

**Supporting Information Available**

**Controlled self-assembly of squaraines to of 1D supramolecular architectures  
with high molar absorptivity**

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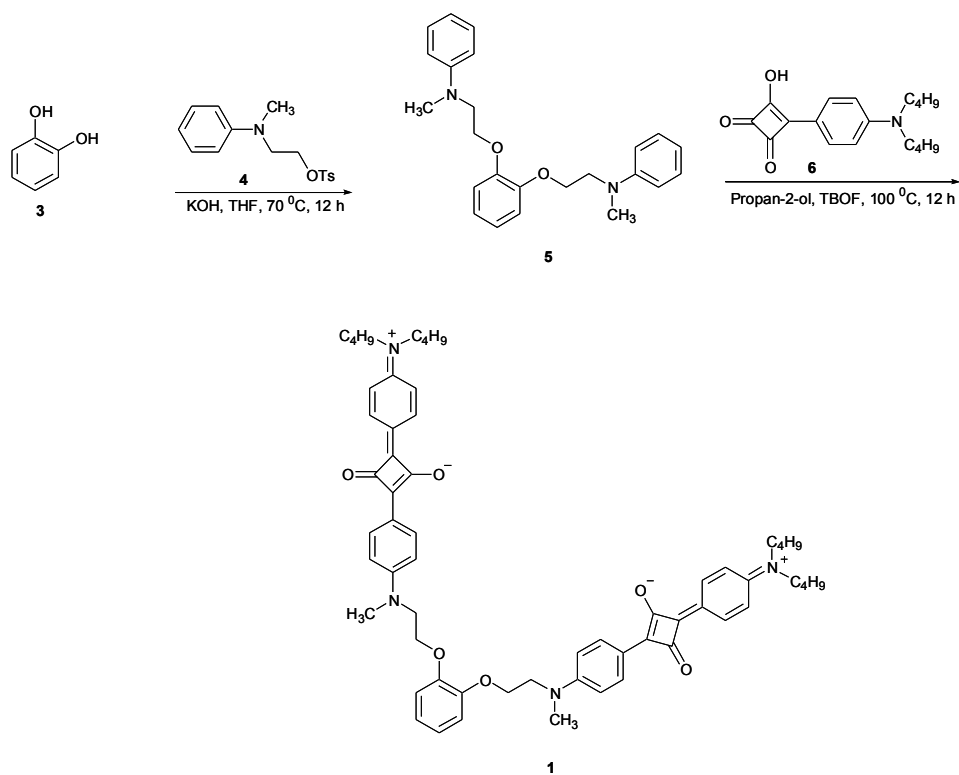
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## Synthetic Methodology



**Scheme 1:** Synthesis of **1**

### General procedure for synthesis:

Synthesis of the precursor molecule **5** was achieved using standard procedures by refluxing catechol **3** with the tosylate **4** in THF in the presence of potassium hydroxide for 12 h. Reaction of **5** under refluxing with 3.3 equivalents of *N,N'*-(dibutylaminophenyl)-4-hydroxy-cyclobut-3-en-1,2-dione (**6**) in propan-2-ol in the presence of catalytic amount (1 mL) of tributyl orthoformate (TBOF) for 20 h resulted in the formation of crude dye **1** which was then purified by column chromatography over silica gel using chloroform/methanol (9:1) as eluent.

**5**: Yield: 54 %. FT-IR (neat):  $\bar{\nu}_{\max}$  3687, 3022, 2929, 1731, 1602, 1514, 1259, 1210, 1045, 927.8, 787.8, 672,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS);  $\delta$  2.94 (s, 6H,  $-\text{NCH}_3$ ), 3.49 (t,  $J=6\text{Hz}$ , 4H,  $-\text{NCH}_2$ ), 3.59 (t,  $J=6\text{Hz}$ , 4H,  $-\text{OCH}_2$ ), 6.69 (t,  $J=9\text{Hz}$ , 6H, Ar-H), 7.21 (t,  $J=9\text{Hz}$ , 8H, Ar-H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ );  $\delta$  38.8, 52.5, 66.4, 68.76, 112, 114.3, 116.2, 129, 133.7, 149 ppm. HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_2$ , 376.2151; found: 376.4912.

**1**: Yield: 17 %. mp  $>320$  °C (decomposition); FT-IR (neat):  $\bar{\nu}_{\max}$  3078, 2954, 2927.9, 1585, 1384, 1359.8, 1344, 1176, 1109, 833, 785, 516  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS);  $\delta$  0.98 (t,  $J=6$  Hz, 12H,  $-\text{CH}_3$ ), 1.2-1.4 (m, 8H,  $-\text{CH}_2$ ), 1.61-1.65 (m, 8H,  $-\text{CH}_2$ ), 3.1 (s, 6H,  $-\text{NCH}_3$ ), 3.44 (t, 8H,  $J=6\text{Hz}$ ,  $-\text{NCH}_2$ ) 3.71 (t,  $J=6\text{Hz}$ , 4H,  $-\text{NCH}_2$ ), 4.14 (t,  $J=9\text{Hz}$ , 4H,  $-\text{OCH}_2$ ), 6.71-6.78 (m, 12H, Ar-H), 8.35-8.39 (m, 8H, Ar-H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 13.8, 20.9, 30.7, 38, 53.3, 58.9, 66.4, 101.9, 112, 114.2, 121, 123, 127, 133.4, 140, 146, 149.7, 151.9, 153.3, 187 ppm. HRMS  $[\text{M}]^+$  calcd for  $\text{C}_{60}\text{H}_{70}\text{N}_4\text{O}_6$ , 942.5295; found: 944.1334 (M+2H).

For syntheses of **2** and **4** refer *J. Am. Chem. Soc.* 2004, **126**, 6590.

For synthesis of **6** refer *Dyes and Pigments* 2001, **49**, 161.

### Experimental Details

Solvents and the reagents were purified and dried by usual methods. All starting materials were obtained from commercial suppliers and used as received. All melting points were determined with Mel-Temp-II melting point apparatus and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR were measured on a 300 MHz Bruker Avance DPX Spectrometer. High Resolution Mass Spectra were recorded with a JEOL JMS600. FT-IR spectra were

recorded using a Shimadzu IR Prestige-21 Fourier Transform Infrared spectrophotometer. The emission spectra were measured on a Spex-Fluorolog F112X spectrofluorimeter. Fluorescence quantum yields were determined using optically matching solutions of 4,4-[bis-(*N,N*-dimethylamino)phenyl] squaraine dye ( $\Phi_f = 0.70$  in chloroform) as standard at an excitation wavelength of 570 nm.

### **Transmission Electron Microscopy (TEM)**

TEM measurements were carried out using JEOL JEM1011 with an accelerating voltage of 90 kv. The samples were freshly prepared by drop casting acetonitrile solution of **1** and **2** as well as  $\text{Ca}^{2+}$  complexes onto a carbon coated grid. TEM images were obtained without staining.

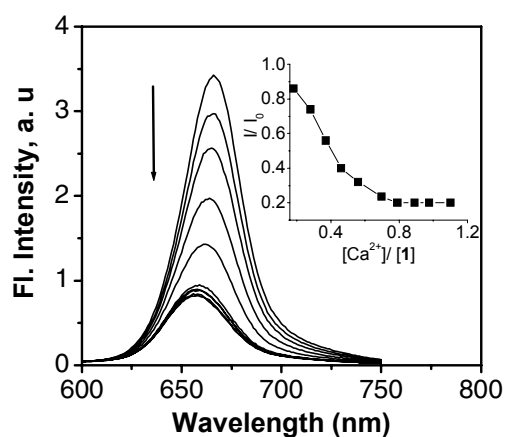
### **Atomic Force Microscopy (AFM)**

AFM images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IV operating in the tapping mode regime. Micro-fabricated silicon cantilever tips (MPP-11100-10) with a resonance frequency of 299 kHz and a spring constant of 20-80  $\text{Nm}^{-1}$  were used. The scan rate varied from 0.5 to 1.5 Hz. AFM section analyses was done offline. Samples for the imaging were prepared by drop casting the solution of **1** and **2** as well as the respective  $\text{Ca}^{2+}$  complexes from acetonitrile on freshly cleaved mica at the required concentrations followed by the removal of the solvent under vacuum.

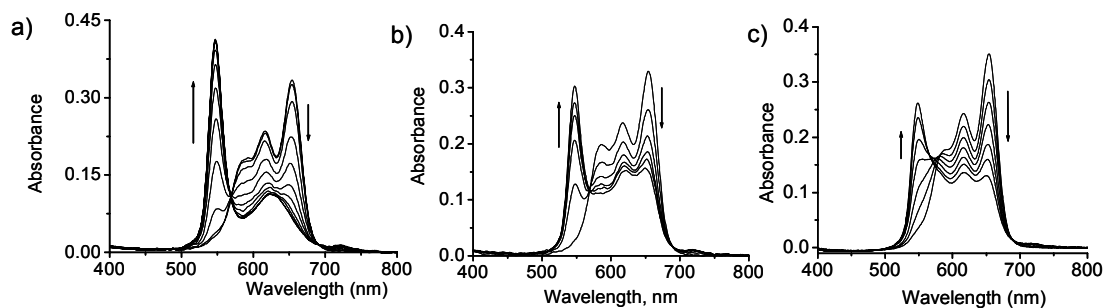
### **General procedure for the complexation of cations with 1 and 2**

Metal perchlorate solutions were prepared in spectroscopic grade acetonitrile. The required bis-squaraine dye was dissolved in acetonitrile ( $10^{-6}$  M) under sonication

followed by slight warming in a water bath. After the addition of one equivalent of the metal salt solution to the solution of the dye, using a microlitre syringe, the solution was shaken well and kept for 1 minute before recording the absorption and emission spectra.

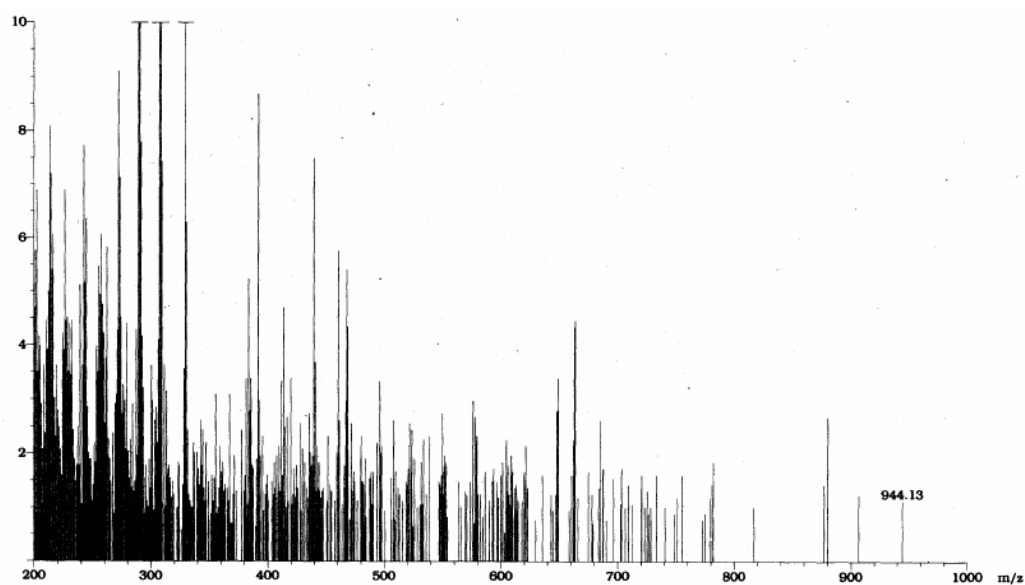


**Figure S1.** Emission spectral changes of **1** ( $1.8 \times 10^{-6}$  M) upon addition of  $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  ( $0 - 2 \times 10^{-6}$  M) in acetonitrile.

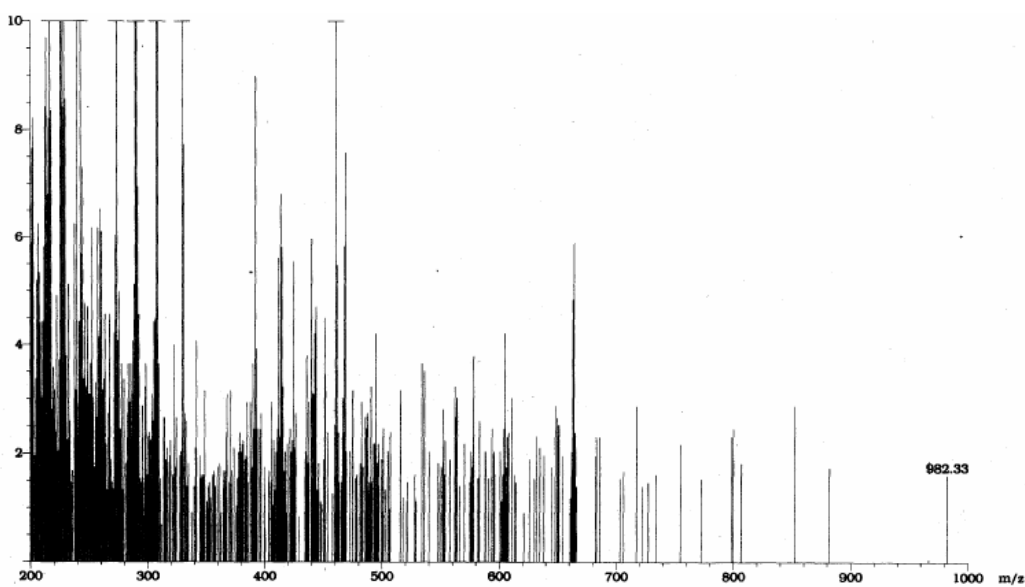


**Figure S2.** Absorption spectral changes of **1** ( $1.8 \times 10^{-6}$  M) upon addition of a)  $\text{Mg}^{2+}$ , b)  $\text{Sr}^{2+}$  and c)  $\text{Ba}^{2+}$  ( $0 - 2 \times 10^{-6}$  M) in acetonitrile.

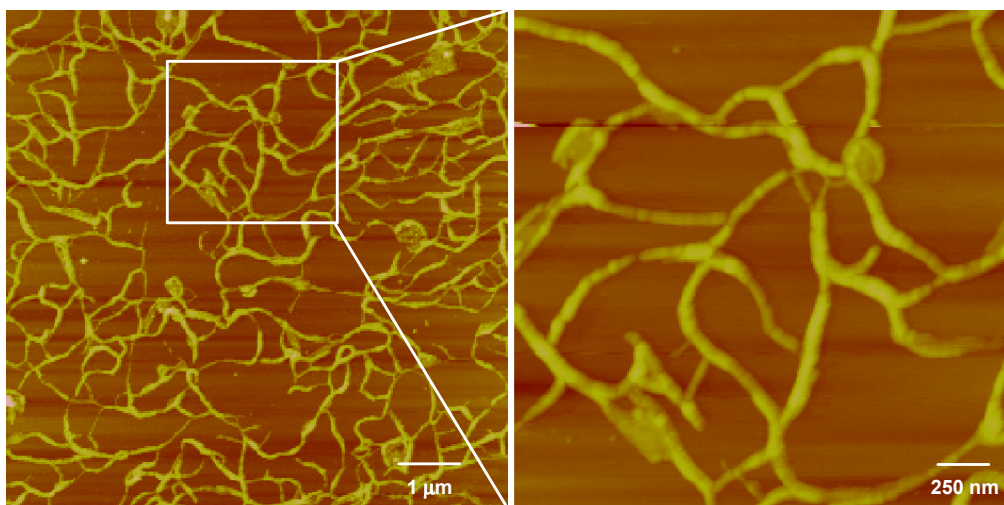
a)



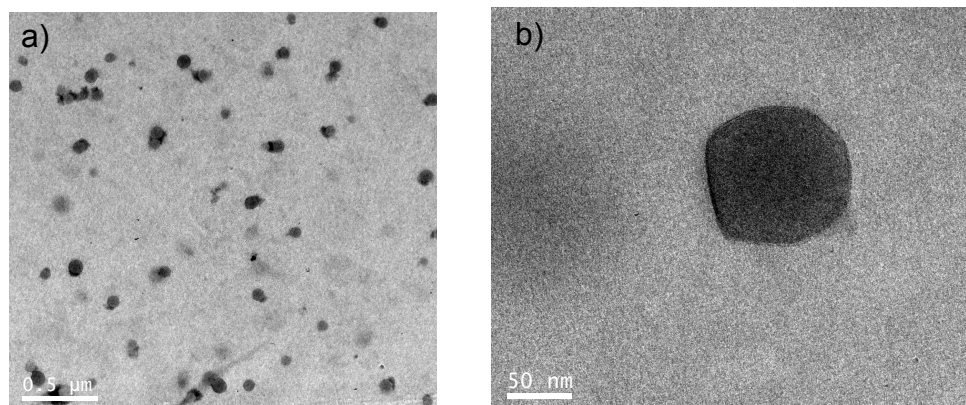
b)



**Figure S3.** MS-FAB spectra of a) **1** alone showing a mass of 944.13 ( $M+2H$ ) and b)  $1.Ca^{2+}$  of mass 982.33 ( $M+Ca^{2+}$ ).



**Figure S4.** Tapping mode AFM height images of **1**.Ca<sup>2+</sup> after 9 h showing no change in morphology. Samples were prepared by casting acetonitrile solution ( $1.8 \times 10^{-6}$  M) over mica (z scale: 40 nm).



**Figure S5.** Transmission Electron Microscopic (TEM) images of **2** ( $1.8 \times 10^{-6}$  M) casted from an acetonitrile solution over a carbon coated grid. a) Shows spherical morphology and b) zoomed image of the same.