Two-Way Energy Transfer

Vectorial Control of Energy-Transfer Processes in Metallocyclodextrin Heterometallic Assemblies**

Johanna M. Haider, René M. Williams, Luisa De Cola, and Zoe Pikramenou**

In recent years, the importance of miniature photomolecular devices in nanoscale technology has led to the design of polymetallic supramolecular assemblies.[1–3] The employment of polyelectronic metal centers in a single supramolecular structure provides the basis for the development of molecular energy-conversion systems and wires in macromolecular systems.[4–7] Multistep reactions are usually required to link metallic building blocks together by means of covalent bonds; such multistep processes result in poor yields and synthetic complexity. Noncovalently assembled systems, in contrast, may allow control of the photoinduced processes by a simple choice of the assembled photoactive components. The noncovalent assembly of units in water presents other opportunities, not only to mimic natural processes, but also to provide easily accessible architectures. Self-assembled systems between ruthenium–bipyridine centers and various electron or energy acceptors have recently attracted much interest.[8–10] We are interested in studying photoinduced processes between metal units assembled in water through noncovalent interactions. We have previously introduced photoactive metals onto cyclodextrin rims for the assembly of photoactive units brought together by the cyclodextrin cavity.[11–14] Herein, we present a ruthenium tris(bipyridyl) cyclodextrin "wheel", $[Ru(\beta\text{-CD-mbpy})_3]^{2+}$ (**1**; β-CD-mbpy = 6-mono[4-methyl(4′-dimethyl-2,2′-bipyridyl] permethylated β-cyclodextrin which was isolated as the PF_6 salt **1**-$(PF_6)_2$ and which could be converted into the Cl salt **1**-Cl_2 to enhance its solubility) that acts as both energy donor and acceptor leading to a versatile system for communication between the inner metal core and the outer guest unit by energy transfer; metal-complex guests based on osmium(II) and iridium(III) terpyridine species with biphenyl or adamantyl tails attached to one of the ligands have been employed to examine the importance of the included tail in the photoinduced process (Figure 1).

Compound **1**, is an attractive luminescent receptor molecule with three cyclodextrin cups available for recognition. Solutions of **1** in water with 10 % acetonitrile exhibit luminescence at room temperature at 622 nm ($\Phi = 0.027$, $\tau_{\text{aerated}} = 460$ ns, $\tau_{\text{degassed}} = 640$ ns) upon excitation at the metal-to-ligand charge transfer (MLCT) band at 436 nm. Comparison of the photophysical properties of this complex with the parent complex $[Ru(mbpy)_3][PF_6]_2$, (mbpy = 4,4′-dimethyl-2,2′-bipyridine) which bears no cyclodextrins, indicates that cyclodextrin substitution does not have a significant effect.

Osmium(II)-based guests, have been employed to play the role of energy acceptors whereas iridium(III)-based guests were used as energy donors for the Ru^{II} center. The guests have hydrophobic biphenyl and adamantyl tails to ensure high binding constants in the cyclodextrin cavity. The nature of the hydrophobic tail, aliphatic versus aromatic, is selected to examine its effect in the photoinduced processes. Considering the excited-state energies of the metal units (2 eV for Ru (620 nm), 1.7 eV for Os (730 nm), and 2.36 eV for the Ir complexes (525 nm))[15] we can estimate the driving force for the energy-transfer processes; for the energy transfer from Ru^{II} to Os^{II} this is estimated to be $\Delta G = -0.3$ eV, and for the energy transfer from Ir^{III} to Ru^{II} $\Delta G = -0.36$ eV. The shift of the $\lambda_{\max}$ of the emission spectra of the photoactive components (Figure 2a) show the relative trend of their excited-state energies, indicating the dual role of the ruthenium cyclodextrin complex as an energy donor or acceptor for the Os^{II} and Ir^{III} guests, respectively. A pictorial description of the excited-state energies of the photoactive metal components is presented in Figure 2b.

Photoinduced energy transfer from the ruthenium center of **1**-Cl_2 to the $[Os(biptpy)(tpy)]Cl_2$ (biptpy = 4′-(4-biphenyl)-2,2′:6′,2″-terpyridine, tpy = 2,2′:6′,2″terpyridine) complex bound in the cyclodextrin has been studied by time-resolved luminescence spectroscopy. Upon addition of a 22-fold excess of the guest in an aqueous solution of the ruthenium receptor, a high percentage (around 83 %) of a short-lived component of 20 ps in the ruthenium luminescence lifetime is detected (Figure 3a) corresponding to the energy-transfer process. In these conditions about 87 % of the cyclodextrin cups are filled[11] which agrees with the percentage of the short

---

[*] Dr. Z. Pikramenou, Dr. J. M. Haider
School of Chemical Sciences
The University of Birmingham
Edgbaston, Birmingham B15 2TT (UK)
Fax: (+44) 121-414-4446 or 4403
E-mail: z.pikramenou@bham.ac.uk

Prof. Dr. L. De Cola, Dr. R. M. Williams
Molecular Photonic Materials
Institute of Molecular Chemistry
Faculty of Science, University of Amsterdam
Nieuwe Achtergracht 166, 1018 WS Amsterdam (Netherlands)
Fax: (+31) 20-525-6456
E-mail: ldc@science.uva.nl

[**] We are grateful to The Leverhulme Trust and The Royal Society for funding.

DOI: 10.1002/ange.200250164

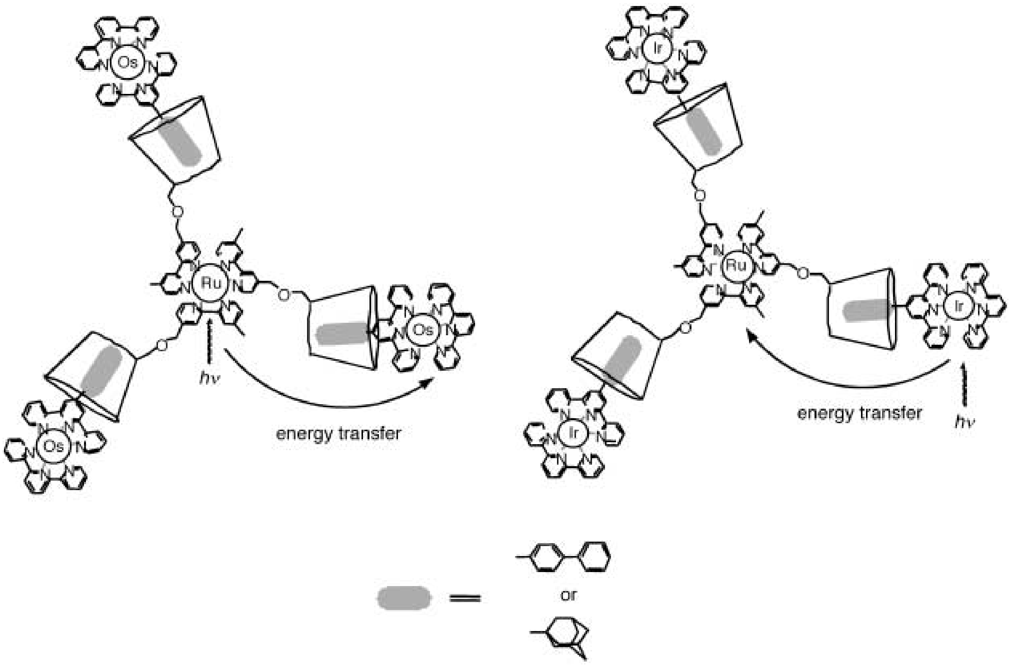

Figure 1. Assembled Os^{II} or Ir^{III} metal-complex guests with **1** allows photoinduced energy transfer from and to the ruthenium core.

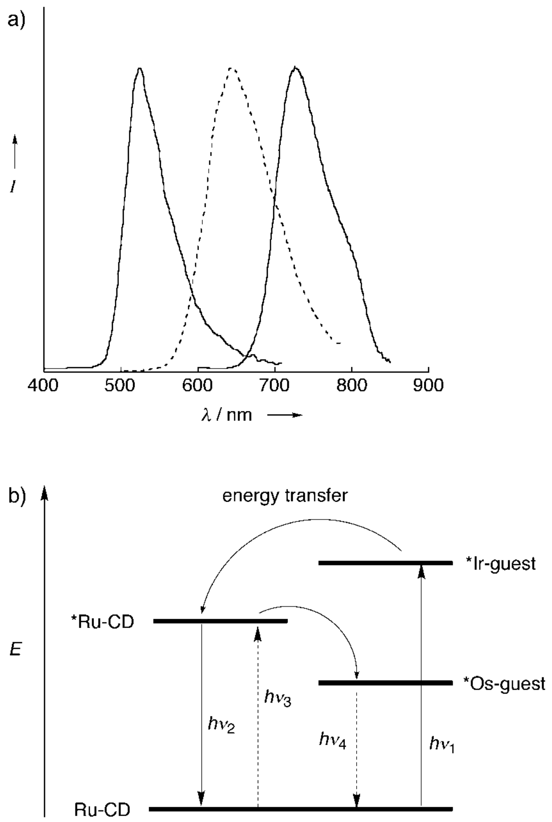

Figure 2. a) Steady-state emission spectra of [Ir(tpy)(tpy-ada)][NO$_3$]$_3$, **1**-Cl$_2$, and [Os(tpy-ada)(tpy)][NO$_3$]$_2$ (from left to right) in aqueous solution, observed at room temperature. The intensities are not to scale. b) Simplified energy diagram of the excited states of the photoactive components.

component. According to $k=(1/\tau)-(1/\tau_0)$, an energy-transfer rate of $8.3\times10^{10}\,s^{-1}$ is calculated. Furthermore upon excitation at the same wavelength, 324 nm, a rise time of the osmium luminescence signal at 730 nm of 13 ps confirms the photoinduced energy transfer from the ruthenium center to the guest through noncovalent bonds These results confirm that in spite the relatively long metal–metal distance (≈ 16 Å, calculated from an MM2 model) and the noncovalent nature of the bridge, light excitation of the ruthenium-based unit in the heterometallic [Ru(β-CD-mbpy)$_3$–Os(biptpy)(tpy)]$^{4+}$ supramolecular assembly leads to an efficient-energy transfer process, in aqueous solutions.

To study the influence of the hydrophobic tail in the energy-transfer process between the Ru^{II} and Os^{II} centers, similar experiments were performed with [Os(tpy-ada)(tpy)][NO$_3$]$_2$ (tpy-ada = 4′-(1-adamantyl)-2,2′:6′,2″-terpyridine). The ruthenium luminescence is partially quenched, hence the appearance of a long component in the lifetime; the short component of 1.08 ns agrees with an observed rise time in the osmium emission of 1.12 ns (Figure 3b). An energy-transfer rate of $6.4\times10^{8}\,s^{-1}$ is calculated for the process. These results clearly show that the nature of the hydrophobic tail unit has a strong effect on the energy transfer process. Taking into consideration that the adamantyl tail should bring the metals closer together than the biphenyl one, the slowing down of the energy-transfer process is attributed to the effect of the orbital overlap, which implies a contribution from the Dexter mechanism, controlled by the electronic interaction between cyclodextrin and biphenyl, or cyclodextrin and adamantyl. In covalently linked systems aliphatic spacers are known to lead to a slower rate of energy-transfer than conjugated spacers.[16–22] However, in most of those cases the spacer affects the spatial disposition of the photoactive centers, whereas in our case this factor is eliminated.

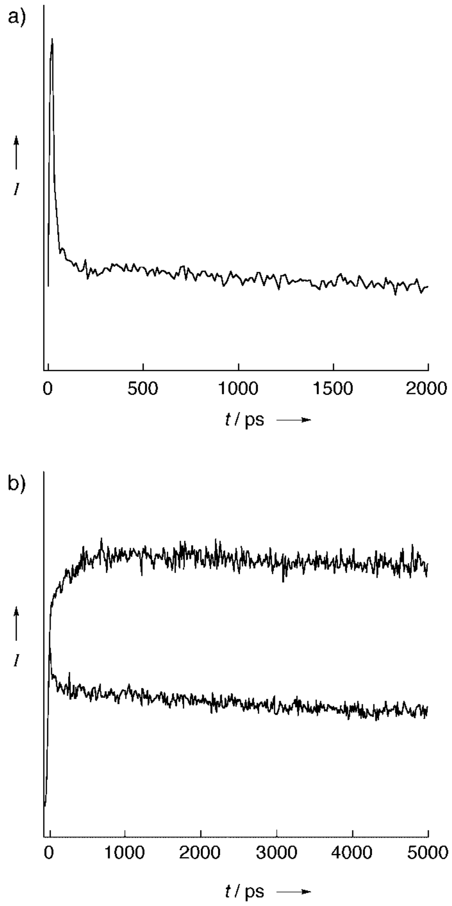

Figure 3. a) Time-resolved emission of an aqueous solution of **1**-Cl_2 (1.8×10^{-5} M) with [Os(biptpy)(tpy)]Cl_2 (3.8×10^{-4} M). Excitation at 324 nm, detection at 600 nm. b) Time-resolved emission of an aqueous solution of **1**-Cl_2 (1.8×10^{-5} M) with [Os(tpy-ada)(tpy)][NO_3]$_2$ (1.4×10^{-4} M). Excitation at 324 nm, detection at 600 nm (lower trace) and at 730 nm (upper trace).

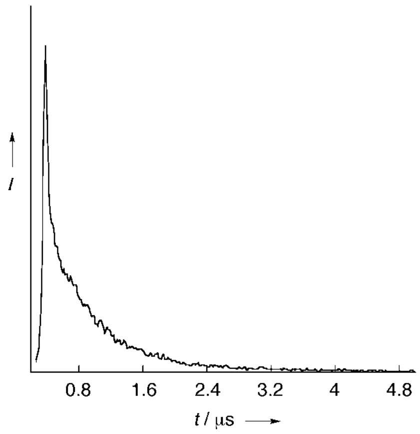

Figure 4. Time-resolved emission of an aqueous solution of [Ir(tpy-ada)(tpy)][NO_3]$_3$ (2.5×10^{-5} M) with **1**-Cl_2 (3.7×10^{-5} M). Excitation at 330 nm, detection at 570 nm.

To monitor the luminescence of the iridium guest, excess of the ruthenium complex was used to ensure binding of most of the guests (80–95%) in the cyclodextrin cups. Monitoring of the iridium luminescence lifetime (at 525 nm) upon excitation at 330 nm showed the presence of a fast component with an amplitude determined by the amount of complexed iridium compound, with a lifetime of $\tau = 3$ ns for [Ir(biptpy)(tpy)][NO_3]$_3$ and $\tau = 35$ ns [Ir(tpy-ada)(tpy)][NO_3]$_3$ (Figure 4). Besides the short components there was also a long component present, which was 1.2 µs for the biptpy and 0.5 µs for the tpy-ada system, which correspond to the lifetimes of the separate complexes. Monitoring of the emission of the ruthenium center at 620 nm does not show any change in the ruthenium luminescence lifetime, which excludes the presence of an electron-transfer process as the dominant pathway. The ruthenium–iridium photoinduced communication through noncovalent bonds is attributed to an energy transfer from the iridium guest to the ruthenium core. The energy-transfer rates are estimated to be 3.3×10^{8} and 2.9×10^{7} s^{-1} for the biphenyl and the adamantly guests, respectively. In accordance with the osmium case we observe a slowing down of the rate by changing of the hydrophobic tail of the guest from an aromatic to an aliphatic moiety.

In summary, we have demonstrated that photoinduced energy transfer through a cyclodextrin cavity establishes communication between metal centers in water mediated by noncovalent interactions. The ruthenium "wheel" cyclodextrin system allows vectorial control of energy transfer between metal centers in aqueous solutions. The system allows switching of the two-way communication between the inner metal core and the outer ones by simply changing the photoactive metal-complex guests.

Experimental Section

The ligands 6-mono[4-methyl(4′-methyl-2,2′-bipyridyl)]-permethylated β-cyclodextrin (β-CD-mbpy),[12] 4′-(4-biphenyl)-2,2′:6′,2″-terpyridine (biptpy),[23] 4′-(1-adamantyl)-2,2′:6′,2″-terpyridine (tpy-ada) and the metal complexes[12] were prepared by analogous procedures to those previously reported. The time-resolved emission experiments were performed by time-correlated single-photon counting system employing a frequency doubled DCM dye laser which is synchronously pumped with a mode locked Argon ion laser resulting in 324 nm 20 ps FWHM pulses; details of the instrument have been previously described.[11]

1-(PF_6)$_2$ ^{1}H NMR (300 MHz, CD_3CN): $\delta = 8.5$, 8.4 (s, 6H, H-3, H3′), 7.9–7.5 (m, 6H, H-6, H-6′), 7.4–7.2 (m, 6H, H-5, H-5′), 5.2–5.0 (m, 21H, H_{Glu}-1), 4.7 (br dd, 6H, H-7), 4.2 (br d, 3H, H_{Glu}-6), 3.9–3.0 (m, -OCH_3 and H_{Glu}-2,3,4,5,6), 2.5 ppm (s, 9H, CH_3). ROESY ^{1}H NMR spectroscopy has been carried out to detect NOE connectivities and confirm assignments. Electrospray MS (MeOH): m/z: 2448 $\{M-2[PF_6]\}^{2+}$. Elemental analysis: calcd (%) for **1**-Cl_2: $C_{219}H_{348}Cl_2N_6O_{108}$–$Ru_1\cdot 20H_2O$ ($M_r = 5325.46$) C 49.39, H 7.34 N, 1.58; found: C 49.19, H 6.97, N 1.66.

Received: September 16, 2002 [Z50164]

Keywords: cyclodextrins · energy transfer · metal–metal interactions · N ligands · ruthenium

---

[1] M. Barboiu, J.-M. Lehn, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 5201.

[2] S. Encinas, L. Flamigni, F. Barigelletti, E. C. Constable, C. E. Housecroft, E. R. Schofield, E. Figgemeier, D. Fenske, M. Neuburger, J. G. Vos, M. Zehnder, *Chem. Eur. J.* **2002**, *8*, 137.
[3] S. Serroni, S. Campagna, F. Puntoriero, C. Di Pietro, N. D. McClenaghan, F. Loiseau, *Chem. Soc. Rev.* **2001**, *30*, 367.
[4] a) F. Barigelletti, L. Flamigni, *Chem. Soc. Rev.* **2000**, *29*, 1; b) A. El-ghayoury, A. Harriman, A. Khatyr, R. Ziessel, *Angew. Chem.* **2000**, *112*, 191; *Angew. Chem.* **2000**, *39*, 185.
[5] L. De Cola, P. Belser, *Coord. Chem. Rev.* **1998**, *177*, 301.
[6] D. J. Cardenas, J.-P. Collin, P. Gavina, J.-P. Sauvage, A. De Cian, J. Fischer, N. Armaroli, L. Flamigni, V. Vicinelli, V. Balzani, *J. Am. Chem. Soc.* **1999**, *121*, 5481.
[7] P. F. H. Schwab, M. D. Levin, J. Michl, *Chem. Rev.* **1999**, *99*, 1863.
[8] Y.-Z. Hu, S. Tsukiji, S. Shinkai, S. Oishi, I. Hamachi, *J. Am. Chem. Soc.* **2000**, *122*, 241.
[9] H. F. Nelissen, A. F. J. Schut, F. Venema, M. C. Feiters, R. J. M. Nolte, *Chem. Commun.* **2000**, 577.
[10] M. D. Ward, *Chem. Soc. Rev.* **1997**, *26*, 365.
[11] J. M. Haider, M. Chavarot, S. Weidner, I. Sadler, R. M. Williams, L. De Cola, Z. Pikramenou, *Inorg. Chem.* **2001**, *40*, 3912.
[12] J. M. Haider, Z. Pikramenou, *Eur. J. Inorg. Chem.* **2001**, 189.
[13] M. Chavarot, Z. Pikramenou, *Tetrahedron Lett.* **1999**, *40*, 6865.
[14] S. Weidner, Z. Pikramenou, *Chem. Commun.* **1998**, 1473.
[15] J.-P. Collin, I. M. Dixon, J.-P. Sauvage, J. A. G. Williams, F. Barigelletti, L. Flamigni, *J. Am. Chem. Soc.* **1999**, *121*, 5009.
[16] F. Barigelletti, L. Flamigni, M. Guardigli, A. Juris, M. Beley, S. Chodorowski-Kimmes, J.-P. Collin, J.-P. Sauvage, *Inorg. Chem.* **1996**, *35*, 136.
[17] V. Balzani, F. Barigelletti, P. Belser, S. Bernhard, L. De Cola, L. Flamigni, *J. Phys. Chem.* **1996**, *100*, 16786.
[18] B. Schlicke, P. Belser, L. De Cola, E. Sabbioni, V. Balzani, *J. Am. Chem. Soc.* **1999**, *121*, 4207.
[19] M. Frank, M. Nieger, F. Voegtle, P. Belser, A. von Zelewsky, L. De Cola, V. Balzani, F. Barigelletti, L. Flamigni, *Inorg. Chim. Acta* **1996**, *242*, 281.
[20] L. De Cola, V. Balzani, F. Barigelletti, L. Flamigni, P. Belser, A. von Zelewsky, M. Frank, F. Voegtle, *Inorg. Chem.* **1993**, *32*, 5228.
[21] L. S. Kelso, T. A. Smith, A. C. Schultz, P. C. Junk, R. N. Warrener, K. P. Ghiggino, F. R. Keene, *J. Chem. Soc. Dalton Trans.* **2000**, 2599.
[22] P. T. Gulyas, T. A. Smith, M. N. Paddon-Row, *J. Chem. Soc. Dalton Trans.* **1999**, 1325.
[23] N. W. Alcock, P. R. Barker, J. M. Haider, M. J. Hannon, C. L. Painting, Z. Pikramenou, E. A. Plummer, K. Rissanen, P. Saarenketo, *J. Chem. Soc. Dalton Trans.* **2000**, 1447.