Competitive photoinduced electron transfer by the complex formation of porphyrin with cyclodextrin bearing viologen

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Supporting information

Table of Contents *Page*

1. Preparation and Spectroscopic characterization *S2*
2. 2D ROESY ^{1}H NMR spectra of acceptor **3** with and without AdCA *S4*
3. Circular dichroism spectral changes of TCPP upon addition of **3** *S*5
4. Absorption spectral changes of TCPP upon addition of *β*-CD *S*5
5. Fluorescence changes of TCPP upon addition of **1** *S*6
6. Fluorescence changes of TCPP upon addition of **2** *S*6
7. Fluorescence changes of TCPP upon addition of **3** *S*7
8. Fluorescence decay of TCPP in the presence of acceptor **2** and **3** *S*8

Preparation and Spectroscopic characterization:

Measurements

IR spectra were recorded on a FT/IR/410 JASCO instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JOEL-GSX 400 at 400MHz Instrument. 2D NMR (ROESY) experiments were recorded at 400 MHz on a VARIAN UNITY plus NMR spectrometer. Chemical shifts were referenced to the solvent values.Elemental analyses were recorded on an Elementar Vario EL-III instrument.UV-Vis spectra were record on a SHIMADZU UV-2500PC instrument. Fluorescence spectra were record on a HITACHI f-2500 instrument. Fluorescence lifetimes of TCPP were measured by time correlated single-photon counting method under air saturation; Sp Tsumani Ti:Sa laser was used for the excitation of porphyrin. Excitation wavelength was set at 420 nm (Laser Pulse width = 100 fs); Measurements were carried out at room temperature.

Syntheses

Acceptor 1: Ethyl 3-(1'-methyl-[4,4']bipyridine-1-yl)propionate

4,4'-Bipyridine (1.6 g, 1.1 mmol) was dissolved in dried $CHCl_3$ 20 ml, and cooled with ice both, CH_3I (0.62 ml, 1 mmol) was dissolved in acetone 20 ml, the CH_3I solution was added slowly to the 4,4'-bipyridine solution with stirring at 4℃. The mixture was stirred for 1 hour in an ice bath and overnight at room temperature. The precipitate was collected by suction filtration, washed with dry $CHCl_3$, and dried in vacuum. Recrystallization from 95% ethanol. The solid (20 mmol, 6.0 g) was dissolved in dry DMF 30ml, and ethyl 3-bromo-propionate (5.1 ml, 40 mmol) was added, and then stirred at 120℃ for 4 hrs, then in room temperature overnight. The precipitate was collected by suction filtration, washed with dry DMF, and orange solid was obtained in a 75% yield.

IR: (cm^{-1}) 2999, 1731, 1638, 1560, 1183.

^{1}H NMR (DMSO-d_6, 400 MHz): δ(ppm) 9.38 (d, 2H, viologen), 9.27 (d, 2H, viologen), 8.75(m, 4H, viologen), 4.92(t, 2H, -CH_2-), 4.43 (s, 3H, N-CH_3), 4.08(t, 2H, -CH_2-COO), 1.17(t, 3H, C-CH_3); the signal of -CH_2-N- obscured by H_2O peak.

^{13}C NMR (D_2O and DMSO-d_6 mixture, 300 MHz): δ(ppm) 169.7 (C of –CO-), 148.6, 147.9, 146.5, 146.2, 126.0, 126.0 (C of viologen), 60.6 (C of O-CH_2), 56.3 (C of N-CH_2), 48.0 (C of CO-CH_2), 34.1 (C of N-CH_3), 14.0 (C of CH_3).

Acceptor 2: Mono-6-deoxy-3-[3-(1'-methyl-[4,4']bipyridine-1-yl)-propionamide] cinnamoyl-*β*-CD

3-(1'-Methyl-[4,4']bipyridine-1-yl)propionic acid (0.13 mmol, 40 mg) and mono-6-dexoy-[3-aminocinnamoyl]-*β*-CD (0.13 mmol, 160 mg) were dissolved in DMF (5 mL) and water (1 mL). The mixture was cooled with ice bath and stirring for 1 hr, and 1-(3-dimethylaminopropyl)-3-ethylcarbodimide hydrochloride (3 eq) was added stirring in an ice bath 1 hr more, and another 3 days at room temperature. After cooled to room temperature, the solution was poured into acetone (50 mL). The resulting precipitate was dried under vacuum to get crude product. The crude product was purified by HP 20 column. The eluent was concentrated and washed by ethanol to give 142 mg of the desired product in a 71% yield.

IR: (cm^{-1}) 3395, 2925, 1638, 1418, 1153, 1026.

^{1}H NMR (DMSO-d_6, 400 MHz): δ(ppm) 10.74 (br, 1H, -CO-NH-), 9.46 (d, 2H, viologen), 9.27 (d, 2H, viologen), 8.76 (m, 4H, viologen), 7.63 (br, 4H, phenyl), 7.56 (d, 1H, -CH-), 6.55 (d, 1H,

-CH-), 5.75-5.66 (m, 14H, O(2) and O(3) of β-CD), 5.01 (s, 3H, methyl), 4.87-4.82 (m, 7H, C(1) of β-CD), 4.49-4.32 (m, O(6) and C(6') of β-CD), 3.62-3.26 (m, overlaps, with HOD), 2.89-2.73 (m, 4H, -CH_2-).

^{13}C NMR (DMSO-d_6, 300 MHz): δ(ppm) 167.9, 166.0 (C of –CO-), 148.6, 148.0, 146.4, 146.3, 129.0, 129.0 (C of viologen), 140.5, 126.1, 126.0, 119.0 (C of phenyl), 143.8, 116.3 (C of CH=CH), 101.9 (C(1) of β-CD), 81.5 (C(4) of β-CD), 73.1 (C(3) of β-CD), 72.4 (C(2) of β-CD), 72.0 (C(5) of β-CD), 59.9 (C(6) of β-CD), 56.9 (C(6') of β-CD), 48.0 (CH_2-viologen), 36.4 (C of CH_3), 30.7 (-CH_2-).

Anal. Calcd for $C_{65}H_{93}O_{37}N_3Cl_2 \cdot 9.8\ H_2O$: C, 44.46; H, 6.46; N, 2.39. Found: C, 44.49; H, 6.62; N, 2.31.

Acceptor 3: Mono-6-deoxy-3-[3-(1'-methyl-[4,4']bipyridine-1-yl)-propionamide] hydrocinnamoyl-*β*-CD

3-(1'-Methyl-[4,4']bipyridine-1-yl)propionic acid (0.13 mmol, 40 mg) and mono-6-dexoy-[3-aminohydrocinnamoyl]-*β*-CD (0.13 mmol, 160 mg) were dissolved in DMF (5 mL) and water (1 mL). The mixture was cooled with ice bath and stirring for 1 hr, and 1-(3-dimethylaminopropyl)-3-ethylcarbodimide hydrochloride (3eq) was added stirring in an ice bath 1 hr more, and another 3 days at room temperature. After cooling to room temperature, the solution was poured into acetone (50 mL). The resulting precipitate was dried under vacuum to get crude product. The crude product was purified by HP 20 column. The eluent was concentrated and washed by ethanol to give 130 mg of the desired product in a 65% yield.

IR: (cm^{-1}) 3395, 2925, 1638, 1153, 1026.

^{1}HNMR (DMSO-d_6, 400 MHz): δ(ppm) 10.27 (bs, 1H, -CO-NH-), 9.43 (d, 2H, viologen), 9.26 (d, 2H, viologen), 8.76 (m, 4H, viologen), 7.43 (d, 2H, phenyl), 7.1 2(d, 2H, phenyl), 5.70 (m, 14H, O(2) and O(3) of β-CD), 4.98 (s, 3H, methyl), 4.78 (m, 7H, C(1) of β-CD), 4.42-4.27 (m, O(6) and C(6') of β-CD), 3.82-3.16 (m, overlaps, with HOD), 2.76-2.72 (m, 4H, CH_2 of phenyl and viologen), 2.59 (t, 2H, CH_2 of phenyl).

^{13}C NMR(DMSO-d_6, 300 MHz): δ(ppm) 171.9, 167.3 (C of –CO-), 150.8, 148.6, 146.4, 146.3, 128.3, 128.27 (C of viologen), 136.5, 135.5, 126.0, 119.1 (C of phenyl), 101.9 (C(1) of β-CD), 81.5 (C(4) of β-CD), 73.0 (C(3) of β-CD), 72.4 (C(2) of β-CD), 71.2 (C(5) of β-CD), 59.9 (C(6) of β-CD), 57.0 (C(6') of β-CD), 48.0 (CH_2-viologen), 36.3 (C of CH_3), 34.9 (C of -CH_2-CO), 29.6, 29.8 (C of -CH_2-).

Anal. Calcd for $C_{65}H_{93}O_{37}N_3Cl_2 \cdot 8.3\ H_2O$: C, 44.03; H, 6.23; N, 2.37. Found: C, 44.02; H, 6.35; N, 2.56.

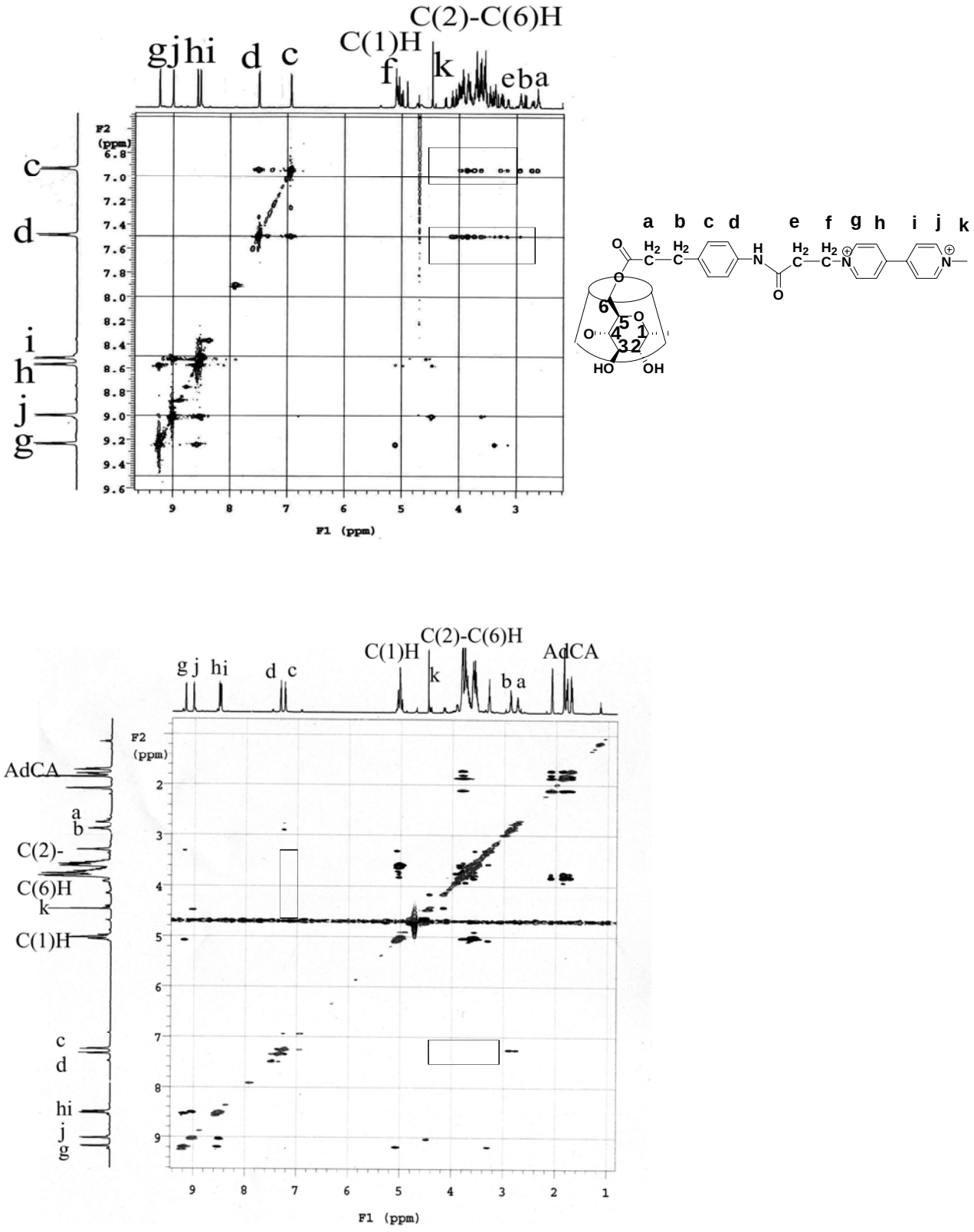

Figure 1. 500 MHz 2D ROESY ^{1}H NMR spectra of acceptor **3** at the absence (upper) and presence of AdCA at1.5 mM in D_2O.

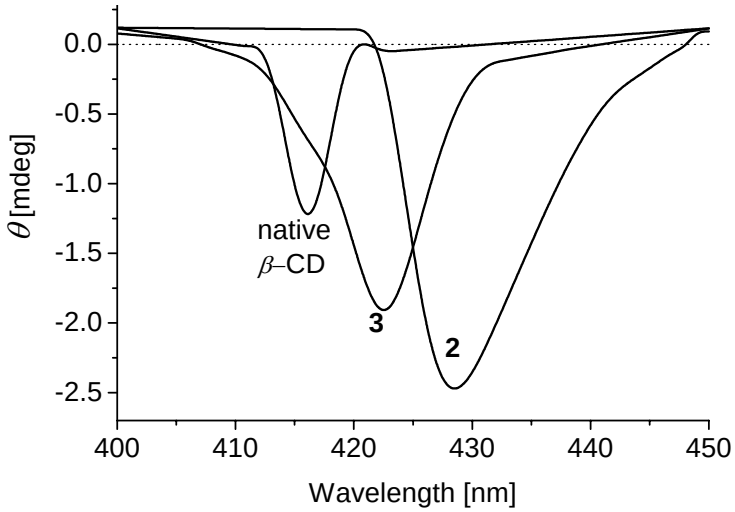

Figure 2. Circular dichroism spectral changes of TCPP (10 μM) in 0.05 M phosphate buffer with native β-CD (black line), quencher 2 (green line) and quencher 3 (red line) at 0.90 mM.

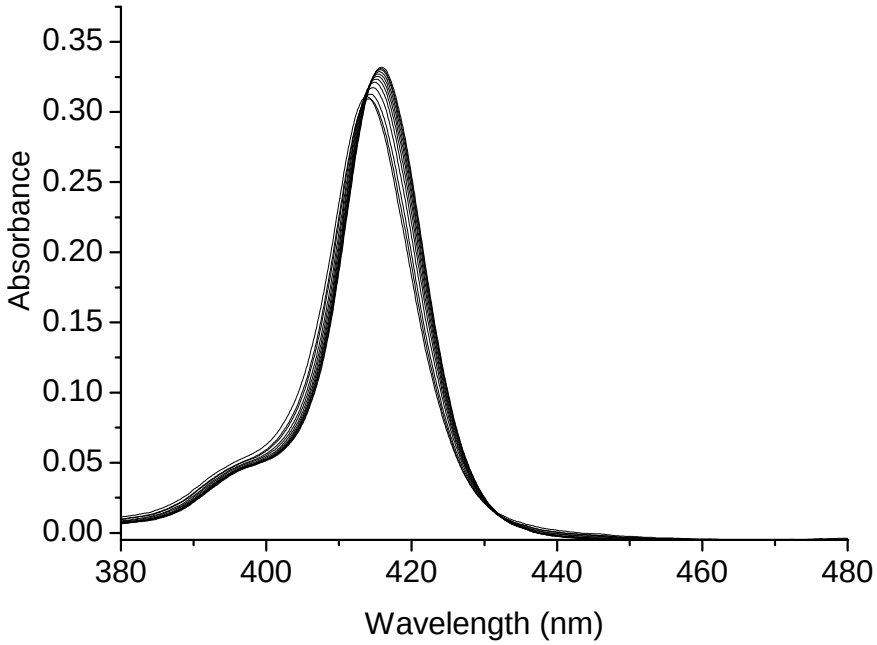

Figure 3. Absorption spectral changes of TCPP (1.0 μM) in 0.05 M phosphate buffer at pH 7.0 upon addition of β-CD from 0 to 2.0×10^{-5} M at 25 ℃.

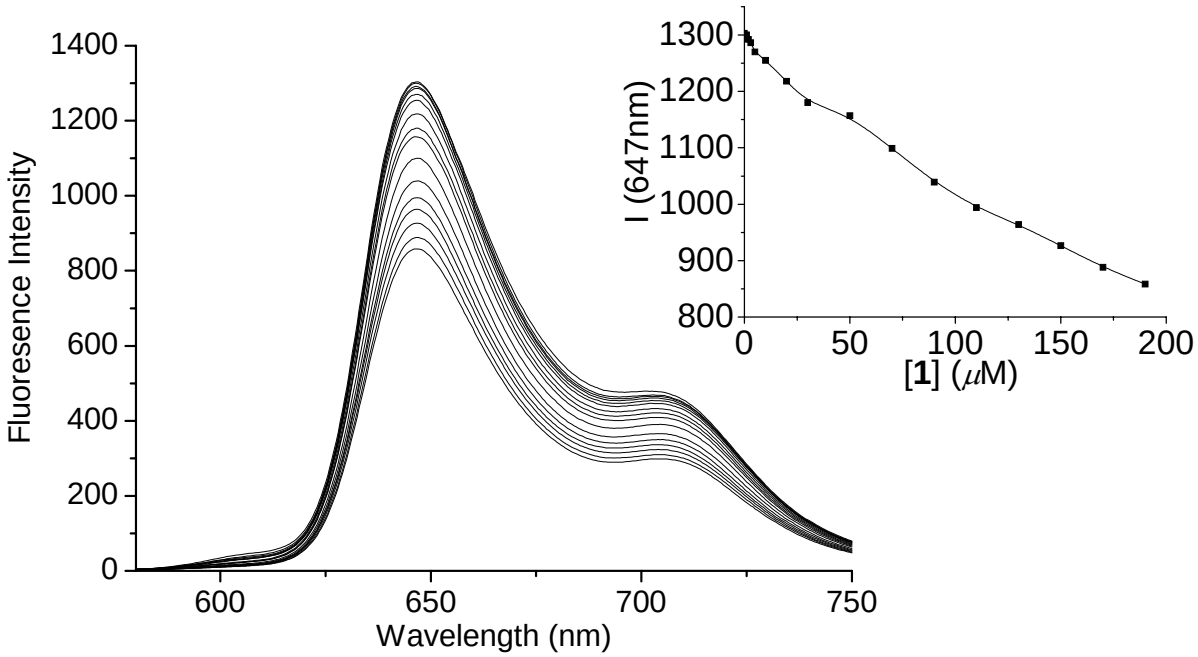

Figure 6. Fluorescence changes of TCPP (1.0×10^{-6} M) in 0.05 M phosphate buffer at pH 7.0 upon addition of **1** from 0 to 190 μM at 25℃, λ_{ex}=418 nm.

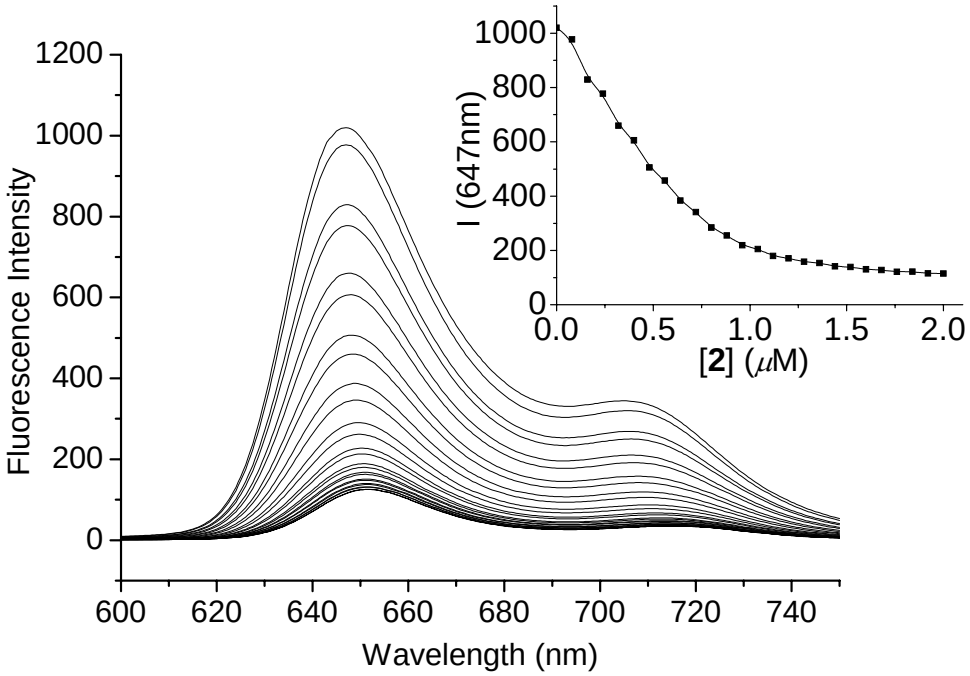

Figure 7. Fluorescence changes of TCPP (1.0 μM) in 0.05 M phosphate buffer at pH 7.0 upon addition of **2** from 0 to 2.0 μM at 25℃, λ_{ex}=420 nm.

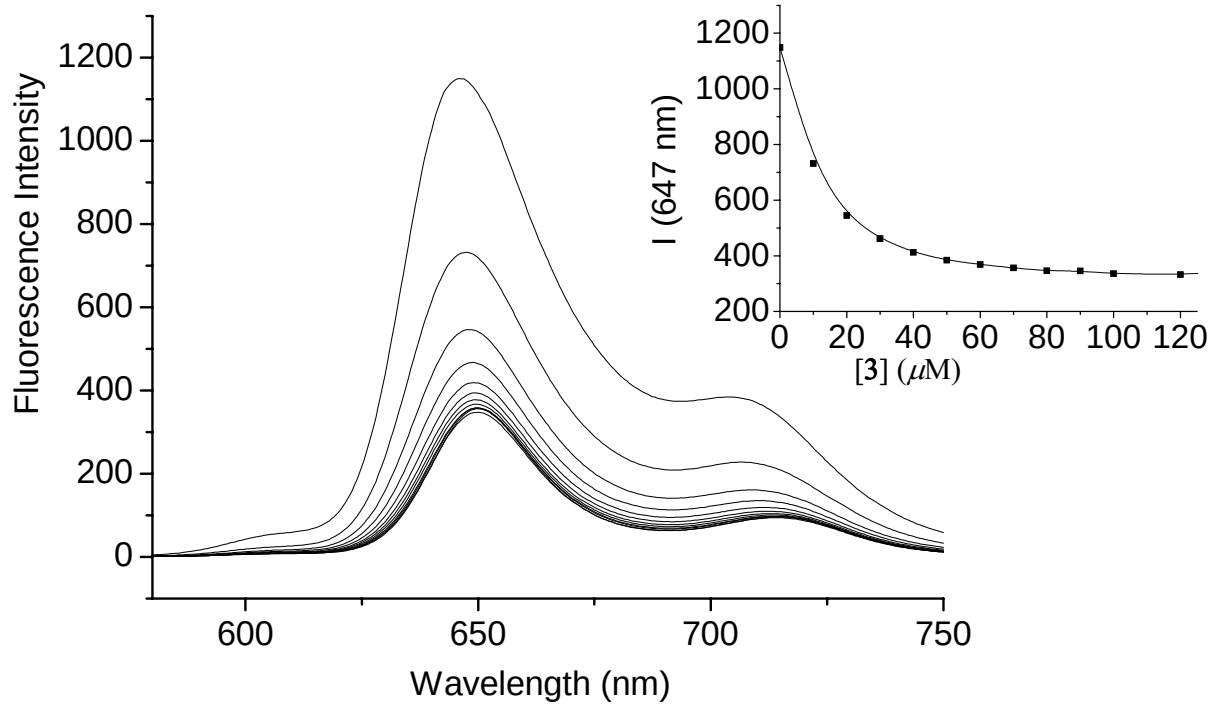

Figure 8. Fluorescence changes of TCPP (1.0 μM) in 0.05 M phosphate buffer at pH 7.0 upon addition of **3** from 0 to 190 μM at 25℃, λ_{ex}=417 nm.

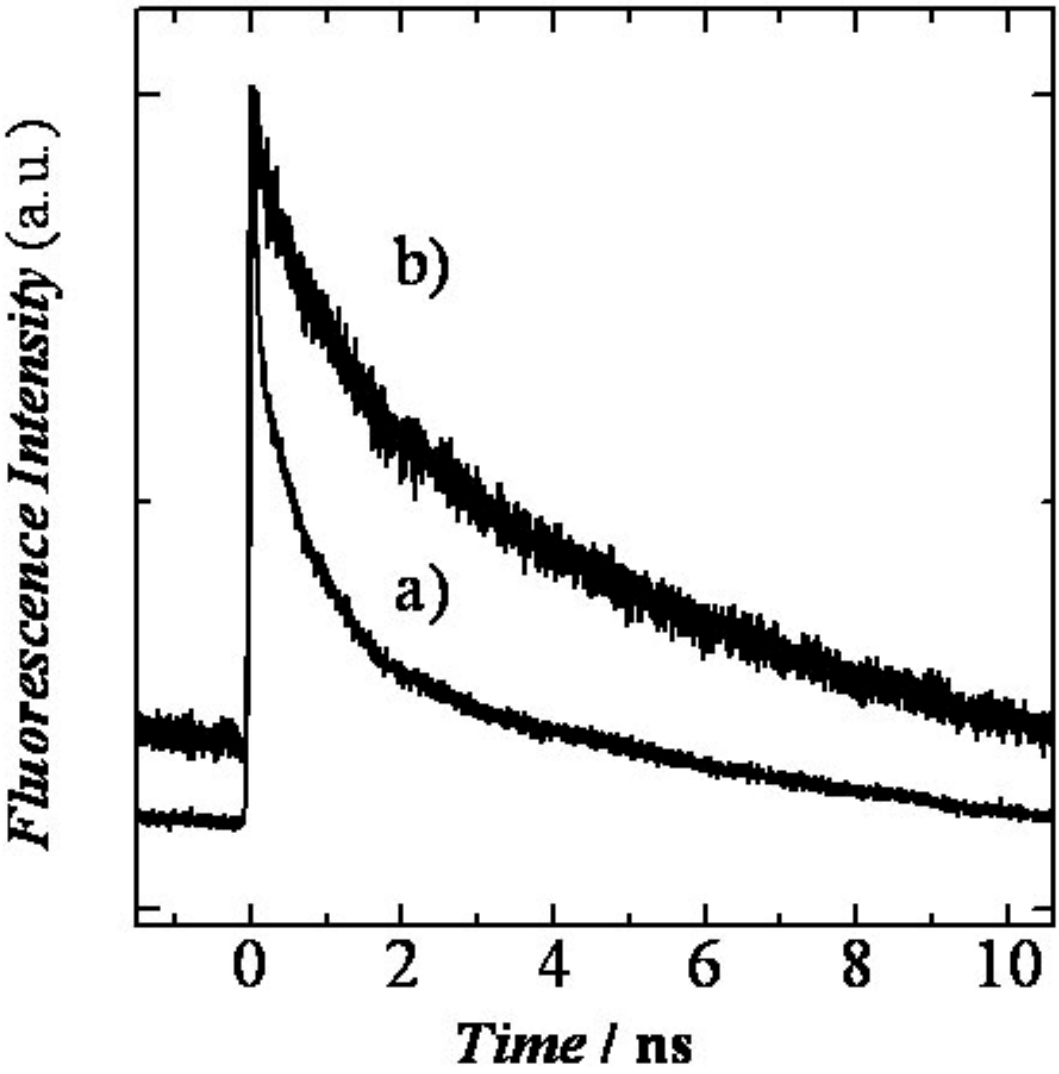

Figure 9. Fluorescence decay profiles of TCPP (1.0 μM) in the presence of acceptor **2** (1 μM, a) and acceptor **3** (80 μM, b) in 0.05 M phosphate buffer at pH 7.0 exciting at 420 nm.