COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Coordinative control of photoinduced electron transfer: bulky carboxylates as molecular curtains

Irene Bruseghini, Luigi Fabbrizzi,* Maurizio Licchelli and Angelo Taglietti
Dipartimento di Chimica Generale, Università di Pavia, Viale Taramelli 12, 27100 Pavia, Italy.
E-mail: luigi.fabbrizzi@unipv.it

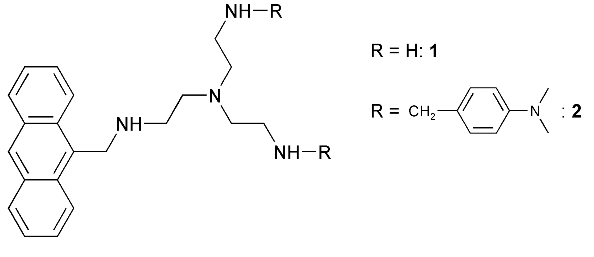
Received (in Cambridge, UK) 3rd March 2002, Accepted 8th May 2002
First published as an Advance Article on the web 23rd May 2002

An intramolecular photoinduced electron transfer which takes place in a Zn^{II} polyamine complex can be interrupted through coordination of a bulky carboxylate anion, acting as a curtain.

Electron transfer, the most elementary chemical reaction, plays a key role in processes of relevance to life.[1] During the last decade, a large number of model compounds for studies on electron transfer has been provided. Models typically consist of a photoexcitable fragment, exhibiting for instance acceptor properties (A), covalently linked to an electron donor (D). In some cases, the two subunits communicate electronically and the efficiency of the D-to-A* photoinduced electron transfer (PeT) can be tuned by varying the *through-bond* distance between D and A.[2] However, a few examples refer to systems capable of direct *through-space* PeT,[3] and even fewer examples have been reported about control and modulation of PeT processes through the complexation of guest molecules, which intercalate between the donor and the acceptor.[4]

In the past years, we have reported some examples of systems in which a PeT process can be established by taking advantage of metal–ligand interactions.[5,6]

We report here a DA system in which it is possible to address and modulate a through-space intramolecular PeT process by means of metal–ligand interactions, taking place in a Zn^{II} polyamine complex. In particular, we were interested to control a PeT process from D to A, simply lowering, between D and A, a molecular 'curtain' capable of interrupting the electron transfer, and to drive this insertion through a coordinative interaction. In this connection, we have synthesized the polyfunctional system **2**,† in which one anthracene substituent (An) and two *N*,*N*-dimethylaniline (DMA) subunits are appended, through –CH$_2$– spacers, to the terminal nitrogen atoms of the tripodal tetramine tren. The precursor system **1**, containing the sole An substituent, was also considered for comparative purposes.



The photophysical behavior of **1** and **2** in solution (MeOH–H$_2$O, 4 : 1, v/v) was first investigated by carrying out spectrofluorimetric investigations at varying pH. First, a solution of **1**, containing excess acid, was titrated with standard base. Under acidic conditions (pH < 2.5), the strong and characteristically structured emission band of An was observed. Then, on increasing pH, the fluorescence intensity, I_F, decreased until almost complete quenching at pH ≥ 8 (Fig. 1(a), grey triangles). Progressive fluorescence quenching has to be associated to the fact that the deprotonation of the ammonium groups of **1** makes the lone pair of each amine nitrogen atom available for a PeT process to the proximate An fragment. A second spectrofluorimetric titration was carried out on an identical solution, to which 1 equiv. of Zn^{II} had been added. An I_F decrease was still observed until pH ~4.5, where emission started to increase, as a result of Zn^{II} complexation to the tetramine (Fig. 1(a), black triangles). In fact, upon complexation, amine lone pairs become engaged in the coordination of the metal and are no longer available for any PeT process: as a consequence, fluorescence is restored.[7] The [Zn^{II}(**1**)]$^{2+}$ complex shows a trigonal bipyramidal stereochemistry, with a solvent molecule (*i.e.* H$_2$O) occupying the vacant axial position. The moderate fluorescence quenching occurring at pH ≥ 7 has to be associated to the deprotonation of the axially bound water molecule, which induces the occurrence an intra-complex PeT process from the metal bound OH$^-$ ion to the An* subunit.[8] The same titration experiment was repeated in presence of 1 equiv. of triphenylacetic acid (TPA), and gave a profile perfectly superimposable on that of the second experiment (Fig. 1(a), open triangles).

Then, the same titration set was carried out with system **2**. Titration of the metal-free solution of the D–A system **2** gave similar results to those observed for **1**, as shown in Fig. 1(b) (shaded circles). Titration of **2** in presence of an equimolar amount of Zn^{II} produced a different profile than observed for **1**: in particular, I_F kept decreasing even beyond pH = 4.5, where the Zn^{II} tetramine complex begins to form (Fig. 1(b), filled circles). We ascribe this behaviour to the metal complexation, which brings the photoexcited fragment An* and the DMA subunits close enough to allow the occurrence of an intra-complex through-space PeT process.[5,6] In particular, An* behaves as an electron acceptor and DMA as a donor. Notice that the DMA-to-An* PeT process is less efficient that the amine nitrogen-to-An* process, as indicated by the less pronounced negative slope of the titration profile in presence of Zn^{II}, compared to the steeper profile obtained in absence of Zn^{II}. However, when the titration is performed in presence of TPA, at pH ≥ 4.5 a sharp enhancement of fluorescence is observed, with almost full recovery of the initial emission at pH = 7–8 (Fig. 1(b), open circles). This behaviour is associated to the formation of the Zn^{II} polyamine complex and to the simultaneous binding

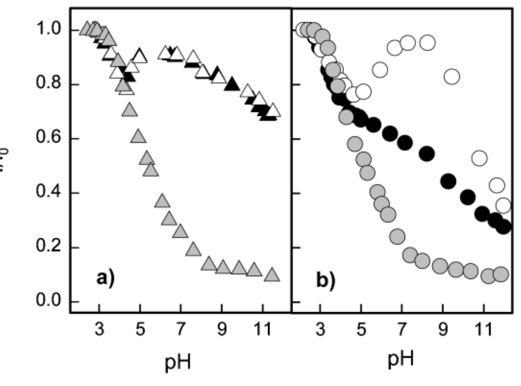
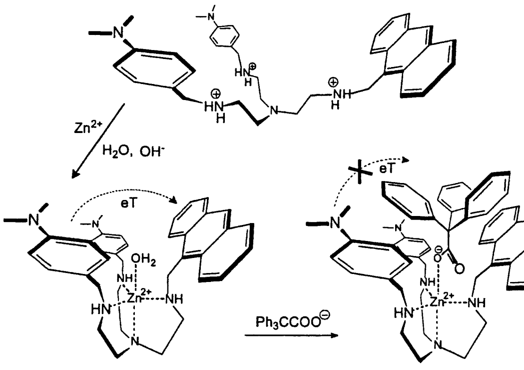


Fig. 1 Spectrofluorimetric pH-titrations of MeOH–H$_2$O (4 : 1 v/v) solutions of (a) **1** (grey triangles); **1** + 1 equiv. Zn^{2+} (black triangles); **1** + 1 equiv. Zn^{2+} + 1 equiv. TPA (white triangles) and (b) **2** (grey circles); **2** + 1 equiv. Zn^{2+} (black circles); **2** + 1 equiv. Zn^{2+} + 1 equiv. TPA (white circles).

DOI: 10.1039/b202815h

of the TPA anion to the axial site of the metal complex. While the bulky carboxylate coordination does not produce any change in the emission of reference compound $[Zn^{II}(\mathbf{1})]^{2+}$, in the case of the $[Zn^{II}(\mathbf{2})]^{2+}$ binding of the TPA anion brings the triphenylic moiety amid An* and DMA fragments, thus disturbing and almost completely removing the intramolecular eT process. Molecular modelling studies (MM+) indicated that binding of TPA to Zn^{II} induces a divarication of the An and DMA substituents, whose reciprocal distance is remarkably increased. In particular the distance between C(10) of An and the nitrogen atom of each DMA fragment increases from about 8 Å to 11.5–12.5 Å. However, in absence of crystal structural data, the proposed stereochemical arrangements must be considered as an only a hypothesis. The cascade binding of Zn^{II} and TPA anion to **2** is pictorially illustrated in Scheme 1.



Scheme 1

In order to corroborate the proposed mechanism, we carried out further spectrofluorimetric titration experiments, by adding a variety of carboxylate anions to an MeOH solution of the $[Zn^{II}(\mathbf{2})]^{2+}$ complex. Titration profiles are reported in Fig. 2.

On titration with acetate and cyclohexylcarboxylate, the solution remained poorly fluorescent (open and filled circles in Fig. 2). A moderate I_F increase was observed on titration with 1-adamantanecarboxylate and benzoate (white and black squares).

On the other hand, titration with the TPA anion (filled triangles) induced a significant increase of the anthracene emission. It should be noted that none of the considered carboxylates induced any I_F increase when added to a methanolic solution of the reference system $[Zn^{II}(\mathbf{1})]^{2+}$. Non-linear least-squares analysis of the titration profiles (spectrofluorimetric and/or spectrophotometric) confirmed the formation of 1:1 carboxylate–complex adduct, whose formation constants K are reported in Table 1. Log$K$ values range between 4.4 and 5.6 and do not seem to correlate with the bulkiness of the anion substituent, thus excluding steric repulsive effects between the anion and the substituents on the polyamine framework.

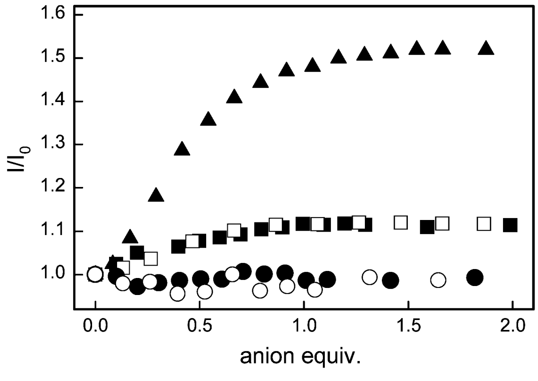


Fig. 2 Spectrofluorimetric titrations with carboxylates of a MeOH soloution of $[Zn^{II}(\mathbf{2})]^{2+}$. Anions added: acetate (○), cyclohexylcarboxylate (●), benzoate (■), 1-adamantanecarboxylate (□), TPA (▲).

Table 1 Log$K$ values for adduct formation equilibria in MeOH, at 25 °C: $[Zn^{II}(\mathbf{L})]^{2+}$ + carboxylate $\rightleftharpoons$ $[Zn^{II}(\mathbf{L})(\text{carboxylate})]^{+}$

Anion	logK^a $[Zn^{II}(\mathbf{2})]^{2+}$	$[Zn^{II}(\mathbf{1})]^{2+b}$
Triphenylacetate	5.6 ± 0.1 (5.5 ± 0.1)	(5.3 ± 0.1)
1-Adamantanecarboxylate	4.5 ± 0.2	
Benzoate	5.2 ± 0.1 (5.1 ± 0.2)	(4.9 ± 0.2)
Cyclohexylcarboxylate	(4.4 ± 0.2)^b	
Acetate	(4.4 ± 0.2)^b	(4.7 ± 0.2)

[a] As determined from fluorescence and UV/Vis (in parenthesis) titrations. [b] No emssion changes were detected.

By contrast, anion bulkiness has a profound effect in controlling the efficiency of the intramolecular electron transfer in $[Zn^{II}(\mathbf{2})]^{2+}$: in particular, the anion bearing the bulkiest substituent, TPA, prevents the occurrence of a PeT process from DMA to An*, so that the excited fluorophore can undergo its normal radiative decay. This behaviour is ascribed to the fact that the sterically hindering TPA anion fills the cavity which interfaces An* and DMA substituents, preventing any occasional contact and extruding solvent molecules. Moreover, the metal bound TPA anion, even if containing π-fragments, is not favourably oriented for being permeable to electrons, thus behaving as an insulating material.

This work has demonstrated that the powerful fluorescent signal can be switched ON by insulating D and A with an interfacing molecular fragment, the process being driven by a metal–ligand interaction. This work has been supported by the European Union (RTN Molecular Level Devices and Machines) and by the Italian Ministry of University and Research (PRIN 2001-Dispositivi Supramolecolari).

Notes and references

† *Preparation* of **2**: a solution of 4-dimethylaminobenzaldehyde (5.1 mmol in 40 ml of MeOH) was added dropwise over 2 h under magnetic stirring to a solution of **1** (2.5 mmol in 60 ml of MeOH), whose synthesis was reported elsewhere.[5] The solution was kept at 40 °C for 36 h. Then $NaBH_4$ was carefully added in small portions and the solution was heated at 50 °C overnight. The solvent was then removed and the resulting sticky solid was suspended in 70 mL of water. The aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The organic phase was dried with $MgSO_4$ and the solvent was distilled off, giving L as a dark orange oil, which was washed with several portions of diethyl ether. Yield: 75%. ESMS: *m*/*z* (%) 603.4 (100) (M + H+).

1 *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley, VCH, 2001.
2 K. D. Jordan and M. N. Paddon Row, *Chem. Rev.*, 1992, **92**, 395; K. A. Jolliffe, T. D. M. Bell, K. P. Ghiggino, S. J. Langford and M. N. Paddon Row, *Angew. Chem., Int. Ed.*, 1998, **37**, 916; H. Han and M. B. Zimmt, *J. Am. Chem. Soc.*, 1998, **120**, 8001; T. D. M. Bell, K. A. Jolliffe, K. P. Ghiggino, A. M. Oliver, M. J. Shephard, S. J. Langford and M. N. Paddon Row, *J. Am. Chem. Soc.*, 2000, **122**, 10661.
3 T. Arimura, S. Ide, Y. Suga, T. Nishioka, S. Murata, M. Tachiya, T. Nagamura and H. Inoue, *J. Am. Chem. Soc.*, 2001, **123**, 10744 and references therein.
4 J. N. H. Reek, A. E. Rowan, M. J. Crossley and R. J. M. Nolte, *J. Org. Chem.*, 1999, **64**, 6653.
5 G. De Santis, L. Fabbrizzi, M. Licchelli, A. Poggi and A. Taglietti, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 202.
6 L. Fabbrizzi, M. Licchelli, P. Pallavicini and A. Taglietti, *Inorg. Chem.*, 1996, **35**, 1733; M. Di Casa, L. Fabbrizzi, M. Licchelli, A. Poggi, A. Russo and A. Taglietti, *Chem. Commun.*, 2001, 825.
7 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.
8 L. Fabbrizzi, M. Licchelli, A. Perotti, A. Poggi, G. Rabaioli, D. Sacchi and A. Taglietti, *J. Chem. Soc., Perkin Trans. 2,* 2001, 2108.