

Electronic Supplementary Information : Calix[4]arene sulfonate as a template for forming fluorescent thiazole orange H-aggregates.

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- I. Material and Methods**
- II. Absorption spectrum of TO in water**
- III. Job Plot for the binding of TO to calix[4]arenesulfonate**
- IV. Fluorescence Excitation spectrum of TO H-aggregate**

I. Material and Methods.

Thiazole orange (TO) ultra pure grade with p-toluenesulfonate as the counter ion was purchased from AnaSpec (California, USA) and used without further purification. Calix[4]arenesulfonate was synthesized according to the method of Atwood et al. (J. L. Atwood, W. G. Orr, N. C. Means, F. Hamada, H. Zhang, S. G. Bott and K. D. Robinson, *Inorg. Chem.* **1992**, *31*, 603-606.). Briefly, calix-[4]-arene (200 mg, 0.471 mmol, Sigma-Aldrich, Canada) was added to concentrated H₂SO₄ (3.0 mL) and stirred at 85°C for 5 hr, then allowed to cool to room temperature overnight. The resultant solution was poured into brine (10 mL), and the resulting mixture was heated to boiling then allowed to cool to room temperature. A pale pink solid was obtained by filtration, and repeatedly recrystallized from a minimum of hot distilled water until colourless crystals formed, giving calix[4]arenesulfonic acid (322.3 mg, 0.435 mmol, 92%).

Solutions were made from 18MΩ cm⁻¹ water, the pH was adjusted by adding NaOH (Sigma-Aldrich, Canada). The maximum ionic strength was 0.7 mM.

Absorption and Fluorescence spectroscopy. Absorption spectra were recorded using a Varian Cary-50 single beam spectrophotometer. The fluorescence spectra were recorded using a Photon Technology International (PTI) quanta master spectrofluorimeter operated

in CW mode. Excitation of the samples was set at 350 nm. The fluorescence spectra were not corrected for changes in the absorbance at the excitation wavelength. For both measurements, the solutions were placed in a quartz (Suprasil) cell of 0.4 cm width 1 cm path length (Hellma, Belgium).

II. Absorption spectrum of TO in water.

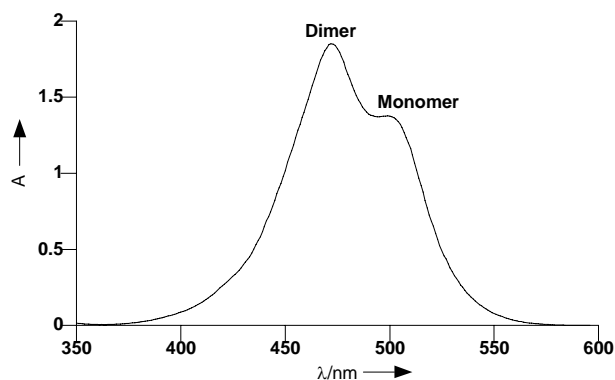


Figure S1: UV/Vis absorption spectrum of TO in water (100 μM).

As can be seen in figure S1, the absorption spectrum of TO in aqueous solution indicates a mixture of both monomeric (500 nm) and dimeric (472 nm) forms of the molecule.

III. Job Plot for the binding of TO to calix[4]arenesulfonate.

The Job plot, also known as Continuous Variation Method is a very popular method to determine binding stoichiometry. In this method, the sum of total host $[\text{H}]_0$ and total guest $[\text{G}]_0$ remains constant (α), and the concentration of $[\text{G}]_0$ is varied from 0 to α . The maximum obtained for the plot provides the stoichiometry (for mathematical development, see Hirose K. in *Analytical Methods in Supramolecular Chemistry*, ed. Christoph A. Schalley, Wiley-VCH, Weinheim, ch. 2, pp. 17-54.).

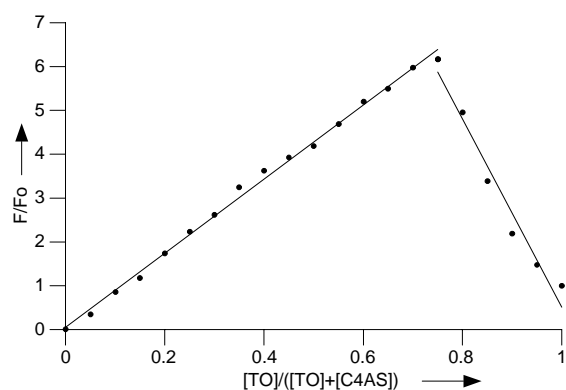


Figure S2: Job plot (continuous variation method) of thiazole orange (tosylate) in the presence of calix-[4]-arenesulphonate to a total concentration of 0.1 mM in water. The concentration of DMSO is negligible (<0.05%). Fluorescence enhancement is obtained from fluorescence at 641 nm.

IV. Fluorescence Excitation spectrum of TO H-aggregate.

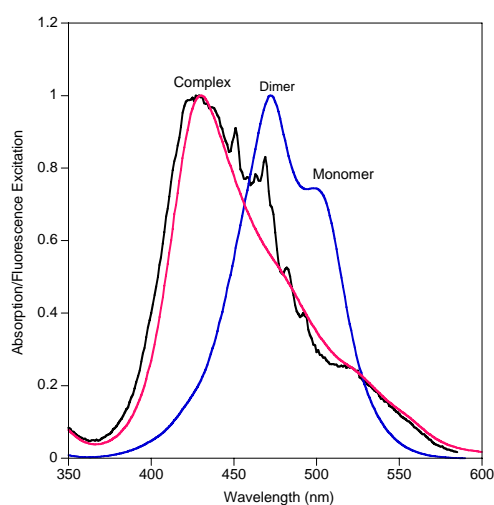


Figure S3: Absorption spectra of TO (100 μ M) in water in the absence (blue) and the presence (red) of calix[4]arenesulphonate (30 μ M). Fluorescence excitation spectrum of TO (100 μ M) in presence of calix[4]arenesulphonate (30 μ M), $\lambda_{em} = 641$ nm.

As can be seen in figure S3, the fluorescence excitation spectrum of the complex formed between TO and calix[4]arene sulfonate matches with the absorption spectrum. In the

fluorescence excitation spectrum detail from the high energy absorption band (429 nm) and the low energy absorption band (562 nm) can be identified. In addition, vibrational structures can be observed. This is not surprising since H-aggregates are known to exhibit rich vibrational structures (see Eisfeld, A. and Briggs, J.S., *Chem. Phys.* 2006, 324, 376-384). These vibrational structures can be masked in the absorption spectrum due to the presence of a mixture of the different forms of TO.