

## Supplementary data

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

Tsutomu Ishi-i,<sup>\*a,b</sup> Yoshiki Taguri,<sup>c</sup> Shin-ichiro Kato,<sup>c</sup> Motoyuki Shigeiwa,<sup>\*d</sup>

Hideki Gorohmaru,<sup>d</sup> Shuuichi Maeda,<sup>d</sup> Shuntaro Mataka<sup>b</sup>

<sup>a</sup> *Department 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](mailto:ishi-i@kurume-nct.ac.jp); Fax: +81 942 35 9404; Tel: +81 942 35 9404*

<sup>b</sup> *Institute for Materials Chemistry and Engineering (IMCE), Kyushu University, 6-1 Kasuga-koh-en, Kasuga 816-8580, Japan,*

<sup>c</sup> *Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-koh-en, Kasuga 816-8580, Japan,*

<sup>d</sup> *Mitsubishi Chemical Group Science and Technology Research Center, Inc., 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan.*

## Experimental

**General.** All melting points are uncorrected. IR spectra were recorded on a JASCO FT/IR-470 plus Fourier transform infrared spectrometer and measured as KBr pellets.  $^1\text{H}$  NMR spectra were determined in  $\text{CDCl}_3$  with a JEOL EX-270 and LA 400 spectrometer. Residual solvent protons were used as internal standard and chemical shifts ( $\delta$ ) are given relative to tetramethylsilane (TMS). The coupling constants ( $J$ ) are reported in hertz (Hz). Elemental analysis was performed at the Elemental Analytical Center, Kyushu University. Electron impact mass spectrometry (EI-MS) spectra were recorded with a JEOL JMS-70 mass spectrometer at 70 eV using a direct inlet system. Fast atom bombardment mass spectrometry (FAB-MS) spectra were recorded with a JEOL JMS-70 mass spectrometer with *m*-nitrobenzyl alcohol (NBA) as a matrix. Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a PerSeptive Biosystems Voyager-DE spectrometer using delayed extraction mode and with an acceleration voltage of 20 keV. Samples were prepared from a solution of dichloromethane using dithranol as the matrix.

Gel permeation chromatography (GPC) was performed with a Japan Analytical Industry LC-908 using JAIGEL-1H column ( $20 \times 600$  mm) and JAIGEL-2H column ( $20 \times 600$  mm) eluting with chloroform ( $3.0 \text{ mL min}^{-1}$ ). Analytical TLC was carried out on silica gel coated on aluminum foil (Merck 60 F<sub>254</sub>). Column chromatography was carried out on silica gel (KANTO 60N). DMF was distilled from calcium hydride under reduced pressure, and stored under an argon atmosphere. Chloroform was stored in the presence of silver foil. Compounds **3**<sup>1</sup> and **6**<sup>2</sup> was prepared according to a method reported previously.

**4-Bromo-7-[4-(diphenylamino)phenyl]-2,1,3-benzothiadiazole (4).** To a mixture of 4,7-dibromo-2,1,3-benzothiadiazole (**3**) (294 mg, 1.0 mmol), tetrakis(triphenylphosphine)palladium(0) (69 mg, 0.06 mmol) in deaerated benzene (40 mL) were added 2,2-dimethyl-1,3-propanediol

4-(diphenylamino)phenylboronate (429 mg, 1.2 mmol), deaerated ethanol (10 mL), and deaerated aqueous 2 M sodium carbonate solution (20 mL) at 60 °C under an argon atmosphere and heated at 85 °C for 3.5 h. The reaction mixture was poured into water, extracted with dichloromethane, and washed with brine. The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography (KANTO 60N) eluting with hexane/chloroform (2:1, v/v) to give **4** in 64% yield (282 mg, 0.635 mmol) as a red solid. An analytical sample was obtained from recrystallization from dichloromethane/hexane. Mp 64–66 °C; Found: C, 62.48; H, 3.54; N, 8.98. Calcd for C<sub>24</sub>H<sub>16</sub>BrN<sub>3</sub>S: C, 62.89; H, 3.52; N, 9.17%;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3030, 1607, 1590, 1502, 1479, 1328, 1317, 1280, 882 and 881;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 7.07 (t, *J* 8.1, 2 H, ArH), 7.17–7.20 (m, 6H, ArH), 7.26–7.33 (m, 4 H), 7.54 (d, *J* 8.1, 1 H, ArH), 7.80 (d, *J* 8.1, 2 H, ArH) and 7.90 (d, *J* 8.1, 1 H, ArH); *m/z* (FAB, NBA) 457, 459 (M<sup>+</sup>).

**4-Bromo-7-{2-[4-(diphenylamino)phenyl]ethenyl}-2,1,3-benzothiadiazole (5).** A stock solution was prepared from palladium acetate (4 mg, 0.01 mmol) and tris(2-methylphenyl)phosphine (6 mg, 0.02 mmol) in dry DMF (9 mL) at 80 °C under an argon atmosphere. The stock solution was added to a solution of **3**<sup>1</sup> (269 mg, 0.91 mmol) and 4-diphenylaminostyrene (271 mg, 1.0 mmol) in deaerated triethylamine (2 mL) and dry DMF (27 mL) at 100 °C under an argon atmosphere and heated at 110 °C for 15 h. The reaction mixture was poured into water and extracted with chloroform. After the organic layer was neutralized with aqueous 1 N hydrochloric acid solution, it was washed with brine, dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography (KANTO 60N) eluting with hexane/dichloromethane (3:1, v/v) and GPC eluting with chloroform to give **5** in 30% yield (134 mg, 0.28 mmol) as a orange solid. An analytical sample was obtained from recrystallization from dichloromethane/hexane. Mp 140–141 °C; Found: C, 64.59; H, 3.78; N, 8.79. Calcd for C<sub>26</sub>H<sub>18</sub>BrN<sub>3</sub>S: C, 64.47; H, 3.75; N, 8.67%;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 1588, 1505, 1490, 1330, 1284, 1175, 969, 888, 837, 749, 695, 622 and 499;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>)

7.03–7.15 (m, 8 H, ArH), 7.28 (t,  $J$  8.4, 4 H, ArH), 7.46 (d,  $J$  16.3, 1 H, olefinic H), 7.50 (d,  $J$  8.7, 2 H, ArH), 7.52 (d,  $J$  7.7, 1 H, ArH), 7.82 (d,  $J$  7.7, 1 H, ArH) and 7.91 (d,  $J$  16.3, 1 H, olefinic H);  $m/z$  (EI) 483, 485 ( $M^+$ ).

**5,10,15,20-Tetrakis{4-[7-[4-(diphenylamino)phenyl]-2,1,3-benzothiadiazole-4-yl]phenyl}-21H,23H-porphine (1a).** To a mixture of **4** (243 mg, 0.53 mmol), tetrakis(triphenylphosphine)palladium(0) (35 mg, 0.03 mmol) in deaerated DME (15 mL) were added 5,10,15,20-tetrakis[4-(4,4-dimethyl-2,6-dioxa-1-boracyclohexanyl)phenyl]-21H,23H-porphine (**6**) (120 mg, 0.11 mmol) and deaerated aqueous 2 M sodium carbonate solution (7.5 mL) at 60 °C under an argon atmosphere and heated at 80 °C for 16 h. The reaction mixture was poured into water, extracted with dichloromethane, and washed with water. The organic layer was dried over anhydrous sodium sulfate and evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography (KANTO 60N) eluting with dichloromethane and recrystallized from dichloromethane/hexane to give **1a** in 23% yield (53 mg, 0.025 mmol) as a violet solid: mp >350 °C; Found: C, 78.35; H, 4.37; N, 10.27. Calcd for  $C_{140}H_{90}N_{16}S_4 \cdot 0.2CH_2Cl_2$ : C, 78.63; H, 4.25; N, 10.46%;  $\nu_{max}$  (KBr)/ $cm^{-1}$  3458 ( $\nu_{NH}$ ), 1590, 1482, 1326, 1280, 966, 888, 829, 800, 753 and 697;  $\delta_H$  ( $CDCl_3$ ) -2.60 (s, 2 H, NH), 7.10 (t,  $J$  7.3, 8 H, ArH), 7.23–7.35 (m, 40 H, ArH), 7.93 (d,  $J$  7.1, 4 H, ArH), 8.00 (d,  $J$  8.3, 8 H, ArH), 8.15 (d,  $J$  7.1, 4 H, ArH), 8.45 (s, 16 H, ArH) and 9.07 (s, 8 H, ArH),  $m/z$  (MALDI-TOF, dithranol) 2124.26 ( $M^+$ ,  $C_{140}H_{90}N_{16}S_4$  requires 2123.65).

**5,10,15,20-Tetrakis {4- {7- {2-[4-(diphenylamino)phenyl]ethenyl} -2,1,3-benzothiadiazole-4-yl} phenyl}-21H,23H-porphine (1b).** According to a method similar to the preparation of **1a**, **1b** was obtained in 9% yield (8 mg, 0.0035 mmol) from **5** (80 mg, 0.165 mmol), tetrakis(triphenylphosphine)palladium(0) (18.5 mg, 0.016 mmol), deaerated DME (8 mL), **6** (40 mg, 0.037 mmol), and deaerated aqueous 2 M sodium carbonate solution (4 mL). The mixture was heated at 80 °C for 16 h. The crude product was purified by silica gel column chromatography (KANTO

60N) eluting with dichloromethane and by recrystallization from dichloromethane/hexane. Mp >350 °C; Found: C, 79.39; H, 4.76; N, 9.60. Calcd for  $C_{148}H_{98}N_{16}S_4 \cdot 0.2CH_2Cl_2$ : C, 79.26; H, 4.42; N, 9.98%;  $\nu_{max}$  (KBr)/ $cm^{-1}$  3446 ( $\nu_{NH}$ ), 1589, 1505, 1490, 1325, 1278, 1174, 965, 889, 835, 799, 751, 695 and 498;  $\delta_H$  ( $CDCl_3$ ) -2.62 (s, 2 H, NH), 7.05–7.18 (m, 32 H, ArH), 7.17–7.32 (m, 16 H, ArH), 7.59 (d,  $J$  8.8, 8 H, ArH), 7.68 (d,  $J$  16.2, 4 H, olefinic H), 7.91 (d,  $J$  7.7, 4 H, ArH), 8.05 (d,  $J$  16.2, 4 H, olefinic H), 8.06 (d,  $J$  7.7, 4 H, ArH), 8.43 (s, 16 H, ArH) and 9.06 (s, 8 H, ArH);  $m/z$  (MALDI-TOR, dithranol) 2227.45 ( $M^+$ ,  $C_{148}H_{98}N_{16}S_4$  requires 2227.71).

**5,10,15,20-Tetrakis{4-[7-[4-(diphenylamino)phenyl]-2,1,3-benzothiadiazole-4-yl]phenyl}-21H,23H-porphine zinc (1c).** A solution of **1a** (30 mg, 0.014 mmol) and palladium acetate dihydrate (31 mg, 0.14 mmol) in argon-bubbling chloroform (5 mL) was stirred at room temperature for 8 h under an argon atmosphere. The complexation was monitored by disappearance of NH proton signal in  $^1H$  NMR spectra. The reaction mixture was evaporated in vacuo to dryness. The residue was dissolved in 1,1,2,2-tetrachloroethane and subjected to silica gel column chromatography eluting with argon-bubbling dichloromethane to give **1c** in 78 % yield (24 mg, 0.011 mmol) as a reddish brown solid: mp >350 °C;  $\nu_{max}$  (KBr)/ $cm^{-1}$  1590, 1480, 1328, 1281, 998, 885, 812, 795, 753 and 697;  $\delta_H$  ( $CDCl_3$ ) 7.10 (t,  $J$  7.3, 8 H, ArH), 7.22–7.34 (m, 40 H, ArH), 7.93 (d,  $J$  7.3, 4 H, ArH), 7.99 (d,  $J$  8.8, 8 H, ArH), 8.16 (d,  $J$  7.3, 4 H, ArH), 8.45 (s, 16 H, ArH), 9.17 (s, 8 H, ArH);  $m/z$  (MALDI-TOF, dithranol) 2185.39 ( $M^+$ ,  $C_{140}H_{88}N_{16}S_4Zn$  requires 2185.56).

**4-Bromo-7-(4-tolyl)-2,1,3-benzothiadiazole (7).** According to a method similar to the preparation of **4**, **7** was obtained from **3** (2.94 g, 10.0 mmol), tetrakis(triphenylphosphine)palladium(0) (583 mg, 0.5 mmol), deaerated benzene (100 mL), 4-tolylboronic acid (1.50 g, 11.0 mmol), deaerated ethanol (25 mL), and deaerated aqueous 2 M sodium carbonate solution (50 mL). The mixture was heated at 80 °C for 17 h. The crude product was purified by silica gel column chromatography (KANTO 60N) eluting with dichloromethane/hexane (1:3, v/v) to give **7** (2.71 g) as an inseparable mixture including the

mono-substituted product and **3** (**3**/mono/**7**, 27:56:17, mol/mol/mol). Without further purification, **7** was used to the next reaction. Yellow solid;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.44 (s, 3 H,  $\text{CH}_3$ ), 7.34 (d,  $J$  8.1, 2 H, ArH), 7.56 (d,  $J$  7.6, 1 H, ArH), 7.79 (d,  $J$  8.1, 2 H, ArH) and 7.91 (d,  $J$  7.6, 1 H, ArH).

**4-[4-(Diphenylamino)phenyl]-7-(4-tolyl)-2,1,3-benzothiadiazole (2a).**<sup>3</sup> According to a method similar to the preparation of **4**, **2b** was obtained in 28 % (263 mg, 0.56 mmol) from **7** (610 mg, 2.0 mmol), tetrakis(triphenylphosphine)palladium(0) (120 mg, 0.11 mmol), deaerated benzene (20 mL), 2,2-dimethyl-1,3-propanediol 4-(diphenylamino)phenylboronate (1.07 g, 3.0 mmol), deaerated ethanol (5 mL), and deaerated aqueous 2 M sodium carbonate solution (10 mL). The mixture was heated at 80 °C for 6 h. The crude product was purified by silica gel column chromatography (KANTO 60N) eluting with dichloromethane/hexane (1:4, v/v) and by GPC eluting with chloroform. Mp 192–194 °C (lit.,<sup>3</sup> 192–194 °C);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  1590, 1482, 1316, 1276, 1186, 887, 818, 745, 698, 624, 523 and 509;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.45 (s, 3 H,  $\text{CH}_3$ ), 7.07 (t,  $J$  7.2, 2 H, ArH), 7.17–7.37 (m, 12 H, ArH), 7.75 (s, 2 H, ArH), 7.86 (d,  $J$  8.6, 2 H, ArH) and 7.88 (d,  $J$  8.6, 2 H, ArH).

**4-{2-[4-(Diphenylamino)phenyl]ethenyl}-7-(4-tolyl)-2,1,3-benzothiadiazole (2b).** According to a method similar to the preparation of **5**, **2b** was obtained in 23% yield (232 mg, 0.47 mmol) from **7** (610 mg, 2.0 mmol), 4-diphenylaminostyrene (813 mg, 3.0 mmol), dry DMF (80 + 10 mL), triethylamine (6.0 mL), palladium acetate (16 mg, 0.07 mmol), tris(2-methylphenyl)phosphine (27 mg, 0.09 mmol). The mixture was heated at 110 °C for 18 h. The crude product was purified by silica gel column chromatography (KANTO 60N) eluting with dichloromethane/hexane (1:4, v/v) and by GPC eluting with chloroform. Orange solid; mp 199–200 °C; Found: C, 79.87; H, 5.04; N, 8.61. Calcd for  $\text{C}_{33}\text{H}_{25}\text{N}_3\text{S}$ : C, 79.97; H, 5.08; N, 8.48%;  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  1589, 1506, 1490, 1328, 1280, 972, 821, 750, 695, 511 and 495;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.44 (s, 3 H,  $\text{CH}_3$ ), 7.03–7.15 (m, 8 H, ArH), 7.25–7.36 (m, 6 H, ArH), 7.53 (d,  $J$  8.6, 2 H, ArH), 7.57 (d,  $J$  16.5, 1 H, olefinic H), 7.67 (d,  $J$  7.4, 1 H, ArH), 7.73 (d,  $J$  7.4, 1 H, ArH), 7.85 (d,  $J$  8.1, 2 H, ArH), 7.93 (d,  $J$  16.5, 1 H, olefinic H);  $m/z$  (FAB, NBA) 495 ( $\text{M}^+$ ).

**Spectroscopic measurement.** UV/Vis spectra were measured on a JASCO V-570 spectrophotometer in a 1.0 cm width quartz cell. Fluorescence spectra were measured on a HITACHI F-4500 fluorescence spectrophotometer in a 1.0 cm width quartz cell.

**Measurement of two-photon absorption cross-sections.** Two-photon absorption cross-sections at 700–900 nm were measured by using an open aperture Z-scan method with wavelength variable femtosecond pulses from an optical parametric amplifier (Quantronix TOPAS) excited by an 1 kHz repetition Ti:sapphire regenerative amplifier system (Quantronix Integra). The pulse width is 120 fs and the spatial profiles were characterized by knife-edge method and can be a Gaussian profile. The experimental setup for open aperture Z-scan measurements is schematically shown in Figure 8. The laser beam was split into two parts. One of them was monitored by a Si P-I-N photo-detector (MODEL 818-SL, New Focus) as an intensity reference and the rest was used for the transmittance measurement. After passing through an  $f = 50$  cm lens, the laser beam was focused and passed through a quartz cell filled with the solution sample. The position of the sample cell could be varied along the laser-beam direction ( $z$  axis), so the local power density within the sample cell could be changed under a constant laser power level. The laser power level was controlled at about a 10 mW by inserting ND filters and the power density was changed from 1 to 50 GW/cm<sup>2</sup>. The thickness of the cell is 1 cm. The transmitted laser beam from the sample cell was then detected by same type of the photo-detector as used for reference monitoring. Same measurements were done for a cell filled with the solvent alone. The transmittance can be acquired by dividing the solution-transmitted intensity by the solvent-transmitted intensity. This procedure cancels the influence of surface and interface reflections of the sample cell.

The excitation power dependence of the transmittance was analyzed by the following method.<sup>4</sup> The beam intensity change along the propagation direction ( $z$ -axis) can be described as

$$\frac{dI}{dz} + \alpha I + \beta I^2 = 0, \quad (1)$$

where  $\alpha$  is the attenuation coefficient that is due to linear absorption and scattering and  $\beta$  is the nonlinear absorption coefficient that is due to TPA. Within the approximation of small linear absorption, i.e.,  $\alpha z \ll 1$ , The solution of Eq. (1) is

$$I(z) = \frac{I(0)\exp(-\alpha z)}{1 + \beta z I(0)}, \quad (2)$$

and the transmittance of the nonlinear medium can be written as

$$T(z) = \frac{I(z)}{I(0)} = \frac{\exp(-\alpha z)}{1 + \beta z I(0)} = \frac{T_0}{1 + \beta z I(0)} = T_0 T_i, \quad (3)$$

where  $I(0)$  is the initial intensity,  $T_0$  is the linear transmittance independent of  $I(0)$  and  $T_i$  is the nonlinear transmittance dependent on  $I(0)$ . If the spatial beam profile can be assumed a Gaussian, the nonlinear transmittance  $T_i$  should be rewritten as<sup>5</sup>

$$T_i = \frac{\ln(1 + I_0 L \beta)}{I_0 L \beta}. \quad (4)$$

By fitting the experimental nonlinear transmittance data  $T_i$  with Eq. (4), one can determine the nonlinear absorption coefficient  $\beta$  for a given input intensity  $I(0) = I_0$  and a given sample thickness  $z = L$ . After obtaining the nonlinear absorption coefficient  $\beta$ , the TPA cross section  $\delta$  of one solute molecule (in units of  $\text{cm}^4 \cdot \text{s}/\text{photon}$ ) can be determined by using the following relationship:

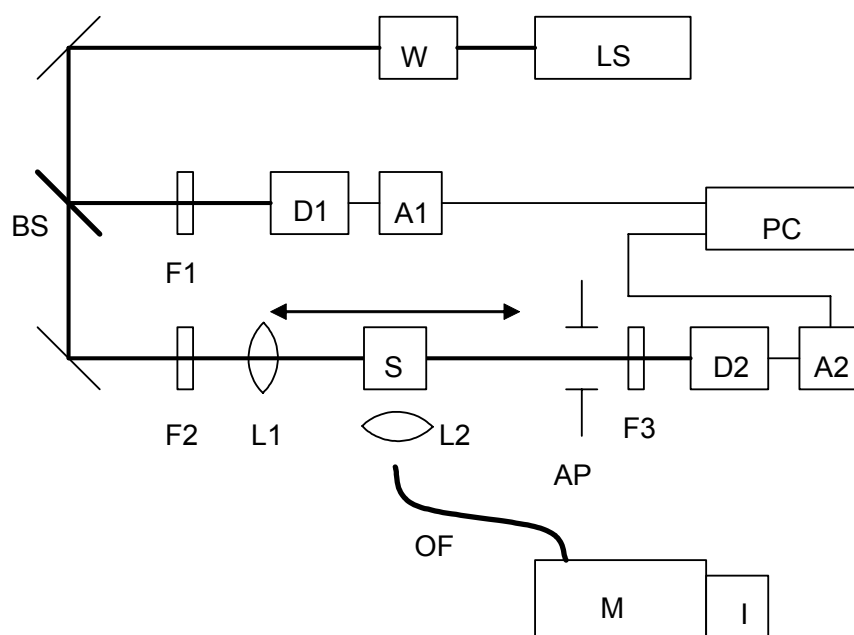
$$\beta = \frac{\delta N_A d \times 10^{-3}}{h\nu}, \quad (5)$$

where  $N_A$  is the Avogadro constant,  $d$  is the concentration of the TPA compound in the solution (in units of M/L),  $h$  is the Planck constant, and  $\nu$  is the frequency of incident laser.

We examined the accumulated thermal effect (ATE) by changing the laser repetition rate, which was varied from 1 kHz down to 10 Hz using optical choppers. The variation of the TPA values was found to be within 5 % in contrast to the Kamada's results.<sup>6</sup> The difference between them might be due to



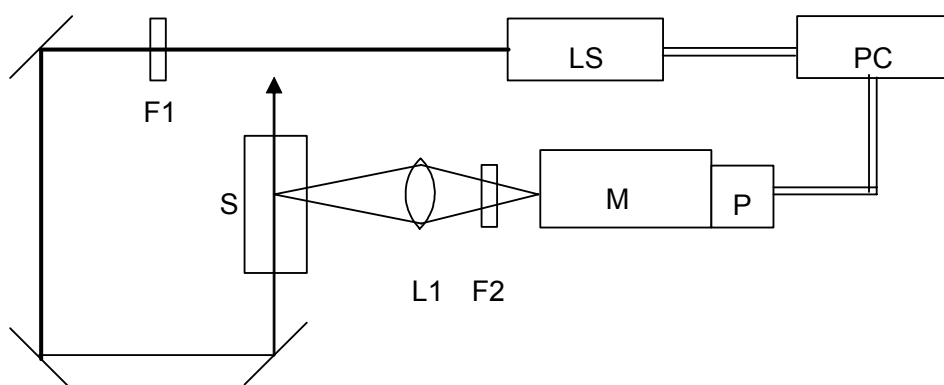
the focusing condition of the laser, where focusing condition of our system is milder than Kamada's system.



**Fig. 1** Experimental setup for two-photon absorption cross section measurement : LS, light source; W, OPA wavelength converter; BS, beam splitter; F1,F2,F3, ND filters and color filters; L1, L2, lens; S, sample cell; D1, D2, detector; AP, open aperture; A1, A2, amplifier; PC, personal computer; OF, optical fiber; M, monochromator; I, I-CCD detector.

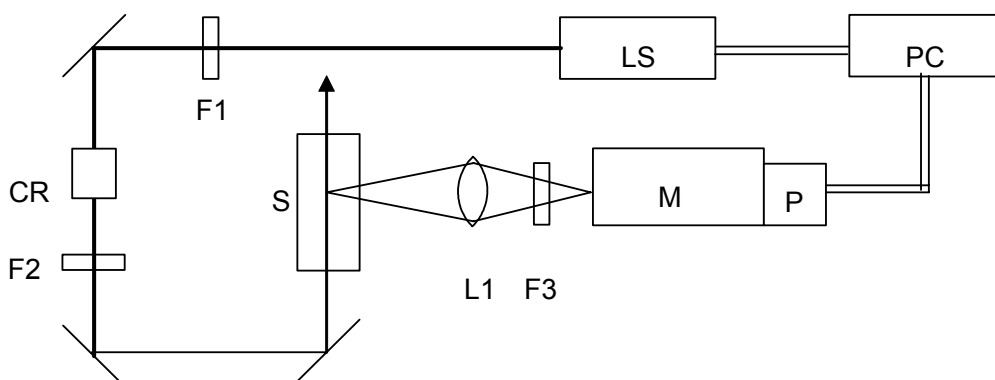
**Measurement of singlet oxygen production photosensitized by two-photon excited dyes.** The amount of singlet oxygen production photosensitized by two-photon excited dyes was determined by a spectroscopic technique. The experimental setup is schematically shown in Figure 9. Phosphorescence from singlet oxygen was measured using 120 fs pulses that were generated from an 1 kHz repetition Ti:sapphire regenerative amplifier system (Quantronix Integra). The wavelength of the

excitation laser was 800 nm, and the average power was about 0.2 W. A beam from a laser illuminated the sample solution from the bottom of the standard quartz cuvette of 1 cm × 1 cm × 4 cm. The concentrations of the samples were written in a caption of Table 3. The phosphorescence was collected by a 2 inch lens and focused onto the entrance slit of a 33 cm single monochromator (Actes, CSM-330) with a grating of 600 grooves mm<sup>-1</sup>. The monochromated light was detected by a liquid-nitrogen-cooled NIR photomultiplier tube (PMT) detector (Hamamatsu, R5509-72). The output of the PMT was pre-amplified and sent to a photon counter (Stanford Research Systems, model400). The photon counter was triggered by the laser and sampling window was set from 5 μs after the trigger and 400 μs duration for a sample signal and from 500 μs after trigger and 400 μs duration for a background signal. The sample signal was corrected by subtracting the background signal in the photon counter and the resultant signal was recorded by a personal computer. To acquire a spectrum, the monochromator was scanned from 1200 nm to 1350 nm. The acquired phosphorescence spectrum was averaged and fitted by a Gaussian, and the peak intensity was calculated.



**Fig. 2** Experimental setup for singlet oxygen detection by two-photon excitation : LS, light source; F1, ND filters; F2: IR transmitting filter; L1, lens; S, sample cell; M, monochromator; P, liquid-nitrogen-cooled PMT detector; PC, personal computer.

**Measurement of singlet oxygen production photosensitized by one-photon excited dyes.** An experimental setup is almost same as the two-photon excited measurement except the exciting laser beam and schematically shown in Figure 10. An 800 nm laser beam from a Ti:sapphire laser was frequency-doubled by a BBO crystal. After the crystal, an 800 nm cut filter was inserted and rest of 800 nm laser beam was blocked. A generated 400 nm laser beam was used to excite sample solution. The average laser power was about 40 mW. The concentrations of the samples in toluene were controlled such that the absorbance at 400 nm was set to  $1.0 \text{ cm}^{-1}$  or  $2.0 \text{ cm}^{-1}$ . Other measurement procedures and data processings are same as two-photon excited measurements.

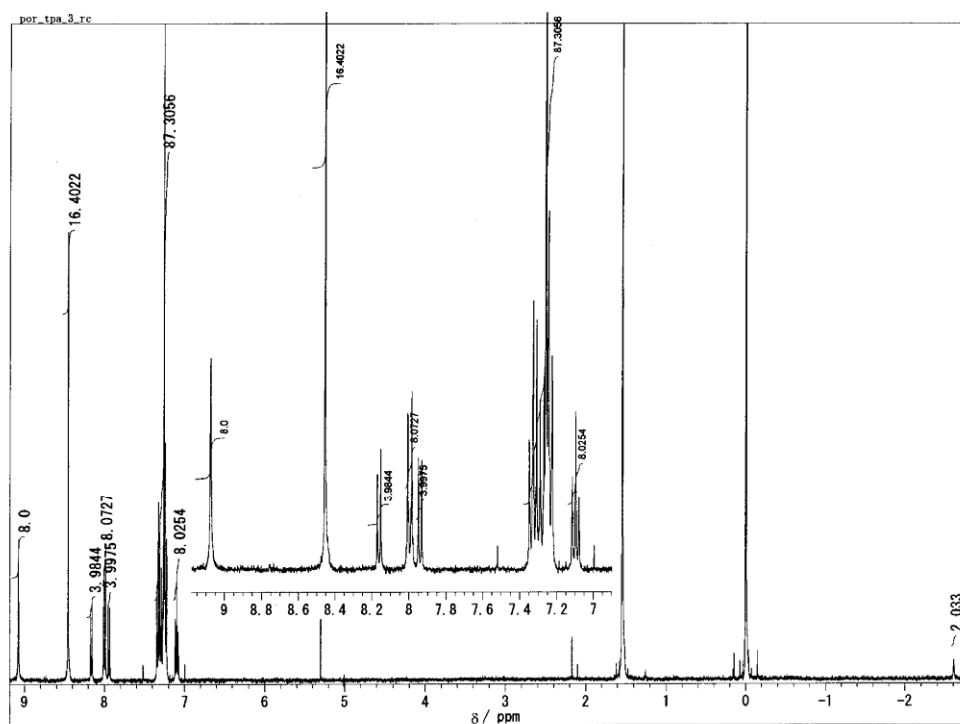


**Fig. 3** Experimental setup for singlet oxygen detection by one-photon excitation : LS, light source; F1, ND filters; F2, 800 nm cut filter; F3: IR transmitting filter; CR, BBO crystal; S, sample cell; L1, lens; M, monochromator; P, liquid-nitrogen-cooled PMT detector; PC, personal computer.

## References

- 1 K. Pilgram, M. Zupan and R. Skiles, *J. Heterocycle Chem.*, 1970, **7**, 629–633.
- 2 T. Imada, H. Kijima, T. Takeuchi and S. Shinkai, *Tetrahedron*, 1996, **52**, 2817–2826.

- 3 S. D. A. Sandanayaka, K. Matsukawa, T. Ishi-i, S. Mataka, Y. Araki and O. Ito, *J. Phys. Chem. B*, 2004, **108**, 19995–20004.
- 4 G. S. He, L. Yuan, N. C. Jayant, D. Bhawalkar, P. N. Prasad, L. L. Brott, S. J. Clarson and B. A. Reinhardt, *J. Opt. Soc. Am. B*, 1997, **14**, 1079–1087.
- 5 L. W. Tutt and T. F. Boggess, *Prog. Quantum Electron*, 1993, **17**, 299–338.
- 6 K. Kamada, K. Matsunaga, A. Yoshino and K. Ohta, *J. Opt. Soc. Am. B*, 2003, **20**, 529–537.



**Fig. 4** <sup>1</sup>H NMR spectrum of **1a** in CDCl<sub>3</sub>.

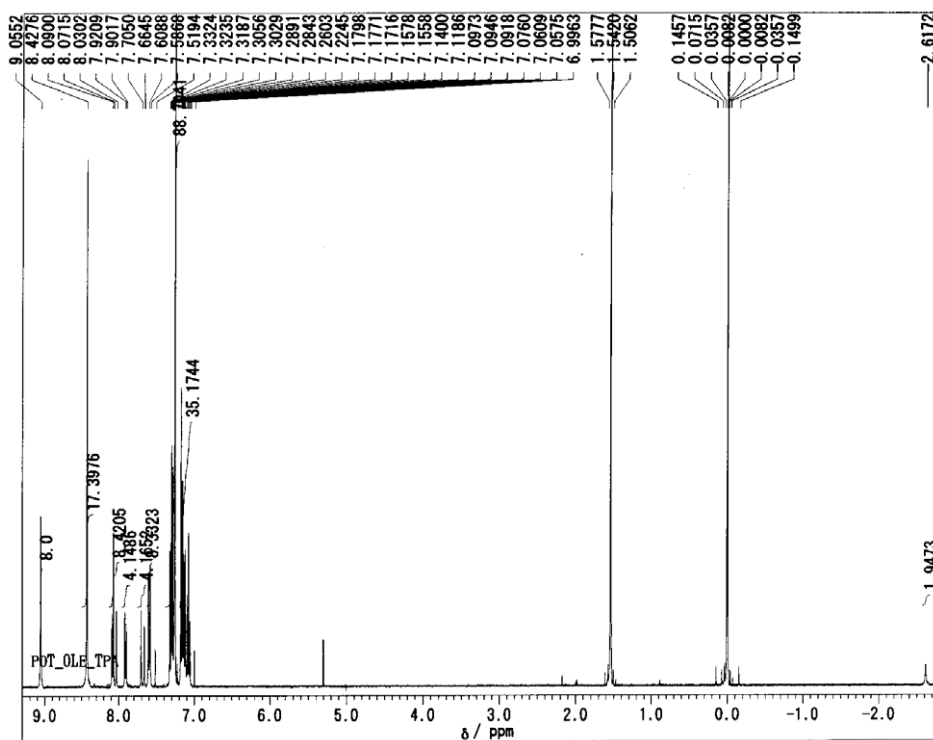


Fig. 5  $^1\text{H}$  NMR spectrum of **1b** in  $\text{CDCl}_3$ .

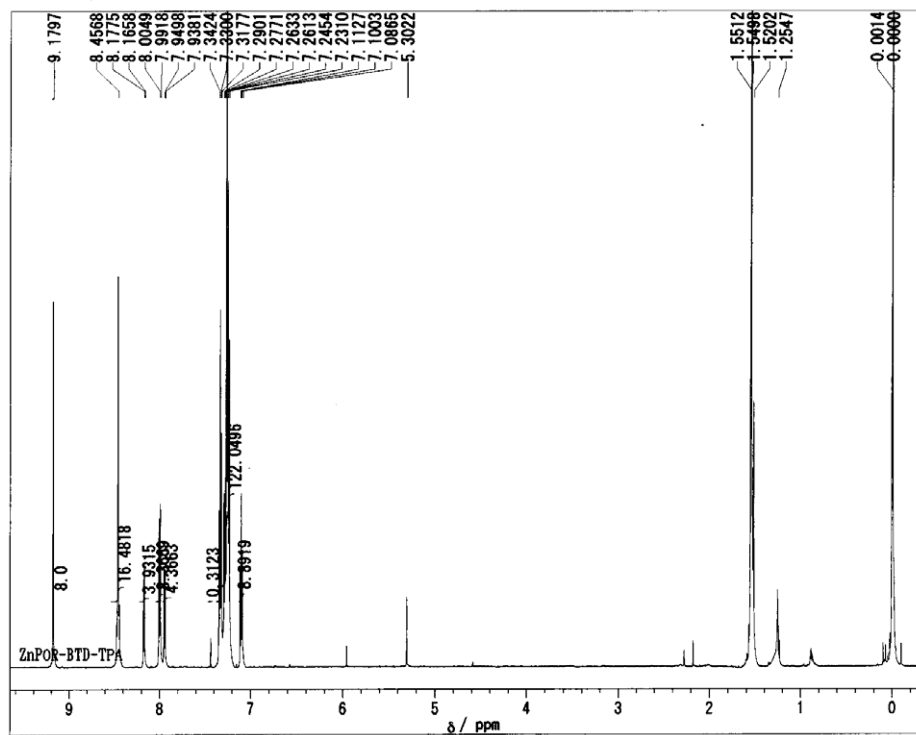
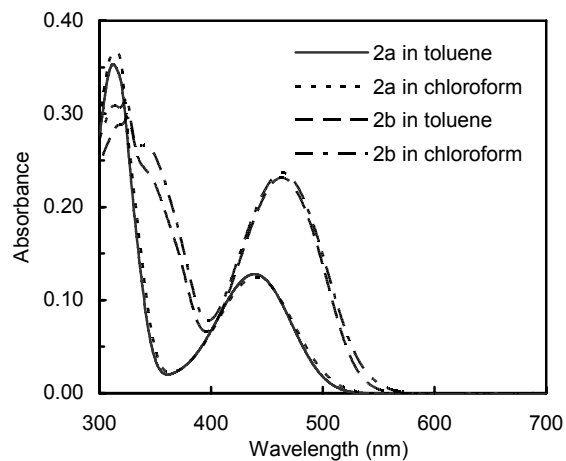
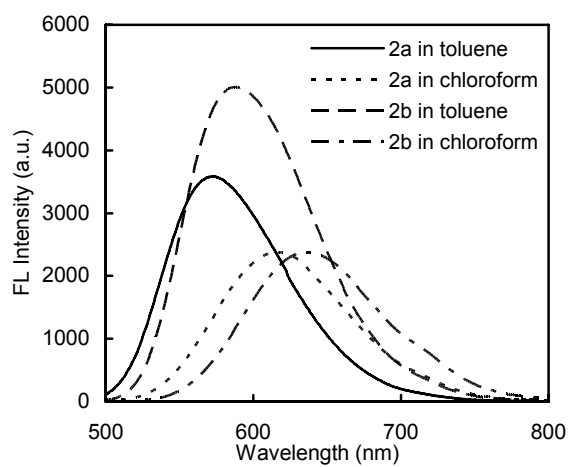


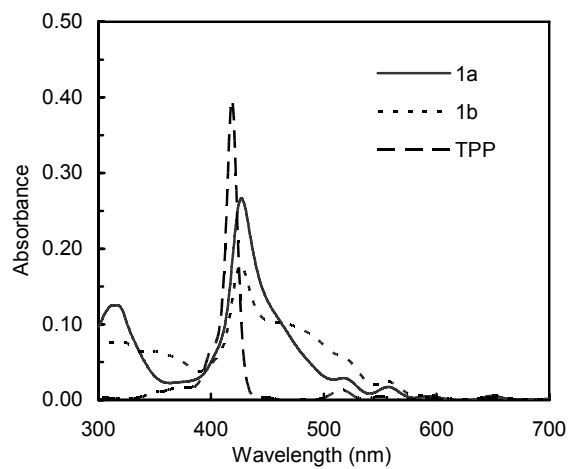
Fig. 6  $^1\text{H}$  NMR spectrum of **1c** in  $\text{CDCl}_3$ .



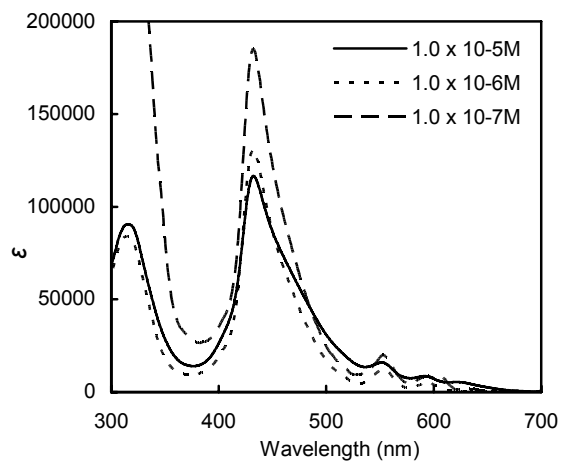
**Fig. 7** UV/Vis linear absorption spectra of **2a** and **2b** in toluene and chloroform ( $10.0 \mu\text{M}$ ).



**Fig. 8** One-photon excited fluorescence spectra of **2a** and **2b** in toluene and chloroform ( $2.0 \mu\text{M}$ ): excited at 438 nm for **2a** and at 464 nm for **2b**.

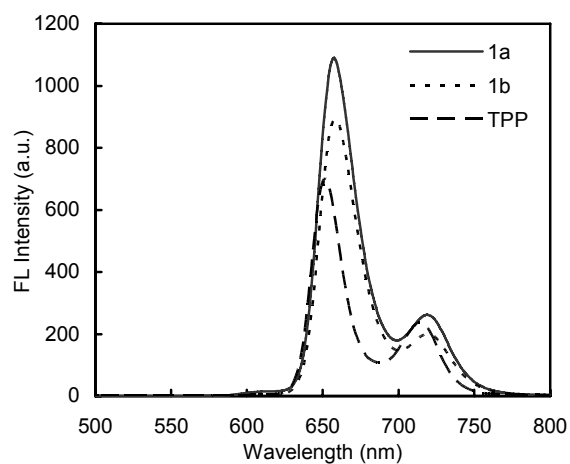


**Fig. 9** UV/Vis linear absorption spectra of **1a**, **1b**, and TPP in chloroform (1.0 μM).

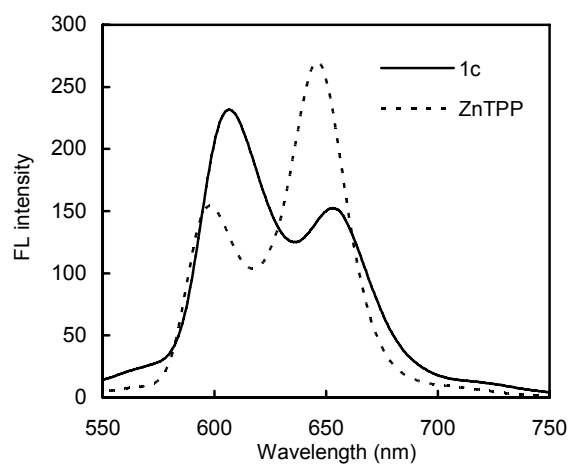


**Fig. 10** UV/Vis linear absorption spectra of **1c** in toluene at 0.1, 1.0, and 10.0 μM.

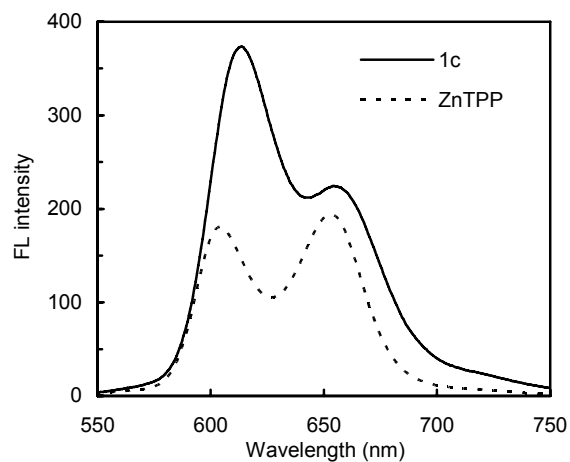




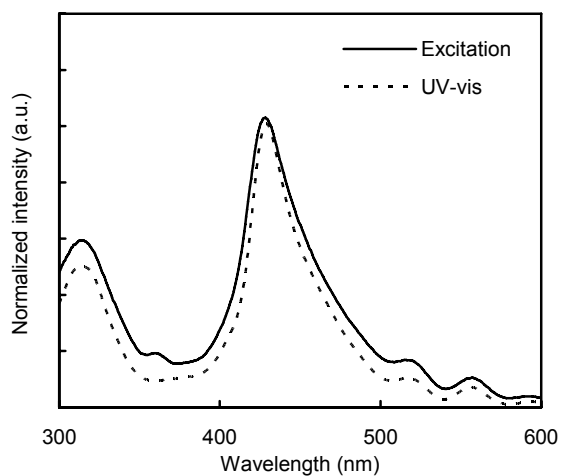
**Fig. 11** One-photon excited fluorescence spectra of **1a**, **1b**, and TPP in chloroform ( $1.0 \mu\text{M}$ ): excited around Soret band (at 427 nm for **1a**, at 426 nm for **1b**, and at 418 nm for TPP).



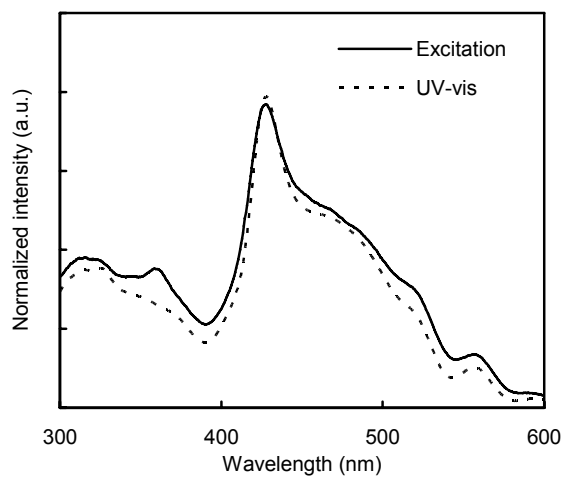
**Fig. 12** One-photon excited fluorescence spectra of **1c** and ZnTPP in toluene ( $1.0 \mu\text{M}$ ): excited around Soret band (at 432 nm for **1c** and at 423 nm for ZnTPP).



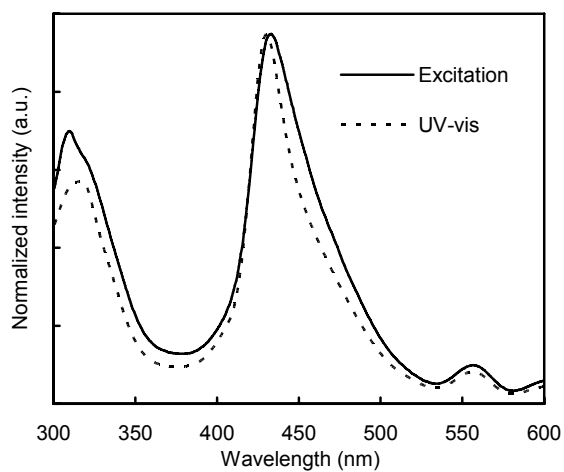
**Fig. 13** One-photon excited fluorescence spectra of **1c** and ZnTPP in chloroform ( $1.0 \mu\text{M}$ ): excited around Soret band (at 430 nm for **1c** and at 424 nm for ZnTPP).



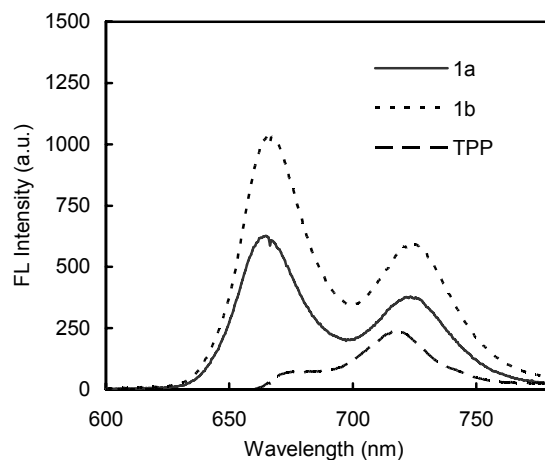
**Fig. 14** UV/Vis linear absorption and fluorescence excitation (at 658 nm) spectra of **1a** in chloroform ( $1.0 \mu\text{M}$ ).



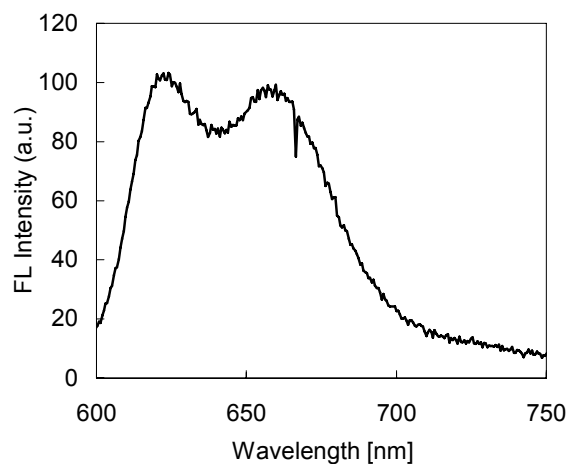
**Fig. 15** UV/Vis linear absorption and fluorescence excitation (at 658 nm) spectra of **1b** in chloroform (1.0  $\mu\text{M}$ ).



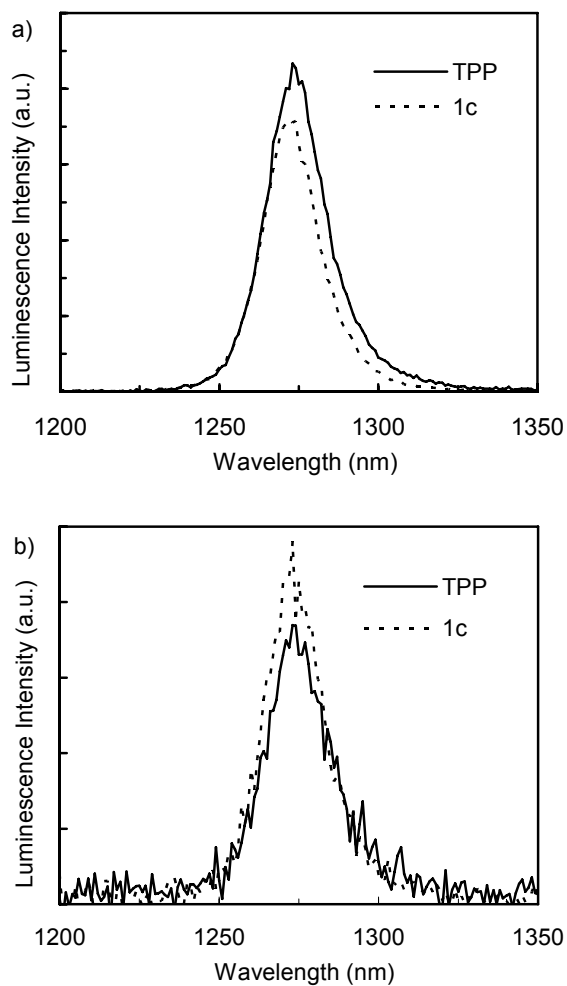
**Fig. 16** UV/Vis linear absorption and fluorescence excitation (at 614 nm) spectra of **1c** in chloroform (1.0  $\mu\text{M}$ ).



**Fig. 17** Two-photon excited fluorescence spectra of **1a** (0.1 mM), **1b** (0.1 mM), and TPP (5.0 mM) in chloroform excited at 800 nm. In the spectrum of TPP, the intensity of shorter wavelength region was reduced due to the re-absorption arising from the high concentration of 5.0 mM.



**Fig. 18** Two-photon excited fluorescence spectrum of **1c** (0.1 mM) in chloroform excited at 800 nm.



**Fig. 19** Oxygen luminescence spectra obtained from (a) 400 nm and (b) 800 nm laser irradiation of air-saturated chloroform solution of **1c** (37.5  $\mu\text{M}$ ) and toluene solution of TPP (25  $\mu\text{M}$  for 400 nm and 5.0 mM for 800 nm).