Supplemental Information for

Host-Guest Assembly of Squaraine Dye in Cucurbit[8]uril: Its Implication in Fluorescent Probe for Mercury Ions

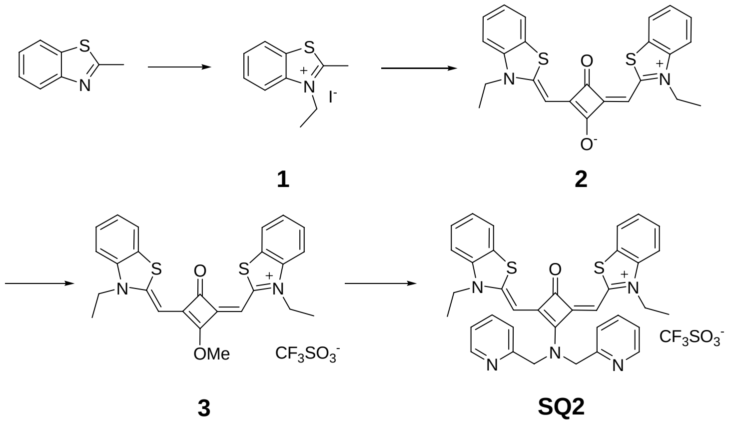
Yongqian Xu, Matthew J. Panzer, Wiley J. Youngs and Yi Pang*

Department of Chemistry & Maurice Morton Institute of Polymer Science, The University of Akron, Akron, OH, 44325
yp5@uakron.edu

1. Materials and general procedure

All the solvents and reagents were of analytic grade and used as received. Water used was ultra filter deionized and purchased from fisher. NMR spectra were collected on a Varian 300 Gemini spectrometer. Mass spectrometric data were obtained on a HP1100LC/MSD mass spectrometry. UV-Vis spectra were acquired on a Hewlett-Packard 8453 diode-array spectrometer. Fluorescence spectra were obtained on a HORIBA Jobin Yvon NanoLog spectrometer. X-ray crystallography data were measured on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.710 73 Å) operated at 2000 W power.

2. Synthesis of SQ



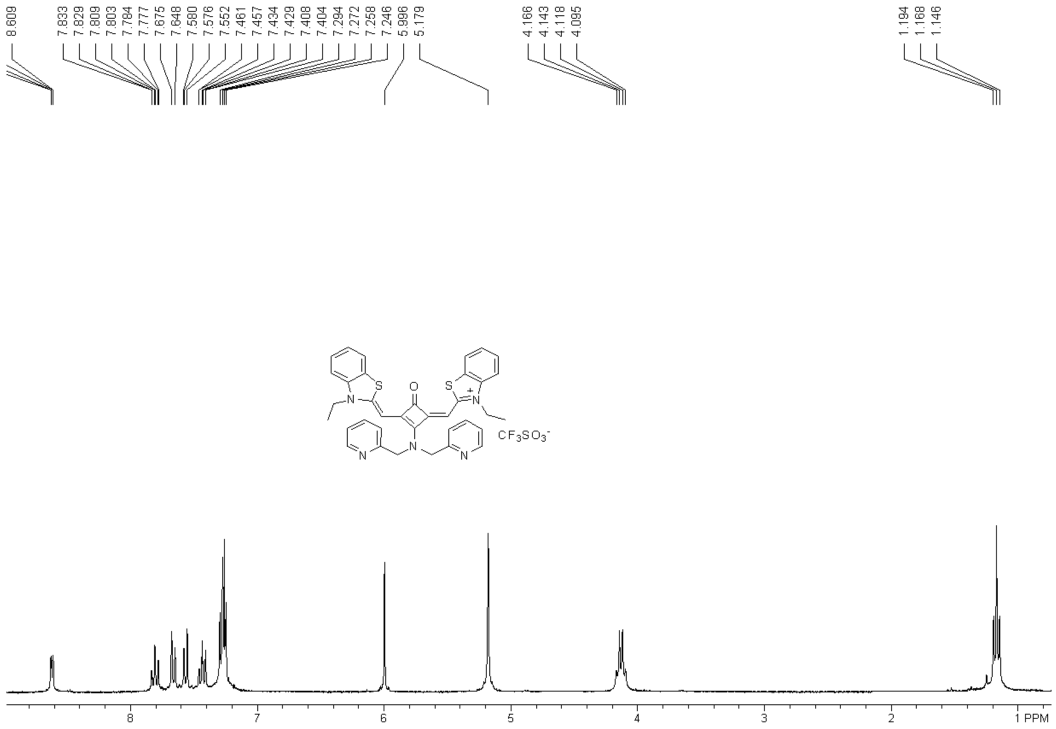
Reagents and conditions: a) CH_3CH_2I, CH_3CN, reflux; b) Squaric acid, n-Butanol/pyridine; c) CF_3SO_3Me, CH_2Cl_2; d) DPA, CH_2Cl_2, RT.

3-Ethyl-2-methyl-1,3-benzothiazol-3-ium Iodide (**1**). A solution of 2-methylbenzothiazole (4.48 g, 30 mmol) and iodoethane 14.03 g, 90 mmol) in acetonitrile (250 ml) was heated under reflux for 24 h. After cooling, diethyl ether (200 ml) was added, the desired salt collected by filtration under reduced pressure and washed several times with diethyl ether. Drying under vacuum. The ether was removed. The process was repeated 1~3 times to achieve a suitable yield as white solid (6.35 g, 69.4%). ^{1}H NMR (CD_3OD, 300 MHz) δ (ppm) 8.33 (d, 2H, J = 7.8 Hz), 8.30 (d, 2H, J = 8.4 Hz), 7.92 (dd, 2H, J = 7.8 Hz, J = 8.4 Hz), 7.81 (dd, 2H, J = 7.8 Hz, J = 8.4 Hz), 4.85 (q, 4H, J = 7.5 Hz), 3.27 (s, 3H), 1.60 (t, 6H, J = 7.5 Hz).

2. Condensed the quaternary ammonium salt (**1**) (0.92 g, 3 mmol) and squaric acid (0.17 g, 1.5 mmol) in BuOH/pyridine (5/1) (60 ml) at reflux for overnight. Purified from silica gel column to get green solid (0.46 g, 70.7%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.53 (d, 2H, J = 7.8 Hz), 7.35 (dd, 2H, J = 7.8 Hz, J = 8.4 Hz), 7.18 (dd, 2H, J = 7.8 Hz, J = 8.4 Hz), 7.12 (d, 2H, J = 8.4 Hz), 5.88 (s, 2H), 4.15 (q, 2H, 7.2 Hz), 1.43 (q, 6H, J = 7.2 Hz).

3. To a solution of **2** (172 mg, 0.4 mmol) in anhydrous CH_2Cl_2 (50 ml), vigorously stirred under N_2 atmosphere, $CF_3SO_3CH_3$ (261 mg, 1.6 mmol) was added at room temperature. After 3~5 h, the mixture was quenched with cold 5% aqueous $NaHCO_3$ solution. The organic layer was dried with anhydrous Na_2SO_4 and the resulting residue was purified from silica gel to get **3** (195 mg, 82.3 %). ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm) 8.04 (d, 2H, J = 7.8 Hz), 7.77 (d, 2H, J = 8.4 Hz), 7.58 (dd, 2H, J = 7.5 Hz , J = 8.4 Hz), 7.42 (dd, 2H, J = 7.2 Hz , J = 8.4 Hz), 6.06 (s, 2H), 4.54 (s, 3H), 4.47(q, 4H, J = 6.9 Hz), 1.29 (t, 6H, J = 6.9 Hz). ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm) 161.96, 158.08, 140.57, 128.53, 127.98, 125.78, 123.51, 114.10, 85.57, 83.70, 61.28, 42.05, 13.10. HRMS (ESI+) found 448.1300 $(M)^+$, calcd for $C_{25}H_{23}N_2O_2S_2$ 448.1279

SQ2. 2,2'-dipolylamine (**DPA**) (1.20 g, 6 mmol) was added to a solution of **3** (0.59 g, 1 mmol) in anhydrous CH_2Cl_2 (30 ml) under N_2 atmosphere, and the mixture was stirred at room temperature for 5-7 days in the presence of catalytic amounts of Et_3N and DMAP [4-(dimethylamino)pyridine]. The mixture was extracted with cold H_2O, and the organic layer was fried over anhydrous Na_2SO_4, solvent was removed in vacuo. The resulting residue was purified from silica gel to get SQ2 (0.58 g, 76.1%).^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.62 (d, 2H, J = 4.5 Hz), 7.79 (dd, 2H, J = 7.8 Hz , J = 7.5 Hz), 7.66 (d, 2H, J = 7.8 Hz), 7.56 (d, 2H, J = 7.5 Hz), 7.44 (dd, 2H, J = 7.8 Hz , J = 7.5 Hz), 7.30-7.25 (m, 6H), 6.00 (s, 2H), 5.18 (s, 4H), 4.13(q, 4H, J = 7.2 Hz), 1.17 (t, 6H, J = 7.2 Hz). ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm) 182.34, 172.15, 157.43, 135.40, 126.52, 123.20, 112.49, 106.04, 87.79, 61.65, 42.51, 29.94, 12.74. HRMS (ESI+) found 614.2048 $(M)^+$, calcd for $C_{36}H_{32}N_5OS_2$, 614.2048



^{1}H NMR of SQ2 in $CDCl_3$.

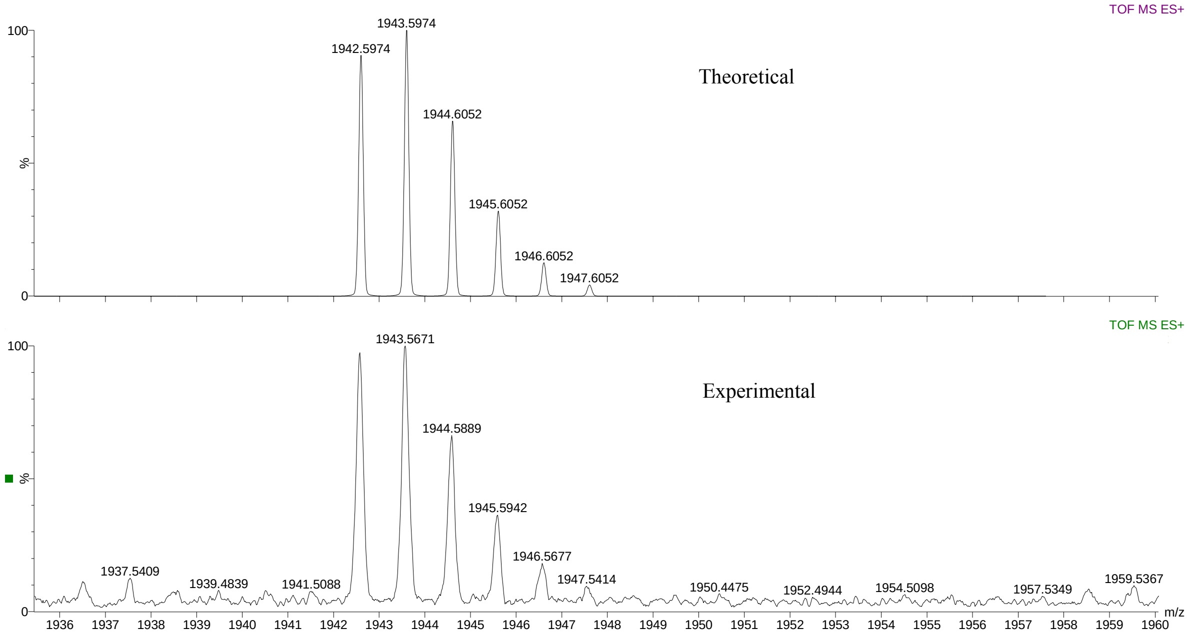


Figure S1. Mass spectra of SQ2:CB8 complex. The experimental isotope pattern of SQ2:CB8 complex (bottom spectrum) matches the theoretical prediction (bottom spectrum) for SQ2+CB8 (without $CF_3SO_3^-$ counter ion).

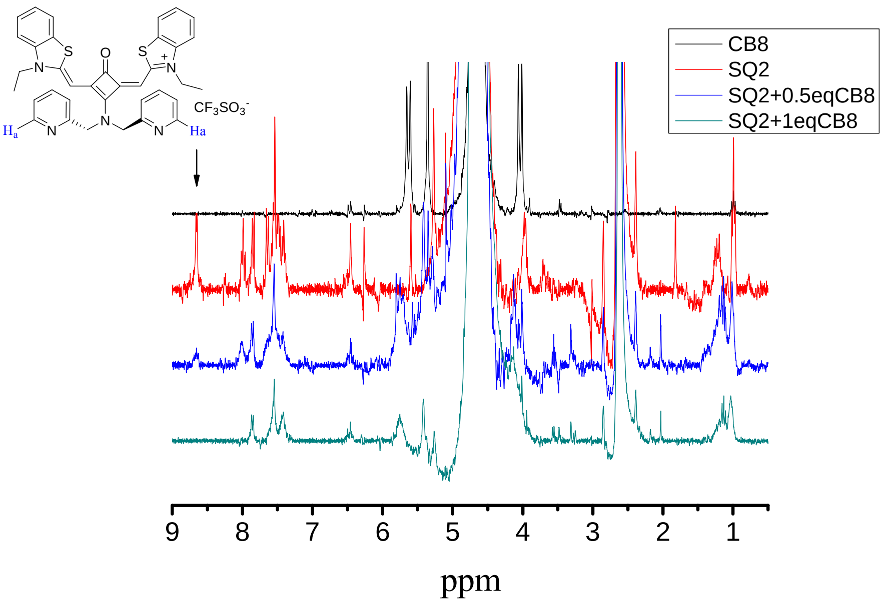


Figure S2. ^{1}H NMR titration of **SQ2** in D_2O/DMSO-d_6(4:1) with different concentration. The pyridyl proton H_a of SQ2 at ~8.6 ppm disappears upon addition of CB[8], indicating the complex formation. Significant noise in the stectrum is due to very poor solubility of the complex.

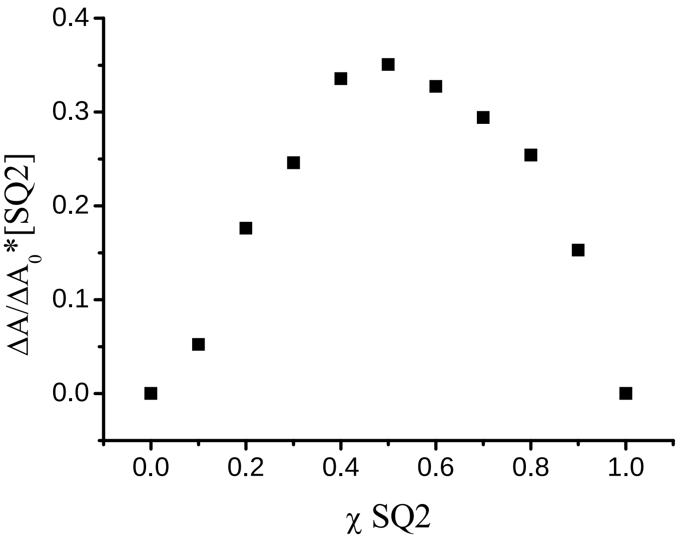


Figure S3. Job plot for the complexation of SQ2 and CB8 in water with 1% MeOH (v/v).

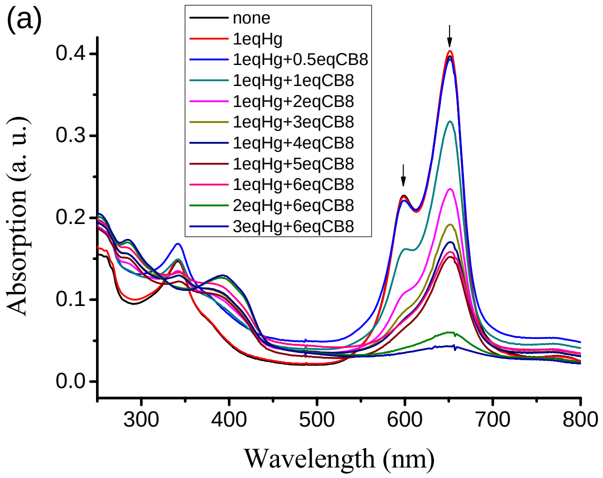


Figure S4. Absorption spectra of **SQ2** (5 uM) in water in the presence of different equivalents of CB8 and Hg^{2+}. The absorption band at ~600 nm is attributed to the H-aggregation.

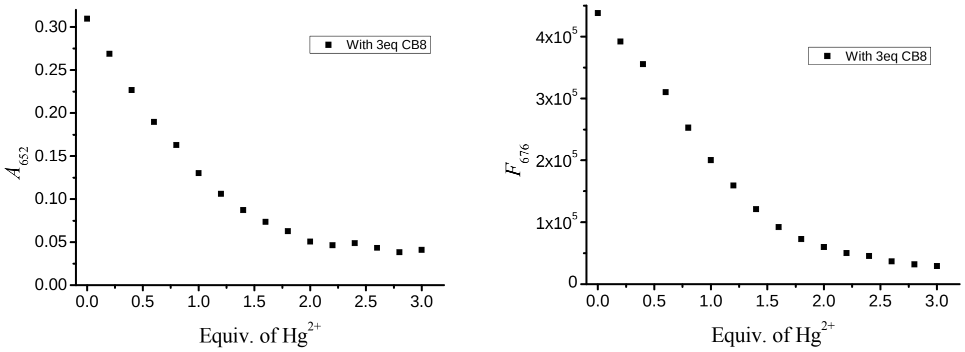


Figure S5. Absorption (a) and fluorescence response (b) of **SQ2** (5 uM) in water with 3 equiv of CB8 upon titration with Hg^{2+} cation. The absorption and fluorescence are monitored at 652 nm and at 676 nm, respectively.

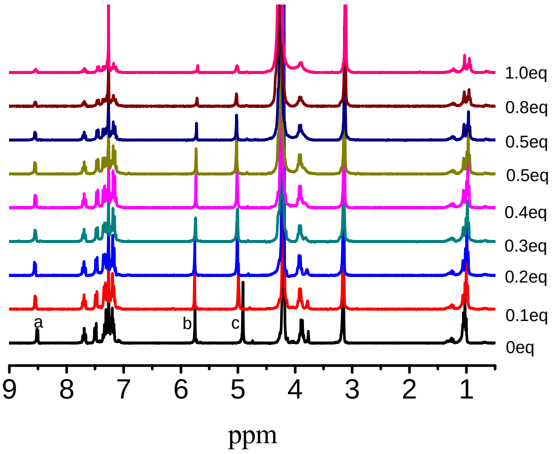


Fig S6. ^{1}H NMR spectra of **SQ2** in $CDCl_3$ and CD_3OD (3:1) with addition of $Zn(ClO_4)_2$ in CD_3OD. The signal at 7.27 and 4.33 ppm is attributed to the $CHCl_3$ and CD_3OD residue.

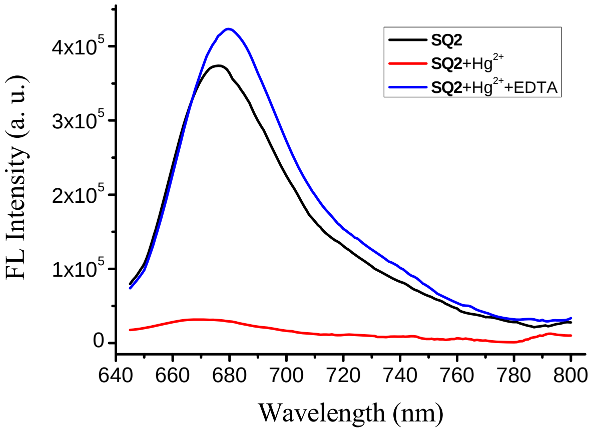


Figure S7. Emission spectra of **SQ2** (5 uM) upon addition of Hg^{2+} (15 uM) and EDTA (60 uM) in aqueous solution with CB8 (15 uM).