

# Redox switchable NIR dye derived from ruthenium–dioxolene–porphyrin systems†

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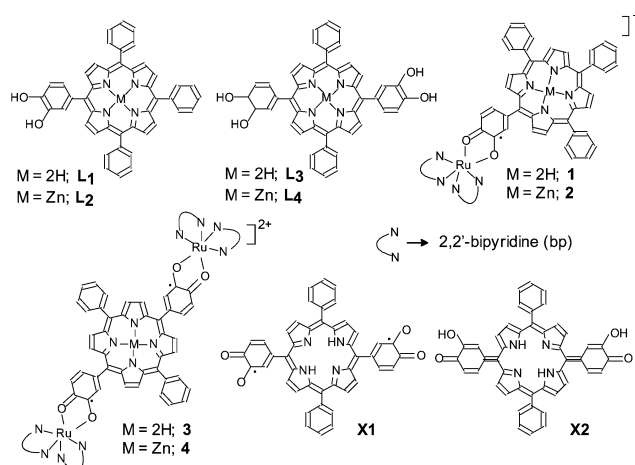
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Newly synthesised Ru(bp)<sub>2</sub>(sq)<sup>+</sup>-derivatives, covalently linked to a porphyrin-core, show very high  $\epsilon$  values in the NIR region; which exhibit fast on/off switching depending on the redox state of the coordinated dioxolene functionality.

Molecular systems, which absorb strongly in the NIR region, are of considerable interest to chemists and material scientists because of their potential in applications such as optical data processing, photodynamic therapy, *etc.*<sup>1</sup> Systems, whose intense NIR absorption can be switched on and off, are even more attractive candidates for applications in optoelectronics. Complexes derived from the Ru(bp)<sub>2</sub>(sq)<sup>+</sup>-fragment<sup>2</sup> are important in this regard as these complexes display an Ru(d $\pi$ )  $\rightarrow$  sq( $\pi^*$ ) MLCT band in the NIR region ( $\epsilon_{890} = 9000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ );<sup>3</sup> while its one-electron reduced (Ru(bp)<sub>2</sub>(cat)) or oxidized (Ru(bp)<sub>2</sub>(q)<sup>2+</sup>) product<sup>2</sup> do not have any significant absorption in this region.<sup>3,4</sup> Additionally, (i) the reversible nature of the sq/cat-redox couple in Ru(bp)<sub>2</sub>(sq)<sup>+</sup>,<sup>2</sup> (ii) thermodynamic feasibility of the photoinduced electron transfer from the donor porphyrin fragment to the acceptor ruthenium–semiquinone unit and (iii) the possibility of fast charge recombination process, makes Ru(bp)<sub>2</sub>(sq)<sup>+</sup> and porphyrin fragments ideal candidates for use in an efficient redox active photochromic dye. With this rationale we have synthesized a set of new bichromophoric complexes **1–4**.<sup>5</sup>



Various analytical data and spectroscopic studies confirm that complexes **1–4** exist as paramagnetic semiquinone forms<sup>3,4,6</sup> and show a featureless room temperature EPR spectrum consisting of a broadened signal centered at  $g_{av} \approx 2.003$  in CH<sub>2</sub>Cl<sub>2</sub>. However, spectra recorded at 77 K are anisotropic, as the molecular orbital containing the unpaired electron(s) of the semiquinone fragment(s) is partially localized

on the ruthenium centre.<sup>4,6</sup> The spectral features of the mono- and bi-radical species, **1–4**, are similar; except that the spectra for **1** and **2** are less broad than those for **3** and **4**. This is presumably due to weak interaction between the two unpaired electrons of the semiquinone fragments. This is not surprising as the two appended ruthenium–semiquinone fragments are separated by  $\sim 14.2 \text{ \AA}$  with an orthogonal orientation with respect to the porphyrin plane (analogous model system is represented as **X1**).<sup>7</sup> To corroborate the presumption, we have employed unrestricted Hartree–Fock (UHF) PM3 calculations<sup>7a</sup> to optimize the geometry of two possible isomeric model compounds **X1** and **X2**.<sup>7b</sup> Calculated results suggest that the triplet form of the biradical **X1** (Fig. 1) is the most stable and more stable than **X2** by 18.7 kcal mol<sup>-1</sup>.<sup>7b</sup>

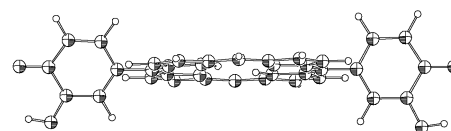


Fig. 1 UPM3 optimized structure of model system **X1**.

Electronic spectral data for ruthenium–dioxolene complexes along with the reduced and oxidized forms of **2** and **4** (Table 1) reveal that bichromophoric systems, **1–4** show expected spectral features of the individual mononuclear components along with an unusually strong absorbance at  $\sim 940 \text{ nm}$  for the Ru(d $\pi$ )  $\rightarrow$  sq( $\pi^*$ ) transition ( $\epsilon = 59000\text{--}83500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). A red shift of  $\lambda_{max}$  ( $\sim 50 \text{ nm}$  for **1–4**, compared to that for Ru(bp)<sub>2</sub>(sq)<sup>+</sup>-species<sup>2</sup>) for this MLCT transition is observed. An even higher red shift of  $\sim 100 \text{ nm}$  for this MLCT band is observed where the coordinated sq-functionality is part of an extended conjugated system.<sup>1d,4</sup> Presumably this higher red shift is due to the more effective lowering of the energy of semiquinone SOMO arising from the extended conjugation.<sup>1d,4</sup> This also indicates the absence of any or little extended conjugation in complexes **1–4** and agrees well with the proposed conformation.

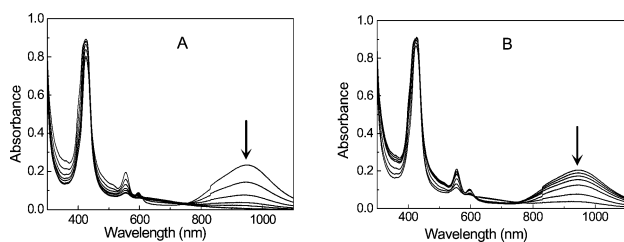
Results of cyclic and square wave voltammetric studies (CV and SWV) for complexes **1–4** (Table 1) also suggest a weak ground-state electronic interaction between the two terminal Ru(bp)<sub>2</sub>(sq)<sup>+</sup>-fragments.<sup>2</sup> All complexes undergo redox processes at potentials consistent with individual mononuclear components. However, redox waves for the cat/sq and sq/q-couples<sup>2</sup> for **3** and **4** are much broader ( $[E_{pc} - E_{pa}] \geq 120\text{--}135 \text{ mV}$ , Table 1) due to the overlapping waves of the two weakly interacting Ru(bp)<sub>2</sub>(sq)<sup>+</sup>-fragments. Spectroelectrochemical studies with complexes **1–4** show that either oxidation or reduction of the semiquinone-fragment causes a complete bleaching of the MLCT band in the NIR region (Fig. 2). Spectral changes are found to be completely reversible and quantitative recovery of the MLCT band at the NIR region occurs upon reversal of the redox processes. This agrees well with the reversible nature of the dioxolene-based redox processes, observed in CV studies for complexes **1–4**. Thus, these complexes fulfil the basic criteria for use as redox switchable photochromic dye.

† Electronic supplementary information (ESI) available: synthesis of complexes **1** and **3**, calculated results for model systems **X1** and **X2**, EPR spectra of **3**, cyclic voltammogram and DPV of **2**. See <http://www.rsc.org/suppdata/cc/b2/b206000k/>

**Table 1** UV–VIS data and redox potential values for complexes **1–4**

	$\lambda_{\text{max}}^a/\text{nm}$ ( $\epsilon \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	$E_{1/2}/\text{V}$ ( $\Delta E/\text{mV}$ ) <sup>b</sup>		
		sq/cat <sup>2</sup>	sq/q <sup>2</sup>	Ru(II/III)
<b>1</b>	292 (44), 419 (329), 515 (16.6), 549 (9.8), 588 (5.4), 927 (59)	−0.68 (75)	0.227 (80)	1.07 (140)
<b>2</b>	291 (51.1), 419 (306), 546 (18.1), 933 (65)	−0.66 (80)	0.14 (70)	1.05 (100)
<b>[2]<sub>red</sub></b>	420 (364), 546 (45.2)	—	—	—
<b>[2]<sub>ox</sub></b>	415 (308), 547 (35.1)	—	—	—
<b>3</b>	286 (107), 418 (298), 514 (17), 548 (9.1), 910 (79.2)	−0.66 (120)	0.14 (125)	1.02 (140)
<b>4</b>	286 (142), 420 (302), 545 (18.2), 945 (83.5)	−0.66 (120)	0.30 (135)	1.06 (126)
<b>[4]<sub>red</sub></b>	424 (333), 555 (61.3)	—	—	—
<b>[4]<sub>ox</sub></b>	408 (289), 558 (43)	—	—	—

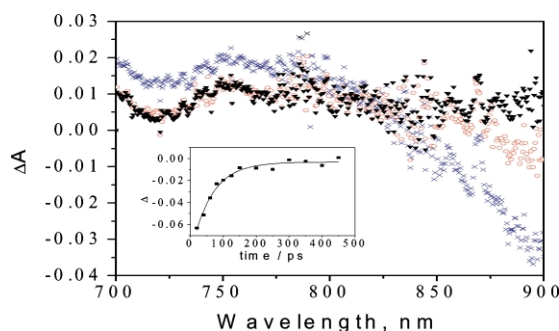
<sup>a</sup> Electronic spectra were recorded in  $\text{CH}_2\text{Cl}_2$ . Spectra of the electro-reduced and oxidised species were recorded *in situ* in presence of 0.1 M [ButN]<sub>4</sub>PF<sub>6</sub> in  $\text{CH}_3\text{CN}$ . <sup>b</sup> CV studies were performed in  $\text{CH}_3\text{CN}$  using 0.1 M [ButN]<sub>4</sub>PF<sub>6</sub>; potential values are reported (scan rate of  $100 \text{ mV s}^{-1}$ ) vs. ferrocene/ferrocenium couple. Pt-as working, Pt-wire as auxiliary and Ag–AgCl as reference electrodes were used for the studies.

**Fig. 2** Change in electronic spectra when complex **4** is subjected to bulk electrolysis at (A) −0.4 V (vs. SCE) and (B) 0.7 V (vs. SCE).

Relative quantum yields, measured with thoroughly  $\text{N}_2$ -purged solutions for the steady state luminescence of the porphyrin core in complexes **1/3** and **2/4** are 0.23 and 0.19, respectively, when compared to **L<sub>1</sub>/L<sub>3</sub>** and **L<sub>2</sub>/L<sub>4</sub>**. A relatively lower fluorescence efficiency and shorter lifetime of **1–4** compared to those of **L<sub>1</sub>–L<sub>4</sub>** are due to photoinduced transfer of an electron from the photoexcited porphyrin to the semiquinone moiety. This is evident from the time-resolved absorption behavior of the systems. Photoexcitation at 532 nm leads to the formation of Ru(bp)<sub>2</sub>(cat)-species<sup>2</sup> effecting bleaching of the NIR absorption (Fig. 3).

The rate constant for the photoinduced intramolecular forward electron transfer process in these complexes is estimated to be  $(1.5\text{--}3.2) \times 10^9 \text{ s}^{-1}$ . The recovery of the bleaching due to back electron transfer process takes place in the picosecond time scale (63 ps for **1**, inset Fig. 3). Thus, complexes **1–4** constitute a unique system which becomes transparent between 800 and 1300 nm on change in redox state of the coordinated semiquinone fragment; initiated either electrochemically or photochemically. There are only a few examples available on inorganic metal complexes,<sup>1a,e,8,9</sup> which have an intense NIR absorption—some with superior  $\epsilon$ -values.<sup>1a,e</sup> However, bleaching and recovery of the NIR band through reversible change in the redox state of the coordinated sq-fragment demonstrate the possibility of using complexes **1–4** as photo or redox-active NIR switches. Further, the fast response time, which is crucial for designing an effective sensor, has provided **1–4** a distinct edge over the others and constitute a novel approach for a real NIR active molecular switch.

In conclusion, **1–4** show an unusually strong absorbance in the NIR region of the spectrum, which disappears when these complexes undergo dioxolene-based one-electron reduction or oxidation process. The NIR absorption band is restored with original intensity upon reversal of the respective redox processes. For photoinduced redox processes, the recovery takes place in the picosecond time scale. Thus, a combination of photoactive porphyrin unit and redox active Ru–semiquinone fragment(s) lead to novel molecular function in complexes **1–4** and make them ideally suited for probable use in redox switchable NIR dyes and sensors for optoelectronic devices.

**Fig. 3** Time-resolved absorption spectra of **1** in  $\text{CH}_3\text{CN}$ : immediately after excitation ( $\times$ ), after a delay of 60 ps and ( $\circ$ ) after 100 ps ( $\blacktriangle$ ). The solution was excited with the second harmonic (532 nm) of an Nd-YAG laser. The FWHM of the excitation pulse was  $\approx 30$  ps. The insert shows the recovery of the bleaching at 925 nm. The data was fit to a function,  $y = y_0 - a_1 \exp(-x/\tau_1)$ . The parameters obtained from this fitting are  $y_0 = -0.0027$ ,  $a_1 = 0.085$  and  $\tau_1 = 63.5$  ps.

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## Notes and references

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- Complexes **1–4** are synthesized by reacting **L<sub>1</sub>–L<sub>4</sub>** (5-(3,4-dihydroxy)-10,15,20-triphenyl-21*H*,23*H*-porphyrin (**L<sub>1</sub>**) or 5,10-bis(3,4-dihydroxy)-10,20-bisphenyl-21*H*,23*H*-porphyrin (**L<sub>3</sub>**) or the corresponding Zn-derivatives, **L<sub>2</sub>** or **L<sub>4</sub>**), with appropriate mole equivalents of Ru(bp)<sub>2</sub>Cl<sub>2</sub> and KOH in ethanol. Analytical data for **1–4** agree well with the proposed formulations.
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