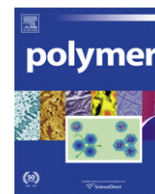




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Feature Article

Three-dimensional conjugated macromolecules as light-emitting materials

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ABSTRACT

In this feature article, we present a short review on the recent development in the construction of structurally perfect red and blue light-emitting materials and highlight such research in our group. We focus mainly on the three-dimensional conjugated structures such as dendrimers, hyperbranched polymers, star polymers, spirobifluorene-based polymers, and spiro-bridged ladder-type oligomers and polymers. Results indicated three-dimensional conjugated structures can efficiently decrease the aggregation of materials, resulting in the improving of the light-emitting efficiency.

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1. Introduction

Organic and polymeric light-emitting materials have attracted considerable scientific and industrial attention due to their potential application in large area flat-panel displays [1]. For full-color displays three primary colors, i.e., blue, green and red light-emitting materials are required. Although great success has been achieved in the development of green light emitters, red and blue light emitters, which fully meet the requirements for commercial application are limited [2].

Over the past decade, polyfluorenes (PFO) have emerged as leading electroluminescent materials with bright blue emission, high hole mobility, and easily tunable properties through modifications and copolymerizations [3–8]. However, an additional green emission and reduced efficiency were observed during operation or annealing the film in air as shown in Fig. 1. There are some different opinions about the origin of this green emission band. For example, such green emission band was once considered to be the emission from the aggregates or excimers in the bulk materials. Chen et al. have also reported that the electric field induction and polar end

group-enhanced aggregation may be the factors for the presence of green emission [9]. Recently, more and more researchers attributed this low energy green emission to the on-chain ketonic defects [10–15]. In solid film, the ketonic defects are low energy trap-sites to which the excited energy can be transferred very efficiently and can completely change the film emission spectra of polymers [16]. To date, these opinions about the origin of this green emission are still under intense debate.

Thus, a challenging goal for researchers is to produce blue light-emitting materials with long-term stability and high efficiency and that are free of blue–green emission. To obtain pure and stable blue light emission, various strategies have been used to reduce the formation of aggregation or ketonic defects for polyfluorenes, including the introduction of bulky side chains [17], spirobifluorene structure [18], cross-linked structure [19], hyperbranched structure, star-like structure [20], and so forth. In most cases, three-dimensional structures can effectively suppress the aggregation of conjugated polymer chains, and thus in some extent block the energy transfer from the polymer backbone to the low energy ketonic defect site, which is helpful to sustain the original blue emission.

Meanwhile, for the red-emitting materials, the relatively low efficiency is the main bottle-neck in the development of red-emitting materials. The nature of red fluorescent materials with

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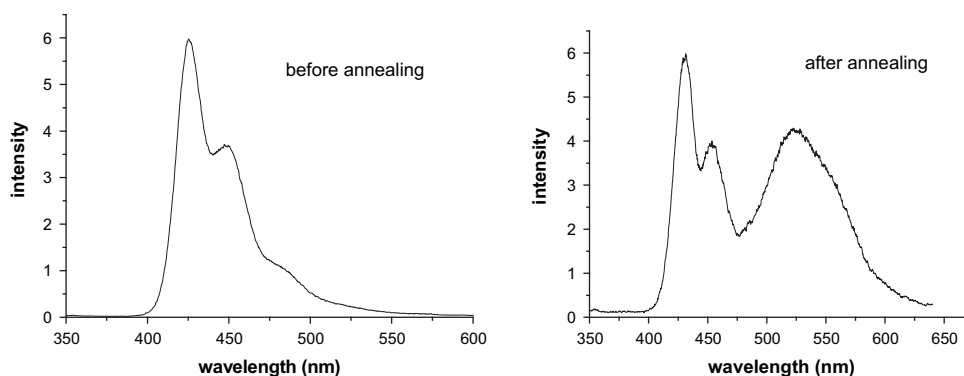


Fig. 1. The green emission of PFO is generated after annealing the film in air.

long enough wavelength (emission maximum wavelength $\lambda_{\text{max}} > 610 \text{ nm}$) are usually polar, such as electron donor-substituted pyran-containing compounds, or nonpolar but extensively π -conjugated, such as polycyclic aromatic hydrocarbon, perylene derivatives [21–28] or porphyrin-type macrocyclic compounds. All these red fluorophores are prone to aggregation in solid state, due to either attractive dipole–dipole interactions or effective intermolecular π -stacking. Therefore, they are highly susceptible to concentration quenching and become either weakly emissive or even not emissive at all in solid state. The guest–host doped emitter system becomes another method for solving the above problem of these red emissive materials when applied for organic light-emitting diodes (OLEDs). However, OLEDs based on dopant are more difficult to adapt for mass production processes than those based on a nondoped host emitter, considering that reproducibility of the optimum doping level requires careful manufacturing control [29]. Although Müllen et al. had carried a lot of significant research of introducing branching units into the perylene bay position to increase its light-emitting efficiency [21–23], efficient red light-emitting materials are still highly needed.

In recent years, conjugated polymers have attracted considerable scientific and industrial attention due to their applications in the fields of OLEDs [1,30–32]. However, conjugated polymers often possess of rod-like and rigid structures. These rigid rod-like

polymers are prone to aggregate which usually lead to fluorescence quenching resulting in lower quantum efficiency. These intrinsic shortcomings stimulate researchers a deep insight into the effects of chemical structures based on polymers as light-emitting materials.

Indeed, the structural perfection of the polymers is very crucial for the application of organic and polymer-based light-emitting materials. Fortunately, the unusual electronic and photophysical properties of the tree-like three-dimensional branched structures have attained growing attention. These three-dimensional conjugated macromolecules such as dendrimers, hyperbranched and star polymers possess themselves of rigid three-dimensional structures, which can effectively suppress the aggregation of polymer chains. Polymers with rigid three-dimensional structures have shown obvious superiority to the corresponding linear structures as light-emitting materials [33,34].

Over the past several years, our considerable effort has been expended to attain novel three-dimensional conjugated polymers or oligomers from design and synthesis points towards improving the efficiency of blue and red light-emitting materials. In the present feature article, we discussed recent related studies, gave some examples in this field, and highlighted such researches in our group. Our strategies mainly focused on designing three-dimensional conjugated structures to reduce the ketonic defect (for blue

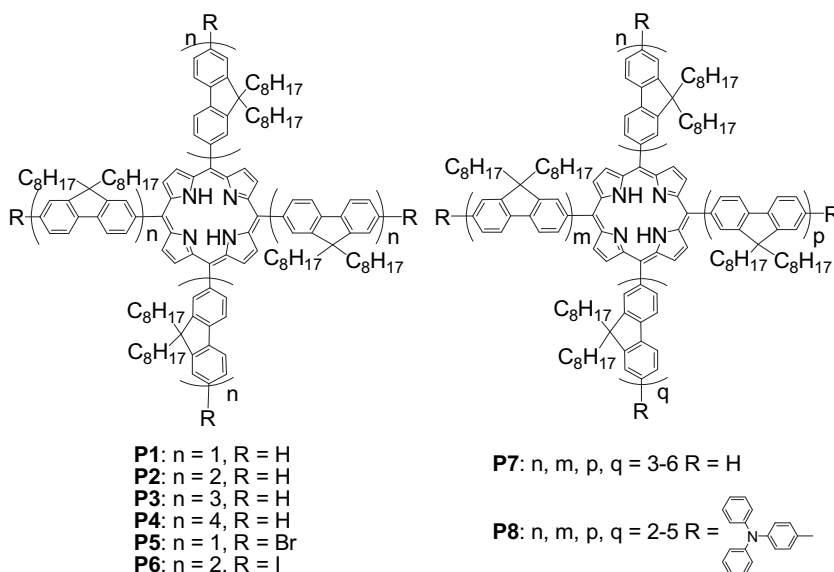


Fig. 2. Structures of the star-shaped porphyrins P1–P6 from Ref. [37] and P7–P8 from Ref. [38].

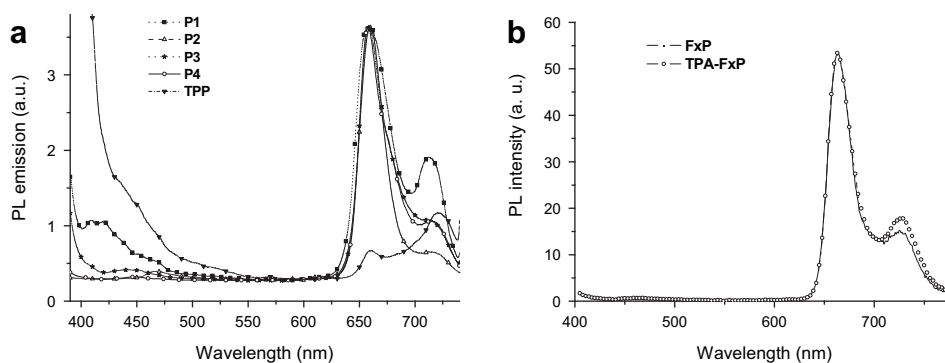


Fig. 3. (a) The normalized photoluminescence spectra of spin-coated thin films of star-shaped porphyrins **P1–P4** and **TPP** from Ref. [37]. (b) The normalized photoluminescence spectra of **P7** (Fxp) and **P8** (TPA-Fxp) in films from Ref. [38].

light-emitting materials) and the aggregation (for blue and red light-emitting materials) of polymers or oligomers with the aim to improve their photoluminescence or electroluminescence efficiency. Designed three-dimensional polymers or oligomers in our group mainly include star polymers or oligomers, dendrimers, hyperbranched and spirobifluorene-based polymers, and spiro-bridged ladder-type oligomers or polymers. Therefore, this feature article is organized in the following way. Section 2 describes the red and blue emitting materials base on the star-shaped structures. Section 3 discusses the studies on the dendrimers as red and blue light-emitting materials. Section 4 introduces hyperbranched polymers as red and blue light-emitting materials. Section 5 describes the recent research on spirobifluorene and spiro-bridged ladder-type polymers or oligomers as blue light-emitting materials.

2. Star-shaped macromolecular architecture based light-emitting materials

As classical definition, star polymers are branched polymers comprising one central core and several linear chains emanating from the core [35]. In the past decade, conjugated molecules with star-shaped structures have gained growing interest [36]. Combination with conjugated character within the arms, a star-shaped architecture would bring new electrical, optical, and morphological properties [36]. Especially, star-shaped oligomers or polymers as light-emitting materials have become very appealing as their branched structures may effectively suppress aggregation.

As known, porphyrins are also planar macrocycles that exhibit saturated red color chromaticity, reasonable fluorescence efficiency, and good thermal stability. While, they are prone to aggregation in solid state due to the intermolecular $\pi-\pi$ stacking. With the combination of the advantages of porphyrin and the properties of star structures, we synthesized a series of monodisperse, well-defined star-shaped porphyrins with four oligofluorene arms at their *meso* positions [37]. The chemical structures of the four-arm oligofluorene porphyrins **P1–P6** are shown in Fig. 2. The key reactions involved in the synthesis were “Lindsey condensation” for porphyrin synthesis and Pd-mediated Suzuki-Miyaura cross-coupling (SMCC) reactions for the attachment of the oligofluorene arms. The idea in this work was to bond the porphyrin guest and the polyfluorene host with conjugated chemical connection, which would lead to through-bond energy transfer. Furthermore, the side octyl chains on the fluorene units can efficiently suppress the aggregation of porphyrin rings and provide good solubility for whole molecules. Star-shaped oligomers showed blue absorption, but emitted in red region due to efficient

energy transfer. As shown in Fig. 3a, the emission spectra of spin-coated films of **P1–P4** exhibited an intense red emission peak at around 658 nm and a shoulder at 715 nm, while tetraphenylporphyrin (TPP) showed two relatively weak emission peaks at around 660 and 720 nm. The photoluminescence quantum yields (Φ) of **P1–P4** in toluene ranged from 0.16 (for **P1**) to 0.22 (for **P4**) in comparison to TPP ($\Phi = 0.11$) as the reference standard.

Based on these results, we further developed an easy one-pot approach to prepare porphyrin-cored star polymers on the gram scales with a reasonable and economical cost (the detailed synthesis routes were shown in Ref. [38]) [38]. Such efficient synthesis can overcome shortcomings of the time-consuming preparation process of monodisperse star-shaped molecules. As shown in Fig. 2, bromo endgroups were blocked by fluorene and triphenylamine (TPA) functional groups to afford star polymers **P7** (Fxp) and **P8** (TPA-Fxp), which exhibited good solubility in common organic solvents, good film-forming ability, and pure saturated red light emission as shown in Fig. 3b. The photoluminescence quantum yields were 0.17 for both **P7** and **P8** in dilute toluene solution with TPP ($\Phi = 0.11$) as the reference standard (irradiated at 423 nm). A single-layer polymer light-emitting diodes (PLED) device with the configuration of ITO/PEDOT:PSS/**P7** or **P8** or TPP/PFO/Al are shown in Fig. 4. The PLEDs of **P7** (or **P8**) showed only a deep red emission at about 662 nm (663 nm for **P8**) and a shoulder at 726 nm (727 nm for **P8**), which indicated an efficient energy transfer from oligofluorene arms to porphyrin core. The doped devices emitted pure red light only when the TPP

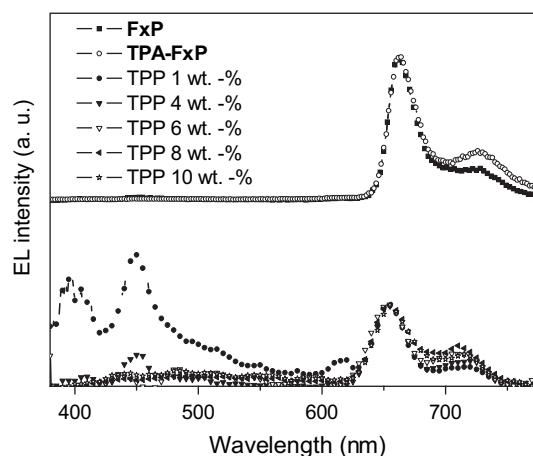


Fig. 4. Electroluminescence spectra of PLEDs based on **P7** (Fxp), **P8** (TPA-Fxp) and TPP/PFO from Ref. [38].

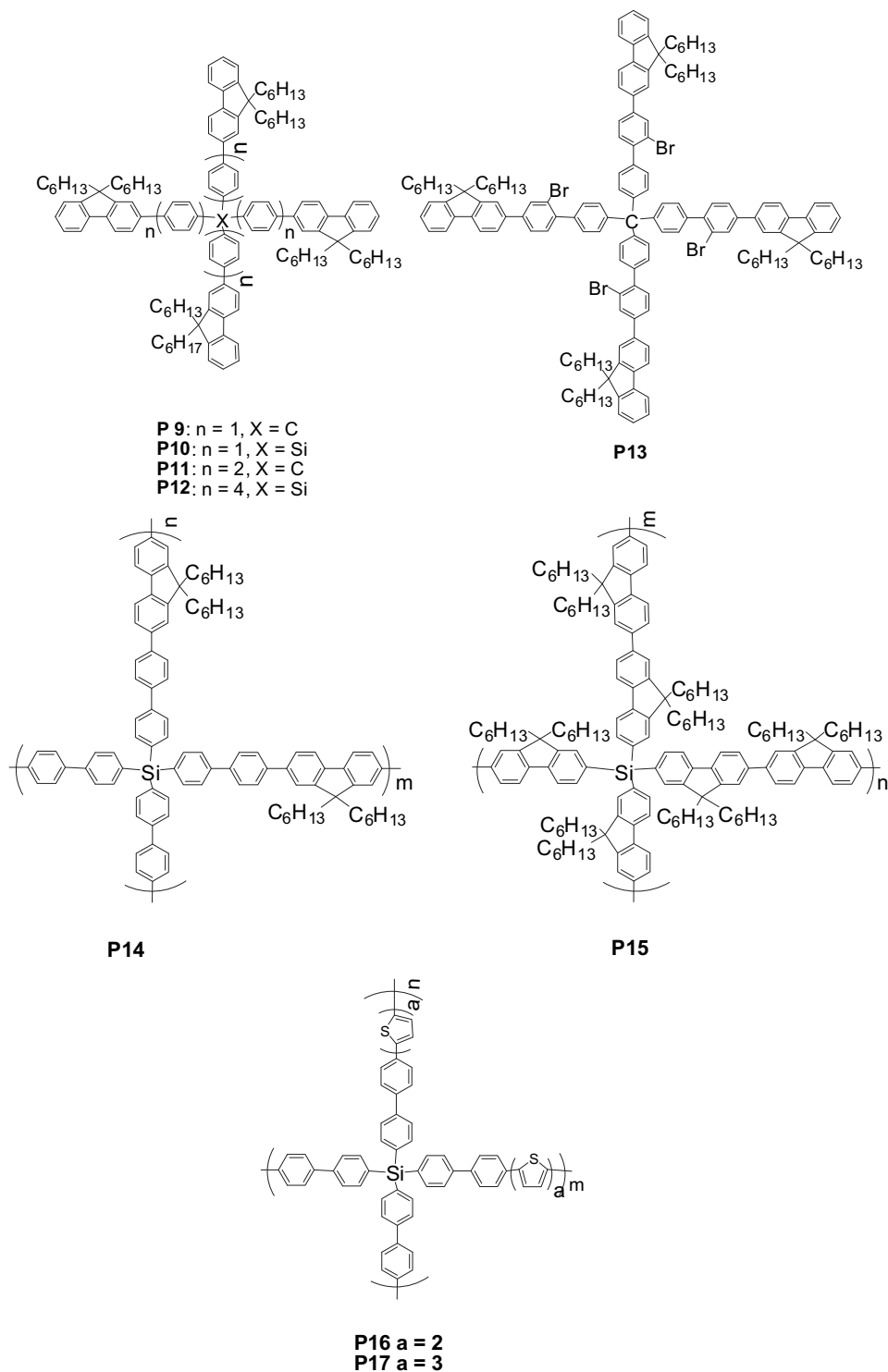


Fig. 5. Structures of star polymers **P9–P13** from Ref. [39] and **P14–P17** from Ref. [40].

concentration was higher than 6 wt.%, while at this concentration the TPP had already aggregated seriously and self-quenching of their fluorescence occurred, which lead to a dramatic decrease in their fluorescence quantum yields. Such results indicated that porphyrin-cored star polymers can be used as potential efficient nondoped red light-emitting materials.

He and coworkers have reported the first blue light-emitting tetrahedral glass-forming molecules (**P9–P13**) derived from fluorene and several tetrahedral core compounds as shown in Fig. 5

[39]. The tetrahedral compounds emitted blue light highly efficiently in both solution and solid state. In a continuation of such research on tetrahedral luminescent materials, they synthesized polymers **P14–P17** by either Suzuki-Miyaura-Schlüter or Grignard polycondensation reactions [40]. Polymers **P14–P17** emitted from blue to red light in the solid state. Their absorption and emission maxima were red-shifted with the increase of conjugation length. Polymer **15** emitted blue light highly efficiently in both solution and solid state.

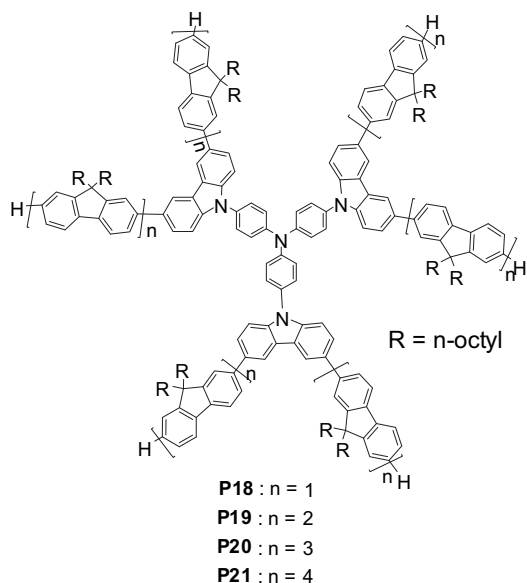


Fig. 6. Structures of star polymers **P18–P21** from Ref. [44].

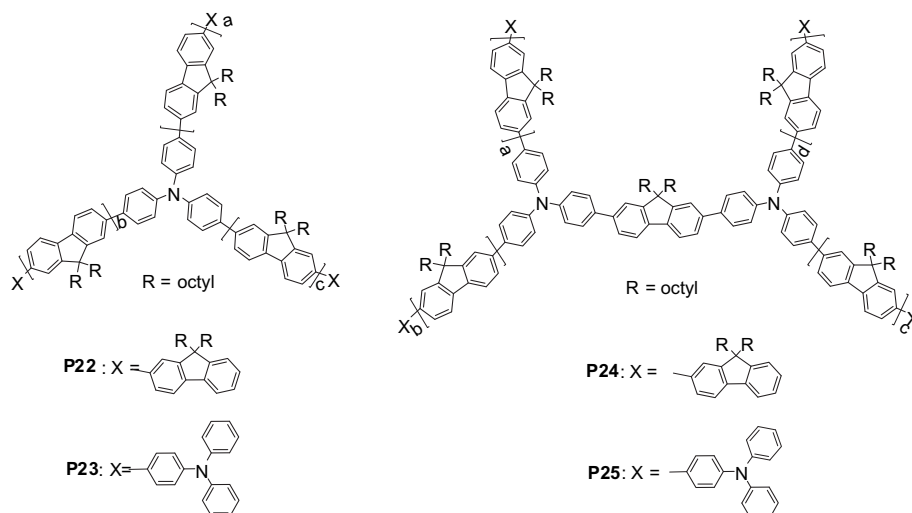


Fig. 7. Structures of three- and four-arm star polymers **P22–P25** from Ref. [46].

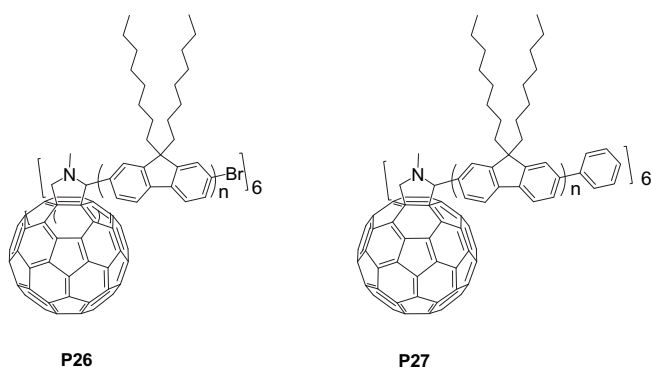


Fig. 8. Structures of polymers **P26** and **P27** from Ref. [51].

Shirota et al. [41,42] have shown that different cores can be used to design star-shaped oligotriarylamines to afford extended conjugation and low oxidation potential compounds. Detailed reviews of such research work on star-shaped molecules have been developed by Shirota et al. and Thelakkat et al. [41–43]. Recently, Ding and his coworkers have synthesized and characterized four monodisperse starburst oligomers bearing a 4,4',4''-tris(carbazol-9-yl)-triphenylamine core and six oligofluorene arms (**P18–P21**) [44] as shown in Fig. 6. The lengths of oligofluorene arms vary from one to four fluorene units. All of the starburst oligomers have good film-forming capabilities and display bright, deep-blue fluorescence both in solution and in the solid state. The photoluminescence quantum efficiencies (Φ) of the films were measured using an integration sphere, which were 0.27, 0.67, 0.81, and 0.88 for **P18**, **P19**, **P20**, and **P21**, respectively. The Φ values for **P20** and **P21** are even higher than those reported for linear polyfluorenes [45]. Deep-blue OLED devices were successfully fabricated using these oligomers as emitters and hole-transporting materials. The presence of the 4,4',4''-tris(carbazol-9-yl)-triphenylamine core was found to be crucial for the hole-transporting process.

In our work, triphenylamine (TPA) and fluorene-based three- and four-arm star polymers were successfully prepared by the

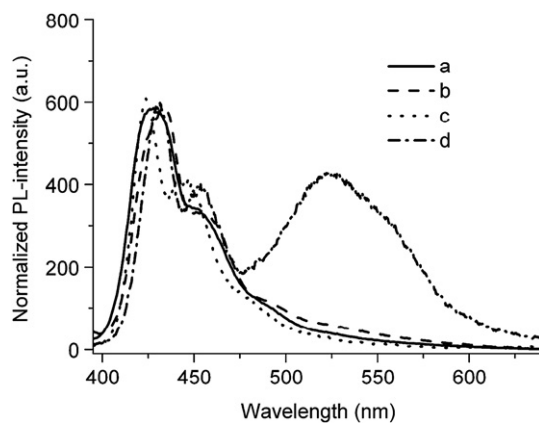


Fig. 9. Film photoluminescent spectra of **P27** before annealing (a) and after annealing at 200 °C for 30 min in air (b); Film photoluminescent spectra of PFO before annealing (c) and after annealing at 200 °C for 30 min in air (d) from Ref. [51].

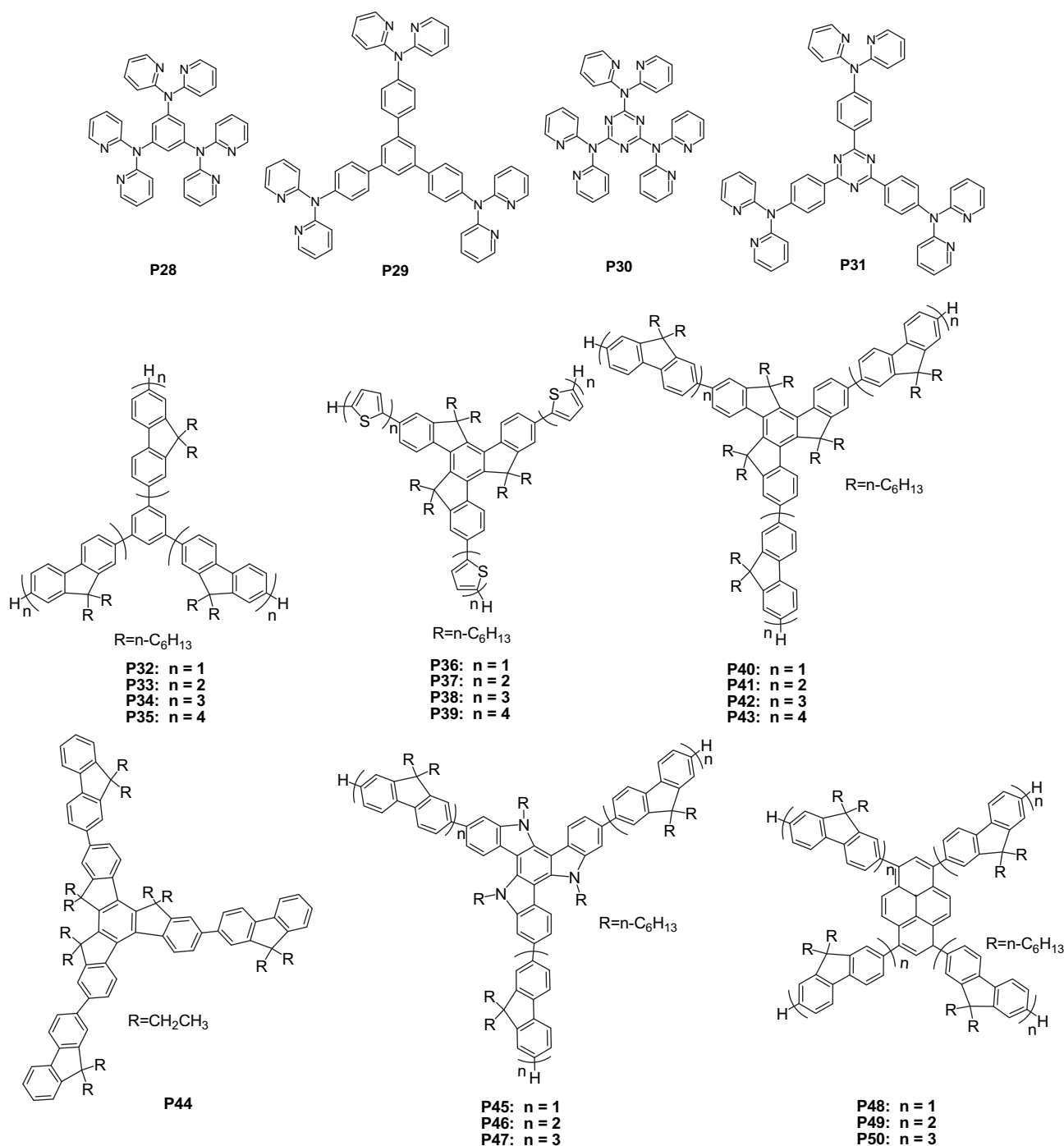


Fig. 10. Structures of polymers **P28–P31** from Ref. [53], **P32–P35** from Ref. [54], **P36–P39** from Ref. [55], **P40–P43** from Ref. [56], **P44** from Ref. [57], **P45–P47** from Ref. [58], and **P48–P50** from Ref. [60].

Suzuki-Miyaura-Schlüter polycondensation (SPC) of multifunctional cores and AB-type monomers [46]. As shown in Fig. 7, star polymers (**P22–P25**) possess of moderate molecular weight and mono-model molecular weight distribution.

It was well known that fullerenes are fascinating molecules with I_h symmetry. Thus, three-dimensional architectures can be afforded by the functionalization of fullerenes using multiple addition reactions [47–50]. In our work, the C60-cored star polyfluorenes **P26–P27** were prepared by Suzuki-Miyaura-Schlüter polycondensation (SPC) of the hexakisadduct core with 2-bromo-9,9-dioctylfluorenyl-4,4,5,5-tetramethyl-[1,3,2]-dioxaborane [51].

Chemical structures are shown in Fig. 8. The modification of the peripheral bromo endgroups of hexakisadducts (**P26**) with Suzuki-Miyaura-Schlüter polycondensation afforded the C60-cored star polyfluorenes (**P27**). The emission spectrum of the C60-cored star polyfluorene **P27** is similar to that of PFO with an emission maximum at 414 nm and shoulder at 435 nm. The film emission spectra of C60-cored star polyfluorene **P27** and PFO before and after annealing at 200 °C for 0.5 h are shown in Fig. 9. Although low energy green emission band at around 525 nm in the control experiment for PFO already became very pronounced, no evident change was found for the emission spectrum of **P27**. As expected,

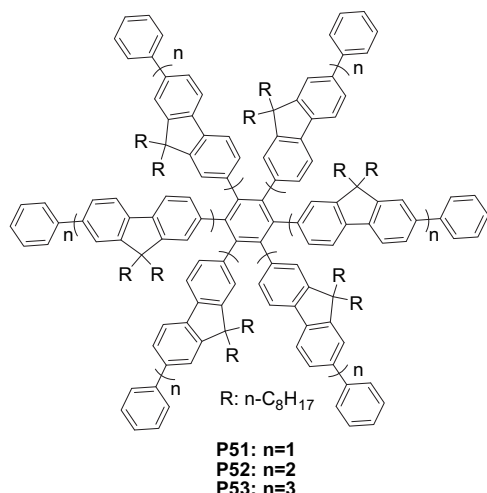


Fig. 11. Structures of polymers **P51**–**P53** from Ref. [61].

the three-dimensional structure can effectively reduce the aggregation of the polyfluorene chains and the detrimental green emission is suppressed.

Three-arm benzene-cored, six-arm truxene-, triazatruxene- and isotruxene-cored star oligofluorenes have been prepared and their optical properties have been investigated [52]. For example, Wang and coworkers [53] have synthesized and characterized four novel star-shaped blue luminescent compounds based on di-2-pyridylamino derivatives of 1,3,5-triazine (**P30**–**P31**) and 1,3,5-trisubstituted benzene (**P28**–**P29**) as shown in Fig. 10. Their research indicated that these four compounds were bright photoluminescent blue emitters. Pei and his coworkers have also presented convenient and efficient approaches to synthesize soluble star-shaped C_3 -symmetric 1,3,5-tri(oligofluorenyl)-benzene derivatives (**P32**–**P35**) [54] and oligothiophene-functionalized polycyclic aromatics based on truxene (**P36**–**P39**) [55].

Perepichka et al. have presented a facile approach to synthesize highly luminescent soluble monodisperse star-shaped oligofluorenes with a truxene central core (**P40**–**P43**) [56]. These star-shaped macromolecules **P40**–**P43** showed very efficient blue

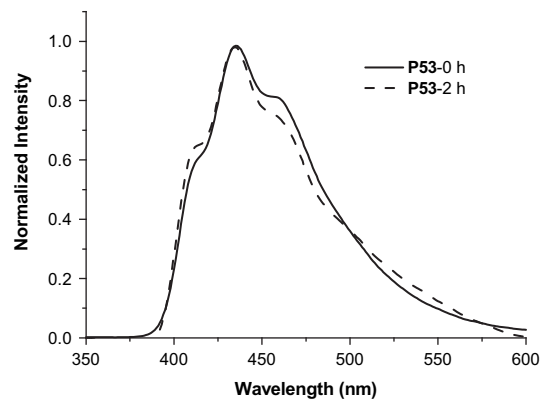


Fig. 12. Film emission spectra of **P53** before and after annealing at 200 °C in air for 2 h from Ref. [61].

photoluminescence at 398–422 nm in both solution ($\Phi = 0.70$ – 0.86) and solid state ($\Phi = 0.43$ – 0.60) with quinine sulfate ($\Phi = 0.546\%$) as a standard.

Yang et al. have developed the first isotruxene-based star-shaped system with an isotruxene core and three fluorene arms (**P44**). **P44** displays promising light-emitting properties and thermo stabilities [57]. Huang and his coworkers have described an effective strategy to achieve highly efficient pure blue electroluminescence (EL) via a novel series of six-arm monodisperse macromolecules based on the triazatruxene and fluorene units (**P45**–**P47**) [58,59]. Moreover, they have also synthesized and characterized a series of starburst materials (**P48**–**P50**) based on a pyrene core with four oligofluorene arms of different length [60]. The single-layered device made of **P50** showed a max brightness of over 2700 cd/m^2 and a max current efficiency of 1.75 cd/A . These preliminary findings show that these starburst materials are promising light-emitting materials.

Recently, we have reported the synthesis of six-arm benzene-cored oligofluorenes [61]. We employed divergent/convergent strategy [62], which start from the repetitive divergent synthesis of symmetrical ethynyl bridged oligofluorenes to the convergent Co-catalyzed alkyne cyclotrimerization. The structures of polymers (**P51**–**P53**) were shown in Fig. 11. These highly substituted star-

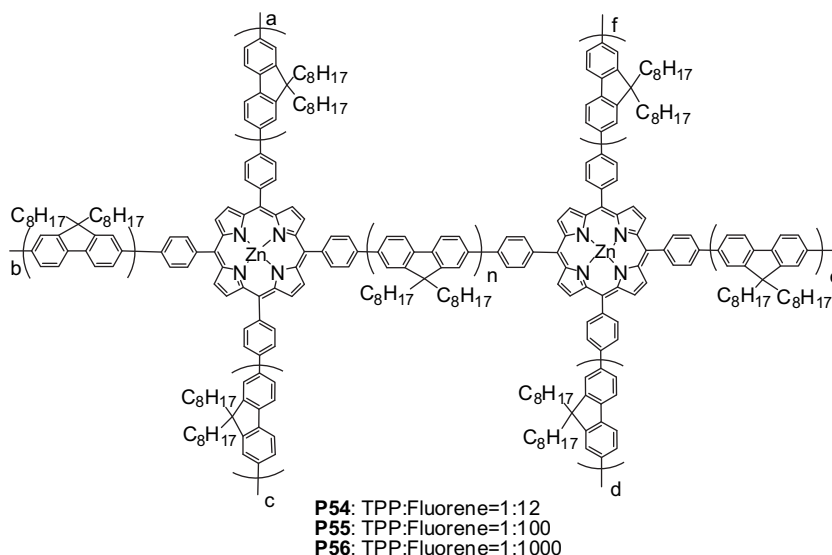


Fig. 13. Structures of polymers **P54**–**P56** from Ref. [63].

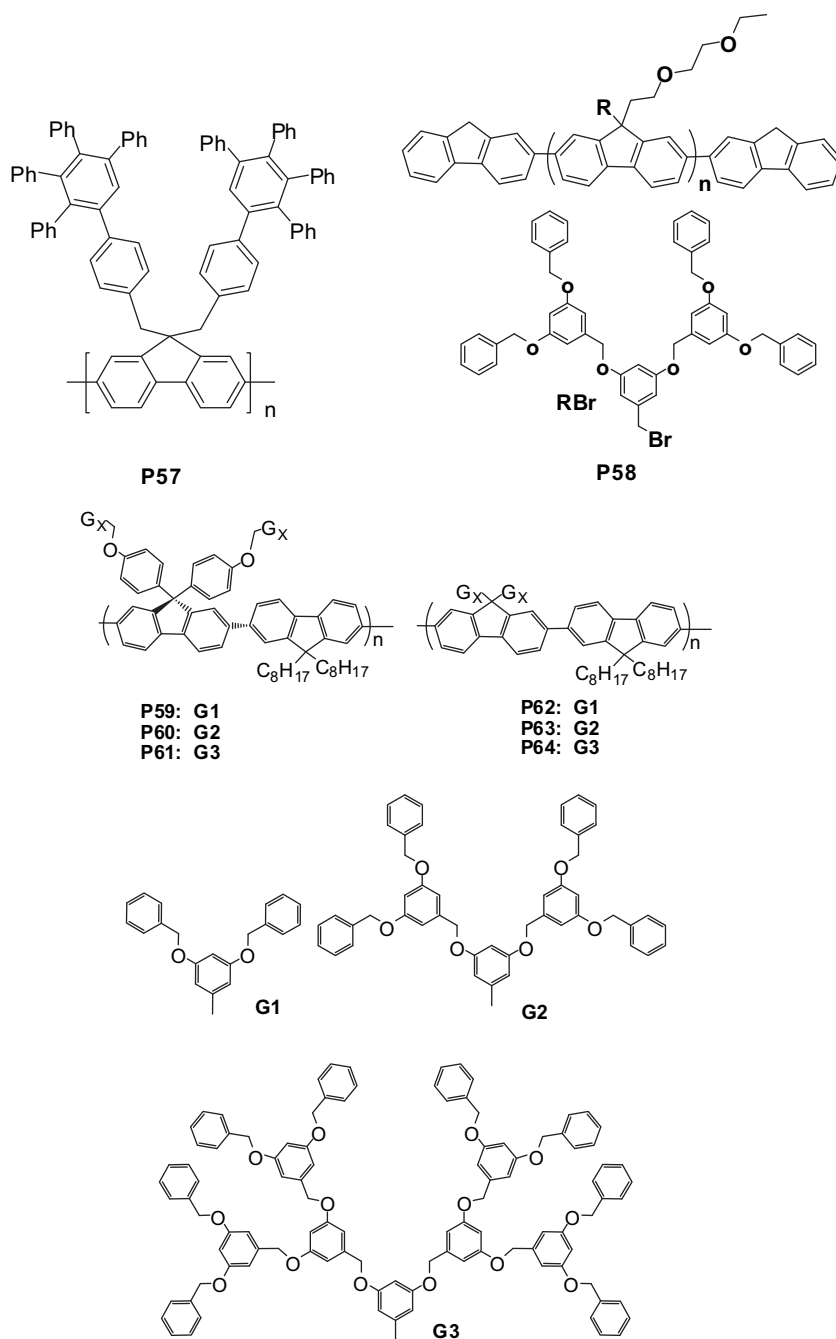


Fig. 14. Structures of polymers **P57** from Ref. [79], **P58** from Ref. [80], **P59–61** from Ref. [73], **P62–P64** from Ref. [81].

shaped oligomers exhibit extremely high fluorescent quantum yields in solution and good thermal and color stabilities in the solid state. The photoluminescence quantum yields (Φ) of star oligofluorenes **P51**, **P52**, and **P53** in dilute THF solution were measured to be 0.95, 0.95, and 0.96, respectively, using 9,10-diphenylanthracene as the reference standard (0.90 in THF). Furthermore, no evident change was found for the emission spectrum of **P53** after annealing at 200 °C in air for 2 h as shown in Fig. 12.

More recently, Li et al. have designed and synthesized three novel zinc tetraphenylporphyrin (ZnTPP)-fluorene copolymers **P54**, **P55** and **P56** [63], with different ZnTPP content based on a facile one-pot Suzuki polycondensation reaction as shown in Fig. 13. The EL devices of **P54**, **P55** and **P56** displayed much lower turn-on

voltages and higher luminance than those of the devices based on TPP/PFO. The maximal luminance and current efficiency are 740, 1040, and 2320 cd/m² and 0.06, 0.23, and 0.45 cd/A for **P54**, **P55**, and **P56**, respectively. **P54** as emitting material showed pure red emission (CIE coordinates of $x = 0.64$, $y = 0.30$) with a narrow fwhm (28 nm) of the EL peak and a luminance of 740 cd/m² at a driving voltage of 17.4 V.

3. Dendronized polymers based light-emitting materials

Dendronized polymers are dendrimers with a central linear polymeric core and have attracted considerable scientific attention due to their unique structures and properties since the mid-1980s

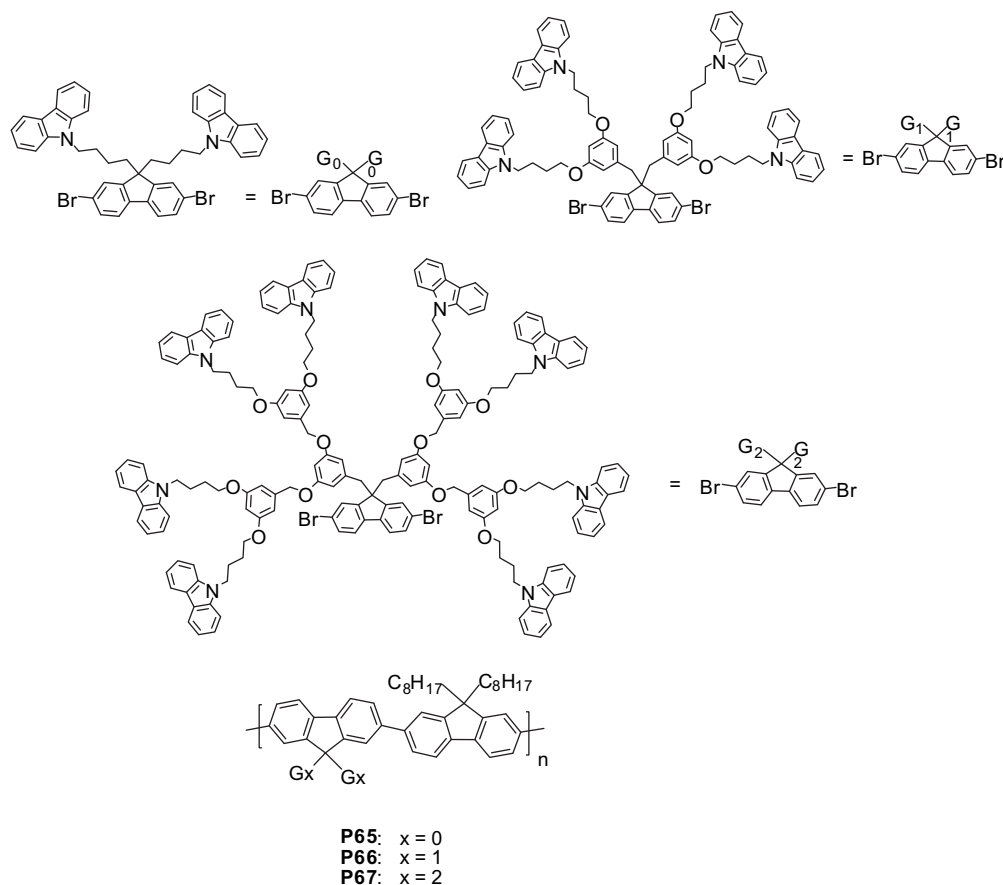


Fig. 15. Structures of polymers P65–P67 from Ref. [82].

[64]. Different parts of dendrimers can be selectively functionalized to give the desired optoelectronic and processing properties. Dendronized polymers with a conjugated polymer backbone are of special interest due to their potential applications as “nanowires” and light-emitting materials. Many conjugated linear polymers were used as backbones of dendronized polymers, including poly(*p*-phenylene)s [64,65], poly(*p*-phenylene-vinylene)s [66], poly(*p*-phenylene-ethynylene)s [67], poly(triacetylene)s [68], poly(acetylene)s [69], poly(thiophene)s [70,71], binaphthyl-based poly(arylene)s [72], and poly(flourene)s [73].

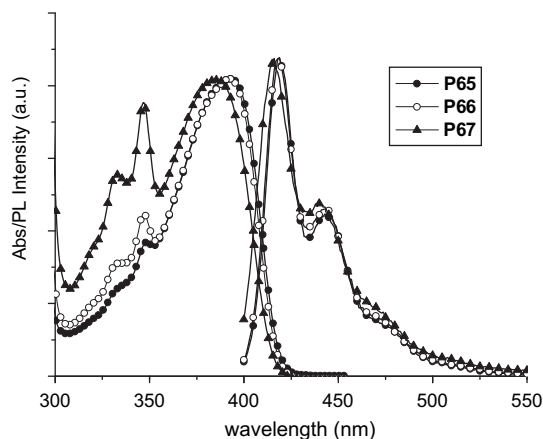


Fig. 16. UV–vis absorption and PL spectra (excited at 388 nm) of dendronized polymers P65–P67 in THF from Ref. [82].

There are a number of potential advantages for dendronized polymers over conjugated polymers and small molecular as light-emitting materials. First, they possess a rod-like, cylindrical shape with the polymer backbone encapsulated into the dendritic envelope. The “site isolation” effect of dendritic wedges can prevent the conjugated backbone from doing cross-talk [74,75]. Second, solubility and especially, optical properties of the molecules can be adjusted by selecting the appropriate surface functional groups. For example, Jiang, Aida, and other research groups have shown that the luminescent activity of the conjugated backbone can be significantly enhanced with the increasing of the generation [76]. Meanwhile, the solubility of the dendrimers opens the way for simple processing required for flat-panel displays. Finally, intermolecular interactions of chromophores can be controlled by the type and generation of dendrons employed.

It was very worthwhile to mention that the syntheses of many kinds of dendronized polymers have been well documented by Schlüter et al. in two recent reviews [77]. In our work, we paid particular attention to the macromonomer route because it can accomplish dendronized polymers carrying structurally perfect

Table 1

The molecular weights, thermal properties, and the photoluminescence quantum yield of P65–P67 in THF and as films measured with 9,10-diphenylanthracene as a reference standard (toluene, $\Phi = 0.9$) from Ref. [82].

Polymer	M_n (g/mol)	P_n	M_w (g/mol)	P_w	M_w/M_n	T_g (°C)	Φ_F in solution	Φ_F films
P65	46700	47	104,000	104	2.21	103	0.93	0.29
P66	131,000	78	157,000	93	1.20	73	0.96	0.55
P67	143,000	47	171,000	60	1.19	73	0.86	0.64

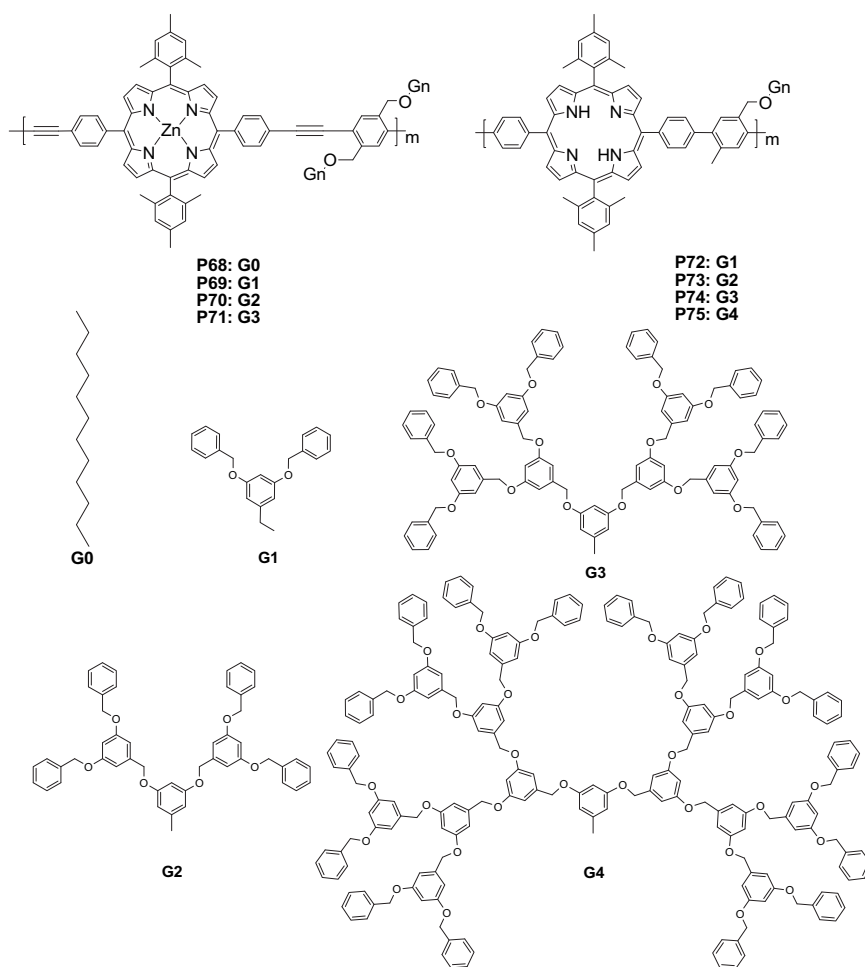


Fig. 17. Structures of polymers **P68–P71** from Ref. [83] and **P72–P75** from Ref. [84].

dendrons. Recently, Burn and Samuel have also made a significant review about how the structure of the light-emitting dendrimers controls key features such as intermolecular interactions and charge transport, which are important for all OLED materials. In their review, advantages of the dendrimer architecture for phosphorescent emitters, the way about how to change the structure to enhance material performance, and device design have been well described [78].

Müllen et al. have prepared polyfluorene **P57** with bulky polyphenylene dendrimer substituent as shown in Fig. 14 [79], which can suppress formation of long wavelength emitting aggregates.

Absorption, emission spectra and molecular modeling confirm that the bulky dendrimer side chains do not cause extra torsion between the fluorene units and give **P57** with pure blue emission. Fujiki group reported an asymmetrically substituted polyfluorene (**P58**) bearing a bulky poly (benzyl ether) dendron and a less bulky 3,6-dioxaocetyl group in the C-9 position. The research results showed that this polymer can give a pure blue photoluminescence with negligible excimer emission around 520 nm [80]. Shu et al. have synthesized dendronized polymers consisting of a conjugated polyfluorene backbone appended with different generations of poly (benzyl ether) dendritic wedges (**P59**, **P60**, **P61**) [73].

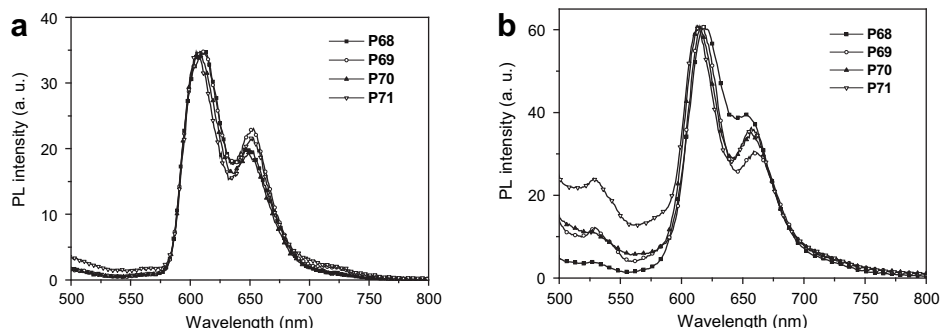


Fig. 18. The photoluminescence spectra of **P68–P71** in toluene (a) and in films (b) (ex at 430 nm) from Ref. [83].

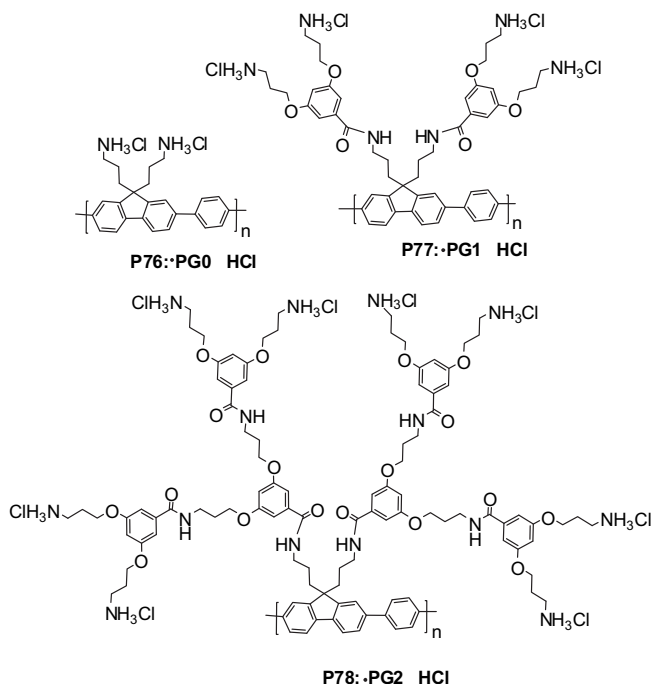


Fig. 19. Structures of polymers **P76**–**P78** from Ref. [86].

Photophysical studies revealed that the size of the dendrimer side chain has a significant influence on the luminescence activity of the dendronized polymers. The large framework of higher generation dendrons, such as **P61**, not only prevents self-quenching, but also suppresses aggregate/excimer formation, leading to an enhancement in photoluminescence (PL) efficiency and luminescent stability. Carter and his coworkers have prepared dendrimers (**P62**, **P63**, **P64**) with several 2,7-dibromo-fluorene monomers containing benzyl ether dendrons at the 9-position [81]. They discovered that there was an apparent optimum size of the dendritic side groups, which leads to aggregation-free solid state spectra and high PL quantum efficiencies.

In our work, we have reported firstly the synthesis of a family of high molecular weight, dendronized poly (fluorene)s carrying peripheral carbazole functional groups by Suzuki-Miyaura-Schlüter polycondensation (**P65**–**P67**) [82]. The structures were shown in Fig. 15. The idea in such molecular structural design was to make

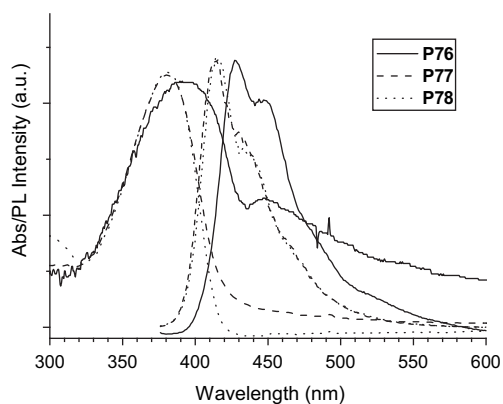


Fig. 20. UV–vis absorption and photoluminescence spectra (excited at 360 nm) of dendronized polymers **P76** (PG0·HCl), **P77** (PG1·HCl), and **P78** (PG2·HCl) in water (1 mg/mL) from Ref. [86].

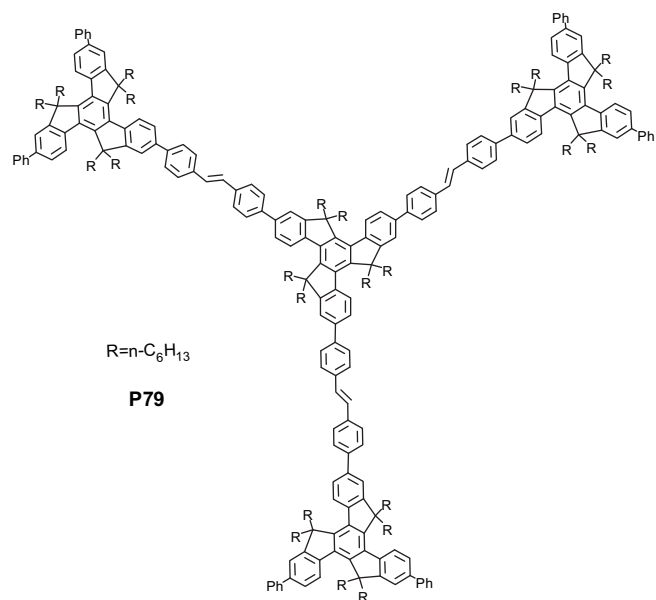


Fig. 21. Structures of polymers **P79** from Ref. [87].

the dendritic wedges play the role of not only site isolation but also hole-transporting. The UV–vis absorption and PL spectra were shown in Fig. 16. The molecular weights, thermal properties, and the fluorescence quantum yield of **P65**–**P67** in THF and as films are summarized in Table 1. Such studies showed that these kinds of dendronized polymers exhibited high quantum efficient yields in solution and films (mainly for second generation **P67**), which were promising blue light-emitting materials.

Planar porphyrin molecules have a tendency to form aggregation in the solid state, which is a disadvantage when they are used as light-emitting materials. In our work, we have successfully

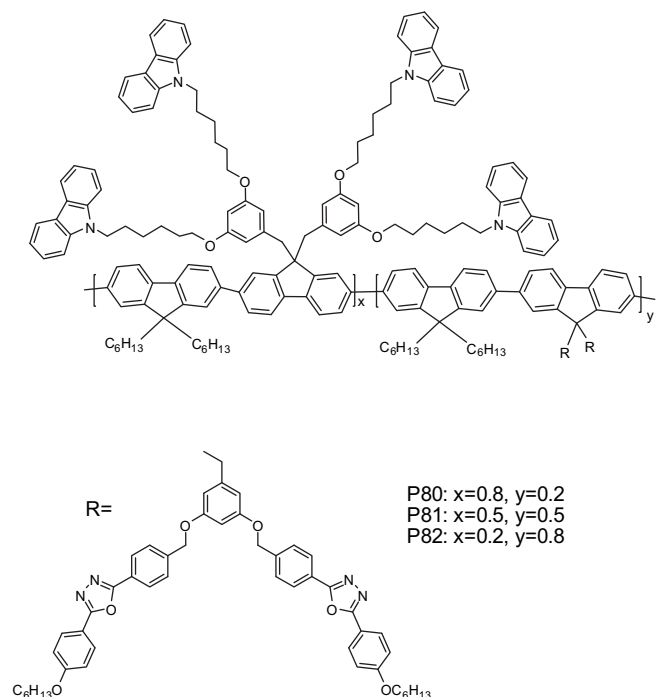


Fig. 22. Structures of polymers **P80**–**P82** from Ref. [89].

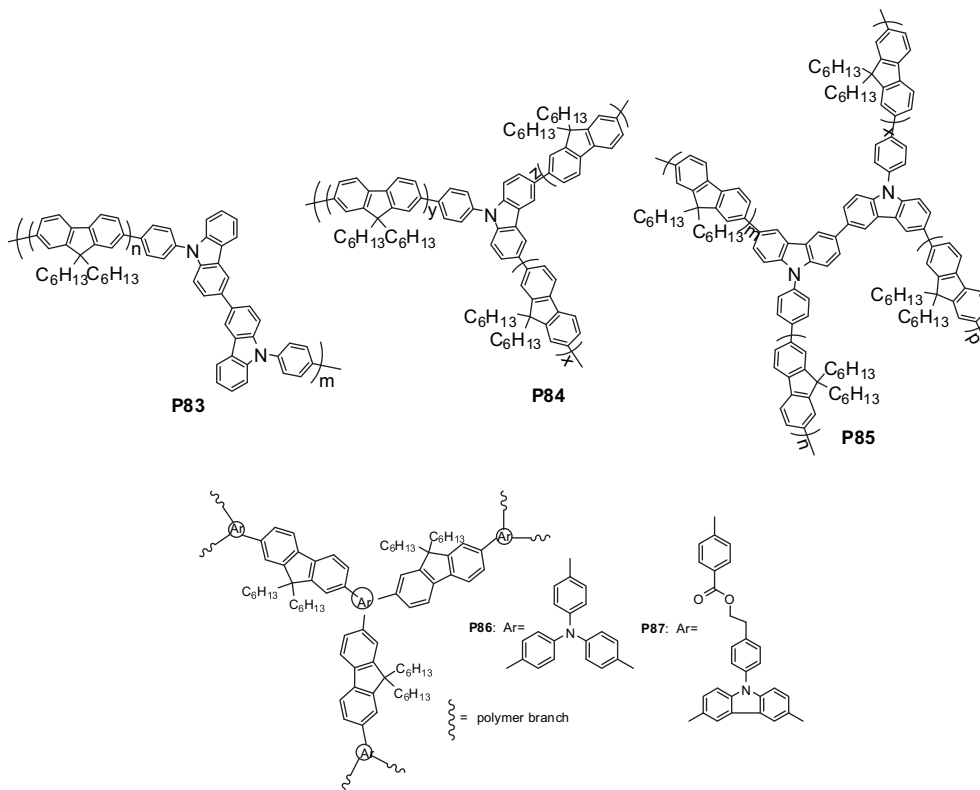


Fig. 23. Structures of polymers **P83–P85** from Ref. [95] and **P86–P87** from Ref. [96].

synthesized a family of red light-emitting dendronized porphyrin polymers (**P68–P71**) [83] by Sonogashira coupling of dendritic macromonomers and porphyrin monomers as show in Fig. 17. The higher generation dendritic wedges of Fréchet-type dendrons (higher than 2) can not only effectively wrap the polymer backbones and reduce their aggregation but also provide good solubility for the conjugated porphyrin polymers serving as red light-emitting materials. As shown in Fig. 18, all the dendronized polymers **P68–P71** exhibited an emission peak at about 605–611 nm and a shoulder at 649–652 nm. The photoluminescence quantum yields of dendronized polymers with ZnTPP as standard ($\phi = 0.033$) in toluene solutions (excited at 425 nm) were 0.048, 0.047, 0.043, and 0.034 for **P68–P71**, respectively.

Continuously, we further synthesized a series of dendronized porphyrin polymers **P72–P75** [84] up to fourth generation **P75** by Suzuki–Miyaura–Schlüter polycondensation. All polymers exhibited an intense red emission peak at around 651 nm and a shoulder at 720 nm, which located in the saturated red light region. The photoluminescence quantum yields of **P73**, **P74**, and **P75** in dilute toluene solution were measured in comparison to TPP ($\phi = 0.11$) to be 0.15, 0.16 and 0.17, respectively, higher than many other porphyrin derivatives. Such results indicated that the higher generation dendronized structure could significantly reduce the aggregation of planar porphyrin chromophores and the quantum yields of the polymers increased with the increasing of the generation of dendrons.

As known, fluorene-based polyelectrolytes often show photoluminescence quantum efficiencies lower than those of typical fluorene-based polymers in organic solvents [85]. This is mainly due to the aggregation of water-soluble conjugated polymer chains in aqueous media. In our work, we incorporated peripheral charged amino groups into a series of cationic water-soluble dendronized polyfluorenes (**P76**, **P77**, **P78**) as shown in Fig. 19 [86]. The

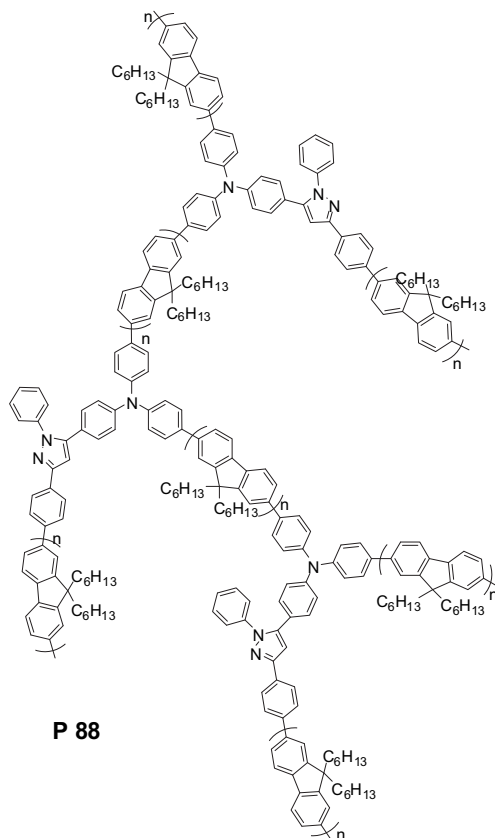


Fig. 24. Structures of polymers **P88** from Ref. [97].

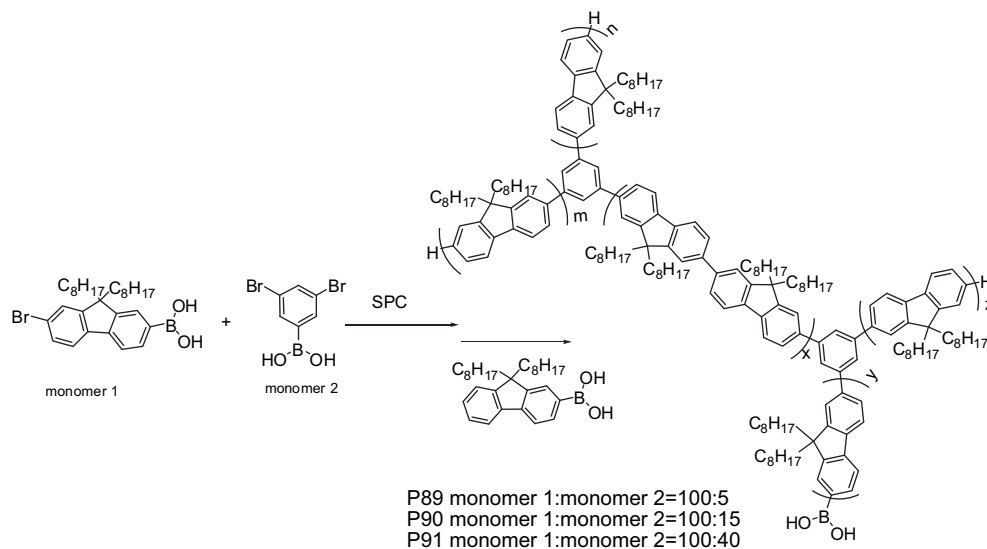


Fig. 25. Structures of polymer **P89**–**P91** from Ref. [98].

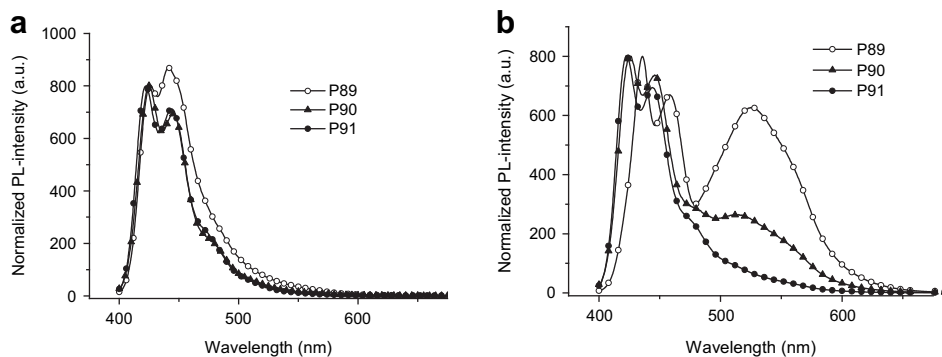


Fig. 26. Photoluminescent spectra of **P89**, **P90**, and **P91** in solid films: (a) before annealing; (b) after annealing at 200 °C for 30 min in air from Ref. [98].

introduction of lateral dendrons, as expected, should not only provide the conjugated polymers with good solubility in water solution through the charged amino groups, but also reduce the aggregation of polymers through the “site isolation” effect of dendrons. The UV–vis absorption and photoluminescence spectra (excited at 360 nm) of **P76**, **P77**, and **P78** in water (1 mg/mL) were shown in Fig. 20. The photoluminescence quantum yields of dendronized polymers in water increased from 0.17 for zero generation **P76** to 0.85 for first generation **P77** and further to 0.94 for second generation **P78** with quinine sulfate ($\Phi = 0.55$) as standard. The extremely high photoluminescence quantum efficiency of the second generation water-soluble dendronized polyfluorene **P78** indicated higher generation with lateral dendrons can effectively prevent polyfluorene chains from aggregation in water solution; the aggregation of polyfluorene chains will quench their fluorescence and result in lower quantum yield.

More recently, Pei et al. have reported a solution-processible fluorescent π -conjugated blue dendrimer **P79** as color-stable deep-blue-emitting OLEDs with high efficiency [87,88]. The structure is shown in Fig. 21. The saturated blue OLED based on **P79** showed the highest luminance efficiency of 5.3 cd/A and 6.6% (external quantum efficiency) at a current density of 10.7 mA/cm² with a luminance of 550 cd/m², and had CIE coordinates of (0.155, 0.086). At the maximum luminance around 17,000 cd/m² and with a current density of 650 mA/cm², the CIE coordinates became

(0.156, 0.091), showing impressive color stability. With such high efficiency at high current density and excellent color stability, the deep-blue fluorescent dendrimer **P79** is promising not only for the application in full-color flat-panel displays but also for the fabrication of white OLEDs in solid state lighting.

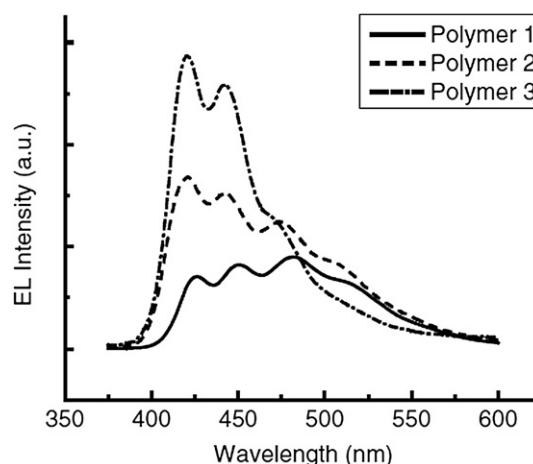


Fig. 27. EL spectra for devices ITO/PEDOT/polymer/Ca from Ref. [99].

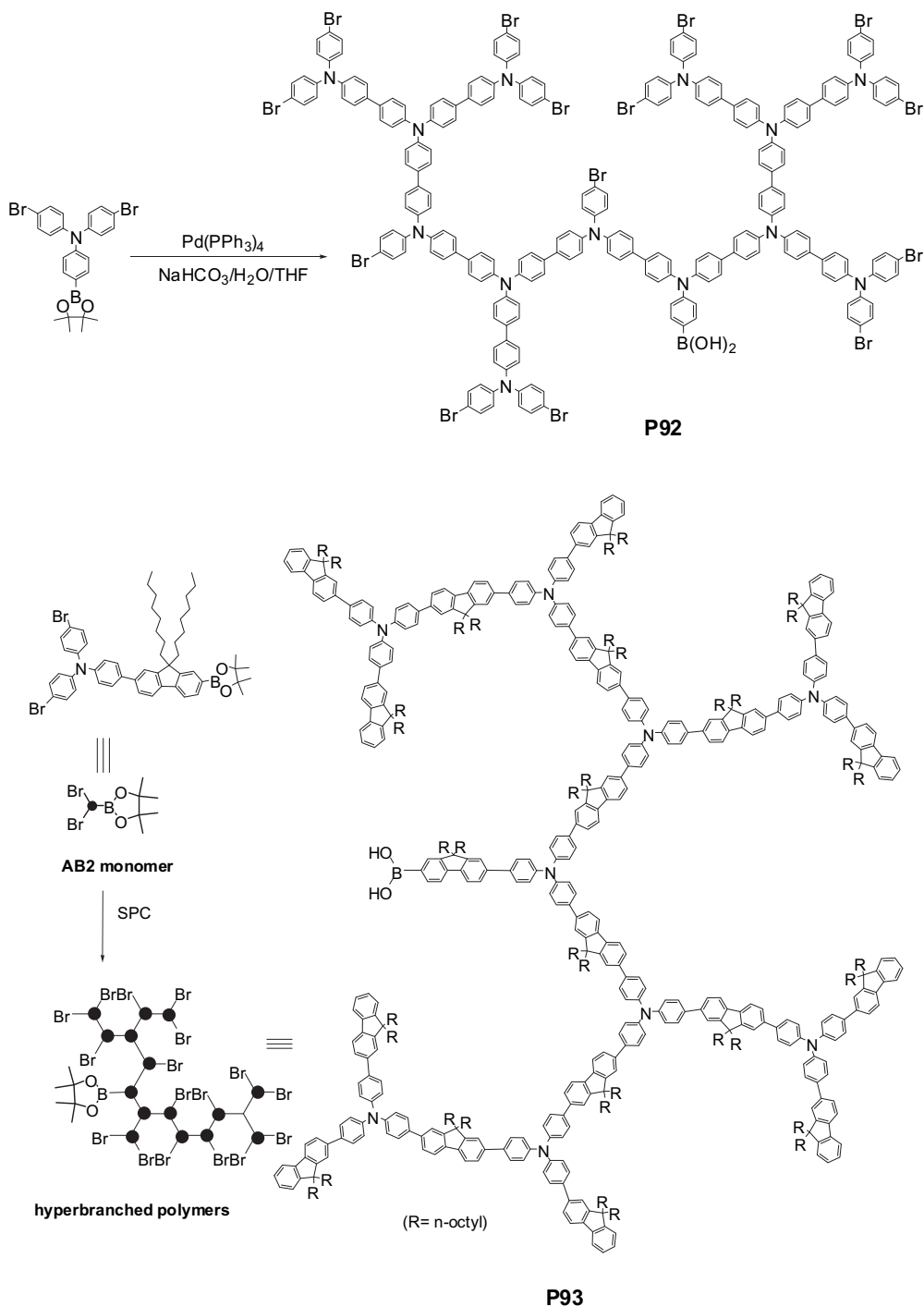


Fig. 28. Structures of polymers **P92** and **P93** from Ref. [101].

Peng et al. have successfully designed, synthesized, and characterized a series of new polyfluorenes **P80**, **P81**, and **P82** with dendritic functional carbazole and oxazole side chains as shown in Fig. 22 [89]. The color quality of photoluminescent and electroluminescent emission was improved very much due to less aggregates of main chains of polyfluorenes with the steric hindrance of dendritic functional carbazole and oxazole units. The electroluminescent devices based on these copolymers as blue emitters and host materials were fabricated and evaluated. The results indicated that these copolymers were promising candidates for both efficient pure blue emitters and host materials for highly efficient phosphorescent PLEDs.

4. Hyperbranched polymers as efficient light-emitting materials

Hyperbranched polymers have attracted increasing scientific and industrial attention in recent years due to their unusual chemical and physical properties such as highly branched and compact three-dimensional structures, large numbers of terminal functional groups, and low intrinsic viscosities [90,91]. The highly branched three-dimensional structure can effectively reduce the aggregation of polymer chains, endow the polymer with good solubility in common organic solvents, and make the polymer form good quality amorphous films [92]. The synthesis of many kinds of



Fig. 29. Structures of polymers **P94**–**P97** from Ref. [102].

hyperbranched polymers has been well documented in several review articles [93]. An elegant synthesis of porphyrin based hyperbranched polymers was achieved by Hecht and Fréchet through an A₂ + B₃ approach [94]. However, there are still limited examples of hyperbranched polymers used as blue and red light-emitting materials.

Table 2

Feed ratios, molecular weights, and polydispersity (PD) of hyperbranched porphyrins **P94**–**P97** from Ref. [102].

Polymers	Feed ratio (AB ₃ monomer/C ₄ monomer)	Mn	Mw	PD
P94	1:0	33400	146,000	4.3
P95	8:1	10600	17,000	1.6
P96	12:1	11200	173,000	1.5
P97	18:1	14300	25,000	1.8

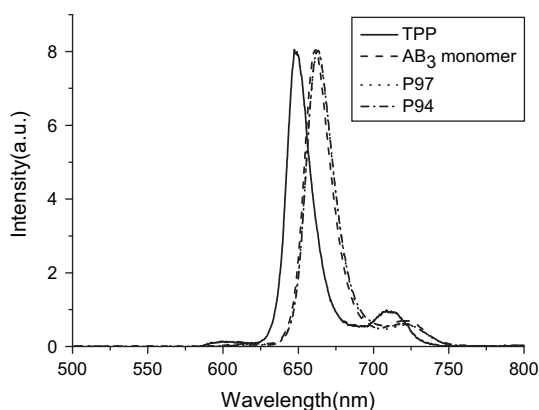


Fig. 30. Fluorescence spectra of TPP, AB₃ monomer, P94, and P97 in THF solution from Ref. [102].

Lin and his coworker have developed a series of novel kinked and hyperbranched carbazole polymers (P83, P84, P85) by the Suzuki coupling polycondensation reaction as shown in Fig. 23 [95]. They introduced disorder packing into the copolymer backbones to decrease the aggregation phenomena. All of these polymers exhibited high blue light quantum efficiencies in solution and solid states and possessed excellent thermal stability by annealing studies under air. Liu and Qin have prepared hyperbranched light-emitting polymers (P86, P87) by copolymerization of tribromoaryl moieties and 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) using “A₂+B₃” approach based on Suzuki-Miyaura-Schlüter polycondensation reaction [96]. P86 and P87 emit strong blue light upon excitation.

Peng et al. prepared a series of hyperbranched, polyfluorenes possessing triarylpyrazoline cores based on the Suzuki coupling protocol [97] as shown in Fig. 24. The device configuration based P88 exhibited good EL properties, which emitted pure blue light with a turn-on voltage of 5.3 V and exhibited an EL efficiency of nearly 2%.

The idea of our work is to introduce branching units into the conjugated polymers to make polymers be of hyperbranched structure, which helps to depress the aggregation of conjugated polymer chains. Directed by these ideas, we have developed an “AB₂ + AB” approach based on Suzuki-Miyaura-Schlüter polycondensation (SPC) to obtain hyperbranched polymer P89–P91 as shown in Fig. 25 [98]. Three polymers P89, P90, and P91 were obtained by taking monomer 1 and monomer 2 in molar ratios of 100:5, 100:15, and 100:40, respectively. Polymer P89–P91 exhibited good solubility in common organic solvents and very good color stability. After thermal treatment of the solid films at 200 °C for 30 min in air, P89 film exhibits the low energy long wavelength emission band at around 525 nm in green-blue region, which might be due to the aggregation and formed excimers of polymer chains. However, for P91 film, no green-blue band emission was observed after thermal treatment of the solid films at 200 °C for 30 min in air as shown in Fig. 26. This result indicated that hyperbranched structure could prevent the aggregation and crystallization of the rigid polymer chains. Furthermore, these hyperbranched conjugated polymers with more benzene cross-points show higher EL efficiency due to the effective exciton confinement and the reduction of intrachain or interchain exciton annihilation as shown in Fig. 27 [99]. It is very interesting to note that this is the first report of hyperbranched polymers being used as blue light-emitting materials.

Triphenylamine (TPA) based polymers have been used as hole-transporting materials for light-emitting diode. TPA-based hyperbranched polymers have been prepared by Tanaka and Wang et al. via Grignard and Negishi coupling reactions. The AB₂ monomers used above are moisture and air sensitive, and used as prepared without further characterization and checking their purities [100]. The drawback obviously limited the application scope of these methods. As shown in Fig. 28, we have developed a more applicable methodology to prepare hyperbranched TPA polymers (P92 and P93) [101]. TPA-based AB₂ monomers carrying two bromo functional groups and one pinacol protected boronic acid group have been designed, prepared, and used for Suzuki-Miyaura-Schlüter

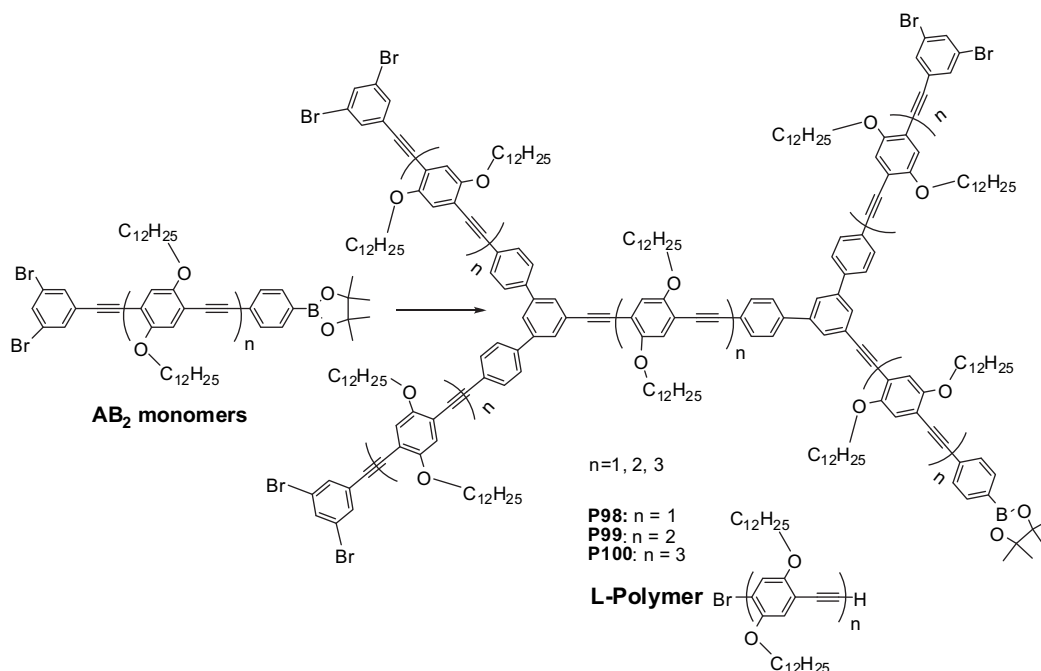


Fig. 31. Structures of polymers P98–P100 from Ref. [103].

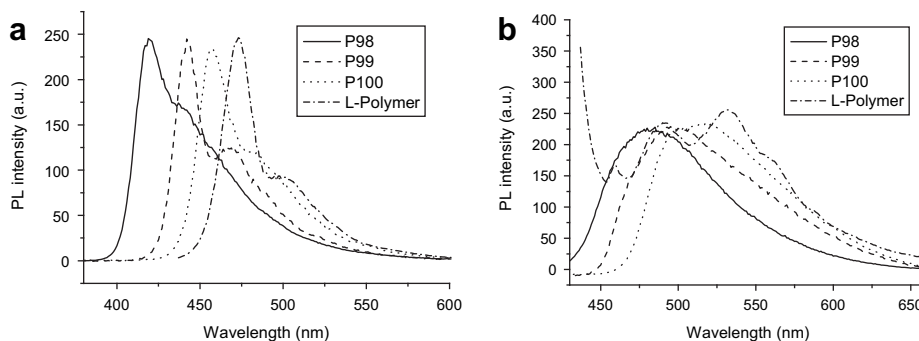


Fig. 32. Photoluminescent spectra of **P98–P100** and L-Polymer in toluene solutions (a) and solid films (b) from Ref. [103].

polycondensation to prepare hyperbranched TPA polymers. The above mentioned AB_2 monomers can be purified by flash chromatography on silica gel and fully characterized by standard characterization methods. Prepared TPA-based hyperbranched polymer **P92** has a number average molecular weight of 7300 and weight average molecular weight of 9800. The introduction of 9,9-dioctylfluorene or its trimer as the core, the solubility of hyperbranched polymers can be increased and the molecular weight of polymer can be controlled by the feed ratio of core molecule to AB_2 monomer. Thus, the polymerization of AB_2 monomer carrying two flexible alkyl chains afforded high molecular weight of hyperbranched polymer

P93 with a number average molecular weight of 146,000 and weight average molecular weight of 169,000, which is fully soluble in common organic solvents and the peripheral bromo functional groups can be further modified. The photoluminescence quantum yields of the hyperbranched polymers in toluene solution were 0.75 and 0.52 for **P92** and **P93**, respectively, which were measured using a dilute solution of 9,10-diphenylanthracene in toluene ($\Phi = 1.0$) as the standard.

We have also developed a highly efficient method to synthesize a novel kind of hyperbranched porphyrin arrays (**P94, P95**) [102] by one-pot Suzuki-Miyaura-Schlüter polycondensations of AB_3

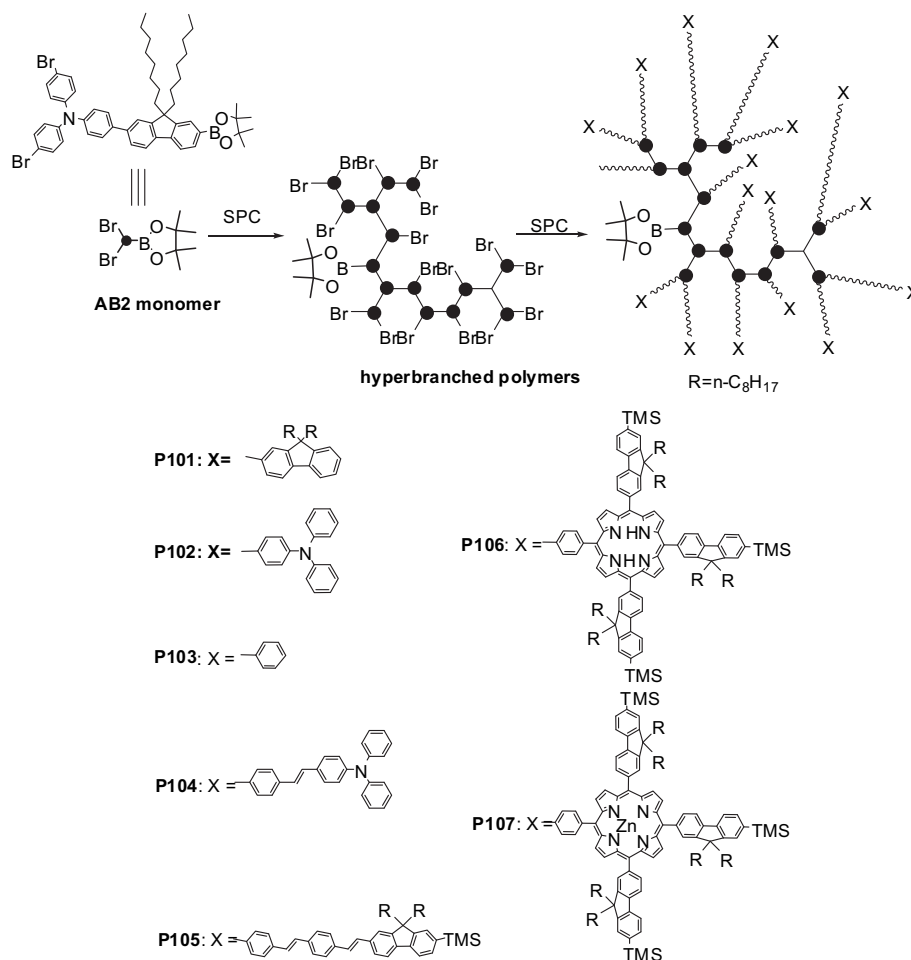


Fig. 33. Structures of polymers **P101–P107** from Ref. [112].

Table 3

Absorption, fluorescence maxima (λ_{\max}), and the photoluminescence quantum efficiency (Φ) of **P102**–**P107** from Ref. [112].

Polymer	Absorption (λ_{\max}/nm)			Fluorescence (λ_{\max}/nm)			Φ
	THF	Toluene	Film	THF	Toluene	Film	
P102	384	384	385	436	430	438	0.51
P103	384	384	381	440	431	444	0.45
P104	393	395	392	460	448	483	0.41
P105	398	399	395	490	466	500	0.63
P106	427	429	434	659	659	663	0.16 ^a
P107	433	438	–	616	620	–	0.03 ^b

^a Tetraphenylporphyrin in the toluene ($\Phi = 0.11$) as the standard.

^b Zn-Tetraphenylporphyrin in the toluene ($\Phi = 0.03$) as the standard.

monomers (**P94**) or $\text{AB}_3 + \text{C}_4$ monomers (**P95**–**P97**) as shown in Fig. 29. We selected fluorene-type porphyrins as monomers, which not only can form conjugated connections, but also the octyl chains on fluorene units can help to increase their solubility. The obtained hyperbranched porphyrin polymers are of high molecular weight and good solubility in common organic solvents. The use of tetraiodo substituted porphyrin, C_4 monomer, as a core molecule in the polymerization of AB_3 monomer, the molecular weight and solubility can be controlled by the fed ratio of the two monomers as shown in Table 2. The emission spectra of TPP, AB_3 monomer, and the polymers in THF solution are shown in Fig. 30. All polymers exhibited an intense red emission peak at around 655 nm and a shoulder at 713 nm. The photoluminescence quantum yields of the hyperbranched porphyrins in toluene were measured to be around 0.15 in comparison to TPP ($\Phi = 0.11$).

As shown in Fig. 31, we have developed a new synthetic strategy of preparing hyperbranched conjugated polymers (**P98**, **P99**, **P100**) with a controllable conjugation length by using monodisperse conjugated oligomers as the AB_2 monomers [103]. These polymers have not only controllable conjugation length, but also the structural feature of hyperbranched polymers. The photoluminescence spectra of **P98**–**P100** and L-Polymer in solutions and films are shown in Fig. 32. The emission maxima bathochromically shifted with the increasing the conjugation length from **P98** to L-Polymer. In solid films, **P98**–**P100** exhibited the emission peaks were much narrower than L-polymer. Such broad peaks of L-polymer were probably due to the formation of aggregation for the linear conjugated polymer chains in solid state. However, the hyperbranched structures of **P98**–**P100** could reduce the aggregation of conjugated polymer chains in solid state to some extent. The photoluminescence quantum yields of **P98**–**P100** in dilute toluene increased from **P98** to **P100** with the increasing of the conjugation length. These results clearly showed that optical properties of the hyperbranched conjugated polymers can be precisely controlled through controlling their conjugation length.

Recently, modification of the large number of endgroups of hyperbranched polymers has attracted more and more interest in the research area of hyperbranched polymers [104–110]. As shown in Fig. 33, we have successfully prepared hyperbranched polymer-cored star polymers **P101**–**P107** by Suzuki-Miyaura-Schlüter polycondensation of AB -type monomer in the presence of hyperbranched

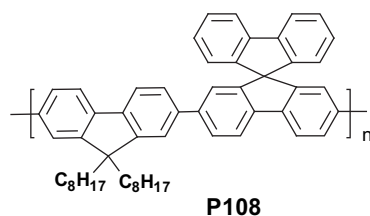


Fig. 34. Structure of polymer **P108** from Ref. [117].

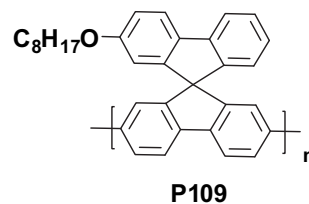


Fig. 35. Structure of polymer **P109** from Ref. [119].

polymers with peripheral bromo functional groups. Hyperbranched polymer-cored star polymers **P101** and **P102** exhibited very good color stability without significant green-blue emission even after annealing at 200 °C for 2.5 h in air [111]. This is due to the three-dimensional hyperbranched structure could effectively suppress the aggregation of the peripheral linear conjugated polyfluorene chains. The large number of peripheral bromo terminal groups of hyperbranched polymers can also be modified by Suzuki-Miyaura cross-coupling reaction to attach different dye molecules to tune their emitting color [111,112] as shown in Fig. 33. As confirmed by their absorption and emission spectra shown in Table 3, the aggregation of the peripheral dyes can also be effectively suppressed by the hyperbranched structures.

More recently, Cao and coworkers [113] have synthesized a novel series of soluble hyperbranched interrupted π -conjugated polymers (HICPs) based on complicated 9,9-diarylfuorenes (CDAFs) branching core and end-capped with high carrier mobility pyrene moieties via Suzuki coupling condensation (the polymers structures are shown in Ref [113]). The aggregation or excimer formation was effectively suppressed by the introduction of the twisted tree-dimensional structure. No obvious low energy green emission band at 520 nm was observed under extreme thermal annealing conditions in air at 200 °C for 12 h. The CDAF1 device shows stable blue emission with the peak at 422 and 447 nm. The Commission International d'Eclairage (CIE) 1931 coordinates is (0.18, 0.16) and the brightness reaches 1051 cd/m^2 at 15.7 V.

5. Spirobifluorene-based light-emitting materials

Compared with the huge amounts of publications on fluorene polymers and copolymers, less attention was paid to spirobifluorene-based polymers. Spiro-annulated molecules utilize the spiro-bridge to connect two conjugated moieties. The tetrahedral bonding atom at the center of a spiro-annulated molecule maintains a 90° angle between the connected conjugated moieties via

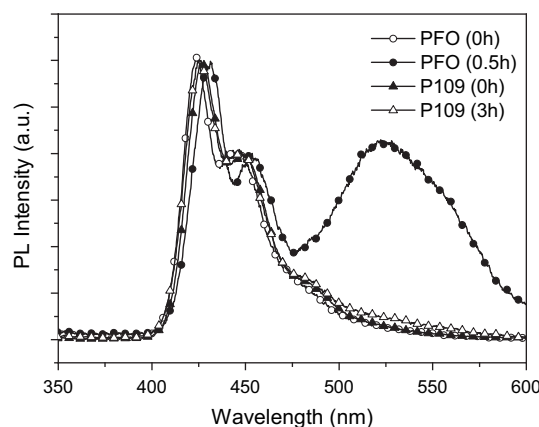


Fig. 36. Photoluminescent spectra of **P109** and PFO in solid films before and after thermal annealing at 200 °C for different times (0.5 h for PFO and 3 h for **P109**) from Ref. [119].

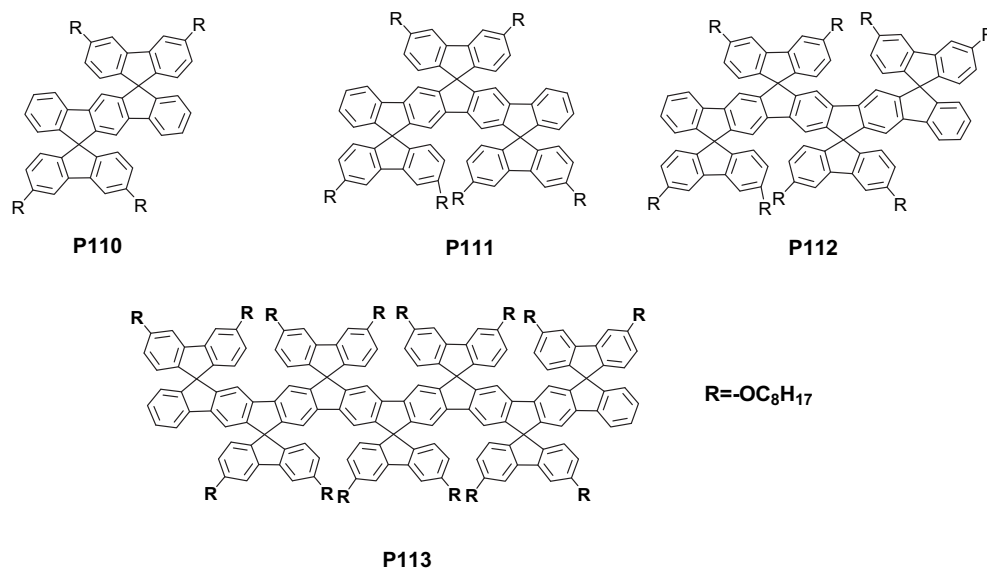


Fig. 37. Structures of oligomer **P110**–**P113** from Ref. [132].

a sp^3 -hybridized carbon atom as a spiro center [114]. This structural feature can minimize the close packing of spiro-annulated molecules in the solid state. Furthermore, the spiro-concept can prevent the photo/thermal oxidation of the 9-position of the fluorene unit to form the undesired ketonic defect. Therefore, the unusual rigid three-dimensional structure makes spirobifluorene an ideal building block in construction of stable blue light-emitting and plastic laser materials [115]. In 2006, Salbeck made a significant review and presented a comprehensive overview of basic physicochemical properties of spirobifluorene containing compounds in solution and in solid state and their practical applications in optoelectronics [116]. However, spirobifluorene-based polymers are not included into this review. Here, we will concentrate on the synthesis and photophysical properties of spirobifluorene-based polymers and spiro-bridged ladder-type oligomers and polymers.

Yu et al. have reported the synthesis and characterization of soluble spirobifluorene and fluorene alternating copolymers (**P108**) as blue light-emitting materials as shown in Fig. 34 [117]. Copolymer **P108** exhibits a more stable and narrower blue emission peak with a smaller tail at longer wavelengths in comparison with conventional alkyl substituted polyfluorenes. Lee et al. have prepared spirobifluorene polymers using Yamamoto coupling

reactions [118]. However, the color stability of the spirobifluorene polymer upon annealing in air was not investigated.

In our work, we have synthesized **P109** through AB-type monomer route via palladium-catalyzed Suzuki-Miyaura-Schlüter polycondensation as shown in Fig. 35 [119]. **P109** exhibited extremely good luminescent stability, no green emission was observed after the polymer film was annealed at 200 °C for 3 h in air as shown in Fig. 36. The photoluminescence quantum yields of **P109** in toluene were measured to be 0.91 with 9,10-diphenylanthracene as a reference standard (cyclohexane solution, $\Phi = 0.9$).

The ladder-type oligomers and polymers possess a rigid coplanar structure, which enhances the conjugation, carrier mobility, and luminescence intensity [120–128]. The synthesis of ladder-type oligo-*p*-phenylenes and the investigation of their photophysical properties have been reported by Scherf and Müllen et al. [120–128]. These ladder-type poly-*p*-phenylenes (LPPP) exhibited blue emission with high fluorescence quantum efficiency. However, similar to polyfluorenes, the ketonic defects also impeded the practical application of ladder-type poly-*p*-phenylenes [129–131]. The structural perfection indeed plays a very important role in determining the film electro-optic properties of the ladder-type poly (*p*-phenylene)s.

In our work, we have synthesized a set of spiro-bridged ladder-type oligomers by Suzuki-Miyaura cross-coupling, oxidation and $\text{BF}_3 \cdot \text{ether}$ -catalyzed cyclization reactions as shown in Fig. 37 [132]. Oligomers **P110**–**P113** possess unique three-dimensional conformation and exhibited intensive emission with a very small Stokes shift. Such unique three-dimensional conformation prevents

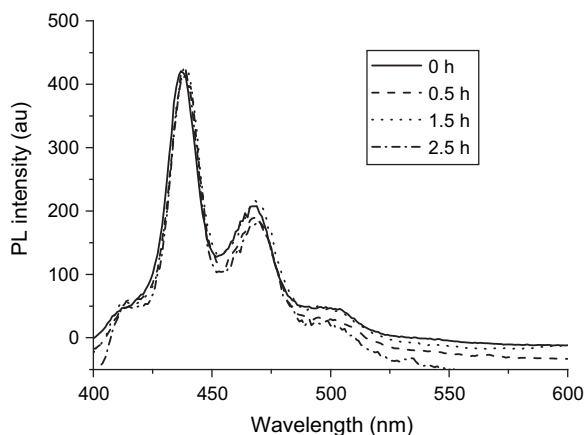


Fig. 38. The normalized film photoluminescence spectra of spiro-bridged ladder-type **P112** before and after annealing at 200 °C in air from Ref. [132].

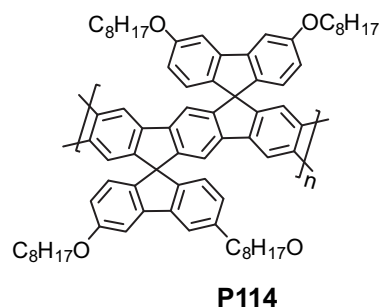


Fig. 39. Structure of polymer **P114** from Ref. [133].

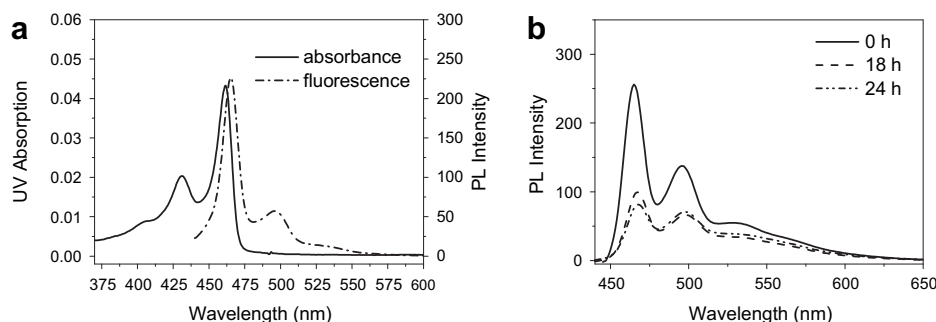


Fig. 40. (a) The UV–vis absorption and photoluminescence spectra of LPPP **P114** in chloroform solutions; (b) the unnormalized film PL spectra of spiro-bridged LPPP **P114** before and after annealing at 110 °C in air from Ref. [133].

planar ladder polymer backbone from aggregation in solid film and displayed very good color stability. With **P112** as an example, no evident photoluminescence spectral change was found after 2.5 h of heating the film at 200 °C in air as shown in Fig. 38.

Recently, we reported a novel route to synthesize spiro-bridged ladder-type polymer **P114** as shown in Fig. 39 [133]. Spiro-bridged ladder-type polymer **P114** possessed good structural perfection, exhibited excellent thermal and color stability, and was free of low energy ketonic defects. The normalized UV–visible absorption and photoluminescence spectra of **P114** in dilute chloroform solution are shown in Fig. 40a. The studies indicated no obvious shift of the UV and the PL spectra on going from solution to film and a very small Stokes shift of 2 nm was observed, which reflects that **P114** is extremely rigid. However, unlike the published results of Me-LPF [130,131], no low energy green emission was observed even after the film of **P114** was annealed at 110 °C for 24 h in air as shown in Fig. 40b. Meanwhile, a single-layer light-emitting diode of the type ITO/PEDOT/ladder-polymer **P114**/LiF/Al was fabricated to investigate the electroluminescence property of the **P114** as shown in Fig. 41. The EL spectrum was almost identical to the PL one, indicating that there was no ketonic defect on polymer **P114**. Spiro-bridged ladder-type polymer **P114** is the first ladder-type poly-*p*-phenylenes (LPPP) that exhibits excellent thermal and optical stability.

More recently, Lin and coworkers [134] synthesized a series of conjugated blue light-emitting copolymers (the structures were shown in Ref. [134]), comprised different ratios of electron-withdrawing segments (spirobifluorene substituted with cyanophenyl groups) and electron-donating segments (tricarbazole-triphenylamines). OLED device evaluation indicated that all the polymers emitted sky blue to deep-blue light when the polymers were used as the emissive layers in the devices with a configuration of ITO/PEDOT:PSS/polymers/CsF/Ca/Al.

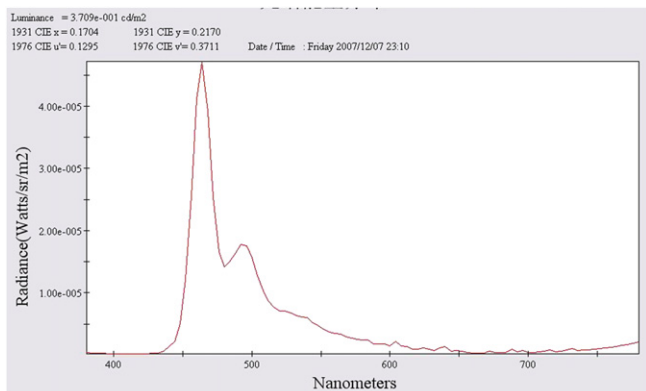


Fig. 41. Electroluminescence of an ITO/PEDOT/**P114**/LiF/Al device from Ref. [133].

6. Conclusion

In recent years, three-dimensional conjugated macromolecules such as dendrimers, hyperbranched and star polymers, spirobifluorene polymers, and spiro-bridged ladder-type oligomers and polymers have been developed as promising light-emitting materials in our group. The rigid three-dimensional structures show superiority to the corresponding linear structures, which can effectively suppress the aggregation of conjugated polymer chains and reduce the self-quenching of their luminescence.

In this feature article, special attention is paid to the recent progress in chemical structure design of three-dimensional conjugated macromolecules as the light-emitting materials and highlight on our studies in detail. These investigations provide us with an important way to improve the OLED efficiency through the modification of the chemical structure. Challenges remain using these three-dimensional conjugated macromolecules to achieve pure red and blue-light-emitting applications. In particular, the structures and components of three-dimensional conjugated macromolecules need to be addressed and optimized to overcome the specific factors, for example, device performance. Since intensive research efforts are ongoing to develop new material designs and device architectures, these advances in the design and engineering of three-dimensional conjugated macromolecules will open new avenues to flat-panel displays and futuristic applications.

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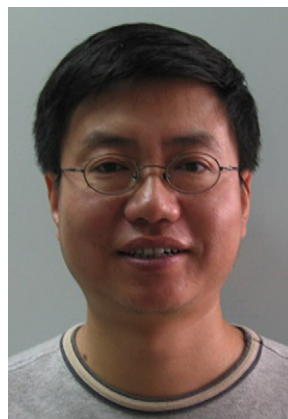
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