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Cucurbit[*n*]urils-induced room temperature phosphorescence of quinoline derivatives

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Abstract

The cucurbit[7,8]urils (Q[7] and Q[8])-induced room temperature phosphorescence (RTP) of quinoline and its derivatives were firstly found in the cucurbit[*n*]urils chemistry. The luminophores (quinolines) and their RTP are affected by the concentration of different Q[*n*]s, heavy metal ions and amounts, and pH. The RTP lifetime of the luminophore has been investigated. In presence of Na_2SO_3, the cation Tl^+ led to stronger Q[*n*]-induced RTP, while the RTP lifetimes of luminophore/Q[7 or 8]/KI were generally longer than that of luminophore/Q[7 or 8]/$TlNO_3$, the RTP lifetimes of these systems were between 0.18 and 47.4 ms. Contrary to the stable 1:2 Q[8]:guest ternary inclusion complexes at lower pHs, as suggested by ^{1}H NMR, electronic absorption and fluorescence spectroscopy, low Q[8]-induced room temperature phosphorescence was observed. However, at higher pHs, high intensity of cucurbit[*n*]urils-induced room temperature phosphorescence of these quinoline derivatives were observed, and a 1:1 Q[8]:guest inclusion complex was formed. Investigations of dependence of RTP intensity on concentration of Q[*n*] revealed that the highest intensity of the Q[*n*]-induced RTP was observed at a low mole ratio of host:guest, which is closed to 1:1. It was presumably resulted from the strong interaction of Q[*n*] and these guests due to the combined hydrophobic cavity interaction and the hydrophilic portal interaction of the cucurbit[*n*]urils with the nitrogen heterocycles guest.

Keywords: Room temperature phosphorescence; Cucurbit[7,8]urils; Quinoline and its derivatives; Potassium iodide; Thallium nitrate

1. Introduction

Triplet-state emission detected by different techniques [1–4] has been observed for a large number of polynuclear aromatic molecules at room temperature [5]. Among the techniques, solid surfaces have been useful for the observation of room temperature phosphorescence (RTP) for different nitrogen heterocycles [6,7]. Detection of these nitrogen-containing heterocyclic compounds is very important in the coal liquefaction. It has been reported that β-cyclodextrin (CD) can induce RTP in selected molecules in the absence or presence of external heavy atoms. The favorable thermodynamic forces cause stable inclusion complexes to be formed between β-cyclodextrin and a variety of small molecules.

Cucurbit[*n*]uril, Q[*n*], is a relatively new family of macrocyclic host molecules [8–11]. They are rigid macrocycles with unique cavities [12] rimmed by carbonyl oxygens. Ingress and egress of guests are controlled by the size of the carbonyl portal. Cucurbit[*n*]urils can form inclusion complexes with organic guests and the strongest complexes formed with positively charged molecules [13–17]. Recently, because of the rapid development of cucurbit[*n*]uril chemistry, photochemical properties [18–34] involving cucurbit[*n*]urils have been investigated intensively. However, to our knowledge, no investigation that dealt with phosphorescence of an organic compound involving cucurbit[*n*]urils has been reported.

In this report, we describe the study of RTP of some nitrogen polynuclear aromatic molecules by incubating them with cucurbit[7 or 8]urils (Q[7] or Q[8]) in the presence of a third molecular species that provides external heavy atoms. These nitrogen heterocycles are quinoline(**1**), isoquinoline(**2**), 7-methyylquinoline(**3**), 2-phenylquinoline(**4**),

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3-aminoquinoline(**5**) and 7,8-phenylquinoline(**6**). The addition of Q[7] or Q[8] leads to intense room temperature phosphorescence. The Q[7] or Q[8]–quinoline derivative complexes have high supramolecular stability at a wide pH range, high phosphorescence sensitivity, and substantial decrease of photobleaching. These properties could enable the sensitive and selective detection of the quinoline derivatives through the molecular recognition by cucurbit[*n*]urils.

2. Experiment

2.1. Instrument

Conventional luminescence spectra were obtained on Varian Cary Eclipse fluorescence spectrophotometer. Absorption spectra of the host–guest complex were recorded on a HP8453 UV–visible spectrophotometer. pH measurements were performed with a SA 720 Model pH meter (ORION). The excitation and emission slits were set at 20 and 20 nm, respectively. For the RTP lifetime measurements the gate time and the delay time were set at 5.0 and 0.2 ms, respectively. RTP lifetime can be derived from the equation: $\ln I_t = \ln I_0 - t/\tau$, where I_t and I_0 stand for the RTP intensities when t is equal to 0 and t. The pH value of the solution was adjusted with H_2SO_4 (1.0 and 0.1 mol L^{-1}) or NaOH (1.0 and 0.1 mol L^{-1}) solution. All the experiments are carried out at room temperature.

2.2. Reagents

Quinoline(**1**) and isoquinoline(**2**) were obtained from Shanghai First Regent Factory, 7-methylquinoline(**3**), 2-phenylquinoline(**4**), 3-aminoquinoline(**5**) and 7,8-phenylquinoline(**6**) were obtained from Aldrich Chemical Co. Ltd. The corresponding HCl salts of these luminophore were prepared by dissolving the quinolines in 5 mol L^{-1} HCl followed by crystallization with ethanol or acetone, collecting them by filtration and drying. Potassium iodide, thallium nitrate and sodium sulfite were obtained from Peijing Regent Factory. All chemicals used in this work were of reagent grade and used without further purification. Cucurbit[7,8]urils (Q[7] and Q[8]) were prepared and purified in our laboratories [10]. The quinoline derivatives were prepared as 1.00×10^{-4} mol L^{-1} aqueous solutions, respectively. Q[8] and Q[7] were prepared as 1.25×10^{-4} mol L^{-1} aqueous solution, respectively. Potassium iodide was prepared as 1.00 mol L^{-1} aqueous solution, thallium nitrate was prepared as 0.20 mol L^{-1} aqueous solution and sodium sulfite was prepared as 0.25 mol L^{-1} aqueous solution.

2.3. General procedure

The aliquot of the quinoline and its derivatives stock aqueous solutions and Q[7] or Q[8] solution were pipetted into 10 mL volumetric flask in turn, respectively. Then appropriate volume of $TlNO_3$ or KI, and Na_2SO_3 were added into the volumetric flask, respectively. Diluted to the mark with milli-Q water, the sample was vigorously shaken by hand for about 1 min, placed for some time and then transferred to a 1-cm quartz cell to measure phosphorescence.

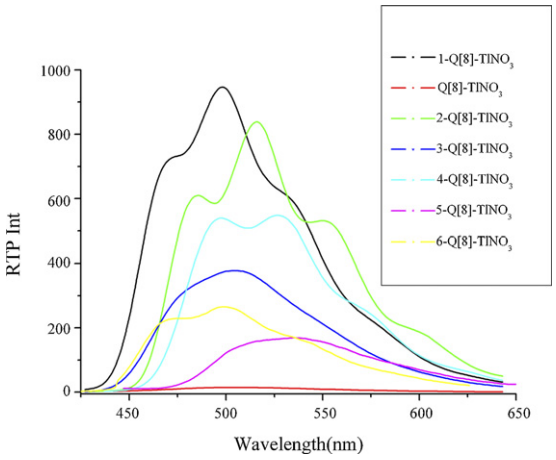

Fig. 1. The RTP spectra of the (**1**, **2**, **3**, **4**, **5**, **6**)–Q[8] systems (in black, green, blue, azure, yellow and pink color) in presence of $TlNO_3$ and Na_2SO_3. [**1–6**] = 1.0×10^{-5} mol L^{-1}; Q[8] = 6.25×10^{-5} mol L^{-1}; [$TlNO_3$] = 4.00×10^{-2} mol L^{-1}; [Na_2SO_3] = 5.00×10^{-3} mol L^{-1}. RTP spectra of Q[8] in presence of $TlNO_3$ and Na_2SO_3 is in red color.

3. Results and discussion

3.1. RTP spectra of the quinoline derivatives induced by Q[8]

The cucurbit[*n*]uril-induced room temperature phosphorescence(RTP) of quinoline and its derivatives were firstly found in the Q[8]–luminophore–$TlNO_3$–Na_2SO_3 systems. Fig. 1 shows the luminescence spectra of these systems. The luminophore **1** showed intense phosphorescence (in black) as a single band with two shoulders in the presence of Q[8] and $TlNO_3$, the RTP emission wavelength of **1** was located at 498 nm. A similar phosphorescence (in green) spectra of luminophore **2** was observed, the RTP emission wavelength of **2** was located at 515 nm. The RTP emission wavelength of the luminophore **3** was located at 505 nm as a single band (in blue). The luminophore **4** and **6** showed similar phosphorescences (in azure and yellow) as twin peaks bands, the RTP emission wavelength of **4** were located at 498 and 530 nm, the RTP emission wavelength of **6** were located at 498 and 530 nm. The luminophore **5** showed intense phosphorescence (in pink) as a single band with a left shoulder, the RTP emission wavelength of **5** was located at 500 nm. The mentioned RTP emission wavelengths of the luminophores were selected as measurement wavelength of emission in this work. There is little background phosphorescence of Q[8]–$TlNO_3$–Na_2SO_3 system (curve g) and luminophore–$TlNO_3$–Na_2SO_3 system (omitted). When the host Q[8] was added to the aqueous solution of the different luminophore–$TlNO_3$–Na_2SO_3 systems, their RTP were strengthened dramatically. This should be attributed to the formation of the inclusion complex of Q[8] and the luminophore(s).

3.2. Dependence of RTP intensity on different Q[n]s and Q[n] concentration

In this work, the experimental results showed that Q[6] and Q[7] can not induce RTP for all of these quinoline derivatives,