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Reversible Light-Driven Redox Switching of Multifunctional Dipolar Ruthenium(III/II) Pentaammine(4,4′-bipyridinium) Complexes

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The achievement of multifunctional molecular switches is of paramount interest in the growing field of molecular electronics.[1,2] Dipolar ruthenium(II) ammine complexes of 4,4′-bipyridinium (bpy) ligands possess unique characteristics as multifunctional redox switches.[3] Actually, the reversible chemical oxidation of these complexes is accompanied by a dramatic change of their linear and nonlinear optical properties. While $\mathrm{Ru^{II}}$ complexes possess distinct linear (absorption maxima in the 580−640 nm region) and nonlinear optical features associated with the their intense, low-energy metal-to-ligand charge-transfer (MLCT) electronic transitions, $\mathrm{Ru^{III}}$ analogues are transparent in the whole visible region and possess negligible second-order optical nonlinearity.[4] In addition, we have recently demonstrated that self-assembled monolayers of these $\mathrm{Ru^{III/II}}$ complexes on an optically transparent metal electrode can be reversibly switched chemically.[5]

Light is a very appealing trigger to switch molecular properties. Its easy manipulation makes light-controlled molecular switches ideally suited to molecular electronics.[2] Indeed, a large variety of examples is reported in the literature.[1] The goal of the present study is the light-controlled, reversible redox switching of multifunctional dipolar $[\mathrm{Ru^{III/II}(NH_3)_5}$-*N*-methyl-4,4′-bipyridinium$](\mathrm{PF_6})_n$ ($\mathbf{1^{III/II}}$) complexes.[6] This represents a difficult task, because photoinduced processes involving $\mathrm{Ru^{III/II}}$ ammine complexes are, in principle, precluded due to their photolability. In fact, $\mathrm{Ru^{III/II}}$ ammine complexes of pyridine and related ligands give photosubstitution in both aqueous solution and nonaqueous solvents.[7] Analogously, the direct or sensitized photoexcitation of $\mathbf{1^{II}}$ leads to photodegradation.[8] To circumvent this problem, we have thus explored alternative strategies.

We report here on the reversible redox photoswitching of $\mathbf{1^{III/II}}$ complexes, which represents the first example of a multifunctional molecular switch involving dipolar metal complexes, having both linear and nonlinear optical properties, exclusively controlled by light.[9] The approach is sketched in Scheme 1. It implies a two-phase (water/benzene) system in which $\mathbf{1^{II/III}}$ salts are soluble only in the water phase. Noteworthy features include (i) photooxidation of $\mathbf{1^{II}}$ by a phenoxy radical generated upon 254 nm irradiation of phenol (PhOH) in the water phase; (ii) photoreduction of $\mathbf{1^{III}}$ at water/benzene interface by irradiation at 528 nm of zinc tetraphenyl porphyrin (ZnTPP) in the benzene phase. The above features, within proper experimental conditions (vide infra), avoid either the direct or sensitized photoexcitation of $\mathbf{1^{III/II}}$ complexes and, hence, any photodegradation. The processes involved in our proposed scheme are described as follows.

Photooxidation Route. This step was photoinitiated by PhOH (5×10^{-3} M), which is in large excess with respect to $\mathbf{1^{II}}$ (10^{-5} M). Under these experimental conditions the 254 nm irradiation of the water compartment leads to the selective excitation of PhOH, which absorbs almost all incident photons (≥95%), thus preventing any significant direct excitation of $\mathbf{1^{II}}$.

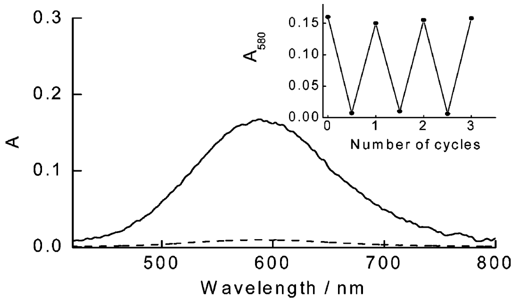
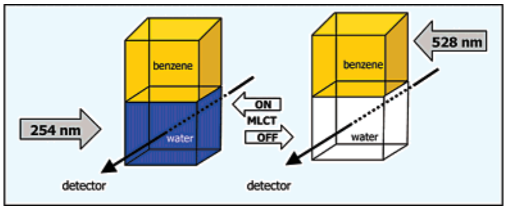
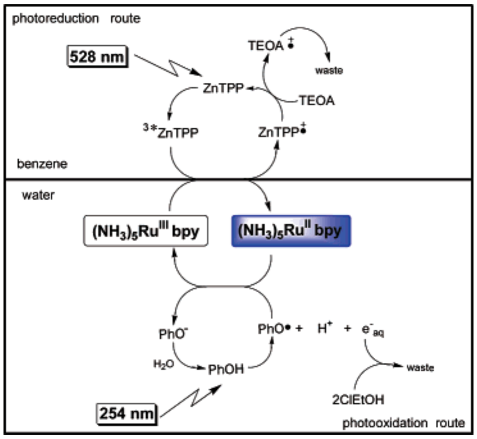


Figure 1. Absorption spectra of **1** in the water phase (—) before and (- - -) after 5 min of 254 nm irradiation. The inset shows the redox-switching of the absorbance maximum (monitored at 580 nm) upon consecutive cycles of 254 and 528 nm irradiation.

Scheme 1



Scheme 2



As displayed in Figure 1, the disappearance of the MLCT optical absorption band is observed after 5 min of steady-state irradiation, according to the oxidation of $\mathbf{1^{II}}$ to the $\mathbf{1^{III}}$ counterpart. The photooxidation route can be explained through the mechanism illustrated in Scheme 2. It is well established that UV irradiation of aqueous solutions of PhOH leads to the formation of hydrated electrons ($\mathrm{e^-_{aq}}$) and phenoxy radicals ($\mathrm{PhO^\bullet}$).[10] $\mathrm{PhO^\bullet}$ offers appropriate thermodynamic and kinetic prerequisites as oxidizing species of $\mathbf{1^{II}}$. Actually, its reduction potential ($E^\circ_{\mathrm{PhO^\bullet/PhO^-}} = +0.72$ V vs SCE),[11] higher than that of $\mathbf{1^{II}}$ ($E^\circ_{\mathbf{1}^{\mathrm{III/II}}} = 0.46$ vs SCE),[4] and its decay on a sufficiently long time scale (hundreds of μs)[12] make feasible the quenching of $\mathrm{PhO^\bullet}$ by $\mathbf{1^{II}}$ through an electron-transfer pathway. Moreover, the presence of an efficient scavenger

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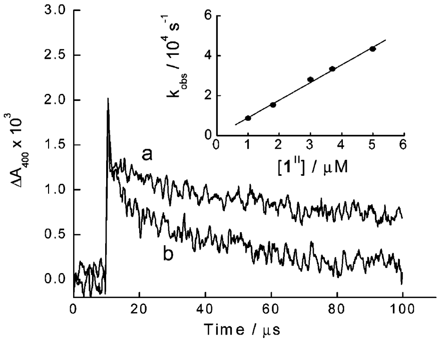

Figure 2. Kinetic traces for the decay of PhO$^\bullet$ observed upon 266 nm laser excitation of PhOH (1×10^{-3} M in aqueous solution) (a) in the absence and (b) in the presence of $\mathbf{1^{II}}$ (3 μM). The faster components of the decay traces are due to ^{3}*PhOH, whose absorption is superimposed to that of PhO$^\bullet$.[15] The inset shows the plot for the quenching of PhO$^\bullet$ by $\mathbf{1^{II}}$.

of hydrated electrons, such as 2-chloroethanol (2ClEtOH),[13] prevents the back reduction of $\mathbf{1^{III}}$ during the steady-state illumination. Noteworthy, the electron transfer between $\mathbf{1^{II}}$ and PhO$^\bullet$ not only switches off the MLCT optical absorption of $\mathbf{1^{II}}$ but also offers the advantage of restoring the starting PhOH (see Scheme 2).[14]

The proposed mechanism is substantiated by complementary nanosecond laser flash photolysis studies in which the PhO$^\bullet$ decay was directly monitored at 400 nm (PhO$^\bullet$ absorption maximum).[12] As shown in Figure 2, PhO$^\bullet$ is efficiently quenched by addition of $\mathbf{1^{II}}$, with a diffusion-controlled bimolecular rate constant ($k_q = 8.5 \times 10^9$ M^{-1} s^{-1}) (see inset Figure 2).

Finally, note that PhOH excited triplet state (^{3}*PhOH), also generated upon UV irradiation, is unable to sensitize photoexcitation of $\mathbf{1^{II}}$ despite the favorable energetics.[15] In fact, under our experimental conditions, ^{3}*PhOH is too short-lived (less than 1 μs)[16] to be quenched by $\mathbf{1^{II}}$. This is supported by the lack of any significant effect of $\mathbf{1^{II}}$, up to 10^{-5} M, on the ^{3}*PhOH kinetic decay.

Photoreduction Route. Photoreduction of $\mathbf{1^{III}}$ was achieved by 528 nm irradiation of ZnTPP (10^{-5} M), which is soluble only in the benzene phase. Visible irradiation of the organic compartment offers the advantage of selectively exciting ZnTPP, thus preventing any direct absorption by $\mathbf{1^{II}}$ while restoring. The photoreduction route makes use of the well-known properties of porphyrins to undergo interfacial electron-transfer reactions with coreactants dissolved in a different phase.[17] In our case, ZnTPP presents suitable prerequisites[18] for a cross-phase photoinduced electron transfer to $\mathbf{1^{III}}$. In fact, the high quantum yield (ca 0.9) of the ZnTPP excited triplet state (^{3}*ZnTPP) photogeneration, its reduction potential ($E^\circ_{\text{ZnTPP}^{\bullet+}/^{3*}\text{ZnTPP}} = -0.55$ vs SCE), much lower than that of $\mathbf{1^{III}}$ ($E^\circ_{\mathbf{1}^{\text{III/II}}} = 0.46$ vs SCE),[4] and its sufficiently long lifetime (ca 1 ms) make feasible the quenching of ^{3}*ZnTPP by $\mathbf{1^{III}}$. According to this view, the complete restoration of the MLCT absorption of $\mathbf{1^{II}}$ is observed after ca. 60 min irradiation of the benzene phase. Although we detected the typical decay signal of ^{3}*ZnTPP at 470 nm by laser flash photolysis measurements, it was not possible to get any reliable evidence for the above quenching process under our experimental conditions.[19] However, the mechanism illustrated in Scheme 2 is supported by the effect of triethanolamine (TEOA) (1 mM) added as a sacrificial electron donor. In fact, no significant degradation of ZnTPP is observed in the presence of TEOA during the photoreduction route. As is well documented,[20] reactions between TEOA and oxidized zinc porphyrins take place very rapidly due to the favorable energetics. In our case, the reaction between ZnTPP$^{\bullet+}$ and TEOA not only prevents the potential back electron-transfer processes but also restores the starting ZnTPP, thus minimizing undesired side reactions.

The suitability of the proposed scheme to achieve the reversible molecular switching of $\mathbf{1^{II/III}}$ complexes was tested by consecutive phototriggered redox cycles. As displayed in the inset of Figure 1, the disappearance/restoration of the MLCT absorption band provides direct evidence that a reversible redox switching occurs.

In summary, we have shown the first example of a molecular switch of multifunctional dipolar $(NH_3)_5Ru^{III/II}$bpy complexes, exclusively driven by light. The adopted strategy allowed the photocontrolled redox switching of such photolabile systems, otherwise not feasible by their direct or sensitized photoexcitation. Such a strategy might represent a general method to accomplish the redox switching of photolabile species. Moreover, the two-phase approach is also of relevance in the perspective of photocontrolled, $Ru^{III/II}$-based self-assembled monolayer molecular switches.[21]

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Supporting Information Available: Details of experimental procedures and laser flash photolysis experiments (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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