Elucidation of acceptor–acceptor interactions in a Ru(II) supramolecular photosynthetic model complex†

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The interaction between the two viologen acceptors in a TEMPO-labeled Ru(II) bisviologen photosynthetic model system assembly has been investigated using EPR spectroscopy; the results are consistent with no viologen–viologen spin exchange in water at temperatures above 5 °C, although upon crystallization ($\leqslant$2 °C) strong spin exchange is observed; the strong spin exchange interaction results in a single broad line at temperatures below 1 °C, unlike the three broad lines measured for free TEMPO upon solvent freezing; this evidence for the TEMPO-labeled complex indicates that there is no interaction of the two viologen acceptors in the supramolecular Ru(II) bis-viologen structure in solution, thus making it indeed a viable model for the photosynthetic reaction center.

A remarkable feature of the photosynthetic reaction center (RC) lies in its utilization of only one of the two nearly identical electron transfer (ET) pathways available from the excited state of the special pair to the Q_A and Q_B quinone acceptors.[1] A large number of covalently linked diads and triads of varying geometry and rigidity possessing excited state electron donors and electron acceptors have been explored as RC model assemblies.[2] These systems are generally aimed at solar energy conversion, and are therefore designed to attain a long lifetime of the charge separated state formed upon photoexcitation. Such *D–A, *D–A_1–A_2, and D–*D–A (*D = photoexcited donor, D = donor, A, A_1, A_2 = acceptors) structures are schematically shown in Fig. 1(a),[3] where in many cases *D is a Ru(II) diimine complex.[4] Although these supramolecular donor/acceptor systems have proven useful in the investigation of long-lived charge separation, only a few can be utilized in the modeling of the dual ET pathways found in the reaction center.[5] Such systems possess two chemically identical acceptors tethered to the donor, A–*D–A [Fig. 1(b)], thus providing a bifurcated pathway for the photoinduced electron transfer. One previously reported A–*D–A supramolecular assembly is of particular importance owing to the similarity in the spatial arrangement of the donor and acceptors compared to that in the RC. This system is of the type $[Ru^{II}(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)]^{4+}$ (dmbpy = 4,4′-dimethyl-2,2′-bipyridine), where the structure of ligand di-V^{2+}-bpy in the complex is shown in Fig. 2(a) and possesses two linked 4,4′-dialkyl viologens.[6] A crucial criteria for the investigation of the charge transfer processes in this supramolecular complex is the assessment of the interaction between the two viologens, since a RC model system should not possess electron exchange between the two acceptors.

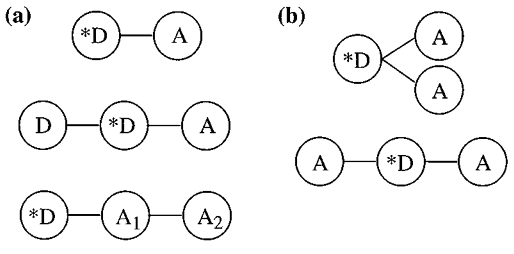

Fig. 1 Schematic representation of donor/acceptor (D/A) asseblies aimed at (a) long charge-separated states and (b) bifurcated ET pathway.

To investigate the interaction between the two viologens in the $[Ru^{II}(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)]^{4+}$ complex we have synthesized the Ru(II) complex with a bis-TEMPO (TEMPO = 2,2′,6,6′-tetramethylpiperidine *N*-oxide) labeled ligand, di-(TEMPO-V^{2+})-bpy, shown in Fig. 2(b). The CW-EPR spectral features of the nitroxide radical in each TEMPO moiety are highly sensitive to dynamics, motion and distance from other radicals. This work presents EPR evidence against the interaction of the two acceptors in the $[Ru^{II}(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)]^{6+}$ model complex.

The synthesis and characterization of $[Ru(dmbpy)(di\text{-}TEMPO)\text{-}V^{2+})\text{-}bipy)]^{6+}$ is given as ESI data.† Elemental analysis is consistent with the expected structure. Transient absorption measurements were conducted on an instrumental setup previously described.[7] The EPR instrument has been previously reported.[8]

As expected from the molar absorption coefficients of the Ru(II)–diimine MLCT (metal-to-ligand charge transfer) transitions and the TEMPO absorption in the visible region, the electronic absorption spectrum of the $[Ru^{II}(dmbpy)_2(di\text{-}(TEMPO\text{-}V^{2+})\text{-}bpy)]^{6+}$ complex is nearly identical to that of

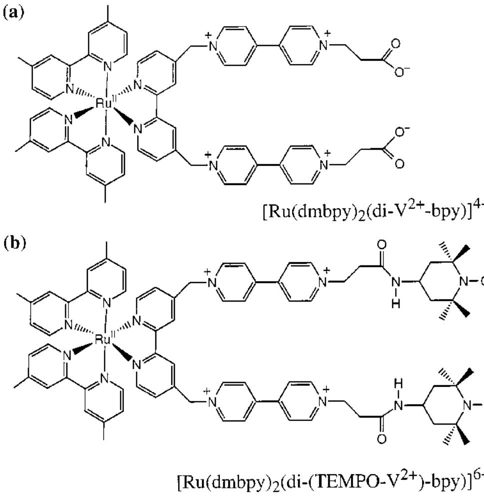

Fig. 2 Molecular structures of the photosynthetic model complex (a) $[Ru^{II}(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)]^{6+}$ and (b) the bis-TEMPO labeled analog $[Ru^{II}(dmbpy)_2(di\text{-}(TEMPO\text{-}V^{2+})\text{-}bpy)]^{6+}$.

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† Electronic supplementary information (ESI) available: synthesis and characterization of $[Ru(dmbpy)_2(di\text{-}(TEMPO\text{-}V^{2+})\text{-}bipy)]^{6+}$, electrospray MS, HPLC, redox potentials and molecular model. See http://www.rsc.org/suppdata/cc/1999/2487/

Table 1 Comparison of the EPR fit parameters for doubly- and singly-TEMPO labeled complexes at 25 °C†

	τ_c/ps	g_{xx}	g_{yy}	g_{zz}	A_{xx}/G	A_{yy}/G	A_{zz}/G
$[\mathrm{Ru^{II}(phen)_2(TEMPO\text{-}phen)}]^{2+}$ [a]	80	2.0097	2.0063	2.0035	6.8	7.5	37.3
$[\mathrm{Ru^{II}(dmbpy)_2(di\text{-}(TEMPO\text{-}V^{2+})\text{-}bpy)}]^{6+}$	50	2.0090	2.0060	2.0030	7.0	7.0	36.5

[a] TEMPO-phen = 4-$\mathrm{(CH)_2OC(O)N}$-(TEMPO)-1,10-phenanthroline, data from ref. 6.

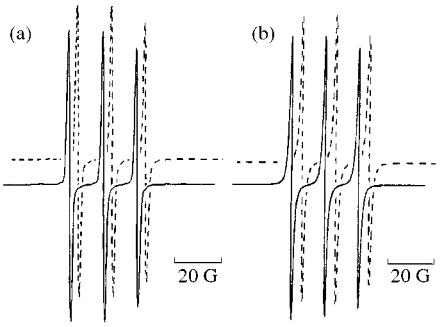

Fig. 3 EPR spectra (——) of 1×10^{-4} M $[\mathrm{Ru^{II}(dmbpy)_2(di\text{-}(TEMPO\text{-}V^{2+})\text{-}bpy)}]^{6+}$ in water at (a) 30 and (b) 5 °C, with their respective computed spectra (– – – –).

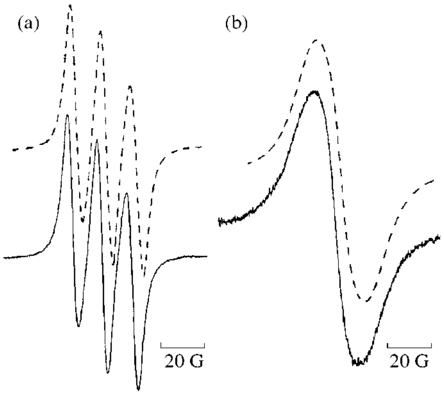

Fig. 4 EPR spectra (——) of 1×10^{-4} M $[\mathrm{Ru^{II}(dmbpy)_2(di\text{-}(TEMPO\text{-}V^{2+})\text{-}bpy)}]^{6+}$ in water at (a) 1 and (b) −3 °C, with their respective computed spectra (– – – –).

$[\mathrm{Ru^{II}(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)}]^{4+}$. Both complexes are non-emissive in deoxygenated aqueous solution and possess similar excited state charge transfer characteristics. In the model complex $[\mathrm{Ru^{II}(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)}]^{4+}$, visible excitation leads to fast ET from the Ru(II) metal center to one of the viologens with risetime of *ca.* 1–2 ps (λ_{exc} = 450 nm, FWHM *ca.* 200 fs).[9] A typical lifetime of the charge separated state, τ_{CS}, of *ca.* 250 ± 20 ns was determined from fits of the monoexponential decay of photoexcited solutions of 5.0×10^{-5} M $[\mathrm{Ru^{II}(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)}]^{4+}$ (λ_{exc} = 532 nm, FWHM *ca.* 4 ns), where the transient absorption of $\mathrm{MV^{\cdot+}}$ was monitored at 610 nm. To ensure that the TEMPO-labeling of the complex did not lead to different ET dynamics, the same experiments were performed on $[\mathrm{Ru^{II}(dmbpy)_2(di\text{-}(TEMPO\text{-}V^{2+})\text{-}bpy)}]^{6+}$, which indicate that within experimental error the risetime and lifetime of the charge separated state are identical. Furthermore, reduction of the TEMPO radicals in $[\mathrm{Ru^{II}(dmbpy)_2(di\text{-}(TEMPO\text{-}V^{2+})\text{-}bpy)}]^{6+}$ complexes was not observed by UV-VIS absorption and HPLC measurements.

Solution CW-EPR measurements of $[\mathrm{Ru^{II}(dmbpy)_2(di\text{-}(TEMPO\text{-}V^{2+})\text{-}bpy)}]^{6+}$ in water were conducted at temperatures ranging from 5 to 30 °C. Selected spectra (5 and 30 °C) are shown in Fig. 3 along with the simulation traces for each experiment.† Throughout this temperature range no spectral broadening was observed at low concentration (< 1 mM), indicative of no interaction between the two TEMPO units within each complex. The solution spectra collected for 1.0×10^{-4} M $[\mathrm{Ru^{II}(dmbpy)_2(di\text{-}(TEMPO\text{-}V^{2+})\text{-}bpy)}]^{6+}$ are similar to those measured for singly TEMPO-labeled Ru(II) complexes. The correlation time for motion, *g*-values, and isotropic hyperfine coupling constants for $[\mathrm{Ru^{II}(dmbpy)_2(di\text{-}(TEMPO\text{-}V^{2+})\text{-}bpy)}]^{6+}$ and a related singly labeled Ru(II) complex are listed in Table 1 from which it is clear that all the parameters for both the singly- and doubly-TEMPO labeled complexes are nearly identical, indicating that the presence of the second TEMPO in the molecule does not affect the motion or magnetic features. In addition, for $[\mathrm{Ru^{II}(dmbpy)_2(di\text{-}(TEMPO\text{-}V^{2+})\text{-}bpy)}]^{6+}$ the correlation time for motion, τ_c, increases as the temperature is lowered, consistent with slower motion at lower temperatures.

Cooling the sample below 2 °C results in the formation of red crystals, prior to solvent freezing at *ca.* 0 °C. The EPR spectra of $[\mathrm{Ru^{II}(dmbpy)_2(di\text{-}(TEMPO\text{-}V^{2+})\text{-}bpy)}]^{6+}$ at 1 °C and −3 °C are shown in Fig. 4. For free TEMPO and most of its derivatives, lowering the temperature below the freezing of the solvent point results in broadening of all three individual lines without the occurrence of exchange broadening, which appears as a single broad line.[10] The observed spectra shown in Fig. 4 are consistent with increased exchange frequency, W_{ex}, as the temperature is lowered with W_{ex} values of 1.0×10^8 and 2.7×10^8 s^{-1} at 1 and −3 °C, respectively. The increased spin exchange between the two viologen units of $[\mathrm{Ru^{II}(dmbpy)_2(di\text{-}(TEMPO\text{-}V^{2+})\text{-}bpy)}]^{6+}$ is only observed upon the formation of crystals (below 2 °C), but not when free in solution. It may be concluded from these observations that only in the crystalline form are the two viologen chains able to interact with each other or with TEMPO units of neighboring complexes within the close-packed lattice.

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