Singlet oxygen generation by two-photon excitation of porphyrin derivatives having two-photon-absorbing benzothiadiazole chromophores†

Tsutomu Ishi-i,*^{ab} Yoshiki Taguri,^c Shin-ichiro Kato,^c Motoyuki Shigeiwa,*^d Hideki Gorohmaru,^d Shuuichi Maeda^d and Shuntaro Mataka^b

Received 26th March 2007, Accepted 8th May 2007 First published as an Advance Article on the web 18th May 2007 DOI: 10.1039/b704499b

Porphyrin derivatives with four two-photon absorbing 2,1,3-benzothiadiazole chromophores at the *meso* positions provide large two-photon absorption cross-sections up to 735 GM as well as large quantum yields of one-photon singlet oxygen sensitization of *ca.* 0.7, leading to generation of singlet oxygen by two-photon excitation of 800 nm. The two-photon singlet oxygen sensitization is discussed on the basis of a parameter of the normalized oxygen luminescence intensity obtained from the two-photon experiment.

Introduction

Two-photon absorbing (TPA) organic molecules have been of much interest in recent years in view of their potential applications for optical power limitation,¹ microfabrication,² three-dimensional optical data storage,³ two-photon laser scanning fluorescence imaging,⁴ and photodynamic therapy.⁵ In particular, in photodynamic therapy, the two-photon excitation technique using red and near-IR region light sources has three advantages: i) increase of penetration depth in tissues, ii) less photodamage, and iii) pin-point excitation by a focused laser beam, which can not be achieved by linear onephoton excitation. Thus, in two-photon-induced photodynamic therapy, TPA organic molecules are required to have both large TPA cross-sections in the red and near-IR region and high quantum yields of singlet oxygen generation. Till now, a limited number of research groups have succeeded in two-photon singlet oxygen sensitization by using difuranonaphthalene,⁶ vinylbenzene,⁶⁻⁹ ethynylbenzene,⁹ and porphyrin derivatives.10-15

The first persuasive report on two-photon sensitized singlet oxygen generation was developed by Ogilby's groups. Difuranonaphthalene and distyrylbenzene derivatives, which provide moderate efficiencies on one-photon singlet oxygen sensitization and two-photon absorbing, display singlet oxygen sensitization by two-photon excitation as monitored by singlet oxygen luminescence.⁶ Later on, they systematically studied a series of water soluble porphyrins and vinylbenzenes.⁷

^cInterdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-koh-en, Kasuga 816-8580, Japan Recently, Rebane's group reported that π -conjugated porphyrin dimers show extremely high TPA cross-sections and high quantum yields of one-photon singlet oxygen sensitization.^{11,12} Correlation between the two parameters 'TPA cross-section and quantum yield of one-photon singlet oxygen sensitization' was discussed to characterize molecular ability in two-photon-induced photodynamic therapy.¹² Another approach was performed by Fréchet's group using fluorescence resonance energy-transfer (FRET) as a key step. In a porphyrin derivative containing eight two-photon absorbing AF-343 chromophores, singlet oxygen can be generated by two-photon excitation of the AF-343 chromophore followed by the subsequent FRET to the porphyrin core.¹³ Recently, this system was developed for use in an aqueous medium.¹⁴

On the other hand, 4,7-diaryl-2,1,3-benzothiadiazoles are known as strongly fluorescent dyes.¹⁶ Further, an electronwithdrawing 2,1,3-benzothiadiazole (BTD) unit was used as an important spacer in semiconducting oligomers.¹⁷ Recently, we have developed BTD-based dyes to produce functional materials such as dichroic fluorescent materials in liquid crystal displays,¹⁸ and light-harvesting antennae as well as energy-transfer reagents in fullerene-dyad systems.¹⁹ More recently, we have created BTD-based two-photon absorbing molecules with red-fluorescent ability on the basis of a combination of the electron-withdrawing BTD unit and electron-donating amino groups to enhance the intramolecular charge transfer character.²⁰ This finding led us to newly develop BTD-based dyes to two-photon singlet oxygen sensitizers. The strategy is based on the combination of a two-photon absorbing BTD-based unit and a singlet oxygen sensitizing porphyrin (Fig. 1). In this article, we report that porphyrin derivatives having four diphenylamino groupcontaining BTD chromophores at the meso positions show high TPA activity as well as one- and two-photon oxygen sensitization. The two-photon singlet oxygen sensitization is discussed on the basis of the quantum yield of one-photon excited singlet oxygen generation and the two-photon absorption cross-section as well as the parameter of the normalized oxygen luminescence intensity obtained from the two-photon experiment.

^aDepartment of Biochemistry and Applied Chemistry, Kurume National College of Technology, 1-1-1 Komorino, Kurume, 830-8555, Japan. E-mail: ishi-i@kurume-nct.ac.jp; Fax: +81 942 35 9400; Tel: +81 942 35 9404

^bInstitute for Materials Chemistry and Engineering (IMCE), Kyushu University, 6-1 Kasuga-koh-en, Kasuga 816-8580, Japan

^dMitsubishi Chemical Group Science and Technology Research Center, Inc., 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan

[†] Electronic supplementary information (ESI) available: synthesis of materials, UV/Vis linear absorption, one-photon excited fluorescence, fluorescence excitation, and two-photon excited fluorescence spectra. See DOI: 10.1039/b704499b



Fig. 1 Structures of TPP, ZnTPP, 1a, 1b, 1c, 2a, and 2b.

Results and discussion

Preparation

Porphyrin derivatives 1a having four (diphenylamino)phenyl group-containing BTD chromophores (DPAP-BTD) and 1b having four (diphenylamino)phenylethenyl group-containing BTD chromophores (DPAPE-BTD) were obtained from a porphyrin derivative having four phenylboronate moieties, **6**,²¹ by Suzuki coupling reactions with the corresponding BTD bromides 4 and 5, respectively, in the presence of a palladium(0) catalyst (Scheme 1). Subsequently, 1a was derived to the corresponding zinc complex 1c by treatment with zinc acetate. The synthetic intermediates 4 and 5 were derived from 4,7-dibromo-2,1,3-BTD 3²² by Suzuki and Heck coupling reactions, respectively. Diphenylamino group-containing BTD dyes 2a and 2b, which correspond to the side chain moieties in 1a and 1b, respectively, were prepared as reference compounds (Scheme 1). Identification of **1a-c** was performed by means of spectroscopic methods, MALDI-TOF mass spectrometry, and elemental analysis.

One-photon absorption and emission properties

The UV/Vis linear absorption spectra of 1a in both toluene and chloroform show a Soret band around 430 nm and Q bands between 550–650 nm (Fig. 2 and Table 1). In addition, a broad charge-transfer (CT) transition band arising from the donor–acceptor DPAP-BTD chromophore in 1a around 440 nm, which coincides with that of reference 2a (ESI†), is overlapped with the intense Soret band.¹⁹ In 1b with an additional olefinic spacer, the CT band from the DPAPE-BTD chromophore shifts bathochromically around to 465 nm, whereas the Soret and Q bands remain at the same positions



Scheme 1 Preparation of 1a, 1b, 1c, 2a, and 2b.

(Table 1 and ESI[†]). The Soret band in **1a** and **1b** was broadened along with a bathochromic shift of *ca*. 10 nm compared to that of TPP, indicating an electronic perturbation from the BTD chromophore to the porphyrin core.²³ Similar UV/Vis spectral behavior was obtained from a comparison of **1c** with ZnTPP (Fig. 3, Table 1, and ESI[†]).²⁴ The strong absorption around 400 nm including both the Soret and DPAP-BTD/DPAPE-BTD bands in **1a–c** is very suitable for



Fig. 2 UV/Vis linear absorption spectra of 1a, 1b, and TPP in toluene (1.0 μ M).

two-photon excitation at 800 nm by using a Ti : sapphire laser source.

References 2a and 2b are strongly fluorescent, emitting an orange-red color with good quantum yields of 0.36-0.72 (Table 2).^{19,20} Upon excitation of the DPAP-BTD and DPAPE-BTD chromophores in 1a and 1b, respectively, such red-orange emissions were quenched completely. Only weak emissions from the porphyrin core were observable around 660 and 720 nm as found in TPP (Fig. 4, Table 2, and ESI[†]). The fluorescent quantum yields (0.06-0.08) in 1a and 1b are comparable to those (0.04-0.05) of the parent TPP (Table 2). Fluorescence excitation spectra of 1a and 1b at he porphyrin emission bands almost coincide with the UV/Vis linear absorption spectra (ESI[†]). The foregoing results indicate that in 1a and 1b the singlet excited state of the DPAP-BTD/DPAPE-BTD moiety is guenched by the porphyrin core via intramolecular energy transfer,²³ then the generated singlet excited state of the porphyrin chromophore converts to a triplet excited state via intersystem crossing as found in many porphyrin derivatives such as TPP. Similar energy transfer and subsequent intersystem crossing are observable in zinc complex 1c (Table 2 and ESI[†]).



Fig. 3 UV/Vis linear absorption spectra of 1c and ZnTPP in chloroform (1.0 μ M).

Table 2 One-photon and two-photon excited fluorescence spectral data, and two-photon absorption cross-sections (δ) of **1a**, **1b**, **1c**, **2a**, **2b**, TPP, and ZnTPP in toluene and chloroform

	Toluene			Chloroform				
Comp.	$\lambda_{\text{SPEF}}^{a}$	$\Phi_{\mathrm{FL}}{}^{b}$	δ^c/GM	$\lambda_{2\text{PEF}}^{g}$	$\lambda_{\text{SPEF}}^{a}$	$\Phi_{\mathrm{FL}}{}^{b}$	δ^{c}/GM	$\lambda_{2\text{PEF}}^{g}$
1a	658, 721	0.07	d		658, 719	0.06	441 ^f	665, 722
1b	659, 721	0.08	d		658, 720	0.06	735 ^f	666, 724
1c	607, 653	0.04	d		614, 656	0.04	469 ^f	621, 660
2a	573	0.72	12^e	569	615	0.51	7.4^{e}	617
2b	588	0.70	23^e	598	635	0.36	38 ^e	647
TPP	653, 717	0.04			653, 715	0.05	2.2^{e}	675 (sh),
								718
ZnTPP	598, 647	0.01			603, 653	0.02		
a F 1								

^{*a*} Fluorescent maxima obtained from one-photon excitation (around Q_1 band: 550–558 nm) at 1.0 μ M. ^{*b*} Rhodamine B ($\Phi_{FL} = 0.65$) was used as a reference. ^{*c*} Two-photon absorption cross-section (δ) at 800 nm was estimated by using AF-50 ($\delta = 45$ GM) as a reference. ^{*d*} Due to the low solubility of **1a**, **1b**, and **1c** (<0.01 mM) in toluene, the σ values could not be measured. ^{*c*} Measured at 5.0 mM. ^{*f*} Measured at 0.1 mM. ^{*s*} Fluorescent maxima obtained from two-photon excitation at 800 nm.

Two-photon absorption and emission properties

The two-photon excited absorption and fluorescence spectral properties of **1a–c** are summarized in Table 2. By two-photon

Table 1 One-photon absorption spectral data of 1a, 1b, 1c, TPP, and ZnTPP (1.0 µM), and 2a and 2b (10.0 µM) in toluene and chloroform

Solvent	Comp.	$\lambda_{\rm max}/{\rm nm} \ (10^{-4} \ e/{\rm M}^{-1} \ {\rm cm}^{-1})$						
		DPAP-BTD/DPAPE-BTD	Soret	Q1	Q ₂	Q ₃		
Toluene	1a	а	429 (24.3)	557 (1.74)	592 (0.48)	652 (0.55)		
	1b	а	428 (18.6)	557 (2.42)	594 (0.58)	652 (0.63)		
	TPP		419 (45.0)	549 (0.69)	590 (0.44)	648 (0.36)		
	2a	439 (1.28)	_					
	2b	464 (2.32)	_					
Chloroform	1a	`a	427 (26.7)	558 (1.74)	594 (0.50)	650 (0.55)		
	1b	а	427 (17.8)	558 (2.41)	592 (0.61)	650 (0.59)		
	1c	а	430 (26.4)	557 (2.29)	599 (1.22)			
	TPP	_	418 (39.7)	550 (0.49)	590 (0.31)	648 (0.32)		
	ZnTPP	_	424 (46.0)	554 (1.90)	595 (0.44)			
	2a	440 (1.25)	—					
	2b	465 (2.37)						
^a The DPAP-BT	D/DPAPE-BTD	absorption band overlapped with the	e Soret band.					



Fig. 4 One-photon excited fluorescence spectra of 1a, 1b, and TPP in toluene (1.0 μ M). The fluorescence spectra were obtained by excitation around Soret band (at 429 nm for 1a, at 428 nm for 1b, and at 419 nm for TPP).

excitation with 800 nm laser pulses, **1a** and **1b** emitted, as expected, frequency upconverted fluorescence from the porphyrin core around 665 and 720 nm (ESI[†]), which shifted slightly to 3–8 nm longer wavelength compared with those obtained by one-photon excitation (Table 2).²⁵ In zinc complex **1c**, the frequency upconverted fluorescence was observable also upon excitation at 800 nm (Table 2).

Two-photon absorption cross-sections (δ) at 700–900 nm were measured by using an open aperture Z-scan method with wavelength variable femtosecond laser pulses. In toluene, the δ values in **1a–c** could not be measured because of their low solubility in toluene (<0.01 mM). In contrast, **1a–c** show good solubility in chloroform (~1.0 mM). In chloroform, plots of two-photon absorption cross-sections against the excitation wavelength exhibited maxima around 800–825 nm (Fig. 5),²⁶ which correspond to the CT transition of DPAP-BTD/DPAPE-BTD chromophores observed in the UV/Vis linear



Fig. 5 Two-photon absorption spectra of **1a**, **1b**, and **1c** in chloroform. The σ value (2130 GM) of **1b** at 760 nm is out of the range of the plot area to retain clarity of the other data.

absorption spectra. The TPA maxima were observed at shorter wavelength positions compared to the one-photon absorption maxima, because the TPA-allowed excited state exists above the one-photon absorption excited state for this kind of centrosymmetrical molecule. The significant increase of δ values observed below 760 nm is interpreted as one-photon resonance enhancement on two-photon transition at a short wavelength near the single-photon transition, as reported previously (Fig. 5).²⁷

At 800 nm, **1a** displays a maximum δ value of 441 GM, which is estimated on the basis of AF-50 (45 GM) used as a TPA benchmark.²⁸ By introducing an olefinic spacer in **1b**, the δ value at 800 nm increases to 735 GM based on an expansion of the π -system (Table 2).²⁶ Zinc complex **1c** displays a maximum δ value of 492 GM at the longer wavelength of 825 nm, which is larger than that (441 GM) of free base porphyrin 1a (Fig. 5). A comparison with TPP having a low δ value of 2.2 GM²⁹ indicates that the large TPA cross-sections in **1a-c** are attributed to the two-photon absorbing nature of the peripheral DPAP-BTD/DPAPE-BTD moiety.²⁰ Compared to references 2a and 2b (7-12 and 23-38 GM, respectively), the δ values in **1a–c** are larger by one order of magnitude (Table 2), indicating an electron-donating effect of the porphyrin core and a cooperative enhancement effect between the four DPAP-BTD/DPAPE-BTD chromophores in the star-shaped structure.³⁰ The porphyrin core is conjugated with the electron-withdrawing BTD moieties by through-bond electronic communication.¹⁵ Such electronic communication can not be created in non-conjugated system.^{13,31}

Singlet oxygen sensitization

Singlet oxygen generation by one- and two-photon excitation of 1a and 1b was measured in toluene. The quantum yield of one-photon singlet oxygen sensitization (Φ_{Λ}) was estimated by monitoring oxygen luminescence at 1275 nm generated by the excitation of 400 nm laser pulses (Fig. 6a). The Φ_{Δ} values of 0.68 in 1a and 0.65 in 1b are comparable to that (0.70) of the parent TPP (Table 3),³² indicating the good performance of 1a and 1b as singlet oxygen sensitizers. In 1c, reliable data could not be obtained because of the very low solubility of 1c in toluene. In chloroform, **1c** displays a Φ_{Δ} value of 0.62, which seems to include a solvent effect of the chloroform.³³ The DPAP-BTD/DPAPE-BTD moiety in 1a-c scarcely affects the oxygen sensitizing nature of the central porphyrin core. A figure of δ × Φ_{Δ} expresses the merit of singlet oxygen generation by two-photon excitation.¹² The $\delta \times \Phi_{\Delta}$ values of 300 GM in 1a and 478 GM in 1b are larger by two orders of magnitude than that (1.5) of TPP (Table 3), indicating the excellent performance of 1a and 1b as two-photon singlet oxygen sensitizers.

In **1a** and **1b**, the oxygen luminescence is detected actually by two-photon excitation of 800 nm laser pulses even at a low concentration of ~10 μ M. In contrast, such oxygen luminescence in TPP could not be detected at the same concentration, and reliable detection required a high concentration of >5 mM (Fig. 6b). The high performance in the two-photon-induced singlet oxygen generation could be ascribed to the throughbond electronic communication between the porphyrin core



Fig. 6 Oxygen luminescence spectra obtained from (a) 400 nm and (b) 800 nm laser irradiation of air-saturated toluene solutions of 1a (16.7 μ M), 1b (11.3 μ M), and TPP (12.5 μ M for 400 nm and 5.0 mM for 800 nm).

 Table 3
 Singlet oxygen generation efficiency by one-photon (400 nm) and two-photon (800 nm) excitation in toluene

Comp.	$\begin{array}{c} \text{One-photon} \\ \varPhi_{\Delta}{}^a \end{array}$	Two-photon δ^b/GM	$\delta \times \Phi_{\Delta}{}^{c}/\mathrm{GM}$	Luminescence intensity ^d
1a	0.68	441	300	298
1b	0.65	735	478	547
1c	0.62^{e}	469	291 ^e	264 ^e
TPP	0.70^{f}	2.2	1.5	1.5

^{*a*} Quantum yield of singlet oxygen generation (Φ_{Δ}) was estimated on the basis of the intensity of singlet oxygen luminescence at 1275 nm (at 16.7 μ M for **1a**, at 11.3 μ M for **1b**, at 37.5 μ M for **1c**, and at 12.5 μ M for TPP). ^{*b*} Two-photon absorption cross-section (δ) at 800 nm was estimated in chloroform by using AF-50 ($\delta = 45$ GM) as a reference. In toluene, the δ values of **1a–c** could not be measured because of the low solubility. ^{*c*} Figure of merit for twophoton singlet oxygen sensitization. ^{*d*} The intensity of singlet oxygen luminescence at 1275 nm normalized by the concentration term (at 16.7 μ M for **1a**, at 11.3 μ M for **1b**, at 37.5 μ M for **1c**, and at 5.0 mM for TPP). The normalized value in TPP was given to be 1.5. ^{*e*} Due to the very low solubility of **1c** in toluene, the measurement was performed in chloroform at 37.5 μ M. ^{*f*} A reported value in reference 32.



Fig. 7 Energy diagram for singlet oxygen generation by two-photon excitation of the benzothiadiazole moiety (DPAP-BTD/DPAPE-BTD) in **1a–c**.

and the BTD moieties in **1a** and **1b**.¹⁵ The oxygen luminescence intensity normalized by a concentration term indicates the order of two-photon oxygen sensitization to be TPP (1.5) << **1a** (298) < **1b** (547) (Table 3). We compared the $\delta \times \Phi_{\Delta}$ values (TPP (1.5 GM) << **1a** (300 GM) < **1b** (478 GM) in Table 3) with these normalized luminescence intensity values. Although the coincidence is not perfect, the trend can be seen clearly. This result demonstrates that Kasha's rule is valid in this oxygen sensitization process irrespective of the excitation method and excited state.^{8,34}

The energy diagram for singlet oxygen generation by twophoton excitation in 1a-c is shown in Fig. 7. The singlet excited state of the benzothiadiazole chromophore generated by two-photon excitation is converted efficiently to the singlet excited state of the porphyrin chromophore, from which the corresponding triplet state is given *via* intersystem crossing to generate singlet oxygen.

Conclusions

In conclusion, we have demonstrated that porphyrin derivatives with four benzothiadiazole chromophores generate singlet oxygen by two-photon excitation at 800 nm. The present two-photon-induced singlet oxygen generation is ascribed to a combination of the two-photon absorbing nature of the peripheral benzothiadiazole dye and the singlet oxygen sensitizing ability of the porphyrin core. This is a new application of benzothiadiazole dye as a functional material. The two-photon oxygen sensitization can be analyzed by a simple parameter of oxygen luminescence intensity obtained only from the two-photon excitation experiment. We believe that the present system will be developed for photodynamic therapy initiated by two-photon excitation.

Acknowledgements

We thank Professor Dr Shigeori Takenaka (Kyushu Institute of Technology) and Dr Keiichi Otsuka (Kyushu University) for the measurement of MALDI-TOF-MS. This work was partially supported by Research for Promoting Technological Seeds, Japan Science and Technology Cooperation (JST).

- 1 G. S. He, J. D. Bhawalkar, C. F. Zhao and P. N. Prasad, *Appl. Phys. Lett.*, 1995, 67, 2433–2435.
- 2 B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I.-Y. S. Lee, D. M. McCord-Maughon, J. Qin, H. Röckel, M. Rumi, X.-L. Wu, S. R. Marder and J. W. Perry, *Nature*, 1999, **398**, 51–54.
- 3 D. A. Parthenopoulos and P. M. Rentzepis, *Science*, 1989, 245, 843–845.
- 4 W. Denk, J. H. Strickler and W. W. Webb, Science, 1990, 248, 73-76.
- 5 (a) C. W. Spangler, J. R. Starkey, F. Meng, A. Gong, M. Drobizhev, A. Rebane and B. Moss, *Proc. SPIE–Int. Soc.* Opt. Eng., 2005, 5689, 141–148; (b) F.-L. Mao, Q.-R. Xing, K. Wang, L.-Y. Lang, Z. Wang, L. Chai and Q.-Y. Wang, Opt. Commun., 2005, 256, 358–363; (c) K. Ogawa, H. Hasegawa, Y. Inaba, Y. Kobuke, H. Inoue, Y. Kanemitsu, E. Kohno, T. Hirano, S. Ogura and I. Okura, J. Med. Chem., 2006, 49, 2276–2283; (d) D. Gao, R. R. Agayan, H. Xu, M. A. Philbert and R. Kopelman, Nano Lett., 2006, 6, 2383–2386; (e) J. W. Snyder, E. Skovsen, J. D. C. Lambert, L. Poulsen and P. R. Ogilby, Phys. Chem. Chem. Phys., 2006, 8, 4280–4293.
- 6 P. K. Frederiksen, M. Jørgensen and P. M. Ogilby, J. Am. Chem. Soc., 2001, 123, 1215–1221.
- 7 P. K. Frederiksen, S. P. Mcllroy, C. B. Nielsen, L. Nikolajsen, E. Skovsen, M. Jørgensen, K. V. Mikkelsen and P. R. Ogilby, J. Am. Chem. Soc., 2005, 127, 255–269.
- 8 (a) C. B. Nielsen, M. Johnsen, J. Arnbjerg, M. Pittelkow, S. P. McIlroy, P. R. Ogilby and M. Jørgensen, J. Org. Chem., 2005, 70, 7065–7079; (b) J. Arnbjerg, M. Johnsen, P. K. Frederiksen, S. E. Braslavsky and P. R. Ogilby, J. Phys. Chem. A, 2006, 110, 7375–7385.
- 9 S. P. McIlroy, E. Clo, L. Nikolajsen, P. K. Frenderiksen, C. B. Nielen, K. V. Mikkelsen, K. V. Gothelf and P. R. Ogilby, *J. Org. Chem.*, 2005, **70**, 1134–1146.
- (a) A. Karotki, M. Kruk, M. Drobizhev, A. Rebane, E. Nickel and C. W. Spangler, *IEEE J. Sel. Top. Quantum Electron.*, 2001, 7, 971–975; (b) M. Drobizhev, A. Karotki, M. Kruk, Y. Dzenis, A. Rebane, F. Meng, E. Nickel and C. W. Spangler, *Proc. SPIE–Int. Soc. Opt. Eng.*, 2003, **5211**, 63–74.
- 11 M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor and H. L. Anderson, J. Am. Chem. Soc., 2004, 126, 15352–15353.
- 12 M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor and H. L. Anderson, *J. Phys. Chem. B*, 2005, **109**, 7223–7236.
- 13 W. R. Dichtel, J. M. Serin, C. Edder, J. M. J. Fréchet, M. Matuszewski, L.-S. Tan, T. Y. Ohulchanskyy and P. N. Prasad, J. Am. Chem. Soc., 2004, 126, 5380–5381.
- 14 M. A. Oar, J. M. Serin, W. R. Dichtel, J. M. J. Fréchet, T. Y. Ohulchanskyy and P. N. Prasad, *Chem. Mater.*, 2005, 17, 2267–2275.
- 15 M. Morone, L. Beverina, A. Abbotto, F. Silvestri, E. Collini, C. Ferrante, R. Bozio and G. A. Pagani, *Org. Lett.*, 2006, 8, 2719–2722.
- 16 (a) J.-M. Raimundo, P. Blanchard, H. Brisset, S. Akoudad and J. Roncali, Chem. Commun., 2000, 939–940; (b) M. Akhtaruzzaman, M. Tomura, M. B. Zaman, J. Nishida and Y. Yamashita, J. Org. Chem., 2002, 67, 7813–7818; (c) M. J. Edelmann, J.-M. Raimundo, N. F. Utesch, F. Diederich, C. Boudon, J.-P. Gisselbrecht and H. Gross, Helv. Chim. Acta, 2002, 85, 2195–2213; (d) K. R. J. Thomas, M. Lin, J. T. Velusamy, Y.-T. Tao and C.-H. Chuen, Adv. Funct. Mater., 2004, 14, 83–90; (e) M. Velusamy, K. R. Justin Thomas, J. T. Lin, Y.-C. Hsu and L.-C. Ho, Org. Lett., 2005, 7, 1899–1902.
- 17 (a) C. Kitamura, S. Tanaka and Y. Yamashita, Chem. Mater., 1996, **8**, 570–578; (b) H. A. M. van Mullekom, J. A. J. M.

Vekemans and E. W. Meijer, *Chem.-Eur. J.*, 1998, **4**, 1235–1243; (c) C. G. Bangcuyo, U. Evans, M. L. Myrick and U. H. F. Bunz, *Macromolecules*, 2001, **34**, 7592–7594; (d) Y.-H. Niu, J. Huang and Y. Cao, *Adv. Mater.*, 2003, **15**, 807–811.

- 18 (a) X. Zhang, H. Gorohmaru, M. Kadowaki, T. Kobayashi, T. Ishi-i, T. Thiemann and S. Mataka, J. Mater. Chem., 2004, 14, 1901–1904; (b) X. Zhang, R. Yamaguchi, K. Moriyama, M. Kadowaki, T. Kobayashi, T. Ishi-i, T. Thiemann and S. Mataka, J. Mater. Chem., 2005, 15, 736–740.
- (a) S. D. A. Sandanayaka, K. Matsukawa, T. Ishi-i, S. Mataka, Y. Araki and O. Ito, *J. Phys. Chem. B*, 2004, **108**, 19995–20004; (b)
 S. D. A. Sandanayaka, Y. Araki, Y. Taguri, T. Ishi-i, S. Mataka and O. Ito, *J. Phys. Chem. B*, 2005, **109**, 22502–22512.
- 20 (a) S. Kato, T. Matsumoto, T. Ishi-i, T. Thiemann, M. Shigeiwa, H. Gorohmaru, S. Maeda, Y. Yamashita and S. Mataka, *Chem. Commun.*, 2004, 2342–2343; (b) S. Kato, T. Matsumoto, M. Shigeiwa, H. Gorohmaru, S. Maeda, T. Ishi-i and S. Mataka, *Chem.-Eur. J.*, 2006, **12**, 2303–2317.
- 21 T. Imada, H. Kijima, T. Takeuchi and S. Shinkai, *Tetrahedron*, 1996, **52**, 2817–2826.
- 22 K. Pilgram, M. Zupan and R. Skiles, J. Heterocycl. Chem., 1970, 7, 629–633.
- 23 B. Li, J. Li, Y. Fu and Z. Bo, J. Am. Chem. Soc., 2004, 126, 3430-3431.
- 24 In toluene, **1c** shows a concentration-dependent change in the UV/Vis linear absorption spectra, suggesting an aggregation of **1c** (ESI[†]). In contrast, in chloroform the UV/Vis linear absorption spectra did not change with changing concentration.
- 25 Z. O. Liu, Q. Fang, D.-X. Cao, D. Wang and G.-B. Xu, Org. Lett., 2004, 6, 2933–2936.
- 26 At 800 nm **1b** did not show a maximum of the two-photon absorption cross-section. However, the linear transmittance component (T_0), explained in the Measurement section, at 800 nm is very close to 1. So the measured cross-section value should be ascribed to the two-photon absorption rather than other nonlinear processes such as excited state absorption.
- 27 K. Kamada, K. Ohta, Y. Iwase and K. Kondo, *Chem. Phys. Lett.*, 2003, **372**, 386–393.
- 28 B. A. Reinhardt, L. L. Brott, S. J. Clarson, A. G. Dillard, J. C. Bhatt, R. Kannan, L. Yuan, G. S. He and G. S. Prasad, *Chem. Mater.*, 1998, **10**, 1863–1874.
- 29 A slightly high σ value (15 GM, 780 nm) in TPP was determined by a two-photon-induced fluorescence method: M. Drobizhev, A. Karotki, M. Kruk and A. Rebane, *Chem. Phys. Lett.*, 2002, **355**, 175–182. In the present work, we used a Z-scan method to determine the σ value (2.2 GM, 800 nm). It is well known that the σ values are highly dependent on the experimental setup, the monitoring wavelength, the intensity level, and the pulse duration: *e.g.*, N. N. P. Moonen, W. C. Pomeranz, R. Gist, C. Boudon, J.-P. Gisselbrecht, T. Kawai, A. Kishioka, M. Gross, M. Irie and F. Diederich, *Chem.-Eur. J.*, 2005, **11**, 3325–3341.
- 30 (a) S.-J. Chung, K.-S. Kim, T.-C. Lin, G. S. He, J. Swiatkiewicz and P. N. Prasad, J. Phys. Chem. B, 1999, 103, 10741–10745; (b) A. Abbotto, L. Beverina, R. Bozio, A. Facchetti, C. Ferrante, G. A. Pagani, D. Pedron and R. Signorini, Chem. Commun., 2003, 2144–2145; (c) Y. Wang, G. S. He, P. N. Prasad and T. Goodson III, J. Am. Chem. Soc., 2005, 127, 10128–10129.
- 31 R. P. Briñas, T. Troxler, R. M. Hochstrasser and S. A. Vinogradov, J. Am. Chem. Soc., 2005, 127, 11851–11862.
- 32 V. A. Ganzha, G. P. Gurinovich, B. M. Dzhagarov, G. D. Egorova, E. I. Sagun and A. M. Shul'ga, J. Appl. Spectroscoc., 1989, 50, 402–406.
- 33 It was reported that the Φ_{Δ} value of ZnTPP decreased from 0.92– 0.93 in toluene to 0.50 in halogenated solvent: F. Wilkinson, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1993, **22**, 113–262.
- 34 A. Gilbert and J. Baggott, *Essentials of Molecular Photochemistry*, CRC Press, Boca Raton, FL, 1991.