Synthesis and Two-photon Properties of New Perylene Bisimide Derivatives

Bo Gao,¹ Changgui Lu,² Jin Xu,² Fanshun Meng,¹ Yiping Cui,^{*2} and He Tian^{*1}

¹Labs for Advanced Materials and Institute of Fine Chemicals,

East China University of Science & Technology, Shanghai 200237, P. R. China

²Advanced Photonics Centre, Southeast University, Nanjing 210096, P. R. China

(Received September 27, 2006; CL-061126; E-mail: tianhe@ecust.edu.cn; cyp@seu.edu.cn)

The synthesis of some novel perylene bisimide derivatives was reported and their linear absorption, emission, and two-photon properties were measured and discussed. Two-photon cross-sections for these compounds were determined to be 8735 GM maximum (nonlinear transmittance, \approx 7 ns, 10 Hz and 850 nm). The frequency upconversion fluorescence was observed under the excitation of 850-nm-nanoseconds laser pulses with the peaks located around 669 nm.

Intense research efforts have been geared toward the synthesis of novel compounds with large two-photon absorption (TPA) cross-sections due to their potential applications in three-dimensional optical storage, two-photon optical power limiting and two-photon upconverted lasing.¹ Perylene and its derivatives are photochemically and thermally stable. They have been widely used as optical and electronic materials.² However, the two-photon properties of perylene were scarcely investigated; only very recently several perylene tetracarboxylic derivatives with large TPA cross-sections were reported by Mendonça and co-workers.³

In this letter, we design and synthesize a series of novel perylene bisimide derivatives by Sonogashira coupling reaction, which have good solubility and attractive optical properties. The molecular structures for these compounds are shown in Figure 1.

Perylene tetracarboxylic bisimides are good chromophores with high fluorescence quantum yield. However, the drawback



Figure 1. The chemical structures of PBI, TPB-PBI, TPB-PBI2, and PBI2.

is its inherent low solubility. To overcome this problem, we introduced 4-methylphenol in the bay region of perylene tetracarboxylic bisimides according to the literatures.⁴ Reaction of N-butyl-1,6,7,12-tetrakis(4-methylpheoxy)-3,4:9,10-perylene tetracarboxylic bisimide with 2-propynyl bromide and sodium hydride in DMF afforded the target compound PBI in 60% yield. Compound TPB-PBI and TPB-PBI2 were synthesized by the Sonogashira coupling reaction of PBI with 1,3,5-tris(4-bromophenyl)benzene. The reactions were carried out in triethylamine/DMF mixture for 6h under the catalyst of $Pd_2(dba)_3$. CHCl₃.⁵ The final products were purified by chromatography (silica gel) in yield of 20 and 13%, respectively. Other attempts (including Pd(PPh₃)₄ or Pd(PPh₃)₂Cl₂ with CuI in triethylamine) gave either considerable amounts of monomer PBI or dimer PBI2 as products.⁶ Compound PBI2 prepared from PBI in triethylamine/THF mixture and catalyzed by Pd(PPh₃)₂Cl₂/ CuI under dry air gave the yield of 60%. All compounds were characterized by ¹H NMR and mass spectra.⁷

The linear optical properties of PBI, TPB-PBI, TPB-PBI2, and PBI2 were studied in CH_2Cl_2 and the data are listed in Table 1. As shown in Figure 2, all compounds show absorption maximum around 573 nm and emission maximum around 603 nm with a shoulder emission at 650 nm; this shows the negligible effect of the different imide substituents on the absorption and emission properties of the perylene bisimide chromophore because of the nodes of the HOMO and LUMO orbital at the imide nitrogen. Therefore, perylene bisimides can be regarded as a closed chromophoric system with an S0–S1 transition (polarized along the extended molecular axis) whose intensity and position remain unaltered by the respective imide substituents.⁸

TPA cross-sections for these compounds in CH_2Cl_2 were determined by nonlinear transmittance method with ≈ 7 ns, 10 Hz and 850-nm-nanoseconds laser pulses.⁷ The concentration



Figure 2. Normalized absorption and fluorescence spectra of PBI, TPB-PBI, TPB-PBI2, and PBI2 in CH₂Cl₂.

Table 1. The optical properties of PBI, TPB-PBI, TPB-PBI2, and PBI2

Compound	$\lambda_{ m abs}^{ m OPA}$ /nm	\mathcal{E} (10 ⁴ mol L ⁻¹ cm ⁻¹)	$\lambda_{ m em}^{ m OPF}$ /nm	Φ^{a}	$egin{array}{c} eta\ \mathrm{cm}\cdot\mathrm{GW}^{-1} \end{array}$	$\sigma_2{}^{\mathrm{b}}$ /GM	$\lambda^{ ext{TPF c}}$ /nm
PBI	572	4.5	602	0.89	0.4	3106	669
TPA-PBI	572	3.8	603	0.81	0.5	3882	—
TPA-PBI2	572	4.1	603	0.74	0.45	8735	660
PBI2	574	6.1	605	0.70	0.6	4659	669

^aFluorescence quantum yield determined using *N*,*N*-dibutyl-1,6,7,12-tetrachloro-3,4:9,10-tetracarboxylic bisimide as the standard.⁸ ($\Phi = 92\%$ in CHCl₃). ^bTPA cross sections in CH₂Cl₂ measured at 850 nm (\approx 7 ns). ^cTPF in CH₂Cl₂ excited by 850-nm-nanoseconds laser pulses, C = 0.005 M for PBI and PBI2, 0.002 M for TPB-PBI2, \approx 1-mm propagation.

for TPA measurements was fixed at 0.005 M (0.002 M for compound TPB-PBI2) in CH₂Cl₂. Typical TPA optical power limiting curve at 850 nm (taking TPB-PBI2 for example) is included in Figure 3. TPA cross-sections values, δ (given in GM = 10⁻⁵⁰ cm⁴ s photon⁻¹ molecule⁻¹) for compound PBI, TPB-PBI, TPB-PBI2, and PBI2 were measured to be 3106, 3882, 8735, and 4659 GM, respectively. The large values of TPA cross-sections are probably affected by excited state absorption (ESA) as "effective" TPA cross-sections.⁹ Owing to the multi-branched structure, TPA cross-section of TPB-PBI2 is larger than that of PBI and TPB-PBI. Compound PBI2 has larger TPA cross-section compared to PBI, may result from the slightly increasing conjugated system which is due to the acetylenic homo-coupling.

A red fluorescence emission could be observed from a sample solution excited by 850-nm-nanosecond laser pulses through 2-PA process. The frequencies of the upconversion fluorescence emission peak are listed in Table 1. All of the emission peaks get slightly red shift because of the strong re-absorption effect in the short wavelength range of the emission band, when the fluorescence beams propagate through such highly concentrated sample medium.

In summary, a series of novel perylene bisimide derivatives have been synthesized and their linear and two-photon photophysical properties were studied. These compounds have relatively large two-photon absorption cross-sections, which have potentials for application as novel TPA materials with high photostability, thermal stability, and fluorescence quantum yields.

This work was supported by the National Natural Science Foundation of China (Nos. 10374013 and 6050811) and Shanghai Scientific Committee.



Figure 3. Measured output intensity versus input intensity of the 850-nm laser pulses of compound TPB-PBI2.

References and Notes

- a) W. Denk, J. H. Strickler, W. W. Webb, Science 1990, 248, 73. b) S. Kawata, Y. Kawata, Chem. Rev. 2000, 100, 1777. c) N. Kawatsuki, T. Tachibana, K. Kamada, Adv. Mater. 2005, 17, 1886. d) K. Ohta, K. Kamada, J. Chem. Phys. 2006, 124, 124303. e) X. Meng, K. Tanaka, S. Murai, K. Fujita, K. Miura, K. Hirao, Opt. Lett. 2006, 31, 2867. f) T. R. Krishna, M. Parent, M. H. V. Werts, L. Moreaux, S. Gmouh, S. Charpak, A. M. Caminade, J. P. Majoral, M. Blanchard-Desce, Angew. Chem., Int. Ed. 2006, 45, 4645. g) Q. Zheng, G. S. He, A. Baev, P. N. Prasad, J. Phys. Chem. B 2006, 110, 14604. h) S. Kato, T. Matsumoto, T. Ishi-i, T. Thiemann, M. Shigeiwa, H. Gorohmaru, S. Maeda, Y. Yamashita, S. Mataka, Chem. Commun. 2004, 2342. i) S. Kato, T. Matsumoto, M. Shigeiwa, H. Gorohmaru, S. Maeda, T. Ishi-i, S. Mataka, Chem. Eur. J. 2006, 12, 2303. j) Q. Zheng, G. S. He, C. Lu, P. N. Prasad, J. Mater. Chem. 2005, 15, 3488. k) G. S. He, T.-C. Lin, S.-J. Chung, Q. Zheng, C. Lu, Y. Cui, P. N. Prasad, J. Opt. Soc. Am. B 2005, 22, 2219. 1) F. S. Meng, B. Li, S. Qian, K. Chen, H. Tian, Chem. Lett. 2004, 33, 470. m) J. Li, F. S. Meng, H. Tian, J. Mi, W. Ji, Chem. Lett. 2005, 34, 922. n) J. L. Hua, B. Li, F. S. Meng, F. Ding, S. X. Qian, H. Tian, Polymer 2004, 45, 7143.
- 2 For examples: a) J. van Herrikhuyzen, A. Syamakumari, A. P. H. J. Schenning, E. W. Meijer, J. Am. Chem. Soc. 2004, 126, 10021. b) C. Hippius, F. Schlosser, M. O. Vysotsky, V. Bohmer, F. Würthner, J. Am. Chem. Soc. 2006, 128, 3870. c) T. Ishi-i, K. Murakami, Y. Imai, S. Mataka, Org. Lett. 2005, 7, 3175.
- 3 a) S. L. Oliveira, D. S. Corrêa, L. Misoguti, C. J. L. Constantino, R. F. Aroca, S. C. Zilio, C. R. Mendonça, *Adv. Mater.* 2005, *17*, 1890. b) L. De Boni, C. J. L. Constantino, L. Misoguti, R. F. Aroca, S. C. Zilio, C. R. Mendonça, *Chem. Phys. Lett.* 2003, *371*, 744. c) D. S. Corrêa, S. L. Oliveira, L. Misoguti, S. C. Zilio, R. F. Aroca, C. J. L. Constantino, C. R. Mendonça, *J. Phys. Chem. A* 2006, *110*, 6433.
- 4 a) G. Seybold, G. Wagenblast, *Dyes Pigm.* 1989, *11*, 303. b) D. Dotcheva, M. Klapper, K. Müllen, *Macromol. Chem. Phys.* 1994, *195*, 1905. c) L. Fan, Y. Xu, H. Tian, *Tetrahedron Lett.* 2005, *46*, 4443.
- 5 J. A. Faiz, N. Spencer, Z. Pikramenou, Org. Biomol. Chem. 2005, 3, 4239.
- 6 a) W.-M. Dai, A. Wu, *Tetrahedron Lett.* 2001, 42, 81. b) D. García, A. M. Cuadro, J. Alvarez-Builla, J. J. Vaquero, *Org. Lett.* 2004, 6, 4175.
- 7 The detailed synthesis of the compounds and the measurement of 2PA cross sections are shown in the Supporting Information, which is available electronically on the CSJ-Journal Website http://www.csj.jp/journals/chem-lett/index.html.
- 8 F. Würthner, Chem. Commun. 2004, 1564.
- 9 a) O.-K. Kim, K.-S. Lee, H. Y. Woo, K.-S. Kim, G. S. He, J. Swiatkiewicz, P. N. Prasad, *Chem. Mater.* 2000, *12*, 284.
 b) R. L. Sutherland, M. C. Brant, D. G. McLean, J. E. Rogers, B. Sankaran, S. M. Kirkpatrick, P. A. Fleitz, *SPIE Proc.* 2004, *5516*, 79. c) K. Kamada, *SPIE Proc.* 2004, *5516*, 97.