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pH-Controlled Photoinduced Electron Transfer in the $[(Mo_6Cl_8)L_6]$− Calix[4]resorcine−Dimethylviologen System

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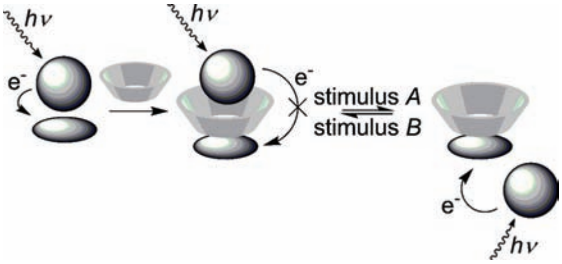
ABSTRACT



A pH-controlled photoinduced electron transfer in the supramolecular system $[(Mo_6Cl_8)L_6]$−calix[4]resorcine−dimethylviologen is reported.

Creation of donor−acceptor molecular systems capable of photoinduced electron transfer is very important because of their potential application in the construction of advanced nanostructured photodevices.[1] Molecular systems with covalently linked ensembles of donor and acceptor moieties have been extensively investigated. Recently, increasing attention is being paid to the development of systems with noncovalently assembled donor−acceptor arrays similar to photobiological systems.[1] In noncovalently linked molecular systems the change in the assembly leads to significant changes in the photoinduced electron transfer processes.[2] A. W. Maverick and H. B. Gray have demonstrated that dimethylviologen (**MV^{2+}**) quenches the luminescence of a cluster anionic complex $[Mo_6Cl_{14}]^{2-}$ by the electron transfer from the excited state of the metal cluster to the **MV^{2+}**.[3] We assumed that the addition of a ditopic receptor capable of the reversible binding of both **MV^{2+}** and $[Mo_6Cl_{14}]^{2-}$ by two

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(1) (a) Wang, M.-Sh.; Xu, G.; Zhang, Z.-J.; Guo, G.-C. *Chem. Commun.* **2010**, *46*, 361. (b) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435. (c) Kim, J. S.; Quang, D. T. *Chem. Rev.* **2007**, *107*, 3780. (d) Cooke, M. W.; Hanan, G. S. *Chem. Soc. Rev.* **2007**, *36*, 1466. (e) Aratani, N.; Kim, D.; Osuka, A. *Acc. Chem. Res.* **2009**, *42*, 1922. (f) Younfblood, W. J.; Lee, S.-H. A.; Maeda, K.; Mallouk, T. E. *Acc. Chem. Res.* **2009**, *42*, 1966. (g) Saha, S.; Stoddart, J. F. *Chem. Soc. Rev.* **2007**, *36*, 77. (h) Balzani, V.; Credi, A.; Venturi, M. *ChemSusChem.* **2008**, *1*, 2. (i) Akiyama, T.; Nitahara, S.; Inoue, S.; Yamada, S. *Photochem Photobiol. Sci* **2004**, *3*, 26. (j) Nishikitani, Y.; Uchida, S.; Asano, T.; Minami, M.; Oshima, S.; Ikai, K.; Kubo, T. *J. Phys. Chem. C* **2008**, *112*, 4372.

(2) (a) D'Souza, F.; Ito, O. *Chem. Commun.* **2009**, 4913. (b) Ferrer, B.; Rogez, G.; Credi, A.; Ballardini, R.; Gandolfi, M. T.; Balzani, V.; Liu, Y.; Tseng, H.-R.; Stoddart, J. F. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 18411. (c) Pellegrin, Y.; Forster, R. J.; Keyes, T. E. *Inorg. Chim. Acta* **2009**, *362*, 1715.

(3) (a) Maverick, A. W.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 1298. (b) Maverick, A. W.; Najdzionek, J. S.; MacKenzie, D.; Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1878.

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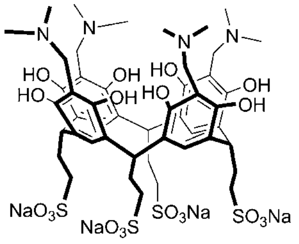
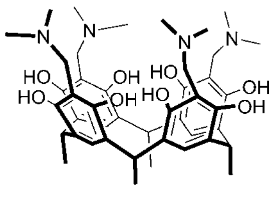
different binding sites results in a reversible separation of the ion pair formed by $\mathbf{MV}^{2+}$ and $[Mo_6Cl_{14}]^{2-}$ and, thus, in making the electron transfer process difficult to perform. Moreover, the changes in the receptor binding properties under external stimuli leads to the release of one of the guests with the following repeated formation of the ion pair capable of the electron transfer process. A pH-switchable derivative of resorcinarene, **1**, with sodium sulfonatoethylene groups on the lower rim and aminoalkylated moieties on the upper rim has been chosen as a ditopic receptor (Scheme 1).[4] Herein, we report a novel three-component supramolecular system composed of the metal cluster $[(Mo_6Cl_8)L_6]^n$ ($L = Cl^-, H_2O, OH^-$),[5] the acceptor $\mathbf{MV}^{2+}{\bullet}2Cl^-$, and the resorcinarene **1** designed for a pH-controlled, photoinduced electron transfer. In acid and neutral aqueous media (pH 2−7), the resorcinarene **1** separates the ion pair $\mathbf{MV}^{2+}{\bullet}[Mo_6Cl_{14}]^{2-}$ through the interaction of the negatively charged lower rim of **1** with the positively charged $\mathbf{MV}^{2+}$ and the protonated aminoalkylated groups of the upper rim with the negatively charged metal cluster. The increase of pH media leads to the deprotonation of the aminoalkylated groups and to the release of the metal cluster from the upper rim of **1** (Scheme 2). In this molecular system as compared to literature analogues, a pH-induced change in the distance between the donor and acceptor of the ion pair forces the photoinduced electron transfer process.

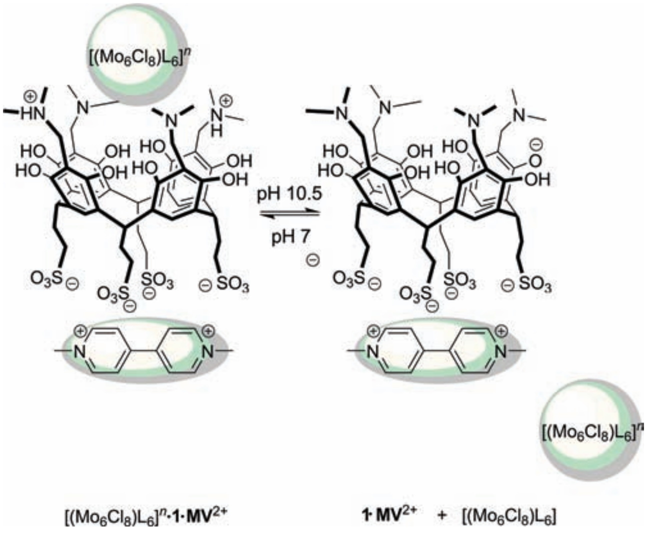
Scheme 1. Calix[4]resorcines **1** and **2**





1 **2**

Scheme 2



Irradiation of an aqueous solution (pH 7) of the mixture $\mathbf{MV}^{2+} + [(Mo_6Cl_8)L_6]^n$ (1:1) at 365 nm in the presence of 20% MeOH (as a sacrificial agent) results in the reduction of $\mathbf{MV}^{2+}$ to cation-radical form $\mathbf{MV}^{+\bullet}$ as evidenced by UV−vis spectroscopy (Figure 1a(A)). The electron transfer from $[Mo_6Cl_{14}]^{2-}$ to $\mathbf{MV}^{2+}$ has been previously investigated.[3]

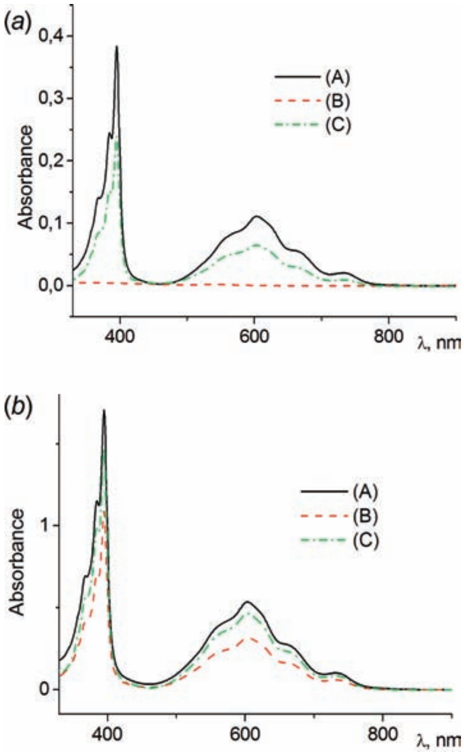


Figure 1. (a, b) UV spectra after 30 min of irradiation at 365 nm of (A) $[(Mo_6Cl_8)L_6]^n + \mathbf{MV}^{2+}$; (B) $[(Mo_6Cl_8)L_6]^n + \mathbf{MV}^{2+} + \mathbf{1}$; (C) $[(Mo_6Cl_8)L_6]^n + \mathbf{MV}^{2+} + \mathbf{2}$ in 20% MeOH aqueous solution at pH 7 (a) and pH 10.5 (b) ($C = 0.05$ mM; the solutions before irradiation were used as a blank reference; the spectra are recorded 10−15 s after irradiation).

In the presence of 1 equiv of **1**, irradiation for 30 min or more does affect the noticeable spectral changes, indicating the absence of the formation of $\mathbf{MV}^{+\bullet}$ (Figure 1a(B)).[6] The

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[4] Korshin, D. E.; Kashapov, R. R.; Murtazina, L. I.; Mukhitova, R. K.; Kharlamov, S. V.; Latypov, Sh. K.; Ryzhkina, I. S.; Ziganshina, A. Y.; Konovalov, A. I. *New J. Chem.* **2009**, *33*, 2397.

[5] $(H_7O_3)_2[(Mo_6Cl_8)Cl_6]$ was used in the experiments. Two axial chloride ions of the metal cluster can be replaced by H_2O and OH^- in aqueous media. They are substituted by H_2O in a neutral aqueous solution and by OH^- in alkaline media. The Mo_6Cl_8 core is unaffected by pH media. The substitution of the axial Cl^- does not efficiently influence the photochemical properties of the metal cluster. (a) Sheldon, J. C. *Nature* **1959**, *184*, 1210. (b) Sheldon, J. C. *J. Chem. Soc.* **1960**, 1007. (c) Adamenko, O. A.; Lukova, G. V.; Golubeva, N. D.; Smirnov, V. A.; Boiko, G. N.; Pomogailo, A. D.; Uflyand, I. E. *Dokl. Phys. Chem.* **2001**, *381*, 275.

[6] During prolonged irradiation of the solution of $\mathbf{MV}^{2+}$ as such and the complex $\mathbf{1}{\bullet}\mathbf{MV}^{2+}$ at pH 7−11, formation of the cation-radical $MV^{+\bullet}$ was not observed either.

difficulty of the photoreduction of **MV**$^{2+}$ is due to the binding and separation of $[(Mo_6Cl_8)L_6]^n$ and **MV**$^{2+}$ by **1**, thus, preventing the electron transfer process. The ion pair **MV**$^{2+}$•$[(Mo_6Cl_8)L_6]^n$ has poor solubility in aqueous media (pH 2−7), but the solubility visibly increases after the addition of **1**. According to NMR and UV−vis data $[(Mo_6Cl_8)L_6]^n$, **MV**$^{2+}$, and **1** form a three-component 1:1:1 supramolecular complex in acid and neutral aqueous media. In the UV−vis spectrum of the solution of $[(Mo_6Cl_8)L_6]^n$ (pH 2), the addition of **1** as such or the mixture of **1** + **MV**$^{2+}$ decreases the intensity of the absorption bands of the metal cluster at 300−350 nm (Figure 2a). This indicates the complex formation between **1** and $[(Mo_6Cl_8)L_6]^n$ both in the presence and in the absence of **MV**$^{2+}$. The stability constant (log *K*) of the 1: 1 complex between $[(Mo_6Cl_8)L_6]^n$ and **1** determined by UV−vis spectroscopic titration is 4.9 ± 0.3 (pH 2) (see Supporting Information, Figure S1(a, b)).[7] The upfield shift of the proton signals of **MV**$^{2+}$ by adding the complex **1**•$[(Mo_6Cl_8)L_6]^n$ in the NMR spectra (pD 7) confirms the binding of **MV**$^{2+}$ by **1** in the presence of the metal cluster (Figure 2b). **MV**$^{2+}$ forms a stable 1:1 complex with **1** at pH 7 as noted by UV−vis and NMR spectroscopies. The stability constant (log *K*) for the complex **1•MV**$^{2+}$ is 4.2 ± 0.2 (pH 7) (see Supporting Information, Figure S2(a,b)).[7]

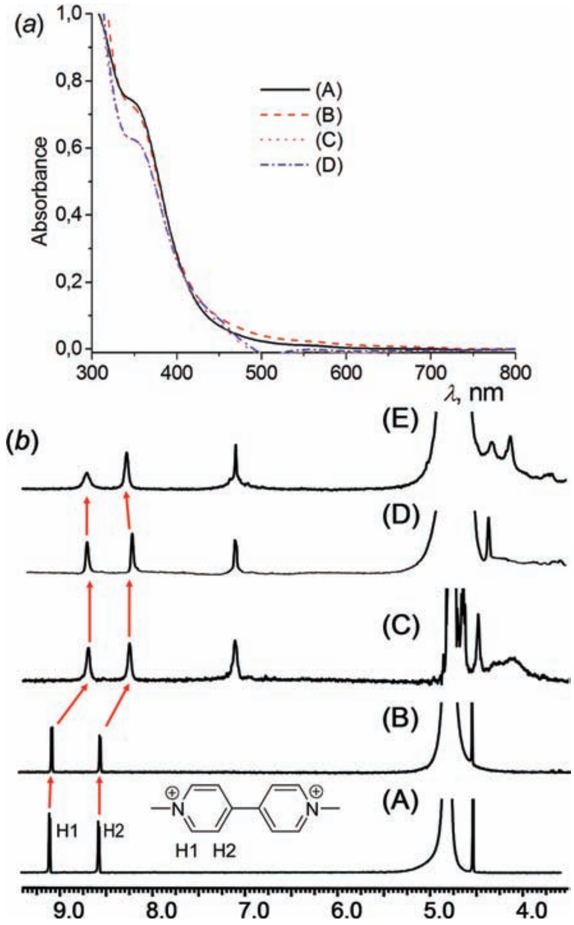

Figure 2. (a) UV spectra of (A) $[(Mo_6Cl_8)L_6]^n$; (B) $[(Mo_6Cl_8)L_6]^n$ + **MV**$^{2+}$; (C) $[(Mo_6Cl_8)L_6]^n$ + **1**; (D) $[(Mo_6Cl_8)L_6]^n$ + **MV**$^{2+}$ + **1** in 20% MeOH aqueous solution (pH 2, $C = 0.33$ mM; in (C, D) a calixarene **1** solution was used as a blank reference); (b) ^{1}H NMR spectra of (A) **MV**$^{2+}$; (B) $[(Mo_6Cl_8)L_6]^n$ + **MV**$^{2+}$; (C) **MV**$^{2+}$ + **1**; (D, E) $[(Mo_6Cl_8)L_6]^n$ + **MV**$^{2+}$ + **1** (CD_3OD/D_2O (1/5); $C = 1$ mM; (A−D) pD 7; (E) pD 10.5).

Irradiation of the binary system with 1 equiv of $[(Mo_6Cl_8)L_6]^n$ and 2 equiv of **MV**$^{2+}$ doubles the formation of the cation radical **MV**$^{+•}$ (see Supporting Information, Figure S3a). In the three-component system with 1 equiv of the mixture ($[(Mo_6Cl_8)L_6]^n$ + **1**) and 2 equiv of **MV**$^{2+}$, irradiation induces the reduction of the viologen unbounded with **1** (see Supporting Information, Figure S3b). Thus, the metal cluster complexed with **1** is able to transfer the electron to the free **MV**$^{2+}$ reducing it.

Earlier, it has been demonstrated that **1** self-assembles in aqueous media by the electrostatic interaction of the upper and lower rims of **1**.[4] The binding of **MV**$^{2+}$ by **1** results in the destruction of the self-assemblies formed by **1** as evident from UV−vis spectroscopy data (see Supporting Information, Figure S4(a,b)). Thus, the experimental data clearly demonstrate that the resorcinarene **1** separates the ion pair **MV**$^{2+}$•$[(Mo_6Cl_8)L_6]^n$ and, therefore, blocks the electron transfer from the excited state of the metal cluster to **MV**$^{2+}$ (Scheme 1).

The increase of pH media (to pH 10.5) leads to the deprotonation of the upper rim of **1** and to the release of the metal cluster. Indeed, according to UV−vis and NMR spectroscopy data, **1** binds **MV**$^{2+}$ but not $[(Mo_6Cl_8)L_6]^n$ in alkaline media. The addition of **1** to the $[(Mo_6Cl_8)L_6]^n$ solution (pH 10.5) does not affect the UV−vis spectrum of the metal cluster. The NMR signals for the **MV**$^{2+}$ protons are shifted upfield upon addition of **1** indicating the formation of the complex (Figure 2b). There is little change in the ^{1}H NMR spectrum of **1•MV**$^{2+}$ after the addition of $[(Mo_6Cl_8)L_6]^n$ which serves to support that there is no influence of the metal cluster on the binding of **MV**$^{2+}$ by **1** in alkaline media. The unbound metal cluster $[(Mo_6Cl_8)L_6]^n$ is once again able to transfer the electron from its excited state to **MV**$^{2+}$. After 30 min of irradiation (365 nm) of the solution of the ternary system $[(Mo_6Cl_8)L_6]^n$ + **1** + **MV**$^{2+}$ (pH 10.5), the characteristic absorption bands of the cation-radical **MV**$^{+•}$ appear in the UV spectrum which confirms the electron transfer from the metal cluster to **MV**$^{2+}$ (Figure 1b(B)). In the binary system $[(Mo_6Cl_8)L_6]^n$ + **MV**$^{2+}$ without **1**, a similar UV−vis spectrum but with a greater absorption was observed (Figure 1b(A)). Apparently, the negatively charged lower rim of **1** shields **MV**$^{2+}$ from the approach of the metal cluster that results in the slower reduction of **MV**$^{2+}$ in the presence of **1**. Also, a small amount of the metal cluster is probably still bound with calixarene at pH 10.5. The formation of a smaller amount of the cation-radical **MV**$^{+•}$ at pH 7, as compared to pH 10.5, is due to \the sacrificial agent (MeOH) being weaker in neutral media and is due to the decreased solubility of $[(Mo_6Cl_8)L_6]^n$ at pH 7.

Irradiation of the **MV**$^{2+}$•$[(Mo_6Cl_8)L_6]^n$ solution in the presence of a calixarene without a negatively charged lower

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(7) Kuzmic, P. *Anal. Biochem.* **1996**, *237*, 260.

rim **2**[8] (Scheme 1) results in the cation-radical formation both at pH 7 and at pH 10.5 (Figure 1a,b(C)). Thus, the results clearly demonstrate that only the binding of both pieces of the ion pair with two different binding sites, and therefore their separation, causes the blocking in the electron transfer process. The binding of only one component of the ion pair (in the systems **2**•$[(Mo_6Cl_8)L_6]^n$ or **1**•**MV**$^{2+}$ at pH 10.5) does not lead to a significant blockage in the electron transfer process.

Although the system $[Mo_6Cl_{14}]^{2-}$ + **MV**$^{2+}$ has been studied before,[3] further research is needed to clarify the mechanism of the photoinduced electron transfer process in this system. We are currently working on such a mechanism.

In conclusion, it has been shown, that the designed supramolecular system $[(Mo_6Cl_8)L_6]^n$•**1**•**MV**$^{2+}$ is able to achieve a pH-controlled photoinduced electron transfer from the excited state of the metal cluster $[(Mo_6Cl_8)L_6]^n$ to **MV**$^{2+}$ followed by its reduction to the cation-radical **MV**$^{+\cdot}$.

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Supporting Information Available: Experimental procedures and UV spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) (a) Matsuskita, J.; Matsui, T. *Tetrahedron Lett.* **1993**, *46*, 7433. (b) Morozova, Y. E.; Kuznetzova, L. S.; Mustafina, A. R.; Kazakova, E. Kh.; Morozov, V. I.; Ziganshina, A. Y.; Konovalov, A. I. *J. Inclusion Phenom. Macrocycl. Chem.* **1999**, *35*, 397.