A photochromic system based on photochemical or thermal chelate exchange on Ru(phen)$_2$L^{2+} (L = diimine or dinitrile ligand)

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In the presence of a bidentate chelate containing two convergent nitrile groups, Ru(phen)$_2$L^{2+} (L = sterically hindering aromatic diimine ligand; phen = 1,10-phenanthroline) undergoes a photochemical reaction leading to quantitative replacement of the diimine by the bis-nitrile ligand; the reverse reaction takes place upon heating, also quantitatively.

Multicomponent molecular systems for which certain parts can be set into motion while others can be considered as motionless are promising models of biological molecular machines and motors as well as potential switches.[1,2] The signals sent to the molecules in order to trigger the movement can be of an electrochemical[3] or chemical[4] nature, photoinduced redox processes being also used in a few cases.[5] In the search for non-sacrificial photochemical reactions usable for moving molecular fragments,[6] it occurred to us that ligand-field (LF) excited states of d^6 transition metal complexes are strongly antibonding and can lead, in some cases, to effective ligand exclusion and substitution by solvent molecules.[7] In the present work, we would like to describe a system in which two different chelates, an aromatic diimine and a dinitrile, can be efficiently and cleanly interchanged under the action of light or heat. In addition, significant photochromism is observed. The ligands used are represented in Fig. 1.

The aromatic diimines 6,6′-dmbp and biq are sterically hindering so that their removal from a ruthenium(II) trischelate complex will be favoured over that of phen, also considering that rotation about the C–C bond between both halves of the chelate facilitates stepwise decoordination. The bis-nitrile dCN has been previously described and used by Angelici *et al.* to make a few complexes (Mn(I), Fe(II) and Pt(II)).[8] Although no structural data are available, dCN is expected to behave as a bidentate chelate.

The following photochemical reactions have been shown to take places quantitatively under light irradiation (300 nm ≤ λ ≤ 800 nm):[9]

$$Ru(phen)_2L^{2+} + dCN \xrightarrow[L = 6,6'\text{-dmbp or biq}]{h\nu} Ru(phen)_2(dCN)^{2+} + L \quad (1)$$
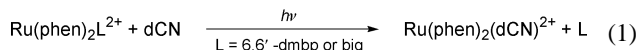
The efficiency of reaction (1) is solvent dependent, the best solvents being acetone or 1,2-dichloroethane (1,2-DCE). The
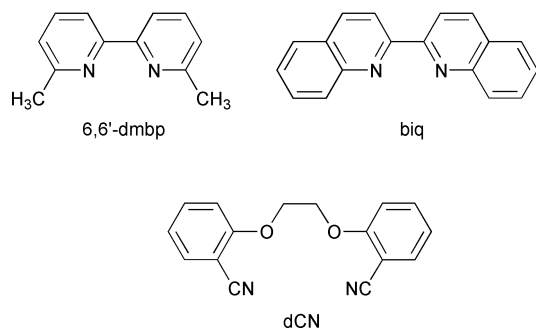

Fig. 1 The various chelates used in photochemically active ruthenium complexes.

photoproduct, Ru(phen)$_2$(dCN)$^{2+}$, was isolated quantitatively and authenticated by comparison with a separately prepared sample.[10] To our knowledge, it is the first example of a photochemical chelate-to-chelate exchange reaction. Crystals were grown from MeOH–*p*-xylene and an X-ray structure of the compound was obtained.[11] The ORTEP diagram is shown in Fig. 2. The ruthenium–nitrogen bond lengths range from 2.04(1) to 2.085(8) Å and are similar to those observed in the Ru(phen)$_3$$^{2+}$ and Ru(phen)$_2$(dpq)$^{2+}$ complexes[12] (dpq = dipyrido[3,2-*d*:2′,3′-*f*]quinoxaline). As also indicated by the N–Ru–N angles the geometry about ruthenium atom is distorted from octahedral. The most noticeable feature is the constraint imposed on the dCN ligand as reflected by the Ru–N(6)–C(40) and Ru–N(5)–C(2) angles (167 and 168° respectively) as well as the large dihedral angle between the two phenyl groups.

In order to demonstrate that dCN and 6,6′-dmbp or biq can be interchanged, it was essential to show that the starting complex can be regenerated. This is indeed the case: reaction (2) takes place quantitatively.

$$Ru(phen)_2(dCN)^{2+} + L \xrightarrow[L = 6,6'\text{-dmbp or biq}]{\Delta} Ru(phen)_2L^{2+} + dCN \quad (2)$$
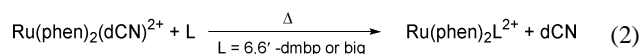
For example, a yellow solution of Ru(phen)$_2$(dCN)$^{2+}$ and biq in ethyleneglycol was heated at 190 °C for 4 h in the dark. The colour of the solution changed to deep red. After removal of the solvent followed by chromatography, Ru(phen)$_2$(biq)$^{2+}$ was obtained in 91% yield. Moreover, the photochemical reaction (6,6′-dmbp or biq release) and the thermal back reaction (dCN
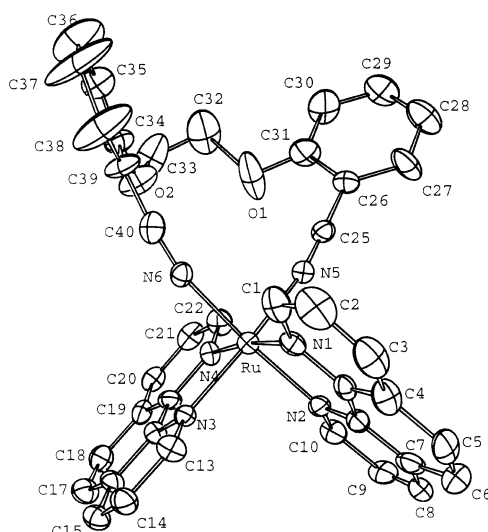

Fig. 2 ORTEP view of the cationic part of [Ru(phen)$_2$(dCN)](PF$_6$)$_2$(*p*-xylene)$_2$(MeOH) with partial labelling scheme. Ellipsoids are scaled to enclose 30% of the electronic density. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ru–N(1) 2.059(9), Ru–N(2) 2.054(9), Ru–N(3) 2.061(9), Ru–N(4) 2.085(8), Ru–N(5) 2.05(1), Ru–N(6) 2.04(1), N(5)–Ru–N(6) 85.1(3), Ru–N(5)–C(25) 168(1), Ru–N(6)–C(40) 167(1), C(26)–C(25)–N(5) 177(1), C(39)–C(40)–N(6) 172(1).
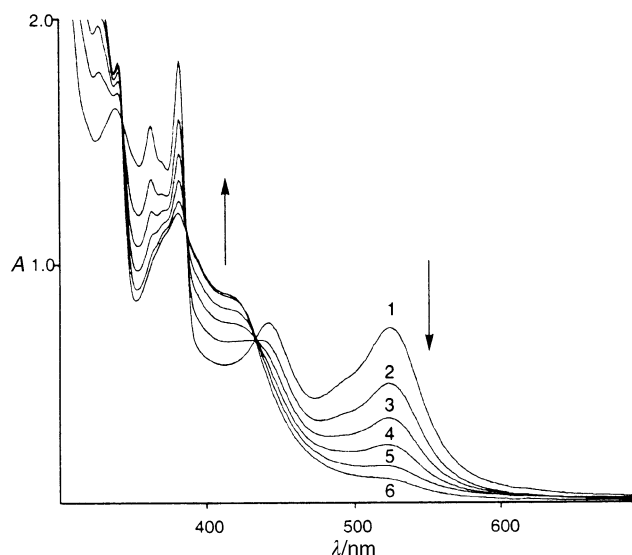
Fig. 3 Electronic spectra of a 1,2-DCE solution of Ru(phen)$_2$(biq)$^{2+}$ in the presence of dCN (10 eq) after visible light irradiation: **1** (0 s); **2** (20 s); **3** (40 s); **4** (60 s); **5** (90 s); **6** (120 s).

release with recoordination of 6,6′-dmbp or biq) could be carried out on the same reaction mixture containing an excess of both ligands, dCN and the aromatic diimine, in addition to the starting ruthenium(II) complex. The solvent, EtOCH$_2$CH$_2$OCH$_2$CH$_2$OH, in which all the components (ligands and complexes) are soluble, turned out to be compatible with both photochemical and thermal processes.

Interestingly, the absorption spectra of Ru(phen)$_2$(dCN)$^{2+}$ and Ru(phen)$_2$(biq)$^{2+}$, for instance, are significantly different. dCN is a poor σ-donor and good π-acceptor, stabilizing the d$_\pi$ orbitals of Ru(t$_{2g}$) and thus leading to a relatively high MLCT (Ru → phen) excited state. In Ru(phen)$_2$(biq)$^{2+}$, the nature of the MLCT bond is different: biq is a better π-acceptor than phen so that the charge transfer is directed from the metal centre to biq and no more to the phen ligands. The photochromism of the system is illustrated in Fig. 3.

Without displaying colour changes as large as those obtained with organic photochromic compounds,[13,14] Ru(phen)$_2$(biq)$^{2+}$ (deep red; λ_{max} = 525 nm in 1,2-DCE) changes colour under irradiation to afford an orange solution of Ru(phen)$_2$(dCN)$^{2+}$ (λ_{max} = 382 nm in 1,2-DCE) within a few tens of seconds.

In conclusion, the present system is particularly promising for the construction of molecular photomechanical devices, combining motion and photochromism.

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9 Photoirradiation was performed in a quartz UV cell (l = 1.0 cm) or in a NMR tube (ϕ = 5.0 mm) by the use of a Hanimex side projector (150 W halogen lamp).

10 A mixture of dCN (79 mg) and *cis*-Ru(phen)$_2$Cl$_2$ (0.272 mmol), EtOH (10 mL) and H$_2$O (10 mL) was refluxed for 2 h under an argon atmosphere. To the mixture was added a KPF$_6$ aqueous solution to form a yellow-orange solid, which was filtered off and washed with water. Chromatography (SiO$_2$, acetone/H$_2$O/KNO$_3$(aq.) = 100/10/1) followed by anion exchange gave [Ru(phen)$_2$(dCN)](PF$_6$)$_2$ as a yellow solid in 53% yield. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 9.93 (dd, J = 5.21 Hz, 1.26 Hz, 2H, phen-2H), 8.82 (dd, J = 8.12 Hz, 1.22 Hz, 2H, phen-4H), 8.46 (dd, J = 8.26 Hz, 1.22 Hz, 2H, phen-7H), 8.33 (dd, J = 8.29 Hz, 5.22 Hz, 2H, phen-3H), 8.30 (d, J = 8.88 Hz, 2H, phen-5H), 8.17 (d, J = 8.88 Hz, 2H, phen-6H), 7.89 (dd, J = 5.30 Hz, 1.24 Hz, 2H, phen-9H), 7.65 (ddd, J = 8.92 Hz, 7.60 Hz, 1.72 Hz, 2H, dCN-5H), 7.59 (dd, J = 8.24 Hz, 5.30 Hz, 2H, phen-8H), 7.46 (dd, J = 7.79 Hz, 1.69 Hz, 2H, dCN-3H), 7.18 (d, J = 8.61 Hz, 2H, dCN-6H), 7.06 (dt, J = 7.64 Hz, 0.52 Hz, 2H, dCN-4H), 4.61 (s, 4H, dCN-CH$_2$); UV/Vis (1,2-DCE): λ_{max} (ε) = 382 nm (14 100 L mol^{-1} cm^{-1}).

11 Crystal data for C$_{57}$H$_{52}$F$_{12}$N$_6$O$_3$P$_2$Ru:[Ru(phen)$_2$(dCN)(PF$_6$)$_2$](*p*-xylene)$_2$(MeOH), yellow crystal: M = 1257.06, orthorhombic, a = 17.9740(6), b = 21.1890(9), c = 29.793(1) Å, U = 11 346(1) Å^3, T = 294 K, space group *Pbca*, Z = 8, D_c = 1.47 g cm^{-3}, μ = 0.422 mm^{-1}. Crystal dimensions: 0.20 × 0.18 × 0.14 mm, F_{000}: 5112, wavelength: 0.71073 Å, radiation: Mo-Kα graphite monochromated, diffractometer: KappaCCD, ϕ and ω scans, *hkl* limits: 0.22/ − 27,27/ − 38,38, θ limits: 2.5/27.49°, number of data measured: 22153, number of data with I > $3\sigma(I)$: 4186, weighting scheme: $4F_o/(\sigma^2(F_o^2) + 0.0064 F_o^4)$, number of variables: 727, $R(F)$: 0.066, $R(F)w$: 0.095, GOF: 1.553, largest peak in final difference: 0.940 e Å^{-3}. Package used: OpenMolen, Interactive Structure Solution, Nonius B.V., Delft, The Netherlands, 1997. CCDC 182/1761. See http://www.rsc.org/suppdata/cc/b0/b004982o/ for crystallograhic files in .cif format.

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