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Photosensitized production of doubly reduced methylviologen followed by highly efficient methylviologen radical formation using self-assembling ruthenium(II) complexes

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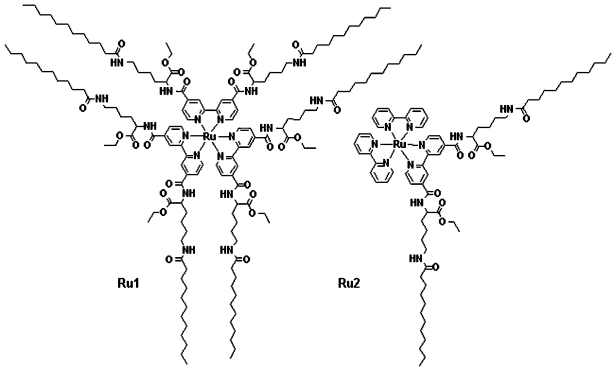
Supramolecular fibers of Ru(II) complexes act as efficient photosensitizers, photochemically generating methylviologen radical ($MV^{\cdot+}$) and then converting it quantitatively to doubly reduced methylviologen, (MV^0), in the presence of triethanolamine.

Viologens, which are 1,1′-disubstituted-4,4′-bipyridinium(II) dications, have been recognized as useful compounds for their electrochromic, photochromic, radical generation, and reversible electron transport properties.[1] Viologens have three common oxidation states with distinct colors: the colorless dication (2+), the generally blue-colored radical cation (+), and the ruddy brown doubly reduced viologen (0). The viologen radical cation is a strong reducing agent, and has been used as an electron relay molecule for many photochemical reactions.[1–8] In contrast, few applications of the doubly reduced viologen (0) species in chemical reactions have been reported;[9] nevertheless, its existence and electrochemical properties are well-known. Doubly reduced viologens are prepared by bulk electrolysis,[10] by chemical reduction using appropriately strong reducing agents such as magnesium metal, sodium metal,[11] as well as by direct photolysis of cyanophenylviologen embedded in a PVA matrix.[1a] Because the doubly reduced viologens are highly reactive in solution, they can potentially be useful as two-electron reducing agents in chemical, electrochemical, and photochemical reactions. Futher, because they are uncharged and lipophilic, doubly reduced viologens are interesting electron transfer mediators for micellar and vesicular electron transport chains.[12] Neutral, doubly reduced charge carriers such as hydroquinones are important in vesicular proton pumps,[13] and doubly reduced viologens, which are analogous photoreduction products, are formed by conproportionation of singly reduced viologens in some micellar systems.[14] In these media, however, they are generally formed in such low concentrations that their presence must be inferred indirectly. To our knowledge, there are as yet no reports of photosystems that quantitatively produce doubly reduced viologens from the fully oxidized dications.

The methylviologen radical ($MV^{\cdot+}$) is easy to produce photochemically using ruthenium(II) polypyridyl photosensitizers in the presence of suitable sacrificial electron donors. In most cases, the experiments are performed using a large excess of methylviologen (MV^{2+}) because quenching of the sensitizer excited state is inefficient at very low MV^{2+} concentration. In addition, the strong absorbance of the $MV^{\cdot+}$ radical cation at 600 and 400 nm makes it difficult to detect doubly reduced methylviologen (MV^0) spectrophotometrically at high viologen concentrations. We describe here the photosensitized production of MV^0 using self-assembling Ru(II) photosensitizers (**Ru1** and **Ru2**). These photosensitizers, which assemble to form nanoscale fibers in certain organic solvents, are good photosensitizers and reduce methylviologen at a substantially higher rate than $Ru(bpy)_3^{2+}$ at low concentrations.[15]

Photochemical reactions were carried out in methanol–toluene (1:1 v/v). A spectroscopic cell (1 cm × 1 cm) containing 1.2×10^{-5} M Ru(II) photosensitizers, 5.0×10^{-5} M $MV^{2+}(PF_6^-)_2$, and 0.1 M triethanolamine (TEOA) was irradiated using a 300 W Xe lamp (ORIEL 500 W Xe and Hg/Xe arc lamp supply model 68811, ORIEL Co.) equipped with a UV cutoff filter (λ > 440 nm). Prior to the measurements, oxygen was expelled by bubbling argon into the solution for 15 min.



When the solutions were irradiated by visible light, the color changed from yellow–orange to red–brown *via* blue. Fig. 1 shows UV–Vis absorption spectral changes for **Ru1** (A) and **Ru2** (B) under visible light irradiation. During the reaction, the absorption bands of $MV^{\cdot+}$ at 605 and 398 nm very quickly increased, and then the absorbance at 605 nm decreased. In addition, a new absorption band at 378 nm appeared and progressively increased. Under the same conditions, the $Ru(bpy)_3^{2+}$ photosensitizer gave very little change in the color to blue, indicating that formation of $MV^{\cdot+}$ was much less efficient than with **Ru1** or **Ru2**. The concentrations of $MV^{\cdot+}$ formed after light irradiation for 3 s, calculated from absorbances at 605 nm (ε = 13400 M^{-1} cm^{-1}) and 398 nm (ε = 42000 M^{-1} cm^{-1}),[16] are 4.3×10^{-5} M for **Ru1** and 3.4×10^{-5} M for **Ru2**: these correspond to conversion of *ca.* 86 and 78% of MV^{2+} to $MV^{\cdot+}$ for **Ru1** and **Ru2**, respectively, in three seconds. The initial rate of formation of $MV^{\cdot+}$ corresponds to quantum yield, per photon absorbed, of approximately 50% at the light intensity used, which was 11 mW cm^{-2}.

Under further irradiation, the absorbance at 605 nm decreased and a new absorption band at 378 nm increased, while the absorbance at 398 nm slightly increased. It is known that MV^0 has absorption bands at *ca.* 398 and 375 nm, but not at 605 nm.[11,16,17] The absorption spectra after irradiation for 2 min are

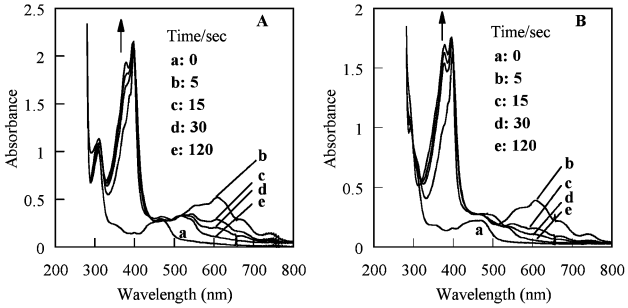


Fig. 1 UV–Vis absorption spectral changes in methanol–toluene containing 5.0×10^{-5} M MV^{2+}, 0.1 M TEOA, and 1.2×10^{-5} M **Ru1** (A) or **Ru2** (B) upon visible light irradiation.

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similar to that of MV^0. Moreover, these absorption changes do not occur in the dark, ruling out the conproportionation reaction of $MV^{\bullet+}$ or the dark reaction of TEOA with $MV^{\bullet+}$ as possible sources of MV^0 in this medium. These spectra show that in the Ru(II) nanofiber systems the photochemical reaction proceeds in two stages, producing first $MV^{\bullet+}$ and then further reducing it to MV^0.

Fig. 2 shows the changes in the concentration of $MV^{\bullet+}$ upon visible light irradiation in the second stage. The production of MV^0 appears to occur by a two-step mechanism involving the uphill reaction of the reduced sensitizer, $\mathbf{Ru1}_{red}$ (or $\mathbf{Ru2}_{red}$) with $MV^{\bullet+}$ according to reaction (1). Once the oxidized sensitizer **Ru1** (or **Ru2**) is produced in this reaction, it reacts photochemically with TEOA to regenerate the reduced form, reaction (2). If we assume that in the second stage of the reaction essentially all of the sensitizer is in the reduced form, then we obtain the linear relation (3), in which C_0 is the $MV^{\bullet+}$ concentration at the beginning of stage 2.

$$\mathbf{Ru1}_{red} + MV^{\bullet+} \xrightarrow{k_{eq}} \mathbf{Ru1} + MV^0 \quad (1)$$

$$\mathbf{Ru1} + TEOA + h\nu \xrightarrow{k} \mathbf{Ru1}_{red} \quad (2)$$

$$C_0(\ln[MV^{\bullet+}]) - [MV^{\bullet+}] = -kK_{eq}[\mathbf{Ru1}_{red}]t + C_0(\ln C_0) - C_0 \quad (3)$$

The inset in Fig. 2 shows that this rate law is followed in the second stage of the reaction. The fact that equilibrium (1) lies very much to the left side explains why the second stage of the photoredox reaction is a much slower process than the first stage. Scheme 1 illustrates the overall process for the two-stage photoreduction of MV^0 from MV^{2+}.

In summary, we describe the photosensitized production of MV^0 using Ru(II) nanofiber photosensitizers under visible light irradiation. The photosensitized reaction occurs in two stages in which $MV^{\bullet+}$ is rapidly formed, followed by slower reduction to

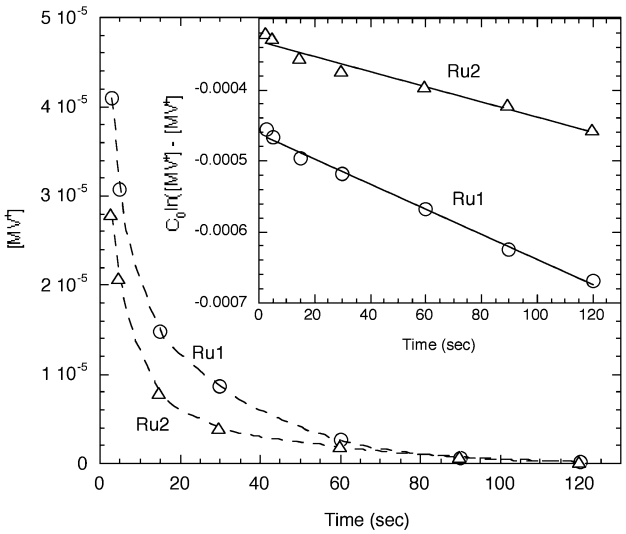
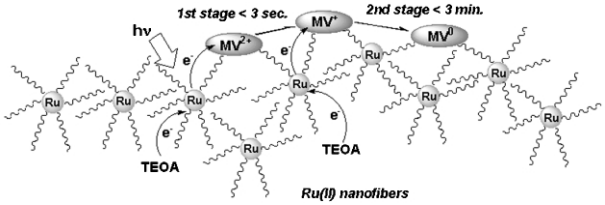


Fig. 2 Changes in the concentration of $MV^{\bullet+}$ for **Ru1** and **Ru2** in methanol–toluene upon visible light irradiation. Inset: linear fits to eqn. (3).



Scheme 1

MV^0. This kind of two-step reduction process may be of particular interest for organized photoredox systems in which neutral charge carriers are needed to carry two reducing equivalents.

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Notes and references

1 (*a*) P. M. S. Monk, *The Viologens: Physicochemical properties, synthesis and applications of the salts of 4,4′-bipyridine*, Wiley, Chichester, 1998, England, and references therein; (*b*) C. L. Bird and A. T. Kuhn, *Chem. Soc. Rev.*, 1981, **10**, 49.

2 (*a*) A. J. Bard, A. Ledwith and H. J. Shine, *Adv. Phys. Org. Chem.*, 1976, **13**, 155; (*b*) A. J. Bard, A. B. Bocarsly, F.–R. F. Fan, E. G. Walton and M. S. Wrighton, *J. Am. Chem. Soc.*, 1980, **102**, 3671; (*c*) A. B. Bocarsly, D. C. Bookbinder, R. N. Dominey, N. S. Lewis and M. S. Wrighton, *J. Am. Chem. Soc.*, 1980, **102**, 3683.

3 (*a*) D. R. Prasad, M. Z. Hoffman, Q. G. Mulazzani and M. A. J. Rodgers, *J. Am. Chem. Soc.*, 1986, **108**, 5135; (*b*) M. Georgopolous and M. Z. Hoffman, *J. Phys. Chem.*, 1991, **95**, 7717; (*c*) H. Feilchenfeld, G. Chumanov and T. M. Cotton, *J. Phys. Chem.*, 1996, **100**, 4937.

4 (*a*) K. Kalyanasudaram, *Coord. Chem. Rev.*, 1982, **46**, 159; (*b*) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.

5 *Homogeneous Photocatalysis (Wiley series in Photoscience and Photoengineering) Vol. 2*, ed. M. Chanon, John Wiley & Sons, Chichester, 1997, ch. 8, p. 246.

6 (*a*) M. M. Alam and O. Ito, *J. Phys. Chem. A*, 1999, **103**, 1306; (*b*) M. Kodaka and Y. Kubota, *J. Chem. Soc., Perkin Trans. 2*, 1999, 891; (*c*) B. A. Parkinson and P. F. Weaver, *Nature*, 1984, **309**, 148.

7 (*a*) I. Willner, A. Riklin and N. Lapidot, *J. Am. Chem. Soc.*, 1990, **112**, 6438; (*b*) I. Willner, N. Lapidot, A. Riklin, R. Kasher, E. Zahavy and E. Katz, *J. Am. Chem. Soc.*, 1994, **116**, 1428.

8 (*a*) E. H. Yonemoto, G. B. Saupe, R. H. Schmehl, S. M. Hubig, R. L. Riley, B. L. Iverson and T. E. Mallouk, *J. Am. Chem. Soc.*, 1994, **116**, 4786; (*b*) D. M. Kaschak, J. T. Lean, C. C. Waraksa, G. B. Saupe, H. Usami and T. E. Mallouk, *J. Am. Chem. Soc.*, 1999, **121**, 3435.

9 M. Mohammad, R. Iqbal, A. Y. Kahn, K. Zahir and R. Jahan, *J. Electroanal. Chem. Interfacial Electrochem.*, 1981, **124**, 139.

10 K. Belinko, *Appl. Phys. Lett.*, 1976, **29**, 363.

11 M. Mohammad, *J. Org. Chem.*, 1987, **52**, 2279.

12 S. V. Lymar and J. K. Hurst, *J. Am. Chem. Soc.*, 1992, **114**, 9498.

13 D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 2001, **34**, 48.

14 J. W. Park, S. H. Ko and J. Y. Park, *Bull. Korean Chem. Soc.*, 1992, **13**, 259.

15 M. Suzuki, C. C. Waraksa, T. E. Mallouk, H. Nakayama and K. Hanabusa, *J. Phys. Chem. A*, 2002, **106**, 4227.

16 T. Watanabe and K. Honda, *J. Phys. Chem.*, 1982, **86**, 2617.

17 C. Lee, Y. K. Lee, Y. Lee and I. C. Jeon, *J. Electroanal. Chem.*, 1999, **463**, 224.