Selective binding of cucurbit[7]uril and β-cyclodextrin with a redox-active molecular triad $Ru(bpy)_3$–MV^{2+}–naphthol†

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A 1:1:1 inclusion complex is formed by the binding interactions among β-CD, CB[7] hosts, and $Ru(bpy)_3$-terminated viologen–naphthalene guest in aqueous solution, in which the positions of both CB[7] and β-CD are closer to the Ru stopper than in the respective 1:1 inclusion complexes, forming a "tightened nut on bolt" structural mode.

In recent years, the chemistry of interlocked supermolecules[1] has been greatly exploited in developing molecular and supramolecular assemblies such as molecular switches[2] and molecular wires.[3] Cucurbiturils (CB[*n*], where n = 5–10), macrocyclic compounds having methylene-bridged glycoluril units and hydrophobic cavities and polar carbonyl groups surrounding the portals, can form very stable host–guest complexes with positively charged molecules.[4–6] Cyclodextrins (CDs) representing hosts with hydrophobic cavities and hydrophilic outer walls generate inclusion complexes with various apolar groups that can be included partially or completely in their cavities.[7] Recently, a ternary complex between CB[6]–CD–dihexaammonium which mainly depended on the supramolecular positive cooperativity were reported.[8] pH-responsive movement of CBs and CDs has been studied.[9] The proton and electron transfer control of the position of cucurbit[*n*]uril wheels in pseudorotaxanes and bistable[3]rotaxane was investigated.[10] Liu and co-workers have also reported a system with a MV-moiety connected to aliphatic chains of different length, where the position of CB[7] could be affected by α-CD.[11] However, a selective binding of CB[7] and β-CD at a different position on a single molecule which has a naphthol moiety, a redox-active $[Ru(bpy)_3]^{2+}$ stopper and the movement of CB[7] driven by β-CD has not been reported before. In our previous work, the photoinduced interaction between CB[8] and MV^{2+} which is covalently linked to a $Ru(bpy)_3$ *via* a four carbon chain has been studied.[12] Here we report a new 1:1:1 guest–host–host complex formed with the molecular triad **1**, CB[7], and β-CD. The triad **1** contains a 2,6-dihydroxynaphthalene unit (Np) and a viologen unit which are linked to each other by flexible chains with a bulky $Ru(bpy)_3$ unit at the terminal (see structures in Chart 1).

The triad **1** was synthesized by following the procedures described in the literature for the synthesis of similar compounds (see supporting information†),[13] and fully characterized by NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). The inclusion complexes of guest triad **1** (1.7×10^{-3} M, the same concentration was used in all ^{1}H NMR measurements) with host β-CD and CB[7] were readily detected by ^{1}H NMR. To study the inclusion complex formation of the triad **1** with β-CD and CB[7], different equivalents of β-CD and CB[7] were added to the solution of triad **1**. In the presence of 0.5 equiv. CB[7], the ^{1}H NMR signals of **1** show that 50% of **1** interacts with CB[7] and 50% is free in solution (see ^{1}H NMR spectrum in supporting information†). In the presence of 1.0 equiv. CB[7], all of **1** forms the inclusion complex. This suggests that triad **1** can form a 1:1 inclusion complex with CB[7] (see ^{1}H NMR spectrum in Fig. 1, A and B). By carefully studying the ^{1}H NMR spectrum of **1** + CB[7] (1:1), it has been found that CB[7] is bound mainly to the MV^{2+} unit as shown in Scheme 1A.

In the presence of 0.5 equiv. of the host β-CD, the ^{1}H NMR signals of free guest **1** can not be observed. The ^{1}H NMR signals of the bound guest change with the increasing equivalents of β-CD. This reveals that the intermolecular host exchange rate between the free guest and the β-CD-bound guest is fast on the NMR time scale. Upon addition of β-CD, a 1:1 inclusion complex in the presence of different equivalents of β-CD is formed. From the detailed ^{1}H NMR investigation, the position of β-CD in the 1:1 inclusion complex is proposed to be on the naphthalene unit (see ^{1}H NMR spectrum in Fig. 1C), as shown in Scheme 1B.

The respective formation of the inclusion complexes of triad **1** with β-CD or CB[7] has been further confirmed by ESI-MS. When 10 equiv. of β-CD were added to the solution of triad **1** (5×10^{-6} M) in water, the ESI-MS spectrum gave a quadruply-charged

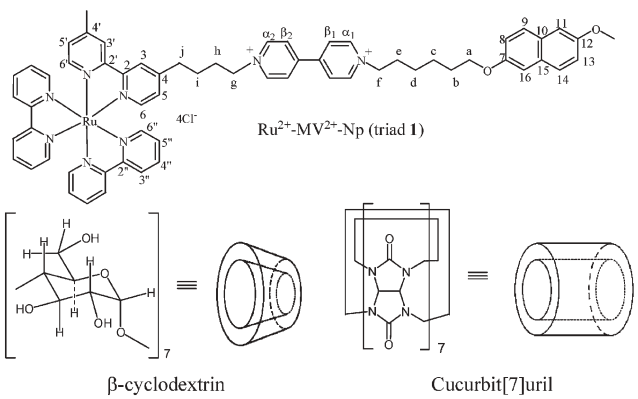

Chart 1 The structures of Ru^{2+}–MV^{2+}–Np (triad **1**), β-CD and CB[7].

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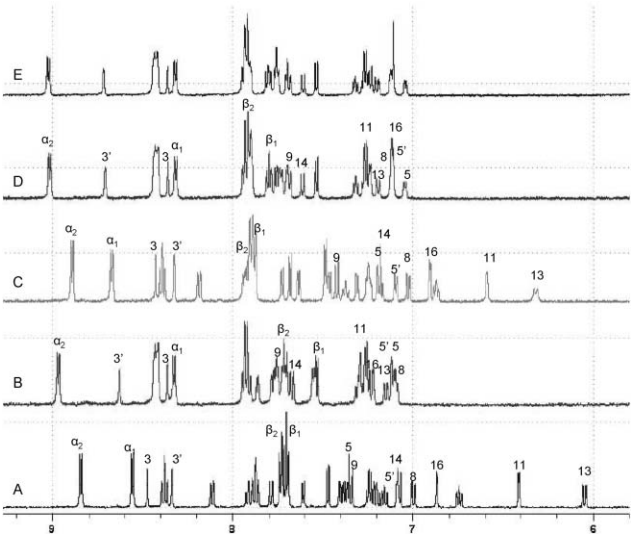


Fig. 1 ^{1}H NMR spectra (500 MHz, D_2O) of triad **1** alone (A), addition of 1 equiv. of CB[7] (B), addition of 1 equiv. of β-CD (C), addition of 1 equiv. of β-CD to the solution of 1:1 inclusion complex of triad **1** and CB[7] (D), addition of 1 equiv. of CB[7] to the solution of 1:1 inclusion complex of triad **1** and β-CD (E).

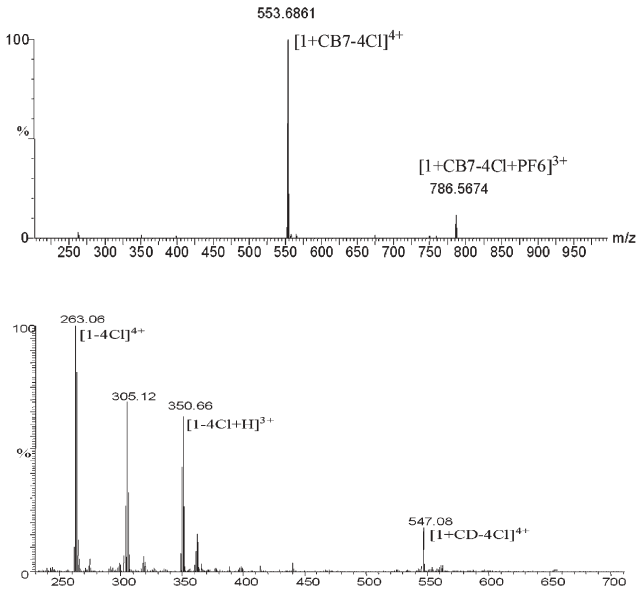
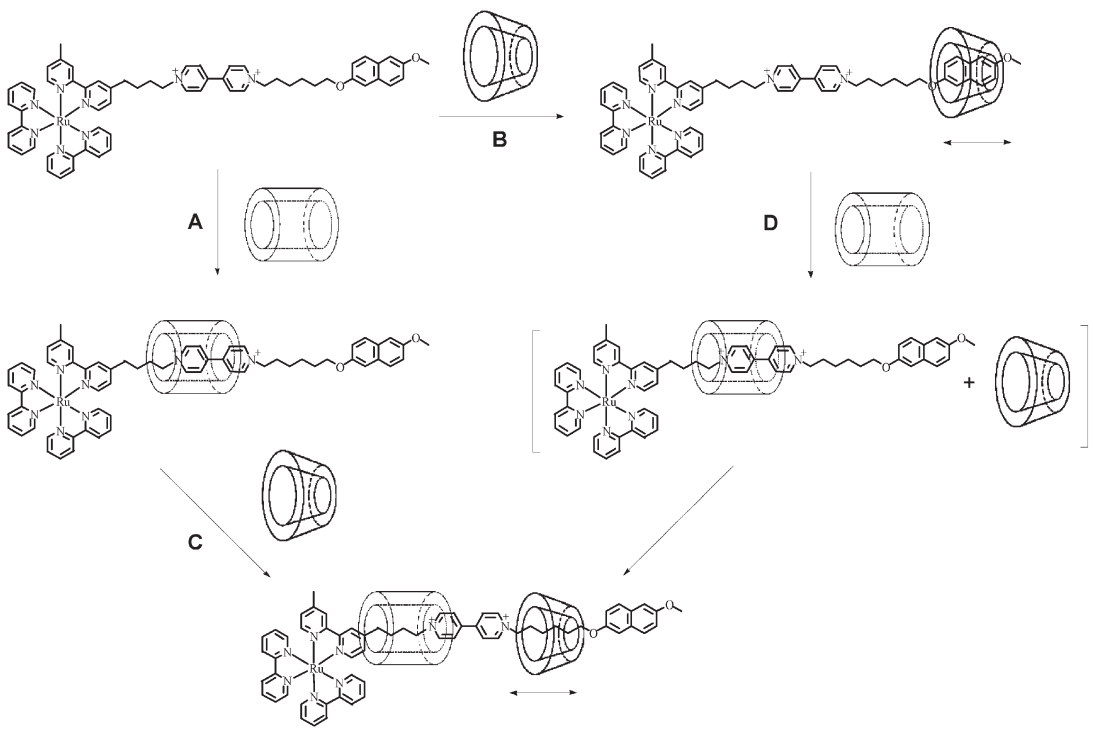


Fig. 2 ESI-MS spectra of 1:1 inclusion complex of triad **1** with CB[7] (top), and with β-CD (bottom).

peak at *m*/*z* 547.0 (calculated for [**1** + β-CD-4Cl$^-$]$^{4+}$, 546.9) (see Fig. 2). When equivalent amounts of triad **1** and CB[7] were dissolved in water, the ESI-MS spectrum gave a quadruply-charged peak at *m*/*z* 553.6861 (calculated for [**1** + CB[7]-4Cl$^-$]$^{4+}$, 553.6869). Both ^{1}H NMR and ESI-MS results provide strong evidence for the formations of the 1:1 host–guest complex of triad **1** with β-CD and CB[7], respectively.

After addition of β-CD into a 1:1 inclusion complex of **1** and CB[7], the CB[7] moved towards the ruthenium moiety which acted as a bulky stopper as shown in Scheme 1C. The β-CD was equilibrating between the bipyridinium and six carbon chain, but mainly located at the six carbon chain. In this case, two of the α-protons of the viologen residue, the protons in the four carbon chain and the half of the 2,2′-bipyridinium ring were inside the cavity of the CB[7]. The other two α-protons and four β-protons of



Scheme 1 Schematic illustration of the interaction of **A**: **1** with CB[7] (1:1 equiv.); **B**: **1** with β-CD (1:1 equiv.); **C**: changes of interaction by addition of equivalent β-CD into a 1:1 inclusion complex of **1** and CB[7]; **D**: formation of the 1:1:1 ternary inclusion complex by addition of equivalent CB[7] into a 1:1 inclusion complex of **1** and β-CD.

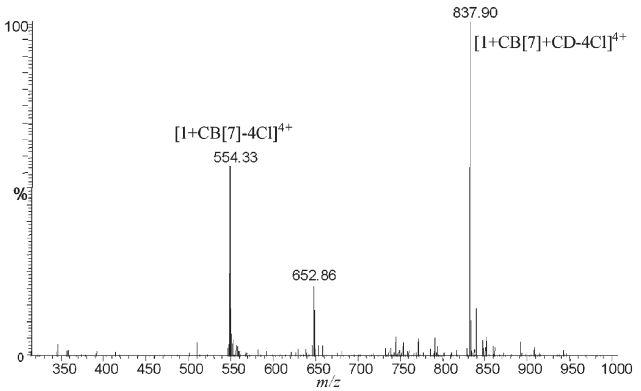


Fig. 3 ESI-MS spectrum of the 1:1:1 ternary inclusion complex of triad **1** with β-CD and CB[7].

the viologen residue were now located outside the cavity of CB[7], while the six carbon chain and viologen residue were dynamically located inside the cavity of β-CD (Fig. 1, D).

Fig. 1E shows the ^{1}H NMR of 1:1:1 inclusion complex formed by addition of 1 equiv. of CB[7] to the 1:1 inclusion complex of triad **1** and β-CD. Fig. 1D and Fig. 1E are almost identical, suggesting that no matter which host (β-CD or CB[7]) is added first, the same 1:1:1 ternary inclusion complex is formed. These observations indicate that CB[7] can displace β-CD from the 1:1 inclusion complex of **1** + β-CD, forming the 1:1 inclusion complex of triad **1** and CB[7] as a transition complex. The β-CD can then moves back to the transition complex and become dynamically located on the viologen residue and six carbon chain with preference of the six carbon chain, shown in Scheme 1D. The binding of CB[7] and the moving of β-CD in these two steps are very fast on the NMR time scale. A possible explanation of the phenomenon that both CB[7] and β-CD are moved closer to the stopper is based on the fact that the β-CD prefers to bind primarily to the naphthol moiety due to the positive charges of the MV^{2+} moiety. When the MV^{2+} is partly included into the cavity of CB[7] the effect of its positive charges has less influence on the β-CD, which then moves primarily to the six-carbon chain, tightening the "nut" on the "bolt". In addition, the positive charges of Ru(II) might also have some influence on this process. This phenomena is in agreement with what Liu and co-workers have observed with the α-CD and CB[7].[11]

Further support for the formation of the 1:1:1 inclusion complex for the triad **1** with β-CD and CB[7] was provided by monitoring the chemical shifts of β-CD in ^{1}H NMR spectra and comparing to the literature.[14] The formation of the ternary **1** + CB[7] + β-CD host–guest 1:1:1 complex (5×10^{-6} M) is also confirmed by ESI-MS, where the major peak at 837.9 can be assigned to [1 + CB[7] + β-CD-4Cl$^-$]$^{4+}$ (Fig. 3).

In conclusion, a 1:1:1 inclusion complex is formed by the binding interactions among β-CD, CB[7] hosts, and Ru(bpy)$_3$-terminated viologen–naphthalene guest. The movement of CB[7] driven by β-CD along the molecular axis can be demonstrated by ^{1}H NMR and ESI-MS. It is interesting to note that in the three-component 1:1:1 inclusion complex, the positions of both CB[7] and β-CD are closer to the Ru stopper than in the respective 1:1 inclusion complexes, forming a "tightened nut on bolt" structural mode. The formation and behavior of the 1:1:1 inclusion complex of the photoactive ruthenium–viologen–naphthalene **1** with β-CD and CB7 provides a base understanding for the future design of more advanced systems with potential applications such as light driven molecular devices and machines. Further studies on the interaction changes triggered by light are in progress.

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