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Square [5]molecular necklace formed from cucurbit[8]uril and carbazole derivative

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ABSTRACT

The formation of square 5-member molecular necklace ([5]MN) is presented by utilizing the host–guest recognition-driven self-assembly between CB[8] and carbazole derivative 1·2Cl[−], which bears two 4,4'-bipyridin-1-ium (BP) arms with a orthogonal geometry. The self-assembly and stimuli-responsive behaviors of square [5]MN are comprehensively investigated by NMR (¹H, COSY, NOSEY, and DOSY), UV–vis, DLS, and SEM methods.

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Over the past two decades, the efficient synthesis of mechanically interlocked molecules such as rotaxanes, catenanes, and knots have attracted wide attention due to not only their amazing supramolecular architectures^{1–3} (e.g., olympiadane,^{1b} pentafoil knot,^{1c} a star of David catenane,^{1d} Solomon links,^{1e} and Borromean rings^{1f}) but also their potential functions, such as molecular machine² (e.g., molecular switches,^{2a} molecular motors,^{2b} molecular sensors,^{2c} molecular catalyst,^{2d} and molecular synthesizer^{2e}) and smart materials³ (e.g., memory devices^{3a} and molecular muscles^{3b}). In these various structures, [*n*]molecular necklaces ([*n*]MN) defined by Kim the first time, as topologic isomers of catenanes, are a class of supramolecular structures in which three or more side rings as molecular 'beads' are threaded onto a central ring as molecular 'chains'.⁴ Sauvage and co-workers unexpectedly observed the formation of a mixture of [*n*]MN (*n* = 4–7) in the metal-template synthesis of multi-ring catenanes, as identified by electrospray mass spectrometry.⁵ After that, supramolecular scientists directly used molecular macrocycles, such as crown ether and cucurbit[*n*]uril, as the 'beads' for forming molecular necklaces via host–guest interactions and/or coordination interactions. For example, Stoddart and co-workers isolated trace crown-based [4]MN from oligocatenanes,^{6a} and then successfully constructed [4]MN and [5]MN with dialkylammonium ions as host–guest interaction sites for anchoring dibenzo-24-crown-8 (DB24C8) macrocycles via the Witting reaction.^{6b}

Recently, Wu and co-workers also used DB24C8 macrocycles to synthesize a kinetically and thermodynamically stable [5]MN.⁷ More interestingly, Li and Stang achieved the orthogonality of coordination-driven self-assembly and crown ether host–guest complexation to successfully obtain a [4]MN with a triangle geometry and [7]MN with a hexagon geometry.⁸ Chiu and co-workers applied four bis-crown-based molecular cages to macrocyclization with flexible linear guests, producing up to a [5]MN.⁹ On another hand, Kim and co-workers introduced cucurbit[*n*]uril (*n* = 6, 8) macrocycles into the self-assembly of molecular necklaces using the coordination of rotaxane-based ligands or host-stabilized charge-transfer interactions to successfully gain cucurbit[6]uril-based [5]MN (*n* = 4, 5)^{4,10} and cucurbit[8]uril-based [6]MN,¹¹ respectively.

CB[8] as a member of cucurbit[*n*]uril family has an enough big cavity which is capable of simultaneously encapsulating two identical or different guest molecules to form a stable 1:2 ternary complex.¹² For example, it can encapsulate an electron-rich guest and an electron-deficient guest to form the stable 1:1:1 complex, which is driven by the charge-transfer interaction between the π -electron donor and acceptor molecules inside the hydrophobic cavity of CB[8].^{12d} Recently, Li and co-workers also found a new 1:2 binding pattern between CB[8] and two 4,4'-bipyridin-1-ium (BP) with a well-defined head-to-tail π - π -stacking geometry in the solid state.^{13a} Due to its unique host–guest recognition properties, CB[8] has been more and more employed as a linking motif to prepare supramolecular organic frameworks,^{13,14} polymers,¹⁵ micelles,¹⁶ vesicles,¹⁷ microcapsule,¹⁸ hydrogels,¹⁹

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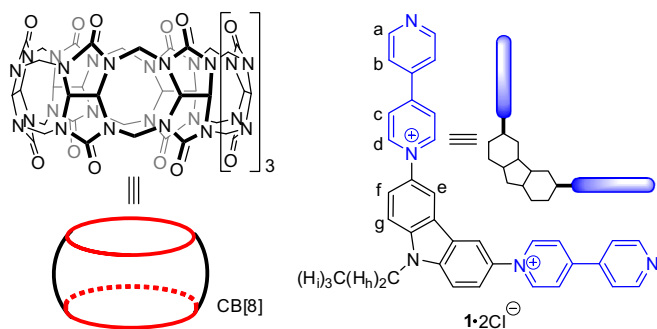


Chart 1. Cucurbit[8]uril and structures of $1 \cdot 2\text{Cl}^-$.

colloids,^{12e} and molecular machines.²⁰ Herein, we report a facile route to achieve the quantitative self-assembly of a square [5]molecular necklace ($\text{CB}[8] \cdot 1$)₄·8Cl[−] from four CB[8] as side rings and four carbazole derivative $1 \cdot 2\text{Cl}^-$ with two 4,4'-bipyridin-1-ium (BP) arms which form the central ring via host–guest interactions, and pH-responsive aggregation behaviors of the square [5]MN.

Our strategy is that rigid linkers with a proper angle and recognition sites could lead to form cyclic geometric shapes such as triangle, square, or pentagon, induced by the host–guest recognition between CB[8] and linkers, and then assemble a structure of molecular necklace. To achieve this idea, we designed and synthesized a 3,6-disubstituted carbazole derivative $1 \cdot 2\text{Cl}^-$ which bears two 4,4'-bipyridin-1-ium (BP) arms with a orthogonal geometry as guest molecules for the investigation of the self-assembly of CB[8]-based [n]MN complex (Chart 1). Compound $1 \cdot 2\text{Cl}^-$ was synthesized by the reaction of corresponding amines with *N*-(2,4-dinitrophenyl) 4,4'-bipyridin-1-ium salts by the Zincke reaction (Supporting information). As shown in Scheme 1, two 4,4'-bipyridin-1-ium arms (blue sticks) of compound $1 \cdot 2\text{Cl}^-$ were located on 3- and 6-sites of the carbazole skeleton that offer two recognition sites with an around 90° angle. Spontaneously, the geometric constraint and the head-to-tail orientation between two stacking BP units determined to form a [4+4] square macrocycle as the central ring of [5]MN (Scheme 1).

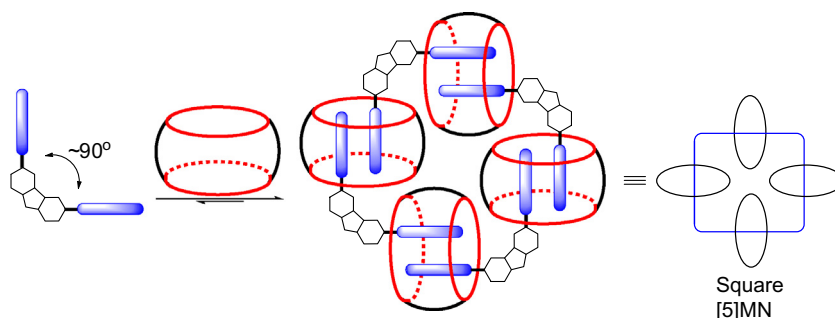
Initially, we investigated the self-assembly behavior of 1 with CB[8] in D₂O using NMR technique. Figure 1a shows the ¹H NMR spectrum recorded for 1 alone in D₂O at room temperature. Adding 0.5 equiv of CB[8] to the guest solution caused the signals of 1 to become more complicated (Fig. 1b). Figure 1b displays distinct resonances for free 1 and the complex of 1 and CB[8], which establishes that 1 undergoes slow exchange on the ¹H NMR time scale. Interestingly, when 1.0 equiv of CB[8] was added to a solution of carbazole derivative 1 (0.5 mM) in D₂O, the signals of free 1 disappeared completely and one new set of signals to come out, indicating the presence of a single thermodynamically stable complex (Fig. 1c). Moreover, no obvious changes could be observed

in the presence of excess CB[8] (2.0 equiv) (Fig. S3), which supports that the stoichiometry of the complex between 1 and CB[8] is 1:1 ratio. In addition, Job's plot using UV–vis spectroscopy displayed a maximum absorption change at 0.5, also suggesting a 1:1 stoichiometry of 1 and CB[8] (Fig. S4). Of particular note is the COSY spectrum that showed that the chemical shifts of protons H_b and H_c upfield shifted by 1.15 and 0.80 ppm, respectively, which are more changes compared with the chemical shifts of H_a and H_d ($\Delta\delta = 0.60$ and 0.10 ppm, respectively) (Fig. S5). It is because the protons H_b and H_c are located at the center of the cavity of CB[8] due to the head-to-tail orientation between two stacking BP units. Furthermore, the NOESY spectrum also revealed the spatial proximity of protons H_b and H_c as head-to-tail stacking of two BP rings (Fig. S6).

In order to obtain information about the constitution of the self-assembled species formed from 1 and CB[8] in D₂O, we performed diffusion-ordered spectroscopy (DOSY) for the self-assembled species ($1 \cdot \text{CB}[8]$)_n. The 2D DOSY NMR spectrum of the self-assembled species ($1 \cdot \text{CB}[8]$)_n revealed that all the signals of 1 and CB[8] gave comparable diffusion coefficient, which further identified the formation of a single complex in the solution (Fig. S7). The diffusion coefficients measured using nine different resonances for ($1 \cdot \text{CB}[8]$)_n averaged $(1.496 \pm 0.052) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Fig. 2). The *D* value of ($1 \cdot \text{CB}[8]$)_n is very close to the tetrameric assemble formed from four cucurbit[7]uril derivatives²¹ ($1.64 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) which strongly suggests the formation of the square assembly ($1 \cdot \text{CB}[8]$)₄. Furthermore, if we assume that ($1 \cdot \text{CB}[8]$)₄ is roughly spherical, the hydrodynamic diameter of ($1 \cdot \text{CB}[8]$)₄ calculated by the Stokes–Einstein equation is about 2.67 nm, and consistent with the computational model (Fig. S8).²²

Next, the self-assembly process of square [5]MN ($1 \cdot \text{CB}[8]$)₄ was studied by UV–vis spectroscopy. A dramatic red-shift from 383 nm to 415 nm of the main absorption peak of the carbazole ring was detected when 0–1 equiv of CB[8] was added to a solution of 1 (Fig. 3a, A–C) accompanying a color change from light yellow to orange. We guess the reason of the color change could be ascribed to the charge-transfer interactions between two BP rings inside the cavity of CB[8] to finally give a central square ring, which caused the elongated conjugation of four carbazole derivative 1 (Fig. S8, MMFF model). Unfortunately, only 1+1 complex of CB[8] and 1 was observed by electrospray ionization mass spectrometry (ESI-MS) because this sophisticated assembly is unstable in the condition of ESI (Fig. S9). Taken together, the ¹H, COSY, NOESY, and DOSY NMR, strongly suggest that the complex of 1 and CB[8] is most likely a single discrete cyclic [5]molecular necklace ($1 \cdot \text{CB}[8]$)₄ with a square geometry.

The response of self-assembly system toward external stimuli, such as temperature, concentration, pH, or some compounds, is very important for potential applications. To know the thermodynamic properties of the square [5]MN ($1 \cdot \text{CB}[8]$)₄, we first studied the response toward changes in temperature and concentration.



Scheme 1. Schematic representation of self-assembly process between cucurbit[n]uril and carbazole derivative $1 \cdot 2\text{Cl}^-$.

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