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A Host-Induced Intramolecular Charge-Transfer Complex and Light-Driven Radical Cation Formation of a Molecular Triad with Cucurbit[8]uril

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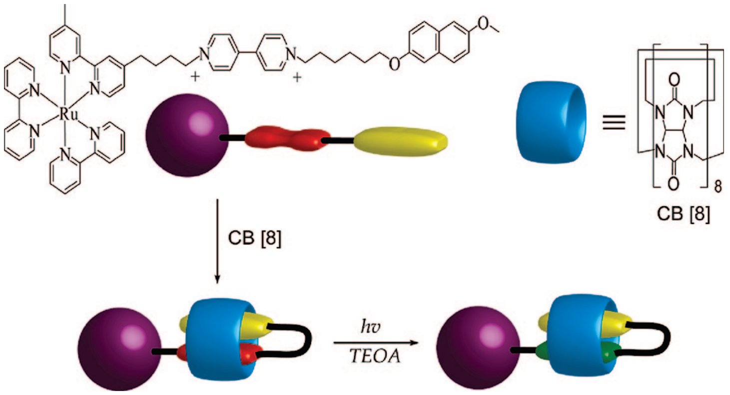

The host−guest chemistry of systems containing a molecular triad Ru(bpy)$_3$-MV^{2+}-naphthol complex (denoted as Ru^{2+}-MV^{2+}-Np, **1**) and cucurbit[8]uril (CB[8]) is investigated by NMR, ESI-MS, UV−vis, and electrochemistry. The Ru^{2+}-MV^{2+}-Np guest and CB[8] host can form a stable 1:1 inclusion complex, in which the naphthalene residue is back-folded and inserted together with the viologen residue into the cavity of CB[8]. The selective binding of Ru^{2+}-MV^{2+}-Np guest with β-CD and CB[8] host is also investigated. We find that CB[8] binds the Ru^{2+}-MV^{2+}-Np guest stronger than β-CD. Upon light irradiation, a MV$^{+\bullet}$ radical cation stabilized in the cavity of CB[8] accompanied by the naphthalene residue has been observed. This novel system may open a new way for design and synthesis of photoactive molecular devices.

Introduction

Recently, great efforts have been made by chemists to construct various interlocked supramolecular systems[1,2] because of their potential applications in many areas, including molecular switches[3] and molecular wires.[4] Cucurbit[n]urils (CB[n], where $n = 5-10$)[5–11] and cyclodextrins (CDs)[12–14] as two different kinds of host molecules have attracted great attention for their special structures and application in the interactions with guest molecules in the past few years. The specific inclusion of the methyl viologen (N,N-dimethyl-4,4-bipyridinium, MV^{2+}), which is a common electron acceptor, in studies of electron transfer

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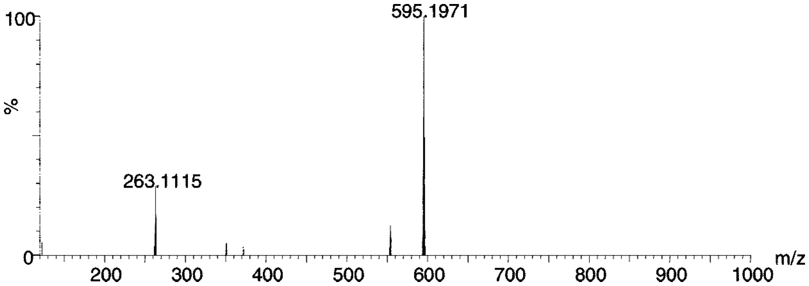
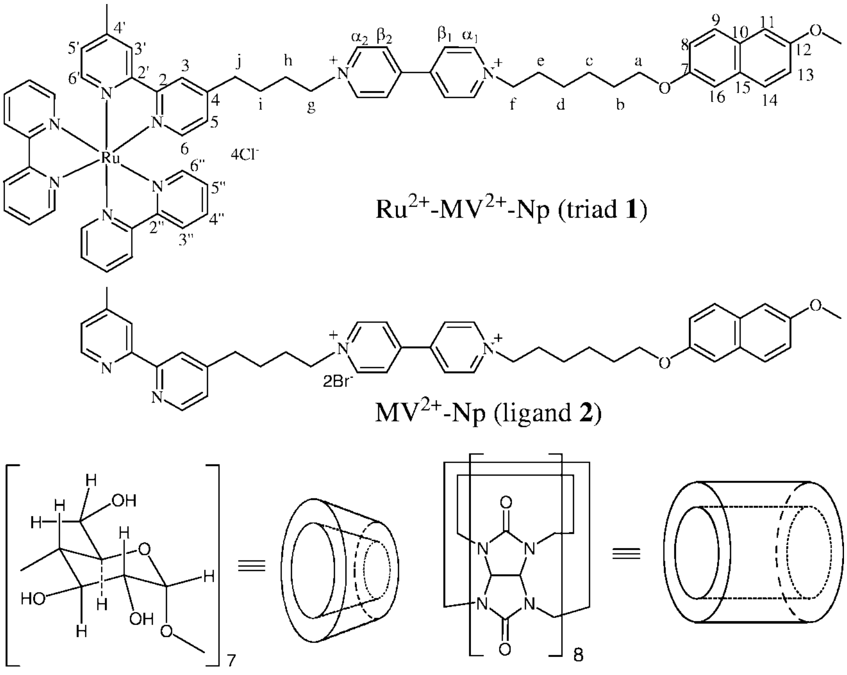


FIGURE 1. ESI-MS spectrum of the 1:1 inclusion complex of triad **1** with CB[8].

CHART 1. Structures of Ru^{2+}-MV^{2+}-Np (1), MV^{2+}-Np (2), β-CD, and CB[8]



Ru^{2+}-MV^{2+}-Np (triad **1**)

MV^{2+}-Np (ligand **2**)

β-cyclodextrin

Cucurbit[8]uril

(ET) reactions[15–17] into the cavity of CB[7] and CB[8] has also been studied extensively.[18–21] Kim and co-workers reported that MV^{2+} can form a stable 1:1 inclusion complex with CB[7] and CB[8], and the methyl viologen cation radical ($MV^{+\bullet}$) dimer is strongly stabilized in the inclusion complex of CB[8]$\cdot$($MV^{+\bullet}$)$_2$.[22,23] They also investigated the stable ternary complexes, in which CB[8] can bind a methyl viologen moiety and a suitable aromatic electron donor inside its cavity,[24] and applied these charge-transfer (CT) complexes for various molecular systems and devices.[25–31] Kaifer and co-workers reported the binding mode of MV^{2+} moieties with CB[7] and designed the switchable molecular shuttles.[32–34] They utilized CB[8] for the redox control of self-assembly[35]and size selection[36] with dendoronized viologens and aromatic electron donors. They also investigated the inclusion complexation of diquat and paraquat by CB[7] and CB[8] and found that one-electron reduction of diquat led to increase binding affinity with CB[7] and CB[8].[37] Reversible

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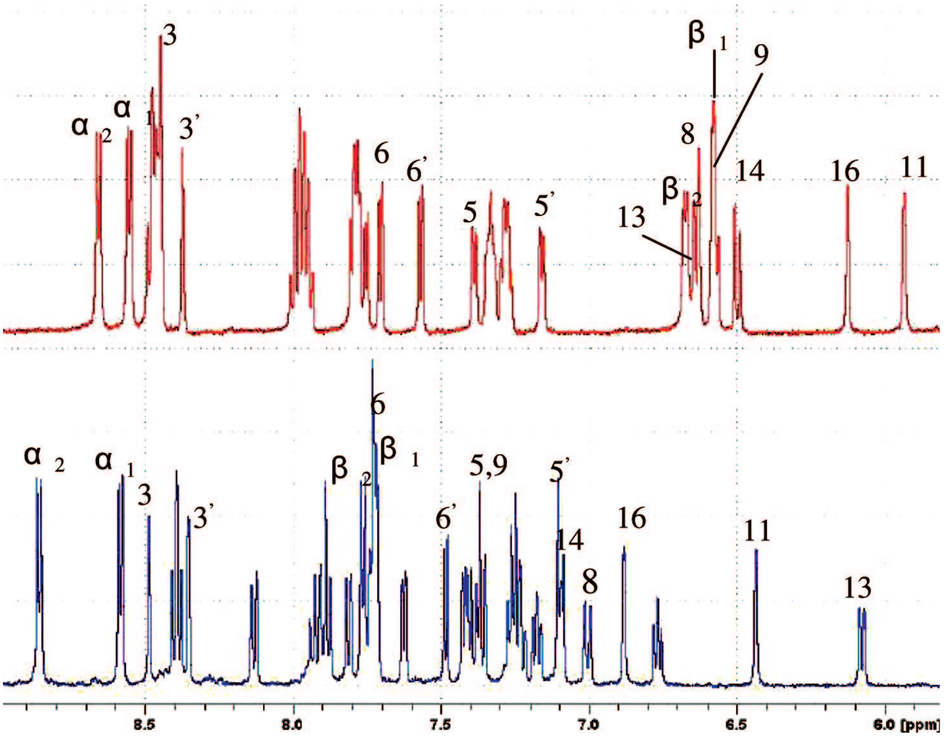
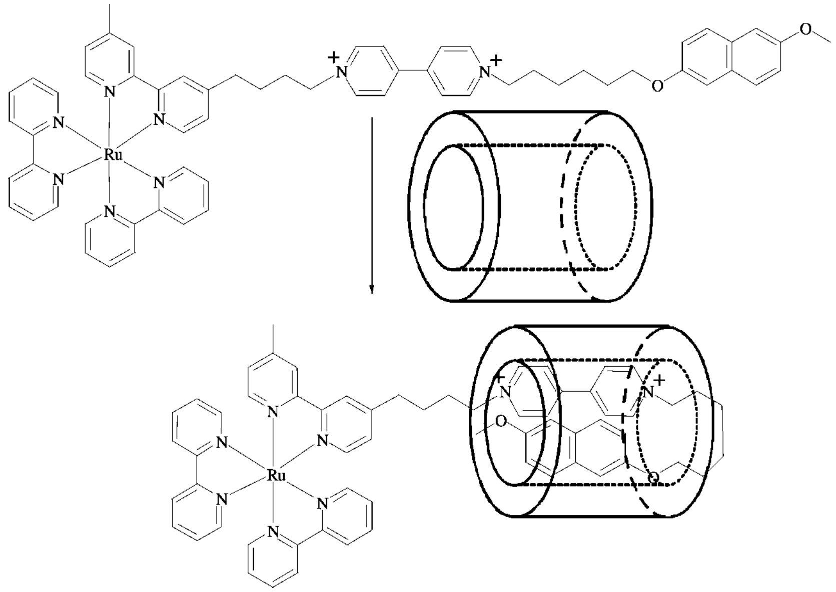


FIGURE 2. ^{1}H NMR spectra (500 MHz, D_2O) of triad **1** in the absence (bottom) and in the presence (top) of 1 equiv of CB[8].

SCHEME 1. Schematic Illustration of the Interaction of Triad 1 with CB[8] (1:1 equiv)



2D pseudopolyrotaxanes based on CDs and CB[6] were also reported by Liu and co-workers.[38] They investigated 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.[39] Despite the many interesting studies involved CB[8] and MV^{2+}, no data have yet been reported on the inclusion of CB[8] with MV^{2+} together with an aromatic donor moiety that is coupled to a redox-active $Ru(bpy)_3$ complex. In our previous work, selective binding of CB[7] and β-CD with a redox-active molecular triad $Ru(bpy)_3$-MV^{2+}-naphthol forming a "tightened nut on bult" inclusion complex has been observed.[40] A photoinduced long-lived charge-separated state of $Ru(bpy)_3$-methylviologen with CB[8] and a light-driven molecular lock have also been studied.[41,42] In this paper we report the host-induced intramolecular CT complex formation between CB[8] and the redox-active molecular triad $Ru(bpy)_3$-MV^{2+}-naphthol (see structures in Chart 1). When this supramolecular system is irradiated with visible light, a radical cation stabilized in the cavity of CB[8] with the presence of naphthalene moiety inside the cavity has been observed in aqueous solution.

Results and Discussion

Interactions of Triad 1 and CB[8]. The triad **1** was synthesized from ligand **2** by following the procedures described in our earlier work.[40] The inclusion complex of triad **1** with host CB[8] was readily detected by ^{1}H NMR spectroscopy (see ^{1}H NMR spectrum in Supporting Information). To study the

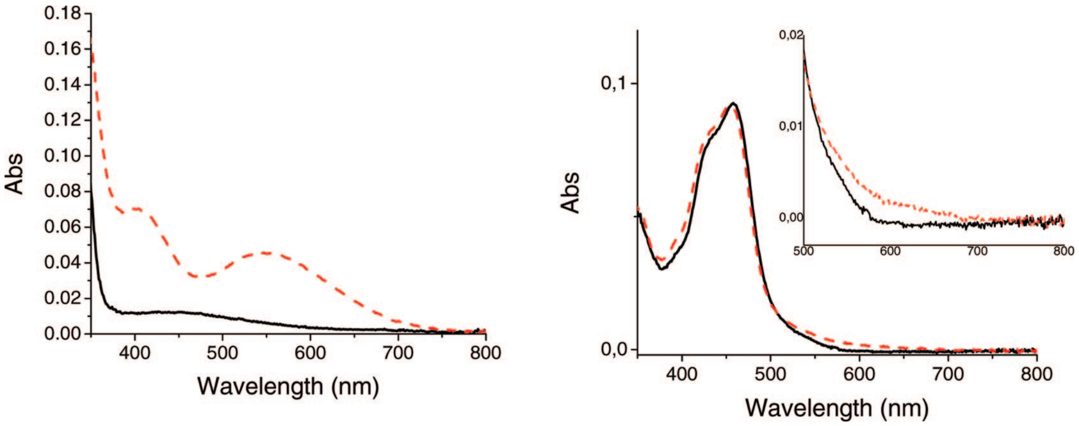


FIGURE 3. Absorption spectra of ligand **2** (left) and triad **1** (right) in the absence (solid line) and in the presence (dashed line) of 1.0 equiv of CB[8].

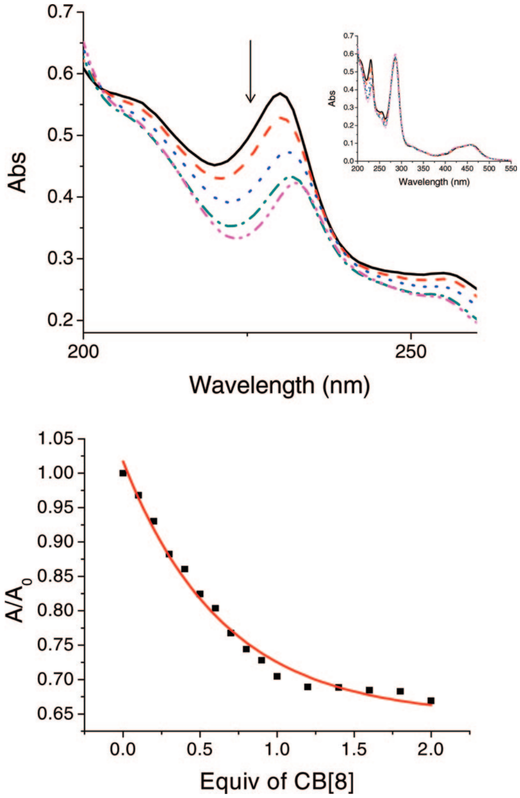


FIGURE 4. (Top) Absorption spectra of triad **1** (8 μM) in water with different concentrations of CB[8]: 0, 1.6, 4.0, 6.4, and 8.0 μM. (Bottom) UV−vis titration curve at 230 nm versus equivalents of CB[8].

complex formation of the triad **1** with CB[8], varying equivalents of CB[8] were added to the solution of triad **1**. In the presence of 0.5 equiv of the host, the proton signals of both bound and free guests are clearly evidenced. Just bound signals were found in the presence of 1.0 equiv of host. In the presence of 2 equiv of CB[8], the proton signals of both bound CB[8] and free CB[8] were observed (see Supporting Information). This can be interpreted that triad **1** can form a stable 1:1 inclusion complex with only 1 equiv of CB[8]. The formation of the stable 1:1 inclusion complex between **1** and CB[8] was further confirmed by ESI-MS. When equivalent amounts of **1** and CB[8] were dissolved in water, the ESI-MS spectrum in positive mode gave a quadruply charged peak at *m/z* 595.1971 (calculated for $[\mathbf{1} + \mathrm{CB[8]} - 4\mathrm{Cl}^-]^{4+}$, 595.1991) (see Figure 1). 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 **1** and CB[8].

When 1 equiv of CB[8] was added to a D_2O solution of triad **1**, the color of the solution changed from red to brown, indicating that a CT complex might be formed.[30,31] To get further information on the nature of the 1:1 inclusion complex, 2D-NMR techniques including COSY, HSQC, and HMBC have been applied. It was noticed that in comparison with the ^{1}H NMR of triad **1** alone, the four β-protons of the viologen moiety in **1** with CB[8] shifted upfield from 7.76 to 6.67 (two protons) and 7.73 to 6.58 (two protons) (Figure 2). The two α-protons shifted upfield from 8.86 to 8.66, and the other two α-protons shifted upfield from 8.58 to 8.56. This result shows that the whole viologen moiety is inserted into the cavity of CB[8]. The five protons of the 2,6-dihydroxynaphthalene moiety shifted upfield from 7.36 to 6.57, 7.09 to 6.49, 6.99 to 6.63, 6.88 to 6.12, and 6.43 to 5.93; only one proton in the 2,6-dihydroxynaphthalene moiety shifted downfield from 6.07 to 6.64. The protons of the six-carbon chain and four-carbon chain in the ^{1}H NMR spectrum of **1** undergo downfield shifts, indicating that the 2,6-dihydroxynaphthalene moiety of **1** folds back to form an intramolecular CT complex with viologen moiety inside the cavity of CB[8], while the proton in the dihydroxynaphthalene moiety beside the methoxy group is not inserted into the cavity of CB[8] (Scheme 1). The protons of methoxy group undergo a downfield shift from 3.39 to 3.71, which means that the methoxy group is not inserted into the cavity of CB[8]. The proton at the 3-position of the substituted bipyridine ligand undergoes an upfield shift from 8.49 to 8.45, the proton at the 5-position undergoes a downfield shift from 7.37 to 7.39, and 6-position undergo an upfield shift from 7.73 to 7.70. The 3′-, 5′-, 6′-protons undergo downfield shifts (data not shown). Small downfield shifts for the protons on the unsubstituted bipyridine ligands can also be observed. All of these NMR data are strong evidence for the formation of 1:1 charge transfer complex as described in Scheme 1. The same phenomenon could also be observed in the case of ligand **2** and CB[8] (see Supporting Information).

The ^{1}H NMR spectrum of triad **1** with CB[8] in D_2O is not affected by the addition of MV^{2+} (up to 3 equiv) which indicates that the 1:1 host−guest complex formed by intramolecular CT interaction is very stable.

UV−vis Absorption. When 1 equiv of CB[8] was added to ligand **2** in H_2O, the color of the solution turned to violet

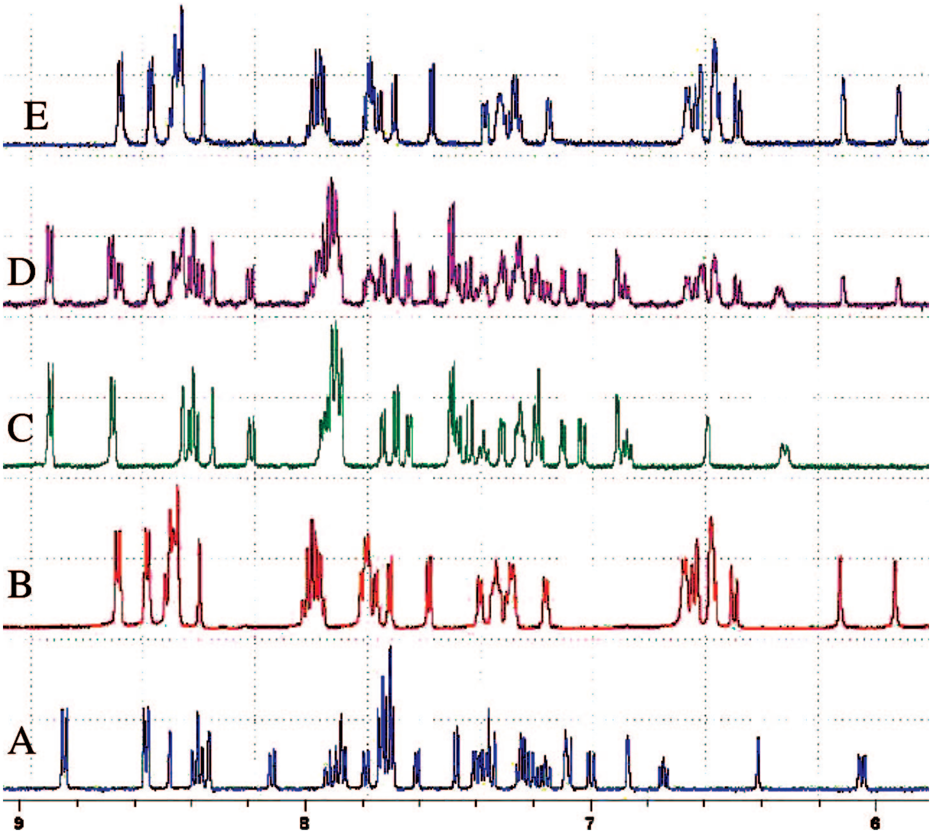
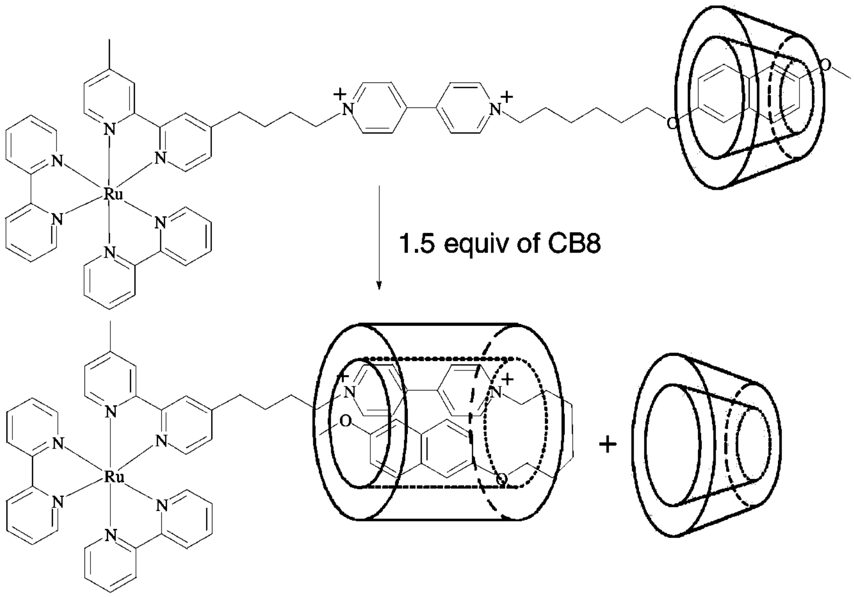


FIGURE 5. ^{1}H NMR spectra (500 MHz, D_2O) of triad **1** alone (A), after addition of 1 equiv of CB[8] (B), after addition of 1 equiv of β-CD (C), after addition of 0.5 equiv of CB[8] to the solution of 1:1 inclusion complex of triad **1** and β-CD (D), and after addition of 1.5 equiv of CB[8] to the solution of 1:1 inclusion complex of triad 1 and β-CD (E).

SCHEME 2. Changes of Interaction by Addition of CB[8] into a 1:1 Inclusion Complex of 1 and β-CD



(λ_{max} = 561 nm) (Figure 3, left), indicating the formation of a CT complex, which is similar to the system previously reported (λ_{max} = 566 nm) by Kim and co-workers.[30,31] In case of triad **1**, the solution turns to brown instead of violet due to the strong absorption (the MLCT transition) of the Ru(bpy)$_3$ moiety at 450 nm; a small increase of the absorption from the CT complex around 560 nm could still be observed in the UV−vis spectrum (Figure 3, right). For both ligand **2** and triad **1**, a red shift around 230 nm in the absorption spectra has been observed upon addition of CB[8] (see Supporting Information). As the equiva-

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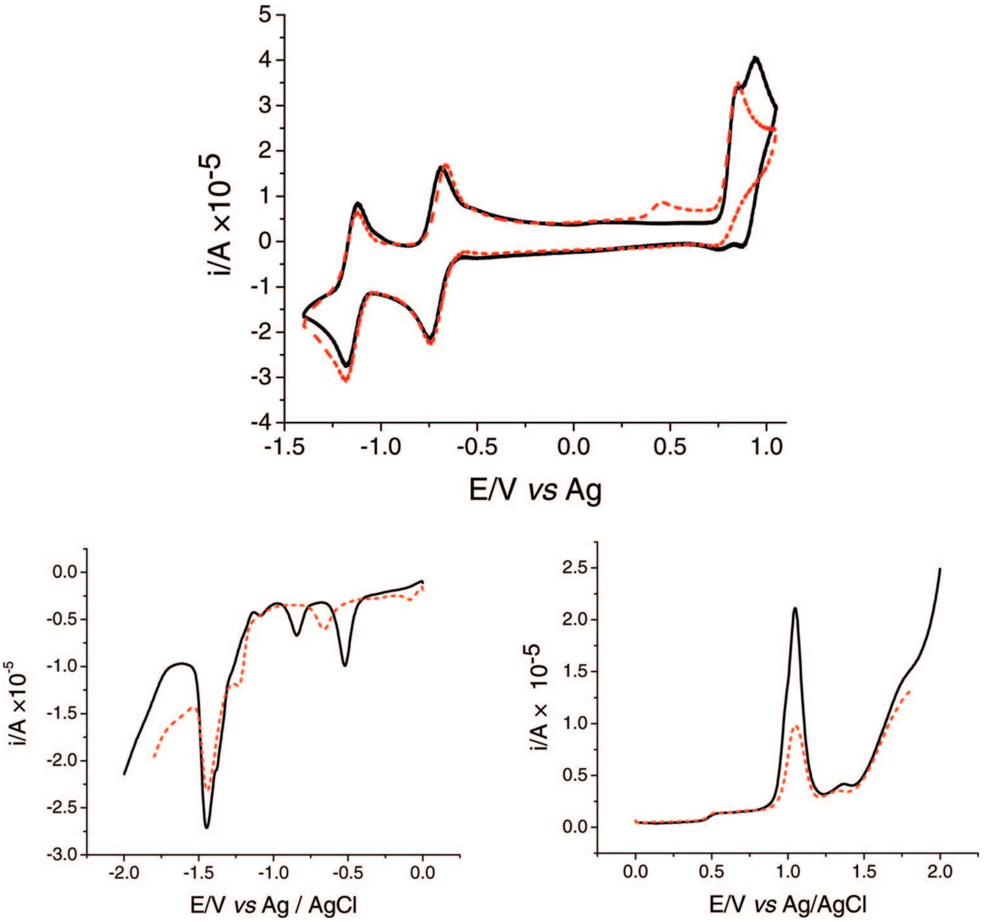

FIGURE 6. (Top) Cyclic voltammograms of triad **1** (1×10^{-3} M) (solid line) and ligand **2** (1×10^{-3} M) (dashed line) in acetonitrile, with Bu_4NPF_6 (0.1 M) as supporting electrolyte, glassy carbon disk as working electrode, and $Ag/AgNO_3$ as reference electrode. (Bottom) Differential pulse voltammograms of triad **1** (1×10^{-3} M) in the absence (solid line) and in the presence (dashed line) of 1 equiv of CB[8] in 0.1 M phosphate buffered (PH 7.0) water solution at room temperature, glassy carbon as working electrode, Ag/AgCl as reference electrode; scan rate: $\upsilon = 0.1$ V s^{-1}.

lents of CB[8] increased, the peak shifted from 230 to 233 nm. This red shift can be attributed to the insertion of the 2,6-dihydroxynaphthalene moiety into the cavity of CB[8] together with MV^{2+} moiety.

The stoichiometry of the binding of triad **1** with CB[8] is further verified by UV−vis absorption titration measurements (Figure 4). After addition of increasing equivalents of CB[8] into an aqueous solution of triad **1** (8 μM), the corresponding UV−vis absorption spectra changes were recorded. Figure 4 shows a plot of the relative absorbance (A/A_0, where A is the corresponding absorbance intensity at 230 nm after addition of different equiv of CB[8] and A_0 is the absorbance intensity before addition of CB[8]) 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 2.62×10^5 L mol^{-1}. This value is very close to the binding constant (3×10^5 L mol^{-1}) of the molecular dyad where $Ru(bpy)_3$ is covalently linked to MV^{2+} by a four-carbon chain as we reported before.[41]

Inclusion of Molecular Triad 1 with CB[8] and β-CD. To study the selective binding of triad **1** with β-CD and CB[8], 1 equiv of β-CD and CB[8] were added to the solution of triad **1**. Figure 5A shows the ^{1}H NMR spectra of triad **1** in D_2O; upon addition of 1 equiv of CB[8], the proton signals of MV^{2+} and naphthalene moiety are upfield shifted (Figure 5B). The protons of the six-carbon chain and four-carbon chain in the ^{1}H NMR spectrum of **1** are downfield shifted, which means the 2,6-dihydroxynaphthalene moiety of **1** folds back to form an intramolecular CT complex with viologen moiety inside the cavity of CB[8], as we have discussed earlier (Scheme 1). However, in the presence of 1 equiv of β-CD, the proton signals of naphthalene moiety shift to downfield. This reveals that the β-CD is equipped with naphthalene moiety as reported in our earlier work (Figure 5C).[39] Upon addition of 0.5 equiv of CB[8] to the above mixed solution of the 1:1 complex of **1** with β-CD, both the 1:1 inclusion complex of **1** with β-CD and the 1:1 inclusion complex of **1** with CB[8] were observed (Figure 5D). When an additional 1 equiv of CB[8] was added to the above solution, only the 1:1 inclusion complex of **1** with CB[8] was observed (Figure 5E). The ^{1}H NMR spectrum of Figure 5E is almost identical to that of Figure 5B, meaning that 1.5 equiv of CB[8] can release β-CD from the triad **1** and form the stable1:1 inclusion CT complex (Scheme 2).

Electrochemistry. The electrochemical behavior of triad **1** in acetonitrile exhibits two consecutive one-electron reduction waves. The first wave corresponds to the reversible reduction of MV^{2+} moiety to the radical-cation $MV^{+\bullet}$, whereas the second wave reflects the reversible reduction of $MV^{+\bullet}$ to MV^0 (Figure 6). The redox properties of the triad **1** in aqueous solution (0.1

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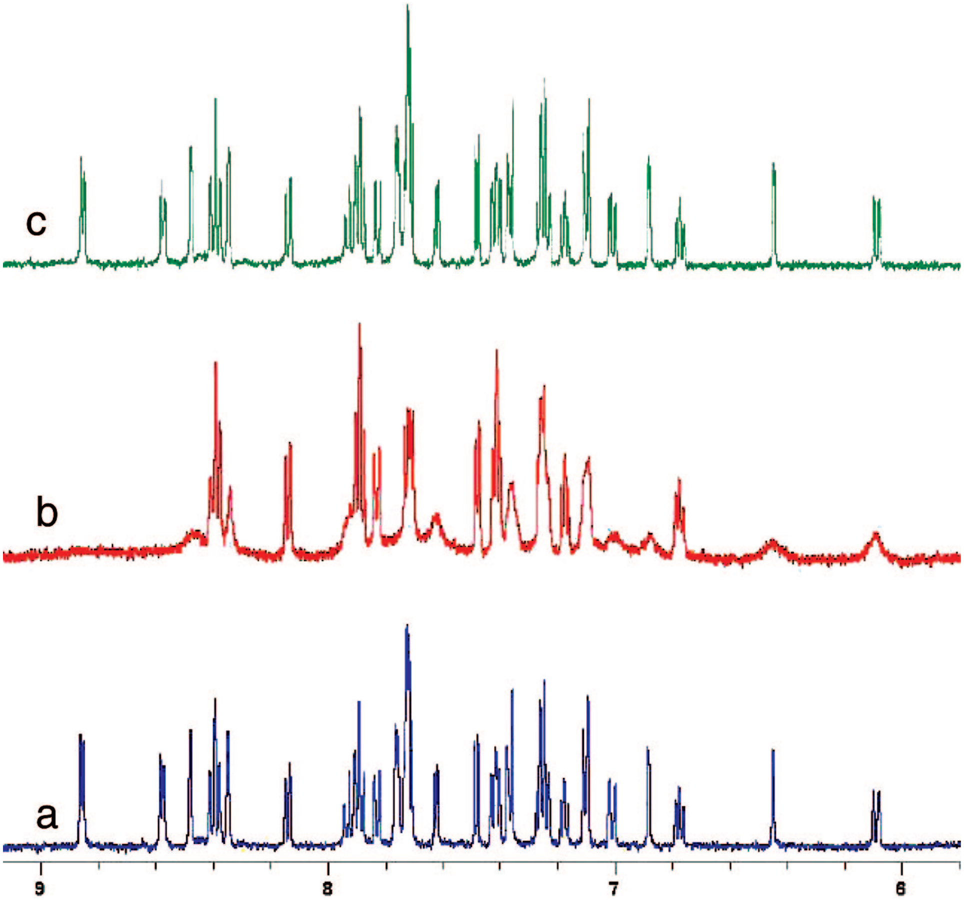

FIGURE 7. ^{1}H NMR (500 MHz, D_2O) of **1**: (a) with TEOA (1:5), (b) after 2 h of light irradiation, and (c) after stopping light irradiation and exposing to air (O_2).

M phosphate buffer (pH 7.0)) were also studied by cyclic voltammetry (CV) (see Supporting Information) and differential pulse voltammetry (DPV). For triad **1** alone, one peak potential at −0.519 V versus Ag/AgCl, corresponding to the reduction of $MV^{2+}/MV^{+\bullet}$, and one peak potential at −0.841 V, corresponding to $MV^{+\bullet}/MV^0$, were observed. By addition of 1 equiv of CB[8] to the solution of triad **1**, the peak potential related to the redox couple $MV^{2+}/MV^{+\bullet}$, $MV^{+\bullet}/MV^0$ appeared at −0.66 and −1.23 V. The half-wave potential ($E_{1/2}$) associated with the oxidation process Ru^{3+}/Ru^{2+} shifts from 1.047 to 1.052 V. This result shows that MV^{2+} moiety in **1** is harder to reduce when it is inserted into the cavity of CB[8], suggesting that the MV^{2+} moiety of **1** is considerably stabilized by CB[8] complexation, while the formation of the 1:1 inclusion complex had less influence on the oxidation potential of the $Ru(bpy)_3$ moiety. This indicates that the electron transfer from the excited state of $Ru(bpy)_3$ moiety to MV^{2+} moiety in **1** becomes slightly harder after the inclusion into CB[8]. The reason why MV^{2+} is harder to reduce is very likely the electron-donating property of the NP moiety in the CT complex within the cavity of CB[8].

Photochemistry. To study the possible photoinduced electron transfer processes in a system containing the triad **1** without the presence of CB[8], an external sacrificial electron donor, triethanolamine (TEOA), was added to the solution of **1**. The light-induced process was followed by ^{1}H NMR. When 5 equiv of TEOA was added, no pronounced chemical shifts are observed in ^{1}H NMR (Figure 7a), indicating that the addition of TEOA does not affect the chemical shifts of the triad **1**. When the NMR tube was degassed with argon and light-irradiated for 2 h, the color of the solution changed to green and the ^{1}H NMR spectrum was taken again. ^{1}H NMR spectral changes have been observed (see Figure 7b). The peaks for the α- and β-protons of the MV moiety shifted outside the normal NMR window due to its radical character, and the peaks for protons of the Np became broad. The peaks for the protons of the substituted bipyridine ligand were also affected, becoming broad. When the light irradiation was stopped and the septum was removed from the NMR tube allowing the air (oxygen) go into the tube, the color of the solution changed back from green to the original orange and the ^{1}H NMR spectrum was restored as shown in Figure 7c. These results strongly support the formation of the Ru^{2+}- $MV^{+\bullet}$ radical in triad **1**. The broadened ^{1}H NMR peaks are due to the paramagnetic effect of the $MV^{+\bullet}$ radical.

To investigate the behavior of $MV^{+\bullet}$ radical in the presence of CB[8], TEOA was added to the 1:1 inclusion complex of **1**+CB[8]. The ^{1}H NMR is shown in Figure 8a. Relative to the ^{1}H NMR spectrum of the 1:1 inclusion complex of **1** and CB[8], no pronounced chemical shifts are observed, indicating that the addition of TEOA does not affect the binding mode of triad **1** with CB[8]. Again, when the NMR tube was degassed with

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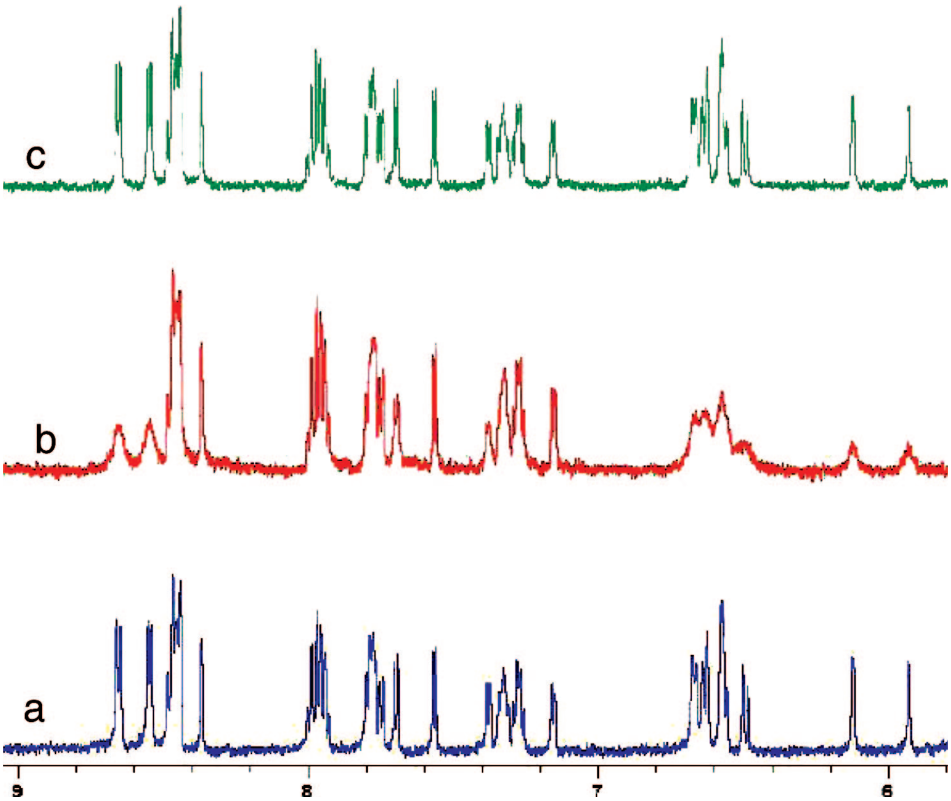


FIGURE 8. ^{1}H NMR (500 MHz, D_2O) of **1**:CB[8] (a) with TEOA (1:1:10), (b) after 3 h of light irradiation, and (c) after stopping light irradiation and exposing to air (O_2).

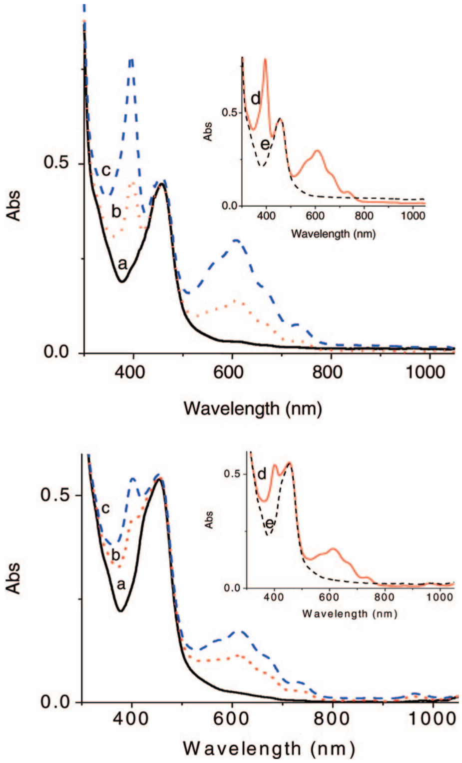
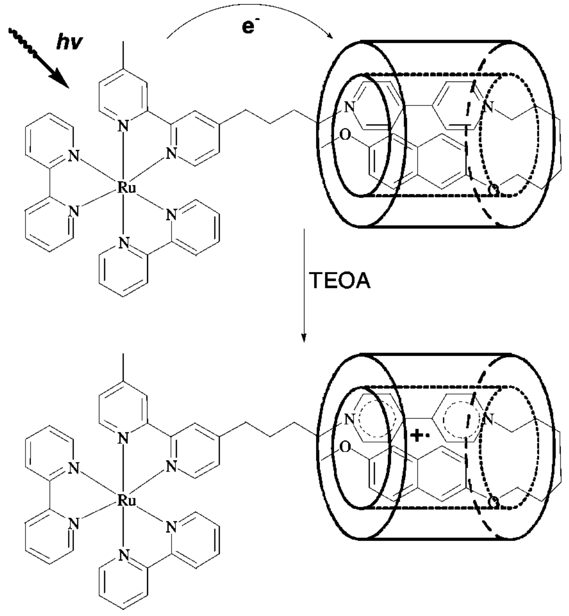


FIGURE 9. Absorption spectra of **1** (4.0×10^{-5} M) and TEOA (5×10^{-2} M) in the absence of CB[8] (top) and in the presence (bottom) of 1 equiv CB[8] (4.0×10^{-5} M): (a) before and (b) after 25 min and (c) after 50 min of light irradiation. Inset: (d) after 50 min of light irradiation, (e) after exposing the cuvette to air (oxygen), the spectral curves return to the original ones.

SCHEME 3. Formation of $MV^{+\bullet}$ Radical in 1:1 Inclusion Complex of 1 + CB[8] after Photoinduced Intramolecular Electron Transfer



argon and irradiated for 3 h with light, the color of the solution changed from brown to dark green; the ^{1}H NMR is shown in Figure 8b. It was found that the peaks related to α- and β-protons for MV^{2+} and protons for the Np moiety became broad. The color of the solution changed back from dark green to brown after exposure of the solution to air, and the ^{1}H NMR spectrum was restored as shown in Figure 8c. These results indicate the formation of Ru^{2+}-$MV^{+\bullet}$ inside the cavity of the CB[8] together with the naphthalene moiety as a partner, which is also supported by the fact that no signals for the $MV^{+\bullet}$ radical dimer inside the cavity of CB[8] was found. In contrast, the formation of $MV^{+\bullet}$ radical dimer inside CB[8] has been observed for a similar complex without naphthalene.[42] The possible explanation of this phenomenon could be that the MV moiety and naphthalene moiety were inserted into the cavity of CB[8], forming a CT complex. In this CT complex, the cavity of CB[8] was occupied by $MV^{+\bullet}$ radical and the naphthalene moiety. There is no room for the second $MV^{+\bullet}$ radical to go into the cavity to form the $MV^{+\bullet}$ radical dimer. This partner radical is so stable that it is impossible for a second $MV^{+\bullet}$ radical to replace the naphthalene moiety in the CB[8] cavity.

A control experiment was performed to support our conclusion. We started the photoirradiation of **1** with TEOA first and then added the CB[8] afterward. ^1H NMR results showed that the same back-folded partner radical inside the CB[8] cavity was observed, indicating that the order of addition of CB[8] before or after the photoirradiation makes no difference for the formation of the charge transfer complex.

The light-induced formation of the stable Ru^{2+}-$MV^{+\bullet}$ radical inside the cavity of CB[8] can be further confirmed by UV−vis absorption as shown in Figure 9. For the aqueous solution of triad **1** and TEOA, two absorption peaks at 399 and 605 nm can be observed after 25 min of irradiation using the same light source as for NMR measurements. These two peaks are due to the formation of free Ru^{2+}-$MV^{+\bullet}$ radical.[26,42] The peak intensity increased as the irradiation time prolonged, and the solution color changed from yellow to dark green (Figure 9 above). The similar phenomenon of color change can be observed as well with addition of 1 equiv of CB[8] into the above-mentioned solution, and the absorption at 401 and 607 nm was observed (Figure 9 bottom). The small red-shifts of peaks can be attributed to the Ru^{2+}- $MV^{+\bullet}$ -Np radical inserted inside the cavity of CB[8]. When the light is turned off and oxygen goes into the cuvette, the initial absorption spectrum can be restored. By comparison of the two systems, we found that the presence of naphthalene moiety inside the CB[8] cavity has no significant effect on the absorption spectrum of $MV^{+\bullet}$ radical; only a weak absorption band appears at ca. 960 nm, which might be related to the interaction between $MV^{+\bullet}$ and the naphthalene partner. The photoinduced electron transfer and the formation of $MV^{+\bullet}$ radical inside the CB[8] are illustrated in Scheme 3.

The mechanism for the above-mentioned photoinduced electron transfer processes can be outlined as follows. Under the irradiation of light, the ruthenium complex **1** was excited to give the excited state *Ru(II)$(bpy)_3$-MV^{2+}-NP, which can transfer an electron intramolecularly to the MV^{2+} moiety, generating Ru(III) and the methylviologen radical $MV^{+\bullet}$, Ru(III)$(bpy)_3$-$MV^{+\bullet}$-NP. However, the back electron transfer from $MV^{+\bullet}$ to the Ru(III) is too fast to be able to observe any change in the NMR spectrum. In the presence of an electron donor TEOA, Ru(III) can be reduced to Ru(II) by oxidation of TEOA, and therefore the back electron transfer from $MV^{+\bullet}$ to Ru(III) is inhibited; thus a stable $MV^{+\bullet}$ radical is formed. Before irradiation, inside the cavity of CB[8], Np moiety as a donor and MV^{2+} moiety as a receptor can form a CT complex. After irradiation, the electron is transferred from *Ru(II)$(bpy)_3$ to the CT complex CB[8](MV^{2+}-NP), forming the charge separated state Ru(III)$(bpy)_3$-CB[8]($MV^{+\bullet}$-NP), followed by the reduction of Ru(III) with TEOA. However, the $MV^{+\bullet}$ radical formation is harder in the presence of CB[8] than with complex **1** alone, due to the more negative reduction potential of MV^{2+} moiety inside the CB[8] cavity caused by the electron donor effect of Np moiety in the CT complex.

Conclusion

Molecular triad **1** can form a stable 1:1 inclusion complex with CB[8] in aqueous solution through a back-folding of the Ru$(bpy)_3$-terminated viologen-naphthalene guest molecule. The formation of this stable 1:1 inclusion complex has been demonstrated by ^1H NMR, ESI-MS, and UV−vis titration. The selective binding among the Ru$(bpy)_3$-MV^{2+}-Np (**1**) guest and CB[8] and β-CD hosts has also been investigated. A self-sorting system is found in which the β-CD can be released from the Np moiety by the addition of CB[8]. Upon light irradiation, a monomeric $MV^{+\bullet}$ radical is formed accompanied by a naphthalene moiety within the triad **1**. This "partner radical" has an absorption spectrum very similar to that of the $MV^{+\bullet}$ radical alone from triad **1**. The formation and behaviors of the 1:1 inclusion complex of the photoactive molecular triad **1** with CB[8] provides basic understanding for the future design of more advanced systems. Further studies on molecular switches from related systems driven by light are in progress in our laboratory.

Experimental Section

General. NMR spectra were obtained on a 500 MHz spectrometer, using TMS as internal standard. High resolution mass spectrometry (HRMS) was performed on a Q-Tof mass spectrometer. Absorption spectra were recorded on a HR2000 high-resolution miniature fiber optic spectrometer. For photochemistry, a multimedia mobile LCD project was used for the light source. Cyclic voltammetry was carried out with a three-compartment cell connected to an Autolab potentiostat with a GPES electrochemical interface. The working electrode was a freshly polished glassy carbon disk (diameter 3 mm). The counter electrode was a platinum wire. Potentials were measured versus a nonaqueous Ag/Ag^+ reference electrode (10 mM $AgNO_3$ in acetonitrile). Solutions were prepared from dry acetonitrile containing 1 mM of the analyte and 0.1 M tetrabutylammonium hexafluorophosphate (electrochemical grade, dried at 373 K for 48 h) as supporting electrolyte. Before all measurement, oxygen was removed by bubbling the solutions for 20 min with solvent-saturated argon, and the samples were kept under argon atmosphere during measurement. In water solution the counterions used were Cl^-, the reference electrode was Ag/AgCl in KCl, and the supporting electrolyte was a pH 7 phosphate buffer solution.

Materials. Triad **1** and ligand **2** were synthesized according to the literature procedure.[40] Other materials and solvents employed were commercially available and used as supplied without further purification.

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Supporting Information Available: Additional ^1H NMR, COSY, UV−vis spectra, and electrochemical data are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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