Regioselective Synthesis of Multifullerenes with Tuneable Solvent Affinities

Der Naturwissenschaftlichen Fakultät
der Friedrich-Alexander-Universität
Erlangen-Nürnberg
zur
Erlangung des Doktorgrades Dr. rer. nat.

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Als Dissertation genehmigt von der naturwissenschaftlichen Fakultät
der Friedrich-Alexander-Universität Erlangen-Nürnberg

Tag der mündlichen Prüfung:

Vorsitzende/r des Promotionsorgans:	Prof. Dr.
Gutachter/in:	Prof. Dr.
	Prof. Dr.

Meinem Doktorvater, Prof. Dr. Andreas Hirsch, gilt mein besonderer Dank für seine fortdauernde Unterstützung und das rege Interesse an meiner Arbeit. In diesem Zusammenhang danke ich auch herzlich meinen Kooperationspartnern, Prof. Dr. Christoph Böttcher (Forschungszentrum für Elektronenmikroskopie, Freie Universität Berlin), Dr. Boris Schade (Forschungszentrum für Elektronenmikroskopie, Freie Universität Berlin) Prof. Dr. Thomas Drewello (FAU Erlangen-Nürnberg) und Prof. Dr. Franziska Gröhn (FAU Erlangen-Nürnberg) für die hervorragende Zusammenarbeit.

Die vorliegende Arbeit entstand im Zeitraum von Januar 2009 bis Dezember 2013 am Institut für organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg

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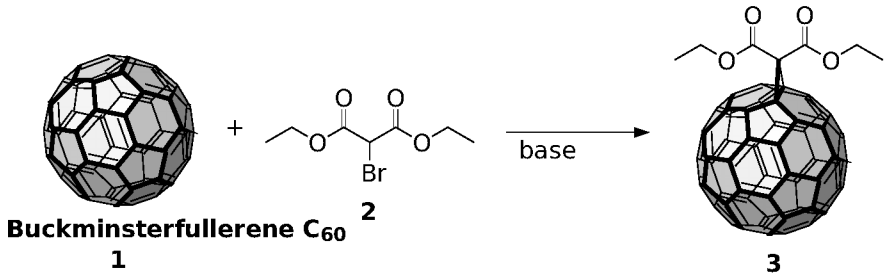
Abbreviation index

ATR: attenuated total reflection
Boc: *t*-butoxycarbonyl
BV: bed volume
CMC: critical micellar concentration
DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene
DLS: dynamic light scattering
SLS: static light scattering
DMA: 9,10-dimethylanthracene
DMAPy: p-N,N-dimethylaminopyridine
DNA: desoxyribonucleic acid
EI: electron beam ionisation, MS ionisation technique
eq.: equivalent
ESI: electrospray ionisation, MS ionisation technique
FAB: fast atom bombardment, MS ionisation technique
Fmoc: (9-fluorenylcarboxyoxy) (protecting group)
FT: fourier transform
HOBt: 1-hydroxybenzotriazole
HPLC: hight-pressure liquid column chromatography
IR: infrared-light spectroscopy
Maldi: matrix assisted laser desorption ionisation, MS ionisation technique
MSA: multivariate statistic analysis
MS: mass spectrometry. See experimental part for matrix abbreviations.
NMR: nucleomagnetic resonance spectroscopy
ODCB: ortho-dichlorobenzene
p: page
P_1-*t*Bu: hexamethylphospintriamide-*tert.*butylimide
Pg: protecting group
Ph: phenyl
RF: reflux
RT: room temperature
SEC: size-exclusion chromatography
stch: stoichiometric
*t*Bu: *tert.* butyl-
TFA: trifluoroacetic acid
THF: furanidine, $(CH_2)_4O$
TOF: time-of-flight
TLC: thin-film liquid chromatography
UV/Vis: ultraviolet-light spectroscopy

1. Introduction

This thesis deals with the addition of malonates to the buckminsterfullerene, which proceeds via the Bingel reaction. The term “Bingel reaction” denotes any cyclic addition of C-H-acidic compounds, with a halogen atom on the C-H acidic carbon, to a fullerene. Its inventor Carsten Bingel discovered this reaction in 1993 (scheme 1).[1]



Scheme 1: A Bingel reaction

1.1. Discovery and Accessibility of the C_{60} Carbon Cage Molecule

The substrate of the Bingel-reaction, the buckminsterfullerene, is obtained in a remarkable way: Fullerenes form from coal vapor under inert atmosphere.[2] It was found to be most efficient to bring the carbon electrodes in direct contact with each other. Since the yield decreases when this is done by a bright arc discharge, either their forming process is light sensitive or the vapor has to be special: Either the ions created in a true arc discharge are less likely to form fullerenes, or the local heating breaks the carbon vapor down to fragments insuitable for the self-forming of these structures. On top of that, no approach to create fullerenes via pure chemical methods had been successful yet. A successful attempt to create C_{60} in a “total” synthesis by dehydrogenating a (perfectly pre-formed) tetrahelicene derivative comprised the use of a laser to perform this last step in a diminishing yield, detectable only in a mass spectrometer.[3] This diligent pathway could rather be seen as a prolonging shunt pathway to identify possible intermediates of the high-temperature rearrangement. This procedure has recently been improved to avoid side-products by fluorinating a defined part of the planar aromatics. This improves the selectivity of the C-C-bond formation.[4] The first discovery of C_{60} happened by a high-temperature reaction that took use of a laser as well.[5]

1.2. The Fullerene's Place in Chemistry

Research in chemistry always receives a refreshing breeze if a new molecular motif is found. This can be a functional group, but also a molecular structure whose skeleton is inherently stable, which undergoes substitution or addition reactions on some variable parts rather than a change in its skeleton. While the aromatic ring and derivatives thereof are the most well-known of those groups, others, as porphyrins, adamantane and the fullerenes are important examples for those cases. From a syntheticists point of view, there is a large difference between fullerenes and these other functional groups: Fullerenes have free addition sites, but no hydrogen atoms that could be substituted. Thus, there are only addition reactions to fullerenes, which do alter the inner electronic structure of the fullerene. Examples of them are mainly Diels-Alder rections, nucleophilic additions (C_{60} is a very strong electron acceptor, see below), and a variety of further cyclisation reactions. This leads to another important facet of fullerenes:

1.3. Ring Strain

Among the typical properties of buckminsterfullerene C_{60} is its enormous ring strain. Due to the cyclopentane rings, the pairs of single bonds have angles of 108° compared to the normal bond angle of 120°. Much of this strain can be relieved by rehybridisation of the carbons when compounds are added to the double bonds. Fullerenes are therefore accessible to a multitude of attacks on their double bonds, plus a set of attacks that involve a prior reduction of its system of double-bonds. When the attack had taken place, however, the ring strain poses an interesting factor: While the usual tetrahedral angle is 109.47°, the constrained angle of 120° on the hexagon rings turns the two bonds of the pentagon ring into the plane, so if the angles of the new bond towards the bonds of the cyclopentane ring were still equal to the tetrahedral angle, the new-formed bond would be formed 95.8° instead of 109.47° towards the former double bond. This newly created strain, which would occur anyway, lowers the step towards a cyclopropanation (where the angle is 60°).[1,6] This makes fullerenes a well-suited substrate for cyclopropanations, aziridine formations,[7] or formations of four-membered rings[8,9,10,11,12] as well. Another reason for this distinct property of fullerenes, of course, is that the lattice rigidity prevents methylene or ethylene groups from accessing more distant points on the fullerene.

1.4. Physical Properties of C_{60}

C_{60} is a brown-black powder. Despite of its compact shape and its total unpolarity, the sublimation point of C_{60} is very high (600°C).[13,14]

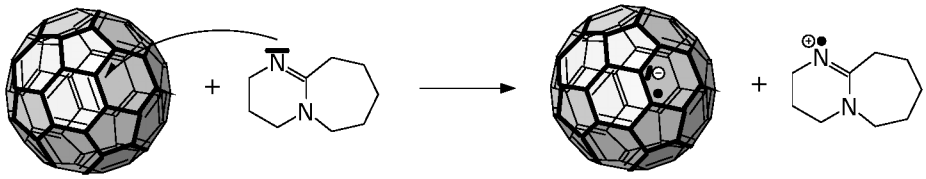
The solubility behavior is an extreme form of what could be expected due to the numerous double bonds on the surface: Especially solvents with numerous free electron pairs give good solubility (table 1).[15,16,17] Amongst unpolar molecules larger, rigid molecules, such as decalines, gain entropy upon mixing with C_{60}, so they are capable of dissolving it as well. The fact that it is completely insoluble as soon as solvents show some polarity, such as acetone, hints that the actual intramolecular forces between solvents and C_{60} molecules are weak compared to entropic factors. The fact that alkyl substitutents on aromatics have a auxilliary effect is most likely due to their higher electron density in their pi-system, which interacts well with the electron-poor one of the fullerene.

solvent	**solubility**
n-hexane	40 mg/L
tetradecane	126 mg/L
decalines	4.6 g/L
chloroform	160 mg/L
dichloromethane	260 mg/L
tetrachlorocarbon	447 mg/L
carbon disulfide	7.9 g/mL
benzene	1.44 g/L
toluene	2.15 g/L
o-xylene	8.7 g/L
1,2,4-trimethylbenzene	17.9 g/L
1,2,3,5-tetramethylbenzene	20.8 g/L
1-methylnaphthaline	33.2 g/L

Table 1: Solubility of C_{60} in adequate solvents

1.5. Electronic Properties

C_{60} exhibits a comparatively high reduction potential, since the atomic skeleton is determinedly electron-poor due to the absence of hydrogens. Due to the extended aromatic system, the HOMO/LUMO gap is only 0.757 eV..[18] The reduction potential is 980 meV. vs. ferrocene.[19] This property makes the system sensitive to nucleophilic additions[20,21,22] and even reduction. Amines will only undergo single-electron transfer reactions (scheme 2),[23] but it can accept up to six electrons from alkali metals, forming a salt.[24] All double bonds of pristine C_{60} are located between two hexagons, at the so-called [6,6]-positions. This has the reason that the pentagonal rings would give them no aromatic stabilisation.[25]



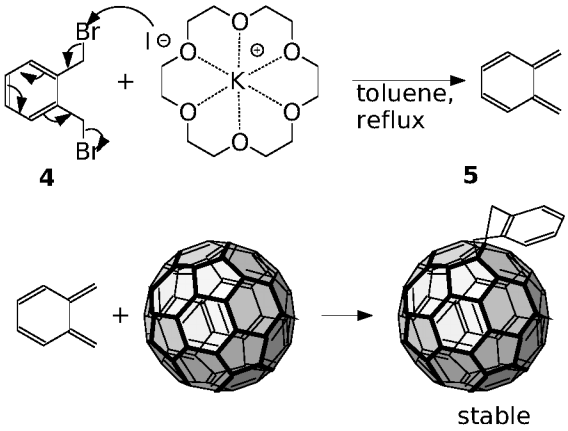
Scheme 2: One (often undesired) reduction of C_{60} by single-electron-transfer from DBU

Electrophilic attacks, however, are very rare.[26,27]

1.6. Diels-Alder Reactions

The most palpable aspect of the electronic properties affects the Diels-Alder reactions on C_{60}. While no Diels-Alder reactions are known that use two conjugated double bonds of C_{60} as diene, C_{60} readily reacts as dienophile with dienes, usually at room temperature.[28,29] Some Diels-Alder reactions, however, are reversible and suffer from a low activation barrier, so these dienes add in an equilibrium.[28,30] Another reason why the fullerenes will not act as dienes is the fact that after such an addition, an unfavorable [5,6]-double bond would be formed.

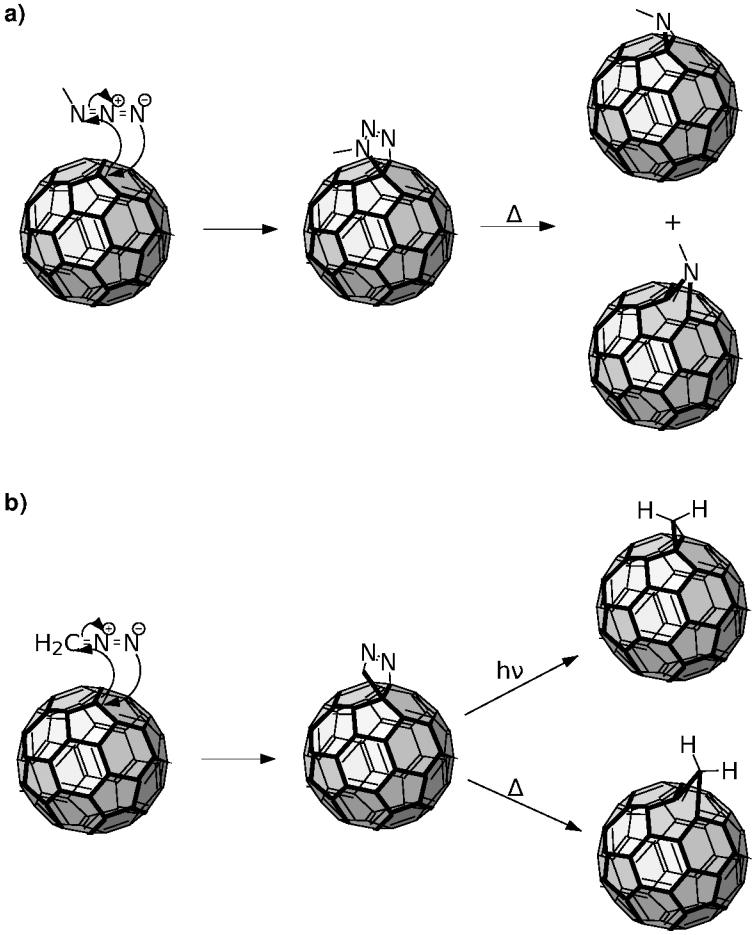
Some unstable addends as **5** for example, generated in situ, cannot be reverted to a stable diene and are therefore irreversibly added (scheme 3).[31,32]



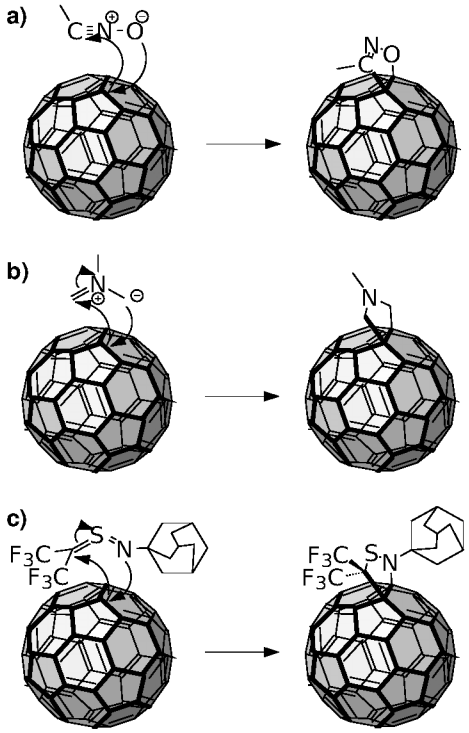
Scheme 3: Increasing the thermodynamic force of the Diels-Alder reaction by highly unstable dienes

1.7. Other Reactions

Reactions not special to fullerenes, but often used for fullerene functionalization, are the fullerene [2+3] cycloadducts of 1,3-zwitterions to the single double bonds of the fullerenes. Among these, the Prato reaction[33] has become the most familar one (scheme 5 b)), due to its facile actability and the stability of products it creates. Another obvious possibility is the addition of azides.[34,35,36] In this reaction, an alkyl azide is added to one double bond, forming a triazoline ring. The ring is unstable and thermally eliminates N_2 and the remaining methylene group is either inserted into a single bond or constitutes a tri-membered cycle together with two atoms of a double bond (scheme 4 a)). Diazomethane[37,38] creates analogous pyrazoline derivatives, where the elimination of dinitrogen can lead to a structure where the nitrogen is attached alone to the double bond, when done photochemically, or be part of a thermal rearrangement which inserts the carbon into a single bond, so the cage is enlarged (scheme 4 b)). Nitrile oxides[39,40] are also good candidates for 1,3-cycloadditions. Formed by deprotonation of α-chlorinated oximes, they readily add to C_{60}, forming an isoxazoline whose single bond is equal to a former [6,6]-double bond (scheme 5 a)).



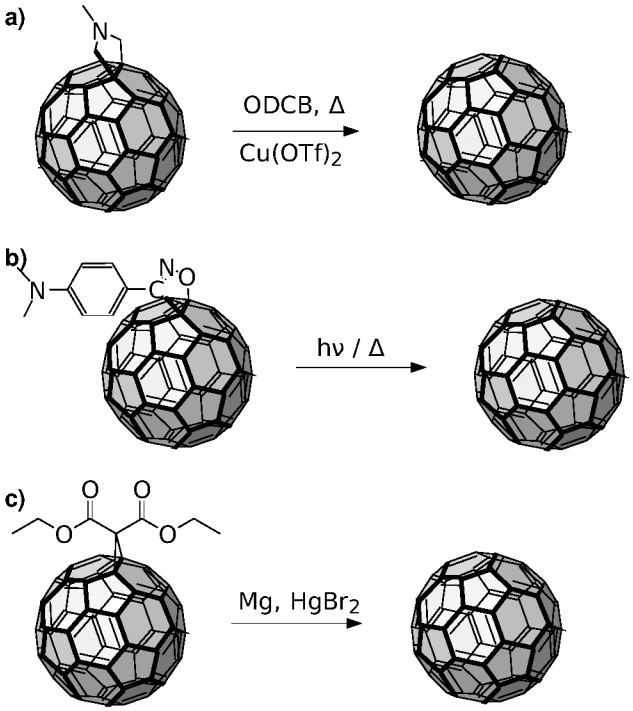
Scheme 4: 2+3-Cycloadditions to fullerenes whose product rearranges by eliminating dinitrogen



Scheme 5: An overview of the several 2+3 cycloadditions to a fullerene double bond

1.8. Some Additions are Reversible

A possibility which will be taken use of in chapter 4.2.1. (page 38) is the restoring of the pristine fullerene. Even when adducts were created by thermodynamically non-reversible addition reactions, there are still special reagents to allow the addend to be cleaved off again. Candidates where this is possible are the Prato reaction,[41,42] the Bingel reaction,[43,44,45] and especially the isoxazoline formation (scheme 6).[46]



Scheme 6: Reactions to remove certain addends

1.9. Formal Description and Conventions

In order to build a closed surface from pentagons and hexagons, one needs at least twelve pentagons, and not more unless the structure is concave. The isolated pentagon rule[47] now tells us that chemical sp^2 carbon structures from pentagons and hexagons are unstable if two cyclopentyl units are annulated onto each other, and C_{60} is the smallest structure that does not violate that rule. The symmetry of the fullerene corresponds to the I_h point group. It is by reason that it has to be so high: if a large, but defined molecule should form under chaotic conditions, even parts of it must be stable. Should these parts gather to a defined molecule in good yield, they must be identical. And if multiple identical parts interconnect, the result is symmetric. The symmetry has also another chemical reason. Due the bent sp^2 carbon atoms, fullerene cages suffer a high ring strain.

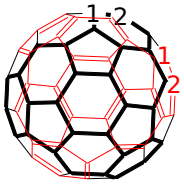
If they were unsymmetric, the strain focusses the lattice deformation to the place with the lowest rigidity. The warp lowers the rigidity even more, forcing the molecule to break on that position or become very reactive there.

In order to express chemical modifications to such cages, the systematic name cannot be used, because the IUPAC naming system is not designed for so great repeating ring structures. One name, created by use of the IUPAC nomenclature by folding two annulated cycles and interconnecting them with the missing bonds would be:

Hentriacontacyclo[29.29.0.$0^{2,14}$.$0^{3,12}$.$0^{4,59}$.$0^{5,10}$.$0^{6,58}$.$0^{7,55}$.$0^{8,53}$.$0^{9,21}$.$0^{11,20}$
.$0^{13,18}$.$0^{15,30}$.$0^{16,28}$.$0^{17,25}$.$0^{19,24}$.$0^{22,52}$.$0^{23.50}$.$0^{26,49}$.$0^{27,47}$.$0^{29,45}$.$0^{32,44}$
.$0^{33,60}$.$0^{34,57}$.$0^{35,43}$.$0^{36,56}$.$0^{37,41}$.$0^{38,54}$.$0^{39,51}$.$0^{40,48}$.$0^{42,46}$]
hexaconta-1,3,5(10),6,8,11,13(18),14,16,19,21,23,25,27,29(45),30,32(44),
33,35(43),36,38(54),39(51),40(48),41,46,49,52,55,57,59-triacontene.

A easier name can be found by stitching two tribenztruxene units together (scheme 7):

"1,3';2,4';3,5';4,6';5,7';6,8';7,9';8,10';9,11';10,12';11,1';12,2'-
Bi(benzo[fghi]benzo[opqr]benzo[x y z aa]truxene)".



Scheme 7: Naming the fullerene as a construct of with two tribenzotruxene units stitched together

It is easier to memorize, but still gives no clear scope over the numbering of the various addition points on the fullerene. A new systematic numbering system was invented in which could be derived more easily.

The systematic numbering is related to the Schlegel diagram (figure 1). The Schlegel diagram is a planar warp of the C_{60} lattice. It begins with the innermost pentagon, follows the first double bond and spirals outwards clockwise. Concerning the chiral configuration, it is obvious that it is meant that this diagraph warps around an actual sphere with the outer rim moving farther away from the spectator. The outer rim constitutes the far side of the fullerene, and is therefore pentagonal, too. The numbering is then done in a clockwise helix beginning from a point at which the highest rotation axis passes. This is true for all other fullerenes. If it is impossible to draw a helix at all from this point, the crossing point of the next lower rotation axis is used.[48] Given a choice of rotation axes with equal count, those which pass rings are prefered towards ones which pass bonds, which in turn are preferred towards axes which pass atoms.

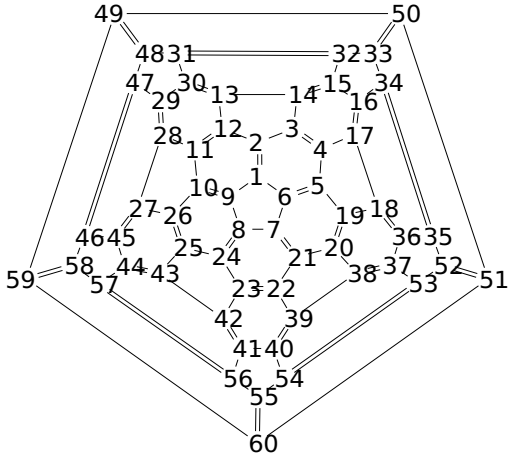
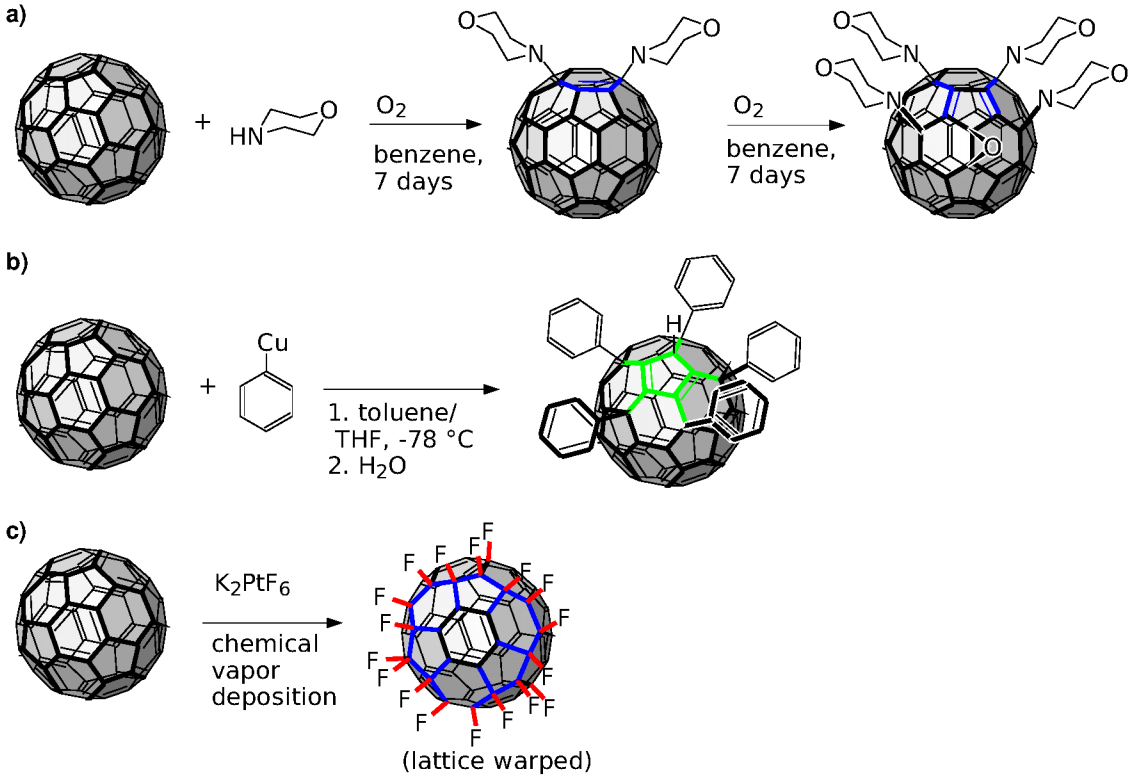


Figure 1: A usual Schlegel diagram

It would be even better to have a term that is based on the symmetry of the fullerene. For this purpose, it is common to write the fullerene's name as ($C_{<n>}$-<symbol>)[<ringsizes>]fullerene, e.g. (C_{60}-I_h)[5,6]fullerene for buckminsterfullerene, while <n> is the carbon count, <symbol> is the symmetry symbol and <ringsizes> is a comma-separated list of the occurring ring sizes. However, it is neither possible to derive the structure of the fullerene nor a numbering scheme. Furthermore, these descriptions may be ambiguous for large fullerenes.

1.10. Identical Addition Sites on the Buckminsterfullerene

Common to fullerenes and all other prevalent skeleton patterns is their property to have multiple identical addition sites. This brings the difficulty to control the count and the relative positions of the addends. Chemists had to develop various and sophisticated methods to direct the addends to certain arrangements on any of these functional groups. Each of these methods generally applies only to their respective moiety, and is not conferrable because it relies on special properties of the group, and any skeleton has its own scope of difficulties. The buckminsterfullerene, especially, has 30 identical addition sites, which are double bonds. An addition of a alkyllithium compound leads to a derivative which now exhibits 58 different places where the next one could be attached. Certain compounds, whose attack causes rearrangement of the double bonds along the fullerene surface, or which create a product susceptible to oxidation in the proximity of the group, control the pattern of their addition on their own (scheme 8).[49,50,51,52]



Scheme 8: Reactions that automatically create a defined addition pattern

If the system of the addend and the fullerene, however, is mirror-symmetric along and orthogonal to the bond on which the addend was attached, there are only nine possible different positions for bisadducts, not regarding chirality. In the Bingel-reaction, the second addend cannot attach on the next position to the first one, obviously due to steric hindrance. The remaining addition sites are accessed in varying percentages.[53,54] As influencing effects, both kinetic and thermodynamic behavior of the electronic system have to be considered. In the case of an aziridine-type monoadduct as precursor, the distribution profile was similar to that with a Bingel- or even a bis-anisolcyclopropane precursor (figure 2).[54]

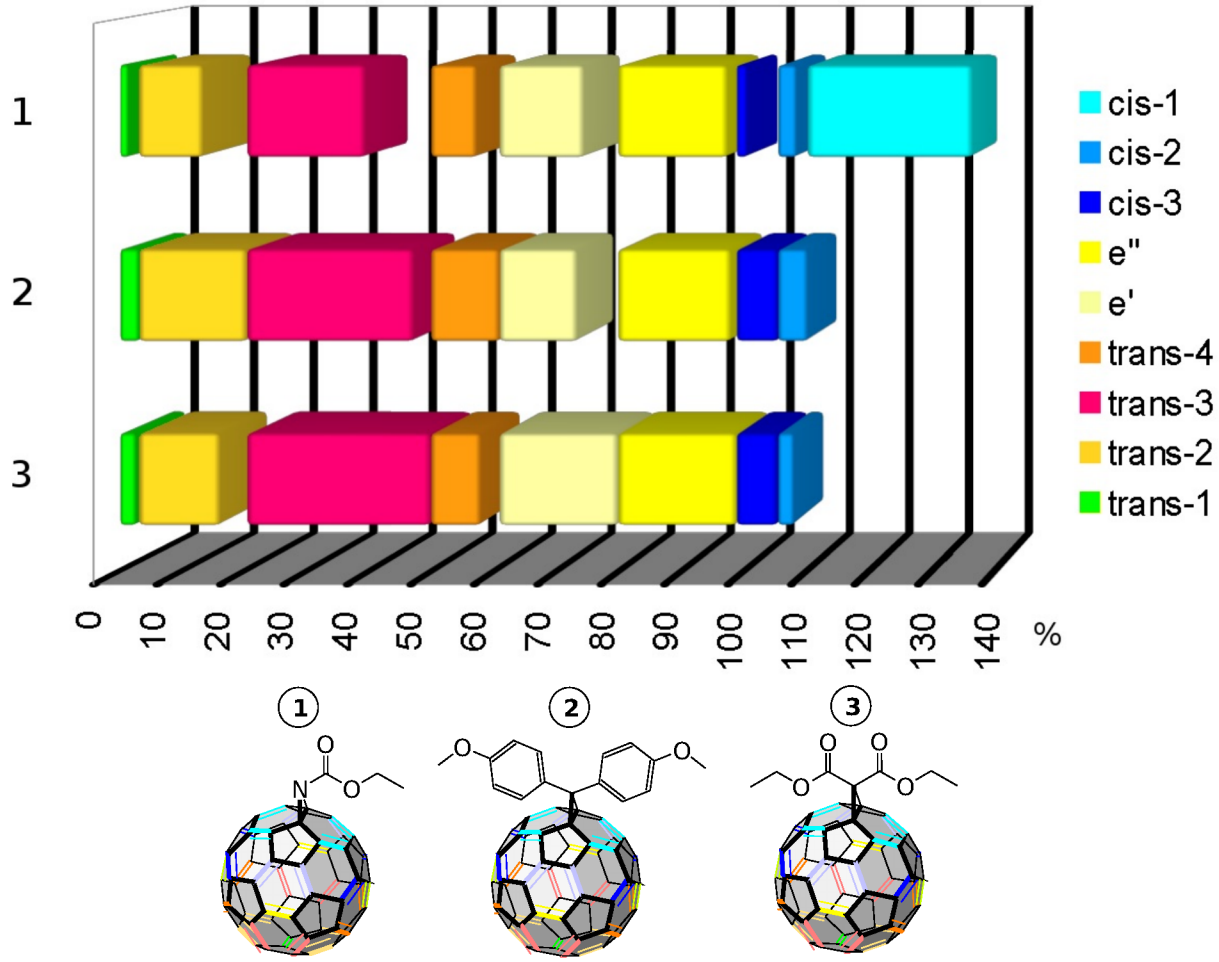
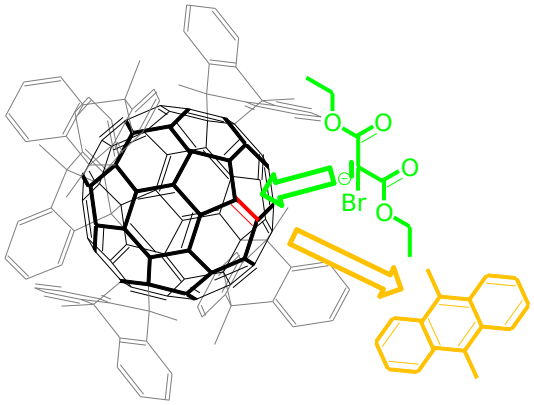


Figure 2: Addition preference of the second diethyl malonate to a monoadduct

We see that unlike the electrophilic aromatic substitution, the selectivity is too low to depend on it. Hence, some tuning of the reaction is required for its use in synthetic pathways. Due to the steric hindrance of the reaction site and the use of general base catalysis, it would be tricky to use a selective catalyst. On the other hand, because of the reversible nature of many additions to fullerene double bonds, the preliminary attachment of groups exerting the desired selectivity by means of the electronic system, or even steric hindrance, is possible. The first successful attempt to do so was done by Iris Lamparth in 1995.[30] Here, most e, e' and trans1 positions were reversibly occupied by dimethylanthracene. The steric hindrance prevented addition to the unwanted positions, too. When one of these addends split off to allow a malonate attach, the remaining ones would still block the unsaturated bonds at the margin of the gap, exposing only the correct site in the middle (scheme 9). In addition, the nearly complete hexakis adduct would have the abundant double bonds already formed to the eight aromatic rings, leaving the remaining site preferred electronically as well.



Scheme 9: Principle of the DMA templatisation: as soon as one addend splits off, the addend lands in the gap

Due to the defined and symmetric electronic system, the spectra of these compounds contain characteristic peaks, one at 314 nm and one at 334 nm. (figure 3)

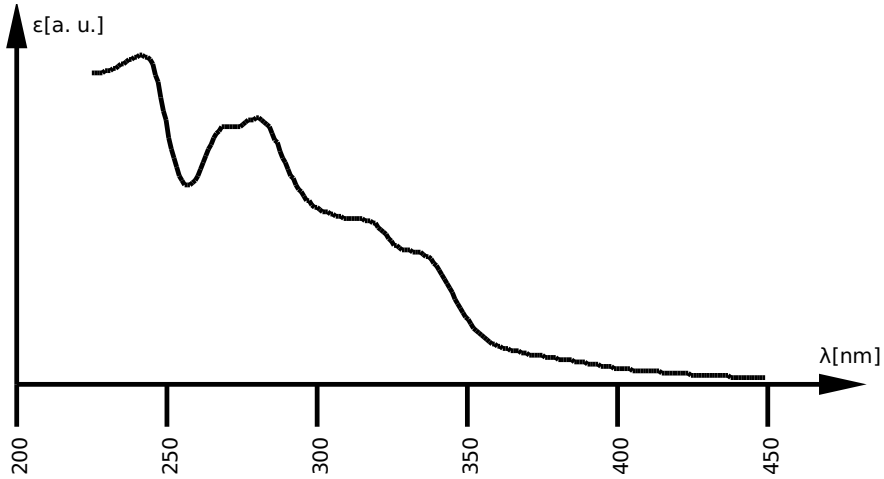
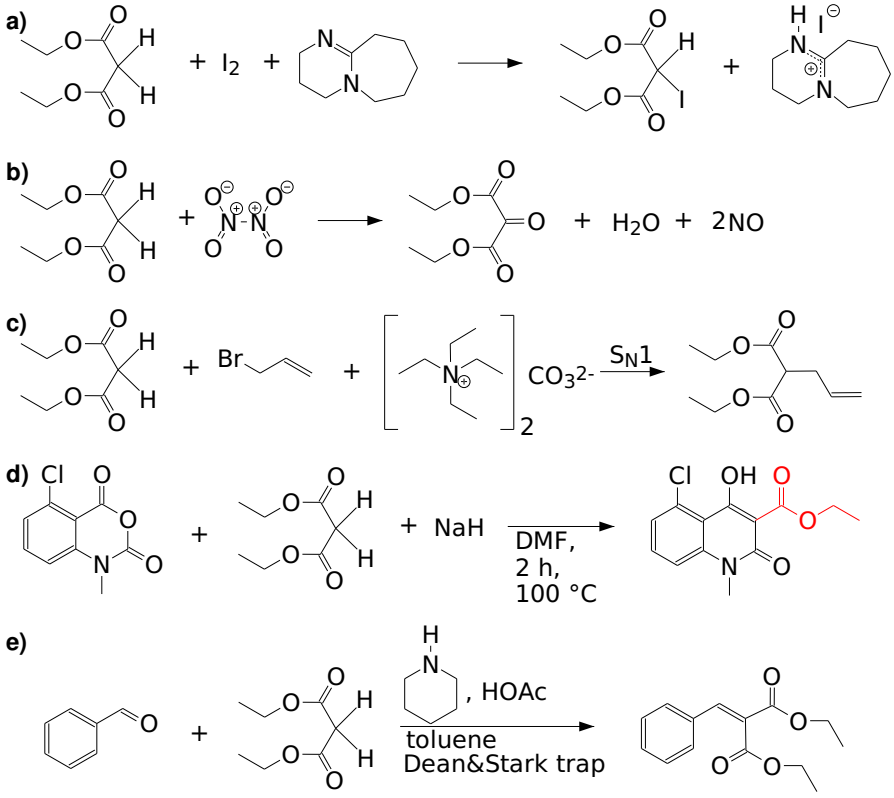


Figure 3: Characteristic spectrum for any T_h symmetric C_{60} Bingel-hexakisadduct

1.11. Malonates

Malonic acid diesters are C-H-acidic moieties with pK_a values around 12.9.[55 p. 197] Due to their negative charge in deprotonated state, their stability against basic transesterification is high. Under strong acidic conditions, they can eliminate alcohol,[56,57] often leading to substitution reactions. If they are halogenated in situ for use in Bingel-reactions, they are usually halogenated in the presence of iodine (scheme 10 b)),[1] bromine or tetrabromocarbon,[58,59] under basic conditions.

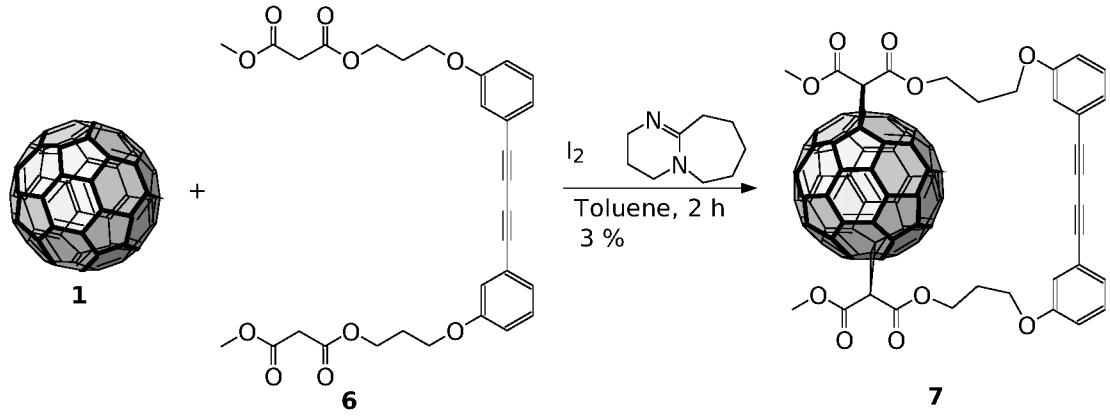
Another scope of their reactivity is that they can be oxidized to the so-called mesoxalates by nitrous gases (scheme 10 a)).[60,61] The most common application for malonates in synthesis is to use the nucleophilicity of their C-H-acidic moiety. This is mainly covered with the Knoevenagel condensation (scheme 10 e)),[62,63] their nucleophilic insertion into rings (scheme 10 d)),[64] and with the synthesis of cinnamic acid derivatives or other α,β-unsaturated acids when the malonate is condensed to carbonyl groups next to groups that stabilize a positive charge on them.



Scheme 10: The reactivity of malonic acid diesters

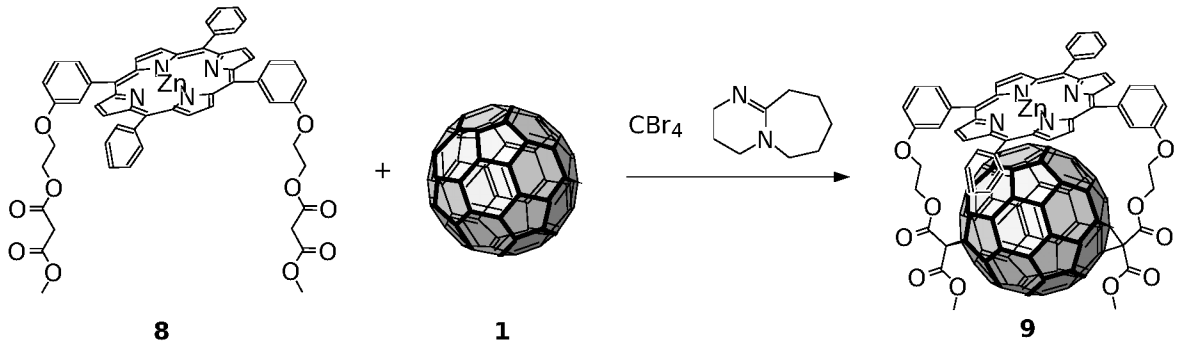
1.12. Earlier Investigations on Selectivity

Our group had undertaken numerous attempts to do accomplish a higher regioselectivity in the pattern of the Bingel-reaction before. In chapter 1.10., the state-of-the-art principle to archieve selectivity has been shown, which was invented by Iris Lamparth.[65] Further attempts, however, have been made to create tethered structures that force the addends into a certain conformation. Jutta Rath had used rigid di-alkyne tethers and especially targeted the trans-1 isomer (scheme 11), which is very difficult to generate due to the steric hindrance a correctly sized tether would undergo during the first Bingel reaction, as the protons of the other malonate would occupy the space the fullerene needs inside the tether ring.[66 p. 129] Such a trans-1 adduct was also statistically deprefered as there is only one single possibility of location for the second malonate compared to four for the trans2-adduct.



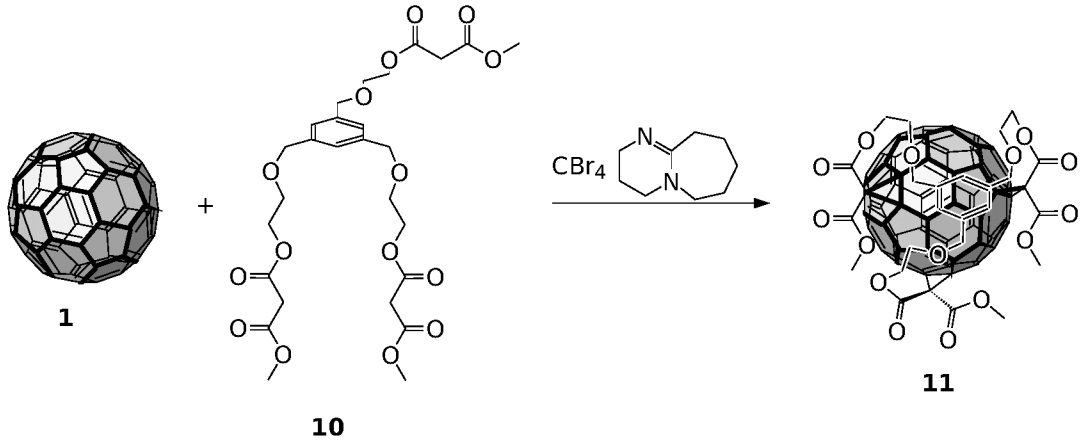
Scheme 11: A tethering mechanism to create the trans1-adduct selectively

The latter form of adduction is an important motif with fullerene-porphyrin conjugates, as those developed by Elke Dietel and Andreas Hirsch (scheme 12).[67] In that synthesis, the fullerene with the correct pattern is selectively formed in 41 % yield.[67] The research was continued by Jörg Dannhäuser[68,69] and Michaela Ruppert.[70]



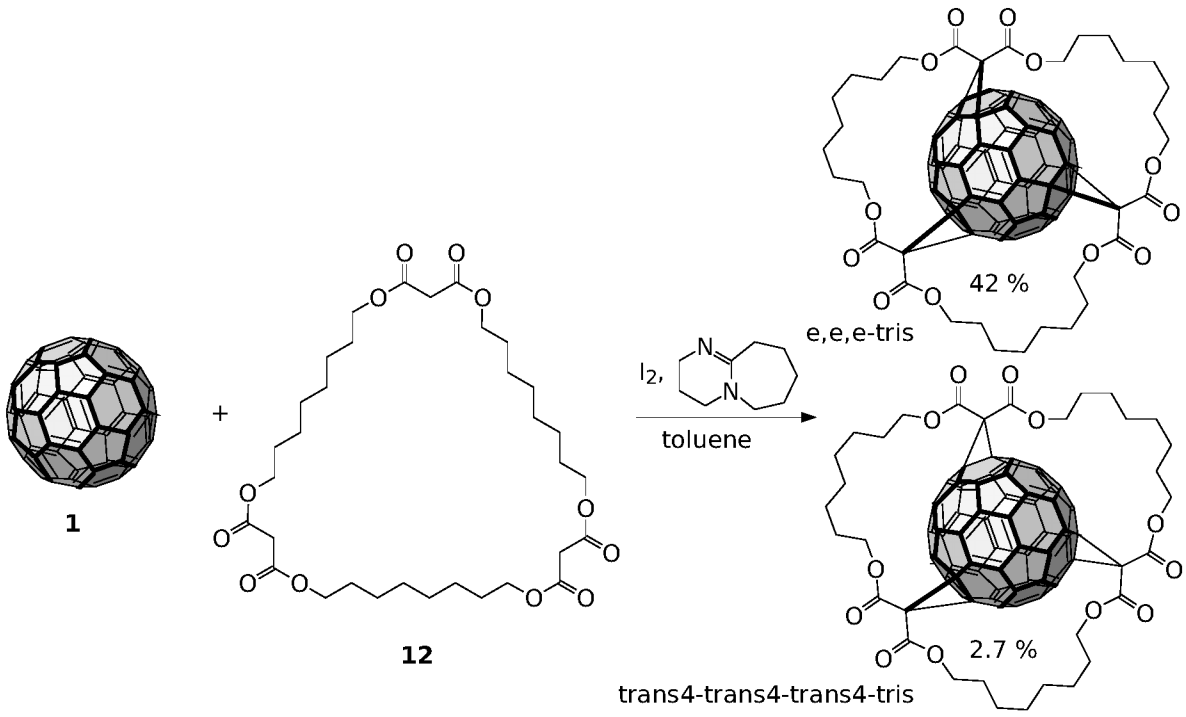
Scheme 12: Adduct formation of porphyrin tethers to fullerenes in close proximity, creating trans-2 adducts. These adducts are being tested for photovoltaic applications.

Florian Beuerle did a selective approach with a central element that held three arms towards the sides (scheme 13). His addend reliably added in a manner that it created an e,e,e-trisadduct.[71,72]

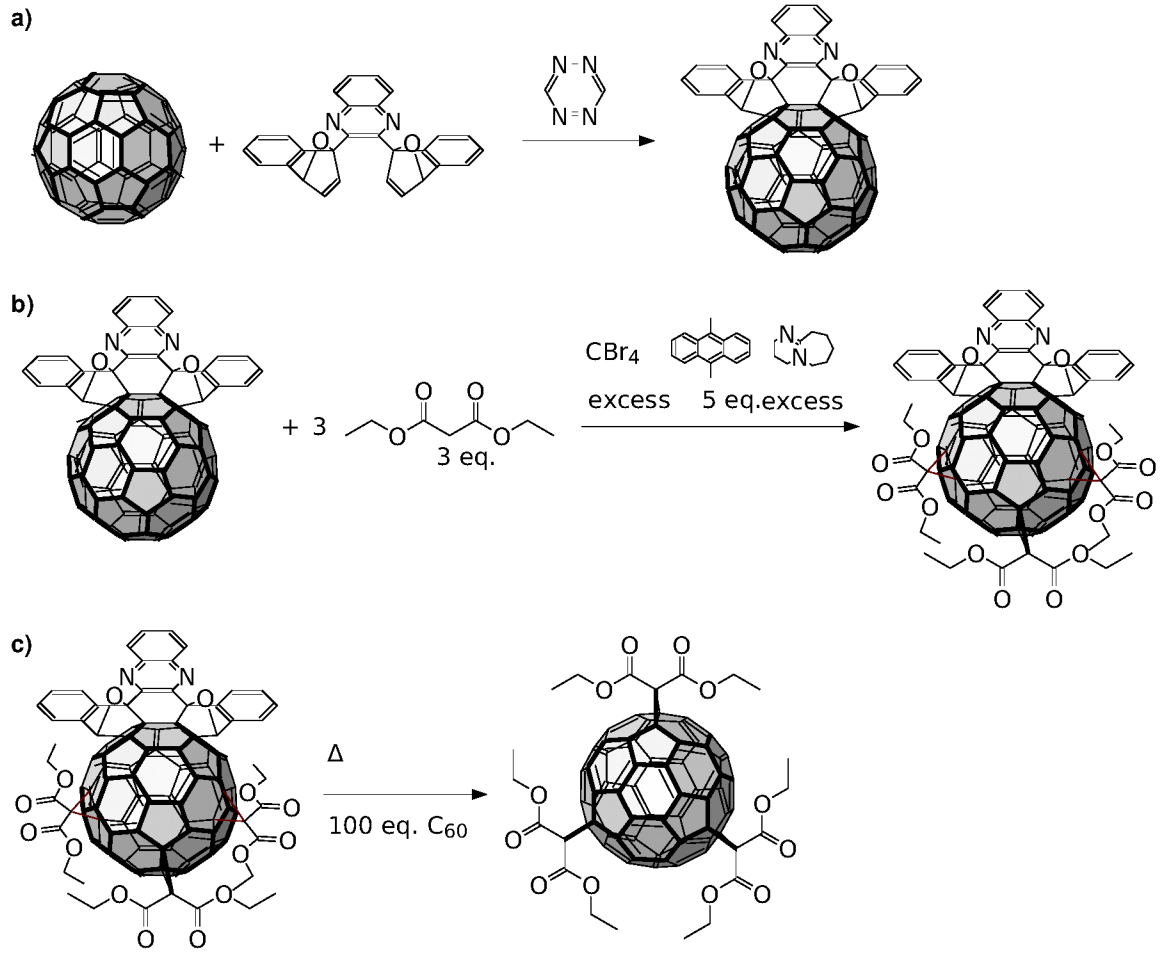


Scheme 13: A center-based tether which selectively creates an e,e,e-trisadduct

Thorsten Brandmüller had discovered a similar templating agent in his systematic screening of the selectivity of oligomeric malonic acid/α-ω-diol cycloesters[73,74]. This happened amongst other findings, which also included a tether directing to a trans4-trans4-trans4-trisadduct (scheme 14). A different, space-consuming templating mechanism to obtain the latter in good yields was invented by Chuang et al. in 2006 (scheme 15).[75]



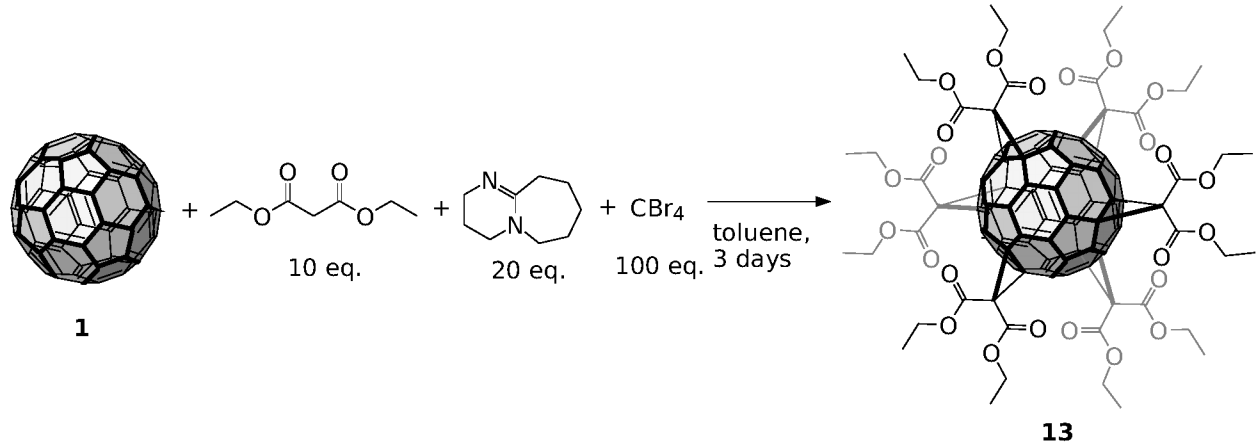
Scheme 14: Selective synthesis of an e,e,e-trisadduct by a tethering of the malonates to a ring of suitable size.



Scheme 15: Complicated steric templating mechanism to selectively generate a trans4-trans4-trans4-Bingel-adduct on a fullerene

A different sort of directing method known by now is the tetrabromocarbon method, which means that an excess of at least 100 equivalents of tetrabromocarbon allows for a selective addition (scheme 16). It was developed by Li et al., who first discovered the benefits of adding an excess of tetrabromocarbon to a DMA-templatized Bingel-reaction[76] and later saw that DMA could be omitted under these conditions.[77]

Despite of a recent theory from my colleague, Frank Hörmann,[78 p. 3891] nothing is known about the mechanism of that reaction, yet.

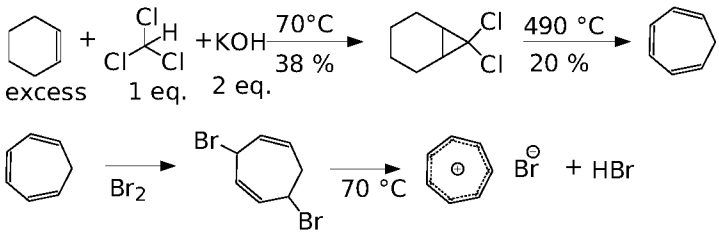


Scheme 16: Tetrabromocarbon-based regioselectivity enhancement

1.13. Tropylium and its Synthesis

Scheme 17: The tropylium ion

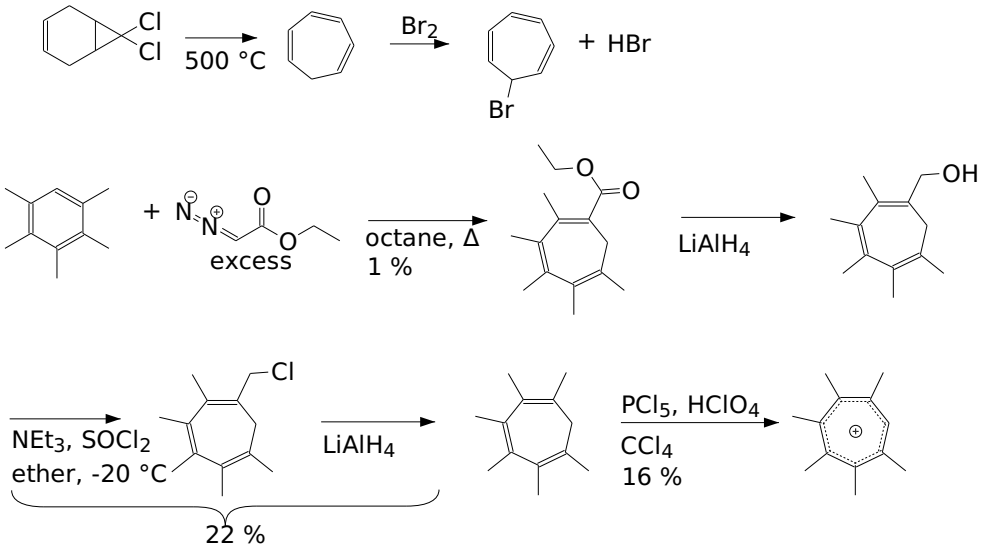
Tropylium (scheme 17) is an aromatic cation with the formula C_7H_7, with its 6 delocalized valence electrons delocalized over a ring of 7 carbons. It is usually synthesized by brominating tropilidene, which, in turn, was created by adding a carbene to hexene (scheme 18), with a total yield of 7.6 %



Scheme 18: Large-scale synthesis for pristine tropylium bromide

Higher substituted derivatives are created from permethylated benzene with a carbene that poses a lower, oxidized carbon synthon (scheme 19). This way, the double bonds are already in place, so thermal rearrangments of the double bonds that would involve the side chains can be omitted. A further advantage of aromatic educts is that the carbenes will attack the protons on the side less likely. They will, however, due to the inert educts tend to dimerize more, so the yield is low either.

Another difficulty is that hydride abstraction becomes increasingly difficult on rings with bulky substituents that also could react in a radical chemistry, so phosphorus pentachloride has to be used, and the yield in the last step is still odd.



Scheme 19: Usual path to synthesize permethylated tropylium

2. Motivation

Fullerenes are, due to the fact that they consist of pure, unsaturated carbon, barely water-soluble. Because it is uninteresting to demonstrate that things behave as expected, our group already had been researching on water-soluble fullerene adducts before,[79,80,81,82,83] creating fullerene adducts which owed their water-solubility to some few, large addends. How would fullerene molecules behave which have many hydrophilic addends, when they are dissolved in water? Can large structures be built from multiple fullerenes and still be solubilized in water? This would require to find a suitable way to bring cations into a molecule that has Bingel reactions in its synthetic pathway, and, which would be seen later, a new approach in creating fullerene adducts with multiple cores. Furthermore, in earlier works of our group, bridged bisfullerenes with complementary ionic substituents had been synthesized,[80,81 p. 130] which had precipitated at neutral pH due to their ionic interaction. Such a hetero-aggregation of the complementary ions would be interesting to put in contrast to a homo-aggregation of the sides of polar/unpolar type macroamphiphiles. Furthermore, the chemistry of the intermediates of these dimers was newly developed and had worked only in certain cases before, so surprising findings concerning the reaction mechanism were possible. And since the new method of templating using tetrabromocarbon[84,85] was not fully understood, it was interesting to find out more about how it worked.

3. Aim

The primary target of this thesis was a fullerene structure consisting of seven fullerenes, with one of them in the middle and the other six ones bearing five Bingel addends with two permanent cations each. The plan was to use the Bingel reaction for this purpose, creating a symmetrical hexakisadduct from one fullerene, connecting the other six fullerenes on it using symmetrical spacers. These other fullerenes should carry the quarternary nitrogen groups on Bingel addends, with an addition pattern being configured in the same manner as the central fullerene. The result would be a molecule which is highly water soluble despite its inner unpolarity, so its solubility behavior could be interesting. This molecule would be well-suited for aggregation studies with desoxyribonucleic acid, which would (due to ionic interaction) wrap around this molecule, whose diameter (about 65 Å) would be in the same order of magnitude as of the natural bobbin for DNA, the histone octamer (about 110 Å).[86 p. 401] Besides aggregation studies, a DNA strand bound to a fullerene may be able to pass biological membranes. The remaining aromatic area of the fullerene could interact with the flexible unpolar ends of the membrane and thus soak up a part of the membrane material on contact, inserting into the membrane and dragging the strand with it, which may be displaced by membrane material during the process, giving it the chance to end in the inside. Patrick Witte had synthesized a similar molecule during his doctoral thesis,[81] however with plain primary ammonium ions as charge carriers. These would be mainly unprotonated at neutral pH.

With the same spacer, of course, one could as well bind just two fullerenes together. This leads to the second aim: To create amphiphiles with one fullerene equipped with unpolar addends and the other one with polar ones. Since these amphiphiles would resemble “enlarged” tenside molecules, they could give a new insight in aggregation phenomena. Also amphiphiles with two polar sides may be useful: The effects of the fully unpolar zones around the “phenyl” rings in an aqueous solvent cage could have various enthalpic effects on the solubility constant and also will affect aggregation in a manner which is unknown yet. On the other hand, with so little hydrophobic surface on the outside, it would be interesting to find out whether they did aggregate at all or not. My job was to synthesize those molecules as samples to investigate this behavior.

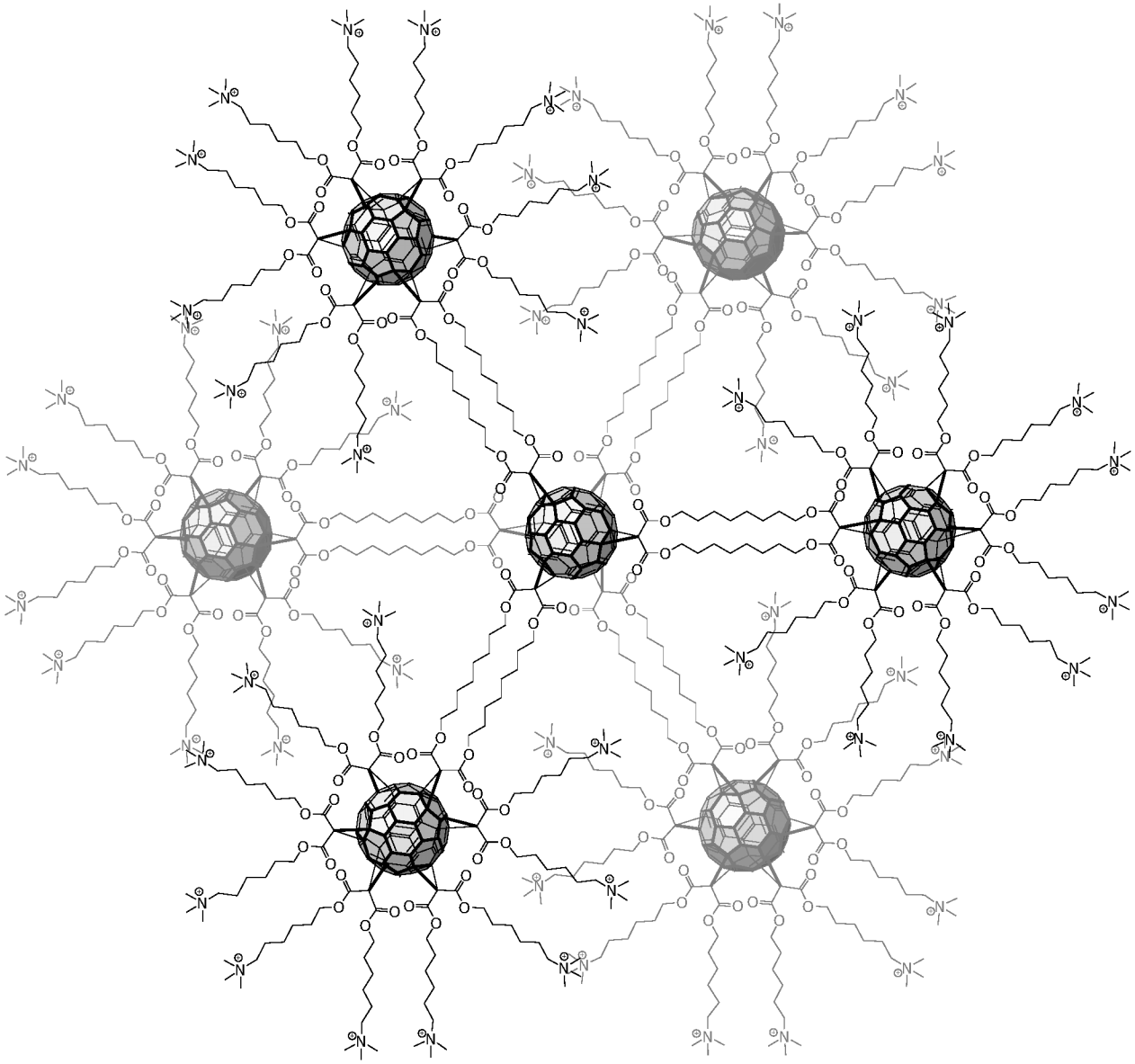
Some expectable problems on these syntheses are well known: The creation of hexakis adducts with one spacer had only worked under certain conditions, variation of seemingly irrelevant factors, such as the choice of base or refraining from creating the activated educts in situ,[81 p. 131] had caused a distinct drop of the yield. To find a reliable way around those troubles, mechanistic investigations were to be conducted, to lighten up the reasons for these problems so they could be aimedly eliminated.

Another point of interest were protecting groups. Our group was investigating a protecting group for one individual double bond on a fullerene, and we asked ourselves whether it could be possible to protect the other educt of the Bingel reaction, the malonate, against the reaction conditions as well. The problem of this idea was that an electrophile had to be attached to a C-H-acidic point, and this would be expected to be so strongly bound that it could be problematic to cleave it off again.

4. Results and Discussion

4.1. First Aim: Cationic Multiadducts of Fullerenes

The initial practical aim of this thesis was to synthesize permanently charged clusters consisting of 7 fullerenes, the macromolecules **14** and **15** (below).



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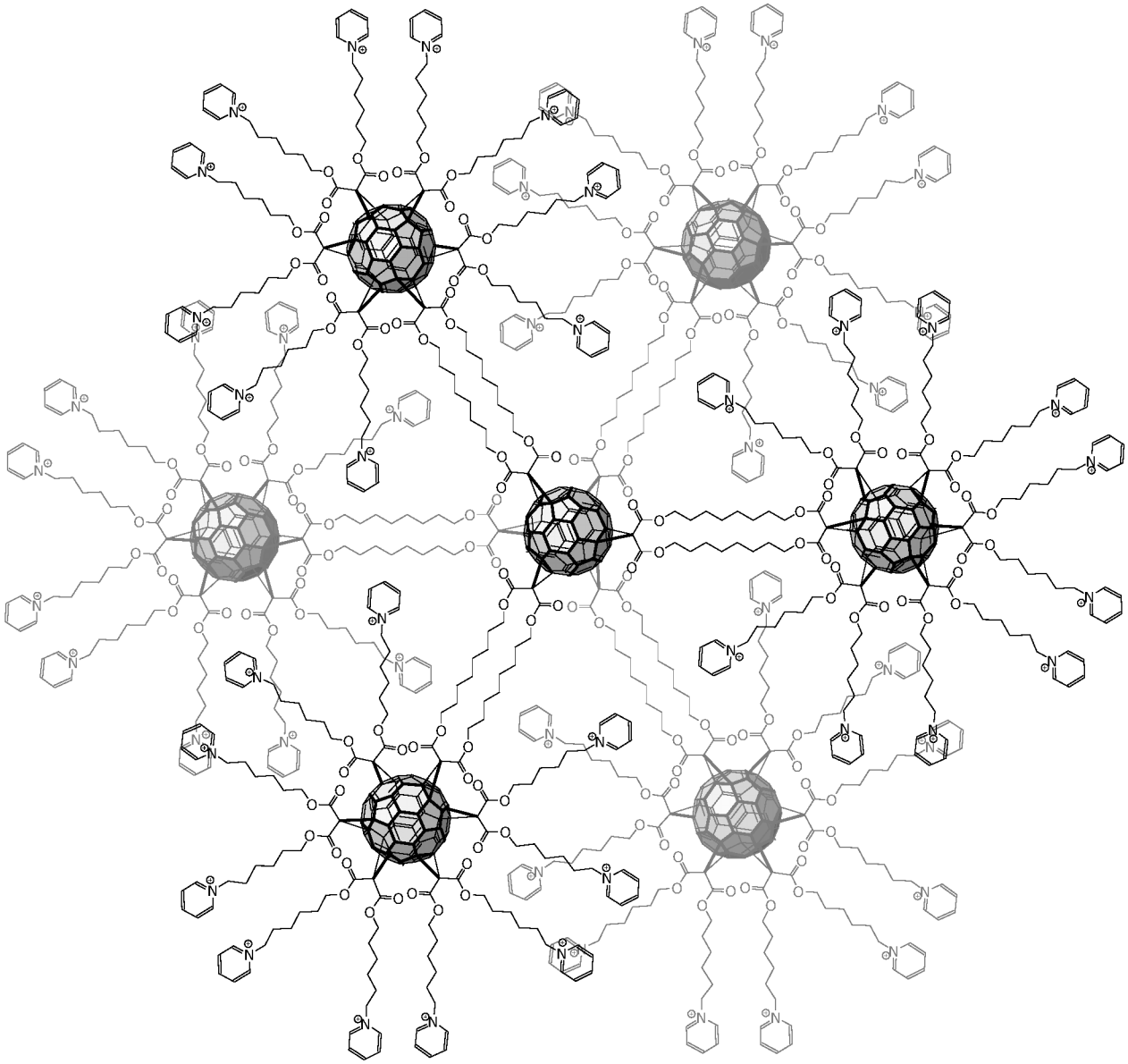
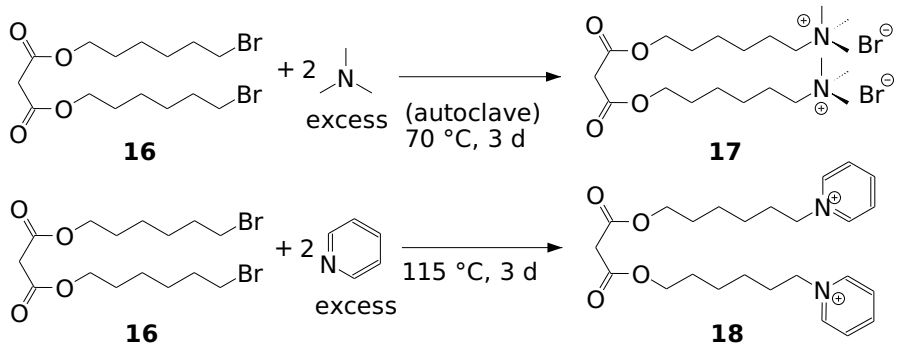
Scheme 20: First draft of a target molecule with permanent ammonium cations.



15

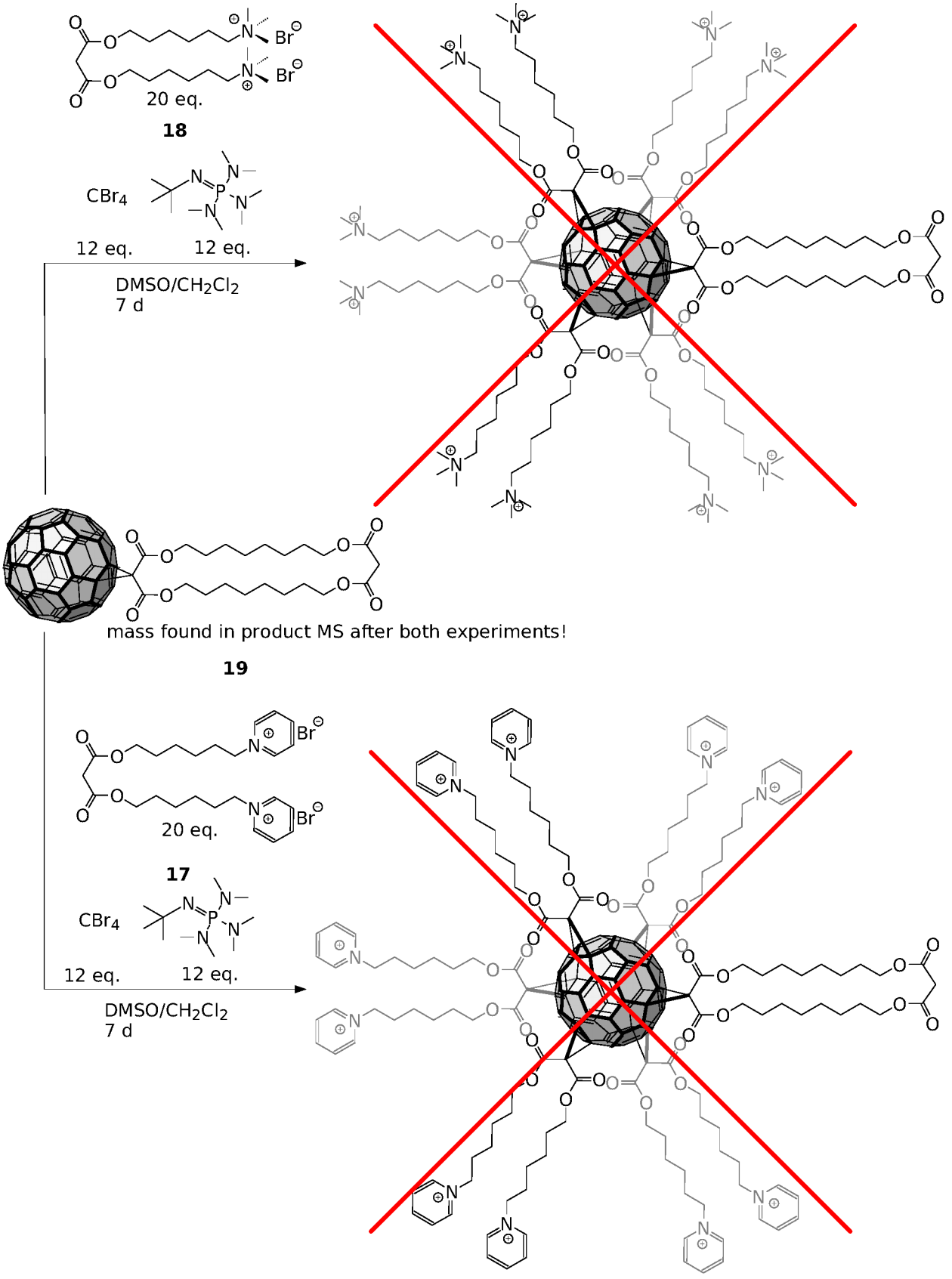
Scheme 21: First draft of a target molecule with quarternary pyridinium cations.

The synthetic route consisted in a convergent approach, in which the outer fullerenes were equipped with their terminal substituents prior to their attachment. This had, in part, statistical reasons, since proceeding otherwise would rise the need to attach thirty malonates in the last stage. Additionally, it was also needed due to solubility problems, since even just two fullerenes, connected with this type of spacer, are almost insoluble.[83] Back in my diploma thesis,[87] a fullerene with a spacer **19**[81] was subjected to a five-fold Bingel reaction with five malonates already carrying the permanent cation residues. Since it had been found out in our group that the reaction proceeds better with in situ bromination of the malonates,[81 table 3.12, p.131] these conditions were applied here. The alternative of using pre-brominated malonates would have suffered from the difficult separability of the different bromination levels of the cationic products, or, when done *vice versa*, from the nucleophilic substitution of the pre-added bromine. As cationic elements on the malonates, triethylammonium and pyridinium residues were used (scheme 22).



Scheme 22: Synthesis of the permanent-cationic malonates

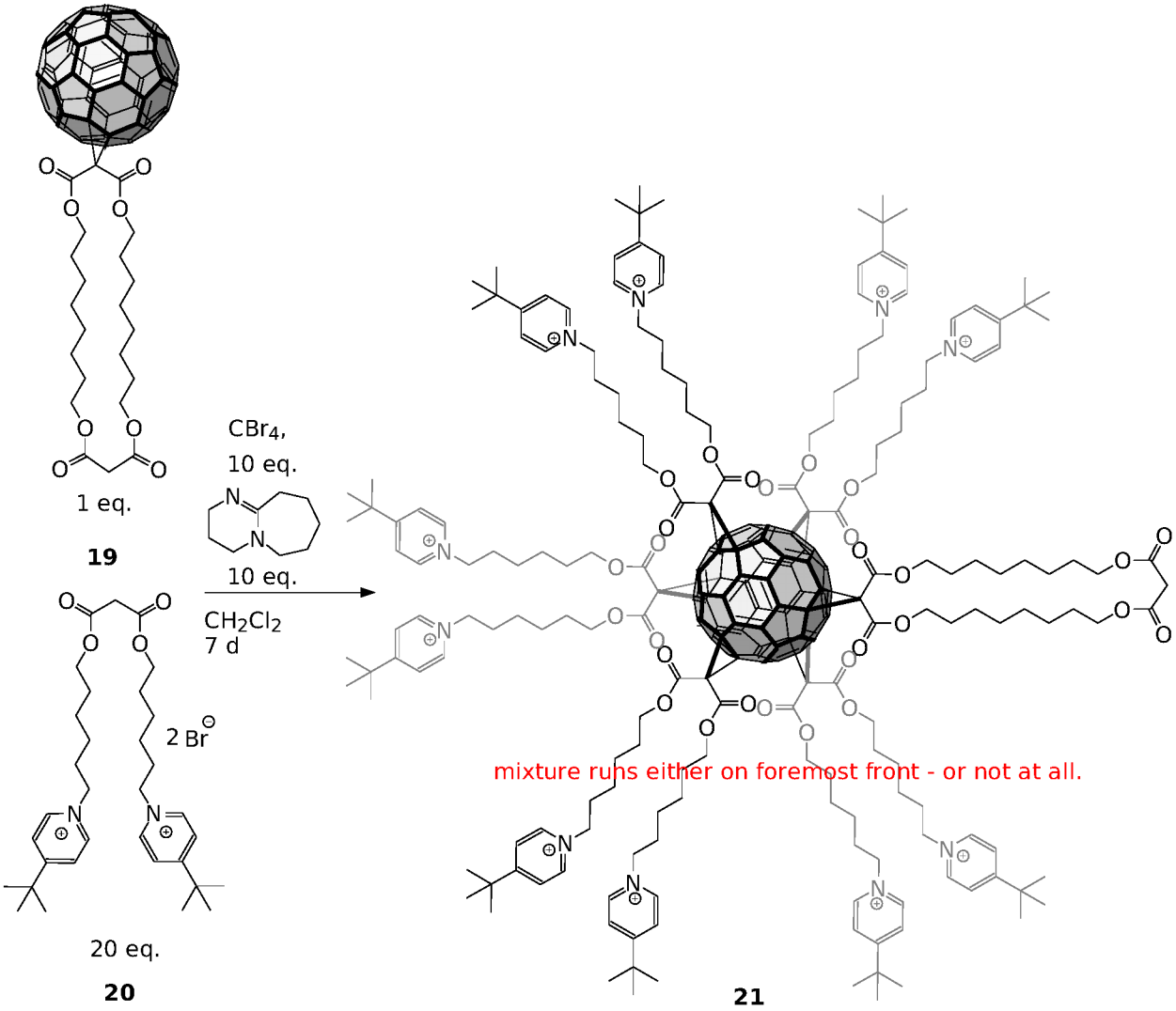
These educts suffered from insolubility in ordinary organic solvents, so dimethylsulfoxide had to be utilized as solvent (scheme 23).



Scheme 23: Failed attempts to affix charged malonates onto a fullerene

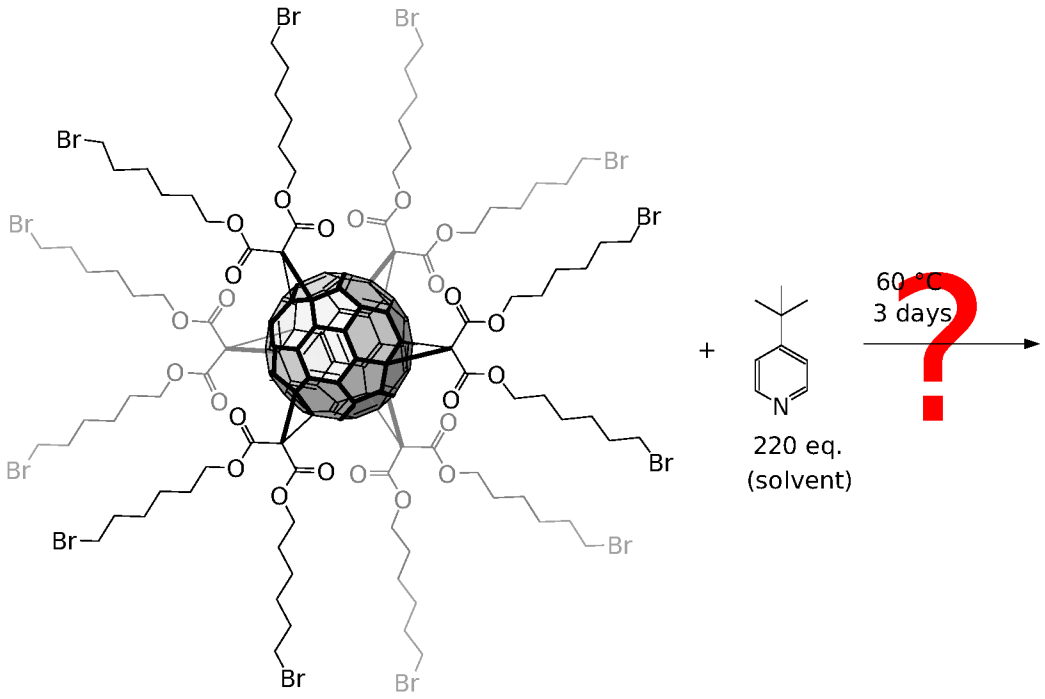
The reaction didn't work. The fact that even unsubstituted educt remained in the reaction mixture after 7 days hinted that the malonates did not even contact the fullerene surface. Obviously, the polar solvent mixture was unsuitable for this reaction. To use solvents which worked better along with C_{60}, more unpolar residues were needed near the cations.

The choice was to replace pyridine by 4-*tert.*-butylpyridine. Although the resulting product mixture was soluble in dichloromethane now, column chromatography was impossible due to the high polarity of the compound. On silica, aluminium oxide and incompletely alkyl-substituted sorbent material, the substance could not be eluted with any solvent (scheme 24).



Scheme 24: Attaching five double-*tert.*-butylpyridinium-malonates fails due to the chromatographic similarity of the side-products!

On completely octadecyl-endcapped silica, the substance eluted along with the foremost edge of the eluent. The same issue was observed with polycaprolactam or starch as a stationary phase with dichloromethane as an eluent. The HILIC[88] method, which means using a mixture of water and acetonitrile, saturated with potassium nitrate, as an eluent with silica as sorbent, led to front-line elution, too. To separate such similar products, there was no big choice of other methods than chromatography, but there was a big choice of methods to generate cations on previously configured fullerenes.



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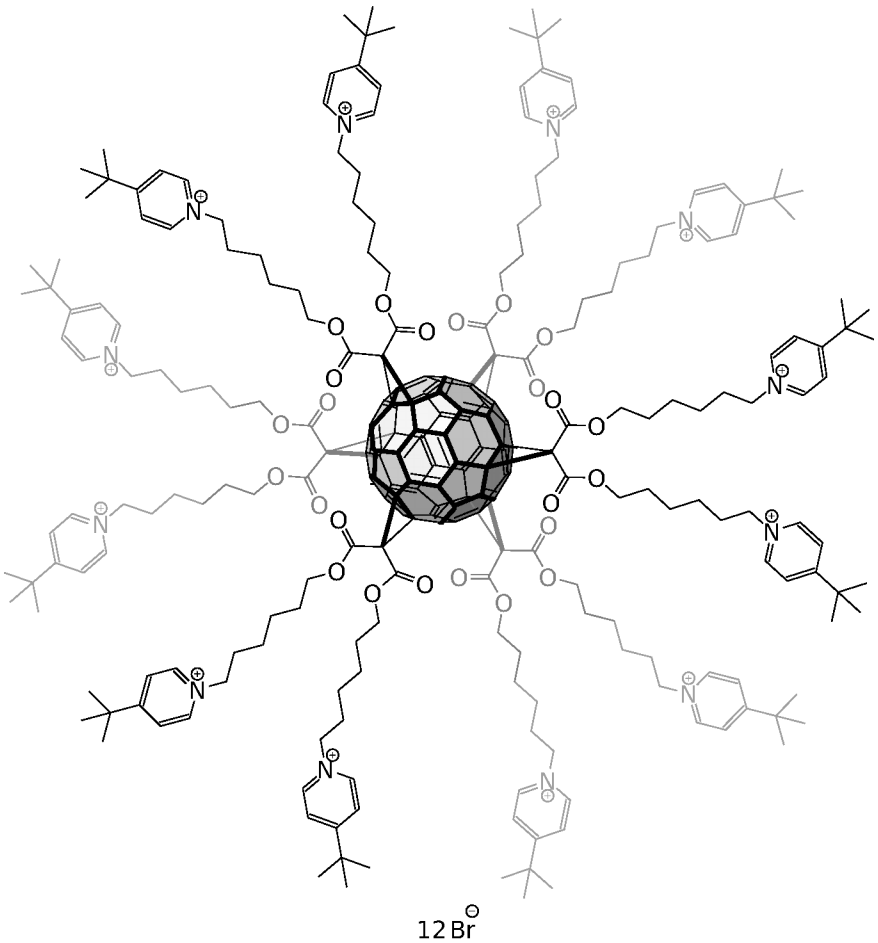


23

Scheme 25: Quarternisation of the purified fullerene adduct *in postum*

Hence, the quarternization had to take place at a time when the addend mixture was separated already.

The first attempt to do this was to synthesize (bis(6-bromohexyl)malonyl)-hexakis[6.0]-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene **22** and add an excess of *tert.*-butylpyridine to it (scheme 25).

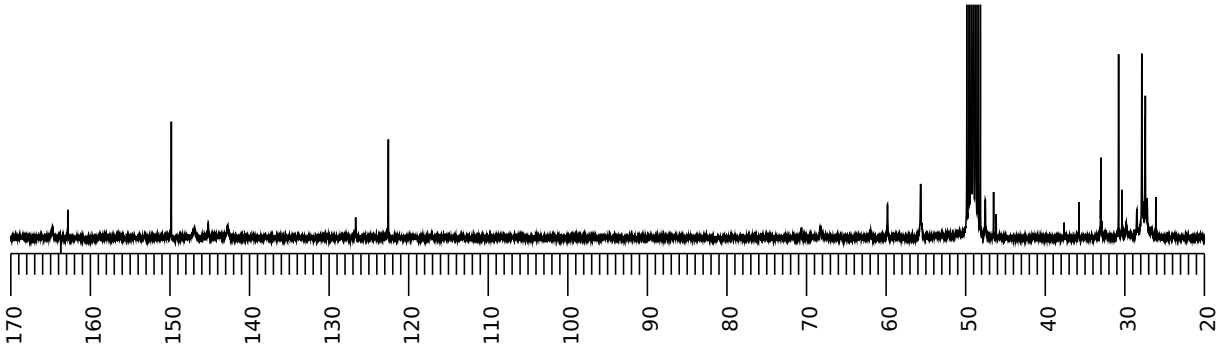
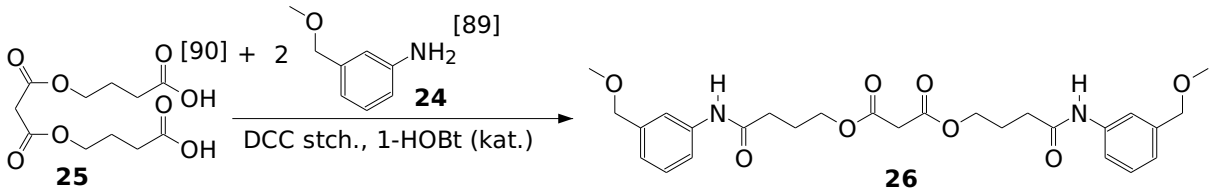
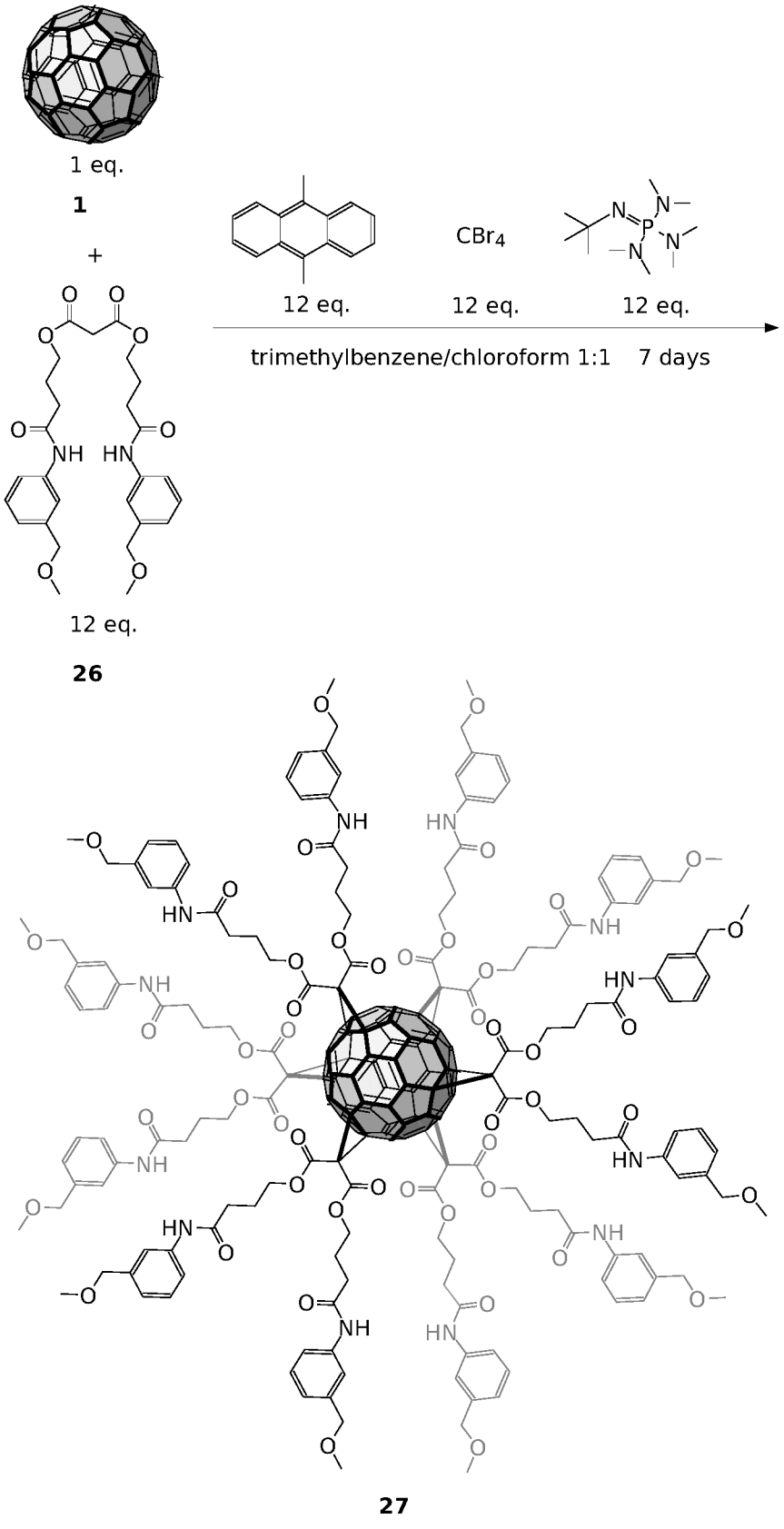


Figure 4: ^{13}C NMR Spectrum after an attempt to quarternize **22** (75.5 MHz, CD_3OD)

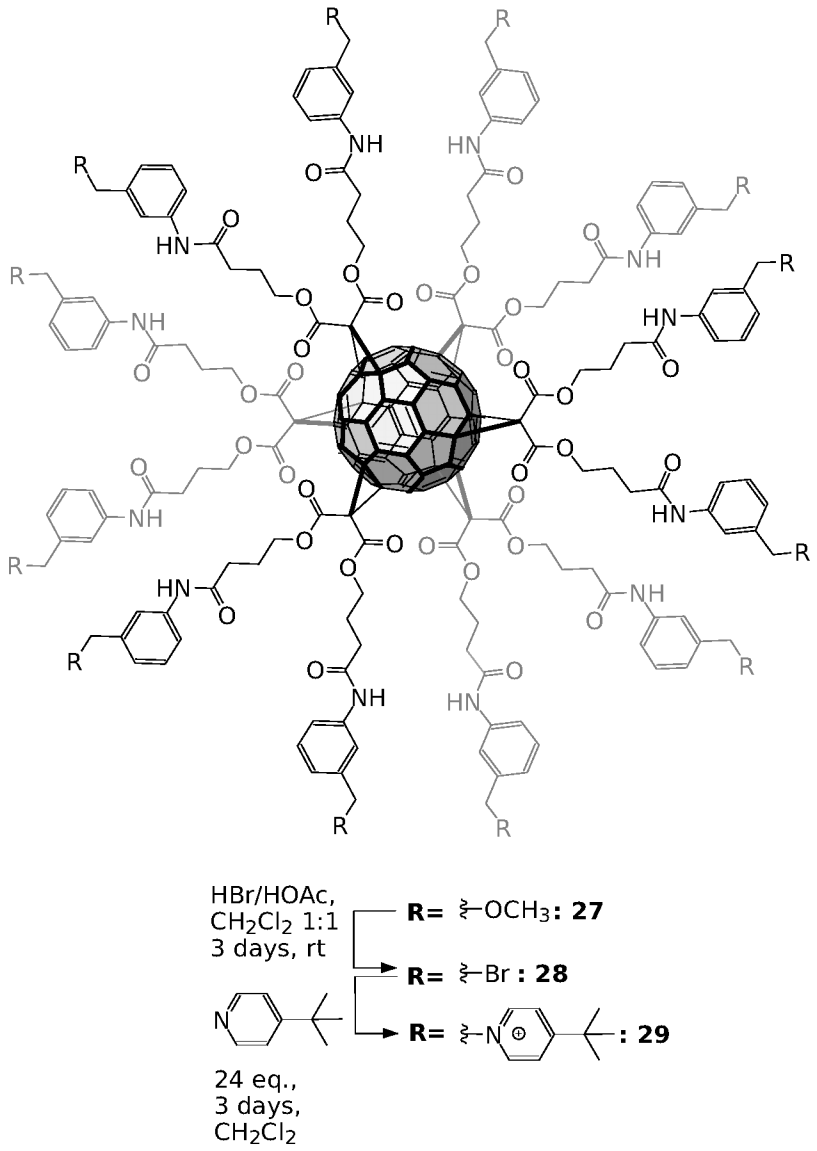
The reaction seemed to work, but the NMR spectrum (figure 4) showed side-products which could not be identified due to the bad separability of permanent cations from each other, and since ESI-MS showed no product signal, a complete substitution could not be verified. A reactive group was needed, which would undergo nucleophilic substitution rapidly enough to have the product transformed to a multi-cation in the last reaction step of the synthetic route. Thus, the meta-methoxy-benzylanilinegroup, invented by Jan-Frederik Gnichwitz of our group just that time,[89] was affixed on the chain ends of a malonate diester (scheme 26).



Scheme 26: Synthesis of a malonate which is to be attached as a precursor rather than an actual cation

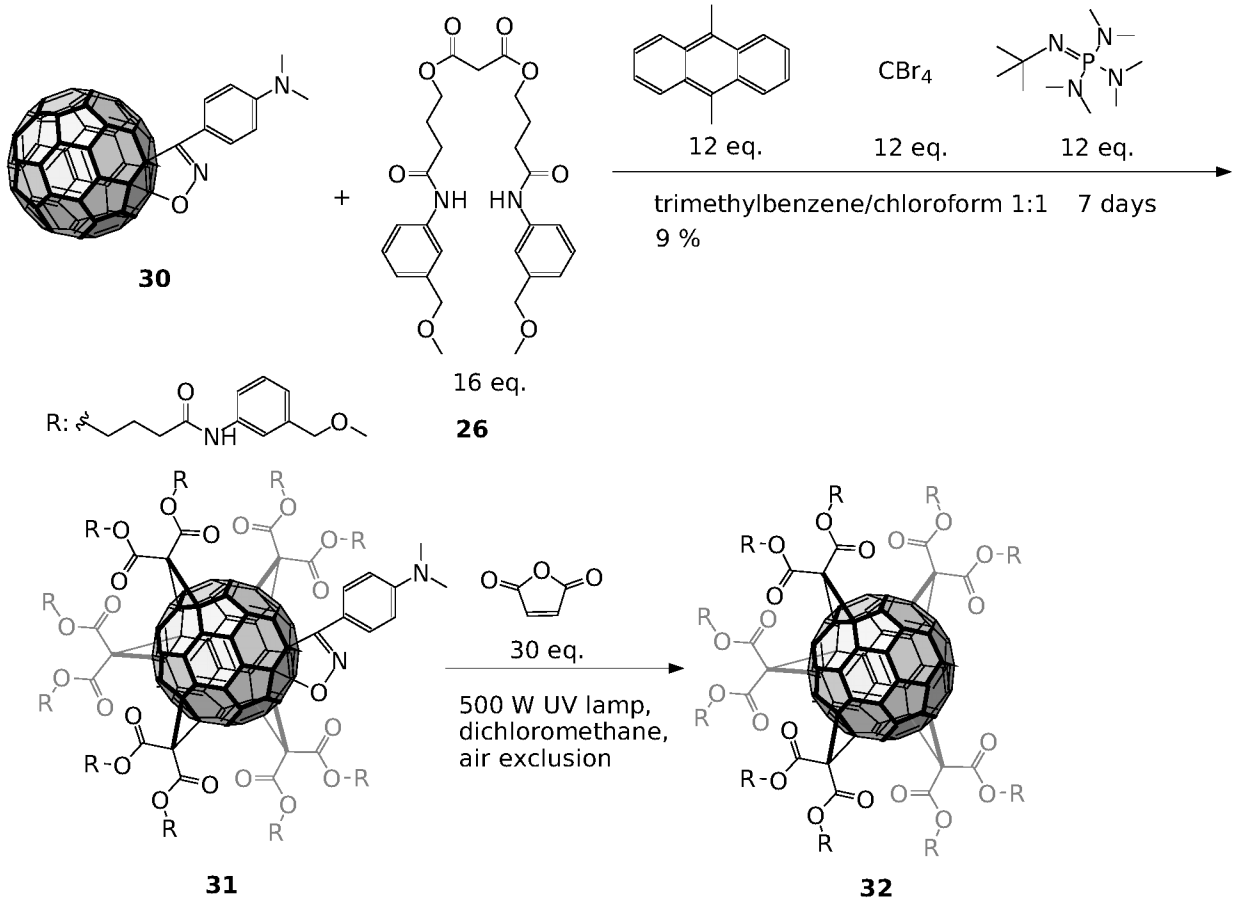


Scheme 27: Trivial approach to the hexakis adduct of the cation precursor, suffering from a untidy workup



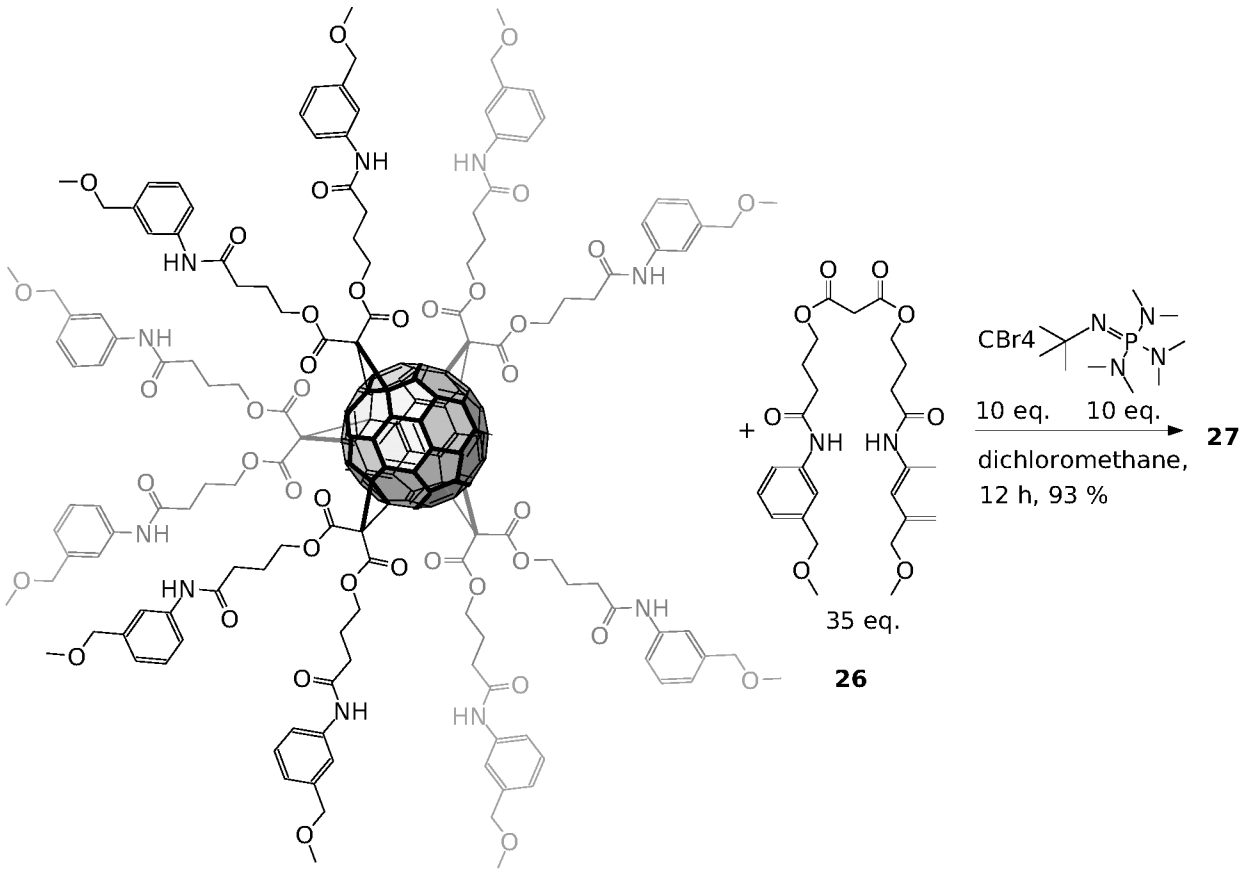
Scheme 28: Final deprotection and generation of the permanent cationic form of **29**.

In this way, a [6.0]-hexakisadduct of symmetric malonates, bearing the aforementioned group with γ-hydroxybutyric acid as a spacer **27** (scheme 27), was created, but the purification of the product was loss-prone and untidy, since precipitation on the silica column was an essential part of the procedure. From a different experiment however (page 37), there was a more efficient, yet more indirect way to create the same substance. Starting from isoxazoline precursor **30**, the mixed [5.1]-pentakisadduct **31** was created (scheme 29). Although a workup using conventional chromatography was still impossible, the eluent mixture toluene:dichloromethane:ethyl acetate:ethanol (3.6:2:3.3:0.95) prove to allow perfect purification on multi-cyclic HPLC (Nucleosil 5 µm), collecting the product after the 12 th run.



Scheme 29: Creation of a pentakis adduct from a malonate with cation-precursor groups

Subsequently, the [6.0]-Hexakisadduct **27** could be made a lot more easily by treating **32** in an excess of **26** and Bingel reagents in a very short time (scheme 30).



Scheme 30: Easier synthesis of a hexakisadduct of malonate **26**, from **31**, which is easier to purify.

The deprotection worked with a dichloromethane - HBr/acetic acid mixture over three days (scheme 28). This yielded the rather unstable product **28**. The *tert.*-butylpyridine group could be quantitatively anchored on it when added in slight excess over three days. The product could be proven by NMR and means of mass spectrometry, as shown in the next chapter.

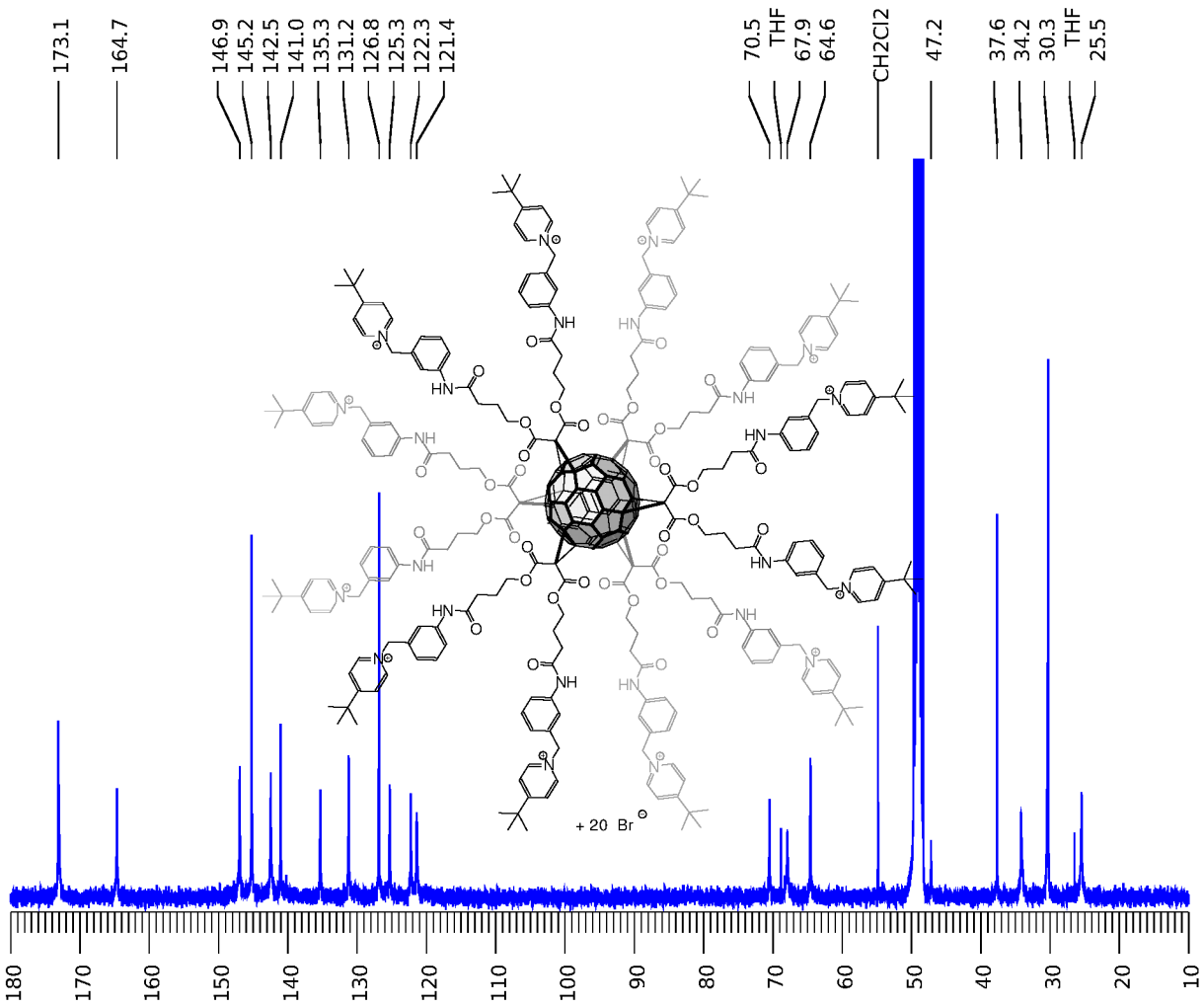


Figure 5: Carbon NMR spectrum of the 12× cationic hexakis adduct **29** (100 MHz, CD_3OD)

A pure hexakis adduction pattern can be observed by the carbon peaks at 146.9 and 142.5 ppm (figure 5). The amide carbonyl carbons resonate at 173.1 ppm, overlapping the quarternary 4-*tert.*-butyl resonances, and malonester carbonyl signals at 164.7 ppm. Two large signals for the 2- and 3-position of the *tert.*-butylpyridine's aromatic ring are found at 145.2 and 126.8 ppm, respectively. The aniline aromatic carbons have their resonances at 141.0, 135.3, 131.2, 125.3, 122.3 and 121.4 ppm. At the characteristic position of 70 ppm, the signals for the sp^3-hybridized C_{60} carbons occur, followed by the alcohol signals at 67.9 ppm and the signals of the methylene group adjacent to the cationic nitrogen at 64.6 ppm. At 47.2 ppm, the signal for the central carbon of the malonate appears. The remaining carbons on the chain resonate at 37.6 ppm and 25.5 ppm. At 34.2 ppm, we see the inner signals of the *tert.*butyl group, and at 30.3 ppm the outer ones. Most importantly, there is no signal for the educt's CH_2Br group at 34.5 ppm, which would mean that some bromides had been left unsubstituted.

4.1.1. Proof of Hexakis Adduct 29 by Secondary-Ion Mass Spectrometry

Thanks to professor Thomas Drewello,[91] MS-MS-spectroscopy was done on this compound.

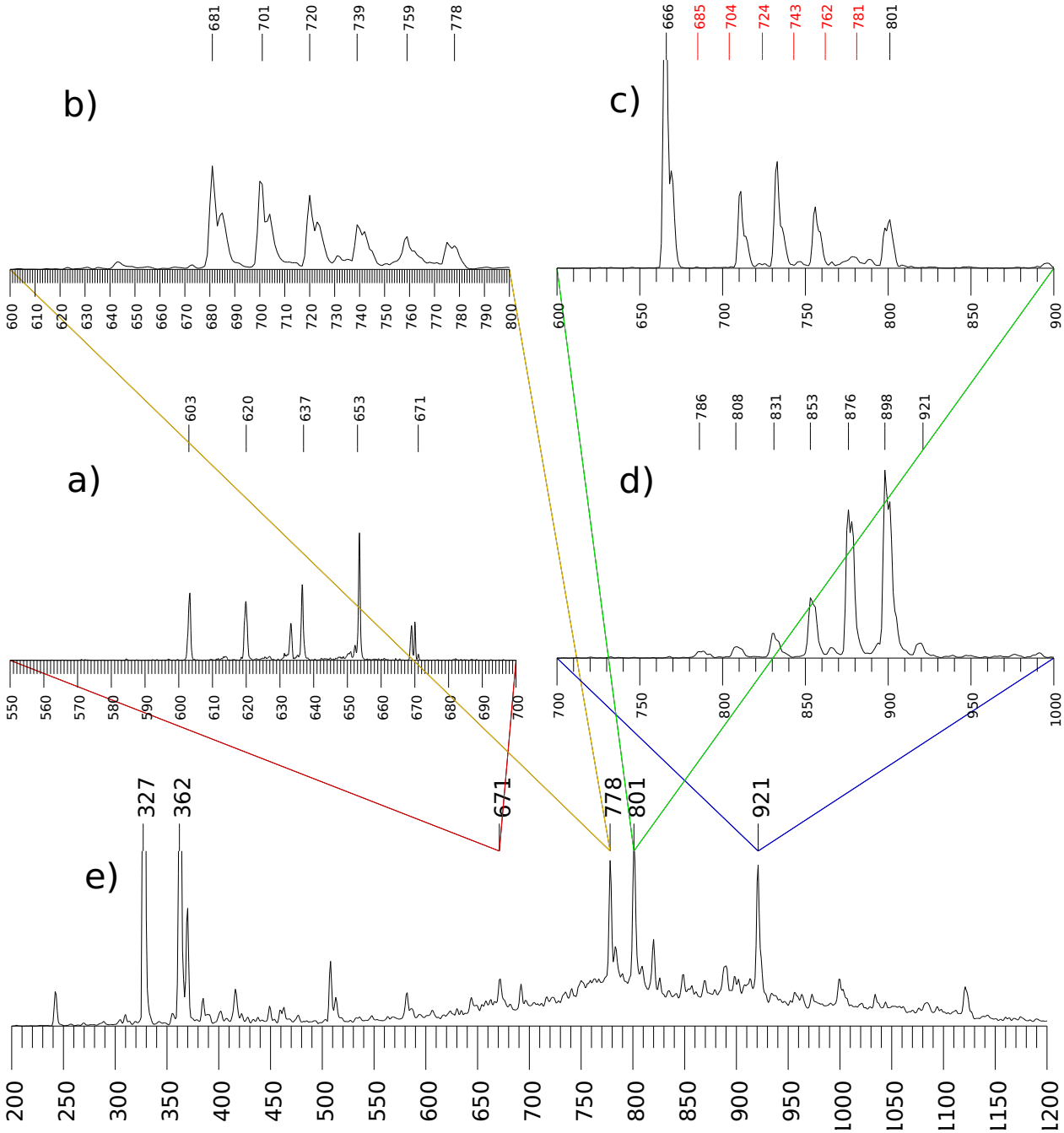


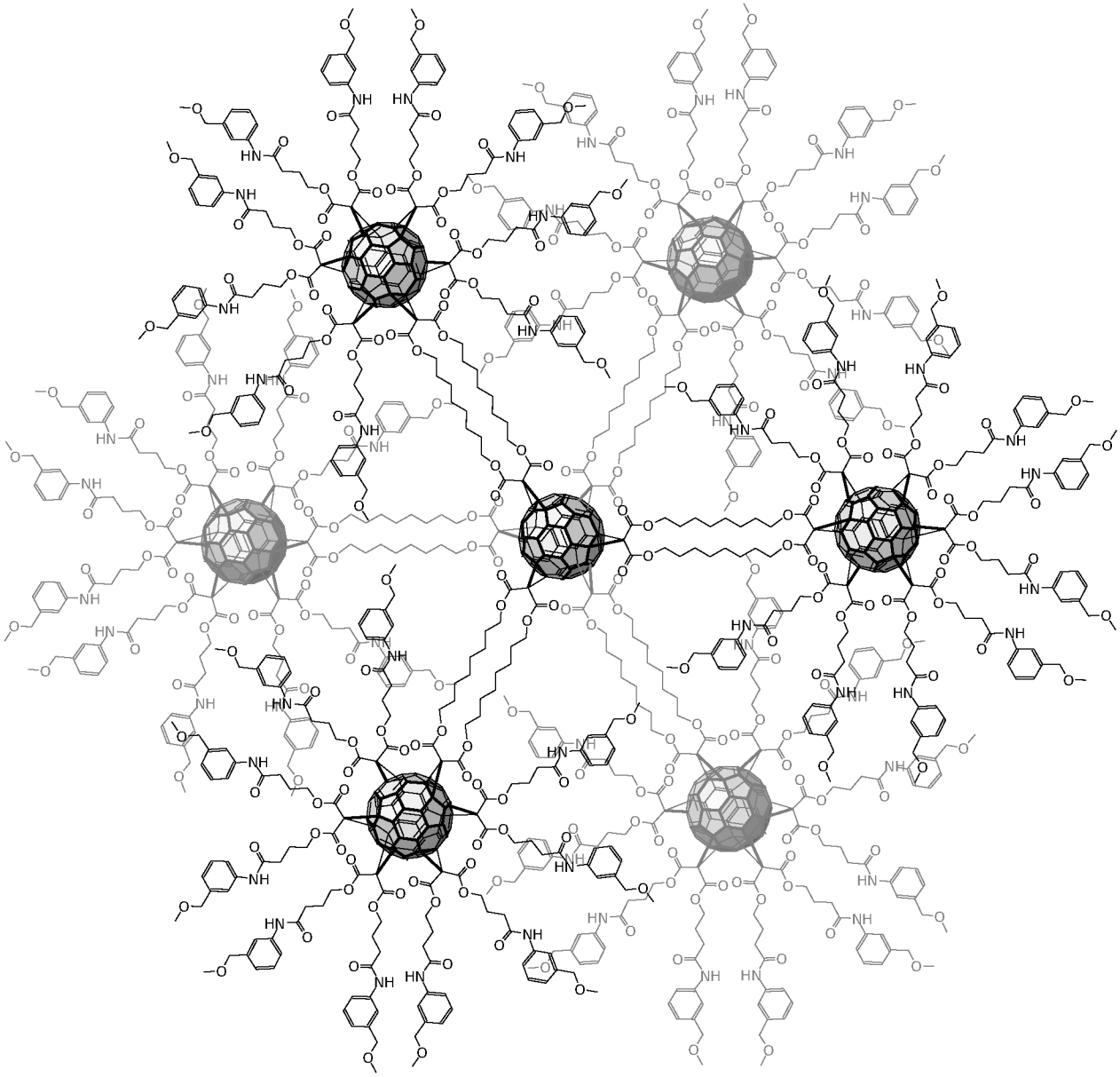
Figure 6: ESI Mother(e)/daughter(a-d) Mass spectrum of **29**. Solvent: MeOH. Spectra recorded by Jing Li/Rolf Kirschbaum from the Drewello group

In figure 6, the daughter ion spectra of four MS peaks are shown. They correspond either to the salt of the molecule, which had lost a defined amount of bromide counterions, ranging from $[M - 6\ Br^-]^{6+}$ (a) $[M - 7\ Br^-]^{7+}$ (b) to $[M - 8Br^-]^{8+}$ (d), but also $[M - 5\ Br^-]^{7+}$ (c). In the daughter ion spectra, it becomes visible that the remaining bromide anions substitute *tert.*-butylpyridine back. In each one, we see one *tert.*-butylpyridine loss peak for each bromide anion left on the torso.

In case (c), however, obviously all possible pyridinium residues are defeated, due to the unusual charge situation, in which charges must be localized on additional other points besides the benzylic groups.

4.2. Forming Macrostructures from Multiple Hexakis Adducts

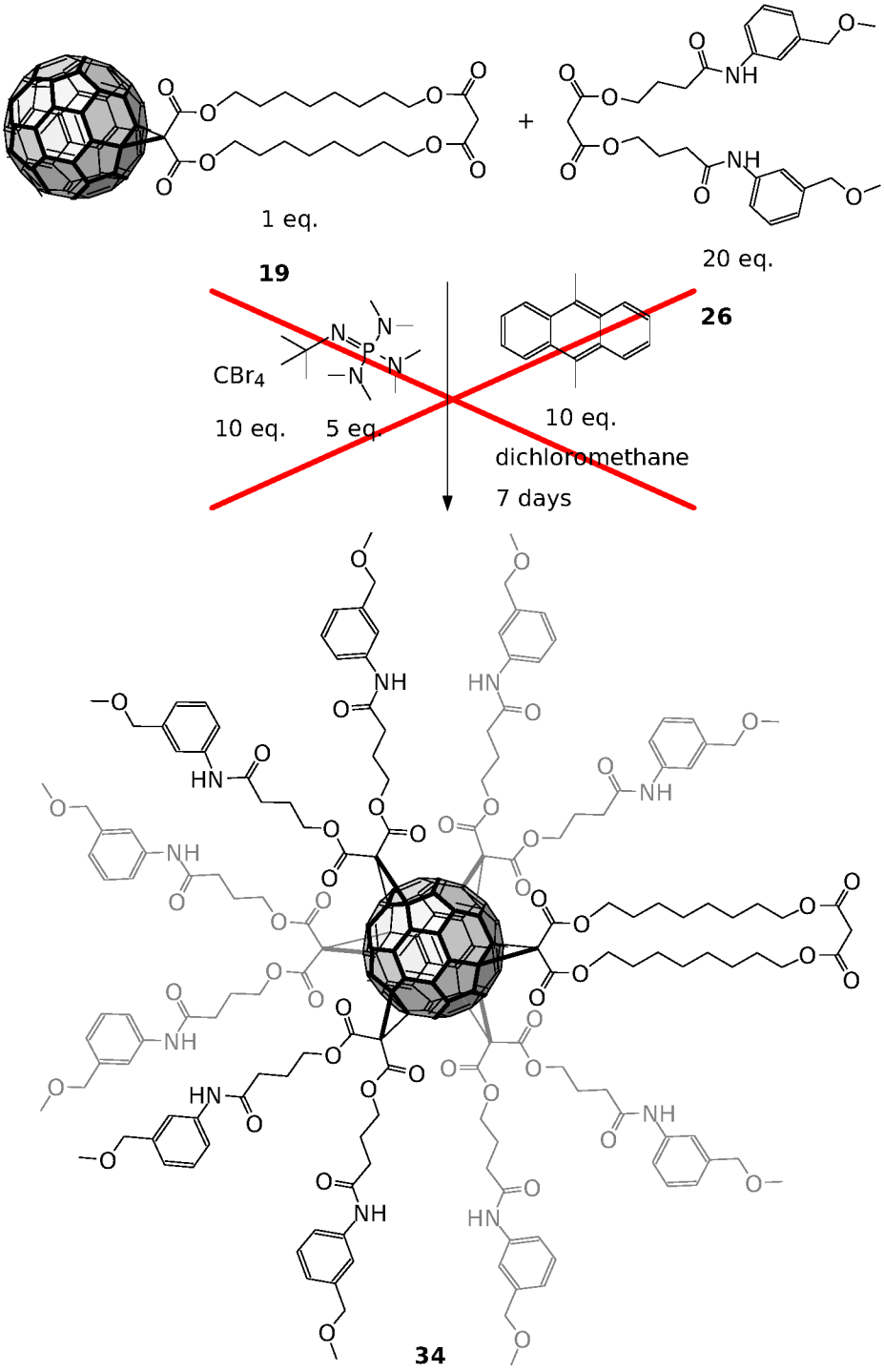
For the molecule that was supposed to resemble a histone octamer, there would be several of those cationic subtituted fullerenes needed to be linked together to a globular shape. This molecule is carrying the positve charges on the ends of its dendritic structure to have them exposed to the outer side, make them bind the negatively charged DNA and effect water-solubility as well (scheme 31).



33

Scheme 31: Intended 60-cation-precursor target molecule

In order to archieve the aim to construct the seven-core fullerene adduct with sixty meta-benzylaniline cation precursors attached to it, molecule **33**, a spacer had to be attached on the fullerene together with those meta-benzylaniline precursors. This was initially tried using the state-of-the-art method of our group. Starting from monoadduct **19** and adding the cation-precursor **26** to it, no evidence for the typical hexakis adduct signals was observed in any eluted fraction or HPLC samples. No indication for an hexakis adduct could be detected in any of the UV/Vis spectra of the eluted fractions.



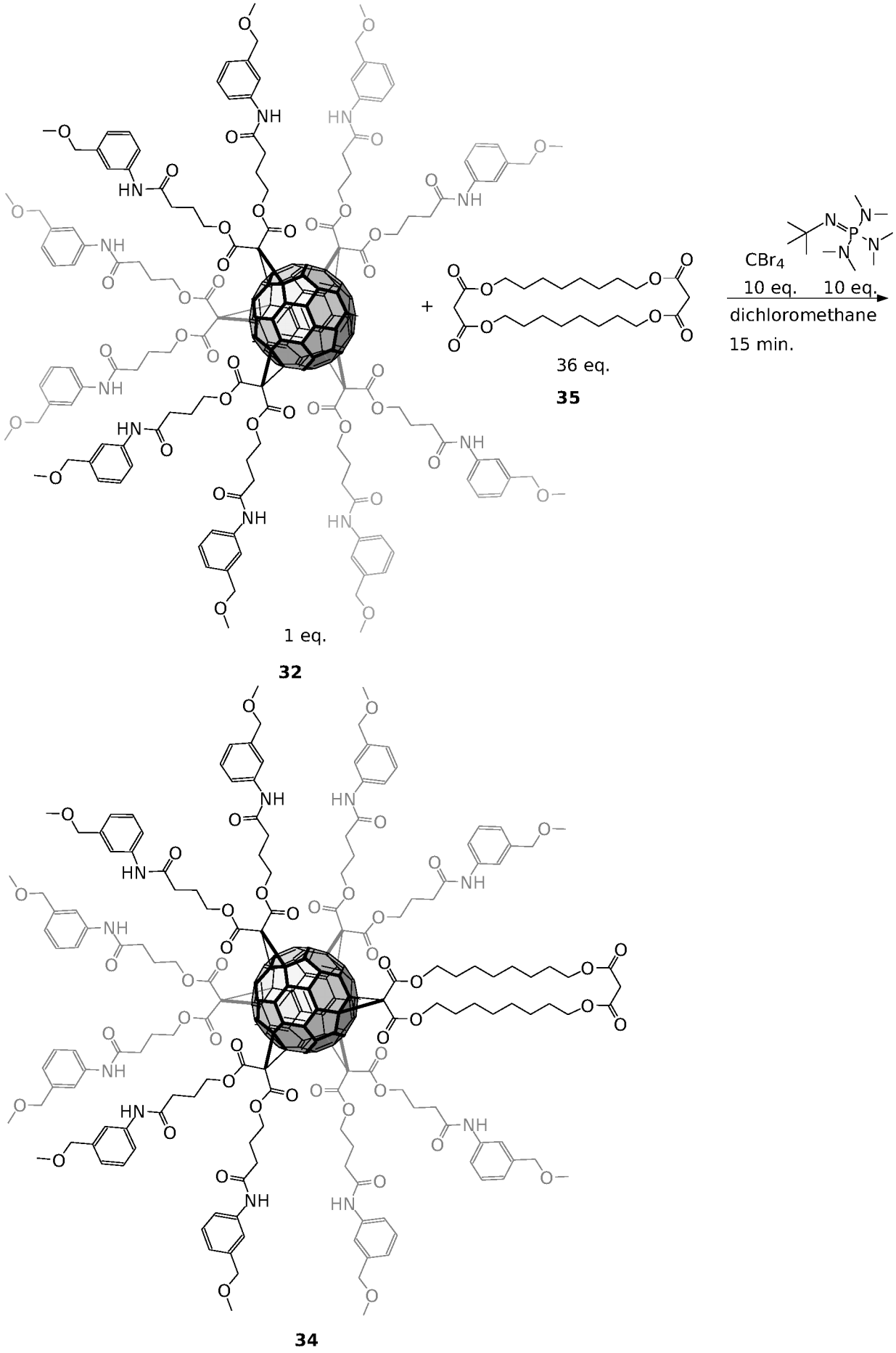
Scheme 32: Trivial approach to the precursor of **33**

4.2.1. Possible Access to Spacer-Equipped Cation Precursors

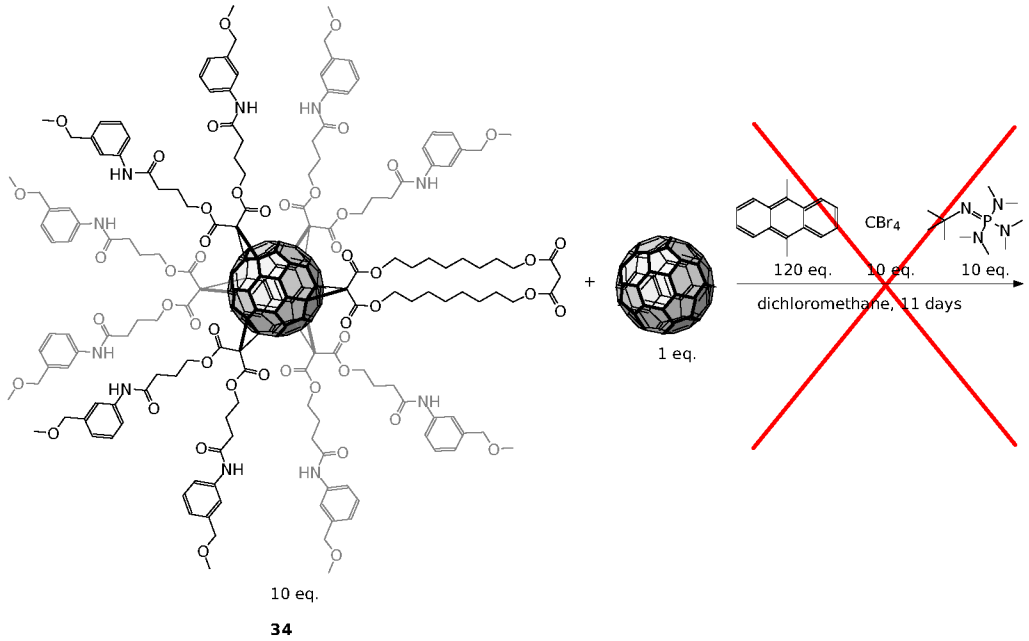
Consequently, a different, indirect approach had to be used. This included the use of the isoxazoline protecting group already mentioned in chapter 4.1. (scheme 29). When the [5.0]-pentakisadduct was subjected to Bingel-conditions in the presence of an excess of the spacer **35**, this gave facile access to the desired [5.1]-adduct (scheme 33).

4.2.2. Attempts to Bind Multiple m-Methoxymethyl Aniline Amide Fullerenes Together

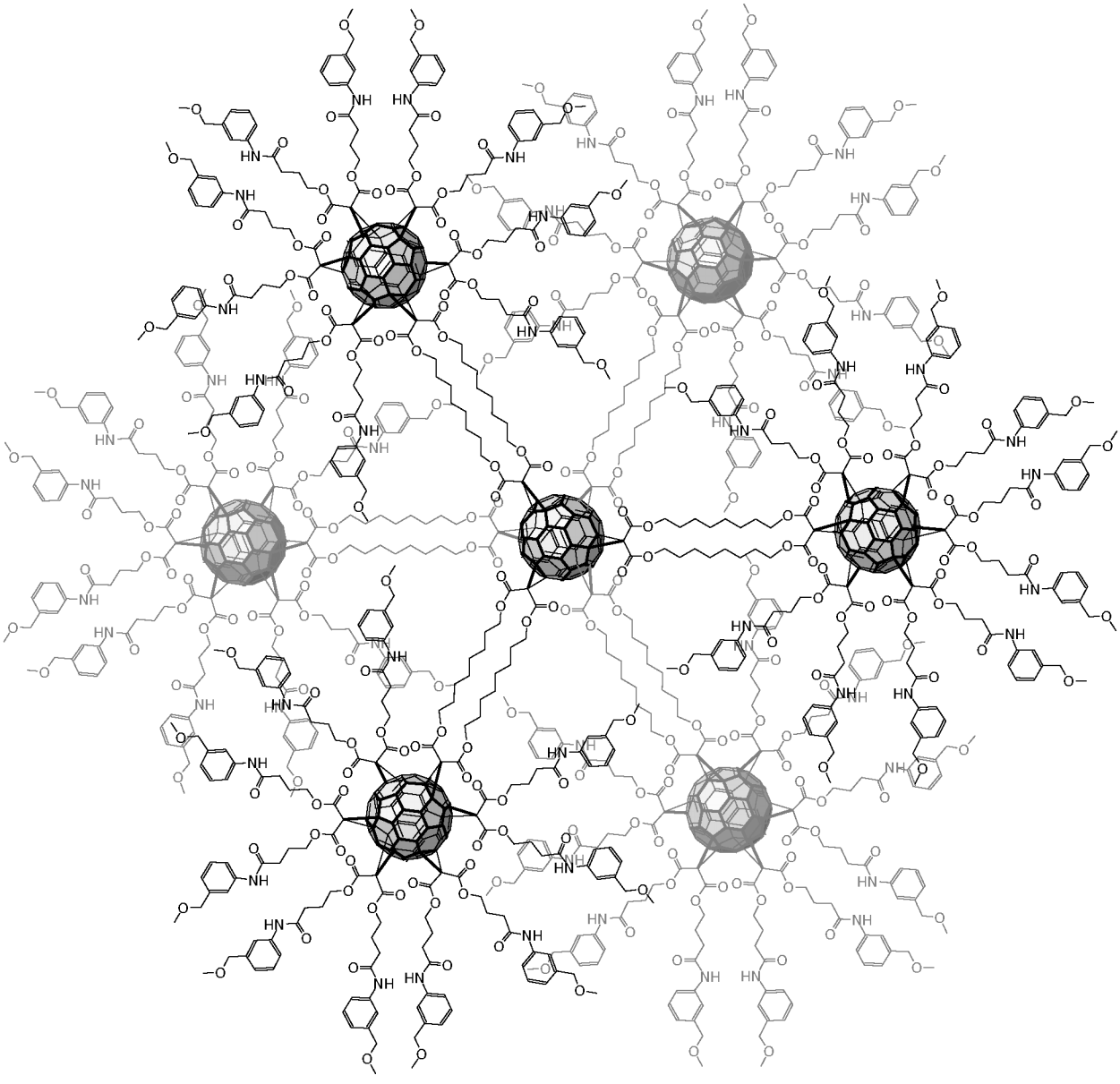
However, it showed to be impossible to affix **34** multiple times to a fullerene. It was subjected in slight excess to the conditions of a DMA-templated hexakis-adduct formation, with P_1-*t*Bu as a base to 1 eq. of C_{60} (scheme 34). After 11 days, nothing could be eluted anymore with the elution mixture used for the educt. When more polar eluents were used (toluene:dichloromethane:ethyl acetate:ethanol 1:3:5:1.5), no fractions that exhibited the characteristic UV/Vis absorptions of hexakis adducts at (314 and 334 nm) were obtained.
Since the product's fullerene spectrum would have mostly consisted of the educts' cores already configured in T_h-symmetric hexakis configuration when inserted, this is a clear clue that decomposition must have taken place on the inserted fullerenes, or the hexakis-configured educts must have become a polymer, and been entirely prevented from elution this way.



Scheme 33: Successful synthesis of the precursor of **33**



34

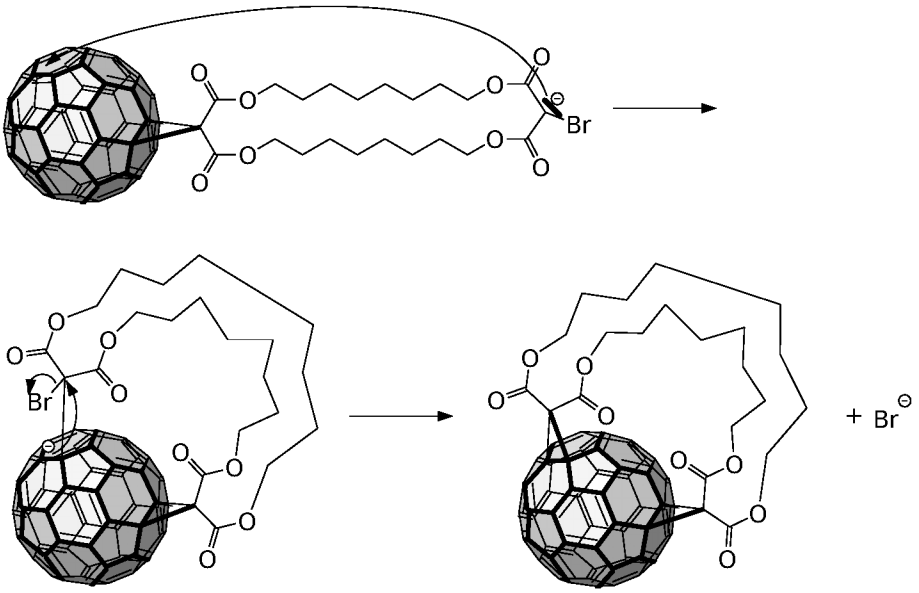


33

Scheme 34: Intended addition of six parts of the molecule to the center

4.2.3. Problems with the Reacting End of the Spacer

The bad results from the spacer-equipped fullerenes during the five-fold Bingel reaction (page 37) hinted on a back bonding of the spacer's end to the fullerene itself in concurrence to the addition of the free malonates. This reaction would be entropically favored, and could only be repressed with a huge excess of malonate addends. Molecular modeling suggested that this back-bonding was energetically possible, with little ring strain along several relative arrangements of both spacer ends.



Scheme 35: Unwanted side-reaction when bismalonate-substituted fullerenes should react

To get an impression on how feasible such a decomposition is, one must compare the calculated energies of the looped decomposition products (figure 8) with the one of a thermodynamic degree of freedom at room-temperature (ca. 2.5 kJ/mol), and consider that intramolecular condensations are entropically favored. The “leashed” addend had to be considered in a concentration that would give the same mean distance of the reacting centers. This distance, in turn, is about half the maximal distance - or even less, if the total stretched conformation has lower entropy than the close bound form. Under the assumption that this distance is 1.3 nm (11×145 nm×cos(35°)), this is a concentration of 136 mol/L, more than the concentration of 70 mol/L the educt had.

The least energetic positions found were the cis2 position and especially the cis3 position. Access to the e position was rather hindered (table 2). according to the formula

$e^{\left(-\frac{\Delta H}{RT}\right)}$

the reaction probability with the end of the spacer would be only 1/20000st as fast as with the malonate, but there may be other influences, as the self-aggregation of the educt (especially cation-precursor malonate **26** which is insoluble in toluene, interestingly), a lower steric hindrance of the spacer's malonate (this malonate would be constrained to meet the fullerene from the side only, with both alkyl chains pointing outward, and the carbonyl bonds and the C-H-acidic carbon in one plane, which is required in the transition state).

conformation	calcd. ΔH_f^{Θ} (Hartrees)	strain energy in comparison to dumbbell (kJ/mol)
cis2	-3722.72083733	65.20
cis3	-3722.73602097	25.33
e	-3722.69253245	139.51
trans4	-3722.64814167	256.06
trans3	-3722.67638360	181.91
mono with spacer - $\Delta H_f^{\Theta}(C_{60})$	-3722.74567079	0

Table 2: Calculated strain of different intra-molecular addition isomers of **35** to C_{60}

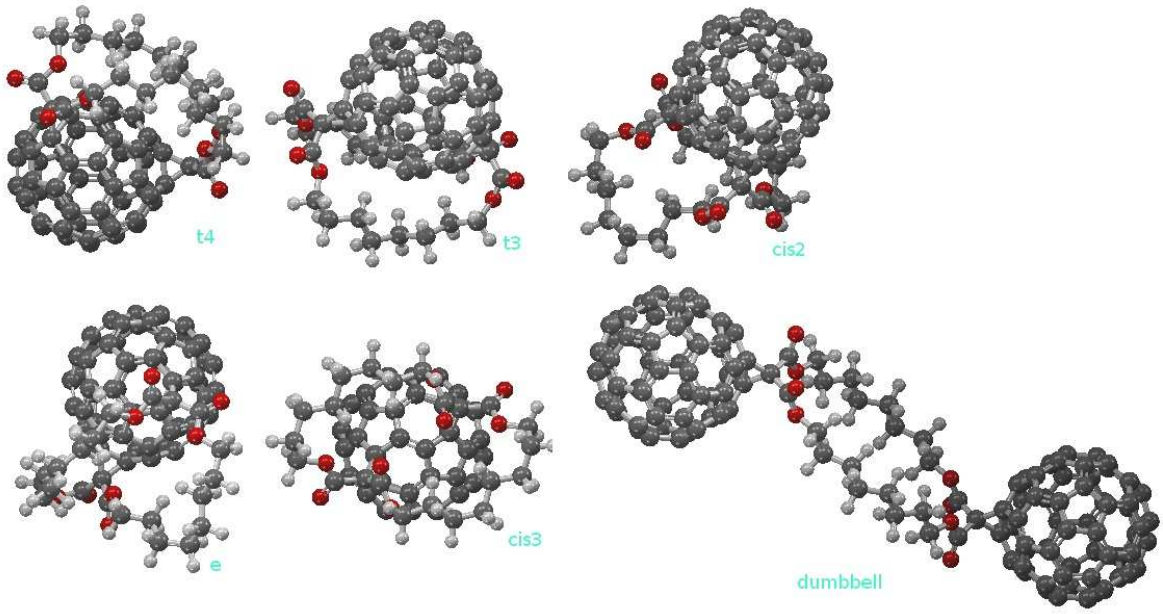
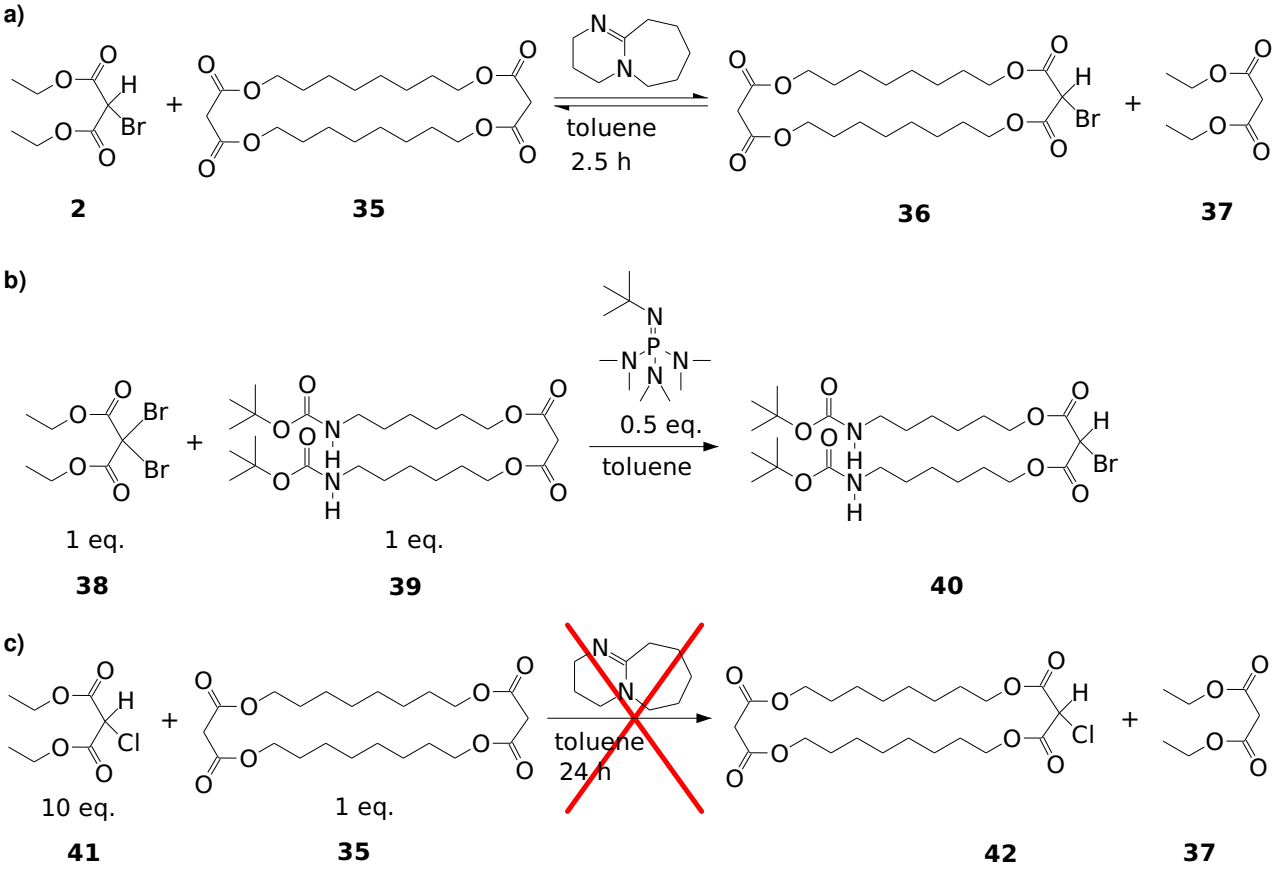


Figure 8: HF-Optimized (cc-pVDZ) models for the various isomers.

4.2.4. Proving Exchange Phenomenon of the Bromyl Cation

Since experiments with pre-brominated malonates had given no better results before,[81] there had to be a possibility how either unbrominated malonates could react, or how bromine could travel between the C-H acidic points of malonates. In order to give evidence for this, an exchange experiment was undertaken. A brominated malonate **2** was added in a flask to a compound with (two) unbrominated malonate sites (scheme 36 a)). After 2.5 h, 14.8 % of **35** had received one bromine atom, so the rate constant of the exchange between two malonates must be at least 2.2×10^{-4} $M^{-1}s^{-1}$ at DBU concentrations of 0.04 mol/L. Because the reaction times for hexakis adduct formations are multiple days and they utilize ten equivalents of addend, this reaction brings the bromination of the spacer-bound malonate near to the equillibrium during the course of the reaction.



Scheme 36: Experiment to prove an exchange of bromine amongst malonates

In experiment a), a substance was isolated, in the carbon spectrum of which a clear split of the alkyl chain signals of **35** can be seen. In the carbon spectrum (figure 9), like in **42**, this split is the smaller, the further the corresponding carbon is distant from the carbonyl groups. At the point of the molecule vital for the proof, the C-H acidic proton, the peak distance between the brominated and non-brominated site is present with 1 ppm, but rather low, due to the opposing effects of the bromine atom to the chemical shift. This lies in accordance with the low carbon shift of the bromine-bound carbons usual for brominated aliphatics. In the proton spectrum (figure 10), there is a clear distinction between the protons at the unreacted end and the reacted end. At the reacted end, the proton signal is split along the molecule's plane. The identity of **36** could also be verified by mass spectrometry (figure 11).

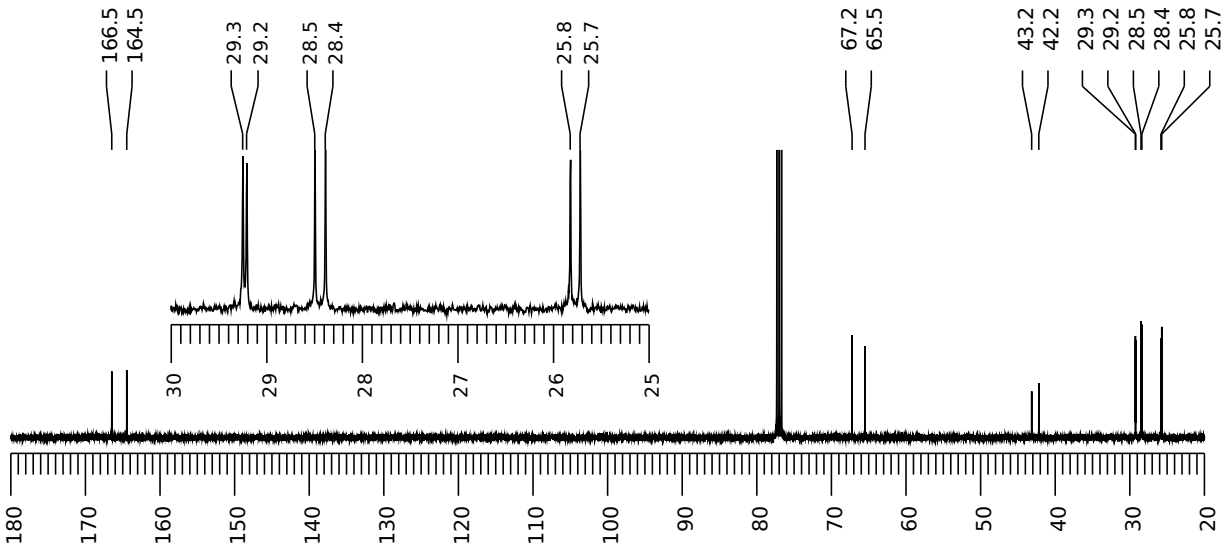


Figure 9: ^{13}C NMR Spectrum of **36** (100 MHz, $CDCl_3$)

The proton NMR spectrum exhibits the typical peak for brominated malonates at 4.83 ppm. The proton signals of the pair of the CH_2-O groups closer to the bromine at 4.20 ppm are split between the differing sides of the molecule's ring plane.

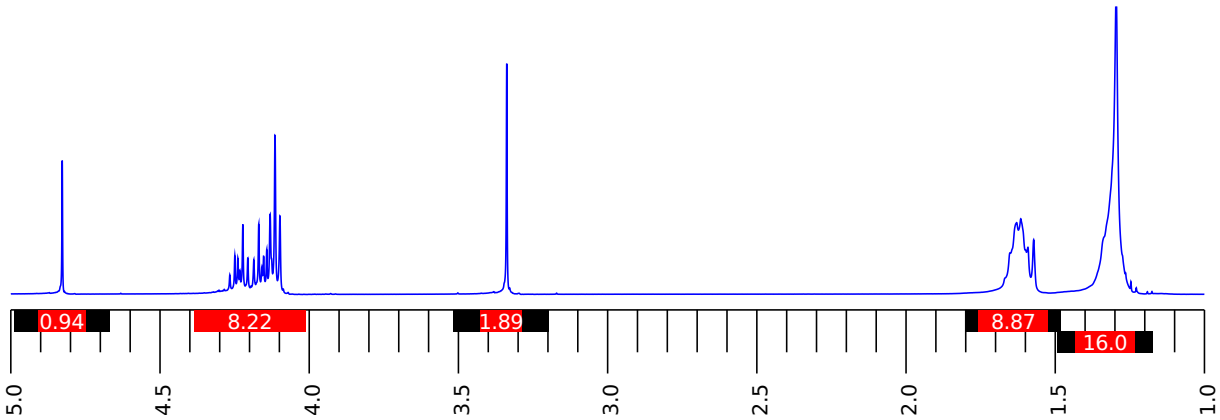


Figure 10: ^{1}H NMR Spectrum of **36** (400 MHz, $CDCl_3$).

Integral zones are shown as red beams

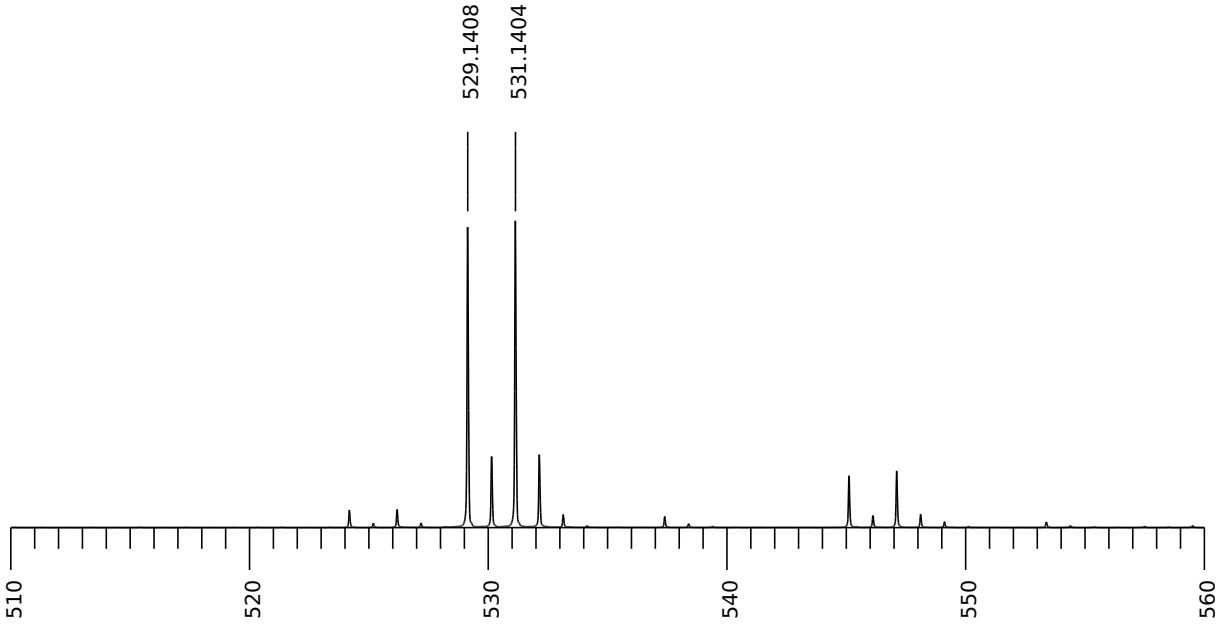
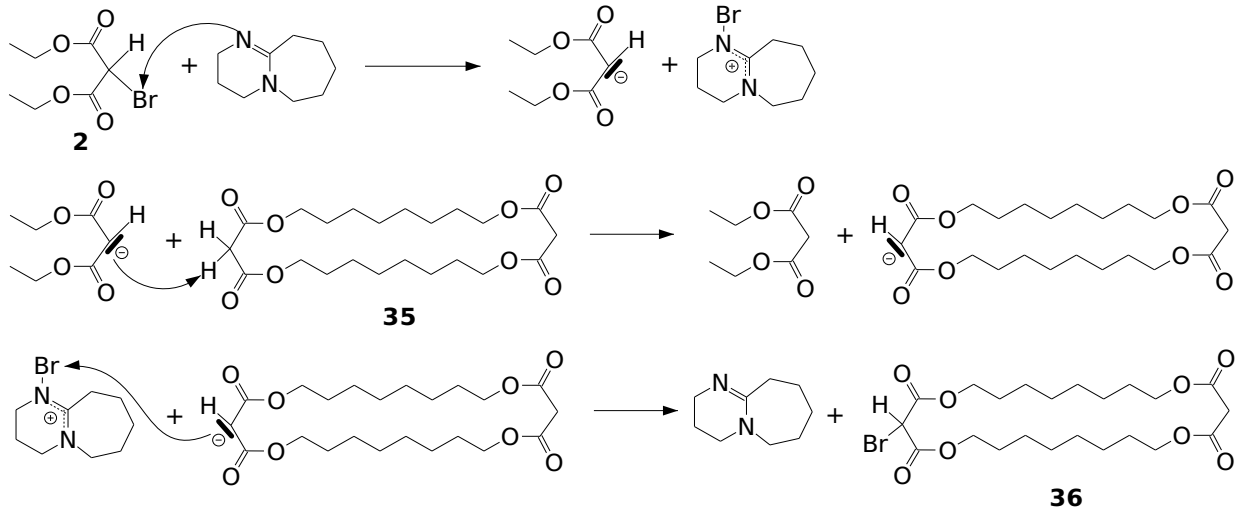
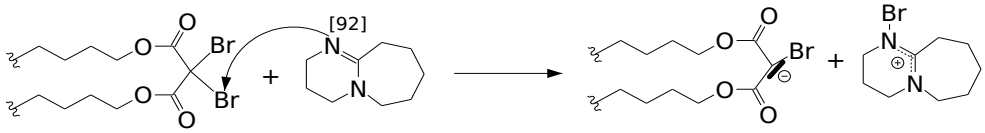


Figure 11: ESI Mass spectrum of **36** $C_{22}H_{35}BrNaO_8$

From this experiment, the reason for the missing selectivity Patrick Witte observed when he added pre-brominated malonates[81 table 3.12, p.131] becomes clear. Because Frank Hörmann saw even dibrominated malonates react (scheme 38),[92] these observations together lead to the assumption that the base can directly attack a bromine atom nucleophilic and carry it to another malonate (scheme 37). This theory would explain both observations with one mechanism.

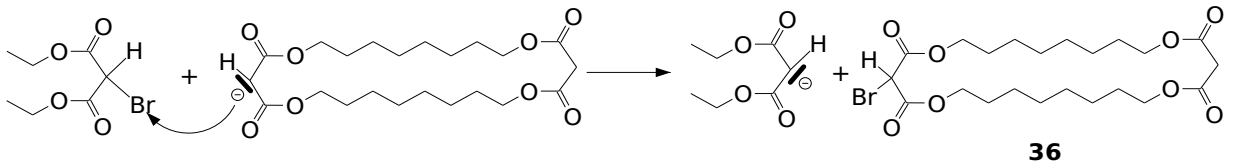


Scheme 37: One proposed mechanism of the bromyl cation exchange



Scheme 38: Explanation for the reactivity of dibrominated malonates by the assumption of a removed bromyl cation

Despite of that, when carbon anions are present, they are assumed to be more nucleophilic than the base, so it is likely that the reaction takes place by means of a direct transfer of the cation (scheme 39).



Scheme 39: Another proposed (direct) mechanism of the bromyl cation exchange

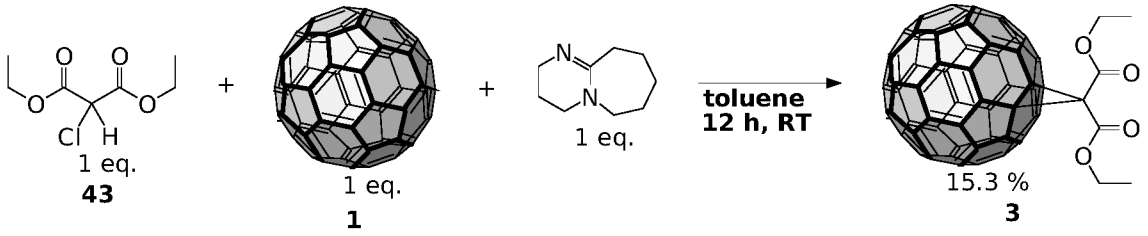
When the bromine changes its place that easily, it is obvious that bromine is unsuitable for a selective activation. Because, as stated, a mechanism is assumed where the halogen carries a positive charge, the side reaction should be greatly repressed when chlorine is used as a halogen. This could be shown in another exchange experiment (scheme 36 c))

4.2.5. The Chlorine Variant of the Bingel Reaction

4.2.5.1. Performing a Bingel Reaction with a Chlorinated Malonate

It had to be checked whether the Bingel reaction would still occur when the leaving group was a chloride anion. While chlorinated malonates had never been used in the Bingel reaction, they had been demonstrated to attack without releasing the halogen in an indirect (Sn2') substitution reaction.[93]

It needed to be observed whether a Bingel reaction was possible with this nucleofugic group.



Scheme 40: A bingel reaction with chlorine as leaving group

The experiment was conducted over a timespan of 12 h, adding only one equivalent of each component, including the base (scheme 40). The yield (15.3 %) was far lower than usual for the brominated malonate (45 %),[59] and only traces of C_{60} could be recovered. This suggests that the reaction occurs more slowly than the radical reduction of C_{60} by the DBU.[23] The resulting carbon spectrum (figure 12) clearly shows fifteen signals that result due to the C_{2v} symmetry after a cyclopropanation, at the same positions as the the monoadduct **19**, and the signal at 71.6 ppm of the C_{60} carbon atoms in the cyclopropane ring is also present, telling us that the malonate was added in the manner of a Bingel reaction indeed.

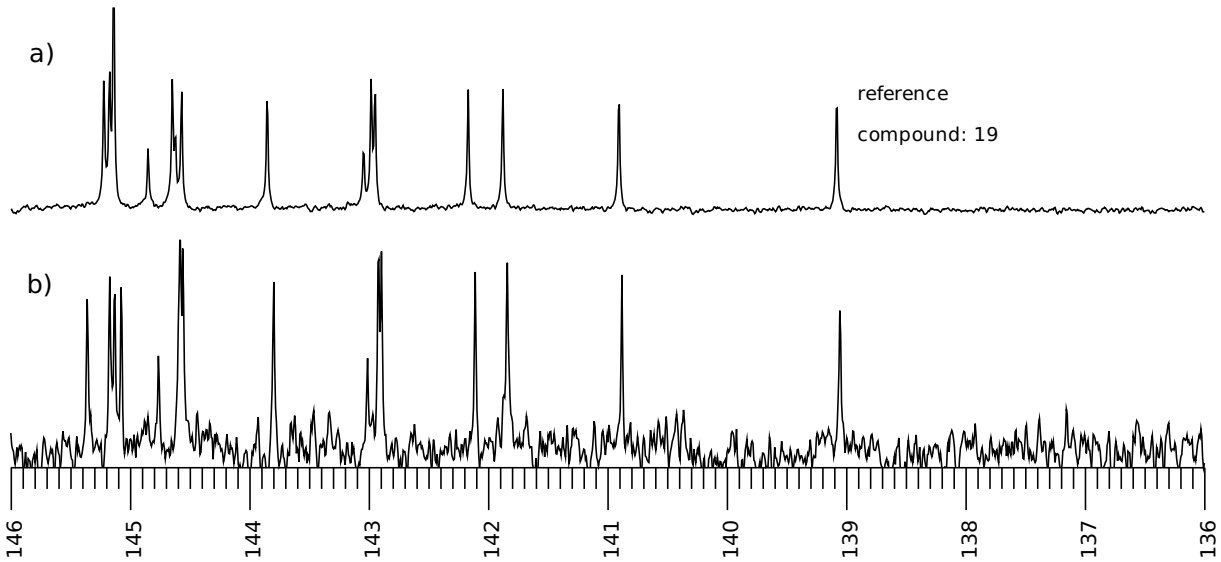
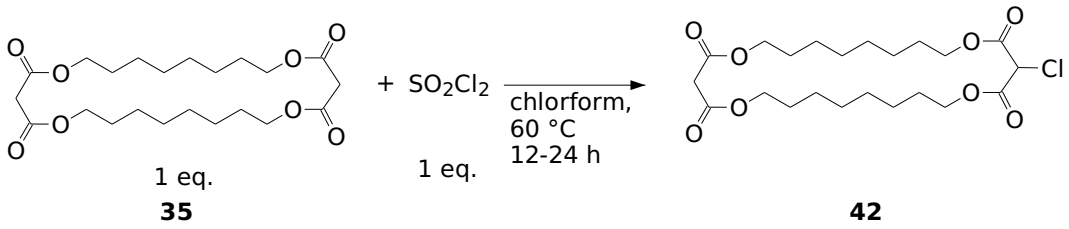


Figure 12: ^{13}C NMR spectrum of **3** a) reference mono-adduct b) product (75.5 MHz, $CDCl_3$)

4.2.5.2. The Feasible Way to Mono-Chlorinate Malonates[94]

In order to mono-chlorinate the malonate, the most obvious procedure which was tried was the halogenation with sodium hypochlorite.[95] However, the need for an unpredictable excess of halogenating agent and the higher reactivity of the product made this method unsuitable - it yielded product in an one-percent-range. A method for selective mono-chlorinating of ketones with sulfuryl dichloride in pyridine[96,97] prove to be more efficient. Here, the premature decomposition of the reagent was so low that stoichiometric addition was possible. The selectivity of mono-chlorinating the bismalonate **35** was sufficent. The best results were obtained with equimolar addition of the reagent in dichloromethane and reaction times between 12 to 24 hours at 60 °C, with 36 % yield (scheme 41). In the carbon spectrum of the substance (figure 14) the split of the carbon signals shows the presence of different environments amongst the malonates. The largest split is seen at the site of modification, as the chlorinated carbon is to 55.8 ppm, 13.67 ppm downfield. In the hydrogen spectrum of **42** (figure 13), a split of the alkoxy protons from the different sides of the molecule's plane can be seen at 4.2 ppm. As unreacted educt could be recycled, the yield based on recovered starting material went up to 70 %. In agreement with Andreas Kratzer's observations, the yield could be observed to drop greatly upon higher dilution, obviously because the mixture's boiling point was lower. Andreas Kratzer found out that the reaction is easier to do with chloroform as solvent.



Scheme 41: Optimal conditions to chlorinate malonates using sulfuryl dichloride.

Workup is done by column chromatography in dichloromethane

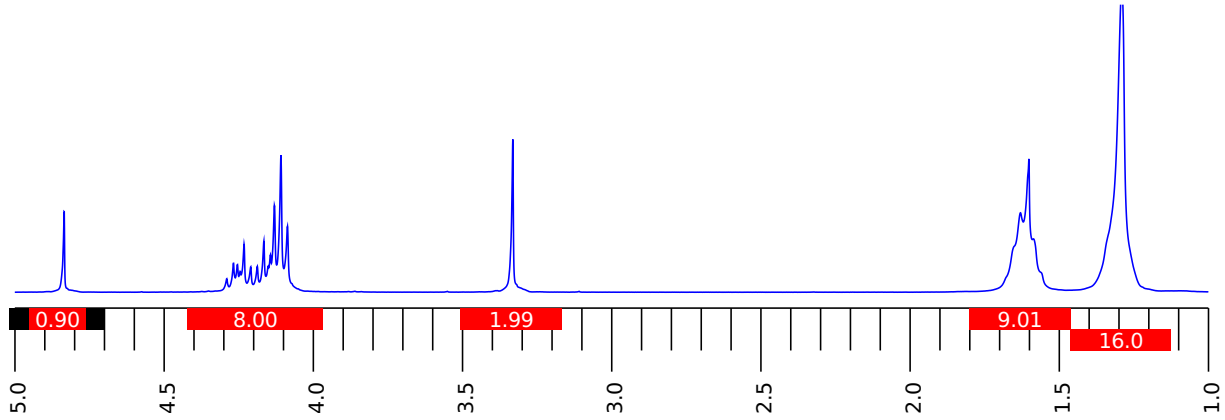


Figure 13: ^{1}H NMR spectrum of **42** (300 MHz, $CDCl_3$).

Integral zones are shown as red beams

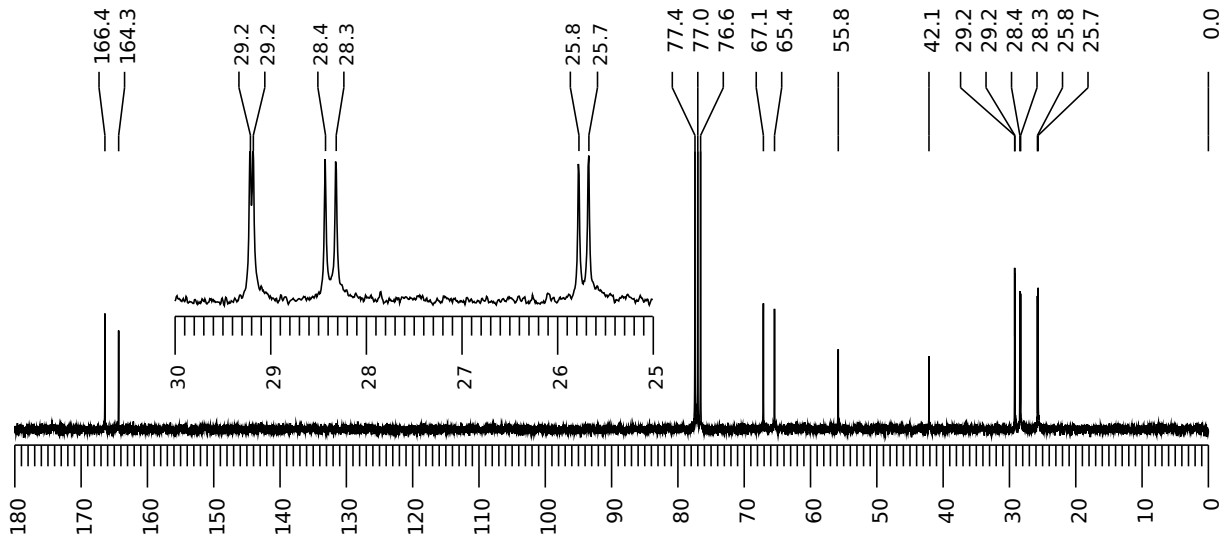


Figure 14: ^{13}C NMR spectrum of **42** (75.5 MHz, $CDCl_3$)

Now, the protected malonates which had been used as cation precursors would be sensitive towards the acidic conditions applied in the monochlorination process. Even worse, usual malonates were so polar that chromatographic separation would not be possible from those little polarity differences of un- and dichlorinated by-products. But is there another use for this selectivity?

Since the templated adduct generation of spacer-bearing fullerene hexakisadducts did not proceed as intended, the synthetic pathway for the 7-fullerene-clusters was amended into a procedure in which the selectivity on the central fullerene is shifted to an earlier step. The keystone was a fullerene carrying the six spacers already bound to it in a T_h-symmetric manner. It would give only one target molecule when reacted with the symmetric pentakis adduct as addend in excess under Bingel-conditions. The most obvious advantage would be that there would not be notable work required to separate the mixture of adducts, as a sufficient combination of reactand excess and reaction time would result in complete substitution of all these core educts. The other reactands would be unable to form larger adducts, so they would differ in their retention behavior enough to allow for trivial chromatographic separation. At least, their retention value would be influenced by a change of the eluent's polarity differently than the big product's one. Of course, this would require reaction times long enough to allow complete conversion.

4.2.6. Usage of the Chloride Addends in Synthetic Procedures

Initial experiments taking use of the selectivity of this addend led to desperating results. When the monochlorinated cycle **42** was added in only ten stoichiometric equivalents to **19** (page 37), the complete reaction mixture solidified to form a fruit gum like gel (figure 15). Under the assumption that no chlorine exchange took place, this could most likely have happened by means of the simple addition of the deprotonated free side of a spacer addend to a fullerene. Due to the chelate effect, this had sufficient stability to be not soluble anymore.

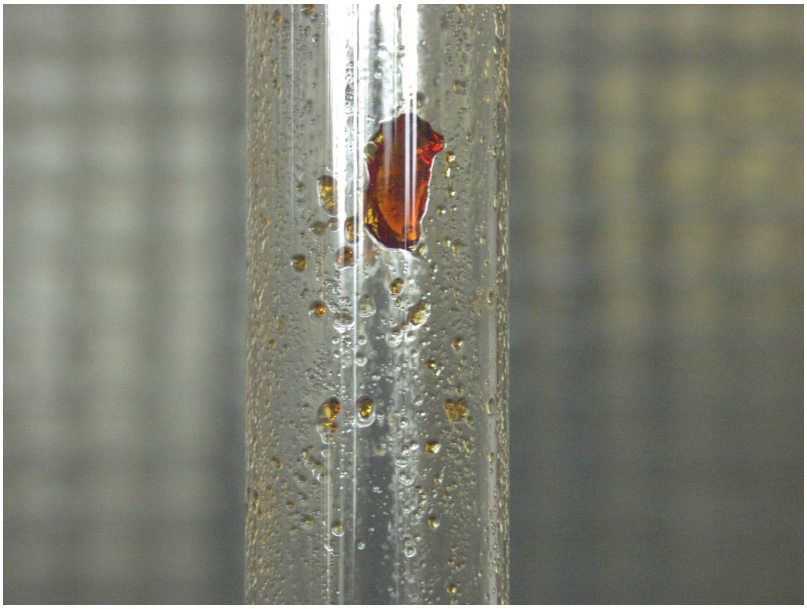
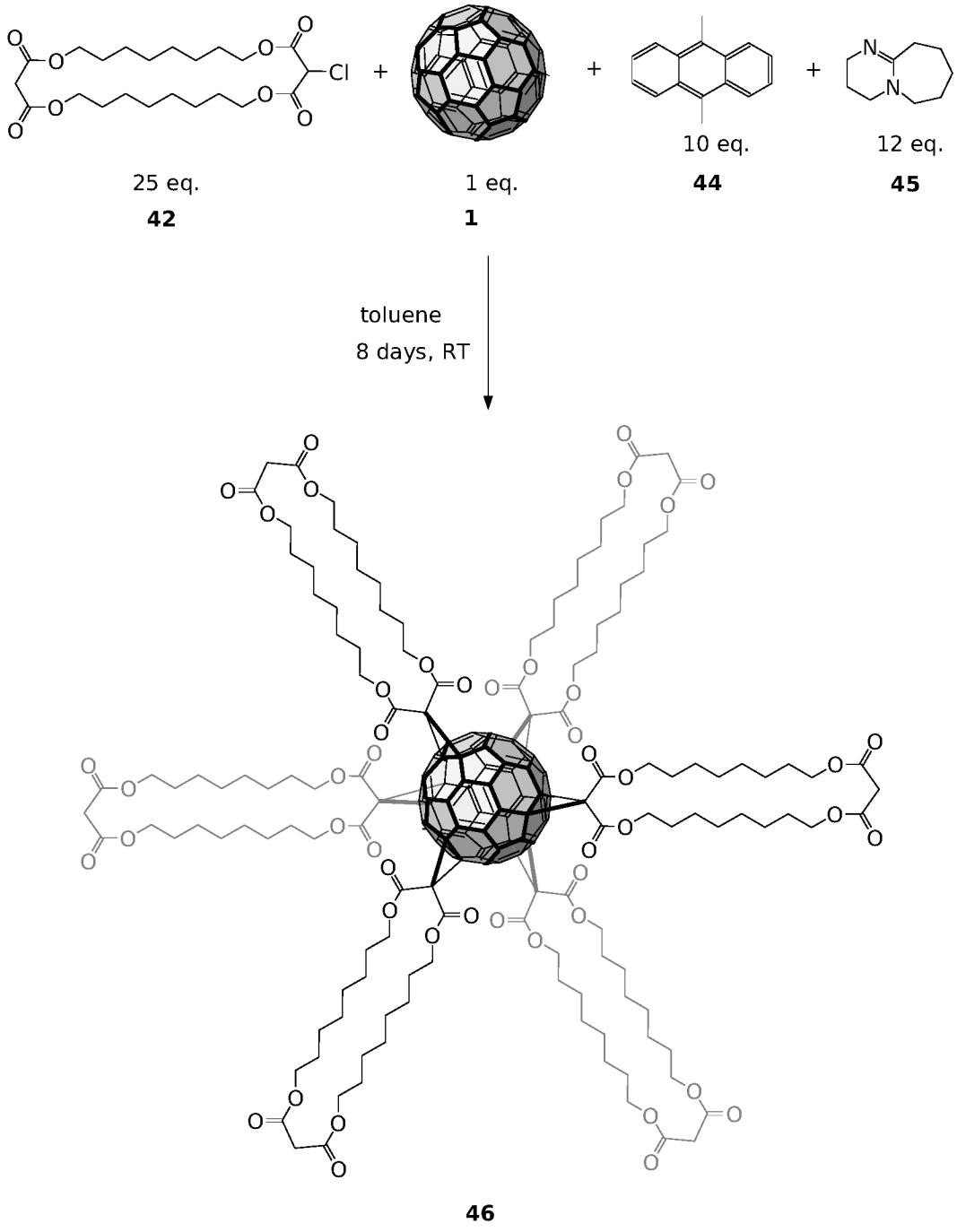


Figure 15: Polymerized product from C_{60} and insufficient excess of **42**

Therefore, the amount of the added **42** had to be increased to 25 to 40 equivalents (scheme 42). The best eluent mixture for the chromatographic purification of this compound turned out to be toluene/ethyl acetate 4:1. Purification consisted of one simple chromatographic purification on silica and another one on a 15 µm flash cartridge. The yields resulting from that reaction, however, were as low as 3.3 % based on the malonate. The yield of 12.3 % based on the C_{60} is less meaningful here, since the fullerene is the cheaper compound now. And as the product is used in low amounts in the next reaction, this yield can even be seen as sufficient.



Scheme 42: Employment of the chlorinated malonates

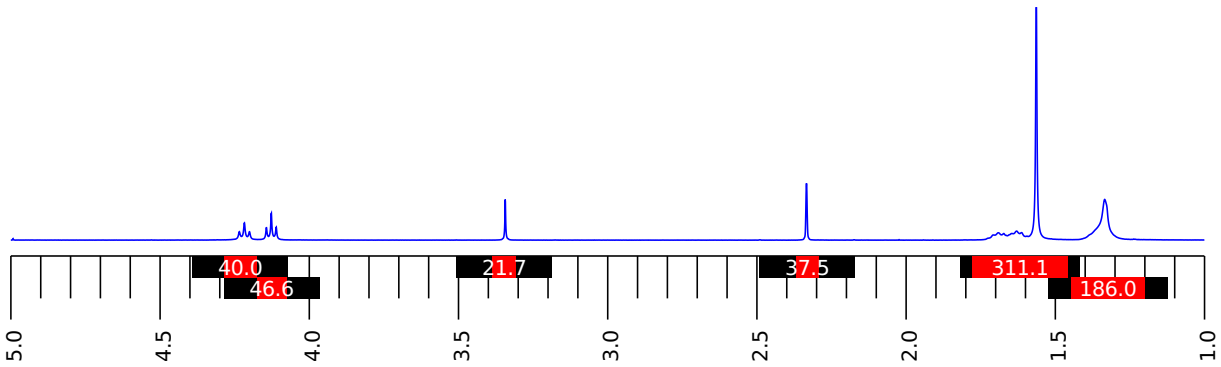


Figure 16: ^{1}H NMR spectrum of **46** (400 MHz, $CDCl_3$).

Integral zones are shown as red beams

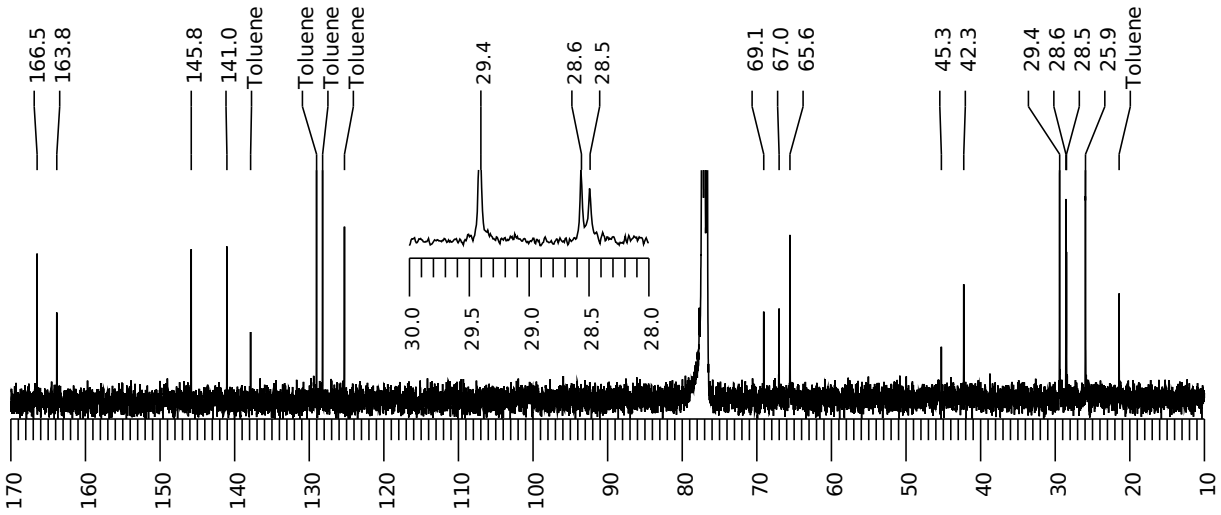


Figure 17: ^{13}C NMR spectrum of **46** (100 MHz, $CDCl_3$)

In the hydrogen spectrum of **46** (figure 16), the α-alkoxy protons of the different ends give discernible signals at 4.22 and 4.13 ppm. In the carbon spectrum of **46** (figure 17), little difference between the corresponding chain atoms on both sides of the spacer can be seen. As characteristic evidence for the product, the C-H-acidic carbons of the free malonates can be seen at 42.3 ppm along with the attached 2-position of the other malonates at 45.3 ppm. The carbonyl groups of the outer malonates at 166.5 ppm are slightly lowfield to the carbonyl groups of the bound malonates at 163.8 ppm. At 67.0 ppm, the carbons of the inner alkoxy groups resonate, next to the carbons of the outer alkoxy groups at 65.6 ppm. The identity of the product could be verified by means of MALDI (figure 18) and ESI (figure 19) mass spectrometry.

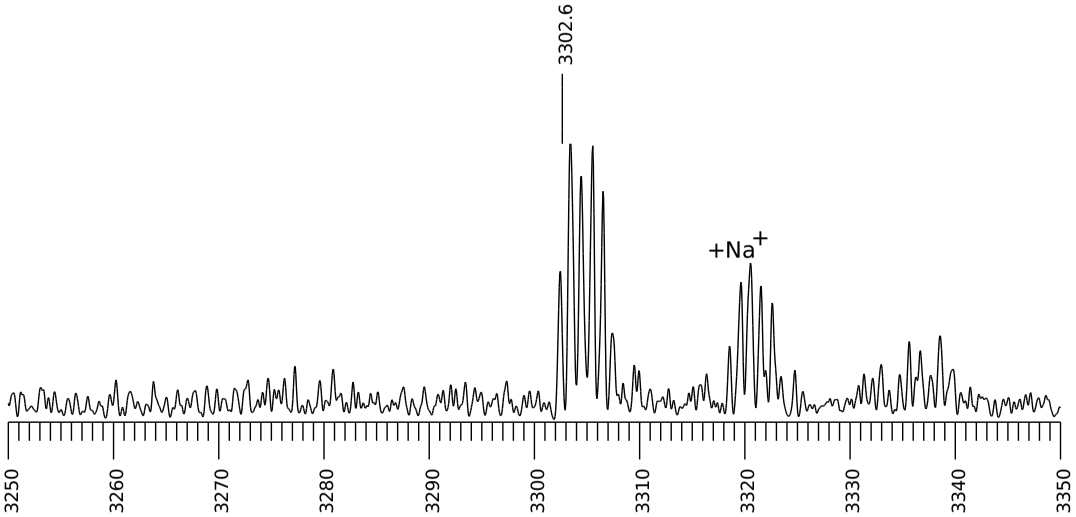


Figure 18: MALDI mass spectrum of **46**

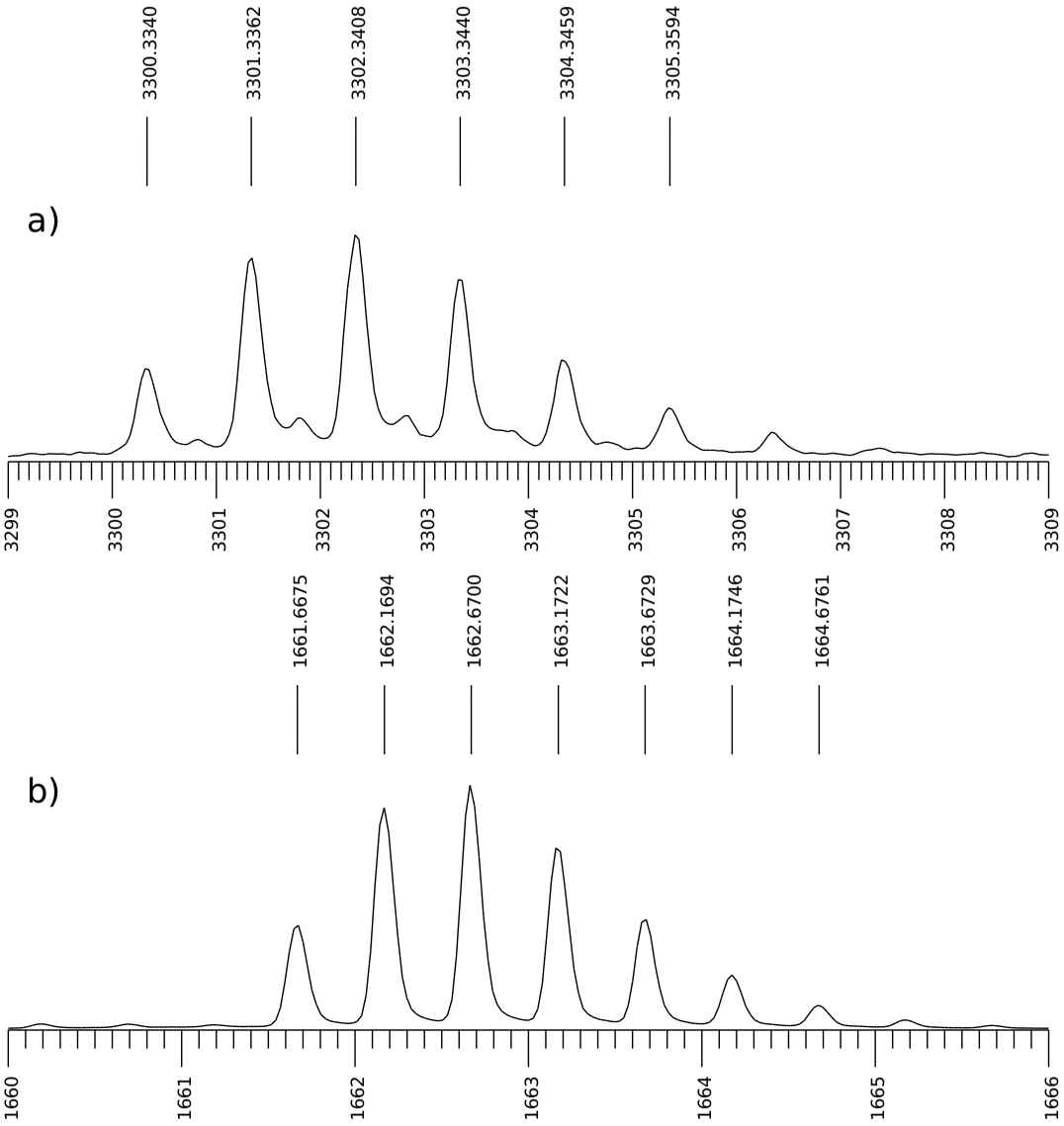
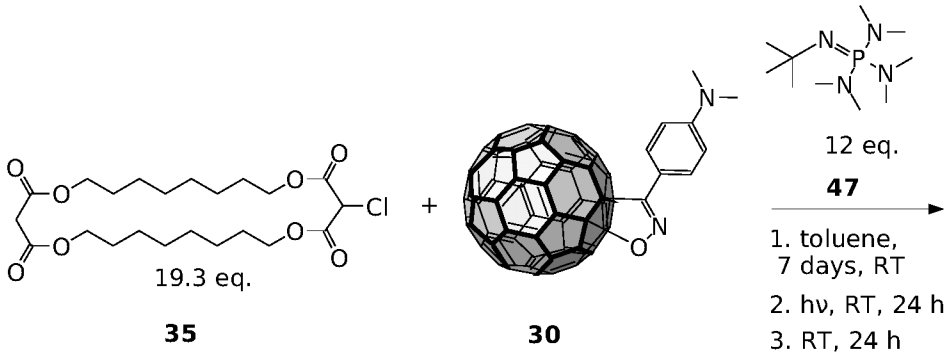
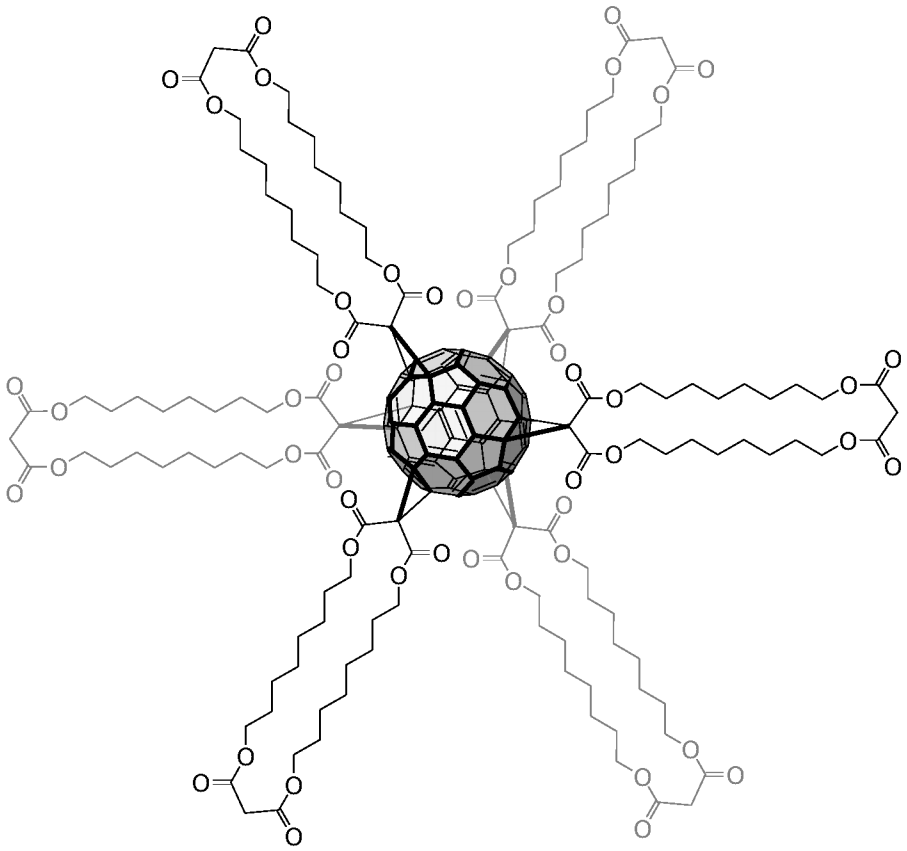


Figure 19: ESI Mass spectra of **46** $C_{192}H_{204}Na_2O_{48}$- a) charged once; b) doubly charged

4.2.6.1. Simplified "One Pot"-Synthesis of 46

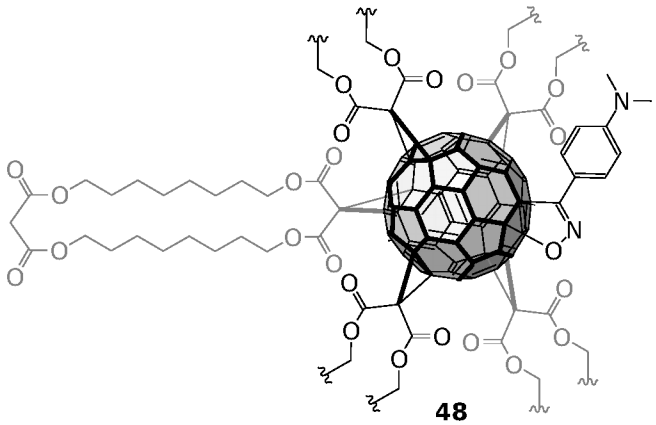
An odd thing of the low yield of the above reaction is that the synthesis of **46** relied almost solely on the advantages of the preactivation by the chlorine. Any problems of this reaction would make this entire approach questionable. To demonstrate the applicability of chlorine as leaving group, this procedure needed further improvement. Following the stated procedure, Andreas Kratzer from our group had obtained a high yield of protected fullerene with five linking-sites **48**, created analogous to **46** but starting from **30**. Since **46** is accessible from this, the difference must either be a beneficial effect of the oxazoline moiety or the DMA blocking the addition of the last addend. One could as well start from isoxazolinofullerene **30** and subject it to the conditions for the synthesis of **46**. In anticipiation of chapter 4.3.1. (page 65), DMA was omitted, so the sixth addend would be attached more easily. After deprotection of the fullerene during the reaction **46** was obtained directly (scheme 43). The reaction indeed was much more effective. Using only 20 equivalents of **42**, added in portions, the obtained yield was 11.6 % based on the malonate (i.e. almost four times as high), and even 33.8 % based on the fullerene.





46

over

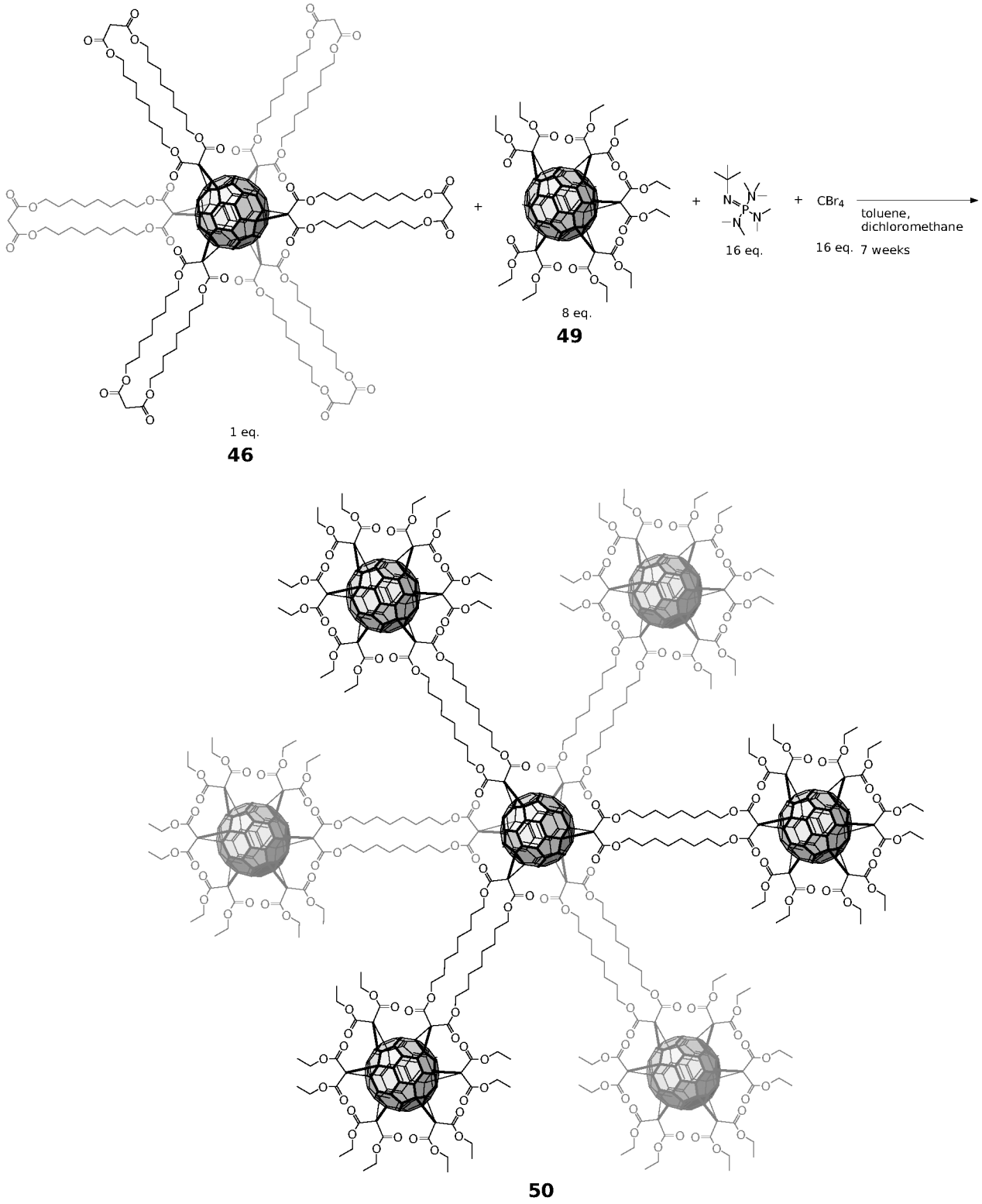


48

Scheme 43: Enhanced "One Pot" Synthesis of **46**

4.2.6.2. Proof of Principle: how Useful is the new Central Moiety?

As proof that this spacer is actually useable, the first simple test-fullerene, pentakisadduct **49**,[98] was attached to this central moiety. It was added in a slight excess (7.5 eq. vs. 6 eq.) to the center (scheme 44). Beginning with a stoichiometric amound of of both **49**, tetrabromocarbon and base(P_1-*t*Bu), the educt/product mixture had precipitated after some minutes in the initial solvent, toluene. After 22 days, it was brought back into solution by adding dichloromethane and the remaining 1.5 eq. of the educt, and after further 44 days, during which another total of 10 eq. of CBr_4 and base were added, the reaction was finished. The workup was interestingly very easy: A plug-filtration (SiO_2; toluene/ethyl acetate 4:1) followed by a cheap chromatographic purification (SiO_2; toluene/ethyl acetate 6:1; then toluene/ethyl acetate 4:1) revealed pure 7-core fullerene **50** in 43 % yield. The compound's mass was proven with ESI and Maldi (figures 23 and 22).



Scheme 44: Example experiment to take use of the pre-substituted central unit **46**

In the proton NMR spectrum (figure 20), two different proton signals for the C**H**$_2$O-groups show up. 120 protons that belong to the 30 diethyl malonates further deep-field, 48 protons for the alkoxy groups of the spacer. Because all malonates in this molecule are attached to a fullerene, no split is observed on the characteristic malonate groups in the carbon NMR spectrum (figure 21).

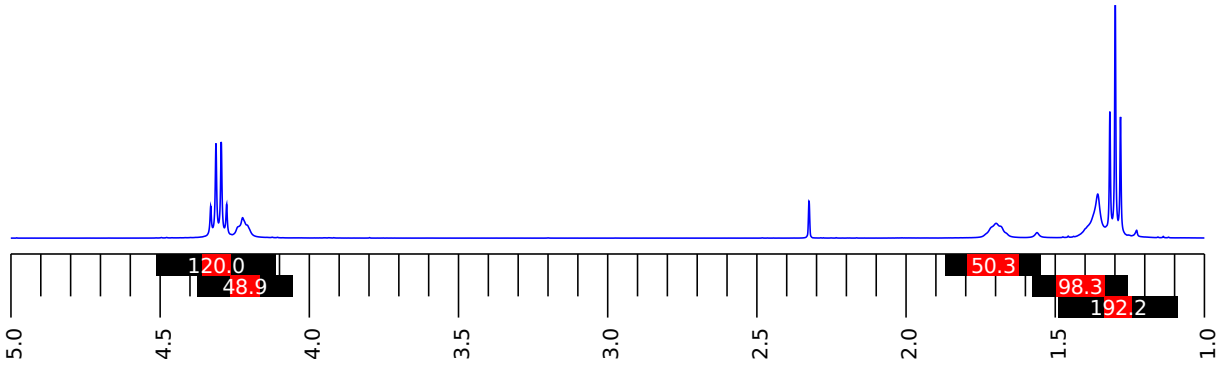


Figure 20: ^{1}H NMR spectrum of **50** (400 MHz, $CDCl_3$).

Integral zones are shown as red beams

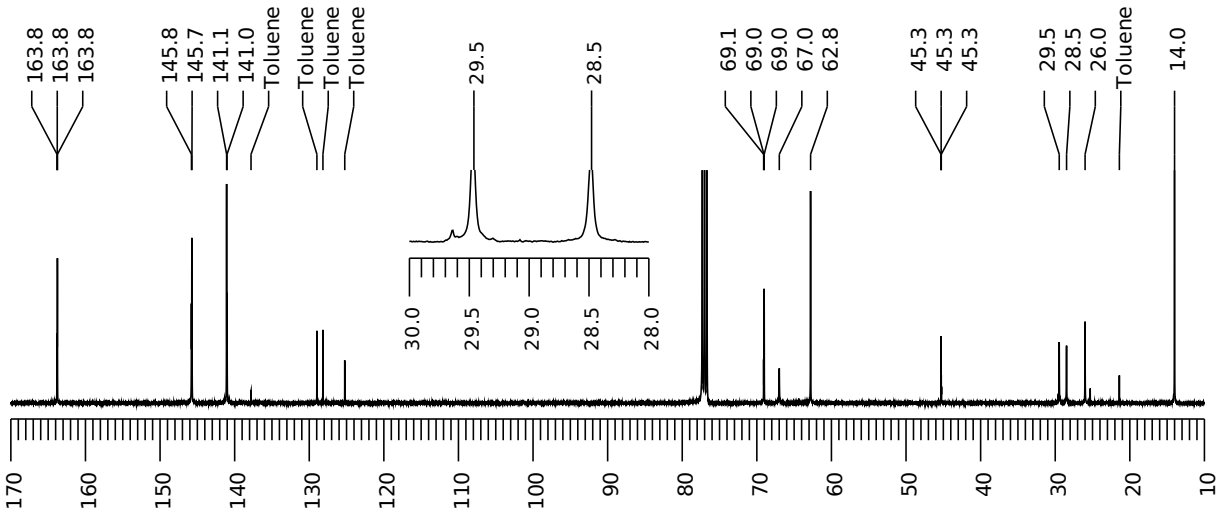


Figure 21: ^{13}C NMR spectrum of **50** (100 MHz, $CDCl_3$)

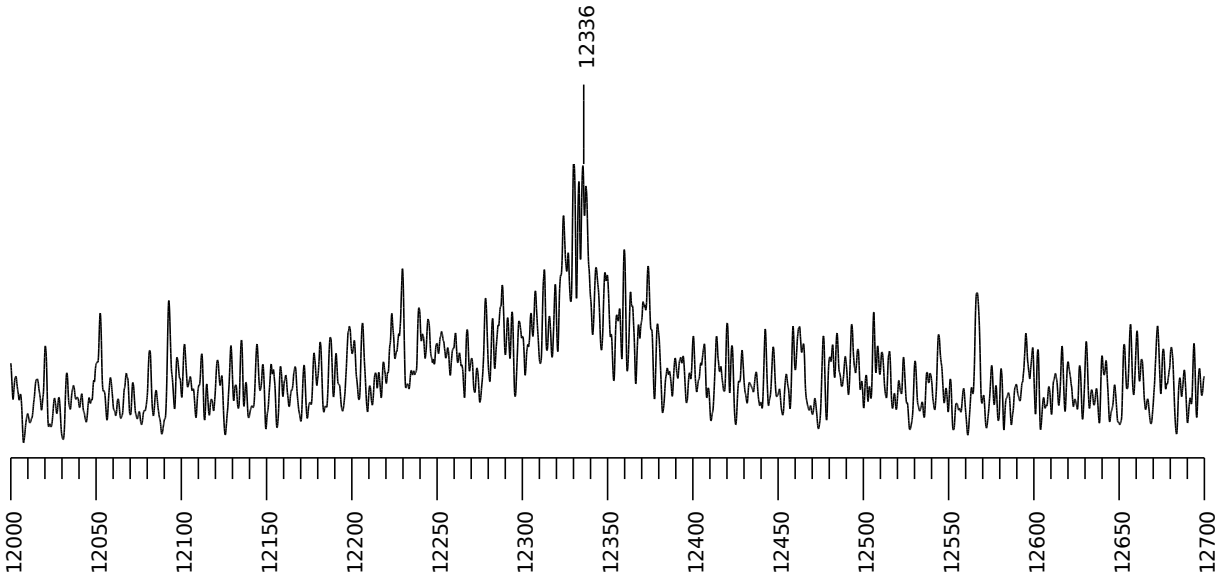


Figure 22: MALDI Mass spectrum of **50** formula: $C_{762}H_{492}O_{168}$ (matrix: dctb)

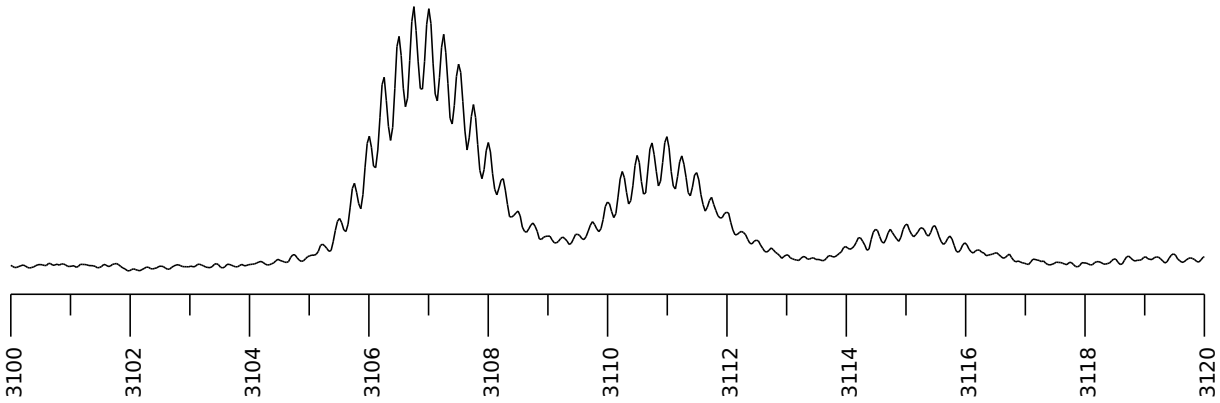
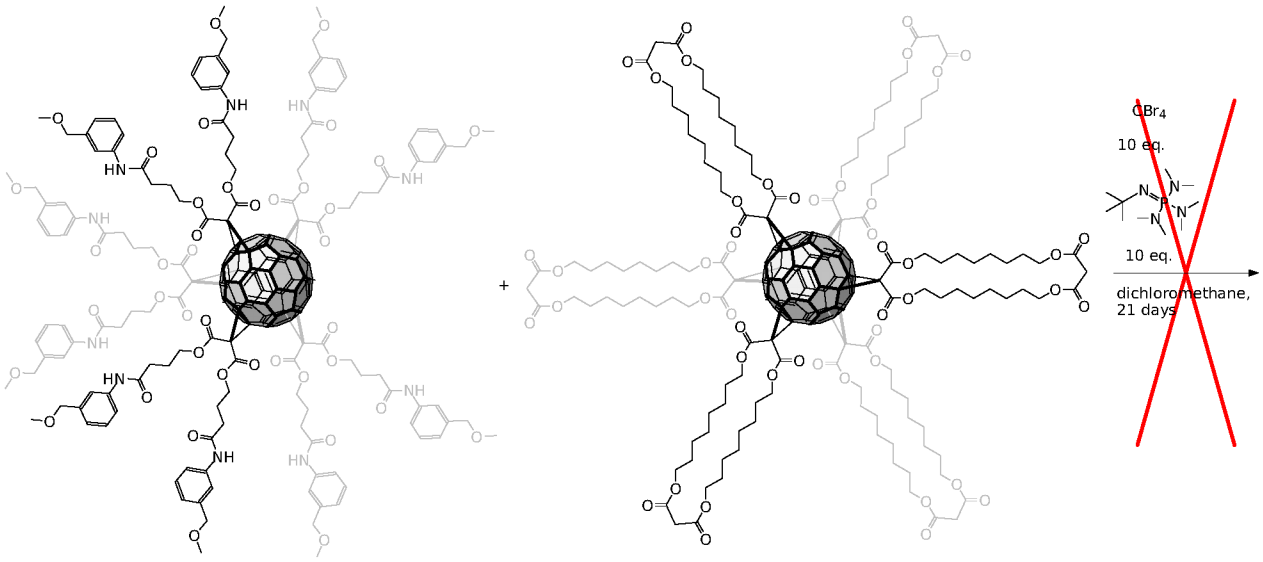


Figure 23: ESI Mass spectrum of **50** $C_{762}H_{492}O_{168}$ (+4 Na)

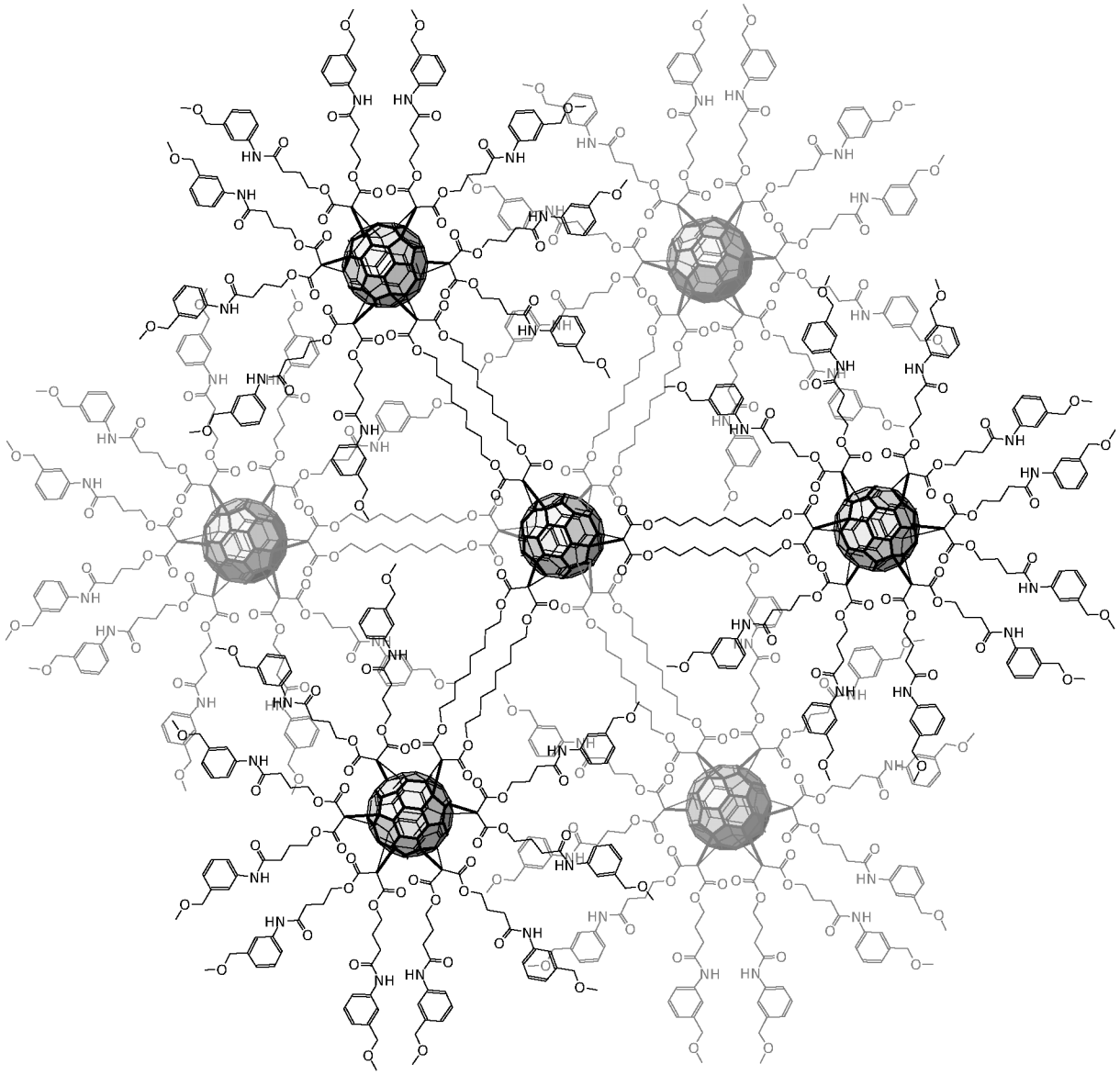
4.2.7. Attempt to Produce Higher Substituted Heptafullerenes

With the discovery of the pre-formed hexakis building block **46**, (page 50) the obvious following step was to add a cation precursor pentakisadduct **32** to the pre-formed central moiety. The usual conditions were applied, adding the tetrabromocarbon and base nearly stoichiometric and waiting for only 21 days (scheme 45). The short duration took in account that the amide arms incline to decomposition under the reaction conditions. But the following result is rather a proof that this fragility was greatly underestimated.



16 eq.
32

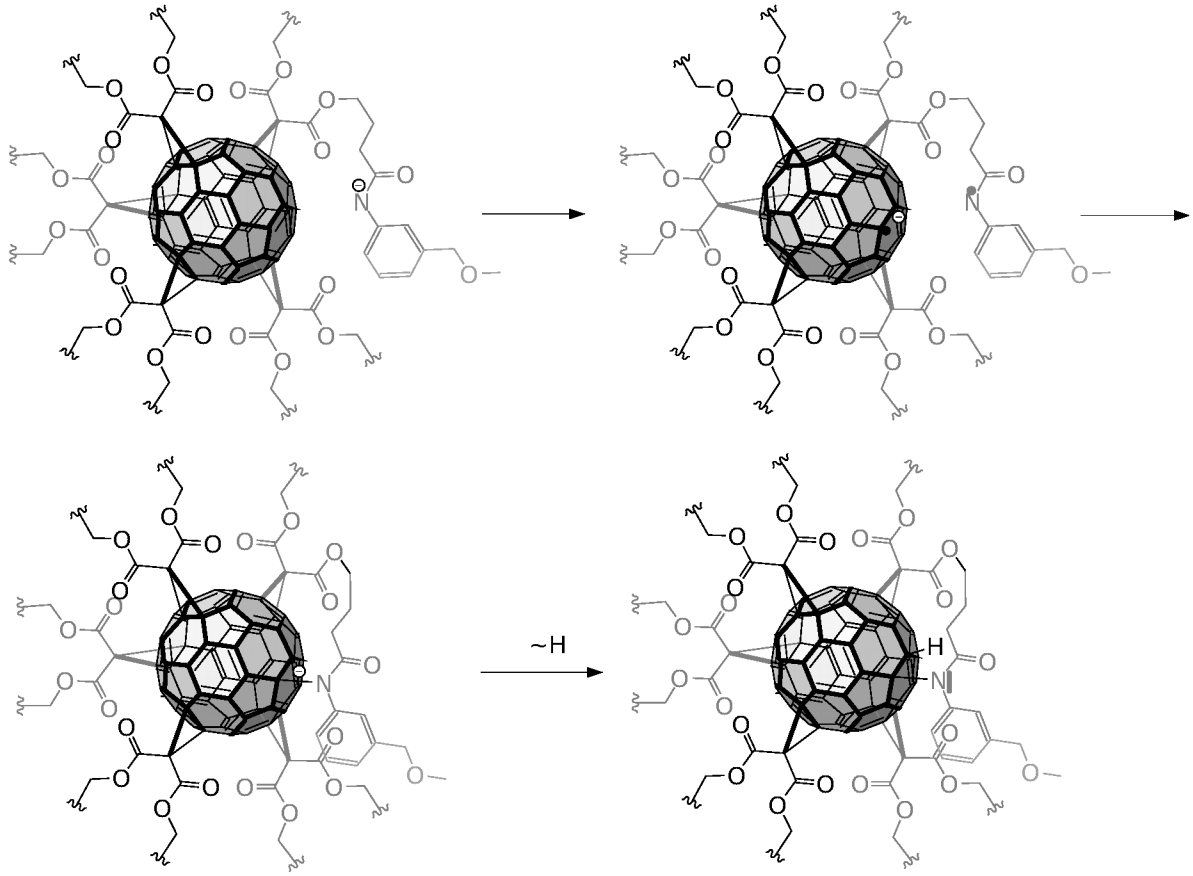
1 eq.
46



33

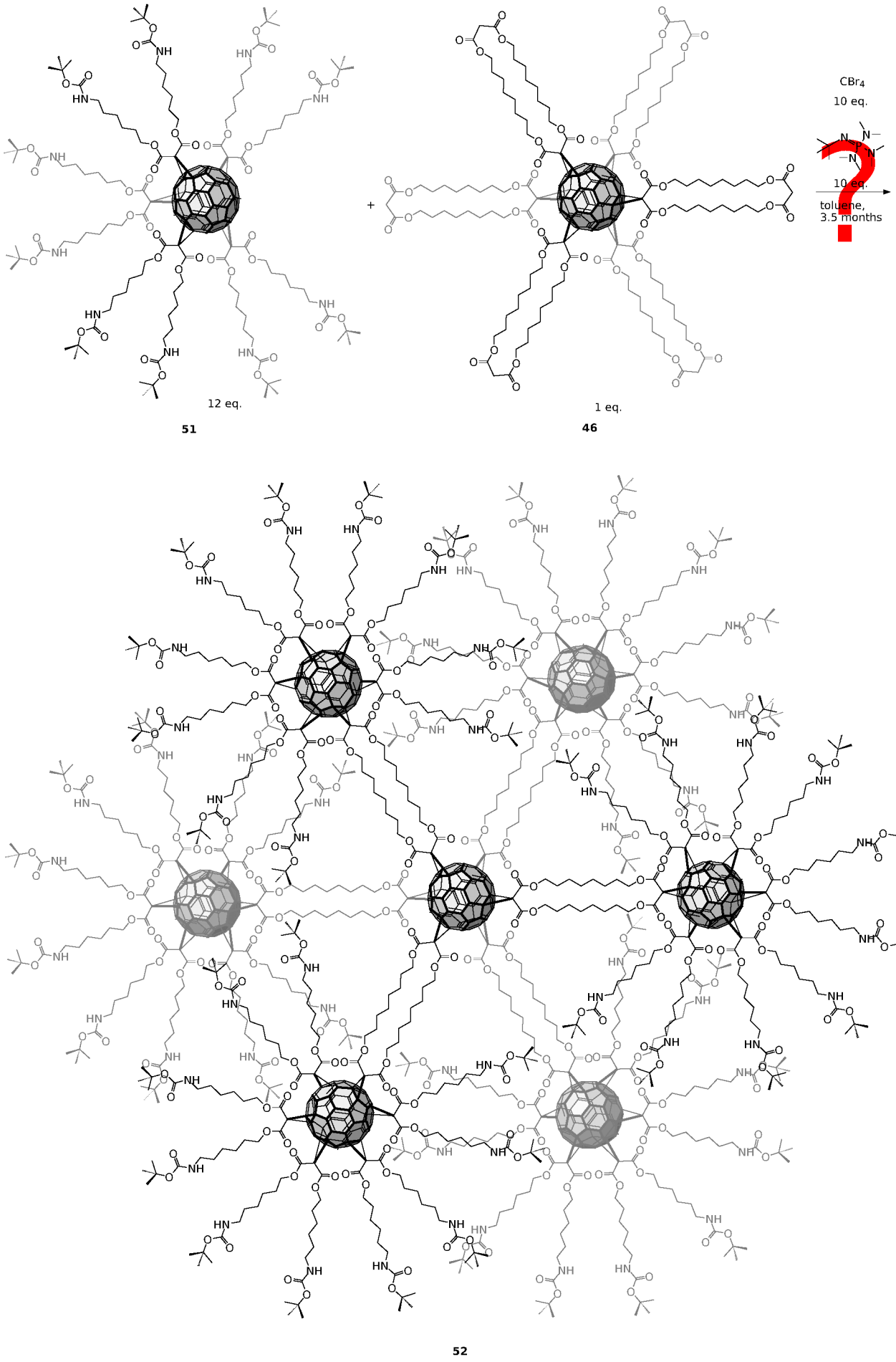
Scheme 45: Attempt to use the presubstituted central element to create heptafullerene **33**

None of the fractions that could be eluted did exhibit any signs of the typical hexakis absorption bands at 314 and 334 nm.[99,100 p. 228] As any adducts formed from the malonate-contributing fullerene would have any cores octahedrally substituted, and there was little possibility that hexakisadducts would decompose under such harmless conditions, it was obvious that the educt had decomposed. Perhaps, the α-carbonylamine moieties had been deprotonated and attacked the open point on the pentakis adducts (scheme 46). The mechanism would, of course, be similar to that known for amines.[23,101] And even if the product decomposed, this can only be because of the only chemical difference to **50**, which are the amide groups.



Scheme 46: Estimative decomposition of pentakisadducts with aniline cation precursors

To have a more simple example of application for the six-malonate-bearing center **46**, the synthesis of the seven-core hexakis adduct **52**, already known from Patrick Witte,[81] was tried in this convergent method from pentakis adduct **51**. The pathway was basically the same as for **50** (scheme 47). Multiple column-chromatographic fractions could be isolated that showed the familiar shoulder peaks at 314 and 334 nm in their UV-Vis-spectrum, but no fraction could be verified by its correct mass in any MS-spectrum. Figure 24 shows the ^{13}C-NMR spectrum of the first hexakis adduct eluted, which was eluted in a mixture of toluene/ethyl acetate 3:2. As the other fractions were eluted much later in much more polar solvents, it is assumable that they must be decomposed fractions or partly deprotected ones. This is more obvious when recalling the knowledge that it is very difficult to separate pentakis adducts from hexakis adducts under conditions of column chromatography, and this gets worse the more branched or otherwise large the product is. This is because a large molecule, consisting of several parts that are connected only with few, flexible bonds, does neglegibly differ in its per-mass solvent affinity from the one of the same components in unconnected form, so the solvent affinity is largely indepentent of the count of these components. If the structure is globular, the contact area to the sorbent is mainly defined to a circular area defined by the length of its arms, but not of the amount of these arms as long as they are sufficient to cover the whole area.



Scheme 47: Experiment to generate a heptafullerene with 60 hexylamine fringe-groups

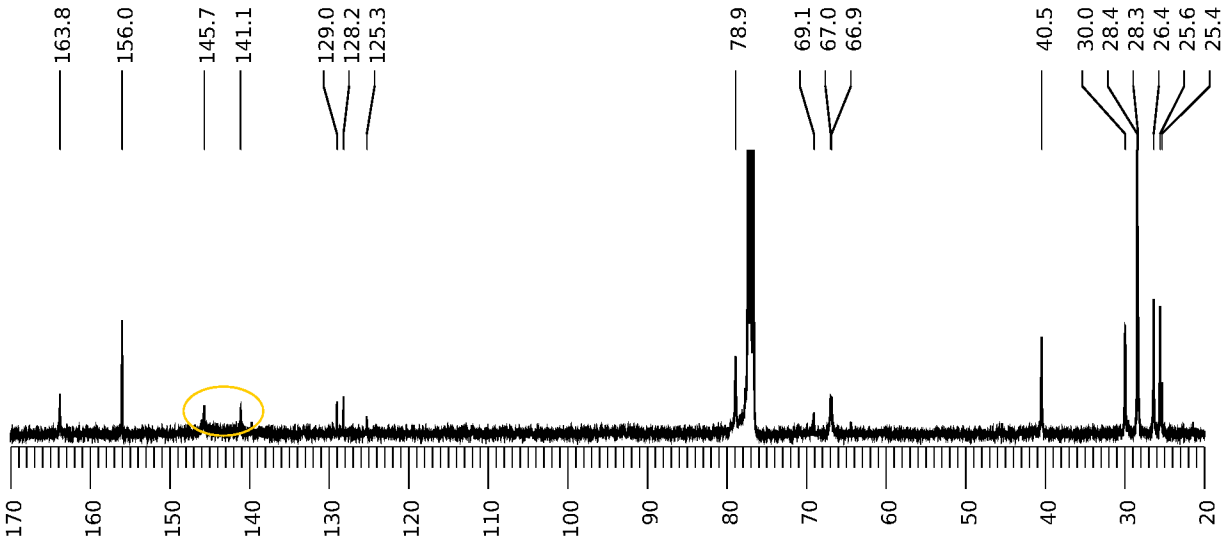
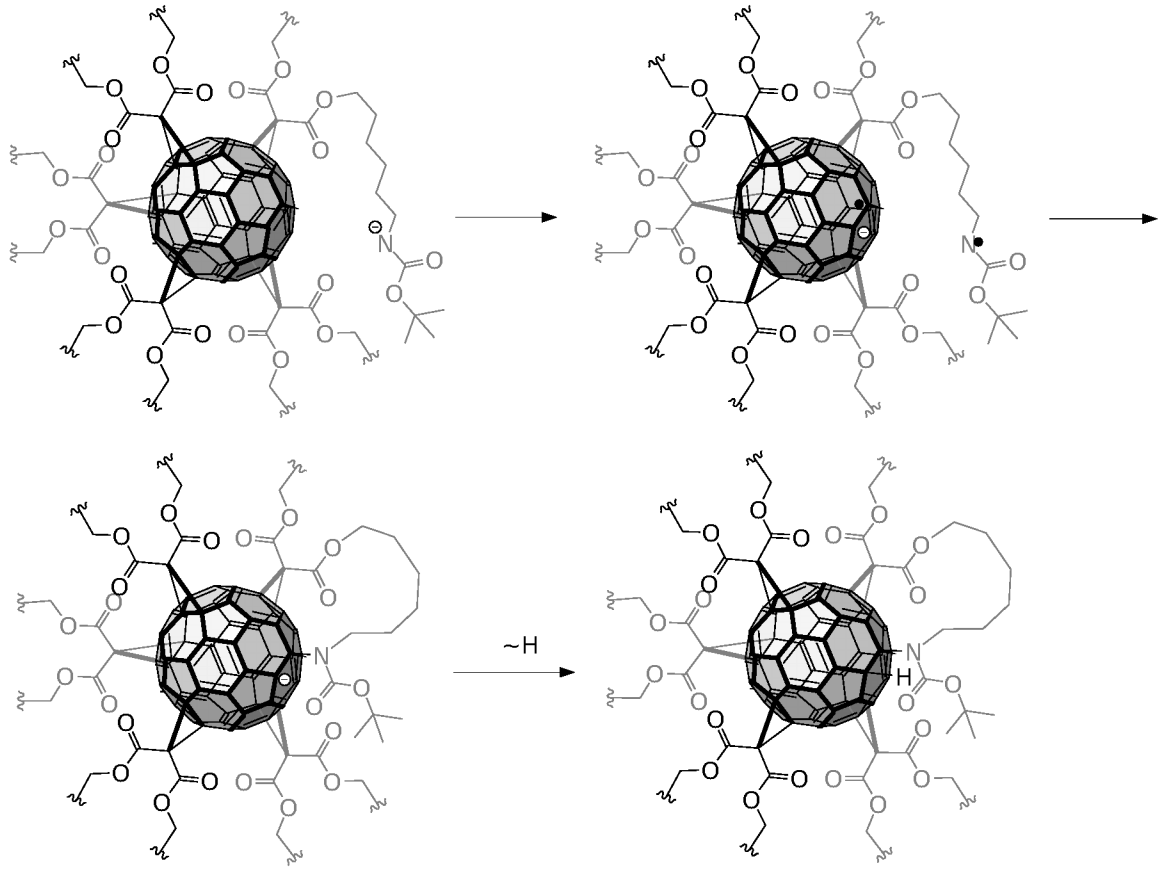


Figure 24: ^{13}C NMR spectrum of the first fraction of experiment 47 that exhibited a hexakis-adduct-typical UV spectrum (100 MHz, $CDCl_3$)

Of course, the main reason for this decomposition might be again a reducing attack of the amide nitrogen to the fullerene core (scheme 48).



Scheme 48: Estimative decomposition of pentakisadducts with boc-protected amines

4.3. Increased Selectivity with Oxazolinofullerenes

The oxazolinofullerenes seemed to exhibit a remarkable improvement of yield in chapter 4.2.6.1.. This led to the question whether they are also capable of improving the selectivity as well, and if it could be of an advantage beyond the addition of spacers. Hence, this experiment was repeated with simple diethyl chloromalonate **41**. To investigate the effect of the oxazoline group on the addition pattern, experiments of hexakisaddition without the known templating were undertaken on a fullerene with no addend, a primitive Prato-type addend and the oxazirene addend.(scheme 49)

4.3.1. Selectivity Effect of Oxazolinofullerenes with Bromides and Chlorides

While no hexakis adduct could be isolated in the case of the Prato-type addend,[33] the oxazolidinofullerene gave a good yield of hexakis adduct when treated with monobrominated malonate (a)). The addition of monochlorinated malonate led to a lower yield of hexakis adduct, however with no noteworthy amount of by-products that would have required purification by HPLC.

4.3.2. Cross-Checks of Selectivity due to Oxazoline

Although the known templating conditions to create T_h-symmetric hexakis adducts[30,65] were seen as innovation, no one had proven yet that T_h-symmetric Bingel adducts are not formed by stochastic reactions without these agents. For this reason, the reaction of an excess of diethyl bromomalonate and diethyl chloromalonate with C_{60} under base influence was tested. In both cases, the desired hexakisadducts could not be found.
In the case of the brominated malonate, the NMR spectrum clearly showed a plethora of C_{60} peaks from different substances, as seen in figure 25. In the case of the chlorinated malonate, TLC control suggested incomplete substitution.

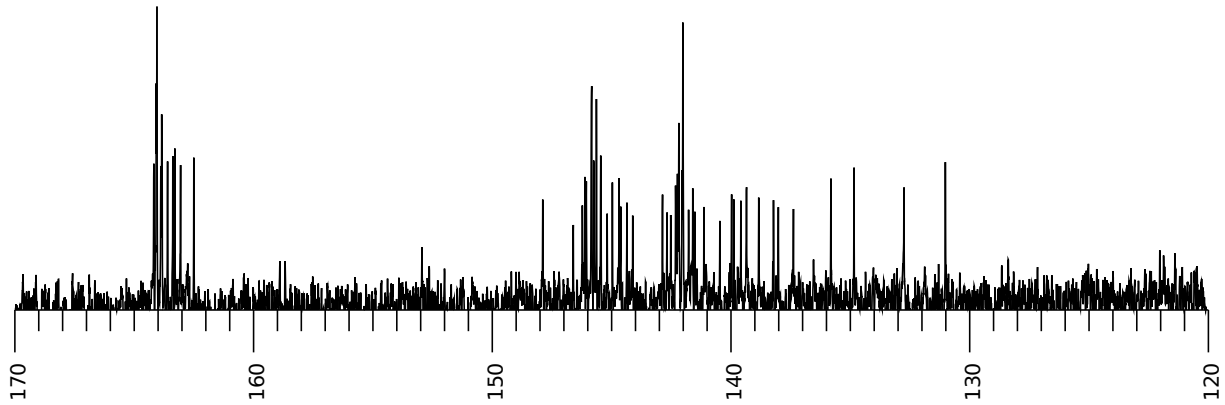
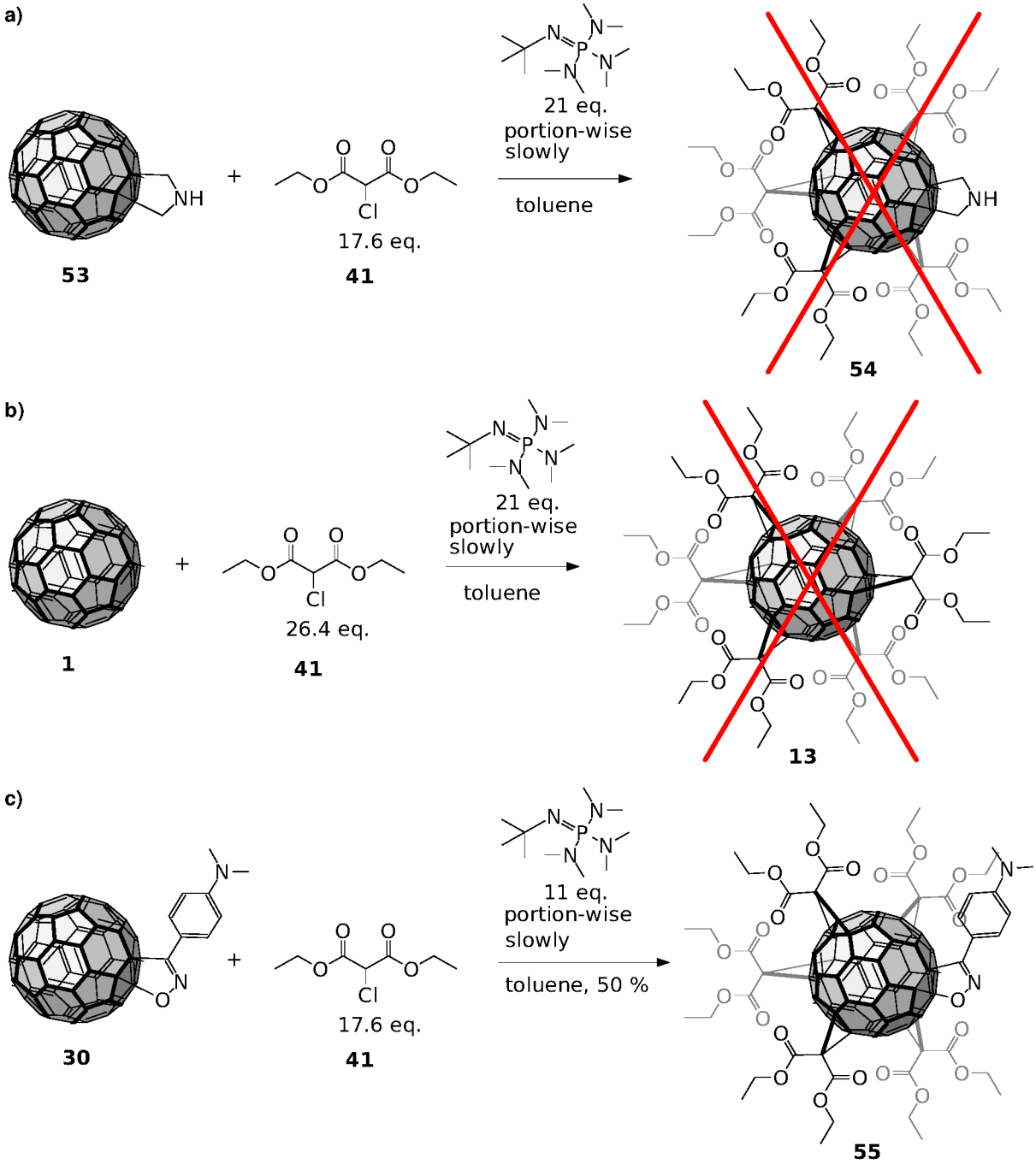
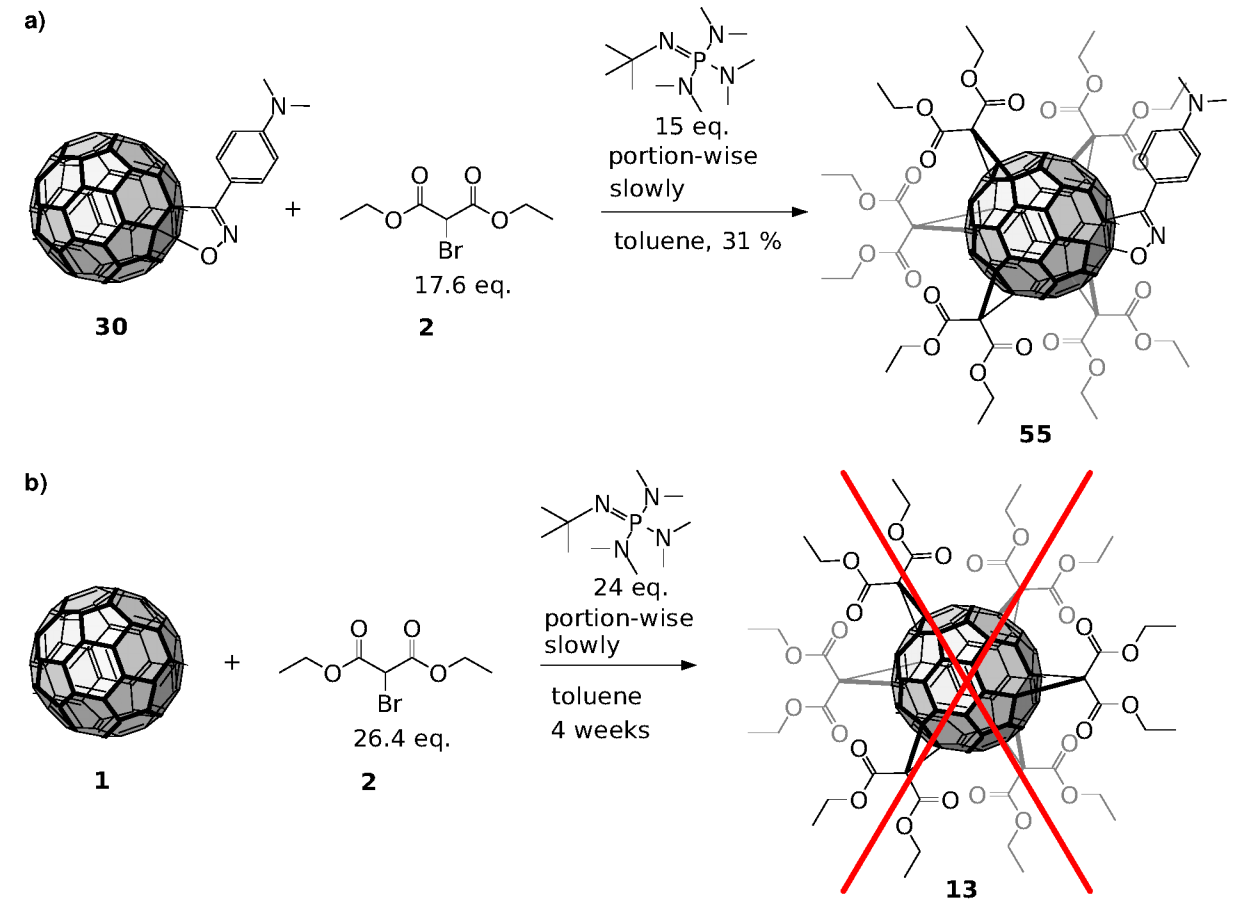


Figure 25: ^{13}C NMR spectrum after treatment of pristine C_{60} with excess of pure monobrominated malonate (75.5 MHz, $CDCl_3$) and DBU



Scheme 49: Experiments showing the beneficial effect of the chloromalonate/isoxazolinofullerene reactand combination

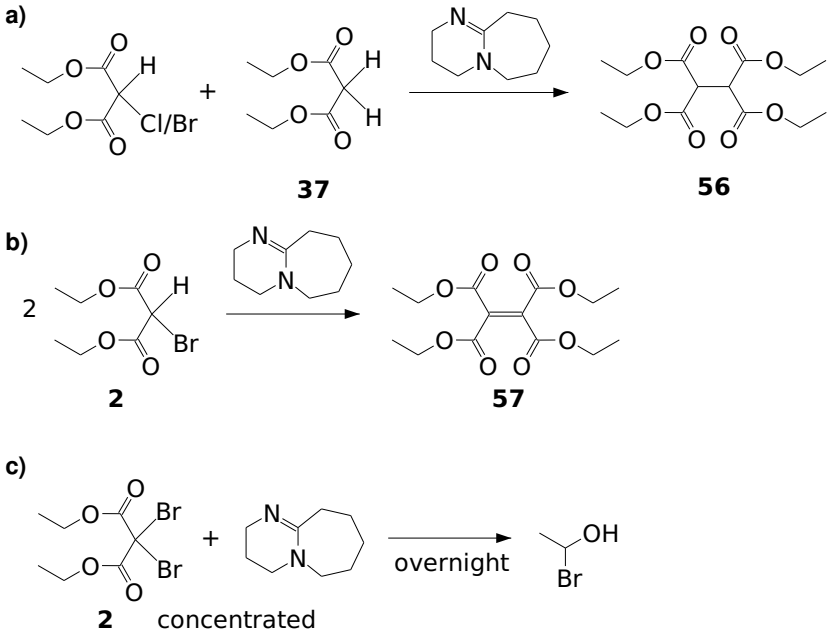


Scheme 50: Cross-check of the selectivity of mono-brominated malonates

4.4. Discovery of Side-Reactions of Halogenated Malonates

The to-date mechanistic knowledge on the Bingel reaction contains little findings about side reactions. In chapter 4.2.6., no definitive explanation for the formation of the polymer was found. Of course, a reversible anion-addition should be pushed back by attachment of further pristine malonate. As this fruit-gum like gel still formed, this was hampered somehow, then.

In the following experiments about halogen exchange, a possible explanation could be found. It is observed that mixtures of monochlorinated and unchlorinated malonates happened to give dimers at the 2 position, obviously by nucleophilic substitution (scheme 51 a)). In the above synthesis, this would decrease the educt amount and, - even worse - could damage the product by chaining further malonate spacers on it. The fact that such side-products were not ovserved in the TLC plates or mass spectra is perhaps due to base depletion consumed by the Bingel-reaction and by this side reaction. When brominated malonates were reacting, this side reaction proceeded even faster and the creation of tetraethyl tetracarboxyethene **57** showed that in that case, it even proceeded between two halogenated malonates, followed by an elimination of HBr from the highly unstable intermediate (scheme 51 b)).

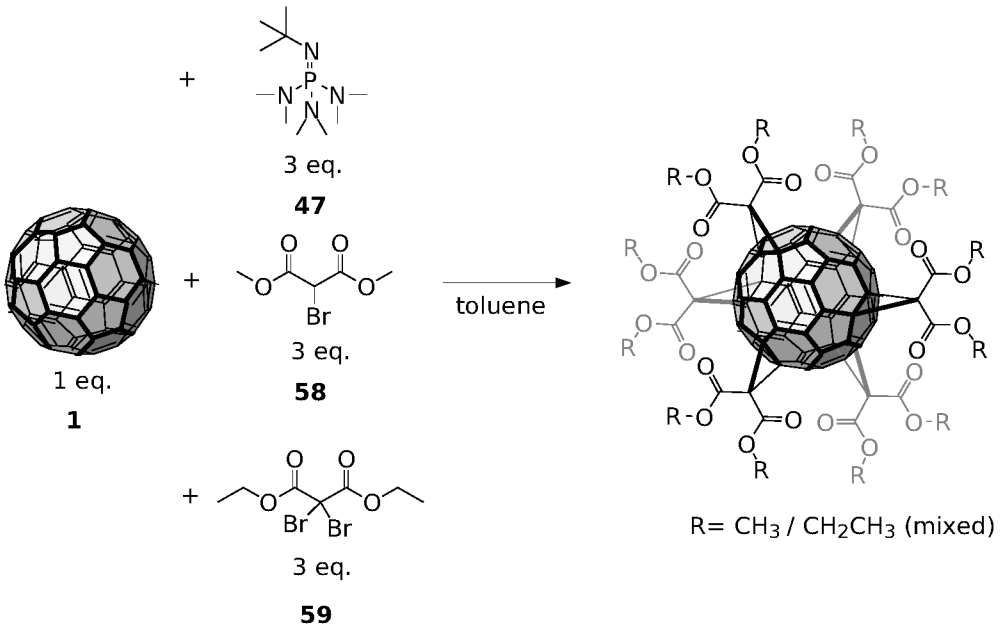


Scheme 51: Actual decomposition reactions on malonates

4.4.1. Mechanistic Investigations of the Tetrabromocarbon Templatisation

Regarding the mechanism of the templating due to tetrabromocarbon,[76,77] the most obvious question was whether the tetrabromocarbon was the true templating agent or if the selectivity was rather due to the dibrominated malonate generated by applying it in excess. If the dibrominated malonate was the active species, adding it directly must give the same results. Adding three eqivalents of both dimethyl bromomalonate and diethyl dibromomalonate and dropwise addition of 3 eqivalents P_1-*t*Bu yielded a notable amount of T_h-symmetric hexakis adduct, proven by NMR due to the characteristic signals at 146 and 141 ppm (figure 26).

The presence of both ethyl and methyl residues on the resulting fullerene adduct did also show that it was impossible to protect a malonate by double-brominating it.



Scheme 52: The initial discovery of the templating effects of dibrominated malonates

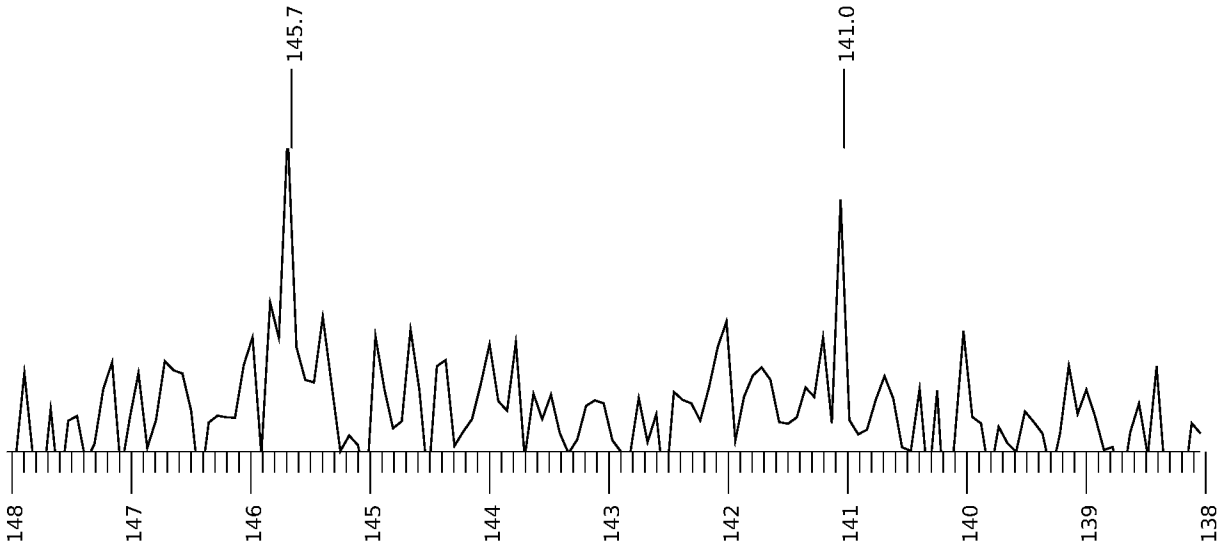
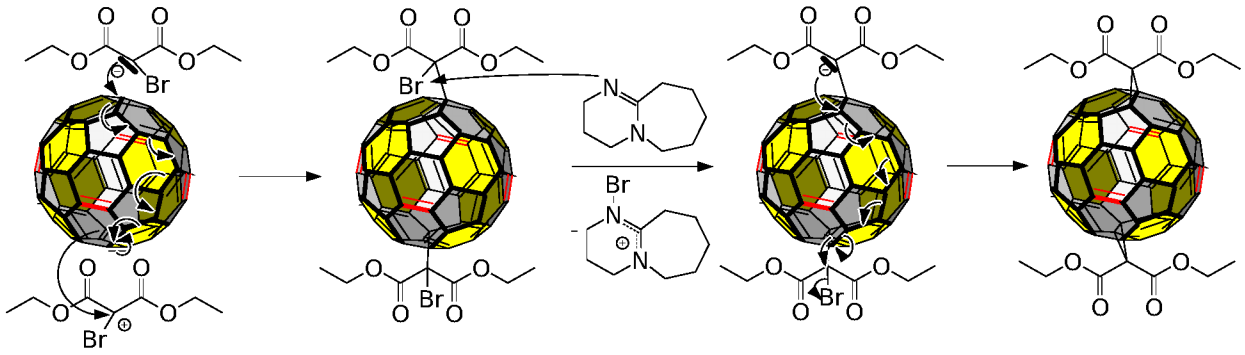


Figure 26: ^{13}C NMR spectrum showing the T_h-symmetric substitution pattern after combined addition of mono- and dibrominated malonates to C_{60} (scheme 52) (100 MHz, $CDCl_3$)

This shows that the presence of dibrominated malonate was capable of causing a selective synthesis. According to *occham's razor*,[102] the assumption that tetrabromocarbon itself does the templating is futile now. Dibrominated malonates, on the other hand, could not be a direct explanation for the selectivity, either, as dibrominated alkylmalonates as such had no reactive side to affix it onto a fullerene's double bond. The “anionic form” with a bromyl cation split off would give no difference towards the simple monobrominated malonate which didn't exhibit that selectivity. If a bromide anion was split off, however, the resulting carbon electrophile would not react with pristine or cyclopropanated C_{60}. On the other hand, it would react with a negatively charged Bingel reaction intermediate that exists directly after the addition of another malonate anion to the fullerene (scheme 53).

That addition reaction would be a heterolytic junction of the cation with the site of the fullerene on which the anion is located. Then, the formation of the corresponding bis-adduct would be expected to occur readily after the remaining bromyl cation of the first malonate was removed from the malonate.The site where the anion is located, of course, would be preferentially the electronically most favorable double bond. Since the e' and e'' and trans sites exhibit the most electronically isolated double bonds, it is a good assumption that the electron would be located there instead of the places which are complete aromatic rings, as aromatic rings tend little to take up further electrons. Another aspect is that the delocalized negative charge would be delocalized into the LUMO area. This LUMO area would be very similar to the LUMO in a monoadduct, which was calculated by Iris Lamparth of our group before and prevalently extended to the e' position.[99] For a feeling about the reactivity of this mechanism, one also must consider that the most stable place for the negative charge to be would be next to the added anion. A delocalisation of the negative charge would correspondingly mostly occur between this position and the most opportune other place.

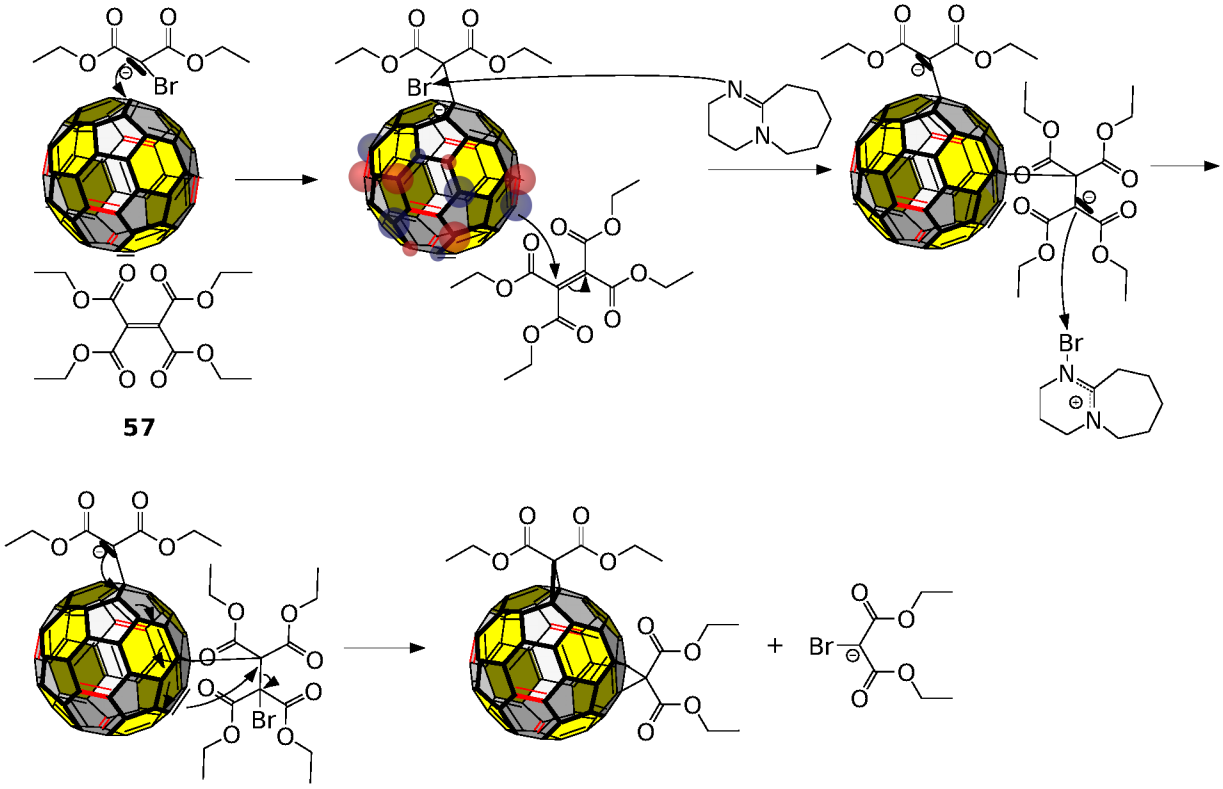
This theory, which involves that two malonates are added cooperatively can be seen very distinct in this experiment if you consider the stoichiometry of reactands of scheme 52: The hexakis adduct is formed even when the sum the malonates are added without any excess, and even with only three equivalents of base, which is the half of what is needed for a complete reaction. This would usually cause an incomplete substitution with statistical distribution of the count of addends, which would barely create a notable amount of hexakis adduct. But cooperative reactions have different statistic conditions.



Scheme 53: Initial theory on the mechanism of the tetrabromocarbon templatisation

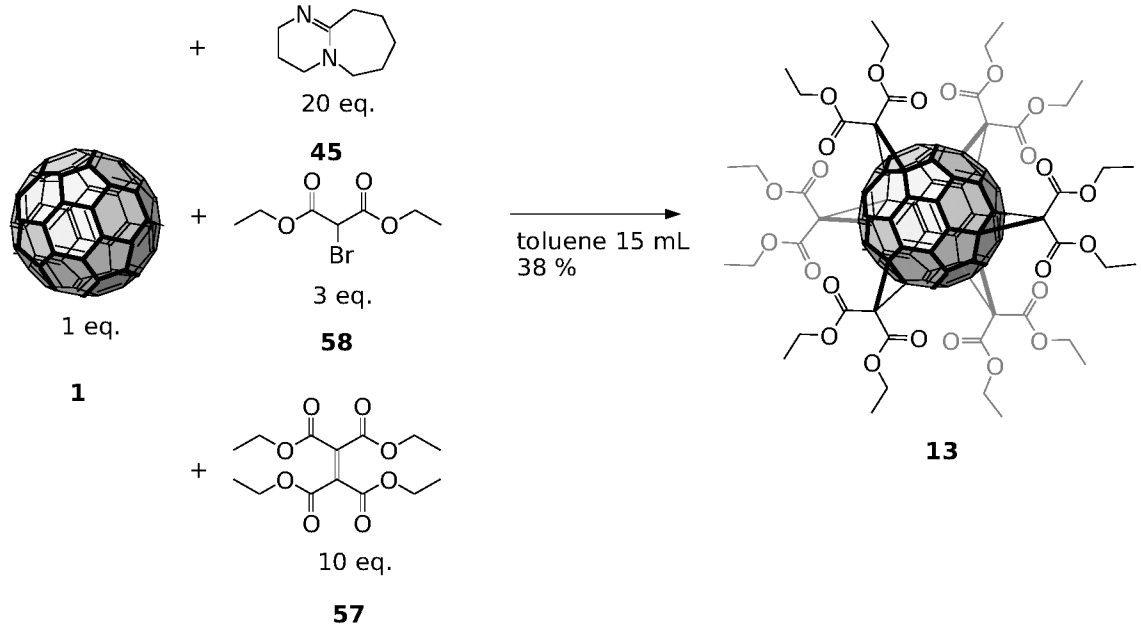
The problem with this theory would be the steric hindrance of the dibrominated malonate.

Could there be a more reactive instance? If we consider the discovery of malonyliden dimer **57**, which has been seen to form under these conditions rapidly (scheme 51 b)), we see that it has a good ability to attack in a cooperative manner (scheme 54).



Scheme 54: Final model of the mechanism of the tetrabromocarbon templatisation

This can be tested by directly inserting tetraethyl tetracarboxyethene **57** under Bingel conditions. Since there is a bad selectivity when there is no templating reagent, as seen in (figure 25), the fact that the yield of hexakis adduct is now very high with 38 %, shows that **57** not only has a templating effect, but also hints that it contributes malonates to the reaction, because the insufficient malonate amount would otherwise lead to lower adduction patterns.



Scheme 55: Experiment to identify the actual reactive instance in the tetrabromocarbon templatisation

Adding 10 equivalents of **57** and 3 equivalents of diethyl bromomalonate **2** to a fullerene, one would definitely expect incomplete substitution if **57** would not react. As it can be seen from graph 27 (b), there was no evidence for incompletely furnished fullerenes in the raw mixture. The yield of the pure product (a) was as high as 38 %!

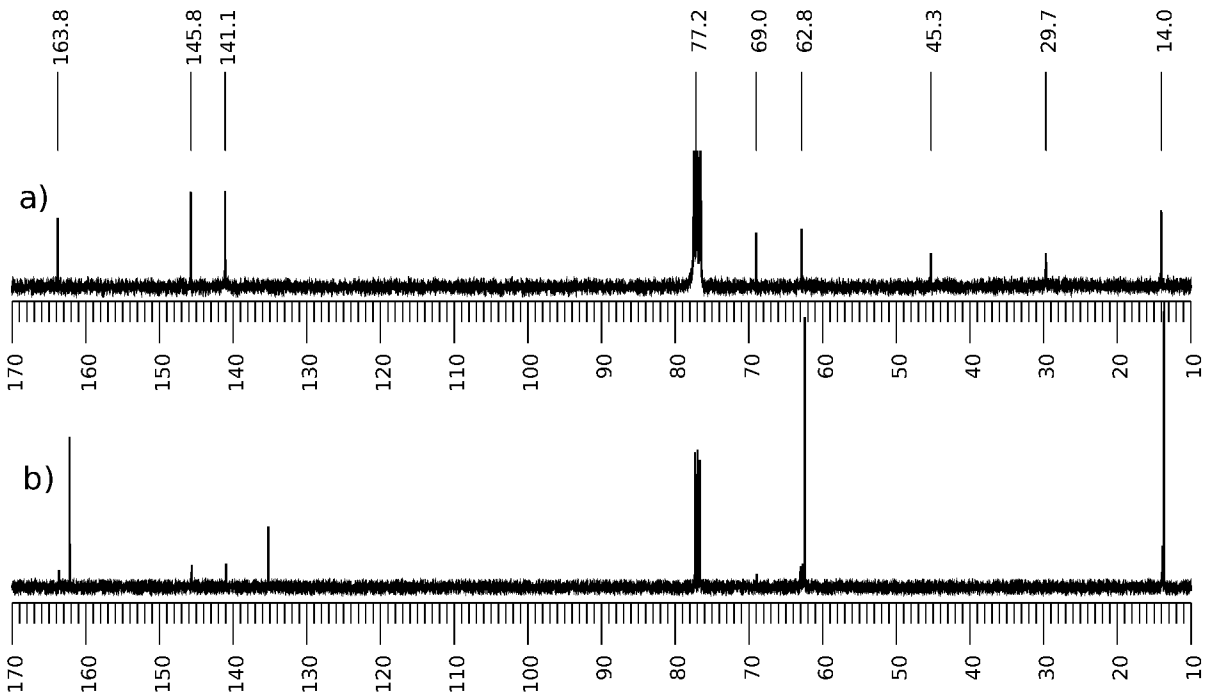
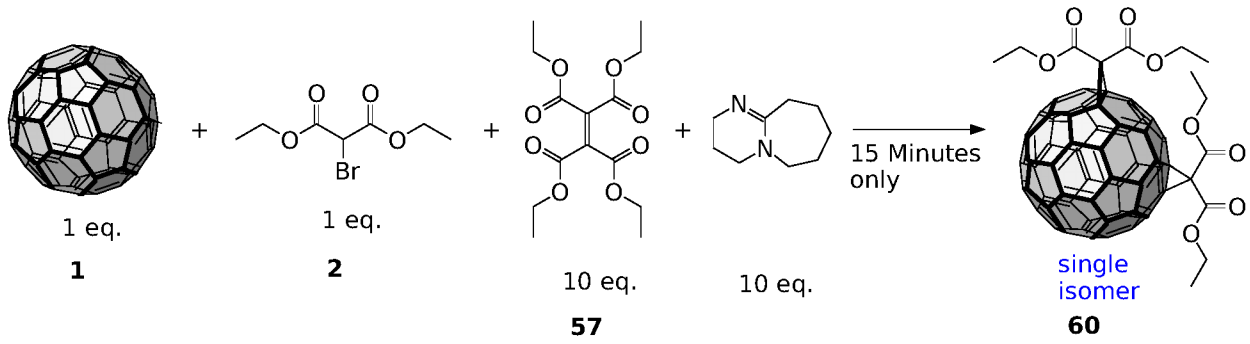


Figure 27: ^{13}C NMR spectra taken from the experiment depicted in scheme 55. Graph a) shows the spectrum of the final product (75.5 MHz, $CDCl_3$), graph b) shows the one of the raw mixture (100 MHz, $CDCl_3$).

The only question remaining on this explanation is why it takes a high degree of dibromination to create a sufficient amount of these alkene dimers. That is a statistic effect: if there are too many unbrominated malonates, they have enough capability to attach wrongly in meantime. Dibrominated malonates react slower, giving them time to "wait" until enough alkene is created. It also could be that the formation of the alkene is more easily done from them, with the dibrominated alkene in first place, which reveals the alkene after one bromyl cation is detached by the base. (The tetraethyltetracarboxyalkene has a very low affinity to bromine: Intentional adding elemental bromine to this alkene was not possible.)

4.4.2. Investigating the Process of the Tetraethyltetracarboxyethene Adduct Formation

If such a templated reaction would occur, the selectively created intermediate would be suited for being isolated. By initiating the Bingel reaction on C_{60} with only one equivalent of brominated malonate and ten equivalents of **57** (scheme 56), and abortion of the reaction after 15 minutes yielded selectively the e adduct.



Scheme 56: Premature abortion of the Bingel reaction with ethylene-based selectivity

The substance was verified by a comparison of the carbon-NMR spectrum (figure 28) to the literature[53] and by Mass spectrometry.

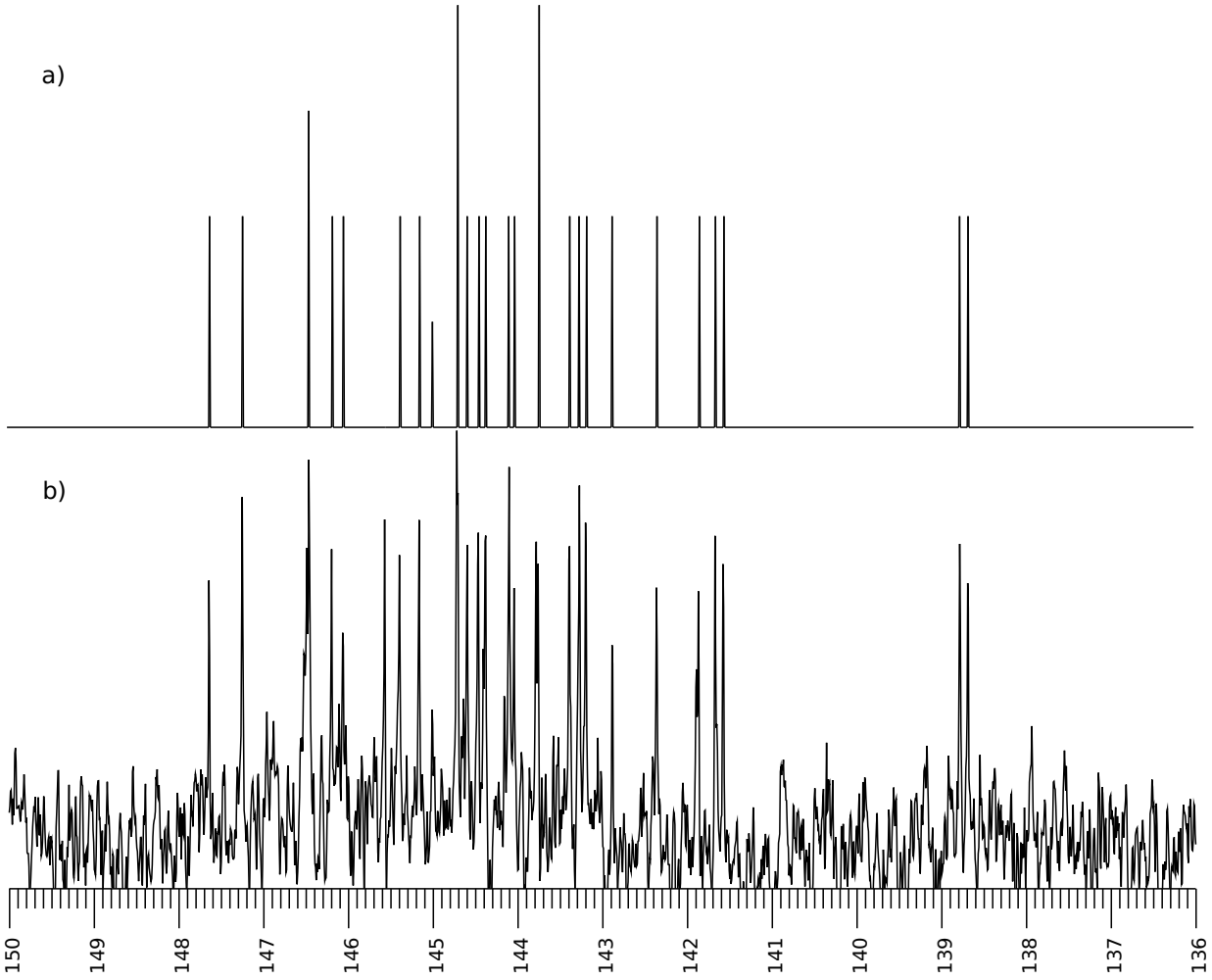


Figure 28: Fullerene-range of the ^{13}C-NMR-spectrum of the product of a tetraethyl tetracarboxyethene-based Bingel reaction which was prematurely interrupted a) reference from literature[53] b) product (75.5 MHz, $CDCl_3$)

Also the UV/Vis-Spectrum (figure 29) hinted at the correct product, distinguishable due to the typical peak at 490 nm for e-bisadducts.[65]

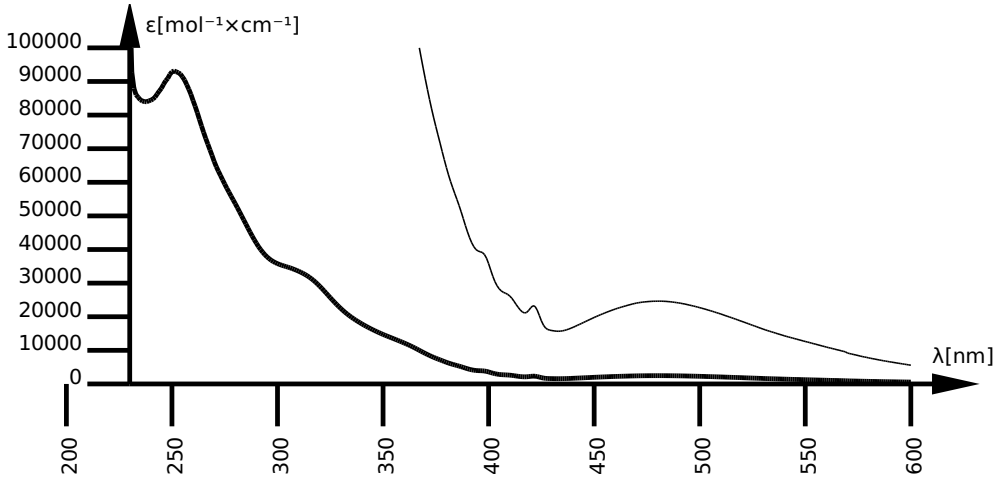
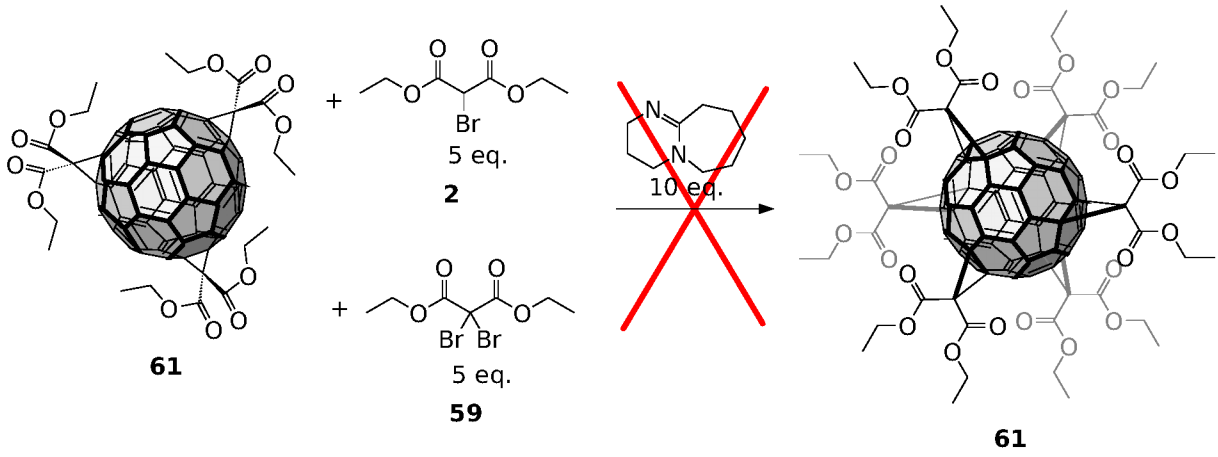
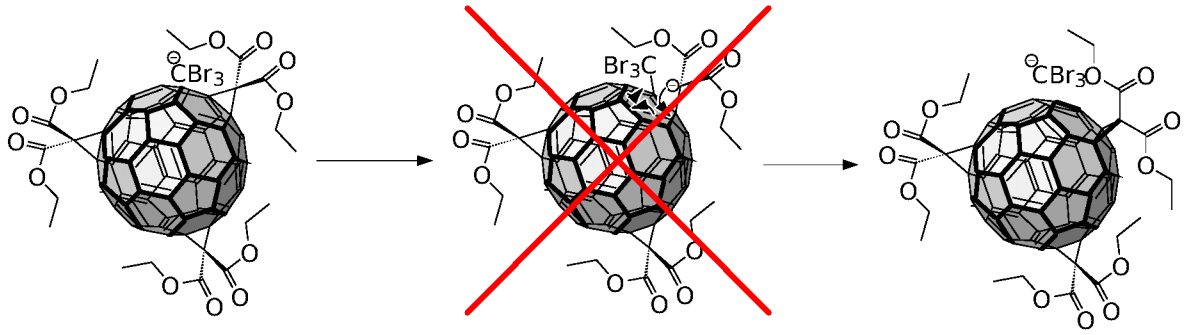


Figure 29: UV-Vis Spectrum of the pure e-bisadduct **60**. Thin line: ×10

An alternative theory for the mechanism of the tetrabromocarbon templatisation necessary to ponder deals with wandering of the malonates on the surface under the influence of dibrominated malonate or some decomposition product thereof. In this case, the selectivity would be due to thermodynamic control, which would favor the T_h symmetric product due to the aromatic stabilisation of the eight remaining benzene rings. In order to examine whether this would be possible, a mixture of mono- and dibrominated diethyl malonate was added under Bingel conditions to a - falsely substituted - trans3,trans3,trans3-trisadduct of diethyl malonate **61** to C_{60}. If wandering was possible, the hexakis adduct **13** should still be able to form, if the reaction conditions were otherwise identical to the conditions that have been proven to be successful when starting with a pristine fullerene. To test this, five equivalents of both the monobrominated and dibrominated malonate were added to bis(diethylmalonyl)-tris-1,2,33,50,46,47-hexahydro[60]-fullerene **61**, together with 10 equivalents of DBU (scheme 57), so the state of the reaction would approximately correspond to the situation when three addends had added under the tetrabromocarbon-templated or dibromomalonate-templated conditions. With this setup, no TLC peaks appeared hinting to the presence of a hexakis adduct until the reaction mixture completely decomposed. This must be seen as evidence that the dibrominated malonate is not capable to enable wandering (scheme 58), which further affirms my theory of the cooperative Bingel reaction.



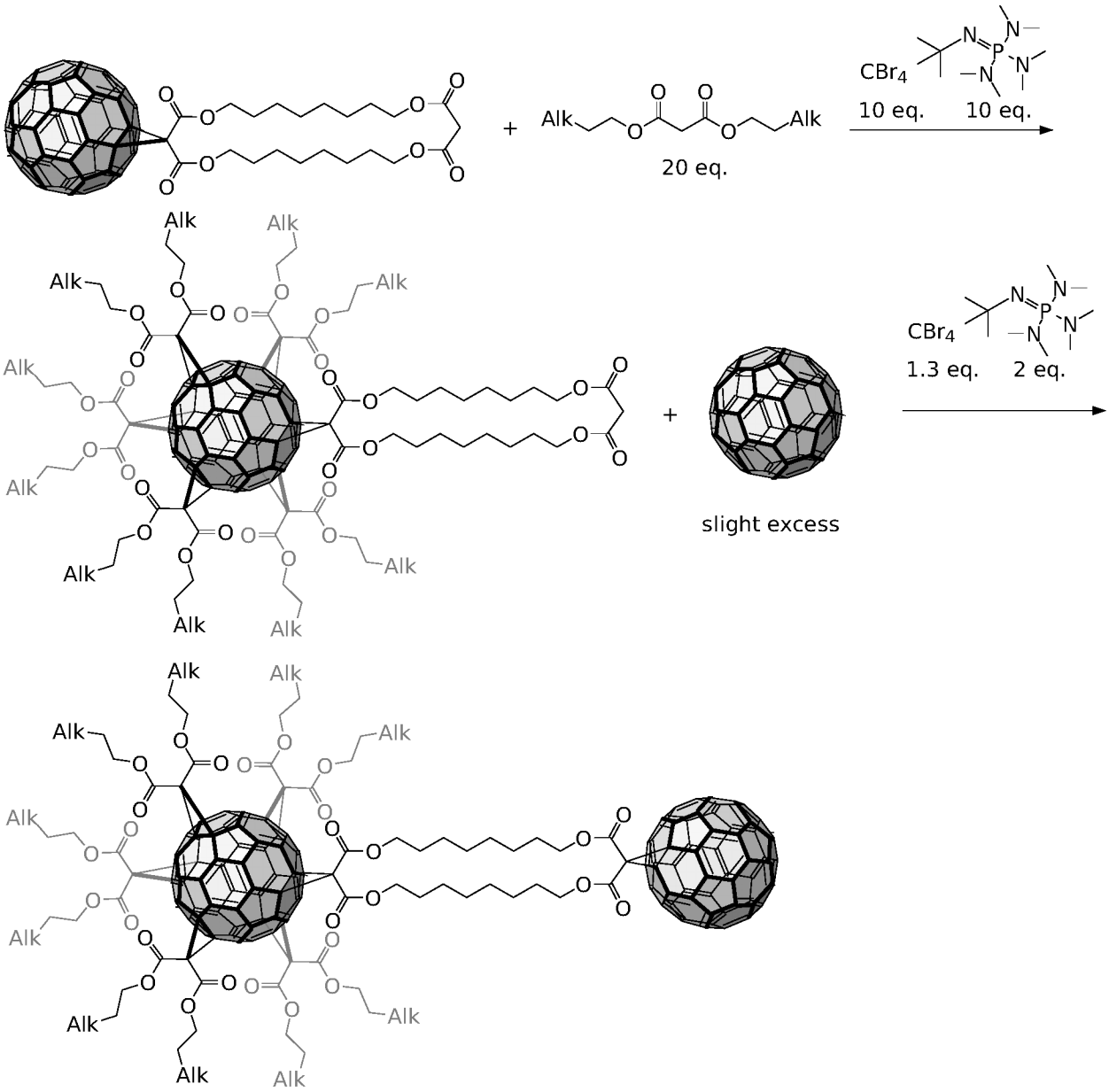
Scheme 57: Experiment to disprove the walk-on-sphere mechanism



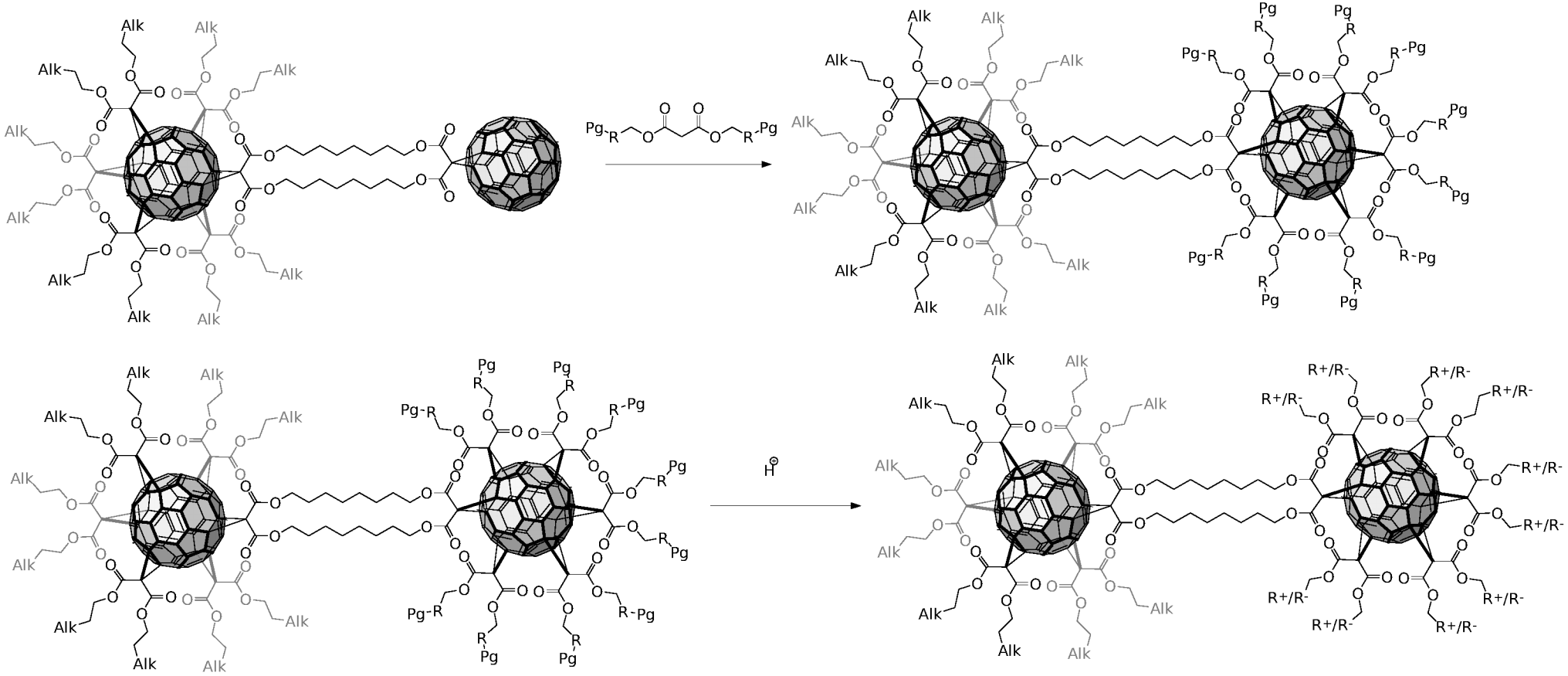
Scheme 58: Immobility of attached malonates

4.5. Second Aim: Investigation of the Aggregation Behavior of Fullerene Amphiphiles

Another topic in my doctoral thesis was the synthesis of a new kind of fullerene amphiphiles for aggregation studies. These molecules consisted of a spacer carrying fullerenes bond on both sides, one of which was functionalized with polar and the other one with unpolar addends. Past aggregation studies with amphiphilic fullerenes were done using predominantly unpolar substituted fullerene hexakisadducts with only one malonate carrying two hydrophilizing dendrimers,[103] with three polar and three unpolar substituted malonates on one fullerene,[104] on mono-adducts with one dendrimer.[105] Other examples were the creation of inverted micelles with bolaamphiphiles as monolayer membranes.[106] The first attempts to construct bifullerenic amphiphiles in this thesis were also made using the method of Patrick Witte, who had created a zwitterionic analogue of this structure before (schemes 59 and 60).[81,107]



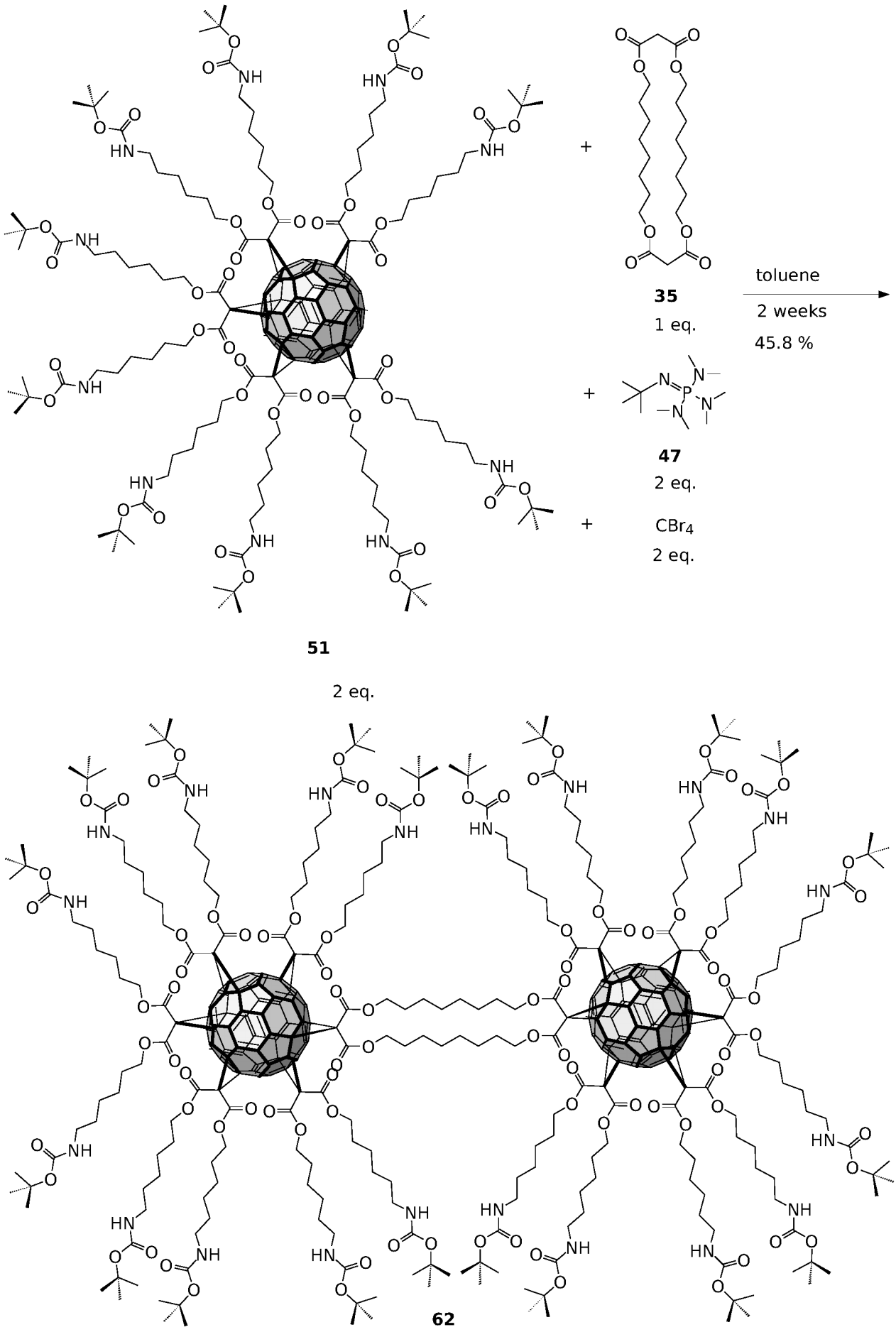
Scheme 59: Synthetic procedure of the synthesis of each amphiphile, formation of the unsymmetric dumbbell



Scheme 60: Synthetic procedure of the synthesis of each amphiphile, second addition and deprotection

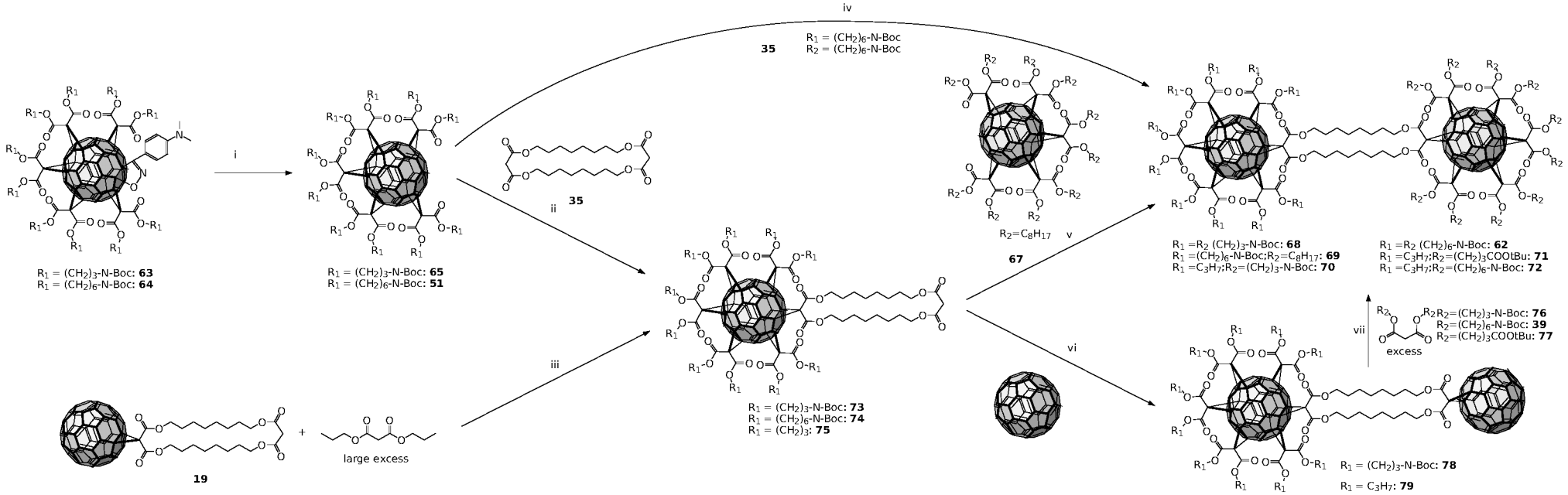
This method, however, suffered from difficult separability of the products, and a low yield, or went out without success for some malonates, which was perhaps due to the aforementioned intramolecular attack of the malonate end back onto the fullerene (scheme 35).

Here again, the difficulties occurred only with the concurring spacer-containing molecules. Also on these molecules, it was necessary to use the protective group of Frank Hörmann.[98] This mainly simplified the way how fullerenes with protected amines could be constructed as spacer bearing addends, but their instability during reactions, especially of those with propyl amine side chains, still yielded the problem of severe purification problems and very low yield. The purification was therefore always done by multi-cycle HPLC, but the low yield was something one must simply live with. The most notable result, from a syntheticist's point of view, was one efficient double-reaction with a stoichiometric addition of educts and reagents (scheme 61). Upon allowing the reaction to run for two weeks, two pentakis adducts of the hexylamine type **51** could be bound together to form **62**. Carbamates on the ligands seemed to inhibit the reaction and molecules react the slower, the bigger they are. If at a low reagent concentration the reaction does still proceed far enough, and the reaction is not hindered by decomposition either, this does hint that the used reagents do not decompose, and that the reagents, in turn, must be responsible for the decomposition that occurs in the cases where they are added in excess.



Scheme 61: Bisaddition of a fullerene pentakisadduct without excess to form a symmetric difullerene

The following chart, scheme 62, shows an overview of all the syntheses of the amphiphiles made.



Scheme 62: Overview of the synthetic routes to the different amphiphiles **80** to **85**

i) toluene, hν, strict air exclusion

ii) CH_2Cl_2, excess, CBr_4, DBU

iii) CH_2Cl_2, 10 eq. DMA, 60 eq. of malonate, 10 eq. CBr_4, DBU,

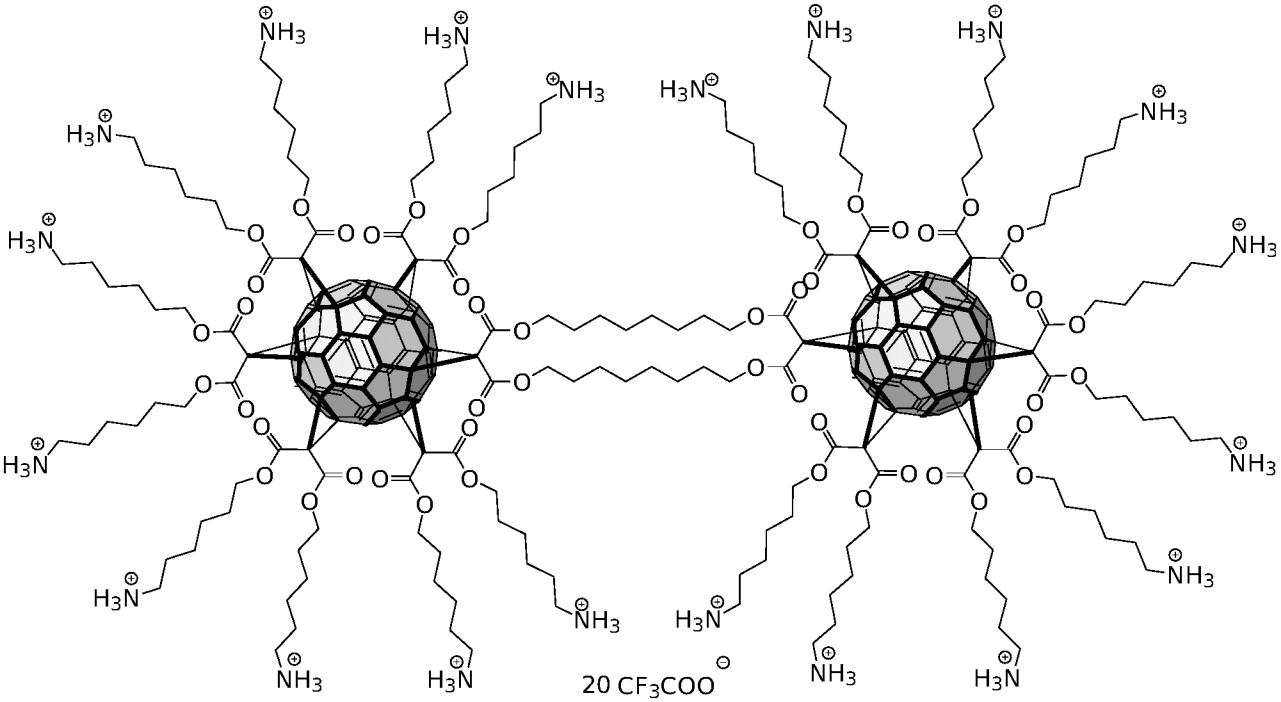
iv) stoichiometric **35**, 2 stch-eq. DBU, 2 stch.-eq. CBr_4

v) CH_2Cl_2, 1.5 eq. **67**, 1 eq. P1-*t*Bu, 1 eq. CBr_4

vi) CH_2Cl_2, 2 eq. C_{60}, 1.5 eq. P1-*t*Bu, 1.5 eq. CBr_4

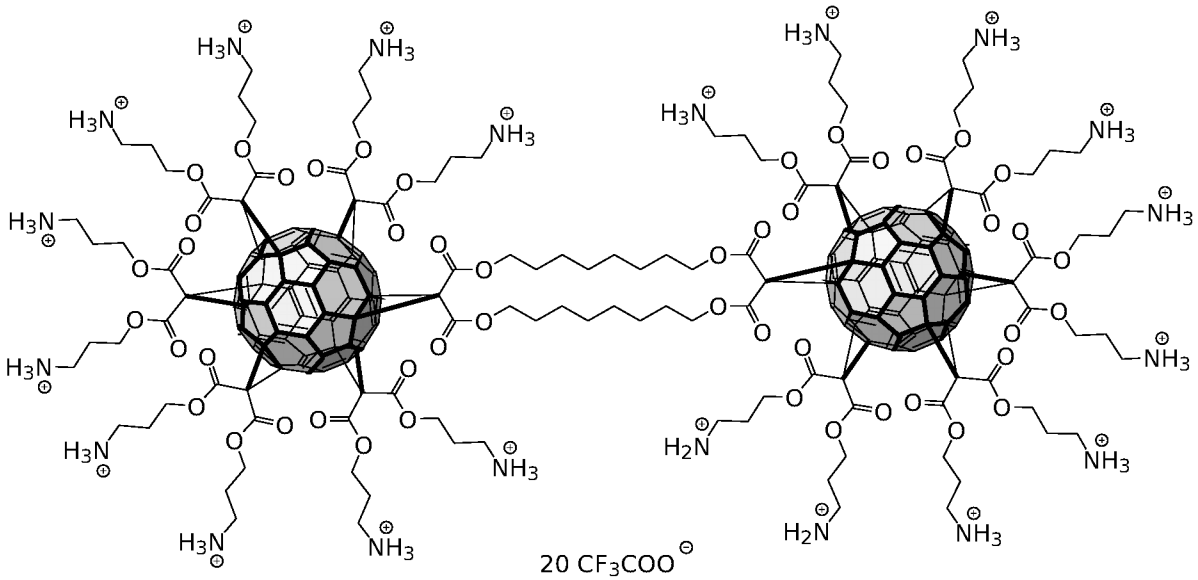
vii) CH_2Cl_2, 20 eq. of malonate, 12 eq.CBr_4, 12 eq. P1-*t*Bu.

In sum, all dumbbell molecules in the schemes **63** to **68** could be made. The bi-hydrophilic molecules **81** and **80** were intended to determine the contribution of the central spacer on the aggregation behavior.



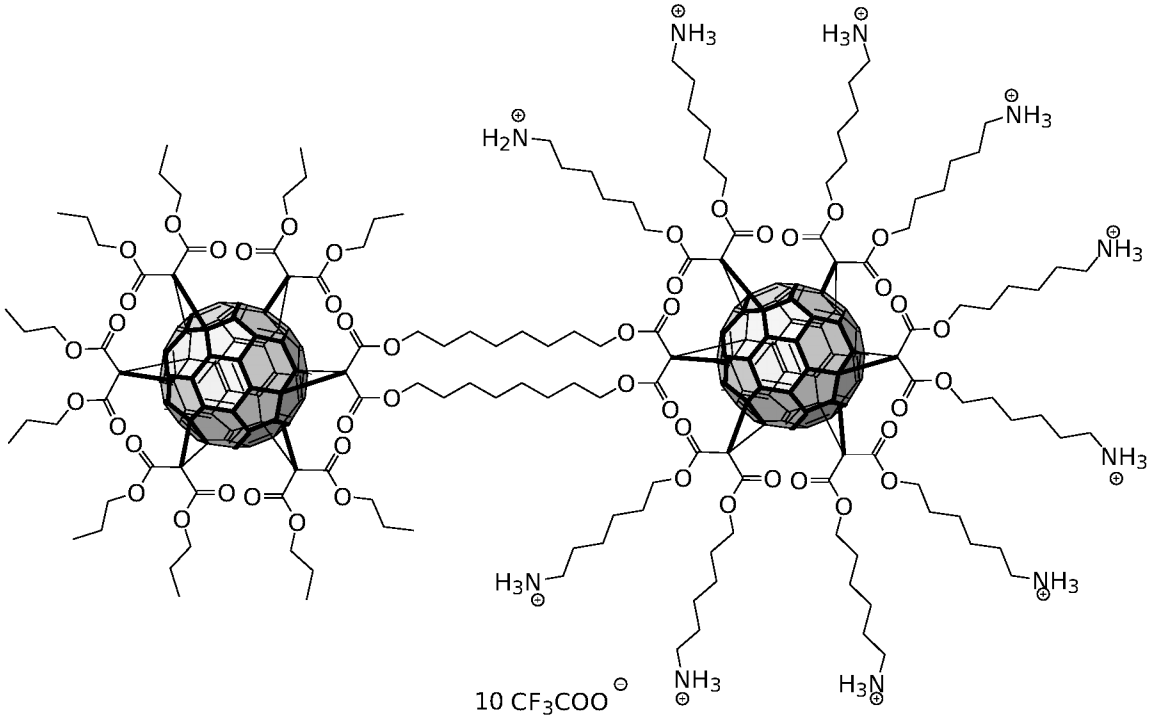
80

Scheme 63: Bi-hydrophile dumbbell with long alkyl chains



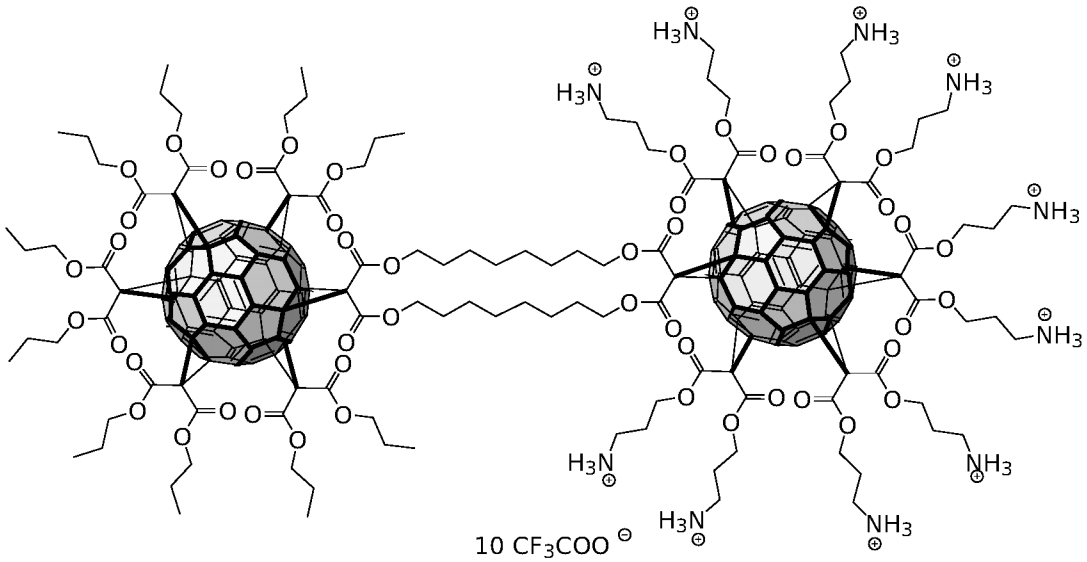
81

Scheme 64: Bi-hydrophile dumbbell with short alkyl chains



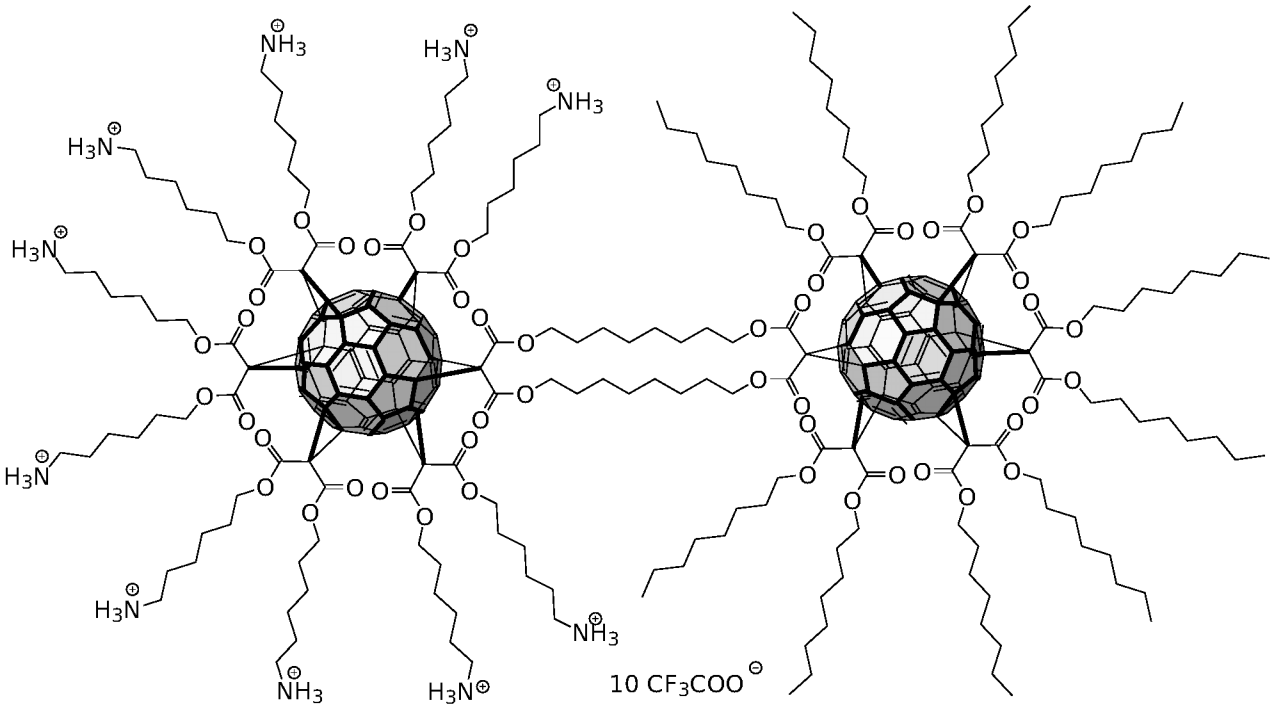
82

Scheme 65: Amphiphile with short alkyl chains on the unpolar side and long alkyl chains on the polar side



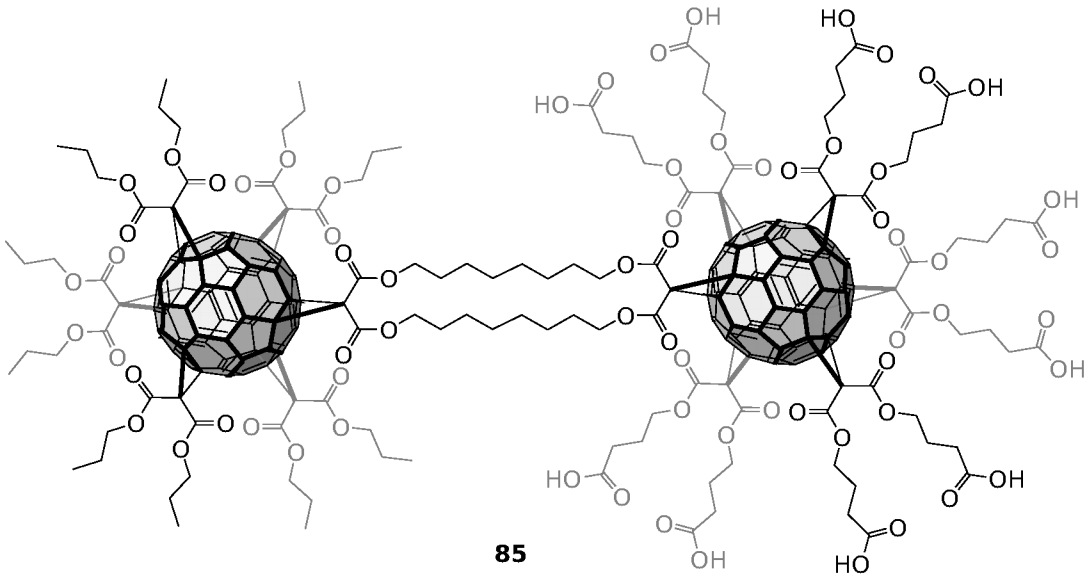
83

Scheme 66: Amphiphile with short unpolar chains and short alkyl chains on the polar side



84

Scheme 67: Amphiphile with long unpolar chains and long alkyl chains on the polar side



85

Scheme 68: Amphiphile with short alkyl chains on the unpolar side and carboxy groups on the polar side. Not water-soluble when protonated

Longer alkyl chains in the polar arms are seen as beneficial for the water solubility due to the greater contact area with water, as it is affirmed by the determined CMC values.

Some discussion of the spectra of the intermediates of the amphiphiles follows to give an overview of all occurring spectral peculiarities. Most of the spectra of the deprotected products gave comparatively broad signals due to aggregation phenomena. Deprotected amphiphiles, such as **80**, were measured in D_2O (figure 30).

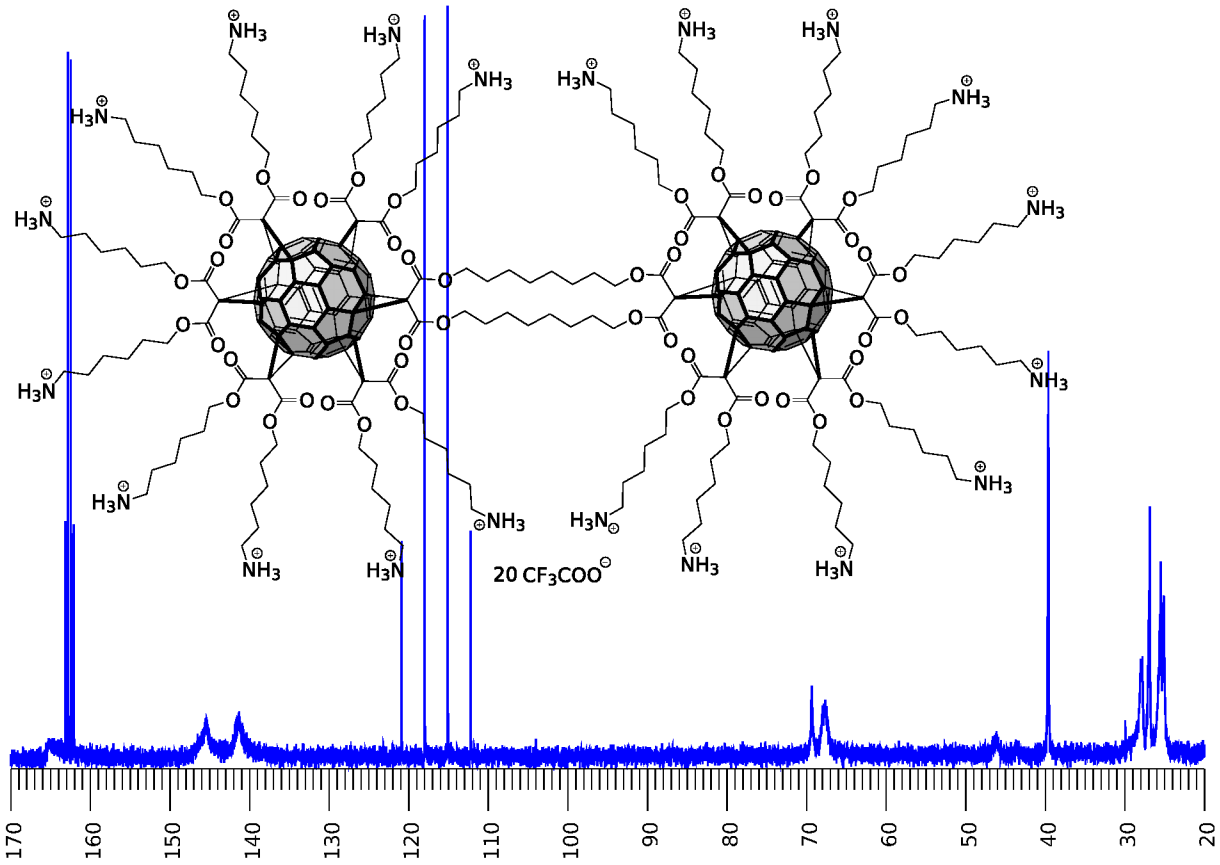


Figure 30: ^{13}C NMR spectrum of the deprotected bi-hydrophile **80** (100 MHz, D_2O)

At 165.5, the carbons of the carbonyl groups can be seen. The sp^2 carbons of the symmetric configured fullerene appear at 145.6 and 141.5 ppm as usual. At 69.4 ppm, the sp^3 carbons of the fullerene are located, at 67.7 ppm, we see the alcohol carbons. A very broad signal at 46 ppm stands for the carbon between the two carbonyl groups of the former malonic acids. The carbons next to the deprotected amines give a strong signal at 39.6 ppm. The remaining aliphatic signals are found at 28.0, 26.9, 25.5 and 25.2 ppm. The trifluoroacetic acid accounts for the sharp quartets at 162.6 (carbonyl) and 116.6 ppm (triflourmethyl group).

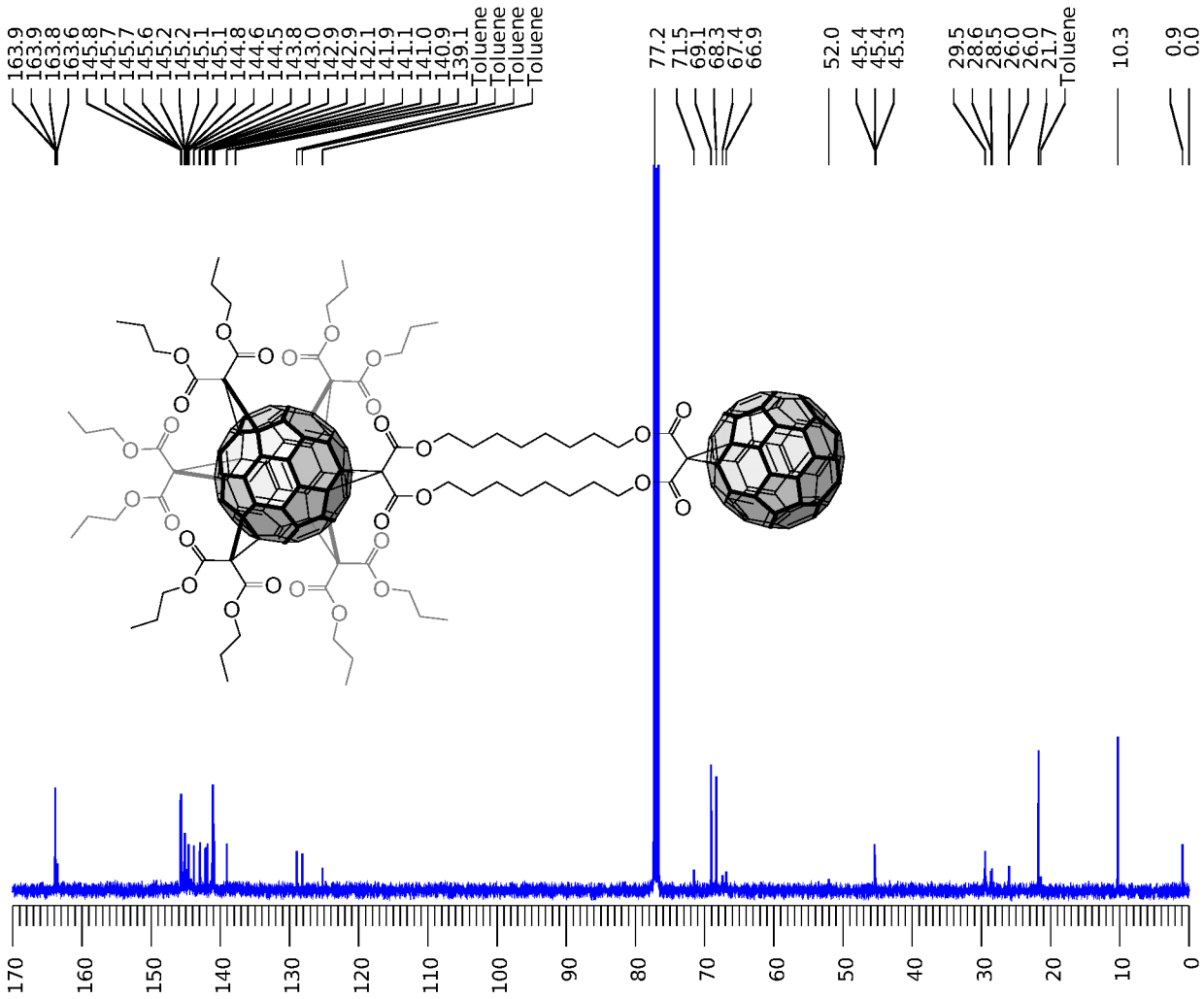


Figure 31: ^{13}C NMR spectrum of the intermediate **79** (100 MHz, $CDCl_3$)

In the carbon spectrum of **79** (figure 31), the most striking eye-catcher are the different carbon signals of the monoadduct between 145.8 and 139.0 ppm. Due to the magnetic effects of the free fullerene, the carbonyl signals are split to four at 163.9 (2×), 163.8 and 163.6 ppm. At 71.6 ppm, the C_{60}-sp^3 signals from the monadduct-sided carbons appear. Further high-field, at 69.6 ppm, the C_{60}-sp^3 signals from the hexakisadduct are located. The protons of the CH_2O groups are distributed the following way: at 68.3 ppm, the ones of the propyl groups are unified in one peak. The signals of the spacer are at 67.4 and 66.9 ppm, for the different ends of the spacer. At 52.0 ppm, the carbon of the 2-position of the monoadduct-side malonate is located. the corresponding carbons on the hexakis-adduct side split due to the asymmetry to 45.43, 45.40 and 45.26 ppm. The carbons in the octyl-chains at the β-position to the oxygens resonate at 29.5 ppm, the ones in the γ-position are split to 28.6 and 28.5 ppm, and, with a smaller split, the carbons in the middle resonate at 26.04 and 25.98 ppm. The mid carbons of the propyl chains appear at 21.7 ppm, and the CH_3 carbons at 10.29 ppm.

To exemplify the NMR spectra on a comprehensive example, the most complex NMR Spectrum, the one of **69** (figure 32), is used. At 145.5 and 141.1 ppm, the signals of the sp^2 carbons of the fullerenes resonate. They are slightly, and irregularly broadened both due to the different environment of both fullerenes and the [5.1]-substitution pattern. At 163.8 ppm, the (irregularly formed) bands of the ester carbonyl groups appear. The carbonyl signals of the amides appear at 156.0 ppm. We observe the signal of the center of the *tert.*-butyl groups at 79.0 ppm, at 69.1 ppm, the sp^3-signals of the fullerenes appear. At 66.9 ppm, an irregular group of signals for the CH_2O-groups is observed. The carbons of the 2-position of the malonates appear at 45.4 ppm. The strongest signal in the aliphatic region is at 28.4 ppm, where the signals of the methyl groups of the neobutyl group appear. At 40.6 ppm, the methylene group next to the nitrogen appears. The third- and fourth- last signals of the aliphatic end-chains appear at 31.8 and 29.9 ppm. The second- last and last signals of it, of course, come at 22.6 and 14.1 ppm. We see the aliphatic signals in β-position to the alcohols at 29.2 ppm. Some small signals are visible at 29.6, 26.1 and 25.3 ppm, which are related to the α, β and γ-position to the spacer. At 28.3, 26.4, 25.8 and 25.6 ppm, the remaining aliphatic carbons appear, one of which must be hidden in the left shoulder of the signal at 28.4 ppm.

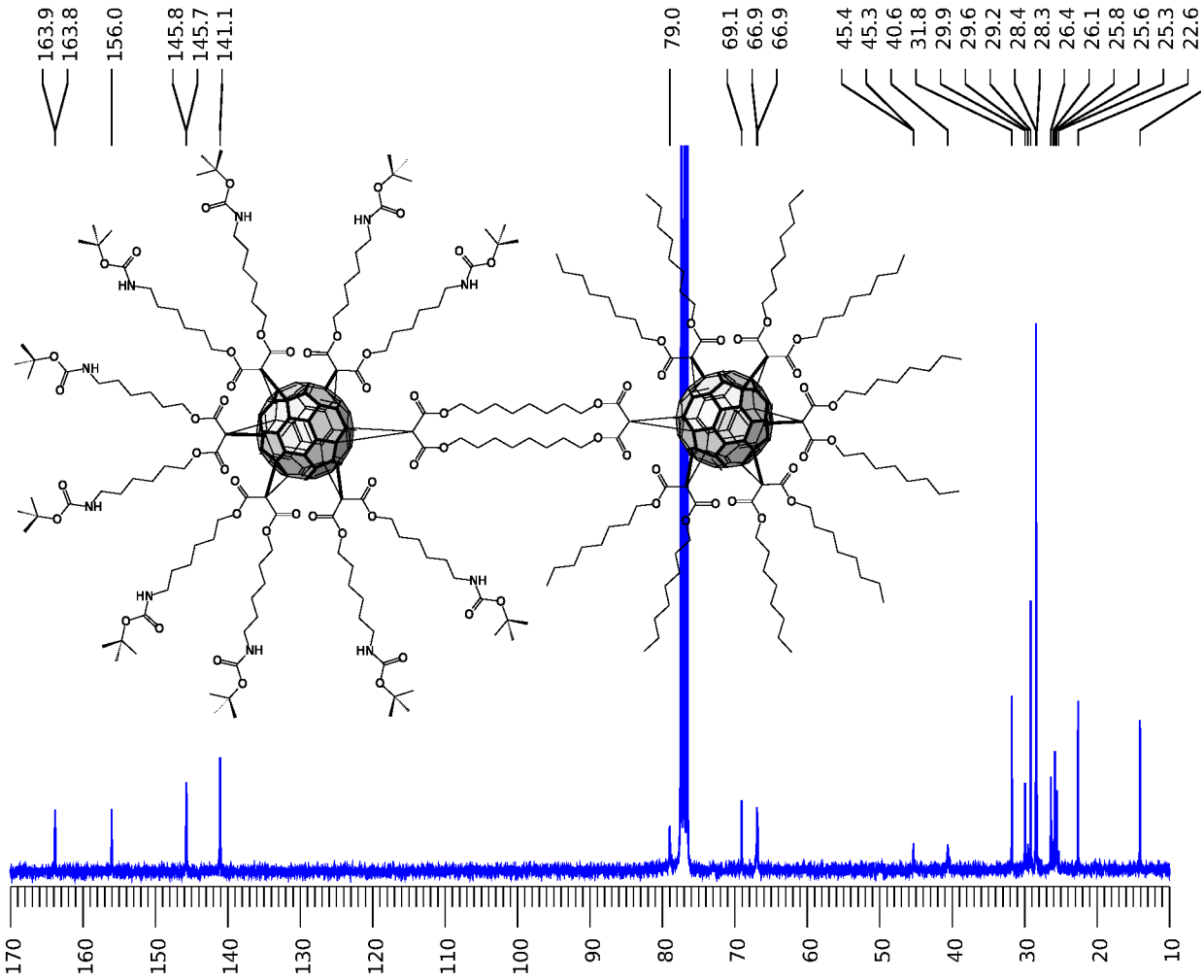


Figure 32: ^{13}C NMR spectrum of the protected amphiphile **69** (75.5 MHz, $CDCl_3$)

4.5.1. Investigation of the Micellar Aggregation

The investigation of the micellar aggregation behavior in aqueous solution included the measurement of the critical micellar concentration. Afterwards, the constitution of the micelles could be studied by means of cryo-TEM at concentrations above the obtained critical micelle concentration.
The structure was discovered by means of transmission electron microscopy, and the size was verified by dynamic light scattering.

4.5.2. Conductometric Titration

The cationic derivatives were highly water-soluble. Of each substance, 1 mg of it would dissolve in 20 µL of water.

In order to get an initial clue about the aggregation behavior, the critical micellar concentration of the compounds was determined by conductometric titration. Each measurement was undertaken starting from 9.5 mL of pure (electrolyte-free) water. The substance was diluted to a specific concentration in water and added to the measurement cell in portions with equal volume and delay. The step in the derivative of the conductivity was seen as critical micellar concentration. The droplet size was 10 to 20 microliters, the added amount of sample solution was about 1 mL.

Results can be seen in table 3.

From the measured graph of the conductivity against the concentration, an arbitrary linear term was subtracted, to make the expected kink more clearly visible along the counterion term. In compound **80**, additional, softer arrangement transition points at 6.9 µmol/L and 580 µmol/L have been observed, as shown in figure 34

82	4.037	µmol/L
83	10.044	µmol/L
80	50.6	µmol/L
84	0.679	µmol/L

Table 3: Critical micellar concentrations of the amphiphiles

The titration curves (figure 33) were fitted with two straight lines along the ranges of the graph which ocularly were not part of the actual elbow of the kink. The intersection point of these straight lines was seen as the critical micelle concentration. As this method has a subjective element, and had deviations of up to 20 % (in the case of **83**, the accuracy is assumed to be not better than 30 %, since both weighing and pipetting errors could be around 5 % each.

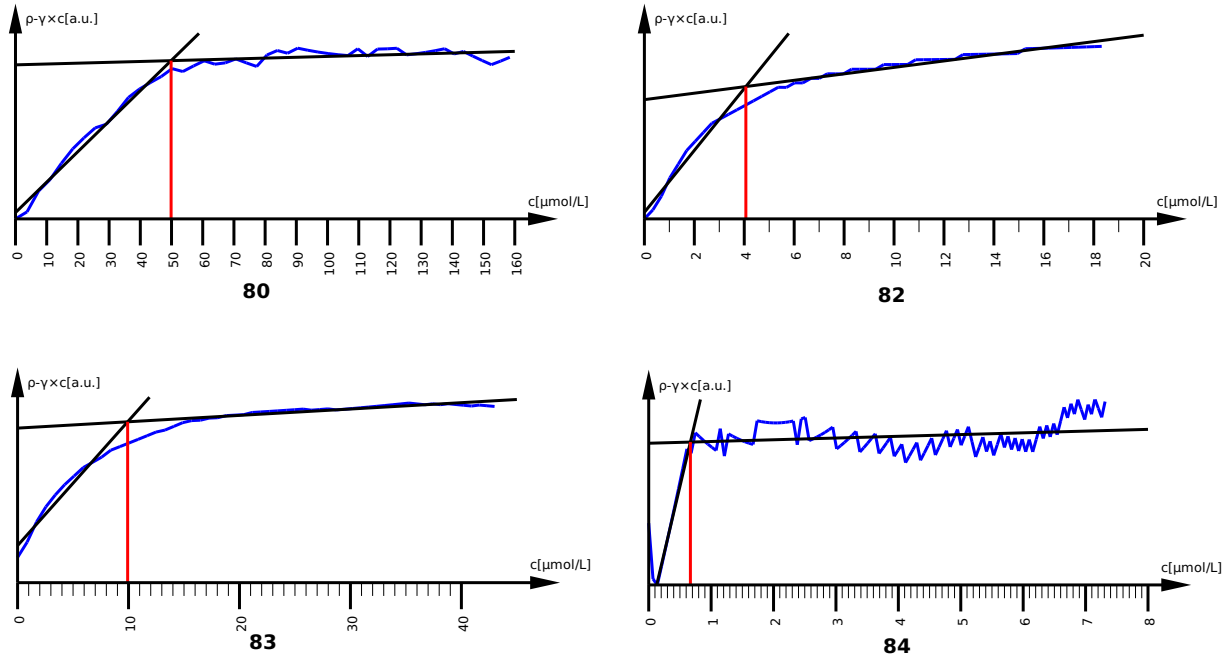


Figure 33: Conductometric titration curves to determine the CMC. To make the kink more visible, a straight was subtracted to make the graph end nearly horizontal

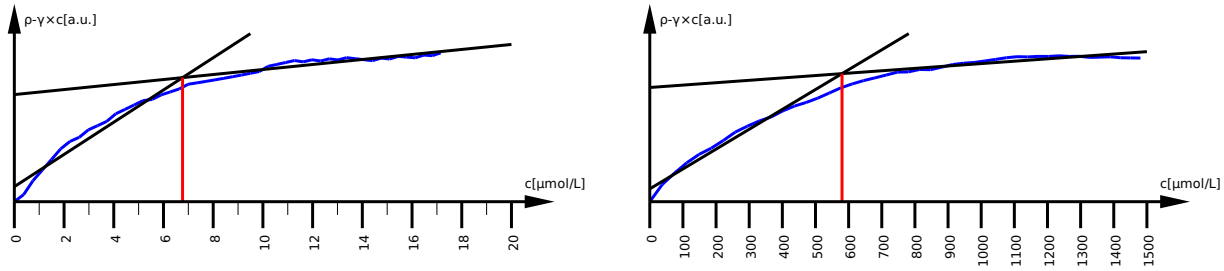


Figure 34: Further titration curves of **80** showing more diffuse kinks. To make the kink more visible, a straight was subtracted to make the graph end nearly horizontal

4.5.3. Transmission Electron Microscopy (TEM)

Thanks to Christoph Böttcher and co-workers,[108] CRYO-TEM pictures were taken from all aqueous aggregates of the amphiphilic compounds. The transmission electron micrographs show predominantly well-defined micelles which were only a few nanometers large (figure 35). This means, although the predominant amount of the compounds' surface is unpolar, the molecules do not form contacts on most of these points. No regular micelles were observed. The only other type of aggregation encountered were straight, non-branched rods with a defined, invariable thickness.

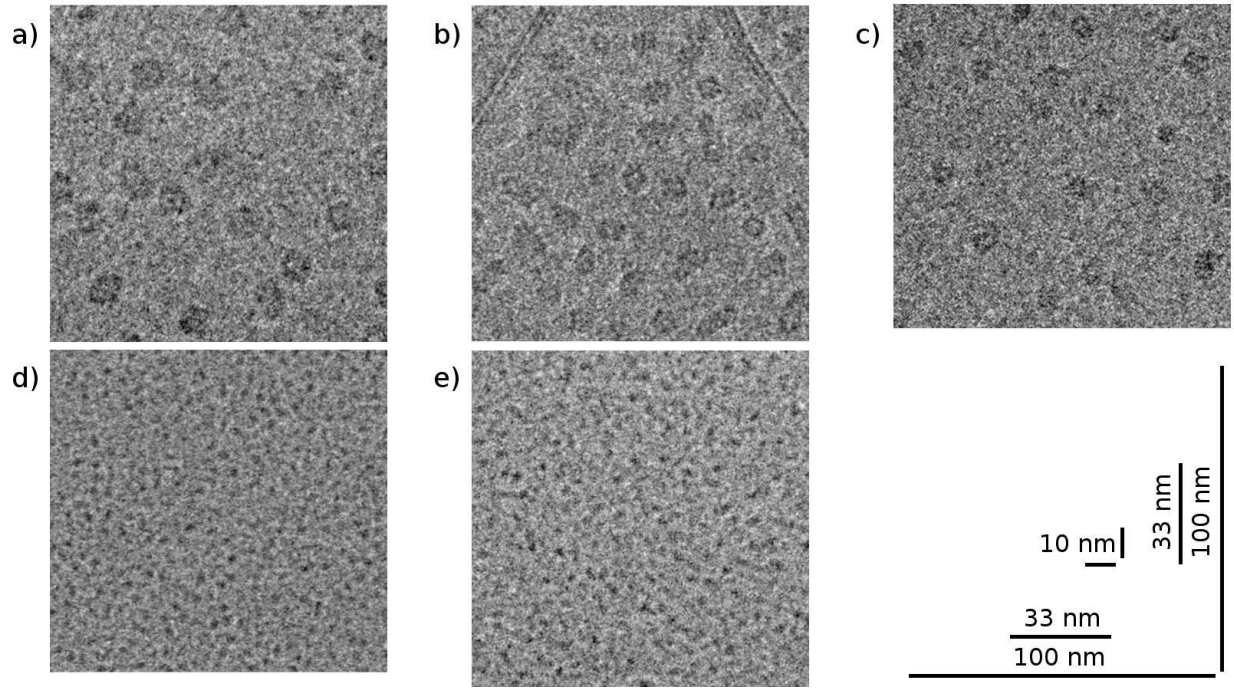


Figure 35: Micrographs of the compounds in pure water. a) **84** b) **83** c) **82** d) **81** e) **80**

A very likely explanation how such a good water-solubility could be possible amongst these molecules would be that the free fullerene hexagon rings were hydrated. This can be made more obvious when comparing the molecules with the simple fullerene, which can also be solubilized in water by giving it a stable hydrate hull.[109] Moreover, Beuerle and co-workers have observed a salt-like behavior Thus, mainly the spacer areas of the molecule consitute the force responsible for the aggregation. This lies well in accordance with the size of the aggregates of the bolaamphiphilic molecules **80** and **81**, which was calculated by Boris Schade[108] to be similarly large. The hydrophilic molecules **80** and **81** did not aggregate or just dimerize, so the unpolar substituents of the molecules must be necessary for the aggregation as well. The tendency that the alkyl chains barely effect aggregation lies in accordance to the fact that longer unpolar chains, as in **84**, lead to no higher aggregation than the said micromicelles.

When the hydrophilicity of the substances was attempted to raise by reducing the pH amongst the ammonium amphiphiles (figure 36), the aggregates became shapeless and bigger, but did not form more elongated structures. If the pH was raised amongst the carboxy-amphiphiles (figure 37), which were linear aggregates anyway, these aggregates build larger and thicker rods, but still with straight corners. The explanation for the counterintuitive behavior could be the increase of the ionic strength. A more notable insight in both cases is that, judging from the straightness of the shapes, the elongated structures are some sort of crystalline arrangements, not random forms of clotting.

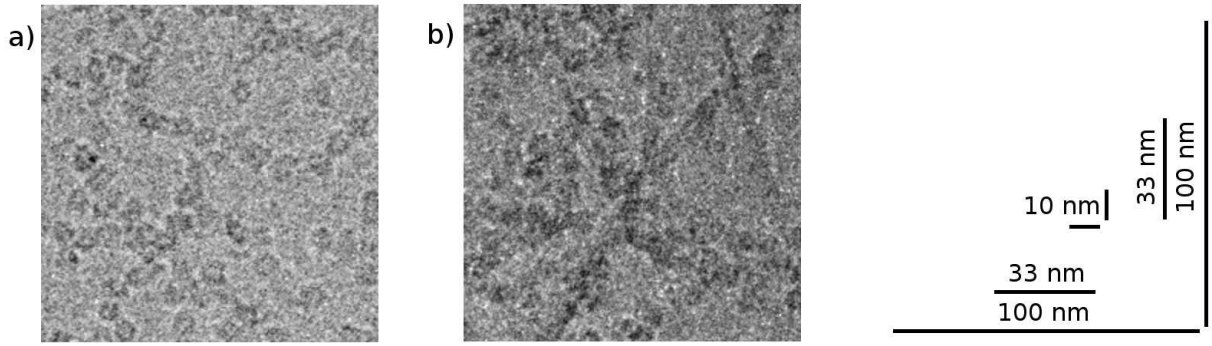


Figure 36: Aggregates of the compounds **81** (a) and **82** (b) dissolved in overly acidic water

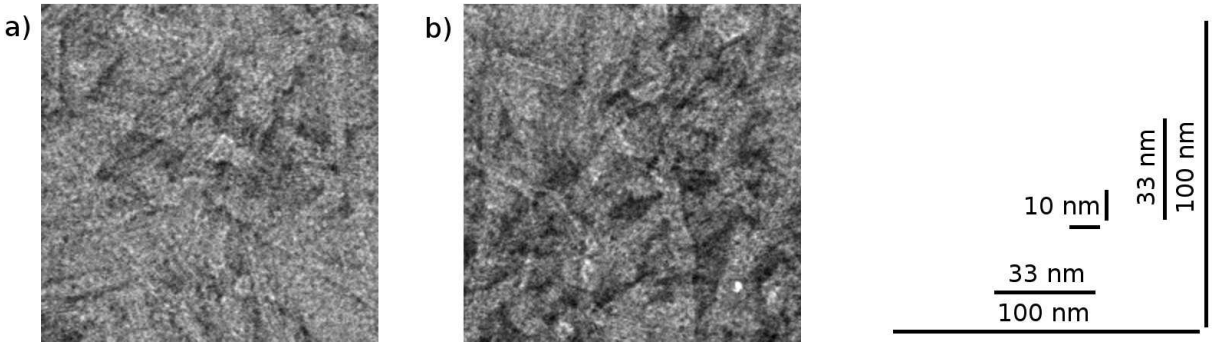


Figure 37: Anionic compound **85** dissolved in overly basic conditions

4.5.4. Dynamic Light Scattering Experiments

Thanks to Jasmin Düring,[110] from **82**, **80** and **84**, the micellar size was determined by means of dynamic light scattering (table 4). The results found matched the TEM results very well. Each measurement revealed the presence of larger particles, which had no correspondence in the TEM pictures. An explanation for them would be the polyelectrolyte effect.[111] This effect dampens friction of polymers in a certain range of concentration. In DLS, they would move farther and appear bigger, so both experiments can be seen as mutually supporting each other, though.

Compound	TEM radius	DLS	
		radius	peak width
80	1-2 nm	0.6 nm	0.09 nm
81	1-2 nm	n. A.	n. A.
82	3-4.5 nm	3.2 nm	0.4 nm
83	3.5-5.5 nm	n. A.	n. A.
84	4.75-6.5 nm	5.1 nm	0.18 nm

Table 4: Comparison of micellar radii of the amphiphiles measured with DLS and TEM

4.5.5. Theoretical Aspects of the Micellar Aggregation

Interpretation of these results was done by Christoph Böttcher, Kai Ludwig and Boris Schade.[112] In their work, they evaluated large sets of thousands of molecule images using the *multivariate statistical analysis*[113] to generate three-dimensional images of the pictures. Their theory resulting from these evaluation now refers to the size of those globular aggregates. It is not possible to give a direct explanation for the ratio of unpolar residues to the aggregate size due to increase of stickyness. Such a construction would either include exposition of surface area to the outside of simple micelles, which expose binding capacity for a varying number of addends. An increase of the inter-micellar binding sites would result in branching, creating higher dimensional polyaggregates than spheres. The other way stickiness could directly affect size would be, that the surface amphiphiles had to shelter a higher amount of unpolar dendrimer area inside of them. As the ratio of inner area to outer area increases linear with the diameter, the micellar size would be controlled by its surface-to-volume ratio. This theory has three drawbacks: First, the smaller micelles (see figure 38 c)) are so small that they have both sides exposed to the surface. As thus, even unpolar parts are exposed, any further increase of lipophilicity would result in condensation of the free, unpolar ends, to a precipitate. Second, the aggregates found seemed to be highly defined. A micelle with an inner area of unpolar content, but with even some polar ends of stray molecules inside, would be expected to be chaotic since the disorder requires entropy. But most obvious is that the micelles were filled with water. This means that the size is determined by some other effect than the ratio of hydrophilic and hydrophobic area, which is nearly size-independend on water-filled constructs. Taking in account that any of the unpolar substances is constrained to its polar counterpart, the reason becomes clear: to hide the molecule totally in the micelle, the polar part would also have to enter, which is unfavorable.

Thus, the big micelles must form from aggregation of defined smaller adducts, which define a finite aggregation pattern whose shape defines the size. The obvious starting point for theories about the structure were the aggregates of the bolaamphiphiles. They were considered as prototype for the smaller micelles. Although it could not be determined how many molecules they contained, and much less what their structure was, it was reasonable to assume that they were aggregating at the unpolar spacer part. Such constructs could consist of 2, 3 or 4 dumbbells (figure 38).

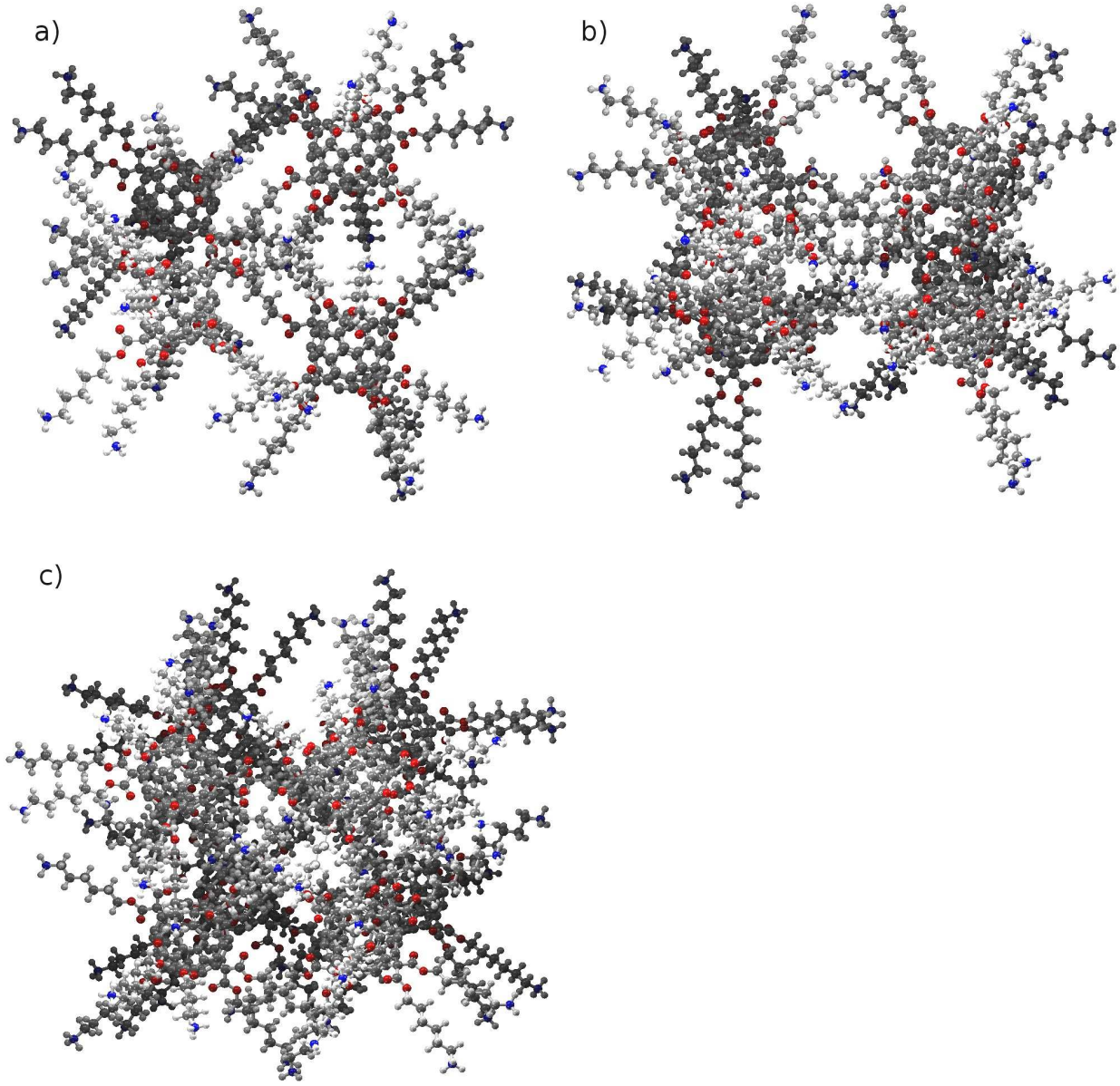


Figure 38: Computer models of different possible aggregates of **80**. a) dimer; b) trimer; c) tetramer

In order to match the size of the aggregates, the best symmetric model for the macroaggregates would consist in a dodecahedral arrangement, where twenty of those micelles constitute a dodecahedron. At least four molecules of **83** or **84** must build a micelle, so that this micelle has three unpolar “connection sites” on the outside around a three-fold rotation axis, while there are hydrophilic sites on both sides of the plane built by these sides.

The cubic micromicelles forming such a compound from them would have their (originally tetrahedral) symmetry distorted. While the three unpolar outer sides that connect them to aggregates need to be exposed, the fourth would be exposed to the very fringe of the sphere. It would be energetically preferred to be drawn further inside of a micromicelle (figure 39 c)). And since the inner of each hydrophilic points has a different environment than the other on the outside, its angle can be warped to be different from 90 degree. In order to seperate the lipid area better from the aqueous one, it could be favored to pull it into the micelle, lowering the inner tip angle below 90 degree (b).

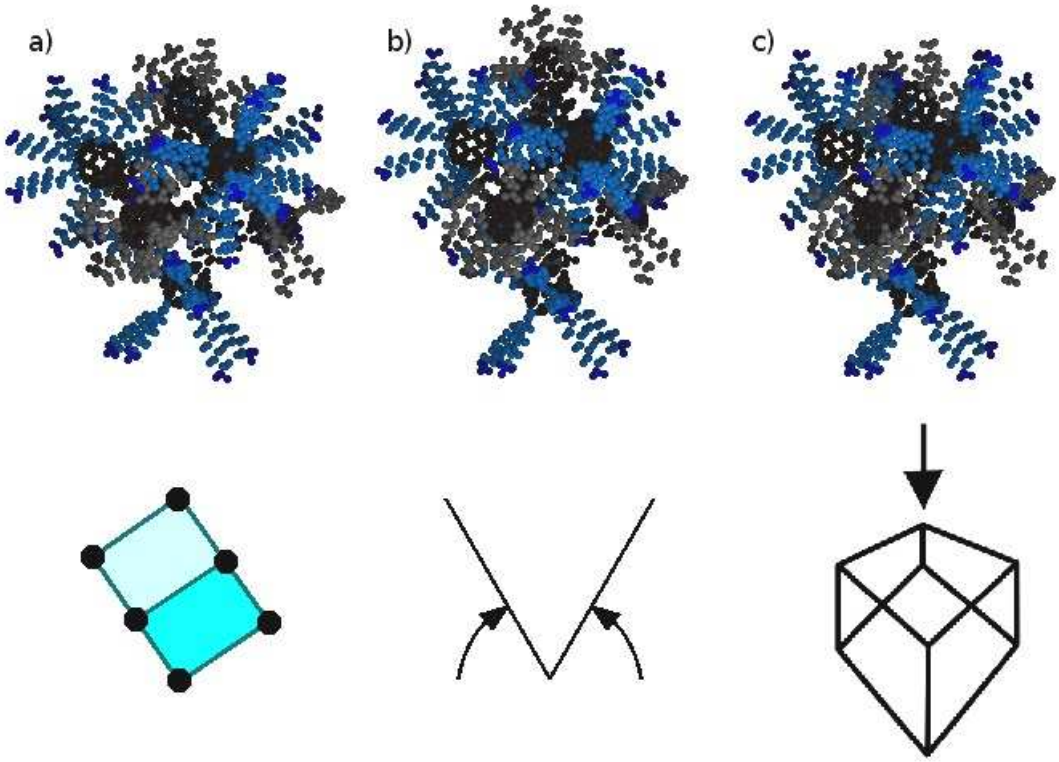


Figure 39: Warps expected on a micromicelle when forming a symmetric larger aggregate
The chains on polar ends are dyed blue for better visibility

The big aggregates are now formed so that the (polar) inner tip points to the inside (figure 40).

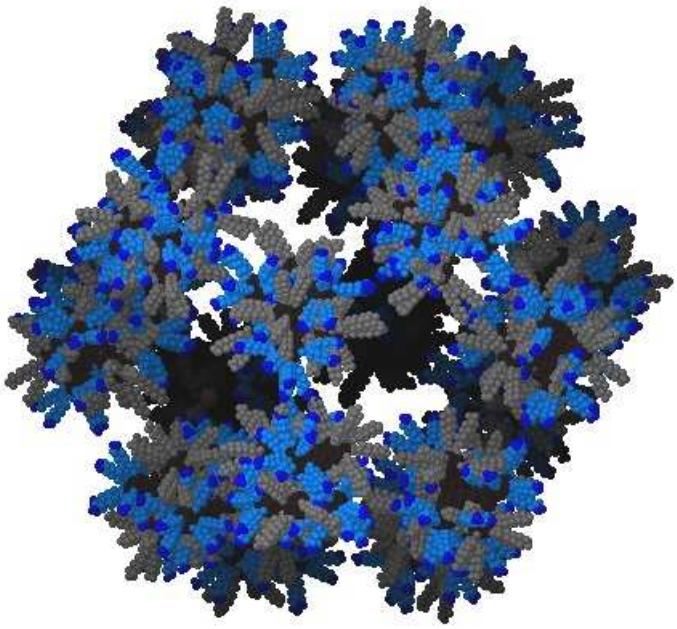


Figure 40: Dodecahedral aggregate of amphiphile precursor **84**
The chains on polar ends are dyed blue for better visibility

It was also seen that **82** would form another form of smaller arrangements, which can be best described so that the micromicelles resemble the points of a cuboctahedron, but with little further difference from the dodecahedral structures (figure 41).

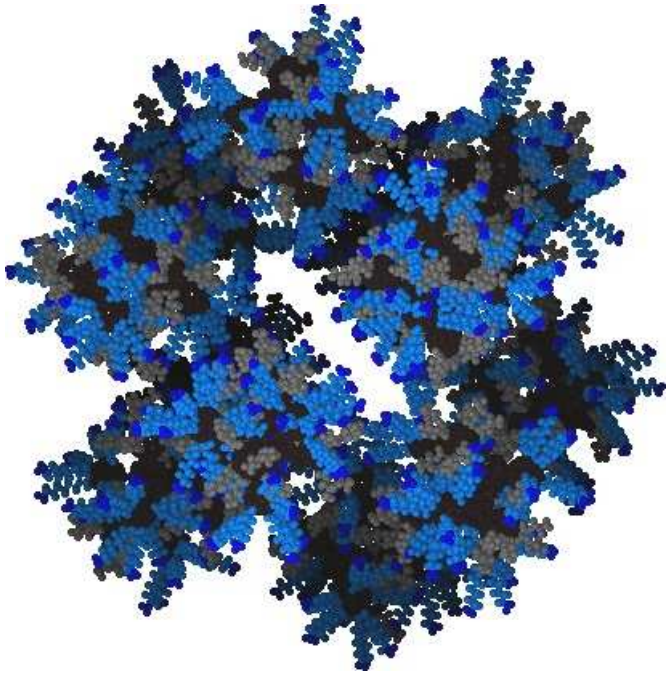


Figure 41: Cuboctahedral aggregate of cationic amphiphile **82**
The chains on polar ends are dyed blue for better visibility

The one-dimensional structures found now consist in 6-membered rings, similarly formed as the spherical structures. Multiple of those rings form a tube, so the micromicelles are still intact in this case. This form of arrangement has been shown by exploring the different side-views, as well as from occurrences where the rod direction was perpendicular to the image plane (figure 43, detail). Assuming it is a hexagonal structure, it must consist of two stripes from the side where a plane points towards the viewer, and of three stripes when an edge of the hexagon points towards the viewer. Exactly these two views were found when averaging the side-views of the rods (figure 42).

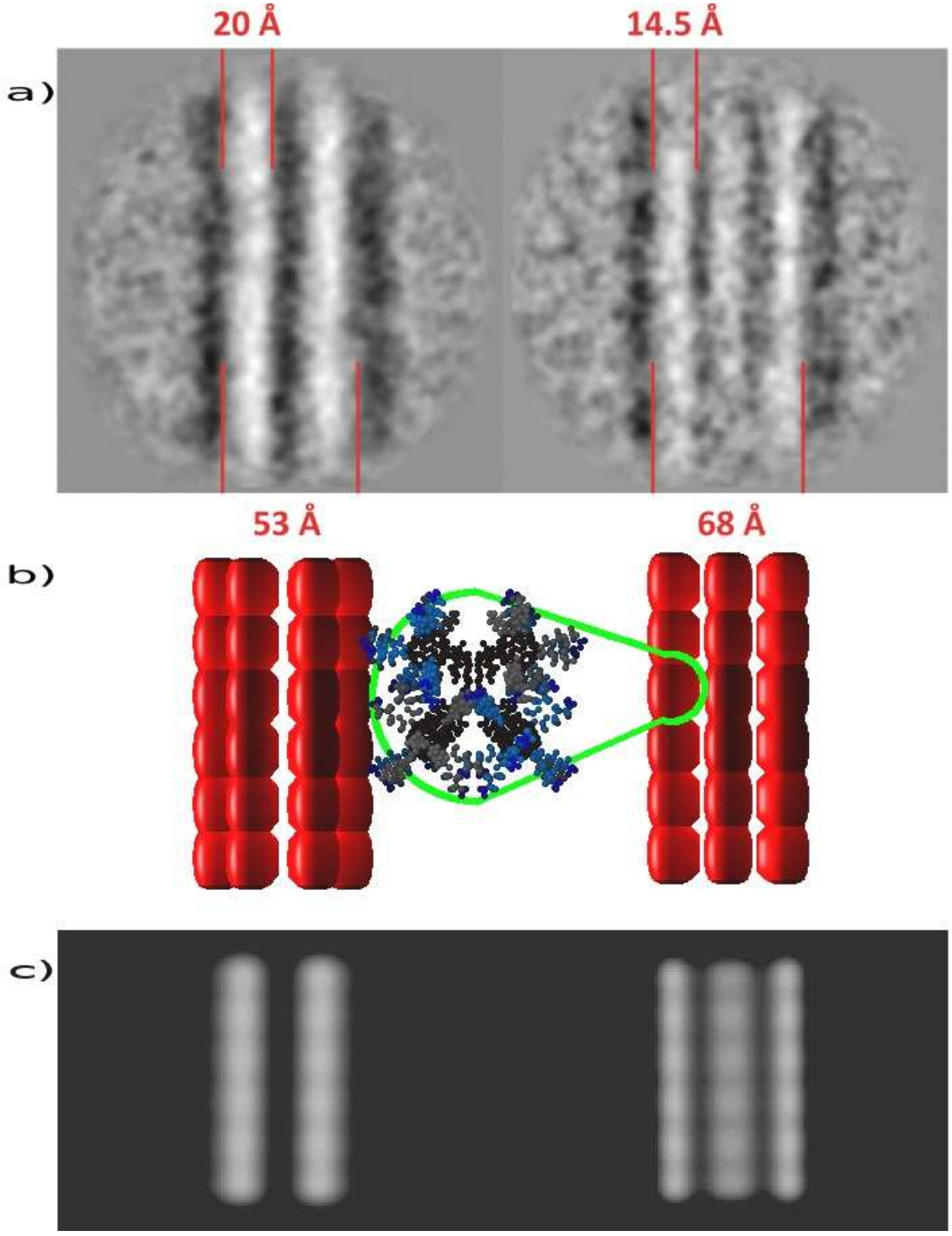


Figure 42: Projection of a tube side into the plane. Averaged from TEM pictures (a), modeled (b) and calculated (c)

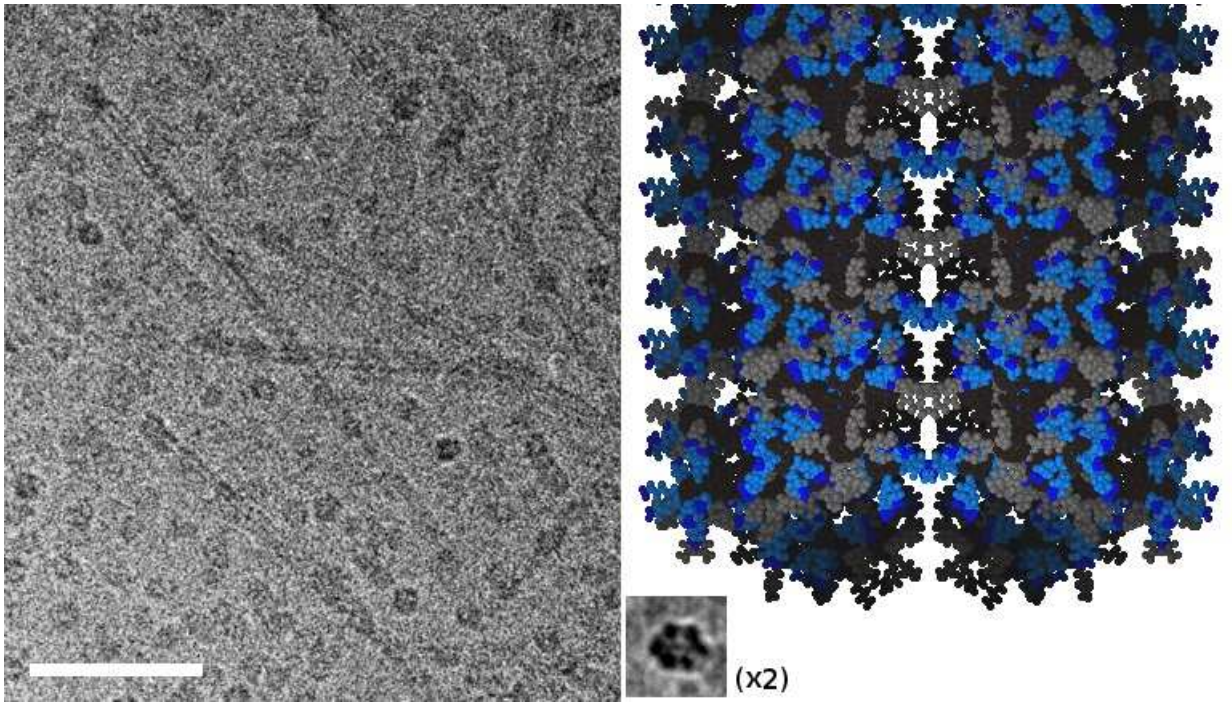


Figure 43: The tubular structure formed from **83** depreferentially without buffer.
Scale length = 50 nm The chains on polar ends are dyed blue for better visibility.
Detail in the middle: Top-view on end of rod.

In order to investigate whether the type of hydrophilic residues was responsible for the uniformity of the aggregates, another amphiphile, **85** was tested. This amphiphile was “anionic”, it carried carboxy groups. Since it is a known fact that Bingel-carboxylates get hydrolyzed in pH above 9,[65,82] the substance was created in protonated form. It was unsoluble in pure water. When the pH-Value was carefully raised using buffers, it was soluble at pH values starting from 8. Because of the needed buffer (sodium phosphate), conductometric titrations were impossible, but TEM micrographs were measured under these conditions (figure 44).

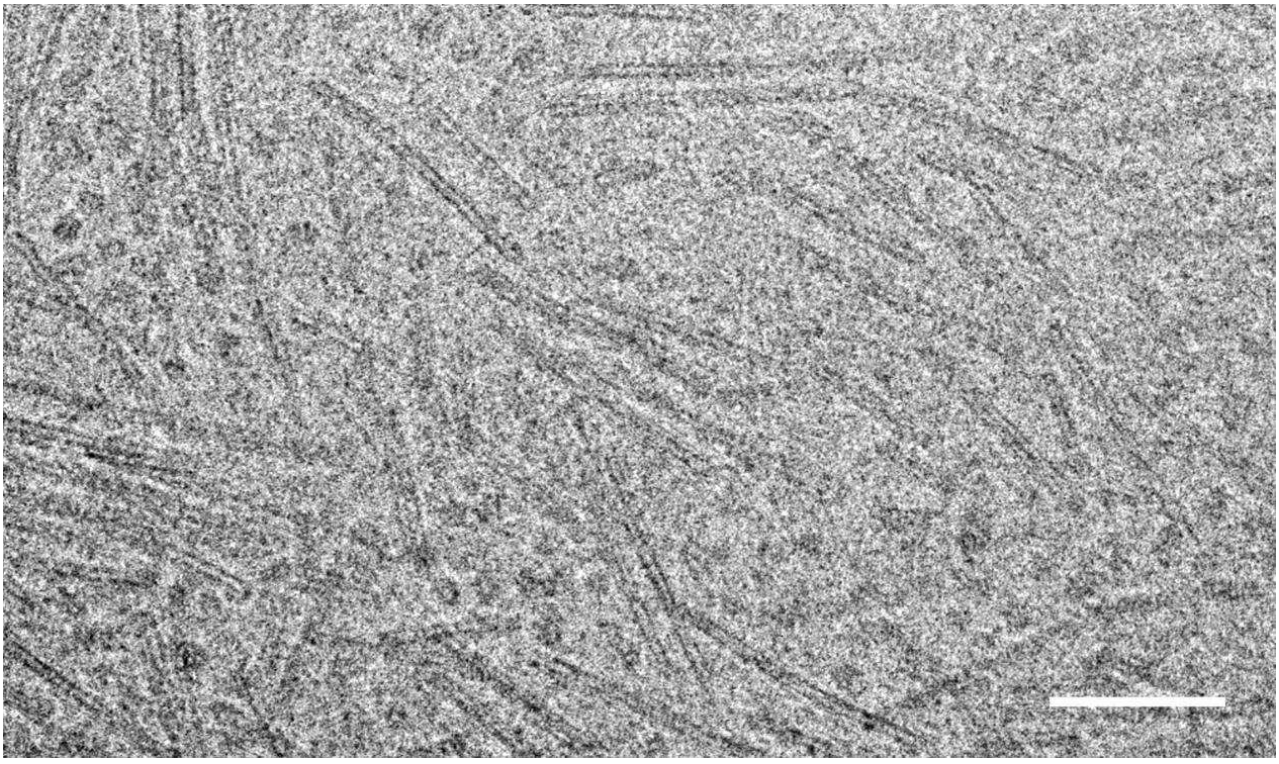


Figure 44: TEM picture showing the aggregation of amphiphile **85**. Scale length: 50 nm

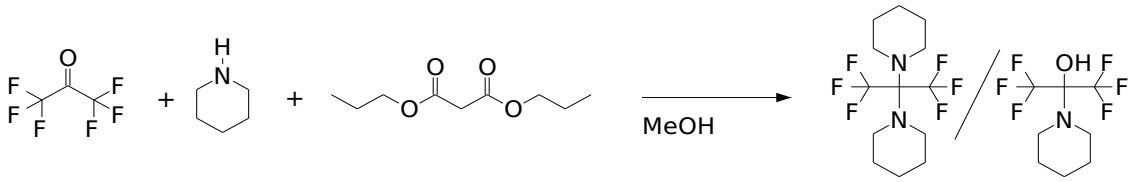
Due to the imperfect deprotonation and polarity of the buffered water, well-defined rods built up instead of spherical aggregates. In an attempt to dissolve this compound in water, 23 mg of it were first dissolved in 1 mL of water and 4 mL of methanol. Then the methanol was evaporated at 48 °C and 100 mbar. The residue was 850 mg of a gel (figure 45). It was not possible to dilute this gel with water. The gel kept its shape and did not mix with further added water.

Figure 45: Gel-like structure build up from **85** in a 100 mL round-bottom flask

Due to the lack of a crystal structure of this amorphous aggregate, the reasons for this behavior can only be guessed, but it is likely that it forms domains of unpolar residues at high concentrations, which do not allow water to pass, so blobs of water are trapped inside of unpolar domains. The aqueous domains, in turn, prevent collapsing of the structure, which in turn prevents the remaining methanol from leaving, resulting in a mutual stabilisation of the phases.

4.6. Finding a Protecting Group for the C-H-Acidic Position of Malonates

Despite of this success, a tempting question was how to create a real protecting group for malonates. The selectivity archieved by the chlorides is usable for the intended purpose of feasibly linking fullerenes together. On the other hand, the malonates on the unchlorinated end did not become entirely unreactive. They are still nucleophiles, which can do unwanted attacks. Obvious substrates for this attack are the chloride atoms on the activated malonates, or other keto-groups. This could limit the substrate scope of the Bingel reactions. Also, as the mono-addition experiment told, the reaction still went worse than the usual Bingel reaction. With that given, it is still of interest to find an actual protecting group. Many substances, as aldehydes or alkyliodide reagents are capable of attacking the carbanions of a deprotonated malonate. But since a protecting group must fulfill the condition of being able to be cleaved off again, such irreversible addends would not be of any help. 9-(Methyl)fluorene-1'-yl, or Fmoc groups are designed to be cleaved of under basic conditions, so they have no protecting effect during a Bingel reaction. The needed molecules had to be hard Lewis acids. Hexafluoroacetone was a candidate. It had been used as protecting group before for alphahydroxycarboxylic acids.[114] The attempted reaction did not occur with DBU as a base. When piperidine was added as a base, fluorine containing piperidine adducts were resulting (scheme 69). It was easily to conclude that perfluoroacetone did not attach either due to steric hindrance or the inability to form a double bond to the malonate (which would be due to steric self-hindrance of the planar product as well).

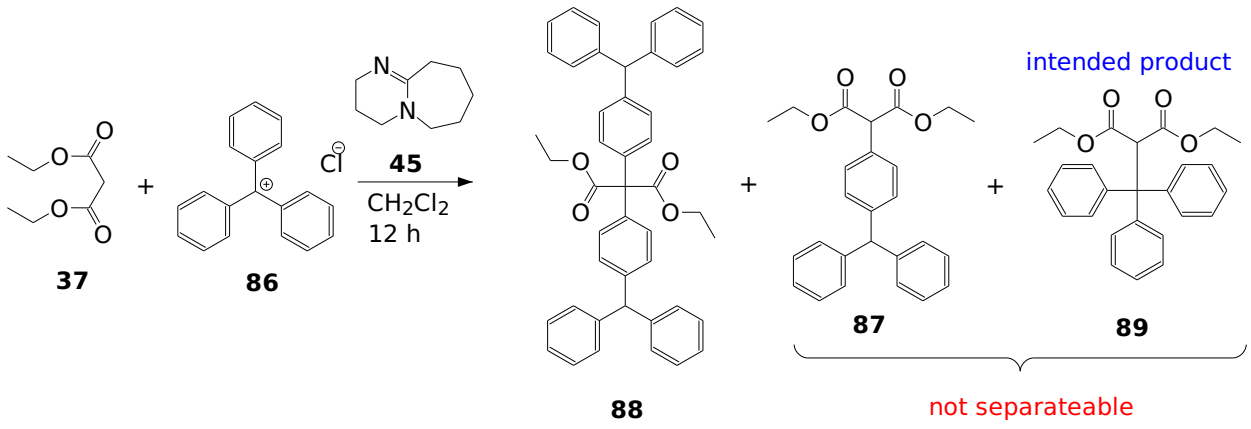


Scheme 69: Side-reaction of Hexafluoroacetone with the base rather than the deprotonated malonate

4.6.1. Triphenylmethyl Cation as Protecting Agent

Triphenylmethane is another carbon electrophile. Its steric hindrance and capability of stabilizing a positive charge would make it a proper candidate for reversible protection of a C-H acidic point. As the cation had been added to diethyl-malonate before using an alcoholate base, and the hydrolysis of triphenylmethane/malonate adducts had been done successfully in ethanol/water mixtures,[115] protecting the malonate with triphenylmethane seemed to be a promising approach.

In order to avoid the use of an alcoholate base, which would be incompatible with the ester groups in the Bingel adducts, the addition (scheme 70) was undertaken with DBU as base - a reaction which was successfully applied to tropylium, see chapter 4.6.3.. Although the yield was rather low (13.5 %), formation of a mixture of end-on adduct of triphenylmethane, triphenyladduct **87**, was observed, interestingly accompanied with an equal amount of the di-adduct **88** (12.7 % Yield). This showed that a single group did not really work as a protecting agent, as due to the low steric hindrance, substances like triphenylmethyl chloride **86** could bind. Attaching it twice posed a statistic difficulty on the intended stochastic reaction, on which a spacer with two malonates had to be (completely) protected on one side but be left unsubstituted on the other.

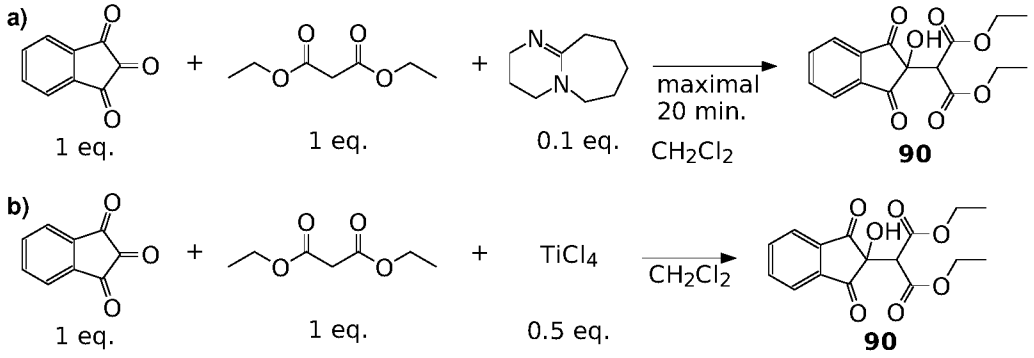


Scheme 70: Attempts to use the triphenylmethyl cation as protecting agent

The doubly triphenylmethane-substituted malonate can furthermore not be deprotected anymore. Neither HBr/acetic acid nor boiling in water could cleave off the diphenylmethylphenyl groups. Because of the low yield and the difficulty to separate from triphenyladduct **87** from **89**, which would have become even worse on more complex malonates, this approach was withdrawn.

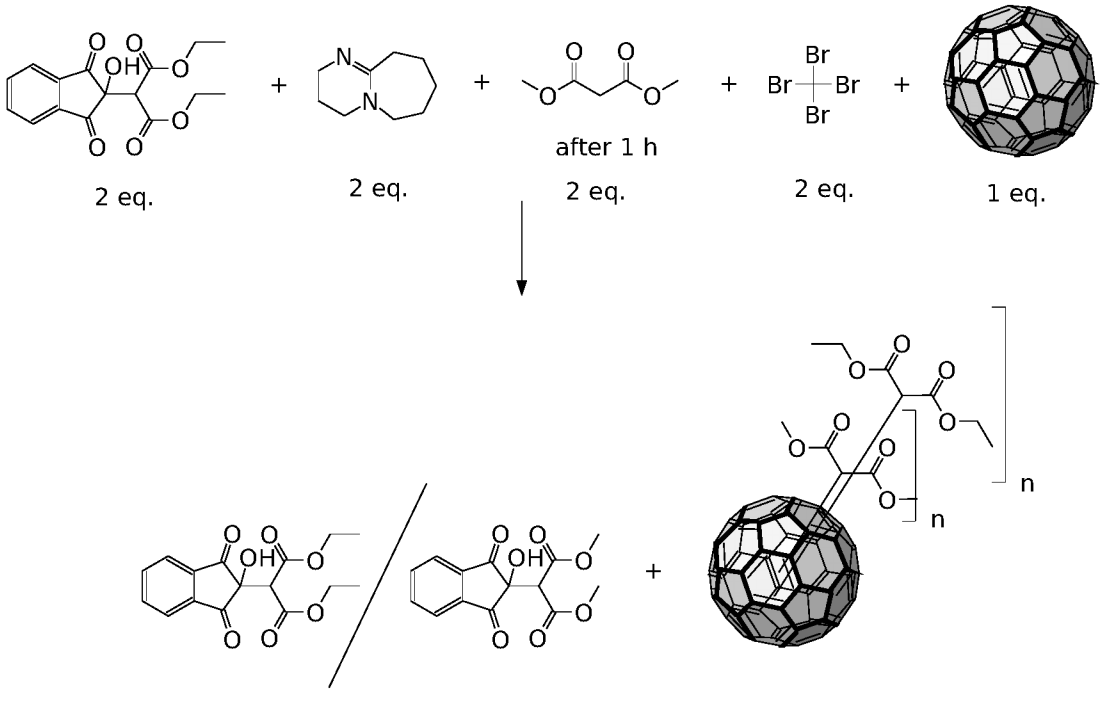
4.6.2. Ninhydrin as Protective Agent

As in theory, any stable electrophile attached to a malonate would do, also the central carbon atom of ninhydrine might be able to protect diethyl malonate. Addition of ninhydrine, with DBU as base to diethyl malonate went smootly at room temperature in dichloromethane and was finished after 20 minutes (scheme 71).



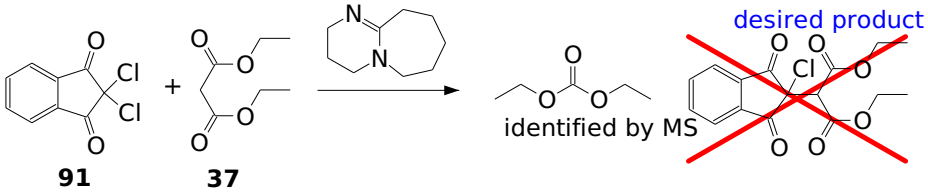
Scheme 71: Binding Ninhydrine to the C-H acidic position of malonates

However, when a malonate, which was protected this way, was subjected to the Bingel conditions in the equimolar presence of an unprotected malonate, and one equivalent of base, sufficient to attach one malonate only (scheme 72), the resulting fullerene fractions were equipped with an equimolar share of both malonates, while the recovered "protected" malonate had all of its carbonyl signals split, suggesting that it did shuffle under those conditions. Evidently, the addition of the malonate was reversible under basic conditions.



Scheme 72: Ninhydrin-protected diethyl malonate is still attached to a fullerene in concurrence to dimethyl malonate

Any attempt to protect the alcohol from double-bonding back to the fullerene failed, as no reaction occurred with addition of any electrophile to it. Substances that were tried were methyl iodide, trimethyl silyl chloride, and acetyl chloride. Sulfuric acid was also tried in order to cleave off the alcohol and the attached proton as water, but it led to no reproducible results. Titanium tetrachloride also failed in an attempt to cleave off the alcohol, but interestingly, it accomplished the attachment of the diethylmalonate to the ninhydrine. Replacement of ninhydrine by 1,3-indanedione-2,2-dichloride **91** was another approach to combat the basic instability of the adduct. The nucleophilic adduct of diethyl malonate to 1,3-indanedionedichloride would be protected by a pre-formed leaving group, the chloride anion, which would require a hydrolysis of a C-Cl bond to be cleaved off again, which could be possibly stable under the Bingel conditions, or cleave off immediately to form a double bond. When indanedionedichloride **91** was subjected to the addition conditions, no substituted malonate was observed (scheme 73). The alcohols on the malonate were later found as a carbonate, possibly by some complex rearrangement of the unstable product.

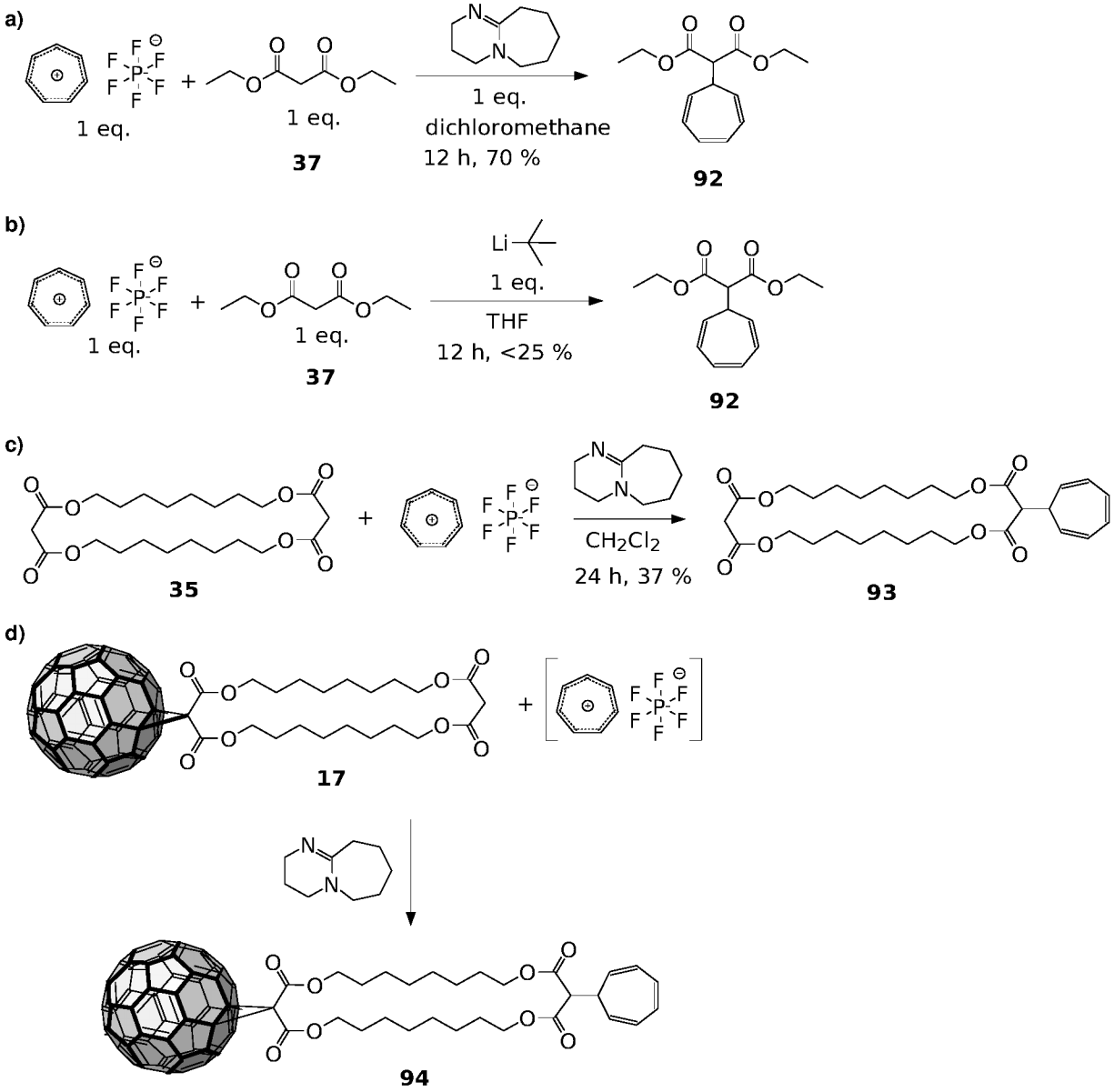


Scheme 73: Strange decomposition reaction of Indandione dichloride

These findings suggested that building up a double bond from the malonate to a moiety which is unstable enough to be cleaved off again would result in no stable adduct.

4.6.3. Tropylium as a Protecting Group

As a protecting group, tropylium seemed to fulfill the requirements: It was an electrophile, so it could attach a deprotonated malonate. An adduct would sterically hinder an attack on the remaining C-H - acidic proton - or at least on the anion remaining after such an attack. As a carbocation, tropylium would fulfill the second requirement, which is to have enough stability to be cleaved off again.
The connection of the tropylium ion to the spacer **35** under base addition worked as expected (scheme 74 c)).



Scheme 74: Addition of tropylium to a malonate using a base

Unlike **42** or **36**, the carbon NMR spectrum of **93** (figure 47) shows no split of the alkyl signals. There is a splitting of the carbonyl signals, though, and a small split of the alkoxy signals. In the proton spectrum (figure 46), the multiplet of the tropilidene-side C**H**$_2$O groups (which is split between the different sides of the ring plane) is superimposed with the one on the other side. The actual proof for the product is the simultaneous presence of the C-H-acidic protons of the dublet at 3.62 ppm for a substituted malonate and the one at 3.36 ppm for an unsubstituted one, having the correct 1 to 2 intensity ratio.

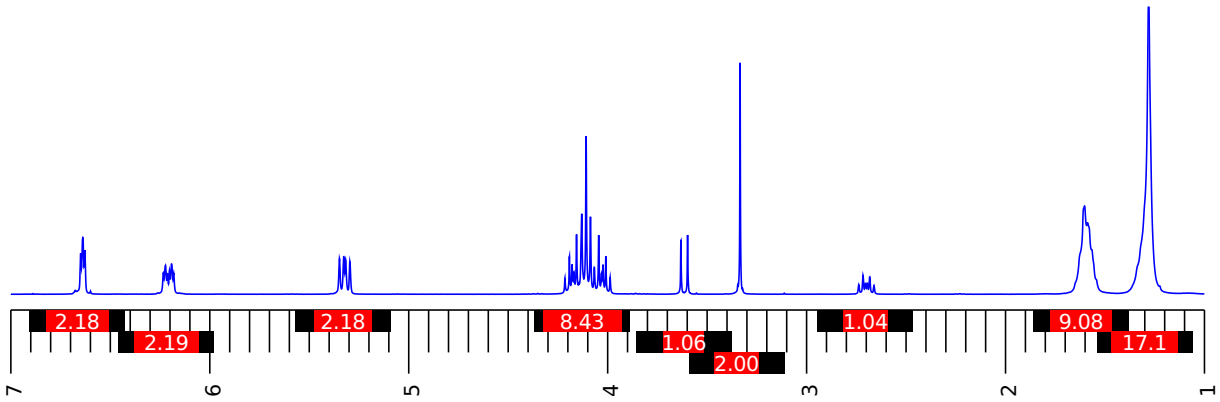


Figure 46: ^{1}H NMR spectrum of a tropylium-protected spacer **93** (300 MHz, $CDCl_3$). Integral zones are shown as red beams

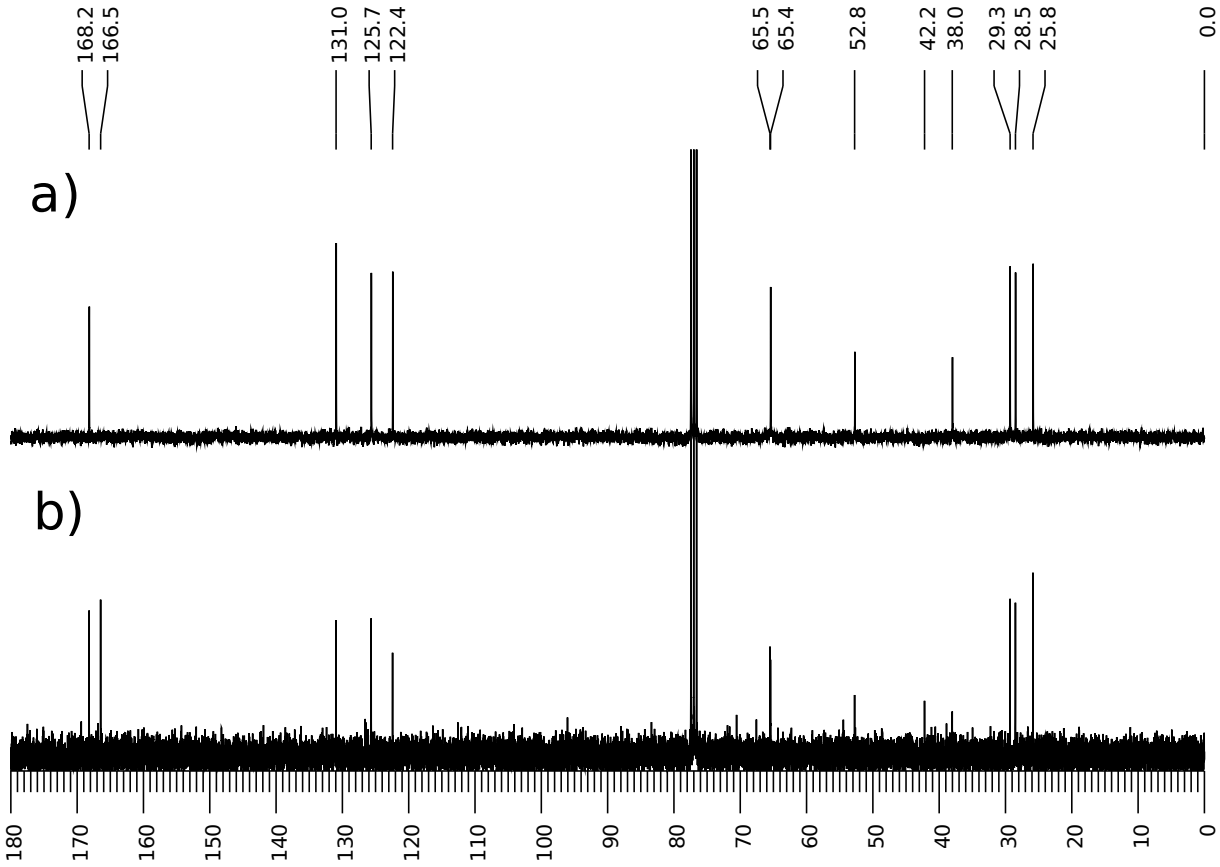
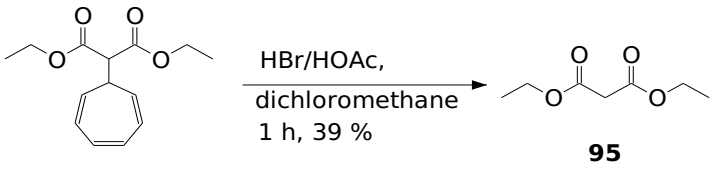


Figure 47: ^{13}C NMR spectrum of a tropylium-protected spacer. a) doubly protected; b) **93** (75.5 MHz, $CDCl_3$)

Another hardpoint of tropylium was that it could be cleaved off again. Multiple acids were tried, including sulfuric acid, and cyanide and fluoride salts, but the onliest effective reagent was hydrobromic acid in anhydrous acetic acid (scheme 75). The strongly acidic conditions needed were orthogonal to the reaction conditions in a Bingel reaction. However, it seemed inappropriate that they had to be so harsh.

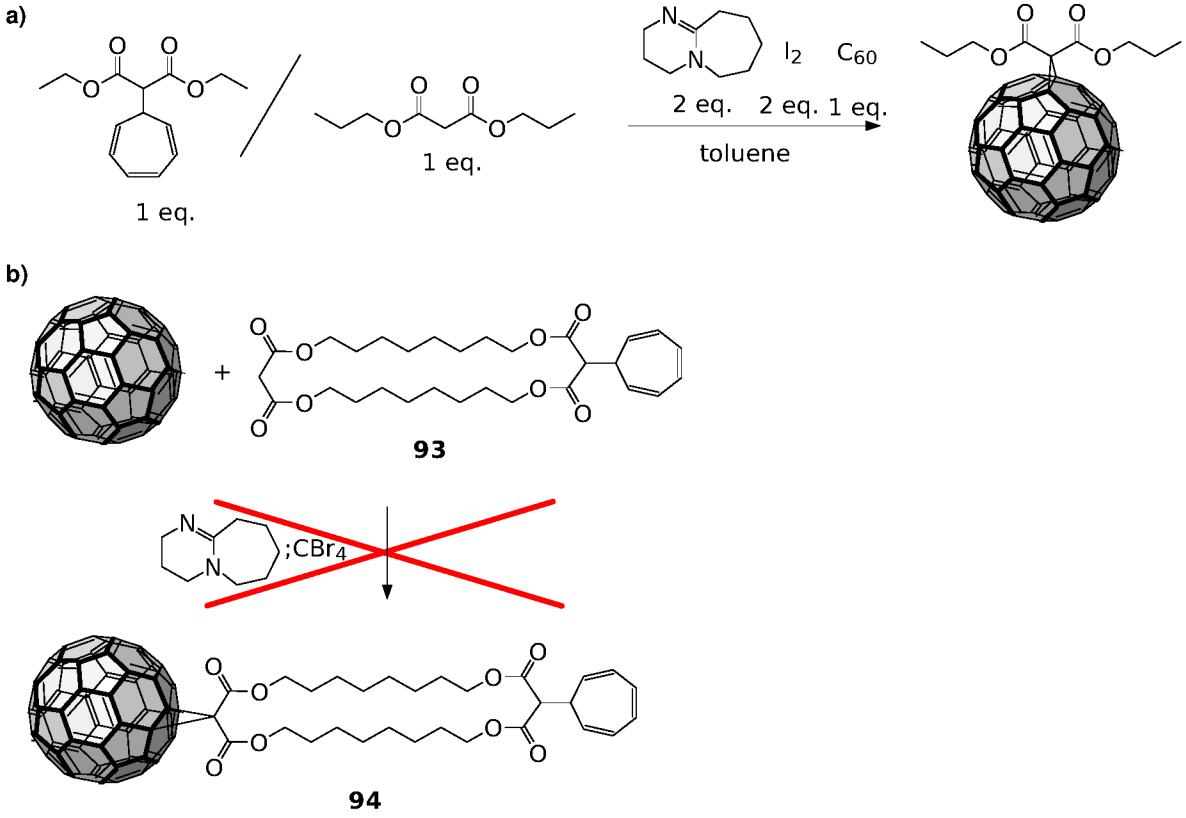


92 **95**

Scheme 75: Cleavage of the tropilidene protective group from a malonate

Literature investigation later revealed that the addition of a malonate to tropylium was already discovered.[116] However, the author was primarily interested in decarboxylating or hydrolyzing the malonate rather than setting it free again.

Now about the effectiveness of tropylium as a protecting group. As seen in scheme 76, only the unprotected malonate added to the fullerene. The protected malonate, however, was only recovered with an impurity, for which unresolvable signals in the aromatic region were observed that were different each time. My guess is that these signals occur due to rearrangement in the triene unit, yielding different types of aromatic rings. Interestingly, this decomposition did not occur if the protected malonate only was exposed to the Bingel conditions (DBU, CBr_4, fullerene) with no free malonate present. In experiment b), the addition of the one-side protected spacer did not give a clean product due to the same syndrome of decomposition.

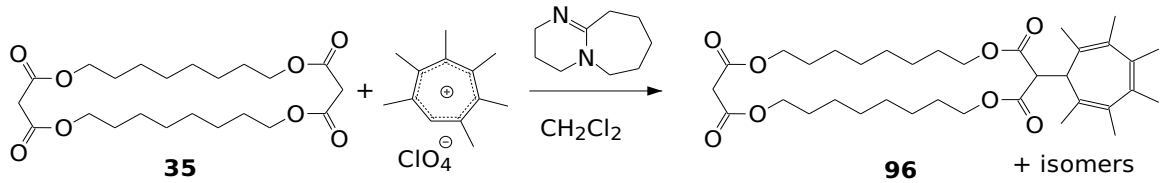


Scheme 76: Experiments on the usability of tropilidene as a protecting group

4.6.4. Attempts to Find a Bulk-Synthesis for the Heptamethyltropylium Ion

In order to get these problems under control, it must be understood that the tropilidene, as which tropylium is constituted in its attached form, is an alkene. As a such, it will undergo addition reactions to several reagents, including bases, the bromyl cation, and similar fragments formed under any reaction conditions. However, alkenes loose much in reactivity when the steric hindrance is large enough.[117,118,119,120]

To check whether the use of this compound was feasible, a preliminary experiment was done whether permethyltropylium would be able to attach to the malonate at all, especially whether electronic effects of methylated tropylium ions would prevent its attachment or not (scheme 77). Hexamethyltropylium was created following the common method of Knoche (scheme 19 a) and c)), and could be successfully added to the spacer **35** to form **96**.



Scheme 77: Addition of hexamethyltropilidene to cyclo[2]-octylmalonate **35**, yielding an adduct mixture

The sole MS peaks of this adduct (figure 48) at 603 ($[M]^+$), 625 ($[M - H + Na]^+$) and 641 ($[M - H + K]^+$) prove clearly that the reaction succeeded as intended. The R_f value in dichloromethane/ethyl acetate 19:1 of this product amounts, according to the fact that an unpolar residue was attached, to 0.63, in comparison with 0.5 observed for pure **35**. A more unpolar peak was observed with R_f=0.71, which was likely due to the bisubstituted educt.

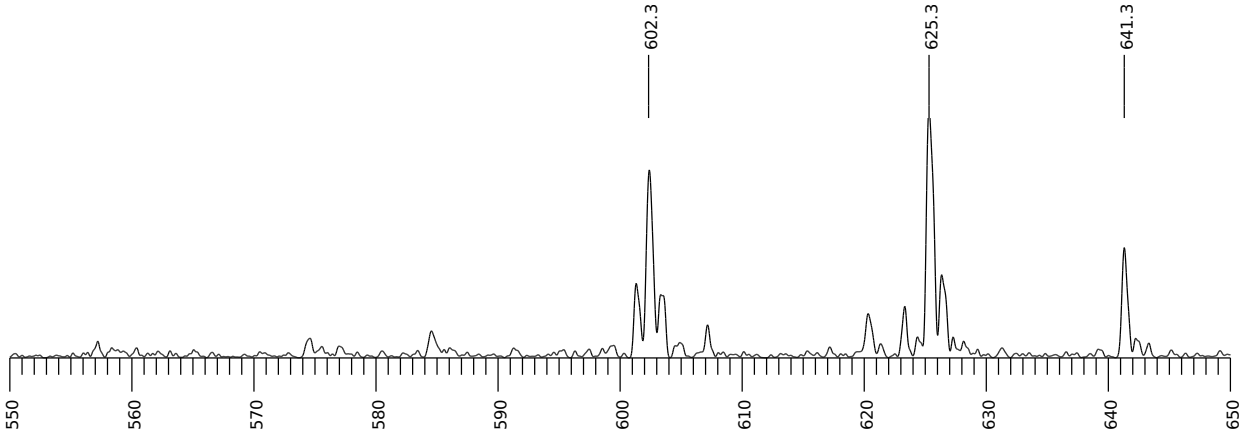


Figure 48: MALDI-Mass spectrum of **96** $C_{35}H_{54}O_8$ (matrix: sin)

The NMR spectrum contained several peaks in the area of the C-H - acidic protons. Obviously, these different peaks must occur due to different regioisomers of the added spacer. No methyl proton signals were found between 2.8 and 2 ppm, proving that no aromatic ring had been formed.

Even if this adduct was suitable as protected substrate, the chaotic crowd of signals would make it unsuitable for spectroscopic verification of the intermediates during use of this group (figure 49). To overcome this, the protecting group aimed to be synthesized had to have at least C_7-symmetry.

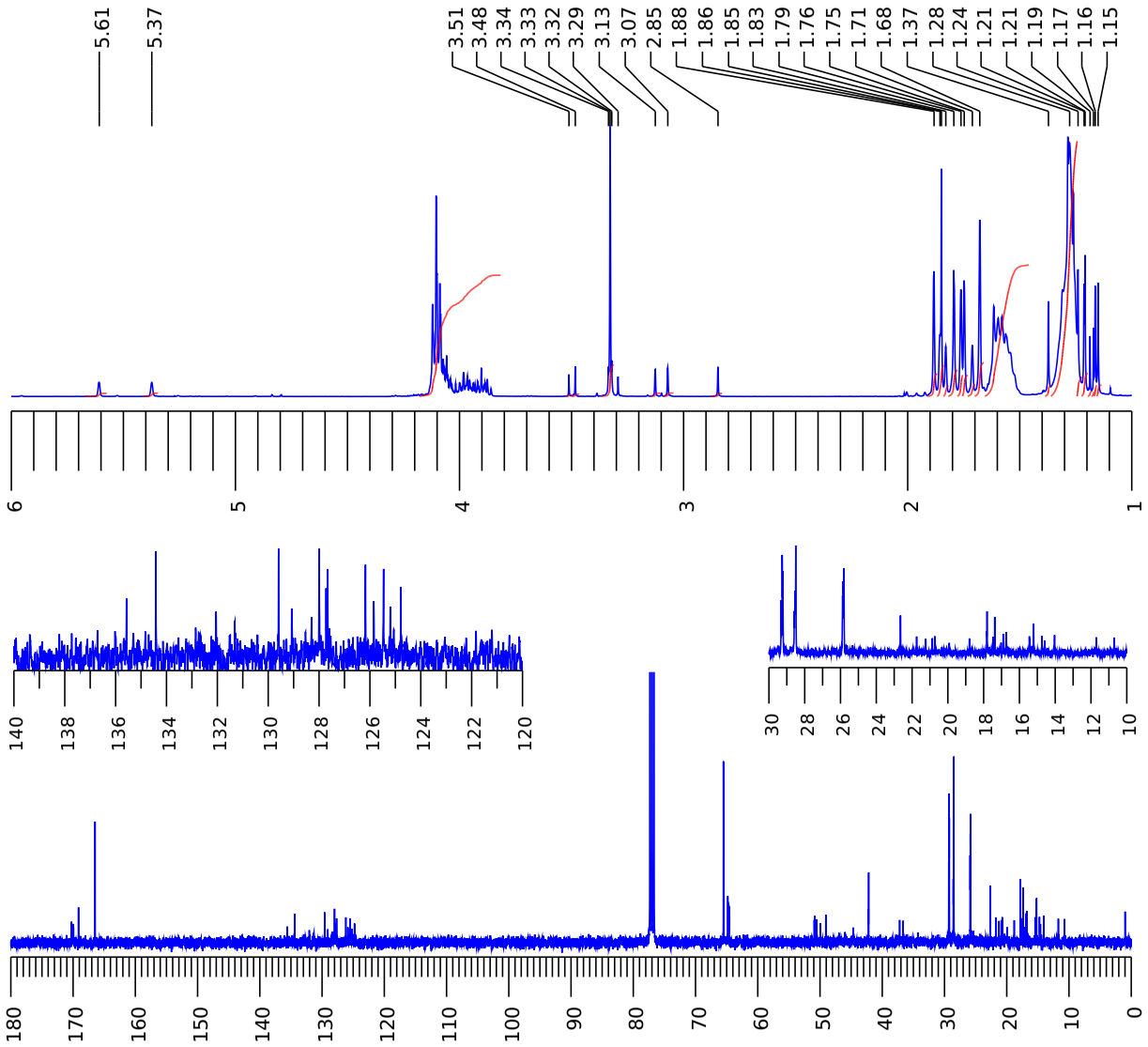
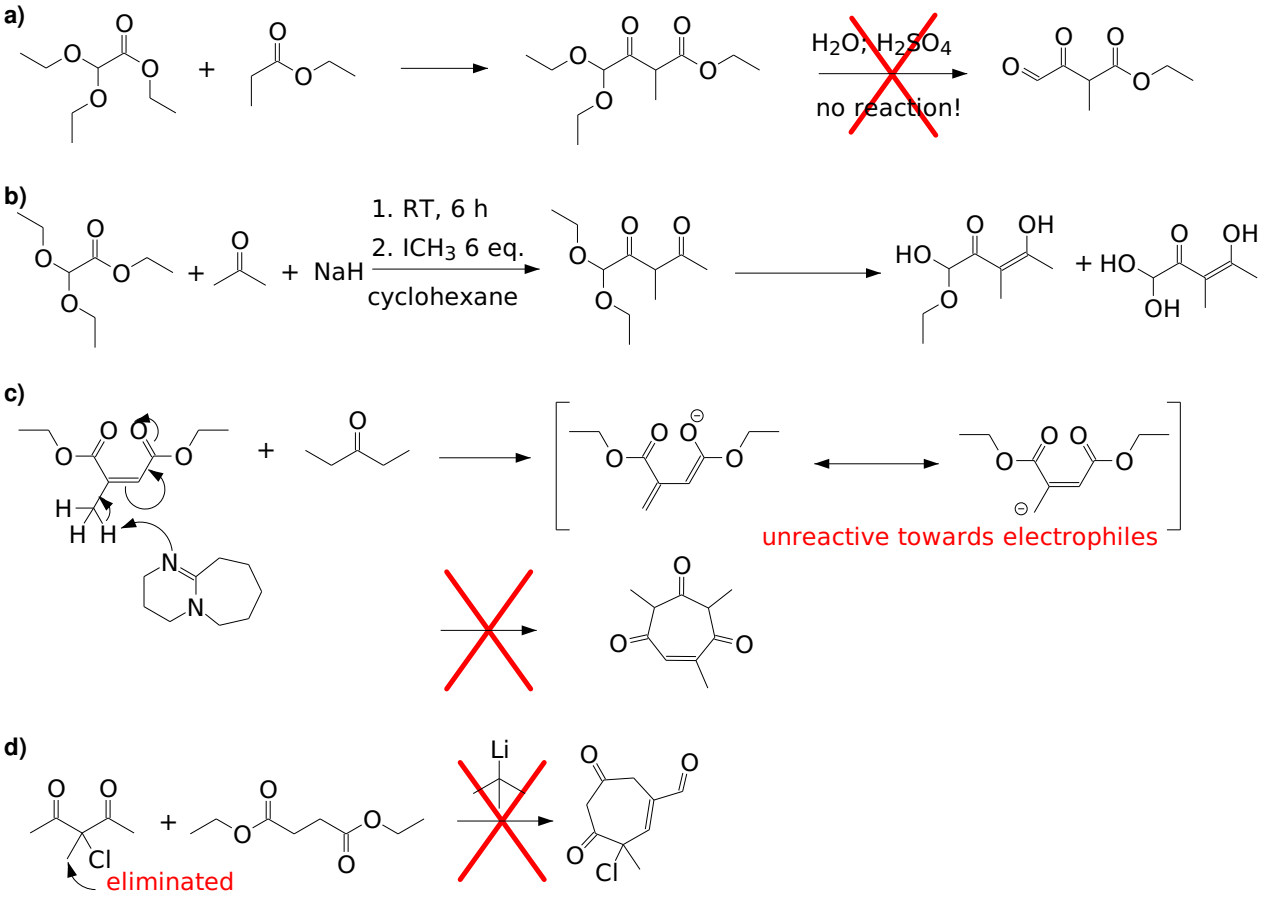
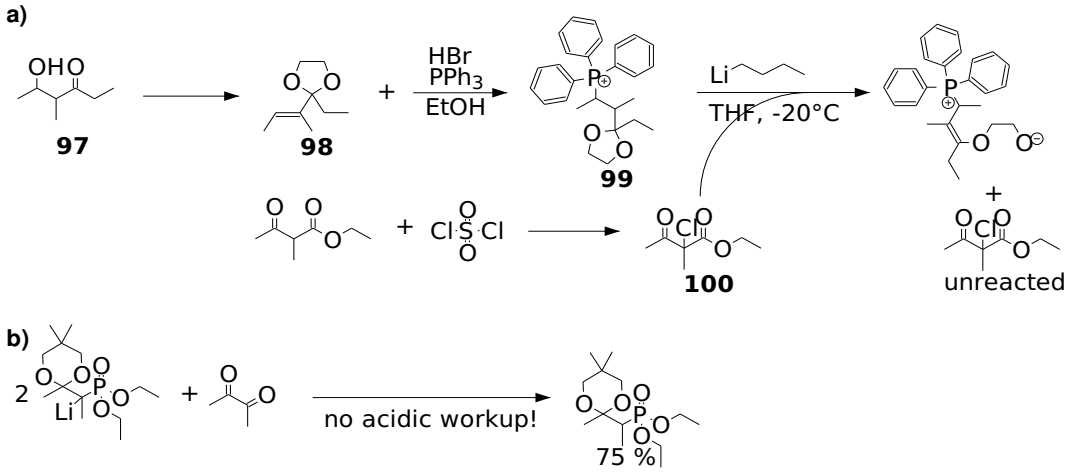


Figure 49: NMR spectra of **96** (75.5 MHz, $CDCl_3$) (400/100 MHz, $CDCl_3$)

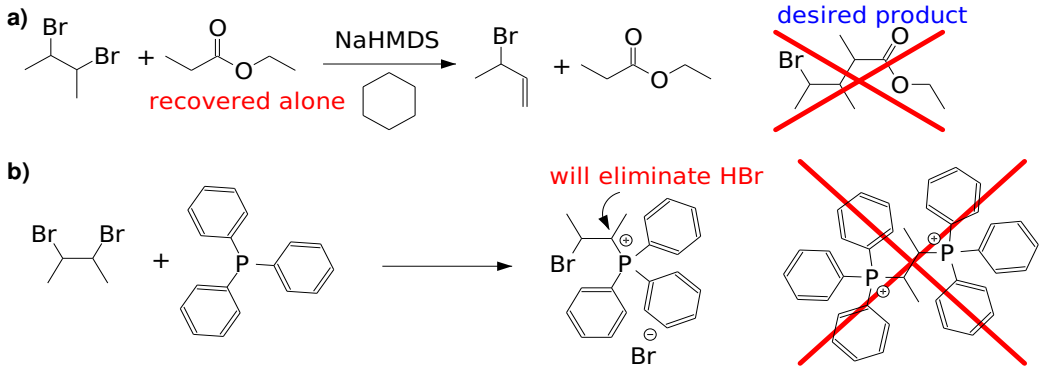
The largest problem to create such highly substituted heptane cycles was the close proximity of reacting functional groups to each other. This is, until now, the primary reason why none of my approaches was successful. In general, my basic method was to conduct a nucleophilic coupling reaction, between two components that would both exhibit an additional reaction site in order to accomplish a later cyclization. And these additional reaction sites were problematic because they had to be in α-, β- or γ-Position to the reacting one in order to cyclize a 7-membered ring from two halves. The atoms between thoses sites had to be prepared to be transformed to a double bonded with another CH_3-group. This gives the need to keep them reactive, which favors the problem with side-reactions amongst them even more. A methyl group already attached between these sides can still be a problem by providing a proton for elimination, as seen in scheme 78 or 79. The most abundant side-reactions consequently were eliminations in the nucleophilic part, or, regarding the part intended as electrophile, polymerisiation and steric hindrance due to the keto/enol-equillibrium of these carbonyl compounds.



Scheme 78: Attempts to create higher substituted tropylium derivatives by means of the Claisen condensation

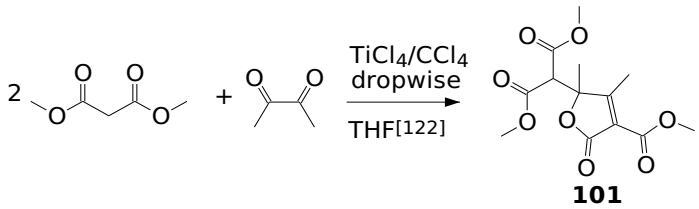


Scheme 79: Problems with unwanted deprotonation during the Wittig reaction



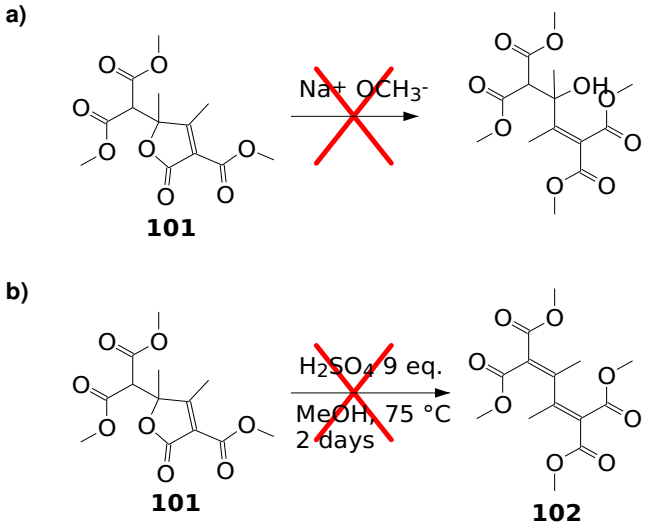
Scheme 80: Parasitic elimination of HBr from dibromobutane (a): alkene not identified, postulated from failing

The most obvious way to create such unsaturated and highly substituted adducts would be the Knoevenagel reaction.[121 p. 527] However, butanedione failed to react under ordinary Knoevenagel conditions, and the attempt to create bisadducts under conditions specialized for ketones[122] led to a compound that resulted from a parasitic transesterification (scheme 81).



Scheme 81: Attempts to form an unsaturated and highly substituted alkyl chain by means of the Claisen condensation

Attempts to generate **102** from this cyclic side-product failed in both basic ($NaOCH_3$ in Methanol) and acidic conditions (Methanol, sulfuric acid) (scheme 82).



Scheme 82: Attempts to react the product of the parasitic lactamisation

An attempt to cyclize compound **101** by double Claisen-condensation to acetonitrile led to polymer only.

Phosphonic ester were unable to attach to 2,3-dibromobutane: They prefered the side product which is set free in the Michaelis-Becker reaction,[123] ethylbromide, as a substrate.

5. Conclusions and Outlook

A new method to selectively attach bilateral malonate spacers and similar malonate constructs with multiple reactable sites has been discovered. The simple method of attaching the malonates in concurrence to the spacer's other end has been shown to be unusable. The side-reactions in the Bingel-reaction have been elucidated, giving an explanation why the obvious way of creating a selectivity by pre-bromination did fail. The tetraalkyltetracarboxyalkenes have been demonstrated to be the actual active reagent that effects the famous tetrabromocarbon templatisation (page 69), whose mechanism was not understood until now. This gives access to another, new way of regioselective Synthesis. One further important finding is the selectivity obtained by combining the isoxazoline protecting group and the monochlorinated malonates. It gives us the possibility to conduct a multiaddition reaction which required no isomer-separation at all. Further, the efficiency of meta-benzylaniline cation precursors[89] has proven suitable for quantitatively creating cations on fullerenes. The last two issues are of special importance especially since the separation of different fullerene isomers, which had positive charges all over the surface, showed to be impossible. A series of macroamphiphiles of fullerenes has been synthesized which show a yet unknown aggregation behavior.

They take part in a nested aggregation of small, unstable fragment-aggregates to well defined, obviously hollow, and porous macroaggregates. This happened at very low critical micellar concentrations, but still, their actual solubility was very high. Both the porousness and the final limit of solubility hint on a surprisingly high hydrophilicity of them. Tropylium turned out to theoretically be a protective agent for C-H acidic protons, but the pure form is unsuitable for the Bingel conditions. Because of that, attempts to higher derivatives have been undertaken, the most promising approach of which has been shown to be the titanium tetrachloride variant of the Knoevenagel reaction.

The final star-shaped polycationic fullerene structure still awaits to be synthesized. With the new central moiety **46**, this should be possible, but a more stable alternative to pentakisadduct **32** must be found. What the amphiphiles are concerned, further types of them have to be synthesized, if possibe with more rigid addends, to detect the principles of the newly discovered type of aggregation. Among the amphiphiles, no systems with quarternary ions had yet been made. As this was mostly due to the fact that the product mixture could not be separated, the new method in chapter 4.3.1. (page 65), which seems to create a perfect selectivity amongst the non-decomposed products, could allow access to just this class of compounds from pre-charged malonate units. This would, on one hand, allow to discover the aggregation behavior independently from the pH-Value, and give more defined aggregates, enough to create X-ray structures from them to investigate the aggregation mechanism and their usability for catalytic purposes. And the tropylium ion is obviously no stable protecting agent against Bingel conditions until the hepta<u>e</u>thyl form can be made at least.

5. Zusammenfassung und Ausblick

Es wurde eine neue Methode entdeckt, die es ermöglicht, Malonat-Abstandhalter und ähnliche Konstrukte mit mehreren reaktiven Stellen selektiv reagieren zu lassen. Es wurde auch gezeigt, daß die Vorgehensweise, die Malonate einfach in Konkurrenz zu dem Ende des Spacers reagieren zu lassen, unbrauchbar ist. Es wurden die Nebenreaktionen der Bingel-Reaktion aufgeklärt und so gezeigt, warum der scheinbar einleuchtende Weg, die angreifenden Malonataddenden einfach im Voraus zu bromieren, fehlschlägt. Desweiteren wurde gezeigt, dass die Tetraalkyltetracarboxyalkene die entscheidende reaktive Spezies der Tetrabromkohlenstofftemplatisierung sind, deren Mechanismus bisher noch nicht verstanden war - dies eröffnet ebenfalls neue Möglichkeiten für regioselektive Synthesen.

Eine weitere wichtige Entdeckung ist die Selektivität, die man erhält, wenn man die Isoxazolin-Schutzgruppe und die monochlorierten Malonate miteinander kombiniert. Dies gibt uns nun die Möglichkeit, die Multiaddition durchzuführen, ohne daß eine Isomerentrennung erforderlich wäre. Der meta-Benzylamin - Kationenvorläufer hat sich als geeignet erwiesen, an Fullerenen quantitativ Kationen zu erzeugen. Letztere zwei Punkte sind insbesondere deswegen von Bedeutung, als da die Auftrennung von verschiedenen, an der gesamten Oberfläche vielfach kationischen Fullerenderivaten nicht möglich ist.

Eine Reihe von Makro-Amphiphilen aus Fullerenen ist untersucht worden. Diese wiesen ein bisher unbekanntes Aggregationsverhalten auf. Sie unterlaufen eine verschachtelte Aggregation aus kleinen, instabilen Aggregatsfragmenten, die sich zu größeren, offensichtlich hohlen und porösen Makroaggregaten zusammenlagern. Und obwohl dies einerseits mit ziemlich niedrigen CMC-Werten geschah, war trotzdem die eigentliche Löslichkeit sehr hoch. Sowohl die Porosität der Aggregate als auch die hohe endgültige Löslichkeitsgrenze lassen schließen, daß diese Moleküle eine überraschend hohe Affinität zu Wasser haben.

Tropylium stellte sich als eine im Prinzip geeignete Schutzgruppe für C-H-acide Protonen heraus, aber die reine Form ist ungeeignet für die Bingel-Bedingungen. Deswegen wurde der Versuch unternommen, höhere Addukte von diesem zu erhalten. Als der vielversprechendste Ansatz hat sich hierbei die Titantetrachlorid-Variante der Knoevenagel-Reaktion erwiesen.

Die erwünschte, sternenförmige, vielfach-kationische Fullerenstruktur steht immer noch aus, synthetisiert werden. Mit der neuen Zentraleinheit **46** sollte dies möglich sein, sobald eine stabilere Alternative zum Kationenvorläufer-Pentakisaddukt gefunden ist. Was die Amphiphile betrifft, könnten weitere Konstrukte ausprobiert werden, möglichst mit starren Addenden, um die Gesetzmäßigkeiten dieses neu entdeckten Typs einer Aggregation zu erkunden. Da das Haupthindernis für die Erzeugung permanent-kationischer Amphiphile hauptsächlich die Abtrennung der Isomere war, wäre es mit der in Kapitel 4.3.1. (Seite 65) dargestellten Methode möglich, permanent kationische Varianten mit Hilfe von bereits kationisch eingesetzten Malonaten zu erhalten, um einerseits das Aggregationsverhalten unabhängig vom pH-Wert erkunden zu können, andererseits auch, da sie vielleicht ausreichend definierte Aggregate bilden könnten, um davon eine Struktur mittels Röntgenbeugung zu erhalten. Dadurch könnte man den Aggregationsmechanismus genauer erklären und seine Möglichkeiten als Katalysator ausloten.

Das Tropyliumion wird sich vermutlich weiterhin nicht eignen, um als Schutzgruppe für Malonate unter Bingel-Bedingungen zu fungieren, bis nicht wenigstens die Hepta-Ethyl-Variante zugänglich ist.

6. Experimental Part

6.1. General Remarks and Chemicals

Chemicals & Solvents: Unless otherwise stated, chemicals were purchased from commercial sources and used without further purification. C_{60} was purchased from IO-LI-TEC NANOMATERIALS. Raw solvents were distilled before use, alcohols were distilled from CaO, chloroform, dichloromethane and ethyl acatate were distilled from K_2CO_3, dry THF was dried with KOH and distilled from sodium, dry ether was dried with KOH and distilled. For reactions with fullerenes present, HPLC grade solvents were used.

TLC: MARCHEREY-NAGEL TLC silica gel 60 F_{254}. Developer: $KMnO_4$ (1 % solution in 1 % aqueous KOH).

Column chromatography: MERCK silica gel 60 (230-400 mesh, 0.04-0.063 nm) (deactivated).

Flash chromatography: INTERCHIM puriFlash 430. Column: SIHC-JP 15 µm 40 g. Substance purified portion-wise.

UV/Vis spectroscopy: VARIAN CARY 5000, Solvent: CH_2Cl_2 or H_2O. Absorption maxima given in nm, extinction in $M^{-1}cm^{-1}$.

Conductivity Titration: Conductivity: WTW Cond 330i conductometer. Basis volume: 9.5 mL. Step volume: 10 µL. Solvent: pure water.

Infra-red spectra: BRUKER FTIR Tensor 27 (ATR). Abbreviations: w: weak; m: medium; s: strong.

NMR: BRUKER Avance 400, BRUKER Avance 300, JEOL GX 400. Field strengths given as resonance frequency of the respective nucleus. The chemical shifts are given in [ppm] relative to TMS. Abbreviations: s: singlet; d: doublet; t: triplet; q: quartet; m: multiplet; br: broad. Spectra recorded at room temperature.

MS: Maldi: SHIMADZU Axima Confidence (TOF). ESI: BRUKER Daltonics micrOTOF (TOF). Matrices: dctb: (E)-2-(3-(4-(*t*-butyl)phenyl)-2-methylallylidene)malononitrile; sin: 3,5-dimethoxy-4-hydroxycinnamic acid; dith: 1,8-dihydroxy-10H-anthracen-9-on; dhb: 1,5-dihydroxybenzoic acid.

MSA: Automatic sampling: EMAN software, boxer module.[124] Determination of class sums and 3D calculation: IMAGE SCIENCE IMAGIC-5 software.[125]

DLS: Light source: HeNe Laser (λ = 632.8 nm; 20 mW), correlator: ALV 5000. Goniometer: ALV CGS 3. Range: 30° ≤ θ ≤ 150° (step: 20 °). The intensity autocorrelation function g2(τ) was transformed for each angle to the electrical field's autocorrelation function g1(τ) by means of the Siegert relation. Consecutively, the distribution of the relaxation times was calculated by means of the inverse Laplace transformation.

Computer chemistry: Method: Hartree-Fock. Basis Set: cc-pVDZ. Program: Gaussian09.[126]

Document: HTML rendering was done with wkhtmltopdf-0.9.9, chemical structures were drawn with CS Chemdraw-12[127] and rendered with lhendraw-0.3,[128] spectra were rendered with nmrpaster.[128]

6.2. Substances Synthesized According to the Literature

The following compounds were synthesized in procedures known from the literature.
Hence, their synthesis will not be described in the experimental section.

Bis(3-(*t*-butylcarboxy)propyl) malonate **77**[90]

Bis(3-carboxypropyl)malonate **25**[90]

m-Methoxymethylaniline **24**[89]

Bis(6-(boc-amino)hexyl)malonate **39**[98]

(Bis[6-(boc-amino)hexyl]malonyl)-[5,0]-pentakis-1,2,18,22,23,27,45,31,32,36-decahydro[60]-fullerene **51**[98]

(Diethylmalonyl)-[5,0]-pentakis-1,2,18,22,23,27,45,31,32,36-decahydro[60]-fullerene **49**[98]

Cyclo-[2]-octylmalonyl-1,2-dihydro[60]fullerene **19**[81]

(Diethylmalonyl)-[5,0]-pentakis-1,2,18,22,23,27,45,31,32,36-decahydro[60]-fullerene **49**[98]

6.3. Synthetic Procedures

Synthesis of 4-methyl-hexan-5-ol-3-one 97

According to lit.[121 p. 520], pentanone (27.6 g, 33.9 mL, 321 mmol, 3 eq.), a solution of KOH (0.180 g, 3.21 mmol, 0.03 eq.) in MeOH (1.2 mL) was added. The mixture was cooled to 10 °C. Acetaldehyde (4.71 g, 6.00 mL, 107 mmol, 1 eq.) was added dropwise over 4 h. Then the mixture was warmed to 15 °C and stirred for another 2 h. Acetic acid (200 µL) was added. The mixture was dried with Na_2SO_4, filtered, washing with dichloromethane. The solvent and educt from the filtrate was removed under reduced pressure and the raw product was distilled (75 °C, 9 mbar). Yield: 8.29 g (63.7 mmol, 60 %). d = 0.99 g/cm$^{3.}$

Cation Exchange Experiment Resulting in 2-bromo-cyclo[2]-octylmalonate 36 and Compound tetraethyl tetracarboxyethene 57.

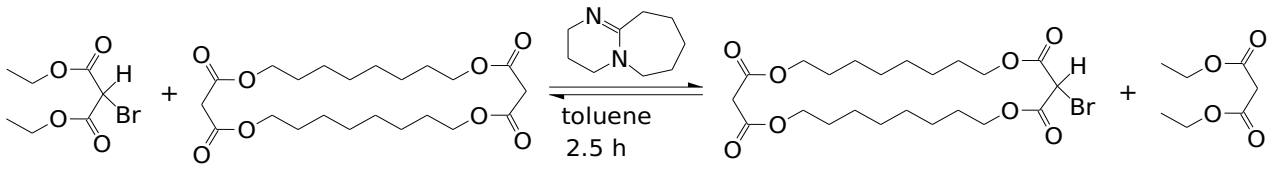
1,3-diethyl-2-bromomalonate (476 mg, 339 µL, 1.99 µmol, 10 eq.), diethyl malonate (319 mg, 302 µL, 1.99 mmol, 1 eq.) and cyclo[2]-octylmalonate **35** (85 mg, 199 µmol, 1 eq.) were dissolved in toluene (5 mL). DBU (303 mg, 297 µL, 1.99 mmol, 10 eq.) was added and the mixture was stirred for 12 h. Acetic acid (0.5 mL) was added and the resulting solution was plug-filtered (SiO_2; dichloromethane/ethyl acetate 1:1) and again (SiO_2; dichloromethane, 6 BV; ethyl acetate; dichloromethane/ethyl acetate 1:1). The resultant was purified by column chromatography (dichloromethane/ethyl acetate 19:1). In the fraction with R_f = 0.11 in dichloromethane, 18 mg of the cycle emerged which was mono-brominated. Furthermore, tetraethyl tetracarboxyethene **57** was found (at least 60 mg), and tetraethyl-1,1,2,2-ethanetetracarboxylate.

Brominated malonate 2-Bromo-cyclo[2]-octylmalonate **36** spectroscopic data:
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.83 (s, 1 H, C**H**Br), 4.35..4.08 (m, 8 H, C**H**$_2$O), 3.34 (s, 2 H, C**H**$_2$(C=O)$_2$), 1.6 (m, 8 H, C**H**$_2$CH$_2$O), 1.3 (m, 16 H, C**H**$_2$C**H**$_2$CH$_2$CH$_2$O) ppm.
^{13}C-NMR{^{1}H} (75.4 MHz, $CDCl_3$) : δ = 166.5 (2 C, CH$_2$(**C**=O)$_2$), 164.5 (2 C, CHBr(**C**=O)$_2$), 67.2, 65.5 (4 C, **C**H$_2$O), 43.2 (1 C, **C**HBr), 42.2 (1 C, **C**H$_2$(C=O)$_2$), 29.3, 29.2 (4 C, **C**H$_2$CH$_2$O), 28.5, 28.4 (4 C, **C**H$_2$CH$_2$CH$_2$O), 25.8, 25.7 (4 C, **C**H$_2$CH$_2$CH$_2$CH$_2$O) ppm.
HRMS (ESI, AcN + MeOH): calcd. for $C_{22}H_{35}BrNaO_8$ [M + Na]$^+$: 529.14061; found: 529.14202.
Proof for tetraethyl tetracarboxyethene **57**. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.29 (q, $^{3}J_{H,H}$ = 7.2 Hz, 8 H, C**H**$_2$O), 1.29 (t, $^{3}J_{H,H}$ = 7.2 Hz, 12 H, C**H**$_3$).
^{13}C-NMR{^{1}H} (75.4 MHz, $CDCl_3$): δ = 162.3 (4 C, **C**=O), 135.3 (2 C, **C**=**C**), 62.6 (4 C, **C**H$_2$O), 13.8 (4 C, **C**H$_3$).
Proof for tetraethyl 2-malon-2-yl-malonate **56**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.24..4.12 (m, 8 H, C**H**$_2$O), 4.09 (s, 2 H, C**H-**C**H**), 1.24 (t, $^{3}J_{H,H}$ = 7 Hz, C**H**$_3$) ppm.
^{13}C-NMR{^{1}H} (100.5 MHz, $CDCl_3$): δ = 167.0 (4 C, **C**=O), 62.0 (4 C, **C**H$_2$O), 51.4 (2 C, (C=O)$_2$**C**H-**C**H(C=O)$_2$), 13.9 (4 C, **C**H$_3$) ppm.
HRMS (ESI, CH_2Cl_2 + AcN + MeOH): for $C_{14}H_{23}O_8$ [M + H]$^+$ calcd. 319.13874. found: 319.13946; for $C_{14}H_{22}NaO_8$ [M + Na]$^+$ calcd. 341.12069. found: 341.12146;

Experiment Showing Unability of Chloryl Cations to Shuffle

1,3-Diethyl-2-chloromalonate **41** (385 mg, 320 µL 1.99 mmol, 10 eq.), and diethyl malonate **37** (319 mg, 302 µL, 1.99 mmol; 10 eq.) were dissolved in toluene (5 mL). Cyclo[2]-octylmalonate **35** (85.3 mg, 199 µmol, 1 eq.) was added and stirred until complete dissolution. The mixture was stirred at room temperature for 24 h. work-up, isolation of the spacer-containing fraction and ^{1}H-NMR spectroscopy gave no evidence for the C-H-acidic proton of the single-chlorinated malonate of 2-chloro-cyclo[2]-octyl malonate **42**.

Cation Exchange Experiment Resulting in 2-bromo-cyclo[2]-octylmalonate 36 and diethyl malonate 37



2 **35** **36** **37**

Scheme 83: Experiment to prove an exchange of bromine amongst malonates

1,3-Diethyl-2-bromomalonate (47.573 mg, 33.9 µL, 199 µmol, 1 eq), cyclo[2]-octylmalonate **35** (85 mg, 199 µmol, 1 eq.) were dissolved in toluene (5 mL). DBU (30.3 mg, 29.7 µL, 199 µmol, 1 eq.) was added and the mixture was stirred for 2.5 h. Acetic acid (100 µL) was added and the resulting solution was purified by column chromatography (SiO_2; dichloromethane). Yield: 13 mg, 12.8 %.

Brominated malonate **36** spectroscopic data:

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.83 (s, 1 H, C**H**Br), 4.35..4.08 (m, 8 H, C**H**$_2$O), 3.34 (s, 2 H, C**H**(C=O)$_2$), 1.6 (m, 8 H, C**H**$_2$CH$_2$O), 1.3 (m, 16 H, C**H**$_2$C**H**$_2$CH$_2$CH$_2$O) ppm.

^{13}C-NMR{^{1}H} (75.4 MHz, $CDCl_3$): δ = 166.5 (2 C, CH$_2$(**C**=O)$_2$), 164.5 (2 C, CHBr(**C**=O)$_2$), 67.2, 65.5 (4 C, **C**H$_2$O), 43.2 (1 C, **C**HBr), 42.2 (1 C, **C**H$_2$(C=O)$_2$), 29.3, 29.2 (4 C, **C**H$_2$CH$_2$O), 28.5, 28.4 (4 C, **C**H$_2$CH$_2$CH$_2$O), 25.8, 25.7 (4 C, **C**H$_2$CH$_2$CH$_2$CH$_2$O) ppm.

Proof for diethyl malonate:

^{13}C-NMR{^{1}H} (100.5 MHz, $CDCl_3$): δ = 166.6, 61.5, 41.7, 14.0 ppm.

ESI-MS(CH_2Cl_2, MeOH, CH_3CN): calcd. for $C_{22}H_{35}BrNaO_8$ $[M + Na]^+$: 529.14075 meas.: 529.14100 Da.

Experiment for Creation of ((Bis[6-(boc-amino)hexyl]malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-[6,0]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 52

Central unit **46** (25 mg, 7.7 µmol, 1 eq.) was dissolved in toluene (7 mL). CBr_4 (17.4 mg, 52.5 µmol, 6.8 eq.) was added. P_1-*t*Bu (14 mg, 15.2 µL, 60 µmol, 7.8 eq.) was diluted with 2 mL toluene and pentakis adduct **51** (152 mg, 47 µmol,6.1 eq) was added immediately afterwards. Twice, once after six weeks and after total 10 weeks, another **51** (152 mg, 47 µmol, 6.1 eq), CBr_4 (8.7 mg, 26.2 µmol, 3.4 eq.) and P_1-*t*Bu (7 mg, 7.6 µL, 30 µmol, 3.9 eq.) (diluted in toluene) were added.

Four more weeks later, the mixture was plug-filtered (SiO_2;dichloromethane/ethyl acetate 1:1) and purified with column chromatography (toluene:ethyl acetate 3:2). The plug residue was also checked by washing it with acetone/ethanol 1:1. Multiple fractions were obtained that exhibited the UV-bands at 314 and 334 nm, but no fraction could be determined as the correct one by a product signal in its MS spectrum.

Oxazoline-Templated Chloromalonate Hexakis-Addition

(p-*N*,*N*-dimethylaminophenylisoxazolino)-mono-1,2-dihydrofullerene **30** (31 mg, 35.1 µmol, 1 eq.), 1,3-diethyl-2-chloromalonate **41** (120 mg, 100 µL, 618 µmol, 17.6 eq.) was added and P_1-*t*Bu (59.8 mg, 64.7 µL, 255 mmol, 7.3 eq.) were added drop-wise in toluene over 30 min. The mixture was stirred over 8 days. P_1-*t*Bu (21.4 mg, 23 µL, 91.3 µmol, 4 eq.) was added drop-wise in toluene and the mixture was stirred for further 4.5 days. The mixture was plug-filtered (dichloromethane/ethyl acetate 1:1) and again (toluene/ethyl acetate 1:1) and purified by means of column-chromatography (SiO_2; toluene:ethyl acetate 10:10:0.75).

Yield: 33 mg (19.7 µmol, 56.1 %)

One-Pot Synthesis of Central unit 46

(p-*N*,*N*-Dimethylaminophenylisoxazolino)-mono-1,2-dihydrofullerene **30** (35 mg, 39.64 µmol, 1 eq.) and 2-chloro-cyclo[2]-octyl malonate **42** (216 mg, 467 µmol, 11.8 eq.) were dissolved in 100 mL of toluene. P_1-*t*Bu (109 mg, 118 µL 0.467 µmol, 11.8 eq.) was added drop-wise in toluene in 70 min. After 13 days, further 2-chloro-cyclo[2]-octyl malonate **42** (106 mg, 229 µmol, 7.5 eq.) and P_1-*t*Bu (43.4 mg, 47 µL 0.185 µmol, 6 eq.) was added and the mixture was stirred for 21 h. The mixture was thoroughly degassed and irradiated with a 500 W high-temperature tungsten soffit lamp for 24 h. After another 24 h, the mixture was plug-filtered (SiO_2; toluene/ethyl acetate 4:1) and purified by means of column-chromatography (SiO_2; toluene/ethyl acetate 4:1) twice, the second time on 15 µm SiO_2 very slowly. Yield: 44 mg (13.4 µmol, 11.6 % based on the total amount of the malonate, 33.8 % based on the fullerene).

Cooperative Bingel Experiment

C_{60} (20.0 mg, 27.8 µmol, 1 eq.) was dissolved in toluene (8 mL). 1,3-Dimethyl-2-bromomalonate (16.8 mg, 10.5 µL, 79.6 µmol, 3 eq.) and 1,3-diethyl-2,2-dibromomalonate **59** (25.3 mg, 15.1 µL, 79.6 µmol, 3 eq.) were added and P_1-*t*Bu (18.7 mg, 20.2 µL 79.6 µmol, 3 eq.) was added dropwise in toluene (3 mL). The mixture was stirred for 18 h. The solution was plug-filtered (SiO_2; dichloromethane/ethyl acetate 1:1) and absorbed on SiO_2 in dichloromethane, washed with dichloromethane (2 BV) and eluted with dichloromethane/ethyl acetate 1:1.

Tetraethyl tetracarboxyethene 57-Templated Generation of Hexakisadduct 13 to Elucidate the Mechanism of the DMA-Templated Bingel Reaction

C_{60} (25 mg, 34.7 µmol, 1 eq.) was dissolved in toluene (15 mL). 1,3-diethyl-2-bromomalonate **2** (24.9 mg, 17.7 µL, 104 µmol, 3 eq.) and tetraethyl tetracarboxyethene **57** (110 mg, 347 µmol, 10 eq.) were added and DBU (105.6 mg, 104 µL, 694 µmol, 20 eq.) was added drop-wise in further 15 mL toluene. The mixture was plug-filtered (SiO_2; dichloromethane/ethyl acetate 1:1). Here, the first NMR spectrum was taken. Further purification was done by another plug-filtration (SiO_2; hexane/ethyl acetate 3:1;hexane/ethyl acetate 2:1 (multiple bed volumes); and finally dichloromethane/ethyl acetate 1:1 to elute the product). Yield: 22 mg (13.2 µmol, 38 %)

Tetraethyl tetracarboxyethene 57-Templated Generation of an e-bisadduct 60 to Elucidate the Mechanism of the DMA-Templated Bingel Reaction

C_{60} (16 mg, 23 µmol, 1 eq.) was dissolved in toluene (15 mL). 1,3-diethyl-2-bromomalonate **2** (5.5 mg, 3.9 µL, 23 µmol, 1 eq.) and tetraethyl tetracarboxyethene **57** (72.5 mg, 229 µmol, 10 eq.) were added and DBU (34.9 mg, 34.24 µL, 229 µmol, 10 eq.) was added directly. The mixture was plug-filtered (SiO_2; dichloromethane). There was a low share of other fullerene adducts in the product mixture. However, most of them were higher fullerene adducts. Further purification was done by column-chromatography (SiO_2; dichloromethane) and (SiO_2 15 µm; dichloromethane). Yield: 4.3 mg (4.1 µmol, 18 %)

^{13}C-NMR: see results (page 75).

MS (MALDI-TOF, sin): m/z = calcd. for $C_{74}H_{20}O_8$ $[M]^+$: 1036.12. found: 1036; calcd. for $C_{74}H_{20}O_8Na$ $[M + Na]^+$: 1059.11. found: 1059;

GP0: General Procedure for Addition/Cleavage experiments

A 100 mL NS29 round-bottom flask was used, usually closed with stopper, or a condenser if reflux conditions were wanted. If not further stated, the reaction was carried out at room temperature (23 °C). The solvent was usually dichloromethane. The solvent was filled in first, then the educts which were not expected to react with each other were inserted. the reagent was inserted last to the well-stirred solution, which was stirred until workup. If bases were present, the mixture was plug-filtered on SiO_2 with some adequate mixture of dichloromethane and ethyl acetate. If acids were present, water was added, then dichloromethane was added and the phases were separated. The dichloromethane phase was dried on $MgSO_4 \times 2H_2O$, which was filtered off after 1 h. The raw mixture was purified on column chromatography if necessary, or the solvent was just distilled off on a rotary evaporator.

GP1: General Procedure for Experimental Forming of Fullerene Multiadducts

This reaction was usually carried out at room temperature (23 °C). The flasks were heated over 100 °C at lower than 20 pa pressure. The solvents used were bought as dry solvents. A nitrogen athmosphere was kept inside the vessel. The C_{60} derivative was put into the solvent and stirred until complete dissolution (if possible). If dimethylanthracene was used, it was added after dissolution of the C_{60}. Not more than 10 eq. of dimethylanthracene were used. The mixture was stirred for at least 2 h, or, if the C_{60} derivative did not dissolve completely, for 3 h. The malonates were added, followed by the halogenating agent. The base was diluted in the solvent and added in over 30 minutes. The mixture was at least stirred over night, usually 7 days.

The success of the reaction could be detected well with TLC. If no yellow spot was seen on TLC, the yield could be expected to be poor.

Workup always started by adding a polar agent into the mixture to adjust the mixture to be the suitable plug filtration eluent. The mixture was immediately applied onto a column pre-packed with that eluent and eluted. If large amounts of dimethylanthracene or CBr_4 were present, another plug filtration was done in which the mixture was first absorbed on silica and washed with dichloromethane, then eluted using the plug-filtration reagent. Afterwards, if large amounts of malonate were present, another plug-filtration was done in hexanes/ethyl acetate mixture that eluted the malonate but not the fullerene. This did not work well with the spacer **35**, which seems to aggregate in unpolar mixtures. The raw mixture was always column-chromatographically pre-purified on 60 µm SiO_2 in the same eluent mixture used for the purification on finer sorbent.

GP2: General Procedure for Preparative Forming of Fullerene Multiadducts WITHOUT tetrabromocarbon templating

On a flask, usually multiple-necked, at least with a nitrogen inlet, had been affixed a dropping funnel. It was flame-dried and kept under a nitrogen athmosphere. It later turned out that the nitrogen atmosphere was of low importance. Either solvent was filled in, followed by adding the fullerene educt as a solid, or a dry solution in the correct solvent of the fullerene educt was added. Isoxazolinofullerenes required trimethylbenzene as solvent. If DMA was used, 10 equivalents of it were added after complete dissolution of the fullerene, and stirred for at least 2.5 hours. If the educt could not dissolve without DMA, as in **22**, the mixture was delayed for 2 more hours. As soon DMA was added, light irradiation was avoided until workup. If the fullerene had an oxazoline protecting group, light irradiation was avoided from the beginning and maintained during workup. After that time, the malonate, (20 eq.) was added. After that, the tetrabromocarbon was added, either stoichiometric to the malonate, lower if only one position should be functionalized, or 100 eq. when CBr_4-templating was used. The base was either DBU (which causes faster reaction, but more decomposition or unselectivity) or P_1-*t*Bu (which is more selective, but the synthesis of **35** from pure C_{60} worked worse with it). CAUTION! P_1-*t*Bu is highly carcinogenic!. The base was added either diluted but rapidly, or diluted and very slowly. It was often beneficial to weigh and definedly dilute larger amounts of CBr_4 or base than needed and insert only the needed fraction of it.

The success of the reaction could be detected well with TLC. If no yellow spot was seen on TLC, the yield could be expected to be poor.

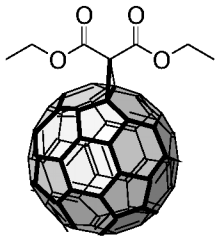
Workup: To remove the dimethylanthracene and its decomposition product, usually the solvent of the mixture was exchanged to dichloromethane (toluene won't do the job), and the mixture was adsorbed on SiO_2. Two bedvolumes of CH_2Cl_2 were passed. Now, the malonate could be washed sometimes off with hexanes/ethyl acetate mixtures! For that, the solvent on the plug had first to be exchanged to pure hexanes to avoid leaking. Afterwards, the mixture is eluted from the plug in the (toluene or dichloromethane)/ethyl acetate mixture used before. Column chromatography required a careful choice of the eluent's composition, and also smaller grained silica. It sometimes required also low elution speeds. Using a HPLC seemed to result in losses.

GP3: General Procedure for Preparative Forming of Fullerene Multiadducts using Tetrabromocarbon Templating

A flask, usually multiple-necked, at least with a nitrogen inlet, was flame-dried and kept under a nitrogen athmosphere. Light irradiation was avoided from the beginning and maintained during workup. Either solvent was filled in, followed by adding the fullerene educt as a solid, or a dry solution in the correct solvent of the fullerene educt was added. Isoxazolinofullerenes required trimethylbenzene as solvent. After that, the malonate, (20 eq.) was added. Then, the tetrabromocarbon (100 eq.) was added and dissolution was awaited. At most 10 equivalents of the malonate may be used, and at least 20 eq. of DBU. The base was added very rapidly. The mixture was stirred for 3 days. Workup proceeded by plug-filtering in toluene/ethyl acetate mixtures with ratios of 1:1 to 3:1.

Workup: To remove the tetrabromocarbon, usually the solvent of the mixture was exchanged to dichloromethane, and the mixture was adsorbed on SiO_2. Two bedvolumes of CH_2Cl_2were passed, or four, if toluene was used instead of dichloromethane. Now, the malonate could be washed sometimes off with hexanes/ethyl acetate mixtures! For that, the solvent on the plug had first to be exchanged to pure hexanes to avoid leaking. Afterwards, the mixture is eluted from the plug in the (toluene or dichloromethane)/ethyl acetate mixture used before. Column chromatography required a careful choice of the eluent's composition, and also smaller grained silica. It sometimes required also low elution speeds. Using a HPLC seemed to result in losses.

1,3-Diethylmalonyl-1,2-dihydro[60]fullerene 3



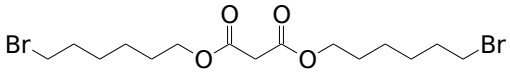
Diethyl chloromalonate (45.5 mg, 37.8 µL, 0.208 µmol, 1 eq.) and C_{60} (170 mg, 236 µmol, 1.13 eq.) were dissolved in toluene (75 mL). 1,8-Diazabicyclo[5.4.0]-undec-7-ene (31.7 mg, 31.1 µL, 1 eq.) were added and the mixture was stirred for 21 h. The mixture was plug-filtered (SiO_2; toluene) and purified with column chromatography (SiO_2; toluene). R_f = 0.726. Yield: 28 mg, 15 %.

Spectroscopy of **3**

^{1}H-NMR (300 MHz, $CDCl_3/C_6D_6$): δ = 4.34 (q, $^3J_{H,H}$ = 7.1 Hz, 4 H, C**H**$_2$), 1.24 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, C**H**$_3$) ppm.

^{13}C-NMR{^{1}H} (75.4 MHz, $CDCl_3/C_6D_6$): δ = 163.4 (2 C, C=O), 145.4, 145.2, 145.1, 145.1, 144.8, 144.6, 144.6, 143.8, 143.0, 142.9, 142.9, 142.1, 141.8, 140.9, 139.1, 63.1, 13.9 ppm.
HRMS (ESI, CH_2Cl_2, AcN + toluene), calcd. for $C_{67}H_{10}O_4$ $[M]^+$: 878.05846; found: 878.05829.

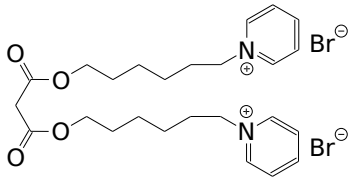
Bis(6-bromohexyl) malonate 16



6-Bromhexan-1-ol (7.5 g, 41 mmol, 2 eq.) was dissolved in dichloromethane (30 mL) and the solution was cooled in an ice bath. Pyridine (3.4 g, 3.46 mL, 42 mmol, 2 eq.) and malonyl dichloride (2.92 g, 2.02 mL, 21 mmol, 1 eq.) were added dropwise over 30 minutes in further 35 mL of dichloromethane. After 15 minutes, the ice bath was removed and the mixture was stirred overnight at room temperature. The organic phase was extracted with water. The solvent was removed under reduced pressure. The raw product was purified by means of column chromatography (SiO_2;hexanes/ethyl acetate 2:1). The product is a liquid.
Yield: 6.9 g (16 mmol, 76 %) based on 6-bromhexanol)
Spectroscopy of **16**

^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ = 4.12 (4 H, t, ^{3}J = 6.7 Hz, C**H**$_2$O), 3.38 (4 H, t, ^{3}J = 6.7 Hz, C**H**$_2$Br), 3.34 (2 H, s, C**H**$_2$(COO)$_2$), 1.84 (4 H, m, C**H**$_2$CH$_2$Br), 1.64 (4 H, m, C**H**$_2$CH$_2$O), 1.44 (4 H, m, C**H**$_2$CH$_2$CH$_2$O), 1.37 (4 H, m, C**H**$_2$CH$_2$CH$_2$Br).
^{13}C-NMR{^{1}H} (100.5 MHz, $CDCl_3$, RT): δ = 166.6 (2 C, **C**=O), 65.3 (2 C, **C**H$_2$O), 41.6 (1 C, **C**H$_2$(COOH)$_2$), 33.6 (2 C, **C**H$_2$Br), 32.5 (2 C, **C**H$_2$CH$_2$Br), 28.3 (2 C, **C**H$_2$CH$_2$O), 27.7 (2 C, **C**H$_2$CH$_2$CH$_2$Br), 25.0 (2 C, **C**H$_2$CH$_2$CH$_2$O).
MS (MALDI-TOF, dctb): m/z = 451, 453, 455 $[C_{15}H_{26}{}^{79}Br_2O_4+Na]^+$, $[C_{15}H_{26}{}^{79}Br^{81}BrO_4+Na]^+$, $[C_{15}H_{26}{}^{81}Br_2O_4+Na]^+$, 250 $[M\ C_6H_{12}Br]^+$.
IR (ATR, Diamant): ῡ = 2937 (m), 2861 (w), 1749 (m), 1732 (s), 1458 (m), 1437 (w), 1411 (w), 1388 (w), 1330 (m), 1264 (m), 1226 (m), 1185 (m), 1148 (s), 1042 (m), 1007 (m), 730 cm^{-1}.

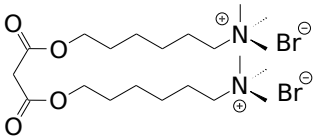
Bis(6-pyridiniumhexyl)malonate dibromide 17



To bis(6-bromohexyl) malonate **16** (2.7 g, 6.2 mmol), 10 mL abs. pyridin were added and the mixture was stirred at 70 °C for 48 h and under reflux for 24 h. The pyridine was removed by distillation and the product was dried at 80 °C for 15 minutes at oil-pump vacuum.
The product is a red-brown, viscous material.
Yield: no loss detectable
Spectroscopy of **17**

^{1}H-NMR (400.1 MHz, D_2O, RT): δ = 8.69 (4 H, d, ^{3}J = 5.5 Hz, o-Pyr), 8.39 (2 H, p-Pyr), 7.92 (4 H, m-Pyr), 4.46 (4 H, t, ^{3}J(H,H) = 7.3 Hz, C**H**$_2$N); 4.01 (4 H, t, ^{3}J = 6.5 Hz, CH_2O), 3.42 (2 H, s, C**H**$_2$(COO)$_2$), 1.87 (4 H, C**H**$_2$CH$_2$N), 1.50 (4 H, C**H**$_2$CH$_2$O), 1.23 (8 H, m, C**H**$_2$C**H**$_2$CH$_2$CH$_2$O) ppm.
^{13}C-NMR{^{1}H} (100.6 MHz, D_2O, RT): δ = 168.7 (2 C, **C**=O), 145.2 (2 C, p-Pyr), 143.8 (4 C, o-Pyr), 127.9 (4 C, m-Pyr), 65.8 (2 C, **C**H$_2$O), 61.4 (2 C, **C**H$_2$N), 40 (1 C, **C**H$_2$(COO)$_2$), 30.1 (2 C, **C**H$_2$CH$_2$N), 27.0 (2 C, **C**H$_2$CH$_2$O), 24.4 (2 C, **C**H$_2$CH$_2$CH$_2$N), 24.1 (2 C, **C**H$_2$CH$_2$CH$_2$O).
IR (ATR, diamond): ῡ = 3028, 2937, 2861, 1725 (s), 1633, 1580 (w), 1487 (s), 1466, 1390 (w), 1330, 1274 (s), 1213, 1175, 1052, 1028, 1001, 881 (w), 775, 730 (w).
UV/Vis (H_2O): λ = 259.5, 362 nm.
MS (MALDI-TOF, dhb): m/z = 508 [M-^{79}Br], 430 [M-2x^{79}Br] Da.
EA(gas chromatography): for $C_{25}H_{36}Br_2N_2O_4$ calcd.: C 51.03, H 6.17, N 4.76; found: C 48.29, H 6.47, N 4.46.

Bis(6-trimethylammonium)malonate dibromide 18



Bis(6-bromohexyl) malonate **16** (4.0 g, 9.3 mmol) was filled into an autoclave together with abs. trimethylamine (20 mL). The mixture was stirred for 3 days at 70 °C. Trimethylamine was evaporated in the autoclave, the residue was transfered into a flask with water and dried in oil-pump vacuum.

The product is a ionic liquid.

Spectroscopy of **18**

^{1}H-NMR (400.1 MHz, D_2O, RT): δ = 4.07 (t, ^{3}J = 6.5 Hz, 4 H, CH_2O), 3.44 (2 H, s, $CH_2(COO)_2$), 3.18 (4 H, m, CH_2N), 2.97 (18 H, C**H**$_3$), 1.67 (4 H, m, C**H**$_2$$CH_2N$), 1.57 (m, 4 H,C**H**$_2$$CH_2O$), 1.29 (8 H, m, C**H**$_2$C**H**$_2$$CH_2CH_2O$) ppm.

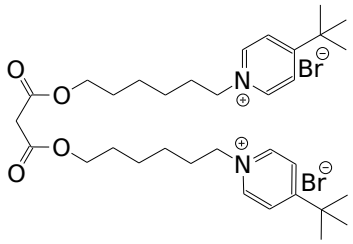
^{13}C-NMR{^{1}H} (75.5 MHz, D_2O, RT): δ = 168.7 (2 C, **C**=O), 65.8 (2 C, **C**H_2N), 65.3 (2 C, **C**H_2O), 52.3 (6 C, **C**H_3), 40.9 (1 C, **C**$H_2(COO)_2$), 26.8 (2 C, **C**H_2CH_2O), 24.7 (2 C, **C**$H_2CH_2CH_2N$), 24.3 (2 C, **C**$H_2CH_2CH_2O$), 21.6 (2 C, **C**H_2CH_2N) ppm.

IR (ATR, diamond): ṽ = 3018 (w), 2942, 2863 (w), 1724 (s), 1630, 1481, 1416,1393, 1334, 1286, 1153 (s), 1054, 1000 (s), 970 (s), 911.

MS (MALDI-TOF, dhb): m/z = calcd. for $C_{20}H_{42}N_2O_4$ $[M - 2\ Br\text{-}CH_2]^+$ 374 Da found: 374 Da.

EA(gas chromatography): for $C_{21}H_{44}Br_2O_4$ calcd.: C 41.19, H 7.24, N 4.57 found: C 44.78, H 7.43, N 4.81.

Bis(6-(*tert.*-butylpyridinium)hexyl)malonate dibromide 20



Bis(6-bromohexyl) malonate **16** (1 g, 2.33 mmol) was dissolved in *tert.*-butylpyridine (3 mL) and stirred at 70 °C for two days and 1 day under reflux. *tert.*-butylpyridine was distilled off at 60 °C at oil pump vacuum. The residue was twice diluted with dichloromethane and washed with toluene.

Yield: 1.6 g (2.28 mmol, 98 %)

Spectroscopy of **20**

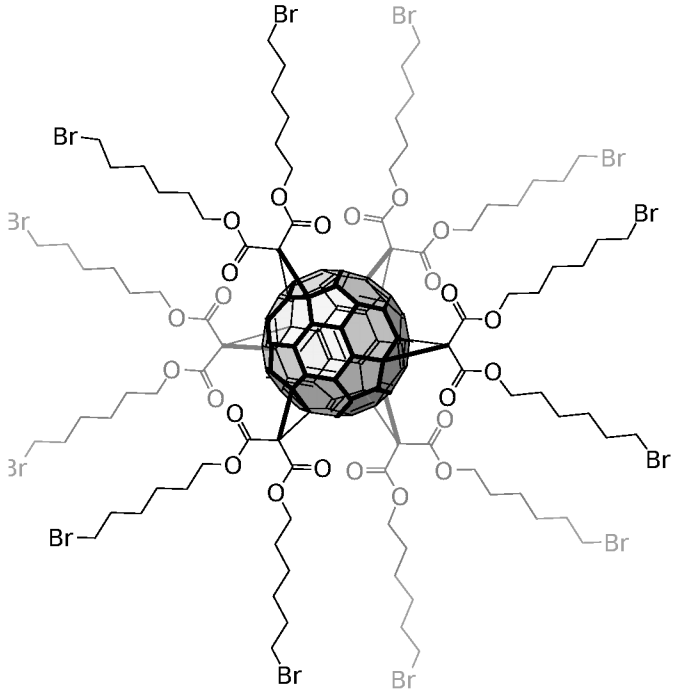
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 9.55 (d, $^{3}J_{H,H}$ = 7 Hz, 2 H, o-pyridine), 7.96 (d, $^{3}J_{H,H}$ = 7 Hz, 2 H, m-pyridine), 4.95..4.85 (m, 4 H, C**H**$_2$O), 4.09..4.03 (m, 4 H, C**H**$_2$O), 3.30 (s, 2 H, C**H**$_2$$(C=O)_2$), 2.29..2.22 (m, 4 H, C**H**$_2$$CH_2N$), 2.11..1.95 (m, 4 H, C**H**$_2$$CH_2O$), 1.67..1.52 (m, 4 H, C**H**$_2$$CH_2CH_2O$), 1.46..1.36 (m, 4 H, C**H**$_2$$CH_2CH_2N$), 1.33 (s, 18 H, C**H**$_3$) ppm.

^{13}C-NMR{^{1}H} (75.5 MHz, $CDCl_3$): δ = 170.5 (2 C, p-pyridine), 166.6 (2 C, **C**=O), 144.6 (2 C, o-pyridine), 125.2 (2 C, m-pyridine), 65.1 (2 C, **C**H_2N), 60.3 (2 C, C**H**$_2$O), 41.7 (1 C, C**H**$_2$$(C=O)_2$), 36.4 (2 C, **C**$(CH_3)_3$), 31.6 (2 C, **C**$H_2CH_2N$), 29.9 (6 C, **C**$H_3$), 28.0 (2 C, **C**$H_2CH_2O$), 25.4 (2 C, **C**$H_2CH_2CH_2N$), 25.0 (2 C, **C**$H_2CH_2CH_2O$) ppm.

MS: m/z = calcd. for $C_{33}H_{52}N_2O_4{}^{79}Br$ [M - Br]$^+$: 619 meas: 619. calcd. for $C_{33}H_{52}N_2O_4{}^{81}Br$ [M - Br]$^+$: 621 meas: 621. calcd. for $C_{32}H_{52}N_2O_4$ [M - 2 Br - H]$^+$: 539 meas: 539.

IR (ATR, diamond): $\tilde{\nu}$ = 2937.1 (m), 1726.0 (s), 1639.2 (s), 1598.7 (w), 1515.8 (w), 1463.7, 1409.7 (w), 1371.1 (w), 1274.7 (w), 1186.0 (w), 1147.4, 1114.7 (w), 1049.1 (w), 995.1 (w), 850.4, 827.3 (w), 732.8 (w), 574.7 (w), 534.2 (w), 462.8 (w), 416.5 (w) cm^{-1}.

(Bis(6-bromohexyl)malonyl)-hexakis[6.0]-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 22



C_{60} (335.1 mg, 465 µmol, 1 eq.) was suspended in dichloromethane (10 mL). Dimethylanthracene (959 mg, 4.65 mmol, 10 eq.) was added. The mixture was stirred for 2 hours.

Bis(6-bromohexyl) malonate **16** (2 g, 4.65 mmol, 10 eq.) and CBr_4 (1.542 g, 4.65 mmol, 10 eq.) were added. P_1-*t*Bu (1.48 g, 1.6 mL, 6.23 mmol, 13.4 eq.) was added drop-wise over 1 hour and the mixture was stirred for 3 days. The raw mixture was plug-filtered (SiO_2; dichloromethane/ethyl acetate 3:1) and purified by column chromatography (SiO_2; toluene/ethyl acetate 19.7:0.3). Then, the raw mixture was purified using HPLC (Nucleosil; toluene/ethyl acetate 1:1).

Yield: 245 mg (74.5 µmol, 16 %) The product is a yellow, translucent, amorphous solid. R_f(SiO_2;dichloromethane)=0.57.

Spectroscopy of **22**

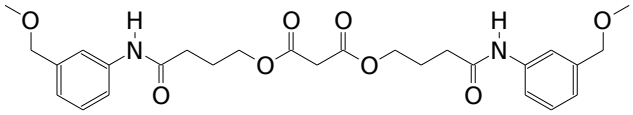
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.32..4.11 (24 H, C**H**$_2$O), 3.44..3.34 (24 H, C**H**$_2$Br), 1.90..1.77 (24 H, C**H**$_2$CH$_2$Br), 1.76..1.64 (24 H, C**H**$_2$CH$_2$O), 1.53..1.23 (48 H, C**H**$_2$C**H**$_2$CH$_2$CH$_2$O)

^{13}C-NMR{^{1}H} (75.5 MHz, $CDCl_3$): δ = 163.6358 (12 C, **C**=O), 145.57, 140.97 (48 C, **C**$_{60}$-sp^2), 68.96 (12 C, **C**$_{60}$-sp^3), 66.60 (12 C, **C**H$_2$O), 45.27 (6 C, **C**(C=O)$_2$), 33.68 (2 C, **C**H$_2$Br), 32.43 (2 C, **C**H$_2$CH$_2$Br), 28.14 (2 C, **C**H$_2$CH$_2$O), 27.55 (2 C, **C**H$_2$CH$_2$CH$_2$Br), 24.92 (2 C, **C**H$_2$CH$_2$CH$_2$O) ppm.

IR (ATR, diamond): $\tilde{\nu}$ = 2936 (m, br), 2859 (m), 2361 (w), 2341 (m), 1743 (s, n), 1462 (w), 1436 (w), 1392 (w), 1263 (s), 1216 (s), 1050 (m, br), 988 (w), 942 (w), 716 (m, n) cm^{-1}.

UV/Vis(CH_2Cl_2): λ = 275, 315, 332 nm.

Bis(*N*-((3-methoxymethyl)phenyl)-butanic acid amid-4-yl) malonate 26



Bis(3-carboxypropyl)malonate **25** (50 mmol, 13.6 g, 1 eq.) and m-methoxymethylaniline **24** (0.11 mol, 15.1 g, 2.2 eq.) are dissolved in dichloromethane. After cooling to 0 °C DCC (45.4 g, 2.2 eq.) and N,N-dimethylaminopyridine (10 mmol, 0.252 g, 0.2 eq.) are added. The reaction mixture is stirred for 36 h. The precipitate is removed and the mixture is purified by column chromatography (SiO_2; ethyl acetate/hexanes 3:1) R_f = 0.22. The solvent was evaporated and traces of ethylacetate were removed in vacuo. Yield: 30 %. Insoluble in toluene!

Spectroscopy of **26**

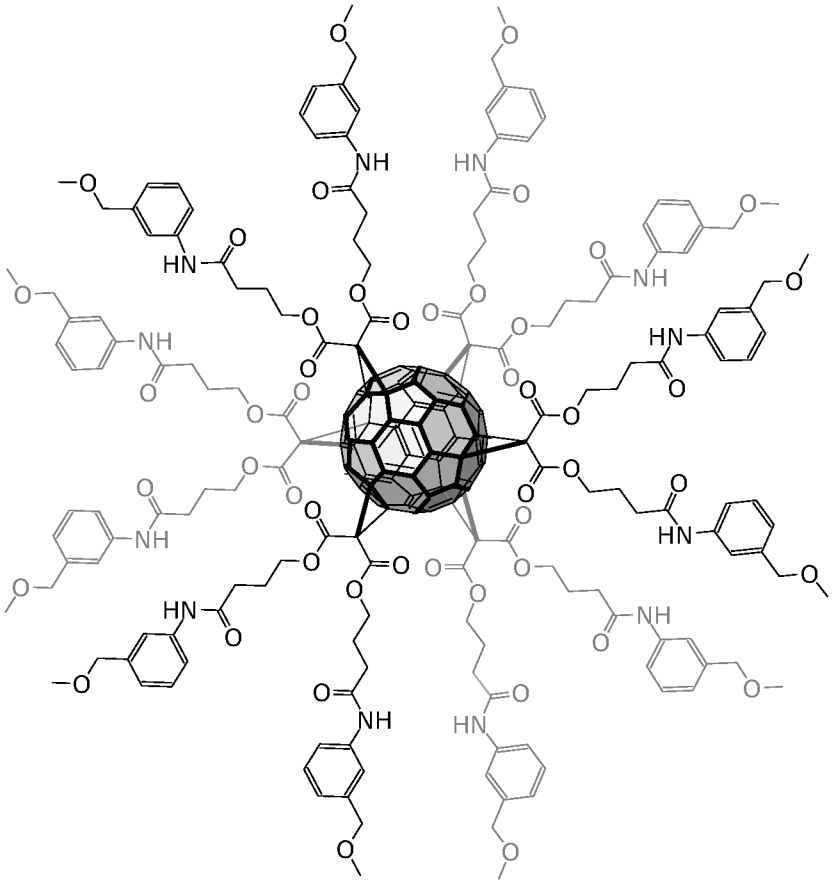
^{1}H-NMR (300 MHz, $CDCl_3$, RT): δ = 8.04 (2 H, s, N-**H**), 7.49 (2 H, s, aniline-2), 7.43 (2 H, d, $^{3}J_{H,H}$ = 9 Hz, aniline-6), 7.24 (2 H, dd, $^{3}J_{H,H}$ = 9 Hz, aniline-5), 7.03 (2 H, d, $^{3}J_{H,H}$ = 9 Hz), aniline-4), 4.37 (4 H, s, C**H**$_2$-O-CH$_3$), 4.23 (4 H, m, C**H**$_2$-O-C=O), 3.37 (2 H, s, C**H**$_2$(C=O)$_2$), 3.33 (6 H, s, C**H**$_3$), 2.43 (4 H, m, **H**$_2$CC=O), 2.07 (4 H, m, CH$_2$C**H**$_2$CH$_2$) ppm.

^{13}C-NMR{^{1}H} (75.5 MHz, $CDCl_3$, RT): δ = 170.5 (2 C, N-**C**=O), 166.8 (2 C, O-**C**=O), 139.1 (2 C, aniline-1), 138.1 (2 C, aniline-3), 129.0 (2 C, aniline-5), 123.4 (2 C, aniline-4), 119.1, 119.0 (4 C, aniline-2, 6), 74.3 (2 C, **C**H$_2$-O-CH$_3$), 64.6 (2 C, **C**H$_2$-O-C=O), 58.1 (2 C, **C**H$_3$), 41.6 (1 C, **C**(C=O)$_2$), 33.5 (1 C, **C**H$_2$-C=O), 24.4 (2 C, CH$_2$**C**H$_2$CH$_2$) ppm.

IR (ATR, RT): $\tilde{\nu}$ = 3380-3210 (m), 2990-2800 (m), 1730 (s), 1660 (s), 1610 (m), 1590 (m), 1550 (s), 1490 (m), 1440 (m), 1380 (w), 1330 (m), 1300 (w), 1270 (s), 1190 (s), 1150 (s), 1090 (s), 1030 (s), 960 (w), 920-890 (w), 880 (m), 790 (s), 730 (m), 700 (s), 650-560 (w), 540 (w) cm^{-1}.

EA(gas chromatography): for $C_{27}H_{34}N_2O_8$ calcd.: C: 63.02 H: 6.66 N: 5.44 S: 0 O:24.87 found.: C: 61.74 H 6.77 N: 6.45 S 0.328

(Bis(*N*-((3-methoxymethyl)phenyl)-butanoic acid amid-4-yl) malonyl)-[6,0]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 27



Pentakisadduct **32** (37 mg, 11.3 µmol) was dissolved in dry dichloromethane (1 mL). Cation-precursor malonate **26** (200 mg, 389 µmol, 35 eq.) and CBr_4 (37.0 mg, 113 µmol, 10 eq.) were added. P_1-*t*Bu (5.3 mg, 22.5 µmol, 2 eq.) was added dropwise in dichloromethane (1 mL) over 15 minutes. The mixture was stirred overnight, plug-filtered (silica; dichloromethane/THF 1:2), absorbed on silica, washed with dichloromethane/ethyl acetate 1:3, eluted with dichloromethane/THF 1:2 and isolated *in vacuo*. Yield: 93 %.

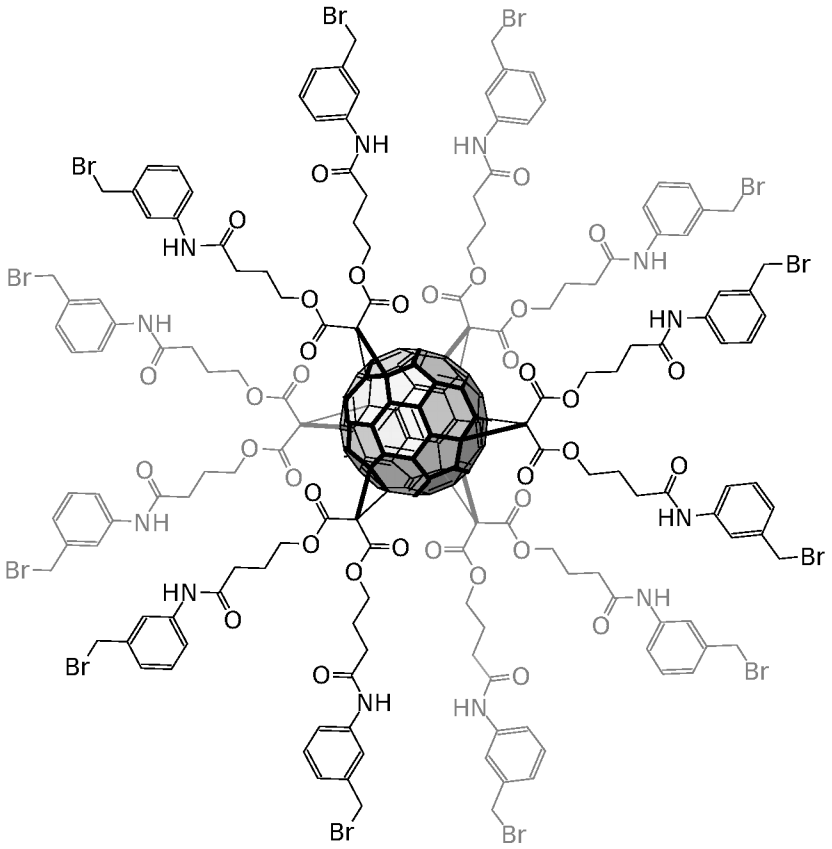
Spectroscopy of **27**

^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ = 8.66 (12 H, s, N-**H**), 7.53 (12 H, s, aniline-2) 7.36 (12 H, m, aniline-6), 7.17 (12 H, m, aniline-5), 6.99 (12 H, m, aniline-4), 4.33 (24 H, s, C**H**$_2$-O-CH_3), 4.26 (24 H, m, C**H**$_2$-O-C=O), 3 (36 H, s, C**H**$_3$), 2.36 (24 H, m, C**H**$_2$CO), 2.02 (24 H, m, CH_2C**H**$_2$$CH_2$) ppm.

^{13}C-NMR{^{1}H} (100.5 MHz, $CDCl_3$, RT): δ = 171.2 (12 C, N-**C**=O), 164.14 (12 C, C(C=O)$_2$), 146.1, 141.6 (48 C, C_{60}-sp^2), 139.4 (12 C, aniline-1), 138.6 (12 C, aniline-3), 129.3 (12 C, aniline-5), 123.9 (12 C, aniline-4), 119.9 (24 C, aniline-2,6), 74.80 (12 C, **C**H_2-O-CH_3), 69.6 (12 C, C_{60}-sp^3), 66.9 (12 C, H_2**C**-O-C=O), 58.6 (12 C, O**C**H_3), 46.1 (12 C, C(C=O)$_2$), 33.4 (12 C, H_2**C**-C=O), 24.5 (12 C, CH_2**C**$H_2$$CH_2$) ppm.

UV/Vis (CH_2Cl_2): λ (ε) = 246 (294000), 260 (181000), 278 (101000), 316 (59000), 334 (48000), 378 (12000), 399 (8000) nm ($M^{-1}cm^{-1}$).

(Bis(*N*-((3-brommethyl)phenyl)-butanoic acid amid-4-yl) malonyl)-[6,0]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 28



(Bis(*N*-((3-methoxymethyl)phenyl)-butanoic acid amid-4-yl) malonyl)-[6,0]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene **27** (88 mg, 23.1 µmol) was dissolved in dichloromethane (3 mL) and a dry, 48 % solution of HBr in acetic acid (3 mL) was added. The mixture was stirred for 3 days. The mixture was poured on water and diluted with dichloromethane. Traces of HBr were removed with solid potassium bicarbonate.

After filtration, the solvent and acetic acid were evaporated and the sample was washed with water. After addition of first dichloromethane, then toluene and evaporation three times, the substance was immediately dissolved in dry THF and subjected to the next step. The mass spectra of the next compound showed that the share of completely transformed product was sufficiently high. Yield: 90 mg (87 %)

Spectroscopy of **28**

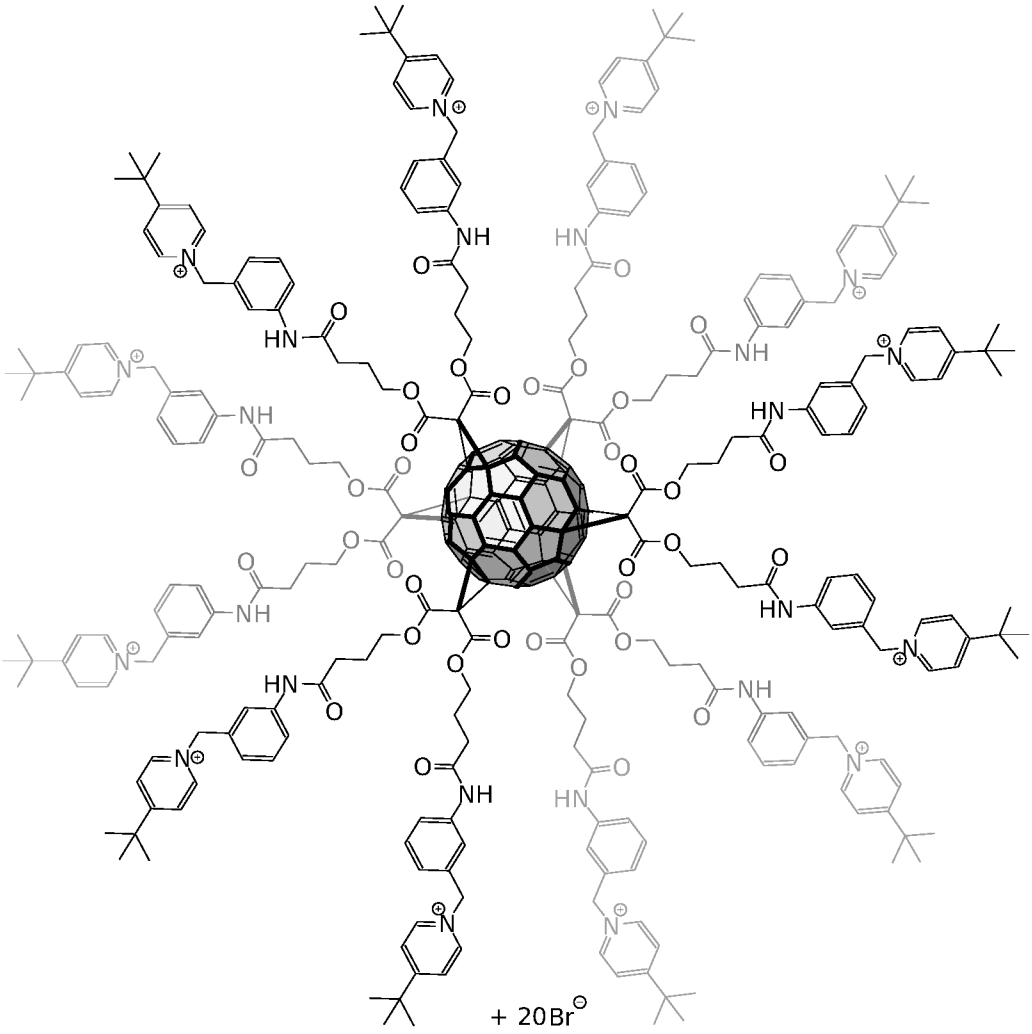
^{1}H-NMR (400 MHz, THF-d8, RT): δ = 9.33 (12 H, N-**H**), 7.70 (12 H, s, aniline-2), 7.53 (12 H, m, aniline-6), 7.18 (12 H, aniline-5), 7.03 (12 H, aniline-4), 4.46 (24 H, s, C**H**$_2$Br), 4.34 (24 H, m, C**H**$_2$O), 2.88 (24 H, C**H**$_2$-C=O), 2.06 (24 H, CH$_2$C**H**$_2$CH$_2$) ppm.

^{13}C-NMR{^{1}H} (100 MHz, THF-d8, RT): δ = 172.1 (12 C, **C**=O-N), 165.1 (12 C, O-**C**=O), 147.7, 141.6 (48 C, **C**$_{60}$-sp^2), 143.1,140.7 (24 C, aniline-1,3), 130.7 (12 C, aniline-5), 125.7 (12 C, aniline-4), 121.8 (12 C, aniline-6), 121.1 (24 C, aniline-2), 71.2 (12 C, **C**$_{60}$-sp^3), 69.2 (12 C, **C**H$_2$-O), 47.6 (6 C, **C**(C=O)$_2$), 35.2 (12 C, **C**H$_2$-Br), 34.6 (12 C, **C**H$_2$-C=O), 27.4 (12 C, CH$_2$**C**H$_2$CH$_2$) ppm.

IR (ATR, diamond:): $\tilde{\nu}$ = 3298 (w, br), 3084 (w), 2962 (m), 2363 (w), 2236 (w), 2082 (w), 1740 (m), 1666 (m), 1610 (w), 1595 (w), 1547 (m), 1487 (m), 1440 (m), 1298 (w), 1259 (m), 1213 (s), 1168 (w), 1093 (m), 1018 (s,br), 883 (w,br), 791(s) cm^{-1}.

UV/Vis (CH_2Cl_2): λ = 280 (100), 315 (59), 336 (46) nm (a.u.).

(Bis(*N*-((3-*tert.*-butylpyridiniummethyl)phenyl)-butanoic acid amid-4-yl) malonyl)-[6,0]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 29



Deprotected hexakis adduct **28** (90 mg, 20 µmol) was dissolved in dry THF (3 mL). 4-*tert.*-Butylpyridine (34 mg, 246.4 mmol, 12 eq.) and 3 mL dichloromethane were added and the mixture was stirred for 3 days. Dichloromethane (10 mL was added) and the mixture was stirred for further 3 days. The liquid was removed and THF and further 4-*tert.*-butylpyridine (34 mg, 0.2464 µmol, 12 eq.) were added. The supernatant was removed and the sample was washed with dichloromethane and diethyl ether.

Spectroscopy of **29**

^{1}H-NMR (300 MHz, CD_3OD, RT): δ = 8.98 (24 H, pyridyl-3), 8.14 (24 H, pyridyl-2), 7.83 (12 H, aniline-2), 7.63 (12 H, aniline-6), 7.34 (12 H, aniline-5), 7.20 (12 H, aniline-4), 5.81 (24 H, s, C**H**$_2$N$^+$), 5.52 (12 C, s, N-**H**), 4.4..4.3 (24 H, m, C**H**$_2$O), 2.52 (24 H, C**H**$_2$CO), 2.04 (24 H, C**H**$_2$C=O), 1.43 (24 H, CH_2C**H**$_2$$CH_2$) ppm.

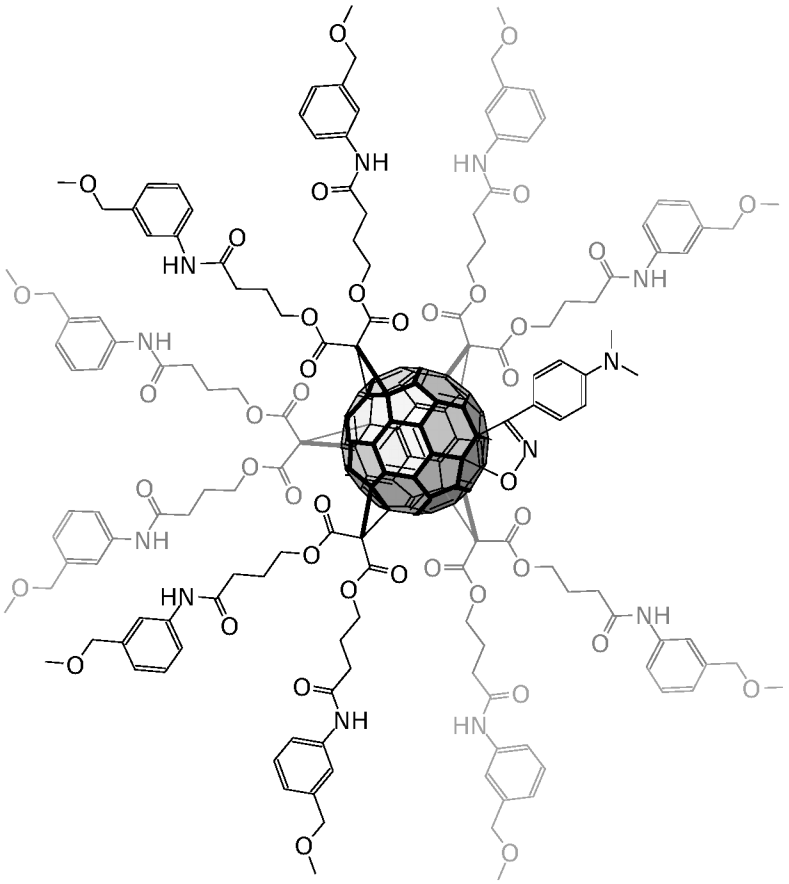
^{13}C-NMR{^{1}H} (100.6 MHz, CD_3OD, RT): δ = 173.1 (24 C, pyridyl-4, N-**C**=O), 164.7 (12 C, O-**C**=O), 147.0 (24 C, C_{60}-sp^2), 145.2 (24 C, pyridyl-2), 142.5 (24 C, C_{60}-sp^2), 141.0 (12 C, aniline-1), 135.3 (12 C, aniline-3), 131.2 (12 C, aniline-5), 126.9 (12 C, pyridyl-3), 125.3 (12 C, aniline-4), 122.3 (12 C, aniline-2), 121.4 (12 C, aniline-6), 70.5 (12 C, C_{60}-sp^3), 67.92 (12 C, **C**H_2O), 64.6 (12 C, Ph-**C**-N^+), 47.2 (6 C, **C**$(C=O)_2$), 37.6 (12 C, **C**H_2(C=ON)), 34.2 (12 C, **C**$(CH_3)_3$), 30.3 (36 C, **C**H_3), 25.5 (12 C, CH_2**C**H_2CH_2) ppm.

IR (ATR, diamond): $\tilde{\nu}$ = 3396 (s), 3051 (w), 2965 (s), 2358 (w), 2341 (w), 1739 (m), 1671 (m,br), 1638 (m), 1609 (m), 1552 (m), 1512 (w), 1491 (m), 1464 (m), 1443 (m), 1417 (m,br), 1373 (w,br), 1263 (s), 1216 (vs), 1173 (m), 1112 (m), 1021 (m,br), 895 (w,br), 851 (m), 791 (m), 769 (m), 712 (m) cm^{-1}.

MS: see chapter 4.1.1..

UV/Vis (MeOH): λ = 282 (100), 318 (54), 335 (43) nm (a.u.).

(Bis(*N*-((3-methoxymethyl)phenyl)-butanoic acid amid-4-yl)malonyl)-((p-dimethylaminophenyl)-1,O-diyl-methaneoxime)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 31



(p-*N*,*N*-Dimethylaminophenylisoxazolino)-mono-1,2-dihydrofullerene **30**[39] (200 mg, 225 µmol, 1 eq.) was suspended in degassed trimethylbenzene (20 mL) and stirred for 1 h. Dimethylanthracene (557 mg, 2.7 mmol, 12 eq.) and degassed chloroform (20 mL) were added and the mixture was stirred for 4 h. (1.8 g, 3.5 mmol, 16 eq.) and CBr_4 (895 mg, 2.7 mmol, 12 eq.) were added. After the malonate was dissolved, P_1-*t*Bu[129] (678 mg, 734 µL, 2.7 mmol, 12 eq.) was added dropwise in degassed trimethylbenzene/chloroform 1:1 and the mixture was stirred for 8 days at room temperature. The mixture and the precipitated raw product was plug-filtered (SiO_2; dichloromethane/THF) and purified by column chromatography (SiO_2; toluene/dichloromethane/ethyl acetate/ethanol 3.66:2:3.33:0.95) R_f = 0.34 (repeated as long as notable volumes of educt and DMA were present) and then purified by means of recycling HPLC (nucleosil; toluene/dichloromethane/ethyl acetate/ethanol 3.66:2:3.33:0.95), collecting the substance after the 12th lap. Yield: 9 % of pure product, sometimes impurified with dibrominated malonate and dimerized (double-bonded) malonate, which will be removed by column chromatography after the deprotection step. Other R_f values: R_f(SiO_2; dichloromethane/THF 2:1): 0.63.

Spectroscopy of **31**

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.75 (s, 2 H, 10 H N-**H**), 7.52 (s, 2 H, 10 H, 2-m-methylaniline), 7.42..7.33 (m, 2 H, 10 H, 6-m-methylaniline), 7.23..7.09 (m, 2 H, 10 H, 5-m-methylaniline), 7.03..7.95 (m, 2 H, 10 H, 4-m-methylaniline), 4.35..4.08 (m, 4 H, 20 H, C**H**$_2$O), 3.29..3.25 (m, 6 H, 30 H, O-C**H**$_3$), 3.24 (s, 6 H, N-C**H**$_3$), 2.45..2.28 (m, 4 H, 20 H C**H**$_2$C=O) 2.08..1.90 (m, 4 H, 20 H, C**H**$_2$CH$_2$O) ppm.

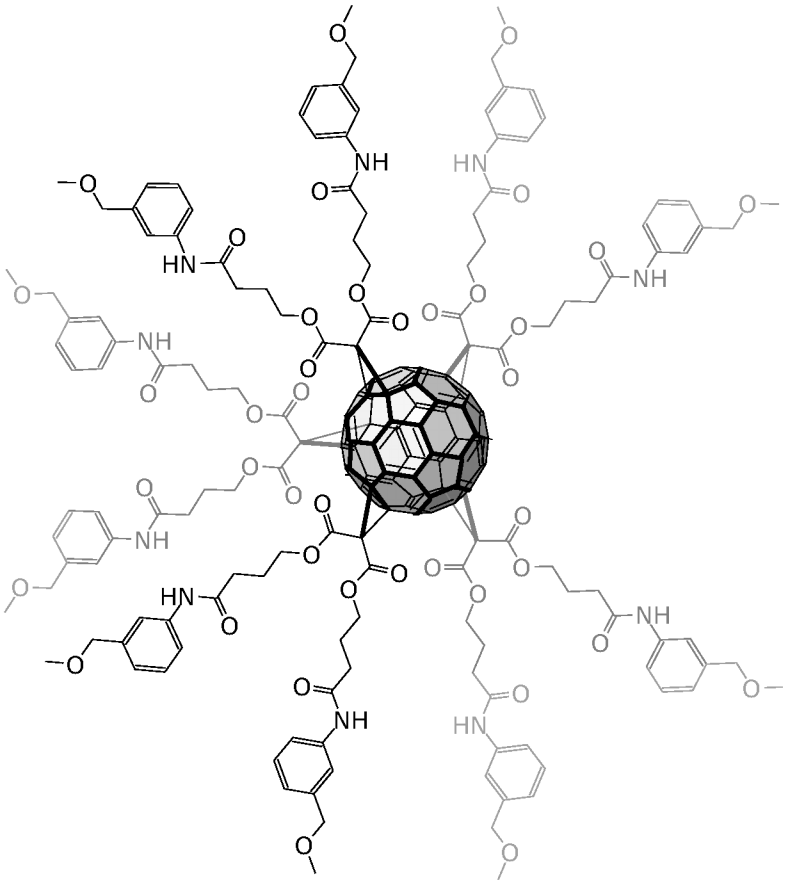
^{13}C-NMR{^{1}H} (75.5 MHz, $CDCl_3$): δ = 170.9 (2 C, C(**C**=O)$_2$ of free dibrominated malonate), 170.7 (10 C, C(**C**=O)$_2$ of product), 167.0 (10 C, **C**=O-N), 146.6, 146.3, 145.9, 145.8, 145.2, 145.1, 144.9, 144.1, 143.4, 142.9, 142.0, 141.8, 141.7, 141.3, 141.0, 140.1, 139.5, 139.3, 139.2, 139.1, 139.0 (48 C, **C**$_{60}$-sp^2), 135.1 (2 C, (C=O)$_2$**C**=**C**(C=O)$_2$, dimerized malonate), 129.3 (2 C, m-dimethylaniline), 138.8 (2 C; 10 C, 3-methylaniline), 138.1 (4 C; 10 C, 1-methylaniline) 128.7 (2 C; 10 C, 5-methylaniline), 123.2 (4 C; 10 C, 4-methylaniline), 119.1 (8 C; 20 C, 1,6-methylaniline), 111.4 (2 C, o-dimethylaniline), 101.0 (1 C, **C**-O of **C**$_{60}$-sp^3), 74.16 (10 C, Ph-**C**H$_2$-O), 69.74, 69.68, 69.1, 67.8, 67.3, 66.4, 65.8 (10 C, **C**H$_2$-O), 57.9 (10 C, **C**H$_3$O), 50.1 (1 C, $CBr_2(C=O)_2$), 45.4 (5 C, $CH_2(C=O)_2$), 39.8 (2 C, (**C**H$_3$)$_2$N), 32.9 (2 C, **C**H$_2$N of free dibrominated malonate), 32.7 (10 C, **C**H$_2$N of product), 24.0 (2 C, **C**H$_2$CH$_2$O of free dibrominated malonate), 23.9 (10 C, **C**H$_2$CH$_2$O of product) ppm.

IR(ATR, diamond): ṽ = 3306 (s, br), 3151 (w), 3087 (w), 2961 (m), 2926 (m), 2855 (m), 2822 (m), 2360 (w), 2341 (w), 1742 (s), 1664 (s), 1610 (m), 1596 (w), 1549 (s), 1488 (w), 1442 (m), 1374 (w,br), 1298 (w), 1260 (s, br), 1216 (s, br), 1167 (w), 1088 (m,br), 1026 (w,br), 898 (vw), 879 (vw), 791 (m), 763 (w), 733 (m), 713 (w), 696 (w) cm^{-1}.

MS (ESI-TOF, MeOH + CH_3CN): m/z = calcd. for $C_{202}{}^{13}C_2H_{170}N_{12}O_{41}Na^{2+}$ [M + 2 Na]$^{2+}$: 1745.5721 meas.: 1745.5810.

UV/Vis (CH_2Cl_2): λ (ε) = 244 (158000), 277 (53000), 283 (50000), 314 (41000), 334 (30000) nm (M^{-1}cm^{-1}).

(Bis(*N*-((3-methoxymethyl)phenyl)-butanoic acid amid-4-yl) malonyl)-[5,0]-pentakis-1,2,18,22,23,27,45,31,32,36-decahydro[60]-fullerene 32



This reaction must be held under strict exclusion of oxygen.
(123 mg, 35.7 µmol, 1 eq.) was dissolved in dichloromethane (50 mL). Maleic anhydride (1.071 g, 11.1 µmol, 1 eq.) was added and the mixture was degassed for 15 minutes. Then, the solution was irradiated with a 500 W halogen lamp for 24 h. The raw mixture was purified by means of column chromatography (SiO_2; dichloromethane/ethyl acetate/ethanol 47.5:47.5:5) and again (SiO_2; ethyl acetate) to remove malonate remaining from the last step. Yield: 70.9 mg (21.7 µmol, 58 %).

Spectroscopy of **32**

^{1}H-NMR (300 MHz, $CDCl_3$): 8.70-8.40 (10 H, N-H), 7.57-7.48 (10 H, aniline-2), 7.43-7.31 (10 H, aniline-6), 7.23-7.11 (10 H, aniline-5), 7.04-6.93 (10 H, aniline-4), 4.47-4.12 (40 H, C**H**$_2$O), 3.32-3.24 (30 H, C**H**$_3$O), 2.53-2.24 (20 H, C**H**$_2$C=O), 2.18-1.87 (20 H, C**H**$_2$CH$_2$O) ppm.

^{13}C-NMR{^{1}H} (75.5 MHz, $CDCl_3$): 170.8, 170.8, 170.7 (10 C, **C**=O-N), 167.4, 165.8, 163.9 C(**C**=O)$_2$, 146.8, 145.9, 145.6, 144.8, 144.6, 144.2, 143.1, 142.1, 139.9, 139.7 (50 C, C_{60}-sp^2), 139.0 (10 C, aniline-3), 138.2 (10 C, aniline-1), 128.9 (10 C, aniline-5), 123.4 (10 C, aniline-4), 119.4 (10 C, aniline-6), 119.2 (10 C, aniline-2), 74.3 (10 C, Ph-CH$_2$-O), 69.2 (10 C, **C**$_{60}$-sp^3), 66.5 (10 C, CH$_2$**C**H$_2$O), 58.1 (10 C, **C**H$_3$O), 33.1 (10 C, CH$_2$**C**H$_2$C=O), 24.1 (10 C, **C**H$_2$CH$_2$C=O) ppm.

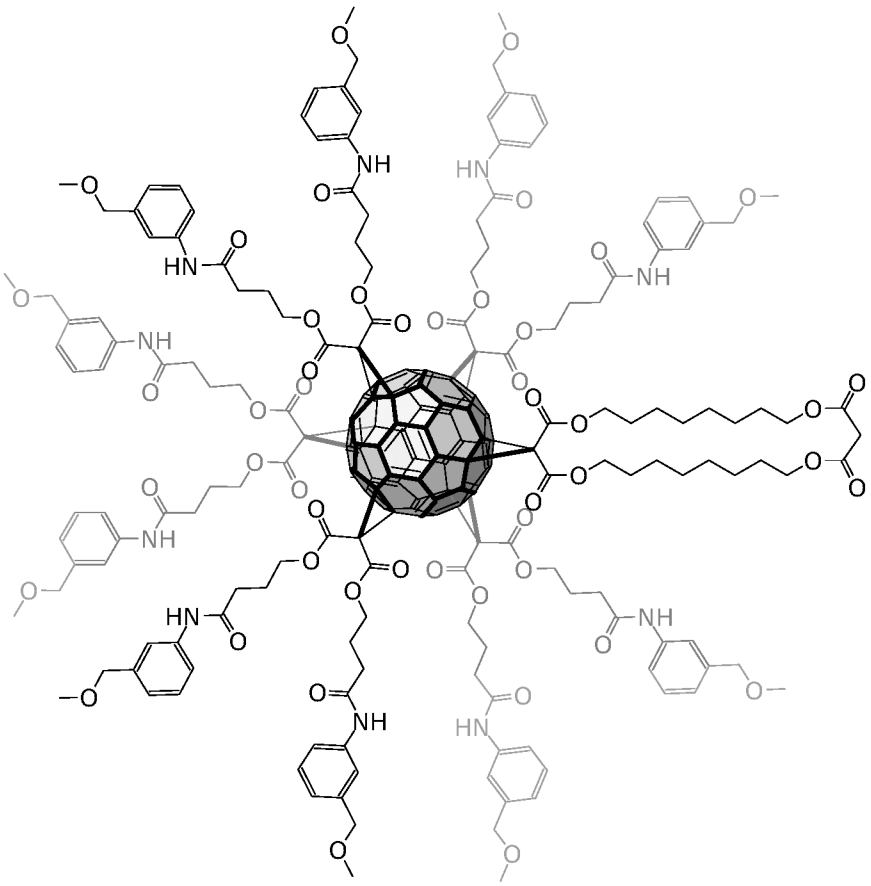
MS (MALDI, sin) calcd.: for $C_{193}{}^{13}C_2H_{160}O_{40}N_{10}Na^+$ $[M + Na]^+$ 3306.0752 meas.: 3306 Da.

MS (ESI-TOF, MeOH/CH_3CN): calcd.: for $C_{193}{}^{13}C_2H_{160}O_{40}N_{10}Na_2{}^{2+}$ $[M + 2\ Na]^{2+}$: 1664.5427 meas: 1664.5323 Da.

IR: 3303 (m), 2926 (m), 2822 (w), 2360 (w), 2247 (w), 1741 (m), 1663 (s), 1612 (w), 1595 (w), 1547 (s), 1488 (w), 1441 (m), 1377 (m), 1256 (s), 1212 (s), 1167 (vw), 1085 (s), 1023 (m), 908 (m), 789 (m), 727 (s), 695 (w), 647 (w).

UV/Vis (CH_2Cl_2): λ (ε) = 277 (48000), 282 (46000), 315 (22000), 341 (13000) nm ($M^{-1}cm^{-1}$).

(Bis(*N*-((3-methoxymethyl)phenyl)-butanoic acid amid-4-yl) malonyl)-(cyclo[2]octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 34



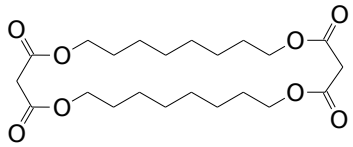
(Bis(*N*-((3-methoxymethyl)phenyl)-butanoic acid amid-4-yl) malonyl)-[5,0]-pentakis-1,2,18,22,23,27,45,31,32,36-decahydro[60]-fullerene (65 mg, 19.8 µmol, 1 eq.) was dissolved in dichloromethane (7 mL). Cyclo[2]-octylmalonate (305 mg, 772 µmol, 39 eq.) and tetrabromocarbon (100 mg, 299 µmol, 15 eq.) were added. P_1 *t*Bu (21 mg, 23 µL, 99 µmol, 5 eq.) were added dropwise over 10 minutes. 5 minutes later, the mixture was plug-filtered (SiO_2;ethyl acetate/ethanol 9:1) and again (SiO_2;dichloromethane/ethyl acetate 2:1 (to elute the addend); ethyl acetate/ethanol 9:1). Yield: 45.5 mg (12.3 µmol, 62 %).

Spectroscopy of **34**

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.39 (s, 10 H, N-H), 7.54 (m, 10 H, aniline-1), 7.38 (m, aniline-6), 7.19 (m, 1 H, aniline-5), 7.02 (m, 1 H, aniline-4), 4.39-4.06 (m, 48 H, C**H**$_2$O), 3.36-3.27 (m, 32 H, O-C**H**$_3$, C**H**$_2$(C=O)$_2$), 2.48-2.30 (m, 20 H, CH_2C**H**$_2$C=O), 2.14-1.95 (m, 20 H, C**H**$_2$$CH_2$C=O), 1.70-1.55 ($CH_2CH_2$C**H**$_2$$CH_2$O), 1.37-1.26 (16 H, C**H**$_2$C**H**$_2$$CH_2CH_2$O) ppm.

^{13}C-NMR{^{1}H} (75.5 MHz, $CDCl_3$): δ = 170.6, 170.5, 170.4 (10 C, **C**=ON), 166.5 (2 C, CH_2(**C**=O)$_2$), 163.8, 163.8, 163.7, 163.7 (14 C, C(**C**=O-O)$_2$), 145.9, 145.8, 145.8, 145.6, 145.6, 141.4, 141.3, 141.2, 141.1, 140.9 (48 C, **C**$_{60}$-sp^2), 139.1 (10 C, aniline-1), 138.3, 138.2, 138.1 (10 C, aniline-2), 128.9 (10 C, aniline-5), 123.5 (10 C, aniline-4), 119.5 (10 C, aniline-1), 74.4 (10-C, Ph-**C**H_2O), 69.3, 69.2, 69.1, 69.1 (12 C, **C**$_{60}$-sp^3), 67.4, 66.4, 65.5, 58.2, 58.1 (10 C, O-**C**H_3), 45.7, 45.6 (6 C, C_{60}-**C**(C=O)$_2$), 42.3 (1 CH_2 -**C**(C=O)$_2$)$_2$, 33.1 (10 C, **C**H_2-C=O), 29.4 (2 C, CH_2(C=O-O-CH_2**C**H_2), 28.5, 28.4 (12 C, C_{60}-**C**(C=O-O-CH_2**C**H_2)$_2$), 25.9, 25.6 (8 C, **C**H_2**C**$H_2CH_2CH_2$O), 24.0 (10 C, **C**H_2**C**$H_2CH_2CH_2$C=O) ppm.

Cyclo[2]-octylmalonate 35



In an improved procedure of Brandmüller,[74] 1,8-octanediol (8 g, 54.7 mmol, 1 eq.) and pyridine (8.66 g, 8.81 mL, 54.7 mmol, 1 eq.) were dissolved in anhydrous dichloromethane (4 l). Malonyl dichloride (7.71 g, 5.32 mL, 1.3 eq.) was dissolved in dry dichloromethane and added portion-wise over 4 days. After stirring for 2 days, the solution was concentrated to 600 mL. Ethyl acetate (67 mL) was added and the mixture was plug-filtered over silica (6×12 cm plug). The solvent was removed and the mixture was chromatographically purified (SiO_2, dichloromethane/ethyl acetate 19:1, diluted, at least 1.5 l bed volume). Yield: up to 2.7 g (23 %).

Spectroscopy of **35**

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.11 (t, $^{3}J_{H,H}$ = 6.7 Hz, 8 H, C**H**$_2$O), 3.33 (4 H, s, COOC**H**$_2$COO), 1.60 (8 H, m, C**H**$_2$$CH_2$O), 1.3 (16 H, m, C**H**$_2$C**H**$_2CH_2CH_2$O) ppm.

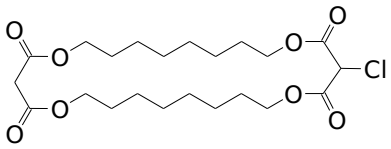
^{13}C-NMR{^{1}H} (100.5 MHz, $CDCl_3$): δ = 166.4 (4 C, **C**=O), 65.4 (4 C, **C**H_2-O), 42.1 (COO**C**H_2COO), 29.2 (4 C, **C**H_2-CH_2-O), 28.4 (4 C, **C**H_2-$(CH_2)_2$-O), 25.8 (4 C, **C**-$(CH_2)_3$-O) ppm.

IR (ATR, Diamond): $\tilde{\nu}$ = 2960 (w), 2922 (m), 2855(m), 1740 (s), 1478, 1389, 1326 (s), 1254 (s), 1217 (s), 1138 (s), 1064 (w), 1028 (m), 1003 (m), 892 (m), 724 (m) cm^{-1}.

MS (MALDI, dhb): m/z = 429 $[M + H]^+$, 451 $[M + Na]^+$.

EA(gas chromatography): for $C_{22}H_{36}$: calculated: C 61.66, H 8.47; found: C 60.93, H 8.35.

2-Chloro-cyclo[2]-octyl malonate 42



To malonate **35** (3.17 g, 1 eq.) suspended in chloroform (4.4 mL) was added sulfuryl dichloride (1 g, 0,599 mL, 1 eq.) and the mixture was heated to 70 °C for 24 h. The result was diluted with dichloromethane (200 mL) and chromatographically purified very slowly over a 200 mL bed-volume plug (SiO_2; dichloromethane). Unreacted educt can be recovered by washing the plug with dichloromethane/ethyl acetate 1:1. Yield: 36 % (70 % BORSM). R_f = 0.15 (prod). Impurities: R_f = 0.35 (both sides monochlorinated). R_f = 0.25 (one side dichlorinated).

Spectroscopy of **42**

^{1}H-NMR(300 MHz, $CDCl_3$): δ = 4.84 (1 H, C**H**Cl), 4.2 (4 H, 2 m, C**H**$_2$O-C=O-CHCl), 4.12 (4 H, t, C**H**$_2$O-C=O-CH_2), 3.33 (2 H, s, C**H**$_2$(C=O)$_2$), 1.63 (8 H, m, C**H**$_2$$CH_2$O) 1.32 (16 H, C**H**$_2$C**H**$_2$$CH_2$$CH_2$O) ppm.

^{13}C-NMR{^{1}H} (75.4 MHz, $CDCl_3$): δ = 166.4, 164.3 (4 C, **C**=O), 67.11, 65.4 (4 C, **C**H_2O), 55.8 (1 C, **C**H-Cl), 42.1 (1 C, C(C=O)**C**H_2), 29.21, 29.18 (4 C, **C**$H_2$$CH_2$O), 28.4, 28.3 (4 C, **C**$H_2$$CH_2$$CH_2$O), 25.8, 25.7 (4 C, **C**$H_2$$CH_2$$CH_2$$CH_2$O) ppm.

HRMS (ESI, AcN + MeOH): calcd. for $C_{22}H_{35}ClNaO_8$ $[M + Na]^+$: 485.19127; found: 485.19089.

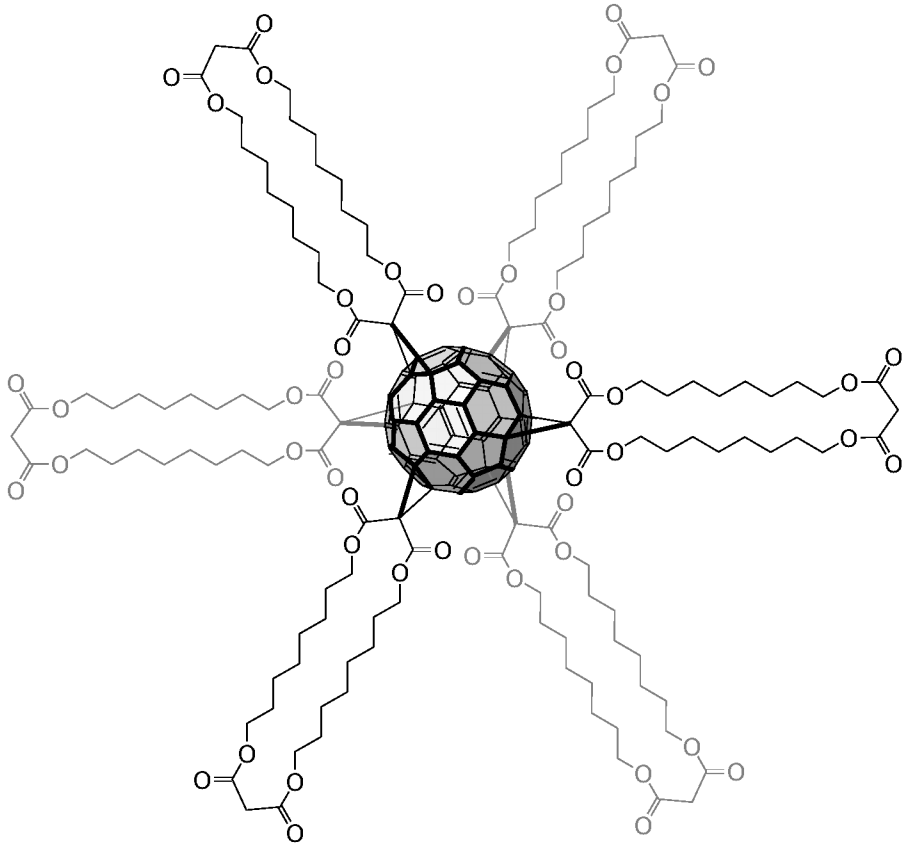
IR (ATR, diamond): $\tilde{\nu}$ = 2935 (s), 2856 (m), 1735 (s), 1469 (m), 1318 (s), 1306 (s), 1282 (s), 1202 (m), 1164 (m), 1147 (m), 1000 (m).

EA(gas chromatography): (mono-chlorinated) for $C_{22}H_{35}ClO_8$ calcd.: C: 57.08 H: 7.62 N: 0.00 S: 0.00 found: C: 56.34 H: 7.618 N: 0.01 S: 0.240

EA(gas chromatography): (di-chlorinated) for $C_{22}H_{34}Cl_2O_8$ calcd.: C: 53.12 H: 6.89 N: 0.00 S: 0.00 found: C: 52.79 H: 6.99 N: 0.00 S: 0.393

mp: mono-chlorinated: 78.3 °C bi-chlorinated: 110 °C

(Cyclo-[2]-octylmalonyl)-[6,0]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 46



Malonate **42** (400 mg, 864 µmol, 25 eq.), 9,10-dimethylanthracene (70 mg, 414 µmol, 12 eq.) and C_{60} (24.9 mg, 34.6 µmol, 1 eq.) were dissolved in toluene (12 mL) and stirred for 3 h. DBU (63.1 mg, 62.0 µL, 414 µmol, 12 eq.) was added and the mixture was stirred for 5 days. Further DBU (15.8 mg, 15.5 µL, 104 µmol, 3 eq.) was added and the mixture was stirred for additional 3 days. Ethyl acetate (4 mL) was added and the mixture was plug-filtered (SiO_2; toluene/ethyl acetate 4:1). The solvent was removed and the raw mixture was purified twice by means of flash chromatography (SiO_2; toluene/ethyl acetate 4:1), the second time on 15 µ grain size SiO_2 and very slowly. Yield: 16 mg (4.88 µmol, 13.7 % based on fullerene, 3.3 % based on the malonate).

Spectroscopy of **46**

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.22 (24 H, $C_{60}C$=O-OC**H**$_2$), 4.13 (24 H, CH_2=O-OC**H**$_2$), 3.4 (12 H, C**H**$_2$(C=O)$_2$), 1.75-1.6 (48 H, C**H**$_2$CH$_2$O), 1.567 (128 H, CH_2CH_2C**H**$_2CH_2CH_2$) ppm.

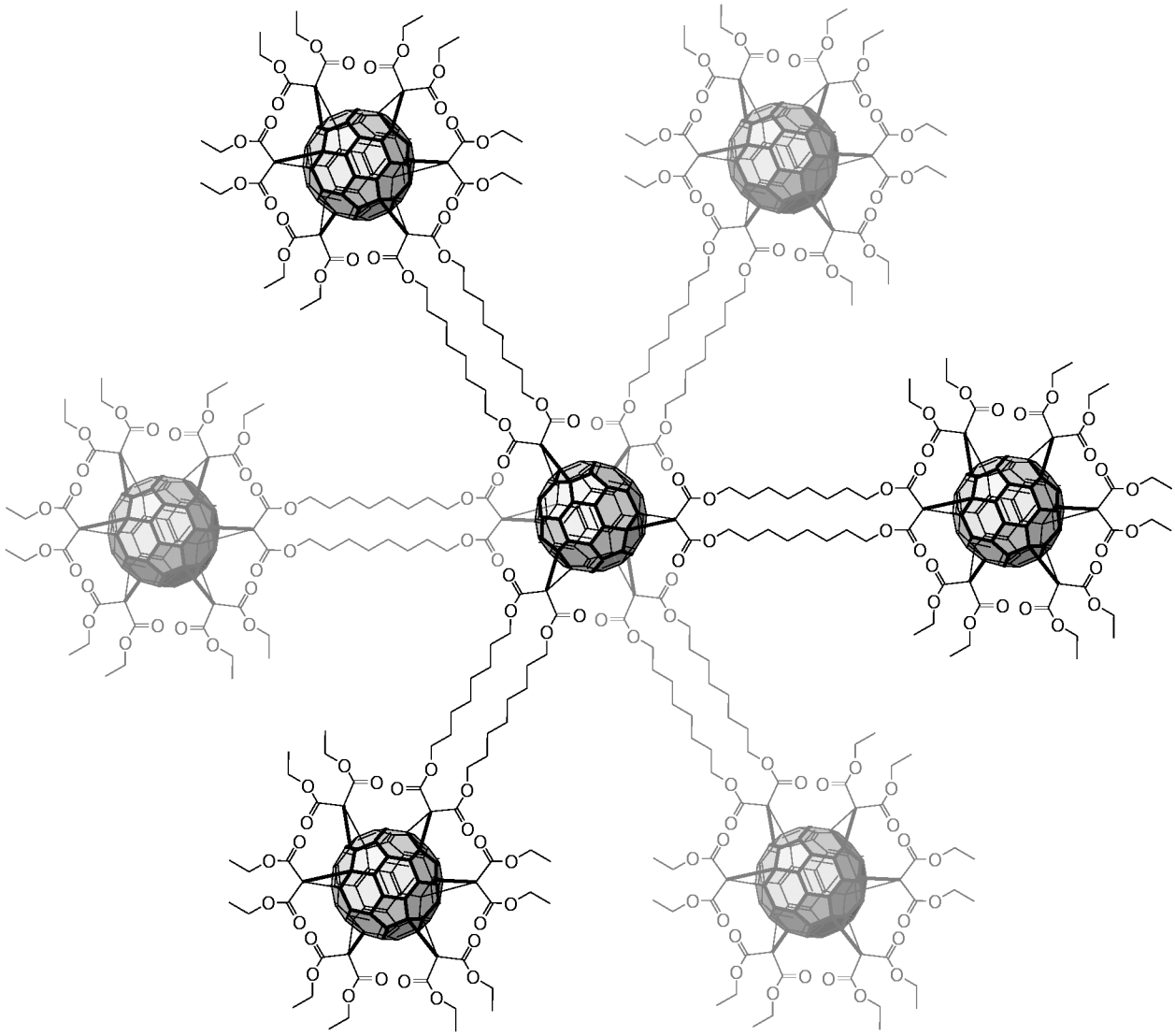
^{13}C-NMR{^{1}H}(100.5 MHz, $CDCl_3$): δ = 166.5 (12 C, CH_2(**C**=O)$_2$), 163.8 (12 C, C_{60}=C(**C**=O)$_2$), 145.8, 141.0 (48 C, C_{60}-sp^2), 69.1 (12 C, C_{60}-sp^3), 67.0 (12 C, C_{60}=C-C=OO**C**H$_2$), 65.6 (12 C, H_2C-C=OO**C**H$_2$), 45.3 (6 C, C_{60}=**C**(C=O)$_2$), 42.3 (6 C, H_2**C**(C=O)$_2$), 29.4 (24 C, **C**H$_2$CH$_2$O), 28.6, 28.5 (24 C, **C**H$_2$CH$_2$CH$_2$O), 25.9 (24 C, **C**H$_2$CH$_2$CH$_2$CH$_2$O) ppm.

MS (MALDI, sin): 3302 $[M+Na]^+$, 3303 $[M + 1H + Na]^+$, 3304 $[M + 2H + Na]^+$, 3305 $[M + 3H + Na]^+$, 3306 $[M + 4H + Na]^+$. HRMS (ESI, AcN + MeOH): calcd. for $C_{192}H_{204}Na_2O_{48}$ $[M + 2H + 2Na]^{2+}$: 1662.67328; found: 1662.67012.

IR (ATR, diamond): $\tilde{\nu}$ = 2929 (s), 2856 (m), 1732 (s), 1465 (w), 1387 (w), 1260 (m), 1212 (s), 1158 (w), 1081 (w), 1019 (m), 802 (m), 715 (w) cm^{-1}.

UV/Vis (CH_2Cl_2): λ (ε) = 245 (87000), 271 (66000), 282 (71000), 317 (45000), 335 (36000), 381 (5000) nm ($M^{-1}cm^{-1}$).

((Diethyl malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-[6,0]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 50



Central unit **46** (31 mg, 9.452 µmol, 1 eq.) was dissolved in 3 mL toluene. A solution of (Diethylmalonyl)-[5,0]-pentakis-1,2,18,22,23,27,45,31,32,36-decahydro[60]-fullerene **49**[98] (114 mg, 75.618 µmol, 8 eq.) in 5 mL toluene was added. The educts precipitated immediately. Be aware that the solution of **49** is oversaturated, so it must be created on demand by concentrating a more dilute solution.

Solutions of CBr_4 (18.8 mg, 56.7 µmol, 6 eq.) and P_1-*t*Bu (13.3 mg, 14.4 uL, 56.7 µmol, 6 eq.) were added and the mixture was stirred for 22 days. Dichloromethane was added until the precipitate was dissolved, and further pentakisadduct (21 mg, 14 µmol, 1.5 eq), CBr_4 (31 mg, 94.5 µmol, 10 eq.) and P_1-*t*Bu (22.2 mg, 24 µL, 94.5 µmol, 10 eq.) were added portion-wise over 2 weeks and the mixture was stirred for another 2 weeks. Ethyl acetate (5 mL) was added and the mixture was plug-filtered (SiO_2; toluene/ethyl acetate 4:1). The solvent was evaporated and the mixture was purified with column chromatography (SiO_2; toluene/ethyl acetate 6:1; toluene/ethyl acetate 2:1). Yield: 50 mg (4.05 µmol, 43 % resp. to **46**)

Spectroscopy of **50**

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.30 (q, $^3J_{H,H}$ = 7.0 Hz, 120 H, $CH_3C\mathbf{H}_2O$), 4.22 (48 H, m, $CH_2C\mathbf{H}_2O$), 1.70 (48 H, $C\mathbf{H}_2CH_2O$), 1.36 (96 H, $C\mathbf{H}_2C\mathbf{H}_2CH_2CH_2O$), 1.30(t, $^3J_{H,H}$ = 7.0 Hz, 180 H, $C\mathbf{H}_3$) ppm.

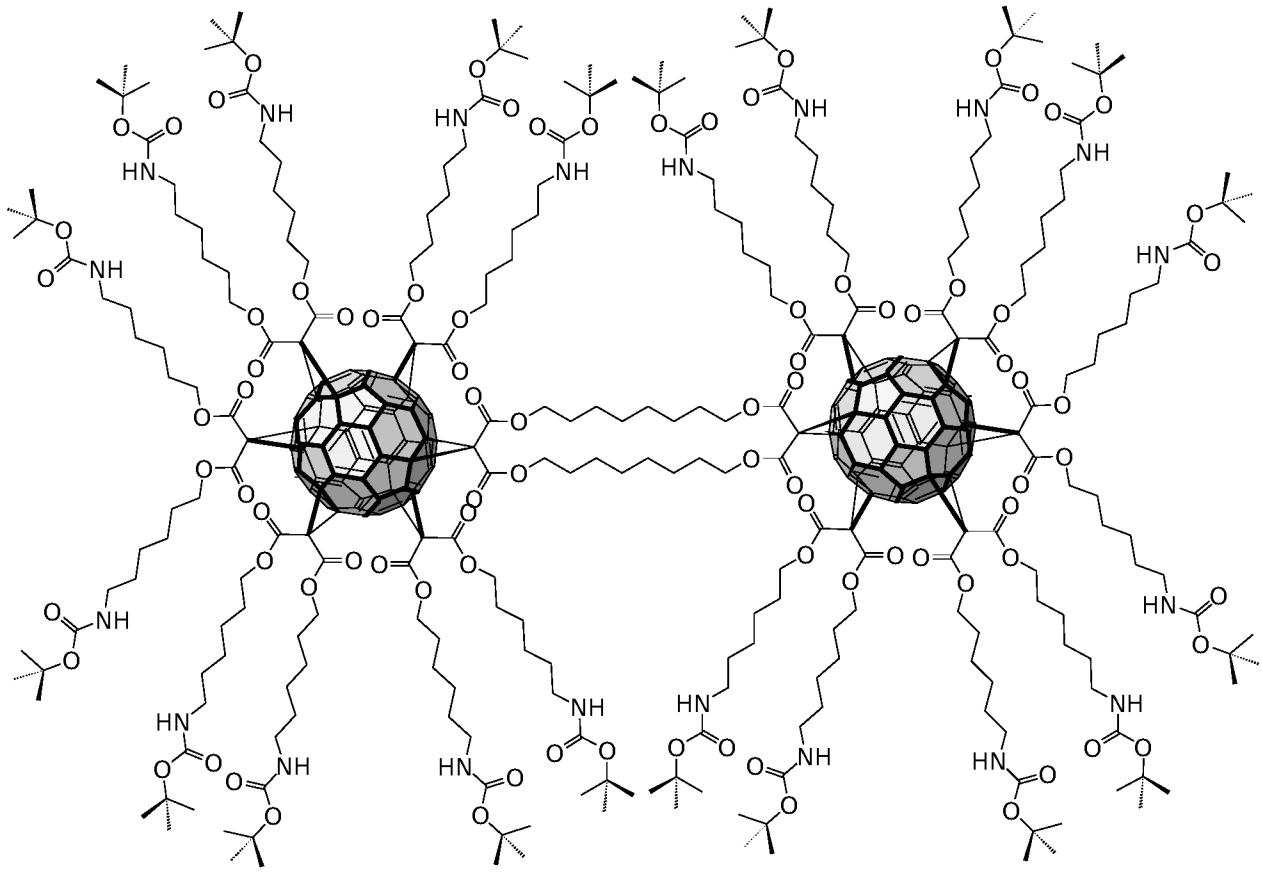
^{13}C-NMR{^{1}H} (100.5 MHz, $CDCl_3$): δ = 163.81, 163.78, 163.75 (84 C, C=O), 145.8, 145.7, 141.1, 141.0 (336 C, $\mathbf{C}_{60}$-sp^2), 69.09, 69.05, 69.01, 67.0 (84 C, $\mathbf{C}_{60}$-sp^3), 62.8 (84 C, $H_2\mathbf{C}$-O), 45.31, 45.29, 45.27, 45.24 (42 C, $\mathbf{C}(C{=}O)_2$), 29.46 (24 C, $CH_2\mathbf{C}H_2CH_2O$), 28.48 (24 C, $\mathbf{C}H_2CH_2CH_2O$), 26.0 (24 C, $\mathbf{C}H_2CH_2CH_2CH_2O$), 14.0 (60 C, $\mathbf{C}H_3$) ppm.

MS (MALDI, dctb): 12336 $[M]^+$; HRMS (ESI, CH_3CN+MeOH+HCOOH): calcd. for $C_{754}{}^{13}C_8H_{492}Na_4O_{168}$ $[M + 4Na]^{4+}$ 3106.74488 found: 3106.75364 Da.

IR (ATR, diamond): ῡ = 2980 (m), 2934 (m), 2857 (m), 1742 (s), 1464 (w), 1368 (w), 1262 (s), 1216 (s), 1079 (m), 1043 (m), 1018 (m), 857 (w), 715 (m) cm^{-1}.

UV/Vis (CH_2Cl_2): λ [nm] = 246 (ε = 418000 $M^{-1}cm^{-1}$), 274 (ε = 415000 $M^{-1}cm^{-1}$), 282 (ε = 403000 $M^{-1}cm^{-1}$), 316 (ε = 333000 $M^{-1}cm^{-1}$), 334 (ε = 290000 $M^{-1}cm^{-1}$), 380 (ε = 71000 $M^{-1}cm^{-1}$) nm.

(Bis[6-(boc-amino)hexyl]malonyl)-((bis[6-(boc-amino)hexyl]malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene) 62



[5.0]-pentakisadduct **51**[98] (228 mg, 70.6 µmol, 2 eq.) was dissolved in toluene (4 mL). Malonate **35** (15.1 mg, 35.3 µmol, 1 eq.), CBr_4 (23.4 mg, 70.6 µmol, 2 eq.) and P_1-*t*Bu (16.54 mg, 17.9 µL, 70.6 µmol, 2 eq.) (dissolved in toluene) were added and the mixture was stirred for 19 days. The mixture was plug-filtered (SiO_2; dichloromethane/ethyl acetate 1:1) and purified via column-chromatography (dichloromethane/ethyl acetate 3:1). Yield: 111 mg, (16.2 µmol, 45.8 %).

Spectroscopy of **62**

^{1}H-NMR(400 MHz, $CDCl_3$): δ = 4.77 (s (br), 20 H, N-**H**), 4.19 (m, 48 H, C**H**$_2$O), 3.03 (m, 40 H, C**H**$_2$N), 1.62 (m, 48 H, C**H**$_2$CH$_2$O), 1.36 (s (br), 180 H, C**H**$_3$) (m, 40 H, C**H**$_2$CH$_2$N), 1.28 (96 H, C**H**$_2$C**H**$_2$CH$_2$CH$_2$O) ppm.

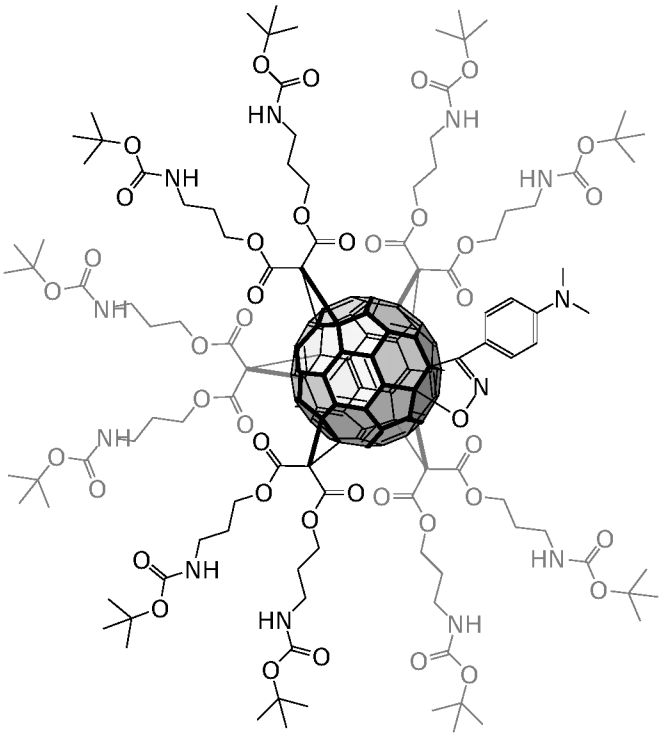
^{13}C-NMR{^{1}H}(100.5 MHz, $CDCl_3$): δ = 163.7 (24 C, C-(**C**=O)O), 155.9 (20 C, N-(**C**=O)O), 145.6, 141.0 (96 C, $\mathbf{C}_{60}$-sp^3), 78.7 (20 C, **C**$(CH_3)_3$, 69.0, 68.9 (24 C, $\mathbf{C}_{60}$-sp^2), 67.0 (4 C, **C**H_2O), 66.7 (20 C, **C**H_2O), 45.3, 45.2 (12 C, **C**$(C{=}O)_2$), 40.3 (20 C, **C**H_2N), 29.8 (20 C, N-$(CH_2)_4$**C**H_2CH_2O), 29.4 (O-$(CH_2)_6$**C**H_2CH_2O), 28.3 (60 C, C(**C**$H_3)_3$), 28.2 (20 C, **C**H_2CH_2N), 26.2 (20 C, **C**$H_2CH_2CH_2N$), 25.9 (O-$(CH_2)_4$**C**$H_2(CH_2)_3O$), 25.4 (20 C, N-$(CH_2)_3$**C**$H_2(CH_2)_2O$) ppm.

MS (ESI, CH_3CN/MeOH): m/z = calcd. for $C_{387}{}^{13}C_5H_{472}N_{20}O_{88}NaK$ $[M + K + Na]^+$: 6934.2757 meas: 6934.2758 Da, calcd. for $C_{387}{}^{13}C_5H_{472}N_{20}O_{88}Na_3$ $[M + 3\ Na]^{3+}$: 2313.4279 meas: 2313.4340 Da.

IR (ATR, diamond): $\tilde{\nu}$ = 2932 (m), 2860 (w), 1742 (m), 1693 (s), 1512 (m, br), 1455 (w, br), 1391 (w), 1365 (w), 1246 (s), 1212 (s), 1166 (s), 1080 (w), 1042 (w), 990 (m), 865 (w), 735 (m), 715 (m) cm^{-1}.

UV/Vis (CH_2Cl_2): λ = 246 (457000), 269 (344000), 283 (362000), 319 (233000), 337 (184000), 386 (31000) nm ($M^{-1}cm^{-1}$).

(Bis[*N*-boc-3-aminopropyl]malonyl)-dimethylaminophenylisoxazolino-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 63



(p-*N*,*N*-Dimethylaminophenylisoxazolino)-mono-1,2-dihydrofullerene **30**[39] (300 mg, 340 mmol) was dissolved in 1,2,4-trimethylbenzene (15 mL). DMA (770 mg, 3.7 mmol, 11 eq). was added and the mixture was stirred for 2 hours.

Bis(3-(boc-amino)propyl) malonate **76** (1.6 g, 4.05 mmol, 12 eq.), chloroform (13 mL), CBr_4 (1.2 g, 4.05 mmol, 12 eq.) and P_1-*t*Bu (1.017 g, 1.101 mL, 4.05 mmol, 12 eq.) were added and the mixture was stirred for 9 days. The mixture was plug-filtered (SiO_2; dichloromethane/ethyl acetate 1:1), dimethylanthracene was washed out (SiO_2; dichloromethane) and the raw mixture was eluted with dichloromethane/ethyl acetate 1:1. The solvent mixture was carefully removed. The raw mixture was dissolved in dry dichloromethane. Again 1 eq. of DMA (70 mg, 338 mmol, 1 eq.), bis(3-(boc-amino)propyl) malonate **76** (1.412 g, 3.375 mmol, 10 eq.) and CBr_4 (0.9 g, 10.6 eq), P_1-*t*Bu (462 mg, 500 µL, 1.84 mmol, 5.45 eq.) were added and the mixture was stirred for another 4 days. Plug filtration was done on SiO_2 with dichloromethane/ethyl acetate 1:1 and again (SiO_2; hexanes/ethyl acetate 3:2; then dichloromethane/ethyl acetate 1:1) in order to remove the malonate and other reagents. HPLC purification was done by means of multi-cycling HPLC (nucleosil; dichloromethane/ethyl acetate 1:1), collecting the product after 3 cycles. Yield: 99 mg (33.4 µmol, 9.8 %).

Spectroscopy of **63**

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, m-aniline), 6.64 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, o-aniline), 5.1..4.85 (s (br), 10 H, N-**H**), 4.43..4.13 (m, 20 H, C**H**$_2$O), 3.2..3.05 (m, 20 H, C**H**$_2$N), 2.93 (s, 6 H, N(C**H**$_3$)$_2$), 1.95..1.75 (m, 20 H, CH$_2$C**H**$_2$CH$_2$), 1.37 (s, 90 H, C(C**H**$_3$)$_3$) ppm.

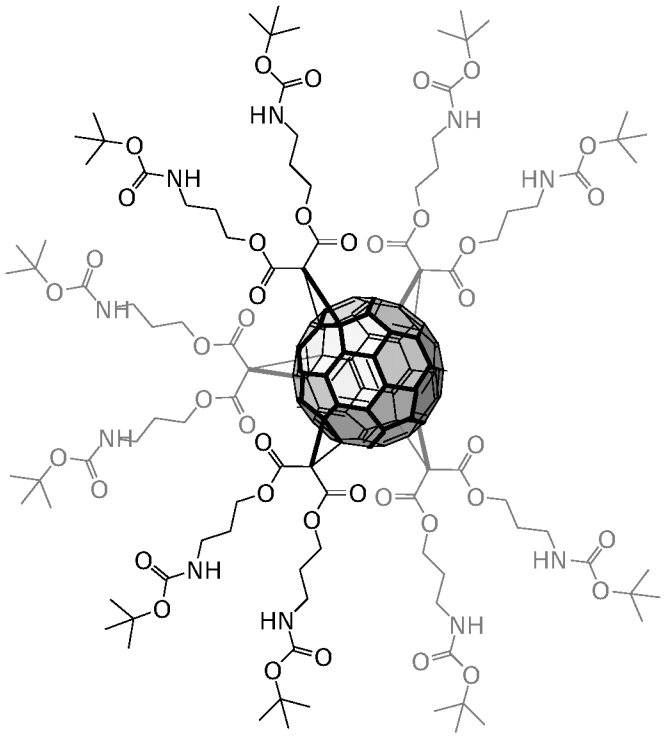
^{13}C-NMR{^{1}H} (100.5 MHz, $CDCl_3$): δ = 163.8, 163.7, 163.6, 163.5, 163.4, 163.3, 163.2 (10 C, **C**=O), 155.9 (10 C, N-**C**=O), 154.3 (1 C, **C**=N), 151.3 (1 C, ipso-aniline), 146.8, 146.6, 146.5, 146.1, 145.9, 145.6, 145.5, 145.4, 145.3, 145.2, 145.2, 144.8, 144.1, 144.0, 143.8, 143.6, 143.2, 143.0, 142.0, 141.6, 141.6, 141.0, 141.0, 140.2, 139.5, 139.4, 139.3, 139.0 (48 C, **C**$_{60}$-sp^2), 129.4 (2 C, m-aniline), 116.1 (1 C, p-aniline), 111.5 (2 C, o-aniline), 101.2 (1 C, C_{60}-C-O), 79.1 (10 C, **C**(CH$_3$)$_3$), 76.8 (1 C, **C-**O-N), 69.7, 69.5, 69.1, 69.0, 67.9, 67.3 (10 C, **C**$_{60}$-sp^3), 64.7, 64.7, 64.2 (10 C, **C**H$_2$O), 53.3, 45.3, 45.2, 44.4, 41.7 (5 C, **C**(C=O)$_2$), 40.0 (2 C, N(**C**H$_3$)$_2$), 37.2 (10 C, **C**H$_2$-N), 28.9 (10 C, CH$_2$**C**H$_2$CH$_2$), 28.3 (30 C, C(**C**H$_3$)$_3$) ppm.

MS (MALDI, dctb): m/z = calcd. for $C_{153}{}^{13}C_2H_{163}N_{11}O_{41}Na$ [M - C-C_6H_4-N(CH$_3$)$_2$ + 3 H + Na]$^+$: 2859.10 meas.: 2859 Da. calcd. for $C_{162}{}^{13}C_2H_{170}N_{12}O_{41}$ [M + H]$^+$: 2966.17 meas.: 2966 Da.

IR (ATR, diamond): 3351 (s), 2973 (s), 2933 (m), 1243 (m), 1690 (m), 1609 (w), 1521 (s), 1454 (w), 1391 (w), 1366 (m), 1249 (s), 1215 (m), 1167 (s), 1040 (m), 714 (w).

UV/Vis(CH_2Cl_2): λ = 245 (81000), 268 (64000), 317 (57000), 337 (43000).

(Bis[*N*-boc-3-aminopropyl]malonyl)-[5,0]-pentakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 65



Protected pentakisadduct **63** (99 mg, 33.4 µmol, 1 eq.) was dissolved in dry, degassed toluene (50 mL). Maleic anhydride (98.22 mg, 1 mmol, 30 eq.) was added. The mixture was degassed for 15 minutes, and irradiated for 1 day with a 500 W halogen lamp under cooling to -5 °C. The amount of the solvent was reduced and the mixture was purified by means of column chromatography (SiO_2; dichloromethane/ethyl acetate 1:1). Yield: 71 mg (25.3 µmol, 76 %).

Spectroscopy of **65**

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.9..4.9 (s, br, 10 H, N-**H**), 4.47..4.16 (m, 20 H, C**H**$_2$O), 3.26..3.04 (m, 20 H, C**H**$_2$N), 1.99..1.74 (m, 20 H, CH_2C**H**$_2$$CH_2$), 1.52..1.3 (s (br), 90 H, C(C**H**$_3$)$_3$) ppm.

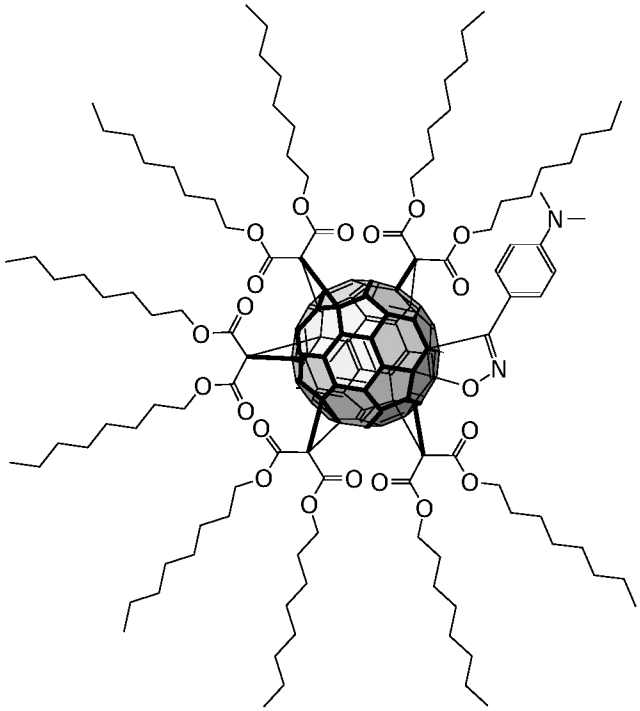
^{13}C-NMR{^{1}H} (75.5 MHz, $CDCl_3$): δ = 163.8, 163.7, 163.2 (10 C, C(**C**=O)$_2$), 156.0 (10 C, N-**C**=O), 148.5, 146.9, 146.1, 145.7, 144.9, 144.6, 144.1, 143.8, 143.1, 142.2, 139.6 (50 C, **C**$_{60}$-sp^2), 79.3 (10 C, **C**(CH$_3$)$_3$), 69.8, 69.4, 69.1 (10 C, C$_{60}$-sp^3), 64.8, 64.8, 64.6, 64.6 (10 C, **C**H$_2$O), 53.9, 45.5, 44.9 (5 C, **C**(C=O)$_2$), 37.2 (10 C, **C**H$_2$N), 29.0 (10 C, CH_2**C**H$_2$$CH_2$), 28.4 (30 C, C(**C**H$_3$)$_3$) ppm.

MS (MALDI, dctb): m/z =calcd. for $C_{153}{}^{13}C_2H_{160}N_{10}O_{40}$ $[M]^+$: 2803.09 meas.: 2803 Da.

IR (ATR, diamond): $\tilde{\nu}$ = 3050 (s), 2976 (s), 2933 (m), 2361 (w), 2341 (w), 1643 (m), 1690 (s), 1609 (w), 1520 (s), 1455 (w) 1392 (w), 1366 (w), 1339 (m), 1251 (s), 1213 (m), 1168 (s), 861 (m), 738 (m).

UV/Vis(CH_2Cl_2): λ = 243 (97000), 282 (79000), 317 (48000) nm ($M^{-1}cm^{-1}$).

(Bis[*N*-boc-3-aminopropyl]malonyl)-dimethylaminophenylisoxazolino-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 66



(p-*N*,*N*-Dimethylaminophenylisoxazolino)-mono-1,2-dihydrofullerene **30** (184 mg, 208 µmol, 1 eq.) was dissolved in toluene (500 mL). Dioctyl malonate (614 mg, 700 µl, 1.84 mmol, 9 eq.) and tetrabromocarbon (6.91 g, 20.842 mmol, 100 eq.) was added. DBU (635 mg, 623 µL, 4.17 mmol, 20 eq.) was added. The mixture was stirred for 3 days. The mixture was plug-filtered (SiO_2; dichloromethane/ethyl acetate 3:1), and purified by means of column-chromatography (SiO_2; dichloromethane) and again (SiO_2 15 µm grain size; dichloromethane). Yield: (110 mg, 43.7 µmol, 21 %)

Spectroscopy of **66**

^{1}H-NMR ($CDCl_3$, RT): 7.85 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, meta-aniline), 6.67 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, ortho-aniline), 4.35..4.07 (m, 20 H, C**H**$_2$O), 2.95 (s, 6 H, (C**H**$_3$)$_2$N), 1.75..1.48 (m, 20 H, C**H**$_2$CH$_2$O), 4.40..1.12 (m, 100 H, C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$CH$_3$), 0.89..0.81 (30 H, CH$_2$C**H**$_3$).

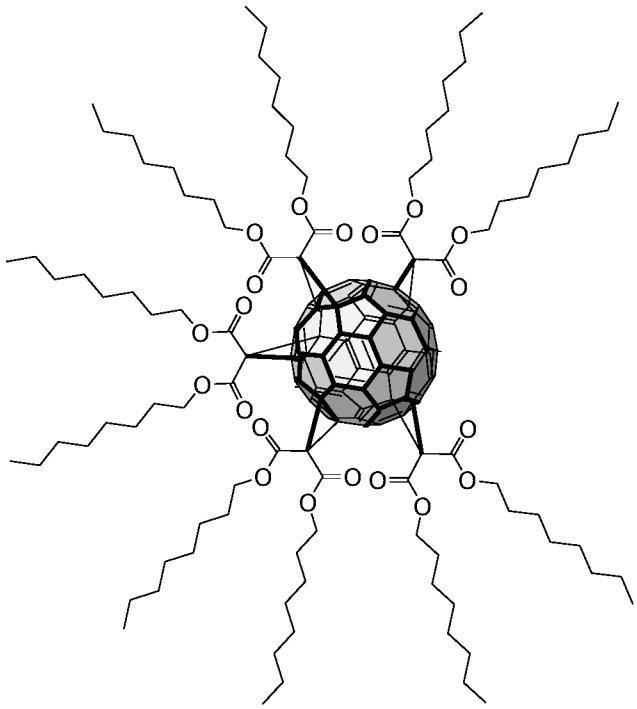
^{13}C-NMR{^{1}H} ($CDCl_3$, RT): 164.0, 163.9, 163.8, 163.6, 163.5, 163.4 (10 C, **C**=O) 154.4 (1 C, ipso-aniline), 151.1 (1 C, **C**=N), 146.7, 146.4, 146.2, 145.9, 145.6, 145.4, 145.3, 145.1, 143.9, 143.6, 143.2, 142.1, 141.8, 141.6, 141.2, 141.0, 140.3, 139.6, 139.5, 139.4, 139.4, (50 C, C_{60}-sp^2), 129.5 (2 C, meta-aniline), 116.7 (1 C, broad, para-aniline), 111.7 (2 C, ortho-aniline), 101.5 (1 C, C_{60}-sp^3, *C*-O), 69.9, 69.6, 69.2, 68.0, 67.4 (9 C, C_{60}-sp^3), 67.0, 66.9 (10 C, **C**H_2-O), 66.5 (1 C, C_{60}-sp^3), 45.5, 45.4, 44.6, 41.9 (5 C, **C**$(C{=}O)_2$), 40.1 (2 C, CH_3-N), 31.73, 31.70 (10 C, **C**$H_2CH_2CH_3$), 29.2, 29.1, 29.1 (20 C, **C**H_2**C**$H_2CH_2CH_2CH_3$), 28.4, 28.3, 28.3 (10 C, **C**H_2CH_2O), 25.8, 25.8, 25.7 (10 C, **C**$H_2CH_2CH_2O$), 22.6, 22.6, 22.5 (10 C, **C**H_2CH_3), 14.0 (10 C, CH_2**C**H_3) ppm.

MS (MALDI, dctb): m/z = calcd. for $C_{153}{}^{13}C_2H_{170}O_{20}$ $[M - C_9H_{10}N_2O]^+$: 2353.23 meas.: 2353 Da, calcd. for $C_{162}{}^{13}C_2H_{180}NO_{10}$ $[M -NO]^+$: 2485.32 meas.: 2485 Da.

IR (ATR, diamond): 2954 (w), 2924 (s), 2854 (m), 1744 (s), 1609 (w), 1525 (w), 1465 (m), 1360 (w), 1255 (s), 1212 (vs), 1123 (w), 946 (w), 714 (w), 669 (m).

UV/Vis: λ (ε) = 246 (81000), 268 (67000), 283 (67000), 316 (66000), 340 (40000) nm ($M^{-1}cm^{-1}$).

(Dioctylmalonyl)-[5,0]-pentakis-1,2,18,22,23,27,45,31,32,36-decahydro[60]-fullerene 67



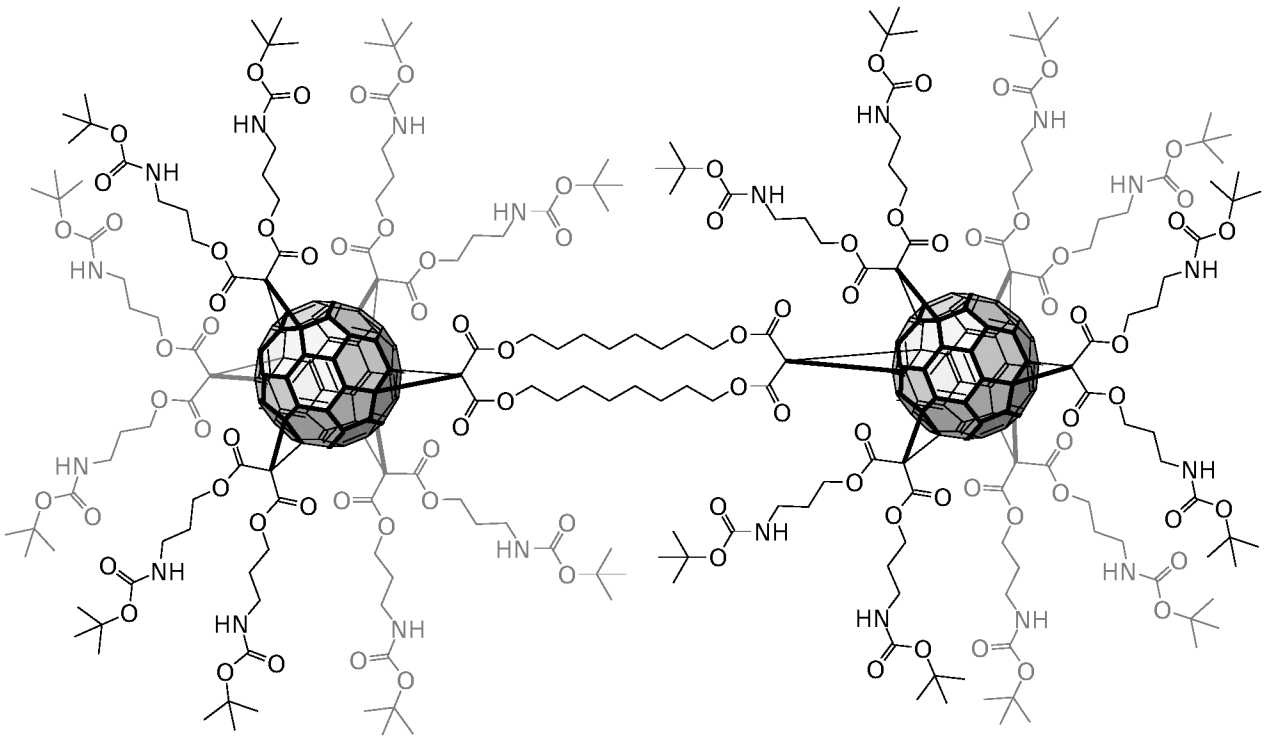
Protected pentakisadduct **66** (104.5 mg, 41.55 mmol, 1 eq.) was dissolved in toluene (50 mL). Maleic anhydride (122 mg, 1.25 mol, 30 eq.) was added.

The mixture was thoroughly degassed by bubbling nitrogen through it, then it was irradiated with a 500 W xenon soffit lamp for 24.5 h. The amount of solvent was reduced *in vacuo* and the solution was directly applied on a chromatographic column (SiO_2; dichloromethane), running the separation slowly. Yield: 69.4 mg (29.49 µmol, 71 %).

Spectroscopy of **67**

^{1}H-NMR (400 MHz, $CDCl_3$): 4.35..4.21, 4.16..4.09 (m, 20 H, C**H**$_2$O), 1.77..1.64 (m, 20 H, C**H**$_2$CH$_2$O), 1.41..1.15 (m, 100 H, (C**H**$_2$)$_5$CH$_2$CH$_2$O), 0.91..0.80 (m, 30 H, C**H**$_3$).
^{13}C-NMR{^{1}H} (100.5 MHz, $CDCl_3$): 163.9, 163.9, 163.8, 163.3 (10 C, **C**=O), 148.4, 146.8, 146.1, 145.7, 145.0, 144.5, 144.2, 144.1, 144.0, 143.0, 142.4, 139.7 (50 C, **C**$_{60}$-sp^2), 70.0, 69.5, 69.4, 69.2 (10 C, **C**$_{60}$-sp^3), 67.0, 67.0, 66.8 (10 C, **C**H$_2$O), 54.0, 45.7, 45.1 (5 C, **C**(C=O)$_2$), 31.7, 31.7, 31.6 (10 C, C**H**$_2$CH$_2$CH$_3$), 29.6, 29.2, 29.2, 29.1, 29.1 (20 C, (**C**H$_2$)$_2$(CH$_2$)$_2$CH$_3$), 28.5, 28.4, 28.4, 28.3 (10 C, **C**H$_2$CH$_2$O), 25.9, 25.8, 25.8, 25.7 (10 C, **C**H$_2$CH$_2$CH$_2$O), 22.8, 22.6, 22.6, 22.4 (10 C, **C**H$_2$CH$_3$), 14.0 (10 C, **C**H$_3$) ppm.
MS (ESI-TOF): m/z = calcd. for $C_{154}{}^{13}C_1H_{170}O_{20}Na$ $[M + Na]^+$: 2375.2210 meas: 2375.2280 Da.
IR (ATR, diamond): ṽ = 2954 (w), 2923 (s), 2854 (m), 1744 (s), 1463 (w, br), 1379 (w), 1351 (w), 1253 (s), 1208 (vs), 1120 (w), 1079 (m), 1025 (m), 990 (w), 942 (w), 883 (w), 804 (w), 714 (m), 667 (w).
UV/Vis(CH_2Cl_2): λ (ε) = 248 (93000), 282 (83000), 322 (39000) nm ($M^{-1}cm^{-1}$).

(Bis[3-(boc-amino)propyl]malonyl)-((bis[3-(boc-amino)propyl]malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene) 68



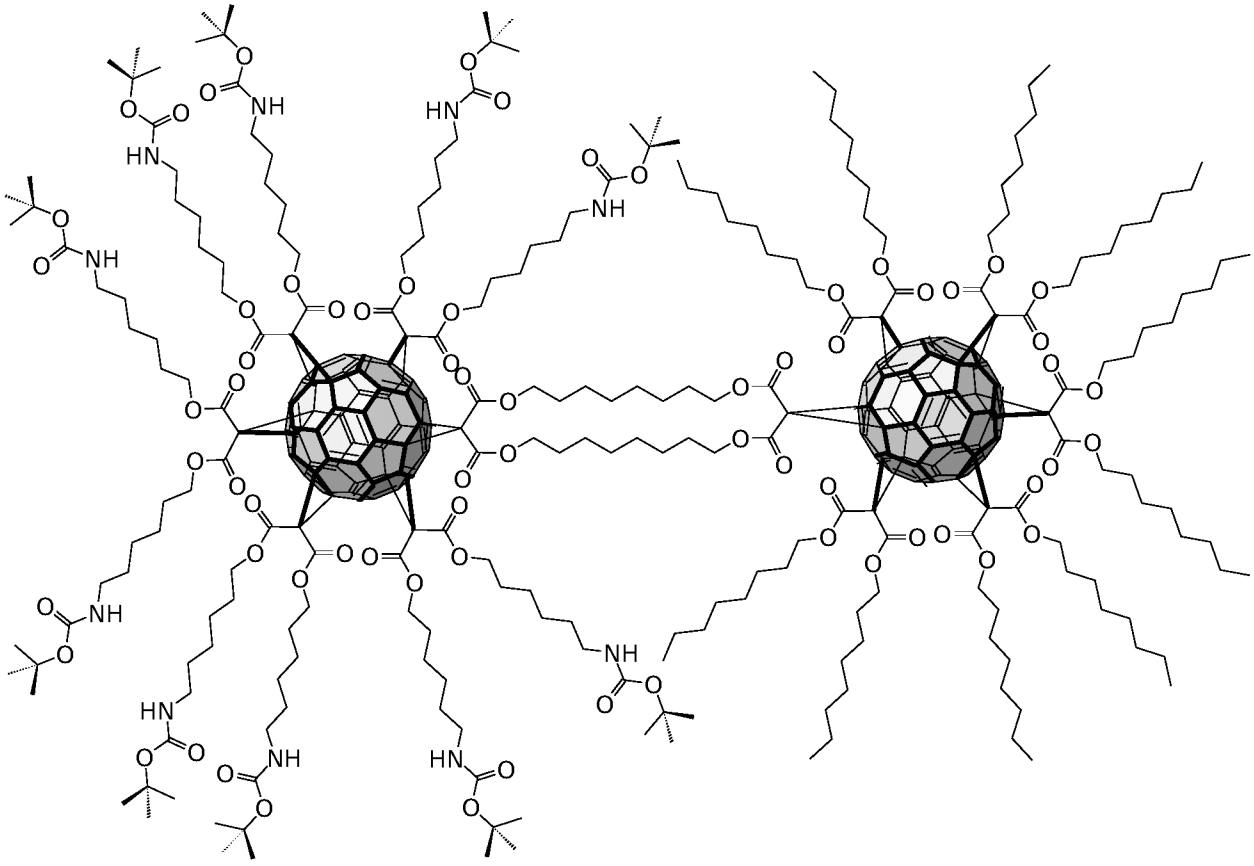
Mixed fullerene dimer **78** (18 mg, 4.559 µmol, 1 eq.) was dissolved in dichloromethane (5 mL). Dimethylanthracene (11.3 mg, 54.7 mmol, 5 eq) was added and the mixture was stirred for 2 hours. bis(3-(boc-amino)propyl) malonate **76** (45 mg, 108 µmol, 24 eq.), CBr_4 (15. mg, 45.59 µmol, 10 eq., in toluene) and P_1-*t*Bu (10.7 mg, 11.6 µL, 10 eq.) in toluene were added. After 8 days, further bis(3-(boc-amino)propyl) malonate **76** (45 mg, 108 µmol, 24 eq.), CBr_4 (15.1 mg, 45.59 µmol, 10 eq., in toluene) and P_1-*t*Bu (10.7 mg, 11.6 µL, 10 eq., in toluene) were added. After 9 days, the mixture was plug-filtered (SiO_2; toluene/ethyl acetate 1:1 and diethylether/dichloromethane/ethyl acetate 10:6:4, combining the eluates). The mixture was purified via column-chromatography (SiO_2; toluene/tetrahydrofurane 2:1) and another (SiO_2; 15 um; toluene/tetrahydrofurane 2:1, slow (12 h)). Yield: 6 mg (0.88 µmol, 19 %).

Spectroscopy of **68**

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.08..4.88 (s (br), 20 H, N-**H**), 4.46..4.13 (m, 48 H, C**H**$_2$O), 3.29..3.04 (m, 40 H, C**H**$_2$N), 2.00..1.78 (m, 40 H, C**H**$_2$CH$_2$N), 1.45..1.38 (m, 180 H, C(C**H**$_3$)$_3$) ppm.

^{13}C-NMR{^{1}H} (100.5 MHz, $CDCl_3$): δ = 163.8 (24 C, C(**C**=O)$_2$), 156.1 (20 C, N-C=O), 145.9, 141.0 (96 C, C_{60}-sp^2), 129.8 (impurity), 122.1 (impurity), 79.3 (20 C, **C**(CH$_3$)$_3$), 70.5, 69.3, 69.2, 69.0 (24 C, C_{60}-sp^3), 64.7, 64.4, 63.0 (24 C, **C**H$_2$O), 47.2 (12 C, **C**(C=O)$_2$), 37.4 (20 C, **C**H$_2$-N), 31.9, 31.7, 29.7 (20 C, C**H**$_2$CH$_2$N)), 29.6, 29.4, 29.1, 28.5 (60 C, C(**C**H$_3$)$_3$), 25.4, 25.4 , 22.7, 22.6, 14.1, 13.9, 11.8 ppm.
UV/Vis (CH_2Cl_2): λ = 246 (69000), 268 (55000), 281 (55000), 319 (31000), 337 (24000), 387 (5000) nm (M^{-1}cm^{-1}).

(Dioctylmalonyl)-((bis[6-(boc-amino)]malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene) 69



Pentakis adduct **51** (20 mg, 5.48 µmol, 1 eq.) and pentakis adduct **67** (12.9 mg, 5.48 µmol, 1.5 eq.) were dissolved in toluene. CBr_4 (1.817 mg, 5.48 µmol, 1 eq.) and P1-*t*Bu (1.29 mg, 1.39 µL, 5.48 µmol, 1 eq.) were added and the mixture was stirred for 2 days. The product was purified by means of column-chromatography (SiO_2; dichloromethane/ethyl acetate 3:1) and again (SiO_2 15 µm; dichloromethane/ethyl acetate 3:1). Yield: 17 mg (2.83 µmol, 51.6 %) R_f (dichloromethane/ethyl acetate 3:1)=0.75.

Spectroscopy of **69**

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.98..4.53 (s, br, 10 H, N-**H**), 4.38..4.10 (m, C**H**$_2$O), 3.07 (m, 20 H, CH_2N), 1.81..1.57 (m, 58 H, C**H**$_2$CH$_2$O, C**H**$_2$CH$_2$N), 1.41 (s, 90 H, C(C**H**$_3$)$_3$), 1.38..1.16 (156 H, C**H**$_2$CH$_2$CH$_2$O, C**H**$_2$CH$_2$CH$_2$N), 0.85 (t, $^{3}J_{H,H}$ = 6.7 Hz, 30 C, CH_2C**H**$_3$) ppm.

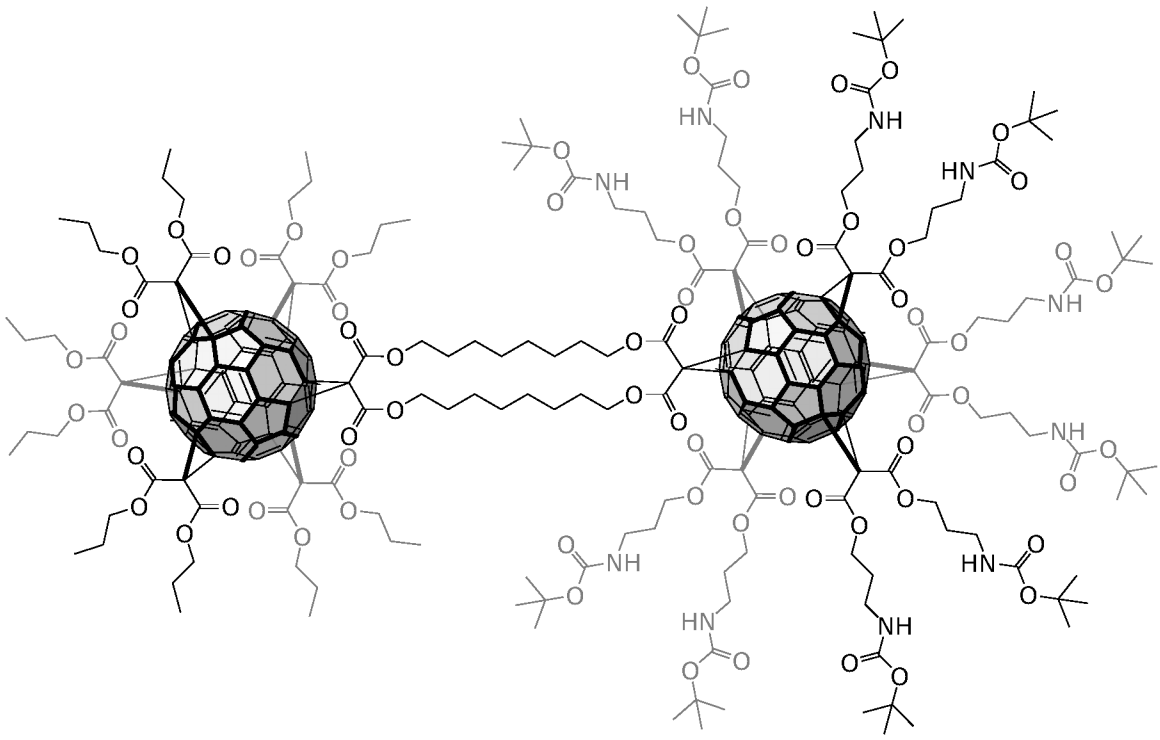
^{13}C-NMR{^{1}H} (75.5 MHz, $CDCl_3$): δ = 163.9, 163.8 (24 C, C(**C**=O)$_2$), 156.0 (10 C, N-**C**=O), 145.8, 145.7, 141.1 (96 C, C_{60}-sp^2), 79.0 (20 C, **C**(CH$_3$)$_3$), 69.1 (24 C, C_{60}-sp^3), 67.0, 66.9 (24 C, **C**H$_2$O), 45.4, 45.3 (24 C, CH$_2$(C=O)$_2$), 40.6 (10 C, **C**H$_2$N), 31.8 (20 C, **C**H$_2$CH$_2$CH$_3$), 29.9 (20 C, **C**H$_2$CH$_2$CH$_2$CH$_3$), 29.6 (4 C, spacer-**C**H$_2$CH$_2$O), 29.2 (40 C, **C**H$_2$CH$_2$CH$_2$CH$_2$CH$_3$, N-(CH$_2$)$_4$**C**H$_2$), 28.4 (30 C, C(**C**H$_3$)$_3$), 28.3 (4 C, spacer-**C**H$_2$CH$_2$CH$_2$O), 26.4 (10 C, **C**H$_2$CH$_2$N), 26.1, 25.8 (10 C, CH$_3$(CH$_2$)$_4$**C**H$_2$), 25.6 (10 C, **C**H$_2$(CH$_2$)$_3$N), 25.3 (4 C, spacer-**C**H$_2$CH$_2$CH$_2$CH$_2$O), 22.6 (**C**H$_2$CH$_3$), 14.1 (10 C, **C**H$_3$CH$_2$) ppm.

MS (ESI-AcN/MeOH): m/z = calcd. for $C_{358}{}^{13}C_4H_{422}N_{10}O_{68}Na_3{}^{3+}$ [M + 3 Na]$^{3+}$: 2023.3227 meas.: 2023.3276 Da, calcd. for $C_{358}{}^{13}C_4H_{422}N_{10}O_{68}NaK^{+}$ [M + Na + K]$^{+}$: 6062.9523 meas.: 6062.9503 Da.

IR(ATR, diamond): $\tilde{\nu}$ = 2927 (s), 2856 (m), 1745 (m), 1714 (s), 1516 (m), 1458 (m), 1391 (w), 1365 (w), 1263 (vs), 1214 (vs), 1171 (m), 1081 (w), 1043 (w), 991 (w), 716 (m) cm^{-1}.

UV/Vis(CH_2Cl_2): λ (ε) = 247 (345000), 269 (226000), 282 (239000), 320 (147000), 338 (118000) nm (M^{-1}cm^{-1}).

(Bis[*N*-boc-3-aminopropyl]malonyl)-((dipropyl malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene) 70



[5,1]/[1,0]-Dumbbell **79** (100 mg, 35.8 µmol) was dissolved in toluene (5 mL). DMA (74 mg, 358 µmol) was added to it and the mixture was stirred for 3 hours. Malonate **76** (187 mg, 446 µmol, 12 eq.), CBr_4 (142 mg, 429 µmol, 12 eq.) was added and P_1-*t*Bu (93 mg, 101 µL, 395 µmol, 11.5 eq.) was added dropwise over 1 hour in toluene. The mixture was stirred for 9 days. CBr_4 (76 mg, 230 µmol) and P_1-*t*Bu (101 mg, 110 µL, 446 µmol, 12 eq.) were added and the mixture was stirred for further 9 days. The mixture was plug-filtered (SiO_2; toluene:ethyl acetate 1:1), and chromatographically purified twice (SiO_2; dichloromethane/methanol 20:0.45), the second time using HPLC. The product was still containing mono- and dibrominated malonate at that point. Yield: 96 mg (9.74 µmol, 27.2 %.).

Spectroscopy of **70**

^{1}H-NMR (300 MHz, $CDCl_3$, RT): 5.25 (s, 1 H, monobrominated malonate CH-Br), 5.00 (s (br), 2 H, N-**H**, brominated malonate), 4.92 (s (br), 10 H, N-**H**) 4.28 (m, 48 H, C**H**$_2$O), 4.17 (m, 4 H, brominated malonate C**H**$_2$O), 3.13 (m, 20 H, product+brominated malonate C**H**$_2$-N), 1.84 (2 m, 48 H, C**H**$_2$-CH$_2$O), 1.66 (m, 4 H, brominated malonate C**H**$_2$CH$_2$O), 1.45..1.30 (m, 16 H, CH$_2$CH$_2$C**H**$_2$CH$_2$CH$_2$), 1.38 (s, 90 H, product+brominated malonate C(C**H**$_3$)$_3$), 0.89 (t, $^3J_{H,H}$ = 7 Hz, 30 H, CH$_2$C**H**$_3$) ppm.

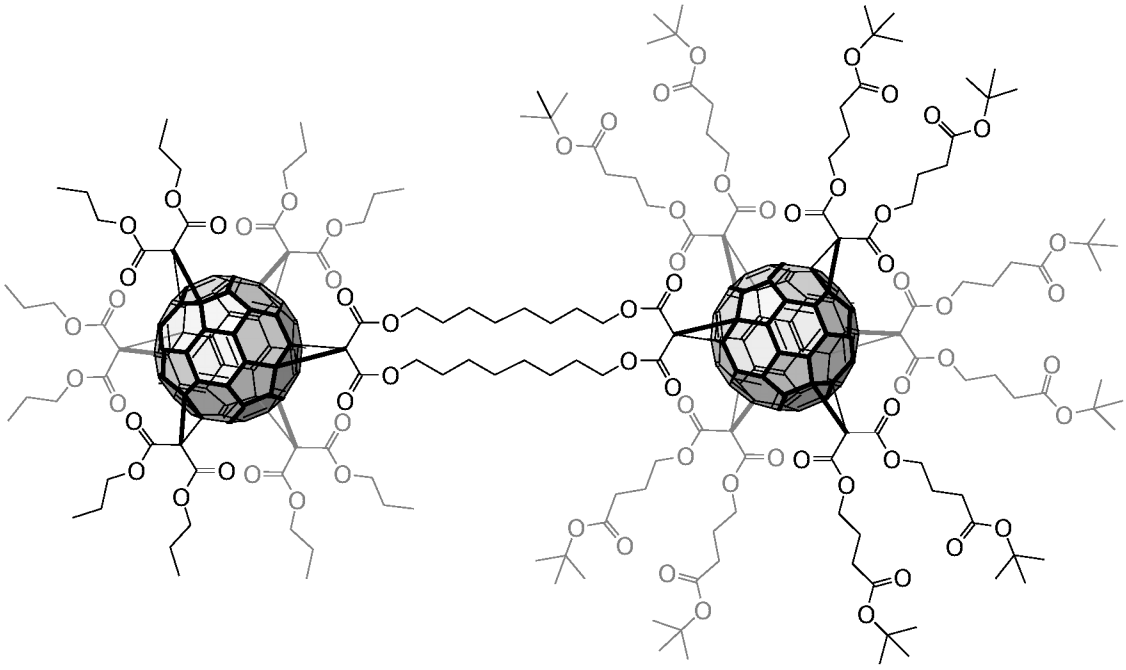
^{13}C-NMR{^{1}H} (75.5 MHz, $CDCl_3$, RT): δ = 163.8, 163.7, 163.6, (24 C, O-**C**=O), 162.2, 162.0 (2 C, 2 C, mono- and dibrominated malonate), 155.9 (10 C, N-**C**=O), 140.6, 141, 140.9 (96 C, $\mathbf{C}_{60}$-sp^2), 79.2 (10 C, $\mathbf{C}(CH_3)_3$), 69.1, 69.0, 68.9 (24 C, $\mathbf{C}_{60}$, sp^3), 64.8, 64.6, 64.3 (24 C, $\mathbf{C}H_2$-O), 53.4 (**C**Br_2, dibrominated malonate) 45.4, 45.2 (12 C, $\mathbf{C}(C{=}O)_2$), 42.2 (**C**HBr, monobrominated malonate).

MS (MALDI, dctb): m/z = calcd. $C_{278}{}^{13}C_3H_{262}N_{10}O_{67}K$ $[M - C{=}O + K]^+$: 4889.71 meas.: 4890 Da.

IR: $\tilde{\nu}$ = 2968 (m), 2934 (w), 1740 (w), 1690 (s), 1514 (m), 1456 (w), 1391 (w), 1365 (w), 1240 (m), 1211 (s), 1166 (m), 1043 (m),735 (w), 716 (w), 529 (w) cm^{-1}.

UV/Vis: λ = 245, 270, 280, 317, 335 nm.

(Bis[3-t-butylcarboxypropyl]malonyl)-((dipropylmalonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene) 71



((Dipropyl malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-1,2-dihydro[60]-fullerene **79** (47 mg, 15.8 µmol, 1 eq.) and DMA (41.6 mg, 202 µmol) were dissolved in dichloromethane and stirred for 3 h. Bis(3-*t*-butylcarboxypropyl) malonate **77** (78.3 mg, 202 µmol, 12 eq.) and CBr_4 (66.86 mg, 202 µmol, 12 eq.) were added, P_1-*t*Bu (98 mg, 25 eq, 419 µmol, 12 eq.) was added dropwise over 40 minutes and the mixture was stirred for 7 days. CBr_4 (66.86 mg, 202 µmol, 12 eq.) and P_1-*t*Bu (30 mg, 128 µmol, 7.7 eq.) were added and the mixture was stirred for further 4 days. The mixture was plug-filtered on SiO_2 in toluene/ethyl acetate 5:2 and purified by column-chromatography (SiO_2; toluene/ethyl acetate 9:1) and HPLC (SiO_2; toluene/ethyl acetate 9:1), followed by another plug-filtration (SiO_2; hexanes/ethyl acetate 10:4;toluene/ethyl acetate 5:2) in order to remove excess malonate. Yield: 47 mg (9.94 µmol, 62.9 %).

Spectroscopy of **71**

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.28, 4.20 (m, 48 H, C**H**$_2$O), 2.29 (m, 20 H, C**H**$_2$C=O), 1.96 (m, 20 H, C**H**$_2$CH$_2$C=O), 1.68 (m, 28 H, CH$_3$C**H**$_2$CH$_2$O, CH$_2$CH$_2$C**H**$_2$CH$_2$O), 1.42 (s, 90 H, C(C**H**$_3$)$_3$), 0.92 (m, 30 H, CH$_2$C**H**$_3$) ppm.

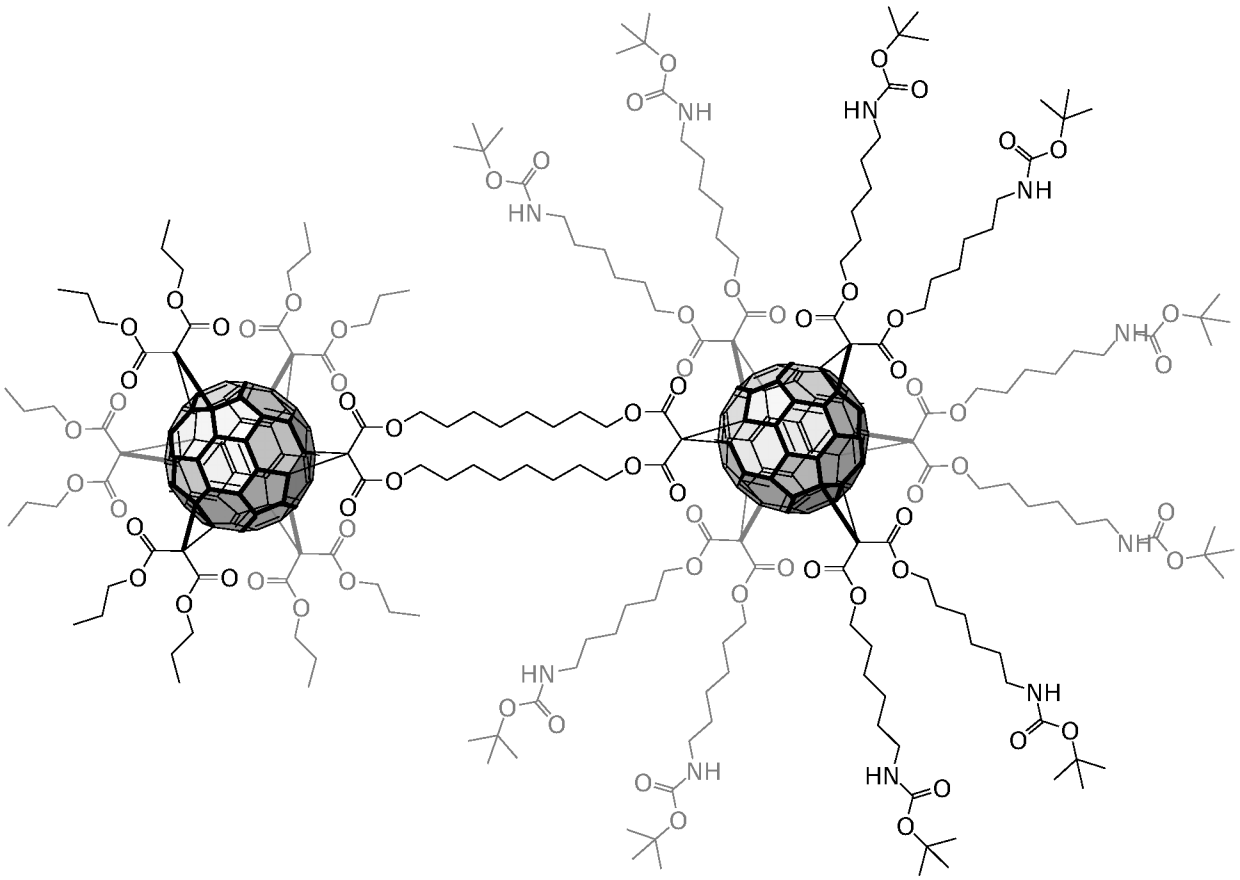
^{13}C-NMR{^{1}H}(100.5 MHz, $CDCl_3$): δ = 171.7 (10 C, **C**=O-O-C$(CH_3)_3$), 163.9, 163.6 (24 C, C(**C**=O)$_2$), 145.8, 145.8, 145.7, 141.2, 141.1, 141.0 (96 C, **C**$_{60}$-sp^2), 80.6 (10 C, C$(CH_3)_3$), 69.1, 69.0 (24 C, **C**$_{60}$-sp^3), 68.4, 66.0 (24 C, **C**H_2O), 45.5, 45.1 (12 C, C(C=O)$_2$), 31.7 (10 C, **C**H_2O), 29.5 (8 C, CH_2CH_2**C**H_2CH_2O), 28.5 (8 C, CH_2**C**$H_2CH_2CH_2$O), 28.1 (30 C, C(**C**$H_3)_3$), 26.0 (8 C, **C**$H_2CH_2CH_2CH_2$O), 24.0 (10 C, **C**H_2CH_2C=O), 21.8 (CH_3**C**H_2CH_2O), 10.3 (**C**$H_3CH_2CH_2$O) ppm.

MS (MALDI, dctb): m/z = calcd. for $C_{279}{}^{13}C_3H_{255}O_{68}$ $[M + 2\ H + H]^+$: 4731.66 meas.: 4732 Da.

IR (ATR, diamond): ṽ = 2970 (m), 2933 (m), 1742 (s), 1726 (s), 1459 (w), 1392 (w), 1367 (w), 1261 (s), 1207 (s), 1152 (s), 1079 (w), 1056 (w), 715 (w) cm^{-1}.

UV/Vis (CH_2Cl_2): λ = 226 (183000), 246 (199000), 269 (150000), 283 (155000), 320 (96000), 336 (78000), 387 (13000) nm (M^{-1}cm^{-1}).

(Bis[*N*-boc-6-aminohexyl]malonyl)-((dipropyl malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene) 72



[5,1]/[1,0]-Dumbbell **79** (68 mg, 24 µmol) was dissolved in dichloromethane (5 mL). DMA (60 mg, 0.29 mmol, 12 eq.) was added to it and the mixture was stirred for 2 hours.

Subsequently, bis(6-(boc-amino)hexyl)malonate **39**[107] (0.24 g, 0.47 mmol, 19 eq.) and CBr_4 (97 mg, 0.29 mmol, 12 eq.) were added and a solution of phosphazene base P_1-*t*Bu (68 mg, 74 µL, 0.29 mmol) was added dropwise over 2 hours. The reaction mixture was stirred for 8 days. CBr_4 (1.1 g, 3.3 mmol, 137 eq.) and phosphazene base P_1-*t*Bu (68 mg, 74 µL, 0.29 mmol, 12 eq.) (dropwise in dichloromethane) were added. After additonal two days, the reaction mixture was plug-filtered (SiO_2; toluene;toluene/ethyl acetate 50:50) and purified via column chromatography (SiO_2; dichloromethane/ethyl acetate 98:2). The product fractions were collected and the solvent was evaporated, yielding the product as residue. Yield: 43 mg, (34 %), red-orange solid.

Spectroscopy of **72**

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.76 (m, 10 H, N**H**), 4.20 (m, 48 H, C**H**$_2$O), 3.06 (m, 20 H, C**H**$_2$N), 1.69 (m, 48 H, C**H**$_2$CH$_2$O), 1.45..1.32 (m, 96 H, C**H**$_2$), 1.40 (s, 90 H, C(C**H**$_3$)$_3$), 0.91 (m, 30 H, CH$_2$C**H**$_3$) ppm.

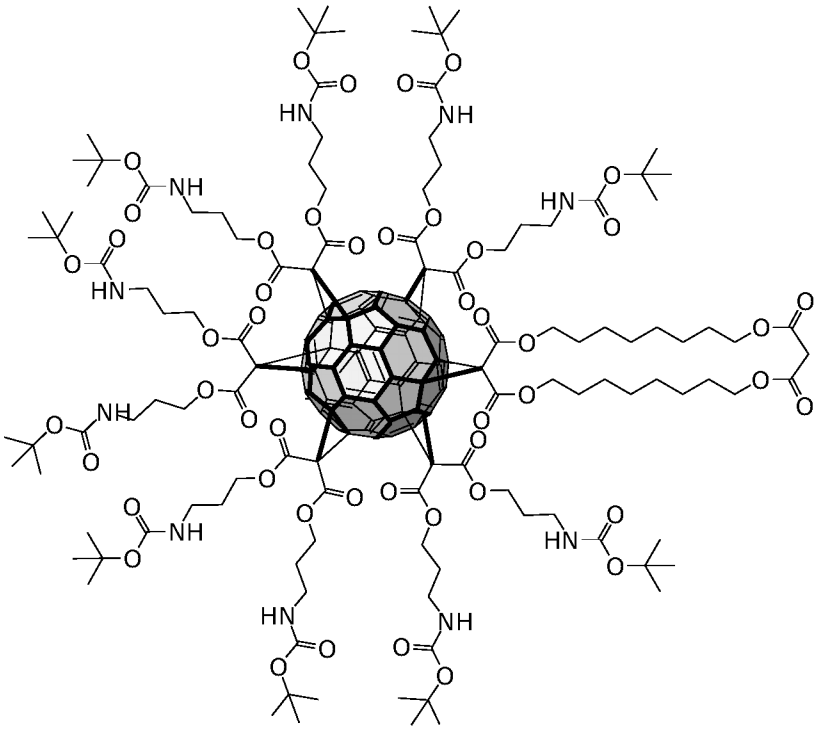
^{13}C-NMR{^{1}H} (75.5 MHz, $CDCl_3$): δ = 163.9 (24 C, **C**H$_2$O), 156.0 (10 C, N**C**OO), 145.7, 141.1 (96 C, **C**$_{60}$-sp^2), 78.9 (20 C, **C**(CH$_3$)$_3$), 69.0 (24 C, **C**$_{60}$-sp^3), 68.3 (14 C, **C**H$_2$O), 66.9 (10 C, CH$_3$CH$_2$**C**H$_2$O), 45.4 (12 C, **C**(COO)$_2$), 40.42 (10 C, **C**H$_2$N), 29.9 (10 C, CH$_2$**C**H$_2$CH$_2$O), 29.5 (4 C, CH$_2$**C**H$_2$CH$_2$O), 28.4 (30 C, C(**C**H$_3$)$_3$, 4 C, **C**H$_2$CH$_2$CH$_2$O), 28.3 (10 C, **C**H$_2$CH$_2$N), 26.3 (10 C, **C**H$_2$CH$_2$CH$_2$N), 26.1 (4 C, **C**H$_2$CH$_2$CH$_2$CH$_2$O), 25.5 (10 C, **C**H$_2$CH$_2$CH$_2$O), 10.3 (CH$_2$**C**H$_3$) ppm.

MS (MALDI-TOF, dctb): m/z = calcd. for $C_{306}{}^{13}C_3H_{315}N_{10}O_{68}$ [M- $CH_2CH_2CH_3$]$^+$: 5256.16 meas.: 5257 Da, calcd. for $C_{309}{}^{13}C_3H_{320}N_{10}O_{68}$ [M - 2 H]$^+$: 5297.20 meas.: 5297 Da.

IR (ATR, diamond): ṽ = 3006 (m), 2989 (m), 2360 (m), 2341 (m), 1745 (m), 1715 (m), 1519 (m), 1459 (m), 1276 (s), 1261 (m), 1219 (m), 1171 (m), 764 (m), 750 (m) cm^{-1}.

UV/Vis (CH_2Cl_2): λ = 244, 271, 282, 317, 334 nm.

(Bis[3-(boc-amino)propyl]malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 73



Pentakisadduct **65** (130 mg, 46.38 µmol, 1 eq) is dissolved in toluene (5 mL). Cyclo[2]-octylmalonate **35** (717.5 mg, 1.675 mmol, 36 eq.), CBr_4 (153.38 mg, 0.4625 mmol, 10 eq.) and P_1-*t*Bu (53.8 mg, 58.2 µL, 230 mmol, 5 eq.) were added and the mixture was stirred for 12 h. The mixture was plug-filtered (SiO_2; dichloromethane/ethyl acetate 1:1) and absorbed on SiO_2, washed with dichloromethane/ethyl acetate 19:1 in order to remove the remaining excess of cyclo[2]-octylmalonate **35** and eluted with dichloromethane/ethyl acetate 1:1. The solvent was removed under reduced pressure. Yield: 35 mg (10.8 µmol, 23.3 %).

Spectroscopy of **73**

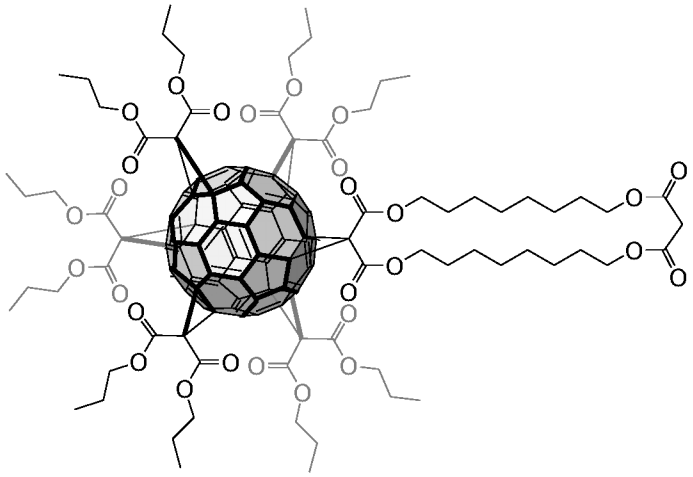
^{1}H-NMR(300 MHz, $CDCl_3$): δ = 5.11..4.81 (s, 10 H, N-**H**), 4.44..4.16 (m, 28 H, C**H**$_2$O), 3.25..3.06 (m, 20 H, C**H**$_2$N), 1.95..1.82 (m, 20 H, C**H**$_2$CH$_2$N), 1.74..1.55 (8 H, CH$_2$CH$_2$C**H**$_2$CH$_2$O), 1.49..1.35 (s, 90 H, C(C**H**$_3$)$_3$), 1.35..1.26 (m, 16 H, C**H**$_2$C**H**$_2$CH$_2$CH$_2$O) ppm.

^{13}C-NMR{^{1}H} (75.4 MHz, $CDCl_3$): δ = 166.4 (2 C, CH$_2$(**C**=O)$_2$), 163.8, 163.7 (12 C, C_{60}-C(**C**=O)$_2$), 156.0 (10 C, **C**=O-N), 145.8, 145.7, 145.7, 145.6, 141.1, 141.0, 141.0, 140.9, 140.9 (48 C, C_{60}-sp^2), 79.2 (10 C, **C**(CH$_3$)$_3$), 69.1, 69.0, 69.0, 67.1 (12 C, **C**$_{60}$-sp^2), 65.5, 64.7 (14 C, **C**H$_2$O), 45.2 (6 C, C_{60}-**C**(C=O)$_2$, 42.2 (1 C, **C**H$_2$(C=O)$_2$), 37.3 (10 C, **C**H$_2$N), 29.6, 29.4 (4 C, CH$_2$CH$_2$**C**H$_2$CH$_2$O), 29.0 (10 C, CH$_2$**C**H$_2$CH$_2$-N), 28.5 (4 C, CH$_2$**C**H$_2$CH$_2$CH$_2$O), 28.4 (30 C, C(**C**H$_3$)$_3$), 25.9 (4 C, **C**H$_2$CH$_2$CH$_2$CH$_2$O) ppm.

MS (MALDI, dctb): m/z = calcd. for $C_{175}{}^{13}C_2H_{196}N_{10}O_{48}$ $[M + H + H]^+$: 3231.33 meas.: 3231 Da. IR (ATR, diamond): $\tilde{\nu}$ = 2922 (s), 2852 (m), 1742 (m), 1690 (s), 1514 (m), 1458 (m), 1391 (w), 1366 (w), 1263 (s), 1209 (s), 1164 (s), 1041 (w), 859 (w), 735 (m), 716 (m) cm^{-1}.

UV/Vis: λ = 246 (138000), 269 (103000), 282 (111000), 320 (69000), 337 (55000) nm ($M^{-1}cm^{-1}$).

(Dipropyl malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 75



Monoadduct **19**[107] (0.40 g, 0.35 mmol) was dissolved in dichloromethane (10 mL). DMA (0.72 g, 3.5 mmol) was added and the mixture was stirred for three hours. Dipropyl malonate (3.9 g, 21 mmol) and CBr_4 (1.2 g 3.5 mmol) were added and a solution of P_1-*t*Bu[129] (0.82 g, 890 µL, 3.5 mmol) was added dropwise under stirring over two hours. The reaction mixture was stirred for seven days. Ethyl acetate (7 mL) was added and the reaction mixture was plug-filtered (SiO_2; dichloromethane/ethyl acetate 3:1). The solvent was evaporated and the product was plug-filtered again (SiO_2; toluene; dichloromethane/ethyl acetate 80:20) and again (hexanes/ethyl acetate 80:20; dichloromethane/ethyl acetate 90:10). Column chromatography (SiO_2; toluene/ethyl acetate 92.5:7.5) was done two times, the solvent was evaporated and the residue was dried 2 hours in vacuum. Yield: 0.11 g (14 %), orange oil.

Spectroscopy of **75**

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.18 (m, 24 H, C**H**$_2$O), 4.11 (m, 4 H, C**H**$_2$O), 3.32 (s, 2 H, C**H**$_2$(C=O)$_2$), 1.66 (m, 28 H, C**H**$_2$CH$_2$O), 1.31 (m, 16 H, C**H**$_2$), 0.90 (m, 30 H, C**H**$_3$) ppm.

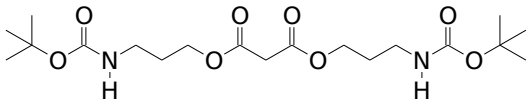
^{13}C-NMR{^{1}H} (75.5 MHz, $CDCl_3$): δ = 166.4 (2 C, $CH_2(\mathbf{C}OO)_2$), 163.8 (10 C, $R_2C(\mathbf{C}OO)_2$), 145.7, 141.0 (48 C, $\mathbf{C}_{60}$-sp^2), 69.0 (12 C, $\mathbf{C}_{60}$-sp^3), 68.3 (10 C, $\mathbf{C}H_2O$), 66.9 (2 C, $\mathbf{C}H_2O$), 65.5 (2 C, $\mathbf{C}H_2OCOCH_2$), 45.3 (6 C, $R_2\mathbf{C}(COO)_2$), 42.2 (1 C, $\mathbf{C}H_2(COO)_2$), 29.3 (4 C, $\mathbf{C}H_2CH_2O$), 28.5 (4 C, $\mathbf{C}H_2CH_2CH_2O$), 25.9 (4 C, $\mathbf{C}H_2CH_2CH_2CH_2O$), 21.7 (10 C, $\mathbf{C}H_2CH_2O$), 10.0 ($\mathbf{C}H_3$) ppm.

MS (MALDI-TOF, sin): m/z = calcd. for $C_{126}{}^{13}C_1H_{104}O_{28}$ $[M]^+$: 2077.67 meas.: 2078 Da, calcd. for $C_{126}{}^{13}C_1H_{104}O_{28}Na$ $[M + Na]^+$: 2100.66 meas.: 2101 Da.

IR (ATR, diamond): ṽ = 2968, 2937, 2880 (w), 2858 (w), 1744, 1462, 1390, 1352 (w), 1264, 1217, 1125 (w), 1079, 1056, 990, 932, 827 (w), 763, 715 cm^{-1}.

UV/Vis (CH_2Cl_2): λ = 281, 315, 333 nm.

Bis(3-(boc-amino)propyl) malonate 76



Malonic acid (8.78 g, 84.4 mmol, 1 eq.) and 3-(Boc-amino)propan-1-ol (34 g, 194 mmol, 2.3 eq.) were dissolved in dichloromethane (100 mL) and cooled to 0 °C. DCC (38.3 g, 2.2 eq., 186 mmol) and N,N-Dimethylaminopyridine (2.06 g, 16.9 mmol, 0.2 eq.) were added. The mixture was stirred for 35 min at 0 °C. After 36 h, the precipitate was filtered off and the filtrate was freed from solvent in vacuo. The residue was dissolved in as little ethyl acetate as necessary (45 °C), and the remaining DCU was crystallized out at 4 °C. The supernatant was concentrated and the mixture was purified by means of column chromatography (SiO_2; hexanes/ethyl acetate 2:3), R_f = 0.64. Yield: 8.20 g (91.7 %).

Spectroscopy of **76**

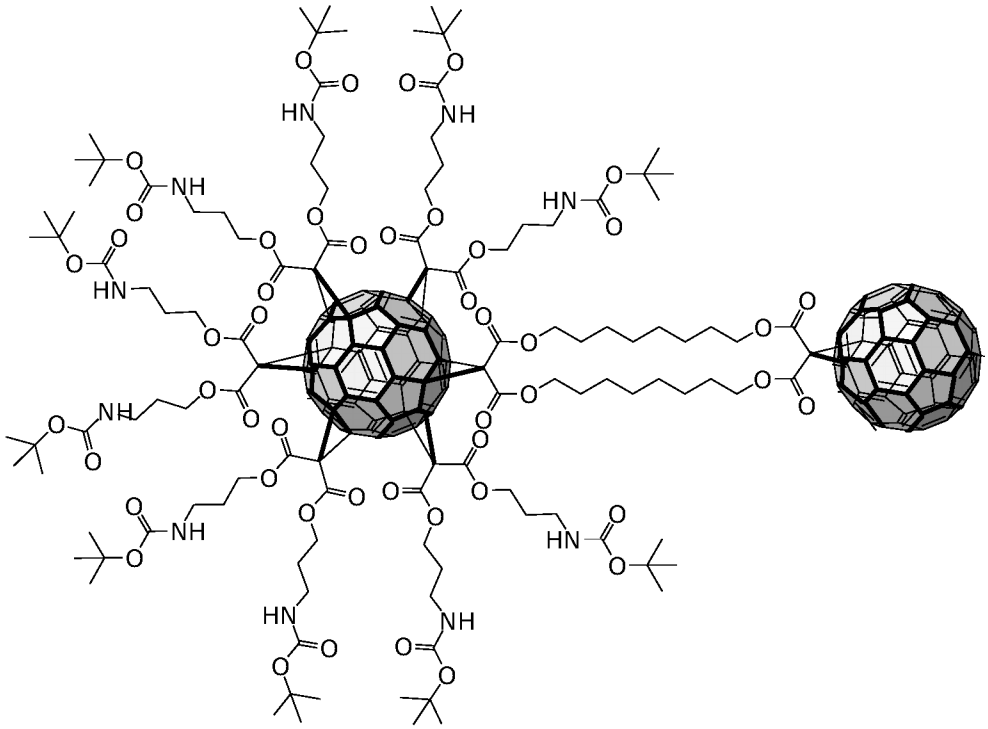
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.81 (s, 2 H, N-**H**), 4.19 (t, $^{3}J_{H,H}$ = 6.1 Hz, 4 H, $C\mathbf{H}_2O$), 3.37 (s, 2 H, $(C=O)_2C\mathbf{H}_2$), 3.17 (m, $C\mathbf{H}_2N$), 1.82 (m, $CH_2C\mathbf{H}_2CH_2$), 1.41 (s, $C(C\mathbf{H}_3)_3$) ppm.

^{13}C-NMR{^{1}H} (100.5 MHz, $CDCl_3$): δ = 166.6 (2 C, $CH_2(\mathbf{C}=O)_2$), 155.9 (2 C, N-$(\mathbf{C}=O)_2$), 79.2 (2 C, $\mathbf{C}(CH_3)_3$), 63.0 (2 C, $\mathbf{C}H_2O$), 41.4 (1 C, $\mathbf{C}H_2(C=O)_2$), 37.2 (2 C, $\mathbf{C}H_2$-N), 28.9 (2 C, $CH_2\mathbf{C}H_2CH_2$), 28.3 (6 C, $C(\mathbf{C}H_3)_3$) ppm.

IR (ATR, diamond): ṽ = 3051 (s), 2973 (s), 2933 (m), 1243 (m), 1690 (s), 1609 (w), 1521 (s), 1454 (w), 1391 (w), 1366 (m), 1249 (s), 1215 (m), 1167 (s), 1041 (w), 738 (w) cm^{-1}.

UV/Vis (CH_2Cl_2): λ = 243 (125000), 355 (24000) nm ($M^{-1}cm^{-1}$).

((Bis[3-(boc-amino)propyl]malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerenyl)-mono-1,2-dihydrofullerene 78



C_{60} (15.623 mg, 21.68 µmol, 2 eq.) and fullerene addend **73** (35 mg, 10.84 µmol, 1 eq.) were dissolved in toluene (7 mL). CBr_4 (7.190 mg, 21.68 µmol, 2 eq.) was added. P_1-*t*Bu (15 mg, 16.1 µL, 6 eq.) was dissolved in toluene (2 mL) and added dropwise. The mixture was plug-filtered (SiO_2 toluene/ethyl acetate 1:1) and purified via column-chromatography (SiO_2 toluene/ethyl acetate 1:1). Yield: 18 mg (4.56 µmol, 42 %).

Spectroscopy of **78**

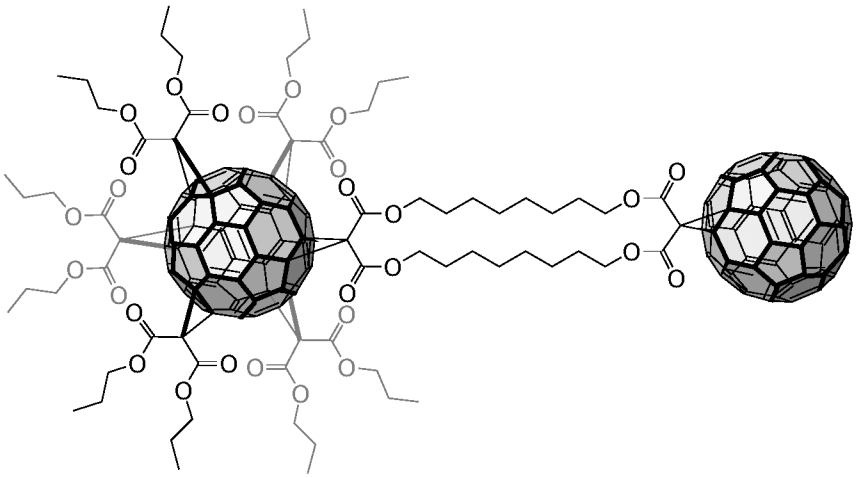
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.09..4.91 (10 H, N-**H**) 4.46 (4 H, mono-C**H**$_2$O), 4.40..4.20 (12 H, hexa-C**H**$_2$O), 3.36..3.00 (20 H, C**H**$_2$N), 2.02..1.80 (20 H, C**H**$_2$CH$_2$N), 1.59..1.32 (106 H, C**H**$_3$, CH$_2$C**H**$_2$C**H**$_2$CH$_2$O), 1.31..1.14 (8 H, C**H**$_2$CH$_2$CH$_2$CH$_2$O) ppm.

^{13}C-NMR{^{1}H} (100.5 MHz, $CDCl_3$): δ = 163.8, 163.7, 163.6 (14 C, C_{60}-C(**C**=O)$_2$), 156.0 (10 C, N-**C**=O), 145.75, 141.1, 141.0 (48 C, hexa-**C**$_{60}$-sp^2), 145.8, 145.7, 145.2, 145.2, 145.2, 144.9, 144.7, 144.6, 143.9, 143.1, 143.0, 143.0, 142.2, 141.9, 141.2, 140.9, 139.1 (58 C, **C**$_{60}$-sp^2), 79.3 (10 C, C(CH$_3$)$_3$), 71.6, 69.2, 69.1, 69.0 (14 C, C_{60}-sp^3), 67.5 (2 C, mono-CH$_2$O), 64.7 (12 C, hexa-**C**H$_2$O), 45.2 (6 C, hexa-**C**(C=O)$_2$), 37.3 (10 C, **C**H$_2$N), 29.7, 29.5 (4 C, CH$_2$CH$_2$**C**H$_2$CH$_2$O), 29.0 (10 C, N-CH$_2$**C**H$_2$CH$_2$), 28.6 (4 C, CH$_2$**C**H$_2$CH$_2$CH$_2$O), 28.4 (30 C, C(**C**H$_3$)$_3$), 26.1, 26.0 (4 C, **C**H$_2$CH$_2$CH$_2$CH$_2$O) ppm.

IR (ATR, diamond) $\tilde{\nu}$ = 2923 (m), 2853 (w), 1742 (m), 1690 (s), 1516 (m), 1456 (w), 1391 (w), 1365(w), 1262 (s), 1208 (s), 1166 (s), 1080 (w), 1042 (m), 736 (m), 716 (m).

UV/Vis(CH_2Cl_2): 246 (138000), 269 (103000), 282 (111000), 320 (69000), 337 (55000).

((Dipropyl malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-1,2-dihydro[60]-fullerene 79



Under dry conditions, C_{60} (0.11 g, 0.15 mmol, 3 eq.) and, upon complete dissolution, fullerene-containing addend **75** (0.11 g, 51 mmol, 1 eq.) and then CBr_4 (17 mg, 66 mmol, 1.3 eq.) were dissolved in 50 mL toluene. Phosphazene base P_1-*t*Bu (16 mg, 17 mL, 66.3 mmol, 1.2 eq.) was added dropwise over 30 min., and the reaction was stirred at room temperature. When after 12 hours TLC showed a considerable amount of educt, CBr_4 (30 mg, 0.12 mmol, 0.25 eq.) and P_1-*t*Bu (28 mg, 30 µL, 0.12 mmol, 0.25 eq.) (dropwise in toluene) were added. This was repeated until the reaction was nearly completed. The reaction mixture was plug-filtered (SiO_2; toluene; toluene/ethyl acetate 92.5:7.5) and purified *via* column chromatography (SiO_2; toluene/ethyl acetate 39:1). Evaporation of the solvent and drying revealed the product. Yield: (68 mg, 48 %), dark-brown solid.

Spectroscopy of **79**

^{1}H-NMR (400 MHz, $CDCl_3$): d = 4.46 (m, 4 H, C**H**$_2$O-mono), 4.25 (m, 4 H, C**H**$_2$O-hexa), 4.20 (m, 20 H, C**H**$_2$O-hexa), 2.33 (s, 2 H, C**H**$_2$(COO)$_2$), 1.86 (m, 4 H, C**H**$_2$CH$_2$O-mono), 1.69 (m, 24 H, C**H**$_2$CH$_2$O-hexa), 1.5 (4 H, C**H**$_2$CH$_2$CH$_2$O-mono), 1.42 (m, 12 H, C**H**$_2$), 0.94 (30 H, C**H**$_3$) ppm.

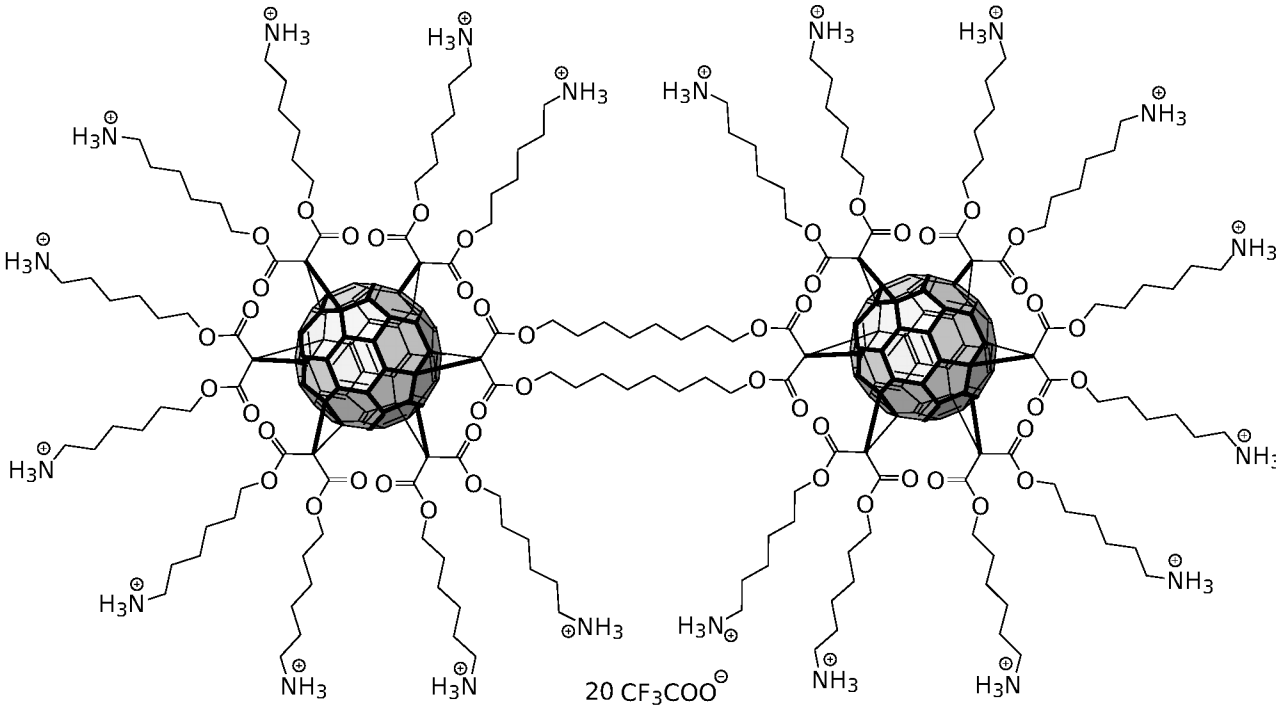
^{13}C-NMR{^{1}H} (100.5 MHz, $CDCl_3$): δ = 163.9 (12 C, **C**=O-hexa), 163.6 (2 C, **C**=O-mono), 145.8, 141.1 (48 C, $\mathbf{C}_{60}$-hexa-sp^2), 145.72, 145.67, 145.62, 145.2, 145.1, 143.8, 143, 142.9, 142.2, 141.9, 141.02, 140.9, 139.07 (58 C, $\mathbf{C}_{60}$-mono-sp^2), 71.6 (2 C, $\mathbf{C}_{60}$-mono-sp^3), 69.1 (12 C, $\mathbf{C}_{60}$-hexa-sp^3), 68.3 (10 C, $\mathbf{C}H_2O$), 67.4 (2 C, $\mathbf{C}H_2O$), 66.9 (2 C, $\mathbf{C}H_2O$), 52.04 (1 C, $\mathbf{C}(COO)_2$-mono), 45.43, 45.40 (5 C, $\mathbf{C}(COO)_2$-hexa), 45.3 (1 C, $\mathbf{C}(COO)_2$-hexa), 29.47 (4 C, $\mathbf{C}H_2$ CH_2O), 28.6, 28.5 (4 C, $\mathbf{C}H_2CH_2O$), 26.0 (4 C, $\mathbf{C}H_2$CH2CH2O), 21.7 (10 C, $\mathbf{C}H_2CH_2O$), 10.3 (10 C, CH_3) ppm.

MS (MALDI-TOF, sin): m/z = calcd. for $C_{185}{}^{13}C_2H_{104}O_{28}$ $[M + H + H]^+$: 2798.68 meas.: 2799 Da.

IR (ATR, diamond): $\tilde{\nu}$ = 2964, 2926 (w), 2853 (w), 1745, 1462, 1395 (w), 1261, 1217, 1081, 1020, 932 (w), 866 (w), 799, 764 (w), 750, 715 cm^{-1}.

UV/Vis (CH_2Cl_2): λ (ε) = 245 (159000), 266 (132000), 280 (112000), 318 (68000), 334 (56000), 425 (4000) nm (M^{-1}cm^{-1}).

(Bis[6-ammoniumhexyl]malonyl)-((bis[6-ammoniumhexyl]malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene) eicosatrifluoroacetate 80



Symmetric double-hexakisaduct **62** was dissolved in TFA (3 mL) and stirred for 3 days. The acid was evaporated and the substance was dried in vacuo.

Spectroscopy of **80**

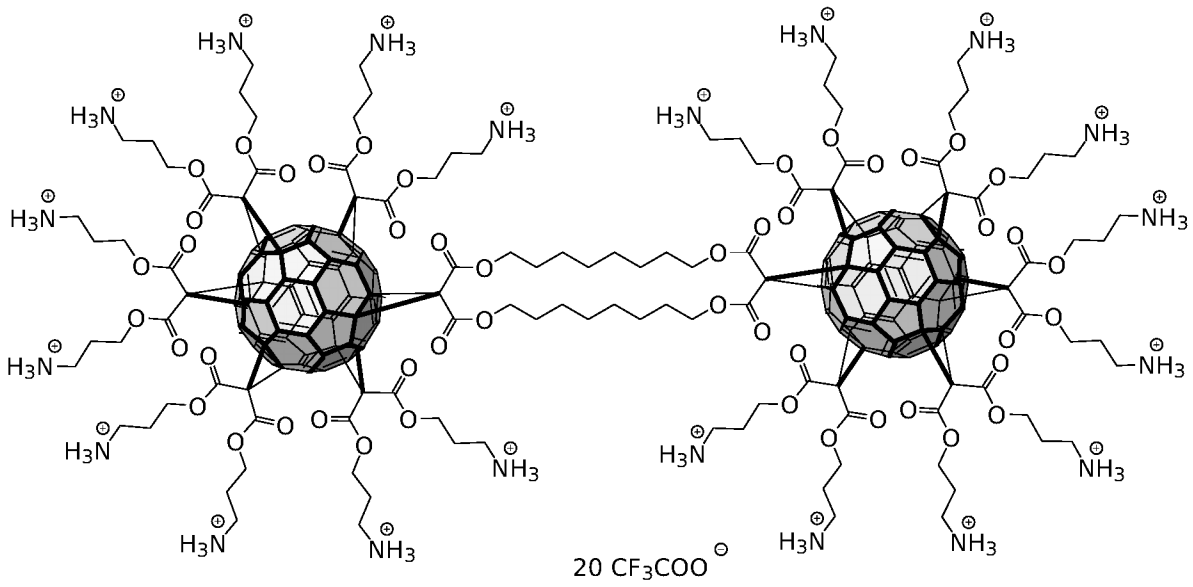
^{1}H-NMR(400 MHz, D_2O): δ = 4.38..3.96 (m, 48 H, C**H**$_2$O), 2.95..2.75 (m, 40 H, C**H**$_2$N), 1.7..3.8 (m, 88 H, C**H**$_2$CH$_2$N, C**H**$_2$CH$_2$O), 1.36..1.06 (m, 96 H, C**H**$_2$C**H**$_2$CH$_2$CH$_2$O) ppm.

^{13}C-NMR{^{1}H}(100.5 MHz, D_2O): δ = 165 (24 C, **C**=O), 145.7, 141.5 (96 C, **C**$_{60}$-sp^2), 69.4 (24 C, **C**$_{60}$-sp^3), 67.7 (24 C, **C**H$_2$O), 46.4 (12 C, **C**(C=O)$_2$), 39.64 (20 C, **C**H$_2$N), 27.9 (20 C, **C**H$_2$CH$_2$N), 26.9 (24 C, **C**H$_2$CH$_2$O), 25.5, 25.1 (**C**H$_2$**C**H$_2$CH$_2$CH$_2$O) ppm.

IR (ATR, diamond): $\tilde{\nu}$ = 2937 (s), 2863 (w), 1742 (m), 1671 (s), 1525 (w), 1466 (w), 1430 (w), 1395 (w), 1261(m), 1198 (s), 1130 (s), 889 (m), 836 (m), 721 (m) cm^{-1}.

UV/Vis(H_2O): λ (ε) = 215 (277000), 246 (153000), 269 (124000), 282 (127000), 319 (82000), 336 (66000) nm (M^{-1}cm^{-1}).

(Bis[3-ammoniumpropyl]malonyl)-((bis[3-ammoniumpropyl]malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene) eicosatrifluoroacetate 81

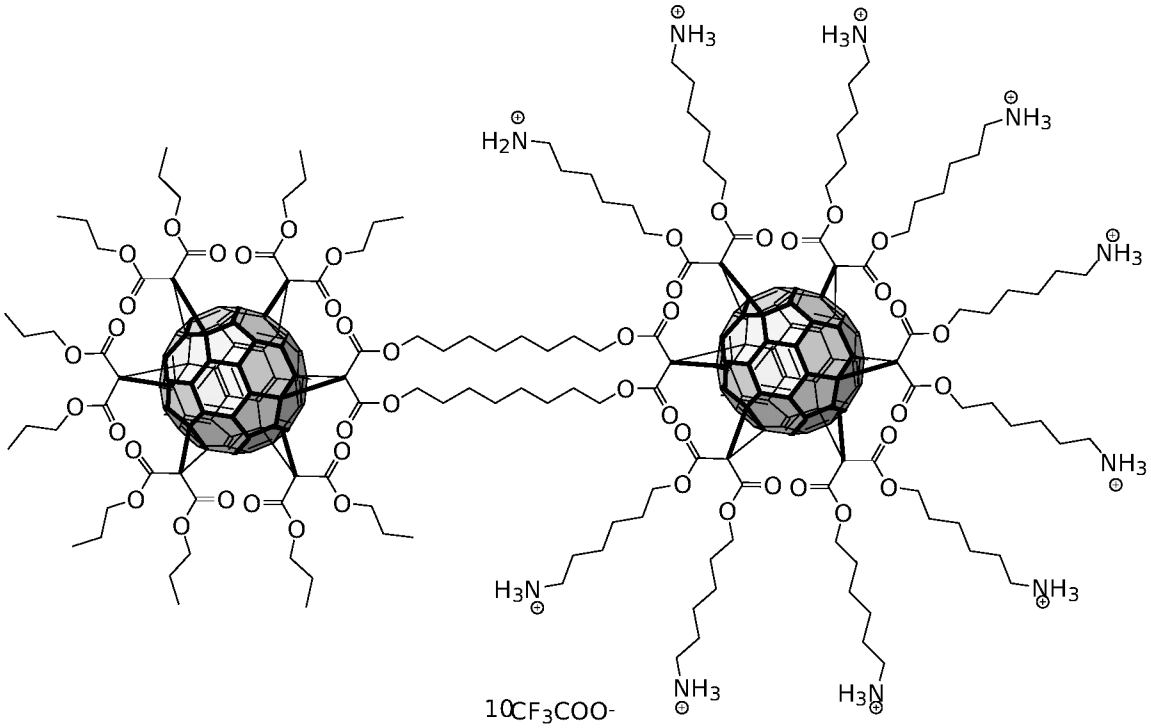


Symmetric double-hexakisaduct **68** (6 mg, 0.878 µmol, 1 eq.) was dissolved in TFA (2 mL) and stirred for 4 days. The acid was removed in vacuo. Yield: 2.5 mg, (6.1 µmol, 70 %).

Spectroscopy of **81**

MS (ESI-TOF, MeOH/AcN): m/z = calcd.: for $C_{210}{}^{13}C_2H_{166}O_{48}N_{10}$ [M +4 H^+ - 10 $C_2H_7O]^{5+}$ 720.1870 meas.: 720.2806 Da, calcd.: for $C_{212}{}^{13}C_2H_{171}O_{48}N_{11}$ [M +4 H^+ - 9 $C_2H_7O]^{5+}$ 728.7955 meas.: 728.8874 Da, calcd.: for $C_{214}{}^{13}C_2H_{176}O_{48}N_{12}$ [M^+ +4 H^+ - 8 $C_2H_7O]^{5+}$ 737.4039 meas.: 737.4958 Da, calcd.: for $C_{216}{}^{13}C_2H_{161}O_{48}N_{13}$ [M +4 H- 7 $C_2H_5N]^{5+}$ 746.0124 meas.: 746.10949 Da, calcd.: for $C_{218}{}^{13}C_2H_{166}O_{48}N_{14}$ [M +4 H- 6 $C_2H_5N]^{5+}$ 754.6208 meas.: 754.7182 Da, calcd.: for $C_{220}{}^{13}C_2H_{171}O_{48}N_{15}$ [M +4 H- 5 $C_2H_5N]^{5+}$ 763.2292 meas.: 763.3302 Da.
UV/Vis (MeOH): λ (ε) = 214 (185000), 245 (114000), 269 (91000), 281 (90000), 320 (55000), 336 (44000), 387 (9000) nm ($M^{-1}cm^{-1}$).

(Bis[6-ammoniumhexyl]malonyl)-((dipropyl malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene) decatrifluoroacetate 82



Under dry conditions, [5,1]/[1,5]-dumbbell **72** was stirred in TFA for 3 days. The acid was distilled off under vacuum, and the remaining solid was taken up three times in methanol and evacuated again in order to remove traces of excess TFA. The substance was taken up in 200 µL methanol again and precipitated with 30 mL of diethyl ether. The supernatant was decanted and discarded, the remaining solid was dried in vacuo to yield the amorphous, red-orange product. Yield: 44 mg (99 %), red-orange solid.

Spectroscopy of **82**

^{1}H-NMR (400 MHz, CD_3OD): δ = 4.88 (s, 30 H, N**H**$_3^+$), 4.35..4.15 (48 H, **C**H$_2$O), 2.90 (20 H, C**H**$_2$N), 1.8..1.6 (68 H, C**H**$_2$CH$_2$N, C**H**$_2$CH$_2$O), 1.39 (56 H, C**H**$_2$), 0.92 (30 H, C**H**$_3$) ppm.

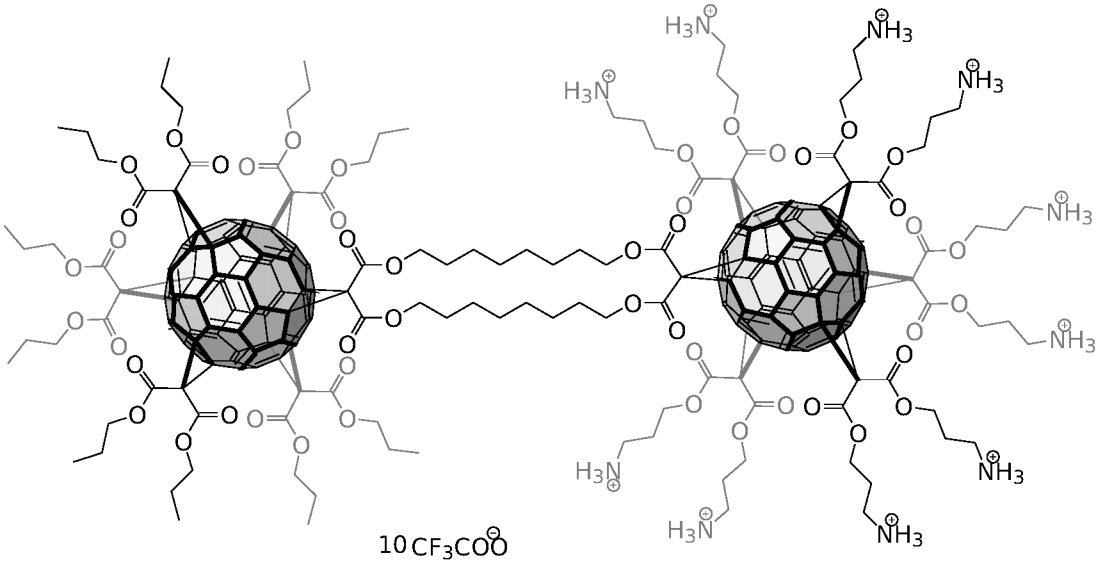
^{13}C-NMR{^{1}H} (100.5 MHz, CD_3OD): δ = 165.0 (m, 10 C, CF_3**C**OO^{-1}), 164.9 (24 C, **C**=O), 146.9, 142.8 (96 C, **C**$_{60}$-hexa-sp^3), 116.1 (m, 10 C, **C**F_3COO^{-1}), 70.6 (24 C, **C**$_{60}$-sp^2), 69.9 (10 C, CH_3CH_2**C**H_2O), 68.2 (18 C, CH_2CH_2**C**H_2O), 47.6 (12 C, (**C**$(COO)_2$), 40.6 (10 C, **C**H$_2$N), 30.3 (4 C, **C**H$_2$CH$_2$O), 29.6 (4 C, **C**H$_2$CH$_2$CH$_2$O), 29.3 (10 C, **C**H$_2$CH$_2$N), 28.4 (10 C, CH$_2$**C**H$_2$CH$_2$O), 26.9 (10 C, **C**H$_2$CH$_2$O), 26.5 (10 C, **C**H$_2$CH$_2$CH$_2$N), 22.9 (10 C, **C**H$_2$CH$_3$), 10.8 (10 C, **C**H$_3$) ppm.

MS (MALDI-TOF, sin): m/z = calcd. for $C_{256}{}^{13}C_3H_{243}N_{10}O_{48}$ [M - 10 CF_3COO^- - 9 H]$^+$: 4299.70 meas.: 4300 Da, calcd. for $C_{256}{}^{13}C_3H_{243}N_{10}O_{48}$Na [M - 10 H + Na]$^+$: 4322.69 meas.: 4322 Da, $C_{256}{}^{13}C_3H_{243}N_{10}O_{48}$K [M - 10 H + Na]$^+$: 4338.66 meas.: 4338 Da.

IR (ATR, diamond): ν̃ = 3059 (m), 2935 (m), 2859 (w), 2361 (w), 1744 (m), 1679 (m), 1537 (w), 1465 (m), 1434 (w), 1393 (w), 1352 (w), 1265 (m), 1205 (m), 1135 (m), 1080 (m), 989 (w), 933 (w), 838 (m), 800 (m), 762 (w), 722 (m) cm^{-1}.

UV/Vis (H_2O): λ = 214 (197000) 244 (125700), 271 (97900). 282 (97800), 316 (60000), 335 (47700) nm (M^{-1}cm^{-1}).

(Bis[3-ammoniumpropyl]malonyl)-((dipropyl malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene) decatrifluoroacetate 83



[5,1]/[1,5]-dumbbell **70** was dissolved in trifluoroacetic acid (3 mL) and stirred for 3 days. The solvent was removed under reduced pressure and the raw product was dissolved in methanol, and dried three times in vacuo. The raw product was subjected to SEC (polyamide) in diluted trifluoroacetic acid (0.36 g/L in H_2O) in order to remove left malonate. Yield: 48 mg (9.57 µmol, 98.2 %)

Spectroscopy of **83**

^{1}H-NMR (400 MHz, CD_3OD): δ = 4.43, 4.27 (48 H, C**H**$_2$O), 2.11 (N-CH$_2$C**H**$_2$CH$_2$-O), 1.7 (28 H, CH$_3$C**H**$_2$CH$_2$O, (CH$_2$)$_6$C**H**$_2$CH$_2$O), 1.4 (16 H, (C**H**$_2$C**H**$_2$(CH$_2$)$_2$O)$_2$), 0.9 (30 H, CH$_3$) ppm.

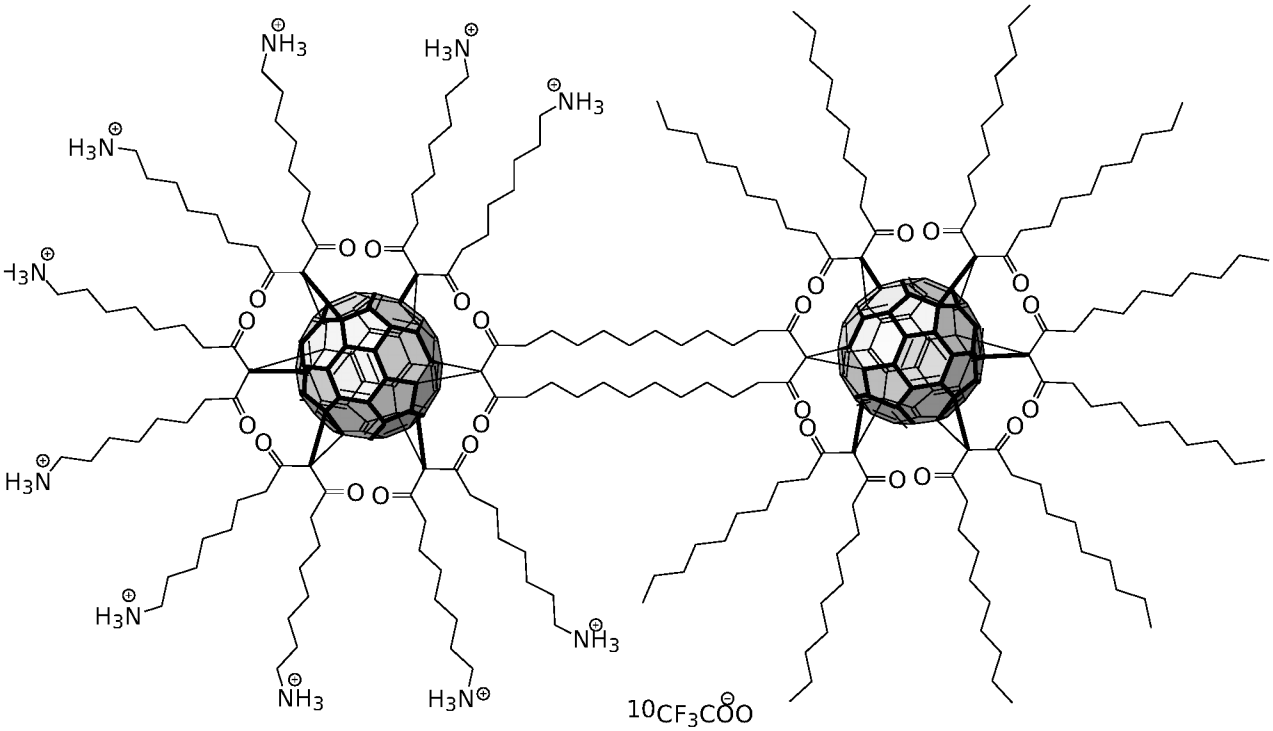
^{13}C-NMR{^{1}H} (100.5 MHz, CD_3OD): δ = 165.7, 165.3 (24 C, **C**=O), 163.7 (q, $^2J_{C,F}$ = 35 Hz, 10 C, CF$_3$**C**OO$^-$), 147.9, 147.74, 147.69, 147.62, 147.56, 143.48, 143.39, 143.18 (96 C, C_{60}-sp^2), 120.9, 117.9 (q, $^1J_{C,F}$ = 1200 Hz, 10 C, **C**F$_3$) 71.4, 71.2, 70.7 (24 C, **C**$_{60}$-sp^3), 66.1 (24 C, CH$_2$-O), 48.4 (12 C, **C**(C=O)$_2$ 38.6 (10 C, **C**H$_2$-N), 31.3 (4 C, CH$_2$CH$_2$**C**H$_2$CH$_2$O), 30.5 (4 C, CH$_2$**C**H$_2$CH$_2$CH$_2$O), 28.6 (10 C, CH$_3$**C**H$_2$CH$_2$O), 27.9 (4 C, **C**H$_2$CH$_2$CH$_2$CH$_2$O), 23.9 (10 C, N-CH$_2$**C**H$_2$CH$_2$-O), 11.72, 11.67 (10 C, **C**H$_3$) ppm.

MS (MALDI, sin): m/z = calcd. for $C_{230}{}^{13}C_2H_{191}N_{10}O_{48}$ [M - 10 CF_3COO^- - 1 H]$^+$: 3886.28 meas.: 3886 Da, calcd. for $C_{230}{}^{13}C_2H_{190}N_{10}O_{48}Na$ [M - 10 CF_3COO^- - 2 H + Na]$^+$: 3908.27 meas.: 3908 Da.

IR (ATR, diamond): $\tilde{\nu}$ = 3250..2750 (s, br), 2965 (m), 2936 (m), 1741 (m), 1673 (s), 1529 (m, br), 1468 (w), 1432 (w), 1397 (w), 1264 (m), 1207 (s), 1129 (s), 1064 (m), 992 (w), 837 (m), 799 (m), 721.4 (s), 598 (w), 529 (m) cm^{-1}.

UV/Vis(H_2O): λ (ε) = 245 (322000), 268 (258000), 281 (265000), 319 (160000), 335 (132000) nm ($M^{-1}cm^{-1}$).

(Dioctylmalonyl)-((bis[6-ammoniumhexyl)]malonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene) decatrifluoroacetate 84



Amphiphile precursor **69** (17 mg, 2.833 µmol) was dissolved in trifluroacetic acid (3 mL). The mixture was stirred for 3 days. The excess trifluoroacetic acid was evaporated in vacuum down to 1 mbar. The mixture was taken up in water and dried in vacuo. Yield: 9 mg (1.47 µmol, 52 %)

Spectroscopy of **84**

^{1}H-NMR (400 MHz, CD_3OD): δ = 4.98..4.82 (30 H, NH_3^+), 4.41..4.29 (m, 48 H, C**H**$_2$O), 3.00..2.92 (m, 20 H, C**H**$_2$N), 1.85..1.62 (68 H, C**H**$_2$CH$_2$O, C**H**$_2$CH$_2$N), 1.53..1.25 (156 H, CH$_2$CH$_2$C**H**$_2$CH$_2$CH$_2$, C**H**$_2$CH$_3$), 0.94 (30 H, C**H**$_3$) ppm.

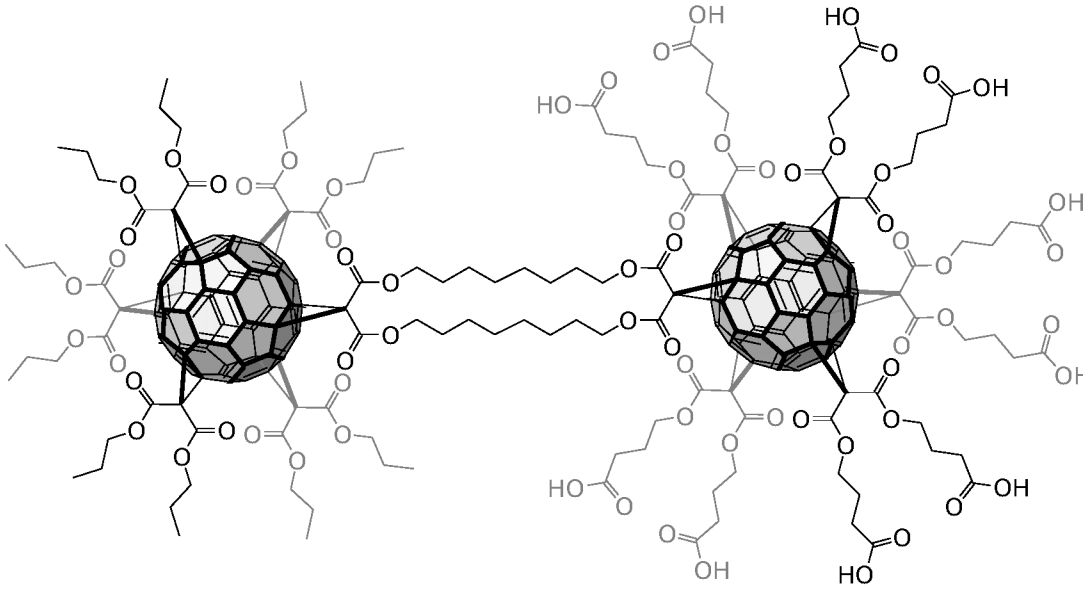
^{13}C-NMR{^{1}H} (100.5 MHz, CD_3OD): δ = 165.7 (24 C, **C**=O), 147.8, 147.7, 147.6, 143.5, 143.4, 143.3 (96 C, **C**$_{60}$-sp^2), 71.4 (24 C, **C**$_{60}$-sp^3), 69.1 (24 C, **C**H$_2$O), 48.4, 41.5 (12 C, **C**(C=O)$_2$), 33.9 (10 C, **C**H$_2$CH$_2$N), 31.3, 31.2, 30.6, 30.2 (**C**H$_2$CH$_2$N, **C**H$_2$**C**H$_2$**C**H$_2$CH$_2$CH$_3$), 29.3, 28.1 (40 C, **C**H$_2$CH$_2$O), 27.9 (20 C, **C**H$_2$CH$_2$CH$_2$N), 27.4 (20 C, **C**H$_2$(CH$_2$)$_4$CH$_3$), 24.7 (40 C, **C**H$_2$(CH$_2$)$_3$N, **C**H$_2$CH$_3$), 15.5 (10 C, **C**H$_3$) ppm.

MS (ESI, AcN/MeOH): m/z = calcd. for $C_{155}{}^{13}C_2H_{176}N_{10}O_{2\ 8}$[M - 6 H - unpolar fullerene + Na + K]$^+$: 2713.23 found: 2713 Da.

IR (ATR, diamond): $\tilde{\nu}$ = 3106 (m, br), 2929 (m), 2858 (w), 1744 (w), 1679 (s), 1437 (w), 1396 (w), 1264 (w), 1206 (s), 1137 (s), 842 (w), 802 (w), 724 (m) cm^{-1}.

UV/Vis(H_2O): λ (ε): 245 (130000), 268 (105000), 282 (110000), 320 (69000), 336 (58000), 387 (9000) nm ($M^{-1}cm^{-1}$).

Bis[carboxypropyl]malonyl)-((dipropylmalonyl)-(cyclo-[2]-octylmalonyl)-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene)-yl-[5,1]-hexakis-1,2,18,22,23,27,45,31,32,36,55,60-dodecahydro[60]-fullerene 85



Anionic amphiphile precursor **71** (47 mg, 9.94 µmol) was dissolved in 3 mL TFA and stirred for 36 h. The acid was evaporated. Thrice, methanol was added and evaporated, thrice dichloromethane was added and evaporated. Twice, the residue was dissolved in ether and precipitated with pentane, removing the supernatant each time. Yield: 24 mg (5.76 µmol, 57.9 %).

Spectroscopy of **85**

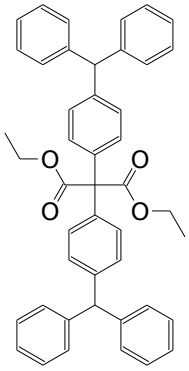
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.53..3.97 (m, 48 H, C**H**$_2$O), 2.63..2.29 (m, 20 H, C**H**$_2$COOH), 2.16..1.88 (m, 20 H, C**H**$_2$CH$_2$COOH), 1.79..1.60 (m, 28 H, C**H**$_2$CH$_3$, CH$_2$CH$_2$C**H**$_2$CH$_2$O), 0.97..0.88 (m, 30 H, C**H**$_3$CH$_2$), 0.89..0.75 (16 H, C**H**$_2$C**H**$_2$CH$_2$CH$_2$O) ppm.

^{13}C-NMR{^{1}H} (75.5 MHz, $CDCl_3$): δ = 178.7 (10 C, **C**OOH), 163.9 (24 C, C_{60}-C(**C**=O)$_2$), 145.8, 145.7, 141.2, 141.1 (96 C, C_{60}-sp^2), 69.1 (24 C, C_{60}-sp^3), 68.4 (24 C, CH$_2$O), 45.5 (12 C, **C**(C=O)$_2$), 29.7, 25.3, 21.8 (10 C, **C**H$_2$CH$_3$), 14.1, 10.3 (10 C, **C**H$_3$) ppm.

MS (MALDI-TOF, sin): m/z = calcd. for $C_{239}{}^{13}C_2H_{163}O_{66}Na$ [M - C=O-OPr - 2 H + Na]$^+$: 4100.94 meas: 4101 Da.

IR (ATR, diamond): $\tilde{\nu}$ = 2961 (m), 2925 (s), 2855 (w), 1742 (s), 1710 (m), 1462 (w, br), 1398 (w, br), 1263 (s), 1216 (s), 1080 (w), 1056 (w), 735 (w), 715 (m) cm^{-1}.
UV/Vis (CH_2Cl_2): λ = 224 (93000), 246 (95000), 269 (72000), 282 (76000), 319 (47000), 336 (38000), 386 (7000) nm ($M^{-1}cm^{-1}$).

2,2-Bis(diphenylmethylphen-4-yl) 1,3-diethyl malonate 88



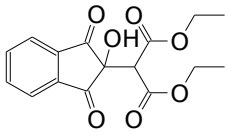
Diethyl malonate was dissolved in dichloromethane (15 mL). Diazabicycloundecene (2.79 g, 2.74 mL, 18.3 mmol, 1 eq.) was added and Triphenylmethyl chloride (5.11 g, 18.3 mmol, 1 eq.) was dissolved in 15 ml dichloromethane and added drop-wise. After 5 h, the mixture was plug-filtered with dichloromethane and purified by means of column-chromatography (SiO_2; toluene). R_f(**88** = 0.86,R_f(**89**/**87**) = 0.62. Yield: (2,2-Bis(diphenylmethylphen-4-yl) 1,3-diethyl malonate **88**) 1.5 g (2.33 mmol, 12.7 %) and a mixture of 2-(Diphenylmethylphen-4-yl) 1,3-diethyl malonate **87** and 2-(Diphenylmethylphen-4-yl) 1,3-diethyl malonate **87** 1.0 g (2.48 mmol, 13.5 %).

Spectroscopy of **88**

2,2-Bis(diphenylmethylphen-4-yl) 1,3-diethyl malonate **88** spectroscopic data:
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.32..7.15 (d, $^3J_{H,H}$=7.2 Hz, 20 H, mono-phenyl), 7.20 (2 H, p-phenyl), 7.10 (m, 4 H, p-phenyl), 7.04 (d, $^3J_{H,H}$=8.5 Hz, 2 H, p-phenyl) ppm.
^{13}C-NMR{^{1}H} (75.5 MHz, $CDCl_3$): δ = 169.9 (2 C, **C**=O) , 143.6 (4 C, **C**-H ipso-;mono-phenyl), 143.0 (4 C, $(C_6H_5)_2$C-H-**C**- p-phenyl), 136.4 (2 C, $(C{=}O)_2$-C-**C**) , 129.44 (4 C, **C**H mono-phenyl), 129.38 (2 C, **C**H p-phenyl), 128.9 (2 C, **C**H p-phenyl), 128.3 (4 C, **C**H mono-phenyl), 126.3 (2 C, **C**H 4-mono-phenyl), 68.0 (1 C, $(C{=}O)_2$-**C**), 61.8 (2 C, **C**H_2O), 56.4 (2 C, $(C_6H_5)_2$**C**-H), 13.8 (2 C, **C**H_3) ppm.
MS(MALDI, dhb): calcd. for $C_{45}H_{40}O_4Na$ $[M + Na]^+$: 667.28 meas: 667 Da.
2-(Triphenylmethyl) 1,3-diethyl malonate **89**2-(Diphenylmethylphen-4-yl) 1,3-diethyl malonate **87** spectroscopic data:

MS(MALDI, dhb): calcd. for $C_{26}H_{27}O_4$ $[M + H]^+$: 403.18 meas: 403; calcd. for $C_{26}H_{26}O_4Na$ $[M + Na]^+$: 425.17 meas: 425; calcd. for $C_{26}H_{26}O_4K$ $[M + K]^+$: 441.15 meas: 441 Da.

2-(Diethyl malon-2-yl)2-hyroxy-1,3-indanedione 90



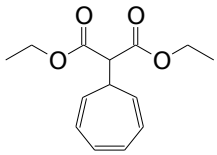
Ninhydrine (1 g, 6.24 mmol, 1 eq.) was suspended in dichloromethane. Diethyl malonate (1 g, 948 µL, 6.24 mmol, 1 eq.) and DBU (95 mg, 93 µL, 0.63 mmol, 0.1 eq.) were added and the mixture was stirred for 20 minutes. Longer reaction times led to decomposition. The mixture was immediately subjected to column chromatography (SiO_2; dichloromethane/ethyl acetate 19:1). Yield: 953 mg (2.98 mmol, 48 %)

Spectroscopy of **90**

^{1}H-NMR: (300 MHz, $CDCl_3$): δ = 8.05..7.98, 7.91..7.83 (2 m, 4 H, C_6H_4), 5.04 (s, 1 H, HOC-C**H**$(C=O)_2$), 4.31..4.10 (m, 4 H, C**H**$_2$O), 3.34 (s, 1 H, O**H**), 1.32..1.16 (m, 6 H, C**H**$_3$).

^{13}C-NMR{^{1}H} (300 MHz, $CDCl_3$): 195.4 (2 C, C_6H_4-$[C=O]_2$), 166.5 (2 C, CH(**C**=O)$_2$,140.2 (2 C, **C**$_2(C=O)_2$), 135.8 (2 C, CH-**C**H=**C**H-CH), 123.4 (2 C, **C**H-CH=CH-**C**H), 72.7 (1 C, **C**-OH), 61.7 (2 C, C**H**$_2$O), 53.1 (1 C, **C**H$(C=O)_2$), 12.9 (1 C, **C**H$_3$).

1,3-Diethyl-2(tropiliden-1-yl)malonate 92



Tropylium hexafluorophosphate (293 mg, 1.24 mmol, 1 eq.) was suspended in dichloromethane (5 mL). Diethyl malonate (200 mg, 210 µL, 1.24 mmol, 1 eq.) and DBU (189 mg, 185 µL, 1.24 mmol, 1 eq.) were added and the mixture was stirred for 12 h. The mixture was filtered and purified using column chromatography (SiO_2; dichloromethane). Yield: 70 %

Spectroscopy of **92**

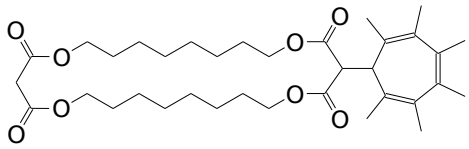
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.68 (2 H, m, CH-CH-CH=CH-C**H**=C**H**), 6.24 (2 H, CH-CH-CH=C**H**), 5.36 (2 H, CH-CH-C**H**=CH), 4.21 (q, $^{3}J_{H,H}$ = 7 Hz, 4 H, C$\mathbf{H}_2$O), 3.65 (d, $^{3}J_{H,H}$ = 10 Hz, 1 H, CH-C**H-**$(C=O)_2$), 2.73 (1 H, m, C**H-**CH-$(C=O)_2$), 1.27 (6 H, t, $^{3}J_{H,H}$ = 7.0 Hz, C$\mathbf{H}_3$) ppm.

^{13}C-NMR{^{1}H} (100.5 MHz, $CDCl_3$): δ = 168.1 (2 C, **C**=O), 130.9 (2 C, CH-CH-**C**H=CH), 126.6 (2 C, CH-CH-CH=CH-**C**H=**C**H), 122.3 (2 C, CH-CH-CH=**C**H), 61.4 (2 C, **C**H_2O), 52.7 (2 C, CH-**C**H$(C=O)_2$), 38.25 (2 C, **C**H-CH$(C=O)_2$), 14.1 (2 C, **C**H_3) ppm.

HRMS (ESI, CH_2Cl_2, AcN + toluene) calcd. for $C_{14}H_{18}NaO_4$ $[M + Na]^+$ 273.10973; found: 273.10998.

IR (ATR, diamond): ṽ = 2983 (m), 2939 (w), 2906 (w), 1728 (s), 1464 (w), 1446 (w), 1369 (w), 1299 (m), 1258 (m), 1229 (m), 1151 (s), 1131 (w), 1096 (w), 1028 (s), 860 (m), 744 (w), 701 (s), 593 (m) cm^{-1}.

2(Hexamethyltropiliden-1-yl)cyclo[2]-octylmalonate 96



Hexamethyltropylium perchlorate, synthesized following the procedure of Okamoto and Co-Workers[130] (34 mg, 0.124 mmol, 1 eq.) and cyclo[2]-octylmalonate **35** (106 mg, 278 µmol, 2.2 eq.) were dissolved in a mixture of 2 mL of tetrahydrofurane and 3 mL of dichloromethane. DBU (18.8 mg, 18.4 µL, 1 eq.) was added and the mixture was stirred for 18 h. Workup was done by means of column chromatography (SiO_2; dichloromethane/ethyl acetate 19:1). R_f =0.63 (doubly: 0.71; educt: 0.50). Yield: 17 mg (28 µmol, 22.7 %).

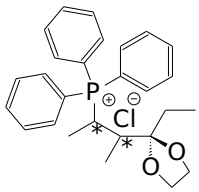
Spectroscopy of **96**

^{1}H-NMR (400 MHz, $CDCl_3$): 5.61 (1 H, **H**C=C), 5.37 (1 H, **H**C=C), 4.15..3.84 (8 H, C$\mathbf{H}_2$O), 3.51, 3.48, 3.34, 3.32, 3.29, 3.13, 3.07, 2.85 (1 H, C-**H**C$(C=O)_2$,), (1 H, 3.33 (2 H, $CH_2(C=O)_2$), (1 H, HC-**H**C$(C=O)_2$), 1.88, 1.86, 1.85, 1.83, 1.79, 1.76, 1.75, 1.71, 1.68 (18 H/15 H, C=C-C$\mathbf{H}_3$), 1.37, 1.24, 1.213, 1.208, 1.19, 1.17, 1.16, 1.15 (3 H, C$\mathbf{H}_3$-CH-CH$(C=O)_2$) ppm.

^{13}C-NMR{^{1}H} (100.5 MHz, $CDCl_3$): 170.2, 170.1, 170.0, 169.9, 169.1, 166.5 (4 C, **C**=O), 135.6, 134.4, 132.1, 129.6, 129.1, 128.0, 127.72, 127.66, 126.2, 125.8, 125.5, 125.2, 124.8 (6 C, **C**=**C**), 65.5, 64.8, 64.7, 64.6 (4 C, **C**H_2-O), 50.92, 50.86, 50.6, 49.9, 49.1 (1 C, C-**C**H$(C=O)_2$), 44.6 (1 C, **C**-CH$(C=O)_2$), 42.2, 42.1 (1 C, C**H**$_2(C=O)_2$), 37.2, 36.6 (1 C, **C**-CH$(C=O)_2$), 29.31, 29.26, 29.2 (4 C, **C**H_2CH_2O), 28.6, 28.54, 28.49 (4 C, **C**$H_2CH_2CH_2O$), 25.90, 25.85, 25.84, 25.81 (4 C, **C**$H_2CH_2CH_2CH_2O$), 22.6, 21.7, 21.2, 20.9, 20.7, 19.9, 18.8, 17.8, 17.5, 17.4, 17.0, 16.9, 16.7, 15.4, 15.2, 14.7, 14.6, 14.0, 11.7, 10.7 (18 C, CH_3)

MS(MALDI,sin): calcd. for $C_{35}H_{54}O_8$ $[M]^+$: 602.38 found: 602. calcd. for $C_{35}H_{54}O_8Na$ $[M + Na]^+$: 625.37 found: 625, calcd. for $C_{35}H_{54}O_8K$ $[M + K]^+$: 641.35 found: 641 Da.

2-Triphenylphosphonium-3-methyl-hexan-4-one glycol acetal 99



Triphenylphosphine (12.2 g, 2.56 mmol, 1 eq.) was dissolved in dichloromethane (72 mL). The solution was saturated with gaseous HCl. 4-methyl-hexa-4-en-3-one gylcol acetal **98** (7.29 g, 2.56 mmol, 1 eq.) was added dropwise in dichloromethane (72 mL). Gaseous HCl was bubbled through the mixture for 10 minutes. The solvent was removed and THF (150 mL) was added. The solution was cooled to -20°C. The upper phase was discarded and the lower phase was recrystallized in THF (59 °C to RT).

Spectroscopy of **99**

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.84..7.57 (m, 15 H, C_6**H**$_5$), 4.00..3.36 (m, 4 H, C**H**$_2$-O), 2.60..2.44 (m, **H**-C-CH-CH-P), 2.43..2.29 (m, 1 H, **H**-C-CH-P), 1.74..1.58 (m, 3 H, CH_3-CH-P), 1.56..1.43 (m, 2 H, C**H**$_2CH_3$), 1.4..1.28 (m, 3 H, C**H**$_3$-CH-CH-P), 0.80..0.67 (m, 3 H, C**H**$_3CH_2$) ppm.

^{13}C-NMR{^{1}H} (75.5 MHz, $CDCl_3$): δ = 134.1 (d, $^{4}J_{C,P}$ = 3.1 Hz, 3 C, para-Ph), 133.9 (d, $^{2}J_{C,P}$ = 8.8 Hz ortho-Ph), 129.7, (d, $^{3}J_{C,P}$ = 12 Hz, meta-Ph), 118.8 (d, $^{1}J_{C,P}$ = 84 Hz, ipso-Ph), 112.3 (1 C, **C**-O_2), 62.6, 62.2 (2 C, O-**C**H_2**C**H_2-O), 35.5 (d, $^{1}J_{C,P}$ = 9.5 Hz, 1 C, P-**C**H), 35.2 (d, $J_{C,P}$ = 34 Hz, P-CH-**C**H), 26.4 (1 C, **C**H_2CH_3), 15.8 (d, $^{2}J_{C,P}$ = 14 Hz, 1 C **C**H_3CH-P), 10.9 (1 C, P-CH-CH-**C**H_3), 7.8 (1 C, CH_2-**C**H_3) ppm.

^{31}P-NMR{^{1}H} (121.5 MHz, $CDCl_3$): 31.05 (1 P, C-**P**$^{+}Ph_3$) ppm.

References

[1] Carsten Bingel, *Chemische Berichte* **1993**, 1957-1959.

[2] W. Krätschmer, Lowell D. Lamb, K. Fostiroupoulos, Donald R. Huffman, *Nature* **1990**, *347*, 354-358.

[3] Margaret M. Boorum, Yury V. Vasil'ev, Thomas Drewello, Lawrence T. Scott, *Science* **2001**, *294*, 828-831.

[4] Mikhail Kabdulov, Martin Jansen, Konstantin Yu. Amsharov, *Chemistry* **2013**, *19*, 17262-17266 .

[5] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl and R.E. Smalley, *Nature* **1985**, *318*, 162.

[6] Tilo Habicher, Jean-François Nierengarten, Volker Gramlich, François Diederich, *Angewandte Chemie* **1998**, *110*, 2019-2022. Tilo Habicher, Jean-François Nierengarten, Volker Gramlich, François Diederich, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1916-1919.

[7] Shin-ya Kuwashima, Masayuki Kubota, Katsuhiko Kushida, Takayuki Ishida, Mamoru Ohashi, Takashi Nogami, *Tet. Lett.* **1994**, *35*, 4371-4374.

[8] Stephen R. Wilson, Nikolas Kaprinidis, Yunhui Wu, David I. Schuster, *J. Am. Chem. Soc.* **1993**, *115*, 8495-8496.

[9] Yosuke Nakamura, Nobutoshi Takano, Tatsuya Nishimura, Eiji Yashima, Mitsuo Sato, Takako Kudo, Jun Nishimura, *Org. Lett.* **2001**, *3*, 1193-1196.

[10] Koichi Komatsu, Guan-Wu Wang, Yasujiro Murata, Motoo Shiro, *Nature* **1997**, *387*, 583-586.

[11] Maurizio Prato, Michele Maggini, Gianfranco Scorrano, Vittorio Lucchini, *J. Org. Chem.* **1993**, *58*, 3613-3615.

[12] Xiaojun Zhang, Alex Romero, Christopher S. Foote, *J. Am. Chem. Soc.* **1993**, *115*, 11024-11025.

[13] Tomaki Sasaki, Katsumitsu Nakamura, *Kenku Kiyo* **2007**, *42*, 229-235.

[14] Arnold F. Holleman, Egon Wiberg, Nils Wiberg*Lehrbuch der Anorganischen Chemie* **1995** 101th Ed., de Gruyter, Berlin.

[15] N. Sivaraman, R. Dhamodaran, I. Kaliappan, *J. Org. Chem.* **1992**, *57*, 6077-6079.

[16] Walter A. Scrivens, James M. Tour, *J. Chem. Soc. Chem. Commun.* **1993**, 1207-1209.

[17] R. S. Ruoff, Doris S. Tse, R. Malbotra, D. C. Lorents, *J. Phys. Chem.* **1993**, *97*, 3379-3383.

[18] Christopher A. Reed, Robert D. Bolskar, *Chemical Reviews* **2000**, *100*, 1075-1120.

[19] Luis Echegoyen, Lourdes E. Echegoyen, *Accounts of Chemical Research* **1998**, *31*, 593-601.

[20] Paul J. Fagan, Paul J. Krusic, Dennis H. Evans, Susan A. Lerke, Eric Johnstont, *J. Am. Chem. Soc.* **1992**, *114*, 9697.

[21] Koichi Komatsu, Yasujiro Murata, Naohiko Takimoto, Sadayuki Mori, Nobuyuki Sugita, Terence S. M. Wan, *J. Org. Chem.* **1994**, *59*, 6101-6102.

[22] Majid Keshavarz-K, Brian Knight, Gordana Srdanov, Fred Wudl, *J. Am. Chem. Soc.* **1995**, *117*, 11371-11372.

[23] Andreas Skiebe, Andreas Hirsch, Holger Klos, Bernd Gotschy, *Chemical Physics Letters* **1994**, *220*, 138.

[24] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, A. R. Kortan, *Nature* **1991**, *350*, 600-601.

[25] Andreas Hirsch, Zhongfang Chen, Haijun Jiao, *Angew. Chem.* **2000**, *112*, 1915.
Andreas Hirsch, Zhongfang Chen, Haijun Jiao, *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 1845.

[26] Toshikazu Kitagawa, Harumi Sakamoto, Kenichi Takeuchi, *J. Am. Chem. Soc.* **1999**, *121*, 4298-4299.

[27] Toshikazu Kitagawa, Yangsoo Lee, Masaaki Hanamura, Harumi Sakamoto, Hirofumi Konno, Kenichi Takeuchi, Koichi Komatsu, *Chemical Communications* **2002**, 3062-3063.

[28] Bernhard Kräutler, Thomas Müller, Alvaro Duarte-Ruiz, *Chemistry - A European Journal* **2001**, *7*, 3223-3235.

[29] Minoru Tsuda, Takayuki Ishida, Takashi Nogami, Sadamu Kurono, Mamoru Ohashi, *Journal of the Chemical Society, Chemical Communications* **1993**, 1296.

[30] Iris Lamparth, Cäcilia Maichle-Mössmer, Andreas Hirsch, *Angewandte Chemie* **1995**, *107*, 1755-1757 .
Iris Lamparth, Caecilia Maichle-Moessmer, Andreas Hirsch, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1607-1609.

[31] Pavel Belik, Andreas Gügel, Jochen Spickermann, Klaus Müllen, *Angewandte Chemie* **1993**, *105*, 95-97.
Pavel Belik, Andreas Gügel, Jochen Spickermann, Klaus Müllen, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 78-80.

[32] Bernhard Kräutler, Josef Maynollo, *Tetrahedron* **1996**, *52*, 5033-5042.

[33] Michele Maggini, Gianfranco Scorrano, Maurizio Prato, *J. Am. Chem. Soc.* **1993**, *115*, 9798-9799.

[34] Thomas Grösser, Maurizio Prato, Vittorio Lucchini, Andreas Hirsch, Fred Wudl, *Angewandte Chemie* **1995**, *107*, 1462-1464.
Thomas Grösser, Maurizio Prato, Vittorio Lucchini, Andreas Hirsch, Fred Wudl, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1343-1345.

[35] M. Prato, Q. Chan Li, F. Wudl, V. Lucchini, *J. Am. Chem. Soc.* **1993**, *115*, 1148-1150.

[36] Johannes Averdung, Jochen Mattay, *Tetrahedron* **1996**, *52*, 5407-5420.

[37] T. Suzuki, Q. Li, K. C. Khemani, F. Wudl, *J. Am. Chem. Soc.* **1992**, *114*, 7301-7302.

[38] Amos B. Smith, Robert M. Strongin, Laurent Brard, George T. Furst, William J. Romanow, Kevin G. Owens, Richard C. King, *J. Am. Chem. Soc.* **1993**, *115*, 5829-5830.

[39] F. Langa, P. de la Cruz, E. Espíldora, A. Gonzalez-Cortes, A. de la Hoz, V. Lopez-Arza, *J. Org. Chem.* **2000**, *65*, 8675-8684.

[40] Hermann Irngartinger, Claus-Markus Köhler, Ursula Huber-Patz, Wolfgang Krätschmer, *Chemische Berichte* **1994**, *127*, 581-584.

[41] S. Filippone, M. I. Barroso, A. Martin-Domenech, S. Osuna, M. Sola, N. Martin, *Chemistry* **2008**, *14*, 5198-206.

[42] Olena Lukoyanova, Claudia M. Cardona, Margarita Altable, Salvatore Filippone, Ángel Martín Domenech, Nazario Martin, Luis Echegoyen, *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 7430-7433.

[43] Nicolle N. P. Moonen, Carlo Thilgen, Luis Echegoyen, François Diederich, *Chemical Communications* **2000**, *2000*, 335-336.

[44] Roland Kessinger, Jeanne Crassous, Andreas Herrmann, Markus Rüttimann, Luis Echegoyen, François Diederich, *Angewandte Chemie* **1998**, *110*, 2022-2025.
Roland Kessinger, Jeanne Crassous, Andreas Herrmann, Markus Rüttimann, Luis Echegoyen, François Diederich, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1919-1922.

[45] M. A. Herranz, C. T. Cox, Jr., L. Echegoyen, *J. Org. Chem.* **2003**, *68*, 5009-12.

[46] N. Martin, M. Altable, S. Filippone, A. Martin-Domenech, R. Martinez-Alvarez, M. Suarez, M. E. Plonska-Brzezinska, O. Lukoyanova, L. Echegoyen, *J. Org. Chem.* **2007**, *72*, 3840-3846.

[47] H. W. Kroto, *Nature* **1987**, 329, 529.

[48] W. H. Powell, F. Cozzi, G. P. Moss, C. Thilgen, R. J. R. Hwu, A. Yerin, *Pure and Applied Chemistry* **2002**, *74*, 629-695.

[49] Georg Schick, Klaus-Dieter Kampe, Andreas Hirsch, *Journal of the Chemical Society, Chemical Communications* **1995**, 2023.

[50] Masaya Sawamura, Hitoshi Iikura, Eiichi Nakamura, *J. Am. Chem. Soc.* **1996**, *118*, 12850-12851.

[51] Olga V. Boltalina, Vitaly Yu Markov, Roger Taylor, Martin P. Waugh, *Chemical Communications* **1996**, 2549.

[52] Ivan S. Neretin, Konstantin A. Lyssenko, Mikhail Yu. Antipin, Yuri L. Slovokhotov, Olga V. Boltalina,* Pavel A. Troshin, Andrei Yu. Lukonin, Lev. N. Sidorov, Roger Taylor, *Angewandte Chemie* **2000**, *112*, 3411-3414.
Ivan S. Neretin, Konstantin A. Lyssenko, Mikhail Yu. Antipin, Yuri L. Slovokhotov, Olga V. Boltalina,* Pavel A. Troshin, Andrei Yu. Lukonin, Lev. N. Sidorov, Roger Taylor, *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 3273-3276.

[53] Andreas Hirsch, Iris Lamparth, Heinrich R. Karfunkel, *Angewandte Chemie* **1994**, *106*, 453-455.
Andreas Hirsch, Iris Lamparth, Heinrich R. Karfunkel, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 437.

[54] Francis Djojo, Andrea Herzog, Iris Lamparth, Frank Hampel, Andreas Hirsch, *Chemistry - A European Journal* **1996**, *2*, 1537-1547.

[55] Clayden, Greeves, Warren, Wothers, *Organic Chemistry*, **2001**, Oxford, ISBN 978-0-19-850346-0.

[56] L. H. Reyerson, Kenneth Kobe, *Chemical Reviews* **1930**, *7*, 479-492.

[57] Otto Diels, Bertram Wolf, *Berichte der deutschen chemischen Gesellschaft* **1906**, *39*, 689-697.

[58] W. H. Hunter, D. E. Edgar, *J. Am. Chem. Soc.* **1932**, *54*, 2025-2028.

[59] Xavier Camps, Andreas Hirsch, *J. Chem. Soc. Perkin Trans. 1* **1997**, 1595-1596.

[60] Richard Sydney Curtiss, *American Chemical Journal*, **1905**, *33*, 603-604.

[61] Elizabeth Gilman, Treat B. Johnson, *J. Am. Chem. Soc.* **1928**, *50*, 3341-3348.

[62] E. Knoevenagel, *Berichte der deutschen chemischen Gesellschaft* **1898**, *31*, 2596-2619.

[63] S. Robert, C. Bertolla, B. Masereel, J. M. Dogne, L. Pochet, *Journal of medicinal chemistry* **2008**, *51*, 3077-80.

[64] I. Tomassoli, L. Ismaili, M. Pudlo, C. de Los Rios, E. Soriano, I. Colmena, L. Gandia, L. Rivas, A. Samadi, J. Marco-Contelles, B. Refouvelet, *European journal of medicinal chemistry* **2011**, *46*, 1-10.

[65] Iris Lamparth, dissertation, Universität Erlangen-Nürnberg, **1996**.

[66] Jutta Rath, dissertation, Universität Erlangen-Nürnberg, **2009**.

[67] Elke Dietel, Andreas Hirsch, Emerich Eichhorn, Anton Rieker, Steffen Hackbarth, Beate Röder, *Chemical Communications* **1998**, 1981-1982.

[68] Fabian Spänig, Michaela Ruppert, Jörg Dannhäuser, Andreas Hirsch, Dirk M. Guldi, *J. Am. Chem. Soc.* **2009**, *131*, 9378-9388.

[69] Jörg Dannhäuser, Wolfgang Donaubauer, Frank Hampel, Markus Reiher, Boris Le Guennic, Björn Corzilius, Klaus Peter Dinse, Andreas Hirsch, *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 3368-3372.

[70] Michaela Ruppert, dissertation, Universität Erlangen-Nürnberg, **2011**.

[71] Nikos Chronakis, Florian Beuerle, Andreas Hirsch, *Chemical Communications* **2005**, 3676-3678.

[72] Florian Beuerle, dissertation, Universität Erlangen-Nürnberg, **2008**.

[73] Thorsten Brandmüller, dissertation, Universität Erlangen-Nürnberg, **2005**.

[74] Uwe Reuther, Torsten Brandmüller, Wolfgang Donaubauer, Frank Hampel, Andreas Hirsch, *Chem. Eur. J.* **2002**, *8*, 2261-2273.

[75] S. C. Chuang, S. I. Khan, Y. Rubin, *Org. Lett.* **2006**, *8*, 6075-8.

[76] Huaping Li, Alex Kitaygorodskiy, Rebecca A. Carino, Ya-Ping Sun, *Org. Lett.* **2005**, *7*, 859-861.

[77] Huaping Li, Sk. Anwarul Haque, Alex Kitaygorodskiy, Mohammed J. Meziani, Maria Torres-Castillo, Ya-Ping Sun, *Org. Lett.* **2006**, *8*, 5641-5643.

[78] Frank Hörmann, Andreas Hirsch, *Chemistry* **2013**, *19*, 3188-3197.

[79] Patrick Witte, Florian A. Beuerle, Uwe Hartnagel, R. Lebovitz, A. Savouchkina, S. Sali, Dirk Guldi, Nikos Chronakis, Andreas Hirsch, *Organic & biomolecular chemistry* **2007**, *5*, 3599-613.

[80] Patrick Witte, Frank Hörmann, Andras Hirsch, *Chemistry* **2009**, *15*, 7423-7433.

[81] Patrick Witte, dissertation, Universität Erlangen-Nürnberg, **2008**.

[82] Michael Brettreich, dissertation, Universität Erlangen-Nürnberg **2000**.

[83] Nikos Chronakis, Uwe Hartnagel, Martin Braun, Andreas Hirsch, *Chemical Communications* **2007**, 607-609.

[84] Huaping Li, Sk., Anwarul Haque, Akex Kitaygorodskiy, Mohammed J. Meziani, Maria Torres-Castillo, Ya-Ping Sun, *Org. Lett.* **2006**, *8*, 5641-5643.

[85] Huaping Li, Alex Kitaygorodskiy, Rebecca A. Carino, Ya-Ping Sun, *Org. Lett.* **2005**, *7*, 859-861 .

[86] Bruce Alberts, Dennis Bray, Julian Lewis, Martin Raff, Keith Roberts, James D. Watson *Molekularbiologie der Zelle*, 3rd Edition, **1995**, Wiley-VCH Verlag GmbH, Weinheim ISBN=3-527-3055-4.

[87] Lennard Wasserthal, diploma thesis, Universität Erlangen-Nürnberg, **2008**.

[88] Petrus Hemström, Knut Irgum, *Journal of Separation Science* **2006**, *29*, 1784-1821.

[89] Jan-Frederik Gnichwitz, Renata Marczak, Fabian Werner, Nina Lang, Norbert Jux, Dirk M. Guldi, Wolfgang Peukert, Andreas Hirsch, *J. Am. Chem. Soc.* **2010**, *132*, 17910-17920.

[90] Frank Hörmann, Michael Brettreich, Wolfgang Donaubauer, Frank Hampel, Andreas Hirsch, *Chem. Eur. J.* **2013**, *19*, 2814-2825.

[91] Prof. Dr. Thomas Drewello, Jing Li, Rolf Kirschbaum, Lehrstuhl für Physikalische Chemie I, Egerlandstraße 3, 91058 Erlangen, Germany.

[92] Frank Hörmann, Andreas Hirsch, *Chemistry* **2013**, *19*, 3188-3197.

[93] Adam D. Darwish, Igor V. Kuvytchko, Xian-Wen Wei, Olga V. Boltalina, Ilya V. Gol'dt, Joan M. Street, Roger Taylor, *Journal of the Chemical Society, Perkin Transactions 2* **2002**, 1118-1121.

[94] Lennard K. Wasserthal, Andreas Kratzer, Andreas Hirsch, *Eur. J. Org. Chem.* **2013**, *2013*, 2355-2361.

[95] Matthew L. Meketa, Yogesh R. Mahajan, Steven M. Weinreb, *Tet. Lett.* **2005**, *46*, 4749-4751.

[96] Fieser & Fieser: Reagents, Volume 1, pages 1128-1129, Wiley & Sons 1967, CCN: 66-27894.

[97] E. W. Warnhoff, D. G. Martin, W. S. Johnsson, *Organic Synthesis Collection* **1963**, *4*, 162.

[98] Frank Hörmann, Wolfgang Donaubauer, Frank Hampel, Andreas Hirsch, *Chemistry- a European Journal* **2012**, *18*, 3329-3337.

[99] Andreas Hirsch, Iris Lamparth, Thomas Grösser, Heinrich R. Karfunkel, *J. Am. Chem. Soc.* **1994**, *116*, 9385-9386.

[100] Francis Djojo, dissertation, Universität Erlangen-Nürnberg, **2000**.

[101] Fred Wudl, Andreas Hirsch, K. C. Khemani, T. Suzuki, P. M. Allemand, A. Kosch, H. Eckert, G. Srdanov, H. M. Webb, *ACS Symp. Ser.* **1992**, *481*, 161.

[102] Roald Hoffman, Vladimir I. Minkin, Barry K. Carpenter, *HYLE-International Journal for the Philosophy of Chemistry* **1997**, 3, 3-28.

[103] Michael Brettreich, Stephan Burghardt, Christoph Böttcher, Thomas Bayerl, Sybille Bayerl, Andreas Hirsch, *Angew. Chem. Int. Ed.* **2000**, *39*, 1845-1848.

[104] Martin Braun, Uwe Hartnagel, Elena Ravanelli, Boris Schade, Christoph Böttcher, Otto Vostrowski, Andreas Hirsch, *Eur. J. Org. Chem.* **2004**, 1983-2001.

[105]Karin Rosenlehner, Torsten Schunk, Norbert Jux, Michael Brettreich, Andreas Hirsch *Org. Biomol. Chem.* **2008**, *6*, 2697-2705.

[106]Tatsuya Homma, Koji Harano, Hiroyuki Isobe, Eiichi Nakamura, *J. Am. Chem. Soc.* **2011**, *133*, 6364-6370.

[107]Patrick Witte, Frank Hörmann, Andreas Hirsch, *Chem. Eur. J.* **2009**, *15*, 7423-7433.

[108]Prof. Dr. Christoph Böttcher, Dr. Boris Schade, Dr. Kai Ludwig, Forschungszentrum für Elektronenmikroskopie, Freie Universität Berlin, Fabeckstraße 36a, Berlin.

[109]Grigoriy V. Andrievsky, Marina V. Kosevich, Oleh M. Vovk, Vadim S. Shelkovsky, Lyudmila A. Vashchenko, *Journal of the Chemical Society, Chemical Communications* **1995**, 1281-1282.

[110]Prof. Dr. Franziska Gröhn, Jasmin Düring, ICMM-Institut für physikalische und theoretische Chemie, Egerlandstraße 3, 91058 Erlangen.

[111]Hu Yang, Qiang Zheng, Rongshi Cheng, *From Colloids and Surfaces, A: Physicochemical and Engineering Aspects* **2012**, *407*, 1-8. .

[112]Boris Schade, Lennard Wasserthal, Kai Ludwig, Christoph Böttcher, Andreas Hirsch, *Chem. Eur. J.* **2014**, DOI: 10.1002/chem.201400153.

[113]Marin van Heel, Joachim Frank, *Ultramicroscopy* **1981**, *6* 187-194.

[114]Jan Spengler, Sergej N. Osipov, Elisabeth Heistracher, Alois Haas, Klaus Burger, *Journal of Fluorine Chemistry* **2004**, *125*, 1019-1023.

[115]Gustaf-Adolf Holmberg, *Acta Academica Aboensis* (chapter 1+2:Hydrolysis of carbon-to-carbon bonds) **1950**.

[116]Kenneth Conrow, *J. Am. Chem. Soc.* **1959**, *81* 5461-5467.

[117]Robert A. Moss, Andrew Mamantov, *Tet. Lett.* **1968**, *9*, 3425-3428.

[118]Donna J. Nelson, Robert L. Henley, *Tet. Lett.* **1995**, *36*, 6375-6378.

[119]Eleni Kassi, Costas S. Patrickios, *Macromolecules* **2010**, *43*, 1411-1415.

[120]Y. V. Kissin, *NMI Press symposium series* **1983**, *4*, 597-615.

[121]Autorenkollektiv, *Organikum*, 22nd Edition, **2004** Wiley-VCH Verlag GmbH, Weinheim. ISBN 3-527-31148-3.

[122]Willy Lehnert, *Tet. Lett.* **1970**, *54*, 4723-4724.

[123]C. A. August Michaelis, Theodor Becker, *Ber. d. dt. chem. Ges.* **1987**, *30*, 1003-1009.

[124]S. J. Ludtke, P. R. Baldwin, W. Chiu, *J. Struct. Biol.* **1999**, *128*, 82.

[125]M. van Heel, G. Harauz, E.V. Orlova, R. Schmidt, M. Schatz, *J. Struct. Biol.* **1996**, *116*, 17.

[126]M. J. Frisch et al. Gaussian, Inc., Wallingford CT, **2004**.

[127]ChemBioOffice2010, **2010** Cambridge Soft/Perkin Elmer .

[128]Lennard K. Wasserthal, unpublished.

[129]R. Schwesinger, C. Hasenfratz, H. Schlemper, L. Walz, E.-M.Peters, K. Peters, H. G. von Schnering, *Angewandte Chemie* **1993**, *105*, 1420-1422.
R. Schwesinger, C. Hasenfratz, H. Schlemper, L. Walz, E.-M.Peters, K. Peters, H. G. von Schnering, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1361-1363.

[130]Kenichi Takeuchi, Yasunori Yokomichi, Takeshi Kurosaki, Yoshihiro Kimura, Kunio Okamoto, *Tetrahedron* **1979**, *35*, 949-956.

Publication List

Lennard K. Wasserthal, Andreas Kratzer, Andreas Hirsch, *Eur. J. Org. Chem.* **2013**, *2013*, 2355-2361.

Boris Schade, Lennard Wasserthal, Kai Ludwig, Christoph Böttcher, Andreas Hirsch, *Chem. Eur. J.* **2014**, DOI: 10.1002/chem.201400153

Poster Contributions

Lennard Wasserthal, Christoph Böttcher, Kai Ludwig, Jing Li, Thomas Drewello, Andreas Hirsch "Fullerene Based Oligo-Cations with a Defined Octahedral Addition Pattern" 3rdEuCheMS Chemistry Congress **2010**, Nuremberg, Germany.

Lennard K. Wasserthal, Andreas Kratzer, Andreas Hirsch, "Mechanistic Effects Relevant for Selectivity of the Bingel Reaction" GDCH Wissenschaftsforum **2013**, Darmstadt, Germany.

Danksagung

Ich bin meinem Doktorvater Herrn Prof. Dr. Andreas Hirsch für die entgegenkommende Themenstellung und seine Geduld zu großem Dank verpflichtet.
Durch ihn hatte ich alle Freiheit, die ich brauchen konnte.
Bedanken möchte ich mich weiterhin für die gute Zusammenarbeit bei all meinen Kollegen:
Meinem Themenvorgänger Patrick "Keulo" Witte,
Dr. Alejandro Montellano López, Dr. Aleksandra Femic, Dr. Alexander "**/-G-/**" Gmehling, Dr. Alexander "Data" Konev, Alexander "Ebelix" Ebel, Alexandra Burger, Andreas "Daeh rohde Blitz" Kratzer, Astrid Herrmann, Astrid Hopf, Dr. Benjamin "Benni" Gebhardt, Bhasem "Ghribby" Gharib, Dr. Boyan Johnev, Chau Vinh, Christian "Panflöte" Methfessel, Christian "Kovi" Kovacs, Dr. Christoph Dotzer, Dr. Claudia Backes, Dr. Cordula Daniela "Cordu" Wessendorf, Dr. Dina "Bragi" Ibragimova, Dr. David "Yoda" Wunderlich, Dominik "Domi" Hasenöhrl, Dominik "Domi" Lungerich, Ekaterini "Kati" Vlassiadi, Dr. Elif Okutan, Eva Kränzlein, Fabian "Fabi" Rodler, Fabian Fritze, Fabian Rodler, Felix "Gimli" Amon, nicht zu verwechseln mit Dr. Felix Grimm, Ferdinand Hof, Dr. Florian "Wessi" Wessendorf, Dr. Florian Andreas "FloB" Beuerle, Dr. Frank "Superbubi" Hörmann, Fraziska "Franzi" Forster, Dr. Hannelore "Hanne" Jasch, Dr. Harald Maid, Dr. Jan Frederik "Freddy" Gnichwitz, Dr. Jan Matthias "Freitaş" Englert, Dr. Jennifer "Jenny" Malig, Jennifer Schimcke, Johannes "Waschl" Holzwarth, Dr. Jutta "Siebenkees" Rath, Jörg "Schöni" Schönamsgruber, Karin "Rosi" Rosenlehner, Katerina "Flexi" Maxouti, Kathrin "Crunchy" Knirsch, Kathrin "Meister" Eder, Dr. Katja Maurer-Chronakis, PD Dr. Konstantin Amsharov, Lillia Mbogo-Wachira, Lukas "Lulu" Zeininger, Mario "Luigi" Marcia, Dr. Mario Adelhardt, Matthias Baaske, Dr. Max von Delius, Michaela "Michi" Ruppert, Dr. Miriam "Mimi" Becherer, Dr. Miriam "Miri" Biedermann, Dr. Nadine Ulm, Dr. Nicolas "Nico" Bernhard, Dr. Nina Kozhemyakina, Dr. Nina Lang, Phillip Vecera, Dr. Prabhpreet Singh, Dr. Radhakrishnan "Radha" Viswanathan, Dr. Rainer "Friseurfürst" Lippert, Regina "Regi" Eigler, René Chris Brachvogel, Rhys Mitchell, Ricarda Schäfer, Dr. Satohiro Sato, Sebastian "Boshido" Bosch, Sebastian "Schlundel" Schlundt, Dr. Siegfried "Sigi" Eigler, Simone Berngruber, Sofia Rohde, Stefan Grimm, Stefan "Steffele" Jasinski, Stefanie "Petzi" Petzi, Stefanie "Pumuckl" Sauer, Prof. Dr. Şule Erten-Ela, Susanne "Cess" Backes, Torsten "Schunki" Schunk, Dr. Tina Andrä, Dr. Tyler Clikeman, Udo Mundloch, Ute Pinkert, Zois Syrgiannis, sowie den effektiven Arbeitskreismitgliedern Leona Toric und Torsten "Torsche" Brandmüller.

Für die wirklich tätige Hilfe bedanke ich mich bei meinen Mitarbeitern:
Kristina Dresbach, die für mich alle Experimente zur Schützung der Ninhydrinaddukte durchgeführt hat,
Armin Neitzel, der die ersten Experimente mit der Tropyliumschutzgruppe durchgeführt hat und ohne dessen vielversprechende Anfangsergebnisse ich das Tropyliumprojekt nicht begonnen hätte und
Judith Kratzel, welche zwei aufwändige Versuchsreihen zu Aufklärung des Mechanismuses der Tetrabromkohlenstofftemplatisierung durchgeführt hat.
Für die Verwaltung und die kooperative Unterstützung danke ich auch den Akademischen Räten und anderen Professoren des Lehrstuhls:
Dr. Michael "Brettl" Brettreich, Marcus "Specki" Speck, Prof. Dr. Norbert "Nobbi" Jux, Prof. Dr. Walter "Waldi" Bauer, Dr. Frank Hauke, Dr. Frank Hampel und Dr. Thomas "Mikro" Röder.
Für die Inspiration zu abwegigen, aber im Erfolgsfall lohnend gewesen wärenden Experimenten danke ich jemandem, der hier sicher nicht genannt werden möchte und dessen Heimatsstadtname grotesk martialisch klingt.
Besonderer Dank gilt auch den Angestellten, die tatkräftig für mich gearbeitet haben:
Zuvorderst den Glasbläsern, Stefan "Glasi" Fronius und Bahram Saberi,
Den Sekretärinnen Erna Erhardt und Heike Fischer
Den Assistenten der Messabteilungen, Christian Placht, Wilfried "Wiff" Schätzke, Wolfgang "Don" Donaubauer, Margarete "Grete" Dziallach und Eva Zeisel, Detlev Schagen, Hannelore "Oschi" Oschmann, Robert "Igor" Panzer,
den Technikern Holger "Bass Booster" Wohlfahrt, Herr Erwin Schreier, Herr Eberhard Rupprecht und Horst Maier,
Sowie Heidemarie "Heidi" Polster und Dr. phil. Alena Slezak
Ganz herzlich möchte ich mich hier auch noch einmal bei den Kooperationspartnern bedanken, die für mich gemessen haben: Prof. Dr. Thomas Drewello, Dr. Jing Li und Rolf Kirschbaum(ESI MS/MS)
Prof. Dr. Franziska Gröhn und Jasmin Düring,(DLS)
und natürlich Prof. Dr. Christoph Böttcher, Boris Schade und Kai Ludwig, die die Transmissionselektronenmikroskopischen Aufnahmen für mich angefertigt und ausgewertet haben.
Ich bin weiterhin dafür sehr dankbar, dass meine Eltern die Zeit meines Studiums lang immer meine Ausbildung unterstützt haben, und mich so die ganze Zeit des Studiums lang von allen erdenklichen Störeinflüssen und nicht-konservativen Arbeitssenken freigehalten haben, so dass ich mich komplett auf das Erreichen meines Abschlusses fokussieren konnte.
Und dann danke noch den netten Leute aus den anderen Arbeitskreisen, die ich näher kannte, Matthias Adam, Andreas Waterloo, Giuseppe "Giu" Rulli, Maximilian Krempe, Vincent "Vince" Oerthel, Julia "Ju" Tyrach, Anja Fingerhut, Christoph Reiter... uvm für die freundliche Atmosphäre, die in allen Arbeitskreisen vorhanden war.

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Diplomarbeit im Arbeitskreis von Prof. Dr. Andreas Hirsch,
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Doktorarbeit im Arbeitskreis von Prof. Dr. Andreas Hirsch,
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Tuneable Solvent Affinities