

## Bridged Triphenylamine Based Molecules with Large Two-Photon Absorption Cross Sections in Organic and Aqueous Media

Zhen Fang <sup>a</sup>, Xinhai Zhang <sup>b</sup>, Yee Hing Lai <sup>c</sup> and Bin Liu <sup>\*a</sup>

<sup>a</sup> Department of Chemical and Biomolecular Engineering, 4 Engineering Drive 4, National University of Singapore, Singapore 117576, cheliub@nus.edu.sg

<sup>b</sup> Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602

<sup>c</sup> Department of Chemistry, 3 Science Drive 3, National University of Singapore, Singapore 117543

### 1. Synthesis and Characterization

#### 1.1 Materials

KI, KIO<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, KOH, butyllithium in hexane (1.6 M), 1,6-dibromohexane and trimethylsilylacetylene were used as received from Aldrich or Fluka. THF was distilled under nitrogen atmosphere over calcium hydride. NBS was recrystallized from deionized water. Acetic acid, triethylamine, trimethylamine, diisopropylamine and other solvents (AR grade) were used without further purification. Bridged triphenylamine **2**,<sup>1</sup> and 4,4'-bis(diphenylamino)stilbene (BDPAS)<sup>2</sup> as TPIF reference were synthesized according to previous methods.

#### 1.2 Characterization Methods

All the new compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, mass spectrascopies and elemental analysis. NMR spectra were collected on a Bruker DPX 300 or DPX 500 spectrometer with d-chloroform and/or d<sub>4</sub>-methanol as the solvent. The UV-

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<sup>1</sup> (a) Hellwinkel, D.; Melan, M. *Chem. Ber.* **1971**, 104, 1001 (b) Hellwinkel, D.; Aulmich, G.; Melan, M. *Chem. Ber.* **1974**, 107, 616. (c) Hellwinkel, D.; Schmidt, W. *Chem. Ber.* **1980**, 113, 358.

<sup>2</sup> Wang, X.; Wang, D.; Zhou, G.; Yu, W.; Zhou, Y.; Fang, Q.; Jiang, M. *J. Mater. Chem.* **2001**, 11, 1600.

vis absorption spectra were recorded on a SHIMAZU UV-Vis 1770 spectrometer. The fluorescence emission spectra were recorded on a Perkin Elmer LS55 fluorometer. EI-mass analysis and elemental analysis were carried out by the Chemical Molecular and Materials Analysis Centre (CMMAC) of the National University of Singapore. Maldi-TOF-mass was tested using a Bruker Autoflex II with THF as the solvent and 2,5-dihydroxybenzoic acid (DHB) as the matrix.

### 1.3 Synthesis

#### **Bridged triphenylamine (BTPHA, 2).**

$^1\text{H-NMR}$  (300MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d, 6H), 7.13 (tr, 3H), 1.64 (s, 18H);  $^{13}\text{C-NMR}$  (75MHz,  $\text{CDCl}_3$ )  $\delta$  131.9, 129.8, 123.4, 122.8, 35.5, 33.1; Mass-EI: 350.4 ( $\text{M}^+$  100), 365.1 ( $\text{M}^+$  14); Anal. Calcd  $\text{C}_{27}\text{H}_{27}\text{N}$ : C, 88.72; H, 7.45; N, 3.83; Found: C, 88.59; H, 7.48; N, 3.90; Mp: 151.3°C-152.2°C.

#### **4,4',4''-Triiodo-bridged triphenylamine (3).**

Bridged triphenylamine **2** (0.1 g, 0.27 mmol) was dispersed in 10 mL of acetic acid. After KI (0.15 g, 0.90 mmol) and  $\text{KIO}_3$  (0.19 g, 0.90 mmol) were added, the mixture was heated to 80 °C and stirred for 2 hours. The reaction mixture was cooled down to room temperature, poured into 20 ml of water and neutralized with saturated  $\text{NaHCO}_3$  solution. The resulting solution was extracted with  $\text{CH}_2\text{Cl}_2$  and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The crude product was purified over silica gel using hexane as the eluent to yield 0.15 g (75 %) of **3** as a light yellow solid.  $^1\text{HNMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59 (s, 6H), 1.56 (s, 18H);  $^{13}\text{CNMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  132.3, 132.1, 131.3, 86.7, 35.3,

32.7; EI-Mass: 742.4; Anal. Calcd C<sub>27</sub>H<sub>24</sub>I<sub>3</sub>N: C, 43.63; H, 3.25; N, 1.88; Found: C, 43.58; H, 3.29; N, 1.87. Melting point: not found, decompose at 260°C, I<sub>2</sub> released.

#### **4,4'-Dibromo-bridged triphenylamine (4).**

To a solution containing bridged triphenylamine **3** (0.5 g, 1.37 mmol) in 40 mL of CHCl<sub>3</sub>, NBS (0.49 g, 2.74 mmol) was added in small portions at 0 °C. The solution was slowly warmed to room temperature and stirred for 1 hour. The reaction solution was poured into water, extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified over silica gel and recrystallized with ethanol several times to yield 0.50 g (70 %) of **4** as a white solid. <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>): δ 7.44 (dd, 4H, *J* = 3.5 Hz), 7.37 (d, 2H, *J* = 7.7 Hz), 7.15 (t, 1H, *J* = 7.7 Hz), 1.61 (s, 12H), 1.59 (s, 6H); <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>): δ 132.2, 131.6, 131.5, 131.2, 131.0, 129.4, 126.5, 126.1, 123.7, 123.5, 115.8, 35.6, 33.0, 32.5, 29.7; EI-Mass: 523.2; Anal. Calcd C<sub>27</sub>H<sub>25</sub>Br<sub>2</sub>N: C, 61.97; H, 4.82; N, 2.68; Found: C, 61.85; H, 4.88; N, 2.70. Melting point: 143.4-144.3°C.

#### **4,4'-Dibromohexyl-bridged triphenylamine (5).**

To a solution containing compound **4** (0.25 g, 0.48 mmol) in 10 mL of anhydrous THF at -78 °C, *n*-BuLi (1.2 mL of a 1.6 M solution in hexane, 4 equiv.) was added dropwise under nitrogen and the reaction was gradually warmed up to room temperature during 1 hour. The mixture was cooled to -78 °C again and 1,6-dibromohexane (0.74 mL, 4.78 mmol) was injected in one portion. Water was added to quench the reaction after the mixture was stirred overnight at room temperature. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified over silica gel

using 8:1 hexane/CH<sub>2</sub>Cl<sub>2</sub> to yield 0.15 g (40 %) of **5** as a colorless oil. <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>): δ 7.36 (d, 2H, *J* = 7.6 Hz), 7.15 (s, 4H), 7.08 (br, 1H), 3.42 (t, 4H, *J* = 6.6 Hz), 2.62 (br, 4H), 1.92-1.83 (m, 4H), 1.70-1.65 (m, 4H), 1.63 (s, 6H), 1.62 (s, 12H), 1.49-1.39 (m, 8H); <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>): δ 136.5, 131.9, 129.7, 129.6, 129.5, 123.5, 123.4, 123.3, 122.6, 35.4, 34.0, 33.2, 32.9, 32.7, 31.3, 28.4, 28.0; EI-Mass: 691.6; Anal. Calcd C<sub>39</sub>H<sub>49</sub>Br<sub>2</sub>N: C, 67.73; H, 7.14; N, 2.03; Found: C, 67.89; H, 7.18; N, 2.00.

#### **4-Bromo-4',4''-dibromohexyl bridged triphenylamine (6).**

To a solution containing compound **5** (0.22 g, 0.32 mmol) in 20 mL of CHCl<sub>3</sub>, NBS (0.071 g, 0.39 mmol) was added at 0 °C. After 0.5 hours, the reaction solution was poured into water, extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified over silica gel with 5:1 hexane/CH<sub>2</sub>Cl<sub>2</sub>, followed by recrystallization from ethanol to yield 0.21 g (87 %) of **6** as a white solid. <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>): δ 7.49 (s, 2H), 7.23 (s, 2H), 7.20 (s, 2H), 3.46 (t, 4H, *J* = 6.8 Hz), 2.69 (t, 4H, *J* = 7.7 Hz), 1.97-1.88 (m, 4H), 1.76-1.74 (s, 4H), 1.66 (s, 6H), 1.60 (s, 12H), 1.55-1.45 (m, 8H); <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>): δ 136.7, 131.7, 131.4, 129.8, 129.5, 129.1, 126.0, 123.8, 123.2, 114.9, 35.6, 35.4, 33.9, 33.5, 32.7, 31.2, 28.4, 28.0, 22.5, 14.0; EI-Mass: 771.2; Anal. Calcd C<sub>39</sub>H<sub>48</sub>Br<sub>3</sub>N: C, 60.79; H, 6.28; N, 1.82; Found: C, 60.90; H, 6.30; N, 1.80; Melting point: 111.4-112.3°C.

#### **4-Trimethylsilylethynyl-4',4''-dibromohexyl-bridged triphenylamine (7).**

A mixture containing compound **6** (0.98 g, 1.27 mmol), Pd(Ph<sub>3</sub>P)<sub>2</sub>Cl<sub>2</sub> (0.044 g, 0.064 mmol), CuI (0.012 g, 0.064 mmol) and 10 mL of triethylamine was bubbled with

nitrogen for 30 mins. A solution containing trimethylsilylacetylene (0.27 ml, 1.91 mmol) in 5 mL of triethylamine was then added. The mixture was stirred at 70 °C for 8 hours under nitrogen. 10 mL of water was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified over silica gel using 7:1 hexane/CH<sub>2</sub>Cl<sub>2</sub> to yield 0.79 g (79 %) of **7** as a yellow solid. <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>): δ 7.47 (s, 2H), 7.16 (d, 4H, *J* = 2.8 Hz), 3.42 (t, 4H, *J* = 6.8 Hz), 2.63 (t, 4H, *J* = 7.2 Hz), 1.93-1.83 (m, 4H), 1.65 (s, 6H), 1.60 (s, 12H), 1.55-1.41 (m, 8H), 0.91-0.84 (m, 4H), 0.29 (s, 9H); EI-Mass: 789.1; Anal. Calcd C<sub>44</sub>H<sub>57</sub>Br<sub>2</sub>NSi: C, 67.08; H, 7.29; N, 1.78; C, 67.28; H, 7.33; N, 1.80; Melting point: 77.5-77.9°C.

#### **4-Ethynyl-4',4''-dibromohexyl-bridged triphenylamine (8).**

To a solution containing compound **7** (0.79 g, 1.01 mmol) in 10 mL of THF, a solution of KOH (0.5 g, 8.93 mmol) in 10 mL of deionized water and 10 mL of methanol was added. The mixture was stirred for 2 hours at room temperature and was extracted with water. The crude product was purified over silica gel using 7:1 hexane/CH<sub>2</sub>Cl<sub>2</sub> as the eluent to yield 0.50 g (70 %) of **8** as a yellow oil. <sup>1</sup>HNMR (500 MHz, CDCl<sub>3</sub>): δ 7.48 (s, 2H), 7.15 (d, 2H, *J* = 7.5 Hz), 3.41 (t, 4H, *J* = 6.6 Hz), 3.09 (s, 1H), 2.63 (t, 4H, *J* = 7.9 Hz), 1.90-1.84 (m, 4H), 1.70-1.63 (m, 4H), 1.66 (s, 6H), 1.59 (s, 12H), 1.51-1.47 (m, 4H), 1.43-1.38 (m, 4H); <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>): δ 136.9, 132.9, 130.0, 129.6, 129.4, 129.3, 127.2, 123.9, 123.3, 84.7, 75.9, 35.5, 33.9, 33.8, 32.8, 31.3, 28.4, 28.0. EI-Mass: 715.2; Anal. Calcd C<sub>41</sub>H<sub>49</sub>Br<sub>2</sub>N: C, 68.81; H, 6.90; N, 1.96; C, 68.95; H, 6.98; N, 2.01

### Neutral tetramer (1N).

A mixture of compound **8** (0.50 g, 0.70 mmol), compound **3** (0.14 g, 0.19 mmol), Pd(Ph<sub>3</sub>P)<sub>2</sub>Cl<sub>2</sub> (0.022 g, 0.031 mmol), CuI (0.006 g, 0.031 mmol) and 10 mL of diisopropylamine was bubbled with nitrogen for 30 mins, which was followed by stirring at 75 °C for 6 hours. The reaction mixture was quenched with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified over silica gel using 3:1 hexane/CH<sub>2</sub>Cl<sub>2</sub> followed by precipitation into methanol to yield 0.35 g (70 %) of **1N** as a yellow solid. <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>): δ 7.62 (s, 6H), 7.58 (s, 6H), 7.18 (s, 12H), 3.42 (t, 12H, *J* = 6.8 Hz), 2.64 (br, 12H), 1.93-1.84 (m, 12H), 1.71 (br, 12H), 1.65 (s, 72H), 1.54-1.41 (m, 24H); <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>): δ 136.8, 132.3, 131.1, 130.2, 129.9, 129.7, 129.5, 129.4, 127.0, 126.7, 123.9, 123.3, 118.2, 116.6, 89.9, 88.8, 35.6, 33.9, 33.8, 32.9, 32.8, 31.3, 30.3, 29.7, 28.5, 28.2, 28.0; Maldi-TOF-Mass: 2505.677. Anal. Calcd. for C<sub>150</sub>H<sub>168</sub>Br<sub>6</sub>N<sub>4</sub>: C, 71.88; H, 6.76; N, 2.24. Found: C, 71.73; H, 6.79; N, 2.27. Melting point: not found, decompose at 212 °C.

### Cationic tetramer (1C).

A solution containing tetramer **1N** (60 mg, 0.024 mmol) in 25 mL of THF was cooled to -78°C. Trimethylamine (~20 drops) was added slowly. The mixture was stirred at room temperature for 15 hours. 3 mL of methanol was added and the mixture was cooled to -78 °C again. Additional trimethylamine (~20 drops) was added and the mixture was stirred at room temperature for another 12 hours. Excess trimethylamine and THF was removed under reduced pressure. The residue was dissolved in methanol and filtered. After methanol was distilled out, the crude product was washed by acetone to afford 35

mg (52 %) of **1C** as a yellow solid.  $^1\text{H}$ NMR (300 MHz,  $\text{d}_4\text{-MeOD}$ ):  $\delta$  7.70 (s, 6H), 7.66 (s, 6H), 7.31 (s, 12H), 3.39 (s, 12H), 3.15 (s, 54H), 2.72 (br, 12H), 1.74 (br, 24H), 1.67 (s, 72H), 1.50 (br, 24H);  $^{13}\text{C}$ NMR (75 MHz,  $\text{d}_4\text{-MeOD}$ ):  $\delta$  138.5, 133.6, 132.3, 131.7, 131.4, 131.1, 131.0, 130.7, 128.1, 127.7, 125.1, 124.6, 120.2, 118.6, 90.7, 89.7, 68.0, 53.6, 36.6, 36.4, 34.0, 33.5, 33.2, 32.5, 29.9, 27.3, 24.0; Maldi-TOF-Mass: 2781.621 (M-Br) $^+$ ; Anal. Calcd. for  $\text{C}_{168}\text{H}_{222}\text{Br}_6\text{N}_{10}$ : C, 70.53; H, 7.82; N, 4.99. Found: C, 70.61; H, 7.79; N, 5.02. Melting point: not found, decompose at 262  $^\circ\text{C}$ .

## 2. XRD structure of BTPHA 2

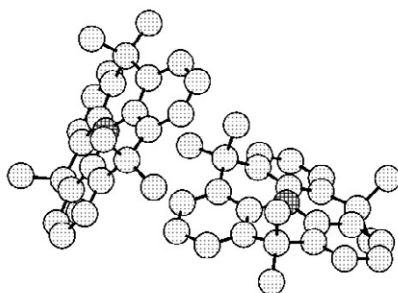


Figure S1 X-ray diffraction structure of single crystal **2**, grey-filled circle: C; black-filled circle: N; H atoms are omitted.

The chemical formula of compound **2** is  $\text{C}_{27}\text{H}_{27}\text{N}$  with the formula weight of 365.50. The unit-cell dimensions are:  $a = 9.8160(5)$   $\text{\AA}$ ,  $b = 18.6778(9)$   $\text{\AA}$ ,  $c = 21.7184(10)$   $\text{\AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90.0680(10)^\circ$ , and  $\gamma = 90^\circ$ . The crystal system belongs to monoclinic, although the beta angle is close to 90 degrees, the intensity symmetry does not support an orthorhombic cell. The unit volume is  $3981.9(3)$   $\text{\AA}^3$  at the temperature of  $223(2)$  K. The space group symbol is  $\text{P}2(1)/c$ ,  $Z = 8$ . The numbers of reflections and independent reflections collected are 22962, and 7020 respectively [ $R(\text{int}) = 0.0555$ ]. The final R values:  $R1 = 0.123$  and  $wR2 = 0.310$  for for 2-theta max of 50 degrees. The high

R values are probably due to the quality of the crystal. The bond lengths, thermal parameters and residual background peaks all appeared to be normal. CCDC no. is 711074.

### 3. Two-photon Absorption Measurements

Two-photon absorption (TPA) spectra were measured using two-photon induced fluorescence (TPIF) spectroscopy.<sup>3</sup> The measurements were conducted with the excitation of 1 kHz pulse train having a typical pulse duration of 120 fs and energy of 0.3 uJ/pulse from an optical parametric amplifier, which was driven by a Ti:sapphire regenerative amplifier. The luminescence was collected in a conventional back-scattering geometry, dispersed in a 50 cm monochromator and detected with a photomultiplier using standard lock-in amplification. The concentrations of solutions were about 10 μM in toluene (**1N**), methanol (**1C**) and water (**1C**) respectively. 4,4'-Bis(diphenylamino)stilbene (BDPAS,  $\lambda_{\text{ex}} < 700$  nm) in toluene and rhodamine B ( $\lambda_{\text{ex}} \geq 700$  nm) in methanol was used as references.<sup>4</sup> TPA cross section was calculated from equation:<sup>5</sup>

$$\frac{\delta_2}{\delta_1} = \frac{F_2 \eta_1 c_1 n_1}{F_1 \eta_2 c_2 n_2}$$

Where  $\delta_1$  and  $\delta_2$  are the TPA cross section,  $F_1$  and  $F_2$  are the TPIF intensities,  $\eta_1$  and  $\eta_2$  are the fluorescence quantum yields,  $c_1$  and  $c_2$  are the concentrations,  $n_1$  and  $n_2$  are the refractive indexes of solvents (1 corresponds to reference, 2 is used for sample **1N** and **1C**).

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<sup>3</sup> Xu, C.; Webb, W. W. *J. Opt. Soc. Am. B* **1996**, *13*, 481.

<sup>4</sup> Makarov, N.S.; Drobizhev, M.; Rebane, A. *Opt. Express* **2008**, *16*, 4029

<sup>5</sup> Oulianov, D.A.; Tomov, I.V.; Dvornikov, A.S.; Rentzepis, P.M. *Opt. Commun.* **2001**, *191*, 235.



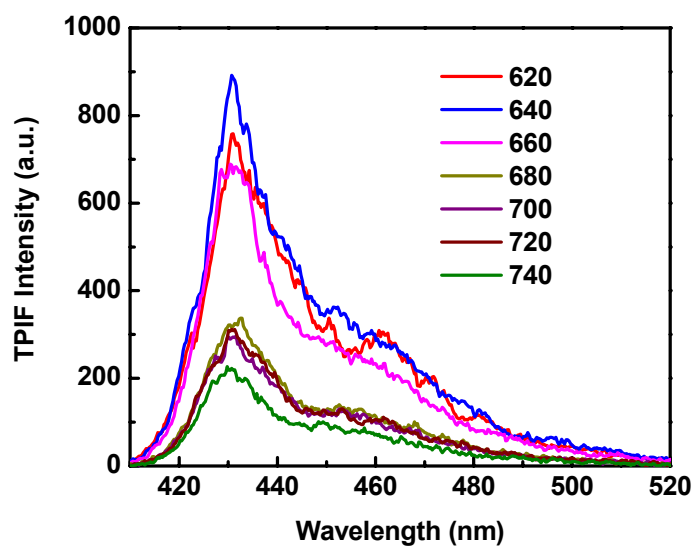


Figure S2. Two-photon induced fluorescence spectra of **1N** in toluene, excited at different wavelength; [1N] = 10  $\mu$ M.

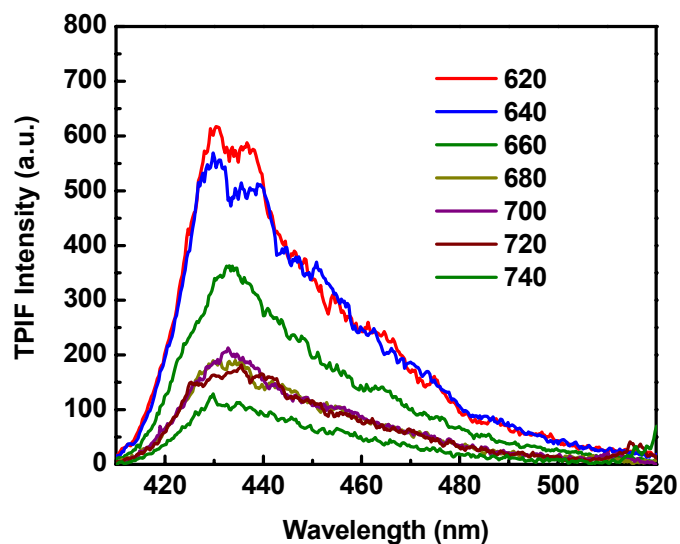


Figure S3. Two-photon induced fluorescence spectra of **1C** in methanol, excited at different wavelength; [1C] = 10  $\mu$ M.

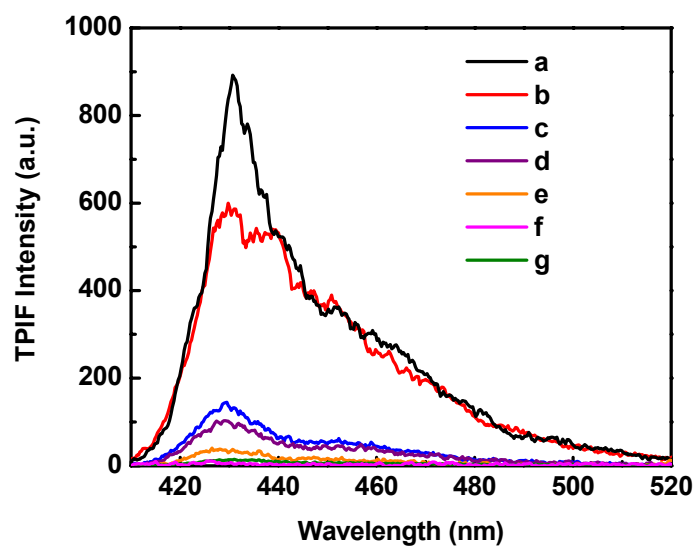


Figure S4. Two-photon induced fluorescence spectra of: (a) **1N** in toluene; (b) **1C** in methanol; (c-g) **1C** in water with different SDS concentrations: 100, 50, 10, 0.2 and 0 mM; excited at 640 nm; [**1N**] and [**1C**] = 10  $\mu$ M.

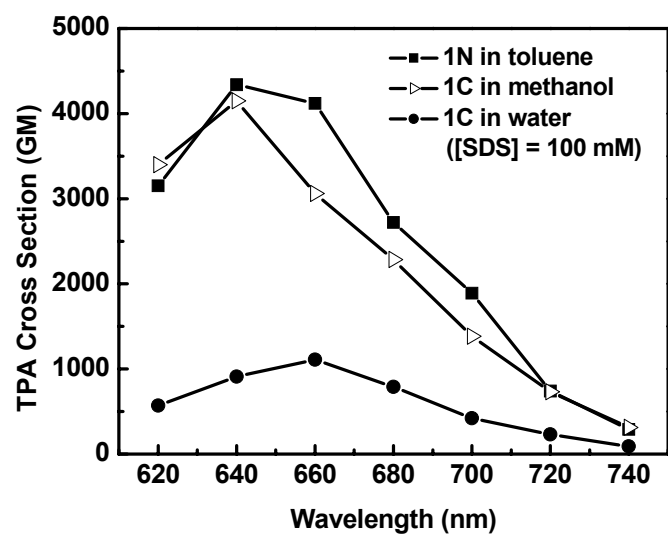


Figure S5. Two-photon absorption spectra of **1N** in toluene, **1C** in methanol, **1C** in water with 100 mM SDS. 620-680 nm: BDPAS in toluene as the reference; 700-740 nm: Rhodamine B in methanol as the reference.  $[1N] = [1C] = 10 \mu\text{M}$ .