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Zinc(II) driven intra-molecular electronic energy transfer in a supramolecular assembly held by coordinative interactions

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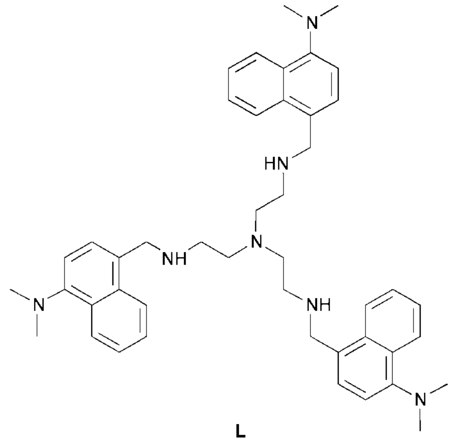
In a MeOH solution the complex $[Zn^{II}(L)]^{2+}$ gives an adduct with the coumarin-343 anion and an electronic energy transfer process takes place from the fluorophore placed on the ligand L to the fluorescent anion, according to a mechanism which can be reversively switched OFF–ON following an acid–base input.

Photonic energy can be transferred from an excited fragment Fl_1 (adsorbing light at wavelength λ_1) to a proximate fragment Fl_2, which emits light at a distinctly higher wavelenth λ_2. A typical mechanism involves the occurrence of a double electron transfer process between Fl_1 and Fl_2, according to a circular pathway, and requires that the two fragments experience occasional van der Waals contacts so that their orbitals can overlap.[1] When Fl_1 and Fl_2 are (or belong to) distinct molecules, a large excess of one of the fluorophores is required in order to ensure the occurrence of the occasional contact: the electronic energy transfer (EET) has an intermolecular nature and the photophysical response (*e.g.* the increase of the fluorescence intensity, I_F, at λ_2) must follow Stern–Volmer behaviour. However, the process can also take place intramolecularly, if Fl_1 and Fl_2 are covalently linked by a relatively short spacer, which makes their encounter much more probable.[2] Intramolecular EET can also be achieved in supramolecular systems in which Fl_1 and Fl_2 belong to distinct moieties held together by non-covalent interactions (*e.g.* hydrogen bonding).[3] EET processes in supramolecular systems are of interest in the fast-growing area of molecular level devices, molecular computing and elementary nanotechnology.[4] We describe here an example of an intramolecular EET process in a system held together by metal–ligand interactions. Metal-mediated inter-component energy transfer has been observed in a few cases.[5] The involved metal is the Zn^{II} cation, which is photophysically inactive and plays an architectural role,[6] bringing Fl_1 and Fl_2 to a suitable distance for the occurrence of an efficient EET process. From this perspective, in the molecule **L** a tripodal tetramine platform has been equipped with three equivalent luminescent fragments that absorb UV light (*N*,*N*-dimethylamine-1-naphthalene: Fl_1; absorption band centred at λ_{max} = 330 nm, emission band centred at λ_{max} = 424 nm).† On the other hand, the dye coumarin-343 was chosen as Fl_2, showing a strong emission at λ_{max} = 475 nm and containing a carboxylic function. Substantial overlap of the absorption band of Fl_1 and of the emission band of Fl_2 fulfils the prerequisite for the occurrence of an EET process.[7]



L

The tetramine **L** must be preliminarily organised through Zn^{II} coordination, according to a process which can be spectrofluorimetrically monitored. In particular, titration of an ethanolic solution of **L** with Zn^{II} induces an increase in the Fl_1 emission intensity, at 330 nm; a limiting value (2.5-fold enhancement) is achieved with the addition of one or more Zn^{II} equivalents. This behaviour is consistent (i) with the formation of a $[Zn^{II}(L)]^{2+}$ complex, and (ii) with the fact that Zn^{II} coordination prevents the occurrence of an electron transfer (eT) process from the proximate amine nitrogen atom to the photoexcited Fl_1 fluorophore—this eT process was responsible for partial quenching of the fluorescence. On formation of the $[Zn^{II}(L)]^{2+}$ complex, full emission of Fl_1 is restored.

Subsequently, an ethanolic solution of $[Zn^{II}(\mathbf{L})]^{2+}$ (1×10^{-5} mol dm^{-3}), irradiated at 330 nm, was titrated with a standard solution of Fl_2. Progressive addition of the titrating solution induced a progressive decrease in the emission band of Fl_1 and the development of an emission band at 475 nm, indicating Fl_2 sensitisation and the occurrence of an EET process involving Fl_1 and Fl_2 (see Fig. 1).

The fluorescence intensity, I_F, of the band at 424 nm *vs.* equiv. of Fl_2 profile (decreasing), as well as the I_F at 475 nm *vs.* equiv. of Fl_2 profile (increasing, see inset in Fig. 1) correspond to the formation of a 1 : 1 adduct between $[Zn^{II}(\mathbf{L})]^{2+}$ and coumarin-343. The log *K* values for the adduct formation equilibrium, calculated through non-linear, least squares treatment of the titration profiles, are 5.98 ± 0.04 (λ = 335 nm) and 6.01 ± 0.03 (λ = 475 nm). This behaviour can be explained considering that: (i) the tripodal tetramine **L** imposes a trigonal bipyramidal stereochemistry on the Zn^{II} ion, leaving one vacant axial position; in the absence of coordinating anions, this

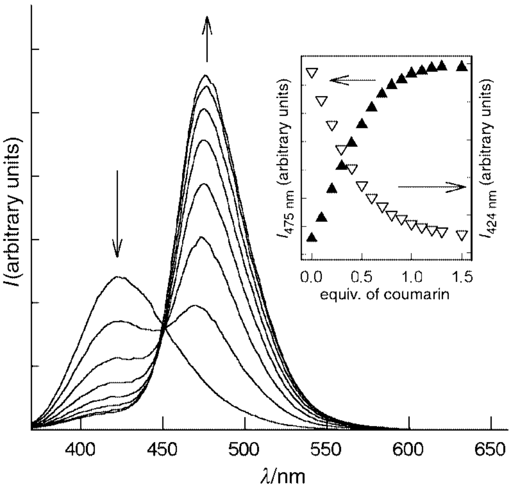


Fig. 1 Selected emission spectra recorded during the spectrofluorimetric titration of a MeOH solution of $[Zn^{II}(\mathbf{L})]^{2+}$ (1×10^{-5} M) with a standard MeOH solution of coumarin-343. The corresponding titration profiles (fluorescence intensity *vs.* equiv. of coumarin) are shown in the inset.

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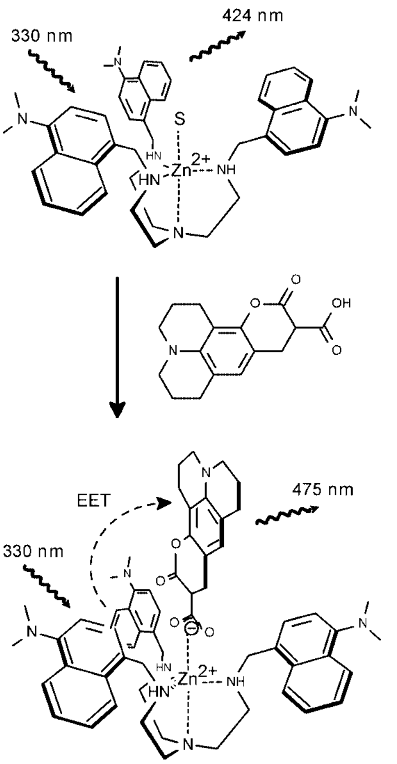

Scheme 1

position can be occupied by a solvent molecule; (ii) the CO_2H group of coumarin-343 deprotonates and the carboxylate fragment replaces the solvent molecule loosely bound in the axial position; (iii) coordination to the metal brings the photoexcited Fl_1 substituent close enough to Fl_2 to ensure the occurrence of an efficient EET process, thus leading to a substantial sensitisation of Fl_2 emission. Any intermolecular contribution to the process was found to be negligible at this low concentration scale of the reagents (10^{-5} mol dm^{-3}). The mechanism of the process is illustrated in Scheme 1.

Thus, the Zn^{II} ion acts as a glue, sticking together the two fluorogenic fragments. It should be noted that an energy transfer rate constant larger than 3.5×10^9 s^{-1} can be calculated from the equation $k_{EET} = (\Phi_0/\Phi - 1)/\tau°$, where $\tau°$ is the lifetime of Fl_1 in the $[Zn^{II}(\mathbf{L})]^{2+}$ complex (2.6 ns), and Φ_0 and Φ are the values of the quantum yield of Fl_1, in the $[Zn^{II}(\mathbf{L})]^{2+}$ complex and in the $[Zn^{II}(\mathbf{L})(Fl_2)]^+$ adduct, respectively.[8]

When the titration experiment is repeated in the absence of the metal cation, no evidence of adduct formation is observed. In this case, a small development of the coumarin emission band at 475 nm occurs, while a small quenching of Fl_1 emission is observed. This behaviour is ascribed to intermolecular dynamic quenching *via* energy transfer, and was found to obey strictly the Stern–Volmer relationship along the investigated concentration range (up to 5×10^{-5} mol dm^{-3}).

In order to check the role of the metal cation in the EET process further, a solution containing equimolar amounts of ligand **L** and of coumarin-343 was titrated with a Zn^{2+} standard solution, whilst recording the emission spectra (λ_{exc} = 330 nm). Addition of the metal ion switches ON the electronic energy flow: the emission at 475 nm increases as Zn^{2+} is added, reaching a *plateau* with the addition of one equivalent of the metal ion. The $[Zn^{II}(\mathbf{L})(Fl_2)]^+$ ternary complex displays an interesting switching behaviour with respect to the addition of standard acid and base. In fact, when a methanolic solution of $[Zn^{II}(\mathbf{L})(Fl_2)]^+$ is titrated with triflic acid, the sensitised coumarin-343 emission decreases and completely disappears upon the addition of 4 equiv. acid (see Fig. 2). In other words, H^+ ions switches OFF the electronic energy flow between Fl_1 and Fl_2. This effect is due to the successful competition of the protons for the amine groups, which leads to demetallation and to the moving away of Fl_1 and Fl_2. The electronic energy flow can be switched ON again on titration with standard base. In particular, upon addition of an ethanolic solution of NaOH, the emission at 475 nm is progressively restored, to reach its original intensity after 4 equiv., thus ensuring the complete formation of the $[Zn^{II}(\mathbf{L})(Fl_2)]^+$ ternary complex. In this sense, the system under investigation shows some similarity to the *plug-and-socket* devices, recently introduced by Balzani and coworkers.[8] Analogy is not complete due to the fact that in the $[Zn^{II}(\mathbf{L})(Fl_2)]^+$ system we do not observe a penetration of the socket by the plug. In any case, previously reported examples were based on weak and reversible hydrogen bonding interactions. In the present study, we took profit from the distinctly stronger metal–ligand interaction, which ensures the formation of an especially stable adduct, thus guaranteeing a firm contact between the two photoactive components. Moreover, the lability of the Zn^{II} cation provides quick reversibility and a prompt ON–OFF response, following the acid–base stimulus.

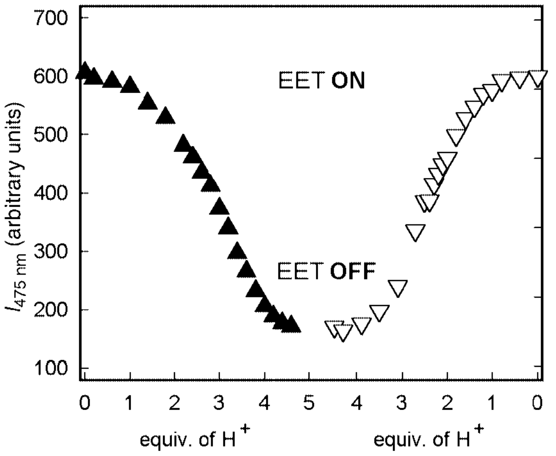

Fig. 2 The effect of an acid–base input on the emission of the $[Zn^{II}(\mathbf{L})(Fl_2)]^+$ system when excited at λ_{exc} = 330 nm.

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Notes and references

† *Preparation* of **L**: a solution of 4-dimethylamino-1-naphthaldehyde (9.1 mmol in 50 mL of MeOH) was added dropwise over 2 h under magnetic stirring to a solution of tris(2-aminoethyl)amine (3 mmol in 100 mL of MeOH). The reaction mixture was kept at 40 °C for 36 h, and then $NaBH_4$ was carefully added in small portions and the reaction was heated at 50 °C overnight. The solvent was then removed under reduced pressure and the resulting sticky solid was suspended in 100 mL of water. The aqueous phase was extracted with CH_2Cl_2 (3×50 mL). The organic phase was dried with $MgSO_4$ and the solvent distilled off, giving **L** as a light yellow oil, which was washed with several portions of diethyl ether. Yield: 67%. FAB MS *m*/*z*(%) 696 (100) M − H^+. ^1H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, 3H, napththyl H), 8 (d, 3H, naphthyl H), 7.45 (m, 6H, naphthyl H), 7.25 (d, 3H, napththyl H), 6.9 (d, 3H, naphthyl H), 4.1 (s, 6H, $HNCH_2$-naphthyl), 3.0–2.5 (m, 30H, NCH_2CH_2NH and NCH_3).

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