

Redox-induced $\text{Ru}(\text{bpy})_3^{2+}$ -methylviologen radical formation and its dimerization in cucurbit[8]uril†

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A redox-induced radical $\text{Ru}(\text{bpy})_3^{2+}-(\text{CH}_2)_n-\text{MV}^{+\bullet}$ ($n = 4, 7$) and its dimerization in cucurbit[8]uril (CB[8]) have been observed concomitantly in aqueous solution, which depends heavily on the length of the carbon chain linkage, in the case of $n = 4$, the characteristic pattern for the radical dimer is predominating, while that for the radical becomes dominated for $n = 7$.

1. Introduction

In recent years, the host–guest chemistry of the cucurbituril family has been making big progress since Kim,¹ Day² and their co-workers reported the preparation of different cucurbit[n]uril (CB[n], $n = 5, 7, 8, 9, 10$) and their homologues. Among them, the inclusion chemistry of CB[8] seems much more interesting, owing to the fact that it can accommodate two identical³ or different⁴ aromatic guests in its cavity. It is noted that the inclusion complex between an electron-rich guest molecule and CB[8] typically requires the presence of an electron acceptor such as methyl viologen (*N,N*-dimethyl-4,4-bipyridinium, MV^{2+}),⁵ because the formation of the ternary complex CB[8]-donor- MV^{2+} is driven by the charge transfer (CT) interaction between the electron donor and MV^{2+} inside the CB[8] cavity. While the dimerization constant of $\text{MV}^{+\bullet}$ (methylviologen radical) in the presence of equimolar CB[8] is estimated to be $2 \times 10^7 \text{ M}^{-1}$, which is much larger than that of the ternary inclusion complex CB[8]-donor- MV^{2+} (normally 10^3 – 10^5 M^{-1}). As soon as MV^{2+} is reduced to $\text{MV}^{+\bullet}$, a 2:1 inclusion radical dimer ($\text{MV}^{+\bullet})_2/\text{CB[8]}$ will be formed immediately, leading to exclusion of the electron rich guest from the CB[8] cavity simultaneously.^{3,5} However, it is not always like this. Some quite uncommon cases have been found since the host–guest interaction of a molecular triad $\text{Ru}(\text{bpy})_3-\text{MV}^{2+}$ -naphthol complex (Scheme 1) and CB[8] was studied,⁶ in which the naphthalene residue is back-folded and inserted together with the viologen residue into the cavity of CB[8]. Upon light irradiation, a $\text{MV}^{+\bullet}$ radical cation stabilized in the cavity of CB[8] accompanied by the naphthalene residue has been observed, the second oxygen atom (in blue, Scheme 1) on the naphthalene ring and the co-existing intramolecular $\text{Ru}(\text{bpy})_3^{2+}$ moiety can be responsible for this quite different results from Kim.⁵

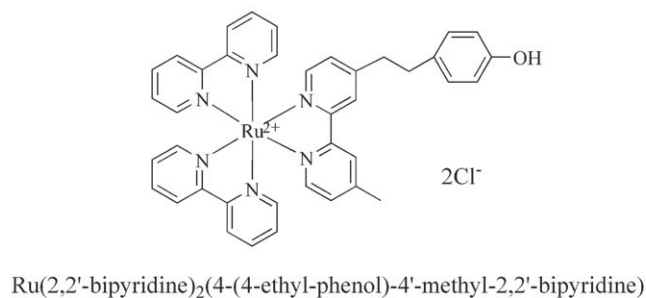
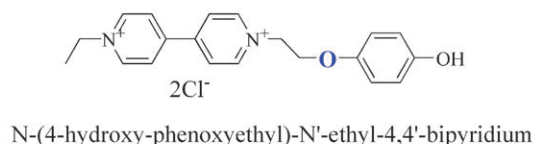
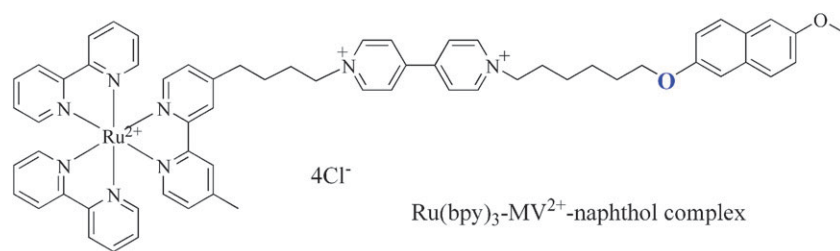
To figure out the real reason and whether the result is a special or a general case, *N*-(4-hydroxy-phenoxyethyl)-*N'*-ethyl-4,4'-bipyridinium (Scheme 1) was further designed by removing the $\text{Ru}(\text{bpy})_3^{2+}$ moiety and replacing the naphthalene ring with a benzene ring to make the system simplified.⁷ As soon as EV^{2+} was reduced to ethyl viologen radical ($\text{EV}^{+\bullet}$), an intramolecular partner radical ($\text{EV}^{+\bullet}\text{-HP}$)/CB[8] was observed in the cavity of CB[8]. Meanwhile, a dynamic balance between the partner radical and the ethyl viologen radical dimer ($\text{EV}^{+\bullet}\text{-HP})_2/\text{CB[8]}$ can be evidenced, demonstrating that this second oxygen atom on the naphthalene ring is one of the main reasons for the above mentioned different result. To study the function of the intramolecular $\text{Ru}(\text{bpy})_3^{2+}$ moiety alone, very recently, a phenol moiety linked ruthenium(II) *tris*-bipyridine complex $[\text{Ru}(2,2'\text{-bipyridine})_2(4\text{-(4-ethyl-phenol)-4'-methyl-2,2'-bipyridine})]$ (Scheme 1) was designed⁸ by removing the second oxygen atom from the molecule, which was found to form a stable ternary host–guest 1:1:1 complex with CB[8] accompanied by MV^{2+} in aqueous solution. In the presence of sacrificial electron donor TEOA (triethanolamine), a stable partner radical trimer existing as “MV and phenol partner radical trimer” in CB[8] cavity can be generated with light, suggesting that the $\text{Ru}(\text{bpy})_3^{2+}$ moiety can play a role for the different result too.

To continue research on this track,^{9,10} herein we report a new supramolecular system in which $\text{Ru}(\text{bpy})_3^{2+}$ moiety is linked to MV^{2+} moiety through a different carbon chain to form ruthenium(II) *tris*-bipyridine complexes $\text{Ru}(\text{bpy})_3^{2+}-(\text{CH}_2)_n-\text{MV}^{2+}$ (**1**, $n = 4, 7$, Scheme 2), while the intramolecular naphthalene residue was removed from their structures and added into the system as free 2,6-dihydroxy-naphthalene ($\text{Np}(\text{OH})_2$), to further investigate the effect of the intramolecular co-existing $\text{Ru}(\text{bpy})_3^{2+}$ moiety, together with the different carbon chain linkage and also the free intermolecular $\text{Np}(\text{OH})_2$ partner on the inclusion chemistry of CB[8]. This system is quite similar to those of Kim,⁵ providing a good possibility to make a comparison between them. The result demonstrated that complexes **1** and $\text{Np}(\text{OH})_2$ form as partners ternary host–guest 1:1:1 complexes with CB[8] in aqueous solution, in the presence of a reducing agent such as sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), a redox induced radical $\text{Ru}(\text{bpy})_3^{2+}-(\text{CH}_2)_n-\text{MV}^{+\bullet}$ and its dimerization in CB[8] have been observed synchronously.

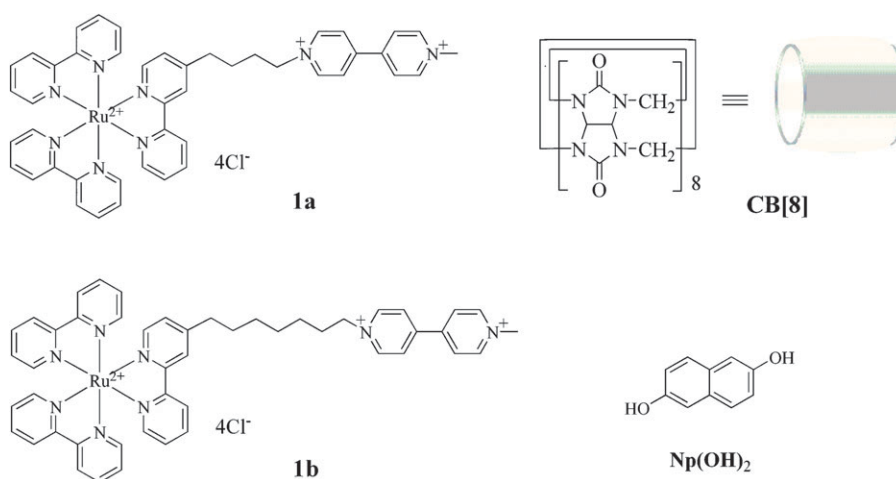
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Scheme 1 Structures of the previously studied complexes



Scheme 2 Structures of complexes **1**, Np(OH)₂ and CB[8]

2. Experimental

Complexes **1** were samples left in our previous work,¹¹ CB[8] was synthesized according to ref. 1, Np(OH)₂, tetrathiafulvalene (TTF) and Na₂S₂O₄ were all of analytical grade and used directly as received. All the water used was distilled water. NMR data were recorded on a VARIAN INOVA-400 spectrometer with chemical shifts reported as ppm, and the solvents were D₂O. Absorption spectra were measured on a Perkin-Elmer Lambda 35 UV/Vis spectrophotometer, and all the UV/Vis spectra were obtained under N₂ atmosphere.

Electrochemical measurements were made with a BAS 100B/W electrochemical workstation at a scan rate of 100 mV s⁻¹ in all

cyclic voltammetric (CV) and 25 mV s⁻¹ in all differential pulse voltammetric (DPV) experiments. All voltammograms were obtained in a conventional three-electrode cell under N₂ at room temperature. The working electrode was a glassy carbon disc (diameter 3 mm) that was polished with 3-μm and 1-μm diamond pastes and sonicated in ion-free water for 15 min prior to use. The counter electrode was a platinum wire and the reference electrode was a saturated calomel electrode (SCE). The experiments were conducted in 0.1 M KCl solutions (pH 7.0) prepared with water. All solutions were deoxygenated by purging with N₂ and maintained under an inert atmosphere during the measurement.

3. Results and discussion

3.1 Inclusion of the ternary complex in CB[8]

The supramolecular interaction of complexes **1** and analogues with CB[8] has been demonstrated in our previous work,^{6,10,11} while those for MV^{2+} , $Np(OH)_2$ and their derivatives have been studied extensively both in our previous works^{6,10,11} and others.^{4,5} There is no doubt that complexes **1**, $Np(OH)_2$ and CB[8] can form a 1:1:1 ternary inclusion complexes in aqueous solution, and the formation of the ternary inclusion complexes can be easily followed on 1H NMR (Fig. S1, S2).[†] Furthermore, a molecular modeling study (HyperChem with AM1 setting) also showed that the $Np(OH)_2$ ring almost paralleled that of the MV^{2+} moiety with a close CT interaction distance (~ 3.6 Å) inside the cavity of CB[8] (Fig. 1), which is in good accordance with the argument in the literatures.^{5–8}

Different length of the carbon chain linkage between $Ru(bpy)_3^{2+}$ moiety and MV^{2+} revealed a negligible effect (compare **1a** and **1b**), due to the fact that only the MV^{2+} moiety in complexes **1** participates in the inclusion interaction. Considering that the carbon chain linkage and the $Ru(bpy)_3^{2+}$ moiety are inert to the reducing agent of $Na_2S_2O_4$, both of them will be working as pure obstacles during the redox induced process. This is quite different from those of a light or electrochemistry induced system,^{4–6,10,11} in which they will take part in the whole process instead.

3.2 UV-Vis and electrochemistry

Fig. 2 illustrated the UV-Vis spectra of complexes **1**, **1** + CB[8] (1 : 1), **1** + CB[8] + $Np(OH)_2$ (1 : 1 : 1) with and without addition of a big excess of reducing agent $Na_2S_2O_4$. Not much difference can be observed for complexes **1** before and after formation of the binary (**1**-CB[8]) and ternary (**1**- $Np(OH)_2$ -CB[8]) including complexes, which is in good accordance with the literature.^{4–6,10,11} In the presence of excess $Na_2S_2O_4$, a redox induced radical $Ru(bpy)_3^{2+}-(CH_2)_n-MV^{+\bullet}$ can be generated for complexes **1** alone, and the typical characteristic pattern for the formation of this radical (two absorption peaks around 395 and 600 nm) can be easily monitored on UV-Vis (red line in Fig. 2) as stated in the literature.^{4–6,10,11}

As for the binary and ternary inclusion complexes of **1a** and **1b**, the characteristic absorption for both the viologen radical and the radical dimer (two absorption peaks around 550 and 950 nm) can be observed concomitantly after addition of excess $Na_2S_2O_4$.^{4–6,10,11} This is quite different from previous results^{4–6,8,10,11} where light together with a sacrificial electron donor TEOA, electrochemistry or a reducing agent such as $Na_2S_2O_4$ were employed to generate the viologen radical, in these cases, a 2 : 1 inclusion radical dimer ($MV^{+\bullet})_2/CB[8]$ will be formed immediately as soon as MV^{2+} is reduced to $MV^{+\bullet}$.

It is noted that the spectra depend heavily on the length of the carbon chain linkage. In the case of **1a**, the characteristic pattern for the radical dimer is predominating, while that for the radical becomes dominated for **1b**. Furthermore, the

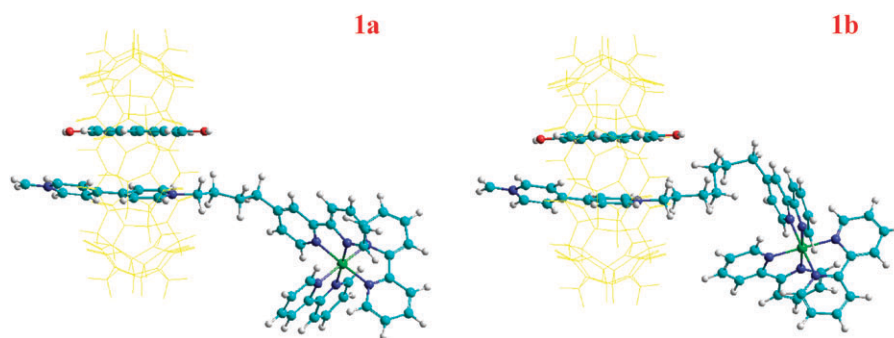


Fig. 1 Optimized molecular modeling of the ternary complexes **1a**- $Np(OH)_2$ -CB[8] (left) and **1b**- $Np(OH)_2$ -CB[8] (right) with N-, O-, C-, Ru, and H-atom in blue, red, cyan, green, and white color illustrated by the geometry-optimized structures by using HyperChem 8.0 software.

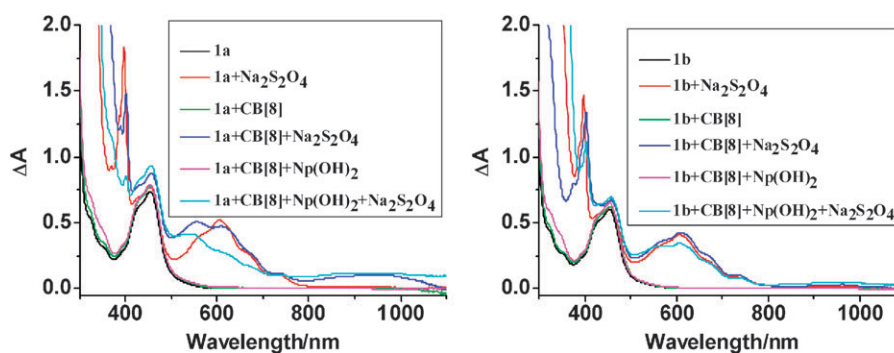


Fig. 2 Absorption spectra of complexes **1** (50 μM), 1 equiv. of CB[8] and 1 equiv. of $Np(OH)_2$ with and without addition of big excess of reducing agent $Na_2S_2O_4$.

absorption for the radical dimer of the ternary inclusion complexes is stronger than that of the corresponding binary inclusion ones, suggesting that the coexisting $\text{Np}(\text{OH})_2$ partner will be helpful in the formation of the radical dimer. All these can be ascribed to the different carbon chain linkage and the coexisting intramolecular $\text{Ru}(\text{bpy})_3^{2+}$ moiety in complexes **1**. The effect was further investigated by using the $\text{Ru}(\text{bpy})_3^{2+}-(\text{CH}_2)_3-\text{MV}^{2+}$ analogous **1c**,¹¹ which bears a shorter bridge (3 carbon chain). Upon addition of $\text{Na}_2\text{S}_2\text{O}_4$ into the aqueous solution of **1c**, a redox induced radical $\text{Ru}(\text{bpy})_3^{2+}-(\text{CH}_2)_3-\text{MV}^{\bullet+}$ was observed in the absence of CB[8] (Fig. 3). In the presence of CB[8], however, only the radical dimer can be observed after reduction by $\text{Na}_2\text{S}_2\text{O}_4$.

The above processes can be interpreted as following. As shown in Scheme 3, after addition of excess $\text{Na}_2\text{S}_2\text{O}_4$, a redox induced radical $\text{Ru}(\text{bpy})_3^{2+}-(\text{CH}_2)_n-\text{MV}^{\bullet+}$ is formed in the system, which can go through a recombination process to form a dimer inside one CB[8] cavity as suggested,^{10a} owing to the significant higher dimerization constant of $\text{MV}^{\bullet+}$ in the presence of CB[8]. However, the hydrophobic carbon chain linkage and the relatively bigger $\text{Ru}(\text{bpy})_3^{2+}$ moiety could cause some hindrance effect on the dimerization process, due

to the fact that only the MV^{2+} moiety in complexes **1** participates in the including interaction.

The experimental results clearly revealed that the content of the radical dimer was dependent on the length of the carbon bridge that links the Ru-complex and MV^{2+} moieties. The hydrophobic carbon chain linkage tends to form coil-like conformation in an aqueous environment, in order to minimize its interaction with the surrounding water molecules. The possibility of forming a coil-like conformation could bring the MV^{2+} moiety closer to CB[8] (as seen from Fig. 1b), which is unfavorable for the dimerization complex formation. In other words, the longer the carbon chain linkage, the stronger the hydrophobic effect, the harder for the MV^{2+} moiety to accomplish dimerization. Meanwhile, the relatively bigger $\text{Ru}(\text{bpy})_3^{2+}$ moiety will act as a pure stopper during the dimerization process, due to the fact that only the MV^{2+} moiety in complexes **1** participates in the including interaction. However, in the case of the ternary inclusion complexes, the radical formation in CB[8] greatly decreases the charge density on methyl viologen, this will weaken not only the CT interaction between methyl viologen and $\text{Np}(\text{OH})_2$ partner, but also the host–guest interaction among methyl viologen,

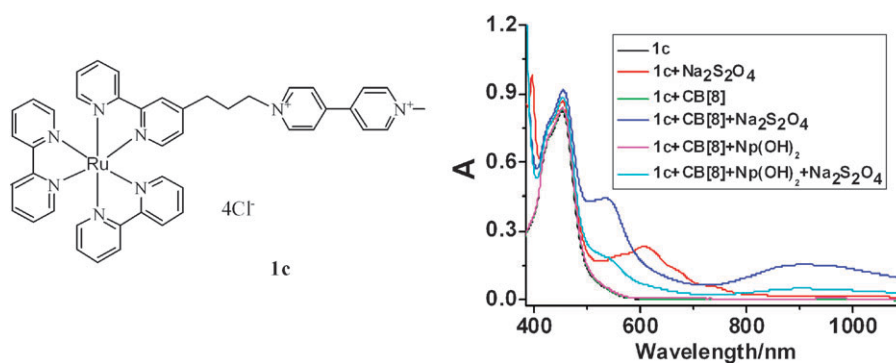
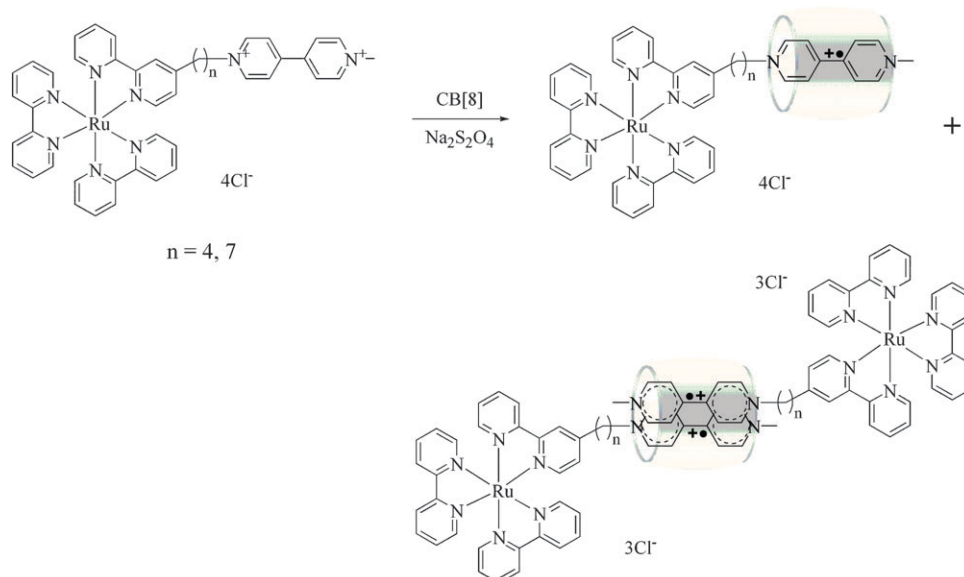


Fig. 3 Absorption spectra of complex **1c** (50 μM), 1 equiv. of CB[8] and 1 equiv. of $\text{Np}(\text{OH})_2$ with and without addition of a big excess of reducing agent $\text{Na}_2\text{S}_2\text{O}_4$.



Scheme 3 A proposed structure for the formation of the stable radical dimer in the solution.

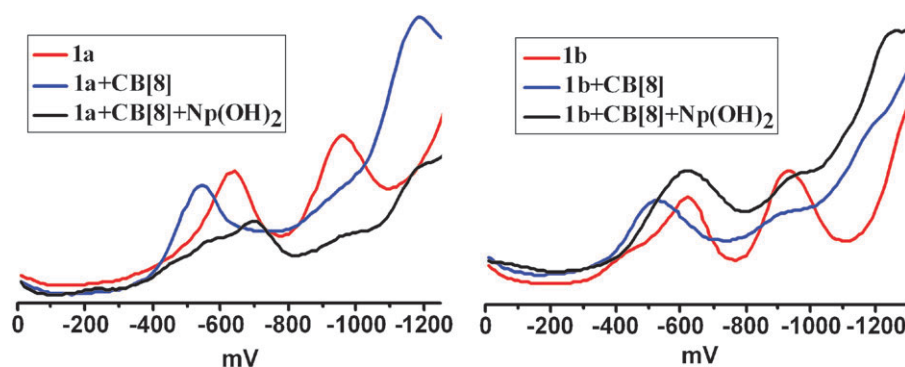


Fig. 4 DPV curves for the system of complex **1**, **1** + CB[8] and **1** + CB[8] + Np(OH)₂ in 0.1 M KCl solution. The concentration used is 1 mM for all the compounds, and the scan rate was 25 mV s⁻¹.

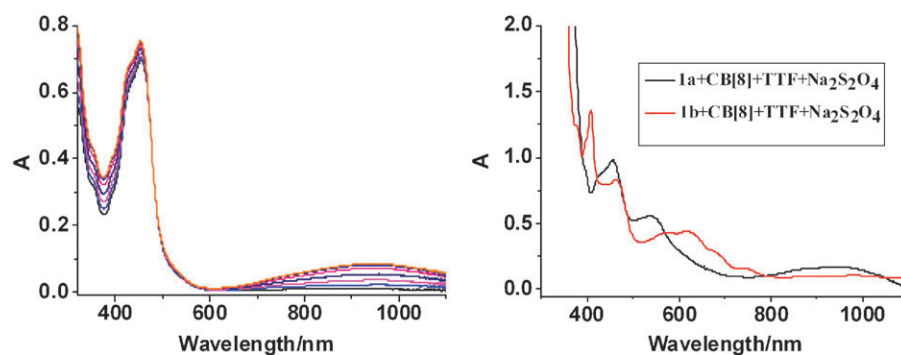


Fig. 5 Left: absorption spectra change for 50 μM **1b**-CB[8] in 1 : 1 ratio in water solution (black) along with gradual addition of TTF (0.2, 0.4, 0.6, 0.8, 1.0, 1.2 equiv.). Right: absorption spectra of complexes **1** (50 μM), 1 equiv. of CB[8] and 1 equiv. of TTF with addition of big excess of the reducing agent Na₂S₂O₄.

Np(OH)₂ and CB[8], leading to a relatively easier recombination of dimerization, accompanied by exclusion of the Np(OH)₂ donor partner from the ternary including complex.

Control experiments were also performed by cyclic voltammetry and DPV for the systems of complexes **1** + CB[8] and **1** + CB[8] + Np(OH)₂ in 0.1 M KCl (pH = 7) solution, to make a comparison with that of complexes **1** alone. The results are shown in Fig. 4.

Not much difference aroused by the different carbon chain linkage can be observed in complexes **1**. According to the literature,^{4-6,8,10,11} the first wave around -0.63 V corresponded to the reduction of MV²⁺ moiety to the cation radical MV^{•+}, whereas the second wave around -0.94 V was attributed to the reduction of MV^{•+} to MV⁰ (red line in Fig. 3). As for the binary (blue line in Fig. 3) and ternary (black line in Fig. 3) inclusion complexes, the peak potentials for the redox couple of MV²⁺/MV^{•+}, MV^{•+}/MV⁰ were shifted to about -0.53 V and -1.2 V, respectively. Meanwhile, those typical peaks for the free radical can still be kept in both systems. Furthermore, the reduction of the MV²⁺ to MV^{•+} changed from reversible to quasi-reversible, while those for the MV^{•+} to MV⁰ from reversible to completely irreversible on CV measurements. This characteristic pattern for the formation of radical and radical dimer is in good agreement with literature precedents.^{4-6,8,10,11} All these provide strong evidence of the formation of a redox-induced radical Ru(bpy)₃²⁺-(CH₂)_n-MV^{•+} (*n* = 4, 7) and its dimer in CB[8].

To provide further information needed in the redox induced process, another electron-rich guest TTF, which has been proven to form a 1 : 1 : 1 inclusion complex with MV²⁺ and CB[8] in the literature,^{5d} was also employed to replace Np(OH)₂ in the above system, and the same procedure was followed as above mentioned, the result is shown in Fig. 5. Taking **1b** as an example, after addition of increasing equiv. of TTF powder into a 50 μM water solution of molecular dyad **1b**-CB[8] in 1 : 1 ratio, a broad new NIR absorption band around 600–1100 nm with λ_{max} = 945 nm appeared in Fig. 4 (left), which can be attributed to efficient intramolecular CT interaction resulting from the 1 : 1 : 1 ternary inclusion complex formation.^{5d,12} In the presence of excess Na₂S₂O₄, the same trend as that in Np(OH)₂ system can be evidenced for complexes **1a** and **1b** (Fig. 4, right), further demonstrated the generality of our result.

4. Conclusions

In conclusion, both the second oxygen atom on the naphthalene ring and the co-existing intramolecular Ru(bpy)₃²⁺ moiety are responsible for the different results from Kim's. A redox-induced radical Ru(bpy)₃²⁺-(CH₂)_n-MV^{•+} (*n* = 4, 7) and its dimerization in CB[8] have been observed simultaneously in aqueous solution, the longer the carbon chain linkage, the harder the dimerization process. The coexisting donor partner such as Np(OH)₂ and TTF will be helpful for the formation of

the radical dimer. These results may provide a new way of constructing supramolecular systems, and can also provide some fundamentals for future design of molecular devices.

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