Supporting Information

Metal Ion Dependent Fluorescence Quenching in a Crown Ether Bridged Porphyrin-Fullerene Dyad

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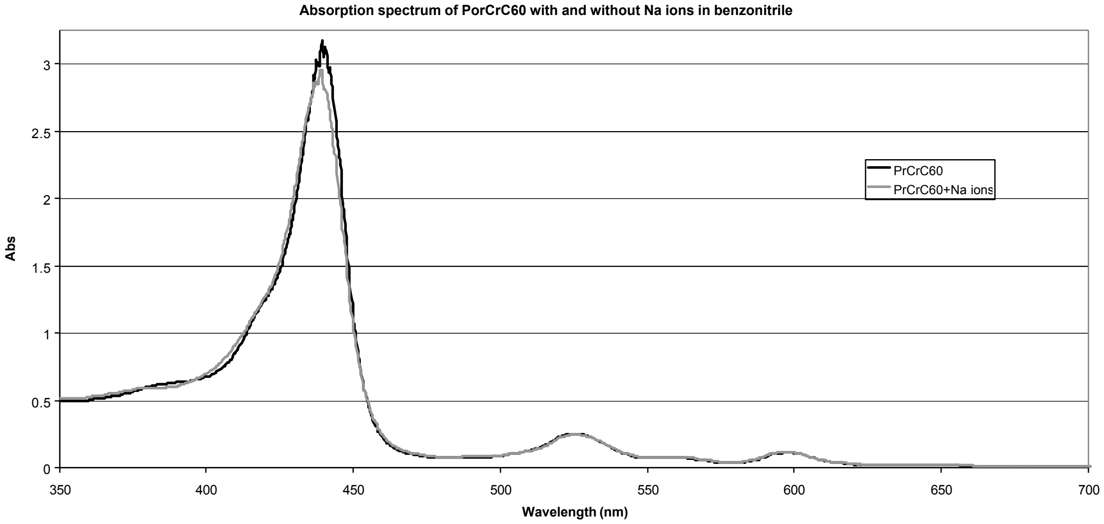
*Preparation of **4***: Porphyrin-crown **3** (25 mg, 0.025 mmol) and hexamethylene tetramine (4 mg, 0.026 mmol) were dissolved in TFA (0.5 mL) and heated to approximately 90°C. Reaction progress was monitored by ^{1}H NMR spectroscopy. Upon completion (2 days), $CHCl_3$ (5 mL) was added to the reaction mixture. The organic layer was collected and washed with H_2O (3×30 mL), then concentrated under reduced pressure. The resulting dark purple residue was chromatographed (silica) with 15 % acetone in chloroform to give the product (major band) as a dark purple solid (13 mg, 49 %). m.p. > 350°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ -2.59, 2 H, br s, inner NH; 4.07-4.18, 8 H, m, OCH_2; 4.23-4.29, 4 H, m, OCH_2; 4.34-4.38, 4 H, m, OCH_2; 6.92, 1 H, d, *J* 8.0 Hz, ArH; 7.04, 2 H, s, quinoxalino H; 7.36-7.42, 2 H, m, ArH; 7.72-7.89, 12 H, m, *meso*-ArH; 8.17 and 8.23, 8 H, dd, *J* 25.3, 6.9 Hz, *meso*-ArH; 8.72, 2 H, s, β-pyrrolic H; 8.91-8.95, 4 H, ABq, *J* 4.8 Hz, β-pyrrolic H; 9.81, 1 H, s, CHO. ^{13}C NMR (100 MHz, $CDCl_3$): δ 68.6, 68.7, 69.7, 69.8, 69.9, 108.5, 110.4, 111.6, 117.1, 117.2, 121.6, 121.7, 126.9, 127.0, 127.5, 127.6, 128.0, 128.1, 128.2, 130.3, 134.1, 134.2, 134.3, 134.6, 138.0, 138.1, 138.2, 139.8, 142.1, 142.2, 142.3, 146.3, 147.7, 149.2, 151.3, 151.4, 152.2, 152.3, 154.2, 154.9. Mass Spectrum (ESI, +ve): found 1027.3822 $[M+H]^+$, calculated $C_{65}H_{51}N_6O_7^+ = 1027.3819$; found 1049.3656 $[M+Na]^+$, calculated $C_{65}H_{50}N_6O_7Na^+ = 1049.3639$.

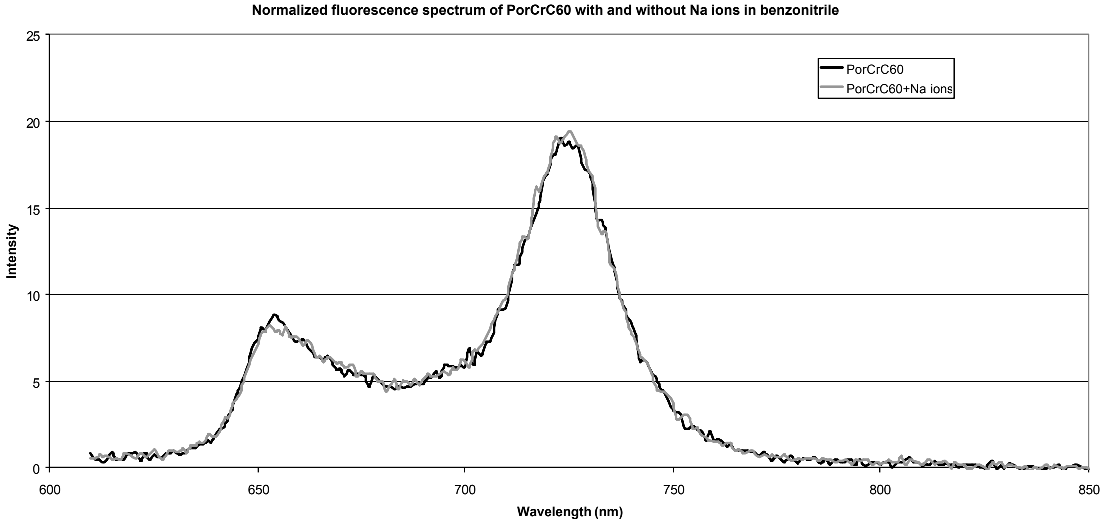
*Preparation of **1**:* To the formylated porphryin-crown **4** (9.2 mg, 8.96 μmol) was added C_{60} (8.2 mg, 13.2 μmol), *N*-methylglycine (1.4 mg, 15.7 μmol) and dry toluene (8 mL). The reaction mixture was refluxed, and reaction progress was monitored by TLC. Upon completion (1.5 days), solvent was removed from the reaction mixture under reduced pressure. The resultant residue was chromatographed (silica) under an argon atmosphere, using 0.5 % to 5 % methanol in toluene. The product was obtained as a brown solid (6.1 mg, 38 %). m.p. 298-300°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ -2.61, 2 H, br s, inner NH; 2.17, 3 H, s, N-CH_3; 4.03-4.22, 16 H, m, OCH_2 and pyrrolidine CH; 4.31-4.35, 4 H, m, OCH_2; 4.71, 1 H, s, pyrrolidine CH; 4.82, 1 H, d, *J* 9.5 Hz, pyrrolidine CH; 6.84, 1 H, br s, ArH; 7.02, 2 H, s, quinoxalino H; 7.14-7.18, 2 H, m, ArH; 7.73-7.87, 12 H, m, *meso*-ArH; 8.13-8.23, 8 H, m, *meso*-ArH; 8.70, 2 H, s, β-pyrrolic H; 8.90-8.94, 4 H, m, β-pyrrolic H. ^{13}C NMR (100 MHz, $CDCl_3$): δ 68.5, 68.8, 68.9, 69.0, 69.2, 69.3, 69.7, 70.0, 83.4, 108.5, 117.1, 117.2, 121.6, 125.5, 126.9, 127.5, 127.9, 128.0, 128.1, 128.4, 129.2, 129.9, 134.1, 134.2, 134.6, 135.6, 135.7, 136.4, 136.5, 137.9, 138.0, 138.2, 139.8, 140.0, 141.5, 141.6, 141.7, 141.8, 141.9, 142.0, 142.1, 142.2, 142.3, 142.4, 142.5, 142.6, 142.8, 143.1, 144.2, 144.3, 144.5, 144.6, 145.0, 145.1, 145.2, 145.3, 145.4, 145.5, 145.7, 145.8, 145.9, 146.0, 146.1, 146.2, 146.3, 146.4, 146.8, 147.1, 147.2, 151.4, 154.0, 154.9, 156.2. Mass Spectrum (ESI, +ve): found 1774.4277 $[M+H]^+$, calculated $C_{127}H_{56}N_7O_6^+$ = 1774.4292; found 1796.4098 $[M+H]^+$, calculated $C_{127}H_{55}N_7O_6Na^+$ = 1796.4112.

Absorption and emission spectra:

Absorption spectra of PrCrC60 (dyad **1**) in benzonitrile in the absence and presence of approx. 0.1 M Na^+.



Normalized fluorescence spectra of PorCrC60 (dyad **1**) in benzonitrile in the presence and absence of Na^+.



Quantum Chemical Calculations: Optimised structures were calculated at B3LYP/6-31G, using Gaussian 03.[S1] Molecular orbital calculations were performed at the HF/6-31G level. LUMO+3 (corresponding to the porphyrin LUMO) in the presence and absence of Na^+ is illustrated in Figure 5 of the manuscript using MOLEKEL 4.0.[S2]

S1. Gaussian 03, Revision B.04, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

S2. MOLEKEL 4.0, P. Flükiger, H.P. Lüthi, S. Portmann, J. Weber, Swiss Center for Scientific Computing, Manno (Switzerland), 2000.