ORIGINAL ARTICLE

A three dimensional framework induced by $\pi\cdots\pi$ stacking of 2,2′-(Alkylene-1,6-diyl)diisoquinolinium from Q[6]-based Pseudorotaxane

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Abstract A bromide salt of 2,2′-(hexane-1,6-diyl) diiso-quinolinium (K6) was designed, synthesized and introduced to construct a novel framework induced by $\pi\cdots\pi$ stacking of 2,2′-(alkylene-1,ω-diyl)diisoquinolinium from Q[6]-based pseudo-rotaxanes. The crystal structure of the compound revealed that the assembled framework based on the Q[6]-2,2′-(alkylene-1,6-diyl)diisoquinolinium pseudo-rotaxanes have stoichiometries of $\{(K6)@(Q[6])\}^{2+}\cdot2Br^-\cdot7(H_2O)$. The compound 1 has a novel three-dimensional framework constructed of two different channels̄one containing stacked isoquinolyl moieties from the K6@Q[6] pseudorotaxanes and the other containing the bromide anions. ^1H NMR spectra analysis was performed and confirmed the pseud-orotaxane interaction model in which the 2,2′-(alkylene-1,6-diyl)diisoquinolinium guest threads into the cavity of Q[6] with the alkyl chain included inside the cavity and the two end isoquinolyl moieties protruding from the two opening portals. Absorption spectrophotometric and fluo-rescence spectroscopic analyses of the host–guest inclusion complex in aqueous solution found that the complexes were most stable at a host:guest mole ratio of 1:1. At this ratio, the complex has binding constants $(K) \sim 10^6$.

Introduction

Q[n]-based supramolecular architectures which have intriguing structures or their potential applications in gas storage or absorption, catalysis, and optoelectronics, have been of great interest in the cucurbit[n]urils (Q[n]s) chemistry [1–10]. Kim and co-workers first demonstrated a kind of supramolecular architectures of Q[n]-based metal–organic coordination polymers was realized by threading cucurbituril (Q[6]) molecules with a long chain with two active ends, and then allowing the resulting pseudorotaxane to coordinate with metal ions [11]. In this strategy, the Q[n]-based supramolecular architectures were constructed through coordination of metal ions to the two active ends from Q[6]-based pseudorotaxanes. More recently, Kim and co-workers demonstrated a cyclic oligomer (molecular necklace) that involves the host guest complex formation between Q[8] and a guest molecule in which an electron donor and an electron acceptor unit are connected by a rigid linker with a proper angle. In this supramolecular architecture, a properly designed guest molecule leads to the host-stabilized intermolecular charge-transfer complex formation in the cavity of the host Q[8] [12].

In present study, a three dimensional supramolecular architecture constructed of the pseudo-rotaxane complexes of Q[6] and a guest 2,2′-(alkylene-1,6-diyl)diisoquinolinium (K6) which has two end isoquinolinium moieties that seem to have a strong tendency to stack together through the $\pi\cdots\pi$

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stacking (Fig. 1). In this 3D framework, the $\pi\cdots\pi$ stacking of the end isoquinolyl moieties from the Q[6]-based pseudo-rotaxanes leads to the formation of this novel supramolecular architecture.

Experimental

Chemicals and synthesis

All commercially available chemicals were of reagent grade and were used as received without further purification. Q[6] was prepared and purified using a method in the literature [13]. The 2,2′-(alkylene-1,6-diyl) diisoquinolinium guest (K6) was prepared using a method in the literature [14]. 0.01 mol 1,6-dibromide-alkyl was added to a stirred solution of isoquinoline (2.58 g, 0.02 mol) in 1,4-dioxane (50 mL) at 373 K for a period of 5 h. After cooling to room temperature, the mixture was filtered, washed with ether, and air-dried. ^{1}H NMR of K6 (D$_2$O, 400 MHz) δ: 9.46(s, 2 H), 8.27(d, J = 6.8 Hz, 2 H), 8.16(m, 4 H), 8.03(m, 4 H), 7.43(d, J = 7.6 Hz, 2 H), 4.52(t, J = 7.2 Hz, 4 H), 1.90(m, 4 H), 1.22(m, 4 H); MS m/z (%): 344 $(M+2)^+$, $170(M/2)^+$, 129 (isoquinolinium ion peak); m.p. 224–225 °C; yield: 65%.

Preparation of single crystals of {(K6)@(Q[6])}$^{2+}$·2Br$^-$·7(H$_2$O)

A mixture of Q[6] (0.12 g, 0.12 mmol) and K6 (0.075 g, 0.2 mmol) in water (25 mL) was heated at 60 °C for 5 h. After the mixture was stirred at room temperature for 3 h, the mixture was filtered. Colorless X-ray-quality crystals were obtained with evaporation of the filtrate and in a yield of ∼50%.

The crystal data for the complex was collected on a Bruker SMART Apex2000 CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) in the ω and φ scan modes. Data was collected at 223 K. Lorentz polarization and absorption corrections were applied. Structural solution and full matrix least-squares refinement
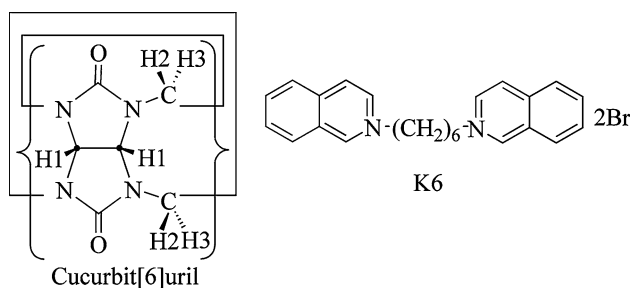
based on $F2$ were performed with the SHELXTL-97 program packages. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically. {(K6)@(Q[6])}$^{2+}$·2Br$^-$·7(H$_2$O): monoclinic, a = 23.5852(19) Å, b = 21.2805(18) Å, c = 13.3985(11) Å, α = 90°, β = 100.999(3)°, γ = 90°, V = 6601.24(18) Å^3, Z = 4, D_{calcd} = 1.635 g cm^{-3}, μ = 1.325 mm^{-1}, unique reflns = 5547, obsd reflns = 4285, params = 493, R [I>2σ(I)]^a = 0.0397, wR [I>2σ(I)]^b = 0.1068. Crystallographic data has also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-732230. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Host–guest complexation

To study the host–guest complexation behavior of Q[6] and the title guest, 2.0–2.5 × 10^{-3} mmol samples of Q[6] in 0.5–0.7 g D$_2$O with guest:Q[6] ratios ranging between 1 and 2 were prepared. The ^{1}H NMR spectra were recorded at 20 °C on a Varian INOVA-400 spectrometer. Absorption spectra of the host–guest complexes were recorded on a HP8453 UV–visible spectrophotometer and fluorescence spectra of the host–guest complexes were recorded on a Varian RF-540 fluorescence spectrophotometer at room temperature. For these absorption and fluorescence studies, aqueous solutions of K6 were prepared with a fixed concentration of 1.0 × 10^{-5} mol L^{-1}, and the samples of these solutions were combined with Q[6] to give solutions with Q[6]:K6: ratios of 0, 0.2, 0.4. 0.6, and so on, up to 3.0.

Results and discussion

Crystal structure of the compound

The single crystal X-ray diffraction analysis of the compound {(K6)@(Q[6])}$^{2+}$·2Br$^-$·7(H$_2$O) revealed a monoclinic crystal lattice with a C2/c space group. It showed that a single unit cell contains three of the same pseudorotaxanes of K6@Q[6]. Each has the guest K6 threading into the cavity of Q[6] (Fig. 2a). The hexyl chain is included inside the cavity, and the two end isoquinolyl moieties protrude from both the opening portals. The two portal planes have an average distance of 6.173 Å, while the length (N13···N13) of the alkyl moiety of the guest is 8.792 Å. Thus, the two N13 cations of the guest protrude 1.31 Å outside the portal planes, and the distance between the N13 cation and the six portal carbonyl oxygen atoms of Q[6]

Fig. 1 The structures of the host cucurbit[6]uril and the guest K6

range between 3.361 and 4.133 Å for the pseudorotaxanes. The dihedral angle between the plane of the six portal carbonyl oxygen atoms of Q[6] and the plane of the closest isoquinolyl moiety of the guest is 59.42°. The two planes of the isoquinolyl moieties of the guest are parallel. The π–π stacking of the protruded isoquinolyl moieties plays an important role in the formation of structurally well-defined frameworks in the crystal structure of the compound. Each protruded isoquinolyl interacts with two neighboring isoquinolyls from the adjacent K6@Q[6] pseudorotaxanes through the π–π stacking (Fig. 2b); the sandwiched isoquinolyl plane and the top isoquinolyl plane are parallel to each other with an average separation distance of 3.164 Å. The dihedral angle between the sandwiched isoquinolyl plane and the bottom isoquinolyl plane is 2.7°, and the distance between the two centers of the two phenyl rings of the isoquinolyl is 3.833 Å.

The π–π stacking induces the formation of a novel three-dimensional opening framework consisting of K6@Q[6] pseudorotaxanes as shown in Fig. 3a, b. Contained within this framework are two repeating "grids" as depicted in Fig. 3c, d. A close inspection of the "grids" reveals that the channels found at the centers of these grids have diameters of ∼7.6 and 5.7 Å respectively. Fig. 3e depicts the interior surface of one of the channels, which is constructed of the portal carbonyl oxygens of the host Q[6]s. This channel includes the stacked isoquinolyl moieties of K6s. Fig. 3f shows the interior surface of the other channel, which is constructed of the methane carbon on the outer surface of the host Q[6]s. This channel includes bromide anions Br1 and water molecules O3W.

^{1}H NMR technique has been proven to be a powerful method to investigate host–guest interactions in the solution state. Fig. 4 shows the ^{1}H NMR spectra of the unbound guest K6 (Fig. 4a) and of the host–guest complex Q[6]–K6 (Fig. 4b). Compared to the proton resonances of the unbound guests, the proton resonances of the included alkyl moieties of the guests experience upfield shifts of 0.2–0.8 ppm. While the proton resonances of the aromatic parts of the included guests are almost the same as those of the unbound guests, the peaks a and g of protons close to the nitrogen atom of the isoquinolyl moieties of the
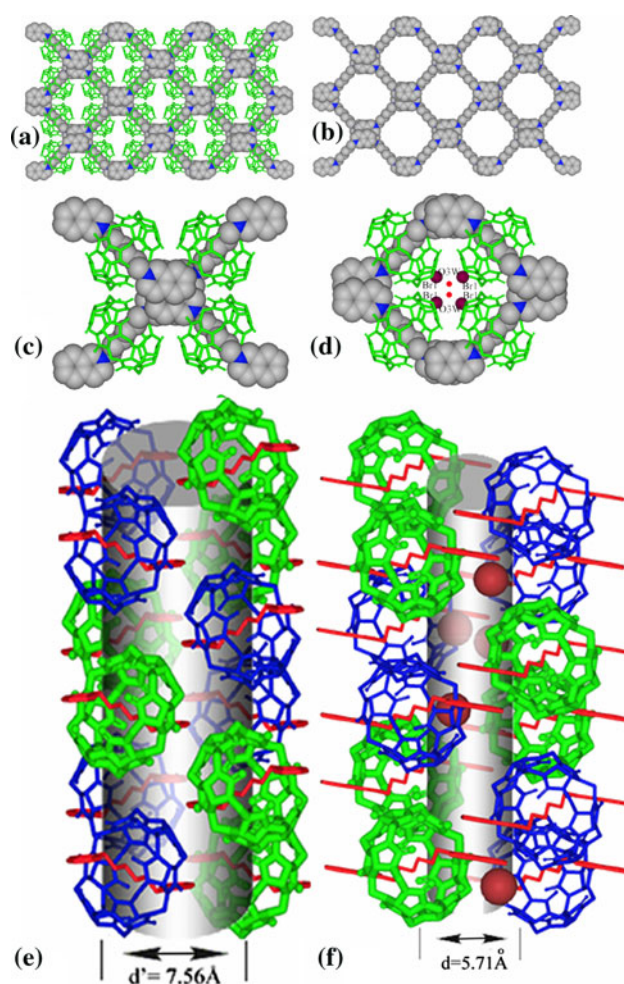

Fig. 3 **a** The 3D framework consisting of K6@Q[6] pseudorotaxanes; **b** The framework omitting the hosts Q[6]; **c** top view and **d** side view of the grid containing the stacked isoquinolyl moieties; **e** top view and **f** side view of the grid containing bromide anions and water molecules. All hydrogen atoms and some water molecules are omitted for clarity

included guest experience downfield shifts of 0.2–0.7 ppm. This indicates that these protons are outside of the shielding realm, at the portals of the host Q[6]; the Q[6] includes the alkyl moiety of the guest in its cavity while the isoquinolyl moieties protrude from both of its opening portals.

Fig. 2 The crystal structure of **a** the K6@Q[6] pseudorotaxane; **b** the basic π–π stacks of the neighboring protruded isoquinolyl moieties of the K6@Q[6] pseudorotaxane (*top view*). All H atoms, Br anions and water molecules are omitted for clarity
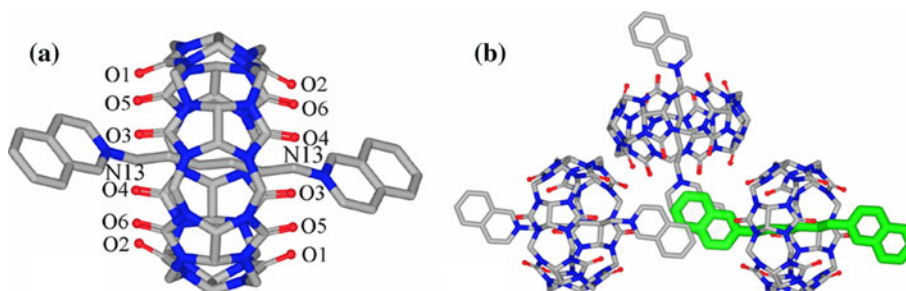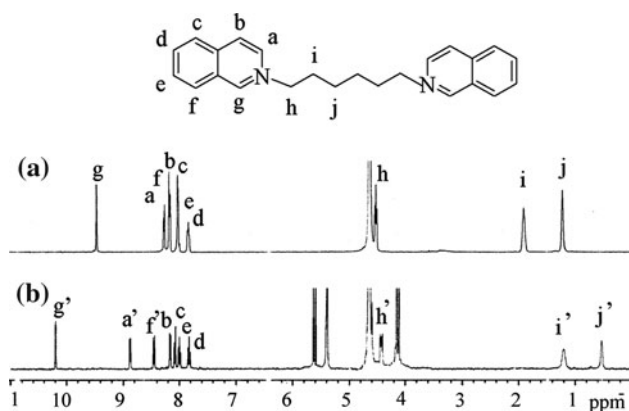
Fig. 4 ^{1}H NMR spectra (400 MHz, D$_2$O) of K6- in the absence of (a) and in the presence of Q[6] (b)

This is consistent with the results observed in the corresponding crystal structures of the Q[6]–K6 inclusion complex.

Spectrophotometric analysis of the interaction between Q[6] and the guest

To further understand the interaction between Q[6] and K6, a ratio-dependent study was pursued using electronic absorption and fluorescence spectroscopy. The free host Q[6] typically shows no absorbance at $\lambda > 210$ nm, and the free guest show the maximum absorption at $\lambda_{max} = 232$ nm for K6. Fig. 5 (top) shows the UV spectra obtained with aqueous solutions containing a fixed concentration of K6 (25mM) and variable concentrations of Q[6]. As the ratio of moles of the host Q[6] to the guest (N$_{Q[6]}$/N$_{K6}$) increases, the wavelength at which maximum absorption occurs progressively blue shifts and the absorption intensity increases. The absorbance (A) and N$_{Q[6]}$/N$_{K6}$ values can be fitted to a 1:1 binding model for the Q[6]–K6 inclusion complex, as shown in Fig. 5 (bottom). Plotting the change in absorbance (ΔA) vs. [N$_{Q[6]}$/(N$_{Q[6]}$+N$_{K6}$)], as shown in the inserts in Fig. 5 (bottom), confirms that the interaction between Q[6] with the guest K6 can be fitted to a 1:1 binding model. The conclusions drawn from the absorption spectra are thus consistent with the results from the ^{1}H NMR study.

Fluorescence spectroscopic studies of the Q[6]–K6 inclusion complex were performed. The free host Q[6] doesn't fluoresce. The wavelength at which maximum emission occurs for the guest is 365 nm for K6. As seen in Fig. 6 (top), the fluorescence intensities of the guests K6 increase with increasing Q[6] concentration. Plots of the fluorescence intensities (I$_f$) vs. N$_{Q[6]}$/N$_{K6}$ and ΔI$_f$ vs. [N$_{Q[6]}$/(N$_{Q[6]}$+N$_{K6}$)] can be fitted to a 1:1 binding model as well as pictured in Fig. 6 (bottom).

The measured data from both absorption spectrophotometric and fluorescence spectroscopy analysis fitted to a
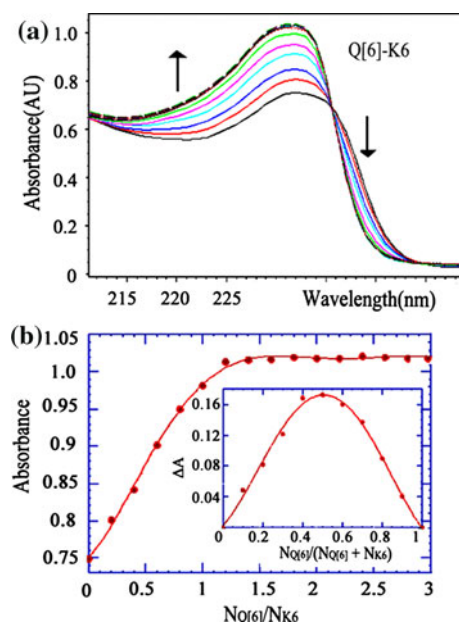
Fig. 5 Electronic absorption spectra (*top*) of the guest K6 in the presence of increasing concentrations of Q[6]. A vs. N$_{Q[6]}$/N$_{K6}$ (*bottom*) and ΔA vs. [N$_{Q[6]}$/(N$_{Q[6]}$+N$_{K6}$)] (*bottom*) curves from the absorption spectra
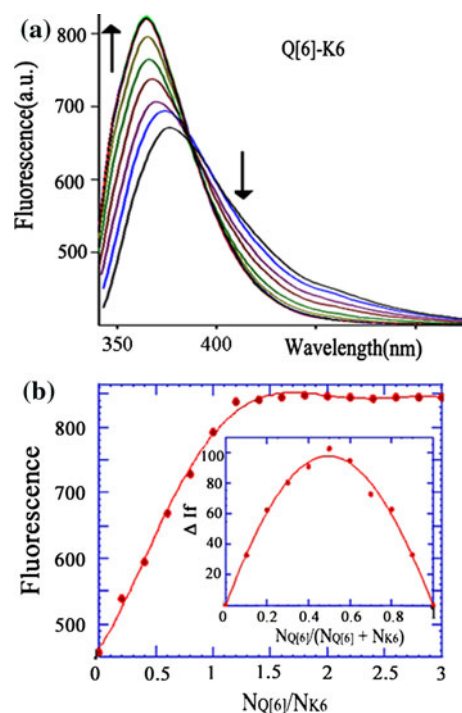
Fig. 6 Fluorescence emission spectra (*top*) of the guest K6 in the presence of increasing concentrations of Q[6]. I$_f$ vs. N$_{Q[6]}$/N$_{kn}$ (*bottom*) and ΔI$_f$ vs. [N$_{Q[6]}$/(N$_{Q[6]}$+N$_{Kn}$)] (*bottom*) curves from the fluorescence spectra

simple 1:1 host: guest complexation, yielded a calculated binding constant (K) of 5.08×10^6 L/mol based on the absorption spectrophotometric analysis and 4.00×10^6 L/

mol based on the fluorescence spectroscopy analysis. The values of K are reasonably consistent, with an average value of 4.54×10^6 L/mol.

Conclusion

Kim and coworkers [11] first reported 2D and 3D frameworks constructed of Q[6]-based pseudorotaxanes that were formed by coordination with metal ions. In present study, we showed that such a 3D framework can be induced by the $\pi \cdots \pi$ stacking of the protruded isoquinolyl moieties. The present study suggests that novel 2D and 3D frameworks could be designed and synthesized by using different linear guests with isoquinolyl ends.

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