Enhanced Nonlinear Optical Activity of Molecules Containing Two D−π−A Chromophores Locked Parallel to Each Other

Chao-Zhi Zhang,[†] Changgui Lu,[‡] Jing Zhu,[‡] Chuan-Yu Wang,[§] Guo-Yuan Lu,*[,†] Chang-Shun Wang,[§] De-Lin Wu,[†] Fang Liu,[†] and Yiping Cui*[,‡]

Department of Chemistry, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, People's Republic of China, Advanced Photonics Center, Southeast University, Nanjing, 210096, People's Republic of China, and Department of Physics, Shanghai Jiao Tong University, Shanghai, 200240, People's Republic of China

Received February 22, 2008. Revised Manuscript Received May 14, 2008

A series of H-shaped second-order nonlinear optical (NLO) chromophores with two parallel and nonconjugated D−π−A units have been synthesized, in which a 9,10-dihydroanthracene is employed as molecular backbone. The measurement results of hyper-Rayleigh scattering (HRS) and UV−vis spectra show that the first molecular hyperpolarizability (β) values of H-shaped chromophores are remarkably increased compared with the corresponding mono-D−π−A unit reference compounds (the enhancements per azo D−π−A unit from 1.2 to 3.0 are observed), without causing a large shift of the absorption band to longer wavelength. Therefore, it gives an available way of solving the trade-off between nonlinearity and transparency in designing NLO chromophores. Furthermore, some main-chain fluoro-containing polyimides embedded with the H-shaped chromophores have also been prepared. The elemental investigation results show that the polyimides exhibit a higher macroscopic nonlinear optical coefficient (d_{33} = 35.0 to ~70.2 pm/V), good thermal stability (T_g 198 to ~210 °C, T_d 240 to ~245 °C), and optical transparency (λ_{max} < 400 nm).

Introduction

Organic and polymeric nonlinear optical (NLO) materials have continuously drawn great interest due to their several advantages that are superior to those of conventional inorganics, such as large nonlinear optical coefficient, ultrafast response, wide response wave band, high optical damage threshold, and easy combination and modification.[1] However, there are still two major challenging topics in designing organic/polymeric second-order nonlinear optical materials. First, for traditional chromophores with D−π−A structure, the first nonlinear hyperpolarizability β of a chromophore molecule increases with increasing length of the conjugated π system and increasing strength of the donor group (D) and/or acceptor group (A) based on the two-state model.[1d,e,2] Unfortunately, an increase in the β value is always accompanied by a bathochromic shift due to a larger π-conjugated length and/or stronger donor and acceptor ability. Therefore, there is always a trade-off between nonlinearity and transparency.[3,4] To overcome the trade-off, several kinds of methods have been developed in designing organic chromophores with both high β value and good transparency, such as employing special conjugated bridge[5] or using different types of conjugation bridge combinations,[6] optimizing the combination of different donors and acceptors.[1d,4,7] Especially in recent years, various kinds of dual (multiple)

* Corresponding authors. E-mail: lugyuan@nju.edu.cn (G-Y.L.), cyp@seu.edu.cn (Y.C.). Fax: +86-025-83317761.
[†] Nanjing University.
[‡] Southeast University.
[§] Shanghai Jiao Tong University.

(1) (a) Marder, S. R.; Kippelen, B.; Jen, A. K.-Y.; Peyghambarian, N. *Nature* **1997**, *388*, 845. (b) Kajzar, F.; Lee, K. S.; Jen, A.K.-Y. *Adv. Polym. Sci.* **2003**, *161*, 1. (c) Shi, Y.; Zhang, C.; Zhang, H.; Bechtel, J. H.; Dalton, L. R.; Robinson, B. H.; Steier, W. H. *Science* **2000**, *288*, 119. (d) You, X.-Z. *Molecular-Based Materials—Opto-Electronic Functional Compounds*; Shanghai Science Press: Shanghai, 2001; Chapter 6, p 165 (in Chinese). (e) Prasad, P.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; John Wiley and Sons: New York, 1991. (f) Service, R. F. *Science* **1995**, *267*, 1921. (g) Senge, M. O.; Fazekas, M.; Notaras, E. G. A.; Blau, W. J.; Zawadzka, M.; Locos, O. B.; Mhuircheartaigh, E. M. N. *Adv. Mater.* **2007**, *19*, 2737. (h) Marder, S. R. *Chem. Commun.* **2006**, *2*, 131. (i) Ma, H.; Liu, S.; Luo, J.-D.; Suresh, S.; Liu, L.; Kang, S. H.; Haller, M.; Sassa, T.; Dalton, L. R.; Jen, A. K.-Y. *Adv. Funct. Mater.* **2002**, *12*, 565.

(2) (a) Barzoukas, M.; Blanchard-Desce, M.; Josse, D.; Lehn, J.-M.; Zyss, J. *Chem. Phys.* **1989**, *133*, 323. (b) Verbiest, T.; Elshocht, S. V.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J. *Science* **1998**, *282*, 913.

(3) (a) Verbiest, T.; Houbrechts, S.; Kauranen, M.; Clays, K.; Persoons, A. *J. Mater. Chem.* **1997**, *7*, 2175. (b) Guo, X.; Zhang, L.; Lu, G. Y.; Zang, C. Z.; Jin, C. M.; Liu, M. H. *Supramol. Chem.* **2005**, *17*, 271.

(4) Ye, C. In *Organic Solids*; Wang, F., Zhu, D., Eds.; Shanghai Science Press: Shanghai, 1999; Chapter 5, p 188 (in Chinese).

(5) (a) Shu, C.-F.; Shu, Y.-C.; Gong, Z.-H.; Peng, S.-M.; Lee, G. H.; Jen, A. K.-Y. *Chem. Mater.* **1998**, *10*, 3284. (b) Zyss, J.; Ledoux, I.; Volkov, S.; Chernyak, V.; Mukamel, S.; Bartholomew, G. P.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 11956. (c) Carella, A.; Castaldo, A.; Centore, R.; Fort, A.; Sirigu, A.; Tuzi, A. *J. Chem. Soc., Perkin Trans. 2* **2002**, *11*, 1791. (d) Hansen, D. J. A.; Becher, J.; Jeppesen, J. O.; Levillain, E.; Nielsen, M. B.; Petersen, B. M.; Peterson, J. C.; Ahin, Y. *J. Mater. Chem.* **2004**, *14*, 179. (e) Tiemann, B. G.; Marder, S. R.; Perry, J. W.; Cheng, L.-T. *Chem. Mater.* **1990**, *2*, 690. (f) Kanis, D. R.; Ratter, M. A.; Marks, T. J.; Zerner, M. C. *Chem. Mater.* **1991**, *3*, 19. (g) Blanchard-Desce, M.; Lehn, J.-M.; Barzoukas, M.; Runser, C.; Fort, A.; Puccetti, G.; Ledoux, I.; Zyes, J. *Nonlinear Opt.* **1995**, *10*, 23. (h) Pushkara Rao, V.; Wong, K. Y.; Jen, A. K.-Y.; Drost, K. J. *Chem. Mater.* **1994**, *6*, 2210. (i) Hennrich, G.; Murillo, M. T.; Prados, P.; Song, K.; Asselberghs, I.; Clays, K.; Persoons, A.; Benet-Buchholz, J.; de Mendoza, J. *Chem. Commun.* **2005**, *21*, 2747. (j) Vocanson, F.; Seigle-Ferrand, P.; Lamartine, R.; Fort, A.; Coleman, A. W.; Shahgaldian, P.; Mugnier, J.; Zerroukhi, A. *J. Mater. Chem* **2003**, *13*, 1596.

10.1021/cm800528a CCC: $40.75
Published on Web 06/25/2008

charge-transfer chromophores have been developed, such as octupolar,[8] star-shaped,[9] Λ-shaped,[10] X-shaped,[11] Y-shaped,[12] U-shaped,[13] etc. In the previous communication,[14] we developed H-shaped second-order nonlinear optical chromophores with two nonconjugated D−π−A units (Figure 1), which exhibit much higher first molecular hyperpolarizability (β) values than the corresponding mono-D−π−A unit reference compounds without red-shift of the absorption band. In this paper, we report further investigation work in detail.

Second, for practical applications, poled polymeric second-order nonlinear optical (NLO) materials should simultaneously have large macroscopic optical nonlinearity, high thermal stability, and good optical transparency;[1b,d,h,i,4,15] therefore, several parameters should be comprehensively considered to solve the nonlinearity−transparency−thermal stability trande-off.[1d,4,15] Many strategies and approaches have been reported for the development of high-quality polymeric NLO materials.[1d,4,15,16] Usually, the effective chromophores are employed to incorporate into main-chain[17] or side-chain[18] polymers by covalent linkages. Moreover, main-chain polymers are usually slower in relaxation of orientation order than the same kind of side-chain polymers.[15,16a,17a,19] Among these, polyimide NLO materials including main chain[20] and side chain[21] have been of more interest since they generally have high physical, chemical, and thermal stabilities.[16a,20–22] Especially, the aromatic main-chain polyimides possess excellent orientation stability and thermal stability owing to their rigid backbone.[16a,20] In addition, the fluorine atoms or fluoro-containing groups are incorporated in the polyimide's structure; the optical losses could be reduced, and the solubility in organic solvent also could be improved.[16a,18m,20a,b,21f–h,22] Therefore, in this paper, we also synthesize some fluoro-containing aromatic main-chain polyimides embedded with the H-shaped chromophores

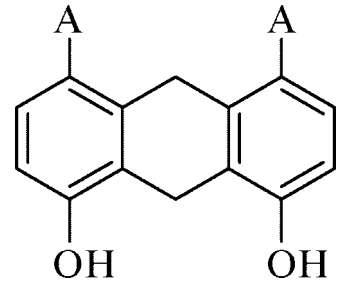


Figure 1. H-shaped chromophores with two parallel nonconjugated D−π−A units.

(6) (a) Luo, J.-D.; Hua, J.-L.; Qin, J.-G.; Cheng, J.-Q.; Shen, Y.-C.; Lu, Z.-.H.; Wang, P.; Ye, C. *Chem. Commun.* **2001**, 171. (b) Kenis, P. J. A.; Kerver, E. G.; Snellink-Ruel, B. H. M.; Van Hummel, G. J.; Harkema, S.; Flipse, M. C.; Woudenberg, R. H.; Engbersen, J. F. J.; Reinhoudt, D. N. *Eur. J. Org. Chem.* **1998**, 1089. (c) Pushkara Rao, V.; Wong, K. Y.; Jen, A. K.-Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1118. (d) Raimundo, J.-M.; Blanchard, P.; Gallego-Planas, N.; Mercier, N.; Ledoux-Rak, I.; Hierle, R.; Roncali, J. *J. Org. Chem.* **2002**, *67*, 205. (e) Abe, J.; Shirai, Y. *J. Phys. Chem. A* **1997**, *101*, 1.

(7) (a) Facchetti, A.; Abbotto, A.; Beverina, L.; Var der Boom, M. E.; Dutta, P.; Evmenenko, G.; Marks, T. J.; Pagani, G. A. *Chem. Mater.* **2002**, *14*, 4996. (b) Zhang, C. Z.; Zhu, J.; Yang, H.; Lu, C.; Lu, G.-Y.; Cui, Y. *Dyes Pigm.* **2008**, *76*, 765. (c) Bublitz, G. U.; Ortiz, R.; Runser, C.; Fort, A.; Barzoukas, M.; Marder, S. R.; Boxer, S. G. *J. Am. Chem. Soc.* **1997**, *119*, 2311.

(8) (a) Alcaraz, G.; Euzenat, L.; Mongin, O.; Katan, C.; Ledoux, I.; Zyss, J.; Blanchard-Desce, M.; Vaultier, M. *Chem. Commun.* **2003**, 2766. (b) Cho, B. R.; Lee, S. J.; Lee, S. H.; Son, K. H.; Kim, Y. H.; Doo, J.-Y.; Lee, G. J.; Kang, T. I.; Lee, Y. K.; Cho, M.; Jeon, S.-J. *Chem. Mater.* **2001**, *13*, 1438. (c) Bozec, H. L.; Bouder, T. L.; Maury, O.; Bondon, A.; Ledoux, I.; Deveau, S.; Zyss, J. *Adv. Mater.* **2001**, *13*, 1677. (d) Bourgogne, C.; Le Fur, Y.; Juen, P.; Masson, P.; Nicoud, J.-F.; Masse, R. *Chem. Mater.* **2000**, *12*, 102. (e) Coe, B. J.; Harris, J. A.; Brunschwig, B. S.; Asselberghs, I.; Clays, K.; Garin, J.; Orduna, J. *J. Am. Chem. Soc.* **2005**, *127*, 13399. (f) Sarkar, A.; Pak, J.; Rayfield, G. W.; Haley, M. M. *J. Mater. Chem.* **2001**, *11*, 2943. (g) Stadler, S.; Braeuchle, C.; Brandl, S.; Gompper, R. *Chem. Mater.* **1996**, *8*, 676. (h) Bartholomew, G. P.; Ledoux, I.; Mukamel, S.; Bazan, G. C.; Zyss, J. *J. Am. Chem. Soc.* **2002**, *124*, 13480. (i) Robello, D. R.; Martines, C. I.; Pangborn, A. B.; Shi, J.; Uranker, E. J.; Willand, C. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 124.

(9) (a) Brasselet, S.; Cherioux, F.; Audebert, P.; Zyss, J. *Chem. Mater.* **1999**, *11*, 1915. (b) Figueira-Duarte, T. M.; Clifford, J.; Amendola, V.; Gegout, A.; Olivier, J.; Cardinali, F.; Meneghetti, M.; Armaroli, N.; Nierengarten, J.-F. *Chem. Commun.* **2006**, *19*, 2054. (c) Chen, M.; Ghiggino, K. P.; Thang, S. H.; Wilson, G. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 4368. (d) Gopalan, P.; Katz, H. E.; McGee, D. J.; Erben, C.; Zielinski, T.; Bousquet, D.; Muller, D.; Grazul, J.; Olsson, Y. *J. Am. Chem. Soc.* **2004**, *126*, 1741.

(10) (a) Coe, B. J.; Harris, J. A.; Brunschwig, B. S. *J. Chem. Soc., Dalton Trans.* **2003**, *12*, 2384. (b) Christopher, R. M.; Ermer, S.; Steven, M. L.; McComb, I. H.; Leung, D. S.; Wortmann, R.; Krdmer, P.; Twieg, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 12950. (c) He, M.; Leslie, T.; Garner, S.; DeRosa, M.; Cites, J. *J. Phys. Chem. B* **2004**, *108*, 8731. (d) Yang, M.; Champagne, B. *J. Phys. Chem. A* **2003**, *107*, 3942. (e) Kuo, W. J.; Hsiue, G. H.; Jeng, R. J. *J. Mater. Chem* **2002**, *12*, 868. (f) Coe, B. J.; Harris, J. A.; Jones, L. A.; Brunschwig, B. S.; Song, K.; Clays, K.; Garin, J.; Orduna, J.; Coles, S. J.; Hursthouse, M. B. *J. Am. Chem. Soc.* **2005**, *127*, 4845.

(11) (a) Kang, H.; Evmenenko, G.; Dutta, P.; Clays, K.; Song, K.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 6194. (b) Kang, H.; Zhu, P.-W.; Yang, Y.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 15974. (c) Yang, Z.; Li, S.; Ye, C. *Synth. Met.* **2003**, *137*, 1519. (d) Kang, H.; Li, S.; Wang, P.; Wu, W.; Ye, C. *Synth. Met.* **2001**, *121*, 1469. (e) Qin, A.-J.; Bai, F.-L.; Ye, C. *THEOCHEM* **2003**, *631*, 79.

(12) (a) Lee, J.-Y.; Kim, J.-H.; Rhee, B. K. *Macromol. Res.* **2007**, *15*, 234. (b) Lee, J.-Y.; Kim, J.-H.; Jung, W.-T.; Park, Y. K. *J. Mater. Sci.* **2007**, *42*, 3936. (c) Ren, J.; Wang, S.-M.; Wu, L.-F.; Xu, Z.-X.; Dong, B.-H. *Dyes Pigm.* **2008**, *76*, 310. (d) Carella, A.; Borbone, F.; Caruso, U.; Centore, R.; Roviello, A.; Barsella, A.; Quatela, A. *Macromol. Chem. Phys.* **2007**, *208*, 1900. (e) De Boni, L.; Silva, D. L.; Neves, U. M.; Feng, K.; Meador, M.; Bu, X. R.; Misoguti, L.; Mendonca, C. R. *Chem. Phys. Lett.* **2005**, *402*, 474. (f) Chou, S.-S. P.; Yu, C.-Y. *Synth. Met.* **2004**, *142*, 259.

(13) Weiss, E. A.; Sinks, L. E.; Lukas, A. S.; Chernick, E. T.; Ratner, M. A.; Wasielewski, M. R. *J. Phys. Chem. B* **2004**, *108*, 10309.

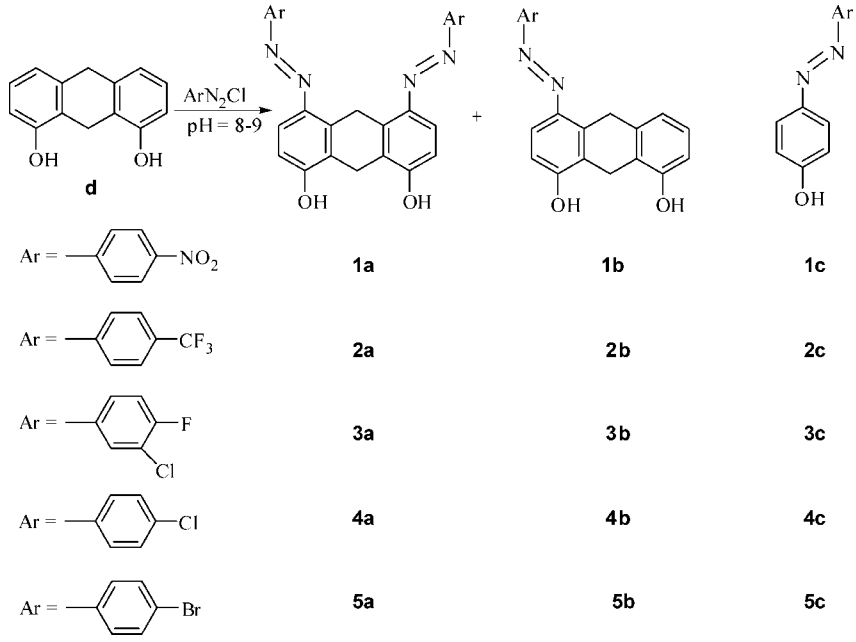
(14) Zhang, C.-Z.; Lu, C.; Zhu, J.; Lu, G.-Y.; Wang, X.; Shi, Z.-W.; Liu, F.; Cui, Y. *Chem. Mater.* **2006**, *18*, 6091.

(15) (a) Dalton, L. *Adv. Polym. Sci.* **2002**, *158*, 1. (b) Dalton, L. R. *Opt. Eng.* **2000**, *39*, 589.

(16) (a) Chang, C. C.; Chen, C. P.; Chou, C. C.; Kuo, W. J.; Jeng, R. J. *J. Macromol. Sci., Polym. Rev.* **2005**, *45*, 125. (b) Luo, J.; Haller, M.; Li, H.; Tang, H.; Jen, A.K.-Y.; Jakka, K.; Chou, C.; Shu, C. *Macromolecules* **2004**, *37*, 248. (c) Willand, C. S.; Williams, D. J. *Ber. Bunsen.-Ges.* **1987**, *91*, 1304. (d) Katz, H. E.; Schilling, M. L.; Fang, T.; Holland, W. R.; King, L.; Gordon, H. *Macromolecules* **1991**, *24*, 1201. (e) Schilling, M. L.; Katz, H. E. *Chem. Mater.* **1989**, *1*, 668. (f) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31.

(17) (a) Li, S.-J.; Ellaya, M.; Dao, L. H. *Mater. Lett.* **2006**, *60*, 1116. (b) Kanai, S.; Totani, K.; Kawazu, Y.; Watanabe, T.; Ogawa, T. *Nonlinear Opt., Quantum Opt.* **2005**, *34*, 107. (c) Huang, D.-Y.; Zhang, C.; Dalton, L. R.; Weber, W. P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 546. (d) Lindsay, G. A.; Roberts, M. J.; Chafin, A. P.; Hollins, R. A.; Merwin, L. H.; Stenger-Smith, J. D.; Yee, R. Y.; Zarras, P.; Wynne, K. J. *Chem. Mater.* **1999**, *11*, 924. (e) Li, Z.; Dong, S.-C.; Yu, G.; Li, Z.; Liu, Y.-Q.; Ye, C.; Qin, J.-G. *Polymer* **2007**, *48*, 5520. (f) Smitha, P.; Asha, S. K.; Pillai, C. K. S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4455. (g) Tsai, H.-C.; Kuo, W.-J.; Hsiue, G.-H. *Macromol. Rapid Commun.* **2005**, *26*, 986. (h) Kimura-Suda, H.; Zhang, Y.-D.; Sassa, T.; Wada, T.; Sasabe, H. *Adv. Mater.* **2000**, *12*, 1196. (i) Luo, J.-D.; Qin, J.-G.; Kang, H.; Ye, C. *Polym. Int.* **2000**, *49*, 1302. (j) Weder, C.; Glomm, B. H.; Neuenschwander, P.; Suter, U. W.; Pretre, P.; Kaatz, P.; Gunter, P. *Adv. Nonlinear Opt.* **1997**, *4*, 63. (k) Heldmann, C.; Warner, M. *Macromolecules* **1998**, *31*, 3519. (l) Qin, A. J.; Yang, Z.; Bai, F. L.; Ye, C. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2846.

Scheme 1. Synthesis of H-Shaped Chromophores and Corresponding Reference Compounds

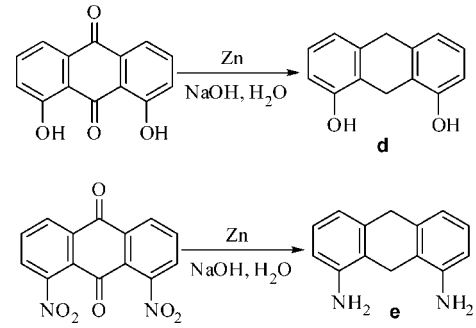


and report the studies on the thermal properties, optical transparency, as well as macroscopic optical nonlinear properties.

Results and Discussion

Synthesis of H-Shaped Chromophores and Fluoro-Containing Polyimides. The H-shaped chromophores were prepared by a diazo-coupling reaction of the 1,8-dihydroxy-9,10-dihydroanthracene (**d**) with a substituted aromatic diazonium salt solutions (Scheme 1). The key intermediate 1,8-dihydroxy-9,10-dihydroanthracene (**d**) was obtained by the reduction of 1,8-dihydroxyl-9,10-anthraquinone with zinc powder in an aqueous solution of sodium hydroxide (Scheme 2). The disubstituted (**1a**, **2a**, **3a**, **4a**, **5a**) and monosubstituted (**1b**, **2b**, **3b**, **4b**, **5b**) products were separated on a silica gel column chromatography. All these crude products were further purified, respectively, by a recrystallization. The weights of these pure compounds (**1a**, **3a**, **4a**, **5a**, **1b**, **3b**, **4b**, and **5b**) are about 0.8 times as much as the weight of corresponding crude compounds. However, weights of pure compounds **2a** and **2b** are, respectively, about 0.6 times as much as the weight of corresponding crude compounds because of more loss in the recrystallization. Because the molar ratios of 2:1 of aromatic diazonium salts to 1,8-dihydroxy-9,10-dihydroanthracene were used in the coupling reactions, the yields of the disubstituted compounds were higher than those of monosubstituted compounds except for **1a** and **1b**. The lower yield of **1a** than **1b** should be ascribed to the larger steric effect of the *p*-nitrophenylazo group, which block the monosubstituted compound continuously reacting with the aromatic diazonium salt. The corresponding mono-D−π−A unit reference compounds (**1c**, **2c**, **3c**, **4c**, **5c**) were also synthesized by the same reaction from phenol

Scheme 2. Synthesis of 1,8-Dihydroxy-9,10-dihydroanthracene and 1,8-Diamino-9,10-dihydroanthracene

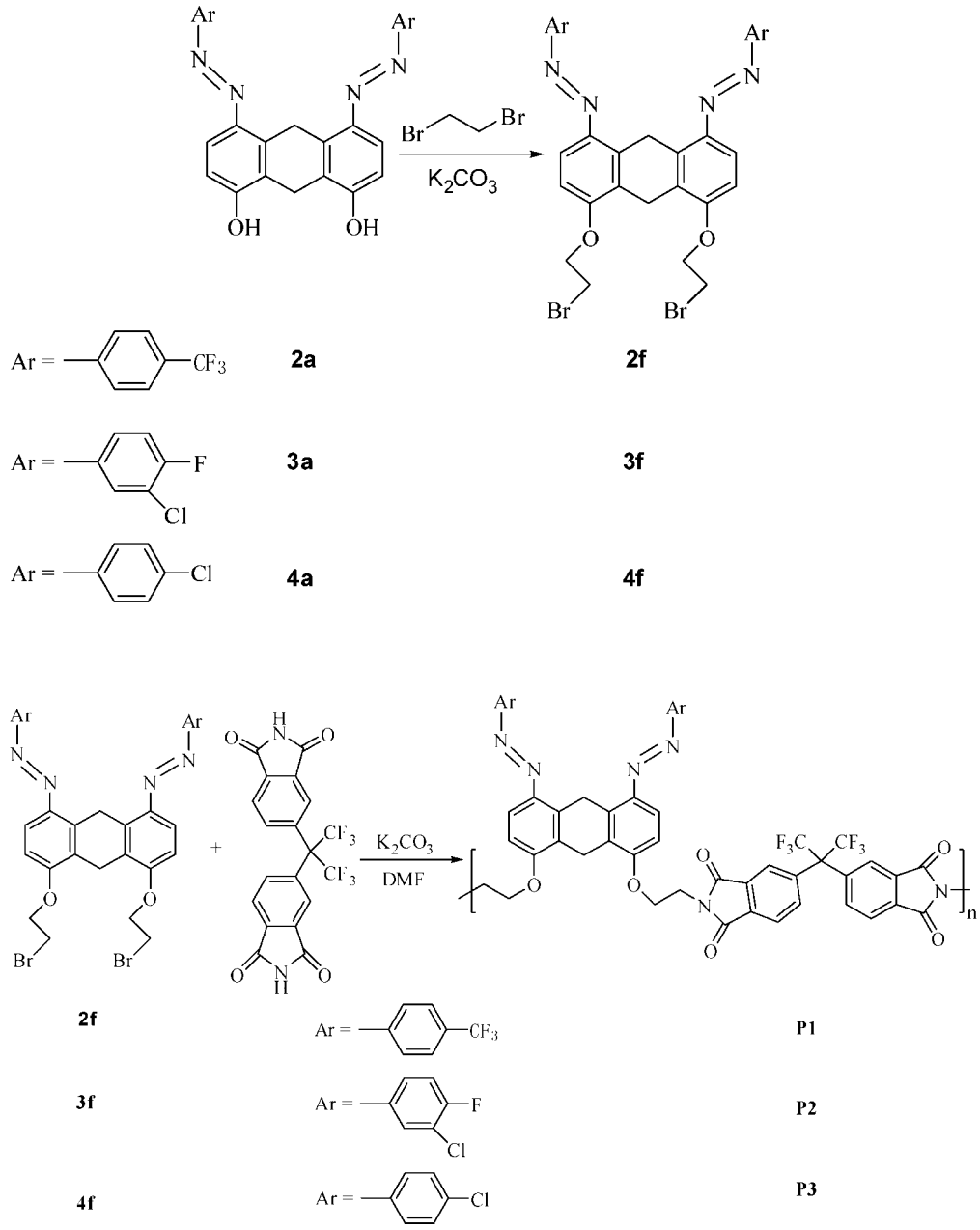


(18) (a) Luo, J.-D.; Haller, M.; Ma, H.; Liu, S.; Kim, T.-D.; Tian, Y.-Q.; Chen, B.-Q.; Jang, S.-H.; Dalton, L. R.; Jen, A. K.-Y. *J. Phys. Chem. B* **2004**, *108*, 8523. (b) Luo, J.-D.; Liu, S.; Haller, M.; Liu, L.; Ma, H.; Jen, A. K.-Y. *Adv. Mater.* **2002**, *14*, 1763. (c) Taylor, D. K.; Samulski, E. T. *Macromolecules* **2000**, *33*, 2355. (d) Jen, A. K.-Y.; Wu, X.-M.; Ma, H. *Chem. Mater.* **1998**, *10*, 471. (e) Zeng, Q.; Li, Z. A.; Li, Z.; Ye, C.; Qin, J.; Tang, B. Z. *Macromolecules* **2007**, *40*, 5634. (f) Nemoto, N.; Miyata, F.; Nagase, Y.; Abe, J.; Hasegawa, M.; Shirai, Y. *Chem. Mater.* **1996**, *8*, 1527. (g) Chittibabu, K. G.; Li, L.; Kamath, M.; Kumar, J.; Tripathy, S. K. *Chem. Mater.* **1994**, *6*, 475. (h) Li, Z. A.; Dong, S.; Yu, G.; Li, Z.; Liu, Y.; Ye, C.; Qin, J. G. *Polymer* **2007**, *48*, 5520. (i) Bai, Y.; Song, N.; Gao, J. P.; Sun, X.; Wang, X.; Yu, G.; Wang, Z. Y. *J. Am. Chem. Soc.* **2005**, *127*, 2060. (j) Liao, Y.; Bhattacharjee, S.; Firestone, K. A.; Eichinger, B. E.; Paranji, R.; Anderson, C. A.; Robinson, B. H.; Reid, P. J.; Dalton, L. R. *J. Am. Chem. Soc.* **2006**, *128*, 6847. (k) Song, N.; Men, L.; Gao, J. P.; Bai, Y.; Beaudin, A. M. R.; Yu, G.; Wang, Z. Y. *Chem. Mater.* **2004**, *16*, 3708. (l) Li, Z. A.; Li, Z.; Di, C. A.; Zhu, Z. C.; Li, Q. Q.; Zeng, Q.; Zheng, K.; Liu, Y. Q.; Ye, C.; Qin, J. G. *Macromolecules* **2006**, *39*, 6951. (m) Ma, H.; Wu, J.; Herguth, P.; Chen, B.; Jen, A. K.-Y. *Chem. Mater.* **2000**, *12*, 1187.

(19) (a) Burland, D. M.; Miller, R. D.; Walsh, C. *Chem. Rev.* **1994**, *94*, 31. (b) Yesodha, K. S.; Pillai, C. K. S.; Tsutstumi, N. *Prog. Polym. Sci.* **2004**, *29*, 45.

(20) (a) Verbiest, T.; Burland, D. M.; Jurich, M. C.; Lee, V. Y.; Miller, R. D.; Volksen, W. *Science* **1995**, *268*, 1604. (b) Miller, R. D.; Burland, D. M.; Jurich, M. C.; Lee, V. Y.; Moylan, C. R.; Thackara, J. I.; Tweig, R. J.; Verbiest, T.; Volksen, W. *Macromolecules* **1995**, *28*, 4970. (c) Li, S.-J.; Yang, Z.; Wang, P.; Kang, H.; Wu, W.; Ye, C.; Yang, M.-J.; Yang, X.-Z. *Macromolecules* **2002**, *35*, 4314. (d) Le Bouder, T.; Maury, O.; Le Bozec, H.; Ledoux, I.; Zyss, J. *Chem. Commun.* **2001**, 2430. (e) Leng, W.-N.; Zhou, Y.-M.; Xu, Q.-H.; Liu, J.-Z. *Polymer* **2001**, *42*, 9253. (f) Kuo, W.-J.; Hsiue, G.-H.; Jeng, R.-J. *J. Mater. Chem.* **2002**, *12*, 868. (g) Qin, A.-J.; Yang, Z.; Bai, F.-L.; Ye, C. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2846. (h) Gubbelmans, E.; Verbiest, T.; Beylen, M. V.; Persoons, A.; Samyn, C. *Polymer* **2002**, *43*, 1581. (i) Lee, J.-Y.; Baek, C. S.; Park, E.-J. *Eur. Polym. J.* **2005**, *41*, 2107. (j) Yu, D.; Gharavi, A.; Yu, L. P. *Macromolecules* **1996**, *29*, 6139. (k) Yu, D.; Yu, L.-P. *Macromolecules* **1994**, *27*, 6718.

Scheme 3. Synthesis of Fluoro-Containing Aromatic Main-Chain Polyimides Embedded with H-Shaped Chromophores



and substituted aromatic amines (Scheme 1). All NLO chromophores were obtained as yellow or red powders. The analytical data of the chromophores (^{1}H NMR, ^{13}C NMR, IR, MS) are in accord with the assigned structures, respectively. For example, in the ^{1}H NMR and ^{13}C NMR spectra of the compound **3a**, the chemical shift values of 5.07, 3.99 ppm (two single peaks) and 25.1, 22.4 ppm are signals of proton and carbon of two methylene groups of $ArCH_2Ar$, respectively. Therefore it is clear that two D−π−A units are bridged by two methylene groups.

The H-shaped chromophores **2a**, **3a**, and **4a** were etherificated with excessive 1,2-dibromoethane to give chromophores **2f**, **3f**, and **4f** with two bromoethyl groups. The main-chain fluoro-containing polyimides (Scheme 3) were synthesized by a condensation[23] of dibromides **2f**, **3f**, and **4f** with 4,4′-(hexafluoroisopropylidene)diphthalic bisimide[24] in an alkaline DMF solution in an yield of 82% to ∼87%.

First Molecular Hyperpolarizabilities of H-Shaped Chromophores. Determination of β of the chromophores was performed using hyper-Rayleigh scattering (HRS) method. The HRS experimental setup was similar to that in the literature.[25] An external reference method (EFM) was utilized in these HRS experiments by choosing *p*-nitroaniline (*p*-NA) as standard.[26] A popular two-level model could be used to estimate their static first hyperpolarizabilities (β_0) which reflect the intrinsic polarizations of the molecules at zero frequency. The two-level model could be expressed as eq 1.[26]

$$\beta(\omega) = \frac{\lambda^4}{[(\lambda^2 - \lambda_{gn}{}^2)(\lambda^2 - 4\lambda_{gn}{}^2)]}\beta_0 \qquad (1)$$

where λ_{gn} was the wavelength corresponding to the transition between the ground and the first excited state, which could be estimated as the peak wavelength λ_{max} in the UV−vis absorption spectra; λ was the wavelength of incident light.

Table 1. Values of First Hyperpolarizabilities (β) and Static First Hyperpolarizabilities (β_0)

compd no.	$\beta/10^{-30}$ esu (THF)[a]	$\beta_0/10^{-30}$ esu (THF)[b]	β enhancement per D−π−A unit[c]
1a	277	105	2.0
1b	208	77	3.0
1c	70	28	
2a	252	117	1.2
2b	207	92	1.9
2c	108	52	
3a	185	86	1.3
3b	115	52	1.6
3c	72	35	
4a	142	66	1.4
4b	127	58	2.5
4c	50	24	
5a	211	97	1.3
5b	162	72	1.9
5c	84	42	
d	85	40	110
phenol	0.39	0.27	
e	118	77	116
aniline	0.51	0.33	

[a] Data of hyperpolarizabilities (β) were determined with concentration 10^{-4} to 10^{-3} mol L^{-1} of compounds at a wavelength of 1064 nm in tetrahydrofuran medium by hyper-Rayleigh scatter (HRS). [b] Static first hyperpolarizabilities(β_0). [c] The value of first hyperpolarizabilities (β) enhancement of each D−π−A unit were calculated according to following methods. For bisubstituted compounds **1a**, **2a**, **3a**, **4a**, **5**, β of bisubstituted compound/($2 \times \beta$ of the corresponding monomer **1c**, **2c**, **3c**, **4c**, **5c**); for monosubstituted compounds **1b**, **2b**, **3b**, **4b**, **5b**, (β of monosubstituted compound $-$ β of phenol)/β of the corresponding monomer **1c**, **2c**, **3c**, **4c**, **5c**; for 1,8-dihydroxy-9,10-dihydroanthracene **d** and 1,8-diamino-9,10-dihydroanthracene **e**, β of **d**/($2 \times \beta$ of phenol), β of **e**/($2 \times \beta$ of aniline).

β_0 was related to the oscillator strength, transition energy, and the difference of the transition dipole moments between the ground and the first excited state. β and β_0 values of the samples are shown in Table 1.

Figure 2 shows profiles of HRS intensity versus molar concentration of **2a** and **2c**. Because the HRS signals have a good linear relationship with the concentrations of the solute, any concentration-dependent effect, such as aggregation and hydrogen bonds, could be ignored. An effect on local fields from solvent could also be ignored, because the D−π−A units of the H-shaped chromophores are similar, and the refractive index change of the solutions of the H-shaped chromophores is neglectable. All profiles of HRS intensity versus molar concentration of chromophores are shown in the Supporting Information.

In order to demonstrate the creditability of the β, HRS spectra around 532 nm (529 to ~535 nm) for the five H-shaped chromophores with two D−π−A units were measured using a fluorescence spectrometer (Edinburgh, FLS920),[27a] which are shown in Figure 3. The HRS spectra demonstrate a sharp peak with bandwidth of 0.3 at 531.8 nm and no other signals nearby. Since there is no background signal from 529 to 535 nm, HRS measurements using a 532 nm interference filter with bandwidth of 3 nm should come to the same results as the spectra measurement above. Moreover, the fundamental limits for β_{0max} (Table 2) were also calculated according to literatures.[27b,c] These data show that experimental β_0 are quite smaller than the fundamental limit. Therefore, these experimental β are convincible.

It is seen from Table 1, the data from the HRS indicate that β of the bisubstituted compounds (H-shaped chromophores, **1a**, **2a**, **3a**, **4a**, and **5a**) are 2.4−4.0 times that of the corresponding monomer compounds (**1c**, **2c**, **3c**, **4c**, and **5c**), i.e., the enhancements of per D−π−A unit from 1.2 to 2.0 are observed. In addition, β values of monosubstituted chromophores (**1b**, **2b**, **3b**, **4b**, and **5b**) are also remarkably increased. In fact, the phenol is also a dipole molecule; its dipole moment is 1.54 D.[28] Thus, the phenol is also a simple D−π−A unit and the direction of the dipole moment is consistent with the azo D−π−A unit in the monosubstituted chromophores (**1b**, **2b**, **3b**, **4b**, and **5b**). Thus, the monosubstituted chromophores are also considered as a H-shaped chromophores. The β of phenol is 0.39×10^{-30} esu based on our HRS experiments (Table 1) under the same condition, which is very close to datum (about 0.25×10^{-30} esu) reported by literatures.[29] Thus, the β values of the monosubstituted chromophores (**1b**, **2b**, **3b**, **4b**, and **5b**) are much higher than the sum of that of the corresponding monomer compounds (**1c**, **2c**, **3c**, **4c**, and **5c**) and the phenol. The enhancements of azo D−π−A unit can be calculated according to the following method: β value of the monosubstituted compounds (**1b**, **2b**, **3b**, **4b**, **5b**) $-$ β value of phenol/β value of the corresponding monomer (**1c**, **2c**, **3c**, **4c**, **5c**). The calculated results indicate that the enhancements of azo D−π−A unit in the monosubstituted compounds (**1b**, **2b**, **3b**, **4b**, **5b**) are 1.6 to ~3.0. Therefore, the H-shaped chromophores with the combined two nonconjugated D−π−A units can result in a remarkable increase of β.

In order to further demonstrate the H-shaped chromophores strategy, 1,8-diamino-9,10-dihydroanthracene (**e**) was also prepared from 1,8-dinitro-9,10-anthraquinone by the reduction with zinc powder in an aqueous solution of sodium

(21) (a) Luo, J.-D.; Haller, M.; Li, H.-X.; Tang, H.-Z.; Jen, A. K.-Y.; Jakka, K.; Chou, C.-H.; Shu, C.-F. *Macromolecules* **2004**, *37*, 248. (b) Yoon, C.-B.; Shim, H.-K. *J. Mater. Chem.* **1999**, *9*, 2339. (c) Kim, E.-H.; Moon, I. K.; Kim, H. K.; Lee, M.-H.; Han, S.-G.; Yi, M. H.; Choi, K.-Y. *Polymer* **1999**, *40*, 6157. (d) Chang, H.-L.; Lin, H.-L.; Wang, Y.-C.; Dai, S. A.; Su, W.-C.; Jeng, R.-J. *Polymer* **2007**, *48*, 2046. (e) Lee, J.-Y.; Bang, H.-B.; Baek, C. S.; Park, E.-J.; Rhee, B. K.; Lee, S. M. *Bull. Korean Chem. Soc.* **2004**, *25*, 605. (f) Lu, J.-X.; Yin, J.; Deng, X.-X.; Shen, Q.-S.; Cao, Z.-Q. *Opt. Mater.* **2004**, *25*, 17. (g) Samyn, C. A.; Van den Broeck, K.; Gubbelmans, E.; Ballet, W.; Verbiest, T.; Persoons, A. *Opt. Mater.* **2003**, *21*, 67. (h) Zhou, Y.-M.; Leng, W.-N.; Liu, X.-J.; Xu, Q.-H.; Feng, J.-K.; Liu, J.-Z. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2478. (i) Jeon, B.-J.; Cha, S. W.; Jeong, M.-Y.; Lim, T. K.; Jin, J.-I. *J. Mater. Chem.* **2002**, *12*, 546. (j) Leng, W.-N.; Zhou, Y.-M.; Xu, Q.-H.; Liu, J.-Z. *Macromolecules* **2001**, *34*, 4774. (k) Chen, T.-A.; Jen, A. K.-Y.; Cai, Y.-M. *J. Am. Chem. Soc.* **1995**, *117*, 7295.
(22) Ding, M. X. *Polyimides: Chemistry, Relationship between Structure and Properties and Materials*; Science Press: Beijing, 2006; p 9 (in Chinese).
(23) Ellwood, M.; Griffiths, J.; Gregory, P. *Chem. Commun.* **1980**, 181.
(24) Sangaiah, R.; Gold, A. *J. Org. Chem.* **1987**, *52*, 3205.
(25) (a) Clays, K.; Persoons, A. *Phys. Rev. Lett.* **1991**, *66*, 2980. (b) Kuzyk, M. G. *IEEE J. Sel. Top. Quantum Electron.* **2001**, *7*, 774. (c) Kuzyk, M. G. *Opt. Lett.* **2000**, *25*, 1183. (d) Chen, Q.; Kuang, L.; Wang, Z. Y.; Sargent, E. H. *Nano Lett.* **2004**, *4*, 1673.
(26) (a) David, R. K.; Mark, A. R.; Tobin, J. M. *Chem. Rev.* **1994**, *94*, 195. (b) Stähelin, M.; Burland, D. M.; Rice, J. E. *Chem. Phys. Lett.* **1992**, *191*, 245. (c) Yang, G.; Su, Z.; Qin, C. *J. Phys. Chem. A* **2006**, *110*, 4817.
(27) (a) Hendrickx, E.; Vinckier, A.; Clays, K.; Persoons, A. *J. Phys. Chem.* **1996**, *100*, 19672. (b) Kuzyk, M. G. *IEEE J. Sel. Top. Quantum Electron.* **2001**, *7*, 774. (c) Kuzyk, M. G. *Opt. Lett.* **2000**, *25*, 1183.
(28) March, J. *Advanced Organic Chemistry*; Kingsport Press: New York, 1977; p 20.
(29) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690.

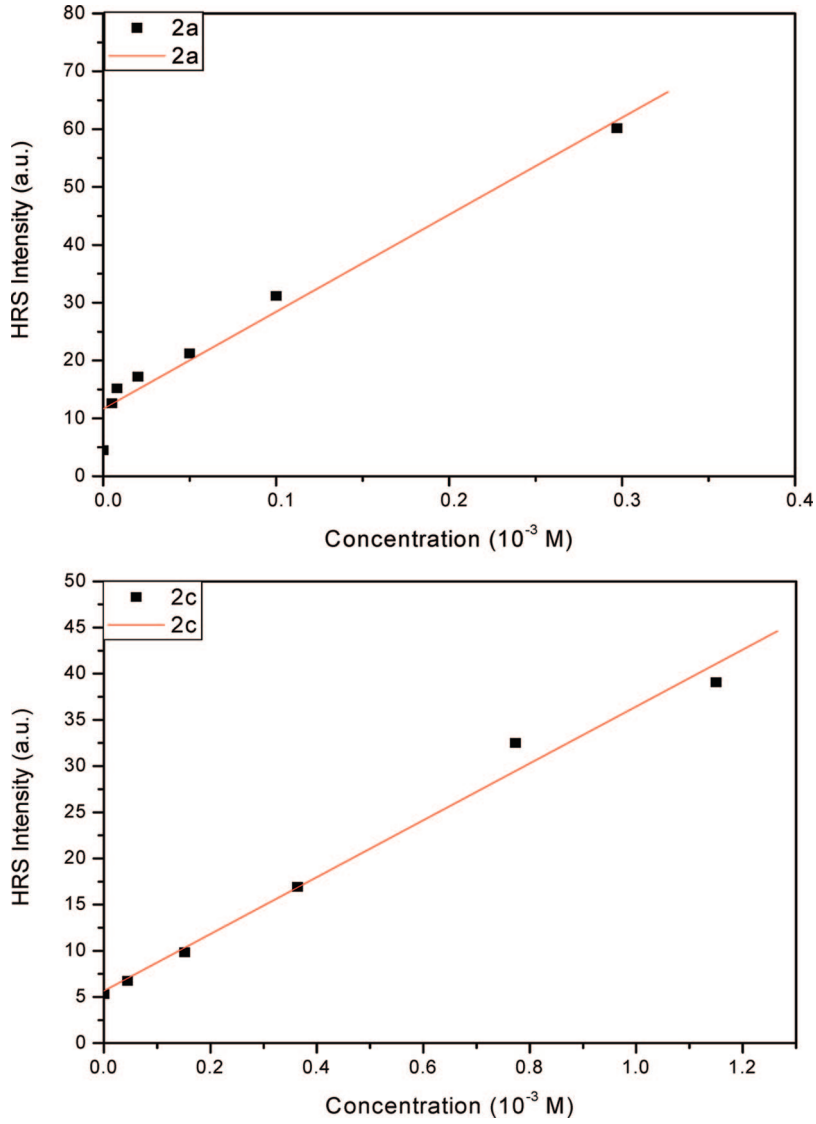


Figure 2. Hyper-Rayleigh scattering (HRS) intensity vs molar concentration of **2a** and **2c**. The solid line is a linear fitting of the experimental data.

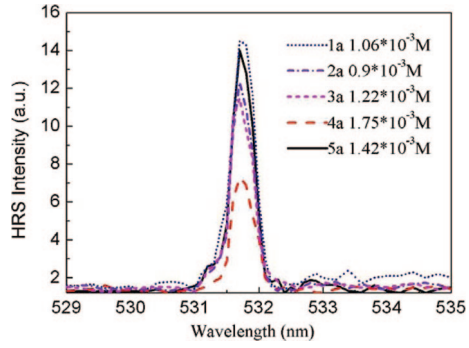


Figure 3. Hyper-Rayleigh scattering (HRS) spectra of chromophores (**1a**−**5a**).

Table 2. Fundamental Limits β_{0max} of Chromophores 1a−5a and 1c−5c

chromophore	λ_{max} (nm) in THF	β_{0max} (10^{-30} esu)	β_0 (10^{-30} esu)	β_0/β_{0max}
1a	398	3267.6	105	0.032
1c	388	1056.8	28	0.026
2a	367	2460.2	117	0.048
2c	357	797.4	52	0.065
3a	365	2413.6	86	0.036
3c	355	774.3	35	0.045
4a	366	2436.8	66	0.027
4c	355	774.3	24	0.031
5a	365	2436.8	97	0.040
5c	357	813.1	42	0.052

hydroxide (Scheme 2). The 1,8-dihydroxy-9,10-dihydroanthracene (**d**) and 1,8-diamino-9,10-dihydroanthracene (**e**) is a dimer of two parallel phenols or anilines connected via two methylene bridges. Therefore, the compounds **d** and **e** are also H-shaped chromophores with two nonconjugated D−π−A units. The β of aniline is 0.51×10^{-30} esu in our HRS experiment (Table 1), which is close to datum (about 1.1×10^{-30} esu) reported by literatures.[29] The β of 1,8-dihydroxy-9,10-dihydroanthracene, 1,8-diamino-9,10-dihydroanthracene, and the corresponding monomer compounds phenol and aniline were determined using the HRS method. It is surprising that the β value of 1,8-dihydroxy-9,10-dihydroanthracene (85×10^{-30} esu), 1,8-diamino-9,10-dihydroanthracene (118×10^{-30} esu) is much higher than a double-β value of phenol and aniline, respectively (Table 1). The enhancements of per D−π−A unit are as high as about 110 (Table 1). Therefore, we can draw a conclusion that the present design with the combined nonconjugated D−π−A units is an effective strategy for increasing β.

Table 3. Crystal Data and Summary of Structure Refinement for 3a

CCDC deposit no.	CCDC 285027
empirical formula	$C_{32}H_{28}Cl_2F_2N_4O_4$
formula weight	641.48
temp	273(2) K
wavelength	0.71073 Å
crystal system, space group	monoclinic, *P*2(1)/*c*
unit cell dimensions	$a = 4.7937(17)$ Å $\alpha = 90°$
	$b = 42.242(14)$ Å $\beta = 107.400(3)$
	$c = 16.031(5)$ Å $\gamma = 90°$
vol	3097.5(18) Å^3
Z, calcd density	4, 1376 kg/m^3
absorption coefficient	0.265 mm^{-1}
F(000)	1328
crystal size	0.30 × 0.28 × 0.14 mm^3
θ range for data collection	1.93−26.00°
limiting indices	$-5 \le h \le 4$, $-52 \le k \le 35$, $-19 \le l \le 1$
reflections collected/unique	16579/6049 [*R*(int) = 0.0419]
completeness to $\theta = 26.00$	99.7%
absorption correction	multisacn
max and min transmission	0.96 and 0.92
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	6049/0/401
goodness-of-fit on F^2	1.056
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0605, wR2 = 0.1203
R indices (all data)	R1 = 0.1019, wR2 = 0.1294
largest diff. peak and hole	0.154 and −0.214 e Å^{-3}

Structures of H-Shaped Chromophores and Their First Molecular Hyperpolarizability. In order to explore the origin of the pronounced increase of the nonlinear second-order optical response of the H-shaped chromophores with two nonconjugated D−π−A units, the crystal structure of **3a** was determined by a Bruker CCD X-ray diffraction instrument.[30] The crystallographic data and selected interatomic distances as well as angles are summarized in Tables 3 and 4, respectively. The ORTEP view of compound **3a** is given in Figure 4. It is found that the two nonconjugated D−π−A units in a single molecule are nearly arranged in the same direction due to the fixing action of the two methylene bridges. The crystal structure data also indicate that all atoms in each D−π−A unit exist almost in a same plane and the planes of the two nonconjugated D−π−A systems in a single molecule make an angle of 10.1° on average.

In addition, the structure geometries of all chromophore compounds were studied by optimizing with the density functional theory (DFT) calculations using Gaussian03 software[31] at the B3LYP/6-31G(d) level.[31,32] Dihedral angles obtained from the geometries indicate that each π-conjugated unit in bisubstituted compounds (**1a/2a/3a/4a/5a**) is almost in a plane and the planes of the two D−π−A units in a single molecule make an angle of 8.4−13.8°. And each π-conjugated units in monosubstituted compounds (**1b/2b/3b/4b/5b**) or monomers (**1c/2c/3c/4c/5c**) is in a plane. The computational results of dihedral angles are well-tallied with that from crystallographic data of **3a**. For example, the computational results of the dihedral angle between the C(1)−C(2)−C(3)−C(4)−C(13)−(14) plane and C(14)−N(1)−N(2)−C(15) plane is 6.1°, and the dihedral angle between the C(15)−C(16)−C(17)−C(18)−C(19)−C(20) plane and C(14)−N(1)−N(2)−C(15) plane is 6.6° in **3a**. Similarly, the computational results of the shortest distance (*R*) (Figure 5) between two π-conjugated units in a molecule are well-tallied with that from crystallographic data of **3a**. For example, the computational results of $R_{C(4)-C(6)}$ in **3a** is 2.540 Å, which is close to the *R* (2.531 Å) from crystallographic data of **3a**. *R* values of some H-typed chromophores with two nonconjugated D−π−A units based on output files of Gaussian 03 after the optimization of the structures of these compounds are shown in Table 5.

Because the H-typed chromophores have two nonconjugated D−π−A units, whereas the reference monomers have only one. The two parallel chains in the H-typed chromophore compounds induce higher hyperpolarizabilities (β) and larger dipolar moment (μ) than the monomer compounds since both β and μ possess an additive property. However, in present works, the β values of H-typed chromophores are higher than that of the sum of the two independent D−π−A units. Di Bella and co-workers[33] reported a theoretical analysis of the NLO response for a hypothetical *p*-NA (*p*-nitroaniline) dimer based on a two-level model. According to their estimation, the NLO response would have a sharp increase, when two D−π−A units of a hypothetical *p*-NA dimer are arranged at the same direction and the distance between them is shorter than 3.0 Å. In the present case, the two D−π−A units in a single molecule are nearly arranged at the same direction and the limited distance (*R*) in the 9,10-dihydroanthracene moiety is 2.531 Å (C4−C6) from the crystal structure data of **3a** or shorter than 3.0 Å from calculations of other H-typed chromophore compounds. Therefore, it implies that these novel H-typed chromophores can exhibit large second-order NLO responses because the close contact between two π-conjugated units in a molecule induces the strong dipole−dipole interaction between two D−π−A units.

It is notable that the β enhancements of per azo D−π−A unit in the monosubstituted chromophores (**1b**, **2b**, **3b**, **4b**, and **5b**) are higher than that of bisubstituted chromophores (**1a**, **2a**, **3a**, **4a**, and **5a**). In fact, the two aromatic rings (Ar−N=N−Ar) of a π-conjugated unit in the bisubstituted chromophores are not in the same plane completely, and π-conjugated electrons could not conjugate well in the whole π-conjugated unit, which is testified from both the structures obtained from output files of Gaussian 03 and the single-crystal structure of **3a**. For example, the angles formed by two aromatic rings (Ar−N=N−Ar) in the same azo D−π−A units of **1a**, **3a**, and **4a** are 13.8°, 10.2°, and 8.5° due to steric effects, whereas for **1b**, **3b**, and **4b**, the angles are 9.1°, 0.5°, and 0.3°. Therefore, a reason of the lower β

Table 4. Selected Interatomic Distances (angstroms) and Angles (deg)

interatomic distance				bondangle			
C4−C5	1.521(3)	C5−C6	1.508(3)	C4−C5−C6	113.3(2)	C11−C12−C12	115.7(2)
C11−C12	1.533(3)	C12−C13	1.512(3)	N2−N1−C14	115.7(2)	N1−N2−C15	114.6(2)
N1−N2	1.248(3)	N3−N4	1.241(3)	N4−N3−C10	114.3(2)	N3−N4−C21	114.4(2)
C4−C6	2.531(3)	C11−C13	2.578(3)				

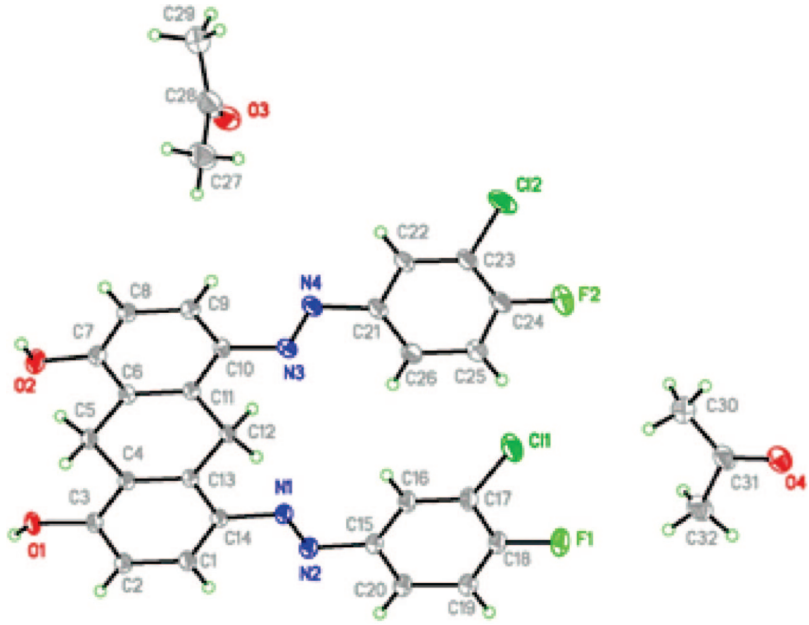


Figure 4. ORTEP drawing of **3a** with 50% probability ellipsoids.

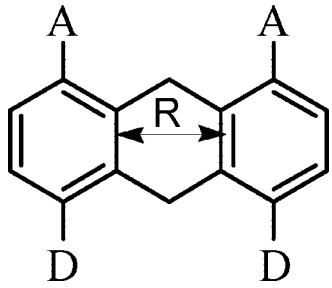


Figure 5. Shortest distances (*R*) between two π-conjugated units of a chromophore molecule with two nonconjugated D−π−A constructions.

Table 5. Shortest Distances (*R*) between Two π-Conjugated Units in Chromophore Compounds

compd no.	**1a**	**1b**	**3a**	**3b**	**4a**	**4b**	**d**	**e**
R (Å)	2.544	2.526	2.540	2.534	2.542	2.516	2.435	2.435

enhancements per azo D−π−A unit in the bisubstituted chromophores compared with monosubstituted chromophores could be the slight noncoplanarity of the π-conjugated unit in the bisubstituted chromophores due to steric effects. On the other hand, the configuration of the two azo groups is trans form at an opposite direction so as that the distances between two substituted phenyl groups or two azo groups of the bisubstituted chromophores (**1a**, **2a**, **3a**, **4a**, and **5a**) are larger than 4.5 Å. For example, in the crystallographic data of **3a** (Figure 4), the distances between nitrogen atoms (N1−N3, N2−N4) of two azo groups are 4.979 and 7.195 Å, respectively. The angle formed by two phenyl rings (C15−C16−C17−C18−C19−C20 and C21−C22−C23−C24−C25−C26) is 8.5°, and the shortest distance between them is 4.783 (C16−C26) and 4.947 Å (C17−C25), which is much larger than 3.0 Å. It means that two azo phenyl moieties in a bisubstituted chromophores are not in close contact. This could be another a reason of the lower β enhancements per azo D−π−A unit in the bisubstituted chromophores compared with monosubstituted chromophores. Indeed, the amazing increase (the enhancements per D−π−A unit are as high as about 110) of the β value of 1,8-dihydroxy-9,10-dihydroanthracene (**d**) or 1,8-diamino-9,10-dihydroanthracene (**e**) compared with a double-β value of phenol or aniline, respectively (Table 1), could be ascribed to the close contact between two π-conjugated units in a molecule.

Maximal UV−Vis Absorption Wavelength (λ_{max}) of the Chromophores. UV−vis absorption spectra of all chromophores in THF, methanol, and ethyl acetate were determined by using a Lambda 25 Perkin-Elmer spectrophotometer, and the maximal absorption wavelength (λ_{max}) data are summarized in Table 6. Figure 6 shows UV−vis spectra of H-typed chromophores **3a**, **3b**, and **3c** in THF. It is can clearly be seen that the H-typed chromophores including the bisubstituted (**1a**, **2a**, **3a**, **4a**, and **5a**) and monosubstituted (**1b**, **2b**, **3b**, **4b**, and **5b**) compounds produce only a little red-shift (8 to ∼18 nm, in THF) in

(30) CCDC 285027 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc-.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, U.K. Fax: +44(0)1223-336033. E-mail: deposit@ccdc.cam.ac.uk).
(31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.
(32) Karna, S. P.; Dupuis, M. J. *J. Comput. Chem.* **1991**, *12*, 487.
(33) (a) Di Bella, S.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 5842. (b) Di Bella, S.; Fragala, I. L.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 682.

Table 6. λ_{max} of the Chromophore Compounds in Different Solvents

compd no.	λ_{max}/nm (THF)[a]	λ_{max}/nm (methanol)[a]	λ_{max}/nm (ethylacetate)[a]	ε_{max} (THF)[b]	red-shift nm (THF)[c]
1a	398	399	393	36 000	10
1b	402	397	394	19 700	14
1c	388	383	382	20 500	
2a	367	363	361	86 900	10
2b	370				13
2c	357	355	353		
3a	365	362	362	30200	10
3b	372	370	367	14 000	17
3c	355	354	352	3820	
4a	366	362	362	37 500	11
4b	370	367	365	11 100	15
4c	355	354	353	8890	
5a	365	362	362	100 600	8
5b	375				18
5c	357	355	354		
d	261				−14
phenol	275				
e	289				−4
aniline	293				

[a] Maximal UV−vis absorption wavelengths (λ_{max}) of compounds were determined in tetrahydrofuran (THF), methanol, and ethyl acetate. [b] Maximal absorption coefficient (ε_{max}) in THF. [c] Red-shift of λ_{max} is the variation of λ_{max} in THF between bisubstituted compounds **1a**, **2a**, **3a**, **4a**, and **5a** or monosubstituted compounds **1b**, **2b**, **3b**, **4**b, and **5b** and the corresponding monomer compounds **1c**, **2c**, **3c**, **4c**, and **5c**.

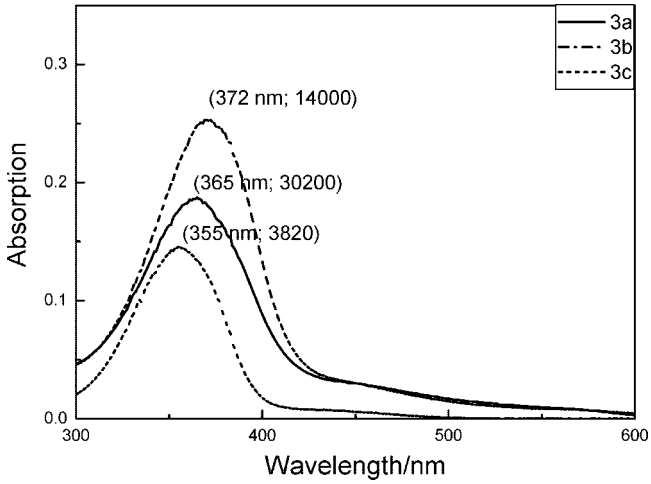


Figure 6. UV−vis absorption spectra of compounds **3a/3b/3c** in THF (λ_{max} and ε_{max} of the compounds in THF are marked on the curves).

comparison with the corresponding reference monomers, because the two D−π−A units in the H-typed chromophores are combined in nonconjugated form via two methylene groups. In addition, 1,8-dihydroxy-9,10-dihydroanthracene and 1,8-diamino-9,10-dihydroanthracene produce a hypsochromic shift (4 to ∼14 nm, in THF) compared with the corresponding reference monomer phenol and aniline. Therefore, the H-typed chromophores with the combined nonconjugated D−π−A units have both an increasing β and good optical transparency.

Properties of the Polyimides Embedded with H-Shaped Chromophores. Thermal properties of the polyimides were examined by thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC). The glass transition temperature T_g and decomposition temperature T_d of **P1**, **P2**, and **P3** are 198 to ∼210 °C and about 240 °C (Table 7), respectively, which indicate that they have higher thermal stability. The molecular weights of the polyimides were estimated by gel permeation chromatography (GPC). **P1**, **P2**, and **P3** have a weight-average molecular weight $\bar{M}_w$ of 0.77, 1.16, and 0.59 ($\times 10^4$ g/mol) as well as a number-average molecular weight $\bar{M}_n$ of 0.38, 0.64, and 0.34 ($\times 10^4$ g/mol) with a polydispersity index of 2.0, 1.9, and 1.7 based on polystyrene standards (Table 7), respectively. **P1**, **P2**, and **P3** are soluble in organic solvents such as THF, DMF, DMSO, because they have lower average molecular weight and the flexible CF_3 groups are incorporated in the polyimides. Therefore, their poling films can be easily prepared for the measurement of macroscopic nonlinear optical coefficient.

The UV−vis spectra of the poled thin films of **P1**, **P2**, and **P3** were measured and the maximal absorption wavelengths (λ_{max}) were 353, 357, and 355 nm (shorter than 400 nm) (Figure 7 and Table 7), without red-shifts in comparison with the corresponding monomer chromophores **2c**, **3c**, and **4c**. It suggests that the main-chain polyimides have good optical transparency.

The macroscopic second-harmonic coefficients (d_{33}) of the polyimides embedded with H-shaped chromophores were determined by Marker fringe method. The experimental setup was similar to that in the literature.[20g,34] The polyimides were dissolved in THF to acquire a mass percent of 8% solution. Then the polyimides were coated on a clear glass by a spinning coater to give polymer thin films. The thicknesses of the thin films were measured by the conventional m-line method to be from 1.3 to 2.4 μm, respectively. The films was poled by applying a 4 kV dc voltage at the approaching their glass transition temperatures between the grid electrode and the conductive glass. The NLO coefficient d_{33} could be deduced by the following equation:[20g,34]

$$d_{33} = d^{(2)}_{zzz(\text{quartz})}[R]^{1/2}\frac{l_c^{\text{quartz}}}{l}F \qquad (2)$$

where R is the relative intensity of SHG, l_c^{quartz} is the relative length of quartz, and l is the thickness of the thin film. The F of thin film can be obtained as the following equation:

$$F^2 \approx \left(0.28\frac{l_c^2}{l^2}\right)\left[1-\cos\frac{\pi l}{l_c}\right] \qquad (3)$$

The l_c is the coherent length of polymer film. When $l < l_c$, function F is approximately a constant ($F = 1.2$). Then the second-order nonlinear coefficient d_{33} can be evaluated utilizing eqs 2 and 3. The values of d_{33} are shown as Table 7, which shows that the fluorine-containing polyimides exhibit a higher macroscopic nonlinear optical coefficient ($d_{33} = 35.0$ to ∼70.2 pm/V) due to containing H-typed active chromophore molecules and a higher percent (48.5−52.3%) of the D−π−A unit in the polyimides. Therefore, the polyimides embedded with H-shaped chromophores have both a higher macroscopic NLO coefficient (d_{33}) and higher thermal stability and good optical transparency.

Conclusion

In this paper, a new strategy in designing second-order nonlinear optical chromophores, i.e., a combination with nonconjugated and parallel D−π−A units at a same direction, was developed. On the basis of the strategy, a series of

Table 7. Physical Properties of Polyimides

polyimides	$^{-}\bar{M}_w$ (10^4 g/mol)[a]	$^{-}\bar{M}_n$ (10^4 g/mol)[b]	polydispersity	T_g (°C)	T_d (°C)	λ_{max} (nm)	d_{33} (pm/V)
P1	0.77	0.38	2.0	198	245	353	70.2
P2	1.16	0.64	1.9	201	240	357	51.5
P3	0.59	0.34	1.7	210	240	355	35.0

[a] Weight-average molecular weight. [b] Number-average molecular weight.

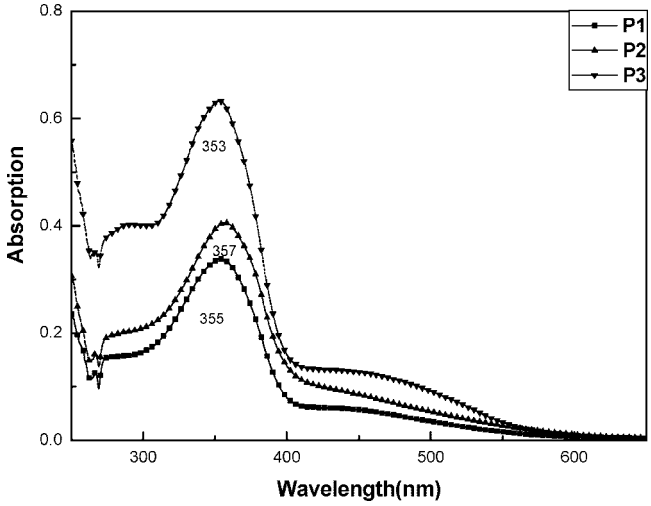


Figure 7. UV−vis spectra of the poled thin films of polyimides.

H-shaped chromophores were synthesized, in which a 9,10-dihydroanthracene was employed as the molecular backbone. The measurement results of HRS and UV−vis spectra demonstrate that the β values of H-shaped chromophores are remarkably increased compared with the corresponding mono-D−π−A unit reference compounds, without causing a large shift of the absorption band to longer wavelength. Therefore, it is an effective strategy for increasing both the first molecular hyperpolarizability and the transparency in designing NLO chromophores. Furthermore, the main-chain fluoro-containing polyimides embedded with the H-shaped chromophores were also synthesized. The elementary investigations indicate that the polyimides exhibit a higher macroscopic nonlinear optical coefficient (d_{33}), good thermal stability, and optical transparency. It could give an alternative way of solving the trade-off between nonlinearity and transparency and thermal stability in designing NLO materials.

Experimental Section

Melting points were determined on a Yanaco micro melting point apparatus (uncorrected). ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AM 300 (Germany), and δ were given in ppm (relative to TMS) and coupling constants (J) in Hz. Mass spectra were recorded under EI mode on a VG-Autospec mass spectrometer and ESI or APCI mode on an LCQ electron spray mass spectrometer (Finnigan). UV−vis spectra were recorded on a Lambda 25 Perkin-Elmer spectrophotometer. IR spectra were recorded on a Bruker Vector 22 spectrophotometer, in which samples were embedded in KBr thin films. Elemental analyses were carried out using a Perkin-Elmer 240C. Preparative column chromatography separations were performed on G60 silica gel, whereas precoated silica gel plates (GF_{254}) were used for analytical TLC. All the solvents were purified by standard procedures. All other chemicals were purchased from Sigma or Aldrich. Thermal analyses were performed by using the SETARAM DSC-131 and TGA−DTA system from TA instruments under nitrogen atmosphere. Molecular weights were determined by GPC with a polystyrene standard using a Waters SEC-244 system at 25.5 °C in THF.

Synthesis of 1,8-Dihydroxyl-9,10-dihydroanthracene, d. Active zinc powder (167 g, 2.6 mol) and 1,8-dihydroxyl-9,10-anthracenedione (10 g, 41.3 mmol) were added to a stirred solution (670 mL) of sodium hydroxide (50 g, 1.25 mol) under a N_2 atmosphere. After the mixture was refluxed for 72 h, and then cooled to room temperature, concentrated hydrochloric acid (570 mL) was added. The reaction mixture was continuously stirred for 1 h, and then filtrated. The solid was dried, followed by recrystallization from toluene (100 mL) to give the pure compound as a yellow crystal 7.3 g, yield 82.6%, mp 206−207 °C. Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.16; H, 5.67. Found: C, 79.22; H, 5.70. ^{1}H NMR ($DCCl_3$): δ = 7.10 (t, 2 H, ^2J = 7.8, ArH), 6.90 (d, 2 H, ^2J = 7.8, ArH), 6.71 (d, 2 H, ^2J = 7.8, ArH), 4.02 (s, 2 H, CH_2), 3.93 (s, 2 H, CH_2). MS (EI): m/z = 211.8, calcd for $C_{14}H_{12}O_2$ [M^+]: 212.1. IR (KBr): ν = 3341.0 (br, O−H) cm^{-1}. UV−vis (THF): λ_{max} = 261 nm (ε = 1610).

Synthesis of 1,8-Diamino-9,10-dihydroanthracene, e. 1,8-Diamino-9,10-dihydroanthracene was prepared from reducing 1,8-dinitro-9,10-anthraquin-one by zinc powder in sodium hydroxide solution (8%) similar to that of 1,8-dihydroxyl-9,10-dihydroanthracene, by using 1,8-dinitro-9,10-anthracenedione (12.3 g, 41.3 mmol) instead of 1,8-dihydroxyl-9,10-anthracenedione. The solid was recrystallized from ethanol to give the pure compound **e** as a green crystal 7.6 g, yield 87.2%, mp 131−133 °C. Anal. Calcd. for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.72; H, 6.70; N, 13.17. ^{1}H NMR ($DCCl_3$): δ = 7.07 (t, 2 H, ^2J = 7.6, ArH), 6.76 (d, 2 H, ^2J = 7.6, ArH), 6.64 (d, 2 H, ^2J = 7.6, ArH), 4.05 (s, 2 H, CH_2), 3.54 (s, 2 H, CH_2). ^{13}C NMR (D_3CCOCD_3): δ = 145.7, 138.1, 135.7, 126.6, 116.8, 112.5 (aromatic C); 35.8, 24.7 ($ArCH_2Ar$). MS (EI): m/z = 210.1, calcd for $C_{14}H_{14}N_2$ [M^+]: 210.1. IR (KBr): ν = 3386.8 (br, t, N−H) cm^{-1}, 1624.9 (C−N) cm^{-1}. UV−vis (THF): λ_{max} = 289 nm (ε = 6390).

Synthesis of 1,8-Dihydroxyl-4,5-bis(4-nitrophenylazo)-9,10-dihydroanthracene, 1a. A solution of 4-nitroaniline (0.83 g, 6 mmol) in a solution of hydrochloric acid (6 mL, 4 M) was added to a solution of sodium nitrite (0.42 g, 6.1 mmol) in 2 mL of water, and the mixture was stirred for 4 h under N_2 atmosphere at 0 −5 °C. Urea (0.01 g, 0.2 mmol) was then added to decompose excessive nitrous acid, and the mixture was further stirred for 30 min. The solution of the diazonium salt was added to a mixture of 1,8-dihydroxyl-9,10-dihydroanthracene (0.63 g, 3 mmol), sodium carbonate (3 g), sodium bicarbonate (0.2 g), and ice (15 g) in ethanol (15 mL) at 0−5 °C. The mixture was stirred for 7 h. Water (100 mL) was then added, and the mixture was heated to 50 °C. After a solution of hydrochloric acid (6.8 mL, 6 M) was added, the mixture was stirred for 20 min, and then filtrated. The solid was dried and purified by column chromatography with chloroform elution, followed by recrystallization from chloroform to give the pure compound **1a** as a yellow powder (272 mg, 0.53 mmol, 17.7%,

(34) (a) Stähelin, M.; Burland, D. M.; Rice, J. E. *Chem. Phys. Lett.* **1992**, *191*, 245. (b) Maker, P. D.; Terhune, R. W.; Nisenoff, M. *Phys. Rev. Lett.* **1962**, *8*, 21. (c) Jerphanon, J.; Krutz, S. K. *J. Appl. Phys.* **1970**, *41*, 1667.

mp ≫ 300 °C). Anal. Calcd. for $C_{26}H_{18}N_6O_6$: C, 61.18; H, 3.55; N, 16.46. Found: C, 60.95; H, 3.46; N, 16.28. ^{1}H NMR (D_3CCOCD_3): δ = 8.40 (d, 2 H, ^2J = 7.1, ArH in dihydroanthracene), 8.32 (d, 4 H, ^2J = 9.0, ArH in nitrophenyl), 8.10 (d, 2 H, ^2J = 7.1, ArH in dihydroanthracene), 7.78 (d, 4 H, ^2J = 9.0, ArH in nitrophenyl), 3.36 (s, 4 H, 2 × CH_2). ^{13}C NMR (D_3CCOCD_3): δ = 148.0, 141.2, 129.9, 129.0, 126.0, 125.6, 124.5, 124.0, 118.8, 117.5 (aromatic C); 23.5, 26.0 ($ArCH_2Ar$). MS (ESI): m/z = 513.8 $[M + H]^+$, calcd for $C_{26}H_{18}N_6O_6$ $[M + H]^+$: 513.5. IR (KBr): ν = 3397.8 (br, O−H), 1641 (N=N) cm^{-1}. UV−vis (THF): λ_{max} = 398 nm (ε = 36 000).

Synthesis of 1,8-Dihydroxyl-4-(4-nitrophenylazo)-9,10-dihydroanthracene, 1b. The above solid was purified by a chromatography column in chloroform elution, followed by recrystallization from chloroform to give another compound **1b** as a yellow powder (468 mg, 1.3 mmol, 43.2%, mp ≫ 300 °C). Anal. Calcd. for $C_{20}H_{15}N_3O_4$: C, 66.48; H, 4.18; N, 11.63. Found: C, 66.26; H, 4.01; N, 11.38. ^{1}H NMR (D_3CCOCD_3): δ = 8.44 (d, 2 H, ^2J = 8.9, ArH in nitrophenyl), 8.13 (d, 2 H, ^2J = 8.9, ArH in nitrophenyl), 7.69 (d, 1 H, ^2J = 8.9, ArH in dihydroanthracene), 6.95 (d, 1 H, ^2J = 8.9, ArH in dihydroanthracene), 7.04 (t, 1 H, ^2J = 7.7, ArH in dihydroanthracene), 6.89 (d, 1 H, ^2J = 7.7, ArH in dihydroanthracene), 6.81 (d, 1 H, ^2J = 7.7, ArH in dihydroanthracene); 4.57 (s, 2 H, CH_2), 3.97 (s, 2 H, CH_2). ^{13}C NMR (D_3CCOCD_3): δ = 159.4, 156.9, 154.7, 148.5, 143.5, 141.1, 137.0, 127.0, 125.1, 124.2, 123.5, 122.1, 119.5, 114.8, 113.5, 113.4, 112.7, 112.6 (aromatic C); 22.3 ($ArCH_2Ar$). MS (EI): m/z = 361.0, calcd for $C_{20}H_{15}N_3O_4$ $[M^+]$: 361.1. IR (KBr): ν = 3438 (br, O−H), 1634 (N=N) cm^{-1}. UV−vis (THF): λ_{max} = 402 nm (ε = 19 700).

Synthesis of 2-Methyl-4-(4-nitrophenylazo)phenol, 1c. A solution of 4-nitrophenyl diazonium salt (6 mmol) obtained by the same method as above was added to a aqueous mixture of 2-methylphenol (0.71 g, 6.6 mmol), sodium carbonate (3 g), baking soda (0.2 g), and ice (15 g) at 0−5 °C. The mixture was stirred for 7 h. After the reaction solution was neutralized with a solution of hydrochloric acid (13.6 mL, 3 M), the mixture was filtrated. The product was obtained by recrystallization from ethanol and water (20 mL, v/v = 4: 1) and dried to give product 1.39 g (5.4 mmol), yield 90%, mp 208−210 °C. ^{1}H NMR (D_3CCOCD_3): δ = 8.39 (d, 2 H, ^2J = 8.4, ArH in nitrophenyl), 8.00 (d, 2 H, ^2J = 8.4, ArH in nitrophenyl), 7.97 (d, 1 H, ^2J = 8.4, ArH in 4-hydroxyphenyl), 7.01 (d, 1 H, ^2J = 8.4, ArH in 4-hydroxyphenyl), 7.90 (s, 1 H, ArH in 4-hydroxyphenyl), 2.43 (s, 3 H, CH_3). MS (ESI): m/z = 257.0,calcd for $C_{13}H_{11}N_3O_3$ $[M - H]^-$: 257.3. IR (KBr): ν = 3417.0 (br, O−H) cm^{-1}. UV−vis (THF): λ_{max} = 388 nm (ε = 20 500).

Synthesis of 1,8-Dihydroxyl-4,5-bis(4-trifluoromethylphenylazo)-9,10-dihydroanthracene, 2a. 2a was prepared and purified in a manner similar to **1a**, by using 4-trifluoromethylaniline (0.64 g, 4 mmol) instead of 4-nitroaniline. A yellow powder was obtained (256 mg, 0.46 mmol), yield 23.0%, mp ≫ 300 °C. Anal. Calcd. for $C_{28}H_{18}F_6N_4O_2$: C, 60.44; H, 3.26; N, 10.07. Found: C, 60.16; H, 3.05; N, 9.80. ^{1}H NMR (D_3CCOCD_3): δ = 8.13 (d, 4 H, ^2J = 8.4, ArH in 4-trifluoromethylphenyl), 7.94 (d, 4 H, ^2J = 8.4, ArH in 4-trifluoromethylphenyl), 7.73 (d, 2 H, ^2J = 8.8, ArH in dihydroanthracene), 7.00 (d, 2 H, ^2J = 8.8, ArH in dihydroanthracene), 5.26 (s, 2 H, CH_2), 4.13 (s, 2 H, CH_2). ^{13}C NMR (D_3CCOCD_3): δ = 159.9, 159.0, 143.2, 140.3, 126.8, 126.7, 123.7, 123.2, 114.8, 113.6 (aromatic C); 25.0, 22.4 ($ArCH_2Ar$). MS (ESI): m/z = 555.3, calcd for $C_{28}H_{18}F_6N_4O_2$ $[M - H]^-$: 555.1. IR (KBr): ν = 3499.6 (br, O−H); 1635.5 (N=N) cm^{-1}. UV−vis (THF): λ_{max} = 367 nm (ε = 86 900)

Synthesis of 1,8-Dihydroxyl-4-(4-trifluoromethylphenylazo)-9,10-dihydroanthracene, 2b. 2b was prepared and purified in a manner similar to **1b**, by using 4-trifluoromethylaniline (0.64 g, 4 mmol) instead of 4-nitroaniline. A yellow powder was obtained by recrystallization from chloroform to give compound **2b** as a yellow powder (68 mg, 0.18 mmol), yield 9.0%, mp ≫ 300 °C. Anal. Calcd. for $C_{21}H_{15}F_3N_2O_2$: C, 65.62; H, 3.93; N, 7.29. Found: C, 65.36; H, 3.85; N, 7.02. ^{1}H NMR (D_3COCD_3): δ = 8.12 (d, 2 H, ^2J = 8.2, ArH in 4-trifluoromethylphenyl), 7.93 (d, 2 H, ^2J = 8.2, ArH in 4-trifluoromethylphenyl), 7.69 (d, 1 H, ^2J = 8.8, ArH in dihydroanthracene), 7.06 (t, 1 H, ^2J = 7.7, ArH in dihydroanthracene), 6.99 (d, 1 H, ^2J = 7.7, ArH in dihydroanthracene), 6.97 (d, 1 H, ^2J = 8.8, ArH in dihydroanthracene), 6.81 (d, 1 H, ^2J = 7.7, ArH in dihydroanthracene), 4.59 (s, 2 H, CH_2), 4.02 (s, 2 H, CH_2). ^{13}C NMR (D_3COCD_3): δ = 159.0, 155.8, 154.7, 143.3, 140.6, 137.2, 130.8, 127.0, 126.8, 126.7, 124.1, 123.3, 122.3, 119.5, 119.0, 114.6, 113.4, 112.6 (aromatic C); 22.3 ($ArCH_2Ar$). MS (APCI): m/z = 383.5, calcd for $C_{21}H_{15}F_3N_2O_2$ $[M - H]^-$: 383.1. IR (KBr): ν = 3425.2 (br, O−H); 1635.9 (N=N) cm^{-1}. UV−vis (THF): λ_{max} = 373 nm (ε = 26 600).

Synthesis of 4-(4-Trifluoromethylphenylazo)phenol, 2c. 2c was prepared and purified in a manner similar to **1c**, by using 4-trifluoromethylaniline (0.97 g, 6 mmol) instead of 4-nitroaniline and phenol (0.62 g, 6.6 mmol). The product was obtained as a yellow powder (1.44 g, 5.5 mmol), yield 90.2%, mp 126−127 °C. ^{1}H NMR ($DCCl_3$)[51]: δ = 7.97 (d, 2 H, ^2J = 8.7, ArH in 4-trifluoromethylphenyl), 7.94 (d, 2 H, ^2J = 6.9, ArH in phenol), 7.78 (d, 2 H, ^2J = 8.7, ArH in 4-trifluoromethylphenyl), 6.98 (d, 2 H, ^2J = 6.9, ArH in phenol). MS (ESI): m/z = 265.2, calcd for $C_{13}H_9F_3N_2O_2$ $[M - H]^-$: 265.1. IR (KBr): ν = 3451.1 (O−H), 1631.5 (N=N) cm^{-1}. UV−vis (THF): λ_{max} = 357 nm (ε = 34 200).

Synthesis of 1,8-Dihydroxyl-4,5-bis(3-chloro-4-fluorophenylazo)-9,10-dihydroanthracene, 3a. 3a was prepared and purified in a manner similar to **1a**, by using 3-chloro-4-fluoroaniline (0.96 g, 6 mmol) instead of 4-nitroaniline. A yellow powder was obtained (602 mg, 1.15 mmol), yield 38.3%, mp > 300 °C. Anal. Calcd. for $C_{26}H_{16}Cl_2F_2N_4O_2$: C, 59.44; H, 3.07; N, 10.66. Found: C, 59.18; H, 3.05; N, 10.35. ^{1}H NMR (D_3CCOCD_3): δ = 7.95 (dd, 2 H, ^3J = 2.4, ^2J = 7.0, ArH in 3-chloro-4-fluorophenyl), 7.88 (ddd, 2 H, ^2J = 8.8, $^2J_{H-F}$ = 4.6, ^3J = 2.4 ArH in 3-chloro-4-fluorophenyl), 7.6 (d, 2 H, ^2J = 8.8, ArH in dihydroanthracene), 7.52 (t, 2 H, ^2J = 8.8, ArH in 3-chloro-4-fluorophenyl), 6.92 (d, 2 H, ^2J = 8.8, ArH in dihydroanthracene), 5.07 (s, 2 H, CH_2), 3.99 (s, 2 H, CH_2). ^{13}C NMR (D_3CCOCD_3): δ = 160.6, 158.9, 157.3, 150.4, 143.0, 138.8, 124.7, 123.2, 122.9, 121.6, 117.7, 114.9, 113.3 (aromatic C); 25.1, 22.4 ($ArCH_2Ar$). MS (APCI): m/z = 522.7/524.7/526.7 (abundance ratio, 9/6/1), calcd for $C_{26}H_{16}Cl_2F_2N_4O_2$ $[M - H]^-$: 523.1/525.1/527.1 (abundance ratio, 9/6/1). IR (KBr): ν = 3421.6 (br, O−H), 1634.0 (N=N) cm^{-1}. UV−vis (THF): λ_{max} = 365 nm (ε = 30 200).

Synthesis of 1,8-Dihydroxyl-4-(-3-chloro-4-fluorophenylazo)-9,10-dihydroanthracene, 3b. 3b was prepared and purified in a manner similar to **1b**, by using 3-chloro-4-fluoroaniline (0.96 g, 6 mmol) instead of 4-nitroaniline. The product was obtained as a yellow powder (280 mg, 0.76 mmol), yield 25.4%, mp ≫ 300 °C. Anal. Calcd. for $C_{20}H_{14}ClFN_2O_2$: C, 65.14; H, 3.83; N, 7.60. Found: C, 64.87; H, 3.66; N, 7.32. ^{1}H NMR (D_3CCOCD_3): δ = 8.07 (dd, 1 H, ^3J = 2.3, ^2J = 7.0, ArH in 3-chloro-4-fluorophenyl), 7.96 (ddd, 1 H, ^2J = 8.8, ^3J = 2.4, $^2J_{H-F}$ = 4.6, ArH in 3-chloro-4-fluorophenyl), 7.62 (d, 1H, ^2J = 8.8, ArH in dihydroanthracene), 7.54 (t, 1 H, ^2J = 8.8, ArH in 3-chloro-4-fluorophenyl), 7.04 (t, 1 H, ^2J = 7.7, ArH in dihydroanthracene), 6.92 (d, 1 H, ^2J = 8.8, ArH in dihydroanthracene), 6.90 (d, 1 H, ^2J = 7.2, ArH in dihydroanthracene), 6.80 (d, 1 H, ^2J = 7.7, ArH in dihydroanthracene), 4.55 (s, 2 H, CH_2), 3.98 (s, 2 H, CH_2). ^{13}C NMR (D_3CCOCD_3): δ = 157.4, 143.0, 140.1, 137.2, 127.0, 124.4, 124.3, 123.8, 122.2, 119.5, 117.8, 117.5, 114.6, 113.3, 112.6 (aromatic

C); 22.3 ($ArCH_2Ar$). MS (EI): m/z = 368.0/370.2 (abundance ratio, 3/1), calcd for $C_{20}H_{14}ClFN_2O_2$ [M^+]: 368.1/370.1 (abundance ratio, 3/1). IR (KBr): ν = 3373.4 (br, O−H), 1620.2 (N═N) cm^{-1}. UV−vis (THF): λ_{max} = 372 nm (ε = 14 000).

Synthesis of 4-(3-Chloro-4-fluorophenylazo)phenol, 3c. 3c was prepared and purified in a manner similar to **1c**, by using 3-chloro-4-fluoroaniline (0.96 g, 6 mmol) instead of 4-nitroaniline and phenol (0.62 g, 6.6 mmol) instead of 2-methylphenol. The product was obtained as a yellow powder (1.43 g, 5.7 mmol), yield 95%, mp 102−103 °C. ^1H NMR (D_3CCOCD_3): δ = 7.97 (dd, 1 H, ^2J = 7.0, ^3J = 2.3, ArH in 3-chloro-4-fluorophenyl), 7.87 (d, 2 H, ^2J = 8.8, ArH in phenol), 7.82 (m, 1 H, ArH in 3-chloro-4-fluorophenyl), 7.29 (t, 1 H, ^2J = 8.6, ArH in 3-chloro-4-fluorophenyl), 6.97 (d, 2 H, ^2J = 8.8, ArH in phenol), 5.64 (s, 2 H, ArOH). ^{13}C NMR (D_3CCOCD_3): δ = 161.7, 160.8, 157.5, 150.0, 146.2, 125.6, 124.3, 123.7, 121.7, 117.6, 116.3 (aromatic C). MS (APCI): m/z = 250.5/252.5 (abundance ratio, 3/1), calcd for $C_{12}H_8ClFN_2O$ [$M + H]^+$: 251.0/253.0. IR (KBr): ν = 3260.9 (br, O−H), 1634.0 (N═N) cm^{-1}. UV−vis (THF): λ_{max} = 355 nm (ε = 3820).

Synthesis of 1,8-Dihydroxyl-4,5-bis(4-chlorophenylazo)-9,10-dihydroanthracene, 4a. 4a was prepared and purified in a manner similar to **1a**, by using 4-chloroaniline (0.76 g, 6 mmol) instead of 4-nitroaniline. A yellow powder **4a** was obtained (689 mg, 1.4 mmol), yield 47.0%, mp ≫ 300 °C. Anal. Calcd. for $C_{26}H_{18}Cl_2N_4O_2$: C, 63.81; H, 3.71; N, 11.45. Found: C, 63.75; H, 3.58; N, 11.14. ^1H NMR (D_3CCOCD_3): δ = 7.95 (d, 4 H, ^2J = 8.7, ArH in chlorophenyl), 7.62 (d, 4 H, ^2J = 8.7, ArH in chlorophenyl), 7.65 (d, 2 H, ^2J = 8.8, ArH in dihydroanthracene), 6.96 (d, 2 H, ^2J = 8.8, ArH in dihydroanthracene), 5.15 (s, 2 H, CH_2), 4.06 (s, 2 H, CH_2). ^{13}C NMR (D_3CCOCD_3): δ = 158.3, 152.3, 143.2, 139.4, 135.7, 129.7, 124.3, 123.5, 114.7, 113.4 (aromatic C); 25.1, 22.4 ($ArCH_2Ar$). MS (APCI): m/z = 486.7/488.7/490.7 (abundance ratio, 9/6/1), calcd for $C_{26}H_{18}Cl_2N_4O_2$ [$M - H]^-$: 487.1/489.1/491.1 (abundance ratio, 9/6/1). IR (KBr): ν = 3502.0 (br, O−H); 1642.0 (N═N) cm^{-1}. UV−vis (THF): λ_{max} = 366 nm (ε = 37 500).

Synthesis of 1,8-Dihydroxyl-4-(4-chlorophenylazo)-9,10-dihydroanthracene, 4b. 4b was prepared and purified in a manner similar to **1b**, by using 4-chloroaniline (0.76 g, 6 mmol) instead of 4-nitroaniline. A yellow powder was obtained by recrystallization from chloroform to give compound **4b** as a yellow powder (168 mg, 0.48 mmol), yield 16.1%, mp > 300 °C. Anal. Calcd. for $C_{20}H_{15}ClN_2O_2$: C, 68.48; H, 4.31; N, 7.99. Found: C, 68.17; H, 4.25; N, 7.71. ^1H NMR (D_3CCOCD_3): δ = 7.95 (d, 2 H, ^2J = 8.8, ArH in chlorophenyl), 7.60 (d, 2 H, ^2J = 8.8, ArH in chlorophenyl), 7.62 (d, 1 H, ^2J = 7.7, ArH in dihydroanthracene), 7.04 (t, 1 H, ^2J = 7.7, ArH in dihydroanthracene), 6.92 (d, 1 H, ^2J = 8.9, ArH in dihydroanthracene), 6.89 (d, 1 H, ^2J = 8.9, ArH in dihydroanthracene), 6.80 (d, 1 H, ^2J = 7.7, ArH in dihydroanthracene), 5.54 (s, 2 H, CH_2), 4.06 (s, 2 H, CH_2). ^{13}C NMR (D_3CCOCD_3): δ = 158.4, 154.7, 152.2, 143.2, 139.9, 137.3, 135.6, 132.8, 129.7, 128.9, 127.0, 124.4, 124.0, 122.3, 119.5, 114.4, 113.3, 112.6 (aromatic C); 22.3 ($ArCH_2Ar$). MS (APCI): m/z = 348.6/350.6 (abundance ratio, 3/1), calcd for $C_{20}H_{15}ClN_2O_2$ [$M - H]^-$: 349.1/351.1 (abundance ratio, 3/1). IR (KBr): ν = 3422 (br, O−H); 1635 (N═N) cm^{-1}. UV−vis (THF): λ_{max} = 370 nm (ε = 11 100).

Synthesis of 4-(4-Chlorophenylazo)phenol, 4c. 4c was prepared and purified in a manner similar to **1c**, by using 4-chloroaniline (0.76 g, 6 mmol) instead of 4-nitroaniline and phenol (0.62 g, 6.6 mmol) instead of 2-methylphenol. The product was obtained as a yellow powder (1.35 g, 5.8 mmol), yield 96%, mp 159−160 °C. ^1H NMR ($DCCl_3$): δ = 7.90 (d, 2H, ^2J = 8.7, ArH in chlorophenyl), 7.85 (d, 2H, ^2J = 8.6, ArH in phenol), 7.49 (d, 2H, ^2J = 8.6, ArH in chlorophenyl), 6.97 (d, 2H, ^2J = 8.7, ArH in phenol), 5.38 (s, 2H, ArOH). IR (KBr): ν = 3226.8 (O−H), 1656.8 (N═N) cm^{-1}. UV−vis (THF): λ_{max} = 355 nm (ε = 8890).

Synthesis of 1,8-Dihydroxyl-4,5-bis-(4-bromophenylazo)-9,10-dihydroanthracene, 5a. 5a was prepared and purified in a manner similar to **1a**, by using 4-bromoaniline (0.69 g, 4 mmol) instead of 4-nitroaniline. A yellow powder **5a** was obtained (202 mg, 0.35 mmol), yield 17.5%, mp > 300 °C. Anal. Calcd. for $C_{26}H_{18}Br_2N_4O_2$: C, 54.00; H, 3.14; N, 9.69. Found: C, 53.79; H, 3.05; N, 9.41. ^1H NMR (D_3CCOCD_3): δ = 7.90 (d, 4 H, ^2J = 8.8, ArH in 4-bromophenyl), 7.79 (d, 4 H, ^2J = 8.8, ArH in 4-bromophenyl), 7.68 (d, 2 H, ^2J = 8.8, ArH in dihydroanthracene), 6.95 (d, 2 H, ^2J = 8.8, ArH in dihydroanthracene), 5.18 (s, 2 H, CH_2), 4.11 (s, 2 H, CH_2). ^{13}C NMR (D_3CCOCD_3): δ = 158.4, 152.7, 143.2, 139.5, 132.8, 124.5, 124.1, 123.6, 114.7, 113.4 (aromatic C); 25.1, 22.4 ($ArCH_2Ar$). MS (ESI): m/z = 577.3/577.3/579.3 (abundance ratio, 1/2/1), calcd for $C_{26}H_{18}Br_2N_4O_2$ [$M - H]^-$: 575.0/577.0/579.0 (abundance ratio, 1/2/1). IR (KBr): ν = 3439.6 (br, O−H), 1630.9 (N═N) cm^{-1}. UV−vis (THF): λ_{max} = 365 nm (ε = 100 600).

Synthesis of 1,8-Dihydroxyl-4-(4-bromophenylazo)-9,10-dihydroanthracene, 5b. 5b was prepared and purified in a manner similar to **1b**, by using 4-bromoaniline (0.69 g, 4 mmol) instead of 4-nitroaniline. A yellow powder was obtained by recrystallization from chloroform to give compound **5b** as a yellow powder (80 mg, 0.14 mmol), yield 7.0%, mp > 300 °C. Anal. Calcd. for $C_{20}H_{15}BrN_2O_2$: C, 60.78; H, 3.83; N, 7.09. Found: C, 60.50; H, 3.73; N, 6.81. ^1H NMR (D_3CCOCD_3): δ = 7.89 (d, 2 H, ^2J = 8.2, ArH in 4-bromophenyl), 7.76 (d, 2 H, ^2J = 8.2, ArH in 4-bromopheny), 7.63 (d, 1 H, ^2J = 8.8, ArH in dihydroanthracene), 7.05 (t, 1 H, ^2J = 8.8, ArH in dihydroanthracene), 6.92 (d, 1 H, ^2J = 8.8, ArH in dihydroanthracene), 6.92 (d, 1 H, ^2J = 8.8, ArH in dihydroanthracene), 6.80 (d, 1 H, ^2J = 8.8, ArH in dihydroanthracene), 4.56 (s, 2 H, CH_2), 4.01 (s, 2 H, CH_2). ^{13}C NMR (D_3CCOCD_3): δ = 158.5, 154.8, 152.5, 143.2, 139.9, 137.3, 132.7, 127.0, 124.6, 122.4, 119.5, 114.5, 113.4, 113.3, 112.7, 112.6 (aromatic C); 22.3 ($ArCH_2Ar$). MS (ESI): m/z = 393.5, calcd for $C_{20}H_{15}BrN_2O_2$ [$M - H]^-$: 393.0. m/z = 430.9 [$M + HCl - H]^-$. IR (KBr): ν = 3405.9 (br, O−H), 1620.2 (N═N) cm^{-1}. UV−vis (THF): λ_{max} = 374 nm (ε = 37 300).

Synthesis of 4-(4-Bromophenylazo)phenol, 5c. 5c was prepared and purified in a manner similar to **1c**, by using 4-bromoaniline (1.04 g, 6 mmol) instead of 4-nitroaniline and phenol (0.62 g, 6.6 mmol) instead of 2-methylphenol. The product was obtained as a yellow powder (1.58 g, 5.7 mmol), yield 95%, mp 153−155 °C. ^1H NMR ($DCCl_3$): δ = 7.90 (d, 2 H, ^2J = 5.7, ArH in 4-bromophenyl), 7.77 (d, 2 H, ^2J = 6.8, ArH in phenol), 7.65 (d, 2 H, ^2J = 5.7, ArH in bromophenyl), 6.97 (d, 2 H, ^2J = 6.8, ArH in phenol). MS (ESI): m/z = 275.5, calcd for $C_{12}H_9BrN_2O$ [$M - H]^-$: 275.0. IR (KBr): ν = 3229.6 (br, O−H), 1659.4 (N═N) cm^{-1}. UV−vis (THF): λ_{max} = 357 nm (ε = 60 300).

Synthesis of 1,8-Bis(2-bromoethoxy)-4,5-bis(4-trifluoromethylphenylazo)-9,10-dihydroanthracene 2f. Potassium carbonate (0.2 g) and **2a** (0.1 g, 0.18 mmol) were added to 1,2-dibromoethane (2 mL, 2.5 g, 13.3 mmol), and the mixture was stirred for 48 h under N_2 atmosphere at 100 °C. After the reaction solution was cooled down to room temperature, the mixture was filtrated. The solid was dried and purified by chromatography column with chloroform elution, followed by recrystallization from acetone to give an orange pure compound **2f** (61 mg, 0.092 mmol), yield 51.2%, mp > 300 °C. ^1H NMR (D_3CCOCD_3): δ = 8.17 (d, 4 H, ^2J = 8.4, ArH in 4-triflouomethylphenyl), 7.82 (d, 4H, ^2J = 8.4, ArH in 4-triflouomethylphenyl), 8.04 (d, 2 H, ^2J = 8.1, ArH in dihydroanthracene), 6.93 (d, 2 H, ^2J = 8.1, ArH in dihydroanthracene), 4.70 (t, 4 H, ^2J = 6.1, OCH_2), 4.50 (s, 2H, CH_2), 3.97 (t, 4H, ^2J = 6.1, $BrCH_2$), 3.82 (s, 2H, CH_2). ^{13}C NMR

(D_3CCOCD_3): δ = 144.8, 143.8, 140.2, 133.7, 129.3, 128.8, 127.6, 126.7, 125.3, 60.0, 51.8, 44.6, 44.2. MS: m/z = 770 [M^+]. IR (KBr): ν = 1631.4 (N═N), 1610, 1504.1 (C═C in ArH) cm^{-1}.

Synthesis of 1,8-Bis(2-bromoethoxy)-4,5-bis(3-chloro-4-fluorophenylazo)-9,10-dihydroanthracene, 3f. 3f was prepared and purified in a manner similar to **2f**, by using 1,8-dihydroxyl-4,5-bis(3-chloro-4-fluorophenylazo)-9,10-dihydroanthracene (0.1 g, 0.19 mmol) instead of 1,8-dihydroxyl-4,5-bis(trifluoromethylphenylazo)-9,10-dihydroanthracene. The solid was dried and purified by chromatography column with chloroform elution, followed by recrystallization from acetone to give an orange pure compound **3f** (28 mg, 0.040 mmol), yield 20.6%, mp > 300 °C. ^{1}H NMR (D_3CCOCD_3): δ = 8.10 (d, 2 H, ^2J = 8.7, ArH in 3-chloro-4-fluorophenyl), 7.98−8.02 (m, 2H, ArH in 3-chloro-4-fluorophenyl), 7.42 (d, 2H, ^2J = 8.7, ArH in 3-chloro-4-fluorophenyl), 7.72 (d, 2 H, ^2J = 8.7, ArH in dihydroanthracene), 6.91 (d, 2 H, ^2J = 8.7, ArH in dihydroanthracene), 4.68 (t, 4 H, ^2J = 6.1, OCH_2), 4.48 (s, 2 H, CH_2), 3.94 (t, 4H, ^2J = 6.1, $BrCH_2$), 3.82 (s, 2H, CH_2). MS: m/z = 740 [M^+]. IR (KBr): ν = 1634.4 (N═N), 1607.3, 1561.2 (C═C in ArH) cm^{-1}.

Synthesis of 1,8-Bis(2-bromoethoxy)-4,5-bis(4-chlorophenylazo)-9,10-dihydroanthracene, 4f. 4f was prepared and purified in a manner similar to **2f**, by using 1,8-dihydroxyl-4,5-bis(4-chlorophenylazo)-9,10-dihydroanthracene (0.1 g, 0.20 mmol) instead of 1,8-dihydroxyl-4,5-bis(trifluoromethylphenylazo)-9,10-dihydroanthracene. The solid was dried and purified by chromatography column with chloroform elution, followed by recrystallization from acetone to give an orange pure compound **4f** (28 mg, 0.041 mmol), yield 20.6%, mp > 300 °C. ^{1}H NMR (D_3CCOCD_3): δ = 8.01 (d, 4 H, ^2J = 8.4, ArH in chlorophenyl), 7.54 (d, 4 H, ^2J = 8.4, ArH in chlorophenyl), 7.94 (d, 2 H, ^2J = 7.5, ArH in dihydroanthracene), 6.91 (d, 2 H, ^2J = 7.5, ArH in dihydroanthracene), 4.64 (t, 4 H, ^2J = 6.1, OCH_2), 4.47 (s, 2 H, CH_2), 3.94 (t, 4 H, ^2J = 6.1, $BrCH_2$), 3.89 (s, 2 H, CH_2). MS: m/z = 704 [M^+]. IR (KBr): ν = 1635.5 (N═N), 1604, 1480 (C═C in ArH) cm^{-1}.

Synthesis of Polyimide 1P. Potassium carbonate (0.2 g), 4,4′-(hexafluoroisopropylidene)diphthalic bisimide (11 mg, 0.026 mmol), and 1,8-bis(2-bromoethoxy)-4,5-bis(4-trifluoromethylphenylazo)-9,10-dihydroanthracene, **2f** (20 mg, 0.026 mmol) were added to *N*,*N*-dimethylformamide (5 mL), and the mixture was stirred for 48 h under N_2 atmosphere at 100 °C. After the reaction solution was cooled down to room temperature, the mixture was filtrated. The solution was dried to obtain an orange solid. The solid was purified by deposition from methanol and water (10 mL, v/v = 1:1) and dried to give a yellow powder product **1P** (25 mg), yield 80.6%. ^{1}H NMR (D_3CCOCD_3): δ = 8.17 (d, 4 H, ^2J = 8.0, ArH in 4-triflouomethyl-phenyl), 8.01 (d, 2 H, ^2J = 8.4, ArH in dihydroanthracene), 7.78 (d, 4 H, ^2J = 8.0, ArH in 4-triflouomethylphenyl), 6.91 (d, 2H, ^2J = 8.4, ArH in dihydroanthracene), 7.84 (s, 2 H, ArH in imide-phenyl), 7.13−7.29 (m, 4 H, ArH in imide-phenyl), 4.68 (t, 4 H, ^2J = 6.1, OCH_2), 3.96 (t, 4 H, ^2J = 6.1, NCH_2), 4.46 (s, 2 H, CH_2), 4.29 (s, 2 H, CH_2). IR (KBr): ν = 1719.0 (C═O), 1645.5 (N═N), 1602.7, 1501.2 (C═C in ArH) cm^{-1}. UV−vis (THF): λ_{max} = 355 nm.

Synthesis of Polyimide 2P. 2P was prepared and purified in a manner similar to **1P** by using 1,8-bis(2-bromoethoxy)-4,5-bis(3-chloro-4-fluorophenylazo)-9,10-dihydroanthracene **3f** (19 mg, 0.026 mmol) instead of **2f**. The product was purified by deposition from methanol and water (10 mL, v/v = 1:1) and dried to give a yellow powder **2P** (26 mg), yield 86.7%. ^{1}H NMR (CD_3COCD_3): δ = 7.95−8.13 (m, 4 H, ArH in 3-chloro-4-fluorophenyl, ArH in imide-phenyl), 7.92 (d, 2 H, ^2J = 8.7, ArH in imide-phenyl), 7.56 (d, 2 H, ^2J = 9.0, ArH in 3-chloro-4-fluorophenyl), 7.53 (d, 2 H, ^2J = 8.7, ArH in imide-phenyl), 7.16 (d, 2 H, ^2J = 8.6, ArH in dihydroanthracene), 7.12 (s, 2 H, ArH in 3-chloro-4-fluorophenyl), 7.06 (d, 2 H, ^2J = 8.6, ArH in dihydroanthracene), 4.66 (s, 4 H, CH_2 in dihydroanthracene), 4.22 (t, 4 H, ^2J = 6.1, OCH_2), 3.96 (t, 4 H, ^2J = 6.1, NCH_2). IR (KBr): ν = 1717.3 (C═O), 1641.5 (N═N), 1598.4, 1497.7 (C═C in ArH) cm^{-1}. UV−vis (THF): λ_{max} = 357 nm.

Synthesis of Polyimide 3P. 3P was prepared and purified in a manner similar to **1P**, by using 1,8-bis(2-bromoethoxy)-4,5-bis(4-chlorophenylazo)-9,10-dihydroanthracene **4f** (18 mg, 0.026 mmol) instead of **2f**. The product was purified by deposition from methanol and water (10 mL, v/v = 1:1) and dried to give a yellow powder **3P** (24 mg), yield 82.8%. ^{1}H NMR (D_3CCOCD_3): δ = 8.01 (s, 2 H, ArH in imide-phenyl), 7.89 (d, 4 H, ^2J = 8.4, ArH in chlorophenyl), 7.86 (d, 2 H, ^2J = 8.6, ArH in dihydroanthracene), 7.72 (s, 2 H, ArH in imide-phenyl), 7.63 (d, 4 H, ^2J = 8.4, ArH in chlorophenyl), 7.02 (s, 2H, in imide-phenyl ArH), 6.91 (d, 2H, ^2J = 7.5, ArH in dihydroanthracene), 4.60 (s, 2 H, CH_2), 4.41 (s, 2 H, CH_2), 4.10 (t, 4 H, ^2J = 6.1, OCH_2), 3.75 (t, 4 H, ^2J = 6.1, NCH_2). IR (KBr): ν = 1718.6 (C═O), 1631.8 (N═N), 1600.7, 1498.3 (C═C in ArH) cm^{-1}. UV−vis (THF): λ_{max} = 353 nm.

Determination of β. The Q-switched Nd:YAG laser pulse (Continuum Precision II, 10 Hz, 8 to ~10 ns pulse width) at 1064 nm was focused by a lens (focal length 50 cm) into a cylinder cell (K9-glass, 50 mm in length, 3 mm in radius). The intensity of fundamental beam could be adjusted by rotating a half-wave plate and was controlled under 0.1 mJ which was monitored by an energy meter. An interference filter at 532 nm (3 nm bandwidth) was mounted at the entrance of the photomultiplier tube (PMT, GDB159) to prevent luminescence at other wavelengths. The HRS signals were detected and averaged by a high-frequency digital oscilloscope (Tektronix TDS 3052, 500 MHz), and the two-photon fluorescence (TPF) around 532 nm was also checked. It was found that TPF contributions could be neglected in these HRS experiments, which was consistent with the facts that their absorption peaks were far away from 532 nm and their absorptions at 532 nm were rather weak.

An EFM was utilized in these HRS experiments by choosing *p*-nitroaniline (*p*-NA) as standard. All the samples and *p*-NA were dissolved in THF, and concentration gradients of the samples were prepared by successive dilution. The first hyperpolarizability of *p*-NA in THF was known to be 21.4 × 10^{-30} esu.[34a] For a two-component solution, the HRS intensity $I_{2\omega}$ could be calculated by eq 4.[35]

$$I_{2\omega} = G(N_1\langle \beta_1^2 \rangle + N_2\langle \beta_2^2 \rangle (I_\omega)^2 e^{-N_2\alpha_2 l} \qquad (4)$$

where I_ω was the incident intensity and G was a parameter reflecting experimental conditions such as instrumental factors, collection efficiency, and local field corrections. N was the number density, and subscripts 1 and 2 referred to solvent and solute, respectively. The brackets indicated the spatial orientational average of the chromophore molecules within the focus area with orientational fluctuations and density fluctuations. The factor $e^{-N_2}\alpha_2 l$ accounted for the losses of HRS signal due to the linear absorption and scattering of the solution at 532 nm.

All the azobenzene samples with the D−π−A structures studied in this work could be considered as line-type molecules, so the popular two-level model could be used to estimate their static first hyperpolarizabilities (β_0) which reflect the intrinsic polarizations of the molecules at zero frequency.

HRS Spectral Experiment for Testing the Creditability of the β. The Q-switched Nd:YAG laser pulse (Continuum Precision II, 10 Hz, 8−10 ns pulse width) at 1064 nm was focused by a

(35) Clays, K.; Persoons, A. *Phys. Rev. Lett.* **1991**, *66*, 2980.

cylindric lens with $f = 50$ mm into the samples. The intensity of the fundamental beam was varied by rotating a half-wave plate and was monitored by an energy meter. HRS spectra around 532 nm (529−535 nm) for the five azo two-D−π−A units chromophores were measured using a fluorescence spectrometer (Edinburgh, FLS920) and are shown in Figure 3. The HRS spectra of all the five two-D−π−A units chromophores demonstrate a sharp peak with bandwidth of 0.3 at 531.8 nm and no other signals nearby. Since there is no background signal from 529 to 535 nm, HRS measurements using a 532 nm interference filter with bandwidth of 3 nm should come to the same results as the spectra measurement above. Therefore, these experimental β are convincible. The fundamental limits for β_{0max} were also calculated and are listed in Table 2. These data show that experimental β_0 are quite smaller than the fundamental limit.

Determination of d_{33} of the Polyimide by the Maker Fringe Method. The polyimides were dissolved in THF to acquire a mass percent 8% solution. The mixed solution was stirred for 30 min and coated on a clear glass by a spinning coater. The thicknesses of the thin films were measured by the conventional m-line method to be from 1.3 to 2.4 μm, respectively. Spin-coating samples were placed together with the conductive glass on the heater. The films was poled by applying a 4 kV dc voltage between the grid electrode and the conductive glass with a distance of 2 cm at the glass transition temperature (T_g) for 20 min, and then films were cooled down to room temperature with the field still being applied. The second-order nonlinear coefficients d_{33} of the samples were measured using the Maker fringe method.[20g,34] The experimental setup was similar to that in the literature.[20g,34] The method is used to change the angle between the incident laser beam and the normal plane of samples by the rotation of samples so as to gain space cycle distribution of second-order harmonic signal. A double optical path system with d_{33} of x-cut quartz as reference was used. A p-polarized Q-switched Nd^{3+}:YAG laser with 16 ns pulse width and 50 Hz repetition frequency was used as the laser source. The wavelength of fundamental light was 1.064 μm, and the maximum output energy was 300 mJ. The film was laid at 45° to the incident beam. Because the molecular centrosymmetry was destroyed, the second-harmonic wave would be generated when fundamental light passed through the corona-poled films. The SHG signals were collected by PMT. The NLO coefficient d_{33} values were deduced by the eqs 2 and 3 in the Results and Discussion section.

Acknowledgment. This work was supported by the National Basic Research Program of China (No. 2007CB925103) and the National Natural Science Foundation of China (No.20774039).

Supporting Information Available: First hyperpolarizabilities of H-shaped chromophores and the corresponding mono-D−π−A unit reference compounds; various spectra of H-typed chromophores (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM800528A