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Rigid aromatic dendrimers

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Abstract. Rigid aromatic dendrimers synthesised by convergent, divergent and combined methods are considered. The potential of practical application of rigid aromatic dendrimers is analysed. The bibliography includes 121 references.

I. Introduction

In the last decades, data on dendrimers have been covered in numerous reviews,[1 – 28] which suggests continuing interest in this unique class of monodisperse highly branched macromolecules with a highly ordered controllable and regular structure. Unlike conventional polymers, dendrimers incorporate the following three main structural components: the central fragment (core), internal branched units and terminal units (Fig. 1). Two main strategies, divergent and convergent, were developed for the synthesis of dendrimers.

The divergent approach is based on iterative coupling and activation steps starting from the polyfunctional core, the growth of molecules proceeding from the centre to the periphery. In the first step (the growth step), monomers (building blocks) are attached to the core to form first-generation dendrimers (Fig. 2). Monomers (A_nB) containing functional groups of different nature are generally used as building blocks. In these monomers, one group (B) is reactive and can be involved in the reaction, whereas other groups (A_n, their number depends on the nature of the monomer) are deactivated. In the next step (the activation step), the passive groups are activated by deprotection or in other ways, after which these groups are ready to be involved in the growth of dendrimers. Therefore, dendrimers grow layer by layer. Theoretical calculations demonstrated that this growth is, however, not infinite.[29] The density of the periphery of the molecule increases from generation to generation, and the resulting steric hindrance limits the growth of dendrimers. As a result of steric restrictions, the molecule assumes a nearly spherical shape. The packing density at the periphery achieved in this step is called the De Gennes dense packing.[29] According to this model, attempts to grow the subsequent layer should lead to the formation of irregular dendrimers (due to the incomplete substitution of functional groups). This problem is particularly acute for rigid aromatic dendrimers.

The functionalisation of dendrimers in the final step of the molecule formation can be performed with the use of monomers containing the necessary functional groups. The difficulties of controlling the transformations of the functional groups are often considered as a drawback of the divergent approach to the synthesis of dendrimers. Not all functional groups of the growing macromolecule can be involved in the growth of a new layer, which in turn can result in defects in the structure of the final product. This problem can be obviated by using excess of the monomer A_nB, which creates difficulties in the step of purification of the final product. Nevertheless, the divergent approach is a method of choice for the synthesis of high-

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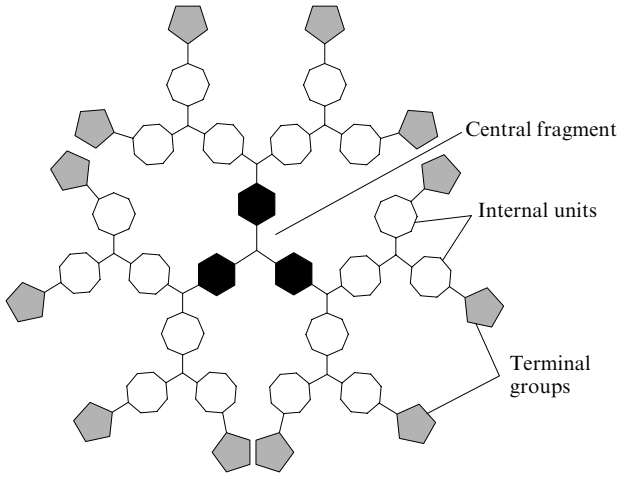


Figure 1. Schematic representation of the dendritic macromolecule.

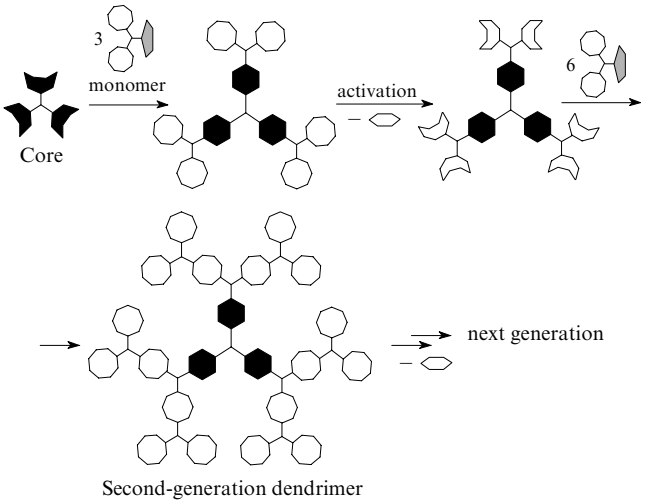


Figure 2. Schematic representation of the synthesis of dendrimers by the divergent method.

generation dendrimers if coupling reactions are selective and efficient.

The convergent approach is also based on the alternation of growth and activation steps. However, the growth of macromolecules occurs from the periphery to the centre, which is achieved due to formation of branched monomers called dendrons, which are attached to the core in the final step of the synthesis. In the first step, a monomer A_nB is attached to the monomer containing peripheral groups of the future dendrimer (the growth step) giving rise to the first-generation dendron (Fig. 3). The activation and coupling of the dendron to the monomer A_nB gives the next-generation dendron. In the last step, the dendrons are attached to the central polyfunctional fragment (core) to form the final dendrimer.

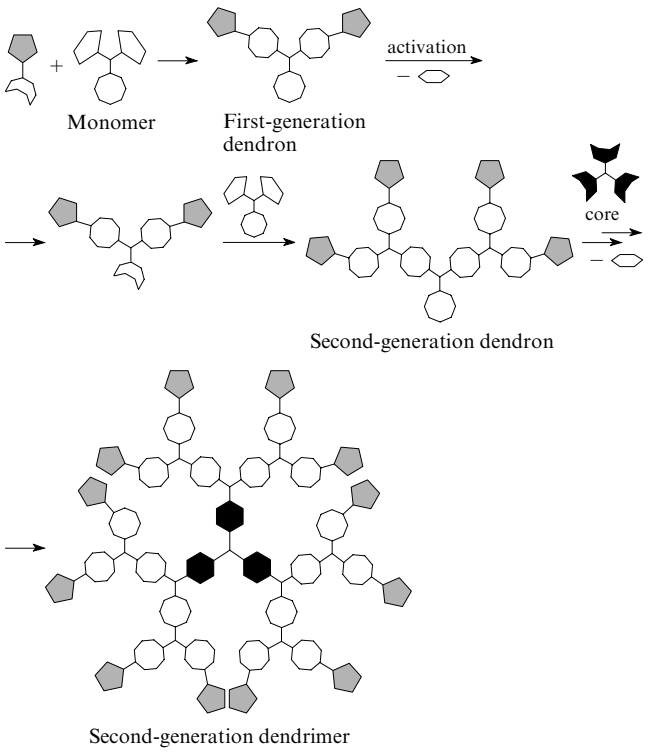


Figure 3. Schematic representation of the synthesis of dendrimers by the convergent method.

The convergent approach also has advantages and disadvantages. The number of reactive functional groups of each molecule involved in the reaction is small and remains constant regardless of the number of generations and the size of the dendron, thus allowing minimisation of the amount of unconsumed groups. The reaction can be brought to completion using a small excess of the monomer (unlike the divergent method). It is much easier to purify the reaction products synthesised according to the convergent approach, because the reaction mixture contains smaller amounts of by-products. The difference in physical properties of the components of the reaction mixture allows the efficient use of chromatographic purification, thus providing the access to individual macromolecules. However, the convergent approach does not allow the formation of high-generation dendrimers (*i.e.*, dendrimers composed of a large number of layers) because of steric hindrance in the step of coupling of the dendron to the core.[1]

An advantage of the convergent method is that it can be used for the preparation of dendrimers containing different functional groups at the periphery of the molecule. To this end, building blocks containing various substituents are used.

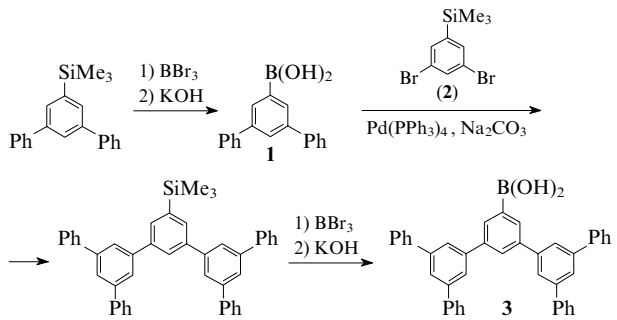
Therefore, the divergent approach is the method of choice for the formation of high-molecular-mass monodisperse dendrimers composed of a large number of layers, whereas the convergent approach is suitable when it is necessary to synthesise monodisperse macromolecules containing a small number of layers and different functional groups at the periphery.[1]

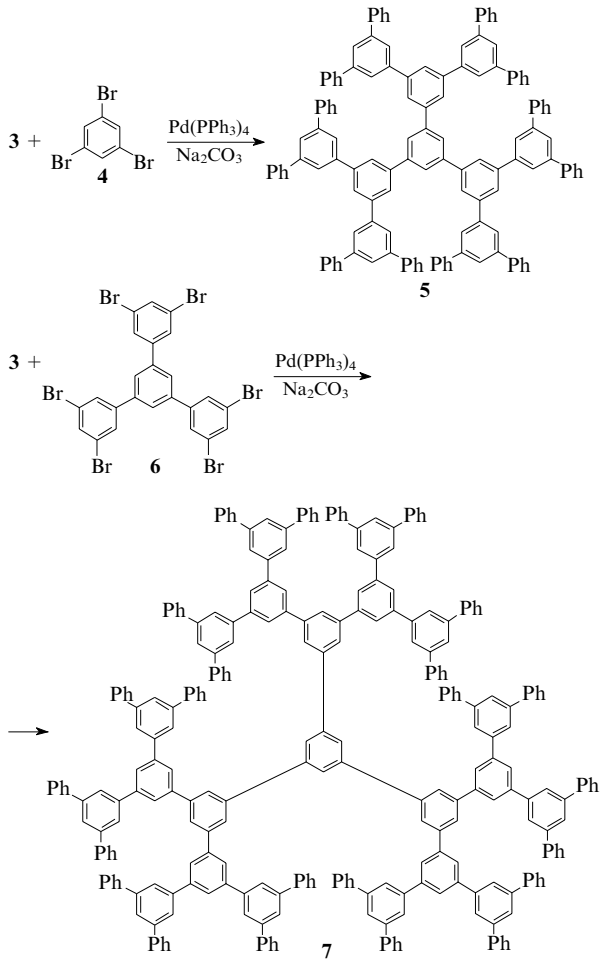
The potential of the synthesis of macromolecules with different architecture and chemical composition can be extended by combining the divergent and convergent schemes.[23, 30–33] For example, a versatile procedure for the synthesis of organosilicon dendrimers [31] is based on the grafting of dendrons, which are prepared according to the convergent scheme onto an oligomeric dendrimer constructed by the divergent method.

In the present review, emphasis is given to rigid dendrimers, because these macromolecules have received little attention in the literature.[34–38] However, these compounds belong to one of the most interesting classes of dendrimers, are characterised by high chemical and thermal stability and are soluble in conventional organic solvents. Rigid aromatic dendrimers of controlled size hold promise in high-temperature catalysis. In addition, aromatic dendrimers with a π-conjugated system can find use in optoelectronic devices.[26, 28, 33, 34, 39–41]

II. Rigid aromatic dendrimers synthesised by the convergent method

Polyphenylene dendrimers have been synthesised for the first time [42, 43] by the convergent method using the Suzuki coupling of substituted phenylboronic acid **1** with aryl bromides.[44] This was used for the synthesis of dendrimers based on 1,3,5-triphenyl-substituted monomers.



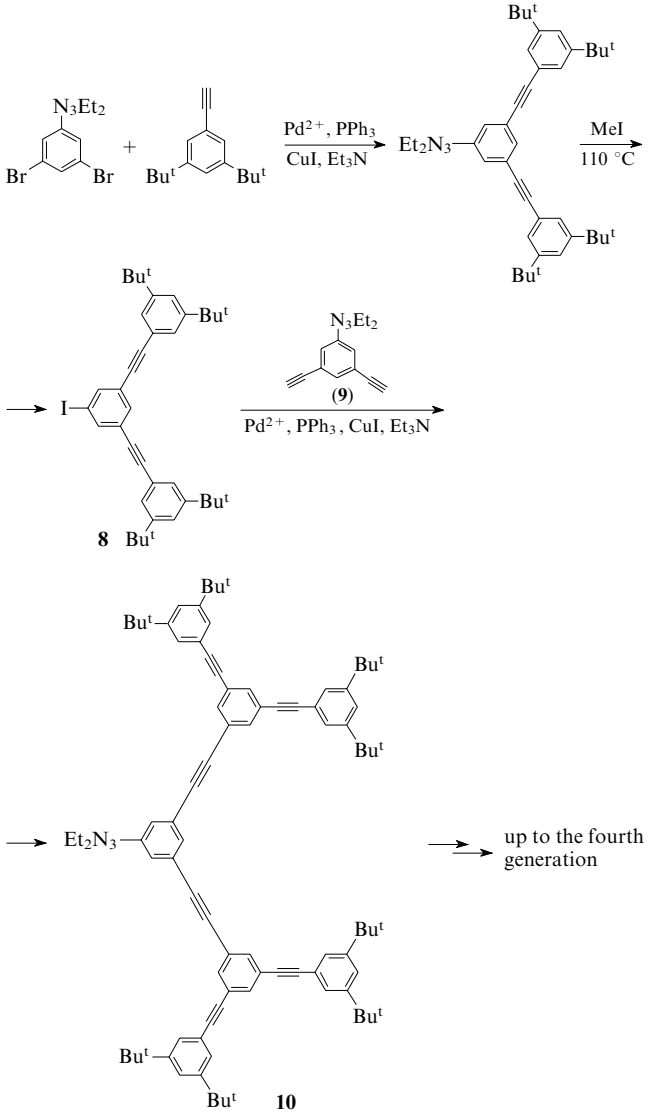


A first-generation dendron was prepared by coupling of 3,5-dibromo-1-(trimethylsilyl)benzene (**2**) with substituted phenylboronic acid **1**. The trimethylsilyl protecting group was removed by treating with boron tribromide followed by hydrolysis, and then activated dendrons **3** were attached to the central fragment, *viz*., to 1,3,5-tribromobenzene (**4**), giving rise to dendrimer **5**. More branched central fragment **6** was used for the synthesis of dendrimer **7**.[43] Monitoring of the reaction of compound **3** with **6** by chromatography demonstrated that the first three bromine atoms are replaced very rapidly, whereas the replacement of other bromine atoms occurs much more slowly due to steric effects. This situation is typical of the convergent synthesis. Due to the presence of a 'rigid' repeating fragment in the dendrimer structure, the shape and size of molecules remain unchanged under different external conditions.

The synthesis of macromolecules based on arylalkyne and phenylacetylene fragments was documented.[26,45] 4-(*tert*-Butyl)phenyl substituents were used as groups increasing the solubility of the final dendrimer; however, their influence on solubility was extended only up to third-generation dendrimers. Fourth-generation dendrimers with 3,5-di(*tert*-butyl)-phenyl terminal groups proved to be somewhat better soluble.[46]

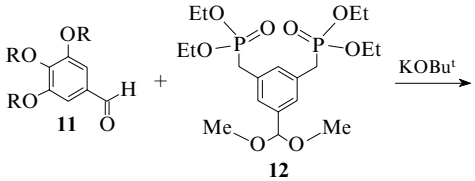
Poly(phenylacetylene) dendrimers were synthesised using dendrons that have been prepared based on the diethynyl monomer containing a triazene protecting group. This dendron is easily activated for the subsequent coupling reaction by replacing the protecting group by a halogen.[47]

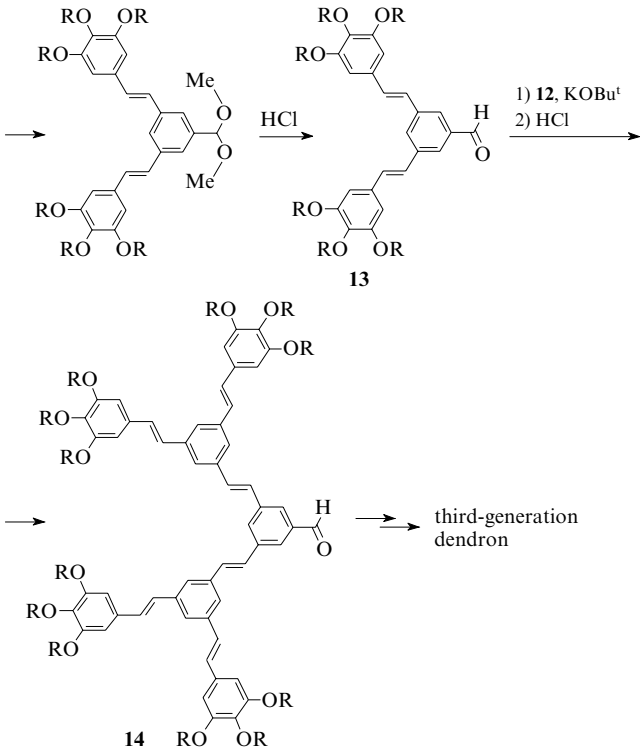
The cross-coupling reaction of first-generation halogen-containing dendron **8** with compound **9** catalysed by a palladium complex afforded second-generation dendron **10**. Due to the rigid defect-free structures of such dendrimers containing conjugated fragments, they possess promising photophysical properties.



Phenylacetylene dendrimers containing Bu^tCO_2 peripheral groups were synthesised by the modified convergent method. Solid-state thermolysis of these systems resulted in the conversion of the Bu^tCO_2 groups into carboxy groups.[48] Since thermolysis of high-generation dendritic molecules is accompanied by partial cross-linking, an alternative procedure for the synthesis of phenylacetylene dendrimers containing carboxy terminal groups was developed. Dendrimers prepared by this method in high yields (up to 90%) are water-soluble compounds.

A first-generation dendron was synthesised[49] by coupling of aldehyde **11** with monomer **12** containing two phosphate groups.

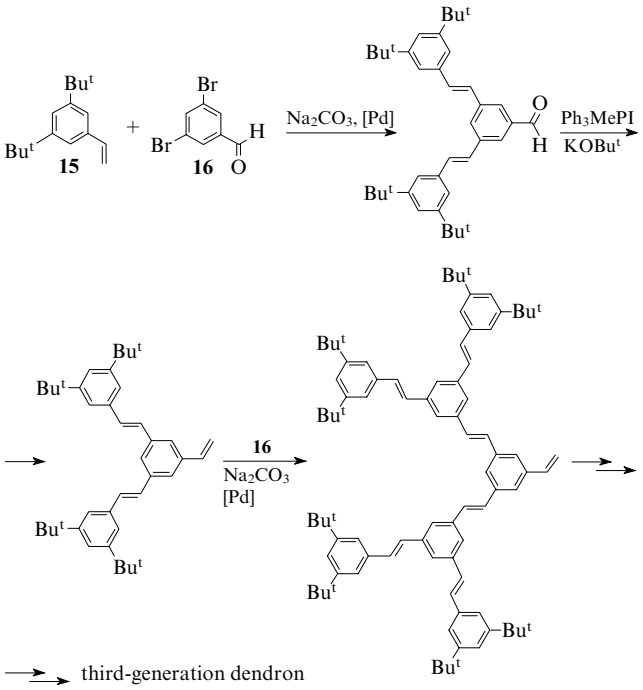




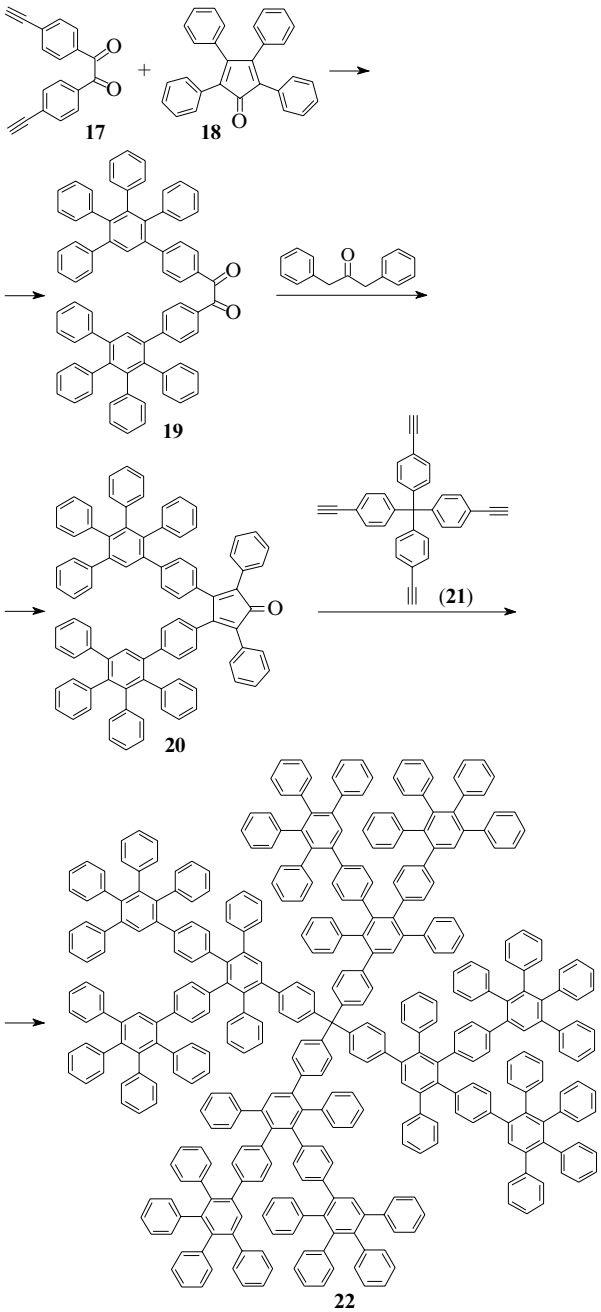
R = n-C_6H_{13}.

Acid hydrolysis leads to the conversion of the acetal group into the aldehyde (compound **13**), which can be involved in the Horner – Wadsworth – Emmons coupling reaction giving rise to second-generation dendron **14**. However, only third-generation dendrons were synthesised by this procedure. The synthesis of the fourth-generation dendron was considered unreasonable because of low yields and long reaction times.

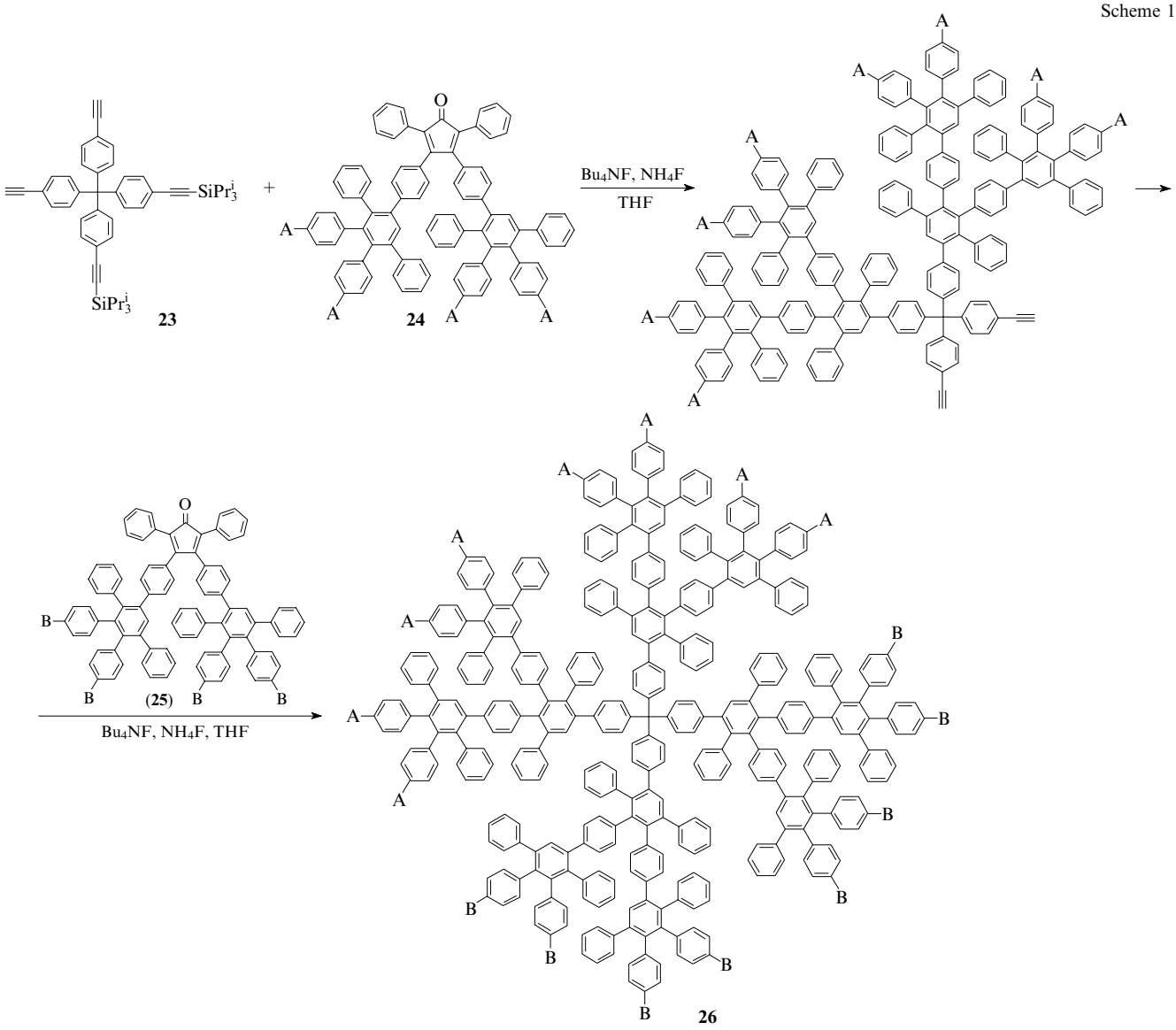
Analogous dendrons were synthesised [50] by Heck coupling [51, 52] of substituted styrene **15** with 3,5-dibromobenzaldehyde (**16**) followed by the Wittig reaction with methylenetriphenylphosphorane iodide. Unfortunately, dendrons of only three generations could be synthesised by this procedure.



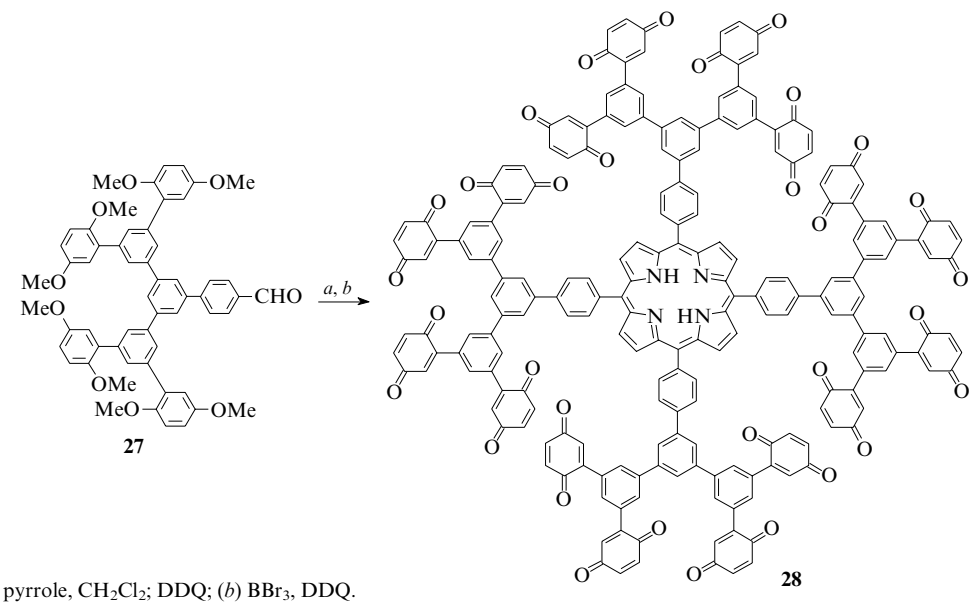
The convergent method was developed [53] for the synthesis of polyphenylene-type dendrimers based on the Diels – Alder reaction. This starts with coupling of 4,4′-diethynylbenzil (**17**) with an excess of 2,3,4,5-tetraphenylcyclopentadienone (**18**). 4,4′-Diethynylbenzil is a monomer A_2B-type because it contains two dienophilic ethynyl groups, which can be involved in the Diels – Alder reaction with dienes, and one ethanedione group, which is inactive in the [2 + 4]-cycloaddition but is helpful for further tranformations. Dendron **19** formed in the growth step is converted by the Knoevenagel reaction with diphenylacetone into reactive second-generation dendron **20**. This undergoes the Diels – Alder reaction with the central fragment, *viz*., tetrakis(4-ethynylphenyl)methane (**21**), to form phenylated rigid second-generation dendrimer **22**. First-, second- and third-generation dendrons were prepared in rather high yields (85% – 89%). Nevertheless, all attempts to make the third-generation dendron react failed because steric hindrance did not allow it to undergo condensation with diphenylacetone. However, identical dendrimers of not only



Scheme 1



Scheme 2



(*a*) $BF_3 \cdot OEt_2$, pyrrole, CH_2Cl_2; DDQ; (*b*) BBr_3, DDQ.

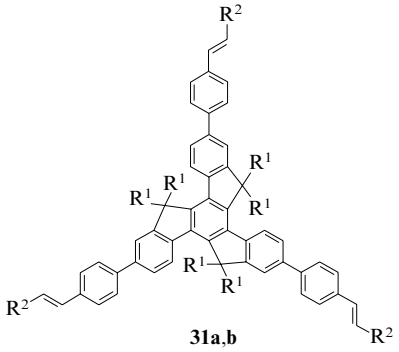
the third, but also the fourth generation can be synthesised using the divergent approach, as will be demonstrated in the next section.

The convergent method was successfully applied to the synthesis of polyphenylene dendrimers containing peripheral substituents of different nature.[38] For this purpose, the central fragment, *viz*., bis(4-ethynylphenyl)bis[4-(triisopropylsilyl)-ethynylphenyl]methane (**23**), with two protected triple bonds was synthesised using a deficient amount of desilylating agents from a tetrasilyl precursor. Then the Diels–Alder reaction with dendrons **24** containing substituents A was carried out. After desilylation, the liberated ethynyl groups were involved in the Diels–Alder reaction with dendrons **25** containing substituents B to give finally dendrimer **26** containing different substituents in one molecule (Scheme 1).

Dendrimers based on porphyrin fragments have attracted interest because of their valuable photophysical properties.[17,54–57] For example, rigid polyphenylene dendrimers containing the porphyrin fragment as the central group have recently been synthesised.[36] Dendron **27**, which has been prepared by the convergent method using the Suzuki reaction, was coupled with pyrrole. The further demethylation with boron tribromide and oxidation with 2,3-dichloro-5,6-dicyano-*p*-quinone (DDQ) produced dendrimer **28** containing peripheral benzoquinone groups (Scheme 2).

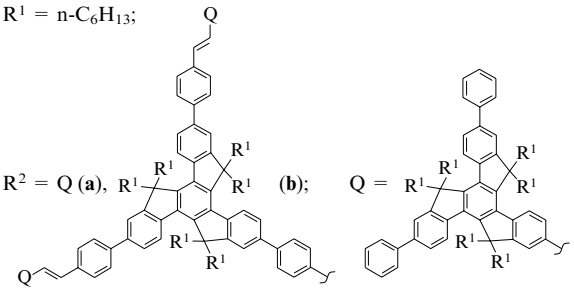
The synthesis of luminescent dendrimers **29** and **30** containing the porphyrin core and carbazole peripheral fragments was documented.[58] Initially, aldehyde precursors were synthesised by a multistep procedure using the Ullmann reaction or the palladium-catalysed Suzuki reaction. Further condensation with pyrrole was carried out under the Lindsey conditions.[59,60]

Due to the presence of large hyperbranched blocks, π-conjugated dendritic molecules possess characteristic three-dimensional architecture, which imparts qualitatively new properties to these molecules compared to linear semiconducting oligomers and polymers.[28] π-Conjugated aromatic dendrimers **31a**,**b** containing stilbene-like groups as bridging fragments were synthesised by the convergent method using the Suzuki reaction and the Horner–Wadsworth–Emmons reaction.[61] These dendrimers show luminescence in the blue region with high quantum yield, which led the authors to conclude that these compounds can be used as materials for light-emitting diodes.



31a,**b**

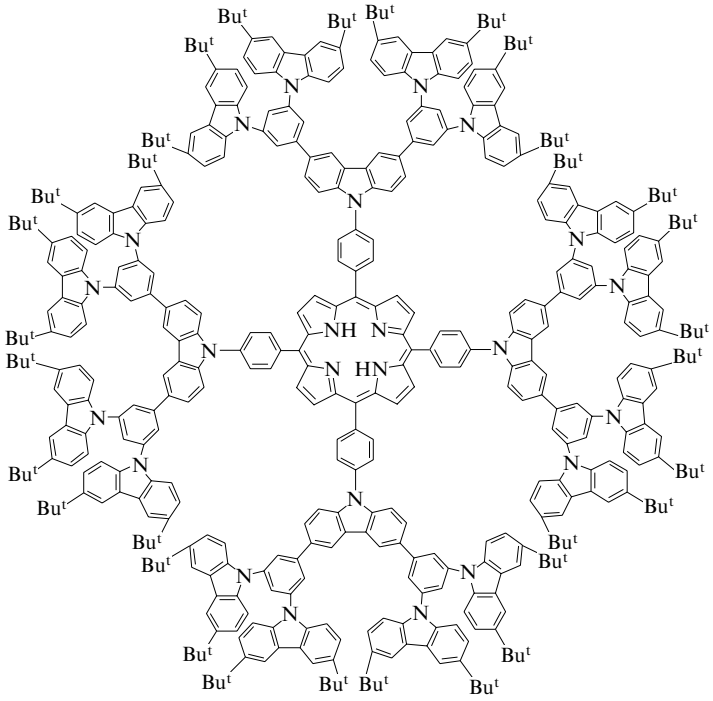
R^1 = n-C_6H_{13};



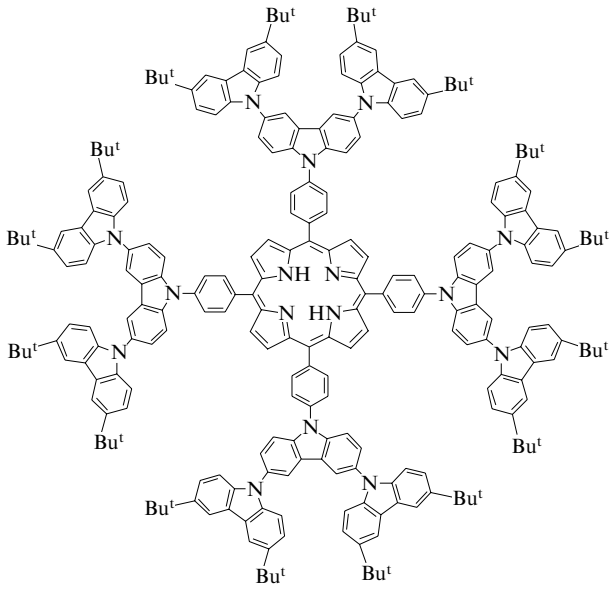
R^2 = Q (**a**), (**b**); Q =

III. Rigid aromatic dendrimers synthesised by the divergent method

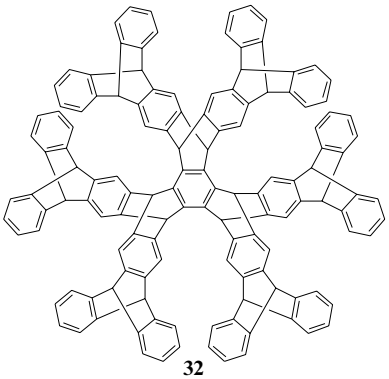
The so-called iptycenes were among the first characterised rigid dendrimers, which were synthesised by the divergent method (using the Diels–Alder reaction).[62] These unique molecules based on the benzene or iptycene cores (compounds **32** and **33**, respectively) are characterised by high thermal stability.



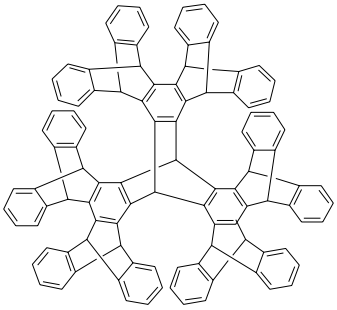
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30



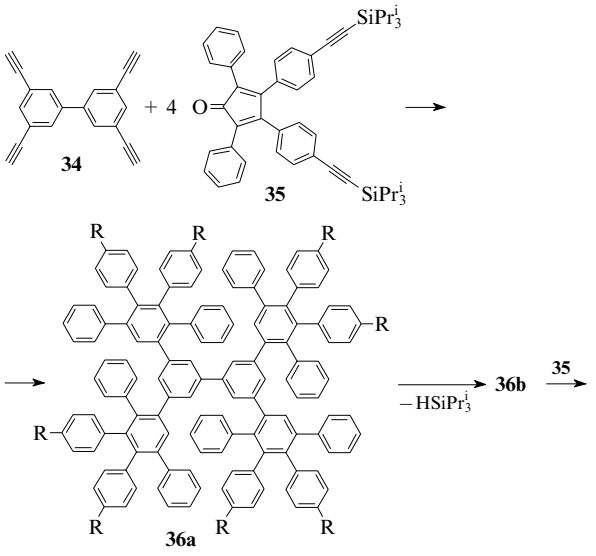
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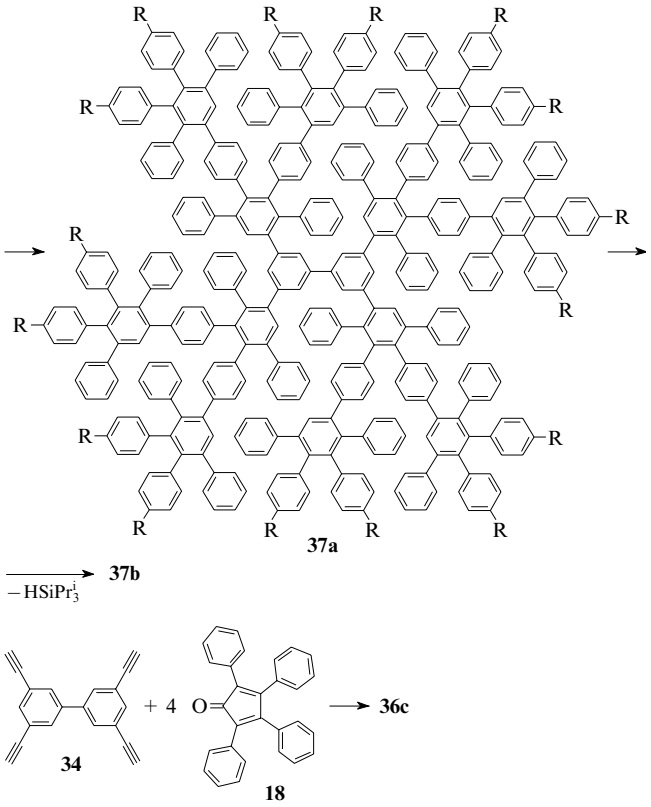


33

Very simple but stringent requirements are imposed on the chemical reactions involved in the main cycle including growth and activation of a molecule: the reactions should be unambiguous, enable complete conversion of the substrates and be feasible. One of the most efficient synthetic schemes for the preparation of polyphenylene dendrimers by the divergent method was developed by Müllen and co-workers.[34, 38, 63–71] This is based on two iterative reactions, *viz*., the Diels–Alder cycloaddition of tetraphenylcyclopentadienones to substituted ethynyl compounds[72] (the growth step) and desilylation of tri(isopropylsilyl)-substituted alkynes (the activation step).

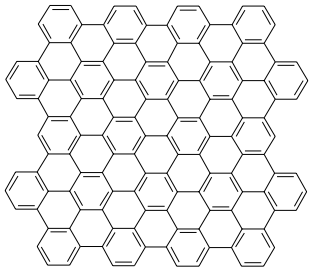
The reaction of 3,3′,5,5′-tetraethynylbiphenyl (**34**) with cyclopentadienone derivative **35** afforded first-generation dendrimer **36a** containing tri(isopropyl)silyl-substituted ethynyl groups. Activated first-generation dendrimer **36b** with eight ethynyl terminal groups was obtained after removal of tri(isopropyl)silyl protection. The reaction of compound **36b** with cyclopentadienone **35** afforded second-generation dendrimer **37a**. As a result, dendrimer **36a** with a molecular mass of 3119 (220 carbon atoms) was transformed into dendrimer **37a** with a molecular mass of 7606 (548 carbon atoms) by the two-step reaction. In spite of the high molecular masses, compounds **36** and **37** are readily soluble in organic solvents.





R = —≡—SiPr$^i_3$ (**a**), —≡— (**b**), H (**c**).

Graphite-like highly fused system **38** was prepared by dehydrocyclisation of dendrimer **36c**.

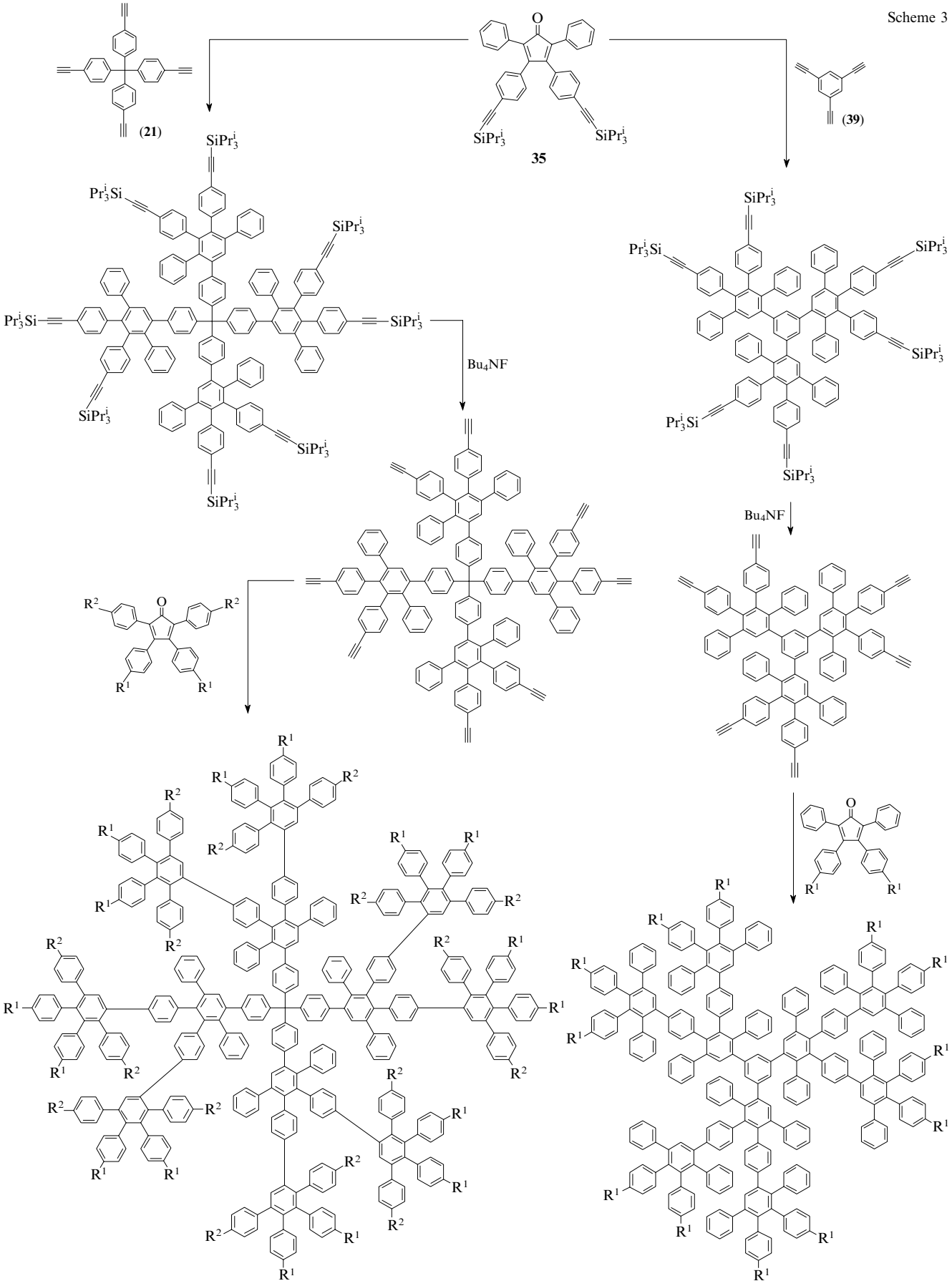


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A series of dendritic polyphenylenes were synthesised based on compound **21** as the core using A_2B-type monomer **35** as the building block (Scheme 3). These dendrimers of four generations exhibit good chemical stability, thermal stability and solubility in many organic solvents. In addition, a series of dendrimers were synthesised[68] using an A_2B block, an A_4B block and various cores [compounds **21**, **34**, 1,3,5-triethynylbenzene (**39**) and 1,2,3,4,5,6-hexakis(4-ethynylphenyl)benzene (**40**)], and their spatial organisation was studied. In the case of an A_2B monomer and cores **21** and **34**, the ability of a dendrimer to grow was demonstrated to be independent of the nature of the core, and the nearly globular shape is achieved only in the fourth generation. On the contrary, the globular shape is achieved very rapidly with the use of an A_4B monomer; however, it is impossible to prepare defect-free dendrimers of generations higher than two.

Alkyl-substituted polyphenylene dendrimers, which are capable of self-assembly on solid surfaces (for example, on graphite), were synthesised[64, 66, 73] starting from 1,3,5-triethy-

Scheme 3



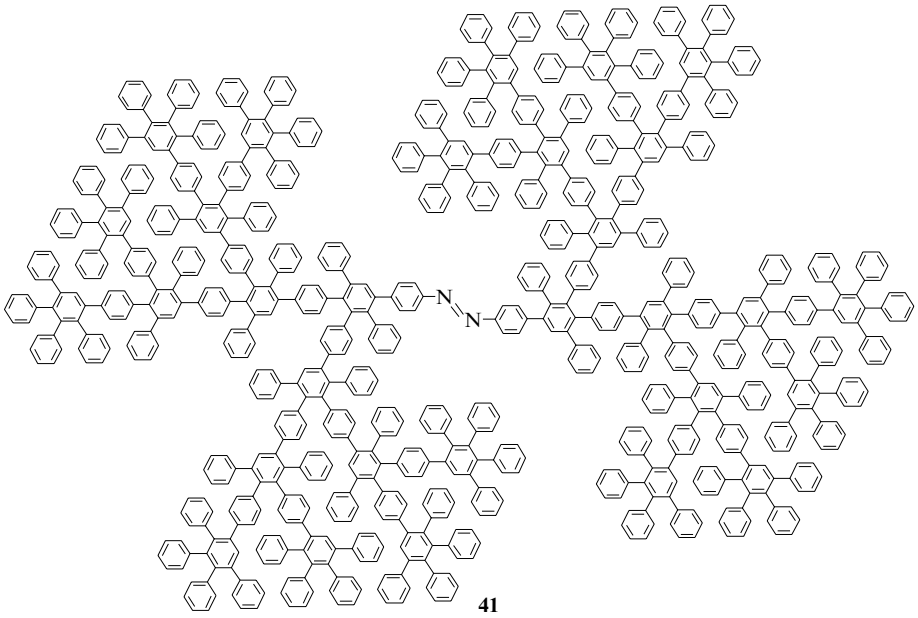
R^1 = n-$C_{12}H_{25}$, H; R^2 = H, n-$C_{12}H_{25}$.

nylbenzene and tetrakis(4-ethynylphenyl)methane (see Scheme 3).

First- and second-generation dendrimers containing the 1,3,5-triethynylbenzene fragment as the core were studied by the molecular dynamics method.[74] It was demonstrated that only four of six possible conformations of second-generation dendritic molecules are stable, and the dendrimer sizes can vary only within 10%.

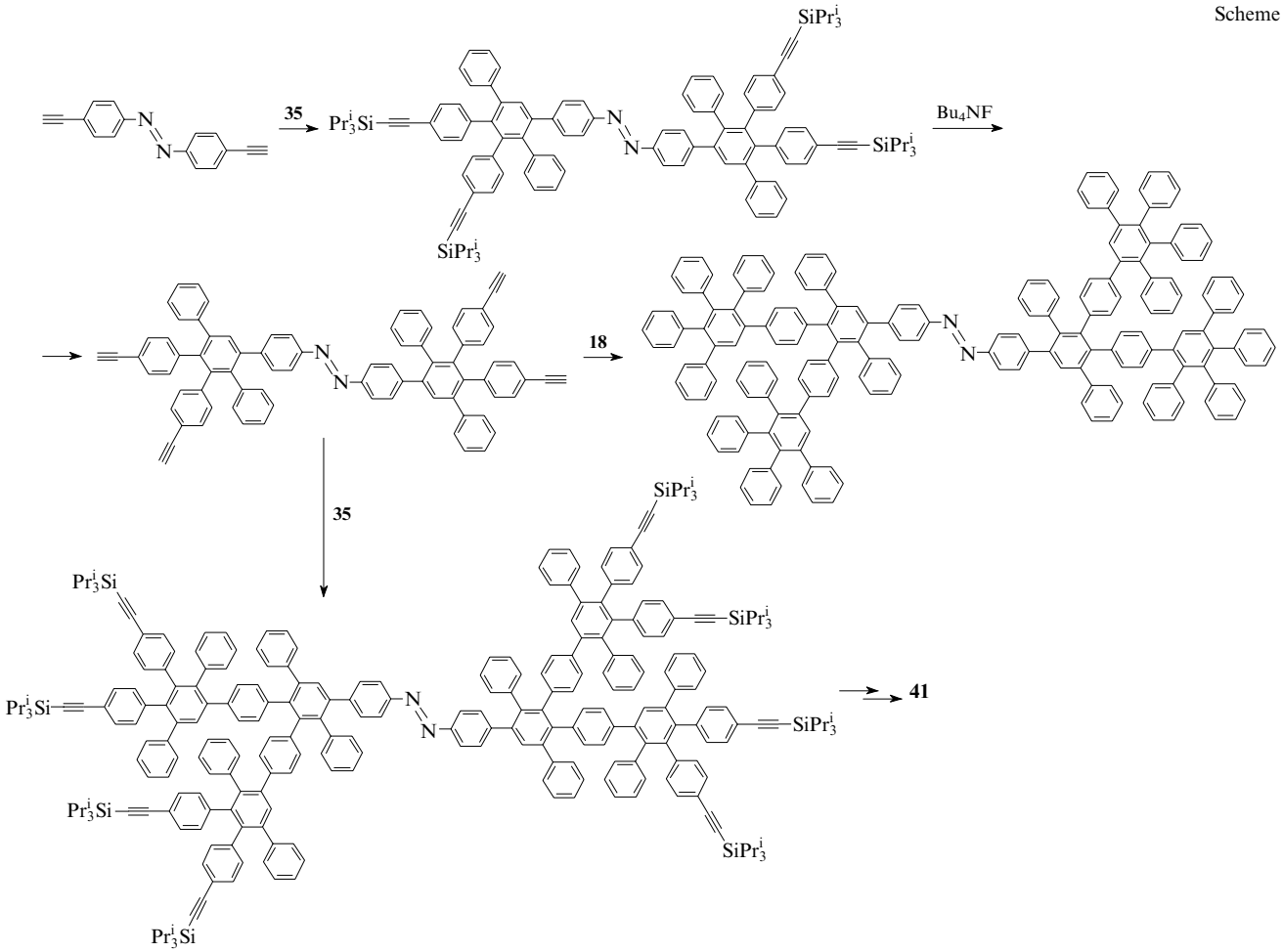
A series of dendrimers containing 4, 10 and 22 symmetrically arranged fluorine-substituted aromatic rings were synthesised.[43] The surface layers of the molecular structures of dendrimers consist of perfluorinated phenyl groups. Dendrimers are rather thermally stable, monodisperse and readily soluble in organic solvents (THF, CH_2Cl_2 or $CHCl_3$). In addition, these dendrimers have good electron-conducting properties and chemical stability. Due to the above-mentioned characteristics, these dendrimers are attractive materials for the design of light-emitting diodes.[75]

A series of polyphenylene dendrimers of four generations (compound **41** is a fourth-generation dendrimer) containing



41

Scheme 4



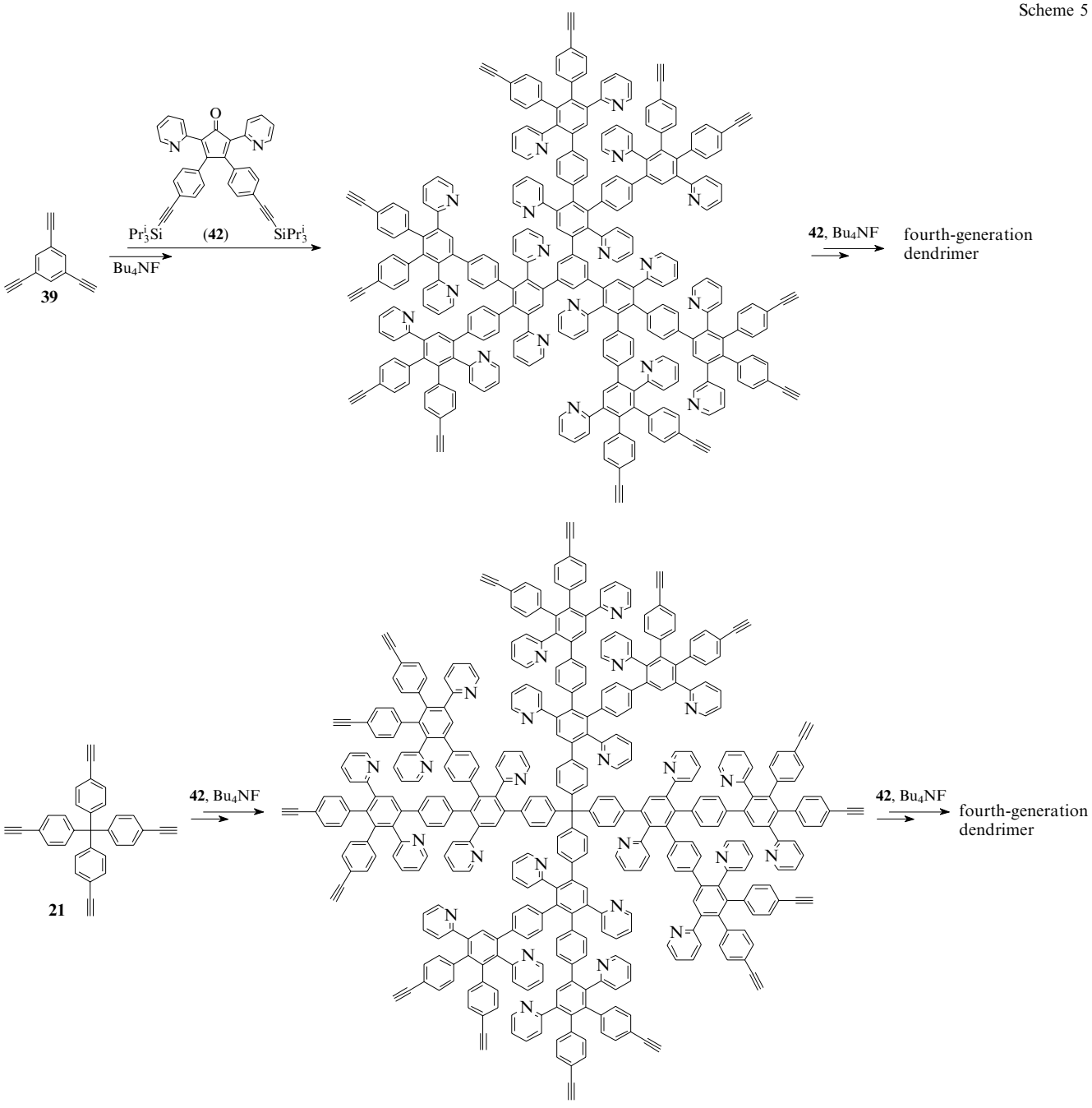
the azobenzene cores were synthesised starting from 4,4′-bis(4-ethynylphenyl)azobenzene (Scheme 4).[71] The resulting dendrimers exhibit reversible photosensitivity under UV-Vis irradiation, which reflects reversible structural changes in the molecule. The influence of the number of the dendrimer generation and the degree of branching of the dendrimers on the kinetic characteristics of photoisomerisation was studied.

In addition to polyphenylene dendrimers containing different functional groups at the periphery and/or in the centre of the macromolecule, dendrimers with different arrangement and compositions of functional groups in the inner sphere were synthesised. Studies aimed at designing polyphenylene dendrimers based on new pyridine-containing monomers, such as 3,4-bis{4-[tri(isopropyl)silylethynyl]phenyl}-2,5-di(pyridin-2-yl)cyclopenta-2,4-dienone (**42**), 3,4-di(pyridin-2-yl)-2,5-diphenylcyclopenta-2,4-dienone (**43**) and 2,3,4,5-tetrakis(pyridin-2-yl)cyclopenta-2,4-dienone, have been carried out.[76–78]

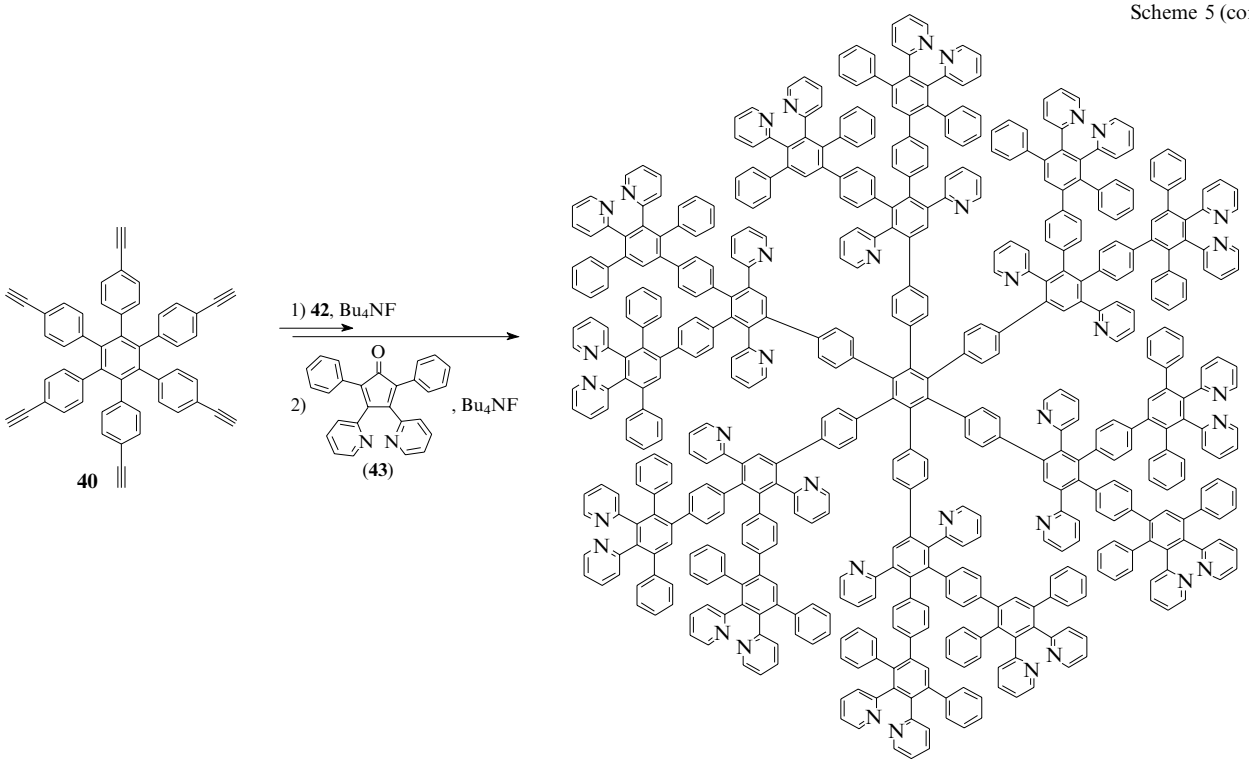
The introduction of pyridine fragments into polyphenylene dendrimers can impart new properties to the latter. The presence of pyridine rings not only at the periphery, but also in the inner sphere of macromolecules extends the potential of functionalisation. Pyridine-containing dendrimers of four generations were prepared using synthetic routes based on the Diels–Alder reaction; however, steric hindrance appears already in the synthesis of the third-generation dendrimer with substituted benzene **40** as the dendrimer core (Scheme 5).

The synthesis of dendrimers of four generations based on core **39** is presented in detail in Scheme 6. In the last step, the third-generation dendrimer containing ethynyl peripheral

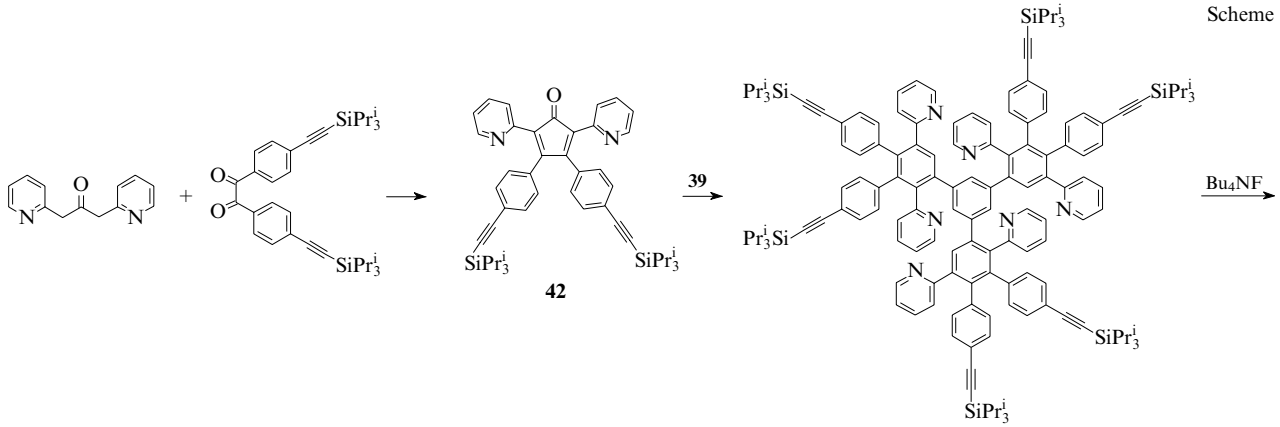
Scheme 5

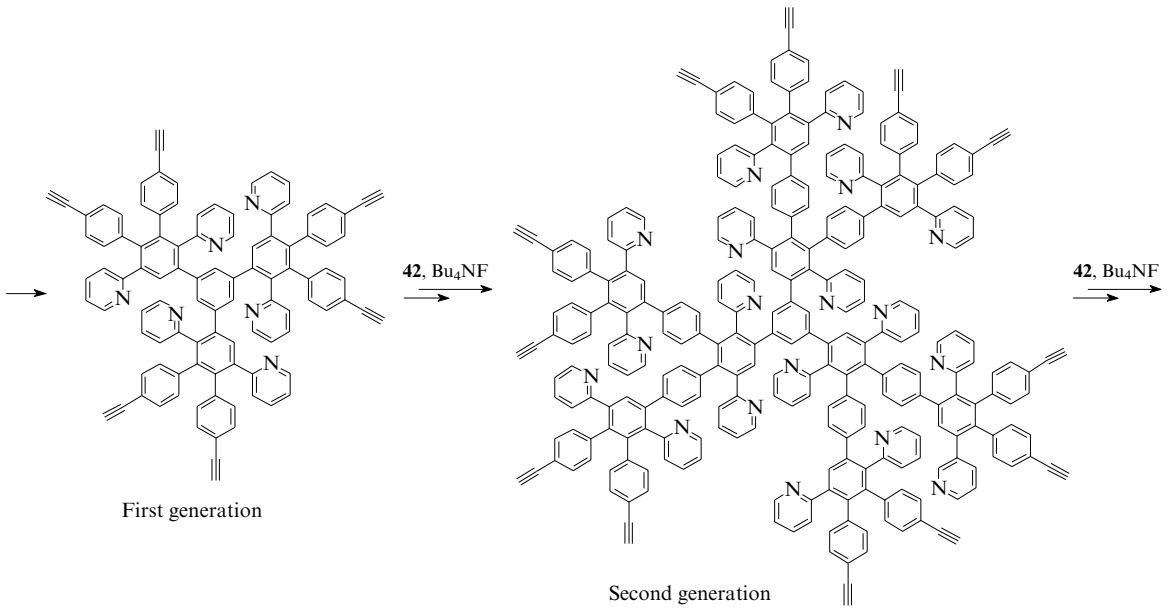


Scheme 5 (continued)

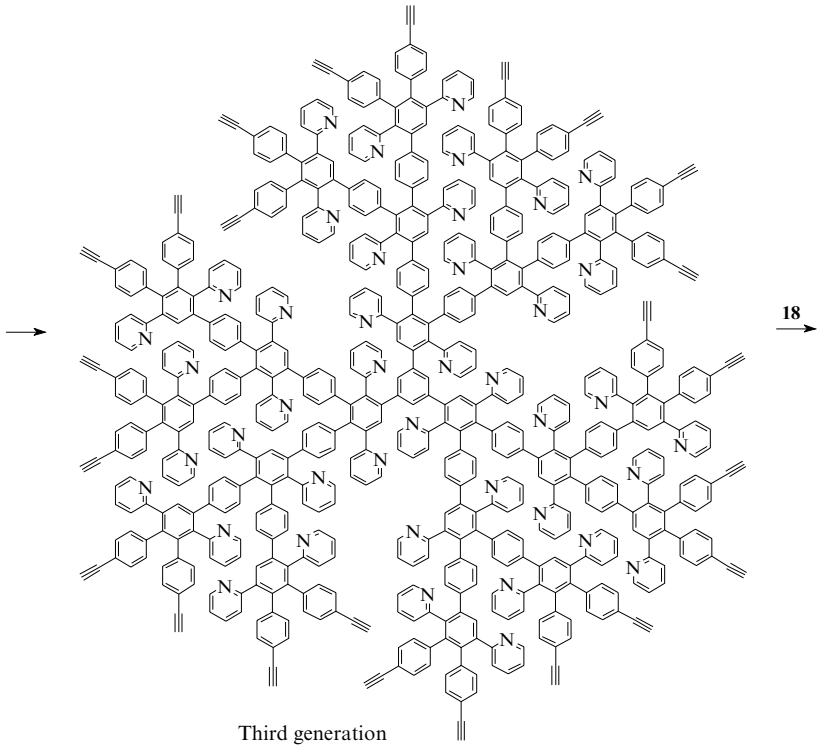


Scheme 6

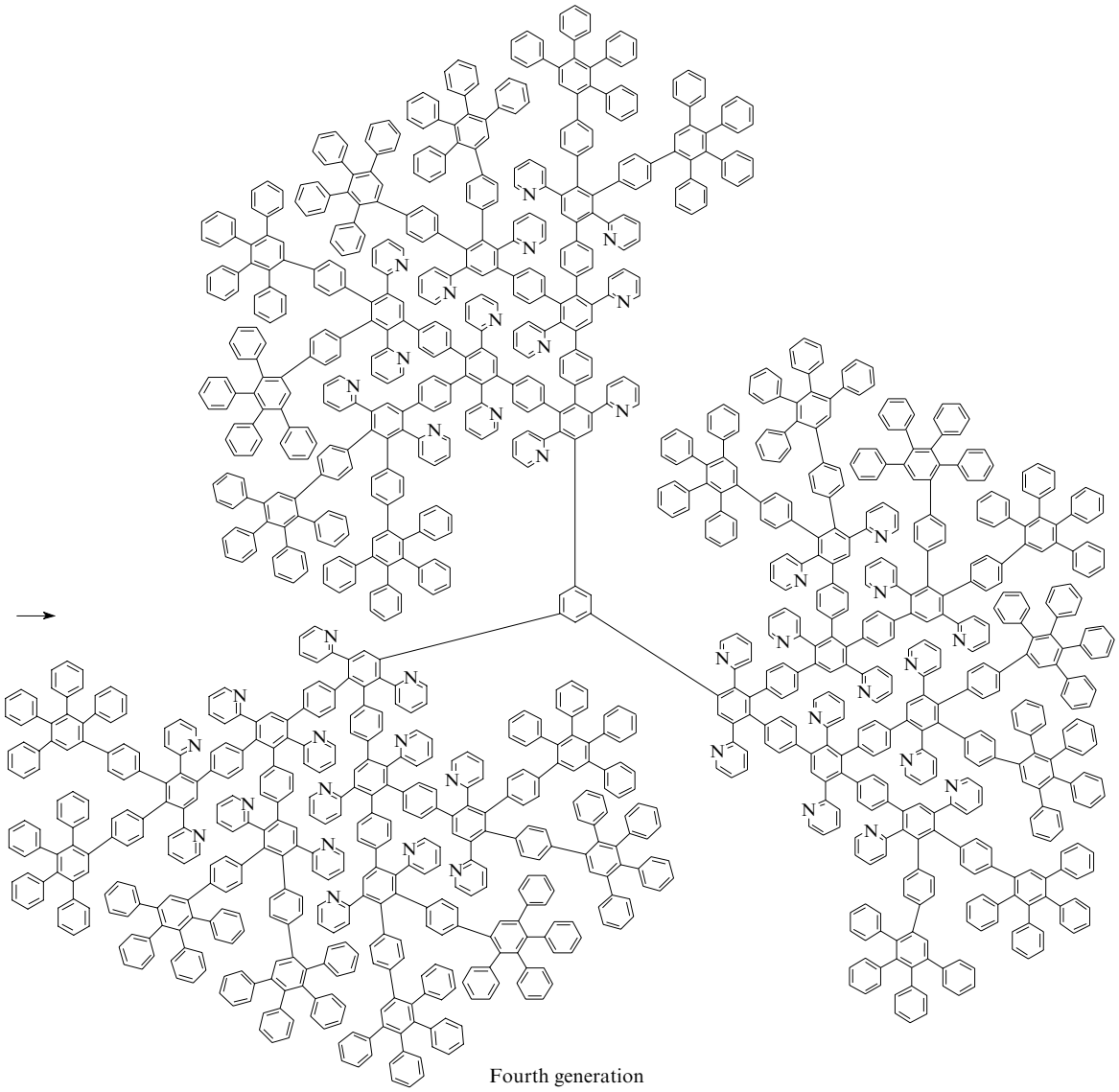




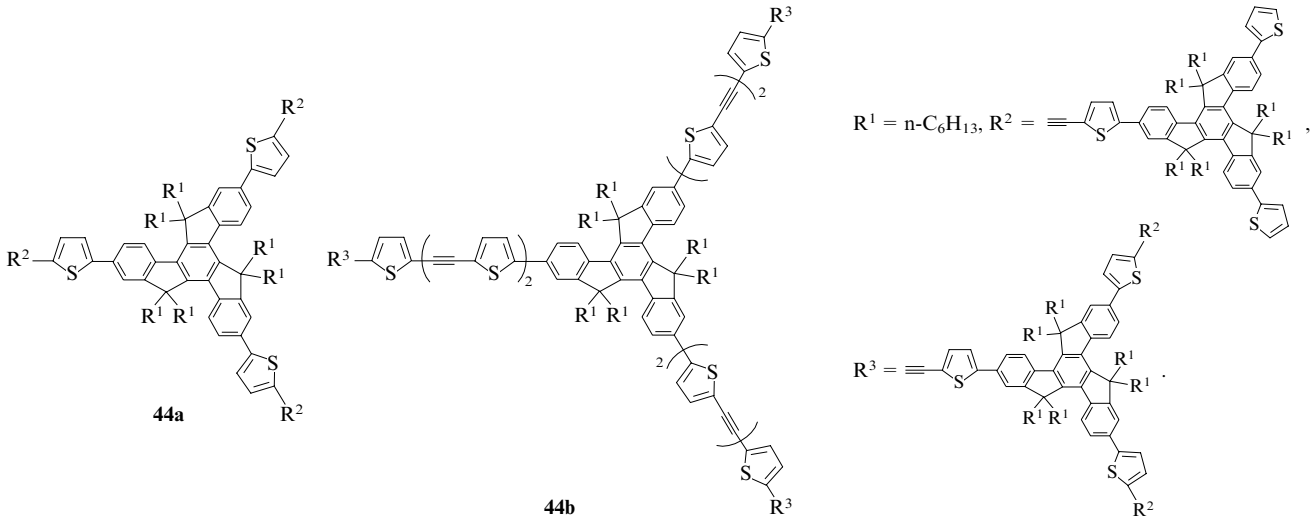
Scheme 6 (continued)



Third generation



Fourth generation



groups is transformed into the fourth-generation dendrimer containing phenyl peripheral groups.

According to the thermogravimetric analysis, all the dendrimers under study are characterised by rather high thermal stability. Thus, a 10% mass loss in air for second–fourth generation dendrimers was observed at temperatures above 480 °C. According to the differential scanning calorimetry, no phase transitions occur in samples of dendrimers up to the decomposition temperature. The structures of the above-mentioned dendrimers are not destroyed even upon treatment with acids or alkalis over a long period of time. Due to high chemical and thermal stability, the resulting macromolecules are unique compounds among other known dendrimers containing the pyridine or amine (imine) functional groups, and these compounds can be used in corrosive media and/or at high temperatures. In addition, these dendrimers can be used in the design of new hybrid (dendrimer–metal) nanostructured systems having catalytic properties.[77]

The efficient combined divergent/convergent synthesis of new conjugated zero-generation (**44a**) and first-generation (**44b**) dendrimers containing oligo(ethynylthiophene) fragments was documented.[33] This method is based on the iterative Sonogashira and Wittig reactions. The dendrimers prepared in high yields (72%–82%) are readily soluble in organic solvents, which made it possible to study in detail the dependence of their properties on the structure. Due to the ability to absorb light in a very broad frequency range, these dendrimers hold promise for the design of light-absorbing materials analogous to natural substances.

The above-considered results show considerable progress in the synthesis of rigid aromatic dendrimers by both the convergent and divergent methods. It is expected that further investigations will be aimed at extending the range of these dendrimers and searching for fields of their practical application.

IV. Possible areas of application of rigid dendrimers

The development of procedures for the synthesis of versatile dendritic matrices, which can be used for the design of special materials for different fields of application (catalysts, optical materials, magnetic nanoparticles and drug delivery agents), is one of the most interesting and important areas in chemistry of dendrimers. Due to predictable, controlled and highly reproducible molecular sizes, dendrimers are ideal standards for mass spectrometry, electronic and atomic spectroscopy and ultrafiltration. The presence of channels and pores in dendritic macromolecules allows their use for encapsulation and immobilisation of small-molecular-mass guest molecules. The possibility of incorporation of guest molecules into dendrimers has been demonstrated,[79] which gave impetus to numerous investigations in this field and the design of new composites of dendrimers with guest molecules.[80,81] Such host–guest composites can find use in biology, medicine, pharmacology and catalysis.[14,23,82,83]

The use of dendrimers as host molecules for the encapsulation of guest metal nanoparticles holds considerable promise. Pioneering investigations in this field date back to 1994.[9] First essential results were published in the late 1990s. The formation of copper nanoparticles in a dendrimeric template was documented.[84,85] Reduction of copper ions in the presence of dendrimers gave rise to colloidal solutions stable at room temperature for more than 90 days. The formation of nanoparticles stabilised by a dendrimeric template was confirmed by UV spectroscopy and electron microscopy. Gold nanoparticles in a dendrimeric template were synthesised by an analogous procedure.[86] It was found that the size of the resulting nanoparticles can be controlled using dendrimers of different generations (from zero to fifth). It was demonstrated that the strategy of the formation of metal nanoparticles inside a dendrimeric nanoreactor can be successfully applied to all transition metals. The introduction of monometallic, bimetallic[90] and semiconducting[87] nanoparticles into dendrimers was examined.[19,83,84,87–93] In this case, dendritic macromolecules are used for efficient stabilisation of supersmall metal particles.

The growing interest in the synthesis of metal nanosized particles in dendrimeric templates was dictated not only by the novelty and simplicity of the procedure, but also by the possible practical applications of nanocomposites, in particular, as catalysts. It was noted[94] that dendrimers allow combination of advantages of homogeneous and heterogeneous catalysis and can provide the control over the structure and size of catalytic particles. For example, Pd and Pt nanoparticles stabilised by a dendrimeric template are characterised by excellent catalytic activity in hydrogenation of simple (for example, allyl alcohol) and electron-deficient (*N*-isopropylacrylamide) alkenes in an aqueous medium.[89] Bimetallic nanoparticles synthesised in the presence of dendrimers are also active in the Heck and Suzuki coupling reactions.[88]

The choice of rigid dendrimers as templates for the formation of metal nanoparticles provides better control over the particle growth and morphology. New hybrid (dendrimer–metal) nanostructured systems based on poly(pyridylphenylene) dendrimers, which have catalytic properties, were studied.[76,77] The catalytic mono- and bimetallic nanoparticles thus synthesised proved to be rather active catalysts for hydrogenation of the triple bond in acetylenic alcohols.[95,96]

Rigid dendritic macromolecules with a strictly defined structure and predictable properties have a high potential for

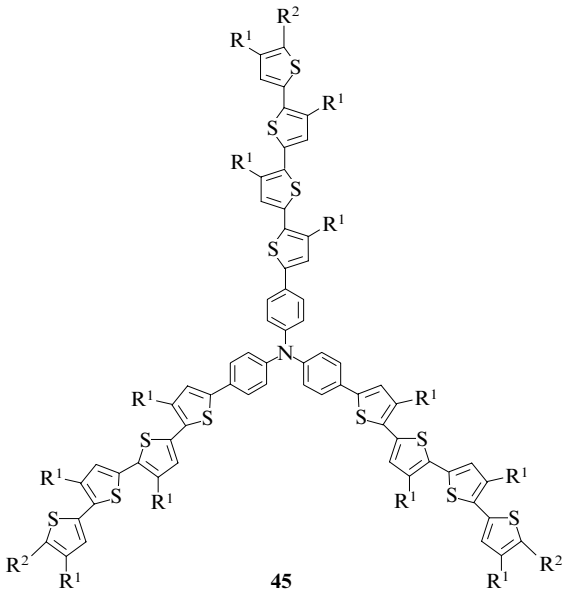
the design of optical and electronic devices. Conjugated phenylacetylene dendrimers [97] containing optically pure 4,4′,6,6′-tetrabromo-1,1′-bi(2-naphthol) diacetate were among the first rigid dendrimers having optical properties, which hold promise for the design of enantioselective fluorescent sensors. Such optically active dendrimers can also be used in the asymmetric synthesis.

Perfluorinated first- and second-generation polyphenylene dendrimers were investigated as materials for organic light-emitting diodes.[98] These systems can be used for the design of blue-light-emitting diodes; however, perfluorinated dendrimers are inferior to linear or branched analogues because of a low degree of conjugation of dendrimers (due to the presence of bulky fluorine atoms) and low electron affinity.

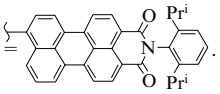
The efficiency of natural light-harvesting systems in plants and bacteria performing the visible light harvesting and conversion of visible light energy into chemical energy stimulated many researchers to design analogous artificial systems. Due to the unique features, conjugated dendrimers are attractive materials for such systems. Numerous dendrimers of different architecture with efficient light-harvesting properties have already been synthesised. For example, the synthesis of conjugated phenylacetylene dendrimers and dendrons,[26, 99–103] phenylenevinylene dendrimers [104] and dendrimers with porphyrin [105, 106] and perylene groups [107–109] was documented.

The above-mentioned conjugated dendrimers [33] containing oligo(ethynylthiophene) fragments are highly promising light-absorbing materials due to the efficient inter- and intramolecular energy transfer and a broad absorption spectrum.

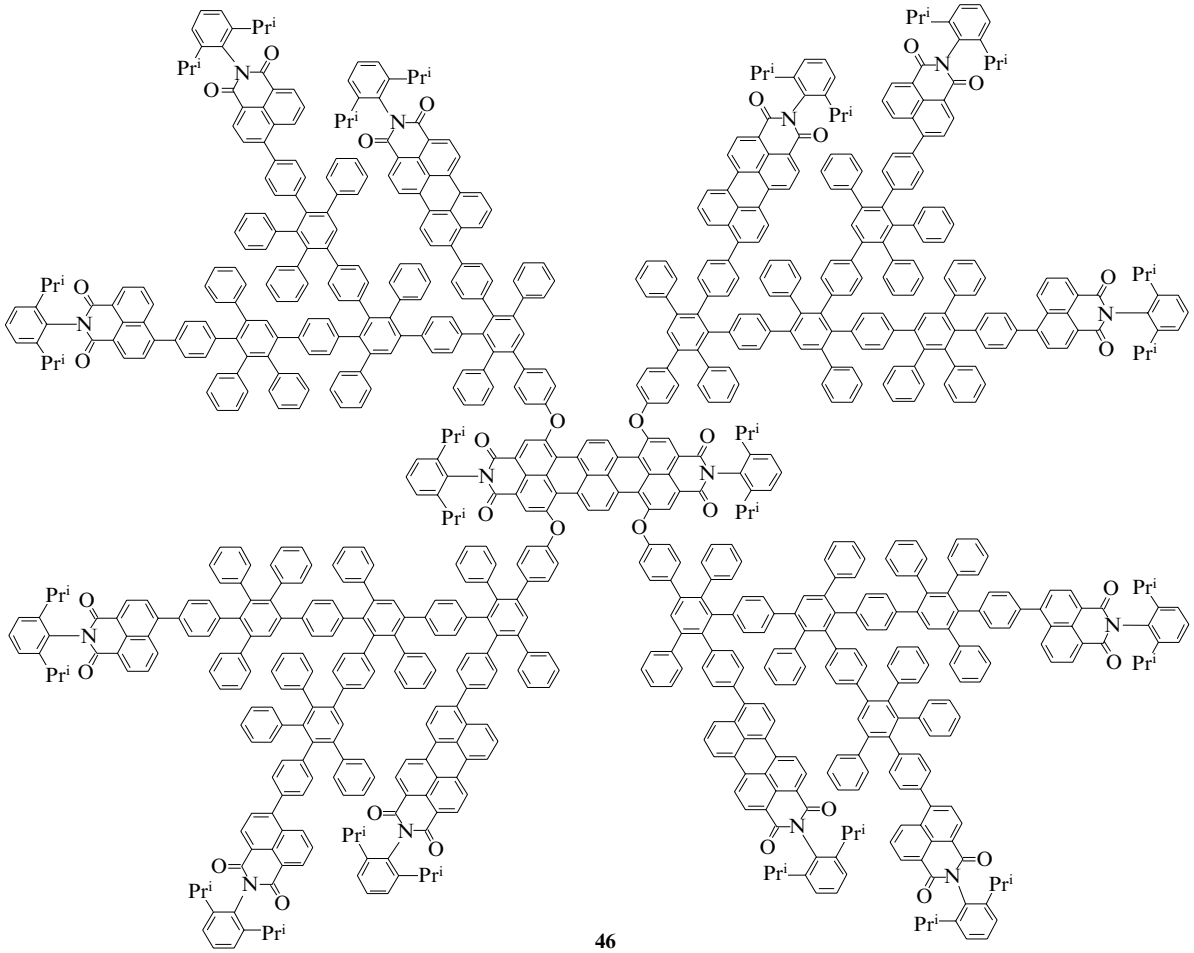
Efficient donor–acceptor systems **45** containing the triarylamine core, oligothiophene side branches and peryleneimide terminal groups were studied.[110] These systems also showed high photochemical activity. The photochemically stable peryleneimide terminal group acts as an electron acceptor; the triphenylamine core, as an electron donor. In different solvents (THF, chloroform or toluene), the luminescence quantum yield decreases with an increase in the solvent polarity due apparently to better stabilisation of the donor–acceptor pair.



45

R^1 = n-C_6H_{13}; R^2 = .

Porphyrin-containing dendrimers are of interest as synthetic analogues of biological systems.[16, 111, 112] Porphyrin-type



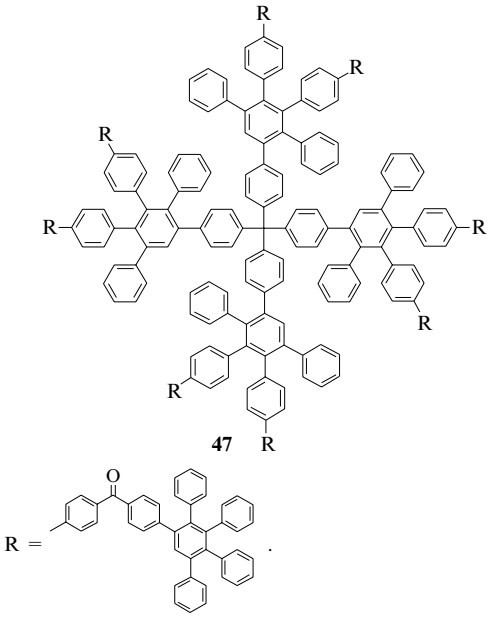
46

dendrimers **29** and **30** with carbazole peripheral groups can be used as efficient light-harvesting antennas.[58] The porphyrin core acts as an energy trap. In addition, porphyrin-containing dendrimers can be involved in various redox reactions.

Multichromophoric system **46** based on rigid polyphenylene dendrimers was stadied.[113] The specified spatial arrangement of chromophore groups and their spectroscopic characteristics provide efficient light absorption throughout the visible region and the energy transfer to the central terrylenediimide fragment, which converts this energy into the IR radiation energy.

The growing interest in the synthesis of dendrimers with unique photophysical properties requires a deeper insight into charge transfer mechanism in these systems. Investigations of symmetrical dendritic molecules did not give an unambiguous answer to these questions. Investigations of phenyleneethynylene dendrimers with asymmetric architecture [100, 101] provided the partial solution to this problem. Intramolecular interactions and the charge transfer mechanism in the systems were considered in more detail.[103] Phenylethynylene dendrimers exhibit highly efficient energy transfer from dendrons to the core, an increase in the generation number of dendrimers having no negative effect on the fluorescent properties of the system. The fluorescence dynamics was studied for symmetrical and non-symmetrical dendrimers both in the presence and absence of an energy trap. The ~50% energy transfer was found to proceed according to a multistep mechanism. Nevertheless, the process is completed in less than one picosecond.

In recent years, bulky macromolecules bearing charged functional groups and having magnetic properties have attracted growing interest. From this point of view, polyphenylene dendrimers are promising nanoobjects.[114] In addition to such advantages as the regular structure and high thermal and chemical stability, polyphenylene dendrimers can stabilise active radical groups with very short lifetimes. In addition to the electronic effects (for example, the resonance effects), dendrimers stabilise radicals due to steric effects by retaining the distance between individual radical groups and preventing them from interacting with each other.[115, 116] The synthesis of a series of dendrimers containing radicals both at the periphery [117, 118] and as the core was documented.[119, 120] In addition, a series of polyphenylene dendrimers (for example, compound **47**) containing definite number of carbonyl groups uniformly distributed in the macromolecular structure were synthesised.



47 R = .

These dendrimers were modified with organolithium reagents with the aim of preparing different types of radicals.[121]

V. Conclusion

Polyaromatic dendrimers have various unique properties different from those of aliphatic analogues. The synthesis of such dendrimers is rather simple and unambiguous because monodisperse dendritic molecules are, as a rule, produced in high yields. Due to the rigid molecular shape, the desired arrangement of functional groups in dendrimers can be achieved with the use of appropriate building blocks. This approach facilitates the introduction of functional groups both into the core of dendrimers or dendritic branches and at the periphery. Some of the above-mentioned features, in particular, the presence of numerous functional groups at the periphery, allows the use of dendrimers as nanosupports for catalysts and chromophore groups. Therefore, polyaromatic dendrimers are attractive as objects of investigation for both organic chemists and experts in the fields of materials science and nanotechnology.

Due to a constant shape, rigid dendrimers are used in studies of electron transfer processes between different redox centres. If one centre is located in the core and another centre is present at the periphery of a dendrimer, the distances, which are necessary to overcome for the electron transfer, can be calculated. In addition, dendrimers containing fragments of two different types of fluorescent dyes at the periphery are of interest in studies of energy transfer processes between these dyes (light-harvesting antennas).

The introduction of fluorescent dye labels into dendritic molecules bearing an active receptor allows the use of such systems in biological objects to determine the degree of binding of the receptor to a biological substrate.

Based on the analysis of the published data, it can be concluded that the development of procedures for the synthesis of dendritic systems and a search for new fields of their application are of great importance. Due to the unique properties, dendrimers are interesting objects of investigation for both fundamental science and various fields of applied studies. Virtually defect-free structures of polyaromatic dendrimers hold promise for the design of various materials having optical, catalytic and magnetic properties. Due to high chemical and thermal stability, such dendrimers are particularly attractive materials for the use in corrosive media and/or at high temperatures.

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