Synthesis of compounds presenting three and four anthracene units as potential connectors to mediate infinite lateral growth at the air/water interface

Author(s):
Münzenberg, Cindy

Publication Date:
2009

Permanent Link:
https://doi.org/10.3929/ethz-a-006053479

Rights / License:
In Copyright - Non-Commercial Use Permitted
Synthesis of Compounds Presenting Three and Four Anthracene Units as Potential Connectors to Mediate Infinite Lateral Growth at the Air/Water Interface

A dissertation submitted to

ETH ZURICH

for the degree of

Doctor of Sciences

presented by

CINDY MÜNZENBERG

Dipl.-Chem., Friedrich-Schiller Universität Jena

born August 23, 1979

citizen of Germany

accepted on the recommendation of

Prof. Dr. Dieter Schlüter, examiner
Prof. Dr. Peter Walde, co-examiner
Prof. Dr. Nicholas Spencer, co-examiner

Zürich, 2009
Acknowledgment

“Whoever wants to reach a distant goal must take small steps.” Helmut Schmidt, former German chancellor (1974 - 1982)

At the outset, I would like to thank cordially Prof. A. Dieter Schlüter for giving me the opportunity to work on this challenging and highly interdisciplinary topic.

Big thanks are due to Dr. Oleg Lukin for his inspiring supervision of this work and all the fruitful discussions we had. I highly appreciate his support, as well as and the model calculations.

I have to thank Prof. Peter Walde for his patient reading my thesis! Thanks so much Peter!

I would like to thank my cooperation partner Dr. Katarzyna Kita-Tokarczyk working in the group of Prof. Wolfgang Meier at the University of Basel for her willingness to introduce me to surface science, her lively way to discuss and her openness for uncommon experiments.

I gratefully acknowledged the inspiring discussions I had with Prof. Paul Smith. Thanks a lot! You were a great teacher!

The support of the following people is highly appreciated: Dr. Kirill Feldman working in the group of Prof. Paul Smith; Reto Fiolka working in the group of Prof. Andreas Stemmer; Prof. Antonella Rossi, Dr. Venkataraman V. Nagaiyanallur, Christian Zinke, Barbora Malisova working in the group of Prof. Nicholas Spencer; Dr. Kerstin Wagner, Dr. Gerald Brezesinski working in the group of Prof. Helmut Möhwald, and Prof. Volker Böhmer. It was a great experience to work with so many different people!

All members of the Schlüter’s group are thanked for the good working atmosphere. Jonas Halter is thanked for his support during his practical course.

I highly acknowledge the support of all members of the mass spectrometry team, especially Rolf Häflinger, the elemental analysis and the help of the NMR team: Dr. Heinz Rüegger and Doris Suter.

I am pleasant to express my gratitude to Prof. Nicholas Spencer and Prof. Ludwig Gauckler for reviewing my dissertation.
But most important, I have to thank my parents, my brother and my grandma who always believed in me. This feeling made me strong whatever happened.
Summary

The present thesis is concerned with the synthesis and characterization of monomers and their photochemically induced polymerization at the air/water interface. It was aimed at preparing amphiphilic monomers which are able to form a monolayer at the air/water interface. Spreading of monomers to generate an ordered monolayer at the interface, i.e. at the air/water is denoted as interfacial approach. UV-light irradiation was utilized to polymerize this monolayer. All monolayer experiments were accomplished by means of the Langmuir-Blodgett-technique. This first attempt towards two dimensional (2D) polymers combines rational monomer design followed by the interfacial approach. A 2D polymer, as understood in this thesis, is characterized through its periodicity, its long-range order, a thickness corresponding to the height of the monomer, and an (almost) infinite lateral extension of the covalently connected monomers.

Two monomer families containing either three or four connective units, named as tripod-and tetrapod-family with regard to their functionality were synthesized. The dimerization of anthracene, a photochemically induced [4+4]-cycloaddition, was chosen to covalently connect the monomers. The synthesis strategy for both monomer families including the incorporation of three or four anthracenes respectively was based on familiar organic reactions in solution, exemplary amide coupling or esterification.

Monomers based on a pentaerythritol scaffold equipped with different polar tails led to a collection of monomers belonging to the tripod-family. Monomers bearing four connective units were accomplished by using cone-shaped calix[4]arenes which allowed the attachment of four anthracenes at the upper rim. Amphiphilicity of the monomers was achieved through the introduction of different tails at the lower rim of the calix[4]arenes. One representative of each monomer-family is depicted in Figure A.
The extent of polymerization depends on the high-yielding anthracene dimerization within the monolayer at the air/water interface. It was challenging to analyze the polymeric monolayer due to the small amount of material involved in a Langmuir-Blodgett-experiment which subsequently required highly sensitive analysis methods. Therefore, the dimerization of different anthracene derivates (Figure B) in solution was preliminary studied to develop insights regarding expectable yields of dimerization and the applicability of spectroscopic methods to characterize the dimers obtained. Yields were found to be in the range of 40 – 70% whereas only the anti-isomer of the anthracene dimers was obtained. The dimers generated from 9-methoxy anthracene for which the syn- and anti-isomer (syn-dim 24 and anti-dim 24) was isolated, the yield increased up to 92%.
Among other spectroscopic methods, IR-spectroscopy was applied to prove the formation of anthracene dimers. The newly formed bridgeheads at 9,9'- and 10,10'- position were consistently observed to appear at around 1454 cm⁻¹ and 1474 cm⁻¹ in the IR-spectrum for the dimers 20, anti-dim 22, anti-dim 23, anti-dim 24 and syn-dim 24. The collected IR-spectroscopy data is in good agreement with already published results.

The potential to dimerize manifold was observed using compound 6 which was found to undergo a threefold intermolecular dimerization with parent anthracene yielding model compound 20, the stoichiometric 1:3 adduct. The UV-Vis spectrum of 20 revealed the complete disappearance of the characteristic anthracene signals. The “homopolymer” out of 6 was observed to show free anthracene signals (end groups) in the UV-Vis spectra - similarly to the “homopolymer” out of monomers 27a at high concentrations (125 mM). The UV-Vis spectra of 27a polymerized at low concentrations (10 mM) elucidated the complete conversion of the anthracenes indicating that this type of monomer and monomers based on 6 allow a manifold dimerization.

The interfacial behavior for 6, 16b, 17 – 19 (tripod-family), and 27a (tetrapod-family) at the air/water interface was concluded from the recorded isotherms. Monomer 6 was found to form a stable and homogenous monolayer, but its reversible formation was not possible,
presumably due to its high crystallinity. Among the tripod-family only 16b was observed to form a stable monolayer which can be reversibly formed. Monomer 27a showed excellent film forming properties, its isotherm was fully reversible. At a surface pressure of 25 mN/m, the monolayer of 27a appeared to be very stable versus time (1800 sec) and its visualization using Brewster angle microscopy (BAM) disclosed a uniform monolayer. The transfer of the non-irradiated and also the irradiated monolayer onto different solid substrates was undertaken to further characterize the monolayer generated at the air/water interface. The layer thickness was determined by ellipsometry. The values obtained for the non-irradiated (17 – 19 Å) and the irradiated layer (20 – 21 Å) corresponded to the height of the monomer 27a, theoretically 24 Å in its fully extend form, the presence of the monolayer was proven. X-ray photon spectroscopy (XPS) for the non-irradiated monolayer verified its theoretical atomic composition. Further, angle resolved XPS revealed increased carbon and decreased oxygen content at high emission angle suggesting the monomer’s orientation: the anthracenes are located at the top of the layer and the polar chains point towards the substrate. Since only the irradiated monolayer of 27a could be visualized by optical microscopy after transfer on a Cu-grid via Langmuir-Schaefer-transfer, cross-linking at the air/water interface was assumed. It was astonishing that a layer with a thickness of about 21 Å could be visualized by optical microscopy! This fact supported the assumption that monomers which were previously synthesized are able to undergo a covalent connection at the air/water interface. For non-irradiated monolayers of 27a, this result was never observed. Infrared-reflection-absorption-spectroscopy (IRRAS) of 27a at the air/water interface supported the assumption of anthracene dimerization since the spectra revealed the absorption of the anthracene bridgeheads as observed for 20, anti-dim22, anti-dim23, anti-dim24 and syn-dim24. The covalent connection at the air/water interface can therefore attributed to the dimerization of anthracenes.
Zusammenfassung


Zusammenfassung

In diesen Fällen lediglich das anti-Isomer des Anthracene-Dimers isoliert werden konnte. Eine Ausnahme bildet das Dimer ausgehend von 9-Methoxyanthracen, für welches das syn- und anti-Isomer (syn-dim 24 und anti-dim 24) mit einer Ausbeute von 92% isoliert werden konnte.

Abbildung B

Zur Charakterisierung der Dimere diente neben anderen spekroskopischen Methoden die IR-Spektroskopie. Die neu entstandenen Brückenköpfe in 9,9'- und 10,10'- Position wurden durchgängig bei 1454 cm⁻¹ und 1474 cm⁻¹ in den IR-Spektren für die Dimere 20, anti-dim 22, anti-dim 23, anti-dim 24 und syn-dim 24 beobachtet. Diese Resultat stimmt mit den in der Literatur veröffentlichten Ergebnisen überein.

Es konnte gezeigt werden, dass die Dimerisierung in einem Molekül mehrfach erfolgen kann, indem ausgehend von Verbindung 6 durch Umsetzung mit Anthracen das 1:3 Addukt erhalten werden konnte. Die so entstandene Modelverbindung 20 zeigte erwartungsgemäß keinerlei Anthracen-Signale im UV-Vis Spektrum mehr. Die „Homopolymerisation“ von 6 weist im Gegensatz dazu auf Anthracen zurückzuführende Absorptionen im UV-Vis Spektrum auf, die die Bildung eines irregularen Netzwerkes mit freien Anthracenen als Endgruppen schlussfolgern lassen. In ähnlicher Weise bestätigt das UV-Vis Spektrum einer 125 mM Lösung von 27a nach Bestrahlung mit UV-Licht das Vorhandensein von Anthracen-Signalen,
Zusammenfassung

Zusammenfassung

die als Endgruppen eines Polymers verstanden werden können. Eine 10 mM Lösung von 27a zeigt nach Bestrahlung das Verschwinden der Anthracen-Signale im UV-Vis Spektrum. Folglich eignen sich Monomere ausgehend von 6 und 27a, um mehrfache Dimerisierungen in einem Molekül zu ermöglichen.

Abbreviations

0D     zero dimensional
1D     one dimensional
2D     two dimensional
3D     three dimensional
AcOH   acetic acid
AFM    atomic force microscopy
ATRP   atom transfer radical polymerization
BnBr   benzyl bromide
Boc    tert-butyloxycarbonyl
CaF₂   calcium fluoride
CFF    consistent force field
C₃ᵥ    symmetry group
C₄ᵥ    symmetry group
DIEA   diisopropyl ethyl amine
DMC    dichloromethane
DIC    differential interference contrast microscopy
DMP    4-dimethylaminopyridine
DMF    dimethylformamide
DNA    deoxyribonucleic acid
DPTS   4-(dimethylamino)pyridinium p-toluenesulfonate
EA     elemental analysis
Et₃N   triethylamine
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDC</td>
<td>N, N’-(3-dimethylaminopropyl)-ethylcarbodiimide hydrogen chloride</td>
</tr>
<tr>
<td>EM</td>
<td>electron microscopy</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
</tr>
<tr>
<td>HCl</td>
<td>hydrochloric acid</td>
</tr>
<tr>
<td>hh</td>
<td>head-to-head</td>
</tr>
<tr>
<td>HOPG</td>
<td>highly oriented pyrolitic graphite</td>
</tr>
<tr>
<td>HOBT</td>
<td>hydroxyl-benzotriazole</td>
</tr>
<tr>
<td>3-HPA</td>
<td>3-hydroxypicolinic acid</td>
</tr>
<tr>
<td>HRMS</td>
<td>high resolution mass spectrometry</td>
</tr>
<tr>
<td>ht</td>
<td>head-to-tail</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz (sec$^{-1}$ or cycles per second)</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>IRRAS</td>
<td>infrared reflection absorption spectroscopy</td>
</tr>
<tr>
<td>J</td>
<td>coupling constant, in Hz</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wave length</td>
</tr>
<tr>
<td>KOH</td>
<td>potassium hydroxide</td>
</tr>
<tr>
<td>LiAlH$_4$</td>
<td>lithium aluminium anhydride</td>
</tr>
<tr>
<td>M</td>
<td>multiplet (NMR)</td>
</tr>
<tr>
<td>M</td>
<td>molar</td>
</tr>
<tr>
<td>[M]$^+$</td>
<td>molecular peak (MS)</td>
</tr>
<tr>
<td>MALDI</td>
<td>matrix assisted laser desorption/ionization (MS)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>MALDI-FT</td>
<td>matrix assisted laser desorption/ionization - time of flight (MS)</td>
</tr>
<tr>
<td>MALDI-TOF</td>
<td>matrix assisted laser desorption/ionization - fourier transformation</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>m/z</td>
<td>mass-to charge ratio in mass spectrometry</td>
</tr>
<tr>
<td>mg</td>
<td>milligram</td>
</tr>
<tr>
<td>MHz</td>
<td>megahertz</td>
</tr>
<tr>
<td>ml</td>
<td>milliliter</td>
</tr>
<tr>
<td>mM</td>
<td>millimol per liter</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>NaN₃</td>
<td>sodium azide</td>
</tr>
<tr>
<td>NH₃(aq)</td>
<td>aqueous solution of ammonia</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>PPh₃</td>
<td>triphenylphosphine</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million (NMR)</td>
</tr>
<tr>
<td>PyBop</td>
<td>benzotriazol-1-yl-oxytrpyrrolidinophosphonium hexafluorophosphate</td>
</tr>
<tr>
<td>SAXS</td>
<td>small-angle X-ray scattering</td>
</tr>
<tr>
<td>S</td>
<td>singlet (NMR)</td>
</tr>
<tr>
<td>¹S*</td>
<td>singlet excited state</td>
</tr>
<tr>
<td>T</td>
<td>triplet (NMR)</td>
</tr>
<tr>
<td>¹T*</td>
<td>triplet excited state</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>ultraviolet-Visible</td>
</tr>
</tbody>
</table>
Table of Contents

Acknowledgment .......................................................... III
Summary ........................................................................ V
Zusammenfassung ........................................................ IX
Abbreviations ................................................................. XIV
Table of Contents ........................................................ XVIII

1 Introduction ........................................................... 1
2 Aim of the thesis ...................................................... 12
3 Literature survey ..................................................... 15
   3.1 Naturally provided 2D polymers ....................... 15
   3.2 Polymerization in confined 2D geometries .......... 19
   3.3 The “flask-type approach” .......................... 33
   3.4 Concluding remarks .................................. 40
4 General Part ............................................................ 42
   4.1 Introduction ................................................. 42
   4.2 Anthracene Dimerization ............................... 42
   4.3 Langmuir-Blodgett Technique ....................... 48
5 Results and Discussion .............................................. 58
   5.1 Tripod Family ............................................... 58
   5.2 Tetrapod Family ......................................... 76
   5.3 Concluding remarks .................................. 96
6 Outlook ................................................................. 97
7 Experimental Section ................................................. 100
   General ............................................................ 100
Table of Contents

7.2 Synthesis  104

8 Literature  119
1 Introduction

During the last decades polymer science has developed numerous concepts for the synthesis of linear polymers and provided advanced conceptual ideas for the creation of related structures such as branched chains, rings, ladders, and dendrimers which are schematically depicted in Figure 1.

![Figure 1: Schematic representation of polymer architectures. Exemplary, a) branched chains, b) rings, c) ladder-polymers, and d) dendrimers are shown.](image)

Regardless of the sophisticated synthetic strategies leading to an almost infinite structural diversity, the polymerization principles are based on monomers capable of forming products with a one-dimensional (1D) polymer backbone. Although polymerization in two dimensions is described manifold, reliable and broadly applicable concepts to synthesize a truly periodic 2D polymer including its structural proof could not be achieved yet. Despite the wide use of the term 2D polymer, a uniform definition is not generally used. Within the scope of the dissertation, a 2D polymer is defined as an one repeating unit thick, covalently bonded, laterally “infinite”, periodic molecular sheet. A descriptive representation of a 2D polymeric sheet is shown in Figure 2.

![Figure 2: Cartoon-like representation of a 2D polymer containing two different chemical functionalities. The monomers are covalently connected in plane (shown as yellow sheet). This type of 2D polymer is formed through preorientated monomers comprised of two different substituents displayed as red dots and blue Y-shaped symbols. For example, these functionalities can be used to introduce hydrophobic, hydrophilic or even supramolecular binding sites. The lateral extension is supposed to be at least in the range of several 100 nm.](image)
The condition of periodicity consequently leads to a long-range order within the sheet-like structure which is illustrated in Figure 3.

![Schematic representation of an arbitrary 2D polymer composed of hexagonal units to illustrate periodicity. Irrespective of the start point and direction of movement, the same structure element can be found. The red arrows indicate the existing long-range order which is meant to be in the order of several hundred nm or even μm. This uniformity in plane leads to an isotropic sheet-like material.](image)

A shining example for a 2D polymer, naturally occurring, is graphene which fulfills above definition. Graphene is an one-atom-thick planar sheet of carbon atoms which are densely packed in a honeycomb crystal lattice. It was taken from graphite. Methods for graphene preparation are versatile. Mechanical cleavage, epitaxial growth and nowadays even chemical synthesis are described in literature. The existence of such an atomically flat sheet amazes many researchers due to its very existence. For this 2D crystal unique properties were reported. Contrary to the naturally occurring graphene, artificially made 2D polymers by means of organic synthesis could provide differently composed 2D structures due to various tailored monomers. The exploration of structural, analytical, technological and theoretical aspects of such 2D polymers is definitely challenging.

The term 2D polymer is not used consistently in literature. For this reason it is necessary to emphasize which types of “2D polymers” described in literature are not considered as such:

- Systems which are self-assembled on surfaces based on non-covalent interaction forces such as hydrogen bonding, π-stacking, dipolar or van der Waals as a directional tool for the design of superstructures are not regarded here.

- Inorganic substances of layered nature where each layer perfectly match the above definition as such are not viewed as 2D polymer because the formation of the 2D polymer is not achieved individually. These 2D polymers were taken from crystals.
From the viewpoint of a synthetic polymer chemist the last-mentioned systems are rather 2D crystals.

So far achieved “2D polymers” rely on monomers confined in 2D as a monolayer which are then covalently connected through random-walk polymerization. The resulting single-stranded polymer is kept in 2D as long as the monolayer remains intact. Without the confining environment of the monolayer at an interface a coiled shape is obtained which is depicted in Figure 4a. This behavior is known from linear polymers in solution. In addition to this practical approach a more theoretical one is the confinement of a linear polymer into 2D which originally existed in a 3D space (Figure 4b). For example, an amphiphilic linear polymer obtained in solution is applied to an interface which resembles 2D space. This way of defining the term 2D polymer was discussed by theoreticians but obviously does not lead to a carpet-like structure. Both cases, summarized in Figure 4, will not provide a true 2D polymer.

Figure 4: Representation how a linear polymer can be confined into two dimensions. Left: a linear polymer restricted in two dimensions due to inherent ordering power of a monolayer which winds and folds upon dissolution. Right: a coiled polymer is artificially restricted in a two dimensionally space, but this consideration is of strong theoretical nature.11

In contrast to the lack of polymerization strategies for regular 2D and 3D structures, a whole tool box for defined 0D and 1D structures is provided by synthetic chemistry to furnish
compounds like natural products\textsuperscript{12}, drugs\textsuperscript{13} or other artificial polymeric substances\textsuperscript{14}. Small organic compounds like bromobenzene or hexane can be considered as 0D or dimensionless due to the restricted spatial extension each atom has. Ill-defined and non-periodic 3D-structures are formed by cross-linking the polymerizable groups in the side chains of a 1D (linear) polymer. Covalent bond formation or the rearrangement of bonds during the reaction course can be mastered with great success, whereby compounds in the size of a few nanometers in size are obtained. It is noticeable that the availability of ordered and well-defined covalently connected 2D and 3D structures is not yet achieved and thus, remains an open space in the landscape of polymer science. These ordered structures can be considered as a major achievement in polymer chemistry and materials science due to the uniqueness of the material and their expected properties.

The carbon allotropes\textsuperscript{15} offer descriptive examples how dimensionality defines material’s properties. The macroscopic properties of graphite, diamond and fullerenes are considerable different resulting from different hybridization states of carbon atoms. In the diamond, the sp\textsuperscript{3}-hybridized carbon atoms form a tetragonal structure in three dimensions leading to a non-conductive, transparent, insoluble and very rigid material, whereas the hexagonal layers of graphite of sp\textsuperscript{2}-hybridized carbon yield a conductive, black, insoluble, and very soft material. In contrast to the equally distributed forces in the diamond crystal, yielding an isotropic solid, graphite has strong in-plane bonds but weak van der Waals forces between the two-dimensionally aligned layers offering the possibility to split this material into individual atomic layers (graphene). A third allotropic modification, in which carbon atoms are arranged in hexagons and pentagons, leads to a cage-like structure, the fullerenes. This soft, black crystalline, soluble, and non-conductive material can be considered as a 0D case.

![Figure 5: Structure of the carbon allotropes: a) graphite, b) diamond and c) C\textsubscript{60}-fullerene.\textsuperscript{16}](image)
Introduction

The current absence of ordered 2D and 3D structures indicates that there is an enormous potential for the exploration of their synthesis and investigation of their physical properties. For example, questions arise about the mechanical stability, brittleness and crack propagation of polymeric sheets which may have the lateral extension of a few square centimeters and represent only one single macromolecule. It would be interesting to know whether an one monomer thick sheet could be seen by eye, how such a sheet behaves during polymerization – does it roll up, does tube formation or back-biting occur, or does it fold in a particular way or crumple?

The exploration of 3D objects generated by a stepwise layer deposition of 2D sheets is another perspective. Furthermore, systematic investigations on the gradual transition of dimensions, from 2D to 3D, and the thickness dependence of properties can be imagined. It might be an exciting objective to investigate whether properties change by each added layer or whether there is a discontinuity of physical properties.

What kind of applications of 2D polymers can one think of? Similarly to studies of ultrathin films, 2D polymers could possibly function as reliable molecular membranes. Regen\textsuperscript{17} and Duran\textsuperscript{18} described ultrathin polymer films which showed permeability (water vs benzene). These new materials may have potential as pressure sensors. Goedel et al.\textsuperscript{19} have shown for a 40 nm thick film spanned over a hole that upon exposure to a slight overpressure an elastic bending of the film was achieved without destruction. Assuming that “true” 2D polymers can be reliably synthesized in adequate quantities and with the proposed structure fidelity, one can image to equip them with defined anchor groups aligned in z-direction for a selective construction of ordered 3D materials. To use 2D polymers as a platform would generally make them interesting systems for catalysis, electrical circuits and molecular electronics.

Which requirements have to be fulfilled to achieve the desired structure without concessions regarding lateral extension, periodicity and thickness homogeneity? For a controlled polymerization constrained in 2D dimension, the elements to control the polymerization are: the monomer design, the connection chemistry involved and the technique chosen to confine the monomers into 2D. Two possible approaches are conceivable: the flask-type approach and the interfacial approach. In order to reach a high level of structure control, both approaches require carefully tailored monomers which allow growth in 2D. The number and position of connective sites incorporated into a rigid monomer scaffold are crucial structural aspects. For
a growth in x- and y- direction at least three connective sites are necessary. In case of a monomer with two connective sites (difunctionality) a linear polymer or an individual stitching within independent planes of an oriented layer of monomers is achieved. For that reason, a difunctional monomer would never furnish a periodic 2D network. In Figure 6 potential monomer geometries with different number of connective sites \( n \) \((n = 3, 4, 6)\) leading to 2D polymers are illustrated in a cartoon-like representation. These geometries are suitable for both approaches. Since the shape-persistency of the main skeleton ensures reduced monomer flexibility, the reactive groups are brought in close proximity. Consequently, polymerization at the predetermined sites as a result of defined availability of the reactive groups should be favored. 

![Figure 6: Schematic monomer geometries and the according possible ways of growth.](image)

Despite the fact that the two approaches have the same prerequisites regarding monomer design, they differ significantly from each other with respect to the ordering power of the environment. The flask-type approach relies on polymerization of dissolved monomers. Assuming that monomers which do not have the ability for form liquid crystals, the dissolved monomers do not form an organized monomer assembly and thus, the connective sites are not compulsorily in one plane. Consequently, the monomer design has to counterbalance this disadvantage. A shape-persistent monomer with more than two connective sites in predetermined positions must allow multiple bond formation events in one plane to avoid an ill-defined 3D-network. After the first bond formation took place, the possibility to have the next binding event in the same plane decreases because of the rotational freedom of the newly formed bond. Apart from that, solubility problems may occur which are mainly due to monomer’s rigidity and bending motions may lead to crumpled or folded objects. These undesired effects interrupt a further growth through the inaccessibility of the polymerizable units. Solubility problems can be in principal regulated by introducing solubilizing structure elements. A more crucial issue might be bending. This would indicate that 2D objects may
reach certain “critical” sizes to which a 2D object can grow. Anyway, polymerization in solution cannot furnish individual polymeric sheets (possibly achievable via the interfacial approach). It is impossible to separate an individual sheet from the polymeric 2D objects in bulk. This may rather lead to sheets of different sizes comparably to the length distribution of linear polymers. However, properties of such a “2D bulk” are supposed to be completely different to the ones found for the linear case. Aside from that, the flask-type approach would provide more quantity of material and therefore characterization and further investigations might be less critical in comparison to handling an individual 2D sheet.

The interfacial approach can rely on the ordering power of the interface to generate well-organized structures. The degree of ordering is a combination of the interface’s nature and the substance applied to it. Schematic representations in Figure 7 elucidate diverse techniques for the creation of ordered structures at an interface.

Advantageously, liquid surfaces allow a relatively uncomplicated lifting-off from the interface so that the transferred film can be further manipulated. To peel off a film from a solid
substrate is not impossible, but more complicated. Among the gas/liquid interfaces, the air/water interface is very common and comparatively easy to handle and thus, preferred in contrast to air/mercury, air/glycerol and others which are occasionally used. The water surface is known to be extraordinary flat. Therefore, water is particularly suitable for ordering monomers in plane. Nevertheless, monomers at the air/water interface can still easily rotate and move laterally. Thus, rigid monomers are required for a suitable alignment of polymerizable functionalities along the network formation axis. The confinement of precisely designed monomers in 2D is achieved by reducing the monomers’ degree of freedom through decreasing accessible space for each monomer. The reduced space capacity at the interface leads to a densely packed film. Thus, a highly regular film prior the polymerization is obtained which can be converted into a covalently constructed 2D polymer utilizing the appropriate connection chemistry. Assuming an accurately preorganized film, a structurally perfect, homogenous 2D polymer is generated - free of domains or other irregularities. It has to be noticed that even though the monomers’ freedom is decreased, the monomers still have a certain degree of rotational freedom at the interface. As a result, the preorganized film is in a dynamic state. This may lead to differently orientated monomers at the time the polymerization event takes place yielding an inhomogeneous material. Another crucial issue for polymerizing orientated monomers at the interface is shrinkage during polymerization which is known from most conventional polymerizations. In case of a highly organized monolayer at the interface, the distance between the monomers before polymerization is close to the van der Waals distance. Covalent bond formation upon polymerization reduces the distance between the monomers and possibly leads to highly ordered, densely packed domains. This may cause a significant interruption of the monolayer’s order. As a consequence, the required shape-persistency of the monomers must be counterbalanced by a certain degree of flexibility which allows to respond to shrinkage.

2D polymers generated through the interfacial approach are extremely light and therefore, require powerful analytical tools to characterize the 2D material. Nevertheless, this method would give access to an individual 2D polymeric sheet representing just one single macromolecule!

The chosen polymerization chemistry must be high yielding and easy applicable in the interfacial approach. Here, the well-established photochemical reaction of [4+4] anthracene dimerization offers an attractive pathway because of the cleanness of the reactions and low
side product generation. No radical inhibitor or catalyst is necessary which disturbs the monolayer order. Irradiation with UV-light ($\lambda > 350$ nm) induces the anthracene dimerization.

![Scheme 1: Dimerization of anthracene which takes place upon irradiation with UV-light. The back reaction is induced by irradiation with UV-light ($\lambda < 254$ nm) or heat.](image)

The following paragraph outlines our strategy towards 2D polymers via the interfacial approach. Due to the convenient handling and the extraordinary surface flatness, the air/water interface is utilized in order to preorganize polymerizable monomers and hence, assure the necessary high level of structure control. The spreading of monomers at the air/water interface is a well-established method which is known as Langmuir technique. This method allows the generation of a monomolecular film at the air/water interface, a monolayer. Amphiphilic monomers which spread at the interface and do not dissolve or form ordered assemblies in the water phase are mandatory for the monolayer formation. The interface strictly confines the monomers spread at the interface forming a layer in 2D. The degree of order within the generated monolayer can be adjusted by controlling the surface pressure. The surface pressure depends on the amount of monomers applied to the surface and on the available space each monomer has. The accessible space for each monomer can be manipulated through movable barriers with which the Langmuir trough is equipped. This is of experimental importance because a densely packed, highly organized monolayer can be obtained.

In Figure 8 the conceptual idea of our approach is summarized. A schematic representation of a trifunctional monomer is shown in its top view. The three “arms” in the space filling model represent the connective sites, the anthracenes. In Figure 8a, the amphiphilic monomers are distributed at the water surface. There is almost no interaction between the monomers. A space decrease through the movable barrier forces the monomers into an ordered monolayer. Exemplary, the trifunctional monomers form a hexagonal structured monolayer as it is depicted in Figure 8b. At this stage, the monomers are not covalently connected. In a second step, the preorganized monolayer is converted into a regular, covalently connected 2D...
polymer by means of selective connection chemistry. One hexagonal structure element is magnified in Figure 8c and Figure 8d to illustrate the formation of covalent bonds between the monomers. To underline the covalent connection in all parts of the monolayer, the magnified hexagon as repetitive structure element is depicted in red (Figure 8e). The polymeric film can be transferred onto a variety of solid substrates. The transfer of a monolayer is known as Langmuir-Blodgett technique. The use of this technique allows the handling and analysis of monolayers.

Figure 8: a) Schematic representation of tripods spread at the air/water interface. Monomers are depicted as space filling models. b) Available space of each monomer is reduced due to compression leading to preorganized monolayer. c) Magnification of a single hexagonal structure element formed due to compression like shown in b). In this densely-packed state, monomers have a distance ideally equal to the van der Waals distance but they are not covalently connected. d) Illustration of a covalently connected hexagonal structure element induced by the photochemical reaction of the anthracenes. e) Sketch of a covalently connected monolayer indicating that polymerization went through the whole layer whereas the red hexagon should represent d).
Summarizing, the polymerization of suitably designed monomers applied to the interfacial approach comprises the following advantages:

- excellent preorganization for precisely designed monomers due to the natural flatness of the water surface,
- the easy generation of films with uniform thickness, and
- the advantage of transferring non-cross linked as well as cross-linked film on various substrates which allows further investigations and in principal post-treatment.

Both, the interfacial and the flask-type approach, justify the confidence that 2D polymers with the above given definition can be obtained if appropriate designed monomers are used and a systematic study of the polymerization performance in 2D is investigated. The accessibility of such structures would be a major achievement in polymer chemistry and certainly of high interest regarding the materials’ properties.
2 Aim of the thesis

The present thesis is part of a long-term project which aims at synthesizing and characterizing laterally infinite, long-range ordered, and one monomer unit thick sheet-like structures which we call 2D polymers. Although there are numerous publications on ultrathin films\textsuperscript{21}, the above definition was not achieved by any of them. Many of these appreciable works fulfill the thickness requirements and the “infinite” lateral dimension, but an internal order of the 2D covalent structure has not been proven yet.

The aim of this dissertation was to design and synthesize suitable monomers for their polymerization at the air/water interface, to polymerize these monomers at the interface and to characterize the polymeric product (2D polymer) obtained. For this purpose amphiphilic monomers with three and four connective sites had to be provided and utilized in the interfacial approach which is practically realized by using the well-established Langmuir-Blodgett technique.\textsuperscript{i} Figure 9 schematically illustrates the two monomer families which were aimed at. Monomers with three and four connective sites are referred to as tripods and tetrapods, respectively. For both monomer families, anthracene was selected as a connective unit which upon exposure to UV-light undergoes a [4+4] cycloaddition. The development of synthetic strategies had to furnish monomers with a high degree of symmetry regarding the connective sites to exclusively lead to a polymerization in-plane. In Figure 9 the simplified structure A suggests symmetry of $C_{3v}$ for the tripod family and structure B implies symmetry of $C_{4v}$ for the tetrapod family if one only considers the upper (anthracene-containing) part of the molecule.

\textsuperscript{i} For more detailed information about Langmuir-Blodgett technique see General Methods (Chapter 4).
The monomers which were synthesized to be polymerized at the interface were investigated towards their capability of reversible film formation at the air/water interface. The morphology of the monolayer during its formation had to be followed by Brewster Angle microscopy (BAM). The monomers able to form a stable monolayer had to be irradiated by UV-light in order to covalently stabilize the monomolecular film. As described by Goedel\textsuperscript{19}, the implementation of anthracene as a photoreactive group in the side chains of a linear polymer can be utilized for cross-linking films at the air/water interface whereby the generation of solvent-free polymer brushes and thin elastic membranes were furnished.

The polymeric film should be characterized at the interface as well as after being transferred onto different substrates. The difference in chemical nature of the monolayer before and after irradiation by UV-light had to be analyzed. For this purpose various surface sensitive techniques such as grazing-incident methods, X-ray photoelectron spectroscopy (XPS) and ellipsometry had to be applied in order to compile a kind of “tool box” which allows a systematic study and characterization of 2D polymers. For this reason collaboration with experts in surface science was mandatory.

Since the dimerization of anthracene is a key step to arrive at a 2D polymer, the dimer formation had to be studied although plenty of literature discussing structural and mechanistic aspects of the anthracene photodimerization is available. Results regarding yields, stability of photoproducts and the influence of oxygen in these publications are inconsistently reported. Therefore, it was an objective to understand and handle photodimerization accordingly to our
needs. Dimerization reactions in solution with different 9-substituted and 1,8-disubstituted anthracenes under varying conditions, e.g. variation of concentrations, solvents and the absence and presence of oxygen had to be accomplished. Tailor-made model compounds and commercially available compounds had to be dimerized and the photoproducts had to be thoroughly investigated by NMR-, IR- and UV-Vis spectroscopy. Analysis of results obtained for the dimerization in solution had to be done to rate the monomers’ potential for multiple intermolecular dimerizations at the air/water interface.

This first attempt started in the present thesis towards 2D polymers should help to disclose the obstacles related with the accessibility and the characterization of such structures and should further direct monomer design as well as applicable characterization methods to a reliable and robust strategy for periodic 2D polymers.
3 Literature survey

3.1 Naturally provided 2D objects

3.1.1 Introduction

A few examples of 2D ordered networks possessing the structural properties like the ones discussed in Chapter 1 are provided by nature. Many works discussing the possibility of the existence of sheet-like structures are present. Theoreticians like Landau\textsuperscript{22}, Peierls\textsuperscript{23} and Mermin\textsuperscript{24} doubted the existence of 2D structures for years. According to theory, thermal fluctuation in the 2D crystallite structure was predicted to lead to an unstable film. Due to film instability, the long-range order is expected to be destroyed. Figure 10 depicts randomly introduced waves resulting in a fluctuating and curved sheet. The amplitude of fluctuation is negligible compared to the lateral extension of the sheet so that the dimension of the structures still remains 2D.

![Figure 10: Representation of a fluctuating and curved sheet based on theoretical assumptions whereas the degree of thermal fluctuation corresponds to the film stability and instability, respectively.\textsuperscript{25}](image)

Thus, a curved sheet-like shown above cannot be excluded from truly 2D structures. However, the degree of curvature is a critical issue because curvature may end up in a tube-like or crumpled structure which does not any longer fulfill the considerations made for 2D networks. Furthermore, island formation and the tendency of decomposition of low dimensional materials as decisive factors for the existence of such structures have been discussed.
Many efforts using different techniques, e.g. chemical exfoliation or mechanical cleavage were undertaken to prove the existence of 2D polymers unprotected from their immediate environment, a 3D crystal. The isolation of single layers out of the crystal involves detachment over microscopic regions. First experiments revealed restacked and scrolled multilayer sheets rather than individual monolayers. The isolation and identification of a layer which is just one repeating unit thick was finally successful. This finding must be considered as a major achievement in many respects. For example, this result motivated physicists to study the properties of condensed matter of low dimensionality.

Chemists may look at the discovery of such thin films from a completely different perspective. The question arises whether 2D polymers like the ones provided by nature can be accessed by organic synthesis by means of polymerizing appropriate designed monomers yielding a 2D polymer. The preparation of graphene using organic synthesis e.g. reduction of graphene oxide with hydrazine does not rely on polymerization of suitable monomers.

### 3.1.2 Graphene

Contrary to all theoretical predictions, Geim et al. isolated naturally provided 2D polymers. Boron nitride, several dichalcogenides, complex oxides (BN, MoS$_2$, NbSe$_2$, Bi$_2$Sr$_2$CaCu$_2$O$_x$), and graphite were take to isolate 2D crystals which were embedded into 3D crystals. The isolation of these sheet-like structures was achieved by applying a repetitive peeling with an adhesive tape. The most prominent example among the named ones is graphene, a single layer of graphite. The structure of graphene is outstanding, it can be characterized as a single layer of covalently connected carbon atoms densely packed in a honeycomb structure with an almost lateral “infinite” extension.
By now it is the thinnest covalently connected monolayer known. In order to prove the existence of this sheet-like structure with a lateral extension in the range of a few micrometers and an almost negligible thickness, bright field transmission electron microscopy (TEM) was applied successfully. Figure 11 shows a TEM image of the sheet which was suspended off the solid substrate and then transferred onto an oxidized silicon wafer revealing that large parts are homogenous and featureless and correspond to a monolayer of graphene. In addition, angle-dependent electron diffraction pattern of the homogenous part of the film confirmed the expected honeycomb structure. The successful structure proof by TEM and electron diffraction is based on the fact that graphene becomes visible on top of an oxidized silicon wafer in the optical microscope. This fact allowed to distinguish between a stack of layers and a single monolayer which was then further analyzed. The visibility of a monolayer (on most substrates) in the optical microscope is somewhat unexpected. However, a monolayer evidently changes the phase of incident light and the difference in optical pathway leads to interference which is different with respect to an empty substrate.

Based on the obtained experimental data, graphene is a strictly 2D material characterized by its long-range order which is closely associated with the term periodicity. The assignment of structure elements originating in periodicity within the honeycomb structure of graphene leads to several proposals. For instance, the \( \text{sp}^2 \)-hybrid orbital of each carbon atom could be formally considered as a repeat unit like it is known for linear polymers. In their case the smallest repetitive chain segment is described as repeat unit. In case of graphene more than one possibility can be considered depending on the formally done fragmentation within the
sheet-like structure. Further repetitive fragments besides the one arising from the carbon orbital are shown in Figure 12. The highlighted hexagons can be viewed as a repeat unit as well. The repetitive element of conventional polymers made so far is based on the skeleton of the monomer they are synthesized from.

Figure 12: a) The hexagonal structure of graphene, a 2D polymer, with some possible repetitive fragments. b) Single possible repetitive fragments of graphene which are only an assumption because the mode of synthesis is not known.6

Since the building block (“monomer unit”) and the mechanism for the graphene formation are not known the assignment of the “true” repeat unit is not possible. Figure 13 illustrates that graphene itself may be considered as a building block for other graphene-based materials irrespective their dimensionalities, e.g. 0D fullerene, 1D carbon nanotube, and 3D graphite. As schematically depicted in Figure 13, 2D polymers may have an enormous potential for generating various molecular architectures.
3.2  Polymerization in confined 2D geometries

3.2.1  Introduction

Plenty of articles can be found reporting about self-assembled monolayers or multilayers at interfaces to confine monomers in two dimensions. The self-assembly of a monolayer generated at gas/liquid and liquid/solid interface followed by covalent stabilization of the layer is a rational pathway towards the generation of synthetic 2D polymers. The examples described herein are based on the fact that monomeric starting material is confined in 2D space before the polymerization takes place.

The described systems differ with respect to the “monomer” nature such as:

- low molecular weight compounds,
- dendrimers and
- polymers.

The goal of confining compounds in 2D was achieved by applying various types of methods and connection chemistry. The following examples cover this research field very selectively. The emphasis was put on characterization. Structures were chosen coming close to the desired
structure of a 2D polymer which is defined by its laterally infinite, and one monomer unit thick and periodic structure.

It is worth to mention that historically clays were also considered to be as an useful stage for film formation followed by a cross-linking event. Blumstein et al. discussed monomers adsorbed between the lamellar layers of montmorillonite-clays to generate a film which can be covalently connected. In particular, methyl acrylate was radically polymerized. The obtained polymer was described as a cross-linked sheet of high rigidity and outstanding mechanical properties were formed.

### 3.2.2 Polymerization of monolayers at the air/water interface

#### 3.2.2.1 Examples of early attempts on polymerization at the air/water interface

Historically the first approach towards polymerization at the air/water interface was published by Gee in 1935. He studied the behavior of β-elaestearin and maleic anhydride on a Langmuir trough. For the generated monolayer of the lipid and its Diels-Alder adduct Gee observed differences regarding the isotherm and the surface potential and concluded that cross-linking took place. The interpretation of the obtained results with respect to the degree of polymerization could not be accomplished due to insufficient analytical tools. The term “2D polymerization” and “2D polymer” was introduced a few years later by Bresler. He suggested the formation of polyaminals by polycondensation of stearic aldehyde and amines at the air/water interface. His assumption for polymer formation was based on the noticed changes in mechanical properties. He also studied other systems at the air/water interface and reported about rubber-like films, taking that result as an evidence for cross-linking. Nevertheless, product characterization regarding the degree of polymerization or structural analysis was not given.

---

\[^{ii}\] unsaturated fatty acid C\(_{18}\)H\(_{30}\)O\(_{2}\)
3.2.2.2 Selected results on polymerization at the air/water interface

Ringsdorf contributed with his systematic and deep studies fundamentally to the field of polymerizing oriented structures like micelles, liposomes and monolayers. He is one of the pioneers in this research area and thus, his approaches and results are given a more detailed discussion.

Ringsdorf’s interest originated from the fascination to simulate biomembranes and to understand their operating principles. In this regard, he published the polymerization of low molecular weight compounds such as monocarboxylic acids containing diacetylenes units at the gas/water interface in 1978. The monomers were converted into a polymer with a conjugated backbone through a UV-induced reaction. This UV-induced topochemical reaction of diacetylenes in solid state and in multilayers was earlier reported by Wegner. The monomers shown in Scheme 2 were spread and UV-treated resulting in a polymerized monolayer with a visually observed red-orange colour. This colour is typical for polymerized diacetylenes and arises from the conjugated backbone. The cross-linked layer was observed to be extremely rigid and it appeared to have an infinite surface viscosity. Pieces could be broken from the layer and manipulated on the water surface by a probe.

\[
\text{H}_3\text{C}-(\text{CH}_2)_{n-1}\text{C}≡\text{C}≡\text{C}-(\text{CH}_2)_8\text{COOH} \xrightarrow{\text{hv}} \text{polymerization}
\]

Scheme 2: Diacetylene monocarboxylic acids (n = 5, 8, 10, 12, 14, and 16) used in order to generate monolayers at the air/water interface which were cross-linked by diacetylene polymerization.

Further the influence of oxygen on the polymerization is discussed. It is worth noting that irradiation done in the absence of oxygen led to a contraction of the layer. The layer exposed to UV-light in the presence of oxygen caused a large expansion presumably due to ozonolysis of the initially formed conjugated backbone. This fact is highlighted at this point and considered to be important because the influence of oxygen is later discussed (see Chapter 4) for our system under investigation.
The polydiacetylene monolayers representing model membranes with a defined hydrophobic and hydrophilic surface were further compressed to bilayers and transferred onto glass substrates. The bilayer with a thickness of approximately 60 Å was visible in a polarizing microscope and showed mosaic pattern indicating a random orientation within the monolayer plane. Moreover the film was stable enough to span it over holes with 0.5 mm in diameter.

Later, in 1987 Ringsdorf described the polymerization of LB-multilayers consisting of 2-eicosenoic acid or octadecyl fumarate. Since these two monomers were found to form stable films they were used to prepare LB multilayers. The progress of UV-light induced polymerization was followed by UV-Vis measurements. The polymer formation was concluded from decreasing characteristic absorption bands of the monomers. In addition, the polymeric multilayer was dissolved from the substrate and the solution was applied to \textsuperscript{1}H-NMR spectroscopy. Broadened signals and the disappearance of monomeric signals confirmed a successful polymerization.

One year later Ringsdorf published the polymerization of LB-multilayers of 1,3-dienes, namely docosa-2,4-dien-1-ol and docosa-2,4-dienoic acid, capable to undergo 1,4- addition leading to linear polymers. The isotherms obtained after spreading of the monomers at the air/water interface indicated a closely packed monolayer from which a well-structured multilayer was built. UV-light induced a topochemical reaction of the monomers proceeding in two steps, depending on the used wavelength. Irradiation with long-wavelength UV-light yielded a linear polymer leading to the formation of the 2,3-double bond which was postpolymerized by energy-rich UV-light. The second step took place under consumption of the newly formed double bond and finally led to an insoluble cross-linked film.

Interestingly enough, the irradiation was done in the presence of air. Apparently no oxygen diffusion within the layers took place and thus, did not cause any oxygen-induced side-reactions. The nature of the monomeric and polymeric film was deeply investigated by UV-spectroscopy, small angle X-ray scattering (SAXS), \textsuperscript{1}H-NMR spectroscopy, and gel permeation chromatography (GPC) confirming the proposed structure. Due to the random walk nature of diacetylene polymerization, no “periodicity” was obtained. The applied connection chemistry successfully led to a covalently stabilized multilayer, but in terms of the 2D polymer requirements the applicability of diacetylene polymerization is limited.
Palacin’s approach\textsuperscript{38} to provide a “true 2D polymer” utilized the formation of LB mono- and multilayer of water soluble, charged and tetrafunctionalized porphyrins, capable to undergo a fourfold intermolecular Glaser coupling. The LB film preparation procedure is called semiamphiphilic, depicted in Figure 14a, since the water soluble monomer is attracted to the air/water interface by Coulomb interactions with a monolayer of a surfactant spread at this very interface.

The water soluble monomer (Figure 14b) was adsorbed from solution onto a stable surfactant layer of hydrogen dihexadecyl phosphate (HDHP). The structure of the precursor film consisting of the two components - the reactive monomer and the phosphate - resembles the structure of the 2D polymer which can be expected after polymerization. Contrary to Ringsdorf’s approach in which the reactive monomer itself is film forming, the semi-amphiphilic method relies on a reactive monomer which depends on a surfactant layer to form a monolayer at the air/water interface.
It became evident from the surface pressure measurements that the investigated films assembled according to the semiamphiphilic method appeared to have high film stability. On the basis of taken BAM micrographs the homogeneity of the films was revealed. The authors claimed that the porphyrins, equipped with four acetylene units, form a tetragonal array at the interface which should allow the cross-linking. The cuprous ions, dissolved in the subphase, necessary for the coupling reaction, came close to the acetylene functionality by diffusion through the layer of HDHP/porphyrin. The Glaser coupling led to a covalent film of diacetylene-porphyrins. The covalent stabilization was applied to monolayers as well as multilayers of HDHP/porphyrin. The multilayered films were transferred onto solid supports.
and the success of the reaction was followed by IR and surface enhanced Raman spectroscopy. Indicative for diacetylene formation was the disappearance of signals resulting from the terminal proton and furthermore the appearance of a new signal at 2245 cm\(^{-1}\) which is characteristic for symmetrical diacetylenes. Based on transmission X-ray experiments of the 2D cross-linked porphyrins a new crystalline phase in the plane of the film was observed. Both monolayers and multilayers were investigated towards their mechanical stability by transferring on grids with different hole-sizes. A covalent bilayer on a grid was obtained by manual horizontal lifting and was visualized in an optical micrograph in which numerous folds and cracks were seen. The authors state that these macroscopic defects are due to the imperfection of the transfer method. Beside the deep studies of cross-linked semiamphiphilic films further investigation was done of the so called chain-free film obtained by applying hydrochloric acid vapour. This treatment was done in order to break the ionic bonds between the porphyrins and the HDHP followed by removal of the aliphatic chains with chloroform. The insolvability of the polymerized porphyrin film in common organic solvents can be understood as an evidence of the covalent character. By electron spin resonance spectroscopy it was found that the porphyrin rings are still lying parallel to the substrate, but no diffraction order upon exposure to the chain-free film to X-rays was observed. Palacin’s idea of creating a 2D molecular thick membrane which must be considered as a 2D polymer is based on the concept of supramolecular engineering and represents thus far the most deeply studied case of covalent ultrathin films. Parallel to the extensive characterization methods the mechanical stability of the bilayer was found to be excellent, but nevertheless a substantial proof of the molecular structure could not be provided.

Regen et al.\textsuperscript{39} generated cross-linked monolayers at the air/water interface. Figure 15a displays the amphiphilic calix[6]arenes which were used as monomers. These monomers were either ionic or covalently connected. A mercury-doped calix[6]arenes with malonate ligandes was spread at the air/water interface. Ionic cross-linking was achieved from the subphase containing monovalent trifluoracetate counter ions which replaced the bivalent malonate ligands, (Figure 15b). The efficiency of cross-linking was revealed, for example, from the significant increase of surface viscosity.
Another example of Regen’s work is the “covalent gluing” of monolayers of aldehydic calix[6]arene in the presence of poly(allyamine) yielding Schiff base formation. Imine formation is supported by the course of the isotherms, X-ray photoelectron spectroscopy and ATR-IR. AFM images of the transferred film onto SiO$_2$ revealed a film that was rich in defect and the peak-to-valley distance implied that the assembly had undergone rearrangements.
Figure 16: Calix[6]arene monomers used by Regen. Aldehyde a) and amine b) yielded the Schiff base c), whereas monomer d) was applied to oxidative coupling in order to cross-link monolayers.

In another approach, based on calix[6]arenes hexathiols arranged in a LB monolayer, Regen et al. carried out oxidative coupling of the thio-groups. Unfortunately, a firm structure proof on the molecular level for all three systems could not be obtained.

Goedel and Heger described the polymerization of monolayers composed of polymeric material which can be cross-linked upon UV-irradiation.

Figure 17: Polyisoprenes equipped with one sulfonate headgroup and anthracene as a photoreactive side group which was utilized for cross-linking the polymer chains within the monolayer. The waved line indicates a statistic distribution of 1,4-cis, 1,4-trans and 3,4-isoprene units. [Ref. 42]

Figure 17 displays the polyisoprenes equipped with one sulfonate headgroup and photoreactive side groups, namely anthracene which was spread at the air/water interface. The
photo-induced cycloaddition of the anthracenes increased the layer stability so that a transfer of the film after cross-linking onto a glass slide was possible. UV-Vis spectroscopy of the transferred polymeric film revealed a significant decrease of the absorption in the region of 330 – 430 nm due to loss of anthracene and due to dimer formation, respectively. Based on the latter spectroscopy result the authors estimated the anthracene dimerization to be more than 90%. Moreover successful transfer on a brass plate with a 0.4 mm diameter hole was achieved. The cross-linked membrane was robust enough to over span this hole. At the same time this membrane was elastic, so that an applied slight overpressure led to visible deformation of the 35 nm thick membrane.

Duran et al. reported on the covalent stabilization of a monolayer generated out of block copolymers which are depicted in Figure 18. The covalent bond formation of amphiphilic star block copolymers that were initially spread at the air/water interface was accomplished. In particular, non-cross linked polybutadiene with poly(ethylene oxide) (Figure 18a) domains was applied to radical polymerization, initiated by AIBN, yielding polymeric material.

![Figure 18: a) Polyisoprene tagged with anthracene side chains and one sulfonate headgroup which were used for monolayer generation by Goedel and Heger. The waved line indicates a statistic distribution of 1,4-cis, 1,4-trans and 3,4-isoprene units. Through the flexibility of the chains anthracenes can come close enough in order to dimerize upon UV-irradiation. b) Star block copolymer used by Duran. Double bonds were cross-linked by radical polymerization at the air/water interface.](image)

The self-condensation of trioxyisilane-functionalized polybutadiene star block copolymers (Figure 18b) under acidic condition furnishing a dark yellow polymeric material was discussed in the same paper. The cross-linked film could be removed from the LB trough with a spatula. For both polymers depicted in Figure 18 isotherms and IR spectra were indicative of cross-linking of the generated monolayers.
Leblanc et al. studied the ability of LB monolayer formation of an amphiphilic PAMAM dendrimer (Figure 19) bearing diacetylene units in the periphery.\textsuperscript{44}

![Figure 19: PAMAM dendrimer equipped with peripheral diacetylene units used for UV-induced polymerization of the diacetylenes.\textsuperscript{44}](image)

Cross-linking of the compressed monolayer was accomplished by UV-irradiation and yielded a polymerized visible blue film. Visualization by BAM disclosed irregularities of the polymeric monolayer.

### 3.2.3 Polymerization on solid substrates

Besides air/liquid interfaces the assembly of polymerizable monomers on solid substrates was used for the confinement of molecules in two dimensions. Monolayers on solid substrates can be either chemisorbed or physisorbed. Chemisorption leads to a covalent connection between the monomer and the substrate, for instance thiols on gold. The limited use of monolayer formation based on chemisorption is discussed elsewhere.\textsuperscript{15}
An original approach towards 2D covalent macromolecular structures generated on highly oriented pyrolytic graphite (HOPG) as solid support was studied by Takami et al.\textsuperscript{45} The authors reported the UV-light induced polymerization of physisorbed self-assembled monolayers of linear hydrocarbon chains (Figure 20a) which were prepared under ultrahigh vacuum conditions. The product obtained was analysed by STM revealing some periodic domains in reasonable dimensions. However, the regularity of the proposed sheet-like structure could not be fully proven.

De Schryver et al.\textsuperscript{46} used a similar topochemical polymerization of diacetylenes to achieve 2D structures. The monomer, a terephthalic acid ester carrying two aliphatic chains with internal diacetylene units, was first spread at the air/water interface and the so formed monolayer was transferred onto HOPG. As indicated in Figure 20b, alternating parallel linear arrays are formed because of hydrogen bonds between neighbouring molecules. These intermolecular interactions caused a lamellar structure which was then polymerized on the solid substrate upon UV-treatment. The structure obtained is of limited size which was revealed from STM investigations.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure20.png}
\caption{Examples of topochemical polymerization of diacetylenes. a) Takami’s UV-induced polymerization of diacetylenes on solid supports.\textsuperscript{45} b) DeSchryver polymerized topochemically linear arrays of diacetylenes.\textsuperscript{46}}
\end{figure}
Huck reported the fabrication of discrete “quasi-2D polymer objects” with nanometer-scale thickness and micrometer-scale lateral dimension using polymer brushes via a surface-templated method. First, poly(glycidyl methacrylate) brushes (PGMA), shown in Figure 21, were grown on a gold-coated silicon wafer patterned with self-assembled monolayers containing initiator headgroups for a surface-initiated atom-transfer radical polymerization (ATRP). Through the ATRP the layer thickness could be controlled.

In a next step, the polymerization of these layers consisting of the PGMA brushes with a thickness of 5 to 30 nm was achieved by immersing them in methanolic sodium hydroxide solution which furnished the ring opening of the epoxide groups of the PGMA brushes and consequently led to cross-linking. The process of covalent bond formation of the layers was followed by IR spectroscopy.

Another example of a 2D cross-linked ultrathin film was published by Lee et al. who succeeded in forming Langmuir-Blodgett films from poly(maleic acid-alt-methyl vinyl ether), poly(allylamine) and sodium dioctadecyl sulfate as a template. In Figure 22 the applied concept of polyion complexes is shown. It was utilized to generate a polyimide network. In particular, a monolayer from the three polyion-complexing components was prepared. The acid and the amine formed the imide upon heating at 180°C the monolayer.
The template enhanced the monolayer stability through complex formation with the amine. The transfer onto a fluorocarbon membrane filter and CaF$_2$ plate of 4 and 8 layers, respectively was achieved and the scanning electron micrographs revealed a polymeric network which was further analyzed by IR spectroscopy and XPS.

The synthesis and polymerization of segmented molecules capable to self-assemble into bilayers was published by Stupp et al.$^{49}$ Figure 23 shows the chemical structure of this molecule. The self-assembled bilayer was formed due to molecular recognition events, driven by the smectogenic biphenyl segments at one terminus of the molecule. These molecular recognition events lead to an internal orientation order and thus, providing a planar confinement of the polymerizable functionalities - the acrylate and nitrile groups - into two different planes. The reactive groups are placed far enough apart in order to avoid a possible formation of ladder-type structures so that two distinguished random walk polymerization processes could proceed. A covalently stabilized 2D object was obtained (5 nm in thickness and lateral extension of about $10^2$-$10^3$ nm) by stitching the acrylates in the main plane und the nitriles in the two corresponding ‘satellite planes’.

Figure 22: Schematic representation of the concept of polyion complexes which was employed by Lee. The subphase containing poly(maleic acid-alt-methyl vinyl ether) and the poly(allylamine) which was spread at the surface formed a complex. The so formed layer was further stabilized by sodium dioctadecyl sulfate that functioned as a template molecule. After the formation of the polyimide network upon heating at 180°C the template molecule was removed.$^{48}$

[Chemical structure images here]
Figure 23: Monomer containing stereocenters that take place in the molecular recognition were used by Stupp et al. to polymerize these monomers.49

This particular monomer design facilitated the polymerization of the cross-linkable functionalities in the individual planes. This led to an individual covalent stitching within the independent planes which are differently coloured as indicated in Figure 23. The polymerization furnished interlocked planes and a sheet-like structure was obtained. However, the polymerization was not directed so that this random-walk process yielded a non-periodic structure which was difficult to characterize on the molecular level due to the small cross-section.

3.3 The “flask-type approach”

3.3.1 Introduction

In this chapter examples are described utilizing the reaction of small fragments in solution in order to furnish larger flat entities. It seems reasonable that the so called “flask-type approach” can furnish the ambitious goal of a 2D polymer. The “flask-type approach” allows to distinguish between two different pathways relying on pure organic synthesis only and on supramolecular chemistry, respectively. The first section will be referred to selected works on the construction of organic nano-objects by means of rational multi-step synthesis. Synthetic methods for the realization of larger structures by coupling of the appropriate building blocks are numerous because of the recent developments in oxidative or transition metal-mediated cross-coupling reactions.50 Consequently, this leads to a huge variety of polyacetylenes and polyarylenes or mixed type of nano-sized molecules owing highly regular linear, branched and planar cycles, in particular trigonal and tetragonal shape-persistent ones. In comparison to the organic chemistry approach the use of supramolecular chemistry as a tool for the generation of 2D structures is addressed in the second part.
3.3.2 Small fragments applied in organic synthesis

The variety of carbon allotropes motivated and encouraged chemists to synthesize all-carbon compounds. Numerous proposals using mainly acetylenic monomers are being discussed to synthesize carbon scaffolds and all-carbon 2D networks in literature.\textsuperscript{51,52} In this regard Diederich\textsuperscript{53} successfully synthesized a family of rigid $\pi$-conjugated monomers. The monomers based on tetracycylethylenes seem to have high potential for the construction of planar 2D carbon networks. Beside the latter mentioned monomers the structure given in Figure 24b was suggested for the creation of network structures via oxidative or transition metal-mediated cross-coupling procedures. The accessibility of such an acetylenic monomer like the unprotected hexaethynylbenzene\textsuperscript{54} is synthetically demanding; and furthermore limited because of its chemical instability.

![Building blocks for all-carbon networks. a) Tetracycylethylenes where R = SiMe$_3$ and other silyl protecting groups as suggested by Diederich. b) The unprotected hexaethynylbenzene is in principle an ideal building block for 2D structures because of its high degree of symmetry, but almost impossible to provide in sufficient quantities because of its chemical instability.\textsuperscript{53,54}](image)

Inevitably, great synthetic efforts are necessary in order to achieve appropriate cyclic molecules with acetylenic groups. The number of bond formations seems to be a critical step for a successful result. This fact was spotlighted in Haley’s work on dehydrobenzo-annules producing large planar structures by intramolecular multiple cross-coupling reactions.\textsuperscript{55} The discussion in the corresponding literature\textsuperscript{55} addresses the problem of generating numerous, simultaneously formed covalent bonds in one final step. Smaller molecules were successfully applied to cyclization; whereas the attempt to hexa[18]annulene, the largest planned structure, led to oligomeric material due to intermolecular alkyne couplings.
Scheme 3: The target structure hexa[18]annulene could not be realized by oxidative coupling. Obviously, multiple intramolecular cyclizations in one single step are difficult to achieve.  

Another example of constructing an all-carbon 2D object was reported by Müllen. He described the conversion of the dendrimer shown in Scheme 4 equipped with rigid, fully aromatic branches into an insoluble planar compound. The resulting so-called nano-graphenes were accomplished through the step-wise synthesis of oligophenylene denrimers. The soluble, fully characterized precursor molecules were in a cascade of intramolecular oxidative cyclodehydrogenations converted into the corresponding fully aromatic entities. The largest structure achieved by the rigid template assisted approach to monodispers graphite sheets was nanographene C\textsubscript{222} with 3.1 nm in diameter. Structure characterization of the obtained black, insoluble material was problematic. Mass spectroscopy revealed that most of the starting material was consumed and most likely converted into the proposed product.
Irrespective of the impressive structure which is shown in Scheme 4, the synthesis was rather complex and the in-depth characterization was difficult due to the insolubility of the planar structures. Therefore, the generation of larger structures obtained by covalent bonds formation in solution is limited.

All-carbon scaffolds were not used exclusively to make periodic 2D polymers in solution. For example, the condensation of a trisalicylaldehyde with ethylenediamine aiming at an ideal hexagonal structure of a salen\textsuperscript{iii} polymer (Scheme 5) was applied by Gothelf.\textsuperscript{58}

\textsuperscript{iii} Salen is an abbreviation for a chelating ligand used in coordination chemistry. The name salen is a contraction for salicylic aldehyde and ethylene diamine which are the precursors to the ligand.
Some local order was revealed from powder synchrotron x-ray diffraction, however, solid state NMR measurements made it evident that the polymer was highly cross-linked in 3D.

A more recent attempt toward the synthesis of sheet-like assemblies was published by Shinkai et al.\textsuperscript{59}. This approach was based on rigid-rod-like conducting polymers as shown in Figure 25a which were aligned parallel. The parallel arrangement was achieved though coordinative interactions between the polymer and a porphyrine-based bidirectional “clip” (Figure 25b). Subsequent template-assisted ring-closing olefin metathesis was intended to furnish poly-pseudo-rotaxane structures. In Figure 25c a cartoon-like representation summarizes the proposed mechanism which should lead to a 2D polymer. The generation of a 2D polymer is questionable because of the rotational freedom of the polymer’s repeating unit so that for the two clips bounded to the same polymer all possible dihedral angles can be assumed. Therefore, it seems reasonable that other structure motifs like bundles are also generated.
a) 

![Chemical structures](image)

b) 

![Chemical structures](image)

R = ![Chemical structure](image)

c) 

![Diagram](image)

Figure 25: The generation of aligned assemblies through supramolecular bundling in solution which was reported by Shinkai et al.\textsuperscript{59} The conjugated polymers (a) were aligned parallel through a bidirectional porphyrin-based supramolecular clip (b) which was able to fix the assembly by reaction of the double bonds via RCM. Cartoon-like summary (c) of Shinkai’s attempt to align rigid-rod polymers into 2D arrays. RCM: ring closing metathesis.

Contrary to the polymerizations done in solution, Baumgartner used solid state polymerization of C\textsubscript{60} fullerene in the presence of sodium in a simple melt-process under inert conditions.\textsuperscript{60}
By this method an alkali intercalated perfect two-dimensional polymeric sheet Na$_4$C$_{60}$ was obtained. The sheet-like and ordered structure of covalently bound fullerene units as confirmed by means of powder diffraction data is depicted in Figure 26. This unique network lacks solubility and hampers further characterization.

### 3.3.3 Small fragments converted to supramolecular assemblies

Lehn et al.\textsuperscript{61} reported the concept of hierarchical self-assembly of small fragments into grid-like supramolecular architectures of discrete size. Generally, hierarchical self-assembly leads to the generation of different organization levels (“hierarchies”) of increasing complexity, diversity and functionality. The concept of hierarchical self-assembly relies on reversible non-covalent interactions such as hydrogen, van der Waals and coordinative bonds between appropriate organic ligands and metal ions which reach under certain conditions the thermodynamic minimum. That means also the formation of monodisperse, grid-like structures like the one shown in Figure 27.
The stoichiometric balance between metal salts and ligands has to be carefully controlled as well, in order to avoid undesired supramolecular structures. For the compound given in Figure 27 a fast equilibrium between a grid-like and a helical structure depending on the metal salt concentration was discussed. Helical structures untwist upon an increased metal salt concentration into grids and thus, the geometry of the intermediate complex must have been changed which is associated with a different ligand shape. The ease of change in ligand shape gives rise to doubts that the metallosupramolecular approach could facilitate 2D polymers of a reasonable, but limited size.

Regardless the beauty of the structures, grid size is in the order of a few nanometers and far beyond an “infinite” extension. The formation of these grid-like structures is a sensitive interplay between the nature of the metal, the steric demand of the ligand, reaction conditions and counterion. The applicability of this approach is further limited due to a possible curvature during grid formation leading to complex curved structures as well as expected insolubility of the higher grids.

### 3.4 Concluding remarks

In Chapter 3, a few examples for the interfacial approach and the flask-type approach were discussed. These examples resemble only a limited insight of the enormous amount of published works towards 2D polymers. The different approaches which were undertaken to
generate a periodic 2D polymer through organic synthesis are manifold. Doubtlessly they are of significant value for the presented project. However, the fundamental question whether one can generate a periodic 2D structure has still to be answered. The obstacles observed for the individual systems which were briefly discussed disclose the challenge to synthesise a 2D polymer.
4 General Part

4.1 Introduction

Among the various methods used in this thesis, two essential ones were put into focus because of their great impact to the presented project. Other techniques applied within this dissertation, in particular to characterize the monolayer, are briefly described in Chapter 5 where the corresponding results are discussed. The first part of this chapter comprises some structural aspects of the anthracene dimerization which was used as key reaction for the covalent stabilization of the monolayer. The Langmuir-Blodgett technique as a tool for preorganization of monomers followed by transfer of the monolayer onto different substrates is described in the second part of this chapter.

4.2 Anthracene Dimerization

In 1867 Fritsche\textsuperscript{63} discovered that a saturated solution of hydrocarbon is converted into ‘microscopic crystals’ upon solar irradiation. The photochemical reaction furnished a product which differed apparently from the initial hydrocarbon compound regarding its physical properties. The product obtained could be reversed back to the starting material by thermal treatment. In 1891 the resulting product was identified by molar mass determination as a dimer of anthracene and shortly afterwards the correct structure was postulated\textsuperscript{64}. Crystal structure analysis, done by Hengstenberg in 1932\textsuperscript{65} and a more precise structure analysis published by Ehrenberg in 1966\textsuperscript{66}, confirmed the proposed dimeric structure.

![Scheme 6: Dimerization of anthracene.](image)

Anthracene itself undergoes intermolecular dimerization upon exposure to UV-light ($\lambda_{\text{max}} \sim 366$ nm). This reaction can be classified as a $[4\pi_e+4\pi_e]$-cycloaddition whereas four $\pi$-electrons of each anthracene react in a suprafacial mode leading to a dimer. Such a concerted reaction passing a pericyclic transition state easily takes place if the orbital symmetry of the
educt in comparison to the product is conserved. In the case of anthracene, orbital symmetry can only be conserved, according to the Woodward-Hoffmann-rules, if photochemical excitation takes places.

The reaction pathway was characterized by dimerization rate constants which were found to be in the range of ca. $0.5 - 2.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. They indicate a very fast reaction, and moreover quantum yield measurements supported the assumption that the $S_1$-state (singlet excited state) is the reactive state for dimerization. The excited molecule combines with a non-excited one to form an excimer (excited dimer). The excimer is converted into the dimer.

\[
1A^* + A \rightarrow 1[AA]^* \rightarrow A_2
\]

Scheme 7: Simplified kinetic pathway of anthracene dimerization in the absence of oxygen. Excimer decay through intersystem crossing, internal conversion or fluorescence decreases the yield of anthracene dimer.

As shown in Scheme 7, processes like intersystem-crossing and internal conversion cause excimer decay and consequently reduce the yield of dimerization. However, it is a general finding that the dimerization rate in solutions correlates with the concentration of anthracene. At higher concentrations aggregates are formed whose reactivity is close to the one in solid state as described for example for the topochemical photodimerization of 9-methylanthracene. For photodimerization in solution it has to be considered that heavy metal solvents decrease or even inhibit photodimerization, for example bromobenzene, $p$-dibromobenzene, 1,3,5-tribromobenzene, 1-bromopropane, and dibromomethane. Heavy atoms are known to favor intersystem-crossing resulting in anthracene in its triplet state which cannot contribute to the dimerization process. But even without any external influence intersystem-crossing can occur due to a defined lifetime of the singlet state resulting in the corresponding triplet state ($1S^* \rightarrow 1T^*$). Anthracene in the triplet state functions as sensitizer for singlet oxygen so that singlet oxygen reacts, if present in the system, in a $[4+2]$-
cycloaddition to form the 9,10-epidioxyanthracene, the so called endoperoxide. Endoperoxide formation (Scheme 8) competes with photodimerization and is therefore an undesired reaction path during the reaction course. It is reported that endoperoxide formation is favored if the $\pi$-system of the anthracene derivative varies too much from planarity.\textsuperscript{73,74,75} Geometrical distortion of compounds such as the one given in Figure 28 favor endoperoxide formation due to the sterical strain which will be released through the reaction with oxygen. Besides this sterical effect the endoperoxide formation depends on structural effects. The reactivity of anthracene derivatives towards singlet oxygen increases with the electron density of the substrate, reflecting the electrophilicity of the singlet oxygen. Endoperoxide formation is also influenced by solvent effects. Polar solvents, e.g. formamide and water reveal an increased rate constant for the endoperoxide formation, assuming the solubility of the compound in the corresponding solvent.\textsuperscript{76}

Scheme 8: a) Irradiation of anthracene in the presence of oxygen can furnish a mixture of products due to the possible formation of endoperoxide and its corresponding rearrangement products.\textsuperscript{77a} b) Proposed mechanism for endoperoxide formation in 9-substituted anthracene derivatives.\textsuperscript{77b}

The impact of the described side-reaction is discussed controversially in literature.\textsuperscript{77} In deoxygenated solvents and at high substrate concentration ($c \geq 10^{-3}$ mol/ L$^{-1}$) this side reaction is reported to be negligible.
Regardless endoperoxide formation, the dimerization yield for 9- substituted and 9, 10-disubstituted anthracene derivatives is also dependent on the substitution pattern. Sterically demanding substituents, a disadvantageous constrain within the anthracene derivative and electronic effects influence the yield. For anthracenes substituted in 9-position isomeric head-to-head (hh) and head-to-tail (ht) dimers as depicted in Scheme 9 are likely. The ht-dimer is favored due to steric reasons. The hh-dimers are usually unstable; they easily undergo the back reaction upon heating. The regioselectivity of photodimerization can be influenced by preorganization of the anthracenes by means of micelles, γ-cyclodextrin or nanoparticles. However, the dimerization also depends on different factors, such as molecular diffusion in solution, surface effects and dislocations in crystals, etc. so that apart from the fundamental information available each system has to be reviewed individually.

The applicability of anthracene dimerization in more complex systems compared to anthracene derivates with relatively simple and sterically non-demanding substitution patterns will be addressed to illustrate the efficiency, broad applicability and hence, usefulness of photodimerization.
Becker investigated the unimolecular chemistry of anthracenes in bichromophoric systems. Apart from the intermolecular dimerization, bichromophoric anthracene based systems are also able to dimerize intramolecularly. In this case the mobility of the photoactive groups determines the dimerization rate. The progress of dimerization, both inter- or intramolecular, was for example followed by UV-Vis-, IR- and NMR-spectroscopy.

The structure shown in Scheme 10 discloses the photodimerization of anthracenes which was utilized to construct a switchable hydrogen bonded supramolecular assembly of 2-ureido-4(1H)pyrimidinone by means of connecting and disconnecting reversibly the anthracenes attached to the UPy-unit. The dimerization yield was estimated to be ca. 80% based on spectroscopy results.

Scheme 10: Construction of hydrogen bonded molecular assembly by means of photodimerization.

Meier et al. reported a successful case of anthracene dimerization whereas the anthracene resembles the highly sterically loaded core of a Fréchet-type dendrimer (Figure 29a). It was observed that uniform anthracene dimers and no side-products in the crude mixture were formed.
Leblanc et al.\textsuperscript{84} reported about a dendrimer (Figure 29b) decorated with anthracene units at the periphery which were applied to UV-light irradiation to initiate dimer formation.

A poly(amidoamine) dendron with an anthryl group (Figure 30a) at the focal point forming smectic phases was investigated by Takaguchi et al.\textsuperscript{85} Dimers were obtained quantitatively upon UV-light irradiation. Surprisingly, only the \textit{ht}-dimer was observed when the liquid crystalline state was irradiated. UV-light irradiation of the dendrimer in solvents led to a mixture of \textit{ht}- and \textit{hh}-dimers (70:30). From this finding, the distribution of the dendron orientation at the ground-state was concluded. The observed regionselectivity was explained by the antiparallel packing of the anthracenes in the smectic phase. The same photoreactive dendron was further used to study the dimerization in an inorganic material.\textsuperscript{86} A dendron-CaCO\textsubscript{3} composite was applied to UV-light. UV-Vis- and \textsuperscript{1}H-NMR-spectroscopy revealed 81\% of dimer.
4.3 The Langmuir-Blodgett Technique

Ordered thin organic film characterized by a thickness of a few nanometers corresponding to a monolayer are conceivable in manifold practical application like electronic circuit components, sensors and detectors. The combination of organic chemistry which allows almost unlimited possibilities of target molecules with defined structure and functionality and advanced thin film deposition technologies permit the generation of such sophisticated systems at the nanometer scale. Methods like thermal evaporation, sputtering, electrodeposition, molecular beam epitaxy, adsorption from solution, self assembly and Langmuir-Blodgett (LB) technique are known for creating thin films. Among these procedures the LB technique is a very powerful one because it allows a precise thickness control of the generated layer, the homogenous deposition of a monolayer over a large area and the possibility of the creation of a multilayer structure. Further, the easy deposition of the layer on almost any kind of solid substrates is another advantage of this method.
Many of poorly water-soluble amphiphilic substances like fatty acids (Figure 31), phospholipids or higher alcohols can be dissolved in commonly used organic solvents, e.g. chloroform or dichloroethane. The dissolved monomers can be spread at a water surface. The solvent, water insoluble and typically with a low vapour pressure, evaporates and the monomers form a more or less ordered layer at the air/water interface. The layer formation further depends on the monomer concentration applied to the water surface and the area available for each monomer. The hydrophilic headgroup tends to be in the aqueous subphase and the hydrophobic part - in case of stearic acid the hydrocarbon chain - extend outward the water subphase towards the air. The first description of such an experiment is bound to Benjamin Franklin, the American statesman. He reported in 1774 the following to the British Royal Society:\(^8^9\):

"At length at Clapman where there is, on the common, a large pond, which I observed to be one day very rough with the wind, I fetched out a cruet of oil, and dropped a little of it on the water. I saw it spread itself with surprising swiftness upon the surface. the oil, though not more than a teaspoonful, produced an instant calm over a space several yards square, which spread amazingly and extended itself gradually until it reached the leeside, making all that quarter of the pond, perhaps half an acre, as smooth as a looking glass."

More than one hundred years later it was Lord Rayleigh who raised the thought that the maximum extension of an oil film on water is equal to the thickness of one molecule.
Simultaneously Agnes Pockels developed a surface balance in her kitchen sink.\(^90\) This rudimentary equipment was used to determine the surface contamination as a function of area of the surfactant for different oils. Based on these findings Langmuir started his systematic studies on monolayers composed of fatty acids, fatty acid esters and alcohols and their transfer on a solid substrate.\(^91\) His fundamental research was awarded with the Nobel Prize in 1932. Studies on multiple deposition of monolayers onto solid substrates have been carried out by Langmuir’s student Katherine Blodgett.\(^92\) The term *Langmuir-Blodgett film* refers to a transferred monolayer onto a solid substrate whereas the term *Langmuir film* describes a floating monolayer of amphiphile which is insoluble in the subphase. A typical Langmuir setup is shown in Figure 32. The Teflon trough is filled with the subphase, e.g. water. The Wilhelmy plate electro-balance is most commonly used to monitor the variation in surface pressure. The Wilhelmy-plate, made from platinum, glass, quartz or filter paper, is suspended in such a way to cross the air/water interface.

Surface tension is caused through the attraction between the liquid’s molecules by different intermolecular forces like van der Waals forces or hydrogen bonding. The attractive force between the same molecules is called cohesion. Between two immiscible phases the liquid’s molecules in bulk are equally pulled in all directions by their neighbours and thus, the net force is zero. At the surface of the liquid, the forces are not equally distributed due to the different nature of the adjacent medium and therefore, molecules are pulled towards the...
aqueous phase as shown in Figure 33. The net force resulting from the imbalanced forces at the interface leads to an energy gain of the molecules at the interface which is lower compared to the molecules in bulk. These molecules are in a higher energetic state. The excess of energy is called surface free energy. In order to minimize the surface free energy the system reduces its interface and contracts. The effect of contraction is limited by the liquid’s compressibility. The surface free energy is described as surface tension $\gamma$ and is given in force per unit length [N/m] and thus, can be understood as a pressure. It is known that pure water has a surface tension of 73 mN/m at 20°C. The surface tension can be decreased by applying amphiphiles which are adsorbed at the interface and thus, strong interactions between molecules in polar liquids are interrupted. The resulting lateral surface tension depends on the concentration of the amphiphile, the temperature and the intrinsic properties of the amphiphile.

![Figure 33: Vectorial representation of unequally distributed forces (the forces are shown as arrows) at the interface between two immiscible phases leading to surface tension. For molecules, depicted as spheres, in bulk (water or air) there is no net force due to an equal force distribution.](image)

At the time the solution of the amphiphile is placed on the water surface, the solution quickly spreads over the available area furnishing a covered water surface. After solvent evaporation took place, the amphiphiles form a monolayer, assuming an appropriate concentration to

---

\(^iv\) A spherical shaped surface represents the smallest and thus, most favourable ratio between surface and volume.
avoid multilayer formation. Supposing that a large area is available for the monomers, the distance between neighboring monomers is large and hence, their interactions are weak.

Amphiphiles in this state represent a two-dimensional gas and, thus, they can be described through equation 1 for an ideal two-dimensional gas assuming that the monomers have negligible size compared to the interfacial area.

\[ \pi A = kT \]  

In equation 1, \( \pi \) corresponds to the surface pressure [mNm\(^{-1}\)], \( A \) corresponds to the area per molecule [nm\(^2\)], \( k \) is the gas constant [8.314 J mol\(^{-1}\)K\(^{-1}\)], and \( T \) [K] is the temperature.

Since the surface tension \( \gamma \) can be comprehended as its two-dimensional analogue of a pressure it is therefore called surface pressure \( \Pi \). The surface pressure \( \Pi \) is the difference between the surface tension of the pure subphase (\( \gamma \)) and the surface tension in the presence of the monolayer (\( \gamma_0 \)).

\[ \Pi = \gamma - \gamma_0 \]  

Surface pressure measurement is for example done by using the Wilhelmy plate-method. The measurement principle is based on the force due to the surface tension on a plate suspended so that it is partially immersed in the subphase. The so determined force is converted into surface tension whereas the dimension of the plate has to be considered. The interplay of gravity, surface tension and buoyancy result in a net downward force \( F \) acting on the plate. The difference of the acting force on the plate between the clean surface and the surface covered with monolayer yields the surface pressure. Assuming a complete wetting of the plate through the liquid and a plate thickness which is almost negligible compared to the width \( w_p \) of the plate leads, the surface pressure obeys equation 2:

\[ \Pi = -\Delta \gamma = -\Delta F/2w_p \]  

Practically, the force pulling the plate downwards is measured by the mass change of the plate which is done by a sensitive electrobalance. Due to the engineering connection between the electrobalance and the movable barriers the surface pressure of a spread monolayer can be easily followed.
The most important indicator of the monolayer properties of an amphiphile is given by measuring the surface pressure as a function of the area of water surface available to each molecule. Recording of the isotherm is carried out at constant temperature and is known as a surface pressure - area isotherm. Very often it is simply named as isotherm. The profile of the isotherms depends on interfacial behavior of the film forming substance and, hence, it is a two-dimensional “fingerprint”. An example of an isotherm characteristic for stearic acid is given in Figure 34. The course of the isotherm usually displays a number of distinct regions which are called phases. The change of phases can be observed while a discontinuity in the isotherm regime appears. The phase behavior of the monolayer depends on the nature of the amphiphile, the subphase and the temperature. In 1952, Harkins et al. introduced the terminology for the phases present at the interface. He distinguished between a gas phase G, a liquid phase L and a solid state S.

Usually an isotherm is recorded by compressing the film (reducing the area with the barriers like depicted in Figure 32) at a constant rate while continuously monitoring the surface pressure. In the gas phase, the area available per molecule is still large and thus, the influence of the amphiphilic material on the surface tension of water is almost negligible. At a certain distance, repulsive forces start to exert influence on neighboring amphiphiles. The decrease in available surface area results in a conversion of the gas phase into the liquid phase L. The liquid phase L can be further divided into the liquid-expanded phase (abbreviated as L₁ or LE, not shown in Figure 34) and the liquid-condensed phase (abbreviated as L₂ or LC, not shown in Figure 34) at higher surface pressure. Further compression reveals the solid phase S in which the amphiphiles are arranged in their closest possible packing. A monolayer in this state is highly incompressible and can be regarded as two-dimensional crystal. Through the limited surface area, an increase of interaction leads inevitably to a significant influence of the surface tension of water.
Further compression of the monolayer in its closest arrangement (solid phase of the monolayer) leads to a collapse of the monolayer as depicted in Figure 35. The pressure at which the collapse takes place is named as collapse pressure $\Pi_c$, furnishing multilayered structures or different aggregations in solution. From the isotherm, the collapse pressure is apparent by an almost parallel course of the isotherm with respect to area per molecule (x-axis). Before the monolayer turns into a multilayered or even disordered system, the area available for each monomer is minimal. Therefore, the mean molecular area ($\text{Å}^2$) of the amphiphile can be revealed from the isotherm before the collapse pressure is reached. This finding allows a first assumption about the degree of order of the monomers arranged at the interface. A clear phase transition or additional kinks in the isotherm are indicative for rearrangements of the amphiphiles at the interface and permit an assumption how the monomers are assembled within the monolayer.

Moreover, the LB technique allows film deposition by means of vertical (Langmuir-Blodgett method) or horizontal (Langmuir-Schaefer method) movement of a solid support, e.g. silicon,
quarz, glass or mica. In order to deposit a tightly packed monolayer the transfer should be done at a surface pressure close to the collapse pressure of the monolayer.

As the film is transferred onto a solid substrate the surface pressure decreases because of a reduced number of molecules remaining at the air/water interface. The transfer process and the quality of the film depend on the surface pressure applied during the deposition. Accordingly to this, the pressure is kept constant by moving the barriers to account for the material loss which corresponds to the material transferred onto the solid. Depending on the nature of the used substrate, amphiphiles can orientate differently. The upstroke of a hydrophilic substrate leads to an attraction of the hydrophilic and polar headgroup towards the surface. The originally hydrophilic surface is then covered by the monolayer and becomes hydrophobic due to the alkyl chains which are exposed to the air. The immersion of a hydrophobic substrate will furnish the contrary situation.

Apart from the substrate, the quality of the transferred film depends on the transfer speed. At high transfer speed the property of the transferred monolayer will mainly be governed by hydrodynamics. In this case, the water layer beneath the monolayer has to be removed in order to have a contact to the solid substrate. At low transfer speed, the quality of the
transferred monolayer will be increasingly controlled by molecular interactions between the monolayer and the solid surface.

Figure 36: Schematic representation of a Langmuir-Blodgett transfer. a) A monolayer formed at the air/water interface. B) Upstroke of a hydrophilic solid substrate which can be either immersed before or after monolayer formation.

The quality of a monolayer transfer can be revealed from the transfer ratio \((TR)\) which is calculated from the relation of the area difference \(A_w\) of the water surface before and after the transfer at constant surface pressure and covered substrate area \(A_S\).

\[
TR = \frac{A_w}{A_S}
\]  

For a quantitative transfer the transfer ratio should be equal to one.\(^{95}\)

As said before, Langmuir monolayers possess a large number of phases which may exhibit a different orientation, tilt angle or rotational degrees of freedom of the molecules. Brewster Angle Microscope has been proven to be a powerful tool in order to visualize the monolayer’s morphology at the microscopic scale (20 - 200 \(\mu m\)). The existence of a Brewster angle is a particularity of \(p\)-polarized light.\(^{96}\) The principle of the method is based on the fact that the reflectivity of an interface between two media of refractive indices \(n_1\) and \(n_2\) depend on the polarization of the incident light and the angle of incident \(\theta\). An interface without roughness
and for which the refractive index changes quickly\(^v\) from the refractive index of the lower phase \(n_1\) to the refractive index of the upper phase \(n_2\) is called Fresnel interface.

![Figure 37: Illustration of the Brewster angle for p-polarized light.\(^9^7\)](image)

For a Fresnel interface and for polarized light in plane of incident (\(p\)-polarized), there is an angle named Brewster angle \(\theta_B\) at which no reflection can be observed. For example, the Brewster angles for the air/water, air/glass and air/diamond interfaces are 53°, 57° and 67.5° respectively.\(^9^8\) In comparison to theory, for a real interface the refractive index \(n\) does not change quickly from one medium to the other. Moreover, an interface has a certain roughness. These facts consequently lead to a minimal reflection at the Brewster angle. The low intensity in reflectivity at the Brewster angle strongly correlates to the interfacial properties. A change in the refractive index \(n\) is for example caused by the presence of the monolayer and, thus, the reflectivity changes measurably. The change of reflectivity is related to the thickness, roughness and anisotropy of the monolayer. As a result, the difference between a two-

\(^v\) The speed of light in vacuum is considered.
dimensional gaseous and a condensed phase of a Langmuir film can be easily visualized by BAM.
5 Results and Discussion

5.1 Tripod-Family

5.1.1 Synthesis

The substance class described here is referred to as tripod-family which is based on the scaffold 4, a trisamino hydroxyl compound. Scheme 11 summarizes the conversion of the commercially available pentaerythritol\textsuperscript{vi} 1 into the trisamino hydroxyl compound 4. In the first step, bromination was carried out in the presence of hydrobromic acid in acetic acid, followed by treatment with sodium azide to yield 3. The trisazide 3 could be handled without any problems regarding the known explosive potential of molecules bearing multiple azides groups. The final step, the reduction of the azide 3 into the corresponding amine 4 proceeded without difficulty as reported in literature.\textsuperscript{99} The reaction sequence was repeated numerous times in a multigram scale. With compound 4 in our hands the attachment of the anthracene units and different hydrophobic tails was now feasible.

Scheme 11: Conversion of pentaerythritol 1 into trisamino hydroxyl compound 4 which was further functionalized.

The introduction of the polymerizable units was achieved by reacting 4 with the commercially available 9-anthracene carboxylic acid 5. Using the peptide coupling reagent PyBop\textsuperscript{vii} in the presence of diisopropyl ethyl amine (DIEA) furnished 6 after column chromatography in 50% yield. The yellow solid 6 was obtained in 3 gram scale. The structure of compound 6 was for example proven by \textsuperscript{1}H-NMR spectroscopy, measured in deuterated chloroform (Figure 38). The aliphatic protons of the scaffold appeared as a doublet at $\delta = 3.61$ ppm and 3.79 ppm, respectively. The triplet of hydroxyl proton emerged at 5.05 ppm. The anthracene signals

\textsuperscript{vi} 2,2-bis(hydroxymethyl)propane-1,3-diol

\textsuperscript{vii} Benzotriazole-1-yl-oxy-tris-pyrrolidino-phosphonium hexafluorophosphate
became visible as expected as multiplets whereas the anthracene proton in 10-position clearly appeared as a singlet. Mass spectroscopy data and elemental analysis were in agreement with theory. Structure 6 represents the first member of the tripod-family while it is doubtful that the hydroxyl group can ensure a sufficient hydrophilic-hydrophobic balance for the desired interfacial behavior.

Scheme 12: Amide coupling yielding the first monomer of the tripod-class.

Figure 38: $^1$H-NMR spectrum of 6 recorded in CDCl$_3$ (300.23 MHz). Solvent marked with (*).

However, it was an aim of this project to study systematically the influence of differently substituted tripod monomers regarding their interfacial behavior. Therefore, the hydroxyl group was esterificated to introduce different polar tails.
Esterification of 6 was achieved by reacting the acids 12 – 14, 15b (Figure 39) and the coupling agents 4-(dimethylamino)-pyridinium p-toluenesulfonate (DPTS) and 1-ethyl-3-(3-dimethylamino-propyl)carbodiimide (EDC). The in situ generated active ester promoted the final coupling to the desired products 16b, 17 - 19. Acid 12 was obtained by a cycle of protection and deprotection (Scheme 13) of the amino- and hydroxyl groups using di-tert-butyl dicarbonate (Boc₂O) and benzyl bromide (BnBr), respectively. The subsequent amide coupling using terephthalic acid monomethylester furnished compound 11. Saponification of the ester yielded the free acid 12. Compound 15a was also applied to saponification using KOH and furnished quantitatively 15b. In order to provide acid 14, the alcohol 2,5,8,11,15,18,21,24-octa oxapentacosan-13-ol was deprotonated using sodium hydride (60% suspended in mineral oil) in dry THF and then let reacted with 4-(bromomethyl)benzoic. The accessibility of the acids 14, 15b was less crucial and yields were always in the range above 70%, whereas 13 was commercially available.

The esterifications (Figure 39) were carried out according to a standard protocol (DPTS/ EDC as coupling agents). All reactions suffered of low yields, typically below 45%. Moreover, the purification of the products obtained by column chromatography was rather difficult. Possibly, the arrangement of polar and apolar subunits of the molecules leading to complex interactions with the silica gel hampered the fractionation of the desired products.
Figure 39: Acids 12 – 14 and 15b applied to esterification furnishing the anthracene-containing tripod monomers 16b and 17-19.
Therefore, preparative GPC was required to isolate pure products which were then characterized by NMR- and mass spectroscopy as well as elementary analysis. Only the crude product of 17 could be applied to column chromatography. Using a solvent gradient the product was obtained in 29% yield. Structure proof of 17 was accomplished for example using mass spectroscopy (MALDI-FT, 3-HPA). The monoisotopic peak was found for [M+Na]+ at 1019.3638 (calculated: 1019.3632). Other coupling agents (DMAP/ EDC, HOBt/ EDC) were completely unsuccessful in these cases.

A collection of amphiphilic and anthracene-containing tripod-monomers (16b, 17-19) was provided and their potential of dimerization under UV-light irradiation investigated. Since these monomers are characterized by anthracenes linked to an amide unit, model compounds starting from 6 were prepared as representative examples. Dimerization experiments in solution were done in such a scale that product isolation followed by product characterization was possible. NMR-, IR- and UV-Vis spectroscopy was used to evaluate the dimerization. It is remarkable that the dimerization in solution - even at high concentration - is not equivalent to an experiment at the interface. Assuming a monolayer in its densely packed state, neighboring anthracenes at the interface are packed close to the van der Waals distance. The π-π interactions between the anthracenes lead to stacks. This state resembles a high level of preorganization which can never be achieved in solution.

At first, a degassed solution of 6 with a fivefold excess of parent anthracene in dichloromethane was irradiated at ambient temperature. The crude product obtained after irradiation was purified by column chromatography yielding 50% of a colorless solid. It is understood that anthracene dimers were generated under the applied conditions. In addition, it is reasonable to assume that beside the 1:3 adduct, compound 20, also the 1:2 and 1:1 adducts between 6 and anthracene were formed. Intramolecular dimerization of two of the three anthracene units of 6 must also be considered as possible side reactions. None of the conceivable side products was isolated and identified.
The structure of 20 was confirmed by NMR- and mass spectroscopy (Figure 40 and Figure 41). The conversion of anthracene was derived from the comparison the $^{13}$C-NMR spectra of 6 and 20 recorded in solution. In particular, the new signals between $\delta = 140$ and 145 ppm and at $\delta = 55$ ppm which correspond to the ortho-phenylene units and the bridgehead carbons were indicative for a successful dimerization. It could be concluded that all three anthracene units individually underwent dimerization. The structure proof is supported by the high resolution mass spectra (Figure 41) which showed beside the monoisotopic peak of $[M+H]^+$ for 20 (1:3 adduct) the monoisotopic peaks for the intermediates loosing successively anthracene leading to $[M+H]^+$ for 6. Because of the straightforward results gained from the previous discussed reaction, multiple intermolecular dimerization events in tri- and tetrapods were assumed to behave similarly.
Monomer 6 was exposed to UV-light applying the same conditions as successfully used for 20, but instead of parent anthracene the monomer 6 should react with itself yielding 21. Due to intra- and intermolecular dimerization an irregular network was expected to be formed. An insoluble yellow precipitate was obtained after irradiation which was filtered off from the yellow supernatant solution and investigated by solid-state NMR, see Figure 40 chart c). It was evident from the typical signals of the newly formed bridgehead signals that dimerization took place. The supernatant solution was applied to column chromatography, but unfortunately structure identification was not possible for any of the numerous side products.
Results and Discussion

Figure 41: High resolution mass spectrum of 20 (IonSpec HiResMaldi, positive mode, matrix: 3-HPA). Monoisotopic peak for [M+H]^+ found at 1280.5347 m/z, calculated: 1280.5361 m/z. The difference between the peaks corresponds to the mass of anthracene.

The possible arrangement of the tripod 6 was regarded from a theoretical point of view. A calculation\textsuperscript{viii} based on 6 by means of molecular mechanics CFF 91 force field suggesting a hexagonal arrangement. Figure 42 represents a favorable state which is calculated for vacuum. However, the monomers preorganized at the interface are still mobile because of the rotational freedom. Therefore, the shown hexagonal structure has to be viewed as an ideal case, but theoretical possible one.

\textsuperscript{viii} Dr. Oleg Lukin is highly acknowledged for calculating the model.
Summarizing, the predicted closed packing at the interface resembles a solid-like state which is, of course, never reached in solution. Nevertheless, the experiments in solution can be considered as a model to comprehend the product formation at the interface. The accessibility of spectroscopic data for dimers generated at the interface is rather difficult because many spectroscopic methods lack sensitivity. Surface sensitive techniques are required to characterize the monolayer.

### 5.1.2 Further Spectroscopic Measurement

#### 5.1.2.1 IR-spectroscopy

Spectroscopic methods mentioned so far were used to confirm the proposed structures; whereas IR- and UV-Vis spectroscopy\(^{ix}\) served to investigate the appearance of the isomeric anthracene dimers in the corresponding spectroscopic method. Since the anthracene dimerization at the air/water interface is important to be proven at a later stage of the project

---

\(^{ix}\) For the IR measurements KBr tablets were prepared. UV-Vis measurements were either done in solution or in solid state, both in transmission.
this IR-study was considered to be useful. Any spectroscopy of a compressed monolayer at an interface is challenging due to the small quantity of molecules involved and thus, the applied analytics need to account for this.

To get deeper insight, the relevant compounds 20 and 21 were investigated as references. According to 68 (and references within), the presence of two distinct absorption bands at approximately 1450 and 1470 cm\(^{-1}\) are indicative of dimer formation in solution or bulk, respectively. These newly formed absorptions bands can be assigned as C-H vibrations of the bridgeheads in 9,9'- and 10,10'- position (Figure 43). In Figure 43, the spectra of 20 and 21 focus on this characteristic region in which the bridgeheads become visible.

![Figure 43: IR-signals of newly formed bridgeheads after dimerization at 9,9'- and 10,10'- position appear at 1454 cm\(^{-1}\) (a) and 1474 cm\(^{-1}\) (b) in IR-spectroscopy. IR-spectra of 6, 20, and 21 recorded in KBr. The photoproducts 20 and 21 clearly show the absorption signals of bridgeheads at 1454 cm\(^{-1}\) and 1474 cm\(^{-1}\) whereas monomer 6 does not show any distinct signals in this region.](image)

Clearly the C-H splitting of the bridgeheads appear at the predicted region. This supports the formation of anthracenic photodimers. Interestingly, the spectrum of 21 exhibits the presence of a complex absorption band around 1600 cm\(^{-1}\) which is not visible in the spectrum of 20. Signals in this region can be assigned to a stretching vibration of benzene rings.\(^{100}\) Formally
the dimerization can be considered as a transformation of anthracene into two ortho-substituted benzene rings and thus, the appearance of signals due to substituted benzene rings was expected. This so-called ring breathing mode was also observed for anthracene dimers by Fox\textsuperscript{101} and Liu\textsuperscript{102}.

\begin{scheme}
\begin{center}
\begin{tikzpicture}
  \node (a) at (0,0) {\includegraphics[width=0.4\textwidth]{anthracene_dimerization.png}};
  \node at (2.5,0) {anti-dim 22};
  \node at (0,-2) {anti-dim 23};
  \node at (2.5,-2) {syn-dim 24};
\end{tikzpicture}
\end{center}
\end{scheme}

Another objective of this IR-study was to understand the appearance of the absorption band at $\nu = 1600 \text{ cm}^{-1}$ as observed in the IR-spectrum of 21. Therefore, the anthracene derivatives 22 - 24 were irradiated and the crude product mixtures were applied to column chromatography and analytical pure products were isolated. Afterwards the IR-spectra were recorded in KBr. Figure 45 compares the IR-spectra of the dimers obtained. The characteristic absorption bands at $\nu = 1454$ and $1474 \text{ cm}^{-1}$ which are indicative of anthracene dimer formation were always present, only a small shift was observed, irrespectively of the substituents, the substitution pattern or the isomeric form. Notably, defined dimers (anti-
**dim22, anti-dim23, anti-dim24, and syn-dim24** do not show any complex signal around $\nu = 1600 \text{ cm}^{-1}$ which was previously assigned in Figure 43, compound 21 as ring breathing mode of benzene. All samples were measured in bulk under the same conditions so that this finding cannot be explained reasonably. Screening the literature for comparable examples either no ring breathing was observed or bands at around $\nu = 1600 \text{ cm}^{-1}$ were not assigned.

Unfortunately, IR-spectroscopy does not allow to distinguish between the two isomers **anti-dim24** and **syn-dim24** because the characteristic bands appear at almost the same position (Figure 45). The initial hope that these isomers possibly differ from each other regarding the position of their absorption bands in the IR-spectrum could not be confirmed. The **syn**-isomers are expected to be formed at the air/water interface since monomers are assumed to be aligned parallel at the interface. The generation on the **anti**-dimer would require monomer rotation of $180^\circ$ leading to an antiparallel alignment. This rotation is unlikely due to monomer’s amphiphilicity which encodes parallel orientation at the interface.
The possibility of endoperoxide formation was also investigated by comparative experiments in the presence and absence, respectively, of oxygen. Endoperoxide formation which might occur in the presence of oxygen can be revealed from absorption bands at $\nu = 880 - 890 \text{ cm}^{-1}$ and $\nu = 1230 - 1260 \text{ cm}^{-1}$.\textsuperscript{67}

Figure 45: Part of the IR-spectra of 22, 23 and 24 and the corresponding dimers which appear constantly with two characteristic absorption signals at (around) 1454 cm$^{-1}$ (a) and 1474 cm$^{-1}$ (b).

However, monomer 22 was applied to UV-light in the presence and the absence of oxygen, time of irradiation was kept constant in either case. Neither the absorption band corresponding to the endoperoxide nor the rearranged endoperoxide yielding a carbonyl compound (see
subchapter 4.2) with its characteristic strong absorption band at \( \nu = 1600 - 1670 \text{ cm}^{-1} \) was observed. The dimer of 22 formed in the presence of oxygen showed the same appearance in the IR-spectrum as depicted in Figure 44. It is therefore concluded that the endoperoxide formation does not compete with dimer formation under the described conditions.

### 5.1.2.2 UV-Vis Spectroscopy

UV-Vis spectroscopy was used to further characterize the dimers obtained based on the tripod-family. As reported in literature, \(^{103}\) absorption maxima for pure anthracene appear at \( \lambda = 252, 323, 339, 356, \) and 374 nm. The used dissolved compounds did not allow the detection of signals below \( \lambda = 250 \text{ nm} \). However, Figure 46a indicates that all characteristic anthracene signals disappeared for the stoichiometric structure 20, no free anthracene groups were detectable.

![Figure 46: a) Comparison of UV-Vis spectra of 6 and 20, measured in transmission. The characteristic UV-absorption of anthracene disappeared completely proving the formation of defined dimeric structure. b) In reflectance measured UV-Vis spectra of 6 and 21 indicate residual anthracenes as expected for dimerization in bulk. (cuvette length = 1cm).](image)

Due to the insolubility of the irregular network 21, the UV-Vis measurements were done in reflection. Figure 46b exhibits free anthracene (end) groups revealing an incomplete dimerization of anthracene. This is caused either by the steric inaccessibility of the remaining anthracenes or the insolubility of the product which was formed during the dimerization.
5.1.3 Interfacial behavior

The previous subchapter confirmed the ability of amide substituted anthracene derivatives to undergo dimerization in solution successfully. Hereby, the assumption that 6 and systems based on 6 behave photochemically similar at the air/water interface is made. A prerequisite for the dimerization at the air/water interface are monomers which are able to form a stable film. Therefore, the tripod series (6, 16b, 17 - 19) were applied to the air/water interface. A chloroform solution of defined concentration (1 mg/ml) was prepared for each monomer and a distinct volume was spread at the air/water interface. After the chloroform was evaporated (5 minutes) the isotherm was recorded at constant temperature (T = 23°C). The quality of the interfacial behavior was derived from recorded isotherms as well as images taken by BAM.

Monomer 6 was applied to the air/water interface using the standard protocol. A first check of the isotherm revealed a collapse pressure at 40 mN/m. In a second experiment the reversibility of the monolayer formation was tested applying a maximum pressure of 30 mN/m in order to ensure a monomolecular layer where no collapse, disorder or multilayer formation was expected. Monomer 6 did not form a stable monolayer; it was not possible to record a reversible isotherm. The BAM image (Figure 47a) which was taken at the surface pressure of 30 mN/m shows that the monolayer appeared to be homogenous - without any noticeable features. Decompression of the layer furnished crack propagation (Figure 47b-c). The formed islands appear to have distinct edges which did not re-spread of complete decompression indicating a very rigid material. This is most likely due to strong hydrogen bonds between the amides.

Monomers 17, 18 and 19 did not form stable monolayers. Irrespective of the volume applied to the subphase, there was no surface pressure detectable. In the case of 17 the surface pressure dropped immediately after the final pressure was reached. Therefore, it seems reasonable that monomers aggregate partially, e.g. to micellar structures or dissolve in the subphase. These observed findings indicate a high degree of hydrophilicity.
Results and Discussion

Figure 47: Visualization of the monolayer of 6 as detected on BAM. a) At a surface pressure of 30mN/m the monolayer appeared homogenous, no defects were visible. b) Decompression of the monolayer furnished a distinct crack within the layer. c), d) Further decompression revealed rapid crack propagation. The size of the images is 430 μm x 498 μm.

Compound 16b differs from the previous ones (17 - 19) since the EO-chains were replaced by a pentaerythritol unit to decrease the hydrophilicity. A reversible monolayer formation was revealed from the isotherm (Figure 48). The target surface pressure of 35 mN/m was previously determined in order to ensure a monolayer regime by increasing the surface pressure until the collapse was reached.

Figure 48: Mean molecular area vs. surface pressure recorded for 16b.

It is noteworthy that the expansion of the monolayer followed a different, but almost parallel course which at a certain surface pressure was slightly shifted towards smaller mean molecular areas. It seems most likely that the time of equilibration was not sufficient to have a
monolayer arrangement in its most favorable state (most densely packed state) at the target pressure. The expanded monolayer was compressed again and the course of the isotherm was similar regarding the slope indicating the presence of a reversible system. The isotherms obtained are featureless and, thus, no conclusion towards phase transitions could be made.

5.1.4 Concluding remarks

The accessibility of the key monomer 6 was high yielding. Other members of the tripod-family (16b, 17-19) synthesized through esterification using 6 and the corresponding acids were relatively low in yield. Purification of 16b, 17-19 was only possible by using preparative GPC. These monomers which can be described as amide-substituted anthracenes were photochemically dimerized. For example, the model compounds such as 20 and 21 furnished through dimerization of anthracenes were synthesized. The IR- and UV-Vis data obtained for the dimeric products was coherent and in agreement with literature. The interfacial behavior was examined at the air/water interface and the isotherm was recorded for the monomer under investigation. Surprisingly, only monomer 16b gave a reversible a monolayer.
5.2 Tetrapod-Family

5.2.1 Synthesis

The substance class described here is referred to as tetrapod-family which was based on the calix[4]arenes. Generally, calix[n]arenes (n = 4, 5, 6, 8) are macrocycles whose skeleton consists of phenol subunits which are linked in ortho-position via methylene groups. The number of the phenol subunits is displayed by [n]. Calix[4]arenes are less flexible and higher in symmetry compared to the higher homologous. Since monomer’s rigidity is considered to be an important property of a molecule that is able to form an ordered film, calix[4]arenes were therefore regarded as promising candidates. Further, the possibilities to chemically modify the upper and the lower rim of calix[4]arenes are intensively reported.\textsuperscript{104}

![Figure 49: a) Calix[4]arene in its cone conformation with para-tert-butyl substituents at its upper rim and hydroxyl groups at its lower rim. b) Schematic representation of a calix[4]arene and its cone shape.](image)

To arrive at calix[4]arene-based tetrapods, the amino compounds \textsuperscript{25}a and \textsuperscript{25}b were prepared according literature\textsuperscript{105} in a multigram-scale. They were then reacted with anthracene-9-carbaldehyde in dry methanol yielding the corresponding Schiff base \textsuperscript{26}a and \textsuperscript{26}b. The purification of the intensively yellow coloured intermediates \textsuperscript{26}a and \textsuperscript{26}b turned out to be rather problematic in that, that they quickly hydrolyzed on silica gel column. This problem could be overcome by adding 5\% triethylamine to the eluent. The acidity of the silica gel column was sufficient to induce the back reaction into educts. The desired compounds \textsuperscript{27}a and \textsuperscript{27}b were then synthesized by reduction of \textsuperscript{26}a and \textsuperscript{26}b, respectively with NaBH\textsubscript{4}. The reaction proceeded quantitatively and no further purification was necessary. The cleanliness of the reaction could be revealed from \textsuperscript{1}H-NMR spectroscopy. In case of the conversion of \textsuperscript{26}a
Results and Discussion

to 27a, the imine proton absorbing at $\delta = 9.36$ ppm disappeared completely after reduction and the generated CH$_2$-group appeared at $\delta = 4.76$ ppm.

Scheme 16: Reagents and Conditions: i) Anthracene-9-carbaldehyde, dry MeOH; ii) a) NaBH$_4$, MeOH, b) LiAlH$_4$, THF.

Figure 50: High resolution mass spectrum of 27a (IonSpec HiResMaldi, positive mode, matrix: DCTB mix). Monoisotopic peak ($^{12}$C$_{124}$H$_{140}$N$_{4}$O$_{20}$Na) for [M+Na]$^+$ 2028.002 found, 2027.9958 calculated.
Results and Discussion

All intermediates were fully characterized by NMR- and mass-spectroscopy as well as elemental analysis. Exemplarily the mass spectrum of 27a is shown in Figure 50. The monoisotopic peak for [M+Na]$^+$ at 2028.002 m/z was in good agreement with the calculated value (2027.9958 m/z).

Since it was an objective to assess the anthracenes’ orientation within a tetrapod-molecule compound 27b was synthesized. This compound should serve as a model compound for 27a. The synthesis of a model compound 27b was necessary because at room temperature 27a was oily due to the EO-chains. Model compound 27b equipped with hexyl-chains at the upper rim was expected to crystallize. Crystal growth was achieved by slow evaporation of DCM; the corresponding crystal structure is shown in Figure 51.\textsuperscript{x} Compound 27b served to estimate the space demand of the anthracene units. This is of particular interest for the later done monolayer studies of 27a described in the subchapter 5.2.2.

Figure 51: Crystal structure of 27b.

The reactivity of compound 27a under UV-light irradiation was also briefly investigated using UV-Vis spectroscopy. It was aimed to synthesize a 1:4 adduct corresponding to the stoichiometric compound 20. After many trials, no stoichiometric compound could be

\textsuperscript{x} The crystal structure was solved by Dr. Volker Gramlich, group of Prof. Walter Steurer (ETHZ).
Results and Discussion

isolated. Unfortunately, even mass spectroscopy did not show the formation of any dimers. These findings are consistent with the reported behavior of anthracene dimers in mass-spectroscopy\textsuperscript{68} which mainly reveal the monomer peak instead of the dimer peak. This observation is in contradiction to the result found for 20 and cannot be explained yet. However, the crude mixtures of these reactions were explored by UV-Vis spectroscopy. It was found that the products obtained after UV-light irradiation strongly depend on concentration. For highly dilute solutions of 27\textit{a} in DCM (0.1 mM) a soluble product was obtained which gave the UV-Vis spectrum depicted in Figure 52. The anthracene-typical resonances had completely disappeared suggesting that under these highly dilute conditions a twofold intramolecular dimerization took place. The possibility of intramolecular dimerization at low concentrations seems reasonable since the crystal structure shown in Figure 51 pointed out that two anthracenes are almost parallel aligned to each other at a close distance. Calix[4]arenes bearing two anthracene units which undergo intramolecular dimerization have been reported in literature.\textsuperscript{106}

![Figure 52: UV-Vis spectra in chloroform comparing tetrapod 27\textit{a} and the product of its irradiation in highly diluted (0.1 mM) (a), and highly concentrated (125 mM) DCM solutions (b).](image)

At much higher concentrations of 27\textit{a} in DCM (125 mM) an insoluble precipitate was formed, so that its UV-Vis spectrum was taken in reflection. With regard to the self-addition of compound 6 yielding 21 some residual anthracene signals were detected and tentatively ascribed to end groups.
5.2.2 Interfacial behavior and monolayer characterization

To explore the ability of monolayer formation of 27a, a surface pressure/area isotherm was recorded by using the same conditions as previously described. Compared to all tripod-based monomers, 27a formed extremely stable, compressible films whose reversibility was superior. Since the surface pressure/area isotherm which is depicted in Figure 53 appeared to be completely featureless, the assignment of phase transitions within the monolayer was not possible.

Figure 53: Surface pressure/area isotherm of 27a. Phase behavior upon compression and decompression is almost identical confirming a good reversibility. The dotted lines indicate the different methods how to determine the mean molecular area at the maximum surface pressure applied.

However, on the basis of these repeatedly obtained curves monomer 27a was selected for an ample investigation and for the initial polymerization experiments. First, the area per molecule was estimated. This can be done in two different ways: A tangent was drawn near the surface pressure of 25 mN/m which intersected the x-axis at approximately 220 Å² (the dashed line in Figure 53). The tangent applied at the maximum surface pressure is understood as an extrapolation. Since there is no consistency in literature how to determine the mean molecular area an alternative value was also obtained by measuring the area at this pressure. Using this method, the area per molecule was found to be at 185 Å² (the dotted line in Figure
53). From the two extreme conformations of stick models shown in Figure 54, the expected value should be somewhere between 100 and 380 Å².

![Figure 54: Molecular models of the two extreme conformations of monomer 27a with the four anthracene units in upright (left) and horizontal orientations (right), respectively. The areas covered by these two conformers differ significantly between approximately 100 and 380 Å².](image)

From the X-ray structure of model compound 27b (Figure 51) an intermediate value can be assumed. A comparison with 27a seems justified since the anthracene geometry is not affected by the substitution at the lower rim.

The film formation upon increasing surface pressure was monitored by BAM. It can be seen from the representative snap shots taken at low pressures (Figure 55) homogenous areas were initially separated by less ordered stripes. At higher surface pressure (typically 25 mN/m), however, a fully homogenous film of 27a was observed. A decrease in surface pressure by opening the barriers revealed the “striped” monolayer appearance as shown in Figure 55.

All transfer and irradiation experiments which are discussed hereinafter were done with a monolayer from 27a at 25mN/m.
Results and Discussion

Figure 55: BAM images of film formation of 27a during increasing surface pressure (from almost 0 mN/m to 25mN/m). The rightmost image indicates a rather smooth monolayer which represents the state at which transfers and irradiations were done. The size of the images is 430 μm x 498 μm.

Before and after irradiation with UV-light BAM images were taken (Figure 56). The images were absolutely identical, no cracks or disordered areas were visible. The right-hand side image in Figure 56 remained after the barriers were opened completely. The open barriers would allow a re-spreading of the monolayer assuming no reaction took place and a BAM image like the one obtained at low surface pressure should have been visible. The re-spreading of the monomer without UV-light treatment was already proven by the behavior of the isotherm (Figure 53) and the BAM picture obtained (Figure 55) after decompression of the monolayer. Since this observation was not made in case of an UV-light treated monolayer of 27a the cross-linking of 27a was demonstrated. As mentioned before, the monolayer stability of 27a over time was excellent. Therefore, the decrease in surface pressure during irradiation could be directly correlated to a photochemically induced reaction at the air/water interface. Referring to the inconsistent viewpoints regarding endoperoxide formation (see Chapter 4.1) a control experiment was done: For a monolayer generated under the same conditions except nitrogen purging while irradiation was done, BAM images before and after irradiation were taken and the contraction due to irradiation was compared. A careful study did not reveal any differences in film morphology and film contraction.
Results and Discussion

Figure 56: BAM images of non-irradiated and UV-light irradiated monolayer of 27a at the air/water interface indicating that irradiation did not cause morphological changes. During irradiation nitrogen was applied. (Images size: 430 μm x 498 μm)

However, the contraction observed during irradiation added up to 40%. Since the dimerization process leads to single bond formation this result cannot be easily understood. One theoretical consideration for this result would be the fact that the tetrapod monomers prefer to arrange into a rectangular lattice structure due to their symmetry which pass into a hexagonal lattice structure while irradiation. The fourfold symmetry of this class of monomers obviously favours a rectangular lattice structure as depicted in Figure 57 which was sustained by molecular modeling. Unfortunately, this assumption could not be experimentally proven.

Figure 57: Proposed rectangular lattice structure for 27a.
Results and Discussion

Since the results for 27a at the interface suggest a polymeric nature of the irradiated monolayer a very simple mechanical experiment was performed to prove the different properties between the monolayer before and after UV-treatment. Both monolayers were scratched with a needle and the response was monitored by BAM. The monolayer which was not treated with UV-light responded immediately. The scratches “healed” instantaneously so that it was almost impossible to take pictures. In contrast, the scratches of the irradiated film remained if the barriers were opened completely. This behavior can be correlated to a solid-like material due to covalent cross-linking. The stiffness of the monolayer after UV-treatment could also be impressively visualized by eye: The filter paper of the Wilhelmy plate was deflected manually and stayed at this particular position.

![BAM images of 27a](image)

Figure 58: BAM images of 27a. a) The scratch can be only seen as a blurry stripe in case of a non-irradiated monolayer. Healing took place immediately. b), c) For an UV-light treated monolayer the scratches remained after the barriers were opened completely. An oscillation of the barriers did not change the observation of partly broken parts of the monolayer. (Images size: 430 μm x 498 μm)

Evidently some reaction took place at the interface. In order to test the mechanical stability of the cross-linked monolayer, transfers on electron microscopy grids with holes sized 45 μm x 45 μm were carried out. The aim was grid coverage with a monolayer without film rupture. Attempts with LB transfer did not work out; however, the horizontal transfer (Langmuir-Schaefer method) was successful. It should be mentioned that the success of coverage was statistically distributed. Figure 59 compares an unsatisfactory and a successful transfer. The images were taken with a conventional optical microscope and the contrast is based on interference. In the unsatisfactory case practically all films over holes had ruptured. Notably, the direction of the cracks was very similar which seems to indicate that during coverage a stress was applied to the entire film while transferring.
Figure 59: Light microscopy images of transferred UV-light treated monolayers of monomer 27a on a Cu-grid with holes sized 45 x 45 = 2025 μm². The image a) shows a case considered unsuccessful because film rupture could not be prevented, the image b) represents a successful case because many holes are over spanned by non-ruptured films. The arrows point towards cracks.

The reason for the crack formation is unknown. The association to drying effects is speculative. In a control test, also the non-cross-linked film was tried to transfer on such a grid; however, it was in none of over fifty attempts possible to cover holes, not even for small parts regardless of horizontal or vertical transfer. Consequently, cross-linking is a prerequisite for such experiments with films from UV-light treated monolayers of 27a. The aging of the cross-linked films was also investigated by optical microscopy. The use of differential interference contrast microscopy (DIC) which enhances the contrast in unstained, transparent samples revealed a micrograph as shown in Figure 60. This image was obtained after 5 days
the film transfer event was carried out. Some of the grid holes are covered (lower part) and some are not (upper part). For example, the grid hole in the center was partially covered. Because of rupture, the film partly folds back on itself, wrinkles, and showed a tendency to roll up at the edge.

Figure 60: DIC image (x40) of a UV-light treated monolayer of 27a taken 5 days after the transfer event. The film is on a Cu-grid with 1600 μm² sized holes some of which are over spanned by non-ruptured films (holes on the right-hand side) and others are not at all (holes on the left-hand side). The holes in the center are partially covered by films and overlaying parts, wrinkles, and rolled-up edges are visible.

For further investigations the non-irradiated film and also the irradiated one of 27a was transferred on silicon wafers and the thickness was determined by ellipsometry. The results, summarized in Table 1, were in good agreement for the estimated height which was determined to be 24 Å in case of the all-trans conformation. Neither the transfer method nor the irradiation of the layer caused a significant change in height, though irradiation may lead to some film thickening. The consistence in height confirms the monolayer nature of the irradiated film which was subsequently transferred onto a Cu-grid.
Table 1: Thickness (Å) of transferred monolayers of 27a and the average value obtained.

<table>
<thead>
<tr>
<th>Vertical transfer</th>
<th>Horizontal transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolayer</td>
<td>UV-light treated monolayer</td>
</tr>
<tr>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>19±1</td>
<td>20±0</td>
</tr>
</tbody>
</table>

After thickness measurements verified the desirable height, the orientation of the monomers within the layer was of further interest. From the polarity of the silicon wafer it was assumed that the ethylene oxide chains point towards the surface and the outmost layer consists of the anthracenes. Therefore, X-ray photoelectron spectroscopy (XPS) which is an information-rich method for surface analysis was used. Beside the qualitative and quantitative analysis of elements present at the surface (except hydrogen and helium), detailed information about organization and surface morphology can be gained. XPS utilizes photoionization and energy-dispersive analysis of the emitted photoelectrons which are characteristic for each element. Figure 61 shows the survey spectrum collected of a non UV-treated monolayer of 27a transferred on a silicon substrate. Carbon, oxygen and nitrogen signals were detected together with the Si2s and Si2p that are due to the substrate. The nitrogen signal, N1s, indicated a successful transfer of the monolayer since this element is the only one that is exclusively present in the monomer. Since no other signals were detected it could also be concluded that the monolayer was free of contamination. Detailed spectra of C1s, O1s, N1s and Si2p were also taken (Figure 62) and the peak areas were used to calculate atomic concentrations and monolayer thickness.
The Si2p spectrum exhibits two signals, one at 99.4 eV and another one at 103.4 eV. The first signal was due to the parent substrate and the second could be assigned to silicon dioxide which was inevitable present.\textsuperscript{107}

The O1s spectrum contains the contributions of both the silicon dioxide at 533.1 eV and the monomer. In fact, the signal that was symmetric in case of pure silicon dioxide showed here an asymmetry at the lower binding energy side due to the presence of oxygen signals of the monolayer. Three different components at 532.6 eV and 533.3 eV were identified upon peak–fitting using the fitting parameters obtained on basis of reference samples analyzed using the same spectrometer settings. They were assigned to the C-O-C chains and to the Ar-O respectively. These values are in agreement with the literature.\textsuperscript{108} The C1s signal was also asymmetric since it contains the signals due to the aromatic rings (284.7 eV) of the calixarene, the anthracenes (285.5 eV) and the C-O-C units at 286.7 eV. The binding energy value of the anthracene units of the monolayer was lower than that of parent anthracene (not shown here) which was attributed to the presence of the donor substituents in the former.
The N1s signal is symmetric at 400.4 eV. This value is 3.4 eV higher than that measured on the pure (drop-casted sample prepared as reference) compound, indicating that the nitrogen atom might be bonded to water molecules. The atomic composition of the monolayer was determined based on the line intensities determined by integration of the fitted Gaussian/Lorentzian model functions after a Shirley background subtraction and corrected for the photoionization cross-sections. The found values are: 82.5% C, 14.8% O, 2.7% N. These findings were in good agreement with the calculated ones: 83.8% C, 13.5% O, 2.7% N. The monolayer thickness was calculated to be 26 ± 1 Å which is significantly larger than the values obtained by ellipsometry but still in agreement with the assumption of a monolayer. Finally, angle resolved XPS measurements were carried out on 27a to get an insight into the monolayer’s orientation. Figure 63 shows the plot of the atomic concentration vs. the emission angle, whereby the latter is the one formed by the direction of the emitted electrons with the surface normal. This plot suggests that the C-O-C units of the monomers are in the inner part of the film while the carbon species seem to be located in the outer part of the monolayer. Thus, the monolayer has an orientation as intuitively thought. The same series of
measurements was done for an UV-light treated monolayer of 27a. Since the molecular composition and the orientation of the layer can be assumed to be identical compared to the non UV-light treated one, the focus was put on the $\pi-\pi^*$ shake-up satellite of the aromatic system. The shake-up satellite corresponds to photoelectrons that have lost energy through promotion of valence electrons from an occupied energy level ($\pi$) to an unoccupied energy lever ($\pi^*$). It was expected to observe a decreased shake-up satellite due to anthracene dimerization which leads to a loss of aromaticity. Surprisingly, neither for the non UV-light treated nor for the UV-light treated film the shake-up satellite of the aromatics was visible. A related study of the dependence on film thickness and visibility of the shake-up satellite was undertaken by our collaboration partner. The data evaluation disclosed the necessity of further experiments to have a reliable data set. The relationship between film thickness and appearance of the shake-up satellite is still under investigation.

![Figure 63: Survey of the angle-resolved XPS measurements of atomic concentrations. A monolayer of 27a showed an increasing carbon content at high emission angles indicating the presence of anthracenes in the outermost layer; whereas the oxygen content decreased at high emissions angles so that the oxygen-containing part of the monomer points towards the silicon substrate.](image)

The prepared samples were also applied to contact angle measurements with water. This method is known in surface science to characterize the wetting of a solid by a liquid which correlates to the nature of the solid.109 Onto the substrate which was previously covered by the monolayer a droplet of water was placed. The angle between the liquid/vapor interface and the solid surface was subsequently determined. Contact angles for SAMs with aromatic units
Results and Discussion

at their surface are known to be on the order of 80-85°. Measurements on the transferred films directly after transfer reproducibly gave contact angles between 32° and 45°. These scattering results were inconsistent with the reported data, and moreover too low for an aromatic system. However, after drying the samples under high vacuum, the values were reproducibly between 82° and 88°, and thus, well within the expected range. This substantial change of contact angle upon drying could be explained by adsorbed water which in the non-dried samples was abundantly available due to the hydrated ethylene oxide chains and could reach the surface through the many pores necessarily present in the cross-linked film. As it was done for the XPS measurements, a reference sample was prepared by drop-casting 27a from a chloroform solution onto a silicon wafer. After solvent evaporation within 3 minutes at atmospheric pressure, the measured contact angle was in the expected range for aromatic compounds, though the compound was applied from bulk. This comparison clearly indicates the influence of water and the drying, respectively.

5.2.2.1 Further monolayer characterization through infrared reflection absorption spectroscopy (IRRAS)

In order to exclude the impact of the monolayer transfer followed by the drying process IRRAS was applied. Similar to conventional IR-spectroscopy IRRAS relies on the molecular structure characterization by detecting molecular vibrations accompanied through changing molecular dipole moments (transition dipole moment). Since the vibrational frequencies and their intensities that are detected are sensitive to molecular conformation, the orientation of the monolayer can be extracted. On the basis of the selection rules for infrared spectroscopy, an infrared-active mode is characterized by its dipole moments which project a non-zero angle from the surface normal as a result of bond vibrations parallel to the surface. However, contrary to the conventional infrared technique, IRRAS allows a direct measurement at the air/water interface and advantageously, any disturbance of the monolayer can be avoided (non-invasive method). The experimental setup (Figure 64) comprises a compartmentalized trough containing a common subphase: the reference trough, which is
monolayer-free, and the sample trough, where the air/water interface is covered by a monolayer. The differential spectrum of both surfaces contains characteristic absorption bands that are due to the film. The use of \( p \)-polarized or \( s \)-polarized light\(^{xi} \) and different angle of incident light allows to determine the orientation and presence of functional groups within the film.

![Diagram of IRRAS setup](image)

**Figure 64:** Schematic representation\(^{112} \) of the IRRAS-setup. A shuttling mechanism allows either the reference or the sample trough to move into the IR spot. Subtracting the reference from the sample spectrum yields the differential spectrum that displays the characteristic absorption bands of the monolayer. The angle of the incident light is given by \( \phi \).

To probe a monolayer of \( 27a \) by means of IRRAS, the monolayer formation and irradiation process were done under the same conditions as previously described. A non UV-light treated and UV-light treated monolayer of \( 27a \) were examined both by \( p \)- and \( s \)-polarized light and various angles of incident. It was an objective of this measurement to arrive at a conclusion whether anthracene dimers were formed at the air/water interface. It was expected to obtain similar spectra like the ones for dimers synthesized in solution. These spectra showed characteristic signals for the newly formed bridgeheads at around 1454 and 1474 cm\(^{-1} \) though

\(^{xi} \) \( p \)-polarized light: light parallel orientated to the wave's direction of travel, \( s \)-polarized light: light perpendicular orientated to the wave's direction of travel (from senkrecht, German for perpendicular)
the precise position differed by a few units in wavenumber depending on the anthracene substitution pattern.

The structure of the collected spectra (Figure 65) for 27a was strongly depended on the polarization and the angle of incident. The use of \( p \)-polarized light and incident angles between 60° and 65° revealed the most information-rich spectra. However, the obtained spectra were very complex and not easily comparable to the ones obtained in bulk. Comparison to literature confirmed the observation that the intensity and presence of absorption bands vary according to the IR-spectroscopic method (measurement done in bulk or at an interface) which was used.\(^{113,114}\) Accordingly, signals which appear for a sample applied to a measurement in a KBr tablet do not necessarily emerge in a spectrum recorded for a system at the interface. The dimerization of anthracene at the interface was concluded from the absorption signals at 1455 cm\(^{-1}\) (2) and 1475 cm\(^{-1}\) (1) which evidently became visible for \( p \)-polarized light at 60°. These data were in very good agreement to previous measurements in bulk. An absorption band at 1600 cm\(^{-1}\) (3) which was assigned as ring breathing mode of the benzene units was also clearly visible. This was in accordance to the IR spectrum of 21 in which a structurally less defined absorption band at 1600 cm\(^{-1}\) was also observed. Since only for 21, presumably an ill-defined network, this absorption band was noticed, inter- and intramolecular dimerization was concluded. In comparison to literature, the photochemical switching of 10-thiodecyl 2-anthryl ether self-assembled on gold was investigated by IR-spectroscopy\(^ {114}\) and an absorption band at 1592 cm\(^{-1}\) after irradiation emerged. It was observed that the disappearance of this band after the back reaction was induced and the repeated appearance under dimerization conditions. Therefore, it was deduced from these findings that the successful dimerization of the anthracenes occurred. The band was assigned as aryl carbon-carbon stretch mode. The emergence of band (3) in our system (Figure 65) was in fair agreement with the data found for anthracene on gold. Interestingly, the characteristic bridgeheads of the dimer of 10-thiodecyl 2-anthryl ether were not observed for the self-assembled system and a comparable measurement in KBr tablet was not provided.
Results and Discussion

Figure 65: IRRAS-spectra of 27a at the air/water interface. The red lines represent a monolayer before irradiated and the blue lines after afterwards. Spectra shown here were obtained using p-polarized light.

At 60° of p-polarized light, an absorption band at 1670 cm⁻¹ (4) became also visible which was never observed for defined dimers measured in KBr (Chapter 5.1.2). Therefore, it is questionable whether exclusively intermolecular dimerization took place or whether the detectability of this band is caused by the orientation within the monolayer and the different method which was used.

Further measurements at higher angles of incident light (65° and 70°) revealed less pronounced bridgeheads (1) and (2) which were clearly detectable at 60°. At 65° the bridgeheads emerged as one absorption band (5) whereas at 70° this band disappeared almost completely. A similar observation was made for the absorption band at 1600 cm⁻¹. At 70° only the absorption band at 1670 cm⁻¹ (8) was visible. The absorption band at 1670cm⁻¹ cannot easily be related to a corresponding structure element present in 27a and the dimer of 27a, respectively. According to commonly used tables for IR-spectroscopy, this region corresponds to a carbonyl vibration. Here, the discussion about endoperoxide formation due to the addition
of singlet oxygen arose again. To approach the question whether endoperoxide formation occurs at the interface, the IRRAS setup was modified manually. A gentle nitrogen flow applied closed to the trough to cover the surface and degassed water was used. The nitrogen flow, even employed very carefully, distorted the smoothness of the interface so that the whole spectrum was less pronounced. Unfortunately, a secured conclusion was not possible, since the observed band intensities were of less informative value due to the signal to noise ration. In order to gain reliable data the setup would require substantial technical modifications.

For comparison, pure 1,8-dichloro anthraquinone was probed with conventional IR-spectroscopy (Figure 66) to locate the carbonyl stretch vibration. The carbonyl stretch was found to be at 1676 cm\(^{-1}\) which was the most intensive band in the whole spectrum.

![Figure 66: IR spectrum of 1,8-dichloro anthraquinone measured in KBr tablet. The most intense absorption band at 1676 cm\(^{-1}\) could be assigned as carbonyl stretch vibration.](image)

Summarizing, the appearance of the spectra obtained in bulk and at the interface differed significantly from each other. A straightforward comparison of absorption bands was not possible. However, the most characteristic absorption bands at 1454 cm\(^{-1}\) and 1474 cm\(^{-1}\) which are indicative of anthracene dimerization were found in bulk and also at the interface. Hence, dimerization of anthracene occurred under the conditions applied. The appearance of the absorption band at 1670 cm\(^{-1}\) which was never observed for dimers furnished in solution,
irrespective of the presence or absence of oxygen. The assignment of this absorption band could not be done yet.

5.3 Concluding remarks

The multi-step synthesis of the monomers 27a and 27b bearing four connective units was accomplished using the calix[4]arene skeleton. The intensive yellowed coloured monomers could be synthesized repeatedly in a multigram scale. Monomer 27a showed superior interfacial behavior and was therefore selected for a detailed study. BAM micrographs of the monolayer out of 27a appeared perfectly homogenous and its formation upon compression and decompression in a Langmuir-Blodgett experiment was repetitively observed. The composition and orientation of a non-irradiated monolayer of 27a was successfully determined by XPS. On the basis of these results the irradiation upon UV-light of the monolayer was reasonable. Covalent connection of 27a within a monolayer after UV-light irradiation was proven by mechanical experiments and transferred onto different solid substrates. In particular, the irradiated monolayer transferred onto a Cu-grid became visible in an optical microscope. The covalently connected monomers were able to over span the holes sized 2025 μm² of the Cu-grid. The thickness of the non-irradiated and the irradiated monolayer of 27a was in accordance with the theoretical expected value of about 24 Å. IRRAS revealed the typical signals for the newly formed bridgeheads upon anthracene dimerization at 1455 cm⁻¹ and 1475 cm⁻¹. These characteristic signals are in conformity with results obtained for dimers formed in solutions as well as examples reported in literature.
6 Outlook

This first approach towards 2D polymers provided tree- and tetra-functional monomers bearing anthracenes as connective units. These monomers were utilized for monolayer formation at the air/water interface in a so-called Langmuir-Blodgett experiment. The monolayer formation could be reliably controlled since the Langmuir-Blodgett technique is well established. The ordered monolayer was then polymerized upon UV-light irradiation. Suitable monomer designs and analytic methods could be evaluated by this first approach and obstacles were disclosed related to these issues.

To further develop the interfacial approach towards 2D polymer, improvements on

- monomer design,
- analytic methods,
- and Langmuir-Blodgett setup

are conceivable.

As said before, monomers with a high degree of symmetry and rigidity are of high interest. The cartoon-like structures in Figure 67 match these requirements.

![Figure 67: a) Schematic representation of a monomer having three anthracenes acting as connective units. The coloured symbols represent different functionalities which ensure amphiphilicity. b-d) Cartoon-like examples how rigid monomers could be equipped to ensure amphiphilicity to apply them at the interface.](image-url)
These structure are grounded on a rigid core which is able to covalently connect three 1,8-disubstituted anthracene derivates. The number of possible cores is limited. Ideally, the core is directly connected to the anthracene to reduce the molecule’s flexibility. In addition, the connection chemistry core-anthracene should be high yielding since the ring closure is less favored due to the loss of entropy.

Triethynylmethanol 28 (Figure 68) seems a potential core for a rigid three-functional monomer.115 Precursor 28 and 1,8-diidoanthracene 29 applied to a Suzuki-Miyaura cross-coupling reaction could possibly lead to the monomer 30 which could be further functionalized by the attachment of a hydrophobic or hydrophilic group, respectively onto the hydroxyl groups.116 The accessibility of 28 and 29 involves a multi-step synthesis. However, the cyclization of the precursors has to be regarded as challenge since, as said before, the entropy will be reduced. During the ring closure, linear structures are also possible and thus, leading to low yields of cycle 30. Notable synthetic efforts would be necessary to generate monomers based on 30. Thus, the development of efficient synthesis strategies to furnish monomers high in symmetry would be noteworthy because intramolecular anthracene dimerizations could be excluded. Furthermore, these monomers could be even applied to dimerization experiments in solution. These monomers polymerized through the interfacial approach and the flask-type approach could be directly compared.

Experiments at the interface based on the non-irradiated and also on the irradiated monolayer of 27a allowed to study the applicability of available analytic methods. It became evident that, for example, XPS- and IRRAS-data could not be easily interpreted for such an organic sheet.
of a thickness corresponding to the monomer’s height. Measurements at different conditions and providing suitable model systems are necessary to further evaluate these analytic methods and the results obtained from them. Beside spectroscopic methods, it seems promising to further develop microscopic methods, e.g. electron or atomic force microscopy in order to prove the periodicity of the covalently connected monolayer. Based on transferred monolayers of 27a, it seems reasonable to take drying of the film due to the ethylene oxide chains which are hydrophilic into account. Therefore, AFM of a wet sample might be mandatory to ensure a thin film without cracks resulting from drying. The improvements of the analytic methods clearly require the collaboration with experts in the corresponding fields.

The Langmuir-Blodgett setup could be modified in such a way that completely inert conditions can be assumed. This change of experimental setup would exclude the discussion of peroxide formation during UV-irradiation. Additionally, it would be helpful to implement into the Langmuir-Blodgett setup a spectroscopic method, e.g. UV-Vis spectroscopy from which the yield of dimerization can be concluded directly.

This first approach towards 2D polymers disclosed the obstacle towards the synthesis and analytics for such a polymer. Even though this project is at the beginning the first results of this highly complex endeavor is very motivating, stimulating and exciting!
7 Experimental Section

7.1 General

7.1.1 Instrumentation

Elemental analyses

The elemental analyses were performed on a Leco CHN-900 or Leco CHNS-932 instrument.

Melting points

The melting points were measured in open capillaries on a Büchi B-540 instrument and were uncorrected.

Mass spectra

EI-, MALDI-FT-MS and MALDI-TOF-MS spectra were measured on Micromass Autospec, Finnigan TSQ 7000, Ionspec Ultima FT-ICR and Kratos Maldi 3, respectively. 3-Hydroxypicolinic acid (3-HPA), DCTB-mix (trans-2-[3-(4-tert-butylphenyl)-2-methprop-2-enylidene]malononitrile were used as matrices for MALDI-FT- and MALDI-TOF-MS.

NMR spectra

$^1$H- and $^{13}$C-NMR spectra were recorded on Bruker Avance 300 MHz at room temperature in the indicated deuterated solvents, which were purchased from Merck or Deutero GmbH. Chemical shifts ($\delta$) of $^1$H- and $^{13}$C-NMR spectra are given in ppm, and coupling constants are ($J$) are in Hz. The resonance multiplicities in the $^1$H-NMR spectra are described as s (singlet), d (doublet), t (triplet) and m (multiplet). Broad resonances are indicated by br.

UV-Vis absorption spectra

UV-Vis spectra were recorded on Perkin Elmer UV/Vis Lambda 20 spectrometer.

FT-IR spectra

FT-IR measurements were performed on Bruker Vector 22 instrument in KBr pellets.

IRRAS spectra

Spectra were acquired with an IFS 66 FT-IR spectrometer from Bruker (Ettlingen, Germany) equipped with an external reflectance unit containing a Langmuir trough setup. The infrared
beam is directed through the external port of the spectrometer and is subsequently reflected by three mirrors in a rigid mount before being focused on the water surface. A KRS-5 wire grid polarizer placed into the optical path directly before the beam hits the water surface. The reflected light collected at the same angle as the angle of incidence. The light then follows an equivalent mirror path and is directed onto a narrow band mercury-cadmium-telluride detector, which is cooled by liquid nitrogen. The entire experimental setup is enclosed to reduce relative humidity fluctuations. The entire experimental setup is enclosed to reduce relative humidity fluctuations.

**Langmuir-Blodgett technique**

Monolayers were prepared by spreading an aliquot of a solution (1 mg/mL in CHCl₃; spectroscopy grade solvents) on Millipore water of pH 7 on a mini Langmuir–Blodgett trough (total area 242 cm²) from KSV, Finland, placed on an anti-vibration table in a dust-reduced environment (no clean-room). After spreading, the solvent was allowed to evaporate for 5 min, followed by compression of the film at 10 mm/min. The surface pressure of the monolayers was measured at a precision of ±0.01 mN/m with a Wilhelmy plate (chromatography paper, ashless Whatman Chr 1) on an electrobalance. Monolayers were compressed at 22 °C.

**Brewster Angle Microscopy**

Monolayer morphology was visualized with a BAM2plus Brewster angle microscope (Nanofilm, Germany), with a 50 mW laser at the wavelength of 532 nm. With a 10× Nikon long-distance objective, the microscope has a resolution of 2 μm; recorded images correspond to 430 μm in width.

**Optical Microscopy**

Optical Microscopy experiments were carried out on a *Leica DM-RP*. 
Ellipsometry

The dry thicknesses of the films were determined by variable angle spectroscopic ellipsometry (VASE, M-2000F, L.O.T. Oriel GmbH, Germany). Measurements were conducted under ambient conditions at three angles of incidence (65°, 70°, and 75°) in the spectral range of 370–995 nm. Measurements were fitted with the WVASE32 analysis software using a three-layer model for an organic layer on a silicon substrate.

Irradiation and Transfer of Monolayers

An UV 250 Watt lamp fitted with a Gallium bulb from UV Light Technology was placed over the trough with a distance of 20 cm. Time of irradiation was 30 minutes. During irradiation the whole setup was purged with a gentle stream of nitrogen. Langmuir-Blodgett and Langmuir-Schaefer-transfer were done according to the protocol. For the Schaefer-transfer a Cu-grid purchased from Plano with a pitch of 45 μm was used.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectra were acquired using a PHI 5700 (Physical Electronics Inc., Eden Prairie, MN) from uncoated film surfaces. The residual pressure during the analysis was 10-7 Pa. The measurements were carried out using a Mg KR (1253.6 eV) radiation source run at 400 W. All the spectra were obtained in digital mode. The lens system was OMNIFOCUS IV and the spectrometer was run in the minimum area mode, defining an analyzed spot size of 0.4 mm in diameter. Constant pass energy of 23.5 eV through the hemispheres of the electron analyzer, operated in the fixed analyzer transmission (FAT) mode, was used for the narrow-scan of O1s, C1s, N1s, Si2s, and Si2p. The wide-scan spectra were acquired with a pass energy of 117.4 eV. The instrument was calibrated using the inert-gas-ion-sputtercleaned reference materials SCAA90 of Cu, Ag, and Au. The accuracy of the binding energy values was found to be (0.05 eV. Sample charging was corrected by referring all binding energies to the carbon 1s signal at 285.0 eV. Angle-resolved XPS measurements were carried out at 28° and 69.8° takeoff angles relative to the sample surface.
Contact Angle measurements

Contact Angle measurements were carried out by means of a Ramé-hart, Inc. NRL C.A. Goniometer (Model No 100-00-230). All reported values are the average contact angles at 3 different spots per sample determined by sessile drop technique.

7.1.2 Chromatography

Analytical Thin Layer Chromatography (TLC)

Reactions were monitored by TLC using TLC silica coated aluminium sheets Alugram by Macherey-Nagel (SIL-G/UV254). The compounds were visualized by 254 or 366 nm UV light.

Column chromatography

Column chromatography purifications were done with silica gel, BIO-RAD Bio-Beads S-X1 [200–400 mesh] or preparative recycling GPC (Japan Analytical Industry Co. Ltd., LC 9101) equipped with a pump (Hitachi l-7110, flow rate 3.5 mL/min), a degasser (GASTORR-702), a RI detector (Jai RI-7), a UV detector (Jai UV-3702, λ = 254 nm), and two columns (Jaigel 2H and 2.5H, 20x600 mm for each) using chloroform as eluent at room temperature.

7.1.3 Materials and solvents

Compounds 1, 5, 7, 13, 22 terephthalic acid monomethylester, anthracene-9-carbaldehyde, and 1,8-dichloro anthraquinone were purchased from Aldrich, Fluka or Acros. Compounds 2–4[69], 8–10[117], 15a[118], 23[119], and 24, anti-dim 24, syn-dim 24[81], 25a[105], and 25b[120] were prepared according literature procedures. Dry solvents, such as diethylether, tetrahydrofuran were distilled from sodium and benzophenone. Dry dichloromethane was distilled over calcium hydride. All syntheses with dry solvents were carried out under inert conditions. Water purified by a Millipore system was used.
7.2 Synthesis

7.2.1 General Procedures

General procedure for the dimerization of anthracene derivatives

The compound was dissolved in dichloromethane and then the solution was degassed. The degassed solution was irradiated with UV-light for 12 h. Then the solvent was removed under reduced pressure and subjected to the preparative GPC purification.

General procedure for esterification

Alcohol (1.45 equiv) and DPTS (1.45 equiv) were added to a solution of acid (1 equiv) in a mixture of dry CH₂Cl₂ and dry DMF at room temperature. After 15 min EDC (1.45 equiv) was added and the mixture was stirred at room temperature overnight. The reaction mixture was diluted with CH₂Cl₂ and washed twice with brine. The organic layer was separated and dried over MgSO₄. The solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography or GPC.

7.2.2 Procedures

**Compound 6.** 9-anthracene carboxylic acid 5 (2.75 g, 12.37 mmol) and 3-amino-2,2-bis(aminomethyl)propan-1-ol trihydrochloride 4 (1.00 g, 4.1 mmol) were dissolved in a mixture of dry CH₂Cl₂ (120 mL), dry DMF (40 mL), and diisopropylethylamine (7.75 g, 60 mmol). The reaction mixture was cooled to 0°C before PyBop (6.76 g, 13 mmol) was added. The cooling bath was removed and the mixture was stirred overnight at room temperature. The solution was diluted with CH₂Cl₂ (300 mL), washed twice with 1 M HCl, and once with brine. The combined organic phases were dried over MgSO₄ and then the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (1:1 hexane/EtOAc) affording 1.51 g (49%) of the product as a yellowish solid.

\[ R_f = 0.46 \text{ (1:1 hexane/EtOAc).} \]
m.p. 248 °C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 3.61$ (d, 6 H, $^3$J$_{H,H} = 6.00$ Hz, CHNH), $3.79$ (d, 2 H, $^3$J$_{H,H} = 6.6$ Hz, CH$_2$OH), $5.05$ (t, 1 H, $^3$J$_{H,H} = 7.05$ Hz, CHO$H$), $7.48$ (t, 6 H, $^3$J$_{H,H} = 7.5$ Hz, Ar$H$), $7.57$ (t, 6 H, $^3$J$_{H,H} = 7.5$ Hz, Ar$H$), $7.97$ (d, 6 H, $^3$J$_{H,H} = 8.4$ Hz, Ar$H$), $8.04$ (d, 6 H, $^3$J$_{H,H} = 8.7$ Hz, Ar$H$), $8.07$ (br, 3 H, CHNH), $8.41$ (s, 1 H, Ar$H$) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 40.08$, $46.96$, $61.09$, $124.61$, $125.41$, $126.95$, $128.08$, $128.79$, $128.87$, $130.67$, $131.02$, $171.76$ ppm.

MS (MALDI-FT, 3-HPA): $m/z$ (%) = 745.2911 [M + H]$^+$, calcd monoisotopic peak ($^{12}$C$_{50}$$^{1}$H$_{39}$$^{14}$N$_{3}$$^{16}$O$_{4}$) 745.2941.

Elemental analysis calcd (%) for C$_{50}$H$_{39}$N$_{3}$O$_{4}$ (745.86): C 80.52, H 5.27, N 5.63; found C 80.67, H 5.29, N 5.66.

**Compound 11.** Compound 10 (2.3 g, 5.18 mmol) and terephthalic acid monomethylester (934 mg, 5.18 mmol) were dissolved in a mixture of dry CH$_2$Cl$_2$ (20 ml), dry DMF (10 ml), and diisopropylethylamine (DIEA, 3.8 ml, 21.8 mmol). The reaction mixture was cooled to 0°C before PyBop (2.84 g, 5.45 mmol) was added. The cooling bath was removed and the mixture was stirred overnight. The solution was diluted with CH$_2$Cl$_2$, washed twice with 1 M HCl, and once with brine. The combined organic phases were dried over MgSO$_4$, filtered and concentrated to dryness. The crude product was purified by column chromatography (10:1 hexane/EtOAc then 3:1 hexane/EtOAc) and afforded 732 mg (52%) of product as colorless oil.

$R_f = 0.44$ (3:1 hexane/EtOAc).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 3.97$ (s, 3 H, CH$_3$), $3.99$ (s, 6H, CCH$_2$), $4.55$ (s, 6H, OCH$_2$Ph), $6.57$ (s, 1H, NH$)$, $7.26 - 7.35$ (m, 15H, Ar$H$), $7.75$ (d, 2 H, $^3$J$_{H,H} = 8.4$ Hz, Ar$H$), $8.04$ (d, 2H, Ar$H$) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 52.35$, $60.39$, $69.01$, $73.45$, $126.97$, $127.6$, $127.66$, $128.38$, $129.75$, $132.48$, $138.19$, $139.39$, $166.37$, $166.49$ ppm.
MS (MALDI-FT, 3-HPA): m/z (%) = 576.2351 [M + Na]+, calcd monoisotopic peak ($^{12}$C$_{34}$H$_{35}$N$_{16}$O$_6$Na) 576.2356.


**Compound 12.** Ester 11 (530 mg, 0.957 mmol) was dissolved in a mixture of THF/MeOH/KOH (aqueous solution, 1M) (10 ml: 10 ml: 10 ml). Additionally, solid KOH (336 mg, 6 mmol) was added. The mixture was refluxed at 100°C for 12 h. The solvent was removed under reduced pressure. The residue was dissolved in water. Precipitation was achieved by adding concentrated HCl (37 %). The solid was separated and dissolved in acetone. The solution was dried over MgSO$_4$ and the solvent removed *in vacuo*. 494 mg (96 %) of 12 as colorless solid were obtained.

$R_f = 0.27$ (1:20 MeOH/DCM).

mp 187 °C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 3.35$ (br, 1H, COO$H$), 3.88 (s, 6H, CCH$_2$), 4.38 (s, 6H, OCH$_2$Ph), 6.74 (s, 1H, NH), 7.14 (br, 15H, Ar$H$), 7.43 (d, 2H, $^3$J$_{H,H} = 8.1$ Hz Ar$H$), 7.74 (d, 2H, $^3$J$_{H,H} = 8.1$ Hz Ar$H$) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 60.46, 68.89, 73.25, 126.54, 127.51, 128.27, 129.12, 136.54, 138.17, 140.45, 167.97, 172.74$ ppm.

MS (MALDI-FT, 3-HPA): m/z (%) = 576.2198 [M + Na]$^+$, calcd monoisotopic peak ($^{12}$C$_{33}$H$_{33}$N$_{16}$O$_6$Na) 562.2200.

Elemental analysis calcd (%) for C: 70.45, H: 5.91, N: 2.49, found C: 70.57 H: 6.01 N: 2.57.
Compound 14. In a thoroughly dried flask, NaH (190 mg, 60% dispersion in mineral oil, 8 mmol) was mixed with THF (15 mL) in an inert atmosphere, and degassed in three freeze-pump-thaw cycles. 2,5,8,11,15,18,21,24-Octaoxapentacosan-13-ol (0.77 g, 2 mmol) was added, forming a slight yellow suspension, and the mixture was let stirred for 15 min before 4-(bromomethyl)benzoic acid (0.48 g, 2.2 mmol) was added. The whole mixture was let stirring overnight. The reaction was worked up by concentrating and filtered through a short plug of silica gel by washing with MeOH/DCM (1:10). The combined filtrate was further purified by column chromatography (silica gel, 1:30 MeOH/DCM to 1:10 MeOH/DCM). 0.77 g (74%) of pure product was obtained as a colorless liquid.

$^1$H NMR (300 MHz, MeOD): $\delta = 3.35$ (s, 6H, OCH$_3$), 3.53 (m, 4H, (CH$_2$)$_2$CH), 3.67-3.61 (m, 24H, CH), 3.78 (m, 1H, CH), 4.79 (s, 2H, CH$_2$Ph), 7.52 (m, 2H, ArH), 8.02 (m, 2H, ArH) ppm.

$^{13}$C NMR (75 MHz, MeOD): $\delta = 60.0$, 72.1, 72.3, 72.6, 73.1, 73.2, 73.7, 79.7, 129.3, 131.6, 132.1, 146.4, 170.7 ppm.

MS (EI): m/z (%) = 518.2727 [M]$^+$ calcd for C$_{25}$H$_{42}$O$_{11}$: 518.2723.

Elemental analysis calcd (%) for C$_{25}$H$_{42}$O$_{11}$ (518.59): C 57.90, H 8.16; found C 58.01, H 8.28.
Compound 15b. Ester 15a (700 mg, 1.124 mmol) was dissolved in a mixture of THF (8 mL), MeOH (8 mL), and 1M aqueous KOH (8 mL). Then solid KOH (756 mg, 13.5 mmol) was added. The mixture was refluxed at 100°C for 12 hrs. The solvent was removed under reduced pressure and the solid residue was dissolved in 40 mL of water. Addition of 5 mL of concentrated HCl to the solution caused precipitation of yellowish solid. The solid was filtered and then dissolved in acetone. The solution was dried over MgSO₄ and the solvent removed under reduced pressure affording 664 mg (97%) of 15b as yellowish oil.

¹H NMR (300 MHz, CDCl₃): δ = 3.33 (s, 9 H, OCH₃), 3.58 – 3.85 (m, 30 H, OCH₂), 4.14 – 4.23 (m, 6 H, OCH₂), 7.29 (s, 2 H, ArH) ppm.

¹³C NMR (75 MHz, CDCl₃): δ = 59.00, 68.90, 69.70, 70.30, 70.50, 70.70, 70.80, 71.90, 126.54, 127.51, 128.27, 109.60, 124.20, 143.21, 152.32, 170.43 ppm.

MS (MALDI-FT, 3-HPA): m/z (%) = 631.2944 [M + Na]⁺, calcd monoisotopic peak (¹²C₂₈H₄₈O₁₄Na) 631.2942.

Elemental analysis calcd (%) for C₂₈H₄₈O₁₄ (608.67): C 55.25, H 7.95; found C 55.43, H 8.04.

Compound 16a. 6 (609 mg, 0.817 mmol) and DPTS (240 mg, 0.817 mmol) were added to a solution of acid 12 (300 mg, 0.56 mmol) in a mixture of dry CH₂Cl₂ (25 mL) and dry DMF (5 mL) at room temperature. After 15 min EDC (157 mg, 0.817 mmol) was added and the mixture was stirred at room temperature overnight. The reaction mixture was diluted with CH₂Cl₂ and washed twice with brine. The organic layer was separated and dried over MgSO₄. The solvent was removed under reduced pressure. 227 mg (23%) of 16a as yellowish solid were collected after the preparative GPC separation. m.p. 148 °C.
Experimental Section

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 3.97$ (s, 6 H, $CH_2NH$), 4.01 (s, 6 H, $CH_2O$), 4.53 (s, 6 H, OCH$_2$Ph), 4.75 (s, 2 H, CCH$_2$), 6.23 (s, 1 H, NH), 7.25 - 7.31 (m, 15 H, ArH), 7.47 - 7.6 (m, 12 H, ArH), 7.69 (d, 2H, $^3J_{H,H} = 8.4$ Hz, ArH), 8.01 (br, 3 H, CONH), 8.04 (d, 6 H, $^3J_{H,H} = 8.1$ Hz, ArH), 8.15 (d, 6 H, $^3J_{H,H} = 6.9$ Hz, ArH), 8.25 (d, 2 H, $^3J_{H,H} = 8.1$ Hz, ArH), 8.52 (s, 3 H, ArH) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 39.84$, 45.81, 60.43, 63.60, 69.94, 73.43, 122.21, 123.77, 124.65, 125.50, 127.07, 127.21, 127.59, 128.18, 128.39, 128.83, 128.94, 130.35, 130.86, 131.17, 131.33, 137.55, 138.15, 166.32, 171.31 ppm.

MS (MALDI-FT, 3-HPA): m/z (%) = 1289.502 [M+Na]$^+$, calcd monoisotopic peak ($^{12}$C$_{83}$$^1$H$_{70}$$^{14}$N$_4$$^{16}$O$_9$Na) 1289.504.

Elemental analysis calcd (%) for C$_{83}$H$_{70}$N$_4$O$_9$ (1267.47): C 78.65, H 5.57, N 4.42; found C 78.73, H 5.61, N 4.45.

**Compound 16b.** The protected alcohol 16a (43.5 mg, 0.034 mmol) was dissolved in EtOH (5 mL) and EtOAc (3 mL) and Pd/C (40 mg, 10% Pd loading) was added. The mixture was placed in a Parr tube and stirred at room temperature under a hydrogen pressure of 3 bar overnight. The solution was filtered through celite and the solvent was removed under reduced pressure. The crude reaction mixture was subjected to the preparative GPC yielding 9.6 mg (28 %) of 16b as colorless oil.

m.p. 148 °C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 3.97$ (s, 6 H, $CH_2NH$), 4.00 (s, 6 H, $CH_2O$), 4.75 (s, 2 H, CCH$_2$), 6.23 (s, 1 H, NH), 7.47 - 7.6 (m, 12 H, ArH), 7.69 (d, 2H, $^3J_{H,H} = 8.4$ Hz, ArH), 8.01 (br, 3 H, CONH), 8.04 (d, 6 H, $^3J_{H,H} = 8.1$ Hz, ArH), 8.15 (d, 6 H, $^3J_{H,H} = 6.9$ Hz, ArH), 8.25 (d, 2 H, $^3J_{H,H} = 8.1$ Hz, ArH), 8.52 (s, 3 H, ArH) ppm.
$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 39.84, 45.81, 60.43, 63.60, 69.94, 122.21, 123.77, 124.65, 125.50, 127.07, 127.21, 128.18, 128.39, 128.94, 130.35, 130.86, 131.17, 131.33, 138.15, 166.32, 171.31$ ppm.

MS (MALDI-FT, 3-HPA): m/z (%) = 1019.3638 [M+Na]$^+$, calcd monoisotopic peak ($^{12}$C$_{62}^{1}$H$_{52}^{14}$N$_{4}^{16}$O$_{9}$Na) 1019.3632.
Compound 17. The preparation of the compound was carried out according to the general procedure for esterification. 6 (250 mg, 0.335 mmol), DPTS (116.7 mg, 0.4025 mmol), acid 13 (59.7 mg, 0.335 mmol), dry CH$_2$Cl$_2$ (15 mL), dry DMF (5 mL), EDC (77.16 mg, 0.4025 mmol) were used in the reaction. The crude product was purified by column chromatography on silica gel (1:1 hexane/EtOAc then 1:1 hexane/EtOAc then EtOAc) affording yellow solid with a yield 89.5 mg (29%).

\[ R_f = 0.3 \text{ (CH}_2\text{Cl}_2/\text{MeOH} 100:1). \]

m.p. 194 – 196 °C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 3.07$ (s, 3 H, CH$_3$), 3.26 (m, 3 H), 3.38 (m, 6 H), 3.54 (m, 3 H), 3.95 (d, 6 H, $^3$J$_{H-H} = 6.3$ Hz, CH$_2$NH), 4.24 (s, 2 H, COOCH$_2$O), 4.51 (s, 2 H, CCH$_2$O), 7.45 – 7.61 (m, 12 H, ArH), 7.99 (d, 6 H, $^3$J$_{H-H} = 8.4$ Hz, ArH), 8.11 (d, 6 H, $^3$J$_{H-H} = 8.7$ Hz, ArH), 8.15 (br, 3 H, NH) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 24.93$, 25.62, 58.59, 63.88, 68.9, 70.05, 70.58, 70.87, 71.60, 124.65, 125.49, 127.0, 128.13, 128.75, 131.02, 131.13, 170.9, 171.34 ppm.

MS (MALDI-FT, 3-HPA): m/z(%) = 906.3766 [M + H]$^+$, calcd monoisotopic peak ($^{12}$C$_{57}$H$_{52}$N$_3$O$_8$) 906.3754.

Elemental analysis calcd (%) for C$_{57}$H$_{51}$N$_3$O$_8$ (906.03): C 75.56, H 5.67, N 4.64; found C 75.68, H 5.75, N 4.66.
Compound 18. The preparation of the compound was carried out according to the general procedure for esterification. 6 (150 mg, 0.2 mmol), DPTS (59.1 mg, 0.2 mmol), acid 14 (69 mg, 0.134 mmol), dry CH2Cl2 (4 mL), dry DMF (1 mL), EDC (38.2 mg, 0.2 mmol) were used in the reaction. The crude product was subjected to preparative GPC yielding 89 mg (53%) of 18 as colorless oil.

1H NMR (300 MHz, CDCl3): δ = 3.97 (s, 6 H, CH2NH), 4.01 (s, 6 H, CH2O), 4.53 (s, 6 H, OCH2Ph), 4.75 (s, 2 H, CCH2), 6.23 (s, 1 H, NH), 7.25 - 7.31 (m, 15 H, ArH), 7.47 - 7.6 (m, 12 H, ArH), 7.69 (d, 2 H, JH-H = 8.4 Hz, ArH), 8.01 (br, 3 H, CONH), 8.04 (d, 6 H, JH-H = 8.1 Hz, ArH), 8.15 (d, 6 H, JH-H = 6.9 Hz, ArH), 8.25 (d, 2 H, JH-H = 8.1 Hz, ArH), 8.52 (s, 3 H, ArH) ppm.

13C NMR (75 MHz, CDCl3): δ = 29.70, 39.73, 58.95, 59.03, 70.46, 70.54, 70.59, 70.90, 71.32, 71.58, 71.87, 71.94, 78.39, 78.74, 96.12, 124.58, 125.47, 127.01, 127.39, 127.74, 128.17, 128.78, 128.84, 130.00, 130.26, 130.76, 171.26 ppm.

MS (MALDI-FT, 3-HPA): m/z (%) = 1246.567 [M + H]^+, calcd monoisotopic peak (12C75H8014N316O14) 1246.564.

Compound 19. The preparation of the compound was carried out according to the general procedure for esterification. 6 (150 mg, 0.2 mmol), DPTS (59.1 mg, 0.2 mmol), acid 15b (81.6 mg, 0.134 mmol), dry CH₂Cl₂ (4 mL), dry DMF (1 mL), EDC (38.2 mg, 0.2 mmol) were used in the reaction. The crude product was subjected to preparative GPC yielding 78.7 mg (44%) of 12 as colorless oil.

¹H NMR (300 MHz, CDCl₃): δ = 3.3 (s, 9 H, OCH₃), 3.36 (s, 6 H, CH₂NH), 3.81 – 3.36 (m, 24 H, OCH₂) 3.94 (d, 6 H, ³J₉H₂H = 4.3 Hz, PhOCH₂CH₂), 4.23 (t, 6 H, ³J₉H₂H = 4.3 Hz, PhOCH₂), 4.65 (s, 2 H, CCH₂), 7.47 - 7.6 (m, 18 H, ArH), 7.62 (s, 2 H, ArH), 8.04 (d, 6 H, ³J₉H₂H = 8.1 Hz, ArH, 3 H, NH), 8.15 (d, 2H, ³J₉H₂H = 8.7 Hz, ArH), 8.52 (s, 3 H, ArH) ppm.

¹³C NMR (75 MHz, CDCl₃): δ = 39.57, 45.94, 58.98, 62.46, 68.84, 69.52, 70.39, 70.54, 70.68, 71.83, 71.92, 72.4, 109.4, 123.67, 124.61, 125.5, 127.0, 128.16, 128.8, 131.18, 143.11, 152.53, 167.28, 171.12 ppm.

MS (MALDI-TOF, DCTB Mix 1:10): m/z = 1358.27 [M + Na]⁺, calcd monoisotopic peak (¹²C₇₈H₈₅N₃O₁₇Na) 1358.58.

Elemental analysis calcd (%) for C₇₈H₈₅N₃O₁₇ (1336.52): C 70.10, H 6.41, N 3.14; found C 70.24, H 6.48, N 3.20.
**Compound 20.** 6 (100 mg, 0.13 mmol) and anthracene (358 mg, 2.01 mmol) were dissolved in DCM (12.07 mL). After three freeze-thaw cycles the solution was irradiated with UV-light for 12 hours. Afterwards the solvent of the turbid mixture was removed *in vacuo*. The crude mixture was purified by column chromatography (3:1 hexane/EtOAc then 1:1 hexane/EtOAc) and yielded 78.3 mg (45 %) of 20 as colorless solid. 

R<sub>f</sub> = 0.32 (hexane/EtOAc 3:1).

m.p. 178 – 179 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 3.61 (d, 6 H, 3<sup>J</sup>HH = 6.3 Hz, CHNH), 3.54 (br, 2 H, CHO_H), 4.45 (d, 3 H, 3<sup>J</sup>HH = 10.81 Hz, CH<sub>bridge</sub>), 4.45 (br, 1 H, 3<sup>J</sup>HH = 10.81 Hz, OH), 4.67 (d, 3 H, 3<sup>J</sup>HH = 10.81 Hz, CH<sub>bridge</sub>), 5.58 (s, 3 H, CH<sub>bridge</sub>), 6.72 – 6.84 (m, 40 H, ArH), 6.9 – 6.96 (m, 14 H, ArH, NH), 7.03 – 7.0 (m, 6 H, ArH) ppm.

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 41.43, 46.86, 53.44, 53.99, 54.22, 62.28, 66.24, 125.37, 125.45, 127.57, 126.38, 126.77, 126.94, 127.07, 127.65, 127.91, 175.76 ppm.

MS (MALDI-FT, 3-HPA): m/z (%) = 1280.5347 [M + H]<sup>+</sup>, calcd monoisotopic peak (12C<sub>92</sub>1H<sub>70</sub>14N<sub>3</sub>16O<sub>4</sub>) 1280.5361.

**Compound 21.** 6 (100 mg, 0.13 mmol) was dissolved in DCM (12.07 mL). After three freeze-thaw cycles the solution was irradiated with UV-light for 12 hours. Afterwards the yellow precipitate which was insoluble in common organic solvents was filtered off.

<sup>13</sup>C CPMAS NMR (75 MHz): δ = 34 - 49, 50 - 58, 63 - 70, 120 - 134, 140 - 150, 168 – 180 ppm.
**Compound anti-dim 22.** 22 (221 mg, 1 mmol) was dissolved in DCM (1 mL) and applied to the general dimerization protocol. 296 mg (67%) of the *anti-dim 22* was obtained as yellowish solid.

m.p. 216 °C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 2.64$ (s, 6 H, CH$_3$), 3.75 (br, 2 H, CH$_{\text{bridge}}$), 3.78 (br, 4 H, CHNH), 6.86 – 6.92 (m, 8H), 7.07 (d, 4 H, $^3$$J_{\text{H-H}} = 4.5$ Hz, ArH) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 36.91$, 56.54, 56.69, 61.9, 125.41, 125.58, 127.53, 142.68, 143.43 (ArH) ppm.

MS (EI): m/z (%) = 221.1198 [M$^+$] calcd for C$_{16}$H$_{15}$N: 221.1204.

Elemental analysis calcd (%) for C$_{32}$H$_{30}$N$_2$: C 86.84, H 6.83, N 6.33; found C 86.91, H 6.88, N 6.35.

**Compound anti-dim 23.** The general dimerization protocol was applied to a solution of 23 (247 mg, 1 mmol) in dichloromethane (1 mL). 116 mg (47%) of *anti-dim 23* was obtained as yellowish solid.

m.p. 246 °C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 2.64$ (s, 6 H, CH$_3$), 3.75 (br, 2 H, CH$_{\text{bridge}}$), 3.78 (br, 4 H, CHNH), 6.82 - 6.91 (m, 8 H, ArH), 7.07 (d, 4 H, $^3$$J_{\text{H-H}} = 4.5$ Hz, ArH) ppm.

$^{13}$C (CDCl$_3$): $\delta = 45.98$, 51.47, 124.58, 125.45, 126.70, 127.05, 127.48, 132.45, 139.14, 144.66 ppm.

MS (EI): m/z (%) = 245.9995 [M$^+$], calcd for C$_{14}$H$_{8}$Cl$_2$: 246.0003.

Elemental analysis calcd (%) for C$_{28}$H$_{16}$Cl$_4$: C 68.04, H 3.26, Cl 28.69; found C 68.09, H 3.28, N 28.63.
Experimental Section

Single crystal X-ray analysis of the sample recrystallized from CDCl₃.

**Compound 26a.** To a solution of 25a (530 mg, 0.42 mmol) in dry MeOH (20 mL) anthracene-9-carbaldehyde (354 mg, 1.72 mmol) was added. The mixture was stirred at room temperature for 3 days. Then the solvent was removed in vacuo. Chromatographic purification (10:1 hexane/EtOAc/ 5% triethylamine then 1: 10 hexane/EtOAc/ 5% triethylamine) afforded 772 mg (92%) of 26a as yellow oil.

$R_f=0.35$ (CHCl₃/acetone 1:1).

$^1H$ NMR (300 MHz, CDCl₃): $\delta = 3.39$ (s, 12 H, CH₃), 3.53 (d, 4 H, $^3J_{HH} = 13.8$ Hz, ArCH₂Ar), 3.57 (t, 8H, $^3J_{HH} = 2.55$ Hz, CH₂), 3.67 – 3. 79 (m, 24H, OCH₂CH₂), 4.07 (t, 8 H, $^3J_{HH} = 4.95$ Hz, CH₂), 3.37 (t, 8 H, $^3J_{HH} = 5.1$ Hz, CH₂), 4.79 (d, 4 H, $^3J_{HH} = 13.2$ Hz, ArCH₂Ar), 7.06 – 7.2 (m, 18 H, ArH), 7.69 (d, 8 H, $^3J_{HH} = 8.1$ Hz, ArH), 8.05 (s, 4 H, ArH), 8.44 (d, 8 H, $^3J_{HH} = 8.7$ Hz, ArH), 9.36 (s, 4 H, CHNAr) ppm.

$^{13}C$ NMR (75 MHz, CDCl₃): 31.55, 59.04, 70.57, 70.69, 71.95, 73.45, 76.62, 120.97, 124.53, 124.76, 125.68, 125.86, 128.49, 130.02, 130.40, 130.67, 135.83, 148.07, 155.19, 158.60 ppm.

MS (MALDI-FT, 3-HPA): m/z (%) = 1997.957 [M + H]$^+$, calcd monoisotopic peak ($^{12}C_{124}^{1}H_{132}^{14}N_{4}^{16}O_{20}$) 1997.951.

Elemental analysis calcd (%) for C₁₂₄H₁₃₂N₄O₂₀ (1998.39): C 74.53, H 6.66, N 2.80; found C 74.73, H 6.75, N 2.88.
**Compound 26b.** Anthracene-9-carbaldehyde (3.52 g, 17.05 mmol) was added to a solution of 25b (3.5 g, 4.27 mmol) in dry MeOH (350 mL). The mixture was stirred at reflux overnight. Size exclusion column chromatography afforded 6.05 g (90 %) of 26b as orange solid.

m.p. 277 °C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 1.03$ (t, 12 H, $^3$J$_{H,H} = 6.6$ Hz, CH$_3$), 1.47 – 1.57 (m, 24 H, C$_H_2$), 2.1 – 2.13 (m, 8 H, OCH$_2$), 3.49 (d, 4 H, $^3$J$_{H,H} = 12.9$ Hz, ArCH$_2$Ar), 4.12 (t, 8 H, $^3$J$_{H,H} = 7.4$ Hz, OCH$_2$), 4.74 (d, 4 H, $^3$J$_{H,H} = 12.9$ Hz, ArCH$_2$Ar), 7.05 – 7.2 (m, 16 H, ArH), 7.7 (d, 8 H, $^3$J$_{H,H} = 8.1$ Hz, ArH), 8.06 (s, 4 H, ArH), 8.7 (d, 8 H, $^3$J$_{H,H} = 8.7$ Hz, ArH), 9.38 (s, 4 H, CHN) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$): 14.17, 22.96, 26.13, 30.43, 31.63, 32.30, 75.72, 120.93, 124.60, 124.74, 125.84, 126.79, 130.39, 130.69, 135.90, 147.74, 155.53, 158.41 ppm.

MS (MALDI-FT, 3-HPA) m/z(%) = 1573.841 [M + Na]$^+$, calcd monoisotopic peak ($^{12}$C$_{112}$H$_{110}$N$_4$O$_4$Na) 1573.845.

Elemental analysis calcd (%) for C$_{112}$H$_{110}$N$_4$O$_4$ (1576.10): C 89.35, H 7.03, N 3.55; found C 89.46, H 7.12, N 3.61.

**Compound 27a.** Sodium borohydride (9.3 mg, 0.25 mmol) was added to a solution of 26a (120 mg, 0.06 mmol) in MeOH (20 mL). The mixture was stirred at room temperature overnight. The excess of sodium borohydride was quenched by the slow addition of hydrochloric acid. The pH of the mixture was adjusted to 12 by addition of 1M NaOH and then extracted times with DCM (3 x 15 mL). The combined organic layers were washed with water, brine, and then dried over MgSO$_4$. The solvent was removed under reduced pressure. No further purification of 27a was necessary. Yellow oil; yield 118 mg (98 %).

$R_f = 0.21$ (CHCl$_3$/acetone 1:1).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 3.18$ (d, $^3$J$_{H,H} = 10.2$ Hz, 4 H, ArCH$_2$Ar), 3.39 (s, 12 H, CH$_3$) 3.59 – 3.56 (m, 40H, OCH$_2$), 3.68 – 3.76 (m, 8H, OCH$_2$CH$_2$),
Experimental Section

4.02 (br, 8 H, OCH₂), 4.21 (br, 8 H, OCH₂), 4.6 (d, 4 H, ³J_H,H = 14.2 Hz, ArCH₂Ar), 4.76 (br, 8 H, ArCH₂NH), 6.48 (s, 8 H, ArH), 6.92 (t, 8 H, ³J_H,H = 7.6 Hz, ArH), 7.13 (t, 8 H, ³J_H,H = 7.5 Hz, ArH), 7.67 (d, 8 H, ³J_H,H = 8.7 Hz, ArH), 7.8 (d, 8 H, ³J_H,H = 8.7 Hz, ArH), 8.06 (s, 4 H, ArH).

¹³C NMR (75 MHz, CDCl₃): δ = 31.6, 41.07, 59.04, 70.57, 70.69, 71.97, 73.16, 112.65, 113.20, 120.54, 120.94, 123.58, 124.56, 125.73, 126.66, 127.35, 128.67, 129.06, 129.31, 129.87, 130.33, 130.90, 131.36, 135.82, 143.45, 148.94 ppm.

MS (MALDI-FT, DCTB mix): m/z (%) = 2028.002 [M + Na]⁺, calcd monoisotopic peak (¹²C₁₂₄¹H₁₄₀¹⁴N₄¹⁶O₂₀Na) 2027.9959.

Elemental analysis calcd (%) for C₁₂₄H₁₄₀N₄O₂₀ (2006.45): C 74.36, H 7.03, N 2.79; found C 74.36, H 7.11, N 2.87.

Compound 27b. LiAlH₄ (9.3 mg, 0.25 mmol) was added to a solution of 26b (120 mg, 0.06 mmol) in THF (20 mL). The mixture was stirred at room temperature overnight. The excess of LiAlH₄ was quenched by the slow addition of water. Then 1M H₂SO₄ was added until the solution became homogeneous and the solution was extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with water and brine and then dried over MgSO₄. The solvent was removed under reduced pressure. Purification of 27b was carried out by means of preparative HPLC GPC. Yellow oil; yield 128 mg (79%).

¹H NMR (300 MHz, CDCl₃): δ = 1.01 (br, 12 H, CH₃), 1.48 (br, 24 H, CH₂), 2.05 (br, 8 H, OCH₂), 3.23 (d, 4 H, ³J_H,H = 14.2 Hz, ArCH₂Ar), 3.98 (t, 8 H, ³J_H,H = 7.4 Hz, OCH₂), 4.6 (d, 4 H, ³J_H,H = 14.2 Hz, ArCH₂Ar), 4.76 (br, 8 H, ArCH₂NH), 6.51 (s, 8 H, ArH), 6.92 (t, 8 H, ³J_H,H = 7.6 Hz, ArH), 7.13 (t, 8 H, ³J_H,H = 7.5 Hz, ArH), 7.67 (d, 8 H, ³J_H,H = 8.7 Hz, ArH), 7.8 (d, 8 H, ³J_H,H = 8.7 Hz, ArH), 8.06 (s, 4 H, ArH) ppm.

¹³C NMR (75 MHz, CDCl₃): δ = 14.17, 22.96, 26.13, 30.43, 31.63, 32.30, 41.13, 75.72, 112.04, 120.93, 124.60, 124.74, 125.84, 126.79, 130.69, 135.90, 147.74, 155.53 ppm.
MS (MALDI-FT, 3-HPA): m/z (%) = 1389.80 [M - C_{15}H_{12}+H]^+; calcd monoisotopic peak (^{12}C_{97}^{1}H_{106}^{14}N_{4}^{16}O_{4}) 1389.8136.

Elemental analysis calcd (%) for C_{112}H_{116}N_{4}O_{4} (1582.14): C 85.02, H 7.39, N 3.54; found C 85.08, H 7.42, N 3.56.

Elemental analysis calcd (%) for C_{92}H_{69}N_{3}O_{4} (1280.55): C 86.29, H 5.43, N 3.28; found C 86.42, H 5.63, N 3.31.
8 Literature


5 http://www.chemgapedia.de


16 http://ruby.chemie.uni-freiburg.de/Vorlesung/strukturchemie_2_2_5.html


33http://hcr3.isiknowledge.com/author.cgi?&link1=Search&link2=Search%20Results&AuthLastName=ringsdorf
&AuthFirstName=&AuthMiddleName=&AuthMailInstName=&CountryID=-1&DisciplineID=0&id=130


69 Quantum yield, Φ: number of defined events which occur per photon absorbed by the system; for photochemical reactions: (amount of reactant consumed or product formed) per (amount of photons absorbed) *IUPAC Compendium of Chemical Terminology*, **1997**, 2nd Edition.


93 http://www.ksvinc.com/LB.htm


95 http://www.ksvltd.com/content/index/keydeposition

97 http://www.ksvltd.com/content/index/BAM300


112 Picture taken from: http://phys.chemie.uni-halle.de/groups/blume/kerth/index.html#Externe%20Infrarot-Reflexions-Absorptions-Spektro


