Proton-controlled photoisomerization: rhenium(I) tricarbonyl bipyridine linked to amine or azacrown ether groups by a styryl pyridine bridging ligand†

Jared D. Lewis, Robin N. Perutz and John N. Moore*

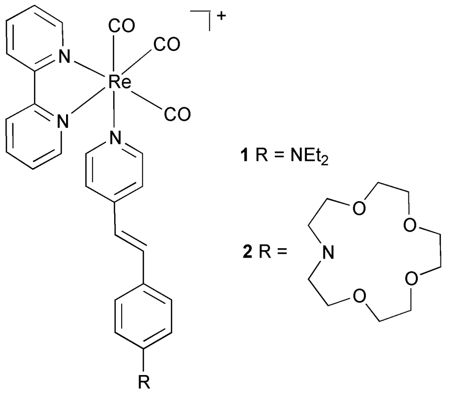
Department of Chemistry, The University of York, Heslington, York UK YO10 5DD. E-mail: jnm2@york.ac.uk

Received (in Cambridge, UK) 20th July 2000, Accepted 25th August 2000
First published as an Advance Article on the web 15th September 2000

Complexes in which *fac*-(bpy)Re(CO)$_3$ is linked by a styryl pyridine to an amine or an azacrown ether show no photoreaction in acetonitrile in the absence of acid, but they photoisomerize readily at the stilbene-like bridging ligand when the terminal amine or azacrown ether group is protonated because an intramolecular energy-transfer mechanism becomes available.

There is widespread interest in the design of molecular photodevices whose properties change on the addition of specific analytes.[1] Devices range from sensors where the analyte turns the emission on or off, to switches where the analyte controls the occurrence or route of a photochemical reaction. Photoinduced intramolecular electron or energy transfer often underlies the mechanism by which the sensing or switching effect occurs. Here we describe a molecular design in which protonation controls a photochemical switching reaction which is driven by intramolecular energy transfer.

We report two new complexes which combine three functional groups: (bpy)Re(CO)$_3$ is linked by a stilbene-like bridging ligand to either an *N*,*N*-diethylamine (**1**) or an aza-15-crown-5 ether (**2**) group.‡ The (bpy)Re(CO)$_3$ chromophore is being used increasingly within molecular sensors and switches because it is luminescent, and its photophysics can be controlled by intramolecular electron and energy transfer.[2] Stilbene has been used as the basis for molecular photoswitches because its well-studied *trans–cis* photoisomerization reaction can be driven by excitation directly to the excited singlet state or indirectly by energy transfer to form the excited triplet state.[3] Crown ethers are attractive as receptors for analytes within many photodevices because cation binding at the crown generally modifies the absorption and emission properties of the attached group, and can control its photochemistry.[1] We report new complexes that combine all three of these groups in a photoswitchable device: photoisomerization at the styryl group is the switch, and proton binding at the amine or azacrown N-heteroatom controls the effect.



The UV/vis absorption spectrum of *trans*-**1** in acetonitrile (Fig. 1) comprises an intense, solvatochromic band at 435 nm and weaker features at 240–350 nm. The 435 nm band is assigned to an intraligand charge-transfer (ILCT) transition localised on the py-DEAS ligand,§ in which charge is transferred from the amine N-atom donor to the pyridyl N-atom acceptor, and the weaker features at *ca.* 300 nm and *ca.* 250 nm are assigned to $\pi \rightarrow \pi^*$ transitions localised on the bpy and py-DEAS ligands, respectively. The dπ(Re) $\rightarrow$ π^*(bpy) metal-to-ligand charge-transfer (MLCT) transition of (bpy)Re(CO)$_3$ complexes typically gives an absorption band at *ca.* 380 nm (absorption coefficient, $\varepsilon \approx 3500$ dm^3 mol^{-1} cm^{-1}), and excitation into this band gives MLCT emission at *ca.* 600 nm which is moderately intense in ambient temperature solution (emission quantum yield, $\Phi_{em} \approx 10^{-2}$).[4] The MLCT absorption band of *trans*-**1** underlies the intense ILCT feature (Fig. 1); excitation at 380 nm, or at any wavelength in the range 300–500 nm, resulted only in very weak MLCT emission, with $\Phi_{em} < 6 \times 10^{-4}$.

Addition of HCl to a solution of *trans*-**1** in acetonitrile resulted in a blue-shift of the ILCT absorption band to *ca.* 320 nm (Fig. 1): this change is attributed to the production of *trans*-**1**-H$^+$, in which protonation at the amine N-atom inhibits charge transfer and raises the energy of the ILCT state. Protonation would not be expected to cause a significant shift in the MLCT absorption band, which is revealed on the long-wavelength edge of the shifted ILCT feature. Excitation of *trans*-**1**-H$^+$ in the range 300–450 nm resulted in one extremely weak emission band at *ca.* 400 nm (excitation peak at *ca.* 330 nm) which is assigned to ILCT emission, and another slightly more intense band at 590 nm ($\Phi_{em} = 1 \times 10^{-3}$) which is assigned to MLCT emission. Excitation spectra recorded on monitoring the emission at $\geqslant$590 nm were found to mirror the expected MLCT absorption profile (excitation peak at *ca.* 355 nm). Only MLCT emission was observed on excitation at $>$400 nm, confirming that irradiation at $>$400 nm excites *trans*-**1**-H$^+$ exclusively to the MLCT state.

Prolonged irradiation¶ of *trans*-**1** in acetonitrile at any wavelength in the range 350–450 nm, exciting to either ILCT or MLCT states, resulted in no change in the UV/vis absorption spectrum, indicating that there is no significant photoreaction.‖

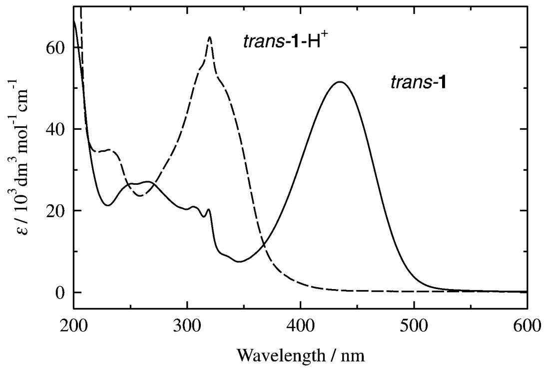


Fig. 1 UV/vis absorption spectrum of *trans*-**1** (2×10^{-5} mol dm^{-3}) in CH$_3$CN (—) and in CH$_3$CN on addition of excess HCl (---).

---

† Electronic supplementary information (ESI) available: UV/vis absorption spectra of **2**. See http://www.rsc.org/suppdata/cc/b0/b005889k/

DOI: 10.1039/b005889k

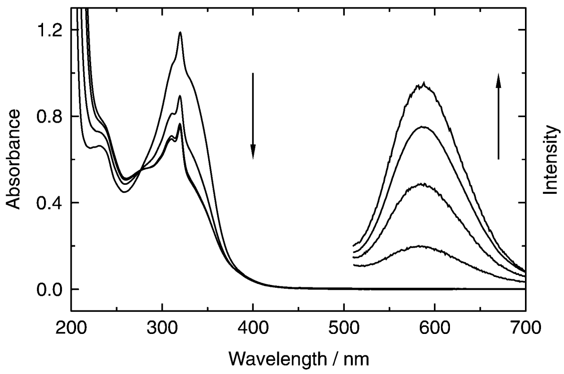
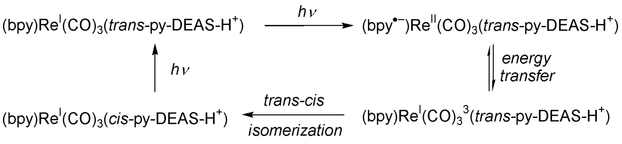


Fig. 2 UV/vis absorption spectra obtained from a solution of *trans*-**1** in CH_3CN (2×10^{-5} mol dm^{-3}), with excess HCl added, after arc-lamp irradiation at 406.7 nm (*ca.* 3 mW) for 0, 30, 120, and 180 min, along with corresponding emission spectra obtained on excitation at 380 nm; no distinct emission features were observed at <500 nm following irradiation.

By contrast, irradiation of *trans*-**1**-H$^+$ at wavelengths in the range 400–430 nm, exciting exclusively to the MLCT state, resulted in pronounced changes in the absorption spectrum, and in a significant increase in the MLCT emission intensity (Fig. 2). The changes in the absorption spectrum of **1**-H$^+$ are consistent with *trans–cis* photoisomerization at the styryl –C=C– bond.[5] This interpretation was confirmed by ^{1}H NMR, which showed the production of new vinylic proton resonances characteristic of the *cis*-isomer;** integration of the *cis*- and *trans*-isomer peaks showed that the photostationary state reached on irradiation of *trans*-**1**-H$^+$ at 406.7 nm consisted of a *ca.* 50 : 50 *cis* : *trans* mixture. These results demonstrate that the photoisomerization of *trans*-**1** in acetonitrile is controlled by protonation.

The MLCT excited state of (bpy)Re(CO)$_3$ complexes typically decays back to the ground state in *ca.* 0.1 μs, by radiative and non-radiative routes, giving moderately intense MLCT emission in ambient temperature solution.[4] The extremely weak emission and the absence of any photochemical reaction for *trans*-**1** indicate that an additional non-radiative decay route that regenerates the ground state is available from the MLCT state of this complex. For complexes in which (bpy)Re(CO)$_3$ is linked to a dialkylamine by a saturated spacer, intramolecular electron transfer from the amine group to the Re centre in the MLCT state can result in the rapid (<1 ns) formation of a charge-separated ligand-to-ligand charge-transfer (LLCT) state which decays non-radiatively back to the ground state.[2,6] Our observations are consistent with this mechanism for the decay of the MLCT state of *trans*-**1**.

The moderately weak emission observed from *trans*-**1**-H$^+$ indicates that, like *trans*-**1**, an additional non-radiative decay route is available from the MLCT state in comparison with typical (bpy)Re(CO)$_3$ complexes. The results of the irradiation experiments show that the mechanism is dependent on protonation, and that *trans–cis* photoisomerization occurs only for the protonated form, *trans*-**1**-H$^+$. Recent studies of complexes in which (bpy)Re(CO)$_3$ is attached to stilbene-like ligands have shown that the MLCT state can decay by intramolecular energy transfer to form a triplet excited state of stilbene from which *trans–cis* isomerization occurs.[7] We attribute the photoisomerization of *trans*-**1**-H$^+$ to this mechanism:



The increase in MLCT emission on irradiation (Fig. 2) can be attributed to the loss of this intramolecular energy-transfer decay route on isomerization to *cis*-**1**-H$^+$ because the energy of the styryl-centred triplet excited state is raised in the *cis*-isomer;[7] $\Phi_{em} \approx 10^{-2}$ is estimated for *cis*-**1**-H$^+$. The significant increase in the MLCT emission intensity on isomerization serves as an effective 'signal' that photoswitching has occurred.

The experiments described above for the diethylamino derivative **1** have been repeated for the azacrown ether derivative **2** (see ESI†). The spectra of these two complexes, and of the free styryl ligands, are similar under all of the conditions studied. As for *trans*-**1**, photoisomerization in acetonitrile was observed only on protonation at the azacrown to form *trans*-**2**-H$^+$.

In addition to describing these complexes as proton-controlled photoswitches, they can also be described as two-input photoionic signal-processing devices:[8] the presence of both protons (ionic input) and visible light (photonic input) is required to give a photonic output change, observed as an increase in the emission intensity.

In summary, we have demonstrated that protonation can be used to control the *trans–cis* photoisomerization reaction of a complex in which (bpy)Re(CO)$_3$ is linked by a stilbene-like bridging ligand to an amine or an azacrown ether. The effectiveness of this approach for the azacrown ether complex provides an opportunity to explore the use of cations within the crown to control the photoisomerization reaction, and such experiments are in progress.

Notes and references

‡ (bpy)Re(CO)$_3$Cl was stirred with an excess of CF_3SO_3H at room temperature for 1 h to yield (bpy)Re(CO)$_3$(CF_3SO_3), which was refluxed overnight in THF under N_2 with <1 equiv of the appropriate styryl ligand, 4-(4-diethylaminostyryl)pyridine (py-DEAS) or 4-(4-aza-15-crown-5-styryl)pyridine (py-AZAS) (see ref. 9 for synthetic method for styryl ligands). The product was metathesized with NH_4PF_6 to yield [(bpy)Re(CO)$_3$(py-DEAS)]PF$_6$ (**1**) or [(bpy)Re(CO)$_3$(py-AZAS)]PF$_6$ (**2**), respectively. The complexes were purified by repeated recrystallization and column chromatography (5% MeOH–CH_2Cl_2 eluting on silica), and were characterized by IR, ES-MS and ^{1}H NMR, which showed that the *trans*-isomers were formed exclusively.

§ The absorption spectrum of the free *trans*-py-DEAS ligand in acetonitrile has a similar profile to that of *trans*-**1**, with an intense, solvatochromic absorption band at 375 nm and a weaker band at 250 nm.

¶ Samples were irradiated in a sealed 1 cm pathlength cell with the output from either a krypton ion laser (350.6 or 406.7 nm; 50 mW) or a xenon-arc lamp (monochromated to 5 nm bandpass; 1–3 mW).

|| No changes were observed in the absorption spectrum of *trans*-**1** following arc-lamp irradiation at 406 nm (3 mW) for 180 min; these conditions are identical to those illustrated for *trans*-**1**-H$^+$ in Fig. 2 except the absorbance at 406 nm was 0.7 for *trans*-**1** (*versus* 0.03 for *trans*-**1**-H$^+$).

** The ^{1}H NMR spectrum showed vinylic proton resonances assigned to *trans*-**1**-H$^+$ (δ 6.95, 7.28; $J_{H\text{-}H}$ = 16 Hz) before irradiation, and to both *cis*-**1**-H$^+$ (δ 6.35, 6.70; $J_{H\text{-}H}$ = 12 Hz) and *trans*-**1**-H$^+$ after irradiation.

1 A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515.

2 K. S. Schanze, D. B. MacQueen, T. A. Perkins and L. A. Cabana, *Coord. Chem. Rev.*, 1993, **122**, 63.

3 H. Görner and H. J. Kuhn, in *Advances in Photochemistry*, ed. D. C. Neckers, D. H. Volman and G. von Bünau, John Wiley & Sons, New York, 1995, vol. 19, p. 1.

4 K. Kalyanasundaram, *J. Chem. Soc., Faraday Trans.*, 1986, **82**, 2401; L. A. Sacksteder, A. P. Zipp, E. A. Brown, J. Streich, J. N. Demas and B. A. DeGraff, *Inorg. Chem.*, 1990, **29**, 4335.

5 H. Mrozek, H. Nikol, A. Vogler and F. Vögtle, *J. Photochem. Photobiol. A: Chem.*, 1994, **84**, 227.

6 K. S. Schanze and D. B. MacQueen, *J. Am. Chem. Soc.*, 1991, **113**, 6108.

7 V. W. W. Yam, V. C. Y. Lau and K. K. Cheung, *J. Chem. Soc., Chem. Commun.*, 1995, 259; V. W. W. Yam, V. C. Y. Lau and L. X. Wu, *J. Chem. Soc., Dalton Trans.*, 1998, 1461; K. S. Schanze, L. A. Lucia, M. Cooper, K. A. Walters, H. F. Ji and O. Sabina, *J. Phys. Chem.*, 1998, **102**, 5577; S. S. Sun, E. Robson, N. Dunwoody, A. S. Silva, I. M. Brinn and A. J. Lees, *Chem. Commun.*, 2000, 201.

8 A. P. de Silva, H. Q. N. Gunaratne and C. P. McCoy, *Nature*, 1993, **364**, 42.

9 A. Juris, S. Campagna, I. Bidd, J.-M. Lehn and R. Ziessel, *Inorg. Chem.*, 1988, **27**, 4007.