Electronic Supplementary Material (ESI) for Dalton Transactions

Cucurbit[5]uril-metal complex-induced room-temperature phosphorescence of α-naphthol and β-naphthol

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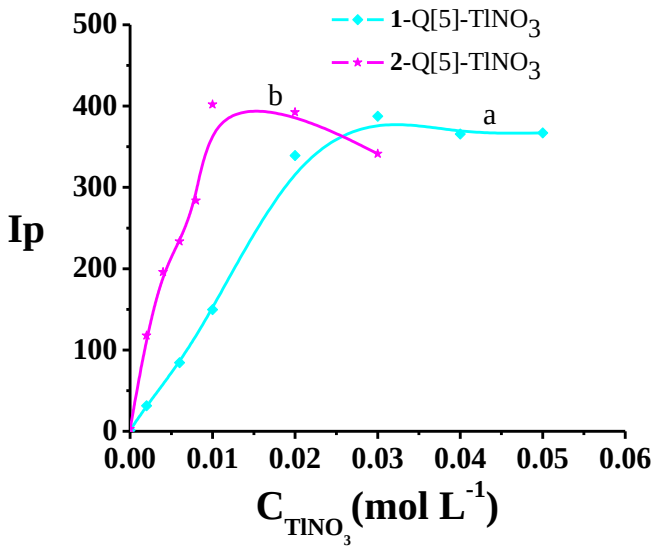
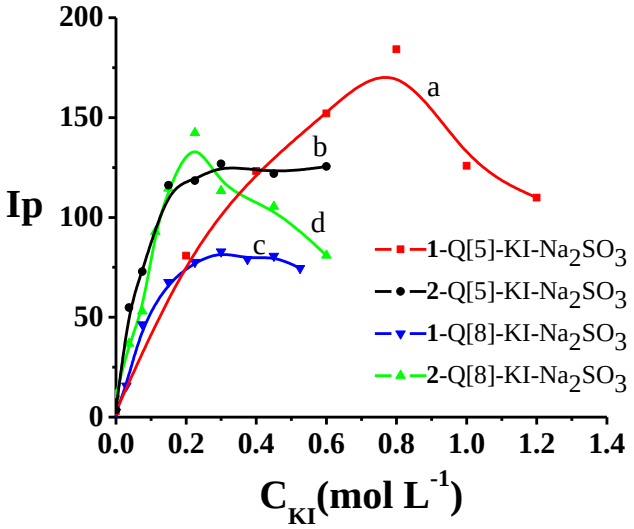
Dependence of RTP intensity on the concentration of heavy atoms

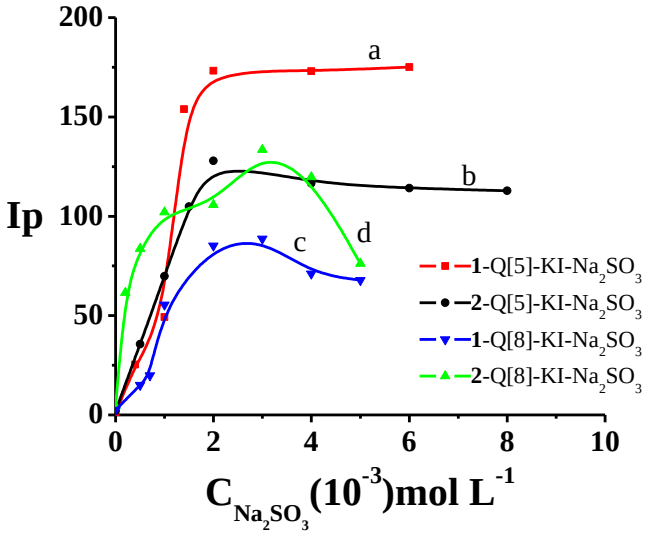


SI-Figure 1 The RTP intensity profiles for **1**-Q[5]-$TlNO_3$(a) and **2**-Q[5]-$TlNO_3$ (b) with increasing amounts of $TlNO_3$. (a): [**1**]=5.0×l0^{-6}mol L^{-1}, Q[5]=3.0×10^{-4}mol L^{-1}; (b): [**2**]=5.0×l0^{-6}mol L^{-1}, Q[5]= 2.5×10^{-4}mol L^{-1}.



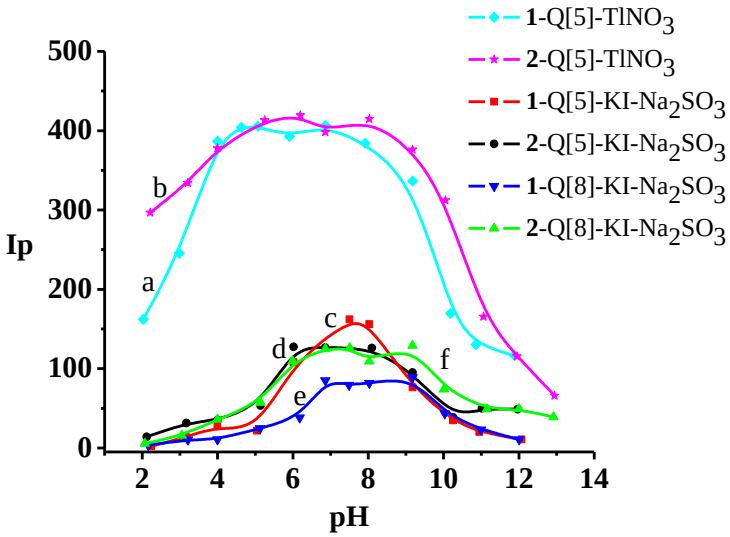
SI-Figure 2 The RTP intensity profiles for **1**-Q[5]-KI-Na_2SO_3 (a), **2**-Q[5]-KI-Na_2SO_3 (b), **1**-Q[8]-KI-Na_2SO_3 (c), and **2**-Q[8]-KI-Na_2SO_3 (d) with increasing amounts of KI. (a): [**1**]=5.0×10^{-6}mol L^{-1}, Q[5]=1.5×10^{-4}mol L^{-1}, [Na_2SO_3]=2.00×10^{-3} mol L^{-1}; (b): [**2**]=5.0×10^{-6}mol L^{-1}, Q[5]=1.5×10^{-4}mol L^{-1}, [Na_2SO_3]=2.00×10^{-3} mol L^{-1}; (c): [**1**]=5.0×10^{-6}mol L^{-1}, Q[8]=6.25×10^{-6}mol L^{-1}, [Na_2SO_3]=2.00×10^{-3} mol L^{-1}; (d): [**2**]=5.0×10^{-6}mol L^{-1}, Q[8]=1.25×10^{-5}mol L^{-1}, [Na_2SO_3]=3.00×10^{-3} mol L^{-1}.

Dependence of RTP intensity on the concentration of sodium sulfite.



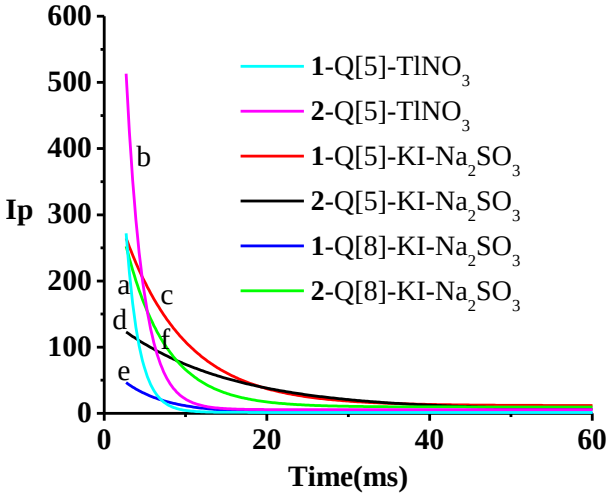
SI-Figure 3 The RTP intensity profiles for **1**-Q[5]-KI-Na_2SO_3 (a), **2**-Q[5]-KI-Na_2SO_3 (b), **1**-Q[8-KI-Na_2SO_3] (c), and **2**-Q[8]-KI-Na_2SO_3 (d) with increasing amounts of Na_2SO_3. (a): [**1**]=5.0×10^{-6}mol L^{-1}, Q[5]=1.5×10^{-4}mol L^{-1},[KI]=0.8 mol L^{-1}; (b): [**2**]=5.0×10^{-6}mol L^{-1}, Q[5]=1.5×10^{-4}mol L^{-1}, [KI]=0.3 mol L^{-1}; (c): [**1**]=5.0×10^{-6}mol L^{-1}, Q[8]=6.25×10^{-6}mol L^{-1}, [KI]= 0.3 mol L^{-1}; (d): [**2**]=5.0×10^{-6}mol L^{-1}, Q[8]=1.25×10^{-5}mol L^{-1},[KI]=0.225 mol L^{-1}.

Dependence of RTP intensity on pH

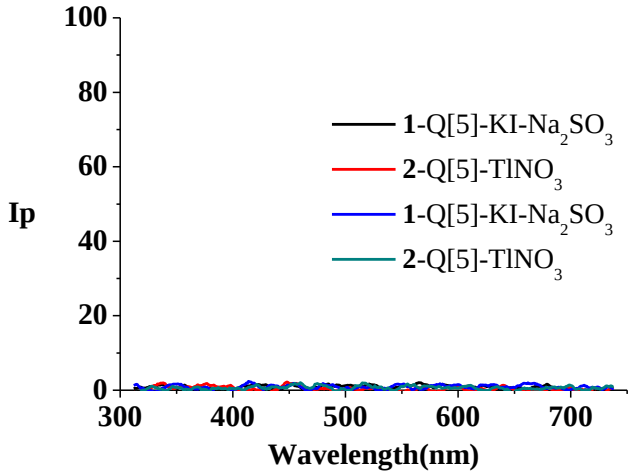


SI-Figure 4 Effects of pH on the Q[5,8]-induced RTP of **1** (a, c and e) and **2** (b, d and f). (a): [**1**]=5.0 × 10^{-6} mol L^{-1}, Q[5]= 3.0×10^{-4}mol L^{-1}, [$TlNO_3$]=0.03 mol L^{-1}; (b): [**2**]=5.0 × 10^{-6} mol L^{-1}, Q[5]= 2.5×10^{-4}mol L^{-1}, [$TlNO_3$]=0.01 mol L^{-1}; (c): [**1**]=5.0 × 10^{-6} mol L^{-1}, Q[5]=1.5×10^{-4}mol L^{-1},[KI]=0.8 mol L^{-1}, [Na_2SO_3]= 2.00×10^{-3} mol L^{-1}; (d): [**2**]=5.0 × 10^{-6} mol L^{-1}, Q[5]=1.5×10^{-4}mol L^{-1}, [KI]=0.3 mol L^{-1}, [Na_2SO_3]= 2.00×10^{-3} mol L^{-1}; (e): [**1**]=5.0 × 10^{-6} mol L^{-1}, Q[8]=6.25×10^{-6}mol L^{-1},[KI]=0.3 mol L^{-1}, [Na_2SO_3]= 2.00×10^{-3} mol L^{-1}; (f): [**2**]=5.0 × 10^{-6} mol L^{-1},Q[8]=1.25×10^{-5}mol L^{-1}, [KI]=0.225 mol L^{-1}, [Na_2SO_3]= 3.00×10^{-3} mol L^{-1};

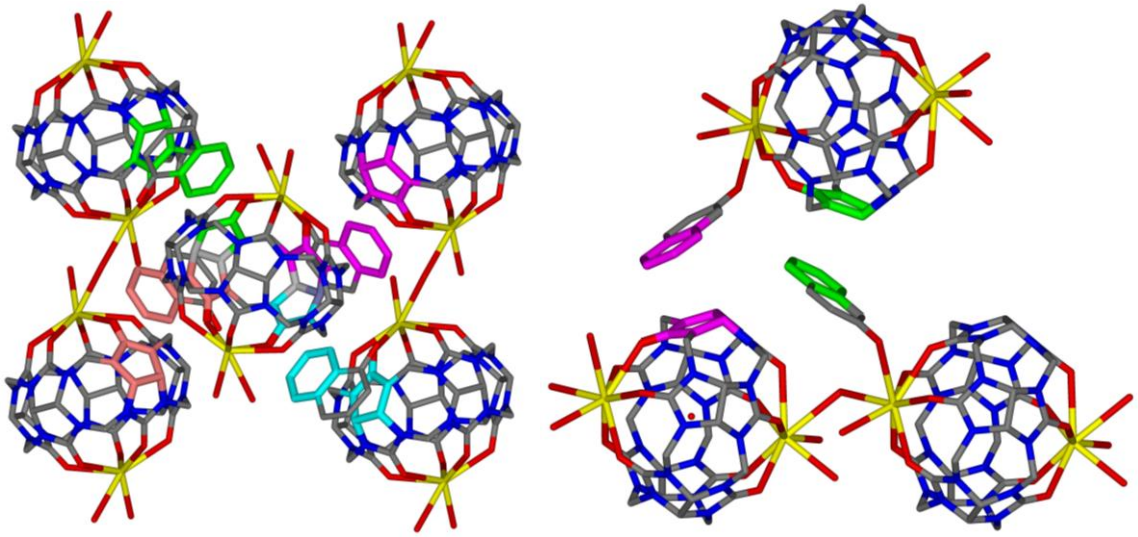
The Q[n]-induced RTP lifetimes of various Q[n] systems.



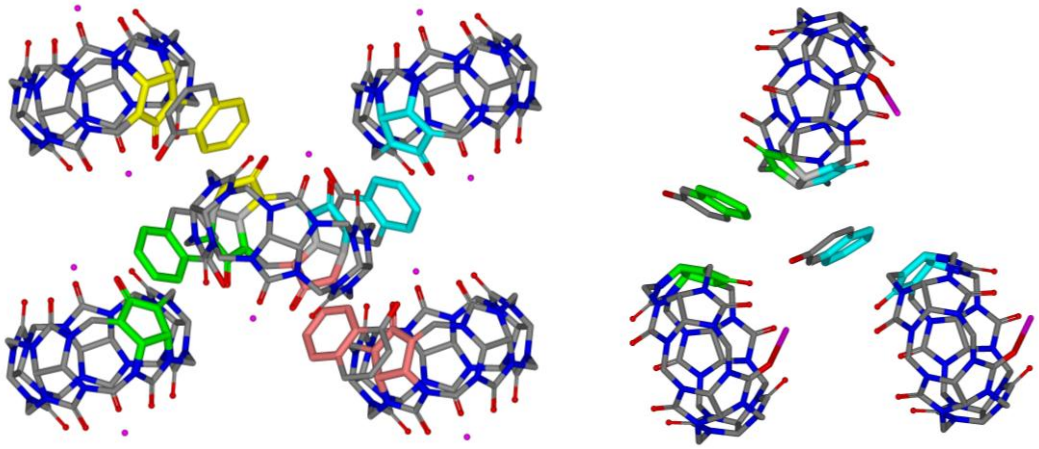
SI-Figure 5 Plots showing RTP intensity vs. time (ms) for the **1**-Q[5]-$TlNO_3$ (a), **2** -Q[5]-$TlNO_3$ (b), **1**-Q[5]-KI-Na_2SO_3 (c), **2**-Q[5]-KI-Na_2SO_3 (d), **1**-Q[8]-KI-Na_2SO_3 (e) and **2**- Q[8]- KI-Na_2SO_3 (f) systems.



SI-Figure 6 The RTP spectra of four compounds in solid state: A (**1**-Q[5]-KI-Na_2SO_3), B (**2**-Q[5]-KI-Na_2SO_3), C (**1**-Q[5]-$TlNO_3$) and D (**2**-Q[5]-$TlNO_3$).



1-Q[5]-KI **2**-Q[5]-KI



1-Q[5]-$TlNO_3$ **2**-Q[5]-$TlNO_3$

SI- Figure 7 stacking of Q[5] and **1** or **2** in the corresponding **1**-Q[5]-KI, **2**-Q[5]-KI, **1**-Q[5]-$TlNO_3$, and **2**-Q[5]-$TlNO_3$ systems

In order to probe the possibility of concentration dependent association occurring for the present systems, saturated solutions of both [Q(5) + KI + 1 napthol] and Q(5) + KI + 2 napthol] were prepared in D_2O and NMR diffusion experiments were run at 25°C using the simulated echo pulse sequence to measure the corresponding diffusion coefficients. Each sample was then diluted by a factor of five, and the diffusion coefficients again measured. The results clearly indicate the presence of a concentration dependent equilibrium in each case.

Each of the 5 monomer units that make up Q(5) has 2 methylene groups (4 protons) and 2 methine groups (2 protons). The protons at each methylene group are non-equivalent and give rise to two signals on either side of the residual HDO signal. The methane protons give one signal as they are equivalent. The attenuations of these peaks in a diffusion experiment were used to determine the diffusion coefficients of the Q(5) molecule in the three samples.

The stimulated echo pulse sequence was used to measure the diffusion coefficients at 25°C. The results for the saturated solutions were as follows.

1. Q(5) + KI + 1-napthol $D = 5.34 \times 10^{-10}\ m^2\ s^{-1}$
2. Q(5) + KI + 2-napthol $D = 4.49 \times 10^{-10}\ m^2\ s^{-1}$
3. Q(5) $D = 3.98 \times 10^{-10}\ m^2\ s^{-1}$

The solutions were diluted by a factor of 5 with D_2O and the diffusion measurements were repeated. The following results were obtained.

1. Q(5) + KI + 1-napthol $D = 6.13 \times 10^{-10}\ m^2\ s^{-1}$

2. Q(5) + KI + 2-napthol $D = 5.97 \times 10^{-10}\ m^2\ s^{-1}$
3. Q(5) $D = 4.51 \times 10^{-10}\ m^2\ s^{-1}$

Attempts to estimate an 'apparent molecular weight' for these systems by employing the likely inappropriate 'solid sphere' model for the associated species followed by 'calibration' of the results obtained against a related measurement for Q(5) alone were stymied when the results showed that Q(5) is itself not monomeric in solution but is significantly associated under the conditions employed (a similar observation has recently been reported for both Q(6) and Q(7) under related conditions). In view of this attempts to further quantify the degree of association present in each of the above systems were discontinued