Cu^{2+}-Induced Blue Shift of the Pyrene Excimer Emission: A New Signal Transduction Mode of Pyrene Probes

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Supporting Information

Materials. All solvents were reagent grade (Merck or Mallinckrodt) unless otherwise noted. THF (HPLC grade) was dried by sodium metal and acetone was dried with calcium chloride before use. All other compounds were used as received. Pentiptycene hydroquinone[1] **3** and 1-bromomethylpyrene[2] **5** were prepared according to the literature procedures.

6,13-Bis{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}-5,7,12,14-tetrahydro-5,14[1',2']:7,12-[1",2"]-dibenzenopentacene (4). A mixture of pentipycene hydroquinone **3** (0.5 g, 1.08 mmol), 2-[2-(2-chloroethoxy)ethoxy]ethanol (0.546 g, 3.24 mmol), K_2CO_3 (0.686 g, 4.97 mmol), and KI (0.1 g, 0.60 mmol) in 30 mL dry acetone was refluxed under N_2 for 6 days. The solvent was removed, and then 100 mL of CH_2Cl_2 was added. The insoluble residue was filtered off and the filtrate was concentrated under reduced pressure to afford the yellowish oily crude product. Upon adding distilled water and stirring for ca. 3 h, white powdered product could be obtained. Recrystallization in $CHCl_3$/MeOH provided the product in needle-type crystals with a 97% yield. (mp 164.5-165.5 °C). ^{1}H NMR (200 MHz, $CDCl_3$): 2.44 (bs, 2H), 3.58-3.74 (m, 16H), 3.91-4.03 (m, 8H), 5.80 (s, 4H), 6.93 (dd, *J* = 5.2 and 3.2 Hz, 8H), 7.34 (dd, *J* = 5.2 and 3.2 Hz, 8H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): 47.97, 61.83, 70.51, 70.69, 71.03, 72.64, 75.04, 123.57, 125.08, 136.53, 145.38, 145.89 ppm; IR (KBr): 1058, 1110, 1259, 1460, 3439 cm^{-1}; FAB-HRMS Calcd for $C_{46}H_{46}O_8$ (M$^+$) 726.3193, Found 726.3192; Anal. Calcd for $C_{46}H_{46}O_8$: C, 76.01, H, 6.38. Found: C, 75.67, H, 6.40.

6,13-Bis{2-[2-(2-(1-pyrenylmethoxy)ethoxy)ethoxy]ethoxy}-5,7,12,14-tetrahydro-5,14[1’,2’]:7,12-[1”,2”]-dibenzenopentacene (1). A mixture of compound **4** (0.49 g, 0.674 mmol) and NaH (0.24 g, 10 mmol) in 15 mL anhydrous THF was stirred at room temperature under N_2 for 40 min. To the mixture was added a 10 mL anhydrous THF solution of compound **5** (0.40 g, 1.35 mmol). After refluxing for 3 days, the THF solvent was removed, and then replaced by CH_2Cl_2. The solution was washed with H_2O and dried with $MgSO_4$. The solvent was removed, and the solid residue was chromatographed on silica gel (CH_2Cl_2 first and then EtOAc) to afford **1** as a light yellowish solid with a 92% yield. (mp 194-196 °C). ^{1}H NMR (200 MHz, $CDCl_3$): 3.56-4.01 (m, 24H), 5.24 (s, 4H), 5.80 (s, 4H), 6.85 (dd, *J* = 5.1 and 3.2 Hz, 8H), 7.31 (dd, *J* = 5.1 and 3.2 Hz, 8H), 7.91-8.16 (m, 16H), 8.36 (d, *J* = 9.2 Hz, 2H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): 47.96, 69.59, 70.49, 70.93, 71.07 (2C), 71.82, 75.17, 123.48, 123.58, 124.42, 124.65, 124.86, 125.01, 125.14, 125.15, 125.85, 126.99, 127.35, 127.38, 127.61, 129.34, 130.77, 131.21 (2C), 131.30, 136.52, 145.40, 145.95 ppm; IR (KBr): 1108, 1257, 1458, 1588 cm^{-1}; FAB-HRMS Calcd for $C_{80}H_{66}O_8$ (M$^+$) 1154.4758, Found 1154.4679; Anal. Calcd for $C_{80}H_{66}O_8$: C, 83.16, H, 5.76. Found: C, 82.83, H, 5.76.

1,4-Bis{2-[2-(2-(1-pyrenylmethoxy)ethoxy)ethoxy]ethoxy}benzene (2). Compound **2** was prepared as described for compound **1**, substituting 1,4-bis{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}benzene (**6**) for compound **4**.

Compound **6** was in turn prepared as described for compound **4**, substituting 1,4-hydroquinone for pentipycene hydroquinone **3**. Compound **6** appears to be sensitive to air and was obtained as dark brownish sluggish oil with a yield of 61%, which was used without further purification (^{1}H NMR (200 MHz, $CDCl_3$): 3.58-3.61 (m, 4H), 3.66-3.72 (m, 8H), 3.78-3.83 (m, 4H), 4.03-4.08 (m, 4H), 6.82 (s, 4H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): 61.51, 67.83, 69.68, 70.14, 70.61, 72.47, 115.48, 152.89 ppm). Compound **2** was obtained as light yellowish solid with a 45% yield. (mp 74-75.5 °C). ^{1}H NMR (200 MHz, $CDCl_3$): 3.66-3.77 (m, 20H), 3.92-3.97 (m, 4H), 5.26 (s, 4H), 6.70 (s, 4H), 7.93-8.17 (m, 16H), 8.38 (d, J = 9.2 Hz, 2H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): 67.90, 69.48, 69.79, 70.66, 70.74 (2C), 71.79, 115.41, 123.51, 124.42, 124.65, 124.86, 125.14 (2C), 125.86, 127.00, 127.33, 127.36, 127.59, 129.33, 130.76, 131.17, 131.21, 131.35, 152.96 ppm; IR (KBr): 1104, 1237, 1452, 1510 cm^{-1}; FAB-HRMS Calcd for $C_{52}H_{50}O_8$ (M^+) 802.3506, Found 802.3499; Anal. Calcd for $C_{52}H_{50}O_8$: C, 77.78, H, 6.28. Found: C, 77.49, H, 6.36.

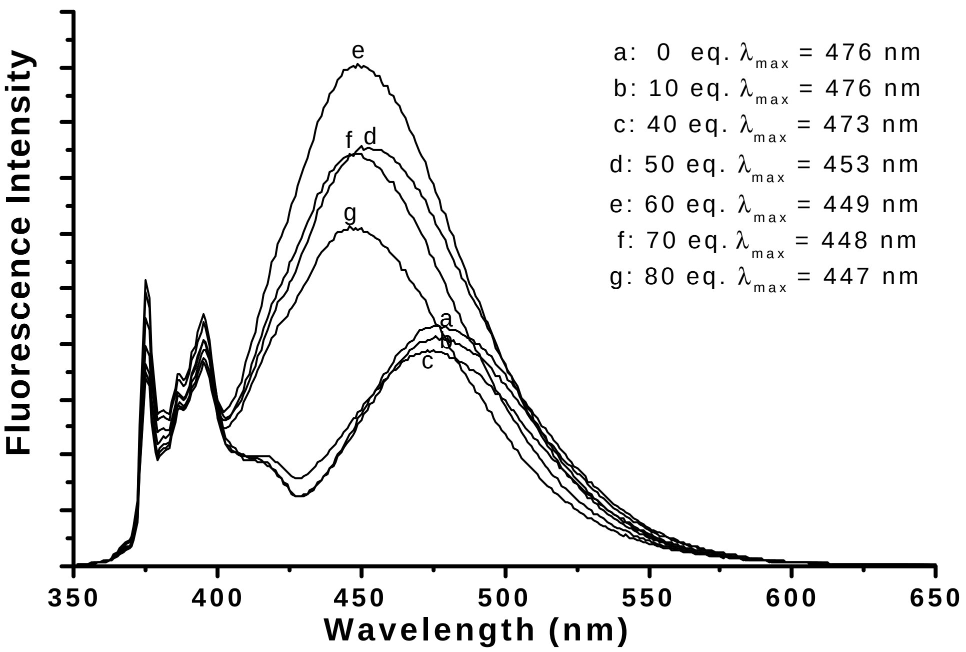
Reference:

(1) Yang, J.-S.; Lee, C.-C.; Yau, S.-L.; Chang, C.-C.; Lee, C.-C.; Leu, J.-M. *J. Org. Chem.* **2000**, *65*, 871-877.

(2) Akiyama, S.; Nakasuji, K.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2231-2236.

Figure S1. Fluorescence spectra of (A) **1** and (B) **2** in MeCN (1×10^{-5} M, excitation at 341 nm) in the presence of (a) 0, (b) 10, (c) 40, (d) 50, (e) 60, (f) 70, and (g) 80 equivalents of $Cu(ClO_4)_2 \cdot 6H_2O$ predissolved in MeCN (0.005 M).

(A)



(B)

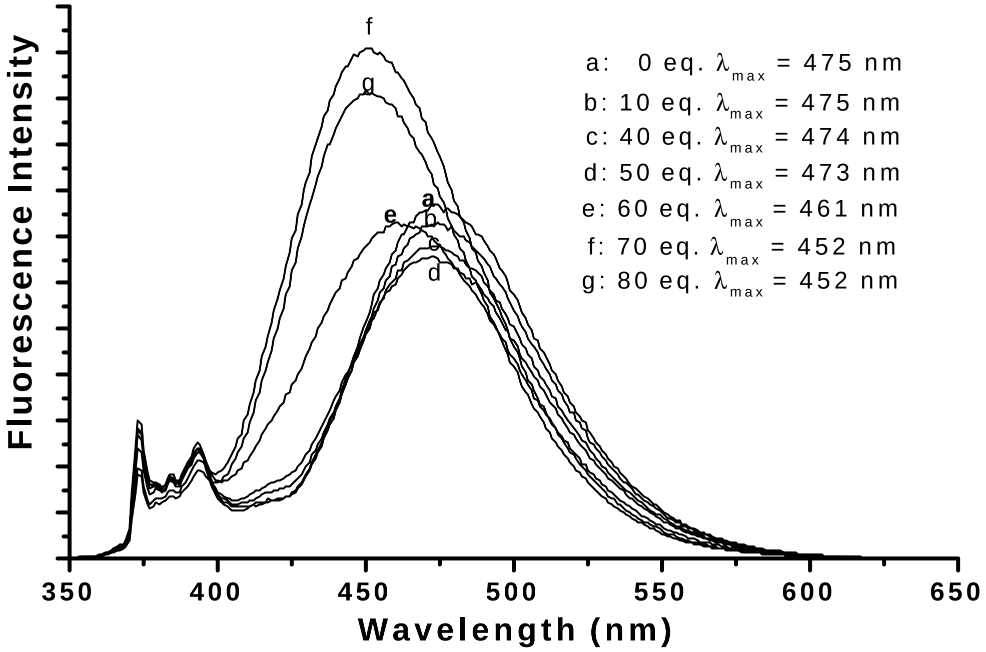
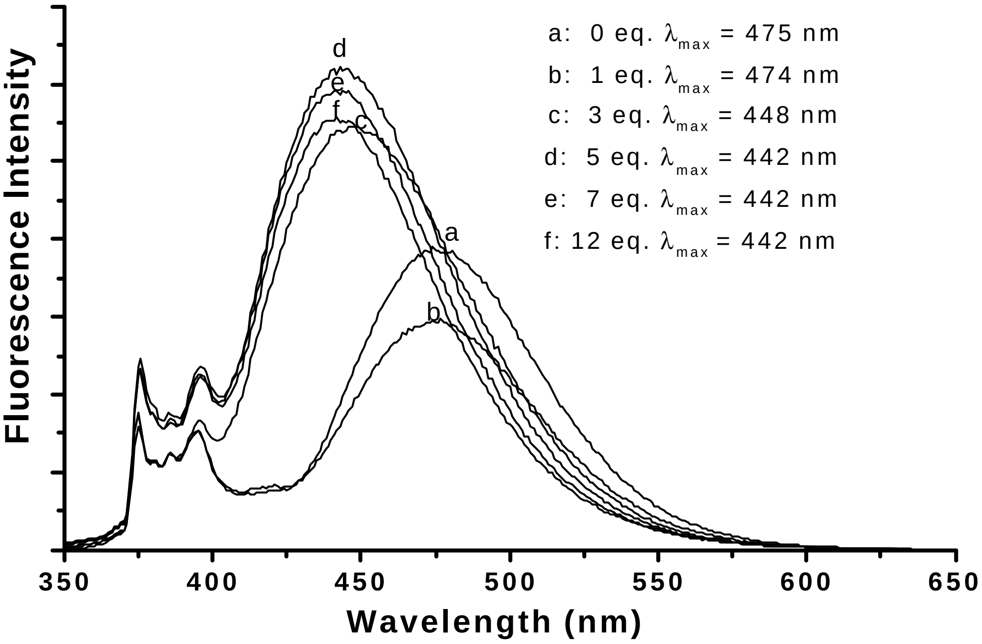


Figure S2. (A) Fluorescence and (B) Absorption spectra of **2** in CH_2Cl_2 (1×10^{-5} M, excitation at 335 nm) in the presence of (a) 0, (b) 1.0, (c) 3.0, (d) 5.0, (e) 7.0, and (f) 12.0 equivalents of $Cu(ClO_4)_2 \cdot 6H_2O$ predissolved in MeCN (0.005 M).

(A)



(B)