## Simple Synthesis, Outstanding Thermal Stability, and Tunable Light-Emitting and Optical-Limiting Properties of Functional Hyperbranched Polyarylenes

## Han Peng, Lin Cheng, Jingdong Luo, Kaitian Xu, Qunhui Sun, Yuping Dong, Fouad Salhi, Priscilla P. S. Lee, Junwu Chen, and Ben Zhong Tang\*

Department of Chemistry, Center for Display Research, Institute of Nano Science and Technology, and Open Laboratory of Chirotechnology of the Institute of Molecular Technology for Drug Discovery and Synthesis, Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China

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In their relentless pursuit of advanced materials, polymer scientists have devoted much effort to the construction of conjugated polymers using aromatic rings as building blocks, in expectation that the resultant polyarylenes would exhibit novel materials properties. A typical example of polyarylenes is polyphenylene, which was first prepared in 1886 and is still under active investigation, with the research frontier now moving from low (linear) to high (ladder, dendritic, and hyperbranched) dimensionalities.<sup>1,2</sup> Our group has worked on the synthesis of hyperbranched polyarylenes by acetylene polycyclotrimerizations initiated by tantalum and niobium halides<sup>3</sup> and have succeeded in the preparation of a completely soluble hyperbranched polyphenylene by the copolycyclotrimerization of 1,4diethynylbenzene with phenylacetylene.<sup>4</sup> While effective to nonpolar monomers, the Ta and Nb catalysts are intolerant of functional groups. In this work, we extended our efforts to the search for robust catalysts and to the creation of functional polyarylenes. In our previous work, we were able to polymerize 3,9-dodecadiyne using CpCo(CO)<sub>2</sub><sup>5</sup> as catalyst at 120 °C, but the product was only partially soluble.3a Instead of heating to the high temperature, in this work, we used UV irradiation to activate the Co catalyst at a lower temperature (65 °C). The photoactivated catalyst initiated the polycyclotrimerizations of functional acetylenes (Scheme 1), and the resultant hyperbranched polyarylenes<sup>6</sup> exhibited unique solution, thermal, and optical properties.

The diyne monomers (1) containing aromatic rings of molecular electronics interest were prepared by palladium-catalyzed coupling of silylacetylene with dihaloarenes followed by base-catalyzed desilylation.<sup>7</sup> The liquid crystalline (LC) monoyne **2c** was prepared by our published procedure.<sup>8</sup> The polycyclotrimerizations were initiated by CpCo(CO)<sub>2</sub> with UV irradiation under nitrogen. The experimental details on the synthesis and characterization of the monomers and polymers can be found in the Supporting Information.

The polymerization results are summarized in Table 1. The copolycyclotrimerization of 4,4'-diethynylbiphenyl (**1a**) with 1-phenylacetylene (**2a**) gave an all-aromatic hyperbranched polyarylene (**3**), which was, however, partially soluble. Replacing the aromatic monoyne with an aliphatic one solved the solubility problem: a completely soluble polymer **4** was produced by the copolymerization of **1a** with 1-heptyne (**2b**). The copolymeriza-



**Figure 1.** <sup>1</sup>H NMR spectrum of **7** in dichloromethane- $d_2$ . Cz = carbazolyl.



**Figure 2.** Absorption and emission spectra of **4** and **5** in dichloromethane.  $\lambda_{ex}$  (nm): 343 (**4**) and 334 (**5**). Polymer concentration: 2 mM.

tion of **1a** with **2c** gave **5** in a high yield—this is remarkable because our early attempts in using **2c** as a comonomer all failed when the Ta and Nb catalysts were used. Similarly, while the Ta and Nb catalysts were ineffective, the CpCo(CO)<sub>2</sub>–hv system initiated polycyclotrimerizations of the functional carbazolyl diyne **1c**, again demonstrating the robustness of the Co catalyst. The polymers all gave unimodal GPC peaks, with their  $M_w$  up to ~29 000 (**5**)<sup>9</sup> and  $M_w/M_n$  down to 1.58 (**7**). Similar to the hyperbranched polyphenylenes prepared by Suzuki coupling,<sup>2b</sup> the polyarylenes exhibited low intrinsic viscosities when dissolved in good solvents such as toluene.

The molecular structures of the polymers were characterized by spectroscopic methods, and all the polymers gave satisfactory spectral data (see Supporting Information for details). The <sup>1</sup>H NMR spectrum of **7** is given in Figure 1 as an example. The spectrum shows no unexpected signals, and all the resonance peaks can be readily assigned. The peaks of the aromatic protons are broad, suggesting that the hyperbranched polymer possesses a random molecular composition, an irregular stereostructure, and a rigid core architecture. This latter point is supported by the sharper peaks of the flexible alkyl chains not directly attached to the rigid aromatic cores. The small peak at  $\delta \sim 3.4$  is due to the absorption of the acetylene protons at the peripheral ends.

We investigated the optical and thermal properties of the soluble hyperbranched polymers using the methods described in our early reports.<sup>10</sup> As shown in Figure 2, **4** absorbs at 309 nm and emits a strong UV light of 398 nm, whose  $\Phi_F$  (0.49) is higher that of poly(1-phenyl-1-octyne) (0.43), a highly luminescent disubstituted polyacetylene.<sup>11</sup> The emission from **5** was much weaker ( $\Phi_F = 0.09$ ), which was possibly quenched by its own absorption in the same spectral region. The lumines-



Table 1. Synthesis<sup>a</sup> and Properties of Hyperbranched Polyarylenes

no.	feed ratio $[2]/[1]^b$	polymer yield (wt %)	$M_{ m w}{}^c$	$M_{\rm w}/M_{\rm n}^c$	$\lambda_{\mathrm{em}}^{d}$ (nm)	$\Phi_{\rm F}{}^{\it e}$	$T_{\mathbf{d}}{}^{f}(^{\circ}\mathbf{C})$	$W_{ m r}{}^g$ (wt %)	$F_{\rm L}{}^h$ (mJ/cm <sup>2</sup> )	$F_{\rm t,m}/F_{\rm i,m}$
1 2 3 4 5 6	1.0 (2a/1a) 1.3 (2b/1a) 1.2 (2c/1a) 2.2 (2b/1b) 1.0 (2a/1c) 1.0 (2b/1c)	73.6 (3) 76.0 (4) 84.9 (5) 83.5 (6) 91.8 (7) 72.6 (8)	4 290 <sup><i>j</i></sup> 20 350 28 570 16 240 6 370 13 420	$     \begin{array}{r}       1.58' \\       2.24 \\       5.78 \\       3.40 \\       1.58 \\       2.15 \\     \end{array} $	398 397 400 399 398	0.49 0.09 0.31 0.20 0.10	585 412 467 474 404	86.0 50.3 75.0 63.7 83.0	343 900 126 577 635	0.21 0.53 0.11 0.35 0.36

<sup>*a*</sup> By copolycyclotrimerizations of diynes (1) with monoynes (2) catalyzed by  $CpCo(CO)_2 - h\nu$  in toluene under nitrogen; [1] = 0.1 M, [cat.] = 10 mM, 65 °C, 6 h. <sup>*b*</sup> Molar ratio. <sup>*c*</sup> By GPC in THF (polystyrene calibration). <sup>*d*</sup> Emission maximum (in dichloromethane). <sup>*e*</sup> Quantum yield of fluorescence (9,10-diphenylanthracene standard). <sup>*f*</sup> Temperature for 5% weight loss (TGA, under nitrogen, heating rate: 20 °C/min). <sup>*g*</sup> Weight of residue at 800 °C in the TGA analysis. <sup>*h*</sup> Optical limiting threshold (incident fluence at which nonlinear transmittance is 50% of initial linear one). <sup>*i*</sup> Signal suppression (ratio of saturated transmitted fluence to maximum incident fluence). <sup>*j*</sup> For soluble fraction of the partially soluble polymer.

cence efficiency of other polymers also changed with the change in the combination of monomer/comonomer pairs (cf. Table 1); that is, the emission property of the polymers can be tuned by altering their molecular structures.

Polymer **4** lost little weight at 585 °C and carbonized in high yield (86%) upon further heating (Figure 3A and Table 1, no. 2). All its structural congeners **5–8** were also thermally stable. Their stabilities are similar to that of poly(*p*-phenylene) (stable up to ~550 °C)<sup>1</sup> but different from those of polyacetylenes (e.g., PPA and PH respectively started to lose their weights at 220 and 150 °C).<sup>12</sup> This is obviously because the polyarylenes are structurally similar to polyphenylene (stable aromatic constituents) but different from polyacetylene (labile polyene backbone).

Molecules of fused aromatic rings may limit optical power,<sup>13</sup> and we checked whether our thermally stable polyarylenes would act as optical limiters. PPA photodegraded under the attack of harsh laser shots,<sup>14</sup> but **4** strongly attenuated the power of intense 532 nm optical pulses (Figure 3B). The optical limiting power of **4** is comparable to that of  $C_{60}$ , a best-known optical limiter.<sup>13–15</sup> Noticing that **4** is a copolymer of **1a** and **2b**, we changed one of its two monomers at one time to see how this change will affect its limiting power. When **1a** and **2b** were respectively changed to **1b** and **2c**, the optical limiting performance of the corresponding copolymers **6** and **5** were respectively improved and



**Figure 3.** (A) TGA thermograms of hyperbranched polyarylenes. (B) Optical responses to 8 ns, 10 Hz pulses of 532 nm laser light, of dichloromethane solutions (0.86 mg/mL) of **4–6** [linear transmittance (%): 92 (**5**), 79 ( $C_{60}$ ), 66 (**4**, **6**)]. Data for poly(phenylacetylene) (PPA; panels A and B), poly(1-hexyne) (PH; panel A), and  $C_{60}$  (panel B) are shown for comparison.

worsened, indicating that the nonlinear optical property can be manipulated by molecular engineering. This is further verified by the data shown in Table 1: the limiting power of the polymers varied in a large range with their molecular structure. Among the polymers, **6** worked best. It limited the laser pulses at a low threshold (126 mJ/cm<sup>2</sup>) and suppressed the optical signals to a great extent (0.11; Table 1, no. 4), which are respectively 2.8- and 2.5-fold better than those achievable by C<sub>60</sub> under comparable conditions.

In summary, in this study, we successfully synthesized soluble functional hyperbranched polyarylenes in high yields by alkyne polycyclotrimerizations initiated by CpCo(CO)<sub>2</sub>-hv,<sup>5</sup> thanks to the functionality-tolerance of the robust Co catalyst. The polyarylenes emitted UV light and limited intense optical pulses. The UV emission is of technological value and may be utilized in the fabrication of full-color light-emitting devices.<sup>16</sup> The excellent optical limiting properties, coupled with their thermal stability and processing advantages, make the hyperbranched polyarylenes promising candidate materials for high-tech applications.

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**Supporting Information Available:** Synthetic procedures and structural characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

## **References and Notes**

- (a) Schluter, A. D.; Wegner, G. Acta Polym. 1993, 44, 59.
   (b) Tour, J. M. Adv. Mater. 1994, 6, 190. (c) Johnen, N. A.; Kim, H. K.; Ober, C. K. ACS Symp. Ser. 1994, 579, 298. (d) Kumar, U.; Neenan, T. X. ACS Symp. Ser. 1995, 614, 518.
   (e) Kim, Y. H. J. Polym. Sci., Polym. Chem. Ed. 1998, 36, 1685. (f) Scherf, U. Top. Curr. Chem. 1999, 201, 163. (g) Watson, M. D.; Fechtenkotter, A.; Mullen, K. Chem. Rev. 2001, 101, 1267.
- (2) (a) Goldschmiedt, G. Monatsh. Chem. 1886, 7, 40. (b) Kim, Y.; Webster, O. W. Macromolecules 1992, 25, 5561. (c) Hecht, S.; Frechet, J. M. J. J. Am. Chem. Soc. 1999, 121, 4084. (d) Wiesler, U. M.; Berresheim, A. J.; Morgenroth, F.; Lieser, G.; Mullen, K. Macromolecules 2001, 34, 187.
- (3) (a) Xu, K.; Tang, B. Z. *Chin. J. Polym. Sci.* **1999**, *17*, 397.
   (b) Tang, B. Z.; Xu, K.; Sun, Q.; Lee, P. P. S.; Peng, H.; Salhi,

F.; Dong, Y. ACS Symp. Ser. **2000**, 760, 146. (c) Lam, J. W. Y.; Luo, J.; Peng, H.; Xie, Z.; Xu, K.; Dong, Y.; Cheng, L.; Qiu, C.; Kwok, H. S.; Tang, B. Z. Chin. J. Polym. Sci. **2000**, 19, 585. (d) Mi Y.; Tang, B. Z. Polym. News **2001**, 26, 170.

- (4) Xu, K.; Peng, H.; Tang, B. Z. Polym. Prepr. 2001, 42 (1), 555.
- (5) While  $Co_2(CO)_8$  was used in the synthesis of benzene-based<sup>1g</sup> and -cored<sup>2c</sup> dendrimers, we were unaware of any previous attempt in utilizing  $CpCo(CO)_2$  as a catalyst to initiate alkyne polycyclotrimerization before our early work reported in ref 3a.
- (6) Hyperbranched polyphenylenes were prepared by Pd(0)and Ni(II)-catalyzed aryl-aryl coupling reactions at high temperatures.<sup>2b</sup> Our approach is, however, conceptually different and offers a new synthetic route to hyperbranched polyarylenes. The simplicity of our methodology and the richness of acetylene chemistry<sup>7</sup> facilitate systematic variations in the structures and properties of the polyarylenes.
- (7) (a) Modern Acetylene Chemistry; Stang, P. J., Diederich, F., Eds.; VCH: New York, 1995. (b) Brandsma, L.; Verkruijsse, H. D. Synthesis of Acetylenes, Allenes and Cumulenes; Elsevier: Amsterdam, 1981.
- (8) Lam, J. W. Y.; Kong, X.; Dong, Y.; Cheuk, K. K. L.; Xu, K.; Tang, B. Z. *Macromolecules* **2000**, *33*, 5027.
- (9) GPC often underestimates molecular weights of branched polymers;<sup>2b</sup> the difference between the relative and absolute molecular weights can be as big as ~40 times: Muchtar, Z.; Schappacher, M.; Deffieux, A. *Macromolecules* **2001**, *34*, 7595. The true molecular weights of our hyperbranched polymers thus could be much higher than those given in Table 1.
- (10) (a) Tang, B. Z.; Xu, H.; Lam, J. W. Y.; Lee, P.; Xu, K.; Sun, Q.; Cheuk, K. K. L. *Chem. Mater.* 2000, *12*, 1446. (b) Huang, Y. M.; Ge, W.; Lam, J. W. Y.; Tang, B. Z. *Appl. Phys. Lett.* 1999, *75*, 4094. (c) Kong, X.; Tang, B. Z. *Chem. Mater.* 1998, *10*, 3352.
- (11) Huang, Y. M.; Ge, W.; Lam, J. W. Y.; Tang, B. Z. Appl. Phys. Lett. 2001, 78, 1652.
- (12) Masuda, T.; Tang, B. Z.; Higashimura, T.; Yamaoka, H. Macromolecules 1985, 18, 2369.
- (13) (a) Tutt, L. W.; Kost, A. Nature (London) 1992, 356, 225. (b) Sun, Y. P.; Riggs, J. E. Int. Rev. Phys. Chem. 1999, 18, 43.
- (14) Tang, B. Z.; Xu, H. Macromolecules 1999, 32, 2569.
- (15) (a) Tang, B. Z.; Leung, S. M.; Peng, H.; Yu, N.-T.; Su, K. C. *Macromolecules* **1997**, *30*, 2848. (b) Peng, H.; Lam, J. W. Y.; Leung, F. S. M.; Poon, T. W. H.; Wu, A. X.; Yu, N.-T.; Tang, B. Z. *J. Sol-Gel Sci. Technol.* **2001**, *22*, 205.
- (16) Lam, J. W. Y.; Dong, Y.; Cheuk, K. K. L.; Luo, J.; Xie, Z.; Kwok, H. S.; Mo, Z.; Tang, B. Z. *Macromolecules* **2002**, *35*, 1229.

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