

Supplementary Information for

# **Self-assembly of amphiphilic fluorescent dyes showing aggregate-induced enhanced emission: temperature dependence of molecular alignment and intermolecular interaction in aqueous environment**

*Takashi Hirose<sup>a,b</sup> and Kenji Matsuda<sup>\*,a,b</sup>*

<sup>a</sup> Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, JST, CREST, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan. <sup>b</sup> Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.

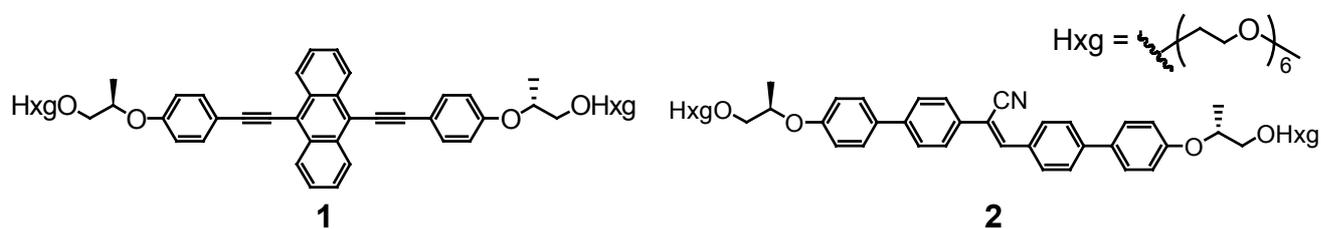
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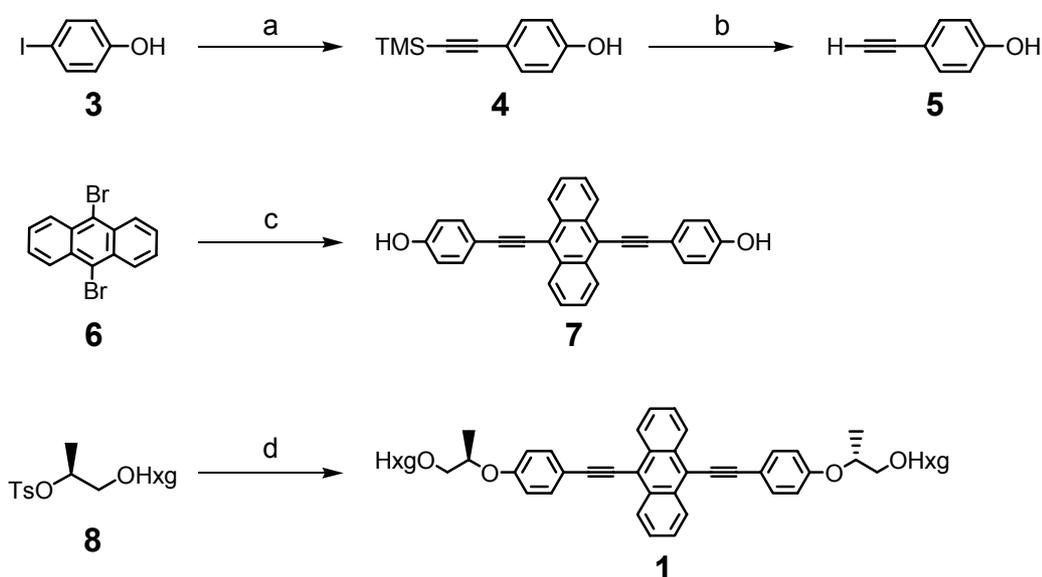
**A. Materials.** All reactions were monitored by thin-layer chromatography carried out on 0.2 mm Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Kanto Chemical, 63-210 mesh). <sup>1</sup>H-NMR spectra were recorded on a Bruker AVANCE 400 instrument. Samples were dissolved in CDCl<sub>3</sub> or Acetone-d<sub>6</sub> and tetramethylsilane was used as an internal standard. Mass spectra were obtained by a JMS-HX110A, and a JMS-SX102A instruments. Compound **8**,<sup>[S1]</sup> **10**,<sup>[S2]</sup> and **13**<sup>[S1]</sup> were prepared according to the method reported previously. *p*-iodophenol (**3**), 9,10-dibromoanthracene (**6**), trimethylsilyl acetylene, 4-bromo-1-cyanomethylbenzene, and *p*-formylphenyl boronic acid were purchased from TCI.

PEAnt derivative **1** and CNBE derivative **2** were synthesized according to Scheme 2 and 3. By the Sonogashira coupling reaction of 9,10-dibromoanthracene **6** with *p*-ethynylphenol **5**, diol precursor **7** was obtained. Tosyl-protected hexaethylene glycol (Hxg) side chain **8** was synthesized according to the literature.<sup>[S1]</sup> In order to obtain compound **1**, diol precursor **7** was reacted with tosyl-protected Hxg chain **8** in the presence of potassium carbonate as a base. Similar strategy was adopted for compound **2**, however, corresponding diol precursor of CNBE did not dissolve in the solvent and the yield of the reaction with Hxg side chain **8** was extremely low. Consequently, Hxg side chain was introduced in advance in order to increase the solubility. 4-Cyanomethyl biphenyl **12** and 4-formyl biphenyl **14**, both having Hxg side chain, were obtained by the Suzuki-coupling reaction. Compound **2** was successfully synthesized by the Knoevenagel condensation of **12** with **14**. The structures of **1** and **2** were confirmed by NMR and MASS spectroscopies.

**Scheme S1.** Molecular structures of amphiphilic fluorescent dyes having Hxg side chains.

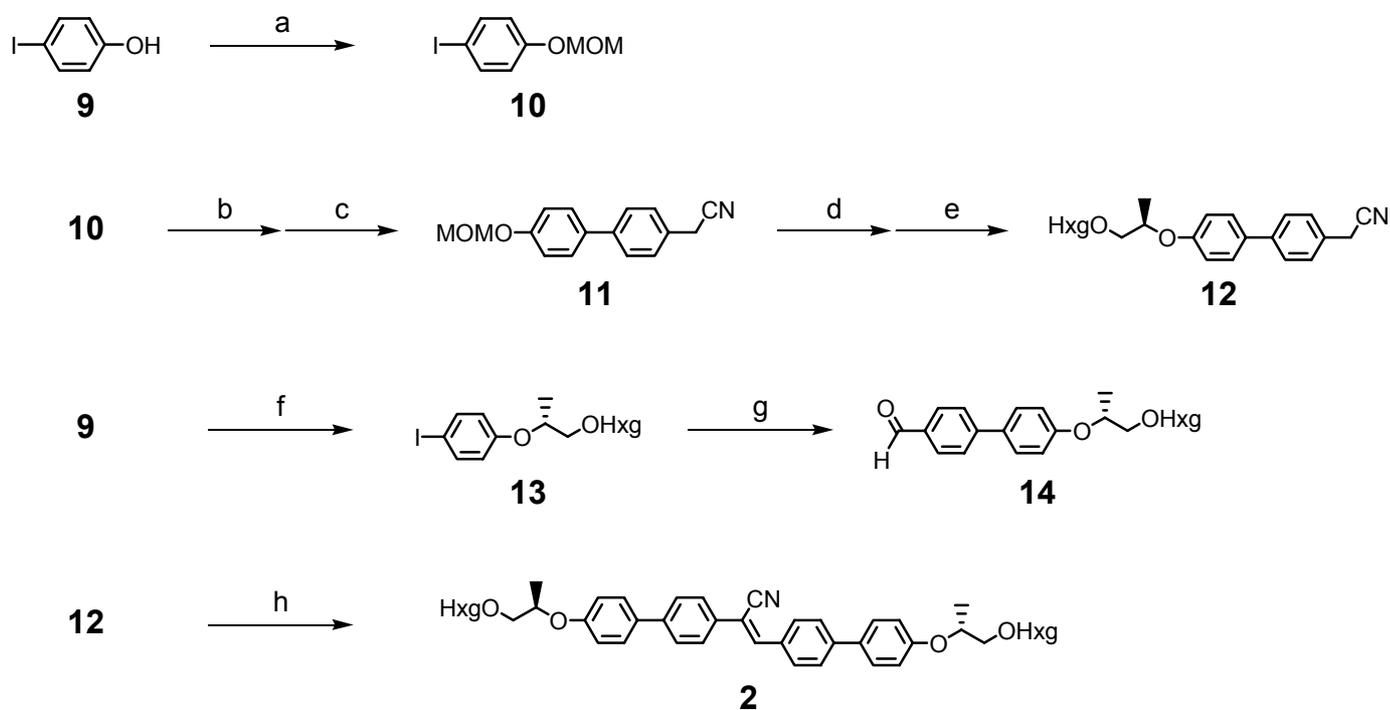


**Scheme S2.** Synthesis of Compound **1**.<sup>a</sup>



<sup>a</sup> Reagents and conditions: (a) trimethylsilylacetylene, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, Et<sub>3</sub>N, quantitative; (b) aq. NaOH, MeOH; (c) **5**, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, THF/Et<sub>3</sub>N, 59% in two steps; (d) K<sub>2</sub>CO<sub>3</sub>, acetone, 60%.

**Scheme S3.** Synthesis of Compound **2**.<sup>a</sup>



<sup>a</sup> Reagents and conditions: (a) MOMCl, THF, quantitative; (b) *n*-BuLi, dry THF, and then (BuO)<sub>3</sub>B; (c) 4-bromo-1-cyanomethylbenzene, aq. Na<sub>2</sub>CO<sub>3</sub>, and then Pd(PPh<sub>3</sub>)<sub>4</sub>, 46% in two steps; (d) conc. HCl, THF; (e) **8**, K<sub>2</sub>CO<sub>3</sub>, acetone, 30% in two steps; (f) **8**, K<sub>2</sub>CO<sub>3</sub>, acetone, 74%; (g) *p*-formylphenyl boronic acid, THF, aq. Na<sub>2</sub>CO<sub>3</sub>, and then Pd(PPh<sub>3</sub>)<sub>4</sub>, 67%; (h) **14**, *tert*-BuOH/THF, and then TBAH, 84%.

**4-Trimethylsilanylethynyl-phenol (4).** To a solution of *p*-iodophenol **3** (5.3 g, 24.5 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (510 mg, 0.73 mmol) and CuI (140 mg, 0.73 mmol) in triethylamine (80 mL) was added trimethylsilyl acetylene (5 mL, 36.1 mmol). The solution was stirred for 3 h at 80 °C under nitrogen atmosphere. The reaction product was filtrated and evaporated. The crude product was purified by silica gel column chromatography (hexane:ethyl acetate = 1:1) to yield **4** (4.7 g, 24.7 mmol, quantitative) as a brown oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz) δ 0.23 (s, 9 H, TMS), 5.36-5.73 (bs, 1 H, OH), 6.76 (d, *J* = 8 Hz, 2 H, Ar), 7.36 (d, *J* = 9 Hz, 2 H, Ar); CI HRMS (*m/z*) [M]<sup>+</sup> calcd for C<sub>11</sub>H<sub>14</sub>OSi<sup>+</sup>: 190.0808, found: 190.0816.

**9,10-Bis-[4-hydroxy phenylethynyl]-anthracene (7).** To a solution of 4-trimethylsilanylethynyl-phenol (**4**) (1.5 g, 7.9 mmol) in methanol (30 mL) was added aqueous NaOH (5 N, 5 mL). The solution was stirred for 2 h at room temperature under nitrogen atmosphere. The resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the organic layer was washed with brine, dried over MgSO<sub>4</sub>, and evaporated to yield **5**, which was used for the next step shortly without further purification. The solution of 9,10-dibromoanthracene **6** (0.98 g, 2.92 mmol) in THF (5 mL) and triethylamine (10 mL) was added to the crude product. After Ar bubbling for 5 min, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (280 mg, 0.4 mmol) and CuI (76 mg, 0.4 mmol) was added and the mixture was stirred for 8 h at 80 °C under argon atmosphere. The reaction product was filtrated and evaporated. The crude product was purified by silica gel column chromatography (hexane:ethyl acetate = 2:1) to yield **7** (700 mg, 1.81 mmol, 58.6%) as a brown powder. <sup>1</sup>H NMR (Acetone-d<sub>6</sub>, TMS, 400 MHz) δ 7.00 (d, *J* = 9 Hz, 4 H, Ar), 7.70-7.78 (m, 8 H), 8.71-8.78 (m, 4 H), 8.93 (bs, 2 H, OH); EI HRMS (*m/z*) [M]<sup>+</sup> calcd for C<sub>30</sub>H<sub>18</sub>O<sub>2</sub><sup>+</sup>: 410.1301, found: 410.1301.

**(*R,R*)-9,10-Bis-[4-(2-{2-[2-(2-{2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-1-methyl-ethoxy)-phenylethynyl]-anthracene (1).** To a solution of 9,10-Bis-[4-hydroxy phenylethynyl]-anthracene (**7**) (50 mg, 0.12 mmol) and K<sub>2</sub>CO<sub>3</sub> (330 mg, 2.4 mmol) in Acetone (1.5 mL) was added Tosyl-protected hexaethylene glycol derivative **8** (TsOCHMeCH<sub>2</sub>OH<sub>x</sub>g) (135 mg, 0.264 mmol). The solution was stirred for 9 h at 70 °C under nitrogen atmosphere. The reaction product was

cooled and poured into aqueous HCl (pH = 2). The resulting mixture was extracted with ether, and the organic layer was washed with brine, dried over MgSO<sub>4</sub>, and evaporated. The crude product was purified by silica gel column chromatography (ethyl acetate:acetone = 1:1) to yield **1** (80 mg, 0.072 mmol, 60.0%) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz) δ 1.37 (d, *J* = 6 Hz, 6 H, Me), 3.37 (s, 6 H), 3.51-3.79 (m, 52 H), 4.58-4.72 (m, 2 H), 7.01 (d, *J* = 9 Hz, 4 H, Ar), 7.60-7.66 (m, 4 H), 7.69 (d, *J* = 9 Hz, 4 H, Ar), 8.65-8.72 (m, 4 H); FAB HRMS (*m/z*) [*M*]<sup>+</sup> calcd for C<sub>62</sub>H<sub>82</sub>O<sub>16</sub><sup>+</sup>: 1082.5597, found: 1082.5597. UV-vis (H<sub>2</sub>O) λ<sub>max</sub> (ε) 450 (19 000); (ethyl acetate) λ<sub>max</sub> (ε) 469 (39 000).

**4-(4-methoxymethoxy)-phenyl-1-cyanomethyl benzene (11).** To a solution of 1-iodo-4-methoxymethoxy-benzene **10** (7.07, 26.8 mmol) in dry THF (110 mL) was slowly added n-butyllithium (BuLi) hexane solution (1.6 M, 17.6 mL, 28.1 mmol) at -78 °C under argon atmosphere. The solution was stirred for 5 min at -78 °C. After the addition of boric acid tri-*n*-butyl ester (10.8 mL, 40.2 mmol), the reaction mixture was further stirred for 1.5 h. The reaction was quenched by the addition of water. 4-bromo-1-cyanomethylbenzene (5.0 g, 25.5 mmol), and aqueous Na<sub>2</sub>CO<sub>3</sub> (20w%, 110 mL), and tetrakis triphenylphosphine palladium (0) (Pd(PPh<sub>3</sub>)<sub>4</sub>) (36 mg, 0.031 mmol) were added to the solution. The solution was refluxed for 23 h under argon atmosphere. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the combined organic layer was washed with brine. The combined organic layer was dried over MgSO<sub>4</sub>, filtrated, and evaporated. The crude mixture was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) to yield **11** (3.0 g, 11.8 mmol, 46.3%) as a pale brown solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz) δ 3.51 (s, 3 H), 3.79 (s, 2 H), 5.23 (s, 2 H), 7.12 (d, *J* = 9 Hz, 2 H), 7.38 (d, *J* = 8 Hz, 2 H), 7.51 (d, *J* = 9 Hz, 2 H), 7.56 (d, *J* = 8 Hz, 2 H); EI HRMS (*m/z*) [*M*]<sup>+</sup> calcd for C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub><sup>+</sup>: 253.1097, found: 253.1100.

**(R)-{4-(4-[2-{2-(2-[2-{2-(2-methoxy)-ethoxy}-ethoxy)-ethoxy}-ethoxy]-ethoxy]-ethoxy)-1-methoxy-ethoxy)-phenyl}-1-cyano-methylbenzene (12).** To a solution of 4-(4-methoxymethoxy)-phenyl-1-cyanomethyl benzene **11** (1.1 g, 4.5 mmol) in THF (30 mL) was added concentrated aqueous HCl (35%, 6 mL). The solution was stirred for 3 h at room temperature. The reaction product was extracted with

CH<sub>2</sub>Cl<sub>2</sub>, and the organic layer was washed with aqueous NaHCO<sub>3</sub> and brine, dried over MgSO<sub>4</sub>, and evaporated. The crude product was dissolved in acetone (40 mL), and then K<sub>2</sub>CO<sub>3</sub> (6.9 g, 50 mmol) and Tosyl-protected hexaethylene glycol derivative **8** (TsOCHMeCH<sub>2</sub>OH<sub>x</sub>g) (2.5 g, 4.9 mmol) was added. The solution was refluxed for 24 h. The reaction mixture was cooled and poured into aqueous HCl (pH = 2). The resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the organic layer was washed with brine, dried over MgSO<sub>4</sub>, and evaporated. The crude product was purified by silica gel column chromatography (ethyl acetate to ethyl acetate:acetone = 1:1) to yield **12** (800 mg, 1.47 mmol, 30%) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz) δ 1.34 (d, *J* = 6 Hz, 3 H), 3.38 (s, 3 H), 3.52-3.75 (m, 26 H), 3.80 (s, 2 H), 4.56-4.66 (m, 1 H), 7.00 (d, *J* = 9 Hz, 2 H), 7.37 (d, *J* = 8 Hz, 2 H), 7.49 (d, *J* = 9 Hz, 2 H), 7.55 (d, *J* = 8 Hz, 2 H); EI HRMS (*m/z*) [*M*]<sup>+</sup> calcd for C<sub>30</sub>H<sub>43</sub>NO<sub>8</sub><sup>+</sup>: 545.2983, found: 545.2987.

**(*R*)-4'-(2-{2-[2-(2-{2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy}-1-methyl-ethoxy)-biphenyl-4-carbaldehyde (14).** To a solution of 1-Iodo-4-(2-{2-[2-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy}-1-methyl-ethoxy)-benzene **13** (300 mg, 0.56 mmol), *p*-formylphenyl boronic acid (93 mg, 0.62 mmol), and aqueous Na<sub>2</sub>CO<sub>3</sub> (20w%, 5 mL) in THF (5 mL) was added tetrakis triphenylphosphine palladium (0) (Pd(PPh<sub>3</sub>)<sub>4</sub>) (36 mg, 0.031 mmol). The solution was refluxed for 15 h under argon atmosphere. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the combined organic layer was washed with brine. The combined organic layer was dried over MgSO<sub>4</sub>, filtrated, and evaporated. The crude mixture was purified by silica gel column chromatography (ethyl acetate) to yield **14** (200 mg, 0.37 mmol, 67%) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz) δ 1.35 (d, *J* = 6 Hz, 3 H), 3.38 (s, 3 H), 3.45-3.78 (m, 26 H), 4.59-4.68 (m, 1 H), 7.03 (d, *J* = 9 Hz, 2 H), 7.58 (d, *J* = 9 Hz, 2 H), 7.72 (d, *J* = 8 Hz, 2 H), 7.93 (d, *J* = 8 Hz, 2 H), 10.04 (s, 1 H); EI HRMS (*m/z*) [*M*]<sup>+</sup> calcd for C<sub>29</sub>H<sub>42</sub>O<sub>9</sub><sup>+</sup>: 534.2823, found: 534.2829.

**(*R,R*)-1,2-Bis-(4'-{1-methyl-2-[2-(2-{2-[2-(2-methoxyethoxy)-ethoxy]-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy}-biphenyl-4-yl)-cyanoethene (2).** (*R*)-4'-(2-{2-[2-(2-{2-[2-(2-Methoxy-

ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy}-1-methyl-ethoxy)-biphenyl-4-carbaldehyde **14** (150 mg, 0.28 mmol) and (*R*)-{4-(4-[2-{2-(2-[2-{2-(2-methoxy)-ethoxy}-ethoxy]-ethoxy)-ethoxy}-ethoxy]-ethoxy-1-methyl-ethoxy)-phenyl}-1-cyano-methylbenzene **12** (150 mg, 0.28 mmol) in a mixsolvent of THF (3 mL) and *tert*-butanol (7 mL) was added tetra butyl ammonium hydroxide (TBAH) (1 M solution in methanol, 0.03 mL, 0.03 mmol). The solution was stirred for 1.5 h at 50 °C under argon atmosphere. The mixture was cooled to room temperature and the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the combined organic layer was washed with brine. The organic layer was dried over MgSO<sub>4</sub>, filtrated, and evaporated. The crude mixture was purified by silica gel column chromatography (ethyl acetate ~ acetone) to yield **2** (250 mg, 0.24 mmol, 84%) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz) δ 1.36 (d, *J* = 6 Hz, 6 H, Me), 3.38 (s, 6 H, Me), 3.45-3.78 (m, 52 H), 4.56-4.68 (m, 2 H), 7.03 (d, *J* = 9 Hz, 2 H, Ar), 7.03 (d, *J* = 9 Hz, 2 H, Ar), 7.56 (d, *J* = 9 Hz, 2 H, Ar), 7.58 (d, *J* = 9 Hz, 2 H, Ar), 7.59 (s, 1 H), 7.64 (d, *J* = 8 Hz, 2 H, Ar), 7.67 (d, *J* = 8 Hz, 2 H, Ar), 7.75 (d, *J* = 9 Hz, 2 H, Ar), 7.98 (d, *J* = 8 Hz, 2 H, Ar); FAB HRMS (*m/z*) [*M*]<sup>+</sup> calced for C<sub>59</sub>H<sub>83</sub>NO<sub>16</sub><sup>+</sup>: 1061.5706, found: 1061.5717. UV-vis (H<sub>2</sub>O) λ<sub>max</sub> (ε) 356 (28 000); (ethyl acetate) λ<sub>max</sub> (ε) 365 (50 000).

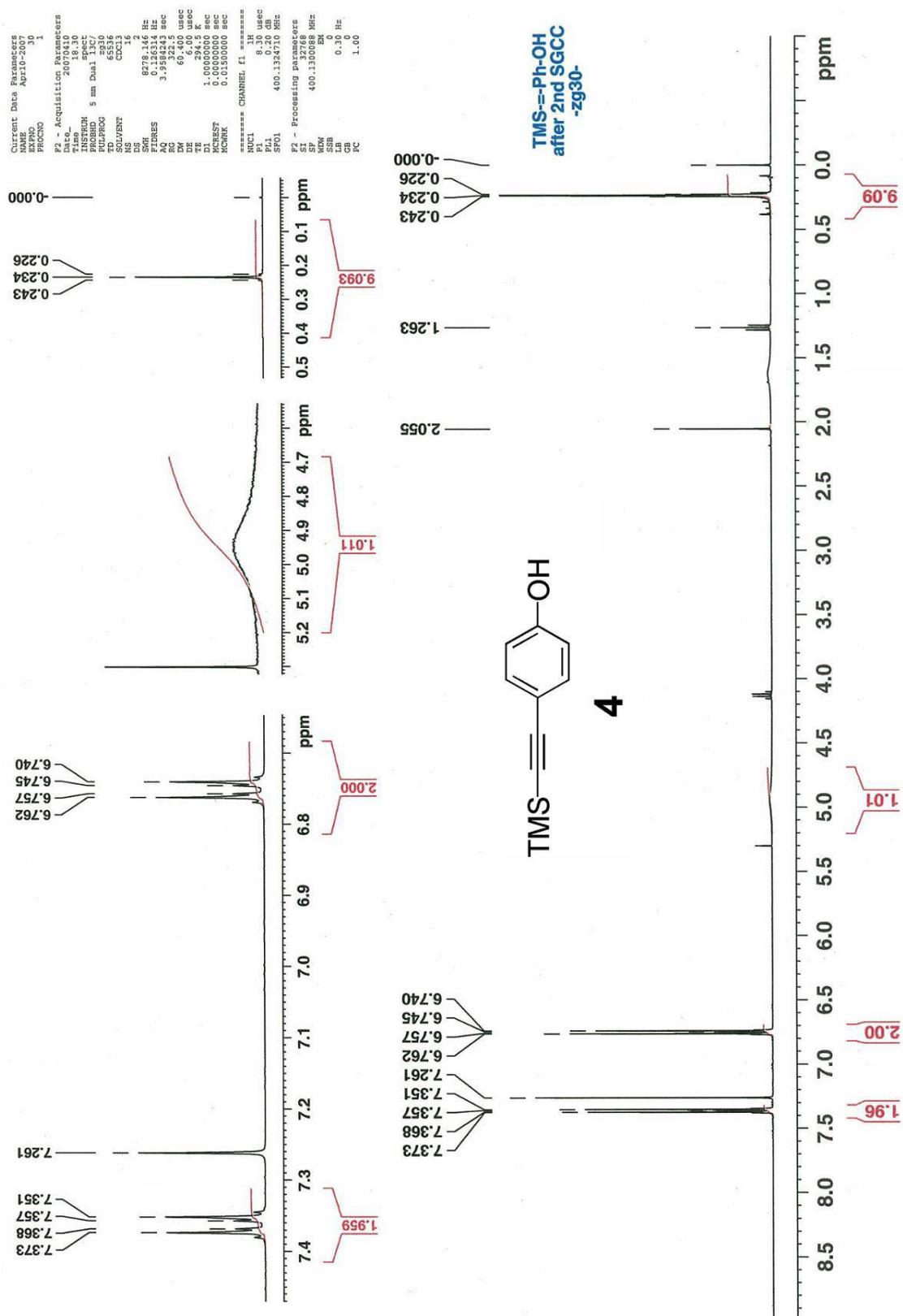


Figure S1. NMR spectra of compound **4** (CDCl<sub>3</sub>, TMS, 400 MHz).

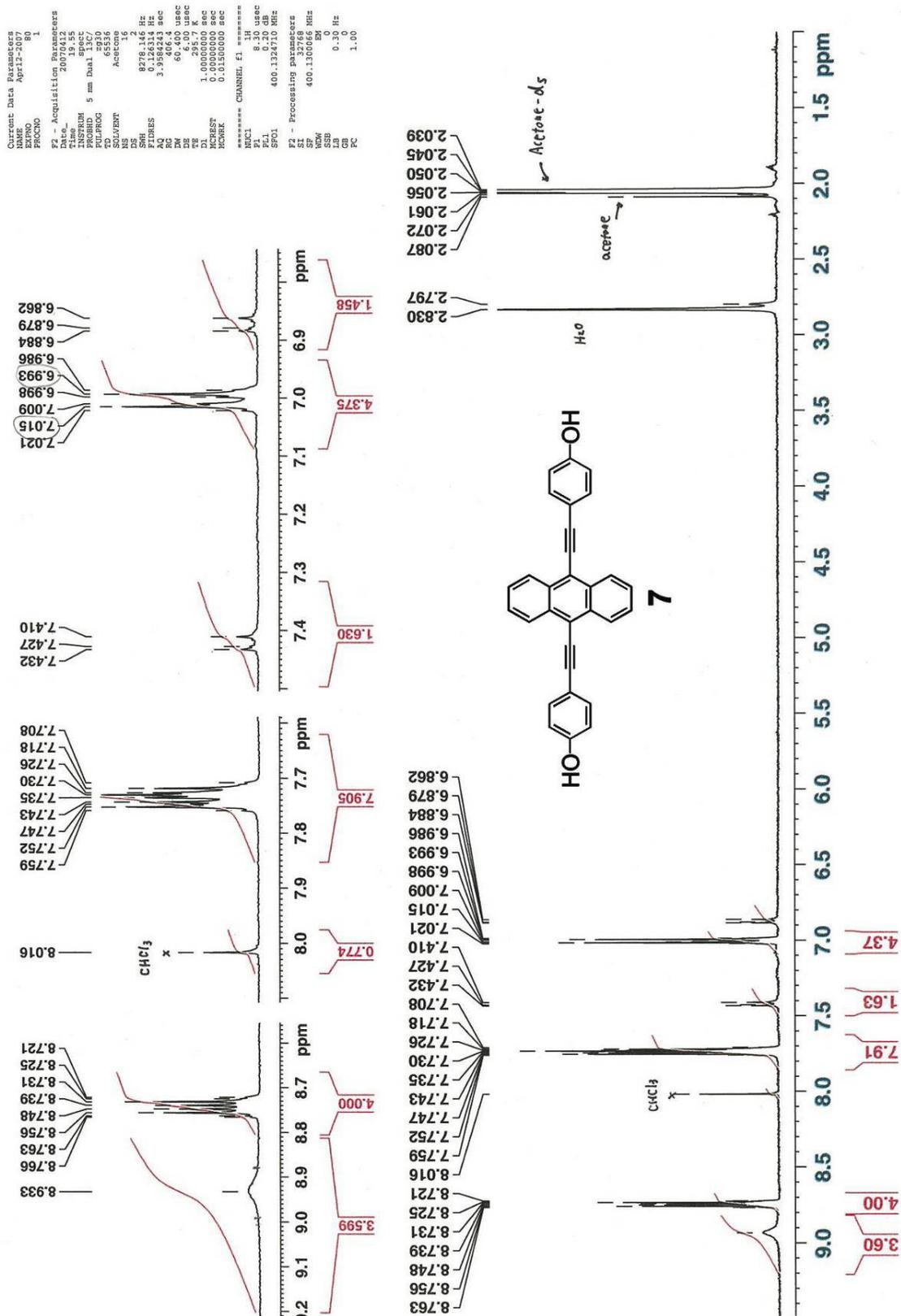


Figure S2. NMR spectra of compound 7 (acetone-d<sub>6</sub>, TMS, 400 MHz).

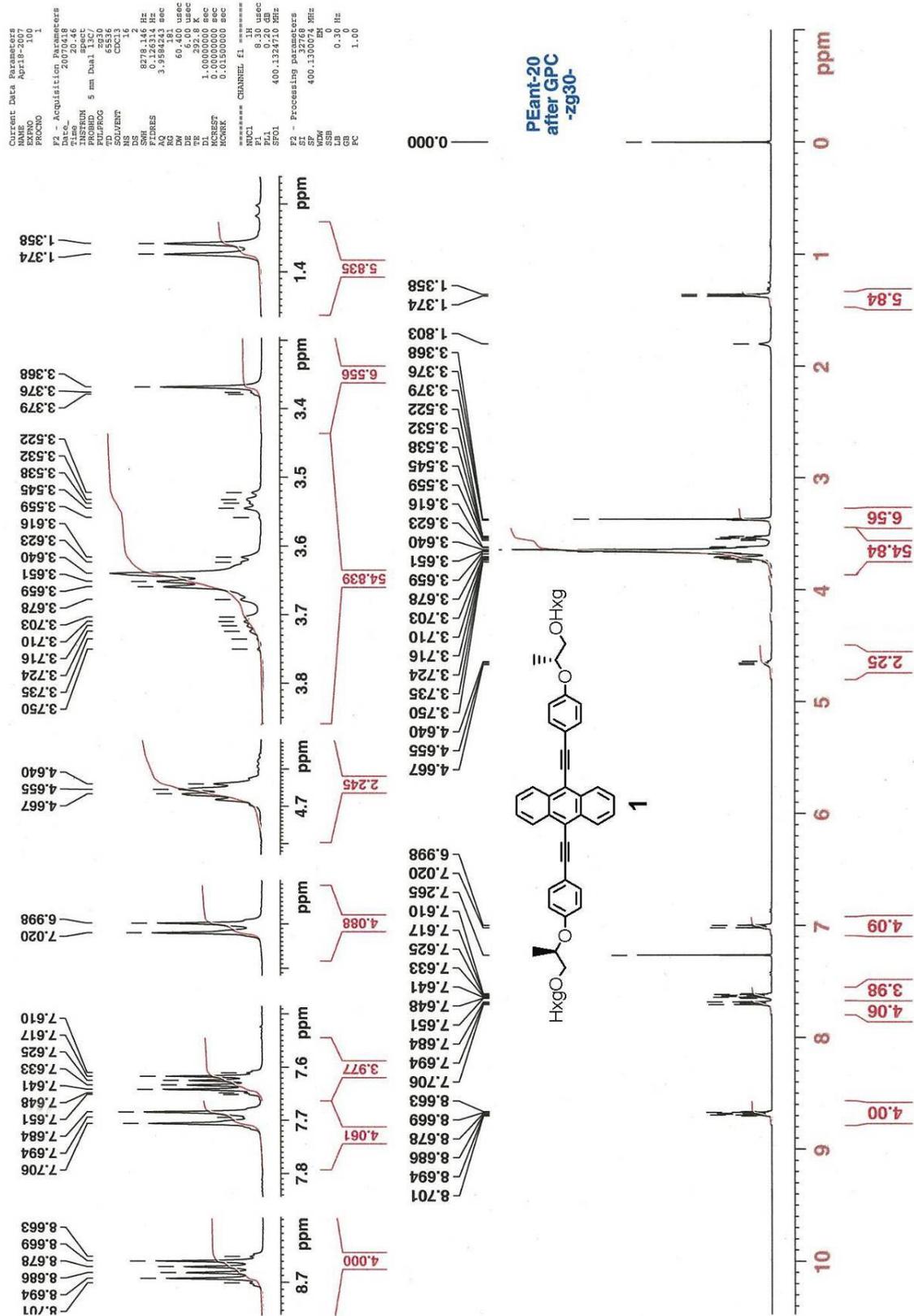


Figure S3. NMR spectra of compound 1 (CDCl<sub>3</sub>, TMS, 400 MHz).

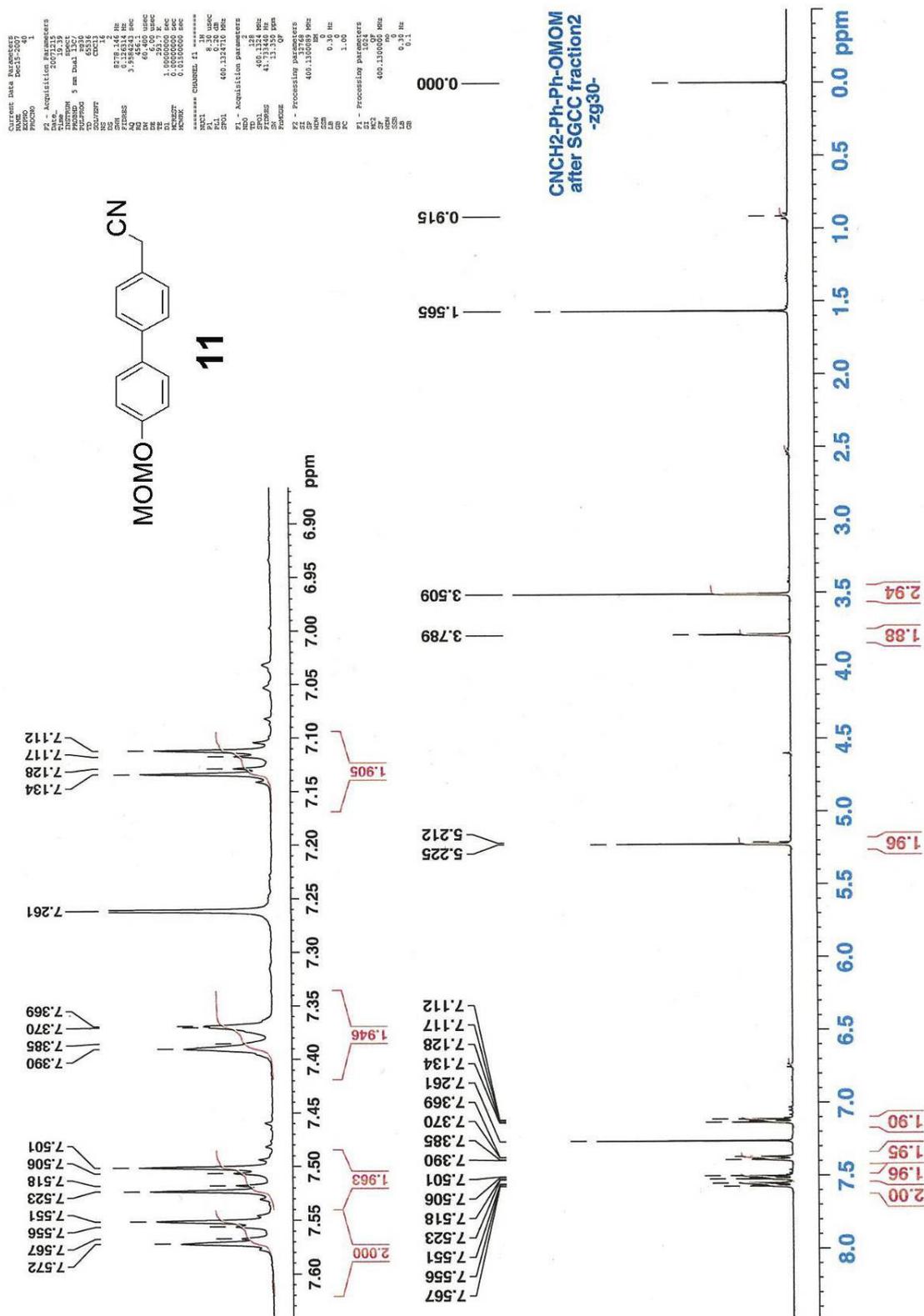


Figure S4. NMR spectra of compound **11** (CDCl<sub>3</sub>, TMS, 400 MHz).





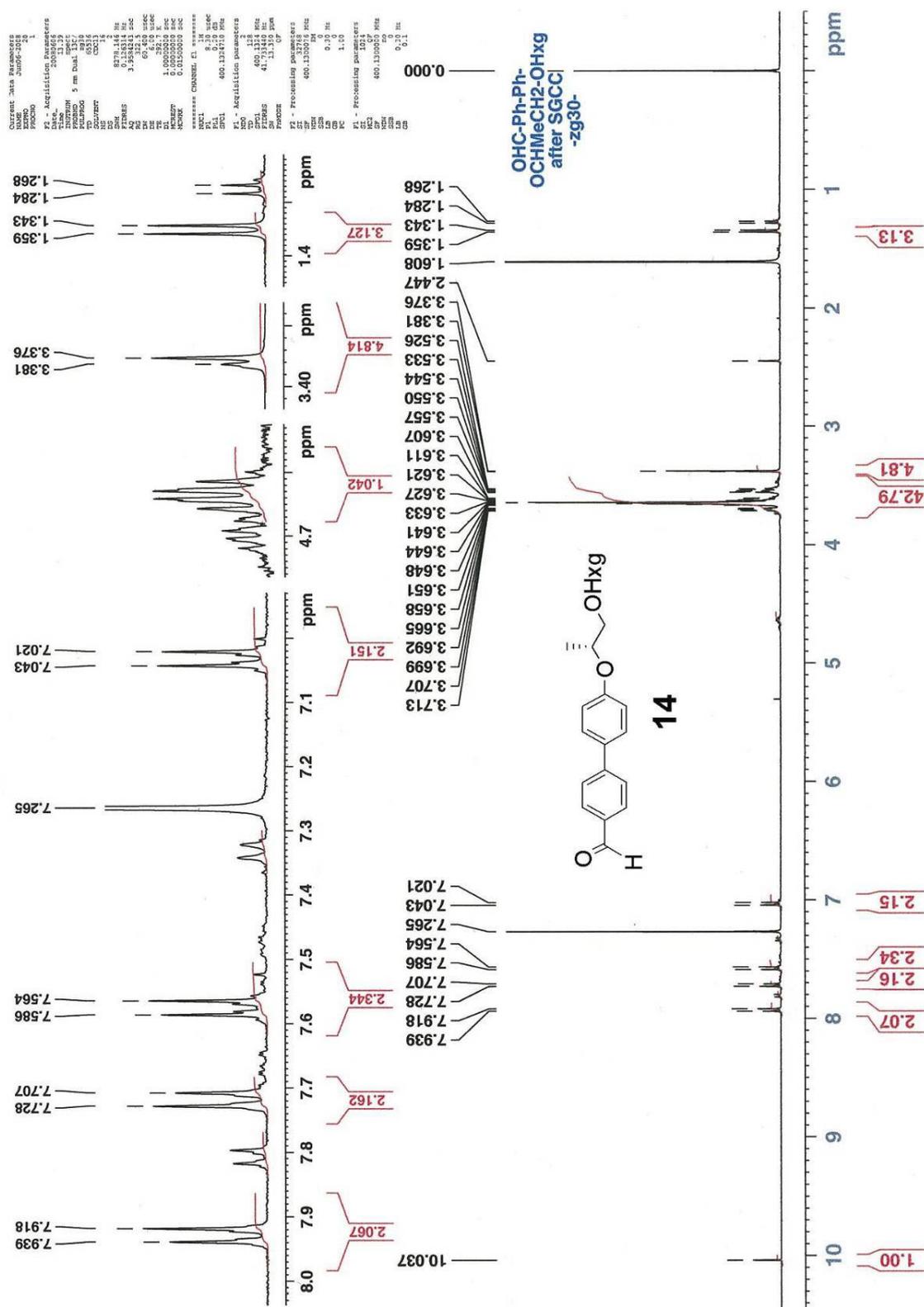
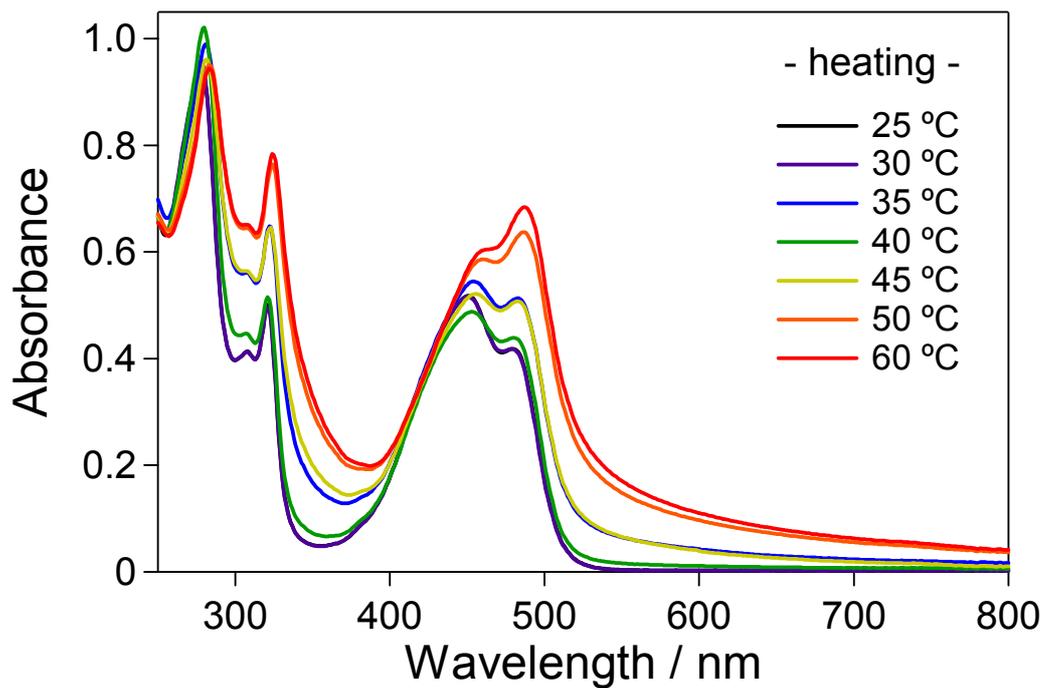


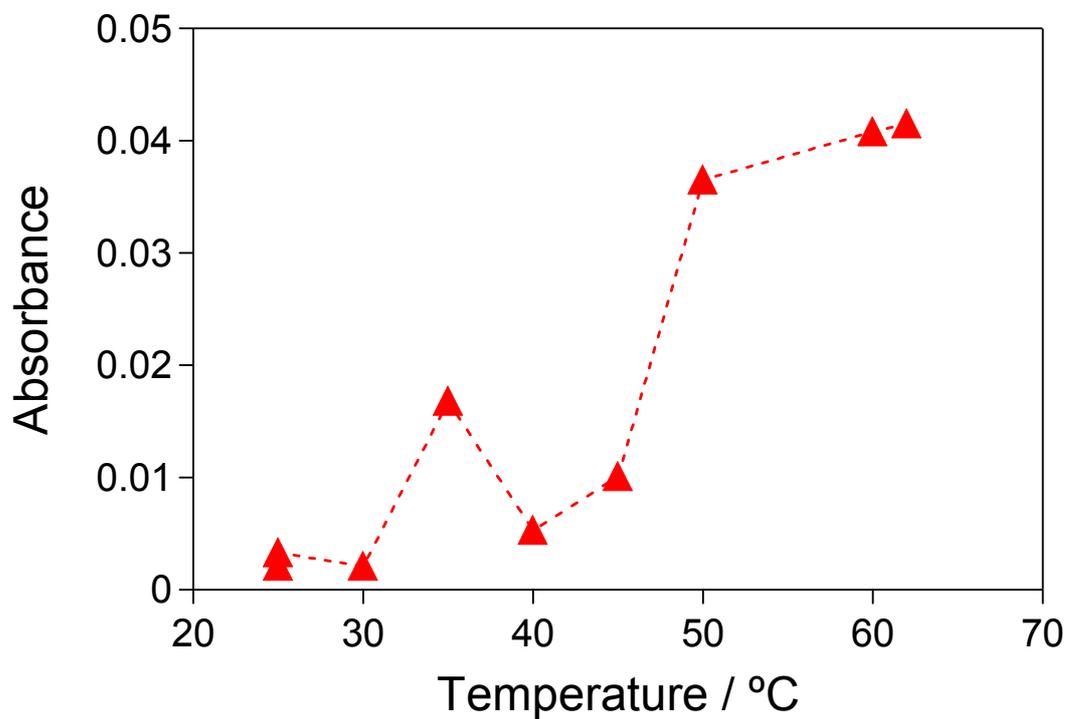
Figure S7. NMR spectra of compound 14 (CDCl<sub>3</sub>, TMS, 400 MHz).



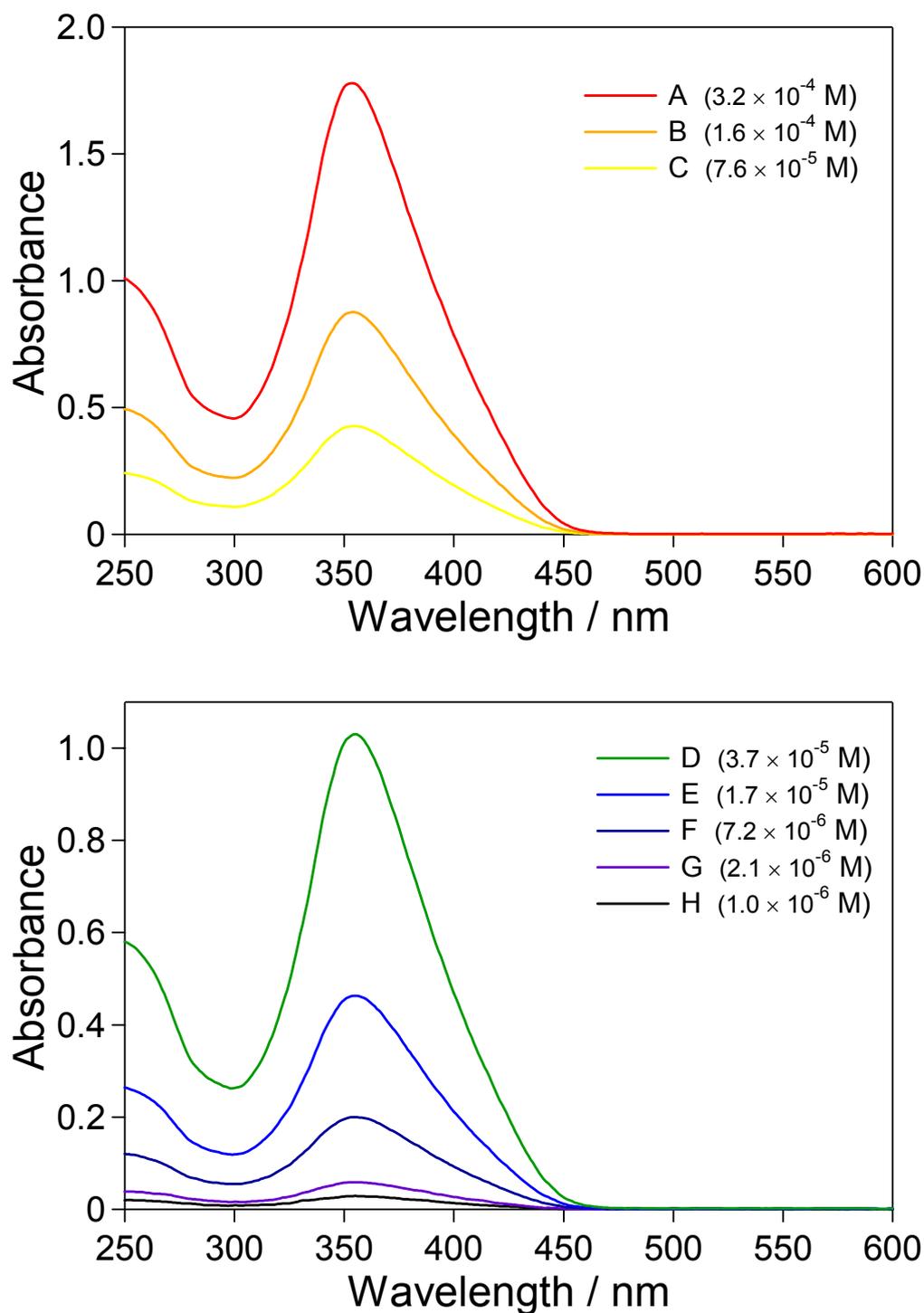
**B. Photochemical Measurement.** Absorption spectra were measured on a spectrophotometer (Hitachi U-3010) equipped with a Peltier-type temperature controller. CD and ORD spectra were recorded on a JASCO J-720S spectrophotometer equipped with a PTC-348WI Jasco Peltier-type temperature controller. Fluorescence spectra were measured on a fluorescence spectrophotometer (Hitachi F-2500) equipped with constant-temperature bath/circulator (Neslab RTE-210). The temperature of aqueous solutions was monitored by a thermocouple attached on the sample cell surface during variable-temperature measurements. Fluorescence quantum yields were determined by using 9,10-diphenylethynyl anthracene in cyclohexane solution ( $\Phi_f = 0.87$ ) for **1** and 9,10-diphenylanthracene in ethyl acetate solution ( $\Phi_f = 1.0$ ) as the reference for **2**. Compound **1** and **2** were purified by reversed phase HPLC (Kanto Chemical co., Mightysil RP-18 (H), CH<sub>3</sub>CN:MeOH:H<sub>2</sub>O = 9:1:2, Flow = 1.5 mL/min, for **1**; CH<sub>3</sub>CN:MeOH:H<sub>2</sub>O = 9:4:1, Flow = 3.0 mL/min, for **2**).



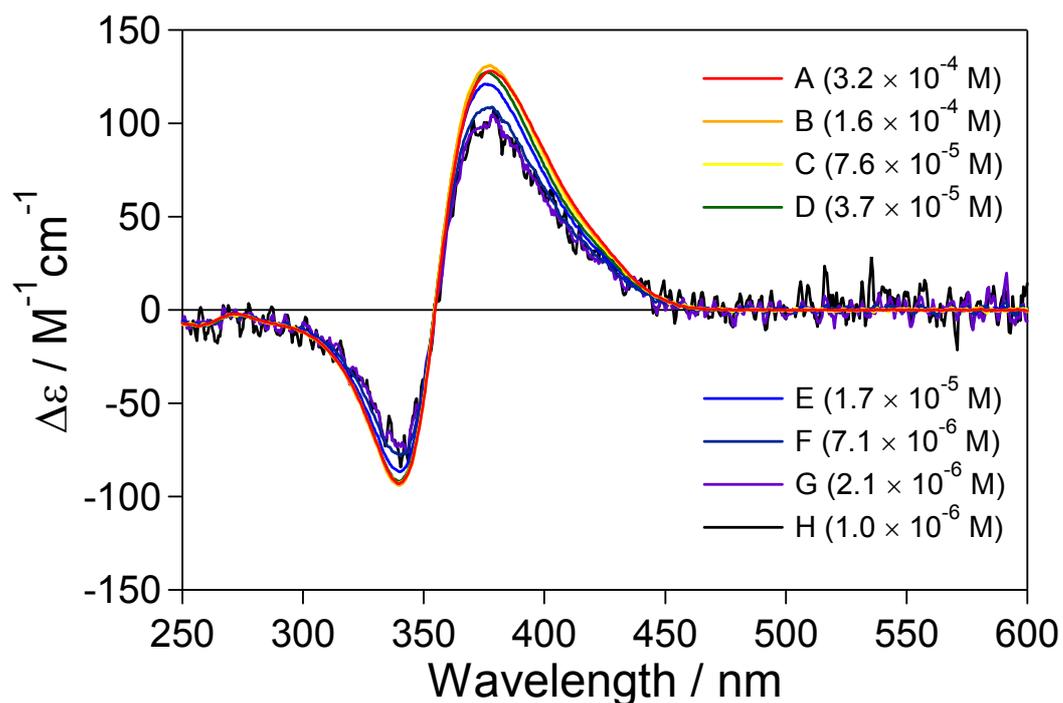
**Figure S9.** Variable temperature UV-vis spectra of an aqueous solution of **1** upon heating.



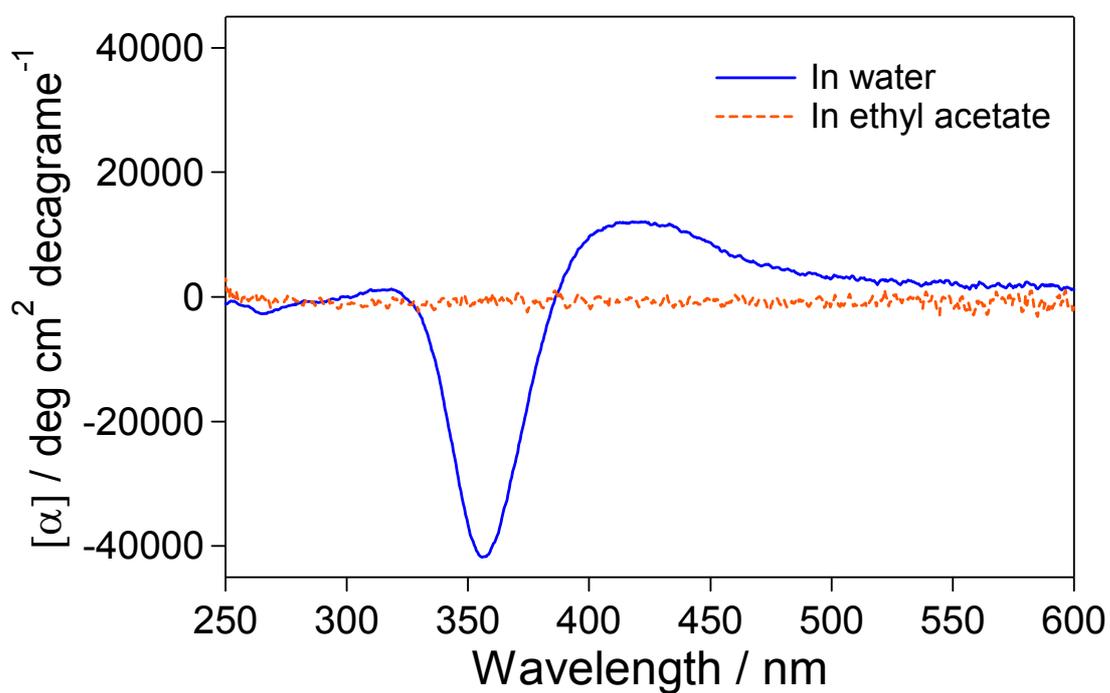
**Figure S10.** The plot of absorbance at 800 nm of an aqueous solution of **1** against temperature.



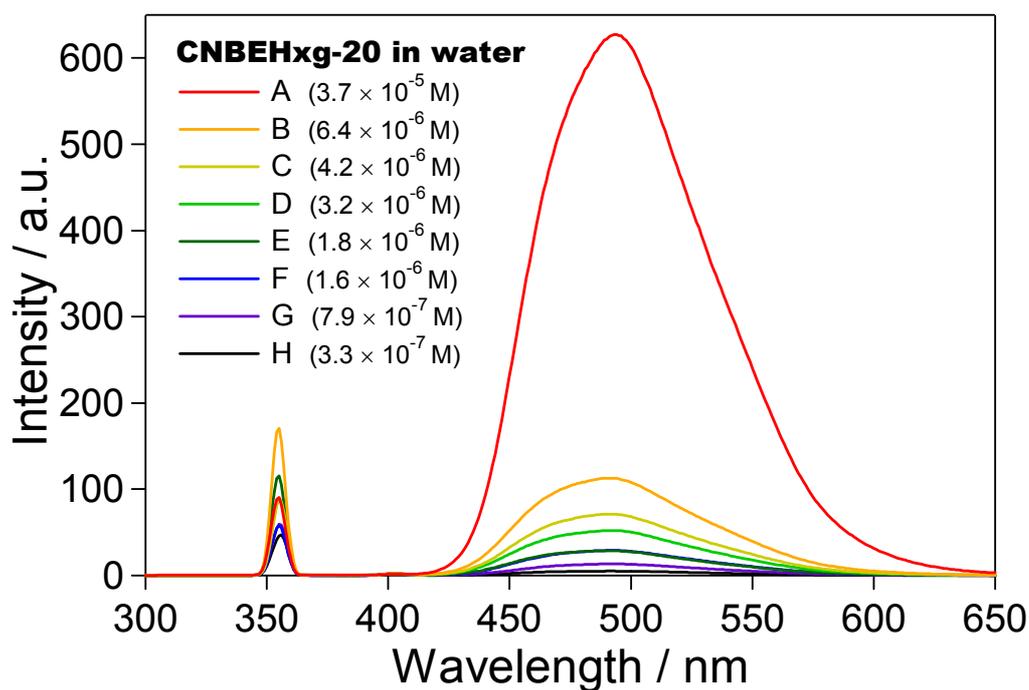
**Figure S11.** Concentration dependence of absorption spectrum of compound **2**. The spectra of sample A, B, and C were measured using a 2-mm cell (upper), and the spectra of D, E, F, G, and H were measured using a 10-mm cell (lower).



**Figure S12.** Concentration dependence of CD spectrum of compound 2. The spectra of sample A, B, and C were measured using a 2-mm cell and the spectra of D, E, F, G, and H were measured using a 10-mm cell.



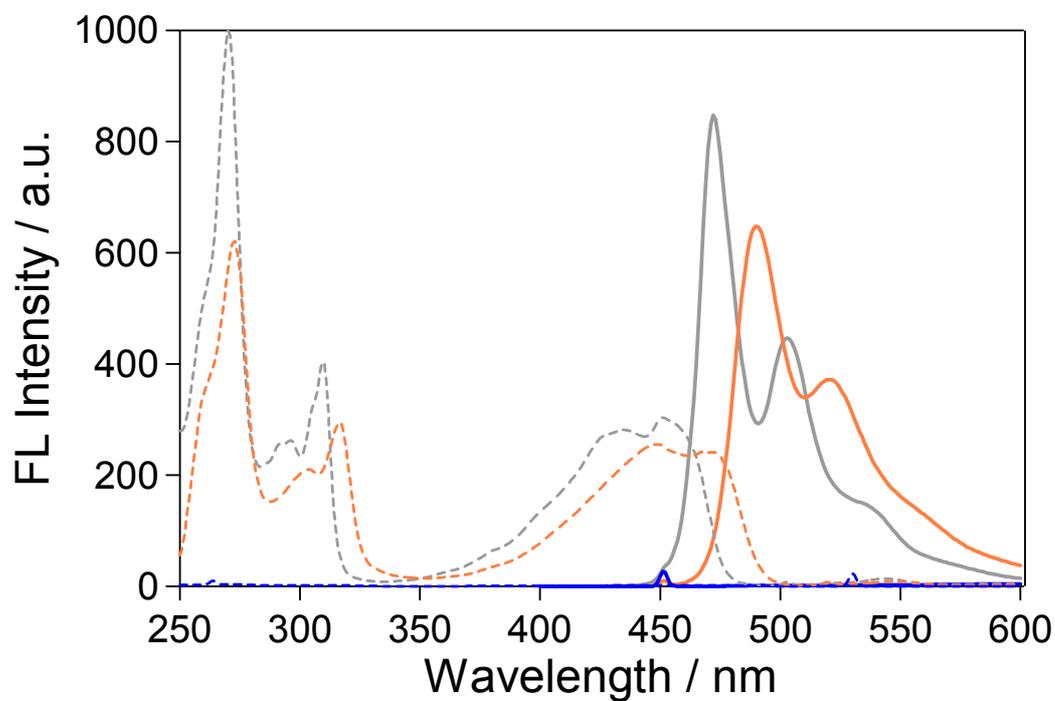
**Figure S13.** ORD spectra of compound 2 in water (blue solid line) and in ethyl acetate (orange dotted line).



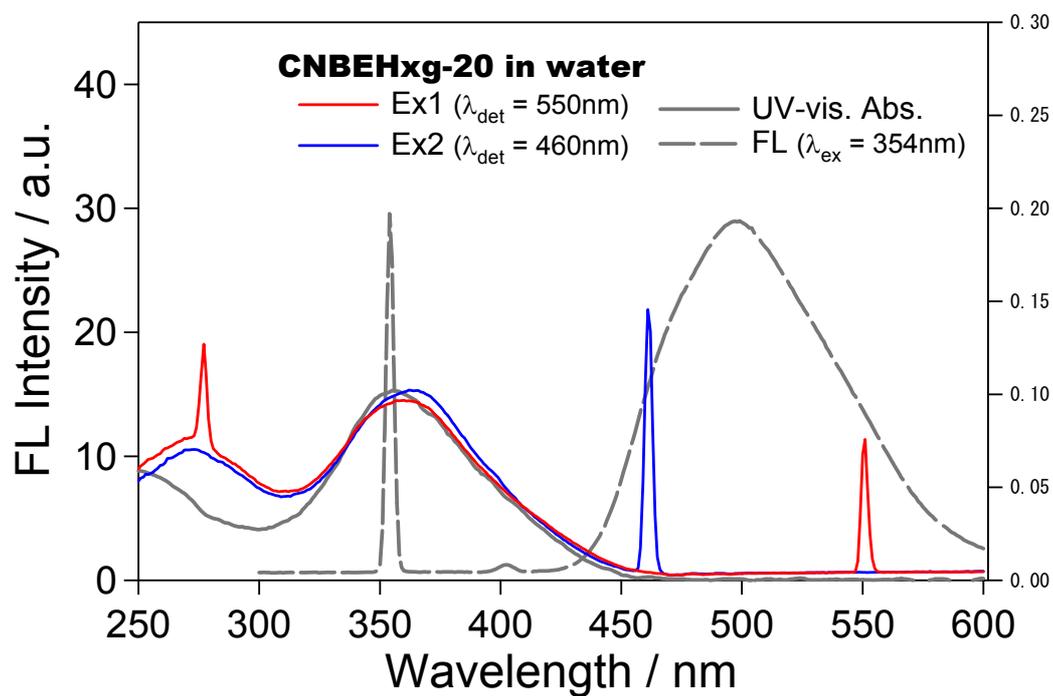
**Figure S14.** Concentration dependence of fluorescence spectrum of compound **2**.

**Table S1.** Concentration dependence of fluorescent property of compound **2** in ethyl acetate and in water. Refractive indexes ( $n_{\text{EtOAc}} = 1.37$  and  $n_{\text{H}_2\text{O}} = 1.33$ ) were adopted for the calculation of fluorescence quantum yield.

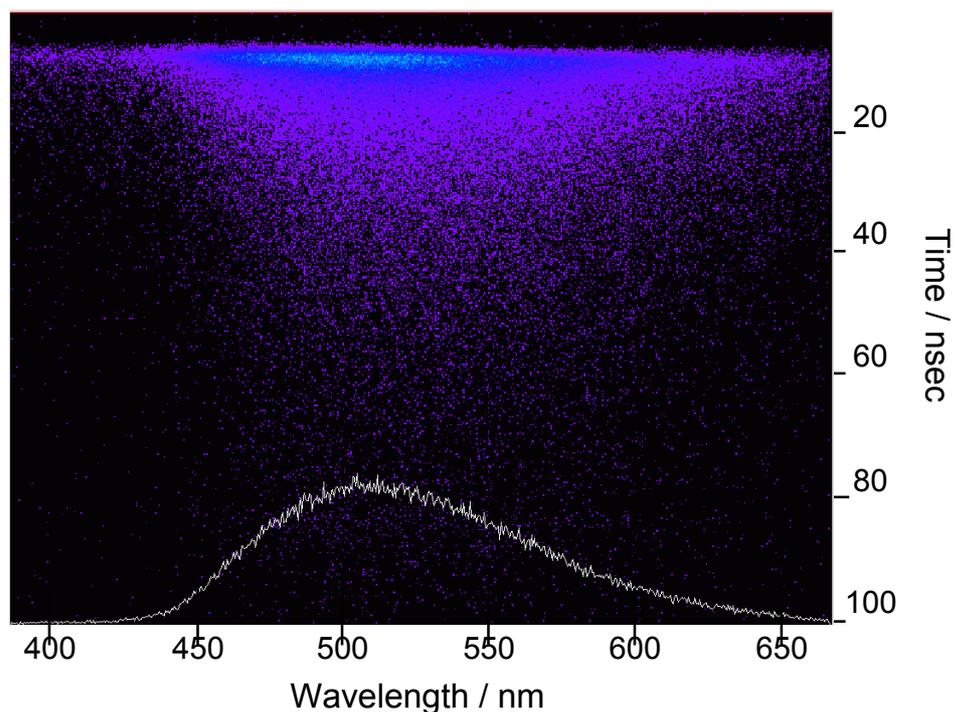
	In ethyl acetate			In water		
	Conc. / M	Abs@354 nm	$\Phi_f$	Conc. / M	Abs@354 nm	$\Phi_f$
A	$5.0 \times 10^{-5}$	2.1545	0.0020	$3.7 \times 10^{-5}$	1.0388	0.021
B	$1.0 \times 10^{-5}$	0.4352	0.0051	$6.4 \times 10^{-6}$	0.1781	0.023
C	$8.0 \times 10^{-6}$	0.3459	0.0051	$4.2 \times 10^{-6}$	0.1180	0.021
D	$6.0 \times 10^{-6}$	0.2589	0.0053	$3.2 \times 10^{-6}$	0.0891	0.021
E	$4.0 \times 10^{-6}$	0.1742	0.0055	$1.8 \times 10^{-6}$	0.0489	0.021
F	$3.0 \times 10^{-6}$	0.1318	0.0060	$1.6 \times 10^{-6}$	0.0452	0.023
G	$2.0 \times 10^{-6}$	0.0857	0.0061	$7.9 \times 10^{-7}$	0.0220	0.022
H	$1.0 \times 10^{-6}$	0.0421	0.0060	$3.3 \times 10^{-7}$	0.0091	0.021



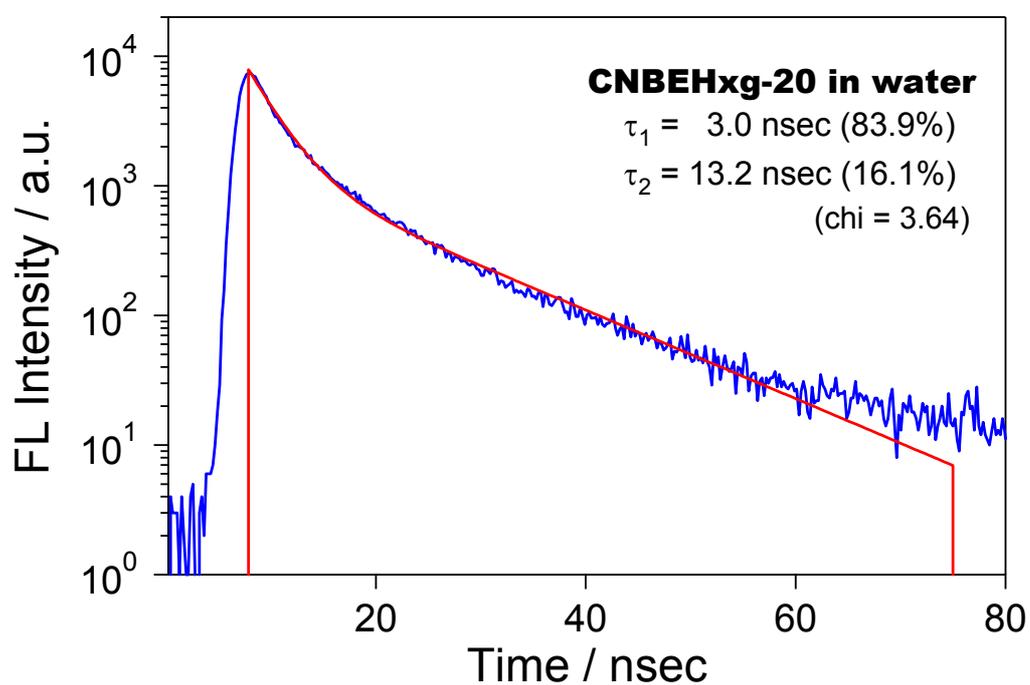
**Figure S15.** Fluorescence spectra of compound **1** in ethyl acetate (orange solid line) and water (blue solid line). Corresponding excitation spectra are shown as dashed lines. Corresponding spectra of 9,10-bis(phenylethynyl)anthracene in cyclohexane are shown as gray lines. The absorbance at the excitation wavelength (ex. 450 nm) was set to 0.09 for all samples.



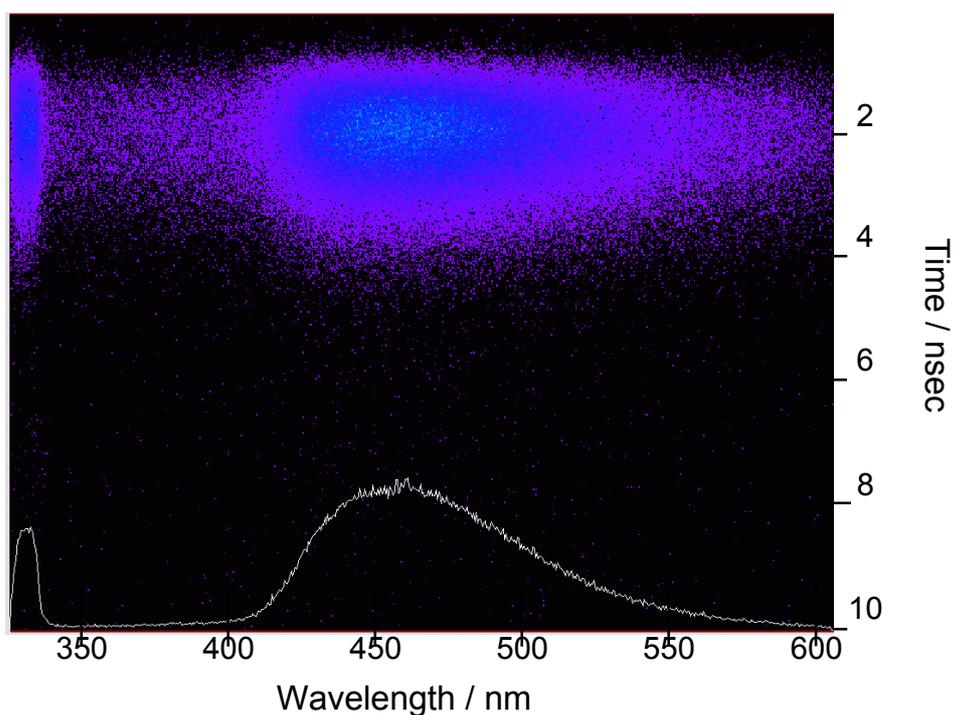
**Figure S16.** Excitation spectra of compound **2** in water detected at 550 nm (red solid line) and 460 nm (blue solid line). Corresponding absorption and fluorescence spectra are shown as gray solid and gray dashed line, respectively.



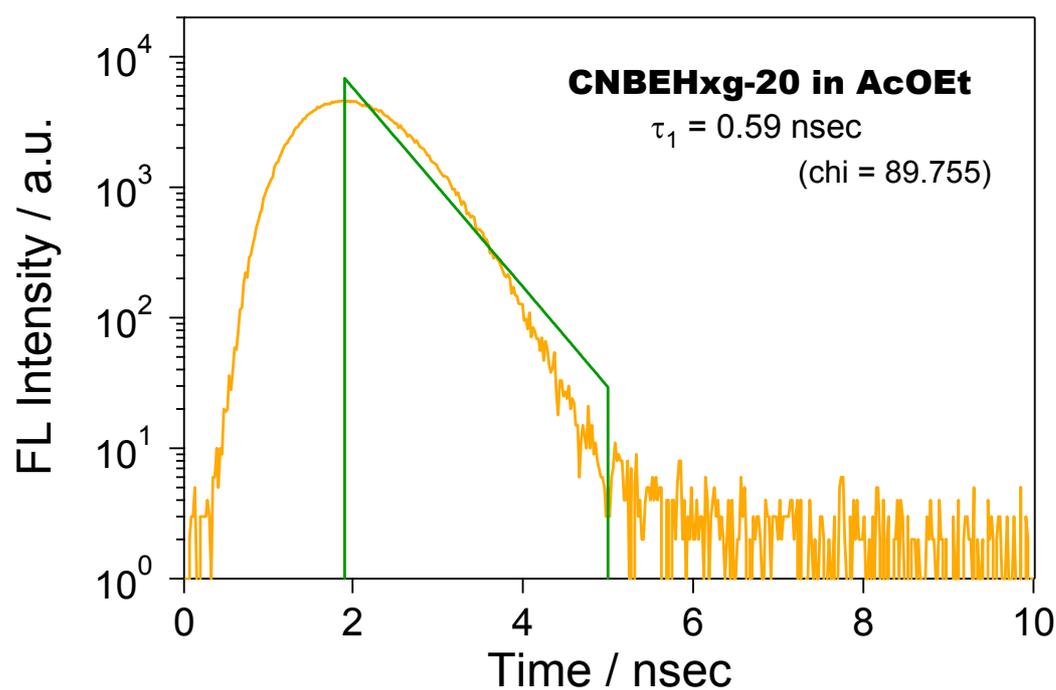
**Figure S17.** Fluorescence lifetime of compound **2** in water. FL lifetime was recorded on a HAMAMATSU C4334 streak scope. Excitation was carried out by a LTB-MNL200 N<sub>2</sub> Laser at 337.1 nm, whose pulse width was about 500 psec.



**Figure S18.** Fluorescence decay curve of compound **2** in water (blue line) and fitting curve (red line). Observed decay curve includes multi-components and the decay curve was fitted with two component model.



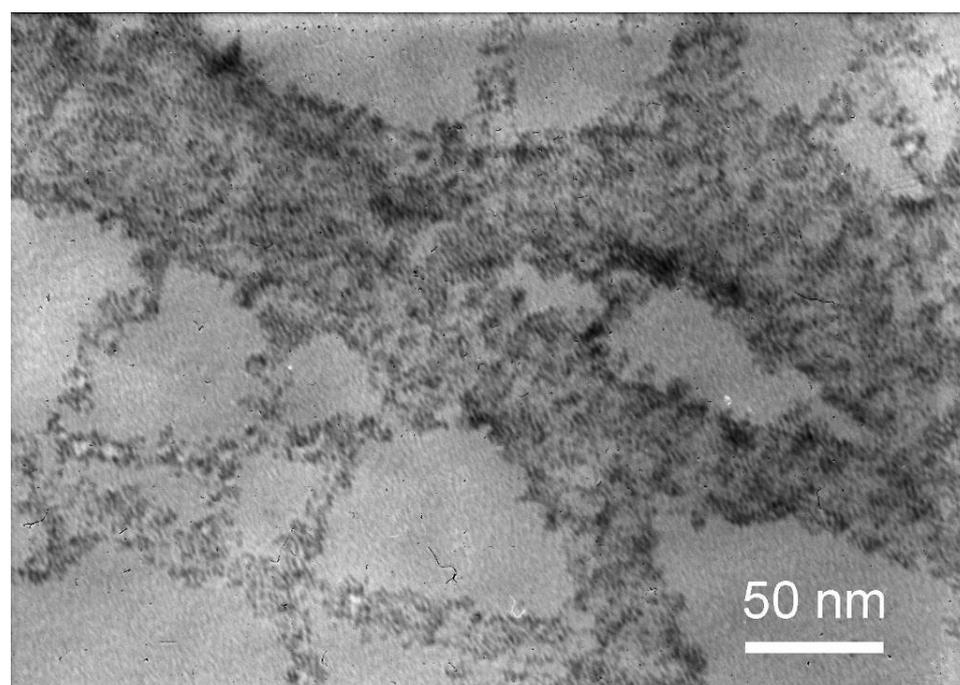
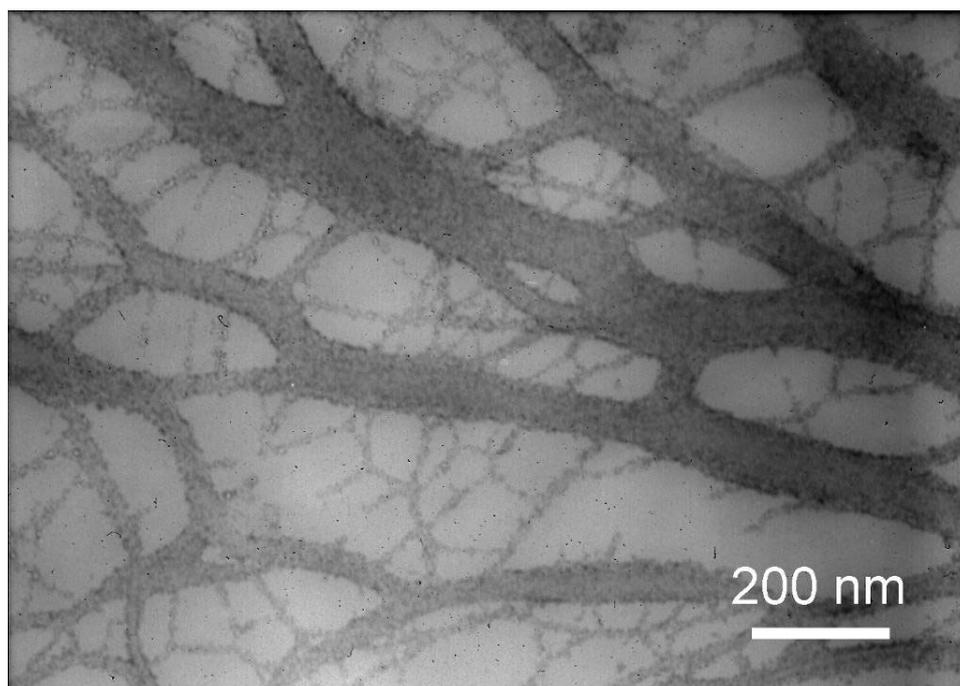
**Figure S19.** Fluorescence lifetime of compound **2** in ethyl acetate. FL lifetime was recorded on a HAMAMATSU C4334 streak scope. Excitation was carried out by a LTB-MNL200 N<sub>2</sub> Laser at 337.1 nm, whose pulse width was about 500 psec.



**Figure S20.** Fluorescence decay curve of compound **2** in ethyl acetate (orange line) and fitting curve (green line). Fluorescence intensity was decayed too fast to determine lifetime.

**C. DLS Measurement.** Particle size distribution was measured on Nicomp 380ZLS particle sizer equipped with 785 nm red laser as light source, using a fixed angle (90°). The samples were filtrated by MILLIPORE Millex membrane filter (0.20 µm) before measurement. The samples were kept 30 °C during measurement. Channel width was selected automatically to 37.0 µsec by the instrument for the case of the aqueous solution of **2**. The data was accumulated for more than 15 minutes. Observed autocorrelation function was analyzed with Nicomp method available for multiple size distribution equipped in the instrument, because of large value of chi squared as Gaussian analysis ( $\chi^2 \sim 27.89$ ). The size distribution was evaluated as scattering-intensity-weighted average, observed at peak#1 = 5.9 ± 0.9 nm (5.2%), peak#2 = 82.4 ± 0.9 nm (3.0%), peak#3 = 2926.7 ± 428.5 nm (91.8%), (Residual = 0.0, Fit Error = 2.26).

**D. TEM Measurement.** Transmission electron microscopy (TEM) was conducted on a HITACHI H-7000 (acceleration voltage, 100 kV). A dilute aqueous solution of **2** ( $\sim 10^{-5}$  M) was dropped on a carbon-coated copper grid ( $\sim 10$  µL), and dried at room temperature for 12 h. After completely dried in vacuo, the copper grid was exposed to OsO<sub>4</sub> vapor for 10 h and observed by TEM. The staining was carried out according to the following procedure. The copper grid was fixed on a slide glass by holding its edge with a cover glass carefully not to damage the carbon coat. A sample tube was filled the bottom with 4% OsO<sub>4</sub> aqueous solution and the prepared slide glass with the copper grid was placed on the top of the sample tube upside down so that the grid was exposed to the OsO<sub>4</sub> vapor.



**Figure S21.** Other TEM images of **2** from an aqueous solution stained with  $\text{OsO}_4$ .

## References.

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[S2] K. Uchida, A. Takata, M. Saito, A. Murakami, S. Nakamura, M. Irie, *Adv. Funct. Mater.* **2003**, *13*, 755-762.