

Light driven formation of a supramolecular system with three CB[8]s locked between redox-active Ru(bpy)₃ complexes†

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Three CB[8]s have been reversibly locked between two Ru(bpy)₃–viologen complexes by light driven electron transfer reactions.

Introduction

The ability to construct and manipulate molecular systems on the atomic level is the key to creating molecular machines and switches. In recent years great effort has been made towards the construction of supramolecular systems such as wires, motors and switches.¹ The cucurbit[n]uril host moiety has been explored due to its excellent binding affinity between its cavity edges and positively charged molecules.² We have recently presented the interaction between the dimethylviologen (DMV)–viologen (MV) system to show movement of a CB[8] host with electrochemical methods,³ as well as a light driven system composed of Ru–MV²⁺–CB[8].⁴ We became interested to know whether the same type of interactions can be performed on more complex systems. The Ru–DMV²⁺–MV²⁺ type systems have previously been investigated as molecular motors with crown ethers,⁵ but no research work has to our knowledge so far been presented with cucurbituril hosts. Here, we report on the first light driven system, composed of molecular triad **1** and CB[8] (Chart 1), where a reversible [5]rotaxane can be formed from two pseudorotaxanes consisting of two ruthenium sensitizers as blockers and three CB[8]s. The triad **1** was synthesized by following the procedures described in the literature for the synthesis of similar compounds and fully characterized by NMR spectroscopy and electrospray ionization mass spectrometry (ESI MS) (see ESI†).

Interaction of triad **1** with CB[8]

The inclusion complex between the guest **1** and host CB[8] was analysed by the ¹H NMR spectral changes (see Fig. 1) and COSY spectra (see ESI†). When up to one equivalent of CB[8] is added to the solution of **1**, the β₁ and β₂ protons of the DMV moiety exhibit an upfield shift from 8.00 and 7.98 to 6.85 and 6.79 ppm respectively, while the α₁, α₂, α₁' and α₂' shift from 8.91, 8.99, 9.00 and 9.09 to 8.74, 8.81, 8.47 and 8.48 ppm (Fig. 1a→c). The β-methyl groups move characteristically upfield from 2.37

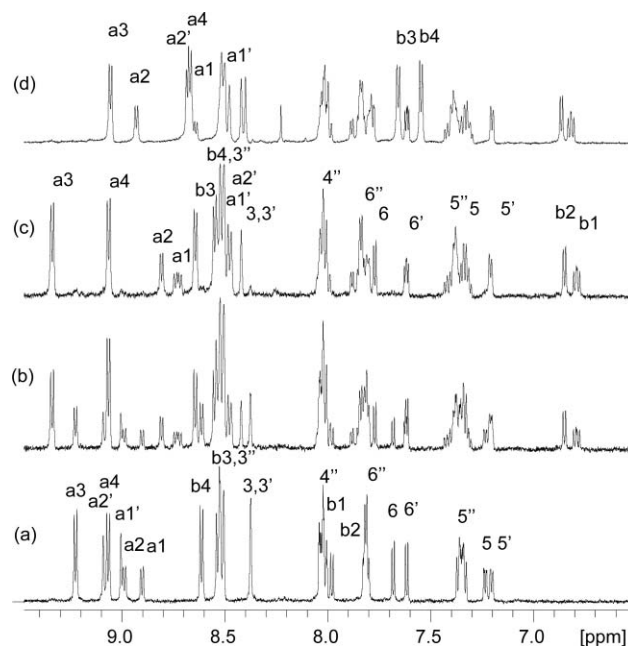


Fig. 1 ¹H NMR spectra (500 MHz, D₂O) of the triad **1** at the concentration of 2.9 mM with CB[8]. (a) **1** only; (b), (c) and (d) show **1** with 0.5, 1.0 and 2.0 equivalents of CB[8] respectively (see ESI for full spectra).

to 1.68 ppm while the protons of the carbon chain a–d and e–g as well as protons 3, 5 and 6 exhibit a downfield shift (see ESI). A downfield shift can also be distinguished on the α₃ and β₃ protons of the MV moiety from 9.22 and 8.51 to 9.34 and 8.64 ppm respectively.

These findings correlate well with previously reported data.³ In the presence of two equivalents of CB[8] the ¹H NMR of **1** (Fig. 1d) showed that the protons at carbon d were moved upfield from 4.88 to 4.85 ppm while no change could be seen at the e, f and g protons of the carbon linker. The protons of the DMV moiety had a split effect where the α₂ and α₂' shifted strongly downfield from 8.81 and 8.48 to 8.93 and 8.69 ppm, while no effect was seen at α₁ and α₁'. A much stronger downfield shift of the protons a, b, c of the MV–DMV linker was seen, as well as strong upfield shifts of the α₃, α₄, β₃ and β₄ protons of the MV moiety from 9.34, 9.06, 8.64 and 8.55 ppm to 9.05, 8.67, 7.65 and 7.54 ppm. These data indicate that the CB host moved slightly away from the DMV moiety and

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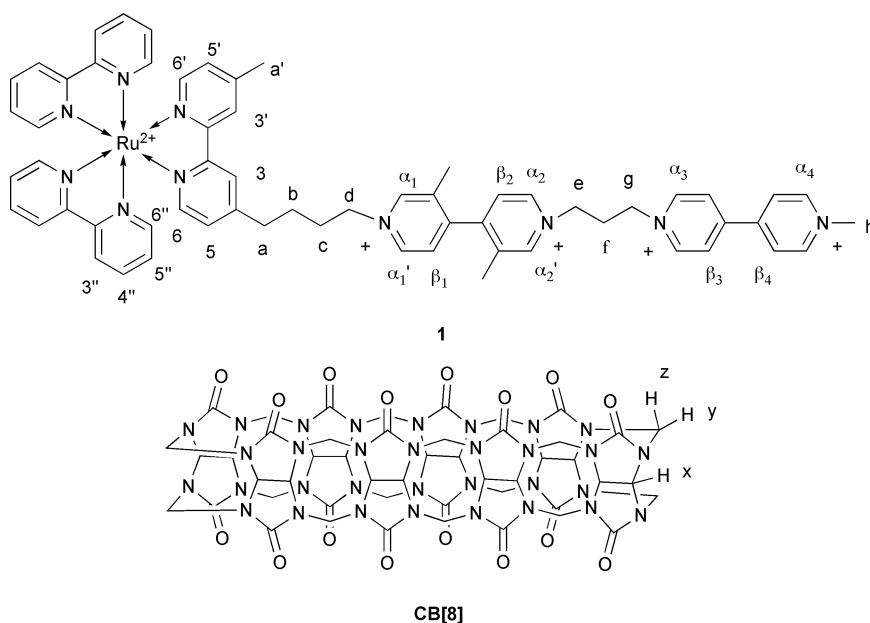
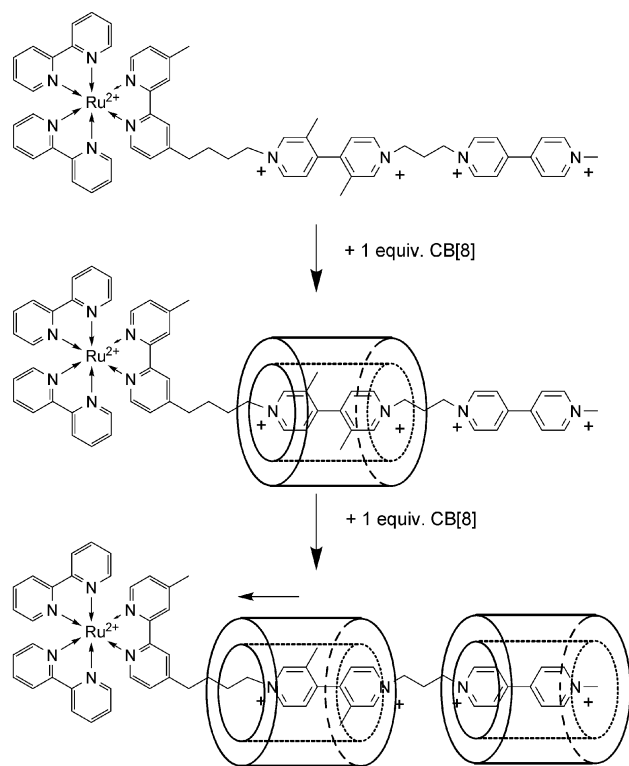


Chart 1 Chemical structures of triad **1** and CB[8].

toward the Ru moiety as depicted in Scheme 1, most likely due to steric effects between the two CB[8]s. This result fits well with reported data where the CB host shows an increased ability to move away from the center of an alkylated viologen compared to methylviologen.⁶



Scheme 1 Schematic presentation of the interactions between **1** and CB[8] based on ¹H NMR spectra (500 MHz, D₂O). The arrows indicate the slight movement of the CB[8].

High resolution mass spectrometry (HRMS)

The interactions between CB[8] and **1** have further been analyzed by HRMS where the formation of 1 : 1 and 1 : 2 inclusion complexes were confirmed. With equivalent amounts of **1** and CB[8] in the solution, the ESMS gave a sextuply charged peak at m/z 394.1364 (calculated for [**1** + CB[8] – 6Cl]⁶⁺, 394.1355), which corresponds to the inclusion of the **1** into the cavity of a CB[8]. When two equivalents of CB[8] were added to a solution of **1**, the ESMS gave a sextuply charged peak at m/z 616.7490 (calculated for [**1** + 2 CB[8] – 6Cl]⁶⁺, 615.5342), which corresponds to the inclusion of the **1** into the cavities of two CB[8]s. Both ¹H NMR and HRMS results thus provide strong evidence for the formation of the 1 : 1 and 1 : 2 host–guest complexes between **1** and CB[8].

Electrochemistry

Electrochemical study is used as a strong indicator for MV^{•+} dimer formation.² The cyclic voltammogram of **1** in acetonitrile shows typical oxidation peaks of Ru(II) and reduction peaks of DMV and MV (Fig. S5†). Differential pulse voltammetry (DPV) measurements in water performed on **1** showed four reduction peaks which are assigned to MV²⁺ → MV^{•+}, DMV²⁺ → DMV^{•+}, MV^{•+} → MV⁰, DMV^{•+} → DMV⁰ (see Fig. 2).

The process with zero and two equivalents of CB[8] was investigated in aqueous solvent and scanned at 0.05 V s^{−1}. With two equivalents CB[8] added to the solution of **1**, the first reduction peak, corresponding to the reduction of MV²⁺ → MV^{•+}, shifts to a more positive value at −0.40 V vs. Ag/AgCl. The second reduction peak of the MV moiety shifted to a more negative value at ca. −1.20 V vs. Ag/AgCl (see Fig. 2). These types of shifts are in accordance with how the reduction potentials of methylviologen shift when forming the radical dimer inside a CB[8] cavity.²

It is worth noting that the positive shift of the reduction potential is smaller compared to a similar reaction with free

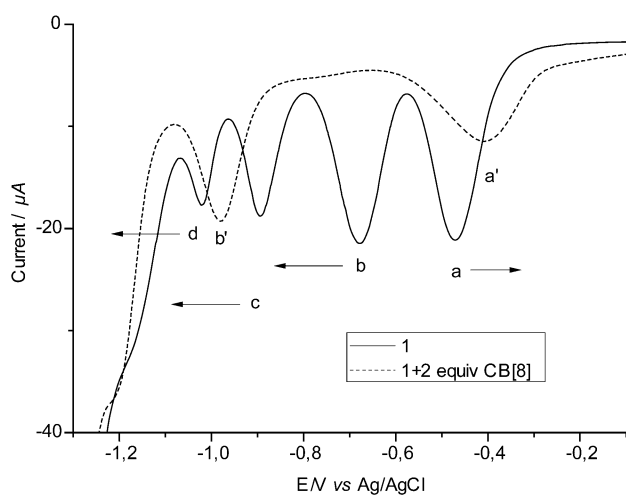


Fig. 2 Differential pulse voltammograms of **1** (solid line) and **1** with two equivalents CB[8] (dotted-dashed) in pH 7 buffer solution at 1 mM, scan rate 0.05 V s⁻¹. The peaks are assigned as: (a) MV²⁺ → MV^{•+}; (b) DMV²⁺ → DMV^{•+}; (c) MV^{•+} → MV⁰ and (d) DMV^{•+} → DMV⁰. With two equivalents CB[8]: (a') MV²⁺ → MV^{•+}; (b') DMV²⁺ → DMV^{•+}; (c') MV^{•+} → MV⁰.

MV²⁺⊂[CB[8]].^{3-4,6} The second reduction peak, corresponding to the reduction of DMV²⁺ → DMV^{•+}, has a remarkable shift of -250 mV compared to its potential in the free triad. At this time the shift is assumed to be due to the synergism of two interactions: (1) the DMV²⁺ moiety inside the cavity CB[8] and (2) the proximity to a formed MV^{•+} dimer. The second reduction peak of the DMV moiety, DMV^{•+} → DMV⁰, is no longer detectable within the solvent window.

Photochemistry

To confirm the formation of the MV^{•+} radical dimer inside CB[8], photochemistry was performed on **1** in the presence of triethanolamine (TEOA) as sacrificial electron donor. For the aqueous solution of **1** (4×10^{-5} M) and TEOA (4×10^{-2} M), two absorption peaks at 398 and 600 nm could be observed after 50 min light irradiation. These peaks are known and attributed to the formation of the free Ru²⁺-DMV²⁺-MV^{•+} radical (see Fig. 3b). With the addition of two equivalents of CB[8] to the solution of **1** and TEOA, no peaks for the free Ru²⁺-DMV²⁺-MV^{•+} radical could be observed after irradiation (Fig. 3d). In this case, however, a very strong peak at 370 nm and a broad peak around 540 nm as well as a broad peak at 870 nm were observed. The blue-shifted peaks are attributed to the formation of a MV^{•+} dimer. The two MV moieties are now “locked” inside the cavity of one CB[8], forming Ru²⁺-DMV²⁺(CB[8])-(MV^{•+})₂(CB[8])-DMV²⁺(CB[8])-Ru²⁺ (see Scheme 2). This is in agreement with previously reported data.⁴ Molecular oxygen can quench the radical dimer leading to the original form of Ru²⁺-DMV²⁺(CB[8])-MV²⁺(CB[8]).

The whole process can be repeated several times without significant photo degradation.

To establish that no losses of cucurbituril occurred when the rotaxane was formed, *i.e.* giving [3] or [4]rotaxanes, ¹H NMR measurements were performed. First a reference test was performed with compound **1**. After addition of TEOA as a sacrificial donor and degassing with nitrogen (Fig. 4a) the NMR tube was irradiated as previously described. From the ¹H NMR

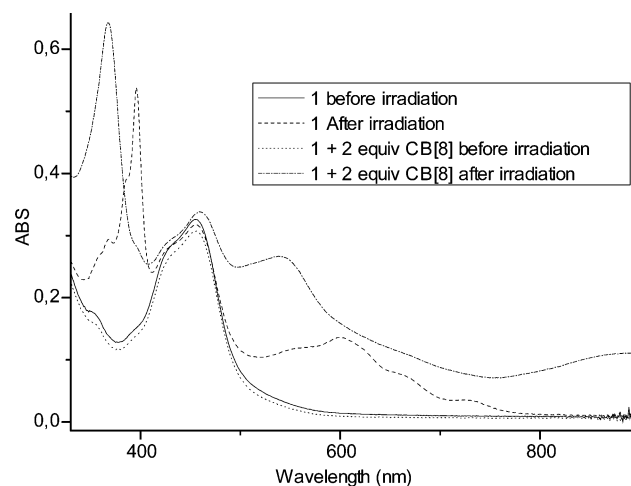


Fig. 3 UV/Vis spectra of **1** (4×10^{-5}) in water solution, with TEOA as sacrificial electron donor: (a) before irradiation (solid); (b) after 50 min light irradiation (dashed); (c) with 2 equiv CB[8] before irradiation (dotted); (d) after 50 min light irradiation with 2 equiv CB[8] (dotted-dashed).

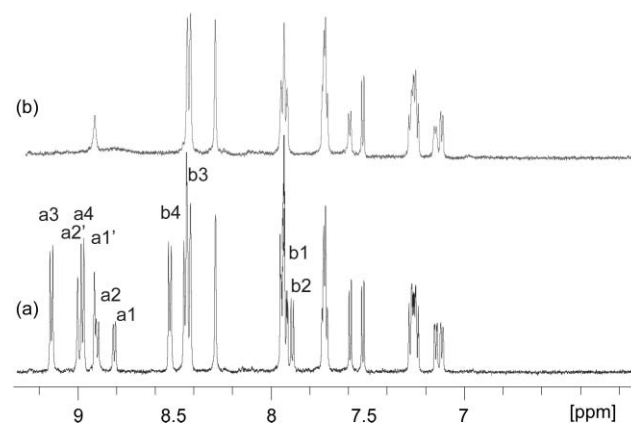
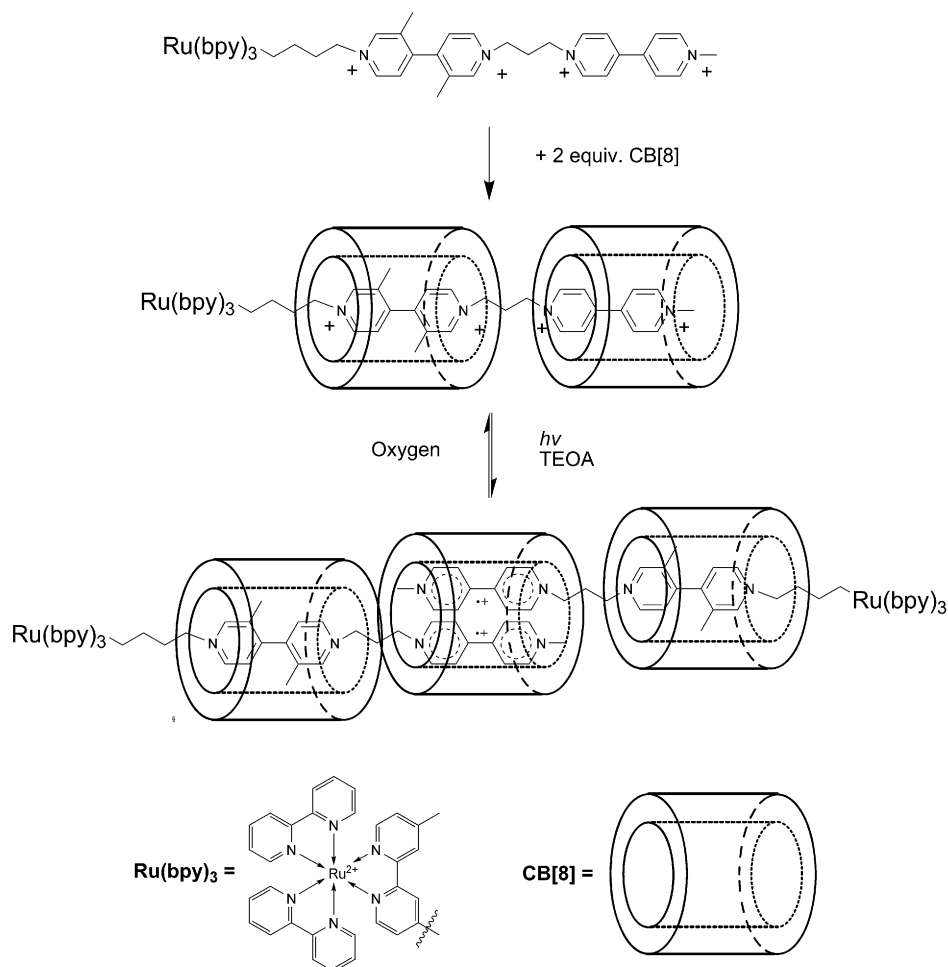


Fig. 4 ¹H NMR spectra (500 MHz, D₂O) of triad **1** and TEOA before irradiation (a) and after 5 min irradiation (b).

measurements, the reduction of both the DMV and the MV moiety can be seen from the disappearance of the α and β peaks corresponding to either viologen moiety from the normal NMR range of these compounds, indicating radical formation (Fig. 4b). The NMR peaks corresponding to the carbon linker and the *N*-methyl group also disappeared while the peaks of the ruthenium moiety were clearly visible, see Fig. S3 for full spectra.^{6†} When two equivalents of the host CB[8] were added (Fig. 5a) and irradiated with light (Fig. 5b) no NMR shift could be observed on the peaks corresponding to the DMV moieties, clearly indicating that the DMV moieties are still inside and stabilized by a CB[8] host.

The peaks corresponding to the α and β protons of the MV moiety become broadened and slightly shifted in position. This is typical behavior of the MV moiety after forming a stabilized radical dimer inside a CB[8] host.⁶

The NMR spectrum clearly shows that both viologen moieties are inside CB[8] hosts when the MV^{•+} radical dimer is formed. This can, in combination with the electrochemical shift of the MV moiety, only be due to the formation of a [5]rotaxane with the DMV²⁺ moieties as well as the MV^{•+} radical dimer inside the cavity of CB[8] host, see Fig. S4 for the entire spectrum.[†]



Scheme 2 Schematic representation of the light driven interaction between **1** and CB[8], forming the [5]rotaxane.

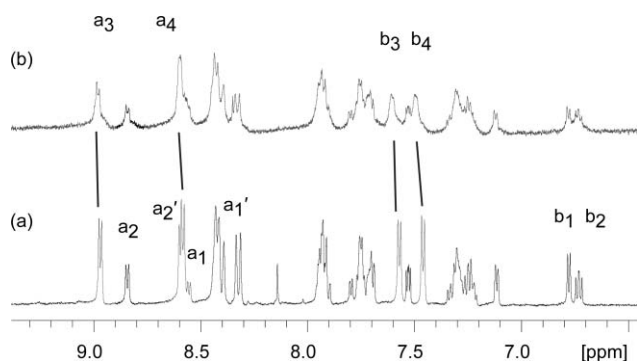


Fig. 5 ^1H NMR spectra (500 MHz, D_2O) of triad **1** with two equiv CB[8] and TEOA before irradiation (a) and after 10 min irradiation (b).

Conclusions

The interactions of CB[8] with the molecular triad **1**, where the two viologens are covalently linked *via* different carbon chains to a ruthenium moiety acting both as a stopper and a photosensitizer, has been studied by ^1H NMR, ESI-MS, electrochemistry and photochemistry. Our results demonstrate that 1 equiv CB[8] can selectively bind to the DMV^{2+} moiety on triad **1**. A second CB[8] can be positioned on the MV moiety. By photochemical

reduction *via* intramolecular electron transfer, the formation of the $\text{MV}^{\bullet+}$ radical dimer inside a CB[8] cavity can be achieved, forming a [5]rotaxane. Molecular oxygen can quench the $\text{MV}^{\bullet+}$ radical and the original structure can be reformed. This result shows that cucurbituril can be used and easily controlled by light even in more complex systems.

Experimental procedures

General

NMR spectra were obtained on a Bruker AVANCE 500 MHz spectrometer, using TMS as internal standard. High Resolution Mass Spectrometry (HRMS) was conducted on a Q-ToF mass spectrometer (Micromass, Manchester, England) equipped with z-spray ionisation source.

Electrochemistry

Cyclic voltammetry was carried out with a three-compartment cell connected to an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie). The working electrode was a freshly polished glassy carbon disk (diameter 3 mm), the counter electrode was a platinum wire. Potentials were measured *vs.* a non-aqueous Ag/Ag^+ reference electrode (CH instruments, 10 mM AgNO_3 in

acetonitrile) and can be converted to SCE by adding 300 mV to the measured value. Solutions were prepared from dry acetonitrile containing *ca.* 0.5 or 1 mM of the analyte, as defined in the text and 0.1 M tetrabutylammonium hexafluorophosphate (Fluka, electrochemical grade, dried at 373 K for 48 h) as supporting electrolyte. Before all measurements, oxygen was removed by bubbling the solutions for 20 min with solvent saturated argon and the samples were kept under argon atmosphere during the measurements. In water solution the counter ions used were Cl⁻ and the reference electrode was Ag/AgCl in KCl. The supporting electrolyte was a pH 7 phosphate buffer solution and can be converted to SCE by subtracting 45 mV to the measured value.

Photochemistry

The measurements were performed using a UV/Vis/NIR spectrometer from Perkin-Elmer. The irradiation to the related systems was achieved with light from a HITACHI Multimedia Mobile LCD Projector.

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