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Light driven molecular lock comprises a Ru(bpy)₂(hpip) complex and cucurbit[8]uril†

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Here, complex **1** ([Ru(bpy)₂(hpip)]²⁺–MV²⁺) and **CB[8]** can form a stable 1 : 1 inclusion complex in aqueous solution, resembling a U-shaped conformation. Upon light irradiation, two complex **1** were reversibly locked through the formation of a MV˙⁺ radical dimer that is stabilized in the cavity of **CB[8]** with Ru complexes as blockers, in which complex **1** was transformed from a U-shaped conformation to a interlocked complex. This study provided a feasible strategy for the fabrication of a photo-driven supramolecular machine resembling a "lock".

Introduction

In recent years, great efforts have been made by chemists to construct and manipulate various interlocked supramolecular systems on the atomic level, such as molecular switches and molecular wires.[1] As a relatively new class of host molecules, cucurbit[n]urils (CB[n], n = 5–8, 10), have attracted great attention due to their special structures and application in interactions with guest molecules.[2] **CB[8]**, one of the members of the cucurbituril host family, with 8 glycoluril motifs linked by methylene bridges forming two hydrophilic carbonylated portals and a hydrophobic cavity, has been shown to accommodate two identical[3] or different[4] aromatic guests in its cavity. For example, **CB[8]** can bind both methyl viologen (N,N-dimethyl-4,4-bipyridinium, MV²⁺) and methyl viologen radical (MV˙⁺) or radical dimer (MV˙⁺)₂ inside its cavity.[5] It is also noted that MV²⁺, a common electron acceptor, is often utilized together with electron donors such as ruthenium poly-bipyridyl complexes to construct donor–photosensitizer–acceptor (D–P–A) systems.[6] And these host–guest systems have been used for the assembly of molecular loop-lock,[7] molecular necklaces,[8] and molecular machines. Kim and co-workers used [Ru(bpy)₃]²⁺ as photosensitizer and MV²⁺ as electron acceptor to study light induced intermolecular electron-transfer (ET) and observed the formation of a MV˙⁺ radical dimer loop inside the CB[8] cavity.[9] Sun and co-workers reported the formation of 1 : 1 inclusion between Ru(bpy)₃–MV²⁺ and **CB[8]**, and observed a long

lived charge-separated state Ru(bpy)₃–MV˙⁺–**CB[8]** upon light irradiation.[10] They also reported that Ru(bpy)₃–MV²⁺ and **CB[8]** could be used to create a light driven molecular "lock" through the formation of a stable dimer (MV˙⁺)₂ inside one **CB[8]** cavity, and this "lock" can be "unlocked" by molecular oxygen.[11] We have presented that Ru²⁺–MV²⁺-Np guest take a U-shaped conformation into the cavity of **CB[8]** and formed a stable 1 : 1 inclusion complex with **CB[8]**. Upon light irradiation, a MV˙⁺ radical cation stabilized in the cavity of **CB[8]** accompanied by the naphthalene residue has been observed.[12] However, to the best of our knowledge, no work has been reported on the interaction between **CB[8]** and MV²⁺ together with an aromatic donor moiety that is coupled to a redox-active [Ru(bpy)₂(hpip)]²⁺(hpip = 2-(4-hydroxyphenyl)-imidazo[4,5-f][1,10]phenanthroline, bpy = 2,2′-bipyridine) complex. Here, we report the formation of a 1 : 1 inclusion complex of **CB[8]** with complex **1**, consisting of a [Ru(bpy)₂(hpip)]²⁺ complex covalently linked to a MV²⁺ *via* a six carbon chain, in which the viologen residue is back-folded and inserted together with the phenol residue into the cavity of **CB[8]**. That is to say, complex **1** takes a U-shaped conformation inside the cavity of **CB[8]** with Ru complex as a blockers. Upon light irradiation, U-shaped conformation was broken, and a molecular "lock" was formed, in which a stable dimer of the (MV˙⁺)₂ inside one **CB[8]** cavity.

Results and discussion

Interactions of complex 1 and CB[8]

The structures of complex **1** used in this study are shown in Scheme 1. Complex **1** was synthesized and characterized by ¹H NMR, ¹³C NMR, and mass spectra analysis (see ESI†). The binding interaction between complex **1** and **CB[8]** in the aqueous solution is determined by ¹H NMR spectroscopy (see ESI†). In the presence of 0.5 equiv. of **CB[8]**, the proton signals of both bound and free guests are clearly evidenced. Upon addtion of 1.0 equiv. of **CB[8]** to the solution of complex **1**, the

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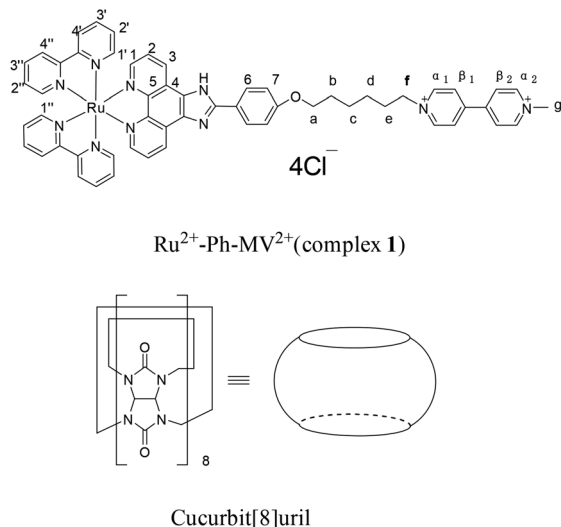
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Scheme 1 Structures of Ru^{2+}-Ph−MV^{2+} (complex **1**) and **CB[8]**.

Scheme 2 Schematic illustration of the interaction of **1** with **CB[8]**.

four α-protons of the viologen moiety in complex **1** shifted upfield from 9.02 to 8.78 (two protons) and 8.84 to 8.20 (two protons) (Fig. 1). The two β-protons shifted upfield from 8.40 to 7.14, and the other two β-protons shifted upfield from 8.36 to 6.95. In the same time, the four phenyl proton signals underwent upfield shifts. Whereas the protons of part of the six-carbon chain (b–f positions) underwent downfield shifts. This can be interpreted that the viologen moiety of complex **1** folds back to form an U-shaped conformation with phenyl moiety inside the hydrophobic cavity of **CB[8]** as shown in Scheme 2. This binding modes is similar with the system reported by Sun's group.[12] ^{1}H NMR titration experiments supported the formation of a 1 : 1 host–guest complex **1** + **CB[8]**. It is also worth to mention that for the host, the peak splitting of the **CB[8]** protons into two sets indicates that the two portals of the **CB[8]** cavity are no longer in identical environment after including the complex **1**.[13]

Furthermore, we performed DOSY-NMR spectra of complex **1** and **1** + **CB[8]**, showing that diffusion coefficient of **1** + **CB[8]** (1.55×10^{-10} m^2 s^{-1}) was slightly smaller than that of **1** (1.70×10^{-10} m^2 s^{-1}), as shown in Fig. S13 and S14 and Table S1.†

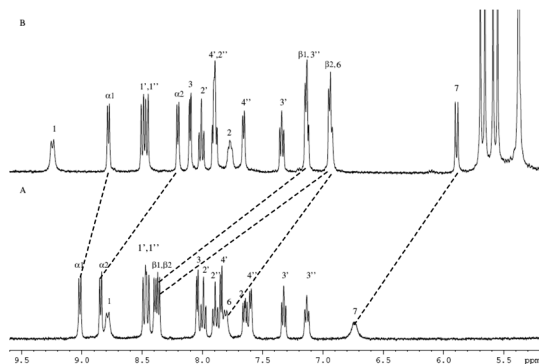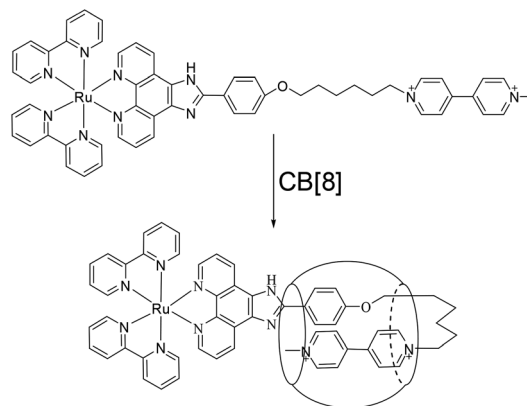The formation of the stable 1 : 1 inclusion complex between complex **1** and **CB[8]** was further confirmed by ESI-MS. When equivalent amounts of complex **1** and **CB[8]** were dissolved in water, the ESI-MS spectrum in positive mode gave a quadruply charged peak at m/z 577.1781 (calculated for [**1** + **CB[8]**]−4Cl$^-$]$^{4+}$, 577.1779. see ESI†). No 2 : 1 or 2 : 2 inclusion complexes were observed. Both NMR and ESI-MS results provide strong evidence for the formation of a stable 1 : 1 host–guest inclusion complex between complex **1** and **CB[8]**. Fig. 2 displays the absorption spectra of complex **1** taken in the course of titration with **CB[8]**. On addition of **CB[8]** to the solution of complex **1**, the intensity of the absorption maxima at 284 nm decreased, accompanied by a slightly red shift to 286 nm. The other strong absorption band around 460 nm can be attributed to the metal-to-ligand charge-transfer (MLCT) transition $\pi^* \leftarrow d\pi$(Ru) of the Ru(bpy)$_2$(hpip) moiety.

The stoichiometry of the binding of complex **1** with **CB[8]** is further verified by titration curve. After addition of increasing equivalents of **CB[8]** into an aqueous solution of complex **1**, the corresponding absorption spectra changes were recorded. Fig. S15† shows a plot of the absorbance as a function of total **CB[8]** concentration. The data can be easily fitted to a 1 : 1 binding model with a binding constant of 4.15×10^4 M^{-1}.
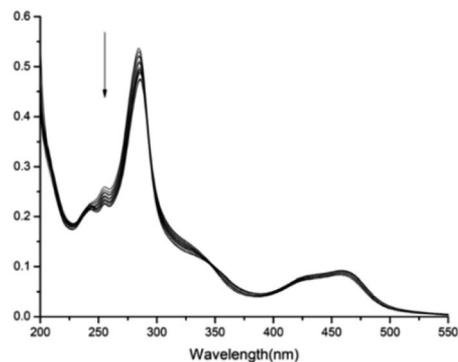

Fig. 1 ^{1}H NMR spectra (400 MHz, D$_2$O) of **1** in the absence (A) and in the presence (B) of 1 equiv. of **CB[8]**.

Fig. 2 Absorption spectra of complex **1** (6 μM) in aqueous solution in the presence of different amounts of **CB[8]** (0−1.6 equiv.).
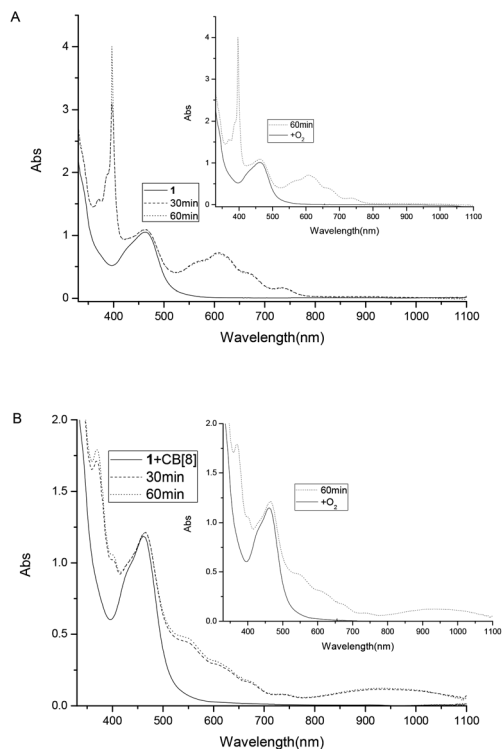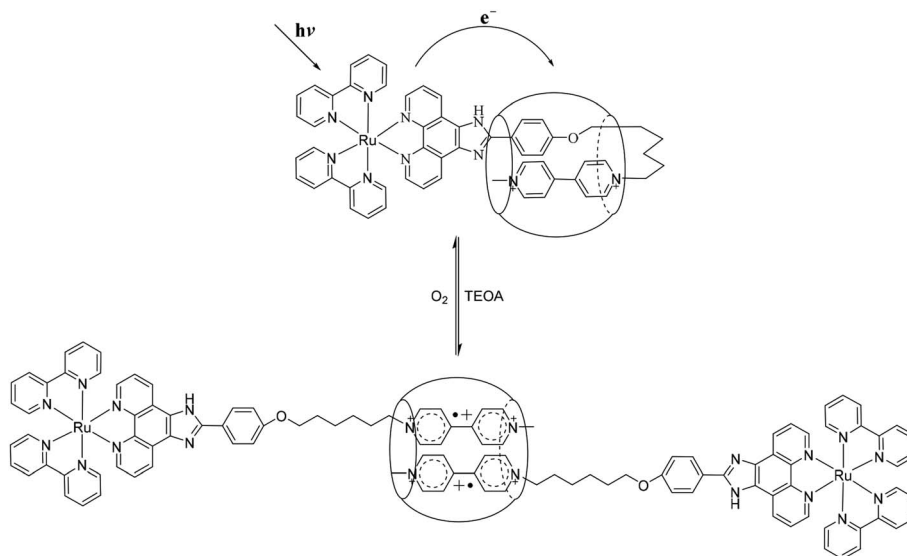
Fig. 3 Absorption spectra of complex **1** (8.0×10^{-5} M) and TEOA (0.1 M) in the absence of **CB[8]** (A) and in the presence (B) of 1 equiv. of **CB [8]**.

Photochemistry

To study the possible photoinduced electron transfer processes in a system containing complex **1**, excess sacrificial electron donor, triethanolamine (TEOA), was added to a cuvette containing complex **1**, and UV-vis absorption was taken as shown in Fig. 3. For complex **1** alone, two absorption peaks around 397 and 607 nm can be easily monitored (Fig. 3A) after 30 min of irradiation, which was due to the formation of redox induced radical Ru^{2+}-Ph–$MV^{\bullet+}$. The color of the solution changed from yellow to dark green and the peak intensity increased as the irradiation time prolonged (Fig. 3A). With the addition of one equivalent of **CB[8]** to the solution of complex **1** and TEOA, no peaks for the free Ru^{2+}-Ph–$MV^{\bullet+}$ radical could be observed after irradiation (Fig. 3B). In this case, however, a very strong peak at 370 nm and a broad peak around 550 nm as well as a broad peak at 950 nm were observed and the color changed from yellow to brown. These three peaks are due to the formation of Ru^{2+}-Ph–$MV^{\bullet+}$ dimer. By comparison of the two systems, we found that two MV moieties are "locked" inside the cavity of one **CB[8]**, forming Ru^{2+}-Ph–$(MV^{\bullet+})_2$(**CB[8]**)–Ph-Ru^{2+} in the presence of **CB [8]** (Scheme 3). This photoinduced ET processes is in agreement with previously reported data.[14]

To establish that the [3]rotaxane was formed, UV-vis absorption of complex **1** with 0.25 or 0.5 equivalent of **CB[8]** were performed as taken in Fig. 4. In the presence of 0.25 equivalent of **CB[8]** in the complex **1**, the characteristic absorption for both the viologen radical (two absorption peaks around 397 and 607 nm) and the radical dimer (three absorption peaks around 370, 550 and 950 nm) can be observed concomitantly after irradiation. However, in the case of 1 : 0.5 mixture of complex **1** and **CB[8]**, only the characteristic absorption for the radical dimer was monitored after irradiation, no characteristic absorption for the viologen radical alone was observed. This indicates that all the viologen radical formed radical dimer inside the cavity of **CB[8]**. In other words, two MV moieties of complex **1** are "locked" inside the cavity of one **CB[8]**, forming a [3]rotaxanes. This experiments supported the formation of Ru^{2+}-Ph–$(MV^{\bullet+})_2$(**CB[8]**)-Ph–Ru^{2+} as shown in Scheme 3. When the light is turned off and oxygen goes into the cuvette, the initial absorption spectrum can be restored. The whole process can be repeated several times without significant photo degradation.

Scheme 3 Schematic representation of the light driven interaction between **1** and **CB[8]**.
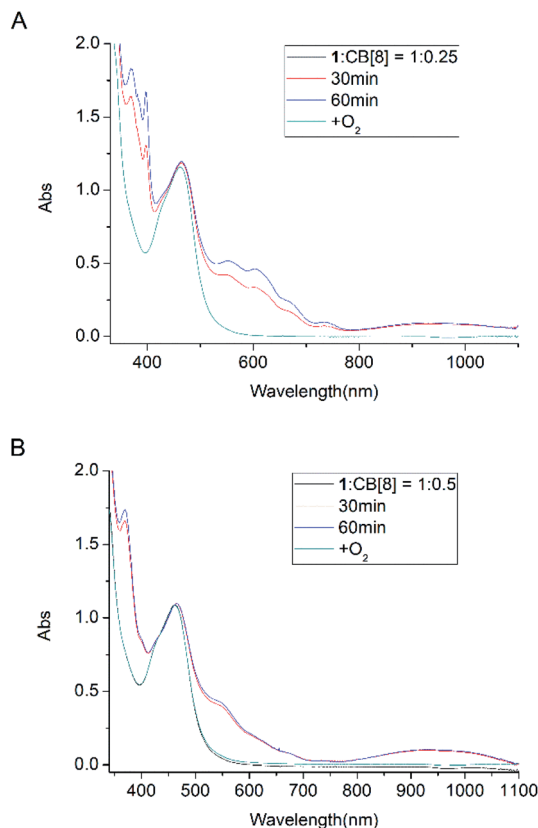
Fig. 4 Absorption spectra of complex **1** (8.0×10^{-5} M) and TEOA (0.1 M) in the presence of 0.25 equiv. (A) and 0.5 equiv. (B) of **CB[8]**: before and after light irradiation under Ar atmosphere.

The light-induced formation of the stable Ru^{2+}-Ph–MV^{+} dimer inside the cavity of one **CB[8]** can be further confirmed by NMR measurements. Upon 5 equivalents TEOA was added to a NMR tube containing complex **1**, the reaction process was monitored by ^{1}H NMR. When the NMR tube was degassed with argon and light-irradiated for 3 h, the color of the solution changed from orange to brown and the ^{1}H NMR spectrum was taken again. As shown in Fig. 5, the peaks for the α1-and β-
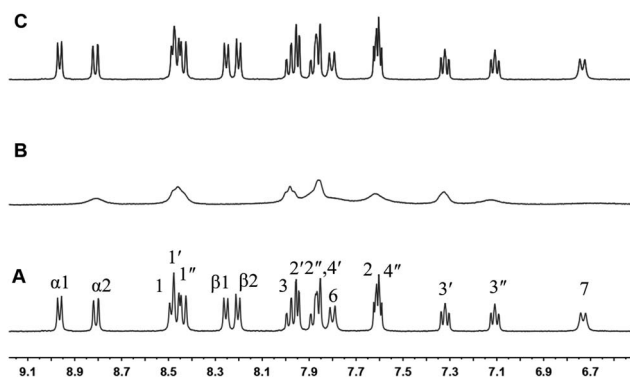
protons of the MV moiety shifted outside the normal NMR window due to its radical character. The peaks for the protons of the phenanthroline ligand, bipyridine ligand and phenol ring were also affected, becoming broad, which are due to the paramagnetic effect of the MV$^{•+}$ radical. When the light irradiation was stopped and the air (oxygen) was allowed go into the tube, the color of the solution changed back to orange and the ^{1}H NMR spectrum was restored as shown in Fig. 5. This experiment strongly support that the Ru^{2+}–MV$^{•+}$ radical was formed in complex **1**.

To investigate the formation of MV$^{•+}$ dimer in the presence of **CB[8]**, TEOA was added to the 1 : 1 inclusion complex of **1** + **CB[8]**, and the effect was followed by ^{1}H NMR. On addition of 5 equiv. of TEOA to a D$_2$O solution of complex **1** (1.0 equiv.) and **CB[8]** (1.0 equiv.), the NMR spectrum was taken again as shown in Fig. 6A. When the NMR tube was degassed with argon, and irradiated for 3 h by the light, the color of the solution changed to dark brown, and the ^{1}H NMR was taken again as shown in Fig. 6B. The peaks corresponding to the α-, β-protons of the MV moiety become broad. This is typical behavior of the MV moiety after forming a stabilized radical dimer inside a **CB[8]** host. Moreover, the NMR peaks corresponding to the phenanthroline ligand, carbon linker and the N-methyl group also broadened while part of the peaks of the ruthenium moiety were clearly visible due to a paramagnetic effect. When the septum was removed from the NMR tube and the air (oxygen) went in, the color of the solution changed back from the dark brown to the original orange, and the ^{1}H NMR spectrum was restored as shown in Fig. 6C. These results suggest the formation of Ru^{2+}–MV$^+$ dimer inside the cavity of one **CB[8]** as illustrated in Scheme 3 and supported by literature data on the behavior of MV^{2+} and related compounds.[14]

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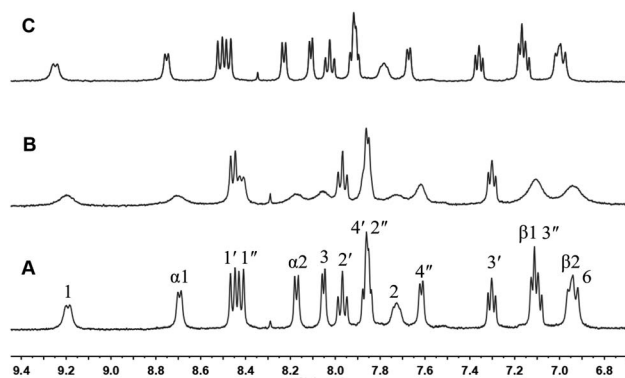

Fig. 5 ^{1}H NMR (400 MHz, D$_2$O) of complex **1** with TEOA (1 : 5) (A), after 3 h of light irradiation (B), and after stopping light irradiation and exposing to air (O$_2$) (C).

Fig. 6 ^{1}H NMR (400 MHz, D$_2$O) of **1** + **CB[8]** with TEOA (1 : 5) (A), after 3 h of light irradiation (B), and after stopping light irradiation and exposing to air (O$_2$) (C).

irradiated for 3 h by the light, the color of the solution changed to dark brown, and the ^{1}H NMR was taken again as shown in Fig. 6B. The peaks corresponding to the α-, β-protons of the MV moiety become broad. This is typical behavior of the MV moiety after forming a stabilized radical dimer inside a **CB[8]** host. Moreover, the NMR peaks corresponding to the phenanthroline ligand, carbon linker and the *N*-methyl group also broadened while part of the peaks of the ruthenium moiety were clearly visible due to a paramagnetic effect. When the septum was removed from the NMR tube and the air (oxygen) went in, the color of the solution changed back from the dark brown to the original orange, and the ^{1}H NMR spectrum was restored as shown in Fig. 6C. These results suggest the formation of Ru^{2+}–MV^+ dimer inside the cavity of one **CB[8]** as illustrated in Scheme 3 and supported by literature data on the behavior of MV^{2+} and related compounds.[14]

Electrochemistry

The redox properties of the complex **1** before and after the inclusion of **CB[8]** were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in 0.1 M phosphate buffer (pH 7.0) water solution (Fig. 7). According to the literature, for the complex **1** alone, the first wave at −0.53 V (for easy comparison, all the half-wave potentials in the context were

determined from DPV peak potentials) corresponded to the reduction of MV^{2+} moiety to the cation-radical $MV^{•+}$, whereas the second wave at −0.84 V was attributed to the reduction of $MV^{•+}$ to MV^0. By addition of 1 equiv. of **CB[8]** to the solution of complex **1**, the peak potential related to the redox couple $MV^{2+}/MV^{•+}$, $MV^{•+}/MV^0$ were shifted to −0.54 and −1.20 V, respectively. The reason why MV^{2+} is harder to reduce is very likely that the formation of radical dimer within the cavity of **CB[8]**. This characteristic pattern for the formation of radical dimer is in good agreement with the literature precedent. In other words, the results further demonstrate the formation of Ru^{2+}-Ph–$(MV^{•+})_2$(**CB[8]**)–Ph-Ru^{2+} dimer in the system.

Conclusions

In conclusion, complex **1** can form a stable 1 : 1 inclusion complex with **CB[8]** in aqueous solution through taking a U-shaped conformation, in which the viologen residue is back-folded and inserted together with the phenoxyl residue into the cavity of **CB[8]**. The formation of this stable 1 : 1 inclusion complex has been demonstrated by ^{1}H NMR and ESI-MS. Upon light irradiation, two Ru(bpy)$_2$(hpip) complexe were reversibly locked through the formation of a $MV^{•+}$ radical dimer stabilized in the cavity of **CB[8]** with Ru(bpy)$_2$(hpip) as blockers, in which complex **1** from a U-shaped conformation transform to a inter-locked complex. This process could be used to create a novel light driven molecular "lock", which can be "unlock" by molecular oxygen. The light driven molecular "lock" and "unlock" processes can be repeated several times with good reversibility. This system may provide some new thinking for further design and synthesis of potential light-driven molecular devices.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 (*a*) N. Yui and T. Ooya, *Chem.–Eur. J.*, 2006, **12**, 6730–6737; (*b*) B. L. Feringa, *Acc. Chem. Res.*, 2001, **34**, 504–513; (*c*) M. J. Frampton and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2007, **46**, 1028–1064.

2 (*a*) J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi and K. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 540–541; (*b*) J. W. Lee, S. Samal, N. Selvapalam, H. J. Kim and K. Kim, *Acc. Chem. Res.*, 2003, **36**, 621–630; (*c*) J. Lagona, P. Mukhopadhyay, S. Chakrabarti and L. Isaacs, *Angew. Chem., Int. Ed.*, 2005, **44**, 4844–4870; (*d*) G. Parvari, O. Reany and E. Keinan, *Isr. J. Chem.*, 2011, **51**,
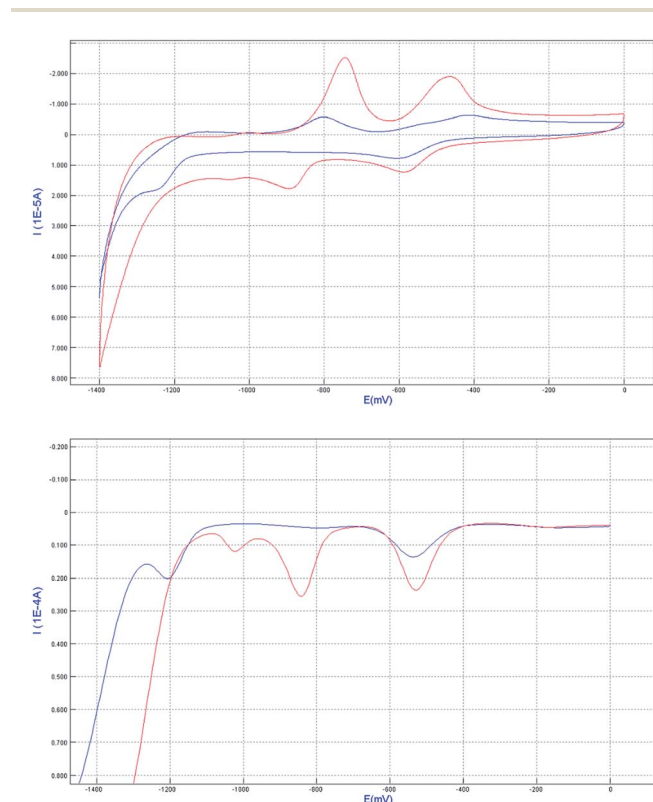

Fig. 7 Cyclic voltammetry (top) and differential pulse voltammetry (bottom) curves of related systems complex **1**(red line) and **1** + **CB[8]** (blue line) in pH = 7 phosphate buffer solution. The concentration used is 1 mM for all the compounds, with glassy carbon disk as working electrode, and Ag/AgCl as reference electrode, the scan rate was 100 mV s^{-1}.

646–663; (*e*) A. Ganguly, S. Ghosh and N. Guchhait, *J. Phys. Chem. B*, 2016, **120**, 4421–4430; (*f*) M. Cao, F. Hu, X. Han, Y. Zhang, D. Wu, S. H. Liu and J. Yin, *Chin. J. Chem.*, 2015, **33**, 351–355.

3 (*a*) K. Moon, J. Grindstaff, D. Sobransingh and A. E. Kaife, *Angew. Chem., Int. Ed.*, 2004, **43**, 5496–5499; (*b*) S. J. Barrow, S. Kasera, M. J. Rowland, J. Barrio and O. A. Scherman, *Chem. Rev.*, 2015, **115**, 12320–12406; (*c*) R. Rabbani and E. Masson, *Org. Lett.*, 2017, **19**, 4303–4306; (*d*) J. Yin, Y. Hu, D. Wang, L. Yang, Z. Jin, Y. Zhang and G. Kuang, *ACS Macro Lett.*, 2017, **6**, 139–143.

4 (*a*) U. Rauwald, J. Barrio, X. J. Loh and O. A. Scherman, *Chem. Commun.*, 2011, **47**, 6000–6002; (*b*) J. Zhang, R. J. Coulston, S. T. Jones, J. Geng, O. A. Scherman and C. Abell, *Science*, 2012, **335**, 690–694; (*c*) W. Jiang, Q. Wang, I. Linder, F. Klautzsch and C. A. Schalley, *Chem.–Eur. J.*, 2011, **17**, 2344–2348; (*d*) F. Tian, N. Cheng, N. Nouvel, J. Geng and O. A. Scherman, *Langmuir*, 2010, **26**, 5323–5328; (*e*) S. Jiang, M. Liu, Y. Cui, D. Zou and Y. Wu, *Eur. J. Org. Chem.*, 2013, 2591–2596; (*f*) S. Jiang, X. Yang, C. Yang, M. Tong, D. Zou and Y. Wu, *Tetrahedron Lett.*, 2013, **54**, 1638–1644; (*g*) S. Li, X. Xu, Y. Zhou, Q. Zhao and Y. Liu, *Org. Lett.*, 2017, **19**, 6650–6653.

5 (*a*) W. S. Jeon, H. J. Kim, C. Lee and K. Kim, *Chem. Commun.*, 2002, 1828–1829; (*b*) K. Kim, D. Kim, J. W. Lee, Y. H. Ko and K. Kim, *Chem. Commun.*, 2004, 848–849; (*c*) S. Andersson, D. Zou, R. Zhang, S. Sun, B. Åkermark and L. Sun, *Eur. J. Org. Chem.*, 2009, 1163–1172; (*d*) T. Zhang, S. Sun, F. Liu,

J. Fan, Y. Pang, L. Sun and X. Peng, *Phys. Chem. Chem. Phys.*, 2009, **11**, 11134–11139.

6 S. Sun, Y. He, Z. Yang, Y. Pang, F. Liu, J. Fan, L. Sun and X. Peng, *Dalton Trans.*, 2010, **39**, 4411–4416.

7 W. S. Jeon, E. Kim, Y. H. Ko, I. Hwang, J. W. Lee, S. Y. Kim, H. J. Kim and K. Kim, *Angew. Chem., Int. Ed.*, 2005, **44**, 87–91.

8 Y. H. Ko, K. Kim, J. K. Kang, H. Chun, J. W. Lee, S. Sakamoto, K. Yamaguchi, J. C. Fettinger and K. Kim, *J. Am. Chem. Soc.*, 2004, **126**, 1932–1933.

9 W. S. Jeon, A. Y. Ziganshina, J. W. Lee, Y. H. Ko, J. K. Kang, C. Lee and K. Kim, *Angew. Chem., Int. Ed.*, 2003, **42**, 4097–4100.

10 S. Sun, R. Zhang, S. Andersson, J. Pan, B. Åkermark and L. Sun, *Chem. Commun.*, 2006, 4195–4197.

11 S. Sun, R. Zhang, S. Andersson, J. Pan, D. Zou, B. Åkermark and L. Sun, *J. Phys. Chem. B*, 2007, **111**, 13357–13363.

12 D. Zou, S. Andersson, R. Zhang, S. Sun, B. Åkermark and L. Sun, *J. Org. Chem.*, 2008, **73**, 3775–3783.

13 W. Ong, M. G. Kaifer and A. E. Kaifer, *Org. Lett.*, 2002, **4**, 1791–1794.

14 (*a*) S. Andersson, D. Zou, R. Zhang, S. Sun and L. Sun, *Org. Biomol. Chem.*, 2009, **7**, 3605–3609; (*b*) S. Sun, W. Gao, F. Liu, F. Li, J. Fan and X. Peng, *Phys. Chem. Chem. Phys.*, 2011, **13**, 570–575; (*c*) S. Sun, S. Andersson, R. Zhang and L. Sun, *Chem. Commun.*, 2010, **46**, 463–465; (*d*) T. K. Monhaphol, S. Andersson and L. Sun, *Chem.–Eur. J.*, 2011, **17**, 11604–11612.