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Synthesis and prospects of application of branched polyarylenes in electroluminescent devices

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Published data on branched organic polymers — polyarylenes possessing photo- and electroluminescence properties — are summarized. Methods for the synthesis of these polymers are presented. Various structures of branched polymers are described, and the relationship between the structure and spectral properties of polymers is considered. Particular attention is given to the possibility of controlling the length of connecting aromatic conjugated units during the synthesis of branched polymers and, consequently, tuning the emission wavelength.
The bibliography includes 206 references.

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I. Introduction

In recent years, substantial progress has been achieved in studies of electronic properties of polymers, the main focus being on investigations of electroconductivity and transport properties,[1,2] which are of particular interest from both the fundamental and practical points of view.

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Electroluminescence of solids was discovered in 1923 by O V Losev.[3] The phenomenon received the official name 'Losev's glow'. A paper[4] published in 1927 described in detail the luminescence which arises in silicone carbide and established the threshold current required for the appearance of this effect. In 1936, this phenomenon was detected by G Destriau on isolated ZnS crystals;[5] in 1955, it found a technological application; and in 1958, this process was surveyed in detail.[6]

The phenomenon of electroluminescence of organic semiconductors was described for the first time for an anthracene single crystal in the early 1960s,[7] while for polymers, it was reported in the 1990s.[8] It should be noted that photo- and electroluminescence behaviour is inherent in polymers that have conjugated chain segments (in the backbone or in the side chain).

Conjugated polymers have been known for a relatively lomg time. The simplest π-conjugated polymers are polyene and polyyne, which consist of regular sequences of double and single or triple and single bonds, respectively. A new impetus to the development of this area of chemistry came from the discovery of metallic properties of doped polyacetylene made in 1977[9] (in 2000, A J Heeger, H Shirakawa and A G MacDiarmid, who took part in this work, were awarded the Nobel prize in chemistry for investigations in the field of semiconducting and conducting polymers).[10,11] The fact that a series of conjugated polymers manifest nonlinear optical properties[12] and photo- and electroluminescence in the visible region,[13,14] associated with their semiconducting properties, predetermines their practical application in micro- and optoelectronics. In turn, this promotes the development of novel advanced methods for

the synthesis of polymers, which is important for creation of electronic and optical devices[15] such as polymeric light-emitting diodes (OLED),[13,14,16,17] photodetectors,[18,19] sensors,[19] field effect transistors,[20] diode lasers[21,22] and other devices.[23,24]

The key element of an organic light-emitting diode is a thin polymer film (with thickness of up to 100 nm) placed between two electrodes of which the cathode injects electrons (n-type carriers) and the anode injects holes (p-type carriers). Upon application of a voltage, electrons and holes move in the active layer from the opposite electrodes and recombine with light emission.[25] It should be noted that the accepted characterization of an organic semiconductor as being of the p- or n-type does not reflect, most often, the ability of the material to transport the holes or electrons but rather describes how easily holes or electrons can be injected from the electrodes into the material.

In optoelectronic devices, polymer layers have a number of advantages over inorganic or low-molecular-mass organic layers: engineering simplicity of production of these layers *via* spin-coating of a substrate, the possibility of easy formation of electronic circuits and, as a consequence, low cost of the produced items. Recently, a method for application of polymer pixels (image elements) using ink-jet printing has been suggested. In this case, a solution of a conjugated polymer was used as the 'ink'.[26]

Among the disadvantages of the known electroluminescent conjugated polymers, one can mention the loss of useful properties upon a contact with water or oxygen (especially during current passage), photochemical instability and the difficulty of accomplishing balanced electron–hole transport, resulting in recombination near the electrode and in quenching of excited states without light emission.[27] Moreover, polyconjugated polymers are often poorly soluble in the solvents used in industry, which essentially restricts the possibilities of their processing.

To improve the solubility and reduce the aggregation of macromolecules, bulky side groups are introduced[28,29] or branched polymers are synthesized.[30] Branching leads to the formation of compact macromolecular objects (globules); therefore, branched polymers demonstrate high solubility in organic solvents and low viscosity of solutions compared to their linear analogues.[31]

To obtain macromolecules with the required properties, *i.e.*, having controlled emission wavelength and possessing electron or hole conductivity, the polymers are synthesized that contain luminophore groups and groups endowing polymers with transport properties. Such polymers or polymeric materials based on them can be successfully used to design optical devices.

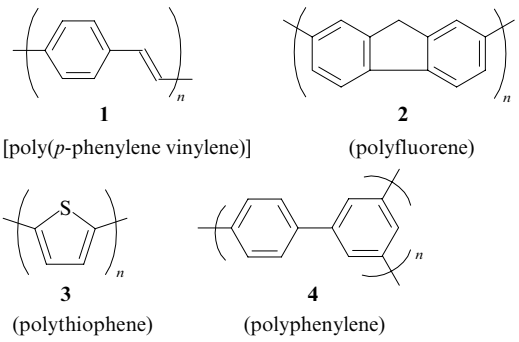
This review is devoted to the synthesis of branched conjugated polyarylenes of different classes and their application as active layers in optoelectronic devices.

II. Photo- and electroluminescent polymers

Polymers containing chromophoric groups and(or) long conjugated segments in the chain exhibit photo- and electroluminescence.[32]

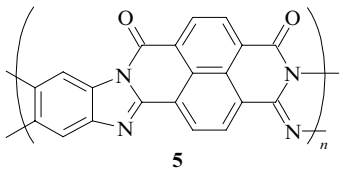
Among photo- and electroluminescent organic compounds, aromatic polymers such as poly(*p*-phenylene vinylenes),[33,34] polyfluorenes,[35,36] polythiophenes[37–41] and branched polyphenylenes[42–45] have acquired the primary significance. Structures **1**–**4** show the basic unsubstituted molecules of the above-mentioned polymers.

Structures 1–4



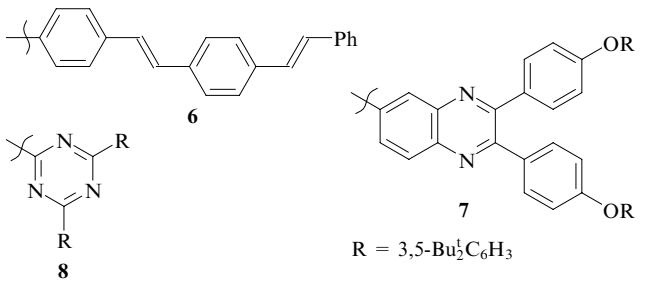
Polymers of these types are relatively stable to environmental impact, and many of their properties can be changed by introduction of substituents. The semiconducting properties of conjugated polymers stem from the presence of π-bond system delocalized along the polymer chain or its section,[46] which provides the mobility of charge carriers. The conjugated polymers of p-type (hole conductors) are poly(phenylene vinylene) (PPV), polyvinylcarbazole (PVC), *etc*. The polymers with high electron affinity such as poly(benzimidazobenzophenanthrolines) (PBBP, **5**)[47] can be used as carriers of n-type (electron conductors).

Structure 5



The electron conduction of a polymer can be provided by the introduction of appropriate groups into the side chains of the macromolecule. For example, these may be fragments of distyrylphenyl (**6**), 2-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole,[48] 2,5-diphenyl-1,3,4-oxadiazole, substituted 2,3-diphenylquinoxaline **7**,[48] 2,5-bis[2-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-5-yl]pyridine,[49] substituted triazines **8**, *etc*.

Structures 6–8



While comparing the photophysical and transport properties of linear and branched polymers, one should bear in mind the possibility of π-aggregation owing to intermolecular interactions in the former case, which diminishes the efficiency of photo- (PL) and electroluminescence (EL).[32,50] Meanwhile, the bulky structure of branched pol-

ymers hampers intermolecular interactions,[51,52] although emission induced by aggregation is still observed.[52,53]

III. From linear to branched macromolecules

Recently, the interest of researchers in branched polymers has been increasing, since their molecular architecture gives rise to properties that cannot be manifested by linear macromolecules.[54–56] Branched polymers are often considered as close analogues of dendrimers despite the fact that the latter are regularly branched macromolecules with high structural order and monodispersity, while branched polymers, as a rule, do not have clearly defined structure and feature a broad molecular-mass distribution (MMD). Branching of the macromolecular chain in branched polymers can be irregular due to single-step synthesis;[57,58] however, these polymers show many properties of dendrimers. They have a globular structure[59–62] and low viscosity characteristics.[63] Moreover, branched polymers have a solubility which essentially exceeds that of their linear analogues.[64]

Depending on the type of branching, branched high-molecular-mass structures can conventionally be divided into five classes (Fig. 1).[65] Representatives of the first three classes have a clearly defined structure, while for the other two classes, branching is random (statistical).

In 1941 Flory[66] used statistical mechanics to determine the molecular-mass distribution of branched polymers and introduced the terms 'the degree of branching' and 'a hyperbranched structure'. Subsequently, he developed the theory of branched polymers and demonstrated that these structures can be obtained in a soluble state (prior to gelation) *via* polycondensation of the monomers, one of which contains only functional groups A and the other one contains two or more groups B able to react with groups A. However, such structural characteristics as degree of branching and the average number of branching points do not reflect the statistical character of polymers. To characterize these systems, the function of molecular-mass distribution was used, which can be calculated by a variety of statistical and kinetic methods.[67,68]

The theoretical description of polycondensation of AB_x type monomers ($x \geqslant 2$) to give branched soluble polymers has aroused researchers' interest. The properties of these polymers were compared to those of linear analogues, although most of the early wokrs in this field were focused on the synthesis of dendrimers.[69–81] Branched macromolecules of dendrimers are obtained in stepwise (repeated) synthesis; therefore, the main difficulty is related to isolation and purification of compounds at each step. Meanwhile, branched polymers, despite the irregular structure, can be obtained in a single step.

As it was mentioned above, branched polymers, in contrast to dendrimers, are polydisperse systems as regards both the molecular mass and the branching factor (degree of branching).[73,74]

Several methods are suitable for the synthesis of these polymers. One of them is the self-condensation of the AB_2 type monomer.[75,76] Correspondingly, the resulting polymers have irregular structure and incomplete branch substitution, these chain defects being non-uniformly distributed over the whole polymer structure.[77]

The first synthesis of branched polymers based on the AB_2 type monomer using aliphatic amines was accomplished in 1978 by Vögtle *et al.*[69] The hyperbranched (cascade) polymers obtained by this method contained free space (pores) in their structure, which was used to introduce inclusion molecules. The suggested approach was based on the reaction of amines with acrylonitrile followed by reduction of the terminal nitrile groups to the amino groups, which were again made to react with acrylonitrile. Schemiatically, this synthetic strategy is presented in Fig. 2. The initial compounds were mono- and diamines as well as polyazamacrocycles. The latter were used to obtain polycyclic systems.

Depending on the number of unreacted functional groups B, three types of repeating units can be distinguished: branching units (dendritic fragments), linear fragments and terminal groups. Whereas dendrimers and

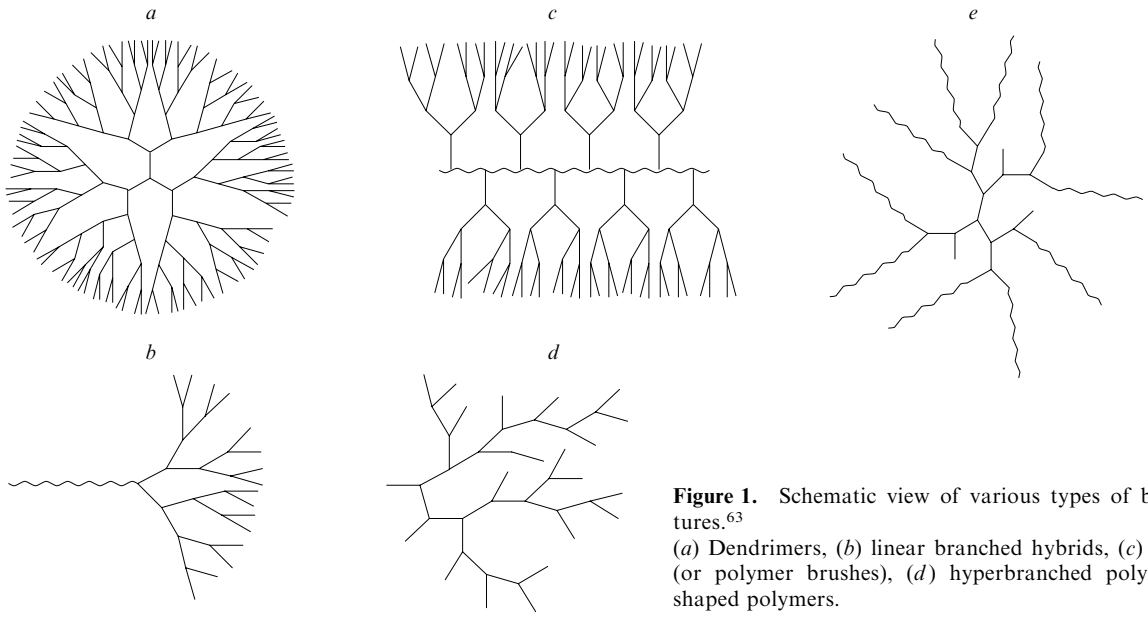


Figure 1. Schematic view of various types of branched structures.[63]
(*a*) Dendrimers, (*b*) linear branched hybrids, (*c*) garft polymers (or polymer brushes), (*d*) hyperbranched polymers, (*e*) star-shaped polymers.

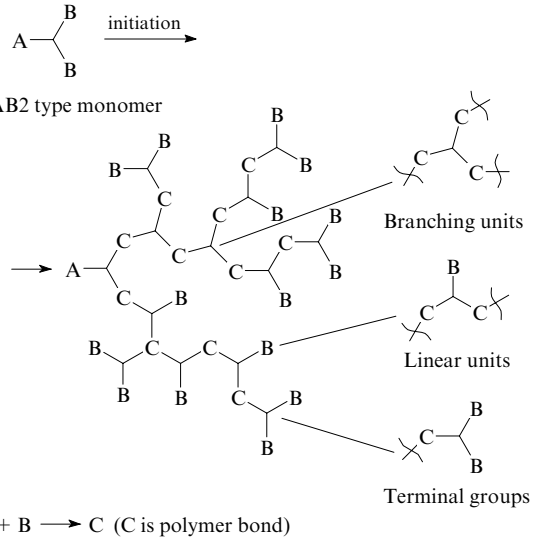


Figure 2. Scheme of homopolycondensation resulting in the branched polymer based on the AB_2-type monomer.[69]

dendrons consist only of dendritic and terminal fragments, branched polymers contain also linear fragments comprising one unreacted group B.

In 1991 Frechet and co-workers[76] suggested the following expression for estimating the degree of branching (DB) of hyperbranched polymers:

$$\mathrm{DB} = \frac{D + T}{D + T + L} \quad (1)$$

where D, T and L are the numbers of dendritic, terminal and linear fragments, respectively. The value of DB can be used to compare the structures of branched polymers with the structures of the corresponding dendrimers and dendrons. Frey and coworkers[78] suggested a modified version of the DB function that takes into account the growth direction

$$\mathrm{DB} = \frac{2D}{2D + L} = \frac{D + T - N}{D + T + L - N} \quad (2)$$

where N is the number of molecules. For branched polymers with high molecular masses, the values of DB calculated by Eqns (1) and (2) almost coincide, because in this case, N in Eqn (2) can be negligibly small. Frey and coworkers suggested[78] that DB of branched polymers obtained by single-step polymerization of AB_2 type monomers usually amounts to ~ 0.5.

For branched polymers resulting from polycondensation of AB_m type monomers, Frey and co-workers[78] also proposed three possible methods for increasing the DB

— increase in the reactivity of terminal fragments;

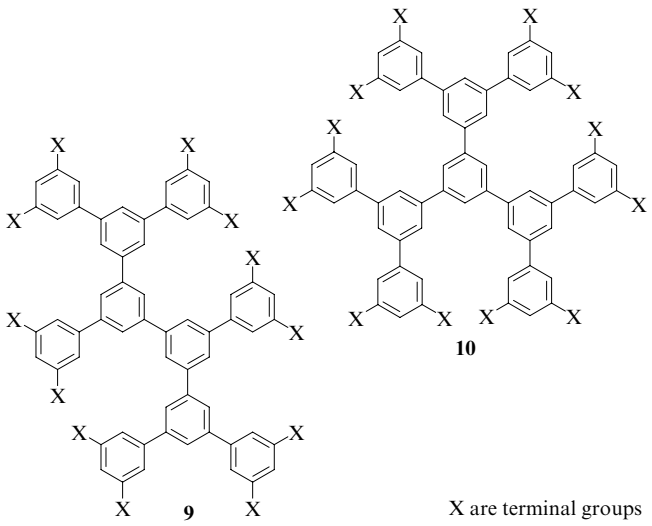
— introduction into the reaction of pre-synthesized defect-free branched fragments;

— slow addition of one of the comonomers to the reaction medium.

If the polymer chain grows symmetrically and the polymer DB is 1, then the structure of the branched polymer will, with a high probability, be the same as the structure of the corresponding dendron.[82]

Note that even at DB = 1, bracnhed polymers have many isomers[63] (see, *e.g.*, structures **9** and **10**).

Strcutures 9, 10



In some cases, the degree of branching of branched polymers can be experimentally determined by NMR identification of characteristic elements of the branched structure. For such compounds as esters and carbonates, the degree of branching can be calculated from the elemental analysis data.[79,80]

IV. Synthesis and spectral properties of branched polyarylenes

The first branched macromolecules were synthesized at the end of the 19th century when Berzelius reported the formation of a resin-like substance from tartaric acid and glycerol.[81] In 1909 Backland presented the first commercial product based on a bracnched phenolic polymer, which had random branching.[83]

Branched polymers are generally prepared by two routes: copolycondensation with participation of two or more monomers[84] or homopolycondensation.[73] The homopolycondensation can be classified into polycondensation of AB_n type monomers,[82] condensation of vinyl monomers,[85] ring opening condensation,[86] and proton transfer condensation.[87] Among the processes of copolycondensation, two main subclasses can be distinguished: polycondensation of the $A_n + B_2$ type monomers (or $A_2 + B_n$, where $n > 2$)[88] and polycondensation of two monomers one of which is formed *in situ* from the AB_n type monomer owing to different reactivity of the fucntional groups.[89]

A variety of star-shaped polymers for the application in OLED as electron- or hole-conducting layers have been reported.[90,91] They contain chromophoric groups such as oligophenyl, oligothiophene, stilbene, tolane, fluorene, carbazole; the branching groups are triphenylamine,[92–94] benzene-1,3,5-triyl,[95–101] 1,3,5-triphenylbenzene,[43,94,96,99,100,102–105] truxene,[106–108] triazatruxene,[109] carbosilane[110,111] and oligothiophene.[112]

As mentioned above, single-step synthesis of branched polymers has a great advantage over syntheses of both linear polymers with multiple side substituents and dendrimers where purification and isolation are required after

the synthesis of each generation. Although it is impossible to control the molecular mass or the shape of resulting macromolecules in branched polymers, these macromolecules have sufficiently extended conjugated segments responsible for efficient luminescence.

IV.1. Branched poly(phenylene vinylenes)

Poly(phenylene vinylenes) form one of the most studied classes of branched polyarylenes with electroluminescence activity. After the publication of Burroughes *et al.*[32] of 1990 devoted to the application of poly(*p*-phenylene vinylenes) in electroluminescent devices (ELD), many research groups started to investigate these structures in detail. Their attractiveness is caused by the ease of regulation of the chemical structure of branched PPV (BPPV), excellent parameters of conversion of electric energy into light and good mechanical properties.

Branched poly(phenylene vinylenes) produced by the Wittig reaction using two different comonomers were reported. Along with B_3 monomer (1,3,5-triformylbenzene), 2,5-dialkoxy-1,4-bis(triphenylphosphinomethyl)benzene bromide and 2,5-dimethoxy-1,4-bis(triphenylphosphoniomethyl)benzene chloride were used as comonomers (Scheme 1, Table 1).[97,113–115]

The optical properties of the resulting PPV **11a–d** were studied in solution and in the solid state (Table 2).[113–115] The absorption and emission spectra of polymers **11c**,**d** are almost identical both in solution and in films, despite the fact that these polymers have different terminal groups.[89] Analogous values of absorption and emission maxima are observed for compound **11a** (see Table 2).[114] Presumably, this can be explained by the fact that the most effective fluorophores in branched poly(phenylene vinylenes) are stilbene groups. The terminal groups can act as chromophoric antennas: they absorb photons, and then the excitation energy is rapidly transferred to the centre through the vinylene connecting units. However, the content of terminal groups in branched poly(phenylene vinylenes) is relatively low. Thus, according to the data on the molecular masses (see Table 1), compounds **11c**,**d** correspond approximately to the fourth generation.

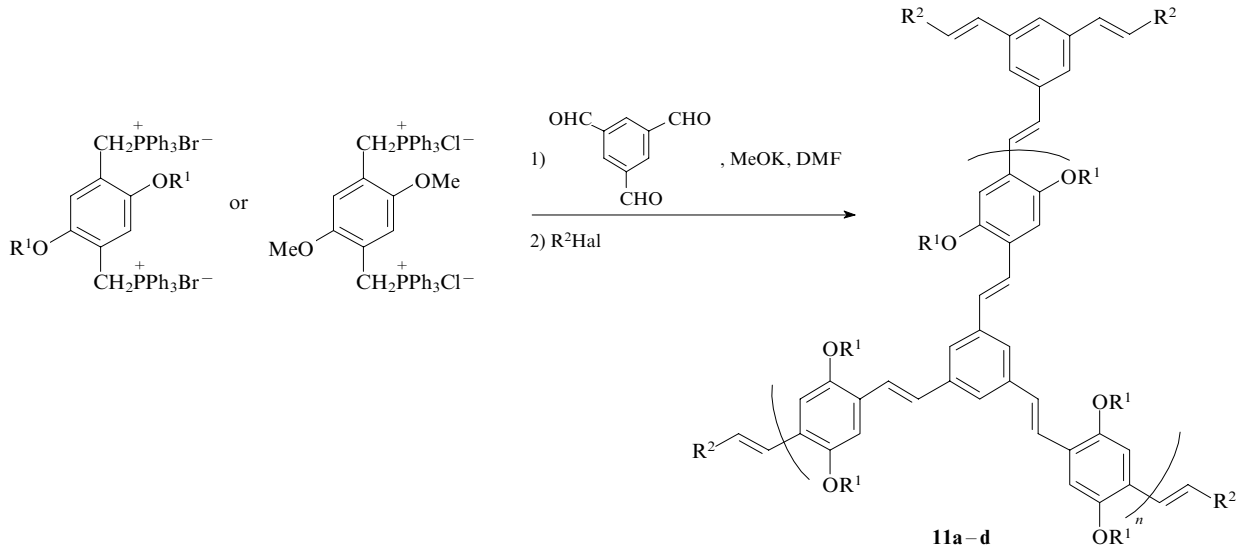
Table 1. Synthesis time and molecular-mass characteristics of branched polymers.

Polymer	Reaction time /h	M_n /Da	M_w /Da	M_w/M_n	Degree of branching	Ref.
11a	10	2 810	6 030	2.14	–	113
11b	–	2 170	5 510	2.54	–	114
11c	–	7 100	28 700	4.10	–	114
11d	–	6 600	28 400	4.30	–	114
12a	10	7 520	19 002	2.52	–	116
12b	10	5 960	12 850	2.15	–	116
13	–	1 930	2 180	1.13	–	113
14	20	35 000	126 000	3.60	–	115
15	20	75 000	239 000	3.20	–	115
16a	16	31 800	52 600	1.65	0.45	117
16b	12	31 900	53 100	1.66	0.53	117
16c	10	32 600	51 300	1.57	0.57	117
16d	6	36 900	63 400	1.72	0.70	117
17	12	34 000	57 200	1.68	–	117

Branched poly(phenylene vinylenes) with the 1,3,5-trisubstituted benzene central core have an almost symmetrical structure, each of the three branches representing a conjugated chain. However, in *meta*-substituted fragments, each conjugated unit can be considered, to the first approximation, as electron-independent. As a result, branched poly(phenylene vinylenes) with the same central core and the connecting units have similar absorption and emission spectra.

The absorption and emission spectra of BPPV in solutions and in films are shifted to the blue region with respect to the spectra of linear poly(phenylene vinylenes). The absorption spectra of BPPV in films are shifted to the blue region and the emission spectra are shifted to the red region with respect to the spectra of solutions. This can be attributed to specific features of polymer conformations. The hyperbranched poly(phenylene vinylenes) in question have additional alkoxy groups in the benzene rings, steric crowding resulting in a more twisted conformation. The

Scheme 1



11a–d

R^1 = Hex, R^2 = 4-Bu^{t}C$_6$H$_4$ (**a**); R^1 = Me: R^2 = Ph (**b**), 4-Py (**c**), 4-Me$_2$NC$_6$H$_4$ (**d**); Hex = n-C$_6$H$_{13}$, Py is pyridyl

Table 2. Optical properties of branched polymers.

Polymer	Solution			Solid state		Ref.
	λ_{abs} /nm	λ_{lum} /nm	φ [a]	λ_{abs} /nm	λ_{lum} /nm	
11a	323, 405	457	0.48	313, 392	502	113
11b	317, 402	453, 480	0.90	307, 389	470, 497	114
11c	330, 405	461, 490	0.24	388	510	114
11d	332, 405	461, 490	0.50	332, 402	510	114
12a	429	509	0.50	422	548	116
12b	430	510	0.12	424	575	116
13	289, 310	359, 369	0.36	305, 325	446	113
14	492	555	0.24	–	600	115
15	478	555	0.42	–	595	115
16a	286, 372	465, 486	–	286, 372	467, 492	117
16b	286, 372	464, 488	–	286, 372	467, 493	117
16c	286, 315, 372	465, 485	–	286, 315, 372	468, 496	117
16d	286, 315, 372	464, 486	–	286, 315, 372	468, 496	117
17	286, 314, 374	464, 488	–	286, 314, 375	468, 496	117

[a] φ is the quantum yield of luminescence.

conformational effect can account for the change in the width of the band gap in branched poly(phenylene vinylenes).

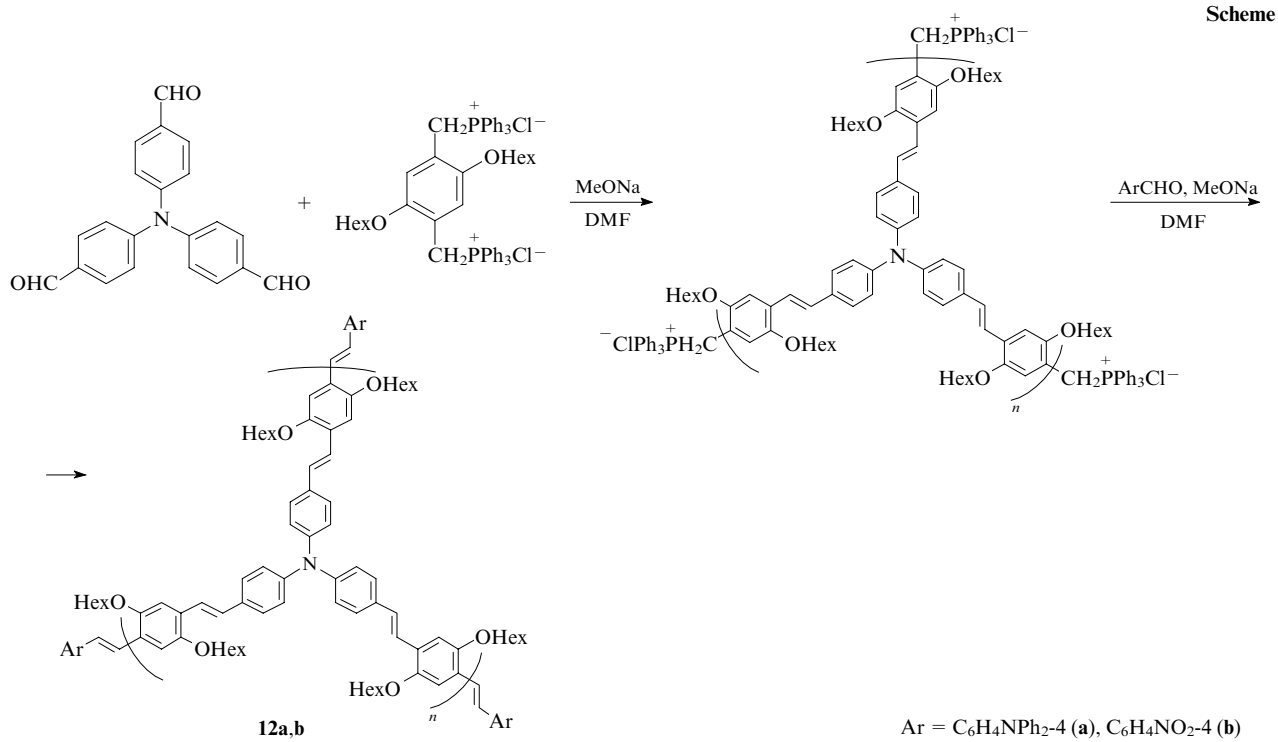
Branched poly(phenylene vinylenes) with terminal diphenylaminophenyl (**12a**) and nitrophenyl (**12b**) groups were prepared by the modified Wittig reaction of 4,4′,4″-triformyltriphenylamine and 2,5-di-n-hexyloxy-1,4-bis(triphenylphosphoniomethyl)benzene chloride monomers (Scheme 2).[116]

The investigations showed that the introduction of alkoxy substituents at the 2,5-positions of the benzene rings of *para*-PPV (to improve their solubility) decreases the width of the band gap and, as a consequence, displaces the luminescence band to longer wavelengths.

The IR spectra of compounds **12a**,**b** show an intense band at 963 cm^{-1}, which refers to *trans*-vinylene moieties, and a very weak band at about 880 cm^{-1} corresponding to *cis*-vinylene moieties (not shown in the scheme). From this, the authors conclude that the *trans*-configuration of the connecting units predominates. Polymers **12a**,**b** are readily soluble in organic solvents (THF, chloroform, dichloroethane and DMF), which is due to the presence of alkoxy side groups in the hyperbranched structure.

The absorption maxima of poly(phenylene vinylenes) **12a**,**b** in solution and in the solid state range from 422 to 430 nm (see Table 2). It is noted that the abosprtion maxima of these polymers in the solid state are somewhat blue-shifted compared to the absorption maxima in a chloroform

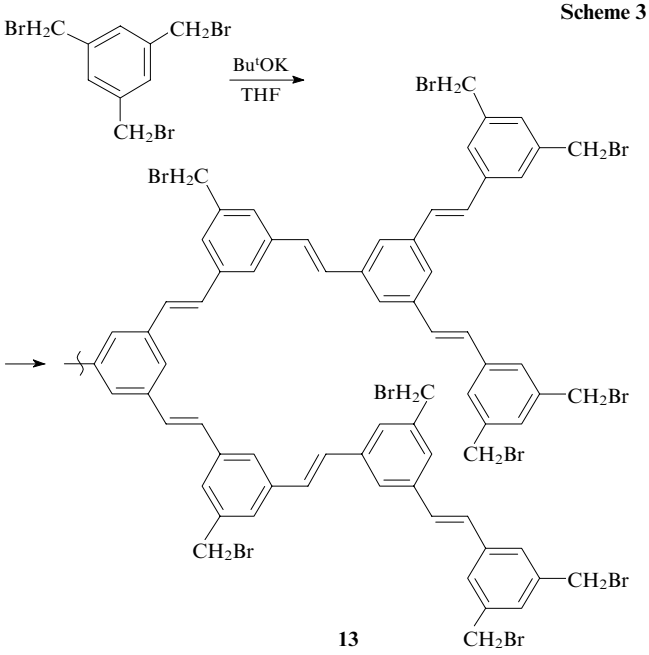
Scheme 2



solution; this shift is not observed for the linear poly(phenylene vinylenes). The authors explain this by the decrease in the contribution of π–π-stacking in the branched structure. In contrast, the fluorescence spectra of polymers **12a**,**b** in the solid state are shifted to longer wavelengths, which may be due to energy transfer between macromolecules. These processes are faster in the solid state than in solution. Furthermore, there are no fluorescence bands of excimers in the long-wavelength region for polymers **12a**,**b**, which indicates a decrease in the probability of excimer formation in the solid state. The fluorescence quantum yield is lower for polymer **12b** than for polymer **12a** (0.12 and 0.50, respectively, see Table 2), which has been attributed to the introduction of electron-withdrawing nitro groups in polymer **12b**.[116]

Branched poly(phenylene vinylenes) **13** with low M_n values were prepared by dehalogenation of A_3-type monomers.[113] Polymers **13** are soluble in THF, chloroform, ethyl acetate and dichloromethane (Scheme 3).

Scheme 3

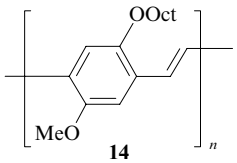


13

The ^{1}H NMR spectrum of polymer **13** exhibits signals in the range of 6.2–7.8 ppm, due to the vinylene and aromatic protons; the signal at 6.5 ppm indicates the presence of *cis*-vinylene units. The maxima at 955 and 700 cm^{-1} in the IR spectrum refer to *cis*- and *trans*-vinylene units, respectively. The photoluminescence spectrum of thin film is shifted to longer wavelengths by approximately 80 nm with respect to the spectrum of solution. In the opinion of the authors,[113] this can be attributed to interchain interactions of macromolecules in the solid state.

Wang *et al.*[117] used comonomers of A_3 type with reactive chloromethylene groups, which contained butoxy substituents in the 1-, 3-, and 5-positions of the benzene ring, to synthesize branched structures. These monomers were obtained by the reaction of 1,3,5-trihydroxybenzene with butyl bromide in the presence of potassium carbonate in DMF followed by the treatment of the resulting product with paraformaldehyde and HCl in 1,4-dioxane. The second comonomer (B_2 type) was synthesized in the analogous manner from hydroquinone. The linear homopolymer (based only on the second comonomer), poly(2-methoxy-5-n-octyloxy-*p*-phenylene vinylene) (**14**), and the copolymer (based on the first and second comonomers), poly(2,4,6-tri-n-butoxybenzene-1,3,5-trivinylene-co-2-methoxy-5-octyloxy-*p*-phenylene vinylene) (**15**), were prepared in the presence of potassium *tert*-butoxide in THF under nitrogen atmosphere.

Structure 14



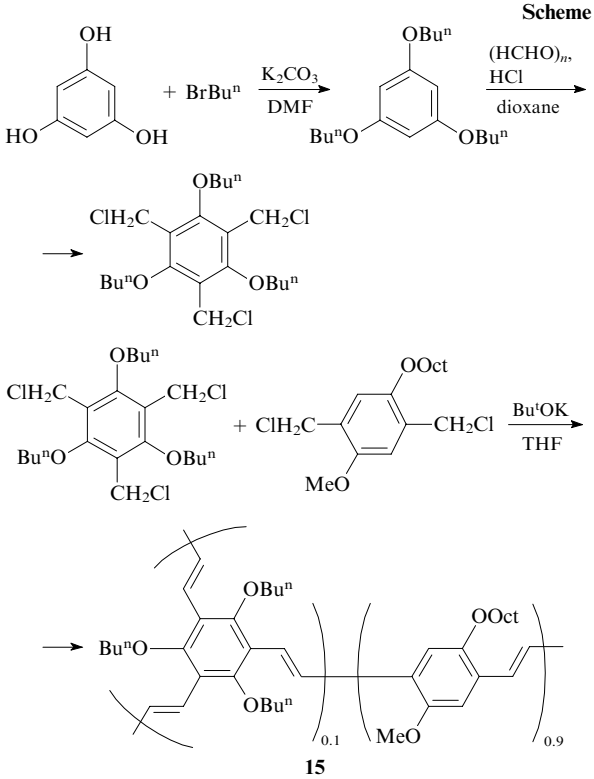
14 Oct = n-C_8H_{17}

The ratio of the branching comonomer and disubstituted comonomer units in copolymer **15** was 1 : 9 (Scheme 4).

The solubility of copolymer **15** appeared to be higher than that of linear homopolymer **14**, which is explained by the decrease in intermolecular interactions of the chains in the branched structure compared to the linear analogue. Some characteristics of polymers **14** and **15** are presented in Tables 1 and 2.

The absorption peak of copolymer **15** is shifted to the blue region relative to the peak of polymer **14** (478 and 492 nm, respectively), which is attributed [118] to decrease in the conjugation length in the copolymer upon the introduction of tributoxybenzenetriyl moieties. In polymer **14**, the chain units are almost coplanar (which creates conditions for the electron transport between the units), while the planar structure of the macromolecule of polymer **15** is violated by the presence of the benzene-1,3,5-triyl moieties with alkoxy substituents. This reduces the conjugation length and gives rise to the observed hypsochromic shift. Meanwhile, the small magnitude of the shift indicates that

Scheme 4

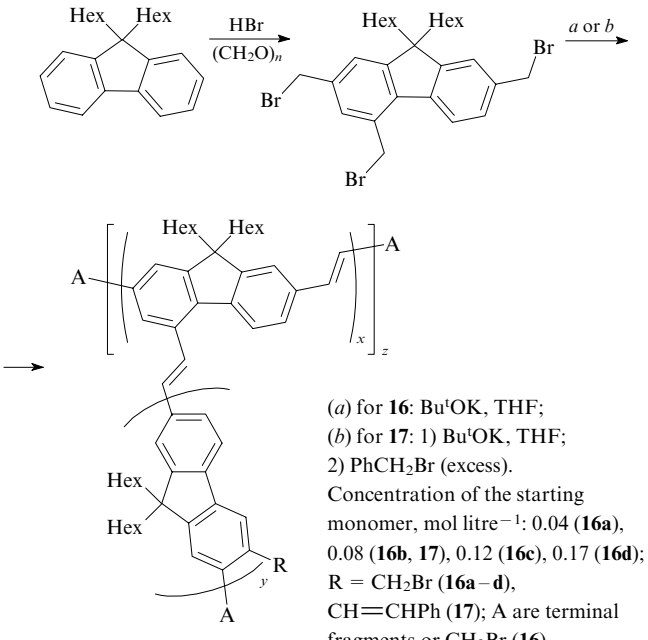


15

the band gaps are nearly equal in the homopolymer and the copolymer. This fact, together with the fact that the benzenetriyl and phenylene moieties alternate in the copolymer in a random manner, suggest that in the extended conjugated chain segments inherent in homopolymer **14** are retained in copolymer **15**. The fluorescence spectra of polymers **14** and **15** in chloroform have similar peaks with maxima at 555 nm, whereas the spectrum of copolymer **15** in the solid state demonstrates a slight hypsochromic shift of the emission maximum compared to the spectrum of homopolymer **14** (595 and 600 nm, respectively). The authors explain the observed displacement by the fact that the steric hindrances and non-planar structure of the copolymer weaken the interactions between the chains in the solid state. This leads to an increase in the band gap and, as a consequence, to a blue shift of the fluorescence maximum of the copolymer. In the authors' opinion, the steric hindrance is also responsible for the lower probability of non-radiative transitions from the excited singlet state, which causes higher fluorescence quantum yield in solution for the copolymer compared to the homopolymer (0.43 and 0.24, respectively).

It is known that the polymer-forming reaction of trifunctional monomers leads to rapid gelation due to formation of a three-dimensional structure; therefore, it is necessary to properly choose the time for polycondensation to prevent the undesirable gelation. In the case of polymer synthesis based on trifunctional 2,4,7-tri(bromomethyl)-9,9-di-n-hexylfluorene monomer, obtained by the reaction of 9,9-di-n-hexylfluorene with paraformaldehyde in the presence of HBr, within several hours after beginning of the reaction, precipitation caused by the start of gelation was observed [119] (Scheme 5). Therefore, branched poly(fluorene vinylenes) (BPFlV) **16** were synthesized in dry THF over different periods of time (from 6 to 16 h) depending on the monomer concentration (see Table 1).

Scheme 5



16a–d, 17

(*a*) for **16**: Bu^{t}OK, THF;
(*b*) for **17**: 1) Bu^{t}OK, THF;
2) $PhCH_2Br$ (excess).
Concentration of the starting monomer, mol litre^{-1}: 0.04 (**16a**), 0.08 (**16b**, **17**), 0.12 (**16c**), 0.17 (**16d**); R = CH_2Br (**16a–d**), CH=CHPh (**17**); A are terminal fragments or CH_2Br (**16**), CH=CHPh (**17**)

The resulting branched polymers were readily soluble in chloroform and dichloromethane; however, the polymers that precipitated from the solution upon the reaction carried out for >16 h were insoluble in organic solvents.

Tsai and Chen [119] also made an attempt to determine the degree of branching by synthesis of compounds modelling various fragments of the the BPFlV structure (linear, terminal, and the branching unit) and by matching their ^{1}H NMR signals with the signals of branched poly(fluorene vinylenes). It was proposed to determine the contents of fragments of the branched structure from the proton chemical shifts of the bromomethyl groups in positions 4 (4.9 ppm) and 2,7 (4.6 ppm). For this purpose, the spectra of polymers **16a–d** in which the terminal bromomethyl groups were not substituted replaced by benzyl bromide were compared with the spectrum of polymer **17**. By comparing the integrated intensities of the signals of characteristic fragments in polymers **16a–d** and comparing them with the corresponding integrated intensities of the signals of the model compounds, the authors estimated the degree of branching of the resulting polymers. A gradual increase in the degree of branching of the polymers (from 0.45 to 0.7) with an increase of the monomer concentration in THF (0.04 to 0.17 mmol litre^{-1}) was noted (see Table 1). Based on these data, it was concluded that the reaction at the bromomethyl groups proceeds more completely as the concentration of the initial monomer increases. The optical properties of the poly(fluorene vinylenes) synthesized are summarized in Table 2.

The absorption spectra of polymers **16b**,**c** in chloroform and in the solid state contain an additional absorption band at 315 nm, which was attributed [119] to an increased degree of branching. The absortpion band (at 372 nm) of branched polymers **16a–d** in solution and in the solid state correlates with the analogous band (at 376 nm) of linear oligo(fluorene vinylenes) containing two repeating units.[118] Quantum chemical calculations for oligo(fluorene vinylenes) showed that the angle between adjacent fluorene fragments is 29°,[120] due to which the conjugation of the backbone is less efficient. In the case of a hyperbranched structure, a similar decrease in the length of conjugation at the branching units is observed.[121] The fluorescence spectra of the solutions of polymers **16a–d** in chloroform contain two emission bands (465 and 486 nm) and do not differ; this provides the conclusion that efficient energy transfer occurs between short oligo(fluorene vinylene) fragments and longer moieties, which serve as more efficient emitters.[121] The fluorescence spectra of the polymers under study in the solid state are shifted by 2–4 nm to longer wavelengths compared to the fluuorescence spectra in chloroform (see Table 2). The effect of terminal bromomethyl groups on the optical properties of branched polyfluorenes can be estimated by comparing the absorption and fluorescence spectra of samples **16b** and **17** (Fig. 3).

The absorption spectra of both samples are similar in the shape and intensity, which suggests that the structures of connecting units and conjugated systems conicide. However, the fluorescnece intensity of polymer **17** is essentially higher than that for polymer **16b**, which can be explained by the presence of more bromine atoms in molecule **16b** than in **17**. The presence of bromine covalently bonded to the polymer molecule or occurring as impurity salts increases the rate of spin-forbidden processes, which enhances the

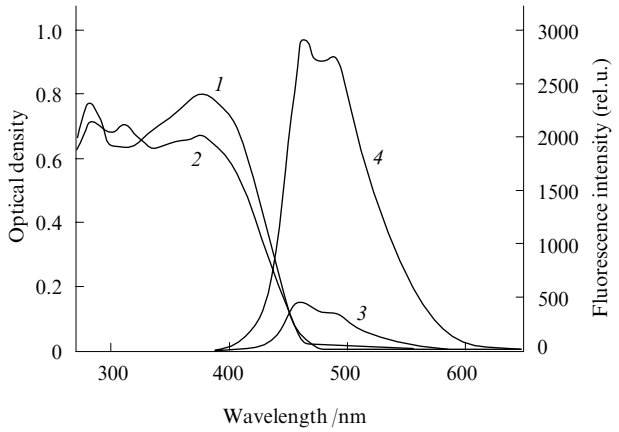


Figure 3. Absorption (*1*, *2*) and fluorescence (*3*, *4*) spectra (excitation wavelength of 380 nm) of samples **16b** (*1*, *3*) and **17** (*2*, *4*) in chloroform ($c = 10^{-5}$ mol litre^{-1}).[119]

spin – orbit coupling and decreases the fluorescence efficiency.[122]

IV.2. Branched poly(arylene ethynylenes)

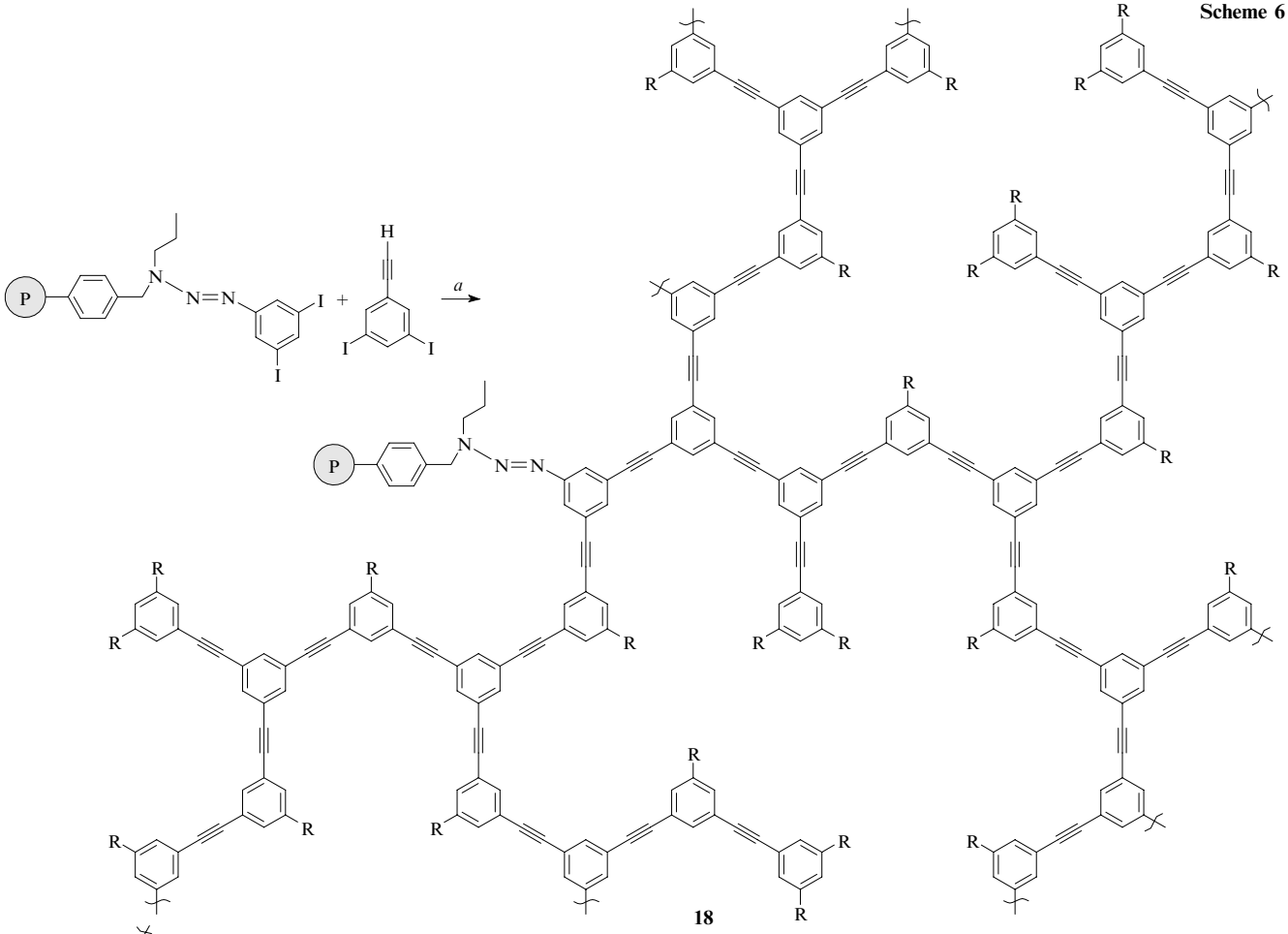
There are numerous examples of synthesis and investigation of optical properties of linear poly(arylene ethynylenes) (see, *e.g.*, Ref. 123). However, branched poly(phenylene ethynylenes) and the corresponding dendrimers have been much less studied.

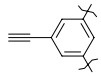
Bharathi and Moore[124] described poly(phenylene ethynylene) **18** synthesized by the Sonogashira reaction on a solid support initially containing terminal secondary amino groups (Scheme 6).

Initially, diiodophenyl fragments were attached to the functional groups of the support. Then, the AB_2-type monomer, 3,5-diiodophenylacetylene, was added gradually to the resulting suspension in the presence of $Pd_2(dba)_3$ in piperidine at room temperature. Polymer **18** was soluble if at the end of the process it was separated from the solid support by the reaction with iodomethane followed by treatment with a large excess of 3,5-di-*tert*-butylphenylacetylene in the presence of $Pd_2(dba)_3$. The molecular mass of the polymer reached 25 kDa and the polydispersity index ranged from 1.3 to 1.5.

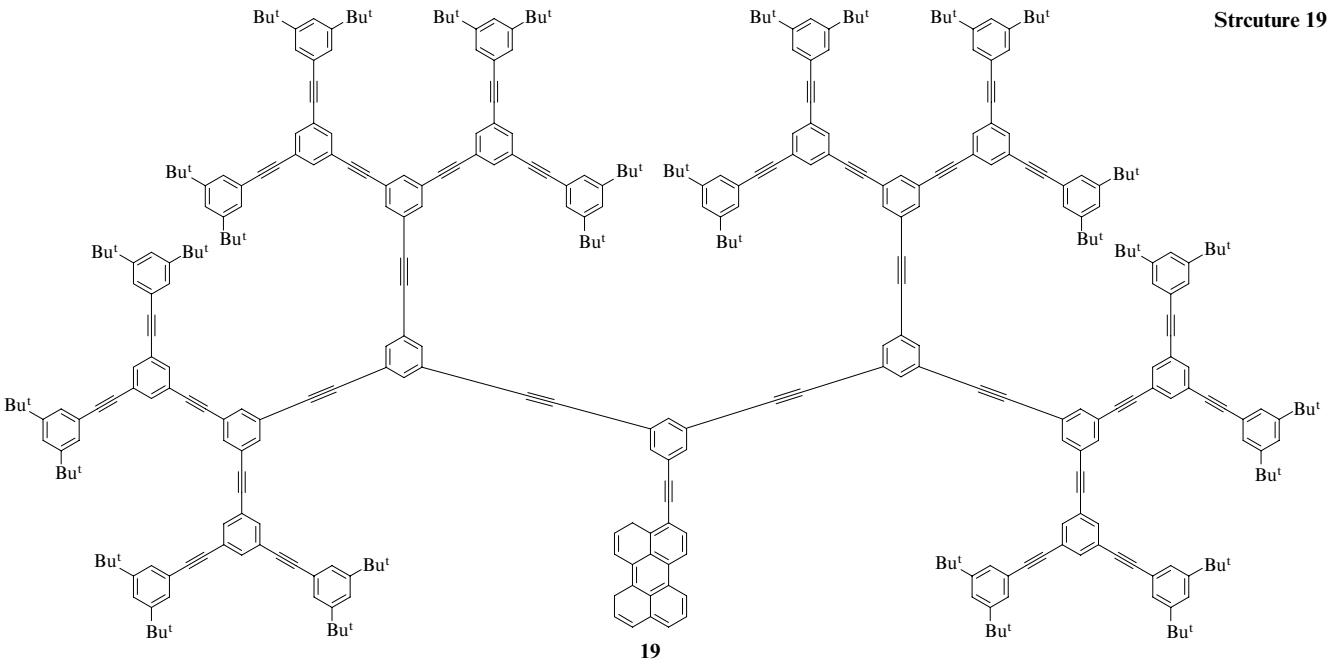
In another study of Moore's research team,[125] slow addition of the AB_2-monomer (3,5-diiodophenylacetylene) to a solution of a multifunctional monomer [*e.g.*, 1-(3,5-diiodophenyl)-3,3-diethyltriazene] afforded high-molecular-mass branched poly(phenylene acetylenes) with molecular masses of 8 – 90 kDa and narrow molecular-mass distributions. It was found that the polydispersity index of the branched polymer decreases as the molecular mass increases.

Scheme 6



R = I,  ; *a* is $Pd_2(dba)_3$, PPh_3, CuI, piperidine; dba is dibenzylideneacetone

Strcuture 19



19

Several dendrimers obtained by Moore's team are also worth mentioning, since this infromation is useful from the viewpoint of synthesis and investigation of branched polymers. They reported [126] dendrimers **19** in which the side branches contain acetylene groups. By controlling the length of conjugated phenylacetylene branches, effective energy transfer can be provided from the dendritic environment to one chromophore core where the absorbed energy is converted to radiation with another wavelength. These conjugated structures demonstrate UV absorption in the range of 250–350 nm, the intensity of which increases with an increase in the number of dendrimer generation. The dendrimer emits light at 350–450 nm. Upon introduction of the perylene groups having a narrower band gap into the dendrimer, the units containing phenylacteylene act as peripheral energy donors and perylene serves as a central energy acceptor.

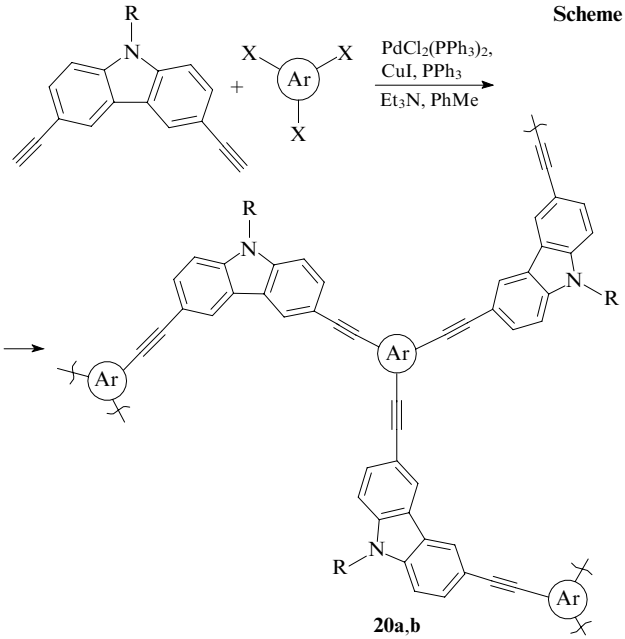
The excitation of dendrimer **19** at 312 nm leads to emission at 450–600 nm, which corresponds to emission of only the perylene moiety. This is accompanied by almost full quenching of luminescence of the phenylacetylene branches.

Phenylacetylene dendrimers are considered also in another publication.[127]

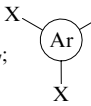
It was noted [128–130] that the symmetry of groups surrounding the focal point is importsnt for efficiency of the antenna.

The synthesis of branched oligo(arylene ethynylenes) **20a**,**b** by the Sonogashira reaction (yields 48%–66%) in a toluene–triethylamine mixture in the presence of triphenylphosphine, copper(I) iodide and dichlorobis(triphenylphosphine)palladium by the '$A_3 + B_2$' reaction type was reported [131] (Scheme 7). The resulting polymers had M_n (according to the data of gel permeation chromatography with UV detection) of about 3500–20 100 Da and polydispersity index of 1.28–2.32. The absorption spectra of polymers **20** in chloroform show two peaks (at 310 and 350–370 nm), which correspond to the carbazole and phenylene ethynylene fragments. The authors note that the long-wavelength maxima of oligo(arylene ethynylenes) with triphenylamine (TPA) branching unit are bathochromically shifted by ~10 nm relative to the maxima of oligomers with benzenetriyl (BTY) branching unit, which indicates a greater length of conjugation in polymers based on triphenylamine. A somewhat greater bathochromic displacement (~40 nm) is observed in the fluorescence spectra of the same oligomers. The fluorescence quantum yields of the resulting oligo(arylene ethynylenes) in chloroform are in the range of 0.09–0.67, which exceeds the luminescence quantum yields of poly(arylene acetylenes) in which the carbazole fragments are present only as the terminal groups.[132]

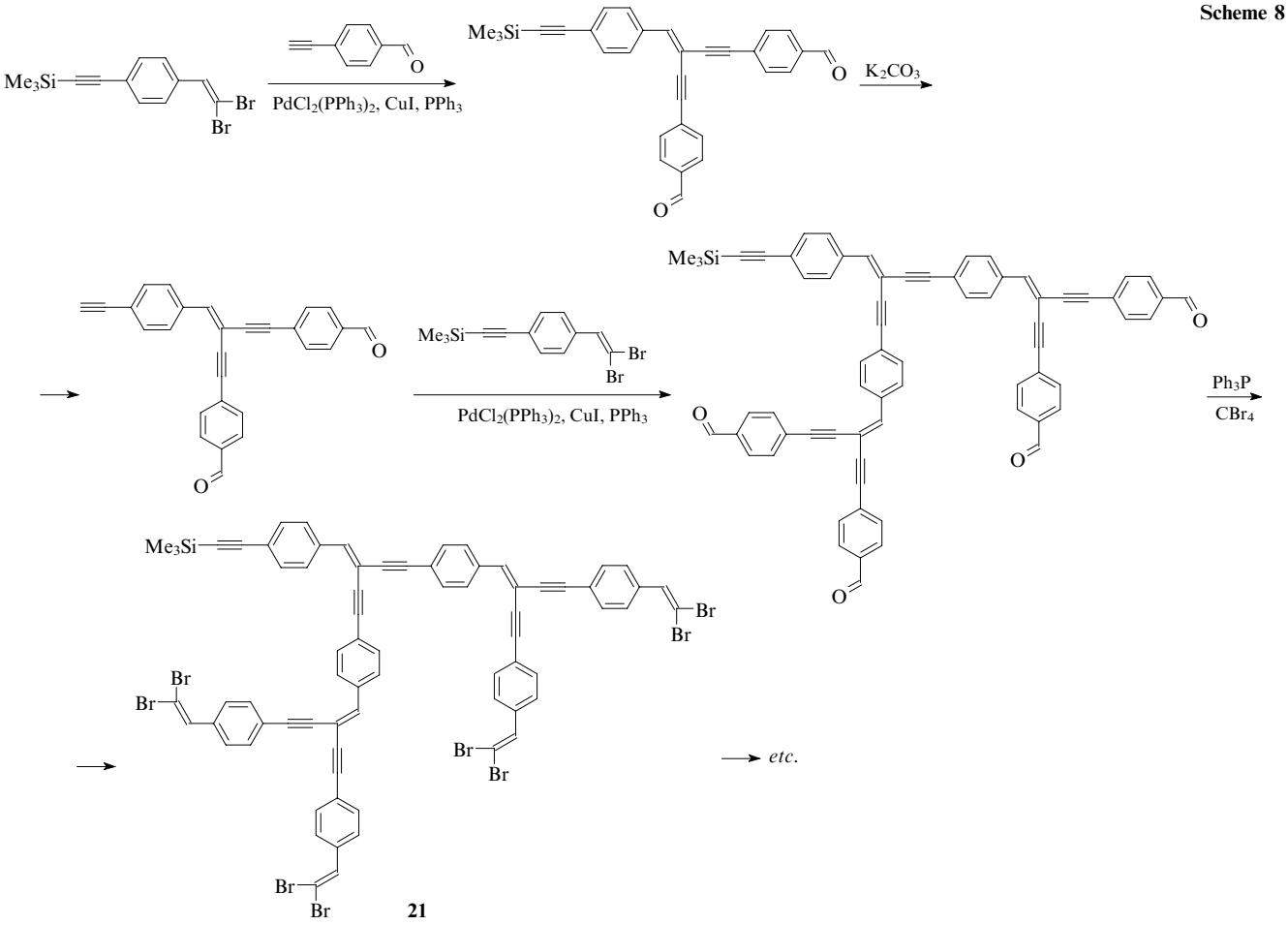
Scheme 7



20a,**b**

R = Oct, n-$C_{18}H_{37}$;  = $N(C_6H_4I\text{-}4)_3$ (**a**), $C_6H_3Br_3$-1,3,5 (**b**)

Scheme 8



The higher values of quantum yields of oligomers with the benzenetriyl branching unit compared to oligomers with the triphenylamine branching unit were attributed to the formation of more rigid structures and decrease in the contribution of non-radiative deactivation of the lower excited singlet state in the former case. It was also noted that with the use of the chloroform – methanol mixture of solvents in the case of oligomers with the TPA branching unit, the intensity of long-wavelength fluorescence (at 500 nm) increases and the blue component (at 410 nm) almost completely disappears. In the case of oligomers with the BTY branching unit, the blue band intensity does not decrease so much and the long-wavelength fluorescence does not appear. The quantum yields decrease twofold in the former case, while in the latter case, they are reduced by 25% – 30%. Relying on this, the authors conclude that oligomers with the BTY unit are more stable to the action of quenching agents.

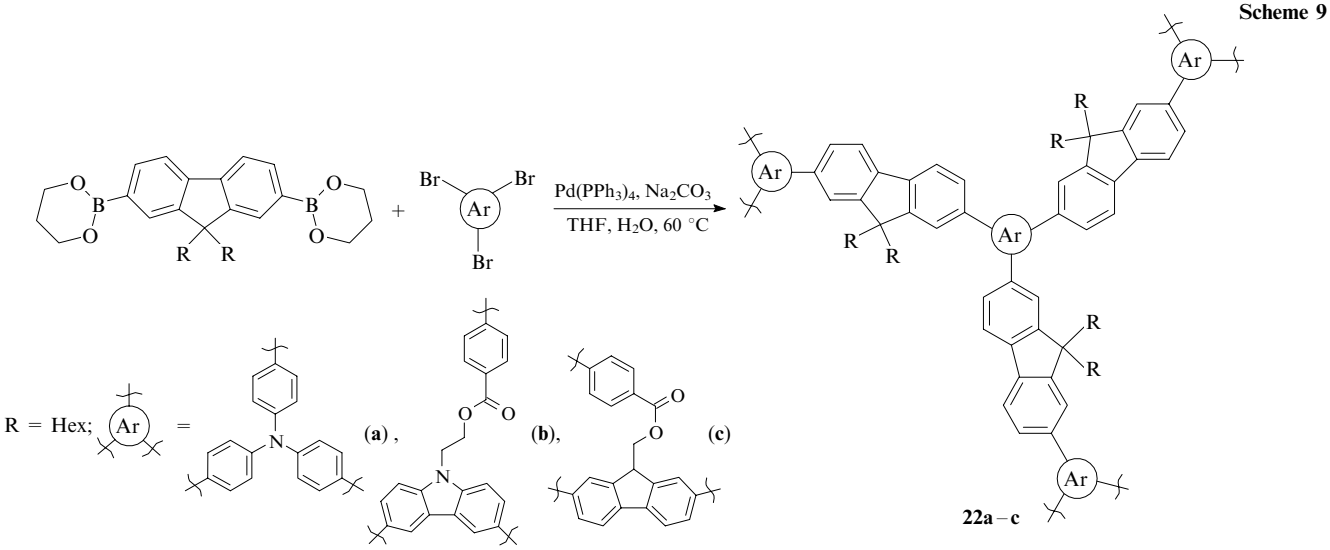
A stepwise synthesis of branched oligo- and poly(ethynylene styrenes) **21** based on β,β-dibromo-4-ethynylstyrene using cross-coupling reaction in the presence of triphenylphosphine, copper(I) iodide and dichlorobis(triphenylphosphine)palladium was reported (Scheme 8).[133] The resulting polymers had molecular mass of about 70 kDa and polydispersity index of ~1.7. They emitted light in the range of 440 – 500 nm, thus being blue emitters. The fluorescence excitation spectra of oligomers **21** in solution exhibit two maxima which are likely to refer to two different conjugated fragments of the macromolecules.[134] The authors assigned the first one to the radiative transition from the lower excited state S_1, while the origin of the second maximum is still unclear.

IV.3. Branched polyfluorenes

Nowadays, the most well studied branched polymers are the polymers with a partial ladder structure — polyfluorenes. Most of the branched polyfluorenes were obtained using metal-catalyzed reactions, most often, the Suzuki reaction, *i.e.*, the reaction of aryl halides with phenylboronic acids (or their esters). The reaction is accomplished upon heating in toluene (or THF) using palladium complex as a catalyst and a 2 M aqueous solution of sodium or potassium carbonate as a base. Various combinations of two and more comonomers are taken, one having at least three functional groups (A_n, where $n \geqslant 3$) and the other having two groups (B_2, C_2, *etc.*). It should be noted that the Suzuki reaction of the $A_n + B_2$ type ($n \geqslant 3$) affords polymers in which the conjugated connecting units have a constant size, allowing one to determine the effective conjugation length, while the Suzuki reaction of the $A_n + B_2 + C_2$ type results in conjugated units of different lengths, which complicates the identification of the luminophore group in the polymers and elucidation of the structure – properties corrleations for these systems.

The synthesis of branched polymers with the branching units based on triphenylamine (**22a**), carbazole derivatives (**22b**) and fluorene (**22c**) by the Suzuki reaction using the corresponding tribromo deriavtives was reported[135] (Scheme 9). The reaction was carried out in THF in the

Scheme 9



presence of aqueous soidum carbonate as a base and $Pd(PPh_3)_4$ as a catalyst.

The authors point out that gelation starts 30 min after the onset of the reaction in the case of polymers **22a**,**b** and within 315 min for polymer **22c**; therefore, the process was ceased several minutes before the gelation. The resulting polymers were characterized by means of IR and NMR spectroscopy. They were soluble in THF and chloroform.

The absorption spectra of polymers **22a**,**c** in THF had one maximum at 372 and 365 nm, respectively, while the absorption maximum of polymer **22b** was hypsochromically shifted (338 nm), which can indicate a shorter effective chain of conjugation in this polymer due to the presence of a dimethylene spacer in the trifunctional monomer.

The fluorescence peaks of polymers **22a**,**b** have almost identical positions (436 and 437 nm) but different widths at half height (57 and 75 nm), which can be explained by different MMD of these polymers.[136] The authors also noted a strong displacement of the fluorescence peak of polymer **22c** to the green region (472 nm), which could be caused by the interaction of fluorene fragments and the reaction by-product, dibromo-substituted dibenzofulvene.

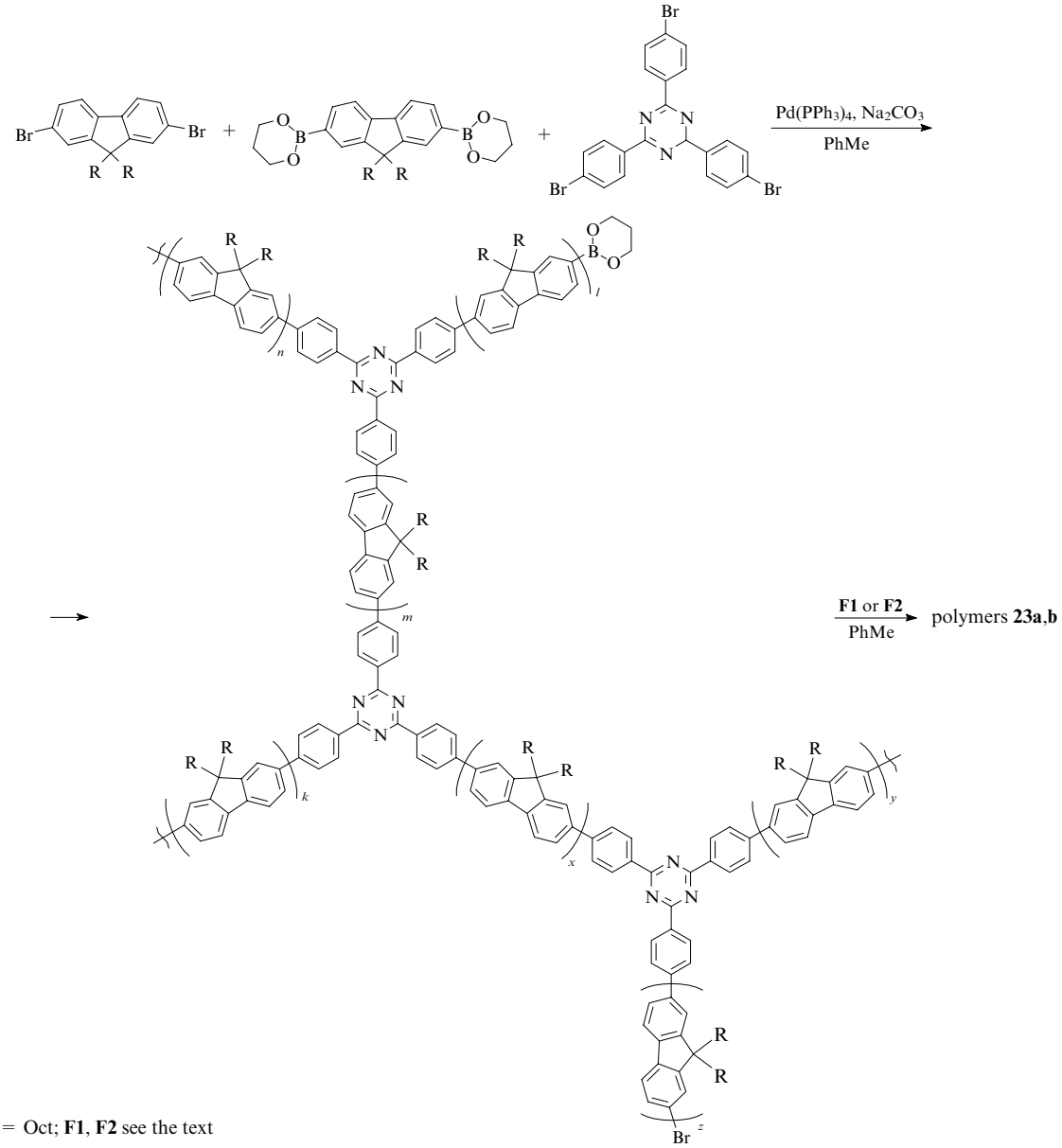
The synthesis of branched polymers by the reaction of the $A_3 + B_2 + B_2'$ type is well developed,[137] and the key reaction conditions (temperature, reaction time, monomer concentration, and solvent) that affect the formation of branched polymers (in particular, the time of gelation) are known. For example, it is known that the Suzuki cross-coupling is better carried out in dilute solutions at low temperatures to avoid the formation of completely cross-linked (and, as a consequence, insoluble) structures. The random character of formation of branched polymers in one step causes the presence of a great number of unreacted (residual) functional groups, which decrease the luminescence efficiency. Therefore, in order to prevent gelation and increase the luminescence efficiency, multifunctional compounds that block the reactive polymer groups are often introducted into the reaction medium in the second step of the polymer synthesis.

The Suzuki reaction of the $A_3 + A_2 + B_2$ type was used to prepare branched polyfluorenes with the 2,4,6-triphenyl-1,3,5-triazine branching unit (Scheme 10).[138] The synthesis was carried out in toluene in the presence of $Pd(PPh_3)_4$ and aqueous solution of Na_2CO_3 at 85 °C for 5 days. The initial monomers, 2,7-dibromo-9,9-di-n-octylfluorene, 9,9-di-n-octylfluorene-2,7-bis(trimethyleneboronate) and 2,4,6-tris(4-bromophenyl)-1,3,5-triazine, were taken in 5 : 6.5 : 1 (polymer **23a**) and 10 : 11.5 : 1 (polymer **23b**) molar ratio. At the second step, multifunctional compounds [2-bromo-9,9-di-n-octylfluorene (**F1**) or 9,9-di-n-octylfluorene-2-trimethyleneboronate (**F2**)] and $Pd(PPh_3)_4$ (0.5 mol.%) were added to the reaction medium, after which the process continued for another 2 days. As a result, amorphous polymers of yellowish colour soluble in most of organic solvents were formed. However, the researchers noted[138] that the solubility of the polymers decreased with an increase in the fraction of 2,4,6-tris(4-bromophenyl)-1,3,5-triazine. The ratios of linear and branching units were determined from the ^{1}H NMR spectra to be 8 : 1 for polymer **23a** and 17 : 1 for polymer **23b**.

The absorption maxima of polymers **23a**,**b** in toluene are located at 386 nm, which corresponds to the $\pi-\pi^*$-transition in the polymer aromatic system. Furthermore, these polymers were found to exhibit solvatochromism (displacement of the fluorescence maximum depending on the solvent polarity): as the solvent polarity increased, the fluorescence maxima shifted to longer wavelengths (positive solvatochromic effect). This implies that the excited state is more polar than the ground state. Of note is also the broadening of fluorescence bands. The fluorescence spectra of polymers **23a**,**b** in the solid state are shifted to longer wavelengths (435 and 436 nm) compared to the fluorescence spectra in solution (418 nm), which has been attributed to a change in the polymer conformation. The fluorescence quantum yields in solution for polymers **23a**,**b** were 40% and 53%, respectively, which is in good agreement with the previously published data.[139] The values of absolute quantum yields for polymers **23a**,**b** in the solid state were measured by the integrating sphere method to be 26% and 32%, respectively.

An analogous work was carried out[140] using a combination of comonomers, 2,7-dibormo-9,9-di-n-octylfluorene (**M1**) and 9,9-di-n-octylfluorene-2,7-bis(trimethyleneboronate) (**M2**), with a trifunctional monomer, 2-(4-bromophenyl)-5-(3,5-dibromophenyl)-1,3,4-oxadiazole (**M3**) (Scheme 11). Polymers **24a**,**b** were obtained at three different

Scheme 10



R = Oct; **F1**, **F2** see the text

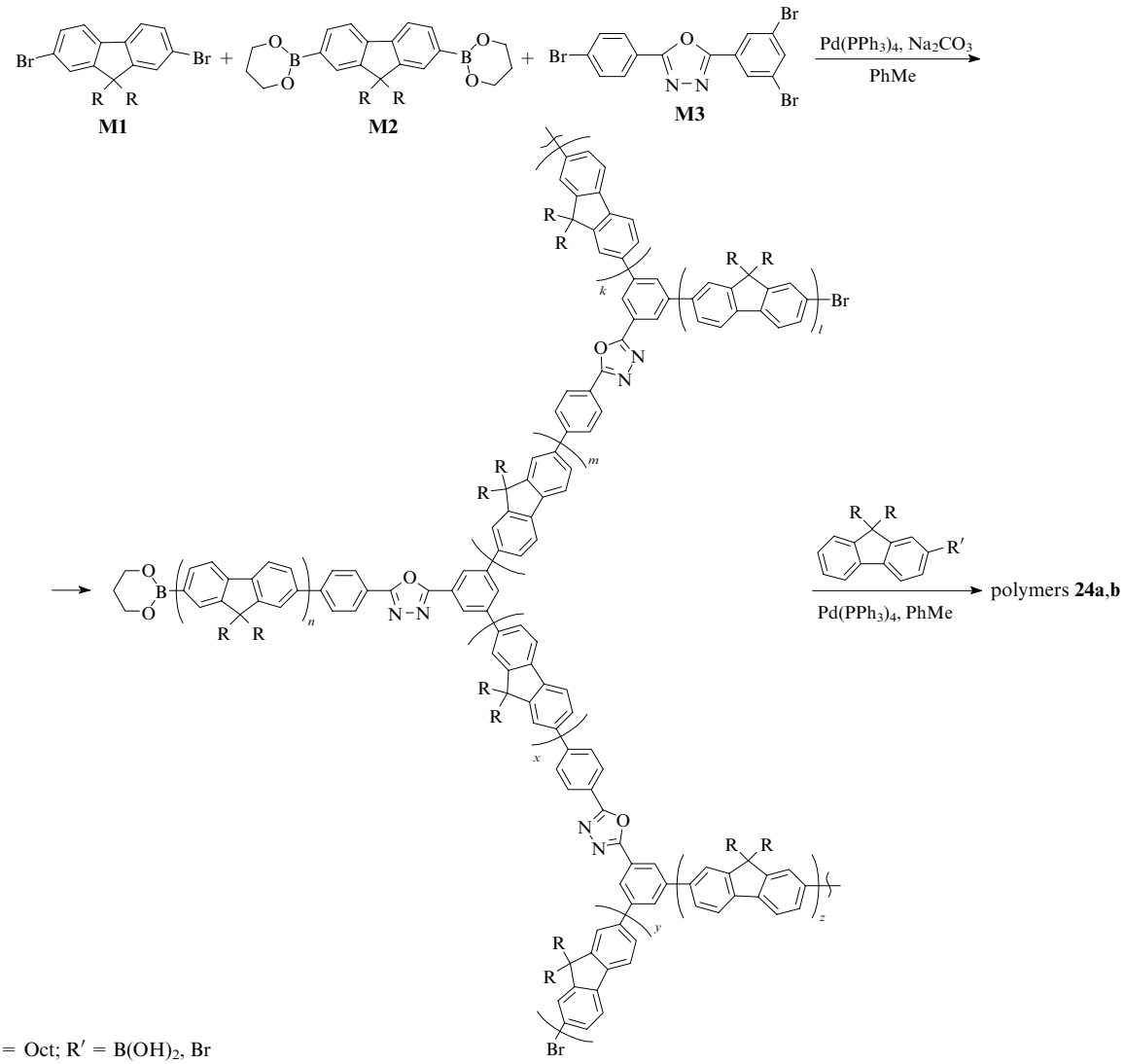
M1 : **M2** : **M3** ratios (5 : 6.5 : 1 and 10 : 11.5 : 1, respectively). The ratio of fluorene chains and branching units was determined based on the signals in ^{1}H NMR spectra and amounted to 9 : 1 for polymer **24a** and 17 : 1 for polymer **24b**. Polymers **24a**,**b** were soluble in toluene, THF, chloroform and dichloromethane, but the authors noted a decrease in the solubility with an increase in the fraction of the oxadiazole moiety in the branched polymers.

There were almost no differences between the optical properties of polymers **24a**,**b** in solution (in chloroform) and in the solid state, but the qunatum yields of fluorescence of polymer **24b** in solution (54%) and in the solid state (42%) were higher than those of polymer **24a** (46% and 32%, respectively),[140] which is a consequence of the greater content of fluorene chains in polymer **24b**.

Another approach to prevention of the π – π-stacking in conjugated polymers in the solid state is application of tetrafunctional branching monomers in which a tetrahedral carbon or silicon atom serves as the branching unit. Thus, the Suzuki reaction of the $A_4 + B_2$-type using 9,9-di-n-hexylfluorene-2,7-diboronic acid and three tetrafunctional comonomers [tetrakis(4-bromophenyl)methane, tetrakis(4-bromophenyl)silane, tetrakis(4-bromobiphenyl)silane or tetrakis(2-bromo-9,9-di-n-hexylfluoren-7-yl)silane] afforded branched polymers **25a** – **d** (Scheme 12).[141, 142] These polymers are soluble in toluene, THF, DMF and chloroform. According to the elemental analysis data, the content of residual bromine was 1.2% – 2.7%.

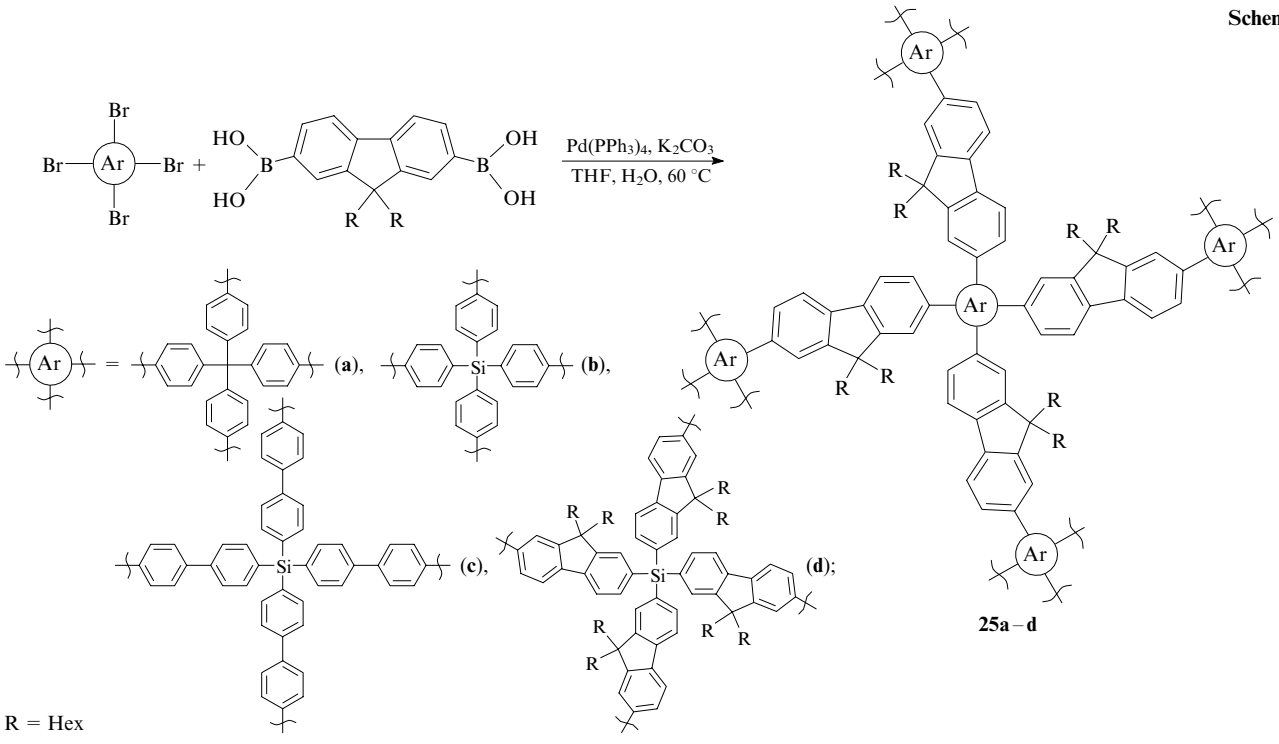
In the authors' opnion, the conjugated moieties in polymers **25a**,**b** are quaterphenyls, which is confirmed by peaks in the absorption (334 and 332 nm) and fluorescence (398 and 397 nm) spectra in a THF solution. The high value of the Stokes shift for polymers **25a**,**b** can be explained by the less rigid structure of the connecting units and the possibility of the conformational transitions in the polymers with a tetrahedral branching unit. The absorption and fluorescence spectra of polymers **25a**,**b** in the solid state are bathochromically shifted by 1 – 11 nm compared to the analogous spectra of the polymers in solution, the absorption spectra are also somewhat broadened but elements of

Scheme 11



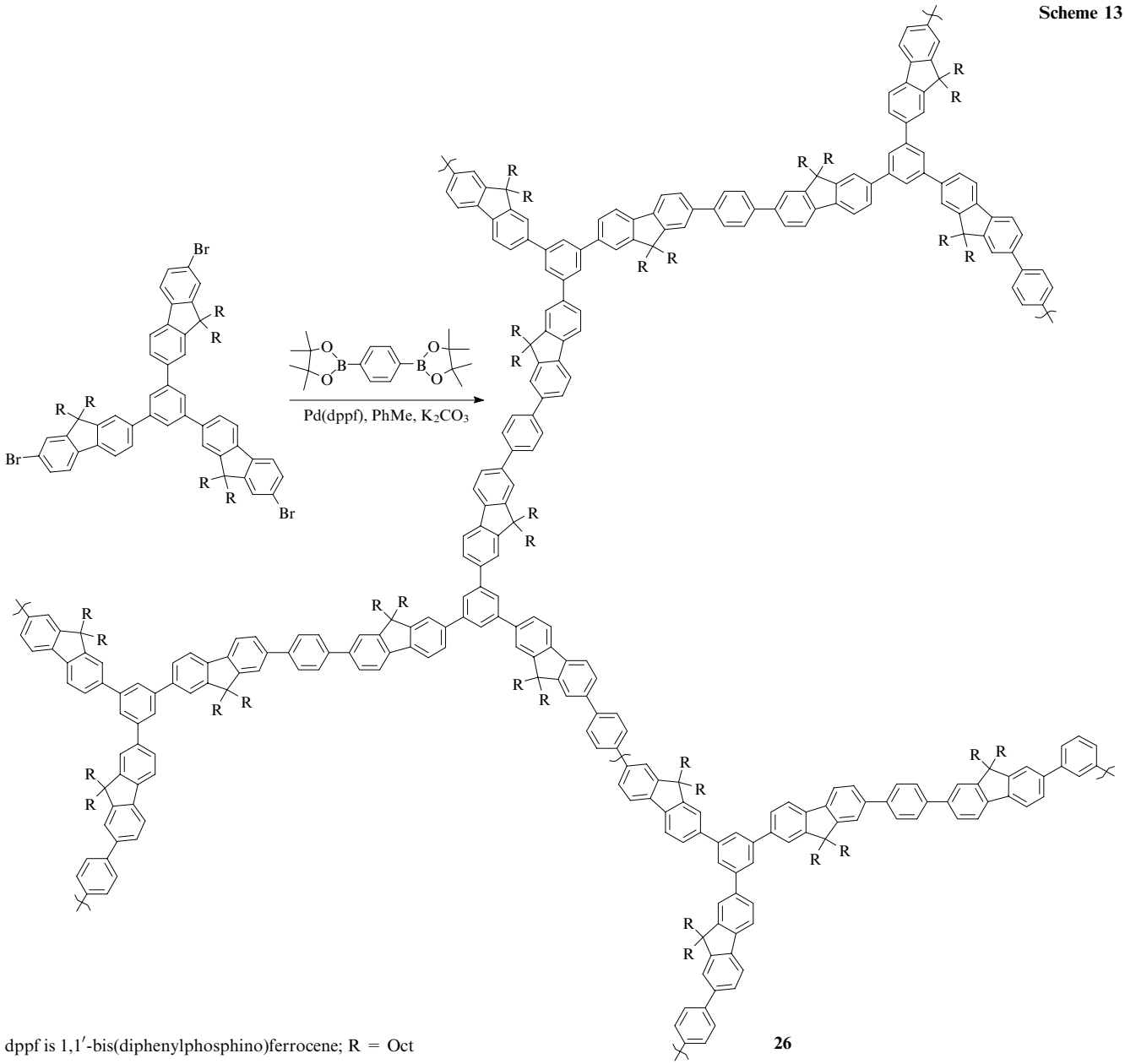
R = Oct; R′ = $B(OH)_2$, Br

Scheme 12



R = Hex

Scheme 13



dppf is 1,1′-bis(diphenylphosphino)ferrocene; R = Oct

26

vibrational structure in the fluorescence spectra do not become more clear-cut. The luminescence quantum yields of polymers **25a**,**b** in the solid state decreased 1.5 – 2-fold compared to analogous parameters in solution. The authors conclude that in the solid state, the intra- and intermolecular interactions of the conjugated moieties are minor.

The absorption and fluorescence peaks of polymer **25c** in solution (luminophore moieties consist of six conjugated benzene rings) are bathochromically shifted relative to the peaks of polymer **25b** by 18 and 9 nm, respectively. The absorption and fluorescence bands of polymer **25d** are hypsochromically displaced relative to the absorption (by 35 nm) and fluorescence (by 3 nm) bands of polymer **25c**. This suggests that in polymer **25d**, the conjugated chain is shorter than the connecting unit due to the steric hindrances associated with the mutual repulsion of n-alkyl side groups. The fluorescence quantum yields in solution and in the solid state for polymer **25d** exceed the analogous values for polyfluorene **25c** by a factor of 1.3 – 1.5.

Fluorenyl dendrimers, 1,3,5-tris(fluoren-2-yl)benzene and 1,3,5-tris(9,9-di-n-octylfluoren-2-yl)benzene, being the model compounds for branched oligo(phenylene fluorenes), were obtained by the cyclocondensation of unsubstituted and dioctyl-susbtituted acetylfluorenes, respectively. Combined polycondensation of *p*-phenylenebis(pinacolboronate) with tribromoarylenes in the presence of ferrocenyl Pd complex *via* the Suzuki reaction of the $A_3 + B_2$-type afforded branched oligo(phenylene fluorenes) **26** (Scheme 13).[143, 144]

The absorption and fluorescence spectra of solutions of the model compounds and oligo(phenylene fluorenes) were studied. The absorption maximum of oligomer **26** is located at 329 nm, and the fluorescence maximum is at 400 nm and has a shoulder at 421 nm. It was shown that no aggregation of luminophore moieties takes place in the branched oligomers synthesized, which favourably distinguishes them from the known linear luminescent polymers.

The Suzuki cross-coupling has been used [145] to obtain a series of polyalkylfluorenes with branched electron-conducting triazine groups and with branched triphenylamine fragments possessing hole conduction. The molecules of these polymers with conjugated segments of different length contained diphenylaminophenyl (hole conduction) and triphenylsilylphenyl groups at the ends of chains. Higher intensity and efficiency of luminescence were observed for the polymers with the triazine core. The luminance and efficiency of 1702 cd m^{-2} and 0.72 cd A^{-1}, respectively, were attained for them. However, the polymers with the triphenylamine branching unit showed a narrower electroluminescence band. As a result, the polymers demonstrated deep blue emission [in CIE(x, y) coordinates: (0.16, 0.09)].† Thus, the study cited [145] deals with the relationship between the molecular structure and thermal stability as well as optical and electroluminescence properties of branched polymers containing groups with electron or hole conduction.

IV.4. Branched polyphenylenes

The role of polyphenylenes as electronic materials stems from the extended system of π-conjugation. Among various branched polymers, branched polyphenylenes are distinguished by the structural order and high thermal stability.[55,146–148]

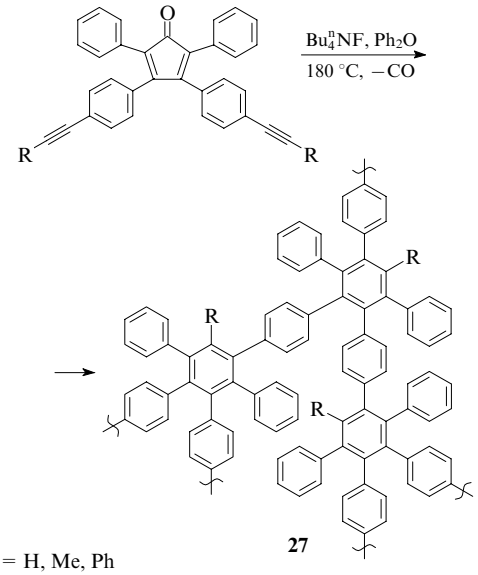
Three main approaches to the synthesis of branched polyphenylenes are used. The first one is the Diels–Alder reaction between ethynyl and cyclopentadienyl groups of aromatic compounds, which serve as polyfunctional monomers (AB_2, A_2, B_3 and other types), resulting in branched polyphenylenes.[148–150] The second strategy is the catalytic cyclotrimerization of diethynyl [151] or diacetyl aromatic [152,153] compounds, in which a new benzene ring is formed and serves as the branching unit. The third approach is the application of metal-catalyzed cross-coupling with the formation of the C–C bond.[75,82,154,155]

†CIE is the International Comission on Illumination (Commission Internationale de l'Eclairage).

IV.4.a. Synthesis of polyphenylenes by the Diels–Alder reaction

Morgenroth and Müllen [149] synthesized structurally ordered hyperbranched systems using the Diels–Alder reaction. Branched polyphenylenes **27** were obtained by the polycondensation of AB_2-type monomers that contained one cyclopentadienone moiety and two phenylacetylene groups as the diene and dienophile, respectively. The polycondensation was carried out in diphenyl oxide at 180 °C in the presence of tetra-n-butylammonium bromide (Scheme 14).

Scheme 14

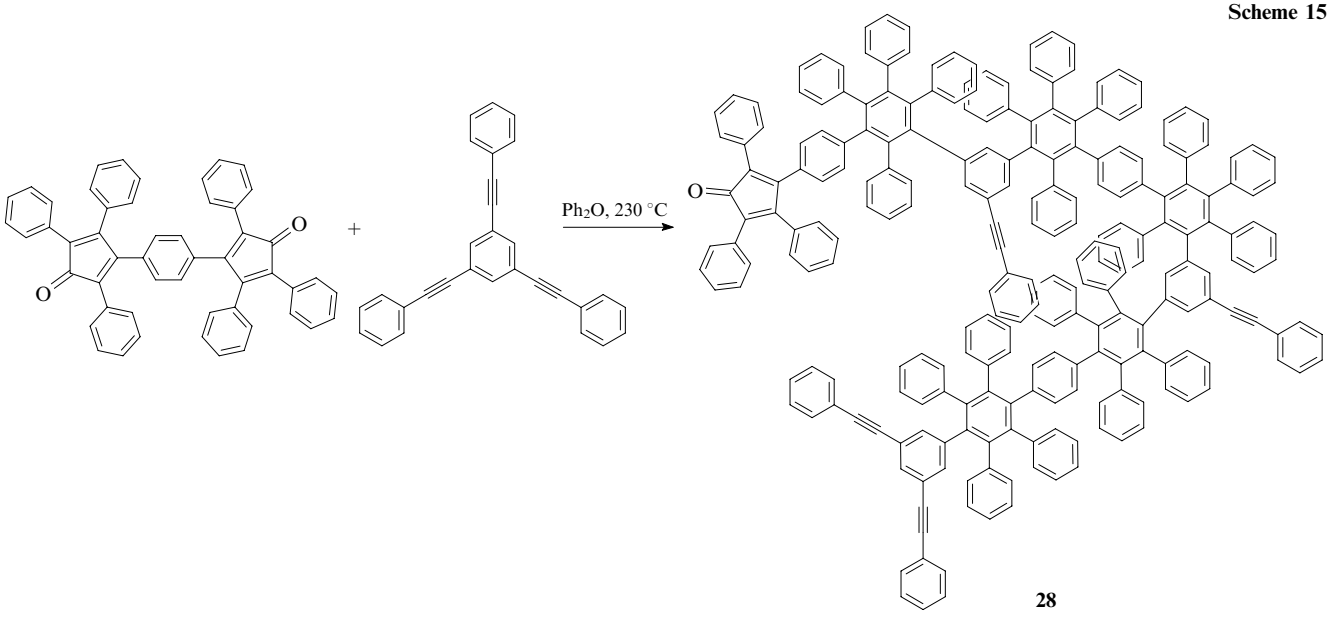


27

R = H, Me, Ph

The average molecular mass of polymer **27** measured by GPC varied from 3 to 100 kDa, the polydispersity index ranged from 1.66 to 6.85 depending on the reaction time and monomer concentration. These polyphenylenes were soluble in toluene and benzene, despite the fact that they consisted of close-packed benzene rings. However, it was found that such polyphenylenes have low luminescence efficiency, pesumably, due to the absence of conjugation at the *p*-phenylene regions of chains.

Scheme 15

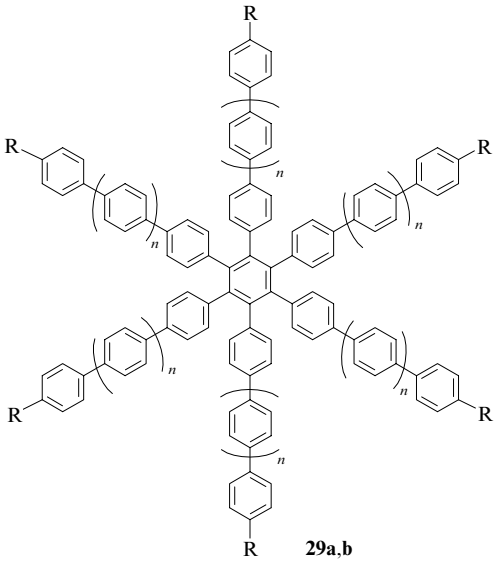


28

The synthesis of branched polyphenylenes **28** by the Diels–Alder reaction has been reported.[150] The polycondensation was carried out by the $A_3 + B_2$-type reaction using bis(cyclopentadienones) and 1,3,5-tri(phenylethynyl)benzene as a dienophile (Scheme 15).

Another study by Müllen and co-workers[156] describes the synthesis of individual branched structures with hexasubstituted benzene ring as the branching unit also by the Diels–Alder cycloaddition. A comparative investigation of the optical properties of 4-alkyl-substituted *p*-phenylenes and hexasubstituted benzenes with branches containing *p*-phenylene moieties was carried out. It was noted that on going from 4-alkyl-substituted linear structures to branched structures with *p*-terphenyl (**29a**) and *p*-quaterphenyl (**29b**) units — hexakis(4-alkyl-*p*-terphenyl)benzene and hexakis(4-alkyl-*p*-quaterphenyl)benzene — bathochromic shifts of the absorption and fluorescence bands take place, which is not fully consistent with the concept of complete independence of the *p*-phenylene branches in structures **29a**,**b**.

Structures 29a,b

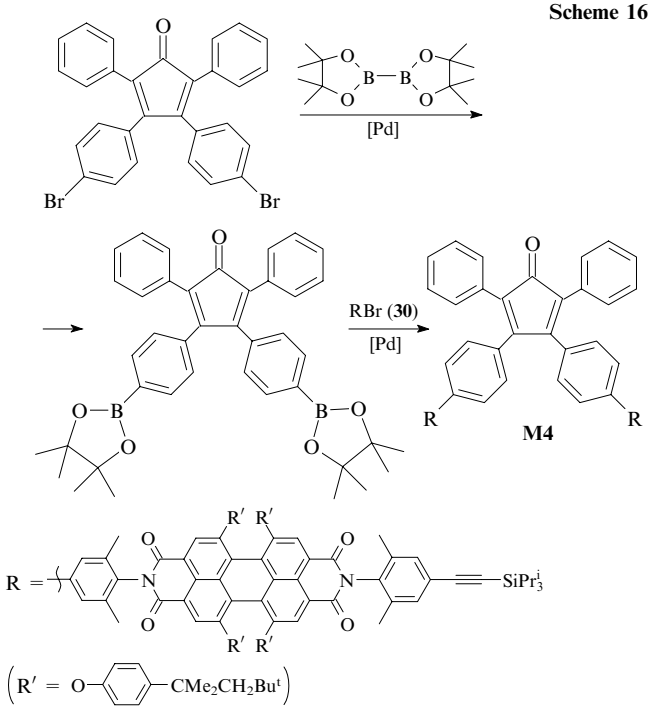


29a,**b**

R = $CMe_2C_{14}H_{29}$-n; *n* = 1 (**a**), 2 (**b**)

The subsequent works of Müllen's reasearch team[157] were devoted to the synthesis of a series of hexasubstituted dendrimers with branches containing highly fluorescent chormophores. In particular, compounds with cyclopentadienone groups and two protected terminal alkyne moieties were used as monomers. The perylene diimide moiety was chosen as the chromophore in this case. Scheme 16 shows the synthesis of one of the monomers (**M4**).

Scheme 16



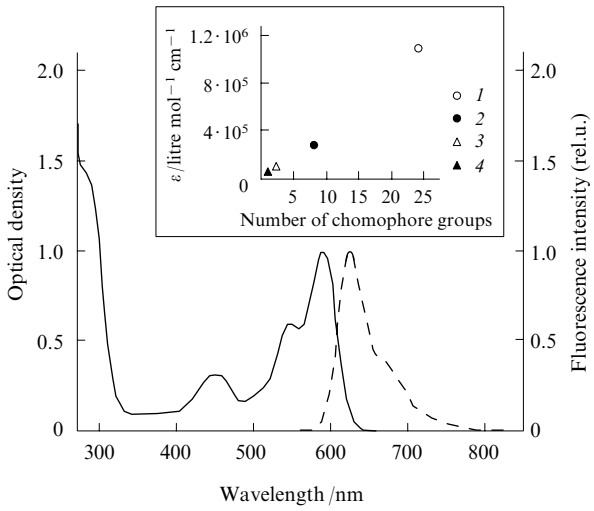
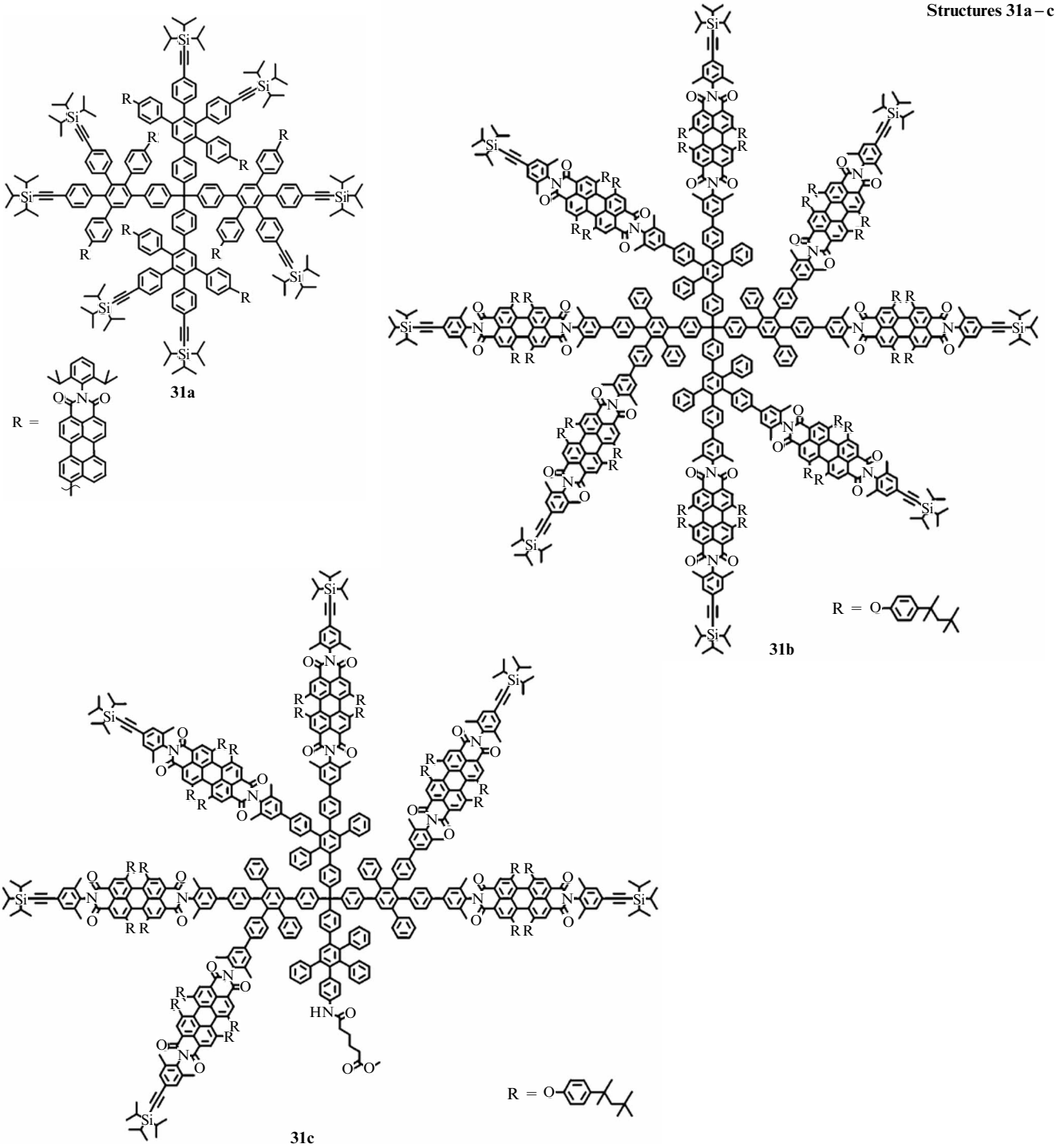


Figure 4. UV absorption (solid line) and fluorescence (dashed line) spectra of first-generation dendrimer **31b** with 8 chromophore groups and second-generation dendrimer **31d** with 24 chromophore groups.[157]
The inset shows the dependence of molar extinction coefficient on the number of chromophore groups: (*1*) **31d**, (*2*) **31b**, (*3*) **M4**, (*4*) **30** (see Scheme 16).

Table 3. Data for dendrimers of the first (**31a**–**c**) and second generations (**31d**).[157]

Compound	Molar extinction coefficient /litre mol^{-1} cm^{-1}	Calculated molecular mass /g mol^{-1}	FD/MALDI-TOF MS data /g mol^{-1}	Theoretical radius /nm	φ_{fl}
31a	282 900	7 122	7 122	2.1	0.95
31b	275 400	14 596	14 619(Na)	3.2	0.96
31c	201 600	11 565	11 588(Na)		0.97
31d	1 090 000	41 705	41 674 (Na)	6.7	0.95

Structures 31a – c



Upon deprotection, the cyclopentadienone and ethynyl groups react as AB_2-monomers. This gives dendrimers **31a – d** of both the first and second generations (Table 3).

Normalized absorption and fluorescence spectra of the resulting compounds virtually coincide (Fig. 4). With an increase in the number of chromophore groups and concomitant increase in the macromolecule size, the molar extinction coefficient grows. All macromolecules demonstrate luminescence quantum yileds close to unity.

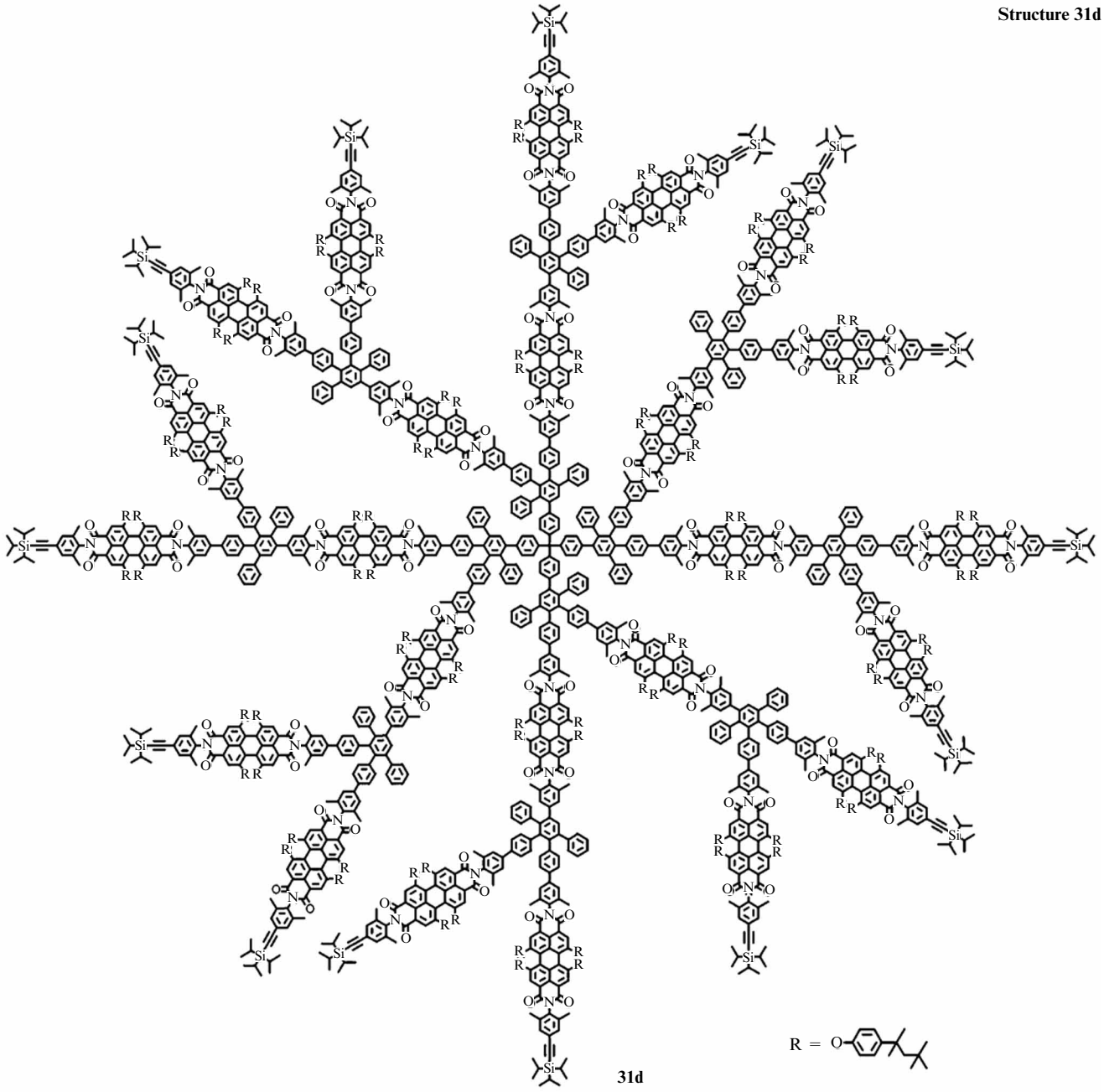
Hence, the optical properties of branched polyphenylenes obtained *via* the Diels – Alder reaction are dictated only by the nature of chromophore groups introduced into the macromolecule.

IV.4.b. Trimerization polycondensation of terminal acetylenes

A great number of works are devoted to the synthesis of branched polymers by the cyclotrimerization of terminal acetylenes, which results, for example, in branched polyphenylenes with 1,3,5- and 1,2,4-trisubstituted benzene rings as the branching units.[95, 158 – 165]

The investigations performed by Chernomordik and Sergeev [158 – 165] in 1971 – 1980 were devoted to the preparation of polymers *via* co-condensation of mono- and dieth-

Structure 31d



31d

ynyl aromatic compounds predominantly in the presence of the Ziegler catalyst ($Bu^i_3Al-TiCl_4$). The authors studied in detail the mechanism of cyclotrimerization and identified the optimal conditions for the formation of the main polymer structure. However, the optoelectronic properties of polymers were not considered at that time.

The problem of synthesis of polyphenylenes by cyclocondensation of terminal acetylenes was addressed again only in the beginning of the 21st century.

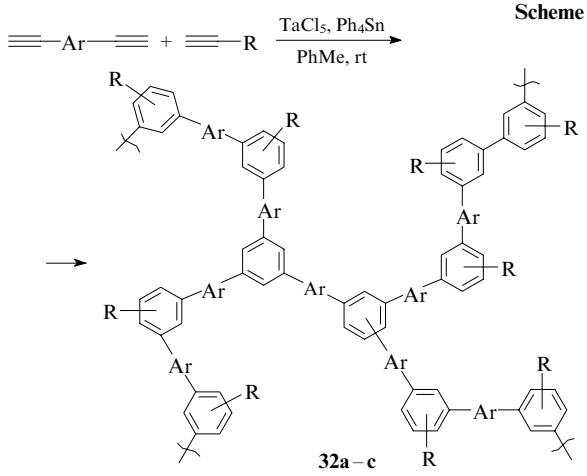
High-molecular-mass branched polyarylenes **32a–c** were synthesized[166,167] by co-polycyclotrimerization of 2,5-diethynylthiophene, 4,4′-diethynylbiphenyl and 2,7-diethynyldibenzothiophene with hept-1-yne and dodec-1-yne in the presence of $TaCl_5-Ph_4Sn$ catalytic system in toluene (Scheme 17).

The resulting polymers had molecular masses from 8600 to 33 500 Da; they were soluble in most of organic solvents and demonstrated high thermal stability. The fluorescence maximum of polymer **32a** in dichloromethane was bathochromically shifted relative to the maxima of polymers **32b**,**c** by ~80 nm, which was attributed to the introduction of thiophenediyl fragments. In the solid state, the fluorescence maxima of all three polymers were slightly displaced to longer wavelengths, which is likely to be caused by weak intermolecular interaction of the connecting units of the oligomers.

Subsequently, these investigations were continued.[166–173] The starting diethynyl compounds contained, for example, triphenylamine moieties,[169] which endowed the branched polymer with better hole conductivity; however, the luminescence quantum yields in this case did not exceed 20%.

For the synthesis of polyarylenes by this method, diethynyl monomers containing carbazole and(or) fluorene as

Scheme 17



32a–c

R = n-C_5H_{11}: Ar is thiophene-2,5-diyl (**a**), biphenyl-4,4 -diyl (**b**);
R = n-$C_{10}H_{21}$: Ar is fluorene-1,7-diyl (**c**)

chromophore moieties were also used. The alkyne polycyclotrimerization proceeded in the presence of TaX_5-Ph_4Sn (X = Cl, Br) and $CpCo(CO)_2$ (Cp = η^5-C_5H_5) catalysts. As a result, soluble branched polyarylenes with the high molecular masses ($M_w \leqslant 1.6\times10^5$ Da) were obtained in almost quantitative yields. Upon photoexcitation, solutions of these polymers emitted blue light (the maximum was at 400 nm) with the fluorescence quantum yield of $\leqslant$90%.[173]

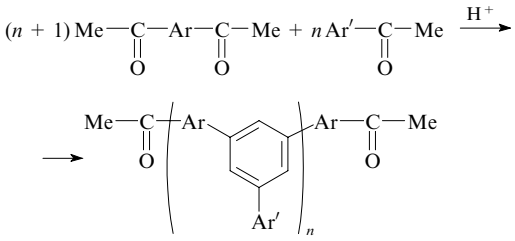
IV.4.c. Trimerization polycondensation of acetyl derivatives of aromatic compounds

The development of methods for polyphenylene synthesis based on the condensation of di- and monoacetyl aromatic compounds is the subject of a series of publications of the 1970s, which are summarized in a review.[152] The formation of polyphenylenes from acetyl derivatives of aromatic compounds or their ethyl ketals,[153,174–181] accompanied by evolution of water or ethanol, in the presence of an acid catalyst (H_2SO_4, $ZnCl_2$, $AlCl_3$, dry HCl, CF_3SO_3H, and so on) represents the trimerization polycyclocondensation (PCC) reactions, *i.e.*, the polyphenylene chain grows *via* the reaction of three acetyl or ketal groups to afford a new benzene ring. At a particular step, the reaction ends in the formation of a gel; therefore, the synthesis was carried out in such a way that soluble polymers were obtained and gelation was avoided. The resulting polymer with a relatively small molecular mass and terminal reactive groups was further subjected to structuring to form a thermally stable three-dimensional polymer.

Given the equal reactivities of groups and without consideration of side reactions, the polycondensation giving rise to branched polyphenylenes **33** can be represented by Scheme 18.

Side reactions are mainly related to incomplete cyclization as well as to different reactivities of two acetyl groups of the monomers at different process steps. The real polymers have a slightly branched chain and a high polydispersity index: the $\bar{M}_w/\bar{M}_n$ ratio is 6.8–9.9.[152] Hence, along with 1,3,5-triphenyl-substituted benzene rings, dypnone (α-methylchalcone) moieties, are formed in the polymer chain upon incomplete cyclization of the acetyl groups. Chemical investigations of polyphenylenes showed that a chain with $n = 7-8$ contains about two dypnone frag-

Scheme 18

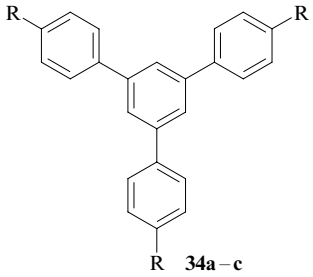


33

Ar = 4,4′-$C_6H_4C_6H_4$, 4,4′-$C_6H_4OC_6H_4$, *etc.*;
Ar′ = Ph, 4-PhC_6H_4, 4-$PhOC_6H_4$, *etc.*

ments.[178] Oligophenylenes with $\bar{M}_n$ = 1500–4000 Da and η_{red} = 0.10–0.15 dl g^{-1} (η_{red} is the reduced viscosity) are soluble in chloroform, benzene, dioxane, DMF, *etc.* Based on the data of model reactions, it was assumed[179–181] that the use of ketals allows one to carry out the PCC process in a more specific manner with the formation of less defective structures. However, presumably, due to the presence of defective structures, these polyphenylenes did not possess luminescence properties. Meanwhile, model cyclotrimers **34a–d** with different lengths of phenylene chains intensively emitted light in the blue visible region (Table 4) and had high luminescence quantum yields in solution.[182]

Structures 34



34a–c

R = H (**a**), Ph (**b**), 3,5-$Ph_2C_6H_3$ (**c**), PhC≡C (**d**)

Table 4. Optical properties of phenylene dendrimers.[182]

Compound	λ_{max} (abs), /nm	ε, /litre mol^{-1} cm^{-1}	λ_{max} (fl) /eV (nm)	φ (%)
34a	253	$0.52\cdot10^5$	3.52 (352)	29
34b	288	$1.10\cdot10^5$	3.42 (363)	43
34c	263,	$1.38\cdot10^5$,	3.44 (360)	72
	290	$1.32\cdot10^5$	72	
34d	308	$1.58\cdot10^5$	3.40 (365)	92

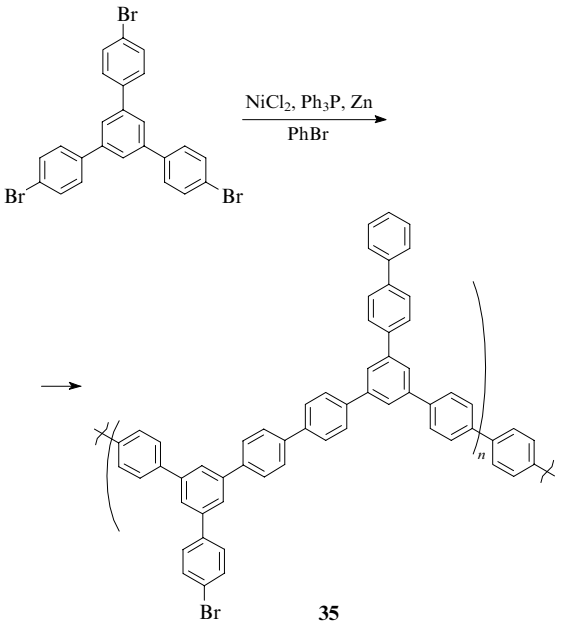
IV.4.d. Synthesis of branched polyphenylenes by cross-coupling reactions

In order to produce materials emitting light in the blue region that would be promising for the application as active layers in polymer light-emitting diodes, hyperbranched oligophenylenes (HOP) with 1,3,5-trisubstituted benzene ring as the branching unit were synthesized by cross-coupling methods based on tribromo- or triiodotriarylbenzenes.[43,182] In order to avoid the formation of cross-linked structures and to reduce the content of terminal bromine atoms, the system functionality was decreased during the

process of polymer synthesis by blocking the terminal groups with bromobenzene.

Branched oligophenylene **35** (Scheme 19) obtained by homopolycondenstaion catalyzed by a nickel complex had the molecular mass of $M_w \approx 4700$ Da and the polydispersity index of ~ 1.3. The degree of polymerization $(p+q)$ was, in this case, close to 12, and the numbers of fragments with (p) and without (q) terminal bromine atoms were almost the same. On average, branched oligophenylene **35** contained 55 benzene rings in each macromolecule. It was readily soluble in most of organic solvents, which is explained by the high degree of branching, weak intermolecular interaction and low solvation energy.

Scheme 19



The structure of oligophenyle **35** was studied using ^1H and ^{13}C NMR spectroscopy.[183] The signals were assigned based on the data for model compounds.

Investigation of the absorption and photoluminescence spectra of oligophenylene **35** in a $CHCl_3$ solution showed that it possesses emission in the blue region. It was established that these polymers are characterized by exceptionally high (up to 96%) quantum yileds of photoluminescence in solution and intense photoluminescence in the solid state. Figure 5 shows the absorption and emission spectra of BOP **35** in the solid state.[184] Coatings with thickness of 30–40 nm were obtained based on quartz plates from solutions of the oligophenylenes in $CHCl_3$ with concentration of 10 mg ml^{-1} at the centrifuge rotation speed of 1000 rpm. The luminescence quntum yield of the film of the resulting sample was 14%.

Upon A_3 type homopolycondensation, the possibilities for the control of the backbone properties are moderate: this can be done only by using monofunctional compounds in the substitution of the terminal halogen atoms.

More possibilities arise upon synthesis of polymers by Pd-catalyzed polycondensation of comonomers of the AA- and BB-types. This method is the Suzuki reaction, *i.e.*, the reaction of aromatic boronic acids or esters with halogen-containing aromatic compounds in the presence of palladium catalysts.[185–187]

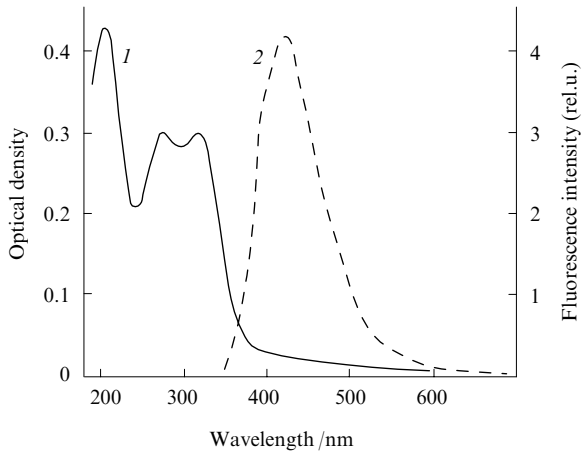
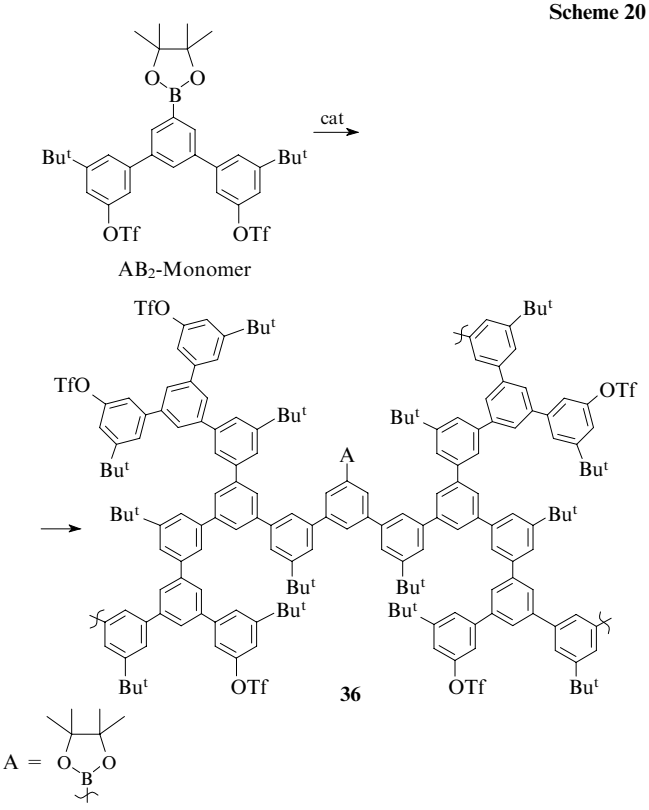


Figure 5. Absorption (*1*) and fluorescence (*2*) spectra of oligophenylene **35** in a film.[184]

A work of Moore's team[31] is devoted to the development of the method of Suzuki polycondensation to prepare branched polyphenylenes **36** (Scheme 20) based on *m*-terphenyl branched AB_2-monomer. The polymer-forming reaction leads to branched poly(*m*-phenylene) **36** with a high molecular mass (MM) and solubility in common organic solvents. The molecular mass and polydispersity index can be controlled by varying the amount of introduced catalyst and the concentration of the starting monomer. The degree of branching was likely to be constant (67%).

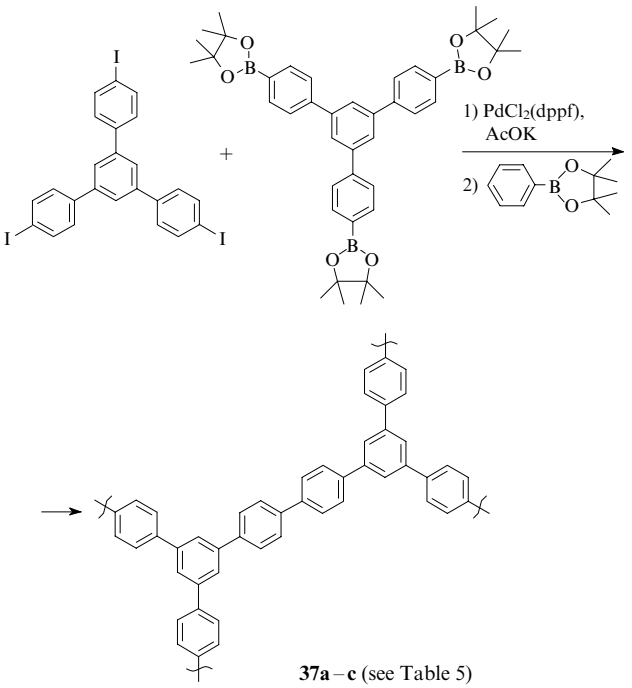
Scheme 20



Branched oligophenylenes **37a–c** were obtained by the Suzuki polycondensation (Scheme 21). The comonomers were compounds with iodine atoms and pinacolborane

groups; at the second step, the terminal halogen atoms reacted with phenylpinacolborane.[188]

Scheme 21



37a–c (see Table 5)

The polymer molecular mass was controlled by variation of the comonomer ratio. At the ~1 : 1 ratio, the first step (before blocking) was expected to give polymers with the maximum possible MM and minimum iodine content, whereas at the ~1 : 3 comonomer ratio, branched oligophenylenes with 16 benzene rings and 6 terminal iodine atoms should have been formed ($M_{theor} \approx 2.0 \times 10^3$ Da). However, in the latter case, the products with $M = 4.2 \times 10^3$ Da and essentially lower iodine content compared to the calculated one were formed. As the fraction of the halogen-containing monomer was increased, the iodine content became higher. Nevertheless, samples with higher mass could be obtained by reducting the percentage of the triiodo-containing monomer (Table 5). The optical properties of model compounds and polyphenylenes have been discussed in detail.[189]

The absorption spectra of branched oligophenylenes **37a–c** are depicted in Fig. 6.

For samples **37b**,**c**, the absorption maximum was observed at 275 nm, this corresponds to the π–π* transition in the aromatic system of the polymer.[188] For oligophenylene **37a**, the absorption maximum appeared to be shifted to longer wavelengths (295 nm), which can be due to a 1.5–2-fold increase in the MM of oligophenylene **37a** compared to oligophenylenes **37b**,**c**. It can be assumed that the absorption wavelength of polymers **37b**,**c** is caused by the presence

Table 5. Some characteristics of branched oligophenylenes **37a–c** obtained at different ratios of comonomers.[188]

Oligophenylene	Molar ratio of comonomers	Iodine content (%)	$M \times 10^{-3}$ /Da	Quantum yield of PL (%)
37a	1 : 1.2	14.2	8.0	25
37b	1 : 1.7	24.8	6.9	16
37c	1 : 2.6	27.5	4.2	12

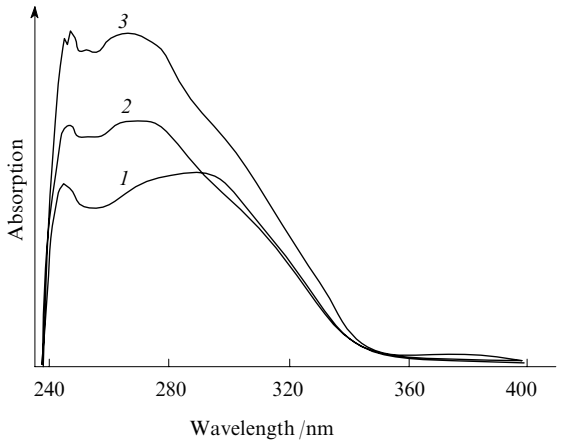


Figure 6. Absorption spectra of branched oligophenylenes **37a** (*1*), **37b** (*2*), **37c** (*3*).[188]

of a considerable number of benzenetriyl branching units with terminal substituted phenyl groups, which accounted for absorption of oligomers with low MM in the range of 260–280 nm. Meanwhile, an increase in MM causes an increase in the percentage of *p*-phenylene connecting units, which is responsible for the observed batchochromic shift (from 275 nm to 295 nm).

Figure 7 shows the photoluminescence spectra of branched oligophenylenes **37a–c** normalized to absortion recorded in chloroform at the excitation wavelength of 275 nm. There are no differences in the peak shapes or positions in the photoluminescence spectra of the oligomers; however, they differed in intensity depending on the halogen atom content at the periphery of the molecule, which is in good agreement with the theoretical concepts about the role of heavy atoms in molecules of organic luminophores.[190] Thus, for oligophenylene **37c** containing 27.5 mass % of iodine, the luminescence intensity was the lowest, whereas for oligophenylene **37a** (14.2 mass % of iodine), it was the highest (see Fig. 5).

Finally, it can be concluded that the effect of the halogen atom content on the efficiency of photoluminescence and the effect of MM can be observed only in the absorption spectra. It should also be noted that the luminescence intensity depends on the wavelength of the exciting

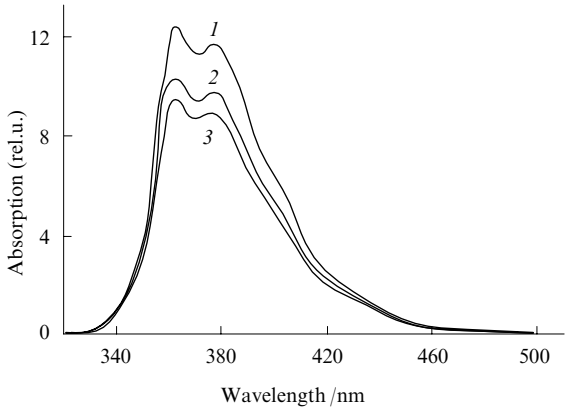


Figure 7. Photoluminescence spectra of oligophenylenes **37a** (*1*), **37b** (*2*), **37c** (*3*).[188]

light. However, in this case, the absortpion maxima of the samples under study are located rather close to each other and the fluorescence intenisty virtually does not change upon excitation at $\lambda = 295$ nm; therefore, the factor that determines the efficiency of luminescence is the halogen (iodine and bromine) content.

A new conjugated polymer containing triphenylamine branching units has been prepated[191] by the reaction of phenylene-1,4-diboronic acid and tris(*p*-bromophenyl)-amine as monomers of the A_2- and B_3 types, respectively. The polymer had a molecular mass of $\sim$5400 and was soluble in chloroform and THF. Its absorption maximum was at 360 nm and the emission maximum was located at 430 nm. From the data of cyclic voltammetry, it can be concluded that the polymer can be potentially used as a charge accumulating material, *i.e.*, for example, as an electrode for storage batteries.

V. Prospects of application of branched polymers in electroluminescent devices

Electroluminescence is light emission by a medium upon transmittion of electric current through it, *i.e.*, direct conversion of electric energy into light energy.[25, 192] Investigations on EL achieved considerable development after the report of 1950 by US researchers Payne, Mager, and Jerome on the design of an electroluminescent lamp.[193] The EL phenomenon serves as a basic principle for various devices, in particular, semiconductor injection light emitting diodes (Losev's battery). In these ELD, emission arises owing to the radiative recombination upon p – n transition in the luminophore layer (active layer).[23, 194, 195] The active layer is placed between two electrodes, of which the cathode injects electrons (n-type carriers) and the anode injects holes (p-type carriers). Upon application of a voltage, electrons and holes move from the opposite electrodes and recombine with energy emission, which switches some of luminophore molecules to the excited singlet or triplet states (excitons). Upon relaxation of singlet excitons, a light quantum is emitted. Besides radiative relaxation of an electron – hole exciton, non-radiative relaxation and dissociation are also possible. In the latter case, upon exciton excitation by a light quantum and effective separation of electrons and holes (in particular, upon the use of donor – acceptor pairs in the active layer), the appearance of photocurrent is possible. This phenomenon forms the principle of action of photoelectric cells — devices that convert solar energy into the energy of electric current.[196, 197]

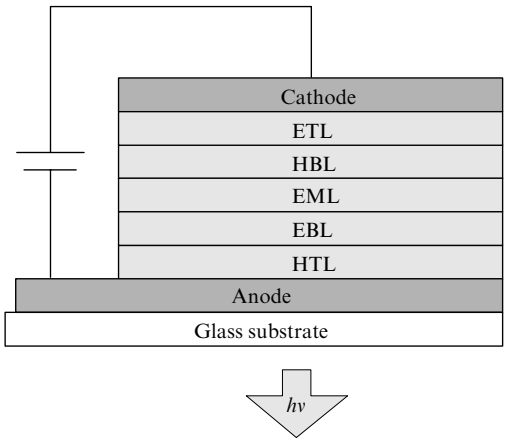
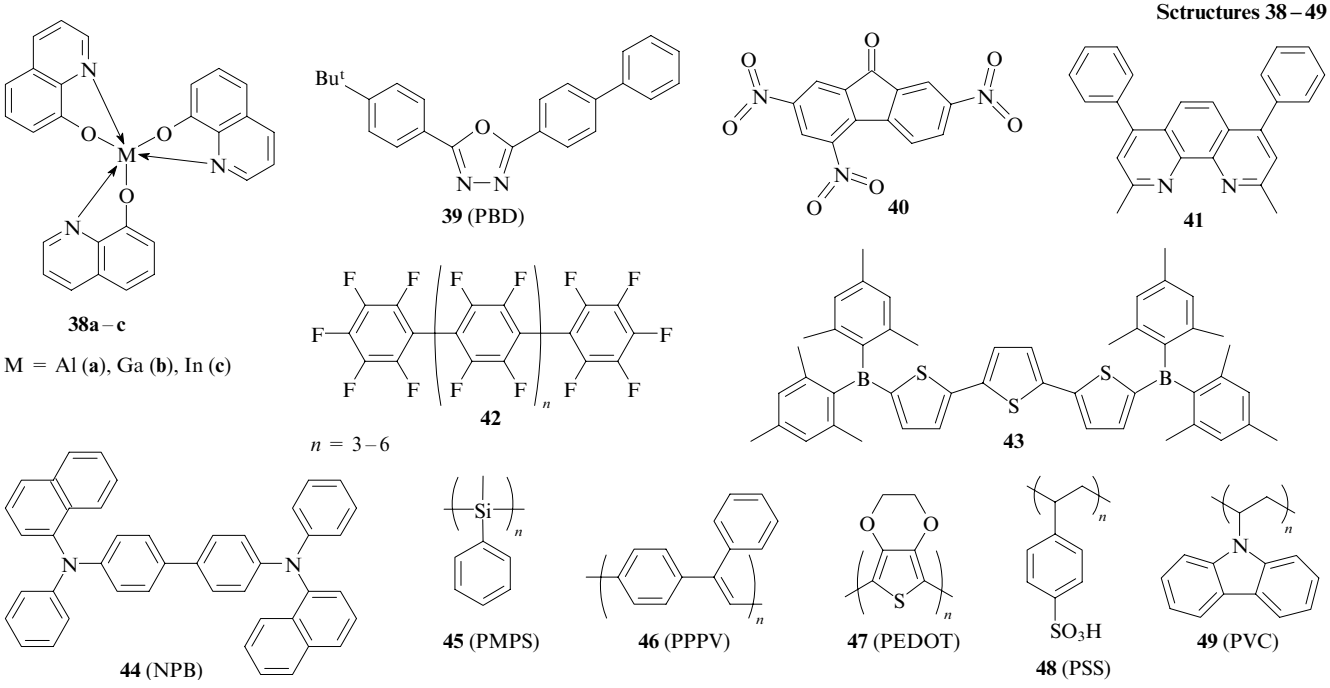


Figure 8. Basic diagram of an OLED.[200, 201]
ETL is the electron conducting layer, HBL is the hole blocking layer, EML is the emission layer, EBL the electron blocking layer, HTL is the hole conducting layer.

For more efficient introduction (injection) of charge carriers into the luminophore layer, additional layers with electron or hole conduction are placed between the luminphore layer and the electrodes (Fig. 8).[2, 198 – 201]

Structures **38** – **43** and **44** – **49** are examples of compounds with electron and hole conduction, respectively.[2, 198]

Sctructures 38 – 49



Polymers **11c**,**d**, **12a** have been used to manufacture ELD.[97] The turn-on voltage for single- and double-layer light emitting diodes based on polymer **12a** was 6 V and that for the diode based on polymer **11** was 3 V. Despite the fact that polymer **11c** possesses high fluorescence properties in solution, single-layer light-emitting diodes based in this polymer have relatively low productivity.

Polyvinylcarbazole (**49**, PVC) is often widely used as a polymeric matrix.[97, 202] In an investigation of mixtures of polymers **11c** and PVC in different ratios, an increase in the electroluminescence quantum yield with respect to neat polymers has been noted.[97] When a PVC–**11c** mixture (in 5 : 1 ratio) was used as an active layer, an enhancement of the luminance of the blue emission to 810 cd cm^{-2} at the voltage of 24 V compared to emission of a single-layer light emitting diode based on polymer **11c** (76 cd cm^{-2} at 20 V) was detected, which was attributed to the improved energy transfer between PVC and polymer **11c**. Moreover, comparison of single layer diodes based on polymer **11c** and a PVC–**11c** mixture showed a 10-fold increase in the efficiency of energy transfer (from 0.025 to 0.27 cd A^{-1}).[97]

Unfortunately, no results of investigation of polymers **12b** and **13** in ELD have been reported;[115] however, in this publication, interesting results of measurement of two-photon absorption and fluorescence are presented and it is shown that these compounds can be of particular interest for such applications as organic lasers and fluorescence microscopy.[203] Single-photon fluorescence is emission from the sample surface (contributions of the secondary absorption and, as a consequence, secondary fluorescence are insignificant), while two-photon absorption can be used to study the samples at a greater depth. In addition, two-photon absortpion induces more intense fluorescence. Upon excitation with a two-photon laser at 800 nm with a frequency of 120 fs, intense fluorescence of PPV **12b** and **13** was observed at 544 and 554 nm, respectively, *i.e.*, it occurred at 35–44 nm longer wavelengths than the single-photon fluorescence in chloroform solutions. This was assumed [116] to be related to the effect of secondary absorption.[204] The higher intensity of two-photon fluorescence compared to single-photon one was also noted, which makes polymers **12b** and **13** promising for practical applications.

The electroluminescence of polymers **14** and **15** was studied in ELD consisting of the consecutively formed layers of indium–tin oxide (ITO)/polyethylenedioxythiophene (**47**, PEDOT, 50 nm)/polymer (60 nm)/**38a** (30 nm)/LiF (1 nm)/Al (200 nm). The electroluminescence spectra of copolymer **15** and homopolymer **14** exhibit two peaks at 582 and 588 nm, which is correlated with the photoluminescence maxima of polymer films. This indicates that the PL and EL spectra reflect the same radiatiave transition from the excited singlet state to the ground state. At the same time, the EL spectra of compounds **14** and **15** demonstrate a shoulder peak at 625 nm, which is absent in the PL spectra; this was attributed to interchain interactions.[117] This assumption is supported by the fact that, in the case of homopolymer **14**, the peak intensity is much higher than that for copolymer **15**. This implies that the branched structure of the copolymer hampers aggregation of polymer chains. For polymer **14**, a lower value of turn-on voltage (4.2 V for **14** and 5.3 V for **15**) and higher luminance (2916 cd m^{-2} at 13.7 V for **14** and 2246 cd m^{-2} at 12.3 V for **15**) are observed, whereas copolymer **15** showed a higher electroluminescence quantum yield (0.17 for **14** and 0.26 for **15**).[117]

Samples **16a–c** and **17** served as an active layer in two-layer ELD of the following structure: ITO/**47**/polymer/Ca (50 nm)/Al (100 nm). The EL spectra of sample **17** completely coincide with the PL spectra of this compound in the solid state. This indicates that the photo- and electroluminescence are produced by the same moieties of the macromolecules. In the case of polymers **16a–c**, the EL spectra compared to the PL spectra show one more broad peak in the long-wavelength region (516 nm), which was assigned [39] to the heavy atom effect on the singlet–triplet transition. The maximum luminance of the emission (2180 cd m^{-2}), the maximum electroluminescence efficiency (8%–9%), as well as the minimum turn-on voltage (17 V) were noted for the ELD based on polymer **17**. For samples **16a–c**, a decrease in the emission intensity (from 184 to 26 cd m^{-2}) and the efficiency of EL (from 9% to 1%) were observed upon an increase in the content of the heavy atom and in the macromolecule degree of branching. The authors assumed the predominant effect of the heavy atom and the thin film morphology on the decrease in the EL efficiency. Also, a decrease in the EL efficiency upon an increase in the turn-on voltage was noted, which was regarded to be due to poor quality of polymer films. Based on a comparison of the EL parameters for the resulting branched polymers and for the reported linear analogues,[136, 205] it was concluded that the use of branched poly(fluorene vinylenes) in ELD is preferred over the use of linear ones.

The electroluminescence of polymers **22a–c** was studied [135] in two-layer ELD structures ITO/polymer/LiF/Al in which the active area was 4 mm^2. The authors note that the EL spectra are in good agreement with the PL spectra of the polymers in the solid state, which suggests participation of the same excited states in both processes. The absence of shoulder peaks attests to weak interactions between the macromolecules owing to their branched structure. The maximum luminance of 142 cd m^{-2} (at the voltage of 15.5 V) was observed for sample **22c**. As the current density increases, the efficiency of EL rapidly grows to reach a maximum (0.18, 0.06 and 0.15 cd A^{-1} for polymers **22a–c**, respectively) and then monotonically decreases. This implies a decrease in the efficiency of recombination of electrons and holes due to their unbalanced injection into the active layer at high voltage values. The low efficiency of EL of polymer **22b** is attributable to weak conjugation of this structure.

The electrochemical properties of branched polyfluorenes with the 2,4,6-triphenyl-1,3,5-triazine branching unit were studied.[138] The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated by the empirical formula [206]

$$E_i = -e(E_j + 4.7)$$

where E_i is the energy of HOMO (LUMO) and E_j are the oxidation (reduction) potentials determined experimentally from the data of cyclic voltammetry for polymers **23a**,**b** in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in acetonitrile at the scanning rate of 100 mV s^{-1} with a platinum electrode and an $Ag/AgNO_3$ (0.1 M) reference electrode. The level of HOMO (LUMO) for polymers **23a**,**b** is 5.60 (2.60) and 5.59 eV (2.50 eV), respec-

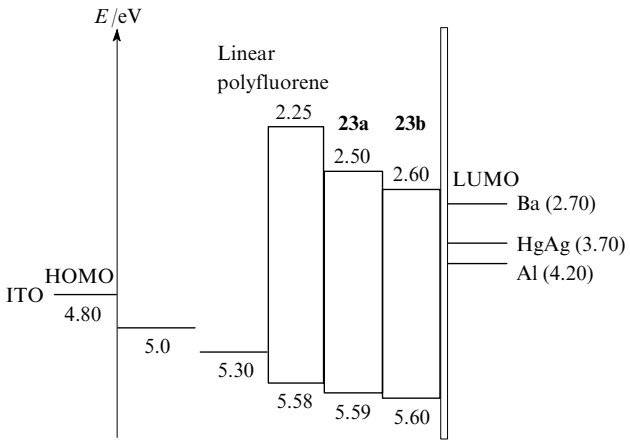


Figure 9. Comparison of the energy levels of linear and branched (**23a**,**b**) polyfluorenes and electrode materials.[138]

tively, which is in good agreement with the data for linear polyfluorenes: 5.58 eV (2.25 eV).[114] The authors note an increase in the LUMO energy of the resulting polymers compared to the linear polymers from 2.25 to 2.50 eV, which they attribute to the introduction of triazine fragments. Hence, owing to the branched structures, the LUMO of polymers **23a**,**b** appeared to be substantially closer to the values of work functions for materials typically used for cathode manufacture (Fig. 9); this may imply a more efficient injection of electrons from the cathode into the polymer layer during ELD operation.

To study EL of polymers **23a**,**b**, ELD of two types were fabricated: ITO/**47** (50 nm)/polymer (70 nm)/Ba (4 nm)/Al (150 nm) and ITO/**47** (50 nm)/**49** (40 nm)/polymer (70 nm)/Ba (4 nm)/Al (150 nm). The polymer films were applied by spin coating from a toluene solution. The shape of EL spectra practically coincides with the shape of PL spectra of thin films; however, the authors detect the displacement of EL maximum of polymer **23b** to longer wavelengths compared to polymer **23a** (463 and 446 nm, respectively, for five-layer diode and 469 and 444 nm for six-layer diode). The maximal value of luminance for polymer **23b** was 1750 cd m^{-2} (at 7.8 V), or 1950 cd m^{-2} (at 13.5 V) for a diode with an additional layer of polymer **49**. Upon addition of PVC, the efficiency of EL of polymers **23a** and **23b** also increased (0.6% and 0.83%, respectively, for a five-layer diode and 1.2% and 1.4% for a six-layer diode), which the authors relate to an increase in the stability of operation of ELD containing the PVC layer.

The electroluminescence[119] of polymers **24a** and **24b** was also studied in ELD of two types: ITO/**47** (50 nm)/polymer (70 nm)/Ba (4 nm)/Al (150 nm) and ITO/**47** (50 nm)/**49** (40 nm)/polymer (70 nm)/Ba (4 nm)/Al (150 nm). The maximum luminance for polymer **24b** was 165 cd m^{-2} (at 12 V) in a five-layer ELD and 1150 cd m^{-2} after addition of the PVC layer. The authors also note the higher efficiency of EL in a six-layer ELD (1.5% for polymer **24b** and 1.0% for polymer **24a**) compared to the five-layer one (0.44% for polymer **24b** and 0.15% for polymer **24a**).

* * *

Branched aromatic polymers such as polyphenylene, poly(phenylene vinylene), poly(phenylene ethylene) or polyfluorene, as well as their linear analogues exhibit photo- and electroluminescence properties. They possess higher molecular masses in combination with higher solubility. The latter circumstance appreciably increases the possibility of their additional purification and fractionation, which is of particular significance from the viewpoint of their potential application, since the modern high technologies impose extremely high requirements on polymer purification. An important feature of this group of polyaromatic systems consists also in the fact that synthetic methods for their production are more suitable for scaling in particular industrial applications.

Based on the results of the performed literature analysis, it is possible to state that the level of structure control achieved to date provides a possibility of targeted synthesis of branched polyaromaric systems with specified spectral characteristics. The development of methods for synthesis and controlling the structure of branched aromatic polymers forms as a separate trend that has high potential for further development.

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