Synthesis, Thermal Stability, and Linear and Nonlinear Optical Properties of Hyperbranched Polyarylenes Containing Carbazole and/or Fluorene Moieties

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ABSTRACT: New diyne monomers containing carbazolyl and/or fluorenyl chromophores, namely, 3,6-diethynyl-9-phenylcarbazole (**1**), 3,6-diethynyl-9-[6-(9-carbazolyl)hexyl]carbazole (**2**), and 2,7-diethynyl-9,9-bis[6-(9-carbazoyl)hexyl]fluorene (**3**), are synthesized. Alkyne polycyclotrimerizations are effected by TaX_5−Ph_4Sn (X = Cl, Br) and $CpCo(CO)_2$−$h\nu$ catalysts, yielding soluble hyperbranched polyarylenes (*hb*-PAs) with high molecular weights (M_w up to ∼1.6×10^5) in high yields (up to ∼100%). The structures and properties of the *hb*-PAs are characterized and evaluated by IR, NMR, UV, PL, TGA, and optical limiting analyses. Most of the *hb*-PAs show outstanding thermal stability (T_d up to 560 °C) with high weight residues (W_r up to ∼86%) after pyrolysis at 800 °C. Upon photoexcitation, solutions of the *hb*-PAs emit strong blue light of ∼400 nm with fluorescence quantum yields Φ_F up to 90%. The *hb*-PAs show excellent optical limiting performance and strongly attenuate the powder of 8 ns pulses of 532 nm laser light.

Introduction

A variety of potential optical and electronic applications have been proposed for conjugated polymers, and the perspective has stimulated dynamic research activities on macromolecules with extended π-conjugations.[1,2] The frontier of research on conjugated polymers is now moving from linear to dendritic and hyperbranched structures.[3−7] Compared to their dendritic cousins,[8,9] hyperbranched polymers enjoy such advantages as ready preparations in large scales by one-pot, single-step reaction procedures.[10−12]

Different synthetic strategies have been developed for preparing hyperbranched polymers.[10−12] The most commonly adopted approach is the self-condensation of AB_n-type monomers with $n \geq 2$.[13−16] This type of polymerization can be carried out in a concurrent mode or by slow addition of the monomer or even in the presence of a core molecule of B_f ($f \geq 1$). Another approach is the copolymerization of A_2 monomers with B_n comonomers ($n \geq 3$).[17−19] The stoichiometric requirement for the functional comonomer pairs are, however, practically difficult to meet, which limits the growth of propagating species, resulting in the formation of oligomeric products with low degrees of branching (DBs). Other polymerization reactions including self-condensing vinyl polymerizations initiated by cationic[20] and radical catalysts[21,22] and ring-opening multibranching polymerizations[23−27] have been explored, mainly for the synthesis of nonconjugated hyperbranched polymers.[28−31]

We have been interested in the synthesis of hyperbranched polymers with electronic conjugation. Our idea on preparing such polymers is via transition-metal-catalyzed alkyne polycyclotrimerization.[32,33] This [2 + 2 +2] polycycloaddition reaction involves a single monomer species, suffers no stoichiometric constraint, and can therefore potentially produce polymers with very high molecular weights. In our previous work, we studied the homopolycyclotrimerizations of *aliphatic* diynes such as 1,8-nonadiyne and 1,9-decadiyne catalyzed by a binary mixture of $TaCl_5$ and Ph_4Sn (Scheme 1).[34,35] Under optimized conditions, completely soluble homopolymers with high molecular weights (M_w up to ∼1.4×10^6) and predominant 1,2,4-trialkylbenzene regioisomeric structures were obtained in high yields (up to 93%). The hyperbranched poly(alkylenephenylene)s (*hb*-PAPs) show outstanding thermal stability, losing little of their weight at temperatures as high as ∼500 °C, although their phenyl rings are separated by the alkyl spacers.

We have extended our efforts to the polycyclotrimerizations of *aromatic* diynes and succeeded in the homopolycyclotrimerizations of organic and organometallic diynes and their copolycyclotrimerizations with aromatic and aliphatic monoynes.[36−44] Unlike the isolated benzene rings in the *hb*-PAPs discussed above, here the "new" benzene rings form by cyclotrimerization and the "old" aromatic moieties from the monomer species are interconnected in the hyperbranched polyarylenes (*hb*-PAs). This enhances electronic communications in the *hb*-PAs and endows them with unique optical and photonic properties such as efficient light emission and excellent optical power limiting.

To enrich the research field of conjugated *hb*-PAs and to gain more information about their structure−property relationships, in this work, we synthesized a series of conjugated *hb*-PAs containing carbazole and/or fluorene chromophores by the homo- and copolycyclotrimerizations of diynes **1**−**3** with monoyne **4** effected by different transition-metal catalysts (Scheme 2) and investigated their thermal and optical properties.

Experimental Section

General Information. Toluene, hexanes, dioxane, 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

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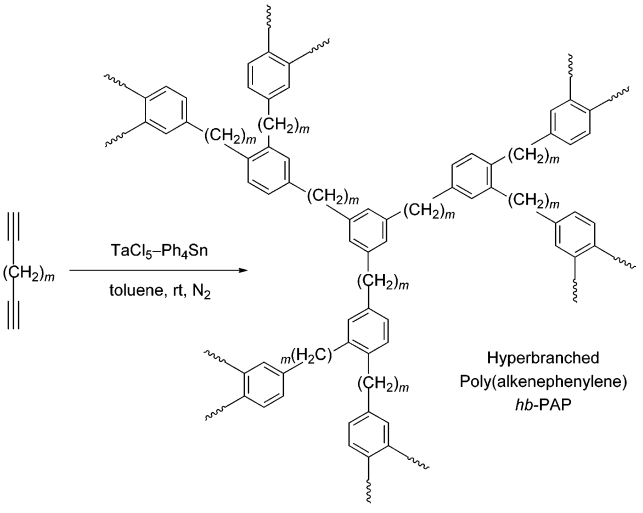
Scheme 1. Synthesis of Hyperbranched Poly(alkenephenylene)s



and stored over sodium hydroxide in a dark, cold place. Metal halides MX_5 (M = Ta, Nb; X = Cl, Br), cyclopentadienyl cobalt dicarbonyl [$CpCo(CO)_2$], tetraphenyltin, dichlorobis(triphenylphosphine)palladium(II) [$Pd(PPh_3)_2Cl_2$], copper(I) iodide, triphenylphosphine, and other chemicals and solvents were obtained from a commercial source (Aldrich) and used as received without further purification. 1-Octyne (**4**) was purchased from Farchan, stored in a dark, cold and dry place, and distilled over calcium hydride prior to use.

Weight- (M_w) and number-average molecular weights (M_n) and polydispersity indexes (PDI or M_w/M_n) of the polymers were estimated by a Waters Associates gel permeation chromatograph (GPC) system in THF using a set of monodisperse linear polystyrenes as calibration standards. IR spectra were recorded on a Perkin-Elmer 16 PC FTIR spectrophotometer using pressed KBr plates. ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 300 NMR spectrometer using chloroform-*d* or DCM-d_2 as solvents and tetramethylsilane (TMS) as internal reference. UV absorption spectra were measured on a Milton Ray Spectronic 3000 array spectrophotometer. Fluorescence spectra were recorded in DCM on a SLM 8000C spectrofluorometer. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer TGA 7 analyzer at a heating rate of 20 °C/min under nitrogen.

Optical limiting experiments were carried out at 532 nm, using 8 ns optical pulses generated from a frequency-double Q-switched Nd:YAG laser (Quanta Ray GCR-3) operating in a near Gaussian transverse mode with a repetition rate of 10 Hz.[45−47] The pulsed laser beam was focused onto a 1 cm square quartz cell filled with a DCM solution of polymer. The incident and transmitted energies were measured by an OPHIR detector (30-A-Diff-SH). Every point of the optical limiting data was the average of at least 15 laser shots. The detector was connected to a computer before and after the optical limiting data were taken. The output stability of the laser equipment was double checked by taking a series of output data by the energy meter every 10 s for an extended period of time.

Monomer Synthesis. The diyne monomers (**1**−**3**) were prepared according to the synthetic routes shown in Schemes 3−5. Typical experimental procedures for their syntheses are given below.

*Preparation of 3,6-Diiodo-9-phenylcarbazole (**6**).* In a round-bottom flask equipped with a condenser were dissolved 5.2 g (21.4 mmol) of 9-phenylcarbazole (**5**), 4.6 g (28.1 mmol) of potassium iodide, and 6 g (28.1 mmol) of potassium iodate in 100 mL acetic acid under gentle stirring. The mixture was heated at 80 °C for 12 h. After the reaction mixture was cooled to room temperature, the crude iodinated product was obtained by filtration. The filter cake was washed consecutively with 100 mL of water, sodium bicarbonate (1 M), sodium thiosulfate solution (1 M), and water. A white solid was obtained after recrystallization from the ethanol/water mixture (2:1 by volume) in 76.5% yield (8.1 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.38 [s, 2H, carbazole (Cz)−H at 4 and 5 positions], 7.59 (m, 4H, Cz−H at 2 and 7 positions and Ar−H at 3 and 5 positions), 7.43 (m, 3H, Ar−H at 2, 4, 6 positions), 7.17 (d, 2H, Cz−H at 1 and 8 positions).

*Preparation of 3,6-Bis[2-(trimethylsilyl)ethynyl]-9-phenylcarbazole (**7**).* To a 500 mL round-bottom flask equipped with a septum and a stirring bar were added 4 g (8.1 mmol) of **6**, 28.1 mg (0.04 mmol) of $Pd(PPh_3)_2Cl_2$, 19 mg (0.1 mmol) of CuI, and 26 mg (0.1 mmol) of PPh_3. Dried Et_3N (100 mL) and THF (100 mL) were injected by a syringe. Under stirring, 2.7 mL (19.2 mmol, 1.9 g) of trimethylsilylacetylene (TMSA) was added. The mixture was stirred at room temperature for 12 h. The formed precipitate was filtered and washed with diethyl ether. The solutions were collected, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography using hexanes/chloroform (1:1 by volume) as eluent. A white powder was isolated in 95.3% yield (3.35 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.22 (s, 2H, Cz−H at 4 and 5 positions), 7.59 (d, 2H, Cz−H at 2 and 7 positions), 7.49 (m, 5H, Ar−H), 7.21 (d, 2H, Cz−H at 1 and 8 positions), 0.23 [s, 18H, $Si(CH_3)_3$].

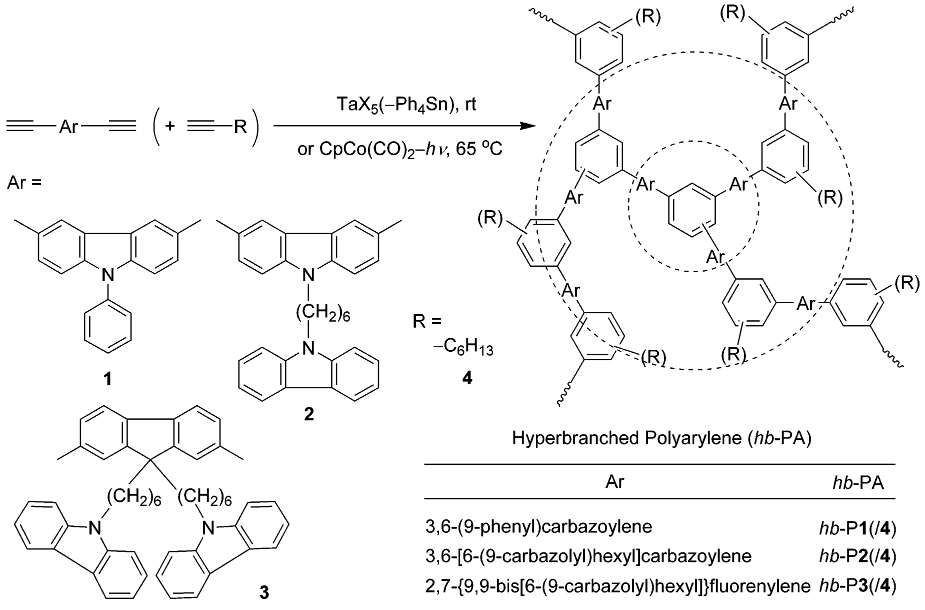
*Preparation of 3,6-Diethynyl-9-phenylcarbazole (**1**).* To a 500 mL round-bottom flask equipped with a stirring bar were added 3.1 g (7.1 mmol) of **7**, 200 mL of methanol, and 1 g (17.8 mmol) of KOH. After stirring at room temperature for 3 h, the solution was concentrated and poured into 500 mL of 1 M HCl solution. The mixture was extracted by chloroform four times. The organic layer was collected, dried over magnesium sulfate, and concentrated by a rotary evaporator. The obtained product was purified by silica gel column chromatography with hexanes/chloroform (3:1 by volume) as eluent to give a white solid (**1**) in 97.8% yield (2.02 g). IR (KBr), ν (cm^{-1}): 3279 (≡C−H stretching), 3065, 3041 (Ar−H stretching), 2099 (C≡C stretching), 1872 (overtone band, substituted benzene ring), 1598, 1501, 1480 (C=C ring stretching), 808 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.25 (s, 2H, Cz−H at 4 and 5 positions), 7.56 (d, 2H, Cz−H at 2 and 7 positions), 7.51 (m, 5H, Ar−H), 7.29 (d, 2H, Cz−H at 1 and 8 positions), and 3.09 (s, 2H, ≡C−H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 139.95, 129.86, 125.74, 123.97, 122.91, 122.37, 120.51, 118.97, 113.12, 108.88, 84.65, 75.79. Anal. Calcd for $C_{22}H_{13}N$: C, 90.69; H, 4.50; N, 4.81. Found: C, 89.36; H, 4.43; N, 4.34.

*Preparation of 3,6-Diiodocarbazole (**9**).* This compound was prepared by a procedure similar to that described above for the preparation of **6** by using 4 g (24 mmol) of carbazole, 5.1 g (31.2 mmol) of potassium iodide, and 6.7 g (31.2 mmol) of potassium iodate in 100 mL of acetic acid. A white solid was obtained by recrystallization from ethanol/water (2:1 by volume) in 73.7% yield (7.4 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.33 (s, 2H, Cz−H at 4 and 5 positions), 8.10 (s, 1H, N−H), 7.68 (d, 2H, Cz−H at 2 and 7 positions), 7.21 (d, 2H, Cz−H at 1 and 8 positions).

*Preparation of 9-(6-Bromohexyl)carbazole (**10**).* Into a 250 mL three-necked flask equipped with a condenser, a nitrogen inlet, and a septum were added 12 g (41.1 mmol) of carbazole, 9.6 mL (61.5 mmol) of 1,6-dibromohexane, and a catalytic amount of tetrabutylammonium bromide in 50 mL of dry toluene. To this mixture was added 50 mL of 50% aqueous KOH, and the reaction mixture was refluxed for 12 h. Toluene was evaporated under vacuum, and the residue was extracted with diethyl ether for three times. The organic layer was further washed with water and brine and was then dried over anhydrous $MgSO_4$. After solvent evaporation, a pale yellow crude product was obtained, which was purified by silica gel column chromatography using hexanes/chloroform (1:1 by volume) as eluent. Yield: 68.7% (9.3 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.08 (d, 2H, Cz−H at 4 and 5 positions), 7.44 (m, 4H, Cz−H at 2, 3, 6, and 7 positions), 7.20 (d, 2H, Cz−H at 1 and 8 positions), 4.30 (t, 2H, N−CH_2), 3.48 (t, 2H, CH_2Br), 1.89 (dd, 2H, NCH_2CH_2), 1.71 (dd, 2H, $BrCH_2CH_2$), 1.43 (m, 4H, $NCH_2CH_2CH_2CH_2$).

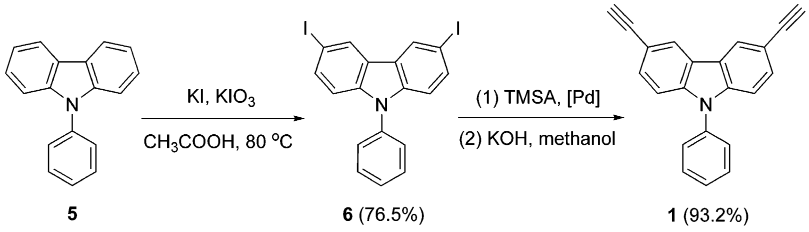
*Preparation of 3,6-Diiodo-9-[6-(9-carbazolyl)hexyl]carbazole (**11**).* This compound was prepared by a procedure similar to that described above for the preparation of **10** using 3.4 g (8.1 mmol) of **9** and 2 g (7.3 mmol) of **10** as reactants. Purification by silica gel column using hexanes/chloroform (1:1 by volume) as eluent

Scheme 2. Synthesis of Hyperbranched Polyarylenes by Alkyne Polycyclotrimerization

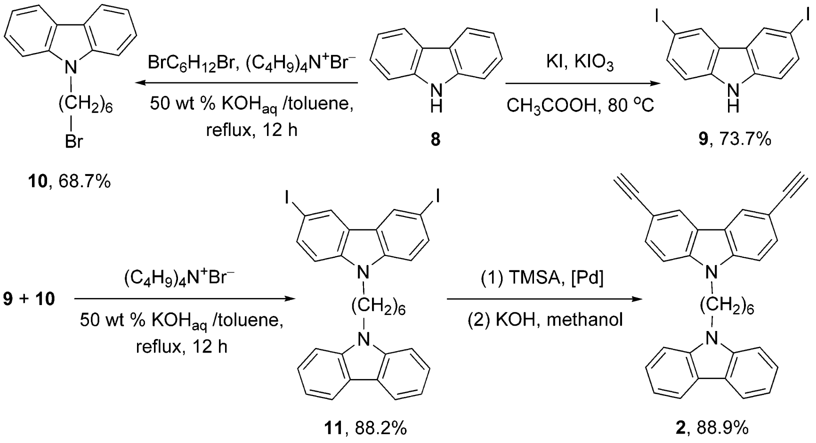


Ar	hb-PA
3,6-(9-phenyl)carbazoylene	hb-P**1**(/**4**)
3,6-[6-(9-carbazolyl)hexyl]carbazoylene	hb-P**2**(/**4**)
2,7-{9,9-bis[6-(9-carbazolyl)hexyl]}fluorenylene	hb-P**3**(/**4**)

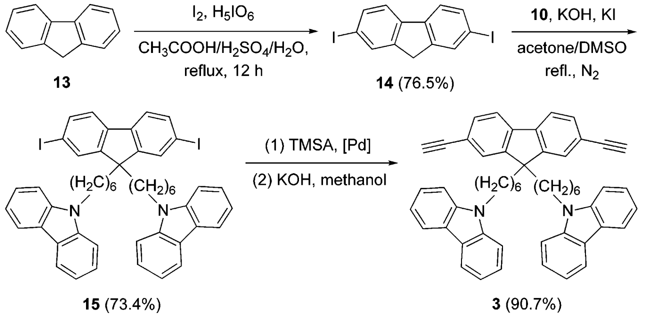
Scheme 3. Preparation of 3,6-Diethynyl-9-phenylcarbazole (1)



Scheme 4. Preparation of 3,6-Diethynyl-9-[6-(9-carbazolyl)hexyl]carbazole (2)



Scheme 5. Preparation of 2,7-Diethynyl-9,9-bis[6-(9-carbazolyl)hexyl]fluorene (3)



afforded a pale yellow solid in 88.2% yield (4.3 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.30 [s, 2H, 3,6-disubstituted carbazole (Cz′)−H at 4 and 5 positions], 8.09 (d, 2H, Cz−H at 4 and 5 positions), 7.65 (d, 2H, Cz′−H at 2 and 7 positions), 7.44 (dd, 2H, Cz−H at 2 and 7 positions), 7.32 (dd, 2H, Cz−H at 3 and 6 positions), 7.23 (d, 2H, Cz−H at 1 and 8 positions), 7.04 (d, 2H, Cz′−H at 1 and 8 positions), 4.26 (t, 2H, CzN−CH_2), 4.12 (t, 2H, Cz′N−CH_2), 1.81 (dd, 2H, NCH_2CH_2), 1.74 (dd, 2H, NCH_2CH_2), 1.26 (m, 4H, $NCH_2CH_2CH_2CH_2$).

*Preparation of 3,6-Bis[2-(trimethylsilyl)ethynyl]-9-[6-(9-carbazolyl)hexyl] carbazole (**12**).* This compound was prepared by a procedure similar to that described above for the preparation of **7**. Purification by silica gel column chromatography using hexanes/chloroform mixture (1:1 by volume) as eluent afforded a pale yellow solid in 93.4% yield (3.5 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.18 (s, 2H, Cz′−H at 4 and 5 positions), 8.08 (d, 2H, Cz−H at 4 and 5 positions), 7.56 (d, 2H, Cz′−H at 2 and 7 positions), 7.44 (dd, 2H, Cz−H at 2 and 7 positions), 7.32 (dd, 2H, Cz−H at 3 and 6 positions), 7.29 (d, 2H, Cz−H at 1 and 8 positions), 7.21

(d, 2H, Cz′−H at 1 and 8 positions), 4.24 (t, 2H, CzN−CH$_2$), 4.13 (t, 2H, Cz′N−CH$_2$), 1.80 (m, 4H, NCH$_2$C*H*$_2$), 1.33 (m, 4H, NCH$_2$CH$_2$C*H*$_2$C*H*$_2$), 0.22 [s, 18H, Si(C*H*$_3$)$_3$].

*Preparation of 3,6-Diethynyl-9-[6-(9-carbazolyl)hexyl]carbazole (**2**).* This monomer was prepared by a procedure similar to that described above, using 3 g (4.9 mmol) of **12** and 0.7 g (12.7 mmol) of KOH as reactants. The product was purified by silica gel column chromatography using hexanes/chloroform mixture (1:1 by volume) as eluent. A pale yellow solid (**2**) was obtained in 95.2% yield (1.05 g). IR (KBr), ν (cm^{-1}): 3260 ($\equiv$C−H stretching), 3049 (Ar−H stretching), 2928, 2854 (CH$_2$ stretching), 2104 (C$\equiv$C stretching), 1626, 1597, 1482 (C=C ring stretching), 1326 (CH$_2$ bending), 754 (Ar−H bending). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 8.19 (s, 2H, Cz′−H at 4 and 5 positions), 8.09 (d, 2H, Cz−H at 4 and 5 positions), 7.56 (d, 2H, Cz′−H at 2 and 7 positions), 7.44 (dd, 2H, Cz−H at 2 and 7 positions), 7.32 (dd, 2H, Cz−H at 3 and 6 positions), 7.29 (d, 2H, Cz−H at 1 and 8 positions), 7.21 (d, 2H, Cz′−H at 1 and 8 positions), 4.24 (t, 2H, CzN−CH$_2$), 4.13 (t, 2H, Cz′N−CH$_2$), 3.07 (s, 2H, $\equiv$C−H), 1.80 (m, 4H, NCH$_2$C*H*$_2$), 1.33 (m, 4H, NCH$_2$CH$_2$C*H*$_2$C*H*$_2$). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 140.63, 140.43, 130.27, 125.75, 124.91, 122.95, 122.37, 120.54, 118.97, 112.97, 109.04, 108.74, 84.96, 75.81, 43.40, 43.15, 29.23, 29.13, 27.44, 27.40. Anal. Calcd for $C_{34}H_{28}N_2$: C, 87.90; H, 6.07; N, 6.03. Found: C, 87.25; H, 6.08; N, 5.92.

*Preparation of 2,7-Diiodofluorene (**14**).* In a 250 mL round-bottom flask equipped with a condenser was dissolved 5 g (32.5 mmol) of fluorene in 60 mL of a solvent mixture of acetic acid, water, and sulfuric acid (100:20:3 by volume) under gentle stirring and heating. To this mixture were added 7.7 g (30.2 mmol) of iodine and 2.3 g (10.1 mmol) of periodic acid dihydrate (H_5IO_6). The resultant mixture was stirred at 65 °C for 12 h. After the reaction mixture was cooled to room temperature, the crude iodinated product was obtained by filtration. The filter cake was washed consecutively with 100 mL of water, sodium bicarbonate solution (1 M), sodium thiosulfate solution (1 M), and water. A white solid was obtained by recrystallization from ethyl acetate/hexanes (1:1 by volume) in 76.5% yield (8.1 g). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.93 (s, 2H, fluorene (Flu)−H at 1 and 8 positions), 7.72 (d, 2H, Flu−H at 3 and 6 positions), 7.54 (d, 2H, Flu−H at 4 and 5 positions), 3.88 (s, 2H, CH$_2$).

*Preparation of 2,7-Diiodo-9,9-bis[6-(9-carbazolyl)hexyl]fluorene (**15**).* A mixture of **14** (2.8 g, 6.7 mmol), **10** (4.4 g, 13.4 mmol), and KI (0.12 g, 0.7 mmol) in 50 mL of acetone/DMSO (9:1 by volume) was stirred at room temperature, to which powdered KOH (1.6 g, 28.5 mmol) was slowly added under nitrogen. The color of the reaction mixture changed from bright yellow to dark green immediately upon KOH addition. The reaction mixture was refluxed for 12 h, concentrated under reduced pressure, poured into water, and extracted with chloroform. The organic extract was washed with water, dried over MgSO$_4$, and concentrated, affording a viscous dark orange oil that crystallized upon standing. Purification was accomplished by silica gel column chromatography using hexanes/chloroform mixture (1:1 by volume) as eluent. A pale yellow crystal was obtained in 73.4% yield (4.5 g). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 8.08 (d, 4H, Cz−H at 4 and 5 positions), 7.59 (d, 2H, Flu−H at 3 and 6 positions), 7.48 (m, 8H), 7.38 (m, 8H), 4.15 (t, 4H, CzN−CH$_2$), 1.82 (t, 4H, Flu−CH$_2$), 1.05 (m, 8H, CH$_2$), 0.51 (m, 4H, CH$_2$).

*Preparation of 2,7-Bis[2-(trimethylsilyl)ethynyl]-9,9-bis[6-(9-carbazolyl)hexyl]fluorene (**16**).* This compound was prepared by a procedure similar to that described above for the preparation of **7**. Purification by silica gel column chromatography using hexanes/chloroform mixture (1:1 by volume) afforded pale yellow crystals in 96.3% yield (3.6 g). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 8.09 (d, 4H, Cz−H at 4 and 5 positions), 7.51 (m, 10H), 7.38 (m, 8H), 4.13 (t, 4H, CzN−CH$_2$), 1.81 (t, 4H, Flu−CH$_2$), 1.61 (m, 4H, CH$_2$), 1.02 (m, 8H, CH$_2$), 0.50 (m, 4H, CH$_2$), 0.19 [s, 18H, Si(CH$_3$)$_3$].

*Preparation of 2,7-Diethynyl-9,9-bis[6-(9-carbazolyl)hexyl]fluorene (**3**).* This monomer was prepared by a procedure similar to that described above for the preparation of **1** using 3 g (3.5 mmol) of **16** and 0.5 g (8.9 mmol) of KOH. The crude product was purified by silica gel column chromatography using hexanes/chloroform mixture (1:1 by volume) as eluent. A pale yellow solid (**3**) was obtained in 94.2% yield (2.35 g). IR (KBr), ν (cm^{-1}): 3283 ($\equiv$C−H stretching), 3048 (Ar−H stretching), 2928, 2854 (CH$_2$ stretching), 2103 (C$\equiv$C stretching), 1626, 1595, 1463, 1452 (C=C ring stretching), 1325 (CH$_2$ bending), 750. ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 8.05 (d, 4H, Cz−H at 4 and 5 positions), 7.57 (d, 2H), 7.43 (m, 8H), 7.25 (m, 8H), 4.11 (t, 4H, CzN−CH$_2$), 3.14 (s, 2H, $\equiv$C−H), 1.82 (t, 4H, Flu−CH$_2$), 1.62 (m, 4H, CH$_2$), 1.04 (m, 8H, CH$_2$), 0.49 (m, 4H, CH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 150.63, 140.86, 140.26, 131.34, 126.35, 125.50, 122.67, 120.90, 120.24, 120.07, 118.60, 108.56, 84.38, 77.56, 54.94, 42.76, 40.01, 29.55, 28.69, 26.76, 23.45. Anal. Calcd for $C_{53}H_{48}N_2$: C, 89.28; H, 6.79; N, 3.93. Found: C, 88.54; H, 6.71; N, 3.75.

Table 1. Homo- and Copolycyclotrimerizations of Diyne 3,6-Diethynyl-9-phenylcarbazole (1) with Monoyne 1-Octyne (4)[a]

run	catalyst	$[M_I]$[b] (M)	M_r[c]	yield (%)	S[d]	M_w[e]	M_w/M_n[e]
1	$TaCl_5$−Ph_4Sn	0	1.0:0	99.9	×		
2[f]	CpCo(CO)$_2$−*hν*	0	1.0:0	99.9	√	2 700	3.9
3	$TaBr_5$−Ph_4Sn	0.108	1.0:1.5	89.2	√	12 200	3.5
4	$TaCl_5$−Ph_4Sn	0.072	1.0:1.0	89.9	Δ	17 500	5.2
5	$TaCl_5$−Ph_4Sn	0.108	1.0:1.5	84.4	√	28 700	7.0
6	$NbCl_5$−Ph_4Sn	0.108	1.0:1.5	94.8	Δ	35 900	10.8
7	CpCo(CO)$_2$−*hν*	0.072	1.0:1.0	76.1	√	3 000	2.9

[a] Carried out under nitrogen in toluene at room temperature for 16 h using a diyne concentration $[M_{II}]$ of 0.072 M and a catalyst concentration [cat.] of 10 mM, except for runs 2 and 7, which were performed at 65 °C and [cat.] = 12.5 mM. [b] Molar concentration of monoyne. [c] Molar ratio of diyne to monoyne: $M_r = [M_{II}]/[M_I]$. [d] Solubility (*S*) tested in common organic solvents such as toluene, DCM, chloroform, and THF: √ = completely soluble, Δ = partially soluble, and × = insoluble. [e] Determined by GPC in THF on the basis of a linear polystyrene calibration. [f] Polymerized for 12 h.

Polymerization Reactions. All the polymerization reactions and manipulations were carried out under nitrogen using the standard Schlenk technique in a vacuum line system or an inert atmosphere glovebox (Vacuum Atmosphere), except for the purification of the polymers, which was done in an open atmosphere. Typical experimental procedures for the copolycyclotrimerization of **3** with **4** are given below as an example.

To a thoroughly baked and carefully evacuated 15 mL Schlenk tube with a stopcock on the sidearm were placed 29 mg (0.05 mmol) of TaBr$_5$ and 22 mg (0.05 mmol) of Ph$_4$Sn under nitrogen in a glovebox. Freshly distilled toluene (3 mL) was injected into the tube using a hypodermic syringe, and the mixture was stirred for 10 min. Monomers **3** (128.3 mg, 0.18 mmol) and **4** (19.9 mg, 0.18 mmol) dissolved in 2 mL of anhydrous toluene were then injected into the catalyst solution. The resultant mixture was stirred at room temperature under nitrogen for 16 h, after which the reaction was quenched by the addition of methanol. The mixture was added dropwise to ∼400 mL of methanol through a cotton filter under stirring. The polymer precipitate was allowed to stand overnight and was then filtered through a Gooch crucible. The isolated polymer was washed with methanol and dried under vacuum at room temperature to a constant weight.

*Characterization Data for hb-P**3**/**4** (Table 3, no. 8).* White powder; yield: 84.6%; M_w: 163 400; PDI: 3.0 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3048 (Ar−H stretching), 2927 (CH$_2$ asymmetrical stretching), 2854 (CH$_2$ symmetrical stretching), 1883, 1766 (overtone band, trisubstituted benzene ring), 1627, 1597, 1484, 1463 (C=C ring stretching), 819 (Ar−H bending), 749, 722. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$), δ (TMS, ppm): 7.94, 7.77, 7.64, 7.24, 7.16 (Ar−H), 4.04 (NCH$_2$), 2.65 (Ar−CH$_2$), 1.96, 1.63, 1.34, 1.12, 0.90, 0.77 (CH$_2$). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$), δ (TMS, ppm): 140.09, 138.99, 125.25, 122.37, 119.86, 118.35, 108.40, 42.53, 40.05, 31.55, 29.55, 28.90, 28.46, 26.66, 26.39, 22.44, 13.66.

*hb-P**1** (Table 1, no. 2).* Pale yellow powder; yield: 99.9%; M_w: 2700; PDI: 3.9 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3293 ($\equiv$C−H stretching), 3065, 3033 (Ar−H stretching), 2103

Table 2. Homo- and Copolycyclotrimerizations of Diyne 3,6-Diethynyl-9-[6-(9-carbazolyl)hexyl]carbazole (2) with Monoyne 1-Octyne (4)[a]

run	catalyst	$[M_I]^b$ (M)	M_r^c	yield (%)	S^d	M_w^e	M_w/M_n^e
1[f]	$CpCo(CO)_2-h\nu$	0	1.0:0	83.7	√	4000	2.9
2	$TaBr_5-Ph_4Sn$	0.108	1.0:1.5	92.9	Δ	7900	4.1
3	$TaCl_5-Ph_4Sn$	0.072	1.0:1.0	99.9	Δ	6700	3.3
4	$TaCl_5-Ph_4Sn$	0.108	1.0:1.5	96.6	√	6800	3.8
5	$NbCl_5-Ph_4Sn$	0.108	1.0:1.5	44.2	Δ	15400	2.8
6	$CpCo(CO)_2-h\nu$	0.072	1.0:1.0	58.0	√	2300	2.2

[a] Carried out under nitrogen in toluene at room temperature for 16 h using a diyne concentration $[M_{II}]$ of 0.072 M and a catalyst concentration [cat.] of 10 mM, except for runs 1 and 6, which were performed at 65 °C and [cat.] = 12.5 mM. [b] Molar concentration of monoyne. [c] Molar ratio of diyne to monoyne: $M_r = [M_{II}]/[M_I]$. [d] Solubility (S) tested in common organic solvents such as toluene, DCM, chloroform, and THF: √ = completely soluble and Δ = partially soluble. [e] Determined by GPC in THF on the basis of a linear polystyrene calibration. [f] Polymerized for 12 h.

Table 3. Homo- and Copolycyclotrimerizations of Diyne 2,7-Diethynyl-9,9-bis[6-(9-carbazolyl)hexyl]fluorene (3) with Monoyne 1-Octyne (4)[a]

run	catalyst	$[M_I]^b$ (M)	M_r^c	time (h)	yield (%)	S^d	M_w^e	M_w/M_n^e
1	$TaBr_5-Ph_4Sn$	0	1.0:0	3	99.9	×		
2	$TaBr_5-Ph_4Sn$	0	1.0:0	1	99.9	×		
3	$TaCl_5-Ph_4Sn$	0	1.0:0	3	97.1	×		
4	$NbBr_5-Ph_4Sn$	0	1.0:0	3	trace			
5	$NbCl_5-Ph_4Sn$	0	1.0:0	3	40.1	×		
6	$NbCl_5-Ph_4Sn$	0	1.0:0	1	22.1	Δ	2500	2.5
7	$CpCo(CO)_2-h\nu$	0	1.0:0	12	70.1	√	7800	3.8
8	$TaBr_5-Ph_4Sn$	0.072	1.0:1.0	16	84.6	√	163400	3.0
9	$TaCl_5-Ph_4S$	0.072	1.0:1.0	16	81.2	√	33 700	2.2
10	$NbCl_5-Ph_4Sn$	0.072	1.0:1.0	16	65.0	Δ	4300	3.7
11	$NbCl_5-Ph_4Sn$	0.108	1.0:1.5	16	34.0	Δ	3100	2.6
12	$CpCo(CO)_2-h\nu$	0.072	1.0:1.0	16	57.5	√	2700	2.4

[a] Carried out under nitrogen in toluene at room temperature using a diyne concentration $[M_{II}]$ and a catalyst concentration [cat.] of 0.036 M and 5 mM for runs 1−6 and 0.072 M and 10 mM for runs 8−11, except for runs 7 and 12, which were performed at 65 °C with $[M_{II}]$ = 0.072 M and [cat.] = 12.5 mM. [b] Molar concentration of monoyne. [c] Molar ratio of diyne to monoyne: $M_r = [M_{II}]/[M_I]$. [d] Solubility (S) tested in common organic solvents such as toluene, DCM, chloroform, and THF: √ = completely soluble, Δ = partially soluble, and × = insoluble. [e] Determined by GPC in THF on the basis of a linear polystyrene calibration.

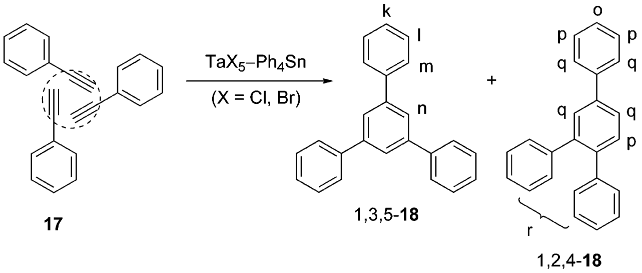
(C≡C streching), 1596, 1500, 1474 (C═C ring stretching), 810 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.38, 8.19, 7.83, 7.64, 7.51, 7.31 (Ar−H), 3.06 (≡C−H). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 139.24, 130.04, 126.90, 124.56, 124.15, 122.32, 120.48, 119.12, 113.20, 109.85.

*hb-P**1**/**4** (Table 1, no. 5).* Pale yellow powder; yield: 84.4%; M_w: 28 700; PDI: 7.0 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3062, 3040 (Ar−H stretching), 2952, 2924 (CH_2 asymmetrical stretching), 2854 (CH_2 symmetrical stretching), 1874 (overtone band, substituted benzene ring), 1597, 1501, 1468 (C═C ring stretching), 810 (Ar−H bending). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.38, 8.13, 7.99, 7.51 (Ar−H), 3.06 (≡C−H, weak), 2.71 (Ar−CH_2), 1.66, 1.28, 0.89, 0.24 (CH_2). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 139.20, 133.39, 130.01, 129.76, 126.97, 125.79, 124.73, 124.56, 124.09, 123.34, 122.52, 121.31, 120.88, 110.24, 109.98, 109.65, 32.89, 31.63, 29.24, 22.52, 18.67.

*hb-P**2** (Table 2, no. 1).* Pale yellow powder; yield: 83.7%; M_w: 4000; PDI: 2.9 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3295 (≡C−H stretching), 3050, 3021 (Ar−H stretching), 2930, 2856 (CH_2 stretching), 2105 (C≡C streching), 1627, 1599, 1484, 1464, 1453 (C═C ring stretching), 1347, 1326 (CH_2 bending), 882, 806 (Ar−H bending), 750. ^{1}H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 8.49, 8.36, 8.24, 8.09, 7.59, 7.23 (Ar−H), 4.20, 4.08 (CzN−CH_2), 3.16 (≡C−H), 1.81, 1.69, 1.37, 1.26 (CH_2). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 140.54, 139.53, 132.89, 130.01, 125.89, 125.41, 123.06, 120.61, 120.13, 119.07, 108.88, 108.42, 42.93, 28.78, 27.11, 26.36.

*hb-P**2**/**4*** (*Table 2, no. 4*). White powdery solid; yield: 96.6%; M_w: 6800; PDI: 3.8 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3049, 3020 (Ar−H stretching), 2926, 2854 (CH_2 stretching), 1598, 1483 (C═C ring stretching), 1325 (CH_2 bending), 805 (Ar−H bending), 749. ^{1}H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 8.43, 8.10, 7.43, 7.18 (Ar−H), 4.30 (CzN−CH_2), 2.69 (Ar−CH_2), 1.79, 1.40, 0.96 (CH_2). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 143.27, 140.32, 137.22, 132.81, 129.12, 128.62, 125.57, 122.75, 120.33, 118.74, 108.55, 42.79, 36.12, 31.52, 29.15, 28.82, 27.03, 22.64, 14.13.

Scheme 6. Synthesis of Model Compounds 1,3,5/1,2,4-Triphenylbenzenes (18) via Cyclotrimerization of Phenylacetylene (17)

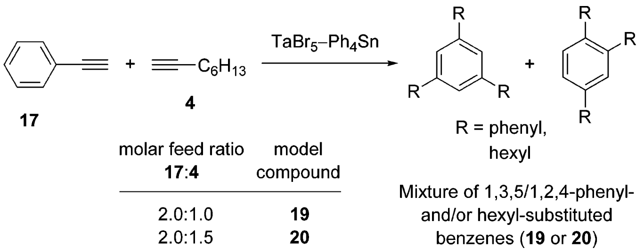


*hb-P**3*** (*Table 3, no. 7*). Pale yellow powder; yield: 70.1%; M_w: 7800; PDI: 3.8 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3292 (≡C−H stretching), 3050, 3023 (Ar−H stretching), 2929 (CH_2 asymmetrical stretching), 2854 (CH_2 symmetrical stretching), 2103 (C≡C streching), 1887, (overtone band, trisubstituted benzene ring), 1626, 1596, 1484, 1463, 1452 (C═C ring stretching), 821 (Ar−H bending), 749, 723 (CH_2 rocking). ^{1}H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 8.02, 7.64, 7.24, 7.15 (Ar−H), 4.08 (CzN−CH_2), 3.24 (≡C−H), 1.92 (Flu−CH_2), 1.61, 1.25, 1.06, 0.62 (CH_2). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 143.27, 140.31, 137.22, 132.81, 129.12, 128.62, 125.57, 122.75, 120.33, 118.74, 108.55, 42.78, 36.12, 31.52, 29.15, 28.82, 27.03, 22.64.

Synthesis of Model Compounds. Two sets of model compounds, i.e., 1,3,5/1,2,4-triphenylbenzenes (**18**) and 1,3,5/1,2,4-phenyl- and hexyl-substituted benzenes (**19** and **20**), were prepared according to the synthetic routes given in Schemes 6 and 7.[40]

*Preparation of 1,3,5/1,2,4-Triphenylbenzenes (**18**).* The regioisomers of triphenylbenzenes **18** were prepared by the cyclotrimerization of **17** (511.5 mg, 5 mmol) catalyzed by a mixture of $TaCl_5$ (18 mg, 0.05 mmol) and Ph_4Sn (22 mg, 0.05 mmol) in 5 mL of toluene by a procedure similar to that used for the polymerization reaction. The product was purified by silica gel using a hexanes/chloroform mixture (1:1 by volume) and isolated in 82% yield. The molar ratio of 1,3,5-**18** to 1,2,4-**18** was 1.0:0.9. The model

Scheme 7. Synthesis of Model Compounds 1,3,5/1,2,4-Trisubstituted Benzenes (19 and 20) via Cocyclotrimerization of Phenylacetylene (17) and 1-Octyne (4)



reaction catalyzed by $TaBr_5$ (29 mg, 0.05 mmol) was carried out under identical conditions, which gave a white solid in 83% yield. The molar ratio of 1,3,5-**18** to 1,2,4-**18** in this case was 1.0:1.4. Pure isomers of 1,3,5-**18** and 1,2,4-**18** were obtained by recrystallizations from ethanol and a mixture of ethanol and hexane (1:1 by volume), respectively.

*Characterization Data for 1,3,5-**18**:* IR (thin film), ν (cm^{-1}): 3058, 3033 (Ar–H stretching), 1595, 1576, 1497, 1411 (–C=C– ring stretching), 873, 762, 698 (Ar–H bending). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.78 (s, 3H, Ar–H n), 7.69 (m, 6H, Ar–H m), 7.47 (m, 6H, Ar–H l), 7.38 (m, 3H, Ar–H k) [the assignments of the resonance peaks k–n were referred to those protons marked in Scheme 6]. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 142.3, 141.1, 128.8, 127.5, 127.3, 125.2 (aromatic carbons). UV (DCM, 2.5×10^{-5} mol/L), λ_{max} (nm)/ϵ_{max} (mol^{-1} L cm^{-1}): 255/41540. MS (CI): *m*/*e* 307.1 [$(M + 1)^+$]; calcd 307.1.

*1,2,4-**18**:* IR (thin film), ν (cm^{-1}): 3055, 3025 (Ar–H stretching), 1599, 1575, 1490, 1474 (–C=C– ring stretching), 756, 697 (Ar–H bending). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.66 (m, 4H, Ar–H q), 7.47 (m, 3H, Ar–H p), 7.35 (m, 1H, Ar–H o), 7.20 (m, 10H, Ar–H r) [the assignments of the resonance peaks o–r were referred to those protons marked in Scheme 6]. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 141.5, 141.1, 141.0, 140.6, 140.4, 139.5, 131.1, 129.9, 129.8, 129.4, 128.8, 127.9, 127.8, 127.4, 127.1, 126.6, 126.5, 126.1 (aromatic carbons). UV (DCM, 2.5×10^{-5} mol/L), λ_{max} (nm)/ϵ_{max} (mol^{-1} L cm^{-1}): 252/34988. MS(CI): *m*/*e* 307.1 [$(M + 1)^+$]; calcd 307.1.

*Preparation of 1,3,5/1,2,4-Phenyl- and Hexyl-Substituted Benzenes (**19** and **20**).* To a thoroughly baked and carefully evacuated 15 mL Schlenk tube with a stopcock on the sidearm were placed 29 mg (0.05 mmol) of $TaBr_5$ and 22 mg (0.05 mmol) of Ph_4Sn under nitrogen in a glovebox. Freshly distilled toluene (3 mL) was injected into the tube using a hypodermic syringe, and the mixture was stirred for 10 min. Monoynes **17** (36.7 mg, 0.36 mmol) and **4** (19.9 mg, 0.18 mmol) dissolved in 2 mL of anhydrous toluene were then injected into the catalyst solution. The resultant mixture was stirred at room temperature under nitrogen for 16 h, after which the reaction was quenched by the addition of methanol. The solvent was evaporated by reduced pressure, and the residue dissolved again in 0.5 mL of hexanes/chloroform mixture (1:1 by volume). The resulting solution was filtered through silica gel. The silica gel was washed thoroughly with another 20 mL of the hexanes/chloroform mixture. Removal of the solvent by a rotary evaporator and drying under vacuum at room temperature gave a colorless viscous oil of **19** in 90.4% yield. Compound **20** was prepared by a similar procedure, using 36.7 mg (0.36 mmol) of **17** and 29.9 mg (0.27 mmol) of **4** in the reaction. The product was isolated in 91.3% yield.

Results and Discussion

Monomer Synthesis. Carbazole- and fluorene-containing polymers such as poly(vinylcarbazole) and poly(fluorene) have been intensively investigated as hole-transporting materials, wide-band-gap energy transfer donors, and blue-light-emitting polymers.[48] To generate functional *hb*-PAs, we designed three new diyne monomers containing carbazole (**1** and **2**) and fluorene moieties (**3**).

Monomer **1** was readily accessible through iodination at the 3 and 6 positions of 9-phenylcarbazole (**5**), followed by palladium-catalyzed Sonogashira coupling with TMSA and deprotection in alcoholic KOH solution (cf. Scheme 3). To synthesize diynes **2** and **3**, one end of 1,6-dibromohexane was attached to the 9 position of carbazole. The resultant monosubstituted product **10** was then coupled with 3,6-diiodocarbazole and 2,7-diiodofluorene, yielding compounds **11** and **15**, respectively. The compounds were subsequently converted to the desired monomers by Sonogashira protocol by reacting with TMSA followed by deprotection with KOH. The hexyl linker does not only connect the aromatic moieties but also help improve the solubility of the resulting hyperbranched polymers. The overall yields were in the range 51–71%.

All the diyne monomers were thoroughly purified and fully characterized by standard spectroscopic methods, from which satisfactory analysis data corresponding to their expected molecular structures were obtained (see Experimental Section for details).

Polymerization Reaction. We first tried to homopolymerize the diyne monomers by tantalum and niobium halides and tetraphenyltin. Reactions conducted in toluene at room temperature give polymeric products in high yields (up to 99.9%), which are, however, unfortunately insoluble in common organic solvents (Tables 1–3). Presumably, rapid intra- and intermolecular cross-linking reactions have taken place, leading to an uncontrolled polymer growth. The high catalytic activity of the Nb- and Ta-based catalysts for the polycyclotrimerization of the functionalized alkynes is somewhat unexpected because these catalysts are known to have little tolerance to polar groups.[49] Attempts to lower the reactivity by diluting the reaction solutions or shortening the polymerization time have met with limited success (e.g., Table 3, run 6).[50] Delightfully, the diynes can be homopolymerized by $CpCo(CO)_2$ catalyst under UV irradiation in high yields (up to 99.9%), although the molecular weights of the isolated polymeric products are low.

To scavenge the unreacted triple bonds and to suppress the undesirable cross-linking reactions, we copolymerized the aromatic diynes with an aliphatic monoyne 1-octyne (**4**). Additionally, the flexible alkyl chain may impart high solubility to the polymer, hence furnishing high molecular weight products. This is indeed the case. As can be seen from the data given in Table 1 (runs 3 and 5), Table 2 (run 4), and Table 3 (runs 8 and 9), most of the copolycyclotrimerization reactions have undergone smoothly, giving completely soluble *hb*-PAs with high molecular weights (M_w up to $\sim 1.6 \times 10^5$) in high yields (up to 96.9%). For the copolycyclotrimerizations of **1** and **2** with **4**, a molar ratio of diyne to monoyne of 1:1.5 is necessary to render the resultant polymers soluble. Only equivalent amount is, however, needed for **3**, thanks to its flexible hexyl chains.

Among the catalysts, the binary mixtures of tantalum or niobium halide and tetraphenyltin generally show higher reactivity than the cobalt complex, producing polymers with higher molecular weights in higher yields. $TaCl_5$-Ph_4Sn is the best catalyst for the alkyne copolymerizations, giving *hb*-P**1**/**4**, *hb*-P**2**/**4**, and *hb*-P**3**/**4** in over 80% yields.

Structural Characterization. The polymers are characterized spectroscopically, and all of them give satisfactory analysis data (see Experimental Section). The IR spectra of diyne **2** and its hyperbranched homopolymer *hb*-P**2** and copolymer *hb*-P**2**/**4** are given in Figure 1. The strong bands associated with ≡C–H and C≡C stretching vibrations of **2** are observed at 3260 and 2103 cm^{-1}, respectively. These absorption bands become weaker

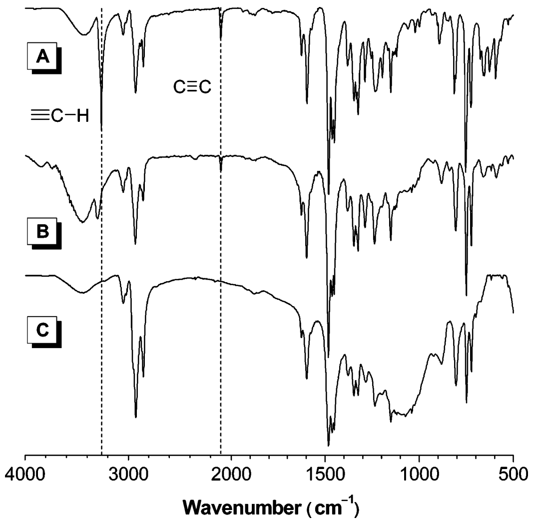


Figure 1. IR spectra of monomer **2** (A), its hyperbranched homopolymer *hb*-P**2** (B), and copolymer *hb*-P**2**/**4** (C, sample taken from Table 2, run 4).

in the spectrum of its homoploymer and completely disappear in that of its copolymer, indicating that the triple bonds have been consumed by the polycyclotrimerization reaction. The absence of acetylene absorptions in the copolymer suggests that 1-octyne has functioned well as a chain terminator and has suppressed the cross-linking reactions. The bands at 2926 and 2854 cm^{-1} associated respectively with asymmetrical and symmetrical methylene strechings are intensified in the spectrum of *hb*-P**2**/**4**, substantiating that the monoyne has been successfully incorporated into the hyperbranched structure. The absorption band of the aromatic C═C skeleton at 1599 cm^{-1} becomes stronger and broader in the spectra of *hb*-P**2** and *hb*-P**2**/**4**, indicating that new aromatic rings have been formed during the acetylene polycyclotrimerization reaction.

The ^{1}H NMR spectra of *hb*-P**1**/**4** and its monomer **1** are shown in Figure 2. The acetylene protons of diyne **1** resonate at $\delta \sim 3.1$ (peak a), which almost completely disappears upon copolycyclotrimerization with 1-octyne. The intensity is very weak, suggesting that almost all triple bonds have been consumed during the polymerization reaction. At the same time, the polycyclotrimerization reaction converts the triple bonds to aromatic rings, giving strong aromatic resonance peaks at $\delta \sim 9-6.5$. The peaks are broad, suggesting that the *hb*-PA possesses an irregular and somewhat rigid steric structure. Accompanying the polycyclotrimerization, the propargyl protons of monoyne **4** are transformed into benzyl protons, whose resonance is observed at $\delta \sim 2.7$ (peak e). The peaks at δ 2−0.5 are unambiguously due to the resonance of the aliphatic protons of the pentyl group (f−j) originally from monoyne **4**. No other unexpected signals are found, and all the resonance peaks can be readily assigned. This confirms the proposed polyarylene structure of the *hb*-PA and completely rules out the possibility that the diynes have been polymerized by a metathesis mechanism.[2]

The molecular structures of the *hb*-PAs are further characterized by ^{13}C NMR spectroscopy. An example of ^{13}C NMR spectrum of *hb*-P**3**/**4**, along with that of its diyne monomer **3**, is shown in Figure 3. The acetylenic carbon atoms of **3** resonate at δ 84.4 and 77.6. These peaks completely disappear in the spectrum of its copolymer. On the other hand, many peaks are observed in the spectral regions where aromatic carbon atoms resonate. These peaks are the sum of the resonance of the aromatic carbons of the fluorene and carbazole moieties as well as the new benzene rings formed by polycyclotrimerization. Moreover, many new carbon resonance peaks are emerged in the aliphatic spectral regions, owing to the incorporation of 1-octyne into the polymer structure.

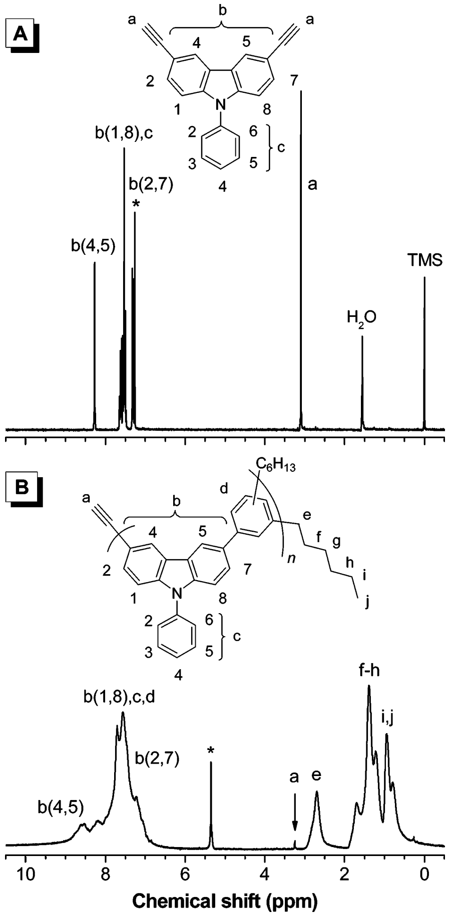


Figure 2. ^{1}H NMR spectra of (A) monomer **1** in chloroform-*d* and (B) its hyperbranched copolymer *hb*-P**1**/**4** in DCM-d_2 (sample taken from Table 1, run 3). The solvent peaks are marked with asterisks.

To gain more insights into the structures of the *hb*-PAs, the areas of their proton resonance peaks are integrated and analyzed. The resonance peak of the methylene protons in the benzyl unit at $\delta \sim 2.6$ (peak e in panel B of Figure 2) is clearly free from the interference by other resonance peaks. Using the integrated areas of the resonance peaks of the aromatic and methylenic protons, ratios of the numbers of diyne units (N_{II}) to those of monoyne units (N_I) in the copolymer can be estimated according to eq 1:

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

where $n_{H,II}$ is the number of acetylenic and aromatic protons in the diyne, and A_{Ph} and A_{Bz} are the integrated areas of the resonance peaks of the phenyl (Ph)[51] and benzyl methylene (Ph−CH$_2$) protons in the copolymer, respectively. The numbers of the diyne and monoyne units inside the copolymer are further related by eq 2:

$$N_I = N_{II} + 3 - 3m \qquad (2)$$

where m is the number of cyclic structures in the *hb*-PA. Assuming that no cyclic structures have been formed via internal

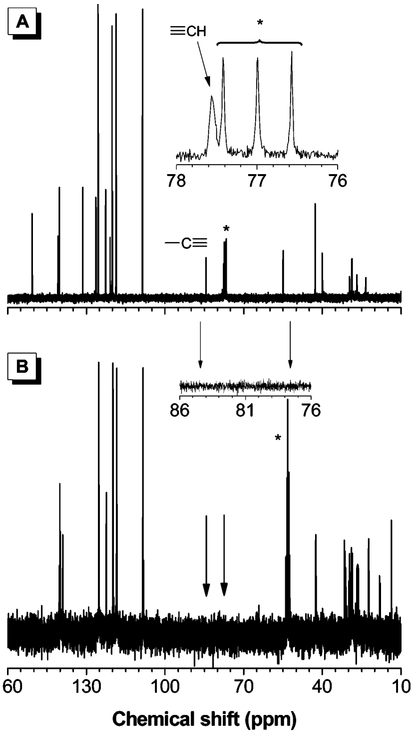


Figure 3. ^{13}C NMR spectra of (A) monomer **3** in chloroform-*d* and (B) its copolymer *hb*-P**3**/**4** (Table 3, run 8) in DCM-d_2. The solvent peaks are marked with asterisks.

Table 4. Molecular Weights of Hyperbranched Polyarylenes Calculated from NMR Data and Estimated by GPC Analysis[a]

no.	*hb*-PA	N_{II}/N_I[b]	N_{II}	N_I	$M_{n,c}$[c]	M_n[d]	$M_{n,c}/M_n$
1	*hb*-P**1**/**4**	0.74	9	12	3940	3490	1.13
2	*hb*-P**2**/**4**	0.49	3	6	2050	1790	1.15
3	*hb*-P**3**/**4**	1.01	(50)	(49)		40850	

[a] Samples taken from Table 1, run 3, Table 2, run 4, and Table 3, run 8. [b] Molar ratio of the number of diyne units (N_{II}) to the number of monoyne units (N_I) in the copolymer. [c] Calculated from the integrated area of resonance peaks in the ^{1}H NMR spectra. [d] Measured in THF on the basis of a linear polystyrene calibration.

cyclizations and backbiting propagations, the number of diyne units can thus be estimated according to eq 3:

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

Combining eqs 1 and 3 gives access to N_{II} and N_I, which enables calculation of number-average molecular weight of a copolymer from its NMR spectral data by eq 4:

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

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 hyperbranched copolymers *hb*-P**1**/**4** and *hb*-P**2**/**4** give a N_{II}/N_I ratio of 0.74 and 0.49 (Table 4), which relate to $M_{n,c}$ values of 3940 and 2050, respectively.

The calculated values are constantly higher than the experimental data obtained from GPC analysis, as commonly observed in other hyperbranched polymer systems.[9−12,34] This difference may be caused by internal cyclization reactions, which lower the monoyne content and thus increase the N_{II}/N_I ratio. Another reason for the lower experimental values may be the fact that the linear polystyrene-calibrated GPC measurements have underestimated the molecular weights of hyperbranched polymers due to the globular sizes of the latter.[52,53] This cause seems predominate in our case, though the first one cannot be completely excluded. The monomer ratio for *hb*-P**3**/**4** has been determined to be 1.01, which indicates that at least one internal cyclization reaction per polymer must have taken place (cf. eq 2). Another possible cause is that *hb*-P**3**/**4** has an ultrahigh molecular weight (cf. eq 2, where $\lim_{n\to\infty} N_{II}/N_I = 1$) with at least a few internal cycles overall in the polymer structure. Unfortunately, upon formation of an internal cycle, the molecular weight of the hyperbranched polymer is no longer dependent on the monomer ratio and consequently cannot be estimated from its NMR spectral data. Assuming that the experimentally determined M_n value of 40 850 is true, *hb*-P**3**/**4** would consist of about 50 monoyne and diyne units together with one internal cyclic structure.

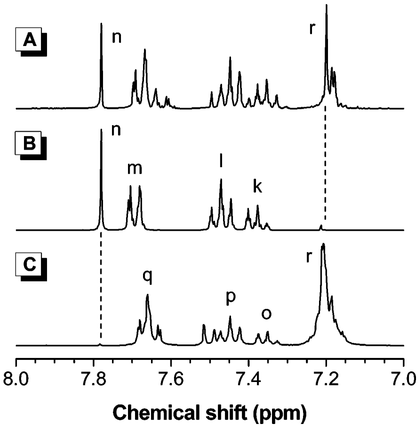


Figure 4. ^{13}C NMR spectra of (A) monomer **3** **18** (A) and pure regioisomers of 1,3,5-**18** (B) and 1,2,4-**18** (C) prepared using TaBr$_5$−Ph$_4$Sn as catalyst.

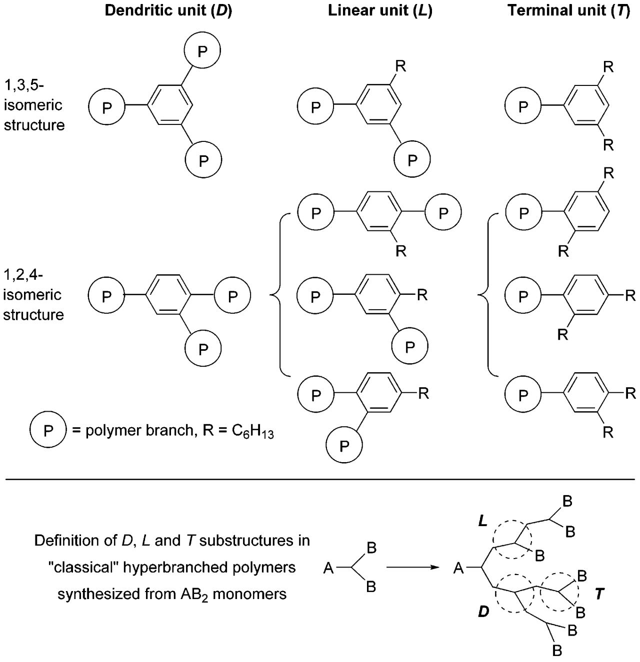
All the above spectroscopic data suggest that the diyne monomers have been polymerized by the transition-metal catalysts via a [2 + 2 + 2] polycycloaddition mechanism. The resonance signals of the newly formed benzene rings in the IR and NMR spectra are, however, overlapping with those of "old" aromatic rings from the monomers and are therefore difficult to confirm and analyze. To provide more evidence for the formation of new benzene rings in the polymer and to make the polymer architecture clearer, we designed and conducted two sets of model reactions. One reaction is the cyclotrimerization of phenylacetylene (**17**), an aromatic monoyne, under similar conditions used for the polymerization of the diynes (cf. Scheme 6). As expected, the reaction yields two triphenylbenzene regioisomers (**18**), i.e., 1,3,5-**18** and 1,2,4-**18**, which can be purified by silica gel column chromatography and isolated by recrystallizations from ethanol and ethanol/hexanes mixture, respectively. Their ^{1}H NMR spectra are shown in panels B and C of Figure 4. All the peaks are well separated and can be readily assigned. The peaks correspond well to those found in the mixture obtained from the cyclotrimerization reaction without any separation or purification (Figure 4A). These results further verify that the transition-metal-catalyzed polymerization has transformed three acetylenic triple bonds into one benzene ring through a cyclotrimerization mechanism.

From the ^{1}H NMR spectra of the mixture of the two regioisomers, the molar ratio of 1,3,5-**18** to 1,2,4-**18** can be calculated according to eq 5:

$$\frac{N_{1,2,4}}{N_{1,3,5}} = \frac{A_r/10}{A_n/3} = \frac{3A_r}{10A_n} \qquad (5)$$

where $N_{1,2,4}$ and $N_{1,3,5}$ are the numbers of 1,2,4- and 1,3,5-

Chart 1. Dendritic, Linear, and Terminal Units of Hyperbranched Polyarylene



trisubstituted benzene units, and A_r and A_n are the integrated areas of resonance peaks r and n, respectively. The calculated molar ratios of 1,3,5-**18** to 1,2,4-**18** are 1.0:0.9 and 1.0:1.4 when TaCl$_5-$ and TaBr$_5-$Ph$_4$Sn are used as catalysts, respectively. The ^{1}H NMR spectra of the isomers obtained from the model reaction of **17** catalyzed by CpCo(CO)$_2-h\nu$ cannot be quantified in the same way, as the peaks are very broad. Possibly, the reaction mixture contains some magnetically susceptible cobalt complexes, which have hindered the proper spinning of the NMR probe. Purification and separation of the crude mixture together with some more detailed studies are currently underway in our laboratories to clarify this issue.

After we have proved that our polymers have indeed formed via the [2 + 2 + 2] cyclotrimerization mechanism, we next tried to shed light on the internal structures of the polymers. From a "classical" definition, a hyperbranched polymer obtained from an AB$_2$-type monomer can have dendritic (*D*), linear (*L*), and terminal (*T*) units, depending on the substitution patterns of their repeat units (Chart 1). Accordingly, if an A group and two B groups have reacted, *D* unit is formed, and if one and none of the B groups have been coupled to another A group, the repeat units are *L* and *T*, respectively. Although the structure of our polymer differs from that of the standard assignment for a classical hyperbranched polymer, we may describe the cyclotrimerization of three diyne triple bonds into a new benzene ring as *D*. Accordingly, the repeat units with two diynes/one monoyne and one diyne/two monoynes can be assigned as *L* and *T*, respectively. Together with our previous findings that the new benzene rings can be substituted in 1,3,5- and 1,2,4-positions, we can imagine a total of 10 different substructures in an *hb*-PA as depicted in Chart 1.

The questions now arise whether all the three units (*D*, *L*, and *T*) are present in our polymers and, if yes, in which quantity or ratio they occur. To clarify these questions, we have designed the second set of model reaction, where we have simulated the copolycyclotrimerization between the aromatic diynes with the aliphatic monoyne. As the aromatic model compound, we have chosen again phenylacetylene (**17**). The compound is cyclotrimerized with aliphatic monoyne **4** in a molar ratio of 2:1 or 2:1.5 to simulate the aromatic and aliphatic acetylenes present in the copolymerization mixtures. By doing so, we should be able to obtain a mixture of model compounds with substructures of *D*, *L*, and *T* units (cf. Scheme 7).

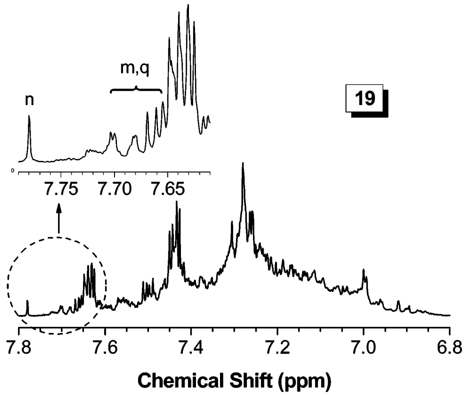


Figure 5. Aromatic proton resonance region in the ^{1}H NMR spectrum of simulated substructures obtained from cocyclotrimerization of **17** with **4** in a molar feed ratio of 2:1.

Figure 5 shows the ^{1}H NMR spectra of model compound mixture **19**. In comparison to the mixture of model compounds **18**, the cocyclotrimerization of **17** with **4** in a molar ratio of 2:1 results in a much more complicated spectrum with many resonance peaks. This should be mainly due to the formation of the linear units as two phenylacetylene and one 1-octyne are needed to generate this substructure. At δ 7.78, however, an isolated peak associated with the three protons of model compound 1,3,5-**6** (peak n) can be identified (cf. Figure 4 and Scheme 6). Additionally, resonance peaks m and q are clearly observed, unambiguously manifesting the formation of triphenylbenzene unit even in the presence of 1-octyne. Unfortunately, at present time, there are no model compounds for the terminal structures available in our laboratories to ultimately confirm the formation of the *T* units. We have, however, successfully identified the formation of the *D* units. Furthermore, all the acetylene triple bonds of both monoynes (i.e., **17** and **4**) have been consumed, as proved by the ^{1}H NMR analysis of the crude mixture of **19**. It is therefore reasonable to believe that the *T* units must have been formed and be part of the remaining aromatic protons in the higher field. The model compound mixture **20**, obtained by the cocyclotrimerization of **17** with **4** in a molar feed ratio of 2:1.5, gives similar results, although the resonance peak of proton n is expectedly smaller (Supporting Information, Figure S1).

Independent of their 1,3,5- and 1,2,4-substitution patterns, the *D*, *L*, and *T* units contain a total of 18, 13, and 8 aromatic protons, respectively, which can be expressed by eq 6:

$$A_{\mathrm{ar}} = A_{\mathrm{D}} + A_{\mathrm{L}} + A_{\mathrm{T}} = 18n_{\mathrm{D}} + 13n_{\mathrm{L}} + 8n_{\mathrm{T}} \qquad (6)$$

where A_{ar} is the integrated area of the aromatic protons, A_{D}, A_{L}, and A_{T} are the integrated areas of the aromatic protons of *D*, *L*, and *T* units, and n_{D}, n_{L}, and n_{T} are the numbers of *D*, *L*, and *T* units, respectively. Comparing A_{ar} with the three protons of A_{n} transforms eq 6 to eq 7:

$$n_{\mathrm{L}} = \frac{3\left(\dfrac{A_{\mathrm{ar}} - A_{\mathrm{n}}}{A_{\mathrm{n}}}\right) - 18n_{\mathrm{D}} - 8n_{\mathrm{T}}}{13} \qquad (7)$$

From our model reactions, we know that

$$n_D = n_{D1,3,5} + n_{D1,2,4} \tag{8}$$

where $n_{D1,3,5}$ and $n_{D1,2,4}$ are the numbers of dendritic 1,3,5- and 1,2,4-substructures, respectively. Furthermore, A_n corresponds to three protons and $n_{D1,3,5}$ can thus be expressed by eq 9:

$$n_{D1,3,5} = A_n/3 \tag{9}$$

Experimentally, $n_{D1,3,5}$ and $n_{D1,2,4}$ are present in a ratio of 1:1.4:

$$n_{D1,2,4} = 1.4n_{D1,3,5} \tag{10}$$

Since n_T and n_D are directly associated with each other ($n_T \approx n_D$),[9-12] we can substitute all the variables in eq 7 and estimate n_L. Knowing all the three substructures gives us access to DB, which is defined as

$$DB = (n_D + n_T)/(n_D + n_L + n_T) \tag{11}$$

If the model compound mixtures **19** and **20** really represent the structural units inside our *hb*-PAs, DB values of 0.11 and 0.05 can be estimated for the polymers obtained from the comonomer mixtures with diyne to monoyne ratios of 1:1 and 1:1.5, respectively. These values are somehow lower in comparison to those of other types of hyperbranched polymers. Nevertheless, the presence of dendritic repeat units, albeit in small quantities, qualifies our polymers as hyperbranched macromolecules.

Thermal and Optical Properties. Thermal properties of the *hb*-PAs are evaluated by TGA under nitrogen. Thanks to their rigid conjugated structures, all the homo- and copolymers show outstanding thermal stability with their degradation temperatures (T_d) well above 400 °C (Figure 6). Among all the polymers, homopolymer *hb*-P**1** shows the highest thermal stability, losing merely 5% of its weight at a temperature as high as 559 °C and carbonizing in a yield as high as 86 wt % when heated to 800 °C (Table 5). Homopolymers *hb*-P**2** and *hb*-P**3** also show high thermal stability and degrade at 538 and 447 °C, respectively. The results are somewhat expected as the presence of aliphatic hexyl chain should lower the thermal stability of the copolymers. In comparison to their homopolymer congeners, all the copolymers start to degrade at slightly lower temperatures due to the incorporation of aliphatic 1-octyne into the polymer structure. The TGA results are consistent with our previous results[49] and further verify hyperbranched structures of the polymers.

The absorption spectra of DCM solutions of monomer **3** and hyperbranched copolymers *hb*-P**1**/**4**, *hb*-P**2**/**4**, and *hb*-P**3**/**4** are shown in Figure 7. All the spectra exhibit absorption peaks at ~260 and ~296 nm due to the absorptions of phenyl and carbazolyl groups. Diyne **3** shows its highest absorption maximum at ~330 nm with a small shoulder peak at ~347 nm associated with the $\pi-\pi^*$ transition of the fluorene chromophore. Its absorption edge locates at ~360 nm. After polycyclotrimerization, the spectrum shifts to longer wavelength and the maximum is now found at ~345 nm. The bathochromic shift suggests that polymer *hb*-P**3**/**4** is electronically better conjugated due to the transformation of the triple bonds to the benzene rings at the 2 and 7 positions of the fluorene chromophore. The spectra of *hb*-P**1**/**4** and *hb*-P**2**/**4** also well extend to 400 nm, again due to the involved extensive electronic conjugation.[54]

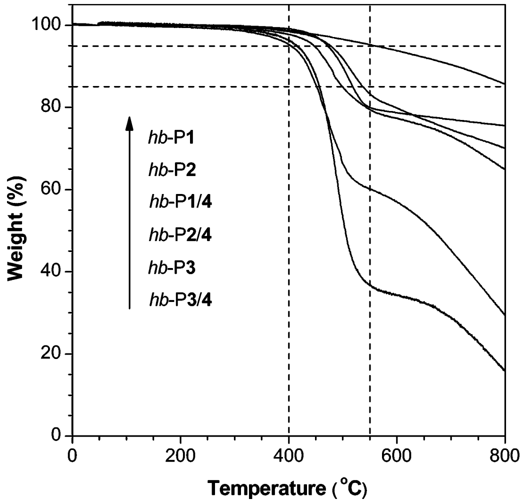


Figure 6. TGA thermograms of hyperbranched polyarylenes recorded under nitrogen at a heating rate of 20 °C/min (samples taken from Table 1, runs 2 and 3, Table 2, runs 1 and 4, and Table 3, runs 7 and 8).

Table 5. Thermal and Optical Properties of Hyperbranched Polyarylenes

no.	polymer[a]	T_d[b] (°C)	W_r[c] (wt %)	λ_{ab}[d]	λ_{em}[d]	Φ_F[e] (%)
			Homopolymer			
1	*hb*-P**1**(E)	559	85.6	296	398	11
2	*hb*-P**2**(E)	538	64.9	295	396	16
3	*hb*-P**3**(E)	447	29.4	332	400	40
			Copolymer			
4	*hb*-P**1**/**4**(A)	477	70.1	301	398	21
5	*hb*-P**2**/**4**(E)	463	74.1	297	397	20
6	*hb*-P**2**/**4**(B)	538	75.5	295	396	19
7	*hb*-P**2**/**4**(E)	463	64.9	295	396	28
8	*hb*-P**3**/**4**(A)	414	15.9	335	402	90
9	*hb*-P**3**/**4**(B)	432	17.9	335	401	50
10	*hb*-P**3**/**4**(E)	427	36.4	331	398	53

[a] Prepared using catalysts $TaBr_5-Ph_4Sn$ (A), $TaCl_5-Ph_4Sn$ (B), and $CpCo(CO)_2-h\nu$ (E). [b] Temperature for 5% weight loss. [c] Weight of residue after pyrolysis at 800 °C. [d] Absorption and emission maxima in DCM solutions. [e] Fluorescence quantum yield estimated using 9,10-diphenylanthracene ($\Phi_F = 0.90$ in cyclohexane) as standard.

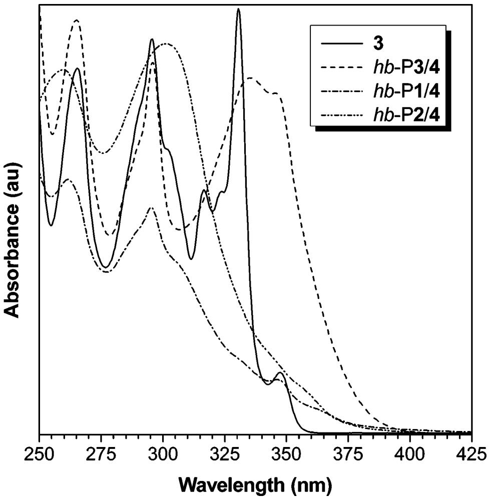


Figure 7. Absorption spectra of DCM solutions of monomer **3** and hyperbranched polymers *hb*-P**1**/**4**, *hb*-P**2**/**4**, and *hb*-P**3**/**4**. Concentration: 12 μg/mL. Samples taken from Table 1, run 3, Table 2, run 4, and Table 3, run 8.

Carbazole and fluorene are well-known luminophores and have often been used as building blocks for the construction of light-emitting macromolecules.[55] We thus studied the photoluminescence of our *hb*-PAs. Upon photoexcitation, the *hb*-PAs emit deep blue light of ~400 nm (Figure 8). In particular, the fluorene-containing copolymer *hb*-P**3**/**4** emits very brightly, whose intensity is much higher than those of their carbazole congeners under comparable experimental conditions. Its emission efficiency (Φ_F) is as high as 90%, more than 4-fold higher than those of *hb*-P**1**/**4** and *hb*-P**2**/**4** (Table 5). The better

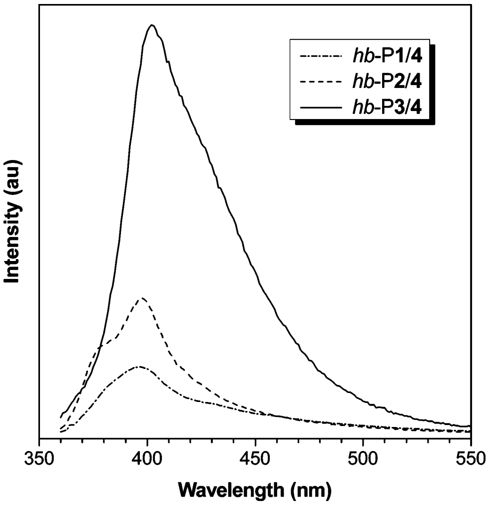


Figure 8. Fluorescence spectra of DCM solutions of hyperbranched polymers *hb*-P**1**/**4**, *hb*-P**2**/**4**, and *hb*-P**3**/**4**. Excitation wavelength (nm): 358 (*hb*-P**1**/**4**, *hb*-P**2**/**4**), 360 (*hb*-P**3**/**4**). Polymer concentration: 12 μg/mL. Samples taken from Table 1, run 3, Table 2, run 4, and Table 3, run 8.

π-electron conjugation in *hb*-P**3**/**4** might be the reason for its more efficient light emission. Interestingly, the Φ_F values of the copolymers are all higher than those of their corresponding homopolymers. This suggests that the flexible hexyl chains not only function as solubilizing groups but also help suppress the nonradiative decay pathways through the mitigation of unfavorable $\pi-\pi$ interactions between the chromophoric branches.

The emission efficiencies of the *hb*-PAs are also sensitive to their molecular structures and the type of catalyst used for the polycyclotrimerization reaction. Whereas the samples of *hb*-P**3**/**4** prepared from $TaCl_5-Ph_4Sn$ and $CpCo(CO)_2$ give respective Φ_F values of 50% and 53%, the sample obtained from $TaBr_5-Ph_4Sn$ shows a Φ_F value as high as 90% (Table 5, nos. 8−10). The reason for the lower Φ_F value for the *hb*-PA obtained from $TaCl_5$-Ph_4Sn might be due to its higher $n_{1,3,5}/n_{1,2,4}$ ratio, as found from the model compounds **18** (1.0:0.9 for $TaCl_5$-Ph_4Sn vs 1.0:1.4 for $TaBr_5-Ph_4Sn$). The poorer π-conjugation along the all-meta-substituted benzene ring might partially block the radiative decay pathways of the excited species and consequently lower the Φ_F value. The weaker emission of the *hb*-PA obtained from the Co complex is likely due to the catalyst residues trapped inside the hyperbranched polymer structure. An evidence for this is the fact that the char residues left in the TGA furnace after pyrolysis become weakly magnetic and could be attracted by a bar magnet.

Fluorene-based polymers such as polyfluorene (PF) are promising for blue light emission applications. However, researchers have often found that green emission bands evolve upon exposing thin films of such polymers to air at elevated temperatures.[56−59] The poor spectral stability has been attributed to the partial oxidation of the PF backbone and the formation of the fluorenone defects. We have examined the fluorescence spectra of our fluorene-containing *hb*-PA. As can be seen from Figure 9, thermally annealing a thin film of *hb*-P**3**/**4** at 100 °C in air for a long time causes little change in its spectral profile. Even raising the temperature to 150 °C and extending the annealing time to 15 h have exerted little effect on the fluorescence spectrum. This excellent spectral stability makes the polymer promising for light-emitting diode applications.

Molecules of fused aromatic rings have often been found to limit optical power.[60−62] The *hb*-PAs may function as optical-limiting materials because they contain numerous aromatic rings.

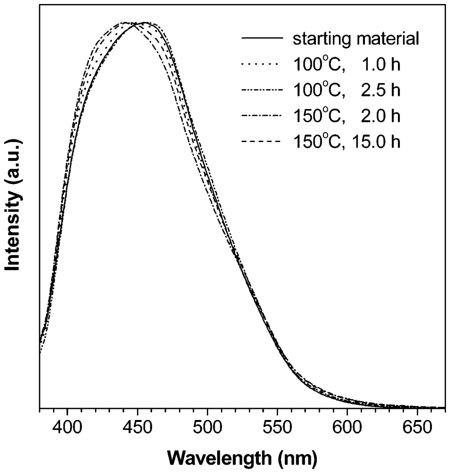


Figure 9. Fluorescence spectra of thin films of *hb*-P**3**/**4** thermally annealed at different temperatures in air. Excitation wavelength: 360 nm.

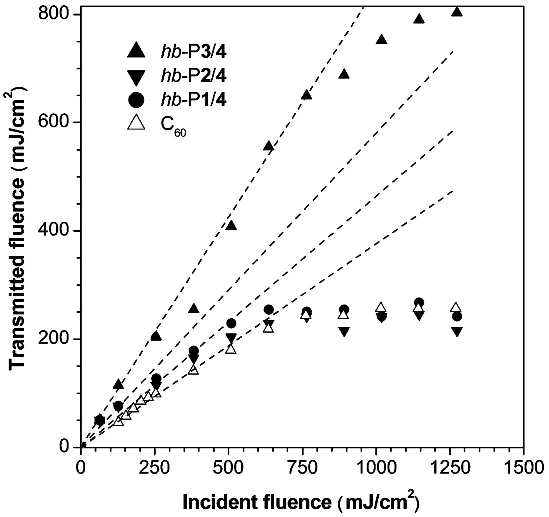


Figure 10. Optical limiting responses to 8 ns, 10 Hz pulses of 532 nm laser light, of DCM solutions of hyperbranched polyarylenes (samples taken from Table 1, run 3, Table 2, run 4, and Table 3, run 8). Polymer concentration: 0.86 mg/mL; light path length: 10 mm. Data for a toluene solution of C_{60} (0.16 mg/mL) is shown for comparison.

Table 6. Optical Limiting Properties of Hyperbranched Polyarylenes

no.	*hb*-PA	F_L[a] (mJ/cm^2)	$F_{t,m}/F_{i,m}$[b]
1	*hb*-P**1**/**4**	1034	0.19
2	*hb*-P**2**/**4**	1050	0.17
3	*hb*-P**3**/**4**	2300	0.63

[a] Optical limiting threshold (incident fluence at which nonlinear transmittance is 50% of initial linear one). [b] Signal suppression (ratio of saturated transmitted fluence to maximum incident fluence).

This is indeed the case: as can be seen from Figure 10, the *hb*-PAs effectively attenuate the power of intense 532 nm laser pulses. The transmitted fluence of *hb*-P**2**/**4** initially increases with an increase in the incident fluence in a linear fashion. It commences to deviate from linearity at an incident fluence of ~380 mJ/cm^2 and reaches a saturation plateau at a transmitted fluence of ~220 mJ/cm^2. Their optical limiting thresholds (F_L) and signal suppression ratios ($F_{t,m}/F_{i,m}$; Table 6) are comparable to those of C_{60}, a well-known optical limiter.[63] In comparison to *hb*-P**1**/**4** and *hb*-P**2**/**4**, *hb*-P**3**/**4** shows inferior optical power-limiting performance as it starts to deviate from linearity at an incident fluence above ~800 mJ/cm^2. This indicates that the optical-limiting performance of *hb*-PA is sensitive to the change in its molecular structure, offering the opportunity to tune its optical limiting properties through molecular engineering endeavor.

Conclusion

New *hb*-PAs are successfully synthesized in high yields by one-pot, single-step, transition-metal-catalyzed homopolycyclotrimerizations of aromatic diynes and their copolycyclotrimerizations with a monoyne. The homo- and copolyarylenes are completely soluble in common organic solvents. The aromatic polymers are thermally and optically stable, losing little of their weights when heated to high temperatures, and show no sign of photodegradation when annealed at elevated temperatures or shot by intense laser pulses. Thanks to their conjugated electronic structure, the *hb*-PAs emit deep-blue light efficiently. Together with their excellent optical power-limiting properties, these novel hyperbranched polymers may find an array of high-tech applications.

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Supporting Information Available: ^{1}H NMR spectrum of substructures obtained from cocyclotrimerization of **17** with **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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