Chem. Mater. **2006,** *18,* 6091−6093

The Second-Order Nonlinear Optical Materials with Combined Nonconjugated $D-\pi-A$ Units

Chao-Zhi Zhang,[†] Changgui Lu,[‡] Jing Zhu,[‡]
Guo-Yuan Lu,[*,†] Xin Wang,[‡] Zheng-Wei Shi,[†]
Fang Liu,[†] and Yiping Cui[*,‡]

Department of Chemistry, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China, and Advanced Photonics Center, Southeast University, Nanjing 210096, P. R. China

Received August 1, 2006
Revised Manuscript Received November 9, 2006

Organic and polymeric second-order nonlinear optical (NLO) materials have attracted much attention in the past two decades because of their potential applications in the fields of telecommunication, optical data storage, and optical information processing.[1] Generally, high performance electro-optic elements, especially those for frequency doubling application, require both high nonlinearities and low optical loss (high transparency). Traditional organic chromophores are organic molecules that contain electron-donating and electron-accepting groups connected via a conjugated π system, i.e., so-called $D-\pi-A$ structure. Generally, the first nonlinear hyperpolarizability β of a molecule increases with increasing length of the conjugated π system and increasing strength of the donor and/or acceptor on the basis of the two-state model.[2] Unfortunately, an increase in the β value is accompanied by a bathochromic shift due to a larger π-conjugated length and/or stronger donor and acceptor ability. Therefore, there is always a tradeoff between nonlinearity and transparency.[3,4] To resolve this problem, three kind of methods have been developed in designing organic chromophores with both high β value and good transparency, (1) employing a special conjugated bridge[5] or using different types of conjugation bridge combinations,[6] (2) optimizing the combination of different donors (D) and acceptors (A),[7] (3) employing dual (mutiple) charge-transfer chromophores, such as octupolar,[8] Λ-shaped,[9] and X-shaped,[10] etc. Willand[11] and Katz[12,13] synthesized polymers or oligomers in which $D-\pi-A$ units were assembled in a head-to-tail arrangement as a part of the backbones of the polymers or the oligomers. The polymers or oligomers that the $D-\pi-A$ units were connected to in series possessed a dramatic enhancement in the EFISH signal ($\mu\beta$) relative to an equivalent concentration of the $D-\pi-A$ unit as a monomer. However, achieving the nonlinearity−transparency tradeoff of the chromophores is still one of the major challenging topics. Therefore, we have recently designed and synthesized a series of novel chromophores (Figure 1) in which 9,10-dihydroanthracene is employed as molecular backbone, on which two $D-\pi-A$ units are incorporated in a nonconjugated fashion and fixed at nearly the same orientation. The chromophores with two $D-\pi-A$ units connected in parallel exhibited a remarkable enhancement in β.

The synthesis of the novel chromophores was achieved by a two-step reaction (Scheme 1), in which the key intermediate 1,8-dihydroxy-9,10-dihydroanthracene was prepared by the reduction of 1,8-dihydroxyl-9,10-anthraquinone with Zn/NaOH, followed by the diazo-coupling with aromatic diazonium salt solutions. Their ^{1}H NMR, ^{13}C NMR, IR, and MS spectra data were in accord with the assigned structures.

The Hyper-Rayleigh scattering (HRS) technique at 1064 nm was employed to measure the first hyperpolarizabilities (β).[14] The excitation source was a Q-switched Nd:YAG laser system (Continuum Precision II 8010) producing an $\sim$8 ns

---

[*] Corresponding author. E-mail: lugyuan@nju.edu.cn (G.-Y.L.); cyp@seu.edu.cn (Y.C.). Fax: 86-025-83317761 (G.-Y.L.).

[†] Nanjing University.

[‡] Southeast 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) Ruslim, C.; Ichimura, K. *Adv. Mater.* **2001**, *13*, 37. (e) Abbotto, A.; Beverina, L.; Bozio, R.; Bradamante, S.; Ferrante, C.; Pagani, G. A.; Signorini, R. *Adv. Mater.* **2000**, *12*, 1963. (f) Xie, H. Z.; Liu, M. W.; Wang, O. Y.; Zhang; Lee, C. S.; Hung, L. S.; Lee, S. T.; Teng, P. F.; Kwong, H. L.; Zheng, H.; Che, C. M. *Adv. Mater.* **2001**, *13*, 1245.

(2) (a) Verbiest, T.; Elshocht, S. V.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J.; Persoons, A. *Science* **1998**, *282*, 913. (b) Alain, V.; Thouin, L.; Blanchard-Desce, M.; Gubler, U.; Bosshard, C.; Günter, P.; Muller, J.; Fort, A.; Barzoukas, M. *Adv. Mater.* **1999**, *11*, 1210. (c) Beckmann, S.; Etzbach, K.-H.; Krämer, P.; Lukaszuk, K.; Matschiner, R.; Schmidt, A. J.; Schuhmacher, P.; Sens, R.; Seybold, G.; Wortmann, R.; Würthner, F. *Adv. Mater.* **1999**, *11*, 536.

(3) Ye, C. In *Organic Solids*; Wang, F., Zhu, D., Eds.; Shanghai Science Press: Shanghai, 1999; Chapter 5, p188 (in Chinese).

(4) (a) Verbiest, T.; Houbrechts, S.; Kauranen, M.; Clays, K.; Persoons, A. *J. Mater. Chem.* **1997**, *7*, 2175. (b) Cheng, L.-T.; Tam, W. *J. Phys. Chem.* **1991**, *95*, 10643. (c) Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, C. R. *J. Phys. Chem.* **1991**, *95*, 10631.

(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.

(6) 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.

(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) Zhao, B.; Lu, W.-Q.; Zhou, Z.-H.; Wu, Y. *J. Mater. Chem.* **2000**, *10*, 1513.

(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.

(9) (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.

(10) (a) Yang, Z.; Li, S.; Ye, C. *Synth. Met.* **2003**, *137*, 1519. (b) Kang, H.; Zhu, P.; Yang, Y.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 15974.

(11) Willand, C. S.; Williams, D. J. *Ber. Bunsen−Ges.* **1987**, *91*, 1304.

(12) Katz, H. E.; Schilling, M. L.; Fang, T.; Holland, W. R.; King, L.; Gordon, H. *Macromolecules* **1991**, *24*, 1201.

(13) Schilling, M. L.; Katz, H. E. *Chem. Mater.* **1989**, *1*, 668.

10.1021/cm0618042 CCC: $33.50

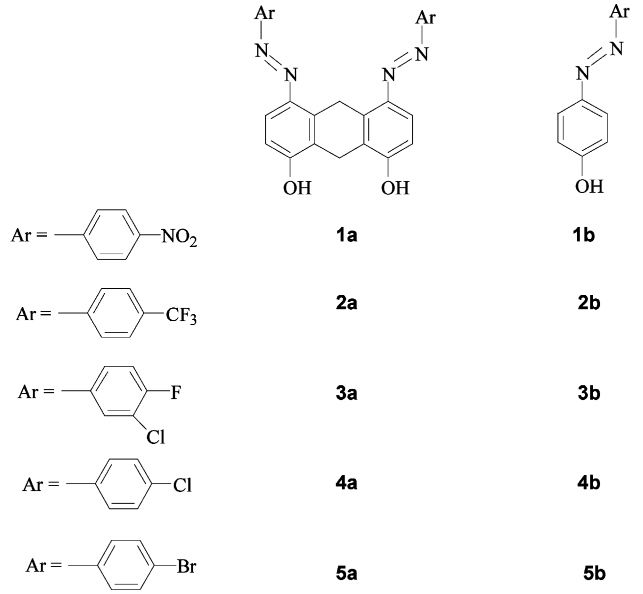
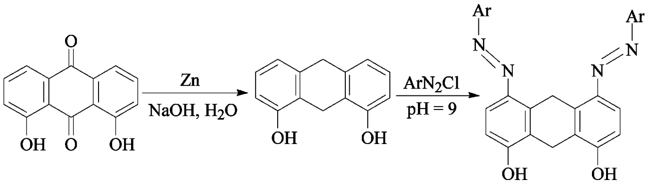


Figure 1. Chemical structures of chromophores (**1a**−**5a**) with two nonconjugated $D-\pi-A$ units and their corresponding mono-$D-\pi-A$ unit analogues (**1b**−**5b**).

Scheme 1. Synthesis of Chromophores with Two Nonconjugated $D-\pi-A$ Units



duration and ~1 cm^{-1} spectral width laser output with a repetition rate of 10 Hz. *p*-Nitroaniline (*p*NA) was used as the external reference.[15] HRS spectra shown in Figure 2 have been measured using fluorescence spectrometer (Edinburgh, FLS920).[16] We can see no fluorescence background in the HRS measurement. The fundamental limits for $\beta_{0\max}$ were also calculated. These data show that experimental β_0 values are much lower than the fundamental limit. Because the HRS signals in Figure 2(1) are quite linear with the concentrations of the solute, any concentration-dependent effect, such as the aggregation and hydrogen bonds, could be ignored. An effect on local fields from solvent could also be ignored, because the $D-\pi-A$ units of the novel chromospheres are the same as that of the corresponding monomers, and the refractive index change of the solutions for the mono-$D-\pi-A$ unit and the double $D-\pi-A$ unit chromophore is neglectable. The linear and the nonlinear properties of the novel chromophores and the corresponding mono-$D-\pi-A$ unit reference compounds are summarized in Table 1. It can be seen that the first hyperpolarizabilities (β) of the chromophores (**1a**−**5a**) with two nonconjugated $D-\pi-A$ units are remarkably increased compared with the corresponding mono-$D-\pi-A$ unit reference compounds (**1b**−**5b**). The enhancements per $D-\pi-A$ unit from 1.2 to 2.0 are observed. Because of the nonconjugated connection between two $D-\pi-A$ units, the absorption bands of new chromophores are only slightly shifted to longer wavelengths compared with the corresponding reference compounds (Table 1). For instance, their absorption maxima in THF solutions are red-shifted for only 8.2−10.7 nm. Therefore, an important advantage of these chromophores is that the resulting remarkable increase in the first hyperpolarizabilities is not accompanied by a large unfavorable red shift of the absorption band.

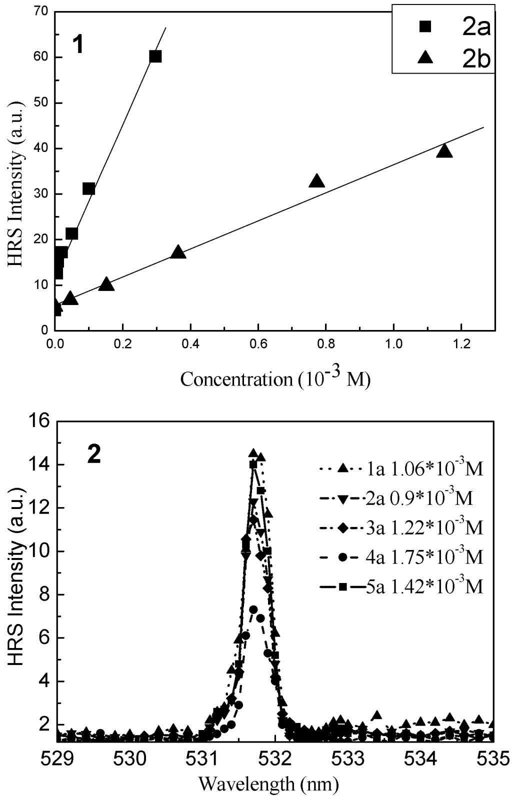


Figure 2. Measurement of the first hyperpolarizabilities (β); (1) HRS intensities versus molar concentration of **2a** and **2b**. Solid lines are linear fitting of the experimental data; (2) Hyper-Rayleigh scattering spectra of chromophores (**1a**−**5a**).

To explore the origin of the pronounced increase of the nonlinear second-order optical response of the chromophores with two nonconjugated $D-\pi-A$ units, we determined the crystal structure of **3a** (Figure 3) by Bruker CCD X-ray diffraction.[17] It is found that the two $D-\pi-A$ units in a single molecule are nearly arranged in the same direction because of the fixing action of the two methylene bridges. The crystal structure data also indicated that all atoms in each $D-\pi-A$ unit exist almost in the same plane and the planes of the two $D-\pi-A$ systems in a single molecule make an angle of 10.1° on average. Di Bella et al.[18] reported a theoretical analysis of the NLO response for a hypothetical

---

(14) (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.

(15) (a) Stähelin, M.; Burland, D. M.; Rice, J. E. *Chem. Phys. Lett.* **1992**, *191*, 245. (b) David, R. K.; Mark, A. R.; Tobin, J. M. *Chem. Rev.* **1994**, *94*, 195.

(16) Hendrickx, E.; Vinckier, A.; Clays, K.; Persoons, A. *J. Phys. Chem.* **1996**, *100*, 19672.

(17) CCDC 285027 contains the supplementary crystallograic 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 Crystallograic data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

(18) Di Bella, S.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 5842.

Table 1. Linear and Nonlinear Properties of Chromophores 1a−5a and 1b−5b

	λ_{max} (nm)[a]						
chromophore	AcOEt	THF	MeOH	red shift[b] in THF (nm)	β ($\times10^{-30}$esu)[c] in THF	β_0 ($\times10^{-30}$esu) in THF	β enhancement per D−π−A unit
1a	393.2	398.0	398.6	10.0	277	105	2.0
1b	381.5	388.0	382.9		70	28	
2a	361.0	367.0	362.7	9.7	252	117	1.2
2b	353.0	357.3	355.0		108	52	
3a	361.8	365.0	361.8	9.8	185	86	1.3
3b	352.0	355.2	353.8		72	35	
4a	361.8	366.0	361.8	10.7	142	66	1.4
4b	352.9	355.3	353.8		50	24	
5a	361.8	365.4	362.0	8.2	211	97	1.3
5b	353.5	357.2	354.6		84	42	

[a] AcOEt = ethyl acetate; THF = tetrahydrofuran; MeOH = methanol. [b] The red shift data of **a** compared with **b**. [c] At 1064 nm,with *p*-nitroaniline (*p*NA) as the external reference.

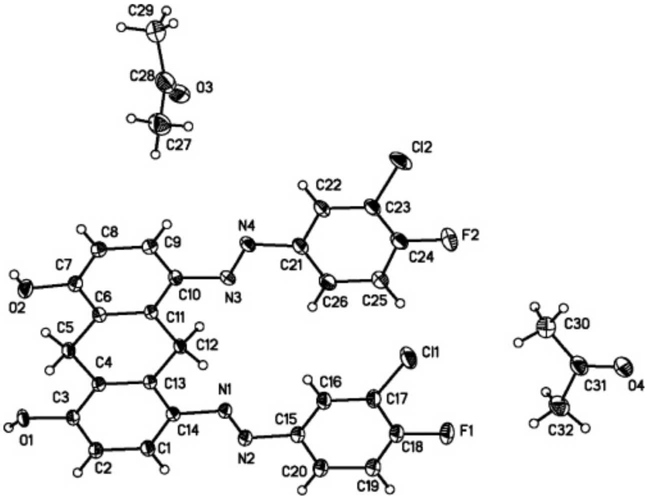


Figure 3. Molecular structure of **3a**, shown with 30% probability level displacement ellipsoids.

*p*NA dimer based on a two-level model using the SOS perturbation. According to the estimation, the NLO response would have a sharp increase when two D−π−A units of a hypothetical *p*NA dimer are arranged in the same direction and the distance between them is less than 3.3 Å. In the present case, the two D−π−A units in a single molecule are nearly arranged in the same direction and the limited distance is 2.531 Å (C4−C6) and 2.578 Å (C11−C13) from the crystal structure data. It implies that the novel chromophores can exhibit large second-order NLO responses. As we know, the signal of HRS is a kind of scattering, which is incoherent. However, in our case, the two parallel D−π−A units of the chromophores are fixed in close proximity. Thus, the radiation from the two D−π−A units would be coherent if they are close enough. The partial coherent HRS signal should be the main reason for enhancement.

In summary, we have synthesized a series of novel NLO chromophores with two non-conjugated D−π−A units oriented at nearly the same direction, and found that they possess much higher first molecular hyperpolarizability (β) values than the corresponding mono-D−π−A unit reference compounds, and these increased β values are not accompanied by a large red shift in the absorption band. We expect that this methodology may provide a new opportunity for dealing with the nonlinearity-transparency tradeoff. The synthesis of further chromophores and the detailed investigation of the reason for the dramatic increase in the first hyperpolarizability are currently in progress.

Acknowledgment. This work was supported by the Science Foundation of Jiangsu Province of China (BK2004085), the National Natural Science Foundation of China (90101018), and the National Science Fund for Distinguished Young Scholars of China (60125513).

Supporting Information Available: Synthesis and structural characterization; various spectra of the new compounds; first hyperpolarizabilities; and HRS experiments This material is available free of charge via the Internet at http://pubs.acs.org.

CM0618042