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Pure Blue-Light-Emitting Materials: Hyperbranched Ladder-Type Poly(*p*-phenylene)s Containing Truxene Units

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ABSTRACT: A series of novel hyperbranched ladder-type poly(*p*-phenylene)s containing truxene units have been prepared through the Pd(0)-catalyzed Suzuki polymerization with an "$A_2 + B_3$" or "$A_2 + B_2 + B_3$" approach. The polymers with different linear length show pure blue light emission from 417 to 465 nm. All the ladder-type polymers exhibit well-resolved absorption and emission spectra and small Stokes shifts in both solutions and thin films, which are the characteristics of full ladder-type poly(*p*-phenylene)s. The three-dimensional structures make the materials soluble in common organic solvents and able to form quality amorphous films, leading to polymer light-emitting diodes (PLEDs) with improved stability and efficiency.

Introduction

Conjugated polymers have been extensively studied recently due to their potential applications as light-emitting materials.[1] For achieving full color displays, the three primary-color-emitting materials, i.e., blue, green, and red, are essential. Compared with the high brightness and efficiency of green- and red-light-emitting materials, blue-light-emitting material does not match requirements for commercially feasible light-emitting diodes.[2] The search for stable light-emitting materials is ongoing. Polyfluorenes (PF),[3] ladder-type poly(*p*-phenylenes) (LPPPs),[4] are generally regarded as the most promising blue-light emitters because of their large band gap, well-defined structure, high luminescence quantum yield, and color tenability. However, all these materials suffer from the low-energy emission generated during either annealing or passage of current in solid states. Recent researches show the source of low-energy emission attributed to aggregates/excimers or ketone defects in the polymer molecular structure.[5]

The synthesis and the investigation of the photophysical properties of ladder-type poly(*p*-phenylene)s (LPPP) were first reported by Scherf and Müllen in 1991.[4a] The conjugated ladder-type polymer possesses a rigid coplanar structure, which enhances the conjugation, carrier mobility, and luminescence intensity, whereas the rigid coplanar structure more easily induces the aggregation in molecular which produces the red-shifted or excimers.[6] To minimize this tendency for aggregation, several attempts have been made such as introduction of bulky side chains, copolymerization with suitable monomers, attachment of sterically demanding end groups, or appending aryl groups onto methylenes.[7] The highly branched and globular features can reduce or eliminate interchain interactions and $\pi-\pi$ stacking interactions between the planar-conjugated molecular chains.[8] Moreover, three-dimensional structures make the materials form good quality amorphous films so as to improve stability and efficiency of PLEDs.[9] Therefore, hyperbranched electroluminescent polymers have become of current interest in terms of developing efficient light-emitting and other optoelectronic devices.

Truxene and its derivatives are widely investigated as starting materials for liquid crystals and fullerene precursors.[10] Recently, a variety of dendrimers and polymers containing truxene were reported as light-emitting materials.[11] The truxene moiety, as the dendric units have unique three-dimensional topology, is easy to functionalize at C-2, C-7, and C-12 positions and C-5, C-10, and C-15 positions, respectively. Usually, six hexyl groups were attached to the C-5, C-10, and C-15 positions of the truxene moiety to increase solubility as well as to release intermolecular $\pi-\pi$ stacking. Truxene can be formally regarded as a derivative of 1,3,5-triphenylbenzene with three $-CH_2-$ "clips" added and accordingly three five-membered rings formed to keep the four phenyls in a planar rigid structure, so the truxene moiety can be introduced into the ladder-type poly(*p*-phenylene) as dentric units to obtain hyperbrached structure.

In this paper, we report on the design, synthesis, and characterization of a series of novel hyperbranched ladder-type poly(*p*-phenylene)s containing truxene units (Figure 1). The hyperbranched polymers containing different linear units show the blue emission color from 417 to 465 nm. The keto-functionalized precursor polymers **HP1**, **HP2**, and **HP3** were prepared by an "$A_2 + B_3$" approach; the other polymer **HP4** was obtained by an "$A_2 + B_2 + B_3$" approach. All the precursor polymers quenched with 4-octyloxybenzene lithium were subsequently treated with the $BF_3 \cdot$ether to afford the hyperbranched ladder polymers **HLP(1−4)** (**HLP1**, **HLP2**, **HLP3**, **HLP4**). The three-dimensional polymers can be easily dissolved in common organic solvents such as chloroform and THF to obtain good quality amorphous films. All the polymers show good both thermal and color stability, which establish them as good candidates for active materials in stable pure blue polymer light-emitting diodes.

Results and Discussion

Synthesis and Characterization. The synthetic route to the desired monomers and polymers is outlined in Scheme 1. To prepare ladder-type poly(*p*-phenylene)s, it is necessary to synthesize the key monomer **MA1**. Starting from the known

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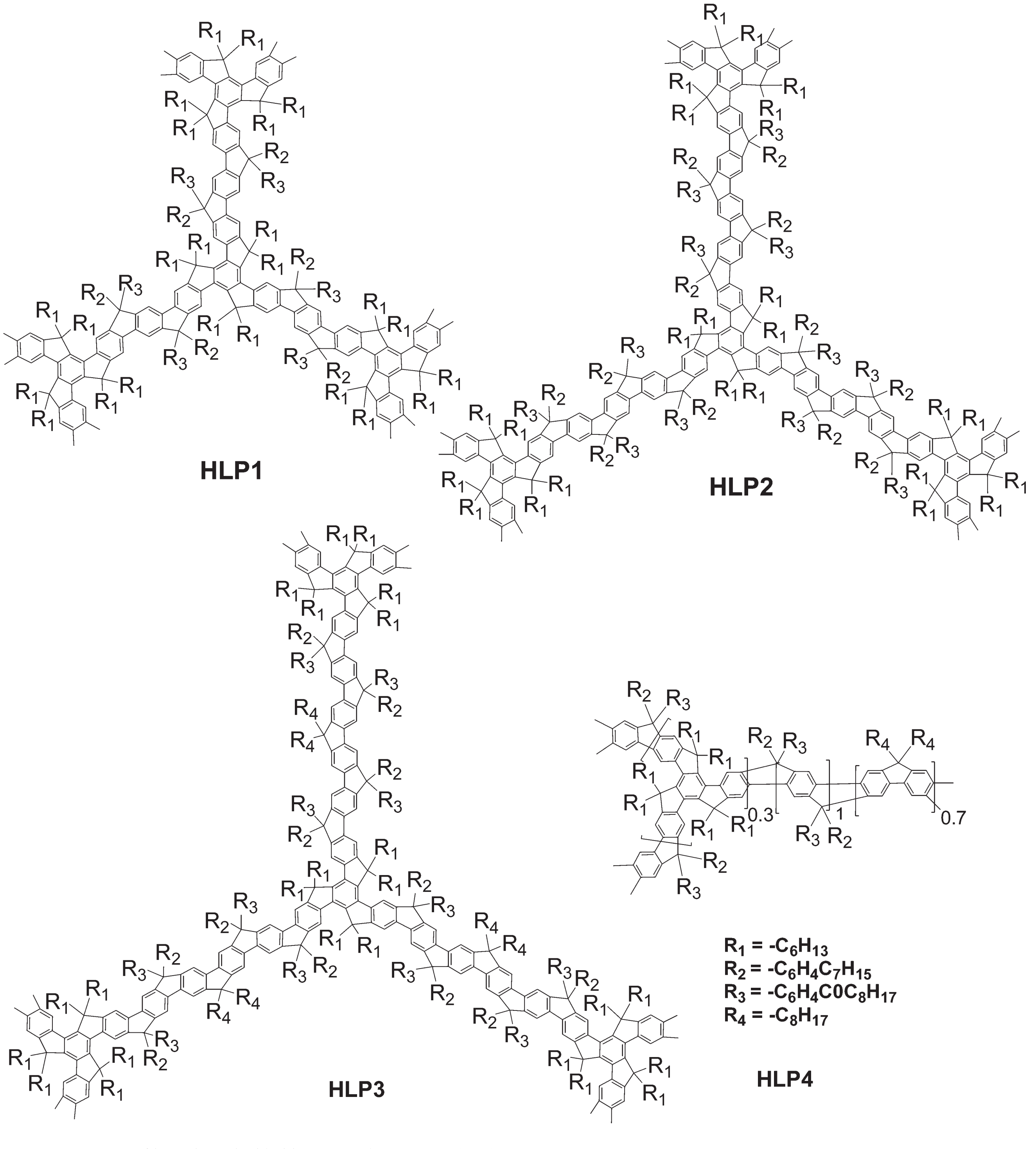
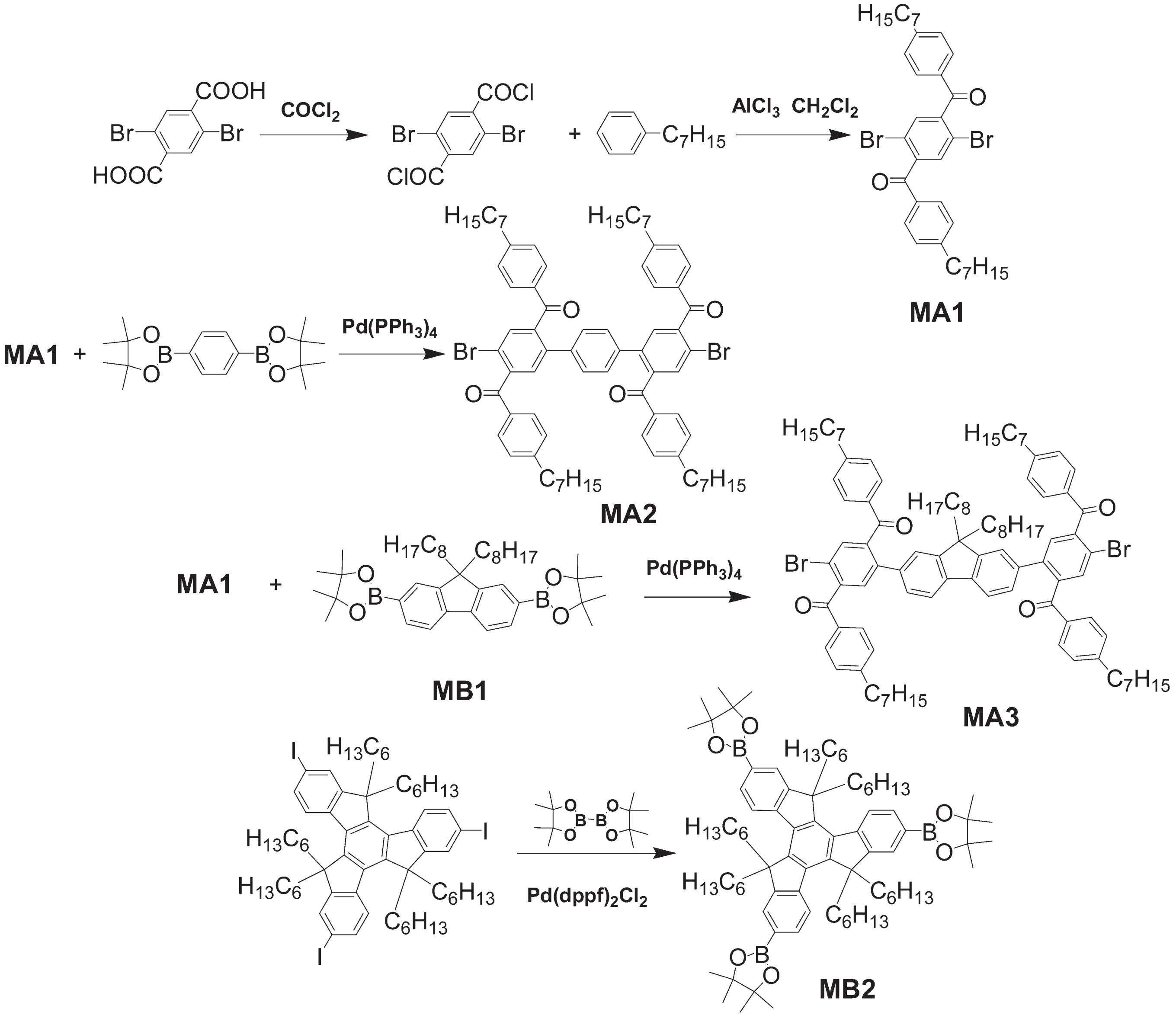


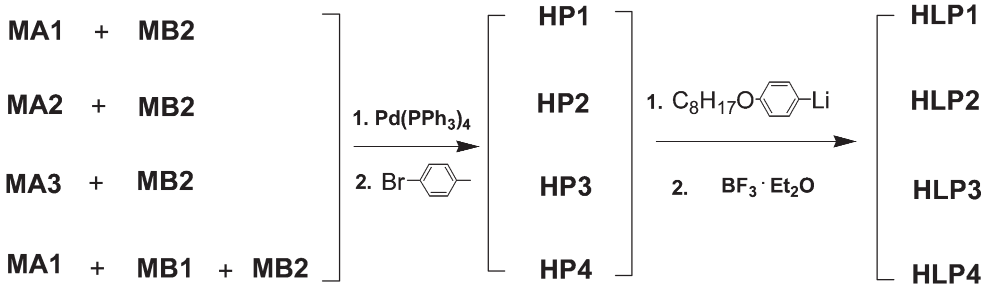
Figure 1. Structure of hyperbranched ladder-type polymers **HLP(1−4)**.

reagent 1,4-dibromo-2,5-benzenedicarboxylic acid, monomer **MA1** was obtained via a two-step synthesis in a total yield 76%. The reaction of excess **MA1** with 1,4-benzenediboronic acid pinacol ester afforded **MA2** through Suzuki coupling reaction in 30% yield. **MA3** was obtained by coupling excess **MA1** and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (**MB1**) using Pd(0)-$(PPh_3)_4$ as catalyst in 43% yield. 2,7,12-Triiodohexaethyltruxene was prepared via the route published by Pei et al.[11f] **MB2** was accomplished in a yield of 54% by the reaction of 2,7,12-triiodohexaethyltruxene and bis(pinacolato)diboron in solution of DMF, CH_3COONa, and $Pd(dppf)_2Cl_2$. The high purity of the monomers was proved by ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, elemental analysis, and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS).

Suzuki polycondensation (SPC) of the macromonomers (A_2: **MA1**, **MA2**, **MA3**) with B_3: **MB2** and B_2: **MB1** was done in a biphasic system (THF/aqueous K_2CO_3) with freshly prepared $Pd(PPh_3)_4$ as a catalyst precursor by the "$A_2 + B_3$" or "$A_2 + B_2 + B_3$" approach. Reactions were kept stirring at reflux for 72 h. 1-Bromo-4-methylbenzene was used to cap the bronic end groups. Standard work-up afforded hyperbranched polymers **HP(1−4)** (**HP1**, **HP2**, **HP3**, and **HP4**) as amorphous solids in yields of 94%, 91%, 92%, and 96%, Scheme 1. Synthesis of Monomers MA(1−3) and MB2



Scheme 2. Synthesis of Hyperbranched Ladder-Type Polymers HLP(1−4)



respectively. The keto groups of hyperbranched polymers were quenched with largely excessive 4-octyloxybenzene lithium to ensure all keto groups reduced completely (Scheme 2). The final products **HLP(1−4)** were obtained by the ring-closure reaction of the corresponding alcohol polymers with boron trifluoride etherate via a intramolecular Friedel−Crafts alkylation in an overall yield 76%, 63%, 75%, and 58%, respectively. All polymers are easily soluble in common organic solvents, such as THF, toluene, chloroform, etc. The molecular structure of the polymers was verified by ^{1}H NMR spectroscopy and elemental analysis. The molecular weights of polymers **HLP(1−4)** were determined by gel permeation chromatography (GPC) with THF as the eluent, calibrated against polystyrene standards. As shown in Table 1 and Figure 2, the GPC analysis indicated that the number-average molecular weight (M_n) and polydispersity index of the polymers are in the ranges $(2.2{-}23.0) \times 10^4$ and 1.5−4.7, respectively.

Table 1. Physical Properties of Hyperbranched Ladder-Type Polymers HLP(1−4)

polymers	M_n	M_w	PD	T_d (°C)
HLP1	35 100	136 300	3.89	359
HLP2	21 500	101 500	4.71	347
HLP3	24 100	69 300	2.87	341
HLP4	233 000	407 400	1.75	335

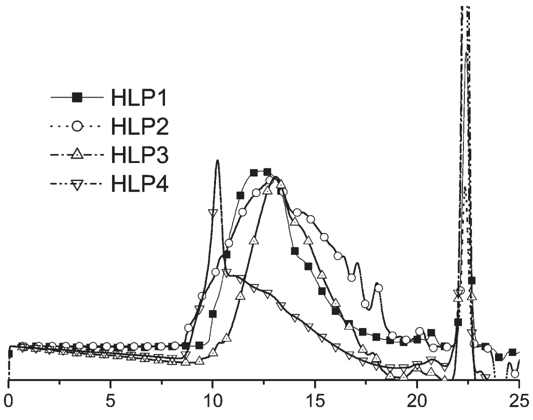


Figure 2. GPC elution traces of hyperbranched ladder-type polymers **HLP(1−4)**.

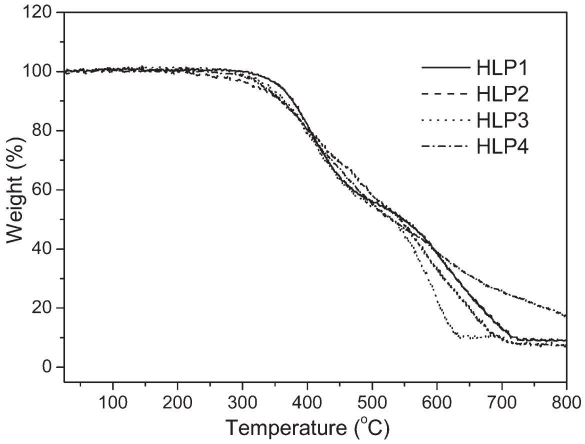


Figure 3. TGA traces of hyperbranched ladder-type polymers **HLP-(1−4)**.

The thermal properties of the hyperbranchced ladder type polymers **HLP(1−4)** were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in a nitrogen atmosphere. All polymers exhibited good thermal stability with onset degradation temperatures (T_d) above 330 °C (Figure 3). Neither a glass transition process (T_g) nor other thermal processes (such as liquid-crystal phase) were observed from 35 to 300 °C in the DSC trace of second heating (10 °C/min).

Optical Properties. All polymers were readily dissolved in common organic solvents such as methylene chloride, toluene, and THF and exhibited bright blue fluorescence in solution. As shown in Figure 4 and Figure 5, the UV−vis absorption and photoluminescence (PL) spectra of the precursor polymers **HP(1−4)** and the ladder-type polymers **HLP(1−4)** in THF solution present an significant difference which can be attributed to the change in the conformation. **HP(1−4)** exhibited similar absorption and emission spectra that were very broad and peaked at around 340 and 470 nm, respectively, while the absorption peaks of ladder-type polymers distinctly shifted toward low energy; on the contrary, the emission peaks shifted toward high energy. The optical properties of the ladder-type polymers were investigated in both solution and solid state. The absorption and emission spectra of **HLP(1−4)** in dilute THF solution are shown in Figure 5. All the ladder-type polymers exhibited well-resolved absorption and emission spectra, which is typical for a rigid, planar, one-dimensional π-system. The absorption and emission maxima red-shifted with the increasing linear length. The Stokes shifts of **HLP(1−4)** are 5, 4, 5, and 6 nm, respectively, indicating that such ladder-type polymers are extremely rigid.

Solid films of ladder-type polymers on quartz plates used for UV−vis and fluorescence were prepared by spin-coating from a 1% THF solution at 1500 rpm. All polymers formed homogeneous films. The UV−vis and photoluminescence spectra of **HLP(1−4)** are shown in Figure 6. The absorption maxima of the ladder-type polymers in thin films were almost identical with those in solution, which indicates that there was nearly no change in conformation of the ladder-type backbone from the solution to the solid state. However, the PL spectra of the ladder-type polymers showed slightly difference when changing from solution to films. Compared with the corresponding to those in solution emission spectra, the peaks of the polymers **HLP1**, **HLP2**, and **HLP3** in solid state showed increasing red-shift values of 3, 5, and 9 nm, respectively. The peak of the polymer **HLP4** shows a red-shift value of 5 nm. There is slight increase in the intensity

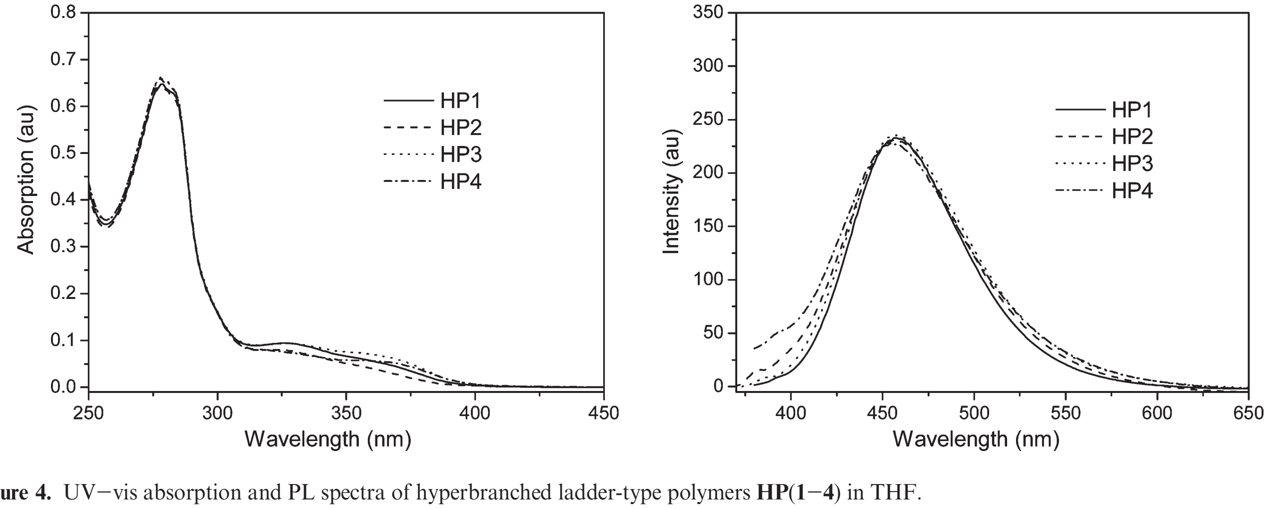


Figure 4. UV−vis absorption and PL spectra of hyperbranched ladder-type polymers **HP(1−4)** in THF.

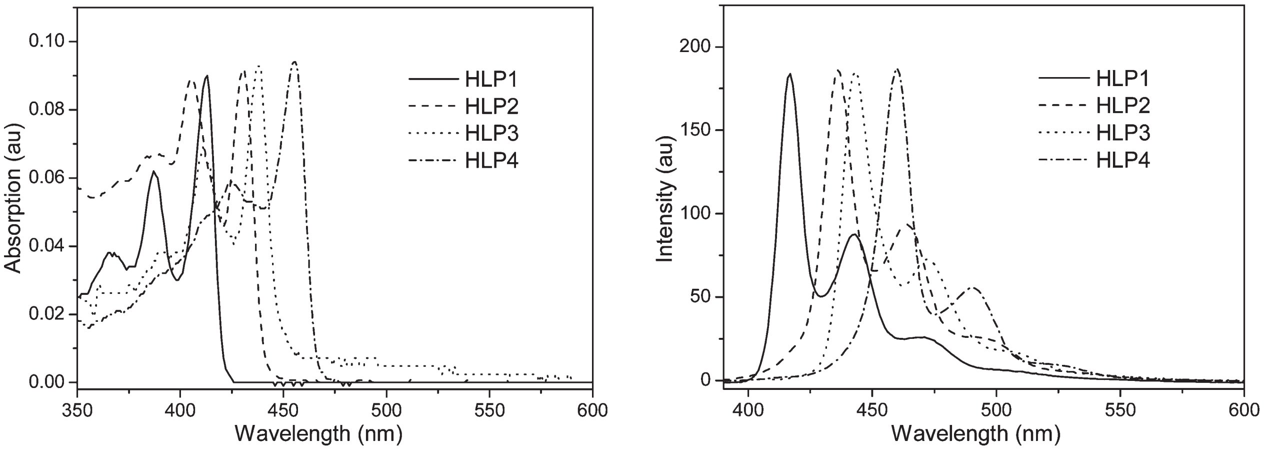


Figure 5. UV−vis absorption and PL spectra of hyperbranched ladder-type polymers **HLP(1−4)** in THF.

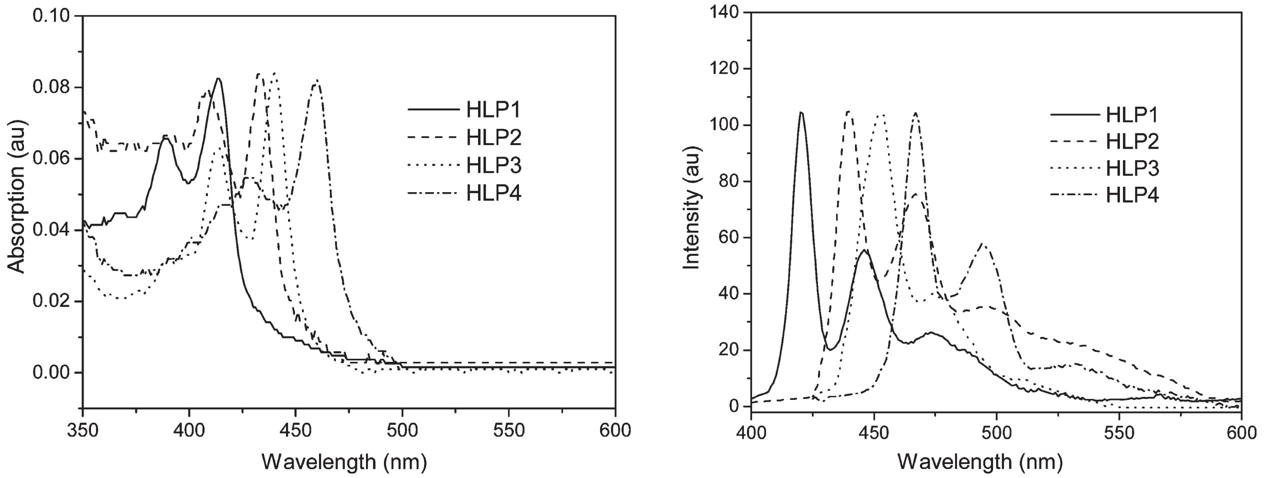


Figure 6. UV−vis absorption and PL spectra of hyperbranched ladder-type polymers **HLP(1−4)** in film.

Table 2. HOMO and LUMO Energies and Band Gap Data of Hyperbranched Ladder-Type Polymers HLP(1−4)

polymers	HLP1	HLP2	HLP3	HLP4
HOMO (eV)	−5.70	−5.68	−5.66	−5.60
LUMO (eV)	−2.79	−2.91	−2.95	−2.97
band gap (eV)	2.91	2.77	2.71	2.63

around shoulder peak and tail rand emissions in films, which is ascribed to the stronger self-absorption effect than that in solution. Generally, the low-energy emission from the fluorenone defects around 550−570 nm was enhanced in the film compared to the corresponding solution because of the increasing interchain energy transfer. However, in the PL spectra of **HLP(1−4)** in solid film, no low-energy tailed peaks was observed. These results indicate that there is barely any fluorenone defect or aggregation in the hyperbranched ladder-type polymers.

Electrochemical Properties. The electrochemical behaviors of polymers **HLP(1−4)** were investigated by cyclic voltammetry (CV) with a standard three-electrode electrochemical cell in acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) at room temperature. The oxidation potentials were measured versus $Ag/AgNO_3$ as the reference electrode and a standard ferrocene/ferrocenium redox system as the internal standard for estimating the HOMO of the ladder-type polymers films. Figure 7 shows the cyclic voltammograms of ladder-type polymers **HLP(1−4)** in films at a scan rate of 30 mV s^{-1} in the range of 0−1.4 V. All the polymers films showed irreversible p-doping processes in the first redox cycle. With increasing linear length, the oxidation peaks of the polymers moved to more negative values. The band gap (ΔE) of polymers **HLP(1−4)** was calculated from the UV−vis absorption onset of the films. The LUMO levels were calculated according to the following equation: $E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + E_{\mathrm{gap}}$. The results are summarized in Table 2. With the increase in the linear length of the ladder polymers, the band gap becomes narrower.

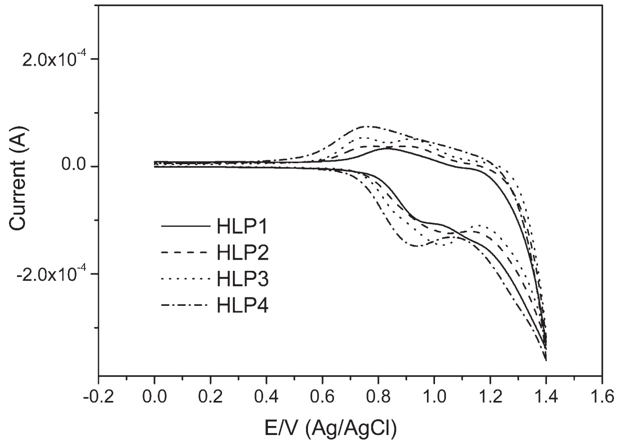


Figure 7. Cyclic voltammograms of hyperbranched ladder-type polymers **HLP(1−4)** in films at a scan rate of 30 mV s^{-1}.

Conclusion

We have successfully prepared a series of ladder-type hperbranched polymers (**HLP1**, **HLP2**, **HLP3**, and **HLP4**) via the palladium-catalyzed Suzuki coupling reaction by an "$A_2 + B_3$" or "$A_2 + B_3 + B_2$" approach. These ladder hyperbranched polymers are soluble in common organic solvents, and their weight-average molecular weights (M_w) were (6.93−40.7) × 10^4 g/mol with polydispersity indexes (PDI) being in the range of 1.75−4.71. All the polymers give strong pure blue emission both in solutions and in film states and exhibit well-resolved absorption and emission spectra, which are the characteristics of full ladder-type polymer.

Experimental Section

General. All chemicals were purchased from Aldrich or Acros and used without further purification. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene,[12] 1,4-benzenediboronic, and 2,7,12-triiodohexaethyltruxene[11f] were prepared according to literature procedures. The catalyst precursor $Pd(PPh_3)_4$ was prepared according to the literature[13] and stored in a Shlenk tube under nitrogen. All solvents were purified and dried by standard methods. The reactions were monitored by TLC with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200−300 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer in $CDCl_3$. The electrochemical behavior of compounds was investigated by using cyclic voltammetry (CHI 630A electrochemical analyzer) with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium tetrafluoroborate solution in CH_3CN at room temperature at atmospheric pressure with a scanning rate of 30 mV s^{-1}. A glassy carbon working electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ (0.01 M in CH_3CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (Fc) redox system and assumption that the energy level of Fc is 4.8 eV below vacuum. Electronic absorption spectra were obtained on a Shimadzu UV−vis spectrometer model UV-2500. Fluorescence spectra were recorded on a Shimadzu RF-5301PC. Elemental analyses were performed on a Flash EA 1112 analyzer. TGA (Pyris 1 TGA) and DSC (TA 2910) measurements were carried out under a nitrogen atmosphere at a heating rate of 10 °C/min to recorded the thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) MS spectrometric measurements were performed on a Bruker BIFLEXIII mass spectrometer.

Synthesis of Monomers and Polymers. *MA1*. 2,5-Dibromoterephthalic acid (3.0 g, 10.5 mmol) was treated with 20 mL of thionyl chloride ($SOCl_2$) (20 mL) and refluxed for 10 h. The excess $SOCl_2$ was removed in a vacuum to give 3,6-dibromo-2,5-phenylenendi(carboxylic acid chloride) as a crystalline yellow solid.

To a solution of heptylbenzene (7.0 mL) and aluminum trichloride (1.8 g, 13.5 mmol), a mixture of all product and 6 mL of CH_2Cl_2 was added dropwise. After stirring at room temperature for 2 h the mixture was poured into ice. The organic layer was washed with 1 M NaOH and water, then dried over Na_2SO_4, and concentrated. The residue was chromatographically purified on silica gel eluting with CH_2Cl_2/hexane (1:2) to afford **MA1** as a white crystal (total yield: 4.5 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, 4H), 7.58 (s, 2H) 7.31 (d, 4H), 2.69 (t, 4H), 1.65 (t, 14H), 1.32−1.28 (m, 16H), 0.88 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.6, 150.8, 143.6, 133.1, 130.7, 129.2, 118.7, 36.4, 32.0, 31.2, 29.5, 29.3, 22.9, 14.3. Anal. Calcd for $C_{34}H_{40}Br_2O_2$: C, 63.76; H, 6.29. Found: C, 63.75; H, 6.24.

MA2. A mixture of **MA1** (2.0 g, 3.1 mmol), 1,4-benzenediboronic pinacol ester (0.1 g, 0.3 mmol), $NaHCO_3$ (0.4 g, 4.8 mmol), H_2O (4 mL), and THF (20 mL) was carefully degassed before $Pd(PPh_3)_4$ (8 mg, 0.082 mmol) was added. The mixture was refluxed for 1 day under stirring. Water and CH_2Cl_2 (50 mL) was added, the organic layer separated, the aqueous layer extracted with CH_2Cl_2 (×2), and the combined organic layers dried over Na_2SO_4. Removal of the solvent, the crude product was chromatographically purified on silica gel eluting with CH_2Cl_2/hexane (1:1, v/v) increasing to CH_2Cl_2 to afford **MA2** as a white solid (0.11 g, 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, 4H), 7.67 (s, 2H), 7.56 (d, 4H), 7.30 (d, 4H), 7.12 (d, 4H), 7.10 (s, 2H), 2.69 (t, 4H), 2.58 (t, 4H), 1.64 (m, 4H), 1.56 (m, 4H), 1.32−1.26 (m, 32H), 0.88−0.84 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 195.0, 151.6, 150.6, 150.0, 142.9, 141.9, 139.7, 138.3, 134.6, 133.8, 133.1, 130.8, 130.5, 129.3, 128.9, 118.7, 36.6, 36.4, 32.1, 31.3, 31.2, 29.6, 29.6, 29.4, 29.4, 23.0, 14.4. MALDI-TOF, *m*/*z*: calcd, 1197.3; found, 1219.9 ($M^+ + 23$).

MA3. A mixture of **MA1** (2.0 g, 3.1 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (**MB2**) (0.1 mg, 0.16 mmol), $NaHCO_3$ (0.4 g, 4.8 mmol), H_2O (4 mL), and THF (20 mL) was carefully degassed before $Pd(PPh_3)_4$ (8 mg, 0.082 mmol) was added. The mixture was refluxed for 1 day under stirring. Water and CH_2Cl_2 (50 mL) was added, the organic layer separated, the aqueous layer extracted with CH_2Cl_2 (×2), and the combined organic layers dried over Na_2SO_4. After removal of the solvent, the crude product was chromatographically purified on silica gel eluting with CH_2Cl_2/hexane (1:1, v/v) to afford **MA3** as a white solid (0.10 g, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, 4H), 7.70 (s, 2H) 7.59 (d, 4H), 7.45−7.42 (d, 4H), 7.31 (d, 4H), 7.22 (d, 2H), 7.16 (s, 2H), 7.06 (d, 2H), 2.68 (t, 4H), 2.53 (t, 4H), 1.64−1.52 (m, 12H), 1.32−1.12 (m, 48H), 0.93−0.80 (m, 22H), 0.26 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.6, 193.7, 151.6, 150.5, 149.7, 142.7, 141.9, 140.4, 140.3, 137.5, 134.0, 133.6, 132.7, 130.8, 130.5, 130.4, 130.2, 129.1, 128.7, 127.8, 123.6, 120.3, 118.2, 55.2, 40.2, 36.4, 36.2, 32.0, 31.9, 31.2, 31.0, 30.3, 29.7, 29.5, 29.3, 29.3, 29.2, 23.8, 22.8, 14.3. MALDI-TOF, *m*/*z*: calcd, 1509.8; found, 1532.0 ($M^+ + 23$).

MB2. A mixture of 2,7,12-triiodohexaethyltruxene (1.0 g, 0.82 mmol), bis(pinacolato)diboron (1.4 g, 5.5 mmol), CH_3COOK (0.61 g, 6.2 mmol), and DMF (30 mL) was carefully degassed before $Pd(dppf)_2Cl_2$ (50 mg, 0.082 mmol) was added. The mixture was stirred for 24 h at 90 °C unde N_2. Water and CH_2Cl_2 (300 mL) were added, and the organic layer was separated and washed with water three times. After removal of the solvent, the crude product was chromatographically purified on silica gel eluting with CH_2Cl_2/hexane (1:3, v/v) to afford **MB2** as a white solid (0.54 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, 3H), 7.87 (d, 3H), 7.85 (s, 3H), 2.92 (m, 6H), 2.15 (m, 6H), 1.42 (s, 36H), 0.88−0.80 (m, 36H), 0.58 (t, 18H), 0.44 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 146.7, 143.4, 138.6, 133.1, 128.4, 124.2, 83.9, 56.0, 37.1, 31.2, 29.7, 25.2, 24.2, 22.5, 14.1. Anal. Calcd for $C_{81}H_{123}B_3O_6$: C, 79.40; H, 10.12. Found: C, 79.38; H, 10.15.

General Procedure for the Synthesis of Hyperbranched Polymers HP(1−4). A mixture of the respective monomers, K_2CO_3, THF, and H_2O was degassed, and $Pd(PPh_3)_4$ was added under a nitrogen atmosphere. The reaction mixture was heated at reflux and stirred under nitrogen for 3 days. 1-Bromo-4-methylbenzene (50 mg, 0.29 mmol) was added to cap the bronic end groups. After refluxing for another 24 h, water and CH_2Cl_2 (200 mL) were added, the organic layer was separated, and the organic layer was dried over Na_2SO_4. After removal of most of the solvent, the residue was precipitated in methanol. The crude polymers were repurified by precipitation from THF into hexane again and dried under vacuum to give polymers **HP-(1−4)**.

Hyperbranched Polymer HP1. MA1 (63 mg, 0.098 mmol), **MB2** (120 mg, 0.098 mmol), K_2CO_3 (0.30 g, 2.2 mmol), H_2O(3 mL), THF (15 mL), and $Pd(PPh_3)_4$ (8 mg, 0.0069 mmol) were used. **HP1** was obtained as yellow-green solid (0.13 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (broad, 3H), 7.78−7.65 (broad, 10H) 7.53−7.63 (broad, 4H), 7.36 (broad, 2H), 7.10 (broad, 4H), 2.83−2.72 (broad, 6H), 2.53−2.40 (broad, 7H), 2.10−1.86 (broad, 6H), 1.68 (broad, 4H), 1.24 (broad, 16H), 0.84 (broad, 42H), 0.59−0.26 (broad, 30H). Anal. Calcd for $C_{104}H_{134}O_2$: C, 88.20; H, 9.54. Found: C, 85.78; H, 9.45.

Hyperbranched Polymer HP2. **MA2** (100 mg, 0.084 mmol), **MB2** (102 mg, 0.084 mmol), K_2CO_3 (0.30 g, 2.2 mmol), H_2O (3 mL), THF (15 mL), and $Pd(PPh_3)_4$ (9 mg, 0.0078 mmol) were used. **HP2** was obtained as yellow-green solid (0.15 g, 91%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.25−8.10 (broad, 3H), 7.71−7.66 (broad, 10H), 7.48−7.26 (broad, 14H), 7.12 (broad, 10H), 2.83 (broad, 6H), 2.58−2.44 (broad, 11H), 2.09−1.85 (broad, 6H), 1.56 (broad, 8H), 1.27 (broad, 32H), 0.87−0.85 (broad, 48H), 0.57 (broad, 18H), 0.27 (broad, 12). Anal. Calcd for $C_{144}H_{178}O_4$: C, 87.66; H, 9.09. Found: C, 85.82; H, 9.05.

Hyperbranched Polymer HP3. **MA3** (100 mg, 0.066 mmol), **MB2** (84 mg, 0.066 mmol), K_2CO_3 (0.30 g, 2.2 mmol), H_2O (3 mL), THF (15 mL), and $Pd(PPh_3)_4$ (8 mg, 0.0069 mmol) were used. **HP3** was obtained as yellow-green solid (0.14 g, 92%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.20−8.05 (broad, 3H), 7.71−7.65 (broad, 12H), 7.48−7.26 (broad, 14H), 7.12 (broad, 10H), 2.83−2.70 (broad, 6H), 2.51−2.43 (broad, 11H), 2.08−1.72 (broad, 10H), 1.56 (broad, 8H), 1.27 (broad, 32H), 0.99−0.83 (broad, 68H), 0.58 (broad, 24H), 0.33 (broad, 16H). Anal. Calcd for $C_{167}H_{214}O_4$: C, 87.76; H, 9.44. Found: C, 87.23; H, 9.47.

Hyperbranched Polymer HP4. **MA1** (100 mg, 0.16 mmol), **MB1** (75 mg, 0.12 mmol), **MB2** (47 mg, 0.038 mmol), K_2CO_3 (0.30 g, 2.2 mmol), H_2O (3 mL), THF (15 mL), and $Pd(PPh_3)_4$ (8 mg, 0.0069 mmol) were used. **HP4** was obtained as yellow-green solid (0.15 g, 96%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.20−8.10 (broad, 1H), 7.66−7.55 (broad, 8H), 7.46 (broad, 4H), 7.31−7.26 (broad, 2H), 7.05 (broad, 4H), 2.80−2.70 (broad, 2H), 2.50−2.37 (broad, 7H), 2.08−1.67 (broad, 5H), 1.50 (broad, 4H), 1.22 (broad, 16H), 0.99−0.84 (broad, 24H), 0.59−0.32 (broad, 15H). Anal. Calcd for $C_{73}H_{94}O_2$: C, 87.37; H, 9.44. Found: C, 86.55; H, 9.27.

General Procedure for the Synthesis of Hyperbranched Polymers HLP(1−4). 4-Octyloxybenzene lithium (5 mL, 3.5 mmol) in ether was dropped into the solution of THF (30 mL) and polymer (60 mg) at 0 °C under nitrogen, and the mixture was stirred for 5 min at 0 °C. Water and CH_2Cl_2 (100 mL) were added, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (×2). The combined organic layers were dried over Na_2SO_4 and concentrated to dryness. The crude polymer was precipitated from THF into hexane. The precipitation was dissolved in dry CH_2Cl_2 (20 mL) and treated with $BF_3 \cdot$ether (0.4 g, 2.61 mmol). After stirring for 5 min at room temperature, 10 mL of ethanol was added to the mixture to destroy the catalyst. Water and CH_2Cl_2 (100 mL) were added, and the organic layer was separated and washed with water three times, dried over Na_2SO_4, and concentrated to dryness. The crude polymer was precipitated from THF into methanol to give hyperbranched ladder-type polymers.

Hyperbranched Ladder-Type Polymer HLP1. A slightly yellow solid (58 mg, 76%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.25−8.05 (broad, 3H), 7.74−7.65 (broad, 8H), 7.52−7.33 (broad, 8H), 7.26−6.85 (broad, 10H), 3.99−3.92 (broad, 4H), 2.80−2.74 (broad, 6H), 2.74−2.45 (broad, 7H), 2.18−2.03 (broad, 6H), 1.85−1.68 (broad, 8H), 1.60−1.12 (broad, 36H), 0.88−0.28 (broad, 78H). Anal. Calcd for $C_{132}H_{174}O_2$: C, 88.43; H, 9.78. Found: C, 85.84; H, 9.68.

Hyperbranched Ladder-Type Polymer HLP2. A slightly yellow solid (52 mg, 63%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.25−8.10 (broad, 3H), 7.68−7.65 (broad, 12H), 7.52−7.26 (broad, 10H), 7.26−6.83 (broad, 24H), 3.93 (broad, 8H), 2.96−2.83 (broad, 6H), 2.84−2.58 (broad, 11H), 2.29−2.03 (broad, 6H), 1.76−1.41 (broad, 16H), 1.26 (broad, 72H), 0.87−0.34 (broad, 90H). Anal. Calcd for $C_{200}H_{258}O_4$: C, 88.11; H, 9.54. Found: C, 84.33; H, 9.25.

Hyperbranched Ladder-Type Polymer HLP3. A yellow solid (60 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.25−8.10 (broad, 3H), 7.69−7.63 (broad, 12H), 7.53−7.26 (broad, 12H), 7.26−6.84 (broad, 24H), 3.92 (broad, 8H), 2.95−2.80 (broad, 6H), 2.59−2.45 (broad, 11H), 2.34−2.09 (broad, 10H), 1.86−1.43 (broad, 16H), 1.26 (broad, 92H), 0.87−0.34 (broad, 100H). Anal. Calcd for $C_{223}H_{294}O_4$: C, 88.14; H, 9.75. Found: C, 83.59; H, 9.61.

Hyperbranched Ladder-Type Polymer HLP4. A yellow solid (48 mg, 58%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.20−8.10 (broad, 1H), 7.65−7.54 (broad, 8H), 7.47−7.26 (broad, 4H), 7.26−6.80 (broad, 12H), 3.91 (broad, 4H), 2.95−2.70 (broad, 2H), 2.57−2.45 (broad, 7H), 2.38−2.00 (broad, 5H), 1.91−1.64 (broad, 8H), 1.28−1.12 (broad, 36H), 0.88−0.30 (broad, 51H). Anal. Calcd for $C_{101}H_{134}O_2$: C, 87.90; H, 9.79. Found: C, 83.29; H, 9.99.

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