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Metal-Free, Regioselective Diyne Polycyclotrimerization: Synthesis, Photoluminescence, Solvatochromism, and Two-Photon Absorption of a Triphenylamine-Containing Hyperbranched Poly(aroylarylene)

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ABSTRACT: A hyperbranched poly(aroylarylene) containing triphenylamine (TPA) moiety (*hb*-P**1**) is synthesized by metal-free polycyclotrimerization of *N*,*N*-bis(4-ethynylcarbonylphenyl)aniline (**1**) in a high yield (86%) with a perfect 1,3,5-regioregularity. The polymer is soluble in common organic solvents such as THF and chloroform and is thermally stable, losing 5% of its weight when heated to a temperature as high as ∼450 °C. The polymer is fluorescent and solvatochromic, whose emission color changes from ∼455 nm (blue) in toluene to 549 nm (yellow) in DMF. The polymer exhibits a large two-photon absorption cross-section due to the intramolecular charge transfer between its electron-donating TPA and electron-withdrawing 1,3,5-tricarbonylbenzene groups.

Introduction

Hyperbranched polymers have attracted much attention in recent years because of the expectation that their unique molecular shapes, branching patterns, and surface functionalities may impart new, unusual properties.[1] In comparison to their dendritic analogues, hyperbranched polymers enjoy ready synthetic access and can be easily prepared in large scales and quantities by single-step reactions and one-pot experimental procedures. Hyperbranched polymers generally possess irregular molecular structures and have excellent macroscopic processability. The novel properties stemmed from their unique molecular architectures may enable them to find technological applications in an array of areas such as nanoscale catalysis, supramolecular assembly, chemical sensor, drug delivery, adhesive coating, and molecular antenna.[2]

Various synthetic strategies have been developed by different research groups for the preparation of hyperbranched polymers.[3] Our group has been working on the development of new protocols for the synthesis of conjugated hyperbranched polymers.[4] In our previous studies, we have found that alkyne polycyclotrimerization and polycouping can readily furnish soluble, stable hyperbranched polyarylenes and polydiynes with unique thermal, optical, photonic, and magnetic properties.[4,5] We have recently discovered that bis(aroylacetylene)s, a group of terminal acyldiynes, can be readily polycyclotrimerized by piperidine, a simple secondary amine, to give 1,3,5-regioregular hyperbranched poly(aroylarylene)s (Scheme 1).[6] Thanks to the numerous benzophenone units in their molecular structures, the polymers are photosensitive and can be readily photo-cross-linked to give photoresist patterns with nanometric resolution.[6]

In our previous work, we used flexible, saturated alkoxy spacers (R) between phenylcarbonylethyne units to ensure good solubility of the resultant polymers (cf., Scheme 1). In this work, we extended our effort to the synthesis of a new hyperbranched poly(aroylarylene), using an acyldiyne containing nonplanar, unsaturated TPA moiety, i.e., *N*,*N*-bis(4-ethynylcarbonylphenyl)-aniline (**1**), as the monomer (Scheme 2). TPA is a famous hole-transporting material that has been widely used in the construction of organic light-emitting diodes because of its good solubility, excellent stability and high luminescence efficiency.[7] It is also a well-known electron donor due to its electron-rich nitrogen atom. Polymer containing such a moiety is thus anticipated to show novel electronic and optical properties.[8] We herein show that efficient electronic communication between the "new" 1,3,5-tricarbonylbenzene units formed by the polycyclotrimerization reaction and the "old" TPA units from the diyne monomer has endowed the resultant polymer (*hb*-P**1**) with high light-emitting efficiency and large two-photon absorptivity.

Experimental Section

General Information. Tetrahydrofuran (THF; Labscan), toluene (BDH), and 1,4-dioxane (Aldrich) were distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. *N*,*N*-Dimethylformamide (DMF) was stirred with calcium hydride overnight, distilled under reduced pressure, and kept in an atmosphere of dry nitrogen. Other solvents were purified using standard procedures. All other solvents and reagents were purchased from Aldrich and used as received without further purification.

^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 300 spectrometer in chloroform-*d* using tetramethylsilane (TMS; $\delta = 0$) as internal reference. IR spectra were taken on a Perkin-Elmer 16 PC spectrometer. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin- Elmer LS 55 spectrofluorometer. Quantum yield of fluorescence (Φ_F) was estimated using quinine sulfate in 0.1 N sulfuric acid ($\Phi_F = 54\%$) as standard. The absorbance of the solutions was kept below 0.1 to avoid internal filter effect. Thermal transition of the polymer was investigated by differential scanning calorimetry (DSC) using a DSC Q1000 at a

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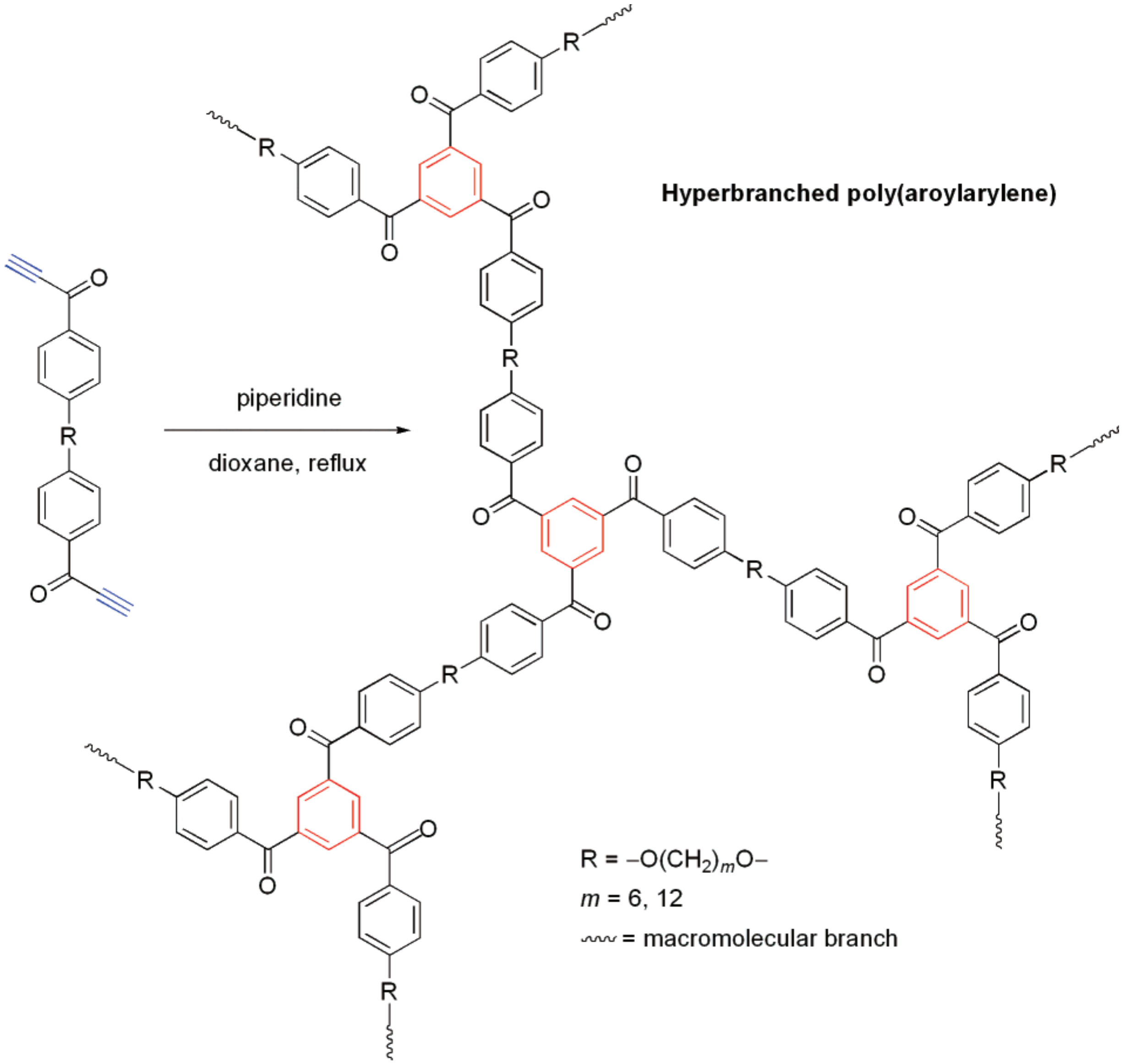
Scheme 1



heating rate of 10 °C/min under nitrogen. Thermal stability of the polymer was evaluated on a Perkin-Elmer TGA 7 under nitrogen at a heating rate of 20 °C/min. Molecular weights (M_w and M_n) and polydispersity index (M_w/M_n) of the polymer were estimated by a Waters 510 gel permeation chromatography (GPC) system, using monodisperse polystyrenes as calibration standards.

Crystal structures of diyne **1** and monoyne **4** (Figure 1) were determined by X-ray crystallography. Single crystals of **1** and **4** were grown at room temperature by slow diffusion of hexane vapor into their dichloromethane (DCM) solutions in closed containers. Crystal X-ray diffraction intensity data were collected at 100 K on a Bruker-Nonius Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation. The intensity data was processed using the SAINT and SADABS routines, and the structure solution and refinement were carried out by the SHELXTL suite of X-ray programs (version 6.10).

Monomer Synthesis. Using Vilsmeier−Haack formylation reaction,[9] 4,4′-diformyltriphenylamine (**2**) was prepared as an intermediate for the synthesis of diyne **1** (Scheme 3). Following the similar procedures,[9] 4-formyltriphenylamine was prepared as an intermediate for the synthesis of monoyne **4**.

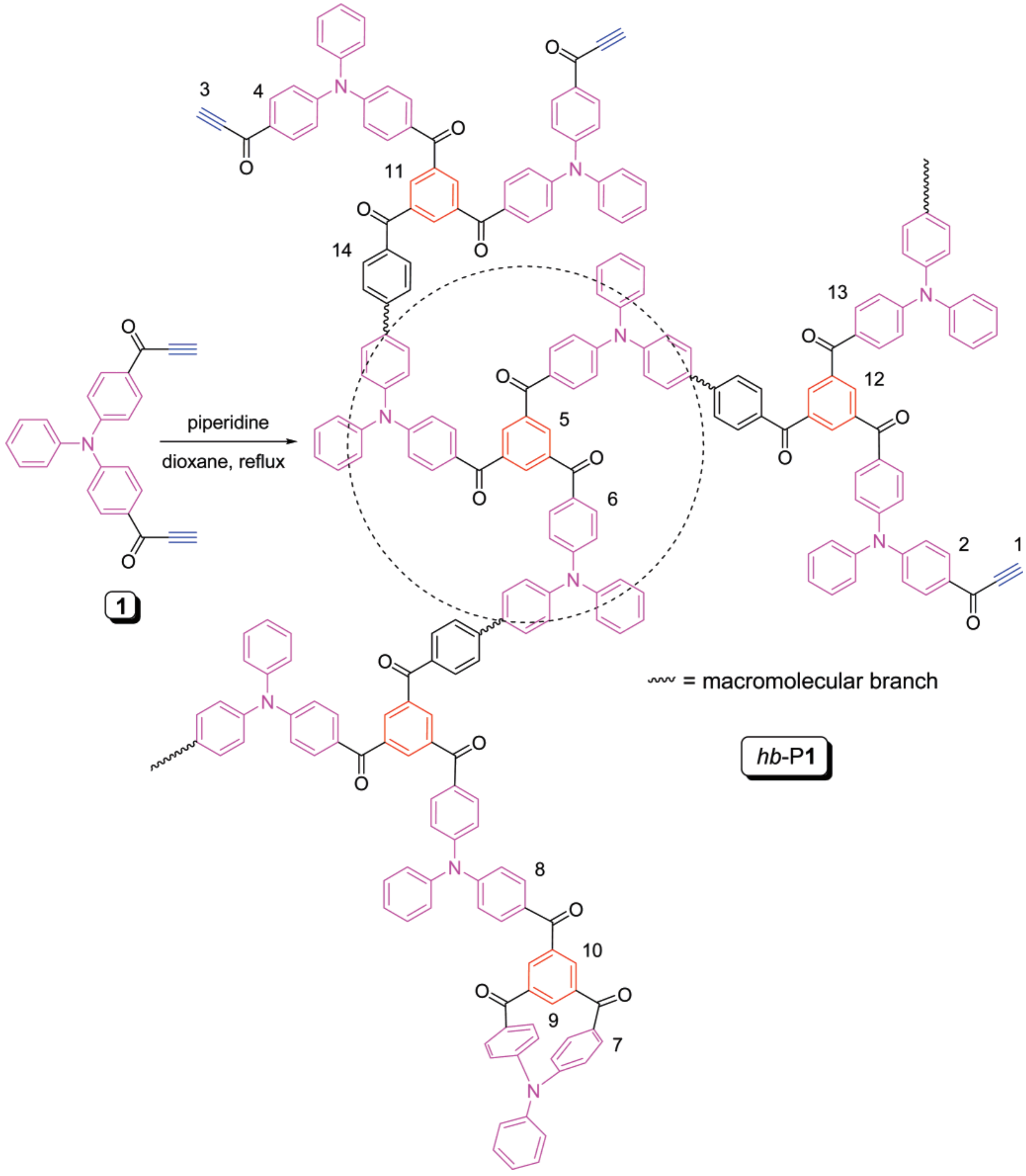
Characterization data of **2**. ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 9.97 (s, 2H), 7.92 (d, $J = 8.6$ Hz, 4H), 7.56 (t, $J = 7.6$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.27 (m, 6H). ^{13}C NMR (75 MHz, DMSO-d_6), δ (ppm): 191.1, 151.4, 145.1, 131.3, 130.9, 130.3, 127.0, 126.3, 122.4.

4-Formyltriphenylamine. ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 9.81 (s, 1H), 7.66 (d, $J = 8.8$ Hz, 2H), 7.34 (t, $J = 7.8$ Hz, 4H), 7.19 (m, 6H), 7.00 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 190.4, 153.3, 146.1, 131.2, 129.7, 129.0, 126.3, 125.1, 119.3.

Synthesis of *N,N*-Bis(4-ethynylcarbonylphenyl)aniline (1). Into a 250 mL two-necked, round-bottomed flask under nitrogen were added 1.2 g (4.0 mmol) of **2** and 40 mL of THF. The solution was cooled to 0 °C, into which 20 mL of 0.5 M (10 mmol) ethynylmagnesium bromide in THF was added dropwise under stirring. The mixture was stirred at room temperature overnight and was then quenched by addition of saturated aqueous NH_4Cl solution. The reaction mixture was extracted with DCM and dried over $MgSO_4$. After filtration and solvent evaporation, **3** was obtained as a yellow solid. Analysis by TLC chromatography shows that **3** was pure enough for the following oxidation reaction.

Into a solution of 0.72 g (2 mmol) of **3** in 100 mL of DCM was added 7.08 g (60 mmol) of 75% manganese(IV) oxide at room temperature. The mixture was stirred overnight and filtered through a short silica gel column to remove the unreacted metal oxide. The crude product was purified by silica gel column chromatography using chloroform as eluent. Light yellow solid of **1** was obtained in 45.8% yield (0.32 g) based on the amount of **2** used. IR (KBr), ν (cm^{-1}): 3244, 2095, 1638, 1605, 1581, 1504, 1257. ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 8.04 (d, $J = 8.6$ Hz, 4H), 7.50 (m, 2H), 7.29 (m, 1H), 7.16 (m, 6H), 3.46 (s, 2H). ^{13}C NMR (75 MHz,

Scheme 2



$CDCl_3$), δ (ppm): 175.5, 152.0, 145.3, 131.4, 131.0, 130.1, 127.1, 126.4, 122.3, 80.3. Anal. Calcd for $C_{24}H_{15}NO_2$: C, 82.50; H, 4.33; N, 4.01. Found: C, 82.17; H, 4.48; N, 4.67.

Synthesis of *N*-(4-Ethynylcarbonylphenyl)diphenylamine (4). This compound was prepared by the experimental procedures similar to those for the synthesis of **1**, using 4-formyltriphenylamine, instead of **2**, as the starting material. Light yellow solid; yield 85.8%. IR (KBr), ν (cm^{-1}): 3267, 2094, 1636, 1582, 1489, 1265. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.96 (d, $J = 8.9$ Hz, 2H), 7.35 (t, $J = 7.7$ Hz, 4H), 7.19 (m, 6H), 6.98 (d, $J = 8.9$ Hz, 2H), 3.32 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 175.3, 153.4, 145.9, 131.5, 129.7, 128.6, 126.4, 125.2, 118.7, 80.6, 79.6.

Synthesis of Model Compound 5. This compound was prepared by the experimental procedures similar to those for the synthesis of *hb*-P**1**, using **4**, instead of **1**, as the starting material (Scheme 4). Into a 25 mL dry Schlenk tube was added 120 mg (0.4 mmol) of **4**. After the tube was evacuated and refilled with nitrogen three times, 3.5 mL of 1,4-dioxane and 0.45 mL of freshly prepared piperidine (0.3 M, 0.135 mmol) in 1,4-dioxane were injected. The solution was stirred and refluxed for 24 h. After the reaction was cooled to room temperature, the solvent was evaporated off and the crude product was purified by a silica gel column chromatography using chloroform as eluent. Product **5** was obtained as a yellowish-red solid in 43.3% yield (52 mg). ^1H NMR (300 MHz,

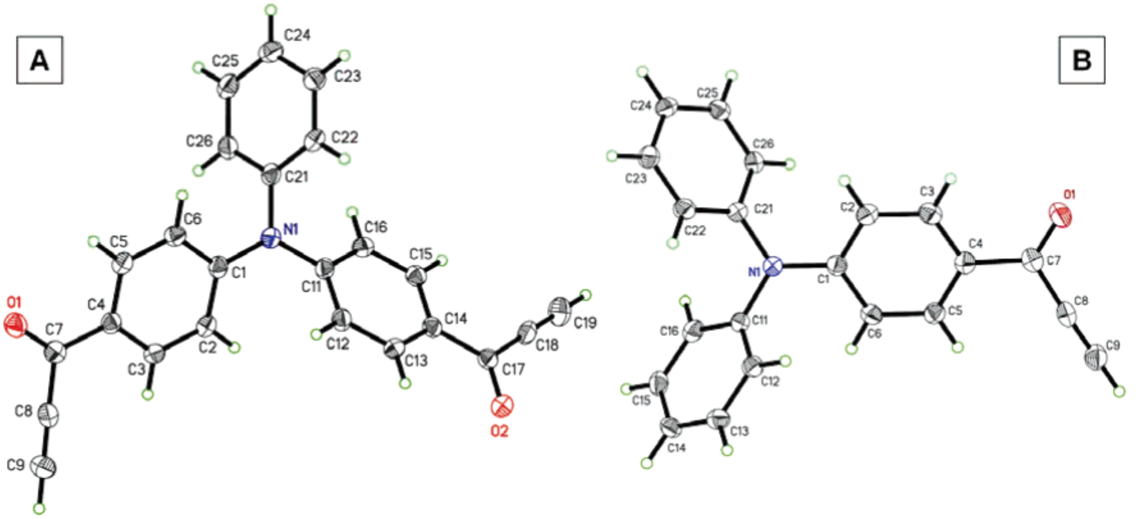
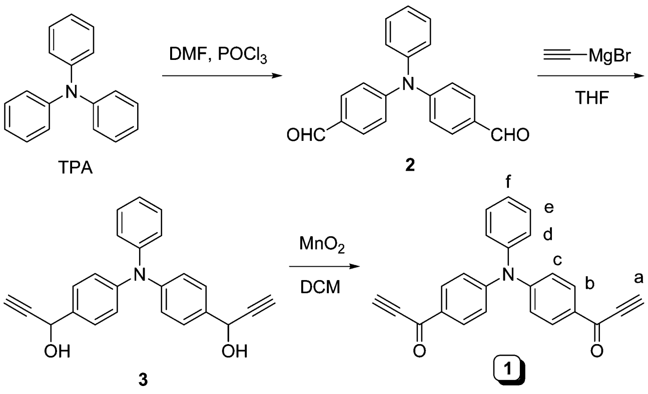
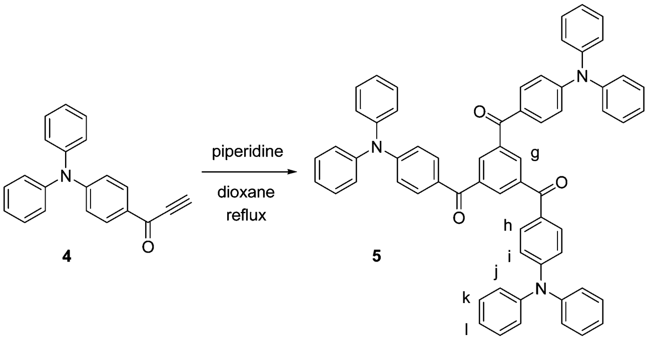


Figure 1. ORTEP drawings of (A) diyne **1** and (B) monoyne **4**.

Scheme 3



Scheme 4



CDCl$_3$), δ (ppm): 8.27 (s, 3H), 7.69 (d, $J = 8.8$ Hz, 6H), 7.33 (t, $J = 8.1$ Hz, 12H), 7.17 (m, 18H), 7.00 (d, $J = 8.8$ Hz, 6H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 193.5, 152.4, 146.2, 138.8, 132.8, 132.1, 129.7, 128.4, 126.2, 124.9, 119.2.

Polymerization Reaction. Into a dry Schlenk tube in a glovebox under nitrogen was placed 140 mg (0.4 mmol) of **1**, 3.5 mL of 1,4-dioxane, and 0.45 mL of freshly prepared solution of piperidine (0.3 M, 0.135 mmol) in 1,4-dioxane. The mixture was refluxed for 24 h. After being cooled to room temperature, the solution was diluted with chloroform and added dropwise to 300 mL of methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight, after which, it was collected by filtration and then dried under vacuum at room temperature to a constant weight. Polymeric product (*hb*-P**1**) was obtained in 86% yield as a yellow powder. M_w 11400; M_w/M_n 2.8 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3281, 2094, 1652, 1584, 1505, 1256. ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 8.56, 8.34, 8.03, 7.74, 7.36, 7.16, 5.78, 3.45. ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 193.4, 188.8, 152.9, 151.9, 151.1, 148.5, 145.9, 145.7, 145.4, 138.5, 137.1, 136.4, 133.7, 133.1, 132.9, 132.0, 131.6, 130.6, 130.1, 129.8, 128.9, 127.1, 126.5, 126.2, 125.7, 125.4, 124.1, 122.6, 122.3, 120.5, 90.7.

Optical Nonlinearity Measurement. A two-photon absorption cross section of *hb*-P**1** was determined by the two-photon excited fluorescence (TPEF) measurement technique, using picosecond laser pulses as described in the literature.[10] A high-energy Nd:YAG laser (Continuum Leopard) provided 35 ps wide pulses of 60 mJ vertically polarized 355 nm radiation at 10 Hz. The beam was pumped into an apparatus of optical parameter amplification and generated 2−3 mJ of tunable idler wavelength with a spectral range of 750−2000 nm. The fundamental intensity was altered by a neutral density filter. The beam from the polarizer was focused on the quartz sample cell (1 × 1 cm; ca. 3 mL) employing a lens with a focus length of 20 cm. The incident beam was adjusted to locate near the cell wall on the collection signal side to avoid self-absorption.

The fluorescence was collected perpendicularly using a silica photodiode after passing a long-wave filter to remove the incident beam. A 10^{-4} M solution of Rhodamine B in methanol was used as reference. The measurements were conducted in a regime where the fluorescence signal showed a quadratic dependence on the intensity of the excitation beam, as expected for TPEF.[11] The polymer concentration was adjusted to 5.5×10^{-5} M to amplify the signal intensity and reduce experimental uncertainty. The two-photon absorption cross section of the polymer was deduced according to the following equation:[10]

$$\delta_s = \delta_r \frac{\Phi_r}{\Phi_s}\frac{I_s}{I_r}\frac{c_r}{c_s}\frac{P_r^2}{P_s^2}\frac{n_s^2}{n_r^2} \qquad (1)$$

where subscripts s and r denotes the sample and reference, respectively, δ is the two-photon absorption cross-section, Φ is the quantum yield, c is the concentration, and n is the solution refractive index. The incident beam power and signal intensity measured by a detector were donated as P and I, respectively.

Results and Discussion

Polymer Synthesis. To synthesize the hyperbranched poly(aroylarylene) containing the TPA moiety (*hb*-P**1**), we designed a bis(aroylacetylene) with its two carbonylethyne units linked by a TPA bridge (**1**) and elaborated a three-step reaction route for its synthesis (cf., Scheme 3). We first converted TPA into its diformyl derivative by the Vilsmeier−Haack reaction.[9] The product (**2**) was subjected to the reaction with ethynylmagnesium bromide, which gave product **3**. We attempted to oxidize **3** by Jones reagent (CrO$_3$/H$_2$SO$_4$) but its TPA core was also oxidized

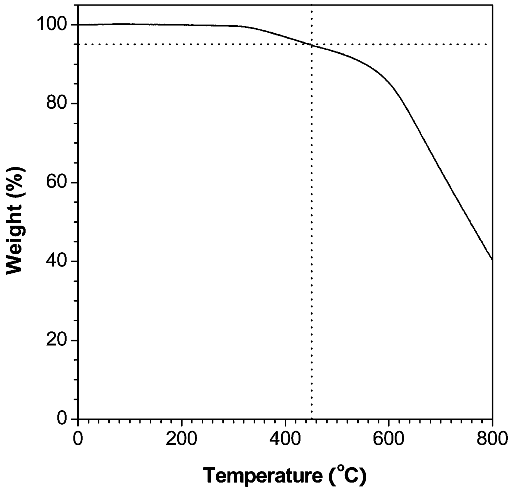


Figure 2. TGA thermogram of *hb*-P**1** recorded under nitrogen at a heating rate of 20 °C/min.

under the harsh reaction conditions. We thus chosen MnO_2, a moderate oxidizing reagent, for the oxidization and delightfully, we obtained the desirable monomer (**1**) as a yellow solid in a satisfactory yield. Molecular structure of **1** was characterized by IR and ^{1}H and ^{13}C NMR spectroscopies as well as X-ray crystallography. The ORTEP drawing of the diyne monomer is given in Figure 1.

In our previous work, we have found that piperidine and 1,4-dioxane are the best catalyst and solvent, respectively, for the polycyclotrimerization of the bis(aroylacetylene)s (cf., Scheme 1).[6] We used the same catalyst and solvent for the polymerization of **1** (cf., Scheme 2). After refluxing for 24 h, we happily obtained *hb*-P**1** in a high yield (86%). The polymer is soluble in common organic solvents, such as THF, chloroform and DCM. GPC analysis gave a weight-average molecular weight of 11400. This relative value is probably considerably underestimated because of the hyperbranched nature of the polymer.[12] Our previous investigation revealed that the underestimation could be as large as 7-fold.[13] The actual or real molecular weight of *hb*-P**1** thus may be much higher than the relative value estimated from the GPC analysis.

The hyperbranched polymer is thermally very stable. As can be seen from Figure 2, the temperature for 5% weight loss is as high as ~450 °C. When the polymer was heated in a DSC cell to 200 °C (the highest temperature allowable for the DSC measurements in our instrumentation center), no any peak was observed. The polymer thus has a very high glass transition temperature (T_g > 200 °C). For the hyperbranched poly(aroylarylene)s containing the flexible alkoxy spacers (cf., Scheme 1), their glass transitions were detected in the temperature range of ~79−103 °C.[6] Obviously, the incorporation of the rigid TPA bridge into the molecular structure of *hb*-P**1** has dramatically enhanced the T_g value of the hyperbranched polymer.

To verify that the triple bonds of **1** are cyclotrimerized to benzene rings of *hb*-P**1**, we conducted a model cyclotrimerization reaction, using *N*-(4-ethynylcarbonylphenyl)diphenylamine (**4**), a monoyne, as a model compound for diyne **1**. Under the similar reaction conditions, **4** is transformed to a sole product with a 1,3,5-tricarbonylbenzene core structure (**5**) without formation of any byproducts (cf., Scheme 4). This proves that **1** has indeed been polycyclotrimerized in a regioselective manner. The moderate yield of **5** is ascribed to the electron-donating effect of the TPA moiety of **4**, which decreases the reactivity of the monoyne.

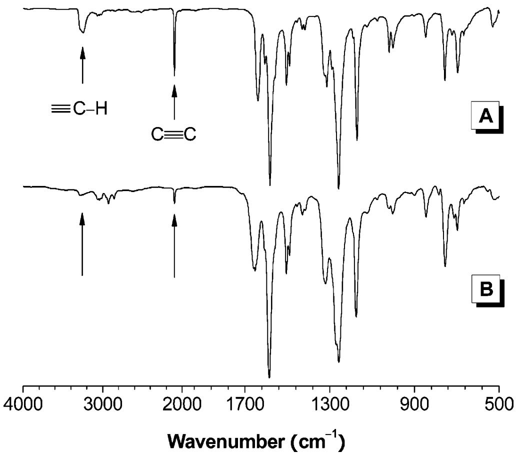


Figure 3. IR spectra of (A) monomer **1** and (B) its polymer *hb*-P**1**.

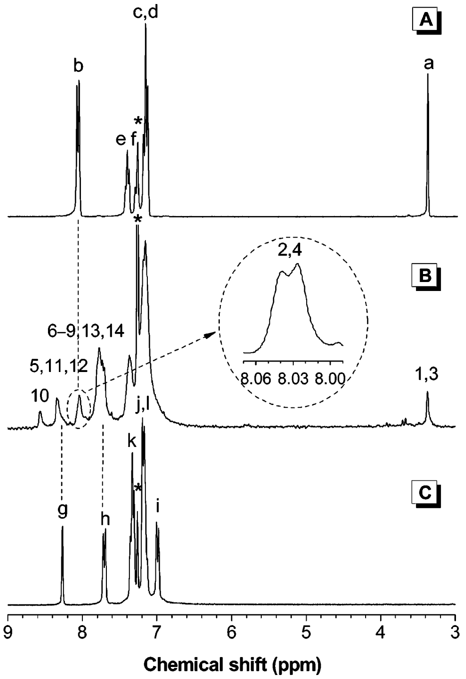
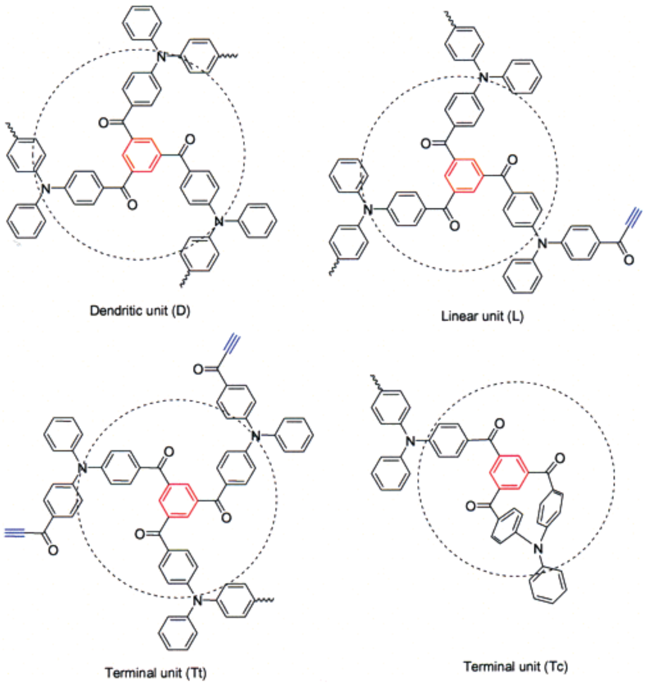


Figure 4. ^{1}H NMR spectra of (A) **1**, (B) *hb*-P**1**, and (C) **5** in chloroform-*d*. Labels of the resonance peaks correspond to those given in Schemes 3 (A), 2 (B), and 4 (C). The solvent peaks are marked with asterisks.

Structure Characterization. We characterized the polymer by spectroscopic methods to collect direct structural information. Figure 3 shows the IR spectrum of *hb*-P**1**; for comparison, the spectrum of its monomer **1** is also shown in the same figure. The diyne monomer shows absorption bands at 3281 and 2095 cm^{-1} due to ≡C−H and C≡C stretching, respectively. These bonds are still observed in the spectrum of *hb*-P**1** at similar wavenumbers but with lower intensities, revealing that most of the triple bonds have been converted to the benzene rings by the polycyclotrimerization reaction.

The ^{1}H NMR spectra of *hb*-P**1** and its monomer **1** as well as model compound **5** are shown in Figure 4. The acetylene proton of **1** resonates at δ 3.46 (a); this peak becomes much weaker after the monomer is subjected to polycyclotrimerization reaction. By comparison with the spectra of **1** and **5**, all the peaks in the spectrum of *hb*-P**1** are readily assigned. The polymerization shifts the resonance of the phenyl protons ortho to the triple bond of **1** at δ 8.04 (b) to δ 7.74 (6−9, 13 and 14), while the phenyl protons on the periphery of *hb*-P**1** resonate at δ 8.03 (2 and 4). The new peak at δ 8.34 (g) is assigned to the proton resonance of the benzene rings newly formed by the polycyclotrimerization. The peak at δ 8.56 (10) arises from the resonance of the tricarbonylphenyl protons of the cyclophane

Chart 1



formed by the end-capping of one triple bond in a terminal branch by two triple bonds in one monomer.[6]

Degree of Branching (DB). As shown in Chart 1, there exist four structural units in *hb*-P**1**: one dendritic unit (*D*), one linear unit (*L*), and two kinds of terminal units including one cyclophane ring (T_c) and two unreacted triple bonds (T_t). Because the resonance peaks of the triple bonds in the linear and terminal units (1 and 3) are hard to discern in the ^{1}H NMR spectrum of *hb*-P**1**, it is difficult to directly calculate the DB of the polymer. Alternatively, we tried to utilize the integrals of the periphery phenyl protons for the DB calculation.

Comparing the ^{1}H NMR spectrum of *hb*-P**1** with those of the monomer and the model compound, the following relationships hold among the contents or fractions (*f*) of the four units (f_D, f_L, f_{Tc}, and f_{Tt}).

$$\frac{4f_{Tt} + 2f_L}{6f_D + 6f_{Tc} + 6f_L + 6f_{Tt}} = \frac{A_{2,4}}{A_{6-9,13,14} - A_9} \qquad (2)$$

$$f_D + f_L + f_{Tt} + f_{Tc} = 1 \qquad (3)$$

where $A_{2,4}$, $A_{6-9,13,14}$, and A_9 represent the integrals of the areas of the resonance peaks (2, 4), (6−9, 13, 14), and 9 as labeled in Scheme 2. According to Scheme 2 and Chart 1, the integrals of resonance peaks 9 and 10, i.e., A_9 and A_{10}, in the cyclophane have the following relationship:

$$A_9 = A_{10}/2 \qquad (4)$$

The ratios can be determined from the ^{1}H NMR spectral data. According to the integrals of the areas of the resonance peaks, we can deduce:

$$\frac{A_{2,4}}{A_{6-9,13,14} - A_{10}/2} = \frac{1.25}{5.29 - 0.21/2} \qquad (5)$$

Combining eqs 2−5, we can get the following equation:

$$2f_{Tt} + f_L = 0.72 \qquad (6)$$

Enlarging the peak at δ 8.03 manifests that it is a doublet with similar intensities. This suggests that the triple bonds in the linear and terminal units are equal in amount. Equation 7 is thus established:

$$\frac{4f_{Tt}}{2f_L} = \frac{1}{1} \qquad (7)$$

Finally, f_L can be calculated as

$$f_L = 0.36 \qquad (8)$$

According to definition, DB of *hb*-P**1** can be expressed as[14]

$$\mathrm{DB} = \frac{f_D + f_{Tt} + f_{Tc}}{f_D + f_L + f_{Tt} + f_{Tc}} \qquad (9)$$

Incorporating eqs 3 and 8 into eq 9 gives the DB value of *hb*-P**1**:

$$\mathrm{DB} = 1 - f_L = 0.64 \qquad (10)$$

This value is higher than those of the "conventional" hyperbranched polymers (commonly ∼50%) and further confirms the hyperbranched structure of the polymer.

Table 1. Photophysical Properties of *hb*-P1 in Different Solvents[a]

solvent	Δf	λ_{ab} (nm)	λ_{em} (nm)	$\Delta\upsilon$ (cm^{-1})	Φ_F (%)
toluene	0.014	397.5	455.5	3203	21.8
1,4-dioxane	0.021	398.0	468.5	3781	22.9
chloroform	0.149	405.5	516.5	5300	16.1
THF	0.210	395.0	498.5	5256	16.8
DCM	0.218	402.0	522.5	5737	16.7
DMF	0.275	392.0	549.0	7295	9.9

[a] Abbreviations: Δf = solvent polarity parameter taken from ref 15, λ_{ab} = absorption maximum, λ_{em} = emission maximum, $\Delta\upsilon$ = Stokes shift, Φ_F = fluorescence quantum yield estimated using quinine sulfate in 0.1 N H_2SO_4 (Φ_F = 54%) as standard.

Optical Properties. As discussed in the Introduction, TPA is an electron donor. On the other hand, the 1,3,5-tricarbonylbenzene unit newly formed in the polycyclotrimerization of **1** is an electron acceptor. Hyperbranched polymer *hb*-P**1** thus may exhibit unique optical properties due to its branched A-π-D structural motif, where A, π, and D denote acceptor, conjugated bridge, and donor, respectively. Residues of transition-metal catalysts are often detrimental to the materials properties, especially optical properties, of polymers. Since no metallic catalyst is used in the polycyclotrimerization reaction, our system is thus well suited for the synthesis of advanced functional materials. The photophysical data of *hb*-P**1** are summarized in Table 1. The absorption spectra of *hb*-P**1** in different solvents are shown in Figure 5. Although the polymer possesses an A−π−D structural motif, the solvent polarity exerts little effect on its ground-state electronic transition: all the spectra are similar, with little shift in the peak maximum (λ_{ab} ∼ 400 nm).

In contrast, the PL spectrum of *hb*-P**1** progressively shifts to red with an increase in the solvent polarity, with λ_{em} moving from 455.5 to 549.0 nm when the solvent is changed from toluene to DMF (Figure 6 and Table 1). The emission color changes from blue in toluene to yellowish green in DCM when the polymer solutions are illuminated under a hand-hold 365 nm UV lamp (Figure 7), which well coincide with their PL spectra. The Φ_F value of the polymer generally decreases when the polarity of the solvent is increased (Table 1). Since the polymer is comprised of D−π−A units, we believe that the solvatochromism is caused by photoinduced intramolecular

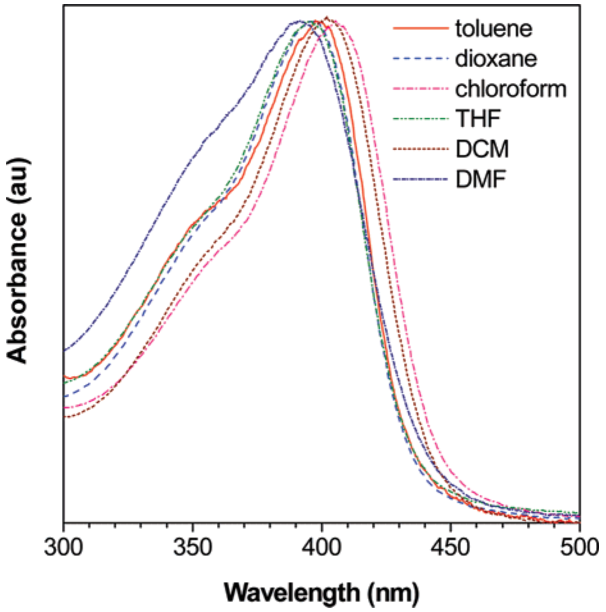


Figure 5. Absorption spectra of *hb*-P**1** in different solvents (concentration: ~10 μg/mL).

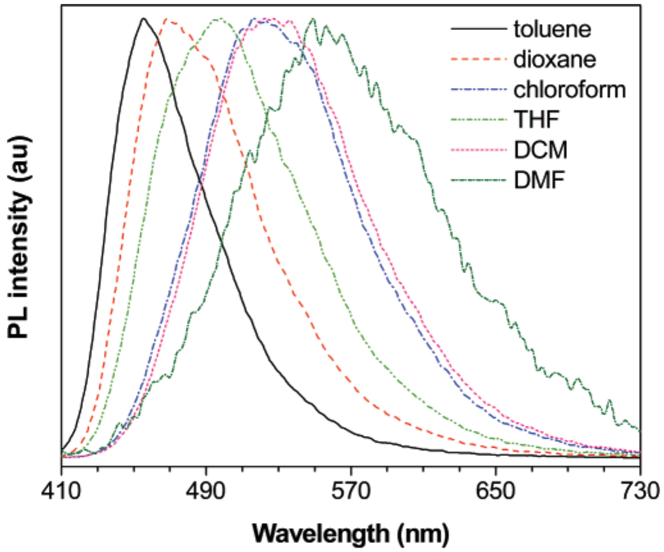


Figure 6. Emission spectra of *hb*-P**1** in different solvents ($c \sim 10$ μg/mL, $\lambda_{ex} = 396$ nm).

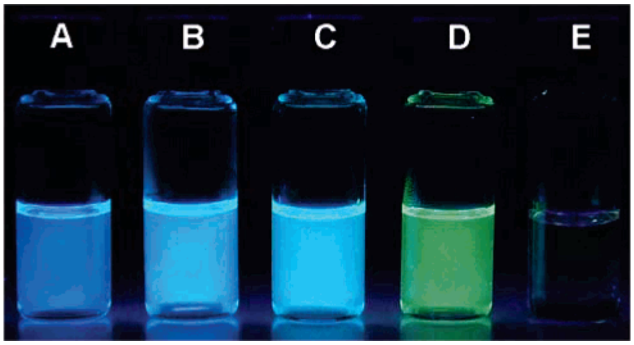


Figure 7. Light emissions from *hb*-P**1** solutions (~10 μg/mL) in (A) toluene, (B) 1,4-dioxane, (C) THF, (D) DCM and (E) DMF. Photographs were taken under illumination of a 365 nm UV light.

charge transfer (ICT) in the excited state. Such chromic behavior is associated with the stabilization of the polar emissive excited states by the polar solvents.[16]

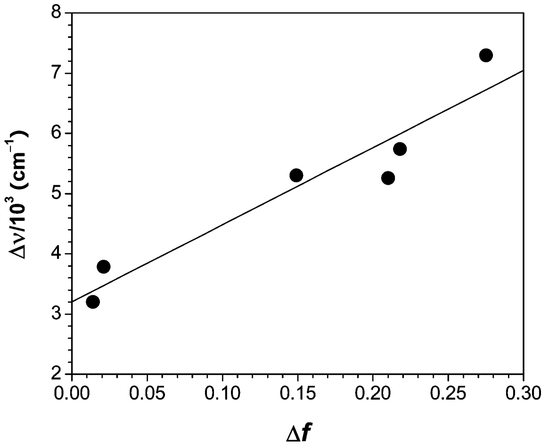


Figure 8. Plot of Stokes shift ($\Delta\nu$) of *hb*-P**1** vs solvent polarity parameter (Δf) of its solution (~10 μg/mL).

To further understand the solvent effect on the PL process of *hb*-P**1**, we calculated its Stokes shifts in different solvents. The Lippert–Mataga equation[17] has been widely used to describe the solvatochromic behavior of a chromophore:

$$\Delta\nu \equiv \nu_{ab} - \nu_{em} = \frac{2\Delta f}{hca^3}(\mu_e - \mu_g)^2 + \text{const} \qquad (11)$$

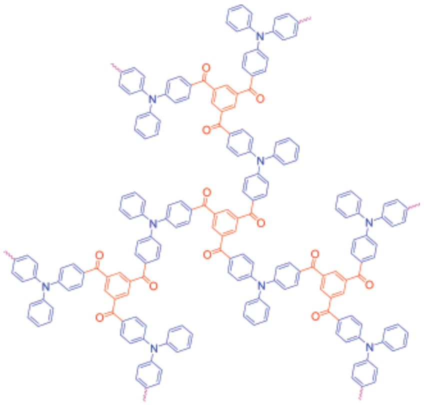
$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad (12)$$

Here $\Delta\nu$ is the Stokes shift, h is the Planck constant, c is the speed of light, a is the radius of the chromophore, μ_e and μ_g are the dipole moments in the excited (e) and ground (g) states, Δf is the solvent polarity parameter, and ϵ and n are the dielectric constant and refractive index of the solvent, respectively. The linear dependence of $\Delta\nu$ on Δf together with the large slope of the $\Delta f - \Delta\nu$ plot (Figure 8) suggests that the ICT excited-state has a larger dipolar moment than the ground state[18] due to the substantial charge redistribution, which is probably derived from the relaxation of the initially formed Franck–Condon excited state (vertical transition from the ground state to the vibrational levels of the excited-state and then relaxation to the ICT state), instead of direct transition from the ground state.[10c]

Materials capable of undergoing two-photon absorption processes have attracted considerable interest because of their potential technological applications in three-dimensional fluorescence imaging, optical limiting, photodynamic therapy, optical data storage, three-dimensional microfabrication, etc.[19] Most of these applications are in the near-infrared region and the two-photon absorption measurements are thus usually performed at ~800 nm.[20] Materials with branched D-π-A structures often exhibit superior two-photon absorption cross sections than their linear counterparts due to cooperative interactions between the branches. It has been found that an increase in the extent of branching in the TPA-containing compounds leads to an increase in their two-photon absorption cross sections.[21] Since *hb*-P**1** is constructed from TPA building blocks and possesses a branched D–π–A structural motif, it is highly likely that it will show a high two-photon absorption cross-section.

To calculate the value of two-photon absorption cross-section, accurate polymer concentration must be known. It is, however, somewhat difficult to determine the molar concentration of a hyperbranched polymers.[22] Fortunately, we can derive the repeating unit of *hb*-P**1** through careful analysis of its molecular structure. As can be seen from Chart 2, each TPA unit is shared

Chart 2



by two newly formed 1,3,5-tricarbonylbene cores. We can therefore distribute one and half of the TPA group to one core. The two-photon absorption cross section of *hb*-P**1** is thus found to be 1347 GM when measured at 800 nm using Rhodamine B as standard, which is comparable to, or larger than, its branched, low molecular weight counterparts previously reported by other groups (1360 GM[8a] and 290 GM[16]).

Conclusion

In this work, we have succeeded in synthesizing a functional hyperbranched poly(aroylarylene) (*hb*-P**1**) by metal-free, regioselective polycyclotrimerization of *N*,*N*-bis(4-ethynylcarbonylphenylene)aniline (**1**). The polymer is soluble in common organic solvents and is resistant to thermolysis at temperatures up to $\sim$450 °C. It is emissive and solvatochromic. Thanks to its branched D-π-A structural motif, the polymer exhibits a two-photon absorption cross-section as high as 1347 GM. These unique linear and nonlinear optical properties make the polymer a promising candidate material for high-tech applications.

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Supporting Information Available: CIF files for, tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths/angles, and anisotropic displacement parameters for, and figures showing an ORTEP drawing of diyne **1** and monoyne **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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