Synthesis, Structural Characterization, and Thermal and Optical Properties of Hyperbranched Poly(aminoarylene)s

Ronghua Zheng,[†] Matthias Häussler,[†] Hongchen Dong,[†] Jacky W. Y. Lam,[†] and Ben Zhong Tang*[,†,‡]

Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China, and Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

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ABSTRACT: A group of new hyperbranched poly(aminoarylene)s (*hb*-PAAs) were prepared by the copolycyclotrimerizations of diynes **1**−**3** and triyne **4** with monoynes **5** and **6** catalyzed by $TaBr_5$ and $CpCo(CO)_2-h\nu$. *hb*-PAAs with high molecular weights (M_w up to 26600) were obtained in high yields (up to 93%). Whereas the *hb*-PAAs synthesized from diphenylaminodiynes contained no internal cyclic structures, their counterparts from triphenylaminotriyne possessed small- and medium-size macrocyclic structures due to the ortho- and meta-linkages of the newly formed 1,2,4- and 1,3,5-substituted benzene rings. All the *hb*-PAAs are thermally very stable with degradation temperatures up to ∼580 °C and emit bright blue lights in dilute solutions as well as in thin films.

Introduction

Polymers and oligomers constructed from diphenylamine (DPA) and triphenylamine (TPA) building blocks are versatile materials that exhibit a variety of advanced functional properties such as high hole-transporting[1−3] and light-emitting efficiencies,[4−8] large two-photon absorption cross sections,[9−11] high photorefractivity[10−13] and photoconductivity,[13−16] and a large stabilization effect on high-spin polyradicals in organic magnets.[17−21] The materials thus promise an array of technological applications in organic electronics, photonics, and spintronics. The multifaceted functionalities of the materials are partially associated with the good coplanarity of the aromatic rings surrounding the central nitrogen atom in the phenylamine unit. The lone-pair electrons on the central nitrogen atom help to enhance the electronic communication along the macromolecular chains and make them to behave as strong electron donors.

Many research groups have worked on the design and synthesis of DPA- and TPA-based linear polymers.[22−30] The frontier of polymer research is now moving from the macromolecules with one-dimensional linear structure to three-dimensional dendritic/hyperbranched structures, in the expectation that the novel molecular architecture of the latter will impart functional properties that are inaccessible by the former.[31−35] Hyperbranched polymers enjoy such advantages as ready preparations in large quantities by one-pot, single-step experimental procedures, while retaining most of the functionalities of their dendritic congeners.[36−40] Inherently, tertiary amines are ideal building blocks for the construction of macromolecules with three-dimensional architectures[41−49] but the synthetic protocols have mainly been the polycondensations of functional AB_2- and (A_2 + B_3)-type monomers through Grignard, Negishi and Suzuki couplings.[47] The AB_2 monomers are normally unstable and their polymerization products are often oligomers with poor solubility in common organic solvents. These drawbacks obviously limit the application scope of this synthetic approach. The polycoupling reactions of A_2 + B_3 monomers sometimes require high temperature and long reaction time, although this synthetic approach offers the freedom in tuning the molecular structures of the hyperbranched polymers by molecular engineering.[47]

Our group has worked on the construction of hyperbranched conjugative polymers via [2 + 2 + 2] alkyne polycyclotrimerizations.[50−56] Through systematic investigations, we have developed effective catalyst systems and optimized polymerization conditions for the synthesis of functional hyperbranched polyarylenes by the homopolymerizations of diynes as well as their copolymerizations with monoynes. The polymers are completely soluble in common organic solvents and are thermally very stable with degradation temperatures (T_d) up to ∼500 °C. The polymers exhibit efficient photoluminescence (PL) with fluorescence quantum yields (Φ_F) up to 98% and optical limiting performance superior to C_{60}, a well-known optical limiter.[51,54] In this work, we extended our research effort in the area. We designed and synthesized a series of hyperbranched poly(aminoarylene)s (*hb*-PAAs) using DPA- and TPA-containing di- and triynes as well as monoynes as building blocks (Scheme 1). The *hb*-PAAs were found to resist thermal decomposition and emit blue light.

Experimental Section

Materials and Instrumentations. Toluene, hexane and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl immediately prior to use. Dichloromethane (DCM) was distilled over calcium hydride. Triethylamine was distilled under nitrogen and stored in a dark place over sodium hydroxide. Tantalum(V) bromide, cyclopentadienylcobaltdicarbonyl [$CpCo(CO)_2$], copper(I) iodide, tetraphenyltin, dichlorobis(triphenylphosphine)palladium(II), triphenylphosphine, lithium fluoride, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), and tris(8-hydroxyquinolinolato)aluminum (Alq_3) were purchased from Aldrich and used as received. Monoynes 1-octyne (**5**) and phenylacetylene (**6**) were purchased from Farchan, stored in a dark, cold, dry place, and distilled over calcium hydride prior to use.

* Corresponding author. Telephone: +852-2358-7375. Fax: +852-2358-1594. E-mail: tangbenz@ust.hk.

[†] Department of Chemistry, The Hong Kong University of Science & Technology.

[‡] Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University (administered by the Ministry of Education of the People's Republic of China).

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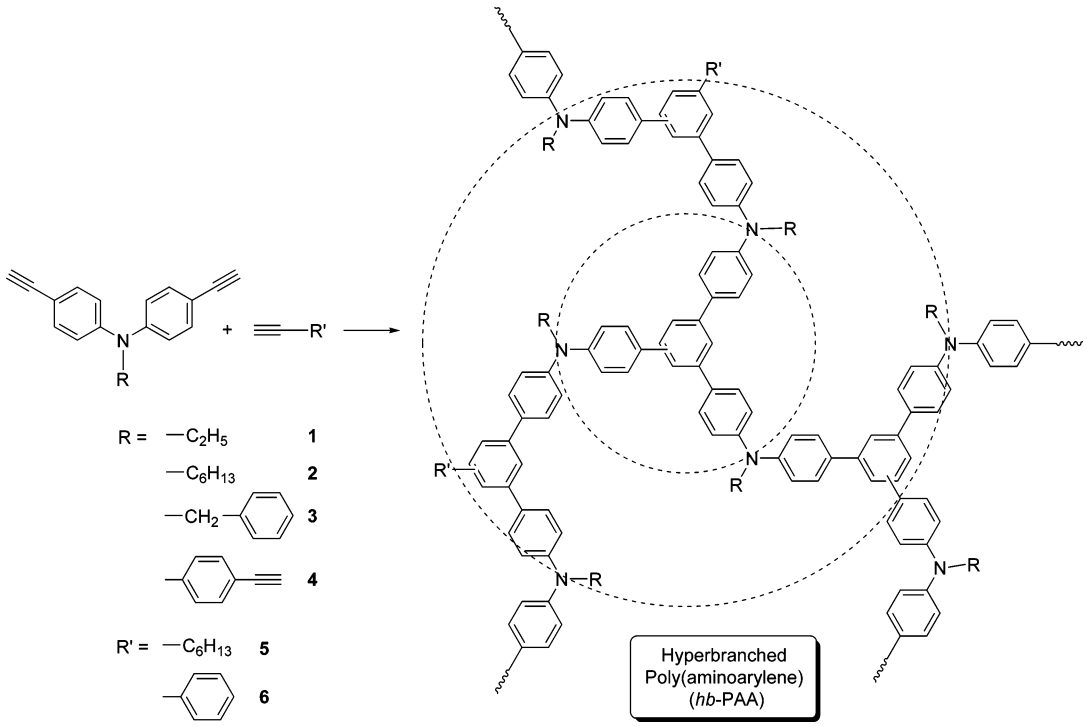
Scheme 1



Weight- (M_w) and number-average molecular weights (M_n) of the polymers and their polydispersity indexes (PDI or M_w/M_n) were estimated by a Waters Associates gel permeation chromatography (GPC) system in THF using monodisperse polystyrene as calibration standard. IR spectra were recorded on a Perkin-Elmer 16 PC FTIR spectrophotometer using pressed KBr disks or thin films. NMR spectra were measured on a Bruker ARX 300 NMR spectrometer using chloroform-*d* or DCM-d_2 as solvent and tetramethylsilane (TMS) as internal reference. Thermogravimetric analyses (TGA) of the polymers were carried out on a Perkin-Elmer TGA 7 analyzer at a heating rate of 20 °C/min under nitrogen. UV absorption spectra were measured on a Milton Ray Spectronic 3000 Array spectrophotometer. PL spectra were recorded in DCM on a SLM 8000C spectrofluorometer. 9,10-Diphenylanthracene was used as standard for quantum yield determination, whose Φ_F in cyclohexane was assumed to be 90% when excited at 355 nm. Thin solid films were prepared using a Spincoater model P6700 (Specialty Coating Systems, Inc.). PL spectra of the films were recorded on Perkin-Elmer LS 50B luminescence spectrometer with Xenon discharge lamp excitation. Electroluminescence (EL) spectra were obtained from a Kollmorgen Instrument PR650 photospectrometer. The luminescence area was 12.6 mm^2, and the current−voltage characteristics of the EL devices were obtained using a Hewlett-Packard HP4145B Semiconductor analyzer.

Fabrication of EL Devices. Indium−tin oxide (ITO) glasses were cleaned in ultrasonic baths of detergent solutions, followed by sequential rinsing with acetone, methanol, and deionized water before drying in an oven at 100 °C. After 25 min of UV−ozone treatment, the glass substrates were transferred into a vacuum chamber with a base pressure of 2×10^{-4} Pa for device preparation. EL devices based on the *hb*-PAAs were fabricated by spin-coating toluene solutions of the polymers onto the ITO glasses, followed by sequential vacuum depositions of multiple layers of other materials. The typical device configuration used in this work was Al(100 nm)/LiF(1 nm)/Alq_3(20 nm)/BCP(20 nm)/*hb*-PAA(50 nm)/ITO, where Al and ITO were cathode and anode, and LiF, Alq_3 and BCP were used as electron-injection (EIL), electron-transport (ETL), and hole-blocking (HBL) layers, respectively.

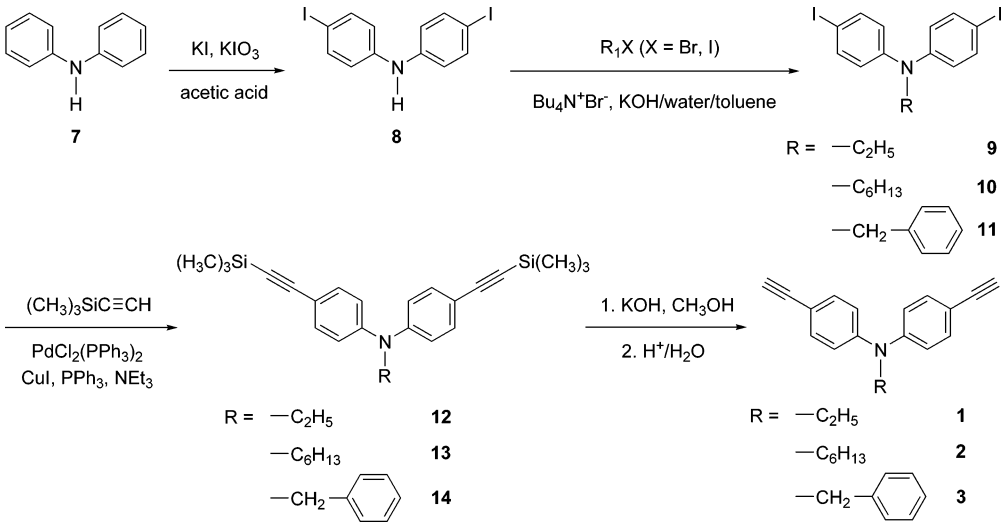
Monomer Synthesis. While monoyne monomers **5** and **6** were obtained from a commercial source, the amine-containing diynes **1**−**3** and triyne **4** were prepared according to the synthetic routes shown in Schemes 2 and 3, respectively.

Bis(4-iodophenyl)amine (8). In a round-bottom flask equipped with a condenser and a magnetic stirring bar were placed 2.54 g (15.0 mmol) of DPA (**7**), 150 mL of acetic acid, 3.65 g (22.0 mmol) of potassium iodide, and 2.35 g (11.0 mmol) of potassium iodate. The content was heated at 100 °C for 24 h under stirring. After the mixture was cooled to room temperature, 50 mL of 0.2 M aqueous solution of sodium sulfite was added. The mixture was then extracted with chloroform three times. The organic solution was collected and washed by deionized water. After solvent evaporation, the crude product was purified by silica gel chromatography using a mixture of hexane/chloroform (1:1 v/v) as eluent. The product was obtained as a light gray powder in 63% yield (3.98 g). IR (thin film), ν (cm^{-1}): 3422 (N−H stretching), 1893 (overtone band, disubstituted benzene ring), 1587, 1498 (aromatic ring C═C vibration), 815 (aromatic C−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.53 (m, 4H, Ar−H, meta to N), 6.80 (m, 4H, Ar−H, ortho to N), 5.65 (s, 1H, N−H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 142.2, 138.2, 119.9, 83.2.

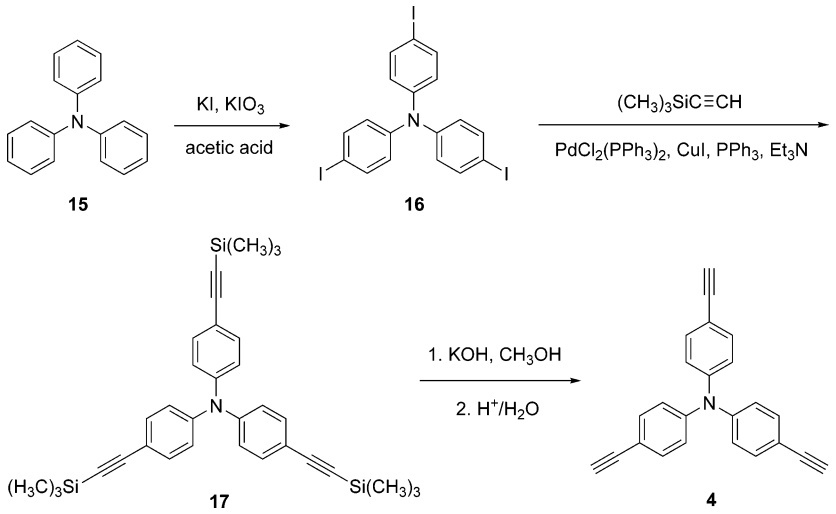
Bis(4-iodophenyl)ethylamine (9). To a 250 mL round-bottom flask equipped with a condenser and a magnetic stirring bar were added 4.21 g (10.0 mmol) of **8**, 50 mL of toluene, 50 mL of 50 wt % KOH aqueous solution, 0.65 g (2.0 mmol) of $Bu_4N^+Br^-$, and 1.87 g (12.0 mmol, 0.96 mL) of iodoethane. The mixture was then refluxed for 24 h under stirring. After this mixture was cooled to room temperature, the organic layer was separated and the water layer was extracted with chloroform three times. The combined organic extracts were washed with $NaHCO_3$ and water and then dried over $MgSO_4$. The crude product was purified by a silica gel column chromatography using hexane/chloroform (1:1 v/v) as eluent. A light gray solid was isolated in 48% yield (2.14 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.52 (m, 4H, Ar−H, meta to N), 6.74 (m, 4H, Ar−H, ortho to N), 3.71 (m, 2H, NCH_2), 1.18 (m, 3H, NCH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 146.8, 138.2, 123.0, 84.0, 46.4, 12.4.

Bis(4-iodophenyl)hexylamine (10). This intermediate was prepared from 2.11 g (5.0 mmol) of **8** and 0.99 g (6.0 mmol, 0.84 mL) of 1-bromohexane, using similar experimental procedures as described above. A colorless liquid was obtained in 44% yield (1.11 g). IR (thin film), ν (cm^{-1}): 2953, 2867 (CH_3 stretching), 2925, 2854 (CH_2 stretching), 1575, 1486 (aromatic ring C═C vibration), 809 (aromatic C−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.52 (m, 4H, Ar−H, meta to N), 6.73 (m, 4H,

Scheme 2



Scheme 3



Ar−H, ortho to N), 3.60 (m, 2H, NCH_2), 1.60 (m, 2H, NCH_2CH_2), 1.27 [m, 6H, $NCH_2CH_2(CH_2)_3$], 0.87 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 147.2, 138.2, 123.0, 83.9, 52.3, 31.5, 27.2, 26.6, 22.6, 14.0.

Bis(4-iodophenyl)benzylamine (11). This intermediate was prepared by the procedures similar to those for the preparation of **9**, using 8.42 g (20.0 mmol) of **8** and 4.11 g (24.0 mmol, 2.85 mL) of benzyl bromide as reactants. A white solid was obtained in 78% yield (7.96 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.49 (m, 4H, Ar−H, meta to N), 7.27 (m, 5H, benzyl protons), 6.81 (m, 4H, Ar−H, ortho to N), 4.93 (s, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 147.1, 138.2, 137.8, 128.7, 127.1, 126.3, 122.7, 84.3, 56.1.

Bis[4-(2-trimethylsilylethynyl)phenyl]ethylamine (12). To a 250 mL round-bottom flask equipped with a septum and a magnetic stirring bar were added 3.95 g (8.8 mmol) of **9**, 218.0 mg (0.31 mmol) $Pd(PPh_3)_2Cl_2$, 15 mg (0.08 mmol) CuI, and 20.3 mg (0.08 mmol) PPh_3. Triethylamine (70 mL) and 30 mL of THF were injected by a syringe. Trimethylsilylacetylene (2.6 mL, 18.6 mmol) was then added under stirring. The mixture was kept stirring at 50 °C for 12 h. The formed precipitate was filtered and washed with diethyl ether. The solvent was removed under reduced pressure. The obtained product was purified by silica gel chromatography using a mixture of hexane and chloroform as eluent. A light brown viscous liquid was isolated in 78% yield (2.69 g). IR (thin film), ν (cm^{-1}): 3039 (Ar−H stretching), 2960, 2898 (CH_3 stretching), 2153 (C≡C stretching), 1597, 1504 (aromatic ring C═C vibration), 1249 (Si−CH_3 bending), 864 (Si−C stretching), 842 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.35 (m, 4H, Ar−H, meta to N), 6.91 (m, 4H, Ar−H, ortho to N), 3.77 (m, 2H, NCH_2), 1.19 (m, 3H, NCH_2CH_3), 0.23 [s, 18H, $Si(CH_3)_3$]. ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 147.1, 133.1, 120.4, 115.6, 105.4, 93.0, 46.4, 12.6, 0.06.

Bis[4-(2-trimethylsilylethynyl)phenyl]hexylamine (13). This intermediate was prepared from 1.89 g (3.7 mmol) of **10** using procedure similar to those for the preparation of **12**. A light brown viscous liquid was obtained in 65% yield (1.08 g). IR (thin film), ν (cm^{-1}): 3040 (Ar−H stretching), 2958, 2871 (CH_3 stretching), 2930, 2859 (CH_2 stretching), 2153 (C≡C stretching), 1596, 1505 (aromatic ring C═C vibration), 1249 (Si−CH_3 bending), 862 (Si−C stretching), 842 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.33 (m, 4H, Ar−H, meta to N), 6.87 (m, 4H, Ar−H, ortho to N), 3.66 (m, 2H, NCH_2), 1.60 (m, 2H, NCH_2CH_2), 1.27 (m, 6H, $NCH_2CH_2(CH_2)_3$), 0.86 (m, 3H, CH_3), 0.24 [s, 18H, $Si(CH_3)_3$]. ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 147.3, 133.0, 120.3, 115.5, 105.3, 92.9, 52.2, 31.6, 27.4, 26.7, 22.7, 14.1, 0.21.

Bis[4-(2-trimethylsilylethynyl)phenyl]benzylamine (14). This intermediate was prepared by procedures similar to those for the preparation of **12**, using 7.92 g (15.5 mmol) of **11**. A white solid was obtained in 50% yield (3.53 g). IR (thin film), ν (cm^{-1}): 3037 (Ar−H stretching), 2958, 2898 (CH_3 stretching), 2153 (C≡C stretching), 1596, 1504 (aromatic ring C═C vibration), 1249 (Si−CH_3 bending), 856 (Si−C stretching), 843 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.33 (m, 4H, Ar−H, meta to N), 7.26 (m, 5H, benzyl protons), 6.98 (m, 4H, Ar−H, ortho to N), 4.98 (s, 2H, CH_2), 0.22 [s, 18H, $Si(CH_3)_3$]. ^{13}C

NMR (75 MHz, $CDCl_3$), δ (ppm): 147.4, 138.1, 133.1, 128.7, 127.1, 126.4, 120.3, 116.0, 105.2, 93.2, 55.8, 0.04.

Bis(4-ethynylphenyl)ethylamine (1). To a round-bottom flask equipped with a condenser and a stirring bar were added 2.34 g (6.0 mmol) of **13**, 100 mL of methanol, and 0.74 g (13.2 mmol) of KOH. After being stirred at 50 °C for 5 h, the mixture was poured into 250 mL of 1.0 M HCl solution. The mixture was extracted with chloroform four times. The combined organic layers were collected and the solvent was removed under reduced pressure. The crude product was purified by silica column chromatography using a hexane/chloroform mixture (1:1 v/v) as elutent. A pale yellow solid was isolated in 53% yield (0.78 g). IR (thin film), ν (cm^{-1}): 3304 (≡C−H stretching), 3038 (Ar−H stretching), 2973, 2897 (CH_3 stretching), 2929, 2869 (CH_2 stretching), 2103 (C≡C stretching), 1595, 1502 (aromatic ring C═C vibration), 830 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.39 (m, 4H, Ar−H, meta to N), 6.94 (m, 4H, Ar−H, ortho to N), 3.79 (m, 2H, CH_2), 3.02 (s, 2H, ≡C−H), 1.21 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 147.3, 133.3, 120.5, 114.6, 83.8, 76.2, 46.4, 12.6.

Bis(4-ethynylphenyl)hexylamine (2). This monomer was prepared by the procedures similar to those for the preparation of **1**. A light brown viscous liquid was isolated in 82% yield. IR (thin film), ν (cm^{-1}): 3289 (≡C−H stretching), 3038 (Ar−H stretching), 2950, 2870 (CH_3 stretching), 2928, 2857 (CH_2 stretching), 2102 (C≡C stretching), 1597, 1502 (aromatic ring C═C vibration), 826 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.38 (m, 4H, Ar−H, meta to N), 6.93 (m, 4H, Ar−H, ortho to N), 3.68 (m, 2H, NCH_2), 3.02 (s, 2H, ≡C−H), 1.63 (m, 2H, NCH_2CH_2), 1.28 [m, 6H, $NCH_2CH_2(CH_2)_3$], 0.87 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 147.7, 133.3, 120.5, 114.5, 83.8, 76.2, 52.2, 31.5, 27.3, 26.6, 22.6, 14.0.

Bis(4-ethynylphenyl)benzylamine (3). This monomer was prepared by the procedures similar to those for the preparation of **1**. A white solid was obtained in 88% yield. IR (thin film), ν (cm^{-1}): 3285 (≡C−H stretching), 3037 (Ar−H stretching), 2102 (C≡C stretching), 1597, 1502 (aromatic ring C═C vibration), 827 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.34 (m, 4H, Ar−H, meta to N), 7.25 (m, 5H, benzyl protons), 6.99 (m, 4H, Ar−H, ortho to N), 4.98 (s, 2H, $-CH_2$), 3.00 (s, 2H, ≡C−H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 148.0, 138.4, 133.7, 129.1, 127.5, 126.8, 120.8, 115.4, 84.1, 76.8, 56.3.

Tris(4-iodophenyl)amine (16). In a 500 mL round-bottom flask equipped with a condenser and a stirring bar were placed 3.92 g (16.0 mmol) of TPA (**15**), 240 mL of acetic acid, 5.84 g (35.2 mmol) of potassium iodide, and 3.76 g (17.6 mmol) of potassium iodate. The content was heated at 110 °C for 12 h. The temperature was cooled and the formed precipitate was collected by suction filtration. The crude product was thoroughly washed with 200 mL water. The solid was dissolved in 100 mL chloroform and consecutively washed with water, 0.2 M aqueous sodium sulfite solution, and $NaHCO_3$. The organic layer was dried over anhydrous $MgSO_4$. After solvent evaporation, a light gray solid was obtained, which was purified by recrystallization from a DCM/hexane mixture (1:2 v/v). A light gray solid was isolated in 90% yield (8.96 g). IR (thin film), ν (cm^{-1}): 3057 (aromatic C−H stretching), 1575, 1483 (aromatic ring C═C vibration), 816 (aromatic C−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.54 (m, 6H, Ar−H, meta to N), 6.81 (m, 6H, Ar−H, ortho to N). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 146.8, 138.7, 126.3, 86.9.

Tris[4-(2-trimethylsilylethynyl)phenyl]amine (17). This intermediate was prepared by the procedures similar to those for the preparation of **12**. A light yellow powder was obtained in 88% yield. IR (thin film), ν (cm^{-1}): 3038 (Ar−H stretching), 2157 (C≡C stretching), 1596, 1505 (aromatic ring C═C vibration), 1249 (Si−CH_3 bending), 864 (Si−C stretching), 843 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.34 (m, 6H, Ar−H, meta to N), 6.98 (m, 6H, Ar−H, ortho to N), 0.24 [s, 27H, $Si(CH_3)_3$]. ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 147.1, 133.3, 124.2, 118.1, 105.1, 94.1, 0.10.

Tris(4-ethynylphenyl)amine (4). This triyne monomer was prepared by the procedures similar to those for the preparation of **1**. A light yellow powder was obtained in 89% yield. IR (thin film), ν (cm^{-1}): 3288 (≡C−H stretching), 3038 (Ar−H stretching), 2105 (C≡C stretching), 1598, 1497 (aromatic ring C═C vibration), 833 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.39 (m, 6H, Ar−H, meta to N), 7.02 (m, 6H, Ar−H, ortho to N), 3.12 (s, 3H, ≡C−H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 147.3, 133.5, 124.3, 117.0, 83.6, 77.1.

Table 1. Synthesis of Hyperbranched Homopoly(aminoarylene)s[a]

run	monomer	cat.	[cat.] (mM)	polymer yield (%)	solubility[b]	M_w[c]	PDI[c]
1	**1**	Co	15	77	□	6300	3.1
2	**2**	Co	15	93	□	6500	2.0
3	**3**	Nb	5	0			
4	**3**	Ta	5	trace			
5[d]	**3**	Ta	10	61	Δ		
6	**3**	Co	15	78	□	6100	2.4
7	**3**	Ta	5	90	×		
8[e]	**4**	Co	15	2	□	3800	1.4

[a] Polymerization reaction carried out under nitrogen in toluene using $CpCo(CO)_2-h\nu$ (Co) at 65 °C for 24 h or $NbCl_5$ (Nb) or $TaBr_5$ (Ta) at room temperature for 6 h. [Diyne] = [triyne] = 0.1 M. [b] Tested in common organic solvents such as toluene, THF, DCM, and chloroform. Symbols: □ = completely soluble; Δ = partly soluble; × = insoluble. [c] Determined by GPC in THF on the basis of a polystyrene calibration. [d] [Diyne] = 0.2 M. [e] [Triyne] = 0.5 M.

Polymerization. All polymerization reactions were carried out under nitrogen atmosphere using a standard Schlenk technique in a vacuum line system or an inert-atmosphere glovebox (Vacuum Atmospheres), except for the purification of the polymers, which was done in an open atmosphere. Typical experimental procedures for the copolymerization of **3** with **5** are given below.

Into a thoroughly baked and carefully evacuated 15 mL Schlenk tube with a three-way stopcock on the sidearm was placed 26.4 mg (0.045 mmol) of $TaBr_5$ under nitrogen in a glovebox. Freshly distilled toluene (1.2 mL) was then injected into the tube using a hypodermic syringe. After this mixture was stirred for 5 min, a solution of 70.0 mg (0.23 mmol) of **3** and 62.7 mg (0.57 mmol, 0.084 mL) of **5** in 1.0 mL toluene was syringed. The polymerization mixture was stirred at room temperature under nitrogen for 6 h. The reaction was stopped by the addition of a small amount of methanol. The mixture was then added dropwise to 300 mL of methanol through a cotton filter under stirring. After the mixture was left to stand overnight, the polymer precipitate was filtered by a Gooch crucible, washed with methanol and hexane, and dried in a vacuum at room temperature. Repeated dissolutions and precipitations as well as careful washing of the polymer solutions with dilute aqueous hydrochloric acid (~3%) were performed to ensure complete removal of any residues of the transition-metal catalyst in the polymer sample.

Characterization Data for *hb*-P3/5. The compound was obtained as a yellow-green powder; yield 38% (Table 2, no. 6). M_w 12300, PDI 2.0 (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 3030 (Ar−H stretching), 2954, 2869, 2926, 2856 (aliphatic C−H stretching), 1601, 1512 (C═C ring stretching), 820 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.49, 7.40, 7.32, 7.19, 7.02 (Ar−H), 5.09 (NCH_2Ph), 2.60 [$Ph-CH_2(CH_2)_4$], 1.60, 1.31, 1.21 [$Ph-CH_2(CH_2)_4$], 0.87 (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 149.50, 148.82, 139.93, 130.98, 129.35, 128.64, 127.64, 127.41, 121.05, 59.18, 37.10, 36.80, 32.56, 32.23, 30.27, 29.89, 23.42, 23.33, 14.68.

hb-**P1.** This was obtained as a brown solid; yield 77% (Table 1, no. 1). M_w 6300, PDI 3.1 (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 3299 (≡C−H stretching), 3036 (Ar−H stretching), 2974, 2932 (aliphatic C−H stretching), 2101 (C≡C stretching), 1599, 1508 (aromatic ring C═C vibration), 821 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.65, 7.38, 7.18, 6.96, 6.58 (Ar−H), 3.81 (NCH_2), 3.03 (≡C−H), 1.22 (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 147.27, 133.30, 131.04, 128.36, 128.11, 124.09, 120.49, 117.36, 83.82, 76.19, 46.41, 12.63.

hb-**P1/5.** This was obtained as a yellow-green powder, yield 23% (Table 2, no. 2). M_w 12000, PDI 1.7 (GPC, polystyrene calibration).

Table 2. Synthesis of Hyperbranched Copoly(aminoarylene)s[a]

run	monomer	M_r[b]	[cat.] (mM)	polymer yield (%)	solubility[c]	M_w[d]	PDI[d]
1	**1/5**	1:1.5	20	9	□	16 400	2.6
2	**1/5**	1:2.5	20	23	□	12 000	1.7
3	**2/5**	1:1.5	20	48	□	14 500	2.7
4	**2/5**	1:2.5	20	32	□	9700	2.1
5	**3/5**	1:1.5	20	79	Δ		
6	**3/5**	1:2.5	20	38	□	12 300	2.0
7	**4/5**	1:1.5	5	99	×		
8	**4/5**	1:3.0	5	25	□	9800	2.2
9	**4/6**	1:3.0	5	76	Δ		
10	**4/6**	1:4.0	5	55	□	26 600	8.4

[a] Polymerization reaction carried out under nitrogen in toluene using $TaBr_5$ as catalyst at room temperature for 6 h. [Diyne] = [triyne] = 0.1 M. [b] Molar ratio (M_r) of [diyne]/[monoyne] or [triyne]/[monoyne]. [c] Tested in common organic solvents such as toluene, THF, DCM and chloroform. Symbols: □ = completely soluble; Δ = partly soluble; × = insoluble. [d] Determined by GPC in THF on the basis of a polystyrene calibration.

IR (thin film), ν (cm^{-1}): 3027 (Ar−H stretching), 2951, 2868, 2926, 2855 (aliphatic C−H stretching), 1600, 1509 (C═C ring stretching), 819 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.55, 7.34, 7.09, 7.03, 6.95 (Ar−H), 3.85 (NCH_2), 2.59 [Ph−CH_2(CH_2)$_4$], 1.60, 1.30, 1.23 (CH_2), 0.86 (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):147.32, 146.34, 143.78, 142.43, 141.57, 140.57, 138.01, 134.23, 131.17, 130.57, 130.20, 129.78, 128.23, 127.99, 127.44, 125.96, 125.41, 124.38, 124.04, 123.42, 121.55, 46.93, 36.56, 36.41, 36.03, 35.86, 33.08, 32.16, 31.92, 29.87, 29.50, 23.03, 14.28, 12.97.

hb-**P2.** This was obtained as a brown solid; yield 93% (Table 1, no. 2). M_w 6500, PDI 2.0 (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 3283 (≡C−H stretching), 3033 (Ar−H stretching), 2952, 2924, 2853 (aliphatic C−H stretching), 2100 (C≡C stretching), 1596, 1505 (C═C ring stretching), 818 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.65, 7.50, 7.40, 7.37, 7.17, 6.99, 6.95, 6.92, 6.88, 6.80 (Ar−H), 3.71 (NCH_2), 3.03 (≡C−H), 1.64, 1.29 (CH_2), 0.87 (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 148.30, 147.62, 133.27, 133.14, 131.03, 128.30, 128.06, 124.00, 120.48, 117.32, 83.83, 75.55, 52.33, 52.18, 31.57, 29.67, 27.29, 26.63, 22.59, 14.01.

hb-**P2/5.** This was obtained as a yellow-green powder; yield 32% (Table 2, no. 4). M_w 9700, PDI 2.1 (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 3031 (Ar−H stretching), 2955, 2870, 2927, 2856 (aliphatic C−H stretching), 1600, 1511 (C═C ring stretching), 819 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.51, 7.39, 7.18, 7.08, 6.95 (Ar−H), 3.74 (NCH_2), 2.59 (PhCH_2), 1.60, 1.30 (CH_2), 0.85 (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 148.10, 134.92, 130.84, 128.58, 128.31, 121.51, 117.52, 53.21, 36.80, 34.79, 32.55, 32.46, 29.89, 28.28, 27.55, 23.42, 14.66, 14.60.

hb-**P3.** This was obtained as a brown powder; yield 78% (Table 1, no. 6). M_w 6100, PDI 2.4 (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 3292 (≡C−H stretching), 3032 (Ar−H stretching), 2926, 2855 (aliphatic C−H stretching), 2102 (C≡C stretching), 1598, 1504 (C═C ring stretching), 822 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.58, 7.27, 7.03 (Ar−H), 5.00 (NCH_2Ph), 3.01 (≡C−H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 148.12, 147.56, 138.01, 133.29, 131.01, 128.69, 127.08, 126.41, 123.34, 120.33, 117.85, 117.38, 114.94, 84.10, 76.33, 56.09.

hb-**P4.** This was obtained as a yellow solid; yield 2% (Table 1, no. 8). M_w 3800, PDI 1.4 (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 3297 (≡C−H stretching), 3035 (Ar−H stretching), 2103 (C≡C stretching), 1594, 1504 (aromatic ring C═C vibration), 826 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.72, 7.61, 7.54, 7.38, 7.05, 7.01 (Ar−H), 3.06 (≡C−H).

hb-**P4/5.** This was obtained as a light yellow powder; yield 25% (Table 2, no. 8). M_w 9800, PDI 2.2 (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 3298 (≡C−H stretching), 3033 (Ar−H stretching), 2955, 2871, 2927, 2856 (aliphatic C−H stretching), 2106 (C≡C stretching), 1600, 1506 (aromatic ring C═C vibration), 832 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.54, 7.23, 7.09 (Ar−H), 3.05 (≡C−H), 2.63 (PhCH_2), 1.64, 1.34 (CH_2), 0.91 (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 147.09, 143.80, 141.54, 140.67, 138.17, 133.43, 130.59, 128.20, 124.52, 36.41, 32.17, 31.92, 29.51, 23.04, 14.31.

hb-**P4/6.** This was obtained as a light yellow powder, yield 55% (Table 2, no. 10). M_w 26600, PDI 8.4 (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 3290 (≡C−H stretching), 3030 (Ar−H stretching), 2099 (C≡C stretching), 1599, 1505 (aromatic ring C═C vibration), 823 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.70, 7.49, 7.42, 7.39, 7.25, 7.12, 7.02 (Ar−H), 3.11 (≡C−H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 148.41, 147.87, 147.45, 146.92, 146.39, 142.67, 142.03, 141.41, 140.83, 139.96, 135.92, 133.57, 131.46, 130.28, 129.24, 128.27, 127.66, 124.96, 123.83, 83.86, 76.95.

Results and Discussion

Monomer Synthesis. We designed the molecular structures of a group of di- and triyne monomers containing DPA and TPA moieties and elaborated multiple-step reaction routes for their syntheses (cf. Schemes 2 and 3). Iodination of DPA (**7**) at 4,4′-positions was achieved by potassium iodide and iodate in acetic acid, which gave aryldiiodide **8**. The amino proton in **8** was replaced by alkyl or benzyl group, using *n*-$Bu_4N^+Br^-$ as catalyst. Palladium-catalyzed Sonogashira coupling of the resulting products with trimethylsilylacetylene and subsequent removal of the trimethylsilyl protection group in alcoholic KOH solution furnished diyne monomers **1**−**3**. Triyne monomer **4** was prepared via similar reaction pathways. Iodination of TPA followed by palladium-catalyzed cross-coupling with trimethylsilylacetylene gave the desired product in an overall yield of 70.5% after deprotection in methanolic KOH solution. All the monomers were obtained as white or pale yellow powders and characterized by spectroscopic methods, from which satisfactory spectral data corresponding to their molecular structures were obtained (see Experimental Section for details).

Polymerization Reactions. We first tried to homopolymerize monomers **1**−**4**. The polymerization results are summarized in Table 1. Using **3** as a model monomer, we evaluated the catalytic activities of different transition metal complexes. $NbBr_5$ was ineffective in initiating the polycyclotrimerization of **3**: no polymer was isolated after 6 h (Table 1, run 3). The pentabromide of its family member tantalum showed a sign of catalytic activity under the identical conditions, with a trace amount of polymeric product obtained. Increasing the catalyst concentration from 5 to 10 mM dramatically increased the polymer yield (Table 1, run 5). The polymer was, however, only partially soluble, probably due to the uncontrolled intermolecular cross-linking reactions. Under irradiation of a UV light, $CoCp(CO)_2$ efficiently initiated the polycyclotrimerization of **3** and a completely soluble hyperbranched polymer *hb*-P**3** was obtained in 78% yield after 24 h reaction. The molecular weight was moderate (M_w = 6100) but the PDI value was normal (2.4), noticing that hyperbranched polymers often possess abnormally large PDI values.[54] Similarly, diynes **1** and **2** were converted into completely soluble *hb*-P**1** and *hb*-P**2** in high yields by the $CoCp(CO)_2-h\nu$ system at 65 °C.

Polycyclotrimerizations of triyne **4** were carried out using $TaBr_5$ and $CoCp(CO)_2-h\nu$ as catalysts. The polymerization of **4** catalyzed by $TaBr_5$ proceeded rapidly and formed an insoluble gel after 20 min. Although $TaBr_5$ was an effective catalyst for the polycyclotrimerization of diynes, it is not surprising that cross-linking reactions were easily induced in the polymerization **4**, a trifunctional acetylene monomer (triyne). Again, only the polymer prepared from $CoCp(CO)_2-h\nu$ was soluble, possibly due to its low molecular weight.

To improve the solubility of the polymers and to increase their molecular weights, we carried out copolycyclotrimeriza-

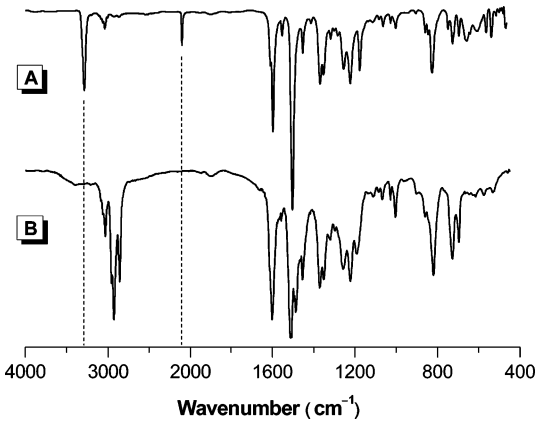


Figure 1. IR spectra of (A) diyne **3** and (B) its copolymer *hb*-P**3**/**5** (sample taken from Table 2, no. 6).

tions of the diynes and triyne with monoyne 1-octyne (**5**; Table 2). The monoyne is expected to terminate some reactive triple bonds, which will help put the vigorous cross-linking reactions under control and at the same time impart solubility to the growing polymer branches, thanks to the long alkyl chain of the monoyne monomer.[50−56] This idea works well and a hyperbranched copolymer, completely soluble in common organic solvents such as chloroform, THF, and toluene, was obtained from $TaBr_5$-catalyzed polycyclotrimerization of **1** in the presence of 1.5 equiv of **5** (Table 2, run 1). The molecular weight increased from 6300 for the homopolymer to 16400 for the copolymer, while the PDI was decreased from 3.1 to 2.6. The yield was, however, still rather low. Increasing the amount of **5** led to a 2.5-fold increase in the polymer yield and produced an *hb*-P**1**/**5** with a molecular weight of 12000 and a PDI of 1.7.

Diyne **2** again showed better polymerizability than **1** and its copolymerization with **5** in a molar ratio of 1:1.5 furnished an *hb*-P**2**/**5** with a high molecular weight of 14500 in 48% yield (Table 2, run 3). Increasing the monoyne concentration lowered the polymer yield and molecular weight. While a diyne-to-monoyne ratio of 1:1.5 was sufficient to produce a soluble copolymer from **1** and **2**, under the same M_r ratio, copolymerization of **3** with **5** gave only a partly soluble product. An increase in the ratio to 1:2.5 helped solve the problem and a soluble copolymer with a molecular weight of 12300 was obtained in 38% yield.

The homopolymerization of **4** catalyzed by $TaBr_5$ was fast, giving a polymeric product in 90% yield in a short reaction time. The catalyst also worked well for its copolymerization with 1-octyne. While a 1:1.5 mole ratio of **4** to **5** produced no soluble product, doubling the monoyne concentration gave a completely soluble copolymer, although in a low isolation yield. To enhance electronic communication, copolymerization of **4** with phenylacetylene was attempted. Unlike the situation in **5**, copolymerization in the presence of 3-fold excess of **6** yielded a gel. A high molecular weight copolymer *hb*-P**4**/**6** was isolated in 55% yield when the amount of **6** was increased to 4-fold (Table 2, run 10).

Structural Characterization. The *hb*-PAAs were characterized spectroscopically, all of which gave satisfactory analysis data corresponding to their expected structures (see Experimental Section for details). An example of the IR spectrum of *hb*-P**3**/**5** is shown in Figure 1, along with that of its diyne monomer. Diyne **3** shows strong absorption bands at 3285 and 2103 cm^{-1} associated with ≡C−H and C≡C stretchings, respectively. These bands completely disappear in the spectrum of its copolymer, indicating that all the triple bonds have been consumed by the polymerization reaction. Meanwhile, the absorption peak at 3030 cm^{-1} assignable to aromatic C−H stretching is intensified. Two new strong absorption bands at 2926 and 2856 cm^{-1} associated with alkyl stretching are also observed due to the incorporation of 1-octyne unit into the copolymer. All these spectral data prove that diyne **3** has been successfully copolymerized with monoyne **5**, producing a hyperbranched polymer via the [2 + 2 + 2] cyclotrimerization mechanism.

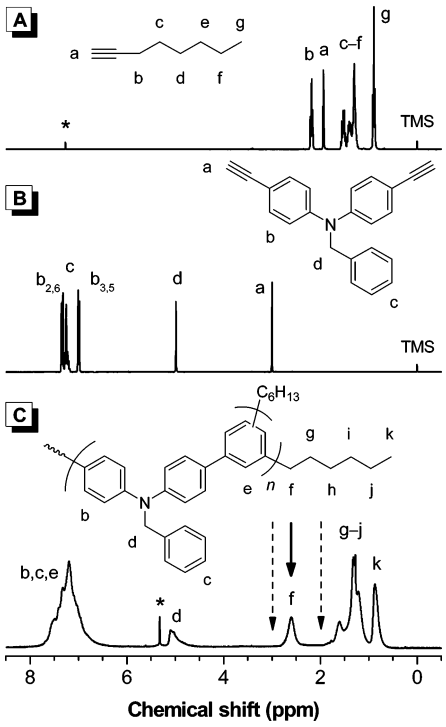


Figure 2. ^{1}H NMR spectra of chloroform-*d* solutions of (A) monoyne **5** and (B) diyne **3** and (C) DCM-d_2 solution of their hyperbranched copolymer *hb*-P**3**/**5** (sample taken from Table 2, no. 6). The solvent peaks are marked with asterisks.

Figure 2 shows the ^{1}H NMR spectrum of copolymer *hb*-P**3**/**5** along with those of its monomers. All the resonance peaks in the copolymer can be readily assigned. Compared with those of its monomers, the peaks of *hb*-P**3**/**5** are broader due to its irregular and rigid structure. The resonance peaks of the ethynyl protons of monomers **3** and **5** are located at δ 3.00 and 1.93, respectively. These peaks are not found in their copolymer, proving that **3** and **5** have been polycyclotrimerized and suggesting that **5** has meanwhile worked as an end-capping agent to terminate the triple bonds in the periphery. The aromatic proton absorptions are intensified after polymerization. Additionally, the peak at δ 2.18 assigned to the propargyl protons of **5** shifts downfield to δ 2.60 in the spectrum of its copolymer, further proving the formation of the new aromatic rings via the [2 + 2 + 2] polycyclotrimerization reaction.

To gain more insights into the structures of the copolymers, the areas of the proton resonance peaks were integrated and analyzed. The methylene absorption of the benzyl unit at $\delta \sim 2.6$ (peak f in panel C of Figure 2) is clearly free from the interference by other resonances. Using the integrated areas of the resonance peaks of the aromatic and methylenic protons, the ratios of the numbers of diyne units (N_{II}) to the numbers of monoyne units (N_I) can be estimated for *hb*-P**1**/**5** and *hb*-P**2**/**5** according to eq 1:

$$\frac{N_{II}}{N_I} = \frac{(A_{Ph} - A_{Ph-CH_2}/2)/10}{A_{Ph-CH_2}/2} = \frac{2A_{Ph} - A_{Ph-CH_2}}{10A_{Ph-CH_2}} \qquad (1)$$

Table 3. Molecular Weights of Hyperbranched Poly(aminoarylene)s (*hb*-PAAs) Calculated from NMR Data and Estimated by GPC Analysis

no.	*hb*-PAA	N_{II}/N_I[a]	N_{II}	N_I	$M_{n,c}$[b]	M_n[c]	PDI[b]
1	*hb*-P**1**/**5**	0.90	27	30	9930	7060	1.4
2	*hb*-P**2**/**5**	0.83	15	18	6500	4620	1.4
3	*hb*-P**3**/**5**	0.88	22	25	9520	6150	1.5

[a] Molar ratio of the number of diyne units (N_{II}) to the number of monoyne units (N_I) in the copolymer. [b] Calculated from the integrated area of the resonance peaks in the ^{1}H NMR spectra. [c] Measured in THF on the basis of a polystyrene calibration.

and for *hb*-P**3**/**5** according to eq 2:

$$\frac{N_{II}}{N_I} = \frac{(A_{Ph} - A_{Ph-CH_2}/2)/15}{A_{Ph-CH_2}/2} = \frac{2A_{Ph} - A_{Ph-CH_2}}{15A_{Ph-CH_2}} \quad (2)$$

where A_{Ph} and A_{Ph-CH_2} are the integrated areas of the resonance peaks of the phenyl (Ph) and benzyl methylene (Ph−CH_2) protons in the copolymers, respectively. Assuming that no cyclic structures have been formed via internal cyclizations and backbiting propagations and that all the triple bonds have been terminated by 1-octyne, the number of diyne units can thus be estimated according to eq 3:

$$N_I = N_{II} + 3 \quad (3)$$

Combining eqs 2 and 3 gives access to N_{II} and N_I, which allows calculations of number-average molecular weights of the copolymers from their NMR spectral data by eq 4:

$$M_{n,c} = N_{II}M_{II,0} + N_IM_{I,0} \quad (4)$$

where $M_{n,c}$ is the calculated number-average molecular weight and $M_{II,0}$ and $M_{I,0}$ are the molecular weights of the diyne and monoyne monomers, respectively. The calculated molecular weights and the experimental values measured by GPC are summarized in Table 3. For all the three copolymers, the calculated molecular weights are higher than the experimental values by 1.4−1.5 times. This difference may be caused by the internal cyclization reactions, which lower the 1-octyne content and thus increase the N_{II}/N_I ratio.

Taking the internal cyclization reactions into consideration, eq 3 will be changed to eq 5:

$$N_I = N_{II} + 3 - 3m \quad (5)$$

where *m* is the number of cyclic structures in the hyperbranched polymer. From eq 5, it can be seen that the presence of one cycle will result in an equal amount of N_{II} and N_I. The N_{II}/N_I ratios for all the hyperbranched copolymers are, however, smaller than 1, indicating that no cyclic structures have formed. Another reason for the lower experimental values from the GPC measurements may be the fact that the polystyrene-calibrated GPC analysis have underestimated molecular weights of hyperbranched polymers due to their globular sizes.[57,58] The latter explanation seems to predominate in our case, although the first one cannot be completely excluded.

Similarly, the molar composition of *hb*-P**4**/**5** can be estimated from the peak integrals of its ^{1}H NMR spectrum. The molar ratio of the number of triyne units (N_{III}) to the number of monoyne units (N_I) can be calculated according to eq 6:

$$\frac{N_{III}}{N_I} = \frac{(A_{Ph} + A_{C\equiv CH} - A_{Ph-CH_2}/2)/15}{A_{Ph-CH_2}/2} = \frac{2A_{Ph} + 2A_{C\equiv CH} - A_{Ph-CH_2}}{15A_{Ph-CH_2}} \quad (6)$$

where $A_{C\equiv CH}$ is the integrated area of the resonance peaks of the protons of the unterminated triple bonds in the copolymer. According to eq 6, the N_{III}/N_I ratio is 0.648 or 1/1.54. Assuming no internal cyclization reactions, theoretically N_I and N_{III} should have the following relationship:

$$N_I = 3N_{III} + 3 \quad (7)$$

This means, for high molecular weight polymers, the N_{III}/N_I should approach a maximum ratio of 0.33 or $^1/_3$. It immediately becomes clear that the assumption of no internal cyclization is not applicable to the case of the triyne monomer. Taking the formation of internal ring structures into account, eq 7 will be changed to eq 8:

$$N_I = 3N_{III} + 3 - 3m \quad (8)$$

Inserting the N_{III}/N_I ratio ($N_{III}/N_I = 0.648$) found by the ^{1}H NMR analysis into eq 8 will lead to the following relationship between N_{III} and *m*:

$$m = 0.486N_{III} + 1 \quad (9)$$

Since we have no information about the number of cycles or the number of monomer units in the copolymer, it is thus not possible to calculate the molecular weight of *hb*-P**4**/**5**. Table 4 shows some examples of N_{III}, N_I and *m* pairs calculated according to eq 9. The corresponding expected molecular weights can thus be estimated according to eq 10:

$$M_{n,c} = N_{III}M_{III,0} + N_IM_{I,0} \quad (10)$$

where $M_{III,0}$ is the molecular weight of the triyne monomer. According to the calculated ratio of triyne to monoyne, a hyperbranched copolymer comprising 10 triyne monomers will require 15 monoynes and 6 internal cycles as building blocks, in which case, a copolymer with a number-average molecular weight of 4830 will be produced (Table 4, no. 1). Increasing the triyne unit to 20 will increase the $M_{n,c}$ to 9810, which matches very well with the molecular weight determined by GPC (cf. Table 2, no. 8). Assuming a 50% underestimation of the molecular weight, *hb*-P**4**/**5** will possess an average of 30 triyne and 2 monoyne monomers along with 16 internal ring structures.

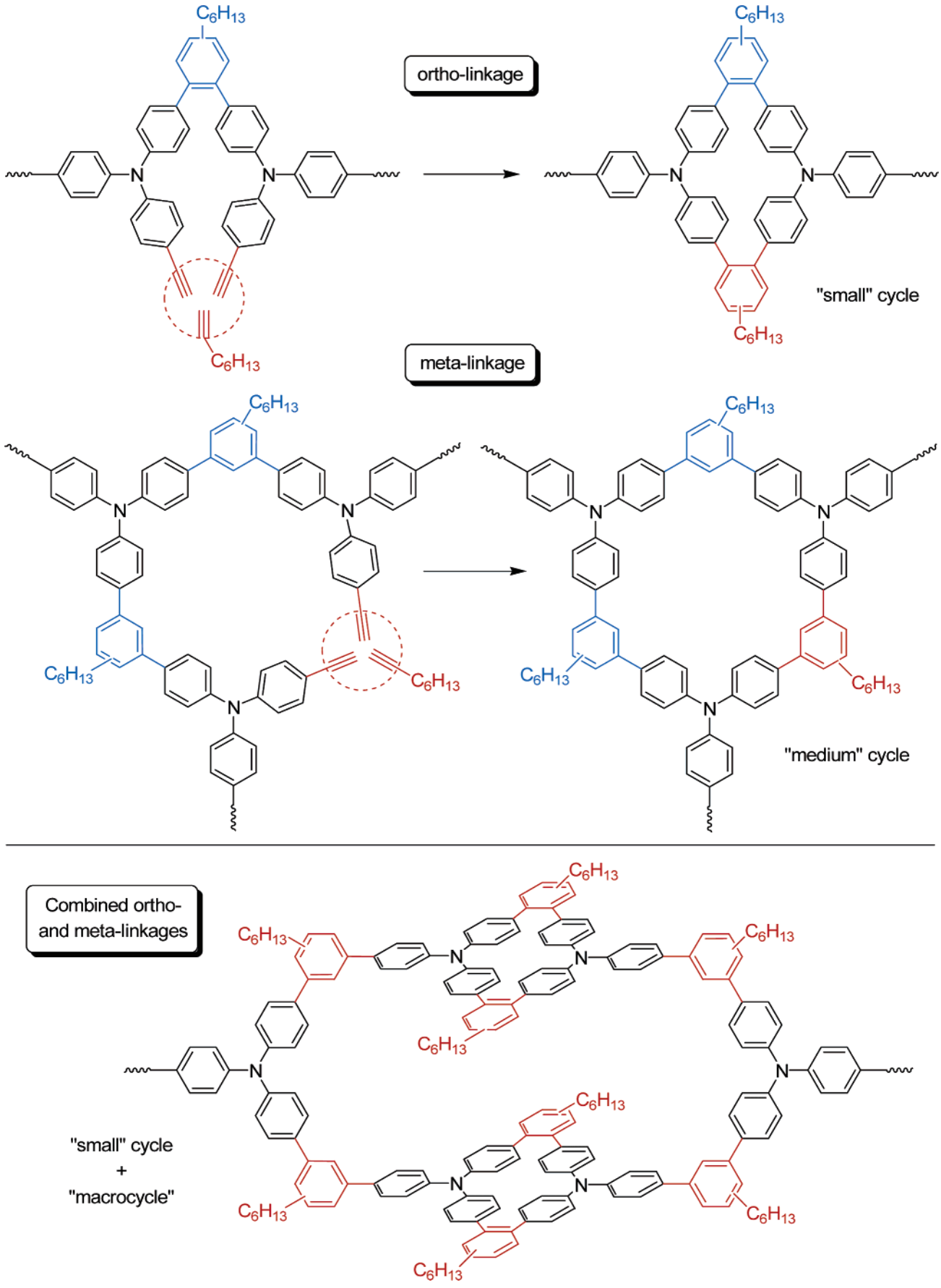
Table 4 clearly shows that the copolycyclotrimerization of triyne **4** with monoyne **5** results in the formation of a hyperbranched copolymer with a significant amount of internal cyclic structures. Why is such a heavily "cross-linked" product still soluble? Previous structural analysis and computational simulation of the hyperbranched polymers prepared from

Table 4. Examples of Calculated Structural Compositions and Molecular Weights of *hb*-P4/5

no.	N_{III}[a]	N_I[b]	m[c]	$M_{n,c}$[d]
1	10	15	6	4830
2	20	31	11	9810
3	30	46	16	14 590

[a] Number of triyne units (N_{III}). [b] Number of monoyne units (N_I) based on the ^{1}H NMR measurement ($N_{III}/N_I = 1/1.54$). [c] Calculated according to eq 9. [d] Calculated according to eq 10.

Scheme 4



polycyclotrimerizations of diynes suggest that the internal cyclizations were proceeded in such a way that the cyclic structures were formed via simple linear and branched propagations.[59,60] Scheme 4 illustrates some proposed propagation modes

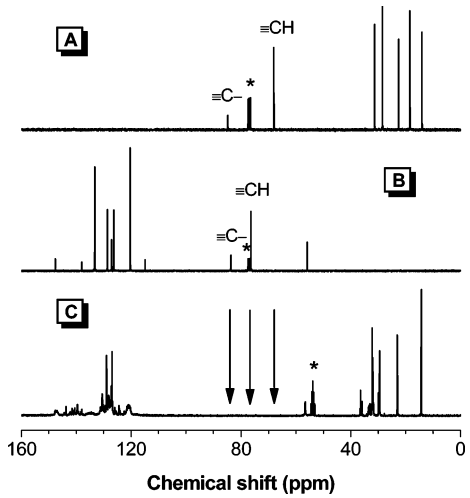


Figure 3. ^{13}C NMR spectra of chloroform-*d* solutions of (A) monoyne **5** and (B) diyne **3** and (C) DCM-d_2 solution of its copolymer *hb*-P**3**/**5** (sample taken from Table 2, no. 6). The solvent peaks are marked with asterisks.

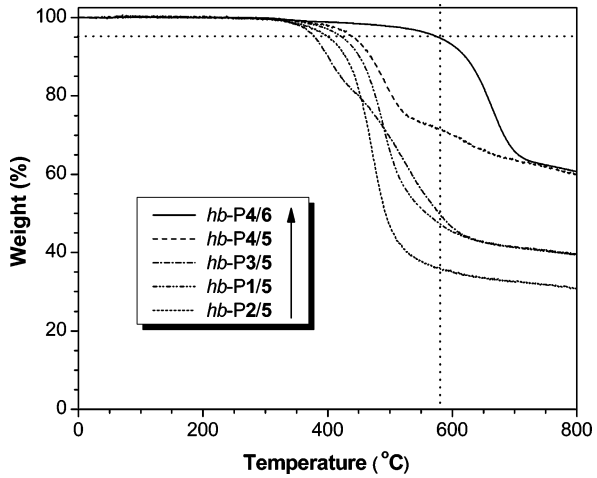


Figure 4. TGA thermograms of *hb*-PAAs recorded under nitrogen at a heating rate of 20 °C/min. Samples taken from Table 2, nos. 1, 4, 6, 8, and 10.

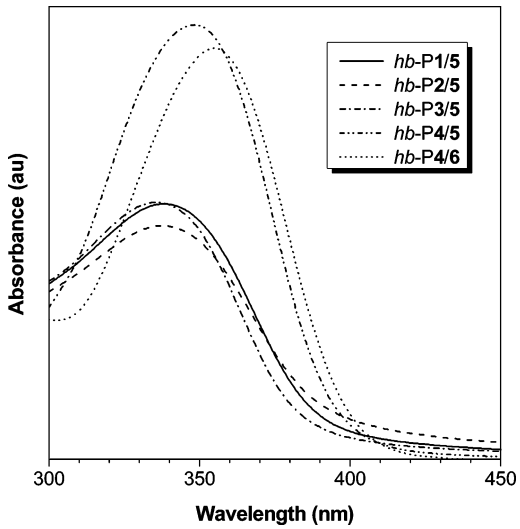


Figure 5. UV spectra of *hb*-P**1**/**5**, *hb*-P**2**/**5**, *hb*-P**3**/**5**, *hb*-P**4**/**5**, and *hb*-P**4**/**6** in DCM solutions with concentration of 12 μg/mL; samples taken from Table 2, nos. 2, 4, 6, 8, and 10, respectively.

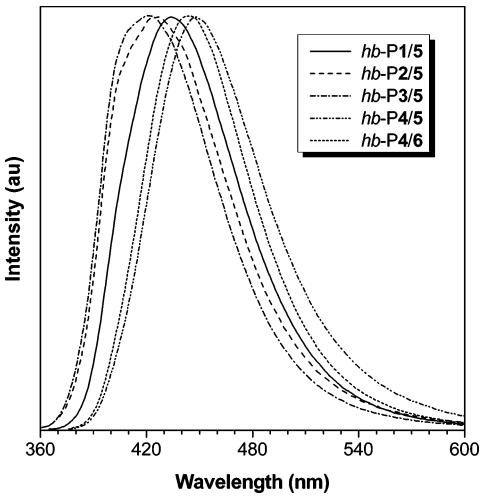


Figure 6. Photoluminescence spectra of DCM solutions of *hb*-PAAs. Solution concentration: 12 μg/mL. Excitation wavelength (nm): 365 (*hb*-P**1**/**5**), 361 (*hb*-P**2**/**5**), 363 (*hb*-P**3**/**5**), 376 (*hb*-P**4**/**5**), and 378 (*hb*-P**4**/**6**). Samples were taken from Table 2, nos. 2, 4, 6, 8, and 10, respectively.

of *hb*-P**4**/**5** accounting the intracyclotrimerization reactions. It is well-known that transition metal-catalyzed alkyne cyclotrimerizations yield mixtures of 1,2,4- and 1,3,5-substituted benzene derivatives. If two triyne monomers are ortho-connected, the close intramolecular proximity of their two acetylene units are likely to be terminated by another triple bond (e.g., from 1-octyne), thus furnishing a second 1,2,4-substituted benzene ring. This intramolecular cross-linking leads to the formation of a "small" cycle, yet the polymer is still soluble due to the overall linear propagation mode.

Another possible pathway is the ring closure of three triyne monomers, which are connected in a meta-fashion and formed with a monoyne via both 1,2,4- and 1,3,5-substituted propagations. Such molecular arrangements are likely to yield "medium"-sized rings, representing a macrodentritic propagation with only three growing arms. Para-substituted polymer branches resulting from 1,2,4-cyclotrimerizations inherently cannot form any ring structures and may only involve the formation of oval-shaped "macrocycles". Such cyclic substructures are possibly formed via the combined ortho- and meta-linkages but have no detrimental effect on the solubility of the resulting polymers as the overall structure is still linearly propagated.

Furthermore, to all these structural discussions, comes the conclusion that the incorporation of 1-octyne should have helped improve the solubility of the polymers. The picture becomes clearer if we compare the solubility of the two copolymers prepared from 1-octyne (**5**) and phenylacetylene (**6**). While a triyne-to-monoyne ratio of 1:3 is sufficient to yield a soluble copolymer *hb*-P**4**/**5**, a ratio of 1:4 is necessary to render *hb*-P**4**/**6** soluble (cf. Table 2, nos. 8 and 10, respectively). The hyperbranched structure of *hb*-P**4**/**6** is somewhat difficult to analyze due to the lack of "segregated" resonance peaks in its ^{1}H NMR spectrum. It is, however, anticipated that it possesses structural features similar to those of its congener *hb*-**4**/**5**.

The ^{13}C NMR spectra of monomers **3** and **5** and their hyperbranched copolymer *hb*-P**3**/**5** are shown in Figure 3. The acetylenic carbon atoms of **3** and **5** resonate at δ 84.1 and 76.8 and at δ 84.8 and 68.0, respectively, which completely disappear after copolymerization. On the other hand, new resonance peaks emerge in the aromatic carbon region in the spectrum of *hb*-P**3**/**5**. The resonance peak of the propargyl carbon ($\equiv$C$-$*C*H$_2$) of **5** shifts from δ 18.4 to δ ~36.0 after polycyclotrimerization. These findings are consistent with the IR and ^{1}H NMR spectral data, proving that all the triple bonds

Table 5. Thermal and Optical Properties of Hyperbranched Poly(aminoarylene)s[a]

				solution			film		
no.	*hb*-PAA	T_d (°C)	W_r (%)	λ_{ab} (nm)	λ_{em} (nm)	Φ_F (%)	λ_{ab} (nm)	λ_{em} (nm)	Φ_F (%)
1	*hb*-P**1**/**5**	423	39.4	338	434	10.4	341	421	2.7
2	*hb*-P**2**/**5**	401	30.8	338	429	10.6	343	420	2.3
3	*hb*-P**3**/**5**	379	39.6	336	423	13.9	342	417	4.6
4	*hb*-P**4**/**5**	443	59.9	348	447	22.9	371	429	19.9
5	*hb*-P**4**/**6**	577	60.7	355	446	21.7	360	433	19.2

[a] Symbols: T_d = temperature for 5% weight loss, W_r = weight of residue left after pyrolysis at 800 °C, λ_{ab} = absorption maximum (DCM solution, 1.2×10^{-5} g/mL), λ_{em} = emission maximum (DCM solution, 1.2×10^{-5} g/mL), and Φ_F = fluorescence quantum yield [for solution and film, determined using 9,10-diphenylanthracene in cyclohexane and poly(methyl methacrylate), respectively, as standard; excitation wavelength (nm): 365 (no. 1), 364 (no. 2), 363 (no. 3), 376 (no. 4), and 378 (no. 5)].

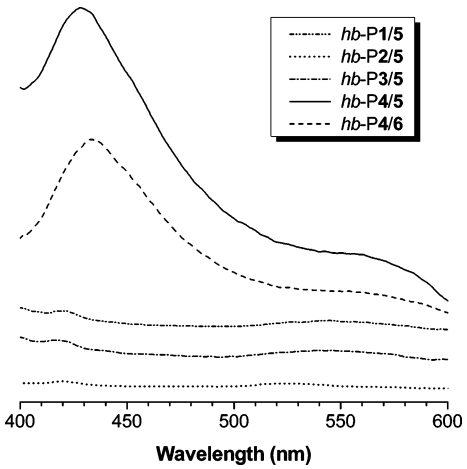


Figure 7. Photoluminescence spectra of thin solid films of *hb*-PAAs. Excitation wavelength (nm): 365 (*hb*-P**1**/**5**), 364 (*hb*-P**2**/**5**), 363 (*hb*-P**3**/**5**), 376 (*hb*-P**4**/**5**), and 378 (*hb*-P**4**/**6**). Samples taken from Table 2, nos. 2, 4, 6, 8, and 10, respectively.

of the monomers have been polycyclotrimerized into benzene rings of the polymers by the transition metal catalysts.

Thermal and Optical Properties. The thermal properties of the *hb*-PAAs were investigated by TGA under nitrogen. All the polymers are thermally stable, showing onset degradation temperatures as high as 400 °C (Figure 4). The thermal stability of the polymer generally increases with a decrease in its alkyl content. Among the polymers, *hb*-P**4**/**6** shows the highest thermolysis resistance, with a weight loss of <5% at 577 °C. The high thermal stabilities of the *hb*-PAAs are consistent with their proposed hyperbranched structures, which are comprised of aromatic rings. While the copolymers prepared from the diyne monomers gives residue weights of 30−40% after pyrolysis at 800 °C, the char yields of *hb*-PAAs built from triyne **4** are as high as 60%, making them promising candidates as precursors to ceramic materials.

All the acetylenic monomers, irrespective of their molecular structures, absorb at 338−342 nm. The *hb*-PAAs prepared from the DPA monomers absorb at similar wavelengths (Figure 5). The absorptions of their congeners with TPA cores, that is, *hb*-**4**/**5** and *hb*-P**4**/**6**, shift bathochromically to 348 and 355 nm, respectively, probably due to better electronic communication between the TPA moieties and the new aromatic rings formed by the polycyclotrimerization reaction. All the absorption peaks are broad, indicative of extensive π-conjugations in the polymers.

TPA is a well-known chromophoric unit and has often been used as a building block for constructing light-emitting and hole-transporting (macro)molecules. It is thus of interest to examine the PL of our polymers. Upon photoexcitation, DCM solutions of the *hb*-PAAs emit bright blue lights with emission maxima (λ_{max}) at 420−450 nm (Figure 6). The λ_{max} values of the TPA-based polymers are red-shifted from those of their congeners containing DPA moieties, due to the higher polarizability of the TPA core. We estimated their Φ_F values using 9,10-diphenylanthracene as standard. The Φ_F values of *hb*-P**1**/**5** and *hb*-P**2**/**5** are estimated to be ~10.5%. Replacement of the substituents of their DPA core from alkyl chains to benzyl group increases the Φ_F value to 13.9% in *hb*-P**3**/**5** (Table 5, no. 3). The TPA-based polymers *hb*-P**4**/**5** and *hb*-P**4**/**6** are more efficient emitters, both of whose Φ_F values exceed 21%. The type of monoyne has exerted little effect on the light-emitting properties of the copolymers.

Many chromophoric (macro)molecules are highly emissive when molecularly dissolved in dilute solutions but become weakly luminescent or even nonemissive when fabricated into solid films.[61] How will the *hb*-PAAs behave in the solid state? Like many other chromophoric polymers, the *hb*-PAAs with DPA cores become practically nonemissive in the solid state (Figure 7). Their PL spectra are virtually flat lines with small

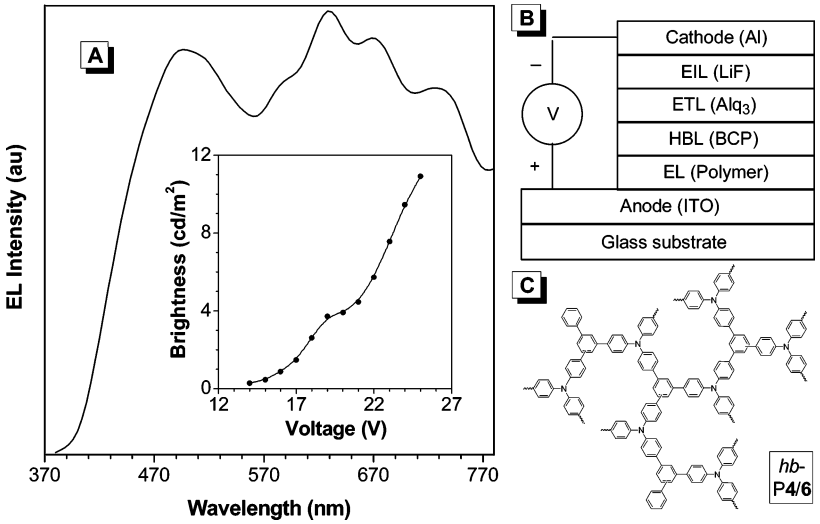


Figure 8. (A) Electroluminescence spectra of a multilayer device of *hb*-P**4**/**6** (sample from Table 2. no. 10) with a device configuration given in panel B. Inset: plot of brightness vs voltage of the device. (C) Chemical structure of *hb*-P**4**/**6**.

humps at ~420 nm, with their Φ_F values dropped to ~2.3−4.6% (Table 5, nos. 1−3). The *hb*-PAAs with TPA cores, i.e., *hb*-**4**/**5** and *hb*-**4**/**6**, show a completely different behavior. Their PL spectra are peaked at ~430 nm, which are, surprisingly, 18 and 13 nm blue-shifted from the emission peaks of their solutions, respectively. Their Φ_F values remain at a high value of ~20% (Table 5, nos. 4 and 5).

The efficient PL of the TPA-cored polymers in the solid-state prompted us to check their EL behavior. We fabricated a multilayer EL device with a configuration of ITO/polymer/BCP/Alq_3/LiF/Al, using *hb*-P**4**/**6** as emitting layer. Despite the use of BCP and Alq_3 as hole-blocking and electron transporting layers, respectively, the EL device performed poorly: it emitted a weak white light with peak maxima at 496, 628, 668, and 728 nm. This suggests that the white light EL is associated with various radiative decay processes. The multilayer device exhibited a turn-on voltage of 14 V and a maximum brightness of 11 cd/m^2 at 25 V. The EL data contradicts with the PL data discussed above, suggesting that the device configuration is yet to be optimized.

Conclusion

In this work, new DPA- and TPA-containing diynes and triynes have been prepared and successfully polycyclotrimerized into hyperbranched poly(aminoarylene)s (*hb*-PAAs) using $TaBr_5$ and $CpCo(CO)_2$- *hν* as catalysts. The *hb*-PAAs constructed from the diyne monomers contain no or negligible amounts of internal cycles, whereas those derived from triyne **4** possess small- and medium-size cyclic structures due to the ortho- and meta-linkages of the newly formed 1,2,4- and 1,3,5-substituted benzene rings. Despite the presence of intramolecular ring structures, the *hb*-PAAs are soluble in common organic solvents. All the *hb*-PAAs are thermally very stable, with degradation temperatures up to ~580 °C. Furthermore, the polymers emit bright blue lights in dilute solutions as well as in thin films, making them promising candidate materials for high-tech applications.

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