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Exclusive Formation of 1:1 and 2:2 Complexes between Cucurbit[8]uril and Electron Donor-acceptor Molecules Induced by Host-stabilized Charge-transfer Interactions

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The exclusive formation of 1:1 and 2:2 host–guest complexes between cucurbit[8]uril (CB[8]) and electron donor-acceptor (D–A) molecules by host-stabilized charge-transfer (CT) interactions is reported. Reaction of CB[8] with D–A molecule 1^{2+} containing dipyridyliumylethylene as an electron-acceptor unit and 2,6-dihydroxynaphthalene as an electron-donor unit, which are connected by a but-2-enyl linker, resulted in the exclusive formation of 1:1 complex 2^{2+} which has been characterized by UV-visible, NMR and mass spectrometry. The ^{1}H-NMR spectrum of 2^{2+} revealed that the acceptor and donor units of 1^{2+} form an *intramolecular* CT complex inside the cavity of CB[8], which was also supported by a molecular modeling study. Another D–A molecule (3^{2+}), which contains a rigid 1,4-xylyl linker to connect a dipyridyliumylethylene unit and 2-hydroxynaphthalene unit reacts with CB[8] to form 2:2 complex 4^{4+} exclusively. In 4^{4+}, two molecules of 3^{2+} form a CT complex with each other while the donor and acceptor units of one guest molecule interact with the acceptor and donor units, respectively, of the other inside the cavities of two CB[8] molecules.

Keywords: Cucurbituril; Charge-transfer complex; Folded conformation; Host–guest chemistry; Self-assembly

INTRODUCTION

The charge-transfer (CT) interactions or donor-acceptor interactions [1,2] between π-systems have been widely exploited in the design and synthesis of self-organizing systems. In particular, the CT interaction between electron deficient 4,4′-bipyridinium derivatives and electron rich aromatics have been extensively employed in synthesizing mechanically interlocked molecules such as rotaxanes and catenanes [3,4], which later led to elegant studies of molecular machines and switches [5–8]. Cucurbit[8]uril (CB[8]), a member of the host family cucurbit[n]uril (CB[n], $n = 5$–10) [9–19], has a hydrophobic cavity, the size of which is comparable to that of γ-cyclodextrin (γ-CD), and two indentical ureido carbonyl-fringed portals. It exhibits remarkable host–guest properties [12–30] distinctly different from those of the smaller homologues, which includes the encapsulation of two identical aromatic guest molecules inside the cavity to form a stable 1:2 host–guest complex [9,15]. Even more remarkably, CB[8] encapsulates two different aromatic guest molecules, an electron-donor and an electron-acceptor, to form a stable 1:1:1 complex [31], which is driven by the markedly enhanced CT interaction between the guest pair inside the hydrophobic cavity of CB[8].

The discovery of the host-stabilized CT complex formation offered a new opportunity to construct novel supramolecular assemblies. For the last several years, we and others reported a wide variety of supramolecular assemblies and their applications [32–40] including molecular necklaces [33], molecular loop locks [34], and redox-controllable vesicles [35], based on this chemistry. In particular, we studied a number of interesting supramolecular assemblies formed from CB[8] and a guest molecule having both electron-donor and electron-acceptor units connected by a suitable linker (D–A molecule). Several different types of supramolecular assemblies were obtained from this approach depending on the length and flexibility of the linker between the donor

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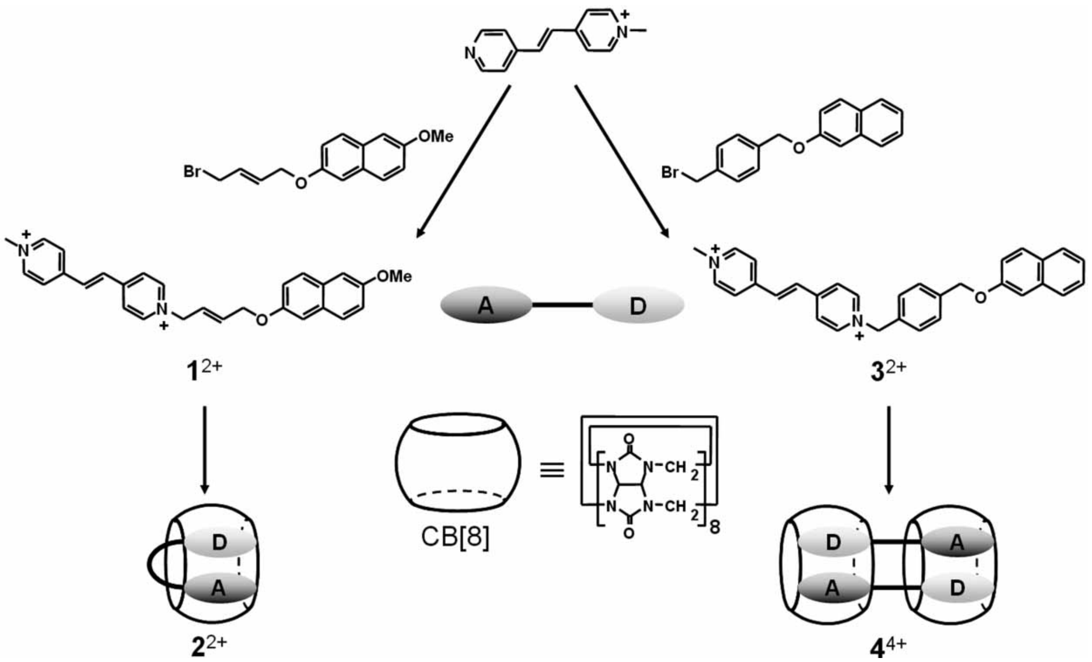

SCHEME 1 Synthesis of $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$ and $\mathbf{4}^{4+}$.

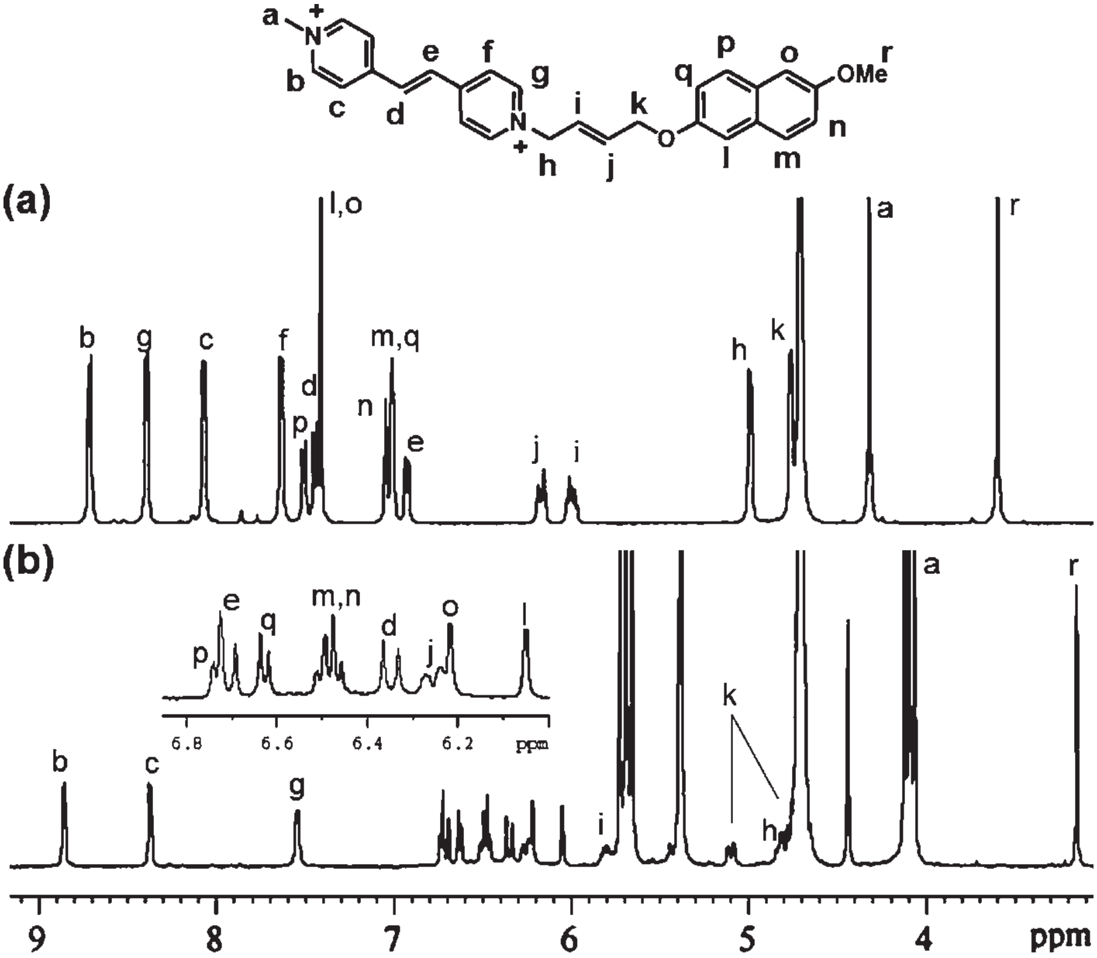

FIGURE 1 Comparison of ^{1}H NMR spectra in D_2O of (a) D–A molecule $\mathbf{1}^{2+}$ and (b) 1:1 complex $\mathbf{2}^{2+}$.

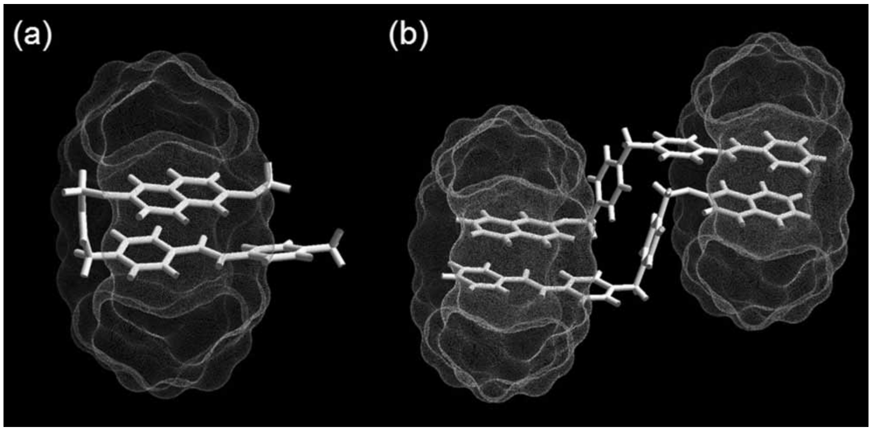

FIGURE 2 Energy-minimized structures of (a) 1:1 complex $\mathbf{2}^{2+}$ and (b) 2:2 complex $\mathbf{4}^{4+}$ obtained by molecular mechanical calculations.

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and acceptor units. A long and flexible linker favored a 1:1 complex by the host-stabilized *intramolecular* CT interaction [36], whereas a short, rigid linker led to a mixture of a 2:2 complex and polymer (or poly(-pseudorotaxane)) [37] by the host-stabilized *intermolecular* CT interaction. Finally, a rigid linker with a proper angle led to a cyclic oligomer or a molecular necklace in which a number of CB[8] beads are threaded on a large "ring" formed by *intermolecular* CT interaction [33].

In an attempt to synthesize a linear polymer (or polypseudorotaxane) using CB[8] and a D–A molecule via the host-stabilized *interamolecular* CT interaction, we synthesized two new D–A molecules with a "rigid" linker. Against our expectation, however, the reaction of the D–A molecules with CB[8] produced either a 1:1 complex or a 2:2 complex exclusively. Here we report the unexpected, exclusive formation of the 1:1 and 2:2 host–guest complexes between CB[8] and D–A molecules by the host-stabilized CT interaction.

RESULTS AND DISCUSSION

With an intention to synthesize a linear polypseudorotaxane by the CB[8]-stabilized *intermolecular* CT interaction, we designed and synthesized D–A molecule $\mathbf{1}^{2+}$ containing dipyridyliumylethylene as an electron-acceptor unit and 2,6-dihydroxynaphthalene as an electron-donor unit, which are connected through a "rigid" but-2-enyl linker to prevent the D–A molecule from folding (Scheme 1). However, the but-2-enyl linker turned out to be flexible enough for $\mathbf{1}^{2+}$ to fold back to form an *intramolecular* CT complex between the donor and acceptor units inside the cavity of CB[8] as described below.

When 1 equiv of CB[8] was added to $\mathbf{1}^{2+}$ in H_2O, the solution turned from yellow to pink ($\lambda_{max} = 522$ nm) indicating the formation of a charge-transfer (CT) complex (Fig. S1). ^{1}H NMR spectroscopy revealed the exclusive formation of a stable host–guest complex ($\mathbf{2}^{2+}$), which can be either a 1:1 or 2:2 complex. However, the ^{1}H-NMR spectrum of $\mathbf{2}^{2+}$ (Fig. 1), the peak assignment of which has been aided by 2D NMR techniques including COSY and ROESY (Fig. S2), is more consistent with a 1:1 host–guest complex in which the guest molecule $\mathbf{1}^{2+}$ folds back so that the dipyridyliumylethylene unit forms an *intramolecular* CT complex with the 2,6-dihydroxynaphthalene unit inside the CB[8] cavity. The signals for the dipyridyliumylethylene (*d*, *e*, *f*, *g*) and naphthalene (*l*, *m*, *n*, *o*, *p*, *q* and *r*) protons, which are now located inside CB[8], shift up-field relative to those of the free guest whereas those for the but-2-enyl unit (*i*, *j*) and a part of dipyridyliumylethylene (*a*, *b*, *c*) unit, which are located outside CB[8], shift down-field. In addition to these observations, the signal corresponding to proton *k* in the complex is split into two sets, which results from the magnetically nonequivalent environments due to the significant conformational restriction. The rotation of the inner pyridinium located inside CB[8] appears to be quite restricted as judged by the somewhat broad signal for proton *g* and the disappearance of the signal for proton *f*, which reappears as a singlet at a higher temperature. Another evidence for the formation of a 1:1 complex rather than a 2:2 complex comes from the size of the supramolecular species estimated from the diffusion coefficient measured by pulsed field gradient NMR techniques (Fig. S3). The estimated hydrodynamic volume of the complex is 1.89 nm^3, only 1.3 times larger than that of CB[8] itself, supporting the 1:1 complex formation. However, the most convincing evidence for the 1:1 complex formation was provided by ESI-mass spectrometry (Fig. S4). A strong peak at 876 corresponding to M^{2+} ion was observed with an isotopic pattern nicely matching the calculated one. Although we have not succeeded in getting the single crystals of $\mathbf{2}^{2+}$ suitable for X-ray work, the

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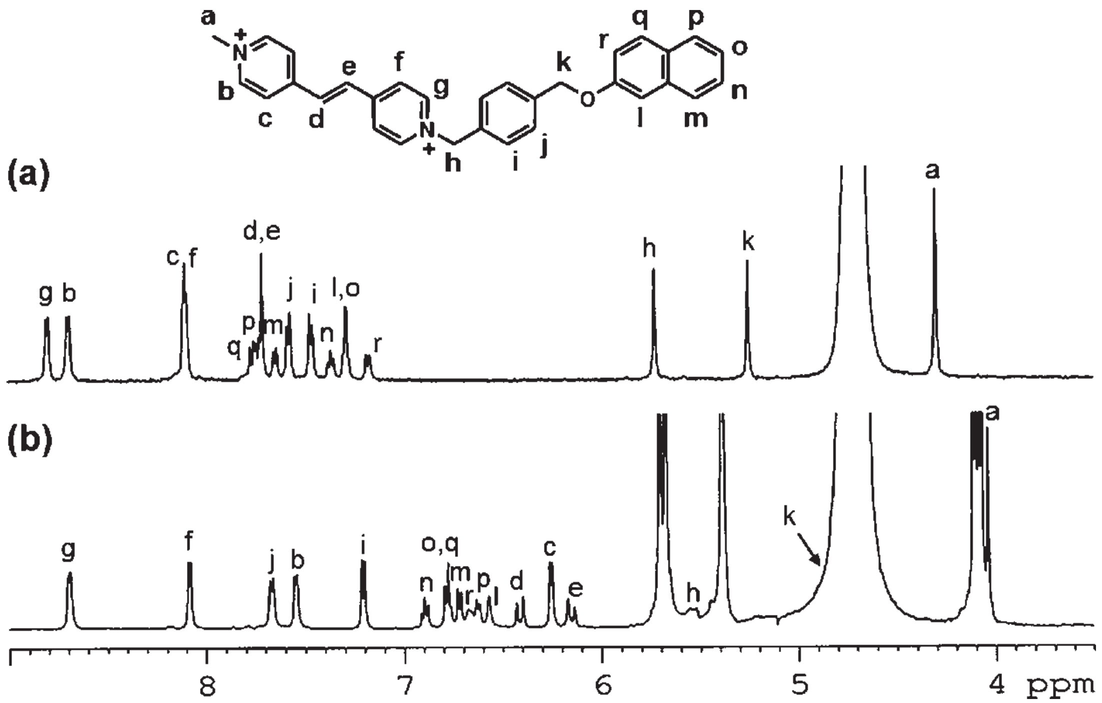

FIGURE 3 Comparison of ^{1}H NMR spectra in D_2O of (a) D–A molecule $\mathbf{3}^{2+}$ and (b) 2:2 complex $\mathbf{4}^{4+}$.

energy-minimized structure of $\mathbf{2}^{2+}$ (Fig. 2) obtained by molecular mechanical calculations (Cerius^2) is congruent with the proposed structure.

The above results led us to design and synthesize another D–A molecule with a rigid linker, $\mathbf{3}^{2+}$, which contains a 1,4-xylyl linker to connect a dipyridyliumylethylene unit and 2-hydroxynaphthalene unit (Scheme 1). The D–A molecule $\mathbf{3}^{2+}$ is similar to the one ($\mathbf{3}'^{2+}$) used for the construction of a polypseudorotaxane on gold [37], except that the electron-acceptor unit is changed from 4,4′-bipyridinium to dipyridyliumylethylene. Most interestingly, while the reaction of CB[8] with $\mathbf{3}'^{2+}$ in solution produced a mixture of a 2:2 complex and polymer (or polypseudorotaxane), that with $\mathbf{3}^{2+}$ resulted in exclusive formation of a 2:2 complex via host-stabilized CT interaction as described below.

Upon addition of 1 equiv of CB[8] to $\mathbf{3}^{2+}$ in H_2O, the color of the solution changed from yellow to orange with a broad CT band around 465 nm in UV spectrum indicating the formation of a CT complex ($\mathbf{4}^{4+}$) (Fig. S5). The ^{1}H NMR spectrum of $\mathbf{4}^{4+}$ (Fig. 3) revealed the exclusive formation of a stable host–guest complex with a binding stoichiometry of 1:1 or its multiples. The ^{1}H-NMR spectrum of $\mathbf{4}^{4+}$, the peak assignment of which has also been aided by 2D NMR techniques including COSY and ROESY (Fig. S6), indicated that the terminal pyridinium unit of dipyridyliumylethylene and 2-naphthol unit are located inside CB[8] cavity. The signals for the terminal part of dipyridyliumylethylene (*a*, *b*, *c*, *d*, *e*) and naphthalene (*l*, *m*, *n*, *o*, *p*, *q*, *r*) protons showed prominent up-field shift relative to those of the free guest. The proton signals of the linking part shifted up-field slightly. The evidence for the formation of a 2:2 complex rather than other possibilities came from the hydrodynamic volume of the resulting supramolecular species estimated from the diffusion coefficient measured by pulsed field gradient NMR techniques (Fig. S7). The estimated volume of the complex is 4.71 nm^3, approximately 3.1 times larger than that of CB[8] itself, which is consistent with a 2:2 complex considering the volumes of two CB[8] and the part of $\mathbf{4}^{4+}$ protruding from CB[8] after the complex formation.

The most convincing evidence for the 2:2 complex formation was provided by ESI-mass spectrometry (Fig. S8). Two strong peaks at 886 and 1203 corresponding to M^{4+} and $[M^{4+} + NO_3^-]^{3+}$ ions, respectively, were observed with isotopic patterns nicely matching the calculated ones. Figure 3 shows the energy-minimized structure of $\mathbf{4}^{4+}$ obtained by molecular mechanical calculations (Cerius^2), in which two molecules of $\mathbf{3}^{2+}$ form a CT complex with each other while the donor and acceptor units of one molecule interact with the acceptor and donor units, respectively, of the other inside the cavities of two CB[8] molecules. This structure is consistent with the prominent up-field shifts of the proton signals for the terminal part of dipyridyliumylethylene (*a*, *b*, *c*, *d*, *e*) and naphthalene (*l*, *m*, *n*, *o*, *p*, *q*, *r*) upon complexation with CB[8]. Presumably, the shielding effect (aromatic π-electrons) of the *p*-xylylene unit of one guest caused the up-field shift of the signals for the methylene protons, *h*, *k*,

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and aromatic proton, *i* of the other guest. The exclusive formation of the 2:2 complex is in contrast to the fact that a similar D–A molecule ($\mathbf{3}'^{2+}$) containing 4,4′-bipyridinium instead of dipyridyliumylethylene as an electron acceptor unit resulted in a mixture of a 2:2 complex and polymer upon complexation with CB[8] [37]. Although the origin of the different behavior of the two D–A molecules is not clear, the dipyridyliumylethylene unit with greater electron-accepting ability with a larger contact area apparently favors the formation of a 2:2 complex upon complexation with CB[8].

In summary, we described the exclusive formation of the 1:1 and 2:2 host–guest complexes between CB[8] and D–A molecules by the host-stabilized CT interaction. Against our expectation, a but-2-enyl linker is flexible enough for a D–A molecule to fold back to form an *intramolecular* CT complex between the donor and acceptor units inside the cavity of CB[8]. The rigid 1,4-xylyl linker prevents the folding of a D–A molecule to form a 1:1 complex with CB[8], but it leads a D–A molecule and CB[8] to form a 2:2 complex exclusively, or a mixture of a 2:2 complex and polypseudorotaxane depending on the size and strength of an acceptor unit, which illustrates that a subtle change in building blocks may result in a huge change in self-assembled structures as frequently observed in supramolecular chemistry.

EXPERIMENTAL

General

Chemicals were purchased from Aldrich Chemical Co. and used without further purification. 1-(4-pyridyl)-2-[4-*N*-(methyl)pyridinio]ethylene iodide was synthesized as reported earlier [37]. NMR experiments were carried out on a Bruker DRX500 spectrometer operating at a proton Larmor frequency of 500.23 MHz. ^{1}H—^{1}H correlation spectroscopy (COSY) and rotating-frame Overhauser effect spectroscopy (ROESY) experiments were performed to assign the proton resonances of $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$ and $\mathbf{4}^{4+}$ at 298 K. UV-visible spectra were recorded on a Hewlett–Packard diode-array 8453 spectrophotometer. Molecular mechanical calculations were carried out by Cerius^2 packages. The electrospray mass spectra were obtained with a JEOL JMS-700T mass spectrometer.

Synthesis and Characterization

2-(4-Bromo-but-2-enyloxy)-6-methoxy-naphthalene

A solution of 6-methoxy-naphthalen-2-ol (85 mg, 0.49 mmol) and 1,4-dibromo-2-butene (1.06 g, 4.94 mmol) in acetone (10 mL) in the presence of K_2CO_3 (0.34 g, 2.5 mmol) was refluxed for 9 h followed by usual aqueous work-up and purification using column chromatography with EtOAc/n-hexane (1:5) to afford the product (62 mg, 41%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.63$ (m, 2H), 7.14–7.08 (m, 4H), 6.21–6.02 (m, 2H), 4.64 (d, $J = 6.90$ Hz, 2H), 4.00 (d, $J = 4.55$ Hz, 2H), 3.89 (s, 3H).

D–A Molecule $\mathbf{1}^{2+}\cdot Br^-\cdot I^-$

A solution of 2-(4-bromo-but-2-enyloxy)-6-methoxy-naphthalene (89 mg, 0.29 mmol) and 1-(4-pyridyl)-2-[4-*N*-(methyl)pyridinio]ethylene iodide (94 mg, 0.29 mmol) in DMF (3 mL) was stirred for 24 h at rt, then the resulting precipitate was filtered, washed with CH_3CN and dried to yield yellow solid $\mathbf{1}^{2+}\cdot Br^-\cdot I^-$ (0.17 g, 97%). ^{1}H NMR (D_2O): $\delta = 8.81$ (d, $J = 6.39$ Hz, 2H), 8.46 (d, $J = 6.43$ Hz, 2H), 8.19 (d, $J = 6.39$ Hz, 2H), 7.73 (d, $J = 6.43$ Hz, 2H), 7.65 (d, $J = 6.44$ Hz, 1 H), 7.55 (m, 3 H), 7.15 (m, 3 H), 7.04 (d, $J = 4.54$ Hz, 1H), 6.24 (m, 1H), 6.07 (m, 1 H), 5.06 (d, $J = 6.90$ Hz, 2H), 4.86 (d, $J = 4.55$ Hz, 2H), 4.40 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (D_2O): $\delta = 156.3$, 153.7, 151.3, 145.8, 144.1, 134.9, 133.8, 133.6, 130.5, 129.7, 129.1, 129.0, 127.3, 126.0, 125.9, 120.2, 119.3, 111.0, 107.1, 67.7, 62.5, 55.8, 48.4; MS (ESI): *m/z* (%): 212.1 (100) $[M]^{2+}$. For elemental analysis, the halide anions were exchanged with NO_3^-. Elemental analysis (%) calcd for $C_{28}H_{28}N_4O_8\cdot 1.5H_2O$: C 58.43, H 5.43, N 9.73; found: C 58.74, H 5.12, N 10.0.

1:1 Complex $\mathbf{2}^{2+}\cdot Br^-\cdot I^-$

To a solution of $\mathbf{1}^{2+}\cdot Br^-\cdot I^-$ (11 mg, 18 μmol) in H_2O (10 mL) was added $CB[8]\cdot(2H_2SO_4)\cdot 30H_2O$ (38 mg, 18 μmol) and the resulting mixture was sonicated with occasional heating until all solid materials were dissolved. Undissolved solid was filtered off and the filtrate was slowly evaporated under a reduce pressure to yield the product $\mathbf{2}^{2+}\cdot Br^-\cdot I^-$ (38 mg, 92%). ^{1}H NMR (500 MHz, D_2O): $\delta = 8.85$ (d, $J = 6.38$ Hz, 2H), 8.37 (d, $J = 6.38$ Hz, 2H), 7.54 (d, $J = 6.38$ Hz, 2H), 6.73 (d, $J = 8.89$ Hz, 2H), 6.71 (d, $J = 16.34$ Hz, 1H), 6.62 (d, $J = 8.89$ Hz, 1H), 6.50 (m, 2H), 6.46 (d, $J = 16.34$ Hz, 1H), 6.34 (br, 1H), 6.25 (m, 1H), 6.21 (s, 1H), 6.04 (s, 1H), 5.80 (m, 1H), 5.72 (d, $J = 16.69$ Hz, 16H), 5.38 (s, 16H), 5.08 (m, 1H), 4.80 (m,2 H), 4.75 (br, 1H), 4.44 (s, 3H), 4.09 (d, $J = 16.69$ Hz, 16H), 3.15 (s, 3H); UV/Vis (H_2O): λ_{CT} (lg ε) = 522 nm (2.84); MS (ESI): *m/z* (%): 876 (100) $[M^{2+}]$, 592 $[M^{2+} + Na^+]^{3+}$.

2-(4-Bromomethyl-benzyloxy)naphthalene

To a solution of 2-hydroxynaphthalene (0.71 g, 4.9 mmol) and K_2CO_3 (3.4 g, 25 mmol) in dried acetone (30 mL) was added α, α′-dibromo-*p*-xylylene (1.0 g, 3.8 mmol). After stirring for 20 h at rt, the resulting mixture was filtered off and purified by column chromatography (EtOAc:Hex = 1:7) to give a white solid (0.43 g, 35%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.75$ (m, 2H), 7.70 (d, $J = 8.12$ Hz, 1H), 7.43 (m, 5H), 7.32 (t, $J = 7.48$ Hz, 1H), 7.21 (m, 2H), 5.16 (s, 2H), 4.50 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 157.0$, 137.9, 137.6, 134.8, 129.7, 129.6, 129.5, 128.2, 128.1, 127.9, 127.3, 124.2, 119.3, 107.5, 69.9, 33.5; MS (EI): m/z 326 [M^+].

D–A Molecule $\mathbf{3^{2+}}\cdot 2NO_3^-$

To a solution of 2-(4-Bromomethyl-benzyloxy)-naphthalene (0.15 g, 0.46 mmol) in 5 mL of DMF was added 1-(4-pyridyl)-2-[4-*N*-(methyl)pyridinio]ethylene iodide (0.12 g, 0.38 mmol). After the mixture was stirred for 24 h at rt, the resulting precipitate was filtered, washed with CH_3CN and dried to yield an orange solid. Anion exchange was performed by adding 1 eq. of $AgNO_3$ to an aqueous solution of this solid and filtered out the precipitated AgBr and AgI using a membrane filter to provide the desired product $\mathbf{3}^{2+}\cdot 2NO_3^-$ (0.18 g, 83%). ^{1}H NMR (500 MHz, D_2O): $\delta = 8.80$ (d, $J = 5.98$ Hz, 2 H), 8.69 (d, $J = 5.98$ Hz, 2H), 8.09 (d, $J = 5.98$ Hz, 4H), 7.76 (d, $J = 8.76$ Hz, 1H), 7.74 (d, $J = 8.12$ Hz, 1H), 7.71 (s, 2H), 7.64 (d, $J = 8.33$ Hz, 1H), 7.57 (d, $J = 8.12$ Hz, 2H), 7.46 (d, $J = 8.12$ Hz, 2H), 7.36 (t, $J = 7.48$ Hz, 1H), 7.28 (m, 2H), 7.17 (d, $J = 8.12$ Hz, 1H), 5.72 (s, 2H), 5.25 (s, 2H), 4.30 (s, 3H); ^{13}C NMR (125 MHz, D_2O): $\delta = 155.7$, 151.7, 151.1, 145.6, 144.6, 139.1, 134.4, 134.0, 133.4, 133.3, 130.2, 129.8, 129.3, 129.2, 127.8, 127.1, 127.0, 126.3, 125.9, 124.6, 119.0, 108.9, 69.7, 64.3, 48.2; MS (ESI): m/z (%): 222.1 (100) [M^{2+}]. For elemental analysis, the nitrate anion was exchanged with Br^-. Elemental analysis calcd for $C_{33}H_{36}N_2O_1\cdot H_2O$: C 59.82, H 4.86, N 4.50; found: C 59.49, H 4.79, N 4.67.

2:2 Complex $\mathbf{4^{4+}}\cdot 4NO_3^-$

To a solution of $\mathbf{3}^{2+}\cdot 2NO_3^-$ (20 mg, 0.035 mmol) in H_2O (7 mL) was added CB[8]$\cdot(2H_2SO_4)\cdot 30H_2O$ (73 mg, 0.035 mmol) and the resulting red mixture was sonicated with occasional heating until all the solid materials had dissolved. Undissolved solid was filtered off and the filtrate was slowly evaporated under a reduce pressure to yield the product $\mathbf{4}^{4+}\cdot 4NO_3^-$ (63 mg, 94%). ^{1}H NMR (500 MHz, D_2O): $\delta = 8.69$ (d, $J = 5.56$ Hz, 2H), 8.08 (d, $J = 5.56$ Hz, 2H), 7.66 (d, $J = 7.55$ Hz, 2H), 7.54 (d, $J = 5.56$ Hz, 2H), 7.20 (d, $J = 7.55$ Hz, 2H), 6.88 (t, $J = 6.76$ Hz, 1H), 6.78 (m, 2H), 6.72 (d, $J = 8.15$ Hz, 1H), 6.68 (br, 1H), 6.62 (d, $J = 7.95$ Hz, 1H), 6.56 (s, 1H), 6.41 (d, $J = 16.69$ Hz, 1H), 6.25 (d, $J = 5.56$ Hz, 2H), 6.15 (d, $J = 16.69$ Hz, 1H), 5.69 (d, $J = 15.10$ Hz, 16H), 5.54 (br, 2H), 5.38 (s, 16H), 4.94 (br, 2H), 4.08 (d, $J = 15.10$ Hz, 16H), 4.01 (s, 3H); UV/Vis (H_2O): λ_{CT} (lg ε) = 465 nm (2.75); MS (ESI): m/z (%): 886.8 (100) [M^{4+}], 1203.0 [$M^{4+} + NO_3^-$].

Diffusion NMR Spectroscopy

The diffusion coefficient measurements were carried out at 25°C using a 5 mm Bruker QNP probe with an actively shielded z gradient coil. Diffusion coefficients were extracted from a series of ^{1}H NMR spectra measured by the bipolar pulse longitudinal encode-decode (BPPLED) pulse sequence as a function of gradient amplitude. In each experiment, gradient duration time was 2.0 ms or 2.5 ms and the amplitudes of the gradient pulses ranged from 1 to 40 G/cm. The diffusion coefficients were calculated from the data using diffusion-ordered spectroscopy (DOSY). The diffusion coefficient of $\mathbf{2}^{2+}$ and $\mathbf{4}^{4+}$ was measured to be $2.61 \times 10^{-10}\,m^2/s$ and $1.91 \times 10^{-10}\,m^2/s$, respectively. The estimated sizes from diffusion coefficient of the complexes, $\mathbf{2}^{2+}$ and $\mathbf{4}^{4+}$, are 1.3 and 3.1 times, respectively, larger than that of CB[8] alone.

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