Skolkovo Institute of Science and Technology

SULFONIMIDE-BASED DENDRIMERS: SYNTHESIS AND APPLICATION FOR SURFACE FUNCTIONALIZATION

Doctoral Thesis

by

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DOCTORAL PROGRAM IN MATERIALS SCIENCE AND ENGINEERING

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I hereby declare that the work presented in this thesis was carried out by myself at Skolkovo Institute of Science and Technology, Moscow, except where due acknowledgment is made and has not been submitted for any other degree.

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Abstract

Dendrimers are unique classes of polymeric macromolecules, composed of branched monomers, characterized by high monodispersity, good biocompatibility, multivalent surface, and the presence of internal cavities. Due to these beneficial features over recent years, dendrimers have been considered attractive materials by detecting and imaging agents, targeting components, or pharmaceutically active compounds. Such a variety of applications exists because the core, branching units, and surface of dendrimers can be created by a wide range of combinations of chemical groups and molecules, causing about fifty families of dendrimers. Despite the growing interest of scientists in these structures, there is still not enough preliminary information for dendrimers' actual use in real-life applications.

In the present work, I focused on one promising type of dendrimers with sulfonimide groups at each branching point. The synthesis of such structures is not so difficult but, at some stage, can be limited to the 4th generation species with considerable drops in yields at the last reaction step. In this work, an improved synthesis method, allowing a high-yield preparation of sulfonimide-based dendrimers via the divergent route, is developed. This route consists of repetitive synthetic steps of selected coupling reactions and allows avoiding the complicated process of purification and allows us for the first time to reach sulfonimide dendrimer up to 5th generation. Although a lot of work on the synthesis of dendrimers has already been done, there is still a large number of problems that must be solved, in particular, the reduction of the synthesis time and optimization of processes. Because of the dendrimer application's importance, one needs to use a powerful set of techniques for the dendrimer characterization to prove their chemical structure, composition, and molecular weight. Methods such as transmission electron microscopy (TEM), optical microscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and nuclear magnetic resonance (NMR) and mass spectrometry (MS) were used to characterize the obtained dendrimers.

In this work, I address the problem of creating a thin film from obtained sulfonimide-based dendrimers of different generations for further surface engineering. The most important for achieving a good hydrophobicity was forming the film made of 5th generation of sulfonimide dendrimer. The creation of a thin layer possessing well-defined repeating fragments at the nanoscale has been a challenge for chemists of various sub-disciplines. Although some success has been achieved, there is still not enough evidence of the existence of constructed dendrimer films that have a thickness of a monomer molecule. Based on the first successful results in making and characterizing synthesized dendrimer structures, I formulate a promising approach to this class of novel polymers. The approach is based on functionalized sulfonimide dendrimers with naphthyl terminal groups capable of forming stable films at the air-water interface with subsequent polymerization in the compressed state. The main advantages of the selected approach are (i) the opportunity to change properties of surfaces at the nanoscale via functionalization of dendrimers, (ii) the capability to transfer films onto a variety of solid substrates, (iii) the possibility of using various analytical tools to characterize the thin film (e.g., optical microscopy, ellipsometry, AFM, SEM and TEM studies), (iv) application such films as protective or sensing coatings.

Keywords: Sulfonimide-based dendrimers, branched-chain, divergent approach, thin films, 5th generation of sulfonimide dendrimer, Langmuir-Blodgett technique, contact angle.

List of Publications

This doctoral dissertation consists of a summary of the following publications:

(1) Bondareva, J.; Rozhkov, V.; Kachala, V. V.; Fetyukhin, V.; Lukin, O. An Optimized Divergent Synthesis of Sulfonimide-Based Dendrimers Achieving the Fifth Generation. Synth. Commun. 2019. https://doi.org/10.1080/00397911.2019.1676909.

(2) Kolotylo, M.; Holovatiuk, V.; Bondareva, J.; Lukin, O.; Rozhkov, V. Synthesis of Sulfonimide-Based Dendrimers and Dendrons Possessing Mixed 1 → 2 and 1 → 4 Branching Motifs. Tetrahedron Lett. 2019, 60 (4). https://doi.org/10.1016/j.tetlet.2018.12.052.

(3) Bondareva, J.; Kolotylo, M.; Rozhkov, V.; Burilov, V.; Lukin, O. A Convergent Approach to Sulfonimide-Based Dendrimers and Dendrons. Tetrahedron Lett. 2020, 152011. https://doi.org/10.1016/j.tetlet.2020.152011.

(4) Bondareva, J.; Luchkin, S.; Dagesyan, S.; Egorov, A.; Evlashin, S.; Lukin, O. Covalent and Noncovalent Films Made up of Sulfonimide-Based Dendrimers. Appl. Surf. Sci. 2020, 146345. https://doi.org/10.1016/j.apsusc.2020.146345.

(5) Bondareva, Julia; Evlashin, Stanislav; Lukin, Oleg. "Sulfonimide-based Dendrimers: Progress in Synthesis, Characterization, and Potential Applications." Polymer Reviews on August 28, 2020

Author's contribution

(1) The author was responsible for performing synthesis procedures to obtain superbranched sulfonyl chloride dendrimer. The same synthetic strategies (coupling and reduction) were used in the present study to prepare the 2nd generation of sulfonimide dendrimer. The author was also responsible for co-writing the manuscript.

(2) The author is mainly responsible for the work. The author was responsible for conducting the experimental work, which leads to the final product and NMR data analysis. Co-authors conducted mass spectrometry analysis. The author was responsible for co-writing the manuscript.

(3) The author was responsible for conducting experiments of convergent synthesis of 2nd and 3rd generation sulfonimide chloride derivatives decorated with naphthyl terminal groups.

(4) The author is mainly responsible for the work. The author conceived and conducted the experiments apart from the SEM and AFM experiments, which were conducted by co-authors. The author was responsible for writing and submitting the manuscript.

(5) The author is mainly responsible for collection and analysis of information in the literature. The author was responsible for writing and submitting the manuscript.

List of Conferences

(1) Gen-Y Young Scientists Cross-Disciplinary Conference, Sochi, Russia, 27 September – 1 October 2017. Poster Title: Synthetic analogs of graphene made of dendrimers.

(2) 3rd annual Skoltech-MIT Conference on “Collaborative Solutions for Next Generation Education, Science and Technology” Moscow, Russia October 15-16, 2018. Poster Title: Sulfonimide-based dendrimers: synthesis and application for surface engineering.

(3) V International Russian-Kazakhstan Conference "Chemical Technology of Functional Materials," Novosibirsk, Russia, 16-18 May 2019. Poster Title: Covalent and noncovalent films made up of sulfonimide – based dendrimers for surface engineering.

(4) XXVII Internatioanal Scientific Conference of Students, Postgraduates and Young Scientists "Lomonosov," Moscow, Russia, planned in October 2020. Poster Title: Synthetic analogues of graphene made of dendrimers for surface coatings.

(5) Bilateral Conference on Functional Materials (BiC-FM) Finland-Russia, October, 8-9, 2020. Flash oral presentation: Naphthyl - functionalized dendrimers can regulate surface properties of materials.

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No one has been more important to me in the implementation of this project than the members of my family. I am incredibly grateful to my parents, Elena and Vladimir, for their love, caring, understanding, kind attitude to life, and continuing support to complete this research work.

Table of Contents

List of Symbols, Abbreviations

AcOH - acetic acid

AFM - atomic force microscopy

BAM - brewster angle microscope

CH_2Cl_2 - dichloromethane

DMF - dimethylformamide

EtOH - ethanol

G - generation

N_2H_4 - hydrazine

Fe - iron

$FeCl_3$-C - iron (III) chloride - carbon

HCl - hydrochloric acid

LB film – Langmuir - Blodgett film

NMR - nuclear magnetic resonance

PAMAM - polyamidoamine

PDI - polydispersity index

PEO - polyethylene oxide

PDMA - poly (N,N-dimethylacrylamide)

POPAM - poly (propylene amine)

PPI - poly (propylene imine)

K_2CO_3 - potassium carbonate

RMS - root mean square

SEM - scanning electron microscopy

3D - three-dimensional

$SnCl_2*2H_2O$ - tin (II) chloride dihydrate

TGA - thermogravimetric analysis

TEM - transmission electron microscopy

TLC - thin-layer chromatography

Et_3N - triethylamine

2D - two-dimensional

UV - ultraviolet

Zn - zinc

GO - graphene oxide

rGO - reduced graphene oxide

Chapter 1. Introduction

1.1 Research Background and Motivation

The quality of human life directly depends on the development of organic synthesis and the industry based on it. We need new drugs with a different spectrum of action, new monomer units for the production of plastics, fibers, and many others. We need more and more chemical compounds with useful properties. This variety of chemical structures lies in the synthesis of molecules that ensure the creation of new substances and materials that a person needs. Available chemical knowledge is often insufficient to arrive at the well-designed target structure. This fact prompts chemists to develop new chemical reactions and optimize the condition of already existed ones. Problems associated with structural analysis of the new chemical species drive, in turn, develop both experimental techniques and computational methods. In the era of multidisciplinary science, the synthesis of a new, previously unknown substance is no scientific interest; therefore, chemists are thinking ahead about the potential application of their synthesized structures. One of the exciting applications of organic molecules, in my opinion, is surface engineering.

Surface functionalization by its modification using chemical compounds has been known for many years, always aiming at improving specific responses of material when interacting with its environment. However, the creation of thin monolayer networks possessing well-defined repeating fragments, mechanically stable enough to cover the surface of materials with the nanometer scale's thickness, has been a challenge for chemists. The reason to consider films a few nanometers thick is the capability of imparting outstanding properties to the surface without changing its inherent properties, such as color, transparency, and morphology. Although some work has been done in this direction, there is still not enough preliminary information to prove the existence of such films and their characterization. Therefore, the development of new monomeric molecules and chemical methods for optimizing surface properties, which afford the specific bonding and adhesion of particular molecules or molecular groups on the surface, is a big challenge of today's research but can be useful in many fields.

The research presented here will be split into two main directions, each of which may be divided into multiple subtasks. The main research directions are (i) synthesis precisely designed dendritic architectures and (ii) dendrimer film formation and investigation. These topics will be discussed separately in the following.

1.1.1 Sulfonimide dendrimers as substances of interest

Dendrimers are repeatedly multibranched compounds. Unlike conventional linear polymers, dendrimers have high structural purity, and their preparation consists of multiple synthetic steps rather than a single polymerization reaction. All dendritic structures contain the core, branching points, the number of which indicates the generation number of a dendrimer, and terminal groups. Latter determine, to a large extent, the properties and applications of a dendrimer.[1] Dendrimers are now thirty years old.[2] The numerous research groups contributed to developing new dendrimer types and their potential applications. Figure 1 illustrates the increasing number of publications on dendrimers in the last two decades in broad fields and materials science. Moreover, this growth is expected to continue.

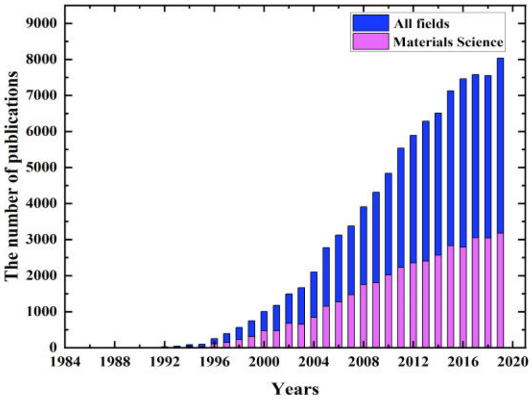


Figure 1. The number of articles related to dendrimer investigation, according to the Scopus database.

This growing interest can be explained by the fact that dendrimers are important in chemistry, biology, medicine, biotechnology, pharmaceutical, and food industries. [3,4] Moreover, dendrimers play an essential role in the investigation of nanoobjects such as nanoparticles. [5] Their physicochemical properties, such as monodispersity, multivalency, and spherical shape, distinguish them from classic polymers and allocate them as a separate class of molecules. Thanks to their inner cavities, dendrimers can create a suitable environment for stabilizing nanoparticles, directly synthesized from metal salts. [6] Despite these properties, very few products using dendrimers, and only one drug has reached the market. [7] The main reason beyond this is an undeveloped synthesis of dendrimers. The absence of a highly efficient synthesis method and the difficulties in purifying an increasingly branched macromolecule have inhibited their transfer from academia to industry. Since many dendrimers have already been obtained and investigated, the amount of information available in the literature is continuously growing. Therefore, we mainly focus on a specific type of dendrimer molecules, namely, sulfonimide-based dendrimers, which contain sulfonimide groups at each branching point. Figure 2 schematically shows the structure of target sulfonimide-based dendrimer where the core is a nitrogen atom, branching points are sulfonimide groups, and naphthalene is a terminal functional group.

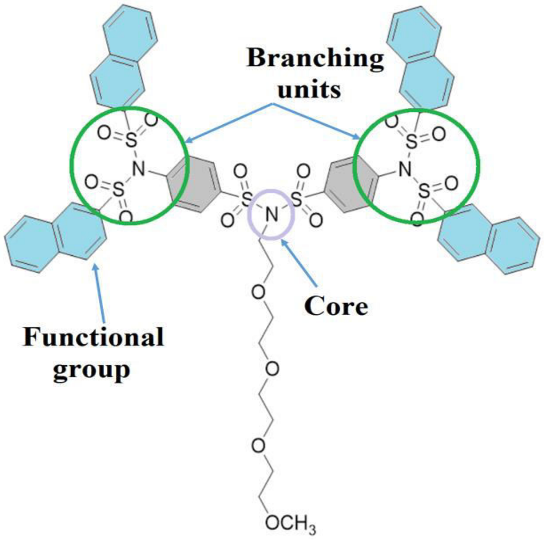


Figure 2. A schematic representation of the 2nd (G2) generation of the sulfonimide-based dendrimer in the form of a planar graph. (Note: the numbers of the generations shown in this scheme are generally admitted for sulfonimide dendrimers. However, following the traditional nomenclature G2 in the Scheme corresponds to G1)

Sulfonimide-based dendrimers were chosen as the materials of interest due to their unique properties, which are absent in other similar branched macromolecules. [8] Among other polybranched compounds, sulfonimide dendrimers possess high melting (>150°C) temperatures, while sulfonimide-based dendronized polymers have high glass transition temperatures (>130°C). Additionally, aromatic sulfonimides are chemically stable. A combination of these properties fits for applications where materials should be stable in the range of temperatures 120–130°C. The main advantage of dendrimers is assigning the desired features by adding the various chemical groups to the dendrimer. Moreover, these substances are non-toxic and biocompatible with the human body that expands the possible application fields. [9] Based on the described characteristic properties of dendrimers in general and for sulfonimide dendrimers in particular, it is possible to identify the main directions shown in Figure 3 for the potential use of sulfonimide dendrimers depending on outer and inner shell functionalization.

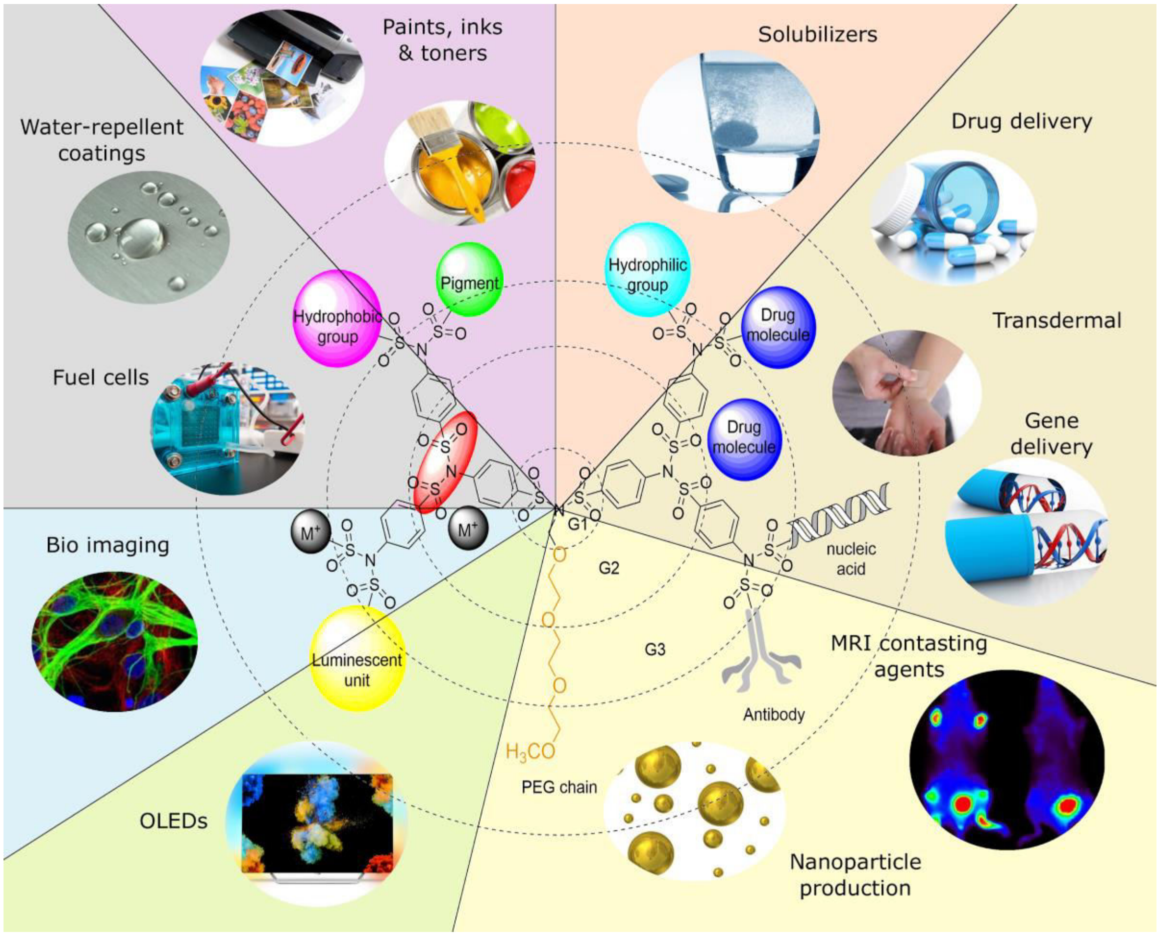


Figure 3. An overview of the possible application of sulfonimide dendrimers depending on outer shell functionalization.

One of the dendrimers' most attractive applications is the formation of thin films on their basis, which impart a useful property to the surface. The properties that can be imparted to a surface using thin films are divided into physicochemical, mechanical, optical, and electrical. This dissertation is devoted to the synthesis and deposition of thin films made from dendrimers, which impart water-repellent properties to surfaces. Each material has its industrial water-repellent coating, the composition of which is adapted for application to a specific surface. There are several hydrophobic coatings currently in active use, such as silicone coatings, silicon-organic solid, wax coatings, Teflon coatings, fatty acid salts, and other substances. The thickness of existing water-repellent surfaces very often varies in wide ranges and can reach up to 5 mm, which leads to a corresponding consumption of material for creating such a film. Also, with such large thicknesses of coatings, the material itself can lose its properties, such as transparency, reflectivity, hardness, etc. Therefore, from a rational point of view, I would like to use the amount of material necessary to create an effective film while not violating the original material properties. Wettability is an easily observed surface property. Water covers evenly over the "hydrophilic" surface and forms droplets on the "hydrophobic" surface. Thus, the material's wettability can be quantified by measuring the contact angle of the water drop on the surface of the material. In high humidity conditions, water can accumulate on the surface of metals and painted coatings destroying the surface layer, which negatively affects materials' quality. Also, the accumulation of water on transparent surfaces such as glass can lead to poor visibility in excess moisture conditions. Therefore, structured and chemically functionalized interfaces with hydrophobic properties are growing interest in technical and medical applications. One way to create such interfaces is the usage of dendrimers, modeled in a particular way. For example, the surface chemistry of a single molecular layer can change wettability by hydrophobization of the outer shell of the dendrimer.

Typically, the literature describes the use of the most prevalent chemical groups for hydrophobic functionalization, among them relatively short regular or branched alkyl groups (up to 6 carbons), long alkyl chains (more than eight carbons), [10] long perfluoroalkyl chains, [11] siloxanes, [12] aryl alkyl, and aryl groups. [13] Also, various phenyl-based aromatic groups (naphthalene, anthracene) can exhibit hydrophobic properties, but they are practically not used for hydrophobization. In this work, it was decided to decorate the target sulfonimide dendrimers with naphthyl groups, which on one side can give hydrophobic properties, but are also undergoing dimerization under the influence of UV radiation that provides an additional opportunity for film formation and stabilization. Finally, the dendrimer synthesis's primary goal has been shifted from approaching as large as a possible number of generations to the rigorous control over the shape and selective functionalization. In our case, continuous generation growth allows increasing the number of outer shell functional groups (naphthyl) groups and, as a result, possibly enhancing the films' hydrophobic properties. At the time of research in the literature, the fourth generation of sulfonimide dendrimers was the highest one. Thus, we set ourselves to achieve at least the fifth generation using the approach we worked out and finding out the generation limit.

1.1.2 Towards sulfonimide dendrimer films

The ability to modify the surface by applying films is essential in many different areas of nanotechnology. Over recent years, dendrimers have been appealing materials as detecting agents, targeting components, imaging agents, or pharmaceutically active compounds. [9] As mentioned above, dendrimers, because of their useful properties and the possibility of functionalizing the outer shell, can be used as materials for surface coatings. Surface modification with a nanoscopic layer of organic molecules can change the interface's properties in a controlled manner. [14] Moreover, the organic molecules are priority materials for creating structured monolayers because they demonstrate an active response to various outside conditions (temperature, pressure, external pollutants, and target molecules). The modifying layer may impart any chemical or physical property required to satisfy the requirements of the end application, or it may be used to study the fundamental phenomenon. There are many methods for creating and depositing surface films from solution substantially thicker than a monolayer on various materials such as spin coating, dip coating, and drop-casting. In addition to the fact that the deposited films in these ways have a large thickness, these methods do not control the process of film formation and require a large amount of substance. Therefore, the choice of method usually depends on the more desirable properties and characteristics of the interface transmitted by the modifier. Besides the diversity of film formation methods from solutions and deposition to surfaces, the thesis is devoted to one of the attractive technologies for solving film formation and deposition problems, such as the Langmuir-Blodgett method. The main advantages of this technique are:

- ➢ Precise control of the number of applied layers during the deposition process.

➢ The ability to design complicated, layered ensembles.

➢ Homogeneous film deposition on a solid substrate.

➢ The method is implemented under normal conditions: does not require creating a vacuum, the presence of high temperatures and pressures.

➢ The ability to receive mono- and multilayers based on deposition technique and various substances.

This study is devoted to demonstrating the possibility of the formation and transfer of thin sulfonimide dendrimers films of different generations to solid surfaces using the Langmuir-Blodgett technique.

Langmuir and Blodgett developed the most common and well-known method of forming and transferring mono- and multimolecular films with controllable particle density in the 1930s. The first films using this technique were obtained for long chains of fatty acids, such as stearic acid, arachidic acid, and their salts. [15] In 1934, Blodgett described the deposition of single-layer films on glass [16], and in 1935 she characterized multilayer monomolecular films on solid surfaces [17], which made the use of Langmuir-Blodgett layers (LB layers) [18] attractive to scientists. The method is based on the interaction of amphiphilic molecules on the water's surface to create an ordered layer of molecules at the liquid-air interface. [19] The oriented molecular layer is densified by applying lateral pressure using a moving barrier, causing an increase in the package's order and density to form a compact molecular layer at the air-water interface. To deposit an LB layer, a Langmuir film is transferred onto a solid substrate only by slowly passing the substrate through the film. Repeated immersion of the substrate into the water can lead to the formation of multilayer films. The orientation of the layer initially depends on the chemical composition of the substrate's surface, the type of molecule that extends to the surface of the water, and the method of transferring the film to a solid.

The surface layer of sulfonimide dendrimers was functionalized with naphthalene terminal groups (from 4 up to 32 groups for the 5th generation synthesized for the first time) that allowed forming two types of films with covalent and noncovalent bonding. The obtained noncovalent and covalent films showed the expected different contact angles due to partial destruction of the naphthyl groups attached to the dendrimer outer side, which can bond intramolecularly or intermolecularly under UV radiation. Thus, a change in the number of naphthyl groups and UV irradiation makes it possible to control the film's hydrophobic properties.

Monolayers can demonstrate new properties that open up new areas for the application of these materials. Langmuir layers still can be used in the manufacture of modern electronics [20] and optic devices [21], chemical and biochemical sensors [22], biological membranes for creating high ordered structural coatings and molecule adsorption processes. [23]

1.1.3 Previous achievements in dendrimer film formation

Nanotechnology's most crucial task is to learn how to embed organic molecules into various ordered structures and layers as new functional elements. Dendrimers can be such attractive organic molecules embedded in coatings. The decision to use dendrimers as monomers to create a film and transfer it to the surface of materials was dictated by the positive experience of other scientific groups working in this direction. There are several examples of the usage of dendrimer molecules as additives to existing coatings to improve their properties or give new functionality to surfaces in the literature. [24,25,26] Due to their specific shape and size, dendrimers are of interest as templates. The dendrimer can be sewn into the net along with a polymer matrix of a different chemical nature and then chemically or thermally removed. This method opens up prospects for obtaining materials with monodisperse nanoporous structure and low dielectric permeability. [27]

Another promising area for the use of crosslinked systems based on dendrimers is getting thin layers. An important feature of monolayers based on dendrimers is their calibrated thickness, determined by dendrimers' size. High functionality and dense globular structure of dendrimers suggest using layers such as coatings with unique barrier properties, modifiers of the chemical nature of the surface, and chemical sensors. Moreover, studying dendrimers' behavior on the surface provides new data on their physical and chemical properties and characteristic interactions with surfaces of different nature.

O. Ozturk et al. in 2005 published an article on the deposition of a film of 4th generation polyamidoamine dendrimer and the same dendrimer encapsulating Pt particles onto a gold surface. [28] Dendrimer films were prepared by delivering the dendrimer solution to the Au surface and evaporating the solvent in a stream of dry nitrogen gas. Based on the average surface area covered by the dendrimer film, the density, and the concentration of dendrimer deposited, the average thicknesses of the films were approximately 200-300 nm. The study aimed to analyze the effect of encapsulating agents (in this case, platinum) on the thermal decomposition rate of the dendrimer layer.

In recent work, dendrimer films with a conjugated microporous polymer were created to give excellent sensitivity to volatile organic compounds. The polymer matrix is fluorescent sensing material, but the aggregation caused quenching behavior due to π–π stacking results in significantly reduced photo functionality and fluorescence sensitivity of the polymer. For enhancing the sensing properties of polymer films for better response, high-density electro-active “branches” dendrimers were added. [29]

Another example is building a self-assembled layer reduced graphene oxide-PAMAM dendrimer for drug sense. Graphene oxide (GO), due to the presence of oxygen-containing functional groups, can be easily decorated with biomolecules and, concerning electrical conductivity, can be reduced to produce more stable reduced graphene oxide (rGO). Some residual oxygen groups on the rGO surface may benefit from chemical functionalization with primary amine ($-NH_2$) extending them to be hydrophilic and increasing its interfacial binding to target materials, thus making it more applicable as a sensing platform for virus detection. Since PAMAM dendrimers are decorated with amino-terminal groups, the combination of polyamidoamine dendrimer (PAMAM) in the form of globules in rGO provides excellent opportunities for increasing detection sensitivity. [30]

Chen Wang et al. reported a new ionic rectification device fabricated by assembling a gold nanoparticles network on the surface of nanoporous anodic aluminum oxide membrane for the ability of enhanced bioanalysis by sensitive capture and detection of circulating tumor cells. Sensitive and selective cell capture plays an essential role in the diagnostics and treatment of cancer. Dendrimer (poly (amidoamine) (PAMAM)) was used as the linkers to connect gold nanoparticles, forming dendrimer nanoparticles network film. Thanks to the high surface-to-volume ratio of the gold nanoparticles and the high density of binding sites of PAMAM, the network has more surface area and can expose more functional groups. The presence of amino groups on the surface promotes anion selectivity. [31]

By the way, in many well-known existing works, as noted above, dendrimers are mainly used **as additives and linkers rather than independent monomers** for film construction. As **methods for applying dendrimers**, the usual spreading of the dendrimer solution to the surface and subsequent drying in the air (drop-casting. dip-coating) are used, which are not characterized by control. These methods **do not control the film thickness** and create thin films since the thickness of the resulting layers was from 200 to 400 nm. Besides, there is no information in the literature on the preparation of films based on sulfonimide dendrimers.

1.2 Research objectives

Based on the available information in the literature, our capabilities, and desires, the research work presented in this dissertation was divided into two parts: synthetic and applied. We took the first step in synthesizing dendritic molecules based on sulfonimide with the idea of providing a set of readily available, intelligently formed structures. We selectively functionalized dendritic platforms for complex applications in science and technology.

The first goal of this PhD project was to achieve a higher generation of designed sulfonimide dendrimers using a simple, selective two-step synthesis that does not require a complex protecting group strategy. High generations are interesting for creating high functionality, which further determines the application field of a synthesized dendrimer. To achieve this goal, several tasks have been set:

1) Selection of appropriate core molecule
2) Perform multistep synthesis sulfonimide dendrimers of the second, third, and fourth generations, decorated with naphthyl functional groups
3) Reach the fifth generation of sulfonimide dendrimer containing 32 naphthyl groups for the first time
4) Optimize the synthesis condition to isolate a gram-scale of substances
5) Carry out purification of the final products
6) Confirm the resulting structures using NMR and mass spectrometry

As one of the applications of the obtained sulfonimide structures, it was planned to use them to prepare and characterize thin films made up of synthesized dendrimers and transferred to various surfaces. In practice, these films can be interesting for changing the properties of polar hydrophilic surfaces to the opposite - hydrophobic ones using minimal amounts of a substance.

The second goal of the project was to show the applicability of sulfonimide dendrimers to prepare films capable of influencing surface properties. In this regard, several tasks were set:

1) Formation of sulfonimide dendrimer films of the second to fifth generations on the water/air interface using the Langmuir apparatus
2) Study of the effect of UV radiation on the process of stabilization of the obtained layers
3) Deposition of created films on different substrates (glass, silicon, mica, copper grids)
4) Characterization of the films by microscopic tools (optical, AFM, SEM, TEM)
5) Measuring thickness, Young’s modulus, contact angles, and nonlinear optical properties of obtained films.

Thus, the achievement of these goals will allow us not only to make progress in the synthesis of dendrimeric structures but also to open new niches for the use of sulfonimide dendrimers for functional surface formation.

Chapter 2. Review of the Literature

2.1 Dendrimer chemistry

2.1.1 A brief historical overview of dendrimers as a new class of synthetic macromolecules

The first mention of substances similar to dendrimer structures referred to 1974 when Vögtle and his colleagues described the use of branched molecules called "octopus molecules" in host-guest interaction with metal ions. [32] Four years later, the same group of scientists described the sequential synthesis of a 1→2 branched dendrimer structure, called ‘‘cascade molecules" based on propylamine molecules [33] via repetitive steps. [34] The term ‘‘cascade" was chosen because it evokes analogies to the repetitive branching of the arms, and with some justification, this type of molecule could have been called dendritic. These molecules were synthesized divergently, utilizing two branching motifs. Further synthesis of new dendrimer structures developed slowly due to the complexity of synthetic procedures and conditions selection. Only in 1981, Denkewalter, together with colleagues, described the synthesis of dendrimers with polylysine branches. The method of obtaining polylysine dendrimers was patented, the product was proposed to be used as metal chelating agents and as substrates for the preparation of pharmaceutical dosages. [35,36] Dendrimers were interesting not only for synthesis but also for the investigation of the spatial structure. In 1982, the concept of dense packing of dendrimer structures was described. [37] Based on an analysis of statistical models, in 1983, de Jenne and Herve demonstrated limits on the growth of branched molecules due to the influence of steric effects. [38] In 1985, Tomalia developed branched polyamidoamines (PAMAMs), coined, and propagated the name ‘‘dendrimer", synthesized using a similar mechanism as described by Vögtle et al., but a numerous repetition of the coupling reaction sequence led to the appearance of dendrimers up to the tenth generation - with a decrease in purity and perfection. [2,39] PAMAM dendrimers were obtained by a divergent method involving the 1→2 branching motif, which means every branching point is capable of attaching two branches or terminal groups. [40]

In 1985, the synthesis of a water-soluble dendrimer containing hydroxyl end groups was presented by Newkome et al. [41,42] Newkome and co-workers demonstrated a divergent synthetic route to water-soluble, highly branched ‘‘arborol systems” with terminal hydroxyl groups. In this case, the 1→3 branching motif was utilized. In the same year, dendrimers containing aromatic hydrocarbons were synthesized. [43,44] Percec and co-workers described an original convergent synthesis of four generations of dendrons with the 1→3 branching motif based on the AB_3 building block methyl 3,4,5-trishydroxybenzoate. [45] Müllen and co-workers reported the four-fold Diels–Alder reaction of functionalized tetraphenylcyclopentadienone (the so-called A_4B building block) with tetraethynylbiphenyl leading to the first and thus far only type of dendrimer with a 1 → 4 branch-ing motif. [46]

As you can see, the initial development of the chemistry of dendrimers over 20 years yielded good results for the further design, synthesis, and even possible application of dendritic molecules. The number of scientific publications in dendrimer chemistry continues to grow year by year and gives scientists inspiration for their further investigation.

2.1.2 Basic concepts in the chemistry of dendrimers

Dendrimers are unique classes of polymeric macromolecules, composed of the core, branched monomers, internal cavities, and functional surface characterized by high monodispersity, good biocompatibility, and multivalency. [47] According to their narrow molecular mass distribution, dendrimers occupy an intermediate position between low molecular weight compounds and high molecular weight compounds. Due to the periodic repeatability of branching points, dendrimeric structures are called fractals. [48] The schematic representation of the dendrimer structure with main structural parts, including generation numbers, is shown in Figure 4. [1]

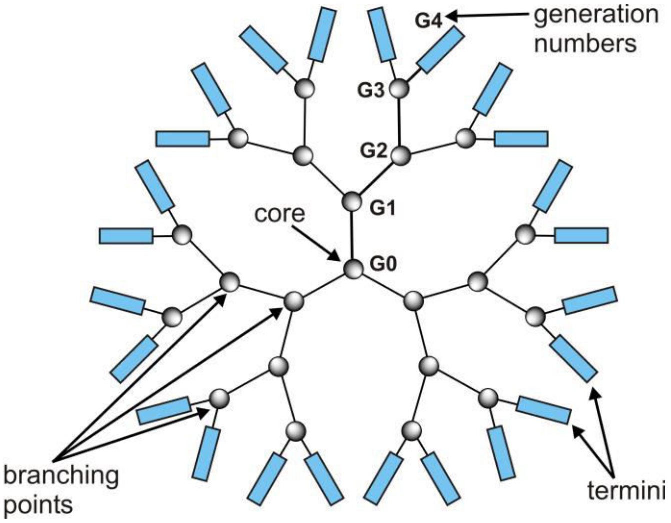


Figure 4. Schematic representation of a dendrimer structure with the key components.

The main structural components of dendrimer include the core, branching points, and terminal or functional groups. The multiplicity of the core and branching units determine the shape and the size of the dendrimer. In some cases, the core can assign a particular function to the dendrimer molecule. Increasing the number of branches increases the number of generations designed as the number of layers fastened to the core and marked as Gn, where n can vary from 0 to 12. [49] If a dendrimer is made by divergent synthesis, and the branching reactions are carried onto the core molecule two times, the resulting dendrimer is considered a second-generation dendrimer and so one.

Moreover, the nature of branching points influences the stability of the molecule itself, the presence of internal voids, and their ability to accommodate guest molecules. The ends group creates the periphery of the molecule and gives unique properties to the dendrimers, such as low/high solubility in different solvents, viscosity, and conformational stability. One of the advantages of the dendrimers, along with other macromolecules, is the presence of an enormous amount of terminal groups, which grows exponentially amplify the desired properties.

2.1.3 The main approaches to the synthesis of dendritic macromolecules

According to the fact that there is an exponential growth of new synthesized chemical compounds [50], the methods for their preparation are still essential, and research and development aimed at improving the processes have not lost their relevance. An analysis of the dendrimer chemical structures and synthesis methods presently available reveals that the synthetic aspects have not been fully explored yet. One of the synthetic issues worth exploring is dendrimers with large aromatic and shape-persistent branches. The reduced flexibility of such structures, together with their chemical inertness, is expected to lead to an exciting addition to the research field in terms of high melting and glass-transition temperatures and possibly new options for chemical modification.

Despite the existence of numerous works on the synthesis of dendrimers, much remains desirable in this regard. There is still a need for even higher generations of all types of dendrimers, as well as for high-performance and optimized synthesis of individual families of dendrimers to endow them with new targeted mono and multifunctionalization. Besides, the development of new various innovative building blocks for the synthesis of dendrimers is essential. Historically, two key synthetic routes to dendrimers known as divergent and convergent have emerged.

2.1.3.1 Divergent synthesis

The divergent route initially formulated by Vögtle [33] and then developed independently by Newkome [42,51] and Tomalia [40] involves repetitive steps of a gathering of monomeric units around a core scaffold structure by coupling and activation reactions. The divergent synthesis method includes a sequential increase in dendrimer generations from the multifunctional core to the periphery. [1] Therefore, in a divergent way, an important parameter is the core unit molecule because it determines a successful chain growth process, the number of branching points, and the stability of the dendrimer itself. This approach is quite efficient, easy to perform, optimize, and allows to achieve a large scale production of the target compounds in contrast to the alternatively used convergent method. The divergent synthesis typically involves the use of inexpensive commercial reagents at each repetitive step resulting in a rapid increase in the mass of the end products with the growth of dendrimer generations. Also, divergent techniques applicable to the synthesis of high generations of the dendrimer. The main disadvantage of this approach is the presence of side reactions that lead to imperfect dendrimer structures and require a purification procedure. From the applied viewpoint, the small defects in high generation dendrimers occurring from either incomplete functionalization or some side processes during the divergent synthesis can be neglected because the synthesis provides essentially monodisperse materials. To minimize this drawback, it is necessary to use a large excess of reagents, extend reaction time, and check the quality of all intermediates. At a certain saturation point, the number of end groups becomes very large, and they will not be able to react further; this gives a limitation for further generation growth by the divergent method. Moreover, the presence of a large number of unreacted dendrimers can make the process of purification of the final product difficult. [52] The schematic representation of the divergent route up to the 4th generation of the dendrimer is shown in Figure 5. [53]

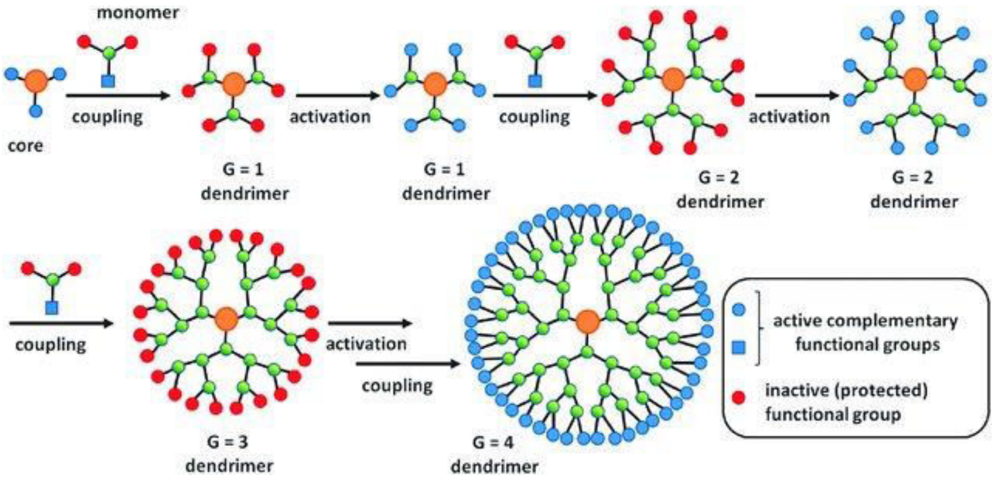


Figure 5. The schematic representation of the divergent synthesis of dendrimers.

Despite some imperfections of this method, the large-scale synthesis of commercially available dendrimers, such as poly(amidoamine), poly(propylene imine), phosphorus-based dendrimers, etc. is carried out by the divergent approach.

2.1.3.2 Convergent synthesis

The convergent dendrimer synthesis devised by Hawker and Frechet [44] and by Miller and Neenan [43] starts with the synthesis of a dendron, which is a wedge-shaped branched species containing one functional group at its focal point and ends by attaching a few dendrons to a multifunctional core. In the convergent method, the synthesis starts from the periphery and ends up at the core. The convergent route allows for complete control over the structural integrity of the dendrimers. In this case, the byproducts of incomplete substitution are easily removed from the target species on account of significant differences in their molecular weights. This method allows to avoid the complicated process of purification and usually leads to higher generation dendrimers. The size and shape of the dendrimer can be tuned by selecting appropriate cores. Although convergent synthesis often uses costly dendrons, it allows producing designer-type dendrimers for specific applications. Using convergent synthesis, we can better control the process, eliminating structural defects. Still, at the same time, the final stage of synthesis may be challenging to proceed due to the steric effect. [44] The schematic representation of the convergent route up to the 3rd generation of the dendrimer is shown in Figure 6. [53]

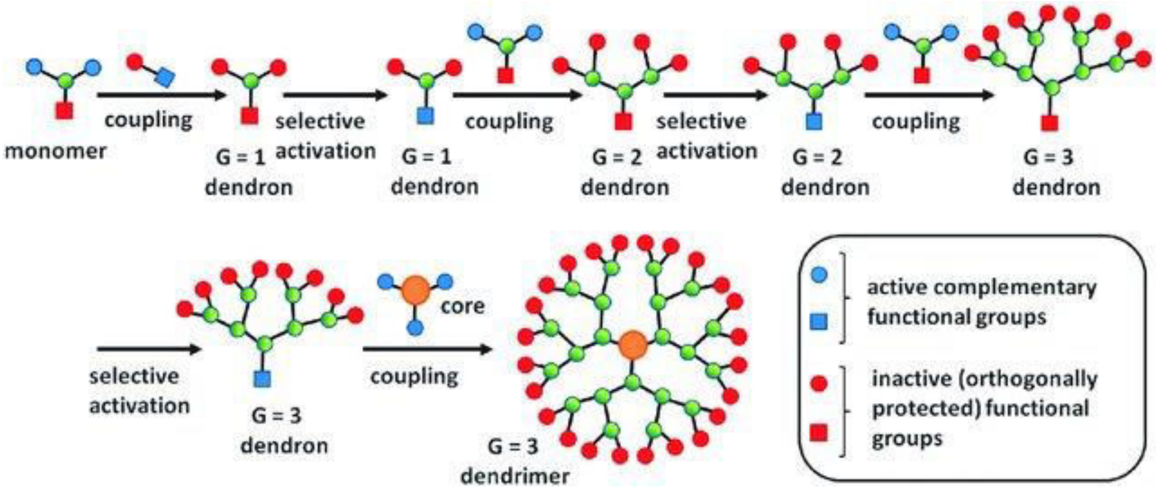


Figure 6. The schematic representation of the convergent synthesis of dendrimers.

Both methods of dendrimer synthesis have their advantages and drawbacks. Thus, the divergent synthesis allows for the fast growth of dendrimer generations and an increase in the mass of the products using at each stage inexpensive commercial reagents. However, the method tends to generate defect structures at higher generations on account of an incomplete functionalization of the dendrimer periphery. [54] The convergent route allows for complete control over the structural integrity of the dendrimer but uses very costly dendrons and often suffers from some incomplete attachments of sizable dendrons to a core due to steric inhibition at the focal point that tends to be wrapped by the branches. However, the small defects in high generation dendrimers occurring from either incomplete functionalization or some side processes during the divergent synthesis can be neglected because the synthesis provides essentially monodisperse materials (usually polydispersity index PDI≤1.08 according to the gel-permeation chromatography analyses) and fully reproducible physicochemical properties. [55] Consequently, the large-scale preparation of commercial dendrimers, such as poly(amidoamine) (PAMAM), poly(propylene imine) (PPI), [56,57] phosphorus-based [58] dendrimers, is carried out via the divergent approach.

2.1.3.3 Double-stage convergent method

In cases requiring a more complicated structure, one may use a combination of the two methods of synthesis called a double-stage convergent way, where the synthesis of building blocks performs with the divergent approach followed by the convergent dendrimer assembly. [59,60] The schematic representation of the divergent route is shown in Figure 7. [53] As you can see from the picture, the first step includes the creation of low-generation multifunctional dendrimer with external coupling sites obtained by divergent synthesis, and the second step consists of the synthesis of a small dendron with an active functional group at the focal point. The resulting reaction consists of the coupling of these two molecules together produced by the convergent route.

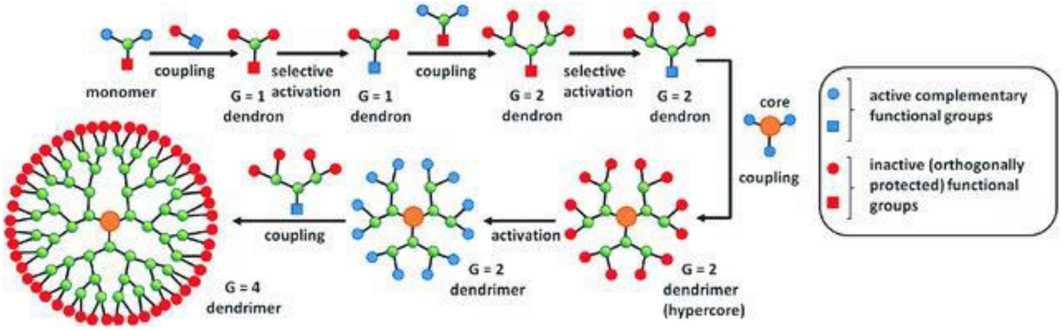


Figure 7. The schematic representation of the combined convergent and divergent synthesis of dendrimers.

This allows creating a needed higher-generation monodisperse dendrimer structure with individual branching points, the number of generations, and specific functional terminal groups modifying their biological and chemical activities.

2.1.3.4 Hypermonomer method

In this method, the number of terminal groups increases faster due to 1⟶ 4 branching with hypermonomeric synthetic building blocks. Four branching units AB4 with an active functional group at the focal point react with active coupling groups of the core molecule, as shown in Figure 8. [53,61]

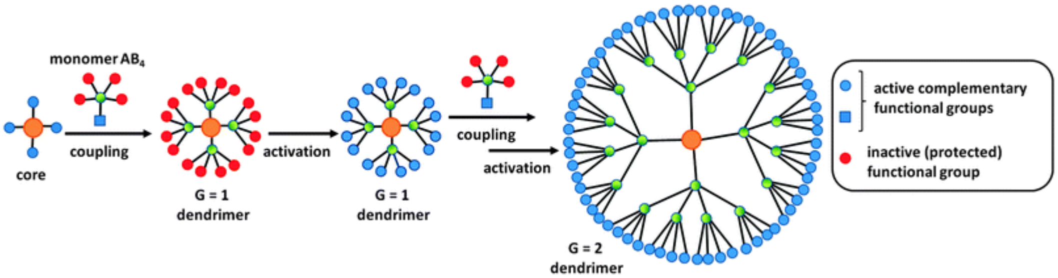


Figure 8. The schematic representation of the hypermonomer method.

2.1.3.5 *Click chemistry method*

Principles of click chemistry were first fully described by K. Barry Sharpless in 2001 in which smaller units are joined together by heteroatom bonds C–X–C where X is heteroatom [62]. The "click reaction" is characterized by high chemical yields; commercially available starting compounds; easily removable or inoffensive by-products; easy product isolation and purification; stereospecific. [63] Click chemistry employs three types of reactions for the synthesis of dendrimer: Diels-Alder reactions, [64] thiol-yne reactions, and azide-alkyne reactions. [62]

Two of the essential goals in the synthesis of dendrimers that should be reached shortly are further development in the target-specific synthetic methodology and the preparation of multigram quantities of these compounds. The achievement of these goals is related to increased control over the selectivity and efficiency of chemical reactions that would allow obtaining dendrimers in fast, simple, high-yield, and purification-free processes.

2.1.4 Types of dendrimers

Dendrimer can be classified based on their shape, branching units, generation number, and method of synthesis. [65] Figure 9 demonstrates the classification of dendrimers.

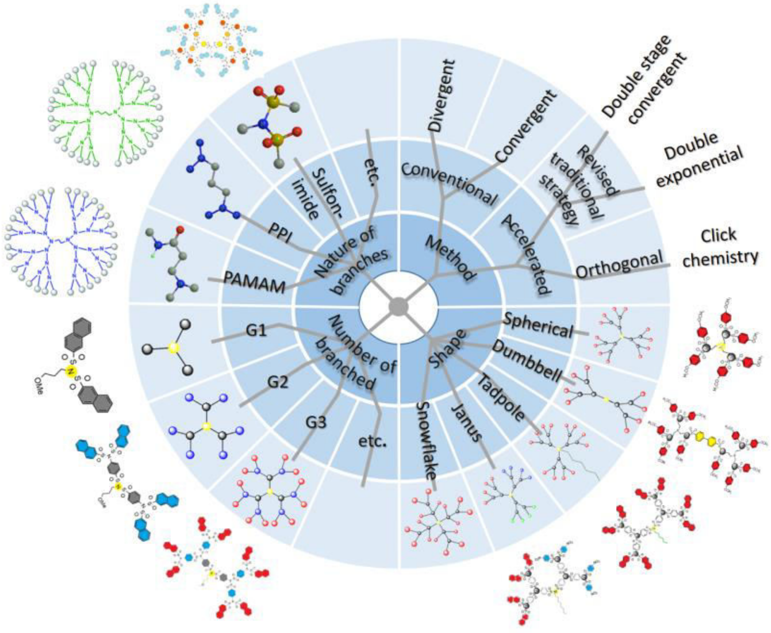


Figure 9. Different types of dendrimers.

With regard to modifications, more than 200 types of dendrimer molecules have been synthesized, among them five widespread families such as polyamide amine (PAMAM), polypropylene imine (PPI), phosphorus, carbosilane, and polylysine dendrimers. Low generations of dendrimers (1^{st}- 4^{th}) mostly have a planar shape. Still, with the increasing number of generations from 5^{th} to 10^{th}, the structure becomes more globular and densely packed at the periphery, with empty cavities inside, that makes the most promising areas for their application is targeted drug delivery of a medical substance to a given area of an organism, organ, or cell. [1] Usually, dendrimers are classified according to the name of the chemical group at the branching point. There are several famous dendrimeric molecules named in such a way, for example, PAMAM (polyamidoamine), PPI (polypropylene imine), carbosilane dendrimers, peptide dendrimers, sulfonimide-based dendrimers, etc. Next, I will consider the most popular dendrimers and their individual properties.

2.1.4.1 PPI

PPI or POPAM (polypropylenimine) is a type of dendrimer with amine-terminated hyperbranched units that belongs to the most widely used representatives because it is commercially available as Astramol® of DSM company, Eindhoven, the Netherlands and Aldrich Chemical Company, Milwaukee, WI. Due to the valency of the nitrogen atom, POPAM is related to 1→2 branching type, and two functional core units give 2^n terminal amino groups for generation Gn. The synthesis of PPI dendrimers is based on the divergent approach developed by Vögtle et al. in 1978, containing addition and reduction reactions. Subsequent repetitive reaction cycles allow the repeated addition of acrylonitrile, followed by reduction until the higher generation is reached. [66] Due to their amino-terminal groups, PPI dendrimers can be easily functionalized with fluorescent dansyl groups [67], ferrocene, cobaltocenium units [68], aza-crown ethers [69], and various other.

2.1.4.2 PAMAM

PAMAM dendrimers were the first dendrimer structures that have been synthesized and investigated. PAMAM (polyamidoamine) dendrimers contain the amide bonds in the molecule. According to the valency of the nitrogen atom, PAMAM is related to 1→2 branching types. In 1985, Tomalia modified the synthetic methodology of Vögtle et al. for the divergent preparation of PAMAM dendrimers by replacing the acrylonitrile reagent used in Michael's addition by methyl acrylate and starting from ammonia or ethylenediamine initiator core reagents. Dendrimers up to ten generations have been obtained in such a way. The PDI of G5-G10 PAMAM dendrimers is less than 1.08, which means that the particle size distribution is uniform for each generation. PAMAM dendrimers are commercially available as Dendritech®, Michigan, (USA) distributed by Aldrich. These are spheroidal or ellipsoidal in shape. [39] It has high solubility and reactivity due to the incidence of several functional end groups and empty internal cavities. [70],[71] Due to the presence of a positive charge on the surface, PAMAM dendrimers are good candidates for the condensation of biological molecules. [72]

2.1.4.3 Peptide dendrimers

Peptide dendrimers are branched macromolecules that contain a peptide branching core or peripheral peptide chains. [72] Peptide dendrimers are divided into three types. The first type has peptides only as surface functionalities, the second category composed of amino acids; the third one has amino acids in the branching core and surface functional groups but having non-peptide branching units. Divergent and convergent methods are mainly used for the synthesis of peptide dendrimers. Peptide dendrimers have been used in industry as surfactants, and in the biomedical field as drug and gene delivery.

2.1.4.4 Hybrid dendrimers

Hybrid dendrimers are a combination of dendritic and linear polymers that structures are possible due to a spherical shape and many surface functional groups of dendrimers. For example, "POMAM dendrimers" [73] are a structural hybrid of combination POPAM and PAMAM dendrimers. The synthesis POMAM started with activation of the amino groups of POPAM via palladium-catalyzed hydrogenation and further reaction with a succinimide ester provide higher-generation POMAM dendrimers.

2.1.5 Synthesis of sulfonimide-based dendrimers

In 2006, O. Lukin et al. reported [74] the divergent synthesis of first representatives of dendrimers with a relatively compact, shape-persistent aromatic sulfonimide-type structure. In contrast to other rigid branched structures, such as poly(phenylacetylene), [75] poly(phenylenevinylene), [76] polyphenylene, [77], and polythiophene [78,79] dendrimers, sufficient availability of commercial arylsulfonyl chlorides allows for faster and cheaper preparation of the aromatic sulfonimide-based dendrimers. [8] The synthesis provides design dendrimers with individual branching points, [52] peripheral functional groups, and branching motifs [80] by selecting the appropriate series of reaction steps. The sulfonimide-based dendrimers, unlike many other branched species, are crystalline solids with high melting points. Dendronized polymers prepared from the first- and second-generation sulfonimide-based dendrons exhibit considerably high glass-transition temperatures that lie in a range attractive for such biomedical applications where heat sterilization plays a role. [81] However, at some stage, it became clear that the divergent growth of dendritic sulfonimides is limited to the fourth-generation species with considerably decreased yields at the final synthetic stages. [82] Tewari et al. have recently reported [83,84] a convergent synthesis of sulfonimide-based dendrimers through linking azide-functionalized persulfonylated dendrons to propargyl functionalized cores using click chemistry. [85,86] Nonetheless, only first-generation dendrimers have been obtained by this procedure, highlighting the importance of the original divergent approach. Therefore, an improved method allowing a high-yield preparation of sulfonimide-based dendrimers up to the fifth generation via the divergent route was described in the present work.

2.1.6 Properties of dendrimer

The currently synthesized dendrimers and dendrite-like polymers are viscous liquids or amorphous solids that are readily soluble in most known organic solvents. To date, the physicomechanical properties of dendrimers and dendrite-like polymers have not been systematically studied. However, the structural features of the considered polymers allow us to draw certain conclusions about the general nature of these properties. Dendrimers are monodisperse, since all macromolecules at each stage of controlled synthesis increase the molecular weight by the same amount, the resulting dendrimers contain macromolecules of the same mass and size. The regularity of the structure of the dendron, the known values of bond lengths and angles allow with high accuracy to calculate the size and molecular weight of the dendritic macromolecules. For dendrimers with a strictly regular structure, such properties of polymers as fiber formation, swelling, and high viscosity of solutions are not typical. The features of dendrimers are determined by the maximum possible diameter of zero generation, the number of generations, and the structure of the skeleton of the macromolecule. A high degree of functionality creates unlimited possibilities for further transformations of dendrimer macromolecules that can lead to designing new nanoscale structures, surface modifications macromolecules.

2.1.7 Application of dendrimers

In chemistry, the discovery of new materials with desirable properties, optimizing the conditions for their production and application is an essential task of theoretical and practical interest for scientists. [87] The perspective materials are needed to enable future technological developments in different areas such as sustainable energy-efficient processes, targeted drug delivery, sensor technology, construction, and many others. The result of such development can be cheaper, lighter, more durable, or more functional material, which can have a significant impact on our lives in the near future. [88]

Dendrimers as new materials have made an essential contribution in different fields such as biomedicine, chemistry, material science, engineering, electronics, and optics. [89] It is not easy to distinguish between installed applications and highly promising future dendrimer chemistry options. Structurally uniform repeatedly branched molecules, called dendrimers, [90,44] as well as their hyperbranched [91] and dendronized [92] polymer congeners play a progressively significant role in many areas of basic and applied science, [93,94] as well as industry. The regular structure of dendrimers and the ability to control their physicochemical properties stimulate significant interest in their further development, study, and application in practice. The choice of peripheral groups allows you to change the chemical, physical, and biological functionality of macromolecules.

The high functional group density at the periphery of dendrimers, high branching combined with control over the molecular structure, makes these synthetic materials a highly useful resource for sensing,[95,96,97] and surface-active [98,99] applications. Moreover, dendrimer molecules have nanoscale dimensions, globular surface, and exciting properties, like low viscosity, high solubility, and reactivity, in combination with the high functionalities, make them prospective candidates in different fields. [100] The widespread applications of dendrimer include gene therapy, chemical sensors [101], drug delivery system, adhesive additives, and coatings, light-harvesting material, catalyst, electronic applications, separating agents. [102] The use of dendrimers as additives in the field of catalysis, sensory technologies, medical diagnostics is the most relevant at present and attracts most researchers. Existing applications of dendrimers and potential applications at the different planning stages are described further concerning their properties.

2.1.7.1 Dendrimer in medicine

Unlike polymers, structural accuracy and, therefore, more uniform dendrimer properties determine them for applications in the biomedical sector. Dendrimers are non-toxic substances, have good solubility, low viscosity, which makes them attractive as biological agents for the medical field. The targeted guest molecules can be attached to the periphery of the dendrimer via functional groups or located in the internal voids of the dendrimer. For example, well-studied PAMAM dendrimers can be used to target cell tumors. [103] Dendrimer based metal chelates can be applied as magnetic resonance imaging contrasting agents. [104] The dendrimer molecule as a contrast agent was used as a diagnostic reagent to identify the tumor using magnetic resonance. [105]

Szoka and Haensler[106] demonstrated applications of PAMAM dendrimers for gene transfection. DNA and organic molecules can be attached to dendrimers and directed to the cell nucleus. The multifunctionality of dendrimers makes them useful as agents for targeted drug delivery of a medical substance to a given area of an organism, organ, or cell. [9] The presence of internal cavities for the drug storage and external functional groups for attaching drug molecules have made their application in pharmaceutical and medicinal chemistry particularly attractive. Drug molecules can be attached to the dendrimer via end groups or can be stored in the internal cavities of a dendrimer. The reason why scientists are looking for new agents for the transport of drug molecules is the imperfection of existing ones. There is still demand new transport systems that will have a high degree of affinity to the human body, affinity to different types of drug molecules, and penetration through the cell membranes. In addition to drug transfer, dendrimers help to overcome some difficulties, for example, low bioavailability, insolubility, toxicity, and decomposition of the drug under biological conditions. [107] So far, PAMAM dendrimers were investigated for oral, ocular, and pulmonary drug delivery. [108,109] Along with these capabilities, dendrimers can also be used for increasing the solubility of dosage forms. Due to the hydrophilic periphery and exterior, dendrimers can dissolve poorly soluble drugs by its encapsulation in dendritic molecules. [110]

2.1.7.2 Dendrimers as additives. Printing inks and paints

The monodisperse "tree-like" structure of dendrimers can be used as additives in toners for color printing. The toners with dendrimer additives can be applied efficiently and uniformly to the surface of the paper, which is essential for printing technology. Moreover, such toners will require less material than their available analogs. Companies producing printing inks are interested in such additives because by adding a dendrimer, a high uniform adhesion of the inks to the surface is achieved, which will significantly reduce ink consumption and reduce the cost of printing. Moreover, in addition to sufficient adhesion to the surface, the ability of dendrimer molecules to form strong bonds with pigment molecules improves print quality. Highly branched dendritic polymers are also used as rheology modifiers; for example, the addition of highly branched polyesters affects the viscosity and surface tension of some compositions. Unlike linear polymers, low viscosity and high molecular density of dendrimer favor their use as an additive in dental chemistry. In this area, materials are required to form crosslinked polymer structures on photo-polymerization of tooth fillings at room temperature with minimum possible loss of volume to avoid slot formation between filling and tooth. During each coupling step of photopolymerization, the Van-der Waals distance is reduced due to a covalent bond formation, commonly decreasing volume.

2.1.7.3 Dendrimers in the sensing technology

Another promising field of application for dendrimers is coating materials. One of the attractive areas where thin coatings can be used is sensory technology—improving the sensor efficiency related to the investigation of new materials. The sensor principle is based on the interpolation of the specific guest compound as an analyte in a coating layer consisting of suitable host molecules such as dendrimers, deposited on the different solid surfaces. [111] The most important structural properties of dendrimers to consider their use in sensors is a three-dimensional structure and numerous terminal functional groups. The ability of dendrimers to distinguish certain carbonyl compounds such as ketones, aldehydes, esters, and amides can be used to analyze aromas in foods to establish the maturity of fruit or cheese. [111] Moreover, dendrimers show long-term stability, which is an advantage for the reproducibility of measurements. Besides food production fields, dendrimers can be used as highly selective sensors for sulfur dioxide, considered responsible for the formation of fog and acid rain. This technique of quality control of valuable products can be used in agricultural research, smart home technologies. One of the priority tasks is developing some smart sensors for refrigerators that can detect the degree of food spoilage. In this case, the dendrimer molecule can store an analyte sensitive to hydrogen sulfide release as a signal of product decomposition. Some studies consider PAMAM dendrimer-based optical sensors for determining pH and cations. [111]

2.1.7.4 Dendrimers as catalysts

The combination of high surface area, high solubility, numerous catalytic centers, and easy extraction process from the reaction mixture make dendrimers useful as nanoscale catalysts. For the efficient use of dendrimers in catalysis, it is necessary to synthesize large generation dendrimers, for increasing the number of active sites available for fixation of catalytically functional moieties.

2.1.7.5 Dendrimer as coatings

Another promising area for the use of dendrimer-based crosslinked systems is the production of thin layers. An important feature of monolayers based on dendrimers is their calibrated thickness, determined by the size of the original dendrimers. High functionality and dense globular structure of dendrimers suggest the possibility of using such layers as coatings, possessing unique barrier properties, chemical modifiers surface, chemical sensors. Also, the study of dendrimer behavior on the surface provides new data on their physical and chemical properties and features of interaction with surfaces of different nature.

Besides the above-listed application of dendrimers, further studies are needed to recognize their absorption, in-vivo stability, coating formation.

2.1.8 Patenting sector for dendrimers

To identify demand areas for dendrimer usage, I carried out a patent analysis of applications of dendrimers in different fields, the distribution according to technology shown in Figure 10. Using the Cipher patent database service (https://cipher.ai), I found 1093 active patents by using the keywords ‘dendrimer’ or ‘dendrimers.’ The searching results reveal an unusually broad area of potential industrial applications for dendrimer technology, ranging from oil, pharma, rubber, automotive, and even cosmetics. There were 48 % of active patents devoted to drug delivery systems involving dendrimer molecules. The next important application of dendrimers is their ability to be as an additive component in resin and coating compositions - 12 % of patents. Application of dendrimers in electrical and optic devices had 9 % of patents, as a film-forming polymer and cosmetic raw material - 8 % of patents.

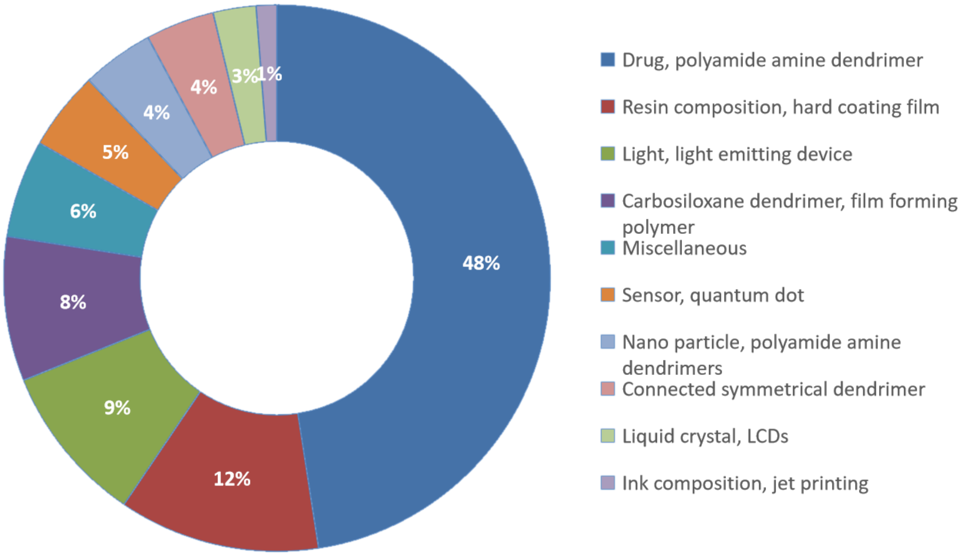
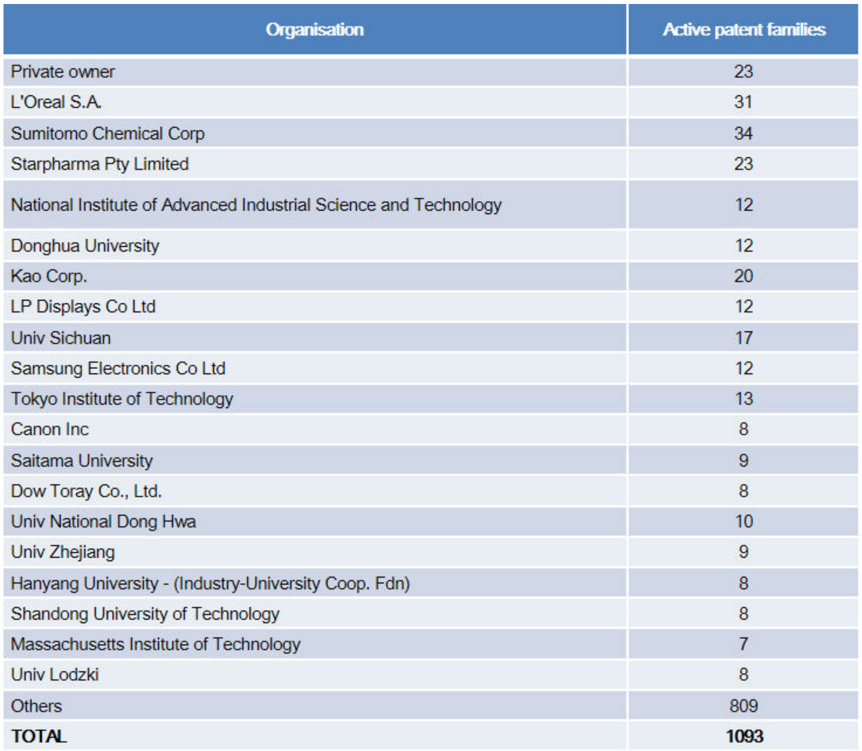


Figure 10. Active patent (granted or pending) families, by technology, according to Cipher patent database service, 2005 - 2020.

Obtaining patents opens up opportunities for further commercialization of results of scientific research. After an analysis of areas in which dendrimer molecules can be used, I consider companies that have patents related to dendrimers and to whom the impact of dendrimer investigation will be attractive. The list of companies and the number of related patents are shown in Table 1. The medical sector is represented by the Starpharma company and the number of universities, including MIT, Tokyo Institute of Technology, and others. Companies producing computer printers and various related products like inks, cartridges, toners such as Canon inc, Industrial Technology, and Kao have related patents. The optoelectronics field is represented by Sumitomo Chemical, LP Display, Samsung Electronics, etc. More information is shown in Table 1.

Table 1. Active patent (granted or pending) families, by an organization, according to Cipher patent database service, 2005 - 2020



Organisation	Active patent families
Private owner	23
L'Oreal S.A.	31
Sumitomo Chemical Corp	34
Starpharma Pty Limited	23
National Institute of Advanced Industrial Science and Technology	12
Donghua University	12
Kao Corp.	20
LP Displays Co Ltd	12
Univ Sichuan	17
Samsung Electronics Co Ltd	12
Tokyo Institute of Technology	13
Canon Inc	8
Saitama University	9
Dow Toray Co., Ltd.	8
Univ National Dong Hwa	10
Univ Zhejiang	9
Hanyang University - (Industry-University Coop. Fdn)	8
Shandong University of Technology	8
Massachusetts Institute of Technology	7
Univ Lodzki	8
Others	809
TOTAL	**1093**

2.2 Langmuir-Blodgett Films

2.2.1 Historical overview

The history of the development of surface chemistry originated in the late 18th century when B. Franklin studied the spreading of a drop of olive oil on the surface of the water. [112] Franklin did not claim to have made a discovery; he designed the first scientific experiment with a thin oil film, made observations, and stimulated further work in the field of surface chemistry. So, at the end of the 19th century, Pockels and Rayleigh demonstrated detailed studies of monolayers on the surface of the water and their transfer to solid substrates. [113,114] Based on the early Franklin's observation, Rayleigh calculated the thickness of the oil film. Agnes Pockels demonstrated a correlation between surface tension and area of films. Langmuir continued to investigate Pockels's ideas and, together with Blodgett, developed the Langmuir–Blodgett trough for film formation and deposition. [17] Langmuir films are monomolecular layers of surface-active organic substances formed and located at the liquid interface (usual water) and gaseous (air) phases. If these monolayers are transferred onto a solid substrate, then a solid monomolecular or multimolecular film, called the Langmuir-Blodgett film, is obtained. The first films using this technique were obtained for long chains of fatty acids, such as stearic acid, arachidic acid, and their salts [15]. These scientific outcomes were further continued in Kuhn's work [115] on the study of the ordering of molecules on the surface. In the field of nanomaterials, it is essential to create a uniform monolayer consisting of ordered particles in the nanoscale. Monolayers can demonstrate new properties that open up new areas for the application of these materials. Langmuir layers still can be used in the manufacture of modern electronics [116,117,20] and optical devices, [118,119,120] chemical and biochemical sensors, [52,121] biological membranes for creating high ordered structural coatings [122] and molecule adsorption processes. [123,124] At the moment, the priority materials for creating structured monolayers are organic molecules because they demonstrate an active response to various outside conditions (temperature, pressure, external pollutants, and target molecules). Monomolecular films at the phase boundary and multilayer solid structures (multilayers) transferred onto solid substrates have a unique set of physical properties that can be useful in various fields of chemistry, physics, and biology.

2.2.2 Dendrimer molecules as a monomer for Langmuir films

One of the exciting types of substances with fascinating architecture is dendrimers. Dendrimers are capable of not only forming stable 3D structures in solution but also tend to organize 2D molecular layers on a water-air interface. [55] Generally, the dendrimer molecules can be modified through the outside group and focal points to manage their self-assembly and functionalization. Since dendronized polymers can retain their shape and can be decorated with the necessary functional groups, they can be used as building monomeric blocks to create thin films using the Langmuir-Blodgett method. In the scientific literature, there are several works devoted to such experiments. Cai-Xia Cheng et al. synthesized polymer containing a hydrophilic block poly-(ethylene oxide) (PEO) and hydrophobic block of dendronized linear poly(N, N-dimethyl acrylamide) (PDMA). [125] PEO45-b-PDMA69 films were obtained using the Langmuir - Blodgett trough, phase transitions, and film morphology at the air/water interface were studied. During this experiment, it was demonstrated that the PEO45-b-PDMA69 under compression could be stacked in close-packed worm-like micelles.

Costa et al. received a nanocomposite with intercalated poly (amidoamine) dendrimer with sodium carboxylate-terminated groups into the layered structure of hydrotalcite by anion exchange and studied the morphology of the resulting films using the Langmuir-Blodgett method. [126] Such intercalation of various molecules in layered adhesive structures through anion exchange leads to materials with expanded functionality to be used for the synthesis of catalysts and ceramic nanocomposites.

Pengfei Duan et al. have demonstrated that with the right combination of hydrophobic and hydrophilic groups in the dendrimer, it is possible to make a surface layer of dendrimers at the water/air interface. Thus, the assembly of a dendron containing hydrophilic peripheral groups of L-glutamate and hydrophobic azobenzene in the core was investigated. The addition of cyclodextrin molecules to the surface of the dendrimer promotes host-guest interaction and can make the film photoactive. [127]

Elizabeth K. Elliott et al. demonstrated the ability to form amphiphilic peptide layers using the Langmuir-Blodgett technique. Such peptides can be integrated into phospholipid membranes and used as carriers of chlorine ions. [128]

The successful preparation of Langmuir monolayers has been achieved with poly(propyleneimine) dendrimers in which the dendritic poly- (propylene imine) part acts as a polar group, and outside long alkyl chains form a hydrophobic moiety. [129] Various authors have described Langmuir-Blodgett formation of several dendrimer monolayers, which include PAMAM structures [28], poly(propyleneimine) dendrimers [29], carbazole [130], poly(aryl ether) dendrimers. [30]

Also, a lot of work has been done by the world-famous Russian scientific group led by Professor Aziz Musafarov, specializing in the synthesis and application of carboxylane dendrimers of different generations decorated by phenyldioxolane, phenylethyl, and ethylene oxide structural fragments. Carbosilane dendrimers are characterized by a practically defect-free, hyperbranched structure capable of carrying many terminal functional groups that form the outer sphere of the molecule. The properties of such dendrimers are determined by the molecular parameters of the outer layer. In this group's scientific works, the influence of the density, nature, and structure of such an outer layer on the behavior and stability of dendrimers at the water-air interface has been studied in sufficient detail. [131]

Despite this fact, in the literature, there is still very limited data on the study of the microstructure and properties of the obtained dendrimer layers, which motivate further investigation of this issue in more detail. There is no data about the application sulfonimide- based dendrimers as a monomer for film formation

2.2.3 Film formation procedure

Langmuir - Blodgett method allows the creation and characterization of monomolecular films at the air-liquid interface and their transfer to solid substrates. The equipment commonly consists of a bath filled with aqueous subphase with high surface tension (usually water) on which a monolayer is formed, two barriers for compressing the floating monolayer, and a force sensor for measuring surface pressure. Technically, the process includes several steps: spreading, compression, and transfer. Before spreading, the bath should be overfilled with pure water; the clean surface is crucial for film formation to prevent some artifacts. After spreading the solution of the dendrimer in a volatile solvent (benzene, toluene, chloroform, $CC1_4$) on the surface of the water, it is needed to wait when the solvent is evaporated. The concentration is selected so that the area of its monolayer does not exceed the area of the working surface of the Langmuir bath. The Langmuir trough is equipped with two barriers to limit the area of the monolayer formation; after evaporation of the solvent is finished, we can compress the monolayer by moving the barriers close to each other. During the compression, we can measure surface tension by using a wetted Wilhelmy plate. The Wilhelmy plate can be made from different materials, but the most favorable is paper a few square centimeters in area. The plate is attached to a balance with a thin metal wire. The force of the liquid pulling down on a plate is measured using a microbalance and used to measure the surface tension γ of the liquid-air interface using the Wilhelmy equation:

$$\gamma = \frac{F}{l\cos(\theta)}$$

where F - capillary force, l is the wetted perimeter equals 2w + 2d, where w is the plate width, and d is the plate thickness, θ is the contact angle between the liquid phase and the plate. [132] Since the paper plate is fully saturated with water, receding and expanded contact angles are zero. [133] The result is obtained as surface pressure that decreases the surface tension of pure water and surface with the film. The principle of the method is shown in Figure 11.

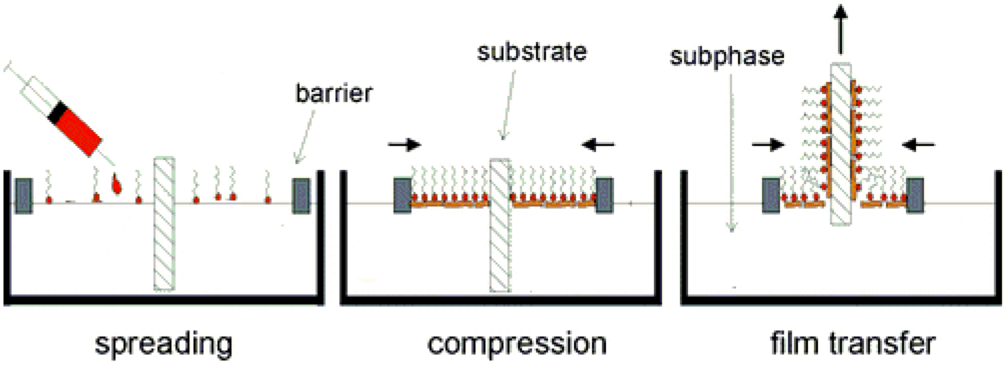


Figure 11. The principle of the LB technique.

2.2.4 Film analysis and characterization techniques

An optical microscope usually investigates the morphology of the transferred films in a bright-field illumination set-up. This fast and straightforward technique allows seeing the film surface with its µm-sized defects as well as overall film morphology. Optical microscopy is a non-destructive and rapid method of obtaining an impression of the layer quality. To get more detailed information on the surface of the LB films, samples were investigated by electron microscopy. Electron microscopy techniques are powerful tools for the characterization of the film morphology. For instance, a transmission electron microscope (TEM) provides resolutions of 1-5 Å and identification of elements in the single-atom scale [134]. Atomic force microscope (AFM) is one of the most modern instruments for studying the morphology and local properties of a solid surface with high spatial resolution. AFM belongs to the family of probe devices that allow visualization of surfaces with atomic resolution. With AFM, one may obtain microscopic maps describing the surface topography. AFM measurements can inform about such parameters as the roughness of the surface, the friction force between the measuring edge and surface of the sample, and Young's modulus. Using this microscope, you can examine both conductive and non-conductive surfaces. In addition, the non-conductive surface examined using AFM does not require the application of a conductive metal coating, which often leads to a noticeable deformation of the surface.

2.2.5 Factors affecting the quality of Langmuir-Blodgett films

The quality of the films is affected by the installation settings, for example, the absence of mechanical vibrations, the constancy of the speed of movement of the sample or proper deposition rate, the constancy of the speed of barrier motion. Also important to create the technological purity of the experiment. For example, by controlling the purity of the starting materials, the use of distilled and deionized water as the basis of a subphase, carrying out preparatory operations, such as etching and washing the substrates, preliminary cleaning of the subphase surface, creating a quasi closed volume in the working area. For successful monolayer formation, the control of surface pressure is essential. The surface pressure should be relatively high in the range of 20 – 50 mN/m and constant during the transferring process to ensure sufficient cohesion in the monolayer. The attraction between molecules in a monolayer is sufficient to prevent the monolayer from falling when transferred to a solid substrate. To determine the right surface pressure, it is needed to compress monolayer until collapse occurs, and the bulk film is formed instead of the monolayer. At the collapsing surface pressure, the stability of the monomolecular layer is disturbed, and it turns into a polymolecular film.

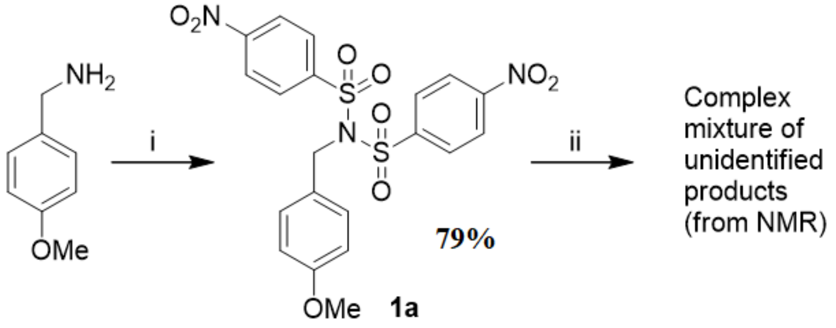
Chapter 3. Dendrimer synthesis. Result and Discussion

3.1 The general approach to the synthesis of sulfonimide-based dendrimers

For the synthesis of the designed dendrimers, I used a divergent approach because this method is easy to perform, and it allows us to achieve a large scale production of the target compounds. [90] In contrast to the alternatively used convergent method [90], dendrimers are synthesized by the stepwise addition of repetitive units.

3.1.1 Selection of the core molecule

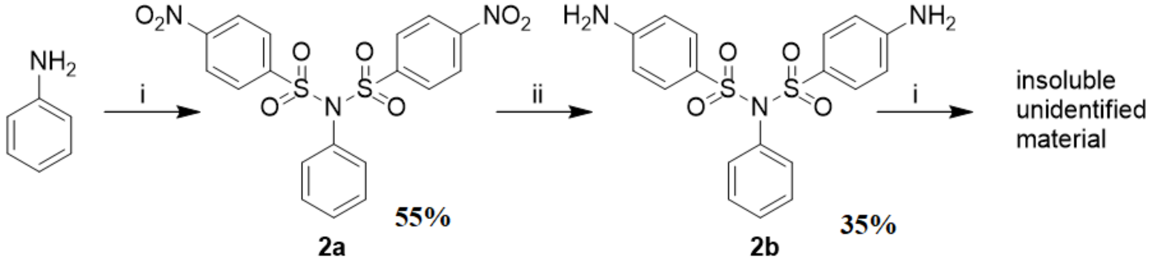
The most crucial step in the divergent synthesis of the dendrimer is the selection of a core molecule because the shape and number of generations will strongly depend on the nature of the core. For this purpose, we carried out a preliminary synthesis with three different primary amines as the potential cores. First, the synthetic utility of 4-methoxybenzylamine was investigated. As shown in Scheme 1, the reaction of the amine with two equivalents of 4-nitrobenzenesulfonyl chloride in the presence of triethylamine in refluxed dichloromethane readily gives sulfonimide **1a** with good yield taking into account filtration and washing.



Scheme 1. An attempt to use 4-methoxybenzylamine as the dendrimer core. Reagents and conditions: (i) 4-nitrobenzenesulfonyl chloride, Et_3N, CH_2Cl_2, reflux; (ii) $SnCl_2{\cdot}2H_2O$, $EtOH/CH_2Cl_2$, reflux.

The second step was the reduction reaction of the obtained dinitroaromatic Compound **1a** with inexpensive tin (II) chloride dihydrate. Tin (II) chloride is widely used as a mild reducing agent to reduce selectively and nearly quantitatively aromatic nitro groups into amino groups under acidic conditions with a simple procedure. [135] However, an attempt to reduce Compound **1a** (Scheme 1) led to a mixture of unidentified compounds. Presumably, some side reactions at the active benzylic position took place.

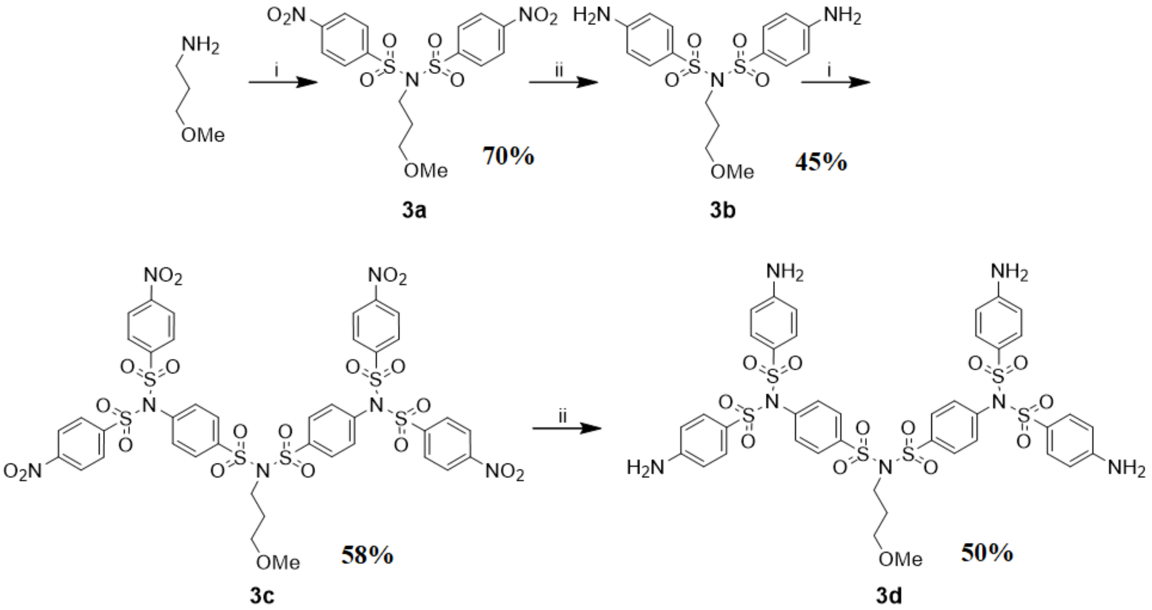
Taking aniline as the starting amine (Scheme 2) resulted in successful both persulfonylation reduction step. For aniline, the resonance of the lone pair at nitrogen atom with the adjacent π system decreases the availability of the lone pair. It makes aniline a poorer nucleophile, and this can result in lower reactivity and, as a result, low yield at the first step. However, an attempt at the persulfonylation of diamine **2b** yielded practically insoluble material limiting any further transformations to 2nd generation structures only.



Scheme 2. An attempt to use aniline as the dendrimer core. Reagents and conditions: (i) 4-nitrobenzenesulfonyl chloride, Et_3N, CH_2Cl_2, reflux; (ii) $SnCl_2 \cdot 2H_2O$, $EtOH/CH_2Cl_2$, reflux.

The negative results with 4-methoxybenzylamine and aniline show the limitations of the divergent synthetic route in which the selection of the core molecule can be time-consuming.

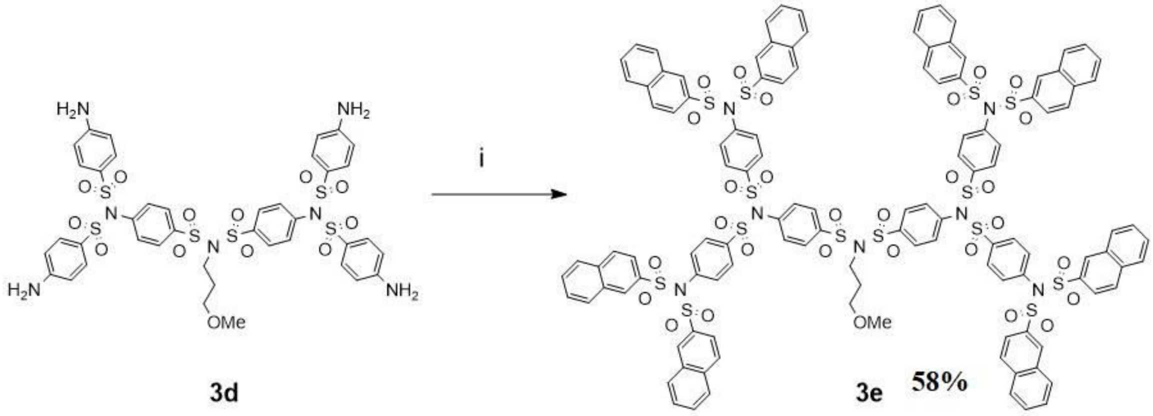
Finally, the use of 3-methoxypropylamine as the core unit turned out to be successful and allow to continue synthesis achieving targeted sulfonimide dendrimers. As shown in Scheme 3, the two repetitive steps of persulfonylation and reduction readily give rise to tetraamine **3d**. For the reduction reactions, the yield decreased due to additional washing of the obtained product



Scheme 3. Using 3-methoxypropylamine as the dendrimer core. Reagents and conditions: (i) 4-nitrobenzenesulfonyl chloride, Et_3N, CH_2Cl_2, reflux; (ii) $SnCl_2\cdot 2H_2O$, $EtOH/CH_2Cl_2$, reflux.

3.1.2 Functionalization of sulfonimide-based dendrimers with terminal naphthalene groups

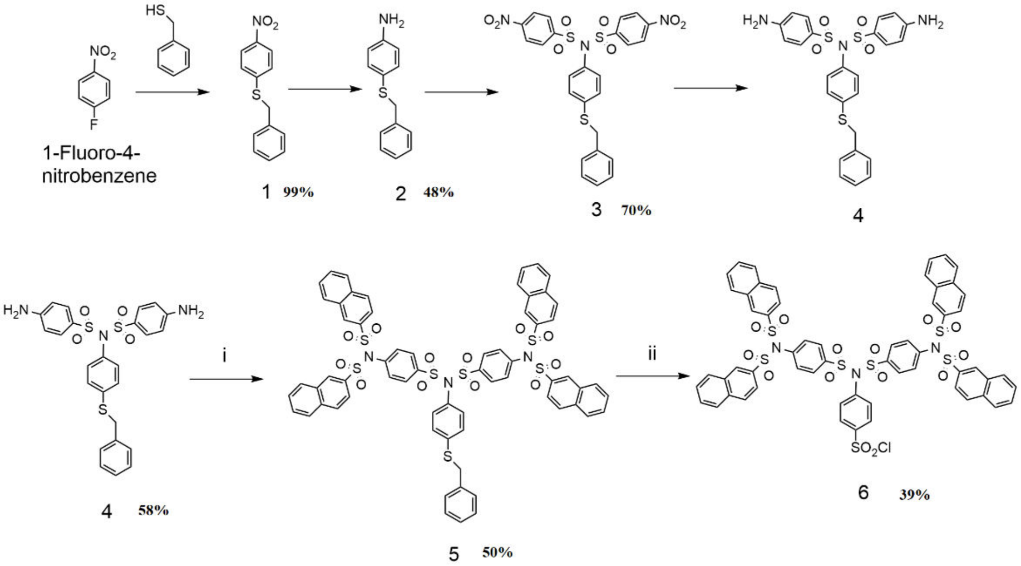
The obtained sulfonimide dendrimers were functionalized with terminal naphthalene groups because naphthalene groups give hydrophobic properties to the dendrimer. The terminal amines of different generations obtained according to repetitive steps shown on Scheme 3 were successfully persulfonylated with 2-naphthalenesulfonyl chloride to give 2nd, 3rd 4th, and 5th generations of dendrimers. The reaction leading to 3rd generation **3e** is shown on (Scheme 4).



Scheme 4. Preparation of the 3rd generation dendrimers. Reagents and conditions: (i) 2-naphthalenesulfonyl chloride, Et_3N, CH_2Cl_2, reflux.

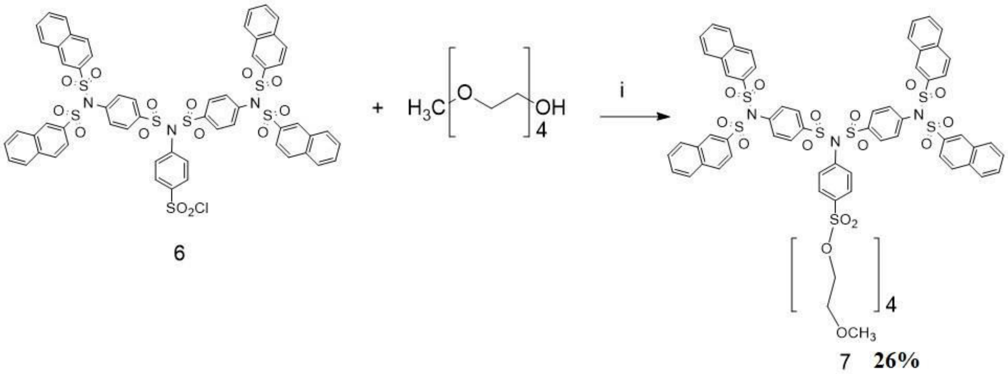
3.1.3 Synthesis of 2nd generation of sulfonimide-based dendrimer

As shown in Scheme 5, the synthesis starts from 4-Fluoronitrobenzene with the nucleophilic displacement of one fluorine group with benzyl thiol in the presence of K_2CO_3. The product **1** was obtained in 99% isolated yield. The nitro group of **1** was reduced to the amino group with $SnCl_2 \cdot 2H_2O$ to furnish amine **2** called 4-(benzylthio)aniline. The yield was drop down due to the purification procedure. The sulfonyl chloride was attached to 4-(benzylthio)aniline **2** to form persulfonylated dinitro Compound **3**. The reaction was carried out in CH_2Cl_2 in the presence of Et_3N. The two nitro groups of compound **3** were reduced to the amino groups with $SnCl_2 \cdot 2H_2O$ to furnish amine **4,** which was obtained as a yellow solid. The obtained amine is a stable compound and can be stored at ambient conditions for a long time without any detectable decomposition. Diamine **4** was persulfonylated in one step with 2-naphthalenesulfonyl chloride in the presence of triethylamine, giving superbranched sulfonimide **5,** which was successfully converted into sulfonyl chloride **6** using *N*-chlorosuccinimide as a chlorinating reagent.



Scheme 5. a) Reagents and conditions: (i) K_2CO_3, DMF, 50°C; (ii) $SnCl_2{\cdot}2H_2O$/EtOH, reflux 2h; (iii) 4-nitrobenzenesulfonyl chloride, Et_3N, CH_2Cl_2, reflux; (iv) $SnCl_2{\cdot}2H_2O$/EtOH, reflux 2h; **b)** (i) 2-naphthalenesulfonyl chloride, Et_3N, CH_2Cl_2, reflux; (ii) *N*-chlorosuccinimide, HCl, AcOH, CH_2Cl_2, 5°C.

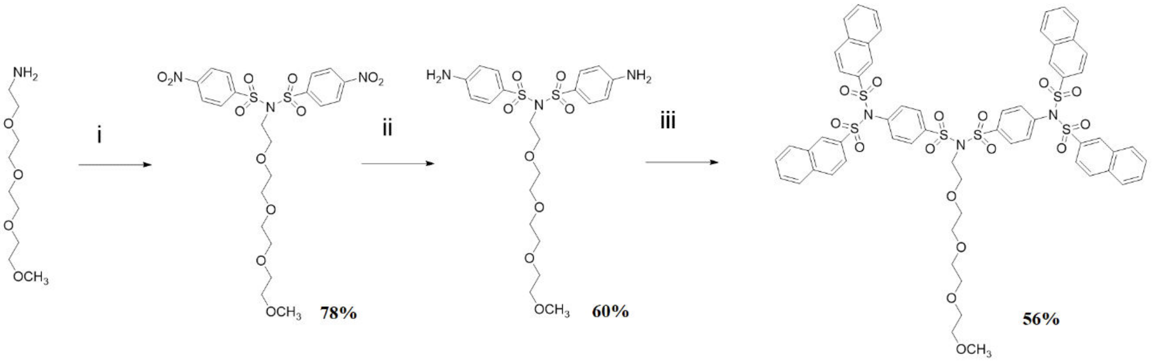
The last step was performed using a convergent approach. Tetraethyleneglycol monomethyl ether was reacted with sulfonyl chloride 6 in acetonitrile in the presence of Et_3N and $NaHCO_3$ as a scavenger to give Compound 7, as shown in Scheme 6, proving that the reactivity of dendron 6 is comparable to that of regular arylsulfonyl chlorides.



Scheme 6. (i) Et_3N, CH_2Cl_2, reflux.

The reaction yield was relatively low, possibly due to the steric effect at the final stage. The dendron production process was laborious and economically unprofitable due to the commercial availability of ready-made arylsulfonyl chlorides.

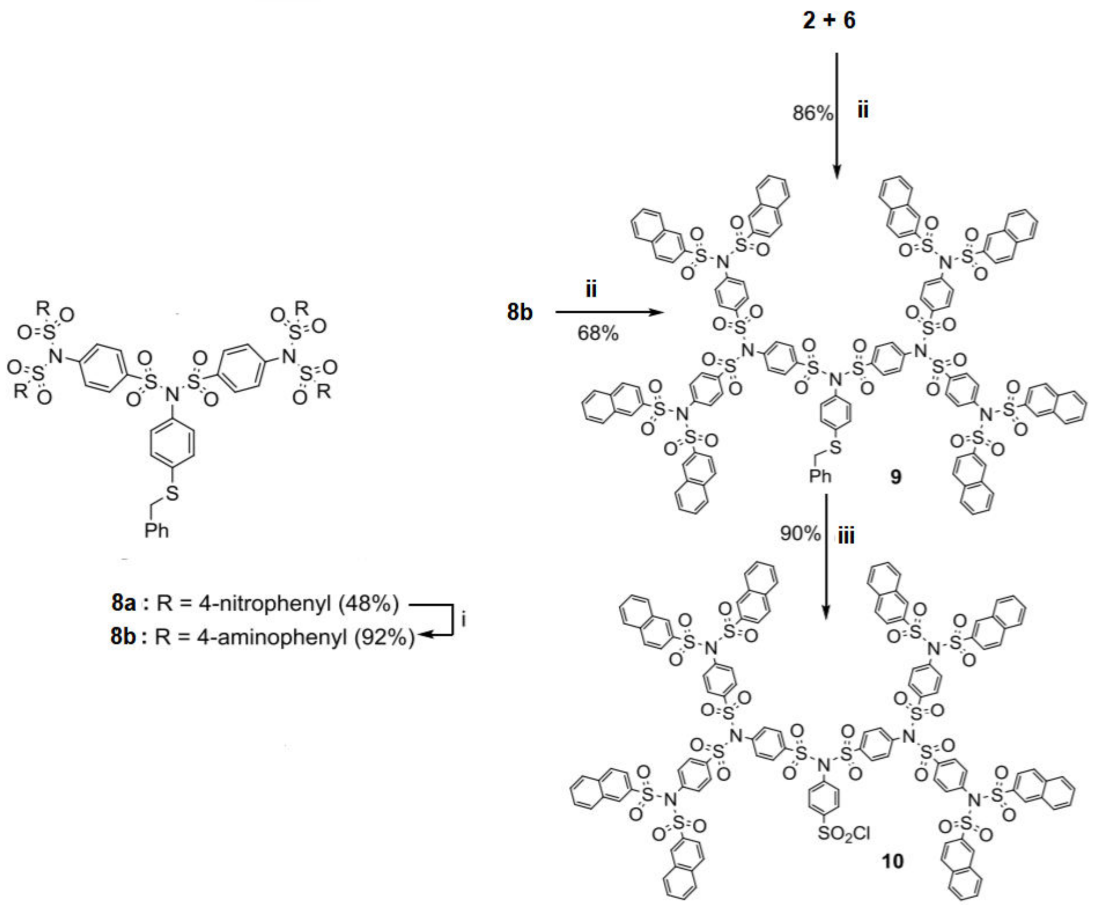
The second generation was also obtained by the divergent method in two steps: coupling and activation. A commercially available primary amine was used as the core molecule. The p-nitrobenzene sulfonyl chloride was attached to methoxypolyethylene glycol amine to form a persulfonylated dinitro compound. The reaction was carried out in CH_2Cl_2 in the presence of Et_3N. The two nitro groups were reduced to the amino groups with $SnCl_2{\cdot}2H_2O$ to furnish amine. Diamine was persulfonylated in one step with 2-naphthalenesulfonyl chloride in the presence of triethylamine, giving second-generation sulfonimide dendrimer. As a result, using a two-stage approach, it was possible to obtain the target second generation, decorated with four naphthyl groups.



Scheme 7. Using Methoxypolyethylene glycol amine as the dendrimer core. Reagents and conditions: (i) 4-nitrobenzenesulfonyl chloride, Et_3N, CH_2Cl_2, reflux; (ii) $SnCl_2{\cdot}2H_2O$, $EtOH/CH_2Cl_2$, reflux. (iii) 2-naphthalenesulfonyl chloride, Et_3N, CH_2Cl_2, reflux.

3.1.4 Synthesis of 3rd generation of sulfonimide-based dendrimer

Since Compound 6 (Scheme 6) showed good solubility in dichloromethane at high concentrations, this made it possible to use this non-commercial dendron for the synthesis of 3rd generation by the convergent method. Both convergent and divergent routes carried out the synthesis of the third-generation dendron. The convergent route combining amine 2 (Scheme 5) and sulfonyl chloride 6 gave third-generation dendrimer 9 in 86% yield. The divergent way of this procedure involved the reduction of tetranitro Compound 8a to yield tetraamine 8b and persulfonylation of the latter with 2-naphthylsulfonyl chloride affording Compound 9 in 68% yield. Sulfide 9 was, in turn, oxidized with N-chlorosuccinimide to yield the third-generation sulfonyl chloride-based dendron 10. (Scheme 8)



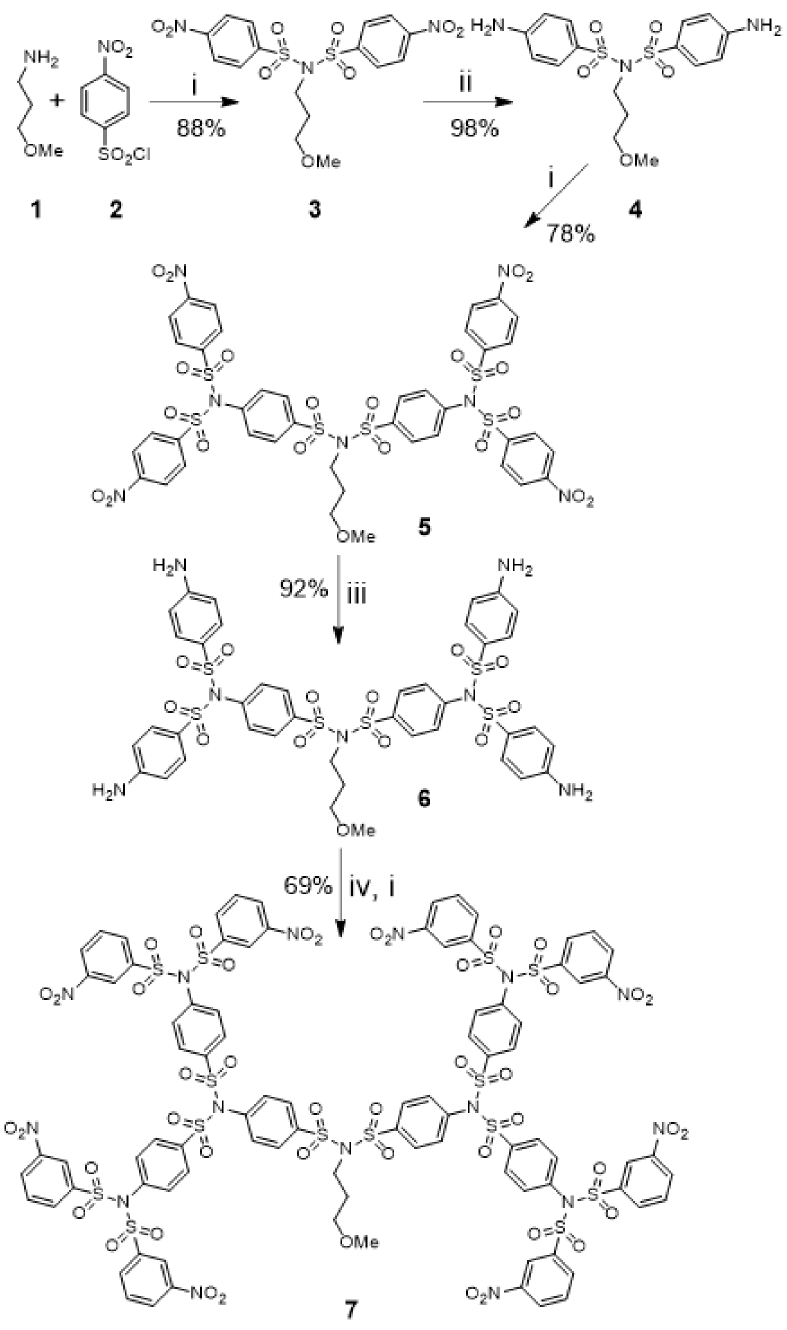
Scheme 8. Convergent and divergent syntheses of 2-naphthyldecorated third-generation dendron 10. Reagents and conditions: (i) $SnCl_2 \cdot 2H_2O$, CH_2Cl_2–EtOH (1:1), HCl, reflux; (ii) $ArSO_2Cl$, Et_3N, CH_2Cl_2, reflux; (iii) N-chlorosuccinimide, HCl, AcOH, CH_2Cl_2, 0°C.

The structure and purity of Compound 10 were fully confirmed by ^{1}H and ^{13}C NMR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis. A reaction of the core amine 2 with three equivalents of Compound 10 in the presence of triethylamine led to the recovery of starting materials in a 90% yield. The LCMS analysis of the remaining part revealed a peak with m/z = 2821.0 that corresponds to monosulfonylated 1+Na^+. This observation seems to indicate that both the steric size and decreased electrophilicity of the sulfonyl chloride unit of 10 do not allow for further convergent growth.

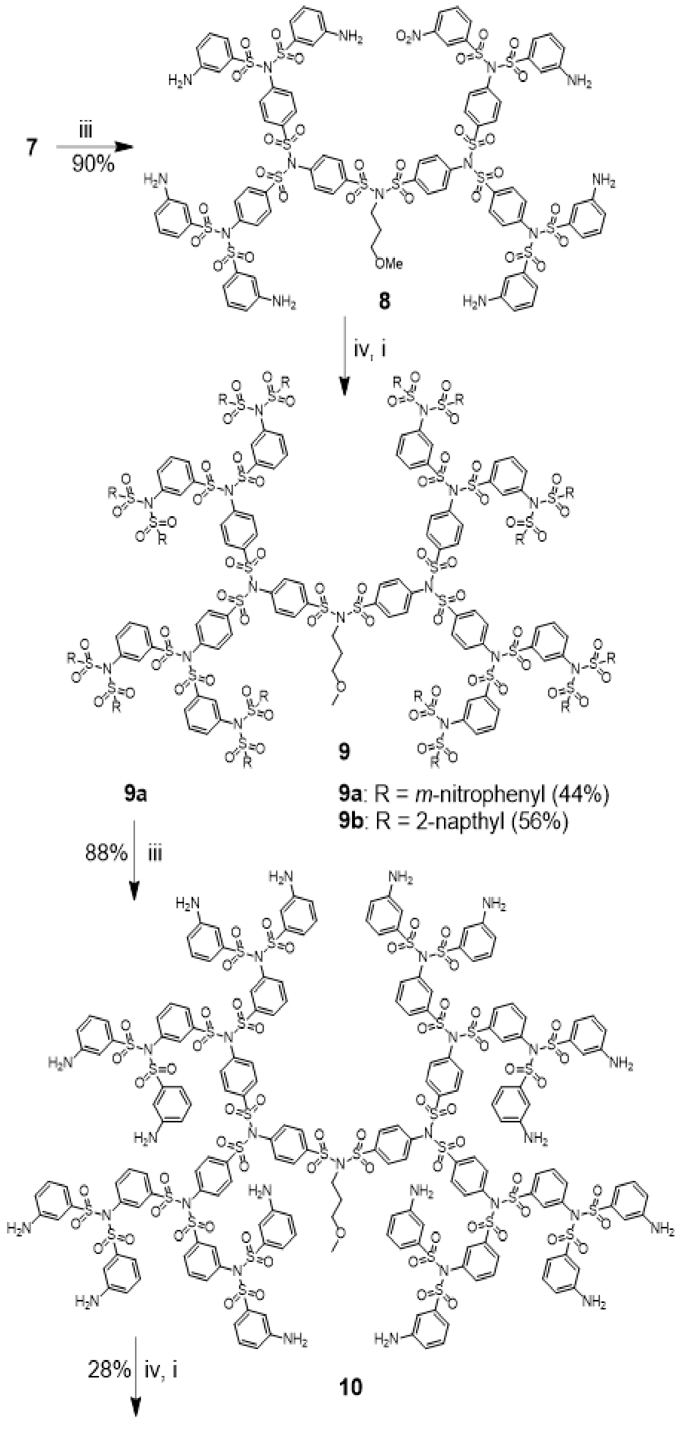
Sulfonimide-based dendrons of first to third generations with chlorosulfo-groups at their focal points presented here can be considered as useful reagents for a convergent acylation of multi functionalized core compounds. Both convergent and divergent synthetic approaches to the sulfonimide-based dendrons were realized with comparable yields of the final structures. It appears that in this case, the convergent route reaches its practical limit at third-generation, whereas the divergent approach has better chances at achieving higher generation sulfonimide-based dendrons. Dendrons of first and second generations have reactivity similar to that of small aromatic sulfonyl chlorides (e.g., tosyl chloride).

3.1.5 Synthesis of 4th and 5th generation of sulfonimide-based dendrimer

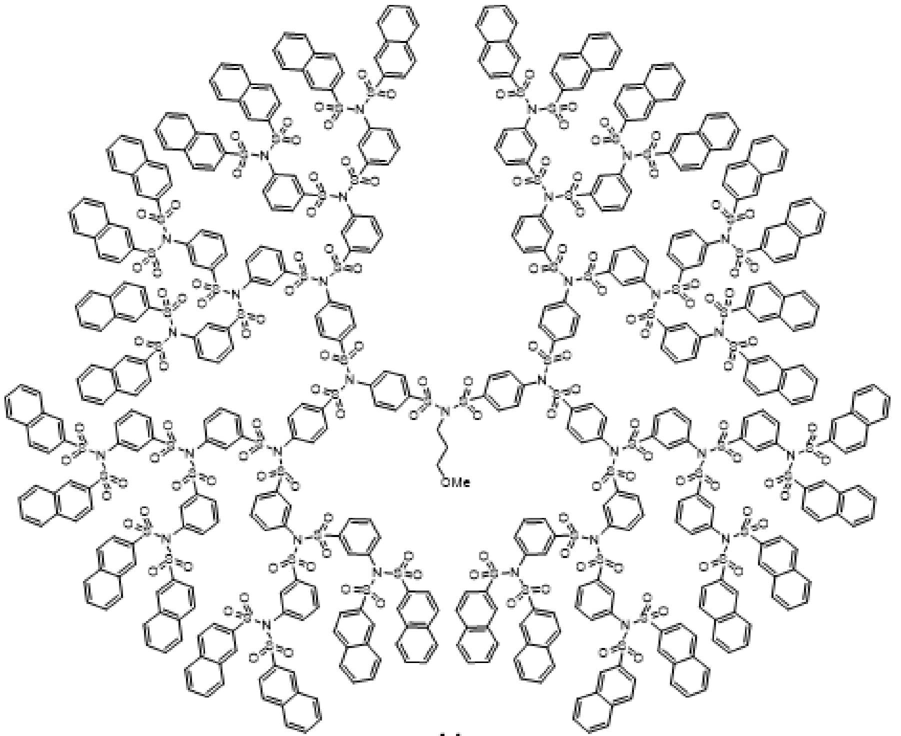
Schemes 9 and 10 illustrate the full synthetic path to the fourth and fifth-generation dendrimer. Synthetic procedures yielding tetraamine **6**, as well as the reduction of nitroaromatic compounds, are similar to those reported formerly. [91] The use of other reducing reagents such as Fe/NH_4Cl, Zn/AcOH, N_2H_4/$FeCl_3$-C gave mixtures of products. The major obstacle causing reduced yields at higher generations is the low solubility of branched species bearing multiple aromatic amino groups in dichloromethane. For example, tetraamine **6** was converted into octanitro-derivative **7** only at 32% yield after being refluxed in dichloromethane for 24h. A part of Compound **6** was not dissolved under given conditions and spread over the flask walls. Presumably, this occurs on account of the aggregation of the oligoamines in the low polar dichloromethane through multiple intermolecular hydrogen bonds. The amines are nicely soluble in more polar acetone or acetonitrile, preventing the aggregation of the solute through hydrogen bonding. However, the persulfonylation reaction in these solvents does not proceed completely. Multiple products of incomplete substitution were isolated. The isolated mixture of products was soluble in pure dichloromethane. Only the sulfonylation of oligoamines in dichloromethane was shown to give products of the complete substitution. [1,84,85,86] Therefore, it seemed reasonable to split the amine persulfonylation into two steps. As mentioned in Scheme 8 and described in the experimental part as amines **6**, **8**, and **10** were first partially sulfonylated in a 1:1 mixture of dichloromethane/acetone giving a combination of incompletely substituted products. The isolated mixture of products was dissolved in pure dichloromethane, and its second persulfonylation step resulted in desired sulfonimides in much better yields compared to formerly described ones; for example, Compound **7** was isolated in 69% yield unlike previously reported 34% yield for similar species. [86] As shown in the earlier study, the use of m-nitrophenyl instead of p-nitrophenyl groups in the third-generation species, such as Compound **7**, was due to the reduced solubility of dendritic sulfonimides with multiple peripheral p-nitrophenyl units preventing their purification completely. [86] The two-step approach allowed for significant scale-up production of higher generation sulfonimide dendrimers. Thus, third-generation octanitro Compound **7** was prepared on a 7g scale in one synthetic run while fourth-generation species **9a** and **9b** were produced on 4g and 5g scales, respectively. The multigram availability of fourth-generation dendrimers prompted us to undertake further steps to prepare fifth-generation sulfonimide dendrimer. The reduction of hexadecanitro Compound **9a** readily gave hexadecaamine **10** in 88% isolated yield. The two-step persulfonylation of 10 with 2-naphthalene sulfonyl chloride resulted in 2g (28%) of the fifth-generation dendrimer **11**. All sulfonimide dendrimers were isolated as crystalline solids with rather high melting points (>130°C).



Scheme 9. The divergent synthesis of sulfonimide-based dendrimers. Reagents and conditions: (i) Et_3N/CH_2Cl_2, reflux 2h; (ii) $SnCl_2{\cdot}2H_2O/EtOH$, reflux 2h; (iii) $SnCl_2{\cdot}2H_2O/EtOH/CH_2Cl_2$, 40° C, 6h; (iv) CH_2Cl_2/acetone, 3-nitrobenzenesulfonyl chloride, reflux 24h.



Scheme 10. The divergent synthesis of sulfonimide-based dendrimers. Reagents and conditions: (i) Et_3N/CH_2Cl_2, reflux 2h; (ii) $SnCl_2 \cdot 2H_2O/EtOH$, reflux 2h; (iii) $SnCl_2 \cdot 2H_2O/EtOH/CH_2Cl_2$, 40° C, 6h; (iv) CH_2Cl_2/acetone, 3-nitrobenzenesulfonyl chloride, reflux 24h.



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Scheme 10. Continuation. The longer reaction times (72h) were required for the synthesis of Compounds **9** and **11**.

The compounds are shown in Schemes 8, and 9 (except for amines **8** and **10**) were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and mass spectrometry (MS). ^{1}H NMR spectrum of Compound **11** recorded in $CDCl_3$ showed considerably broadened signals that are typical for high molecular weight polymers indicating slow conformational changes in the solution. The amine intermediates **8** and **10** were only characterized by ^{1}H NMR and MS and used the same day for persulfonylation steps on account of their tendency to oxidize quickly. Although the yield of 28% for Compound **11** might be considered low from the standpoint of organic chemists but taking into account multiple condensation reaction steps and ca. twofold increase of the molecular weight while going from fourth to the fifth generation, it provides a sufficient amount of the material for applications. Dendrimers **7** and **9a** decorated by eight and 16m-nitrophenyl groups, respectively, exhibited good solubility in cold dichloromethane and chloroform. However, the compounds precipitate completely from the solution upon heating to 40℃ and dissolve again upon cooling to the room temperature as revealed by both variable temperature NMR experiments and the visual inspection. Compounds **9b** and **11** bearing peripheral naphthyl groups are perfectly soluble in these solvents independently on the temperature.

As a result of the synthetic part, all the tasks were completed: the core molecule was selected, the synthesis of 2-5 generations of sulfonimide dendrimers with naphthyl groups was performed. Dendrimers were obtained in sufficient quantities for further purification and analysis. Detailed synthetic procedure and NMR and Mass spectroscopy data are presented in the Appendix Section.

Chapter 4. Film preparation and characterization

4.1 Film preparation

For experiments on the generation and handling of self-assembled and covalent monolayers, a computer-controlled film-balance setup KSV NIMA Langmuir – Blodgett trough, coupled with a Brewster angle microscope (BAM), constructed by KSV Instruments Ltd., Finland, was used. [136] The trough has a working area of 14 × 54 cm^2 and was set on a vibration confinement table and closed in a chamber. The water used was purified using a Milli-Q plus water purification system with an electric resistance of 18.4 MΩ. To prepare a solution for spreading, we dissolved our dendrimer in the ideal solvent. The solvent should be insoluble in the subphase (water), volatile, able to dissolve the substance, and have a positive spreading coefficient, which allows for pulling the dispersed particles out by the spreading of solvents. According to these requirements, we selected chloroform as a solvent with a spreading coefficient of 13.9 mN/m. We prepared solution sulfonimide-based dendrimers with a concentration of 2 mg/ml and spread 40 µl of the solution of our dendrimers in chloroform dropwise by a microsyringe on the Langmuir trough filled with the water subphase. Blank control isotherms were determined before dendrimer spreading to confirm the purity of the surface. After spreading the dendrimer solution on the surface of the water, we need to wait until the solvent evaporates, usually, approximately 20 min. After evaporation of the solvent is finished, we can compress the monolayer by moving the barriers close to each other. During compression, we can measure surface tension by using a wetted Wilhelmy plate. The surface pressure-area (π-A) isotherms were measured by symmetric compression with a constant barrier speed of 5 mm/min. Photoreaction in films was performed with a 250 W UV lamp (254 nm) at a distance of 30 cm, the set up shown in Figure 12. At first, the monolayer was formed by compressing the barriers; then, we irradiated the monolayer on the water surface for 15 min. After the irradiation process, the monolayer was transferred onto the substrate. The monolayer deposition took place only during the pulling out (upstroke) mode. The monolayers on the water surface were transferred to the solid substrates, which were previously immersed in the subphase.

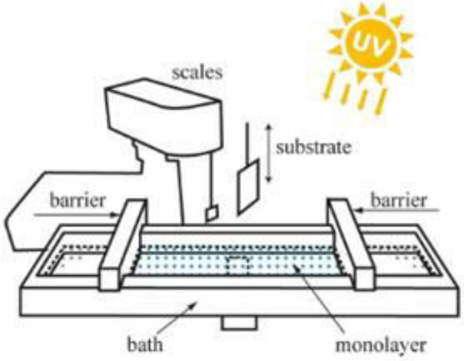

Figure 12. Set up for covalent and non-covalent film formation.

4.1.1 Selection of monomeric units

Film formation refers to a process of creating a thin film and transferring it on different surfaces. The film formation process is essential to the final appearance and functionality of the coating. The possibility of creating chemical film layers is determined by the nature and the number of surface groups, and the type of polymer backbone architecture. As substances for film formation can be used molecules which contain hydrophilic tail and hydrophobic surroundings. Various polymers, such as polyimides, polydiacetylene, and polymer-like structures such as dendrimers, satisfy these conditions. [137] For the investigation of the film formation, four compounds were used in the present study. There are obtained and discussed in the previous chapter sulfonimide-based dendrimers from the 2nd to 5th generation decorated with hydrophobic naphthyl terminal groups for their stable stay on the surface of the water. Upon compression conditions on the air/water interface, the dendrimers molecules can be close-packed in two dimensions (2D) manner and finally collapsed into an unusual three-dimensional (3D) aggregate. [138] It is not necessary to have a long alkyl tail in the structure; dendrimers can be modified using peripheral groups. [139] We introduce a methoxypropyl group in the focal point to create a hydrophilic tail for enhancing interaction with aqueous subphase and decorate a dendrimer with naphthyl groups to create a hydrophobic environment. The schematic structures of prepared substances for monolayer preparation and a possible 3D arrangement of dendrimer molecules are shown in Figure 13.

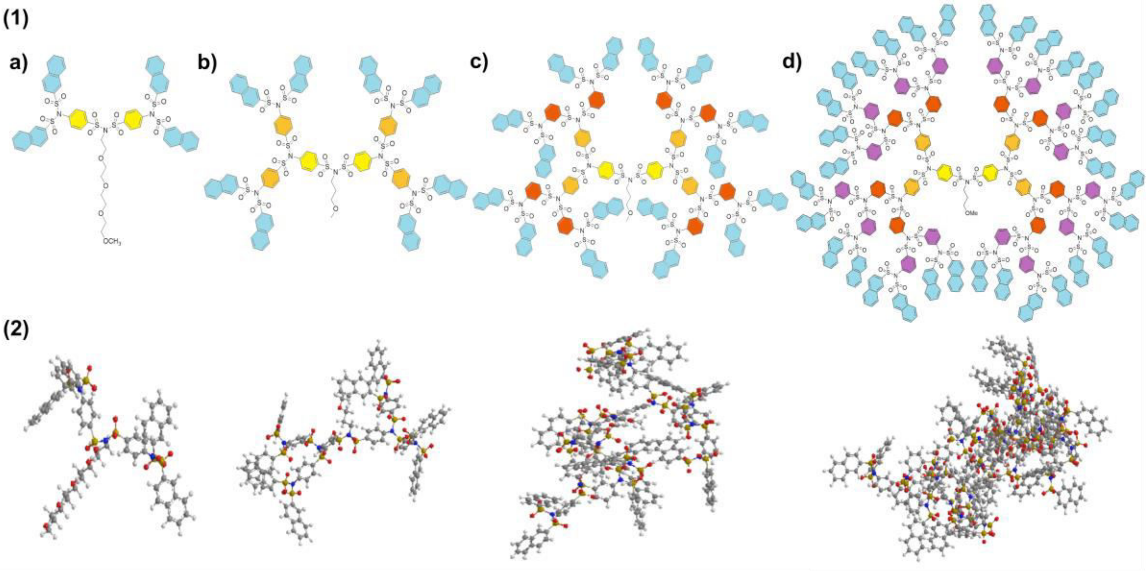

Figure 13. (1) The structure of interest a) 2nd generation G2, b) 3rd generation, c) 4th generation, and d) 5th generation; (2) 3D Chemical Structure View of dendrimers. (Note: the numbers of the generations shown in this scheme are generally admitted for sulfonimide dendrimers. However, following the traditional nomenclature G2 in the Scheme corresponds to G1, G3 to G2, etc.)

From the built 3D models shown in Figure 13 (2), the radii of gyration Rg were theoretically calculated using the formula:[140]

$$< Rg^2 \geq \frac{1}{M} < \left[\sum_{i=1}^{N} m_i \, |r_i - R|^2 \right] >$$

where R is the center-of-mass of the dendrimer, m_i is the mass of the i_{th} atom, and M is the total molecular weight of the dendrimer. The results for G3, G4, and G5are shown in Figure 14. For the second generation, the gyration radius is 9 Å.

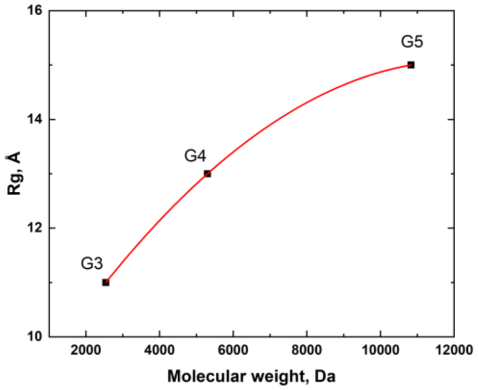

Figure 14. The radius of gyration, R g vs. molecular weight of dendrimers

This study demonstrates the possibility of the formation and transfer of thin sulfonimide dendrimers films of four different generations to the solid substrate using the Langmuir-Blodgett technique. This method allows forming ultrathin films on the water-air interface. We prepared two types of films with noncovalent and covalent bonding for each generation shown in Figure 13. Covalent bonding is carried out using the dimerization of naphthyl terminal groups under the action of UV radiation. [141,142,143] The monolayer was first compacted by moving the barriers. It led to an increase in the probability of the formation of intermolecular covalent bonds between naphthyl groups. Then this film was irradiated by a UV source at a fixed pressure. Still, surface area behavior changed due to the rearrangement of naphthyl groups under UV light. The films with different bonding and generations were analyzed and compared to each other to investigate structure – properties correlations. To visualize the Langmuir layer at the air-water interface, a Brewster angle microscope (BAM) was used. The observation was performed during the compression condition, and the result is shown in Figure 15.

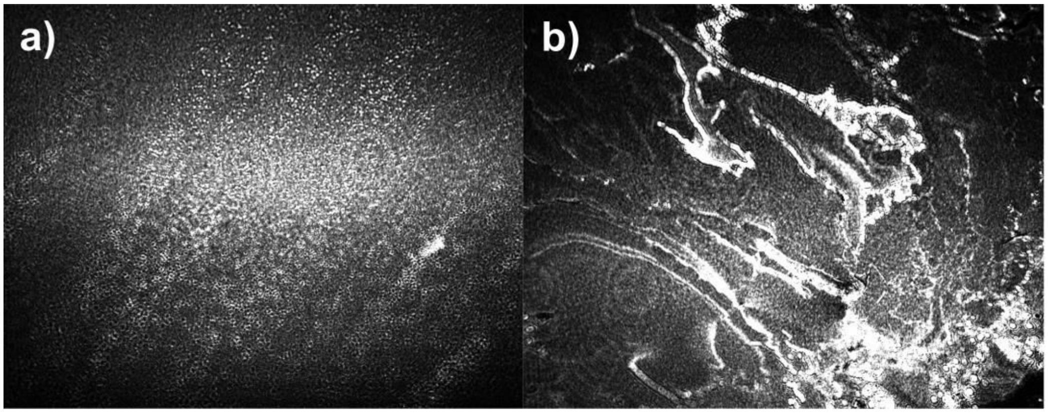

Figure 15. The dendrimer layer of G2 in liquid condensed phase on the Langmuir Trough, imaged by a Brewster angle microscope. a) near critical pressure b) at a pressure higher than critical.

4.1.2 Control of film formation by measuring π - A isotherms

Control of surface pressure is essential for monolayer formation. During the film formation process, the main experimental result is an isotherm of surface pressure versus area per molecule called the π - A isotherm. The capability of G2, G3, G4, and G5 dendrimers to form stable monolayers at the air-water interface was studied by the corresponding surface pressure-area (π-A) isotherms. When the solution of sulfonimide-based dendrimers is spread on the surface of the water at low surface concentrations, the initial molecular organization is random. At very low surface pressures, dendrimer molecules do not interact with each other. At this stage, the film is in the state of an ideal gas. As the surface pressure increases, the molecules remain on the surface and do not form large aggregates. Figure 16 shows the changes in the surface pressure with the area per molecule for the four pure dendrimer generations. In all cases, monolayer compression produces an increase in the surface pressure, indicating the dendrimer surface activity in the air-water interface. According to the results for the 2nd generation dendrimer shown in Figure 16a, it is possible to distinguish different monolayer phases: liquid expanded, liquid condensed, and solid phase. [144]. In the beginning, the surface pressure is close to zero. Upon compression, an inflection point is observed at 5 mN/m in the isotherm, which means that the transition from one phase (type) of the organization to another takes place. Under continuous compression, the surface pressure in the gas phase starts increasing at a surface area of 500 cm^2 or 150 $Å^2$. Through the transition from the liquid expanded to the liquid condensed phase, a solid monolayer phase was formed above 15 mN/m. Further compression resulted in a steep rise in the surface pressure up to 45 mN/m, which is a collapsing pressure, and molecules were forced out of the two-dimensional plane. It should be noted that between G2 and G3, G4, and G5 dendrimers, the only structural difference resides in the focal point. Moreover, the stable isotherm film showed perfect reversibility in successive compression/decompression cycles, as revealed in Figure 16a. The reversibility of the Langmuir monolayer formation was analyzed using successive compression-expansion cycles, and the time stability through isobaric measurements of the film deformation. The study of both properties provides additional information about the interactions established between the dendrimeric molecules, their ability to remain stable in the formation of a monolayer, and the capacity to return to the two-dimensional gaseous state once unzipped the film. At higher surface pressures, before the point of collapse, the second compression isotherm moves to smaller areas, indicating a possible loss of material during compression due to loss of the monolayer forming molecules in the subphase or adhesion of molecules to the Wilhelmy system. As seen from Figure 16b, the critical pressure decreases with increasing generation number, which is probably due to an increase in spatial stress and weaker interaction with the water subphase.

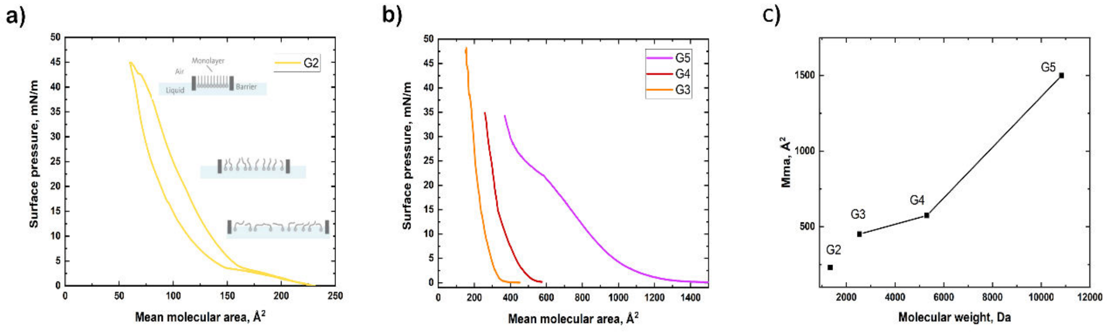

Figure 16. a) The hysteresis curve of the G2 monolayer shows the compression/re-expansion behaviors of the particulate monolayers b) pressure–area isotherms of the G3, G4, and G5 monolayers.

The pressure-area isotherms for the 3rd, 4th, and 5th generation of dendrimers are given in Figure 16b, and the surface compression data are expressed numerically in Table 2. The surface pressure was relatively high in the range of 20 – 50 mN/m. For generations 2nd, 3rd, 4th, and 5th, the first inflection represents the area at which the monolayer enters the liquid expanded phase. The critical pressure is the condition where monolayer still exists. Further pressure increasing results in monolayer collapsing. Moving from the lower generation G3 to the higher one G5, the critical pressure decreases. The primary reason for this behavior is an increase in the steric effect of the molecules of the higher generation of dendrimers. The second possible explanation is that by increasing the dendrimer generation number, it becomes more hydrophobic. Its attraction to the water surface is relatively less as well. It helps to keep the concentration of dendrimer molecules at the air-water interface constant. The first inflection point reaches the maximum for the 4th generation of dendrimers. The average transfer ratio of both dendrimer film types of 2nd, 3rd, 4th, and 5th generation was calculated by KSV NIMA software v 11.1.3 [136] with respect to all initial parameters. The values were equal to 1.1, 0.91, 0.8 and 0.67, respectively.

Table 2. Summary of transition point and critical surface pressure in pressure–area isotherms obtained by using a Langmuir–Blodgett trough.

Generation	First inflection, mN/m	Critical pressure, mN/m
2nd	5	45
3rd	20	49
4th	15	35
5th	20	33

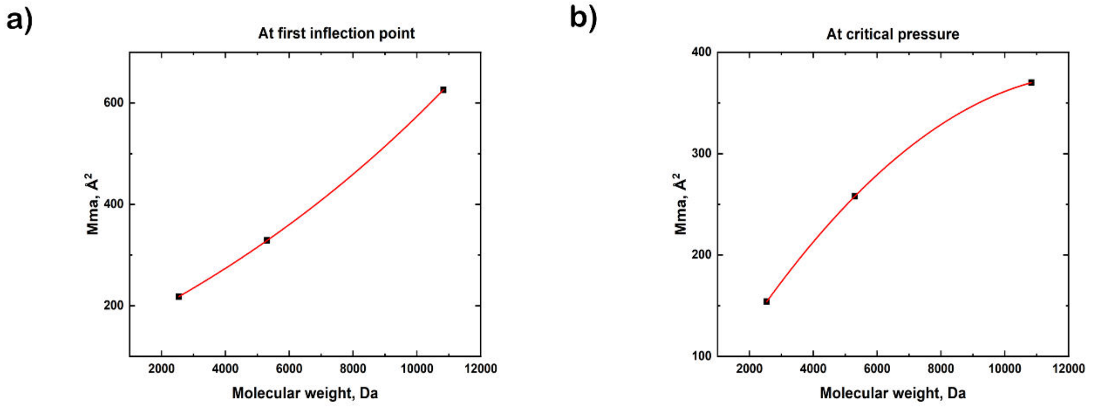

Figure 17. a) Mean molecular area at the first inflection point vs. the molecular weight of dendrimers b) Mean molecular area at critical pressure vs. the molecular weight of dendrimers.

Figure 17 shows that the mean molecular area increases with increasing dendrimer generation and, accordingly, with an increased molecular weight at critical pressure and first inflection. The nature of the dependences is different; for the case with critical pressure, there is a dense packing of dendrimer molecules into a layer on the water/air surface.

4.1.3 Selection of substrates for film deposition

For film visualization, they were transferred on a silicon substrate with 300-nm oxide layers. To measure the contact angle, the films were transferred to the cover glasses. For AFM measurements, mica was used as a substrate, and copper grids were used for TEM investigation. UV Quartz glass (which has high transmission between 200 nm and 2500 nm) is perfect for working within the UV-Visible spectrum. All substrates are shown in Figure 18.

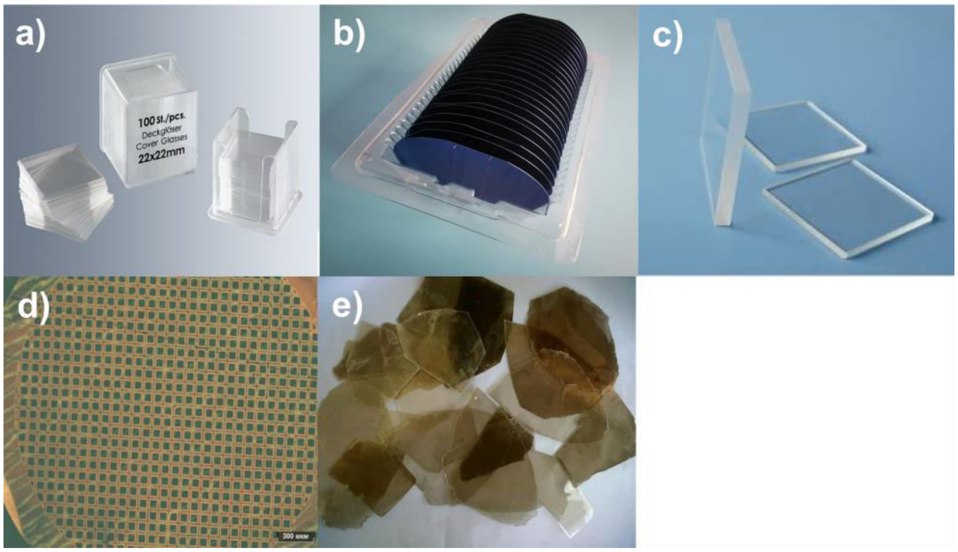

Figure 18. Substrates for film transfer a) cover glass 22x22 mm, b) silicon substrate with 300-nm oxide layers, c) quartz glass plate 10*10*0.5mm, d) copper grid 300 Mesh hole width 58x58 µm, e) mica straps fixed on the glass.

4.1.4 Deposition methods

The LB films of the dendrimers were transferred onto glass, oxidized silicon wafers, and mica by a vertical lifting method with a typical vertical speed of 2 and 5 mm/min. The LB films were transferred on copper grids by the Langmuir – Schaefer method as shown in Figure 19. All substrates before the transfer procedure were first cleaned by isopropanol and acetone and then rinsed several times in distilled water.

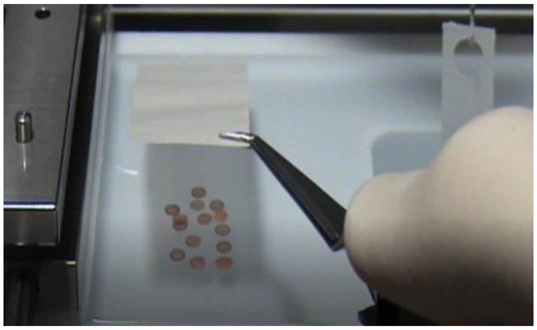

Figure 19. Transfer dendrimer film on copper grids for TEM analysis.

The transfer ratio was defined as A_L/A_S, where A_L decreases the area occupied by the monolayer on the liquid surface, at constant surface pressure, and A_S is the coated area of the solid substrate.

4.2 Film analysis

KSV NIMA Stand-Alone MicroBAM managed the visualization films on the air-water interface. The analysis was carried out using scanning electron microscopy (SEM) by Carl Zeiss (Supra 40) with a voltage of 10 kV and optical microscopy by Carl Zeiss AXIO Scope A1. Ellipsometry measurements estimated the thickness of the films transferred on mica were carried out using a Sentech SE 800 PV and by atomic force microscopy (AFM) Cypher ES High Resolution using the AM-FM Viscoelastic Mapping method [145] with a silicon probe with a resonant frequency of 220 kHz and constant elasticity of 17 N/m. The method with an operating range between 1 MPa and hundreds of GPa is suitable for a wide range of samples from biomaterials and polymers to metals and ceramics. [146]. The Young's modulus was measured by a Hertz sphere indenter with a sphere radius equal to the radius of the curvature of the probe, 10 nm. Images were treated and analyzed using Gwyddion, open-source software for the visualization and analysis of scanning probe microscopy data. UV spectra were obtained by S-3100 UV-Vis Spectrophotometer. The contact angle measurements of the transferred glass thin films were performed by a Drop Shape Analyser – KRÜSS DSA 30. The surface morphology of the free-standing films transferred on a copper grid holder with a hole width of 58x58 μm was determined by transmission electron microscopy (TEM), model JEM 2100F (UHR/Cs), with an acceleration voltage of 200 kV. The nonlinear optical properties of dendrimer films were studied by measuring the nonlinear signal arising from the action of femtosecond laser radiation with a wavelength of 800 nm, a pulse duration of 60 fs, a power of 30 mW, focused by a 5 cm lens, on the sample surface. Laser radiation was incident at an angle of 45 degrees, and a nonlinear signal was recorded by a photomultiplier in the photon counting mode in the direction of the reflected pump beam.

Some parameters need to be analyzed before thin films can be used for real technological applications. It is necessary to check and prove that transfer took place and that the film is deposited on the substrate. For this purpose, the film should be visualized to ensure that the film contains large uniform domains. For visualization, LB films were transferred onto oxidized silicon plates. The choice of the substrate was based on the fact that silicon wafers are used to visualize transparent graphene under an optical microscope. [147] This type of substrate allows visualization of the presence of a film by the naked eye. Optical micrographs were obtained for all investigated films. Figure 20a, d shows an image of the film made up of the 5th generation of the sulfonimide-based dendrimer. As revealed from the picture, the transfer was successfully made, and considering the scale of the image, there are quite large domains without any damage or imperfections. There are no major differences when comparing covalently and noncovalently formed films, which means that sulfonimide-based dendrimers are suitable for both types of film formation.

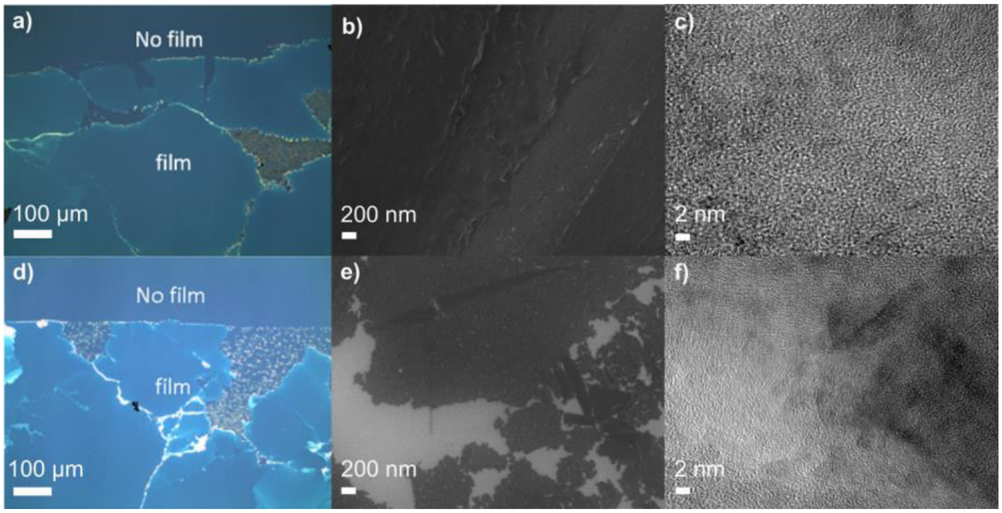

Figure 20. a) Optical micrograph and b) SEM images of UV-stabilized films deposited on an oxidized silicon plate, c) TEM image of UV-stabilized films transferred onto a 300 mesh copper grid, d) Optical micrograph, and e) SEM image of noncovalent films deposited on an oxidized silicon plate and f) TEM image of noncovalent films transferred onto a 300 mesh copper grid.

The possible reasons for the discontinuous LB thin film shown in Figure 20 are a reorientation of molecules during deposition or after deposition and chemical isomerization of naphthyl groups under UV radiation. As a result, the rearrangement of the structure of the monolayer and sitting film is due to vertical transfer. The same pictures were obtained for all generations of the dendrimer in the case of self-assembly and covalent bonding. For scanning electron microscopy, the transfer of the floating films was performed on oxidized silicon plates. Figure 20 b, e shows the microstructure of thin films of the 5th generation with covalent and noncovalent bonding. In the case of noncovalent binding, the film structure is loose packed compared to that with covalent binding, and at high magnification, individual cylindrical-like elements can be seen. Then, as it compresses the barriers, these cylindrical objects form agglomerates. The possibility of transferring the film to the grid and studying it with TEM suggest the sufficient mechanical stability of the prepared film of the 5th generation, in Figure 20 c, f. Thus, the Langmuir films made up of dendrimers can be transferred not only on usual solid substrates but also exist as a free-standing film that is stable enough for analysis.

4.2.1 Thickness measurement

Measurement of film thickness was carried out using two methods, ellipsometry and AFM. The results of two different methods showed good compatibility and are presented in Table 3. The results of the thickness measurements by AFM were obtained for the films of the 4th and 5th generation of dendrimer and equal 3.0 nm and 3.8 nm, respectively. The results for the 2nd and 3rd generations were not available using this method due to the thinness of the film. Thickness measurements by ellipsometry were confirmed by the AFM method and equal 2.6 and 3.8 for the films of the 4th and 5th generations of the dendrimer, respectively. Figure 21 presents the results of the surface investigation for films made of sulfonimide-based dendrimers in terms of height profiles. According to the height profile, the thickness is approximately in the range of 3.0 – 5.0 nm. Comparing the morphology of the surfaces of films with a covalent bond and self-assembled films showed that the films look similar and contain the same cylindrical objects. Still, in the case of the covalent film, the high resolution was achieved due to the stabilization of the films by covalent bonding. Surface roughness was evaluated by atomic force microscopy in terms of RMS roughness (R_a) within a given area. The average roughness was in the range of 0.67 – 0.74 nm, as revealed in Figure 21.

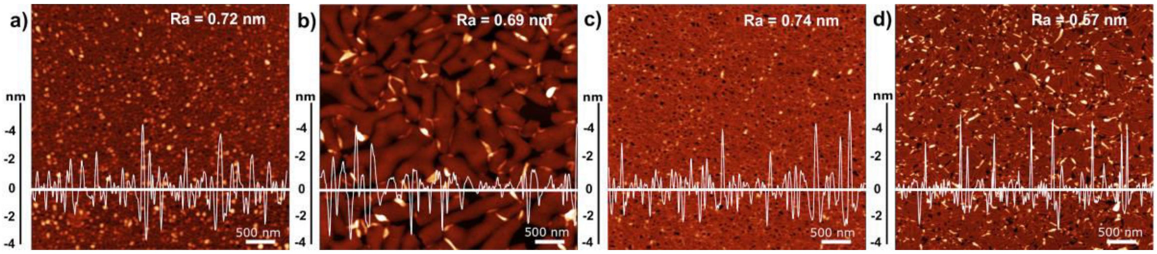

Figure 21. Topography, height profiles, and roughness of the transferred film on mica substrate a) 4th G, not UV irradiated, b) 4th G UV irradiated, c) 5th G, not UV irradiated, d) 5th G UV irradiated.

According to the specification, scanner noise along the vertical z-axis is less than 50 pm. Accordingly, the resolution along the vertical axis should be limited to this value. If you use a probe with a stiffness of more than 1 N / m, then the thermal noise of the probe does not introduce additional noise, so the instrumental error is 50 pm. In this case, the microscope is in a glove box with a chiller, so that the temperature there is constant and thermal fluctuations should not significantly affect the vertical resolution. We also made the first attempt to repeat the deposition process and built up a bilayer. So far, we understood that the bilayer was formed only using an upstroke mode due to the substrate-dendrimer combination. It was proven to measure the bilayer thickness that got doubled.

4.2.2 Young's modulus measurement

To estimate mechanical properties, we measured Young's modulus using AFM. For measurements, we selected the Hertz model for the force curves. [146] The values of Young's modulus for films do not exceed 190 MPa, which corresponds to the soft polymeric material. The difference in Young's modulus values for covalently stabilized and self-assembled films is practically absent. Young's modulus measurements for 4th and 5th generation sulfonimide-based dendrimers are shown in Table 3.

Table 3. Results of thickness and Young's modulus measurements.

Film	Thickness, by ellipsometry, nm	Thickness, by AFM, nm	The average value of Young's modulus, MPa
4th UV irradiated	2.6 ± 0.5	3.0 ± 0.9	150
4th not UV irradiated			155
5th UV irradiated	3.8 ± 0.5	3.6 - 3.8 ± 0.9	184
5th not UV irradiated			186

4.2.3 UV spectroscopy

UV spectroscopy helps in determining the change in the chemical structure of transferred films by detecting chromophores; the intensity of the absorption band is proportional to the number of chromophoric units. To confirm the reaction of intermolecular and intramolecular dimerization of terminal naphthyl groups, the UV spectra of the films of G2-G4 dendrimers transferred to quartz glasses were analyzed. Figure 22 shows that the films give a signal in the range from 200 to 300 nm, which is typical for naphthalene. The signal is more intense for UV unirradiated films than for UV irradiated ones. The presence of weak signals is due to the film thickness since the film thickness does not exceed 6 nm, the concentration of the substance on the surface is too low for analysis of the completeness of the dimerization process. Therefore, the only way to evaluate the changes in the structure of the formed dendrimer film under UV irradiation is by detecting the changes in surface properties, for example, wettability.

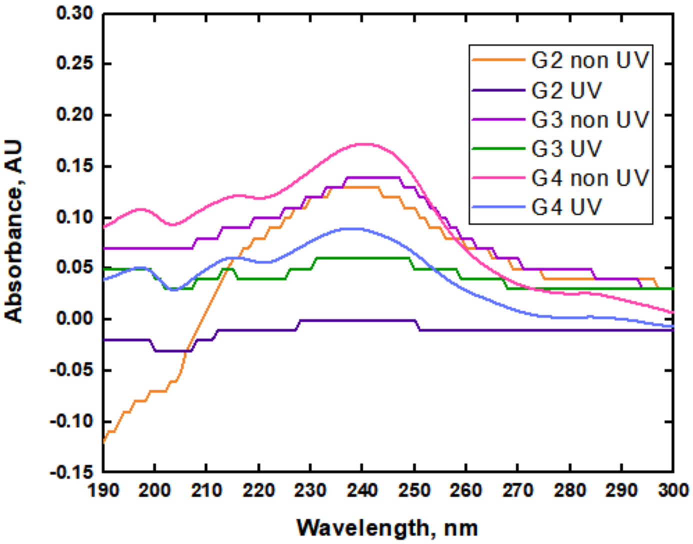

Figure 22. UV spectra of dendrimer films of different generations deposited on quartz glass.

4.2.4 Contact angle measurement

The measurements of the contact angle are used to evaluate the properties of the surface after coating with sulfonimide-based dendrimers. Surface effects are caused by the interaction of its surface morphology and chemical properties. The wetting behavior of sulfonimide-based dendrimer layers is governed by both their chemical composition and geometric microstructure. Since the structures of sulfonimide dendrimers have hydrophobic naphthyl functional groups and can set the hydrophobic properties of the surface, we were interested in measuring the static contact angle between a liquid (water) and a solid (thin film) and checking the wetting ability of the films. When measuring the static contact angle, a regular tendency was observed with increasing generation number, the contact angle increased. In the case of noncovalently formed films, the contact angle was larger than that in the case of covalent films by an average of 3-10º. The values of the contact angles are summarized in Table 4.

Table 4. Contact angle measurements.

Generation	**Contact angle, °**
2nd not UV irradiated	58.2 ±4.9
2nd UV irradiated	31.5 ±6.6
3rd not UV irradiated	72.4 ±12.1
3rd UV irradiated	70.6 ±19.2
4th not UV irradiated	81.6 ±18.0
4th UV irradiated	72.3 ±12.1
5th not UV irradiated	91.9 ±9.9
5th UV irradiated	61.7 ±18.3

Such a difference between covalently and noncovalently bonded films is due to the partial destruction of the aromatic structure under the action of UV light, and as a result, a decrease in the hydrophobicity occurs. The highest contact angle was observed for the noncovalent film of the 5th generation of dendrimer and was equal to approximately 90°. Therefore, such films can be used to create coatings with different hydrophobicities to improve the water-repellent properties of surfaces. The results of contact angle measurements for covalent and noncovalent films of different generations are shown in Figure 23a.

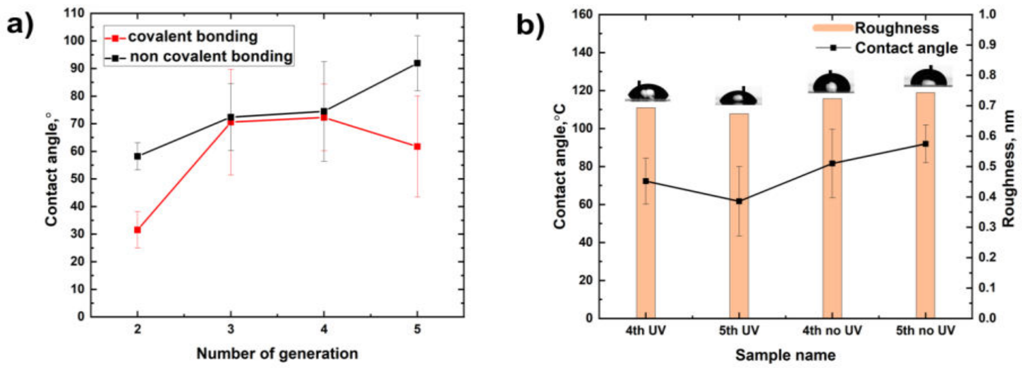

Figure 23. a) Contact angles for different generations, b) Contact angle and surface roughness of sulfonimide-based dendrimer films 4th and 5th generations covalently bonded and noncovalently bonded.

For rough surfaces, the real area of contact is much smaller than the nominal smooth area of contact. The reduction of the contact area can affect adhesion. Figure 23b shows the relationship between the roughness of the surface and wettability. Under UV light, dimerization occurs and leads to decreasing surface roughness due to the more compact organization of molecules. At the same time, the contact angle noticeably decreases with decreasing of roughness. On the other hand, surface roughness increases with increasing the generation of the dendrimer, which is not exposed to UV irradiation that leads to a higher contact angle. It is observed that the contact angle of UV non- irradiated films increases with an increase in surface roughness, which is consistent with the literature.

Two models describe wetting on rough hydrophobic surfaces such as Wenzel [148] and Cassie-Baxter [149]. The Wenzel equation relates to the homogeneous wetting regime (liquid fill-up the roughness grooves) and is corresponded by the following equation for the contact angle on a rough surface:

$$\cos(\theta') = r cos(\theta)$$

here θ' is the apparent contact angle which corresponds to the minimum free energy state for the system, r is the roughness ratio, θ is the Young contact angle. The Cassie-Baxter equation describes the heterogeneous wetting regime (air bubbles trapped inside the grooves) and is shown by the following equation for the contact angle on a rough surface:

$$\cos(\theta') = r_f f cos(\theta) + f - 1$$

where θ' is the apparent contact angle which corresponds to the minimum free energy state for the system, r is the roughness ratio, θ is the Young contact angle, r_f is the roughness ratio of the wetted surface area, and f is the fraction of solid surface area wet by the liquid. To define the suitable model, it is needed to evaluate the experimentally measured parameters such as the spreading coefficient and the work of adhesion. A detailed study of the wettability and the dependence of wettability on the generation of dendrimers is a promising task for further research.

In addition to measuring the wetting angle in the static mode, an analysis of the change in the wetting angle along the entire sample was made. For this, 3 µl drops of water were deposited on the sample; in the area covered by the dendrimer layer, the wetting angle remained unchanged Figure 24a and noticeably decreased when a water drop of the same volume was applied to the region free of the dendrimer film Figure 24b. This observation allows us to conclude that the coating is uniform on the substrate and retains hydrophobic properties.

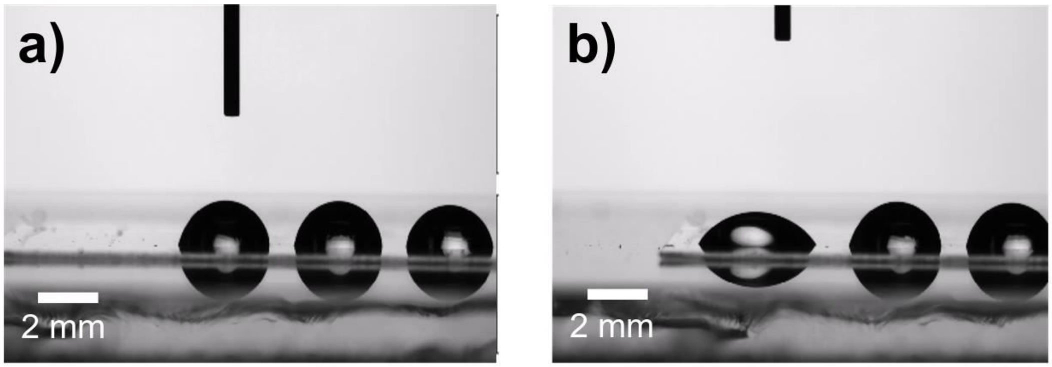

Figure 24. The study of changes in the contact angle along with the sample (V of the drops is 3 μl).

4.2.5 Studies of nonlinear optical interaction in dendrimer monolayer

Two types of monolayers of 5th generation dendrimer molecules on the glass surface grown by the Langmuir – Blodgett method were used as research samples. One of the films was exposed to ultraviolet radiation before being applied to glass, while the second was not. Each plate had a section not covered with the dendrimer film. The power of the nonlinear signal quadratically depended on the pump power in the region up to 70 mW, indicating that a quadratic nonlinear optical process takes place in the samples Figure 25.

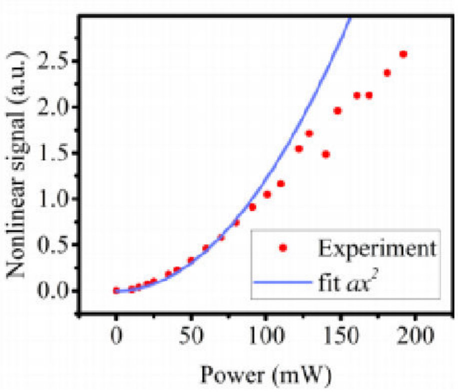

Figure 25. The dependence of the power of a nonlinear signal on the pump power.

For convenience, two studied samples are assembled together, as shown in Figure 26a. Figure 25b shows a map of the distribution of a nonlinear signal obtained by the incidence of p-polarized pump radiation for two samples located next to each other. The scan area was 12 mm x 12 mm. The lower half of the figure corresponds to the sample not exposed to ultraviolet radiation; the upper half of the figure corresponds to the sample irradiated with ultraviolet light. The region 0mm <X <2mm of both glass plates was not covered by a layer of dendrimers. The distribution of the nonlinear signal correlates to some extent with spatial inhomogeneities films visible in the sample photograph Figure 26b

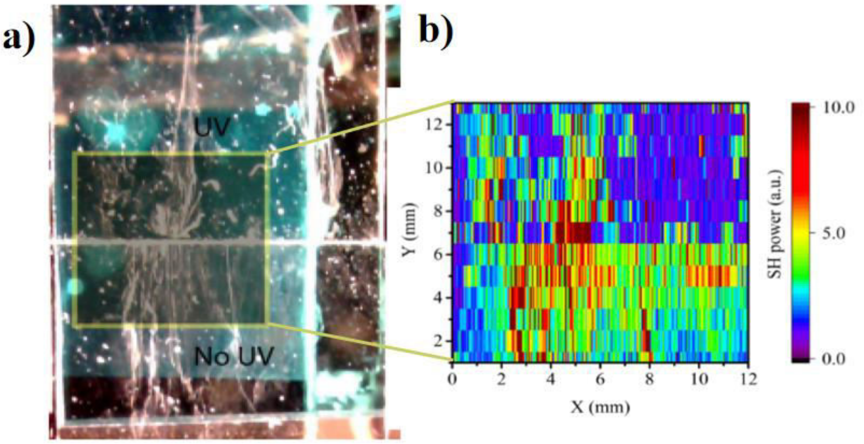

Figure 26. a) Picture of analyzed samples b) Distribution map of the nonlinear signal.

The set of nonlinear signals from two images in several horizontal sections of the map shows the dependences of the non-linear signal on the position of the focus point of the laser beam on the samples in Figure 27a. It can be seen that in the region of the dendrimer film, the non-linear signal increases compared to pure glass, but the signal consists of random emissions. A non-linear signal is present for all combinations of pump polarization and analyzer positions shown in Figure 27b. The existence of non-linear signals is also confirmed by measurements of the power of the non-linear signal depending on the angle of rotation of the analyzer for two pump polarizations Figure 27c.

Analyzer zero position corresponds to their transmission of p-polarized radiation. The curves show the partial polarization of the nonlinear signal.

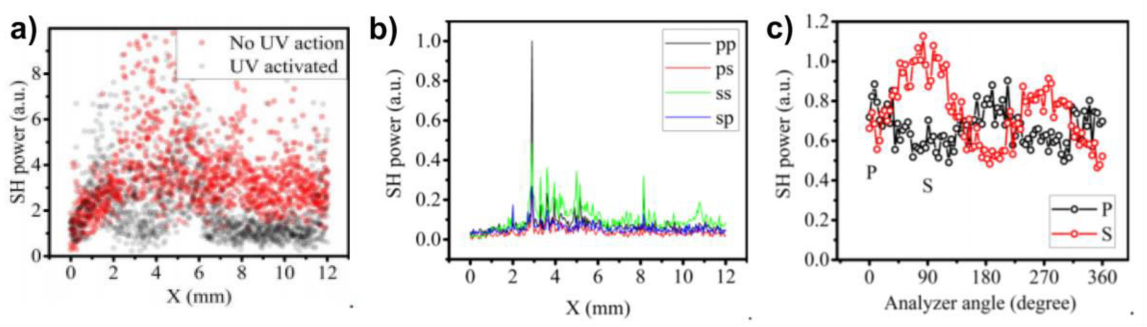

Figure 27. a) The dependence of the nonlinear signal on the position of the focus point of the laser beam on the samples b) The dependence of the nonlinear signal on the position analyzer c) The dependence of the power of a nonlinear signal on the angle analyzer rotation for two pump polarization.

During the experiments, a nonlinear optical signal was detected from the dendrimer film on the glass surface, consisting of a combination of randomly located emissions, which was a consequence of the strong inhomogeneity of the samples. Since the generation of a nonlinear signal occurs at individual points of the sample, this does not allow us to analyze the anisotropy of the nonlinear properties of dendrimer films.

In conclusion, consider the results of pressure-area isotherms and visualization techniques, synthesized sulfonimide dendrimers can be applicable to form two types of films. The obtained films were successfully transferred to various substrates and analyzed following the assigned objectives. The UV stabilization leads to a change in both the morphology and the wettability of the films.

Conclusion

During the synthetic part of this work, the methodology of the synthesis of sulfonimide - based dendrimers decorated with naphthyl groups was developed. Both convergent and divergent synthetic approaches to the sulfonimide-based dendrons were realized. The combination of divergent and convergent ways allows obtaining 2nd and 3rd generations of the dendrimer. As long as the convergent route reaches its practical limit at third-generation, developing the divergent path has better chances at achieving higher generation sulfonimide-based dendrimer.

The divergent synthesis of sulfonimide-based dendrimers was considerably improved and expanded to higher molecular weight species. The yields of the dendrimers were significantly increased compared to those of the formerly available method by utilizing a two-step persulfonylation approach. The multigram availability of the fourth-generation hexadecanitro-dendrimer allowed the synthesis of the fifth-generation sulfonimide-based dendrimer for the first time, on a 2g scale.

For the first time, we created Langmuir-Blodgett thin films made up of sulfonimide-based dendrimers of 2nd, 3rd, 4th, and 5th generations. The Langmuir-Blodgett method allows us to carry out a controlled process of dendrimer microstructuring, which is a way toward real-world applications, and obtain films with thicknesses of 3-5 nm. Moreover, the design of investigated dendrimers allows creating noncovalently and covalently bonded films.

The morphology and structure of obtained films were investigated by microscopic methods. The microstructure of all samples has similar cylindrically-liked objects. Confirmation of the mechanical stability of thin films of dendrimers was achieved by successful transfer to the metal grid holder. For measuring Young's modulus, a technique suitable for the analysis of polymers was selected. Young’s modulus values do not exceed 1 GPa, which, as expected, corresponds to soft polymer materials.

Contact angle measurements evaluated the wettability of dendrimer films. The hydrophobicity of the films made from the 2nd generation to the 5th generation increased. The contact angle of the transferred films increased by 33° for the 5th generation of dendrimer and reached 90º. Also, the results of the apparent contact angle showed a dependence on the surface roughness. Preliminary experiments on the thin-film formation and contact angle measurements show the potential use of fourth- and fifth-generation species for surface engineering applications.

Also, for the first time, nonlinear optical properties of transferred films were investigated. A nonlinear signal was detected for the film sample made of the 5th generation of the dendrimer.

Thus, films from pre-modeled and synthesized dendrimers were successfully obtained and were first thoroughly investigated using the entire spectrum of available methods. The analysis of dendrimer films transferred on solid substrates promises that sulfonimide-based dendrimers can be used as coating materials to modify the properties of solid surfaces at the nanoscale to produce improved materials with hydrophobic properties.

Future work/Directions

Understanding wetting on modified surfaces is essential for designing, controlling, and predicting wetting processes in general. To enhance the hydrophobic properties of the surface, the principle of decorating structures with water repellent functional groups (naphthyl end groups) was used in this work. The structures of dendrimers can be easily tuned by such hydrophobic groups at the periphery in such a way that with an increase of generation, the number of surface projected hydrophobic groups increases by 2n, where n equals generation number. This work showed that introducing hydrophobic groups into the dendrimer structure with further applying such dendrimer as a coating could lead to the appearance of hydrophobic properties of a surface. Factors affecting the wettability are surface roughness, the relative concentration of hydrophilic particles and hydrophobic ones, and their arrangement on the layer. The surface wettability of naphthyl-functionalized dendrimer noncovalent films was characterized by contact angle measurement.

Interestingly, the water contact angle of 3rd and 4th generations of dendrimer samples was equally close to 70 degrees, whereas, for the 2nd and 5th, the difference in contact angles with water was about 33 degrees. This study has focused on the way to alter the properties of surfaces by creating patterned surfaces, for which the wetting properties vary spatially in a controlled way. Interestingly, fabricating such structures requires a careful design strategy, including core selection, synthesis procedure, purification, and, finally, can be limited due to steric effects. It is possible to overcome these problems by putting forward a clearer understanding of future material design strategies, principles for organic end groups that decrease surface free energy. Moreover, it is essential to analyze structural patterns that lead to hydrophobicity, the influence of the number of functional groups, and the effect of their spatial distribution on contact angle values.

Since the surface covered by the film of dendrimers has a roughness, the wettability of rough surface can be explained by two models: Wenzel and Cassie - Baxter. According to the Wenzel model, the water drops on a rough surface are semi-spherical in shape and wets the surface. According to the Cassie - Baxter surface roughness forms voids filled with air, so a drop of water cannot take a spherical shape and rests on a rough texture with air pockets trapped in between. This leads to the low adhesion of the water drop to the surface. To define the suitable model, it is needed to evaluate the experimentally measured parameters such as the spreading coefficient and the work of adhesion. The contact angle of the film coatings with liquids is a basis for the determination of these parameters. Apart from the contact angle, it would be interesting to estimate the rolling angle. If dendrimer films significantly reduce the rolling angle, this will not only benefit the Cassie-Baxter model, but also allow unlocking the potential of such complex and rather expensive materials as dendrimers for real applications, that is, for self-cleaning surfaces, etc.

Along with surface roughness and shape, the size, height, and periodic patterning could also lead to an increase in the surface water contact angle. For example, the distribution of the naphthyl terminal groups can create surface tension and decrease free surface energy or increase surface roughness. The surface tension can be changed by increasing the number of naphthyl groups. Therefore, the evaluation of the dependence of surface tension on the functional group's spatial distributions can help to understand the correlation between the structure of dendrimer and hydrophobic properties.

Thus, a more detailed study of the relationship between surface tension and the branching of the structural patterns of dendrimer can lead to the creation of a model, which helps to predict structure - properties correlations.

Appendix. Experimental section

A.1 Reagents and methods

3-Methoxypropan-1-amine 1, 4-nitrobenzenesulfonyl chloride 2, 3-nitrobenzenesulfonyl chloride, and solvents (dichloromethane, ethanol, and dimethylformamide) were purchased from commercial sources and used without further purification. The monitoring of the reaction course was performed by thin-layer chromatography (TLC) on silica gel-coated aluminum plates (G/UV254 plates of Macherey-Nagel & Co.). Chromatography purification was performed using Merck silica gel 60, 230–400 mesh. Melting points were determined on a Buchi microscope heating unit and are uncorrected. ^{1}H and ^{13}C spectra were recorded on Bruker Fourier 300 and Bruker Ascend 600 NMR spectrometers. Mass spectra were recorded on Agilent 1100 LCMSD SL (ESI), Agilent GC7820A/MSD5977B system (EI, ionization energy – 70eV), and Waters SYNAPT G2-Si (ESI) and FT-MALDI MS (IonSpec Ultra Instrument) spectrometers. MALDI-TOF mass spectra were measured on UltraFlex III TOF/TOF with PNA matrix, laser Nd: YAG, λ = 355nm. Elemental analysis was performed on a Vario Micro cube CHNS analyzer. Samples for the elemental analysis were dried with the aid of an oil vacuum pump (0.05mm Hg) for two weeks. Average values of three independent measurements are reported.

A.2 Procedures

Scheme 1

Compound 1a. 4-nitrobenzenesulfonyl chloride (4.95 g, 22.3 mmol) was added to a mixture of 4-methoxybenzyamine (1.44 g, 10.5 mmol) and triethylamine (6.8 ml, 49.15 mmol) in dichloromethane (100 mL) suspension. The stirred reaction mixture was heated at 80°C in an oil bath for 2 hours. Then DCM was removed by rotary evaporation, and the solid residue was ground to a fine powder with isopropyl alcohol. The colorless precipitated product was filtered and washed with isopropyl alcohol. The yield of product 1a is 4.2 g (78.81%). ^{1}H NMR (DMSO, 300MHz) δ (ppm): 3.82 (s, 3H, OC$\underline{H}_3$), 6.80 (d, 2H, Ar$\underline{H}$), 7.31 (d, 2H, Ar$\underline{H}$), 4.98 (s, 2H, NC$\underline{H}_2$), 7.95 (d, 4H, Ar$\underline{H}$), 8.29 (d, 4H, Ar$\underline{H}$).

^{13}C NMR (DMSO, 75 MHz) δ (ppm): 52.97, 114.07, 124.06, 125.25, 129.54, 131.06, 145.03, 150.56, 160.15.

Reduction of dinitroaromatic compound. Compound 1a (2.5 g, 4.92 mmol) and tin chloride $SnCl_2 \cdot 2H_2O$ (5 g, 22.16 mmol) were dissolved in a mixture of dichloromethane/ethanol (1:1, 150 mL). The reaction mixture was heated at 65°C in an oil bath. After 30 min, a few drops of concentrated hydrochloric acid were added to facilitate a complete dissolution of $SnCl_{2,}$ and the mixture was refluxed for 3 hours. Then the reaction mixture was transferred into a separatory funnel with 400 mL of water and NaOH (in an amount to adjust pH to 10-12). The organic part of the solution was separated, washed with water and then with brine, and dried over $Na_2SO_{4.}$ The solvent was removed by rotary evaporation. According to the NMR analysis, the mixture of unidentified compounds was obtained.

Scheme 2

Compound 2a. 4-nitrobenzenesulfonyl chloride (5.24 g, 23.6 mmol) was added to a solution of aniline (1 g, 10.7 mmol) and triethylamine (2.2 mL, 15.9 mmol) in dichloromethane (100 mL) suspension. The stirred reaction mixture was heated at 80°C in an oil bath for 2 hours. Then DCM was removed by rotary evaporation, and the solid residue was ground to a fine powder with ethanol. The precipitated product was filtered and washed with ethanol. The yield of product 2a is 2.2 g (55%). 1H NMR (DMSO, 300MHz) δ (ppm): 7.14 (m, 2H, Ar$\underline{H}$), 7.52 (m, 2H, Ar$\underline{H}$), 7.59 (m, 1H, Ar$\underline{H}$), 8.10 (m, 4H, Ar$\underline{H}$), 8.50 (m, 4H, Ar$\underline{H}$), ^{13}C NMR (DMSO, 75 MHz) δ (ppm): 125.55, 130.33, 130.49, 131.68, 131.79, 133.08, 143.50, 151.40.

Compound 2b. Compound 2a (1g, 5.89 mmol) and $SnCl_2 \cdot 2H_2O$ (4,6 g, 20.4 mmol) were dissolved in a mixture dichloromethane/ethanol (1:1, 150 mL). The reaction mixture was heated up to 65°C in an oil bath. After 30 min, a few drops of concentrated hydrochloric acid were added to facilitate a complete dissolution of $SnCl_{2,}$ and the mixture was refluxed for 3h. Then the reaction mixture was transferred into a separatory funnel with 400 mL of water and NaOH (in the amount to adjust pH to 10-12). The organic part of the solution was separated, washed with water and then with brine, and dried over Na_2SO_4. Then the solvent was removed by rotary evaporation. The yield of product 2b is 0.4 g (35%). 1H NMR (DMSO, 300 MHz) δ (ppm): 6.33 (s, 4H, N$\underline{H}_2$), 6.60 (m, 4H, Ar$\underline{H}$), 6.91 (m, 2H, Ar$\underline{H}$), 7.36 (m, 4H, Ar$\underline{H}$), 7.39 (m, 3H, Ar$\underline{H}$). ^{13}C NMR (DMSO, 75 MHz) δ (ppm): 112.79, 123.4, 130.72, 131.79, 135.27, 154.56.

Compound 2c. Compound 2b (0.4 g, 0.99 mmol) was added to a solution of 4-nitrobenzenesulfonyl chloride (1,54 g, 6,95 mmol) and triethylamine (0.73 mL, 5.28 mmol) in dichloromethane (100 mL) suspension. The stirred reaction mixture was heated up to 80°C in an oil bath for 2h. Then the solvent was removed under vacuum, and the solid residue was ground to a fine powder with ethanol. The precipitated product was filtered and washed with ethanol. The obtained material was insoluble, preventing its characterization and further use.

Scheme 3

Compound 3a. 4-nitrobenzenesulfonyl chloride (14.9 g, 67.2 mmol) was added to a solution of 3-methoxypropylamine (2 g, 22.4 mmol) and triethylamine (6 mL, 43.37 mmol) in dichloromethane (100 mL) suspension. The stirred reaction mixture was heated up to 80°C in an oil bath for 2h. Then the solvent was removed under vacuum, and the solid residue was triturated with ethanol. The precipitated product was filtered and washed with ethanol. The yield of product 3a is 3.84 g (70%). ^{1}H NMR (DMSO, 300MHz) δ (ppm): 1.95 (m, 2H, $CH_2C\underline{H}_2CH_2$), 3.31 (s, 3H, $OC\underline{H}_3$), 3.40 (t, 2H, $C\underline{H}_2O$), 8.43 (d, 4H, Ar$\underline{H}$), 3.91 (t, 2H, $NC\underline{H}_2$), 8.30 (d, 4H, Ar$\underline{H}$). ^{13}C NMR (DMSO, 75 MHz) δ (ppm): 30.15, 47.97, 58.69, 69.07, 124.46, 129.74, 144.88, 150.84. The melting point is 146°C.

Compound 3b. Compound 3a (2g, 4.4 mmol) and $SnCl_2 \cdot 2H_2O$ (5.95 g, 26.37 mmol) were dissolved in a mixture of dichloromethane/ethanol (1:1, 150 mL). The reaction mixture was heated up to 65°C in an oil bath. After 30 min, a few drops of concentrated hydrochloric acid were added to facilitate a complete dissolution of $SnCl_2$, and the mixture was refluxed for 3h. Then the reaction mixture was transferred into a separatory funnel with 400 mL of water and NaOH (in an amount to adjust pH to 10-12). The organic part of the solution was separated, washed with water and then with brine, and dried over Na_2SO_4. Then the solvent was removed under vacuum. The yield of product 3b is 0.9 g (45%). ^1H NMR (DMSO, 300MHz) δ (ppm): 1.75 (m, 2H, $CH_2C\underline{H}_2CH_2$), 3.19 (s, 3H, $OC\underline{H}_3$), 3.26 (t, 2H, $C\underline{H}_2O$), 7.41 (d, 4H, $Ar\underline{H}$), 3.51 (t, 2H, $NC\underline{H}_2$), 6.60 (d, 4H, $Ar\underline{H}$), 6.26 (s, 4H, $N\underline{H}_2$). ^{13}C NMR (DMSO, 75 MHz) δ (ppm): 30.22, 46.30, 58.23, 69.52, 112.84, 123.94, 130.36, 154.40. The melting point is 178°C.

Compound 3c. Compound 3b (0.9 g, 19.59 mmol) was added to a solution of 4-nitrobenzenesulfonyl chloride (3 g, 13.54 mmol) and triethylamine (0.73 mL, 5.28 mmol) in dichloromethane (100 mL) suspension. The stirred reaction mixture was heated up to 80°C in an oil bath for 2 h. Then the solvent was removed by rotary evaporation, and the solid residue was ground to a fine powder with ethanol. The precipitated product was filtered and washed with ethanol. The yield of product 3c is 3.84 g (58%). ^1H NMR (DMSO, 300MHz) δ (ppm): 1.85 (m, 2H, $CH_2C\underline{H}_2CH_2$), 3.21 (s, 3H, $OC\underline{H}_3$), 3.87 (t, 2H, $C\underline{H}_2O$), 7.41 (d, 4H, $Ar\underline{H}$), 3.50 (t, 2H, $NC\underline{H}_2$), 7.50 (d, 4H, $Ar\underline{H}$), 8.00 (d, 4H, $Ar\underline{H}$), 8.50 (d, 4H, $Ar\underline{H}$), 8.13 (d, 4H, $Ar\underline{H}$). ^{13}C NMR (DMSO, 75 MHz) δ (ppm): 30.11, 47.78, 58.35, 69.10, 125.62, 130.02, 130.51, 133.23, 142.9, 151.57. The melting point is 322°C.

Compound 3d. Compound 3c (1g, 0.877 mmol) and $SnCl_2 \cdot 2H_2O$ (3.56 g, 15.78 mmol) were dissolved in a mixture dichloromethane/ethanol (1:1, 150 mL). The reaction mixture was heated up to 65°C in an oil bath. After 30 min, a few drops of concentrated hydrochloric acid were added to facilitate a complete dissolution of $SnCl_2$, and the mixture was refluxed for 3h. Then the reaction mixture was transferred into a separatory funnel with 400 mL of water and NaOH (in an amount to adjust pH to 10-12). The organic part of the solution was separated, washed with water and then with brine, and dried over Na_2SO_4. Then the solvent was removed under vacuum. The yield of product 3d is 1.4 g (50%). ^1H NMR (DMSO, 300MHz) δ (ppm): 1.77 (m, 2H, $CH_2C\underline{H}_2CH_2$), 2.50 (s, 3H, $OC\underline{H}_3$), 3.20 (t, 2H, $C\underline{H}_2O$), 6.60 (d, 8H, $Ar\underline{H}$), 3.80 (t, 2H, $NC\underline{H}_2$), 7.27 (d, 4H, $Ar\underline{H}$), 7.30 (d, 8H, $Ar\underline{H}$), 7.89 (d, 4H, $Ar\underline{H}$), 6.39 (s, 8H, $N\underline{H}_2$). ^{13}C NMR (DMSO, 75

MHz) δ (ppm): 29.96, 47.57, 58.33, 69.11, 112.90, 122.49, 129.17, 130.88, 133.02, 139.98, 140.48, 154.91.

Scheme 4

Compound 3e. Compound 3d (0.54 g, 0.529 mmol) was added to a solution of 2-naphthalenesulfonyl chloride (1.92 g, 8.46 mmol) and triethylamine (1.17 mL, 8.46 mmol) in dichloromethane (100 mL). The stirred reaction mixture was heated up to 80°C in an oil bath for 2h. Then the solvent was removed under vacuum and the solid residue was ground to a fine powder with ethanol. The precipitated product was filtered and washed with ethanol. The yield of product 3e is 0.25 g (58%). Product 3e was purified on silica gel with 2% ethylacetate/dichloromethane. ^{1}H NMR (DMSO, 300MHz) δ (ppm): 2.01 (m, 2H, $CH_2C\underline{H}_2CH_2$), 3.26 (s, 3H, $OC\underline{H}_3$), 3.37 (t, 2H, $C\underline{H}_2O$), 6.60 (d, 8H, $Ar\underline{H}$), 3.89 (m, 2H, $NC\underline{H}_2$), 7.27 (d, 4H, $Ar\underline{H}$), 7.30 (d, 8H, $Ar\underline{H}$), 7.89 (d, 4H, $Ar\underline{H}$), 6.39 (s, 8H, $N\underline{H}_2$). ^{13}C NMR (DMSO, 75 MHz) δ (ppm): 30.35, 47.86, 58.58, 69.23, 122.71, 128, 129.44, 129.69, 129.72, 129.88, 130.77, 131.81, 132.35, 132.70, 135.47, 135.48, 138.59, 139.61, 140.04, 141.19. Melting point is 153°C.

Scheme 5

Compound 1. 1-Fluoro-4-nitrobenzene (10 g, 0.071 mol) was added to benzyl thiol (8.74 g, 0.07 mol) in the presence of K_2CO_3 in dimethylformamide DMF (50 ml). The stirred reaction mixture was heated up to 50°C in an oil bath for 24h. The reaction mixture was poured into hydrochloric acid (220 ml), and the obtained precipitate was filtered. The yield of product 1 is 17.14 g (99%).

Compound 2. Compound 1 (2.5 g, 0.01 mol) and $SnCl_2{\cdot}2H_2O$ (11.25 g, 0.05 mol) were dissolved in a mixture dichloromethane/ethanol (1:1, 150 mL). The reaction mixture was heated up to 65°C in an oil bath. After 30 min, a few drops of concentrated hydrochloric acid were added to facilitate a complete dissolution of $SnCl_2$, and the mixture was refluxed for 3h. Then the reaction mixture was transferred into a separatory funnel with 400 mL of water and NaOH (in an amount to adjust pH to 10-12). The organic part of the solution was separated, washed with water and then with brine, and dried over Na_2SO_4. Then the solvent was removed by rotary evaporation. The yield of product 2 is 1.2 g (48%).

Compound 3. 4-nitrobenzenesulfonyl chloride (8.9 g, 0.04 mol) was added to a solution of Compound 2 (1.2 g, 0.01 mol) and triethylamine (6 mL, 43.37 mmol) in dichloromethane (100 mL) suspension. The stirred reaction mixture was heated up to 80°C in an oil bath for 2h. Then the solvent was removed by rotary evaporation, and the solid residue was ground to a fine powder with ethanol. The precipitated product was filtered and washed with ethanol. The yield of product 3 is 0.84 g (70%).

Compound 4. Compound 3 (0.84 g, 0.01 mol) and $SnCl_2 \cdot 2H_2O$ (7 g, 0.03 mol) were dissolved in a mixture dichloromethane/ethanol (1:1, 150 mL). The reaction mixture was heated up to 65°C in an oil bath. After 30 min, a few drops of concentrated hydrochloric acid were added to facilitate a complete dissolution of $SnCl_2$, and the mixture was refluxed for 3h. Then the reaction mixture was transferred into a separatory funnel with 400 mL of water and NaOH (in an amount to adjust pH to 10-12). The organic part of the solution was separated, washed with water and then with brine, and dried over Na_2SO_4. Then the solvent was removed by rotary evaporation. The yield of product 4 is 0.5 g (58%).

Compound 5. Compound 4 (0.5 g, 2.49 mmol) was added to a solution of 2-naphthalenesulfonyl chloride (1.92 g, 8.46 mmol) and triethylamine (1.17 mL, 8.46 mmol) in dichloromethane (100 mL). The stirred reaction mixture was heated up to 80°C in an oil bath for 24h. Then the solvent was removed by rotary evaporation, and the solid residue was triturated with ethanol. The precipitated product was filtered and washed with ethanol. The yield of product 5 is 0.41 g (50%).

Compound 6. Compound 5 (0.41 g) and *N*-chlorosuccinimide (0.49 g) were dissolved in a mixture of dichloromethane/AcOH (1:1, 150 mL) in the presence of HCl, AcOH at 5°C for 24 h. The yield of product 5 is 0.32 g (39%).

Scheme 6

Compound 7. Compound 6 (0.32 g, 0.32 mmol) was added to tetraethylene glycol monomethyl ether (0.011 ml) and triethylamine (1.17 mL, 8.46 mmol) in dichloromethane (100 mL). The stirred reaction mixture was heated up to 80°C in an oil bath for 24h. Then the solvent was removed by rotary evaporation, and the solid residue was ground to a fine powder with ethanol. The precipitated product was filtered and washed with ethanol. The yield of product 7 is 0.15 g (26%).

Scheme 7

4-nitrobenzenesulfonyl chloride (8.9 g, 0.04 mol) was added to a solution of Methoxypolyethylene glycol amine (2 g, 9.64 mmol) and triethylamine (6 mL, 43.37 mmol) in dichloromethane (100 mL) suspension. The stirred reaction mixture was heated up to 80°C in an oil bath for 2h. Then the solvent was removed by rotary evaporation, and the solid residue was ground to a fine powder with ethanol. The precipitated product was filtered, washed with ethanol. The yield is 1.56 g (78%). Then prepared dinitro compound (1.56 g, 2.7 mmol) and $SnCl_2 \cdot 2H_2O$ (7 g, 0.03 mol) were dissolved in a mixture dichloromethane/ethanol (1:1, 150 mL). The reaction mixture was heated up to 65°C in an oil bath. After 30 min, a few drops of concentrated hydrochloric acid were added to facilitate a complete dissolution of $SnCl_2$, and the mixture was refluxed for 3h. Then the reaction mixture was transferred into a separatory funnel with 400 mL of water and NaOH (in an amount to adjust pH to 10-12). The organic part of the solution was separated, washed with water and then with brine, and dried over Na_2SO_4. Then the solvent was removed by rotary evaporation. The yield is 1.2 g (60%). The reduced product (1.2 g, 2.3 mmol) was added to a solution of 2-naphthalenesulfonyl chloride (1.92 g, 8.46 mmol) and triethylamine (1.17 mL, 8.46 mmol) in dichloromethane (100 mL). The stirred reaction mixture was heated up to 80°C in an oil bath for 2h. Then the solvent was removed by rotary evaporation, and the solid residue was ground to a fine powder with ethanol. The precipitated product was filtered and washed with ethanol. The yield of the product is 1.12 g (58%).

Scheme 8

Compound 8a. A stirred solution of diamine 4 (1 g, 1.9 mmol), triethylamine (2 g, 20 mmol), and 4-nitrophenylsulfonyl chloride (3.4 g, 15 mmol) in dichloromethane (60 mL) were heated under reflux. After 3h of stirring, a reddish solid substance started to precipitate. The stirring was continued for another 3h. The stirred reaction mixture was allowed to cool to room temperature, and then methanol (60 mL) was added to the mixture. The solvent was removed by rotary evaporation, and the solid residue was ground to a fine powder t with methanol. The precipitated solid was filtered on a glass filter, washed twice with methanol, and dried under ambient conditions. The resulting reddish powder was recrystallized twice from acetone-methanol. The yield of product 8a is 1.2 g (48%), yellowish powder, mp = 200–202°C. [Found: C, 46.52; H, 2.85; N, 7.69; S, 17.79. $C_{49}H_{35}N_7O_{20}S_7$ requires C, 46.48; H, 2.79; N, 7.74; S, 17.72 %]; δH (300 MHz, DMSO-d6) 8.50 (8H, d, J 8.4 Hz, ArH), 8.13 (8H, d, J 8.4 Hz, ArH), 7.84 (4H, d, J 8.4 Hz, ArH),7.47–7.23 (12H, m, ArH), 6.92 (2H, d, J 8.4 Hz, ArH), 4.29 (2H, s, CH_2S); δc (75 MHz, $CDCl_3$) 152.01, 143.25, 140.65, 138.79, 137.51, 137.1, 133.78, 132.1, 130.35, 129.8, 129.3, 129.0, 128.4, 127.78, 126.04, 125.4, 36.3; m/z (MALDI-TOF) 1288.2 (MNa^+).

Compound 8b. 1 g (0.8 mmol) of Compound 8a and 4 g of $SnCl_2{\cdot}2H_2O$ were used in the reaction. Yield: 0.8 g (92%), yellow powder, mp = 209–211°C. δH (300 MHz, DMSO-d6) 8.69 (4H, d, J 8.3 Hz, ArH), 7.34–7.23 (24H, m, ArH), 6.82 (2H, d, J 8.3 Hz, ArH), 6.62 (8H, d, J 8.3 Hz, ArH), 6.38 (8H, s, NH_2), 4.30 (2H, s, CH_2S); m/z (ESI) 1146.2 (MH+).

Compound 9. Method A (divergent): A stirred mixture of tetraamine 8b (0.8 g, 0.7 mmol), triethylamine (1.2 g, 11.4 mmol), and 2- naphthalenesulfonyl chloride (1.3 g, 5.7 mmol) was heated to reflux in a 1:1 mixture of dichloromethane/acetone (40 mL) for 6h. Then the liquid components of the reaction mixture were removed by rotary evaporation. The solid residue was dissolved in dichloromethane (50 mL). Triethylamine (1.2 g, 11.4 mmol) and 2-naphthalenesulfonyl chloride (1.3 g, 5.7 mmol) were added to the solution. The reaction mixture was refluxed with constant stirring for 12 hours. Then the solvent was removed by rotary evaporation, and the solid residue was ground to a fine powder with methanol. The solid precipitate was filtered through a glass funnel filter and thoroughly washed with methanol. Upon drying in vacuum, the crude product was purified by column chromatography on silica gel with CH_2Cl_2/EtOAc (99:1), Rf = 0.35. Yield: 1.3 g (68%), white powder, mp = 177–180 °C. [Found: C, 58.12; H, 3.49; N 3.61; S, 18.08. $C_{129}H_{91}N_7O_{28}S_{15}$ requires C, 58.07; H, 3.44; N, 3.67; S, 18.02%]; δH (300 MHz, $CDCl_3$) 8.45 (8H, d, J 1.7 Hz, ArH), 7.99–7.82 (32H, m, ArH), 7.80–7.72 (12H, m, ArH), 7.71–7.59 (16H, m, ArH), 7.29–7.19 (15H, m, ArH), 7.14 (4H, d, J 8.4 Hz, ArH), 6.91 (2H, d, J 8.4 Hz, ArH), 4.08 (2H, s, CH_2S); δc (75 MHz, $CDCl_3$) 141.98, 140.79, 140.04, 139.61, 138.71, 135.94, 135.46, 135.45, 132.71, 132.26, 131.80, 131.49, 130.78, 130.13, 129.91, 129.72, 128.81, 128.71, 128.15, 128.02, 127.58, 122.69, 37.48; m/z (MALDI-TOF) 2665.1 (MNa+). Method B (convergent): A stirred solution of amine 2 (51 mg, 0.24 mmol), triethylamine (1 g, 10 mmol), and sulfonyl chloride 6 (1.2 g, 9.5 mmol) in dichloromethane (20 mL) were heated to reflux for 6h. The solvent was removed by rotary evaporation, and the solid residue triturated with methanol. The solid precipitate was filtered through a glass filter and washed with methanol. Upon drying in vacuum, the crude product S7 was purified by column chromatography on silica gel with CH_2Cl_2/EtOAc (99:1), Rf = 0.35. Yield: 0.55 g (86%). Melting point and spectral data match those of the compound prepared by method A (divergent).

Compound 10. 1 g (0.38 mmol) of Compound 9, (0.20 g, 1.4 mmol) and N-chlorosuccinimide were used in the reaction. Yield: 0.9 g (90%), white powder, mp = 173–174°C. [Found: C, 55.48; H, 3.29; N 3.78; S, 18.11. $C_{122}H_{84}ClN_7O_{30}S_{15}$ requires C, 55.41; H, 3.20; 1.34; N, 3.71; S, 18.19%]; δH (300 MHz, $CDCl_3$) 8.46 (8H, s, ArH), 8.06–7.75 (48H, m, ArH), 7.72–7.59 (16H, m, ArH), 7.35–7.26 (8H, m, ArH), 7.20 (4H, d, J 8.4 Hz, ArH); δc (75 MHz, $CDCl_3$) 145.79, 140.19, 140.15, 139.56, 139.29, 135.48, 135.48, 132.75, 132.52, 131.82, 130.80, 129.90, 129.72, 128.31, 128.02, 122.71; m/z (MALDI-TOF) 2666.8 (MNa^+).

Scheme 9

Compound 3. A mixture of 3-methoxypropan-1-amine **1** (5 g, 0.056 mol), triethylamine (23 g, 0.225 mol), and 4-nitrobenzenesulfonyl chloride **2** (37 g, 0.168 mol) was stirred in dichloromethane (600 mL) at reflux for 2h. Then the solvent was removed by rotary evaporation, and the solid residue was ground to a fine powder with methanol. The solid precipitate was filtered through a glass funnel filter and thoroughly washed with methanol. The resulting colorless powder was dried in a vacuum. Yield 22.6 g (88%); m.p. 139–140°C.

^{1}H NMR ($CDCl_3$, 300 MHz): d = 8.44 (d, *J* = 9 Hz, 4H), 8.29 (d, *J* = 9 Hz, 4H), 3.88-3.94 (m, 2H), 3.38 (t, *J* = 6 Hz, 2H), 3.31 (s, 3H), 1.92-1.98 (m, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz): d =150.84, 144.88, 129.74, 124.46, 69.07, 58.69, 47.97, 30.15.

MS (EI, 70 eV): *m/z* = 459.0 $[M]^+$.

Anal. Calcd for $C_{16}H_{17}N_3O_9S_2$: C 41.83; H 3.73; N 9.15; S 13.96. Found: C 41.73; H, 3.77; N 9.00; S 13.82.

Compound 4. A mixture of Compound **3** (5 g, 0.011 mol), $SnCl_2{\cdot}2H_2O$ (20 g, fourfold mass excess), and concentrated hydrochloric acid (5 mL) was refluxed in ethanol (300 mL) for 2h, cooled down to room temperature, and then poured onto ice. The pH was adjusted to 10 with 2 M aqueous solution NaOH, and the obtained amine was extracted with dichloromethane, dried over magnesium sulfate ($MgSO_4$), and then evaporated to give Compound **4** as a colorless solid. Yield 4.27 g (98%).

^{1}H NMR (DMSO-d_6, 300 MHz): d = 7.41 (d, *J* = 9 Hz, 4H), 6.59 (d, *J* = 9 Hz, 4H), 6.26 (s, 4H), 3.49-3.54 (m, 2H), 3.38 (s, 3H), 3.26 (t, *J* = 6 Hz, 2H) 1.75-1.80 (m, 2H).

^{13}C NMR (DMSO-d_6, 75 MHz): d =154.40, 130.36, 123.94, 112.84, 69.52, 58.23, 46.30, 30.22. MS (ESI): *m*/z calcd for $C_{16}H_{21}N_3O_5S_2$ $[M+H]^+$ 400.09. Found: 400.1.

Compound 5. A mixture of diamine **4** (4 g, 0.01 mol), triethylamine (8.1 g, 0.08 mol), and 4-nitrobenzenesulfonyl chloride **2** (13.3 g, 0.06 mol) were stirred in dichloromethane (250 mL) at reflux for 2h. During this time, the product slowly precipitated from the reaction mixture. Then the reaction mixture was cooled down to room temperature, and methanol (250 mL) was slowly added at intensive stirring. The solid precipitate was filtered through a glass funnel filter and thoroughly washed with methanol. The resulting colorless powder was dried in a vacuum. Yield 8.9 g (78%); m.p. 220–222°C.

^{1}H NMR (DMSO-d$_6$, 300 MHz): d = 8.49 (d, *J* = 9 Hz, 8H), 8.13 (d, *J* = 9 Hz, 8H), 8.0 (d, *J* = 9 Hz, 4H), 7,48 (d, *J* = 9 Hz, 4H), 3.84-3.89 (m, 2H), 3.33 (t, *J* = 6 Hz, 2H), 3.21 (s, 3H), 1.81-1.86 (m, 2H).

^{13}C NMR (DMSO-d$_6$, 75 MHz): d =151.57, 142.90, 141.20, 138.12, 133.23, 130.51, 130.02, 125.62, 69.10, 58.35, 47.78, 30.11.

Anal. Calcd for $C_{40}H_{33}N_7O_{21}S_6$: C 42.14; H 2.92; N 8.60; S 16.87. Found: C 42.02; H, 2.88; N 8.56; S 16.68.

Compound 6. A mixture of Compound **5** (5 g, 4.4 mmol), $SnCl_2 \cdot 2H_2O$ (20 g, fourfold mass excess), and concentrated hydrochloric acid (5 mL) was stirred at 40 °C in a 1:1 mixture of EtOH/dichloromethane (400 mL) for 6h. During this time, the reaction mixture became uniform, homogeneous. The mixture was cooled down to room temperature, poured into deionized water (800 mL), and transferred into a 2L separatory funnel. An additional portion of dichloromethane (200 mL) was added. The dichloromethane part was separated, washed with water (2x500 mL), 3% aqueous $NaHCO_3$ (2x500 mL), and with brine (2x500 mL), dried over $MgSO_4$, and then evaporated to give Compound **6** as a colorless solid. Yield 4.12 g (92%).

^{1}H NMR (DMSO-d$_6$, 300 MHz): d = 7.89 (d, *J* = 9 Hz, 4H), 7.32 (d, *J* = 9 Hz, 8H), 7.26 (d, *J* = 9 Hz, 4H), 6.60 (d, *J* = 9 Hz, 8H) 6.38 (s, 8H), 3.77-3.82 (m, 2H), 3.30 (t, *J* = 6 Hz, 2H), 3.20 (s, 3H), 1.74-1.79 (m, 2H).

^{13}C NMR (DMSO-d$_6$, 75 MHz): d =154.91, 140.48, 139.98, 133.02, 130.88, 128.17, 122.49, 112.90, 69.11, 58.33, 47.57, 29.96.

MS (ESI): *m*/z calcd for $C_{40}H_{41}N_7O_{13}S_6$ $[M+H]^+$ 1020.11. Found: 1020.12.

Compound 7. A mixture of tetraamine **6** (4 g, 3.9 mmol), triethylamine (4.8 g, 0.047 mol), and 3-nitrobenzenesulfonyl chloride (7.0 g, 0.031 mol) was refluxed in a 1:1 mixture of dichloromethane/acetone (200 mL) at reflux for 2h. Then the liquid components of the reaction mixture were removed by rotary evaporation. The solid residue was dissolved in dichloromethane (200 mL). Triethylamine (4.8 g, 0.047 mol) and 3-nitrobenzenesulfonyl chloride (7.0 g, 0.031 mol) were added to the solution. The reaction mixture was refluxed for 24h. Then the solvent was removed by rotary evaporation, and the solid residue was triturated with methanol. The solid precipitate was filtered through a glass funnel filter and thoroughly washed with methanol. Upon drying in vacuum, the raw product was purified by column chromatography on silica gel with CH_2Cl_2/EtOAc (98:2), $R_f = 0.35$. Colorless powder; yield 6.8 g (69%); m.p. 175–180°C.

^{1}H NMR ($CDCl_3$, 300 MHz): d = 8.75 (s, 8H0, 8.57-8.60 (m, 8H), 8.28 (d, J = 8.1 Hz, 8H), 7.86-7.96 (m, 20H), 7.23-7.30 (7.23-7.30), 3.88-3.93 (m, 2H), 3.42 (t, J = 6 Hz, 2H), 3.29 (s, 3H), 2.04 (br s, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz): d = 148.32, 141.30, 140.55, 140.15, 138.73, 138.29, 134.04, 132.20, 131.07, 130.23, 129.67, 129.26, 123.93, 69.25, 58.55, 47.88, 30.39.

MS (ESI pos., CH_3OH/CH_2Cl_2): *m/z* calcd for $C_{88}H_{65}N_{15}O_{45}S_{14}$ $[M+Na]^+$ 2521.92. Found 2521.91.

Anal. Calcd for $C_{88}H_{65}N_{15}O_{45}S_{14}$: C 42.26; H 2.62; N 8.40; S, 17.94. Found: C 42.15; H 2.70; N 8.27; S, 17.79.

Scheme 10

Compound 8. A mixture of Compound **7** (5 g, 2 mmol), $SnCl_2 \cdot 2H_2O$ (20 g, fourfold mass excess), and concentrated hydrochloric acid (5 mL) was stirred at 40 °C in a 1:1 mixture of EtOH/dichloromethane (400 mL) for 6h. The mixture was cooled down to room temperature, poured into deionized water (800 mL), and transferred into a 2L separatory funnel. Dichloromethane (200 mL) was added. The dichloromethane layer was separated, washed with water (2x500 mL), 3% aqueous $NaHCO_3$ (2x500 mL), and with brine (2x500 mL), dried over $MgSO_4$, and then evaporated to give Compound **8** as a colorless solid. Yield 4.1 g (90%).

^{1}H NMR (DMSO-d_6, 300 MHz): d = 8.15 (d, J = 9 Hz, 4H), 7.84 (d, J 7= 9 Hz, 8H), 7.42 (d, J = 9 Hz, 4H), 7.35 (d, J = 9 Hz, 8H), 7.26 (t, J = 8.1, 8H), 7.05 (s, 8H), 6.85-6.93 (m, 8H), 5.77 (s, 16H), 3.91 (br 2H), 3.25 (t, J = 6 Hz, 2H), 3.13 (s, 3H), 1.76 (br, 2H).

MS (ESI pos., CH_3OH): *m*/z calc for $C_{88}H_{79}N_{15}O_{31}S_{14}$ $[M+H]^+$ 2290.12. Found: 2290.10.

Compound 9a. A mixture of octaamine **8** (4 g, 1.7 mmol), triethylamine (4.3 g, 0.042 mol), and 3-nitrobenzenesulfonyl chloride (6.2 g, 0.028 mol) was refluxed in a 1:1 mixture of dichloromethane/acetone (200 mL) at reflux for 4h. Then the liquid components of the reaction mixture were removed by rotary evaporation. The solid residue was dissolved in dichloromethane (200 mL). Triethylamine (4.3 g, 0.042 mol) and 3-nitrobenzenesulfonyl chloride (6.2 g, 0.028 mol) were added to the solution. The reaction mixture was refluxed for 72h. Then the solvent was removed by rotary evaporation, and the solid residue was ground to a fine powder with methanol. The solid precipitate was filtered through a glass funnel filter and thoroughly washed with methanol. Upon drying in vacuum, the raw product was purified by column chromatography on silica gel with CH_2Cl_2/EtOAc (97:3), $R_f = 0.27$. Colorless powder; yield 4 g (44%), melting region 172–188°C.

^{1}H NMR ($CDCl_3$, 600 MHz): d = 8.75 (s, 16H), 8.57 (d, J = 7.8 Hz, 16H), 8.35 (d, J = 7.8 Hz, 16H), 8.02 (d, J = 7.8 Hz, 8H), 7.95 (d, J = 8.4 Hz, 4H), 7.87-7.90 (m, 24H), 7.73 (t, J = 7.8 Hz, 8H), 7.64 (s, 8H), 7.50 (d, J = 8.4 Hz, 8H), 7.21-7.25 (m, 12H), 3.81 (br, 2H), 3.35 (t, J = 6 Hz, 2H), 3.23 (s, 3H), 2.14 (br, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz): d = 148.32, 141.38, 140.50, 140.09, 138.69, 138.42, 137.20, 134.23, 134.01, 132.25, 131.73, 131.22, 130.62, 130.17, 129.56, 129.30, 123.96, 69.21, 58.51, 29.69.

MS (HR MALDI, dithranol+Na-TFA): *m/z* calcd for $C_{184}H_{129}N_{31}O_{93}S_{30}$ $[M+Na]^+$ 5241.78. Found 5241.68.

Anal. Calcd for $C_{184}H_{129}N_{31}O_{93}S_{30}$: C 42.31; H 2.49; N 8.31; S 18.41. Found: C 42.18; H 2.60; N 8.18; S 18.24.

Compound 9b. A mixture of octaamine **8** (4 g, 1.7 mmol), triethylamine (4.3 g, 0.042 mol), and 2-naphthalenesulfonyl chloride (6.4 g, 0.028 mol) was refluxed in a 1:1 mixture of dichloromethane/acetone (200 mL) at reflux for 4h. Then the liquid components of the reaction mixture were removed by rotary evaporation. The solid residue was dissolved in dichloromethane (200 mL). Triethylamine (4.3 g, 0.042 mol) and 2-naphthalenesulfonyl chloride (6.4 g, 0.028 mol) were added to the solution. The reaction mixture was refluxed for 72h. Then the solvent was removed by rotary evaporation, and the solid residue was triturated with methanol. The solid precipitate was filtered through a glass funnel filter and thoroughly washed with methanol. Upon drying in vacuum, the raw product was purified by column chromatography on silica gel with CH_2Cl_2/EtOAc (98:2), R_f = 0.40. Colorless powder; yield 5.2 g (56%), melting region 155–178°C.

^{1}H NMR ($CDCl_3$, 300 MHz): d = 8.47 (s, 16H), 7.78-7.99 (m, 92H), 7.50-7.63 (m, 40H), 7.35 (d, J = 7.8 Hz, 8H), 7.20 (d, J = 8.7 Hz, 8H), 7.15 (d, J = 8.7 Hz, 4H), 3.76 (br, 2H), 3.17 (t, J = 6 Hz, 2H), 3.08 (s, 3H), 1.80 (br, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz): d = 141.54, 140.45, 140.02, 138.92, 138.50, 137.73, 135.55, 135.48, 132.33, 132.13, 131.82, 130.78, 130.26, 130.03, 129.77, 129.67, 128.02, 127.85, 122.73, 69.12, 58.41, 29.71.

MS (HR MALDI, dithranol+Na-TFA): *m/z* calcd for $C_{248}H_{177}N_{15}O_{61}S_{30}$ $[M+Na]^+$ 5299.28. Found 5299.19.

Anal. Calcd for $C_{248}H_{177}N_{15}O_{61}S_{30}$: C 56.15; H 3.36; N 3.96; S 18.13. Found: C 56.10; H 3.51; N 3.76; S 18.00.

Compound 10. A mixture of Compound **9a** (4 g, 0.77 mmol), $SnCl_2 \cdot 2H_2O$ (16 g, fourfold mass excess), and concentrated hydrochloric acid (4 mL) were stirred at 40°C in a 1:1 mixture of EtOH/dichloromethane (350 mL) for 12h. The mixture was cooled down to room temperature, poured into deionized water (600 mL), and transferred into a separatory funnel. Dichloromethane (200 mL) was added. The dichloromethane layer was separated, washed with water (2x400 mL), 3% aqueous $NaHCO_3$ (2x400 mL), and with brine (2x400 mL), dried over $MgSO_4$, and then evaporated to give Compound **10** as a colorless solid. Yield 3.2 g (88%).

^{1}H NMR (DMSO-d_6, 300 MHz): d = 8.11 (d, J = 8.1 Hz, 4H), 7.96-8.03 (m, 16H), 7.79 (t, J = 7.8 Hz, 8H), 7.56 (s, 8H), 7.49 (d, J = 7.8 Hz, 12H), 7.34 (d, J = 8.1 Hz, 8H), 7.22 (t, J = 7.8 Hz, 16H), 7.06 (s, 16H), 6.90 (d, J = 8.1 Hz, 16H), 6.83 (d, J = 8.1 Hz, 16H), 5.74 (s, 32H), 3.88 (br 2H), 3.20 (t, J = 6 Hz, 2H), 3.03 (s, 3H), 1.78 (br, 2H).

MS (HR MALDI, dithranol+Na-TFA): *m/z* calcd for $C_{184}H_{161}N_{31}O_{61}S_{30}$ $[M+Na]^+$ 4739.21. Found 4739.11.

Compound 11. A mixture of hexadecaamine **10** (3 g, 0.63 mmol), triethylamine (3.1 g, 0.03 mol), and 2-naphthalenesulfonyl chloride (4.6 g, 0.02 mol) was refluxed in a 1:1 mixture of dichloromethane/acetone (180 mL) at reflux for 6h. Then the liquid components of the reaction mixture were removed by rotary evaporation. The solid residue was dissolved in dichloromethane (180 mL). Triethylamine (3.1 g, 0.03 mol) and 2-naphthalenesulfonyl chloride (4.6 g, 0.02 mol) were added to the solution. The reaction mixture was refluxed for 72h. Then the solvent was removed by rotary evaporation, and the solid residue was ground to a fine powder with methanol. The solid precipitate was filtered through a glass funnel filter and thoroughly washed with methanol. Upon drying in vacuum, the raw product was purified by column chromatography on silica gel with CH_2Cl_2/EtOAc (97:3), R_f = 0.27. Colorless powder; yield 1.9 g (28%), melting region 138–173°C.

^1H NMR ($CDCl_3$, 600 MHz): d = 8.46 (s, 32H), 7.77-7.95 (m, 190 H), 7.44-7.58 (m, 92H), 7.31-7.36 (m, 18H), 7.21 (d, *J* = 9 Hz, 12H), 3.75 (br, 2H), 3.00-3.24 (m, 5H), 1.78 (br, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz): d = 141.55, 140.80, 140.00, 138.85, 138.54, 137.74, 137.46, 135.58, 135.42, 135.08, 134.71, 134.52, 132.53, 131.79, 130.95, 130.74, 130.56, 130.25, 129.96, 129.73, 128.00, 127.82, 122.76, 69.12, 58.41, 29.71.

MS (HR MALDI, dithranol+Na-TFA): *m/z* calcd for $C_{504}H_{353}N_{31}O_{125}S_{62}$ $[M+Na]^+$ 10842.48. Found 10842.29.

Anal. Calcd for $C_{504}H_{353}N_{31}O_{125}S_{62}$: C 55.89; H 3.29; N 4.01; S 18.35. Found: C 55.71; H 3.38; N 3.89; S 18.07.

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