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Invited Paper

Intra-molecular Electronic Energy Transfer in Mono- and Di-nuclear Zinc(II) Supramolecular Complexes

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Intra-molecular electronic energy transfer processes have been investigated in systems containing two distinct fluorophores Fl_1 (absorbing photonic energy) and Fl_2 (coumarin 343, brought at a close distance through coordinative interactions, emitting). Fl_1 is covalently linked or incorporated in a polyamine platform containing one or two Zn^{II} ions, while Fl_2 coordinates the Zn^{II} centre(s) through a carboxylate group. Zn^{II} has been chosen for its photophysical inactivity and quick reversibility of the interaction with Fl_2.

Keywords: Electronic energy transfer; Metal ligand interactions; Polyamine ligands; Zn(II) complexes

INTRODUCTION

Electronic energy transfer (EET) is an interesting phenomenon in molecular photophysics. It happens when a fluorophore Fl_1, excited at the wavelength λ_1, transfers its photonic energy to a nearby fluorophore Fl_2, which dissipates the absorbed energy by emitting light at a higher wavelength λ_2. The intimate process involves a double electron exchange (according to a Dexter mechanism) between Fl_1 and Fl_2, according to a circular path. If Fl_1 and Fl_2 belong to two different molecules, EET follows occasional collision and Van der Waals contact between the two fluorophores, which guarantees orbital overlap and electron exchange [1]. Occurrence of the intermolecular process requires that one of the fluorophores is in great excess with respect to the other; in particular, on addition of a fluorophore to the other, the emission intensity at λ_2 increases and that at λ_1 decreases according to a Stern–Volmer behaviour. A more interesting and more rare case concerns intramolecular EET. In this situation, Fl_1 and Fl_2 are brought close to each other by some type of chemical interaction [2–4]. In particular, molecular fragments bearing Fl_1 and Fl_2 can interact through non-covalent interactions (e.g. hydrogen bonding) [5–7], giving rise to a supramolecular assembly. In this case, the efficiency of the EET process is order of magnitudes higher than under inter-molecular conditions.

We are interested in the design of supramolecular systems suitable for the occurrence of intra-molecular EET, based on metal–ligand interactions [8–10]. In particular, we wish to use metals to build up the supramolecular assembly and to bring Fl_1 and Fl_2 close enough to ensure EET takes place. Our preferred metal ion is Zn^{II}, in view of its photophysical inactivity: in fact, (i) it does not possess any redox activity, thus it cannot promote any electron transfer process; (ii) it has a closed shell electronic configuration (d^{10}), thus it cannot be involved in an electronic energy transfer mechanism [11–13].

In this article, we describe EET processes taking place on a platform consisting of a mononuclear and of a dinuclear zinc(II) polyamine complex. The behaviour of the mononuclear complex has been preliminary outlined [14].

RESULTS AND DISCUSSION

Polyamines **L1** and **L2** were used to make the Zn^{II} complexes. The tripodal tetramine **L1** imposes to Zn^{II}

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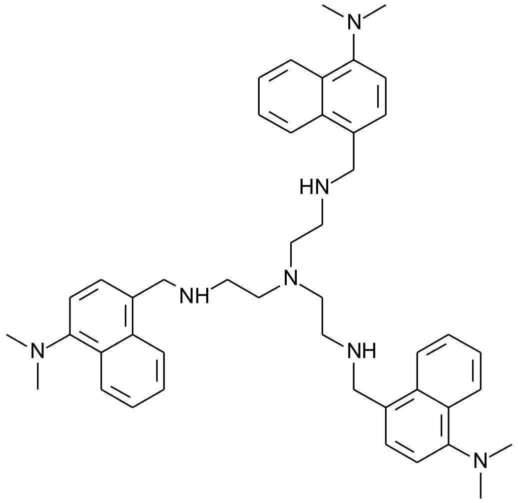
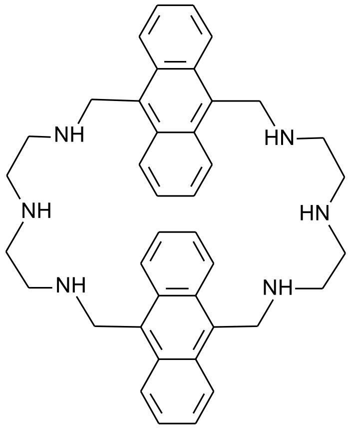


L1



L2

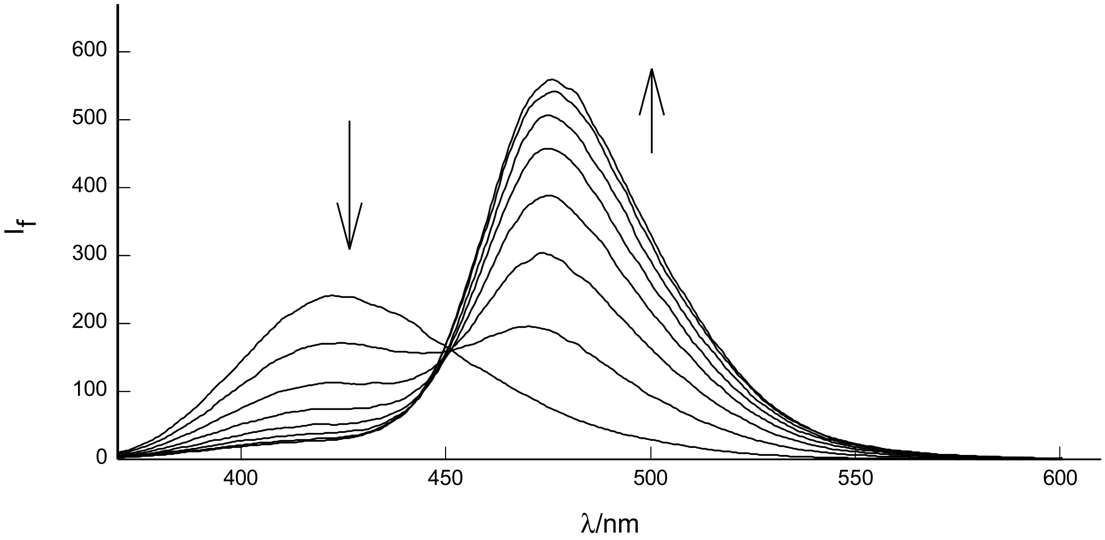
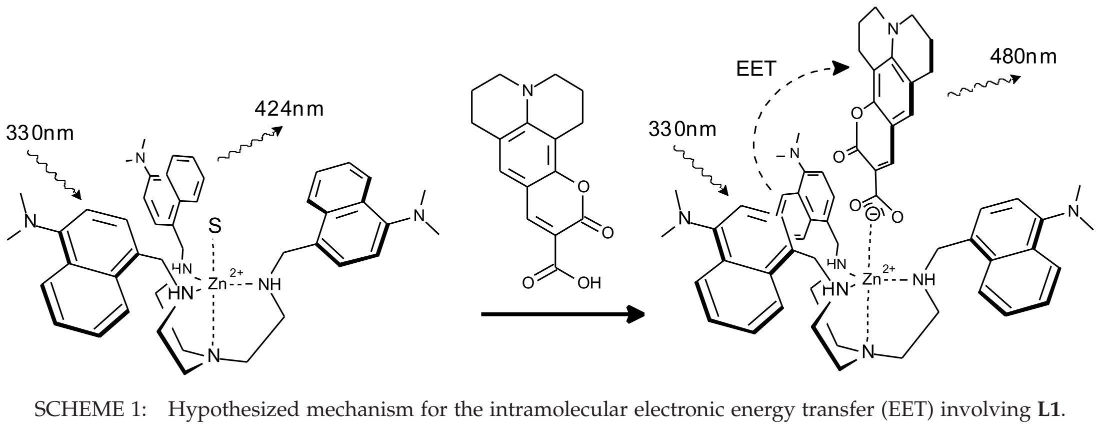


FIGURE 1 Selected emission spectra obtained in the spectrofluorimetric titration of $[Zn^{II}(\mathbf{L1})]^{2+}$ (10^{-5} M in MeOH) with coumarin 343.



SCHEME 1: Hypothesized mechanism for the intramolecular electronic energy transfer (EET) involving **L1**.

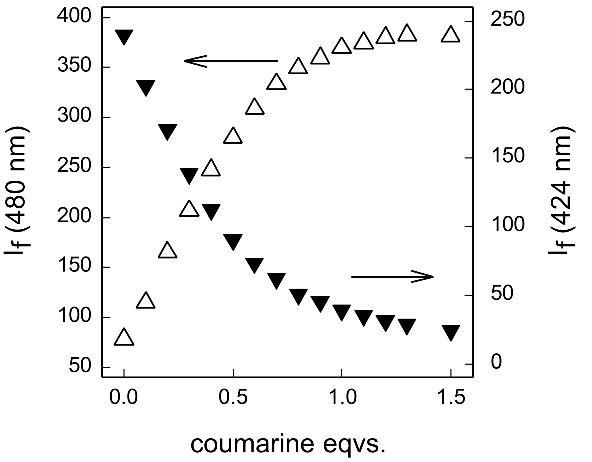


FIGURE 2 Titration profiles obtained adding coumarin 343 to a 10^{-5} M solution of $[Zn^{II}(\mathbf{L1})]^{2+}$ in MeOH.

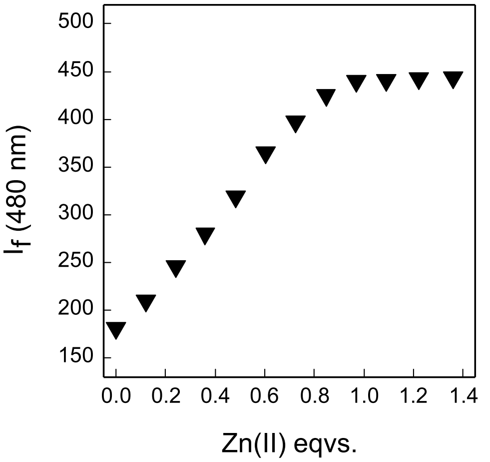


FIGURE 3 The titration profile obtained adding Zn(II) to a solution containing equimolar quantities (10^{-5} M in MeOH) of ligand **L1** and coumarin 343.

a trigonal bipyramidal stereochemistry, leaving one of the two axial positions vacant and available for the coordination of a further ligand, e.g. an anion or a solvent molecule. Moreover, each peripheral amine group has been linked through a methylene group to the fluorophore *N,N*-dimethylamine-1-naphthalene, which possesses an absorption band centred at $\lambda_{max} = 330$ nm and an emission band centred at $\lambda_{max} = 424$ nm. On addition of 1 equivalent of Zn^{II} (as triflate) to a methanolic solution of **L1**, the five-coordinate complex forms, with a solvent molecule occupying the vacant axial position: $[Zn^{II}(\mathbf{L1})(MeOH)]^{2+}$. The solution, irradiated at 330 nm, displays the expected emission band centred at 424 nm. Then, the anionic fluorophore coumarin 343 was added stepwise to the solution. Following the addition, the emission band at 424 nm decreases, while a new band forms and develops at $\lambda_{max} = 480$ nm, as shown in Fig. 1.

The band at 480 nm corresponds to the emission of coumarin 343, indicating the occurrence of an efficient sensitisation. This photophysical behaviour can be explained considering that the carboxylic function of coumarin 343 deprotonates and the carboxylate group displaces the MeOH molecule and axially coordinates the Zn^{II} centre.

A supramolecular assembly forms in which the fluorophores coumarin 343 and *N,N*-dimethylamine-1-naphthalene have been brought rather close. One of the three *N,N*-dimethylamine-1-naphthalene substituents behave as Fl_1, while coumarin 343 behaves as Fl_2. Following irradiation of Fl_1 at 330 nm, photonic energy is transferred to the nearby Fl_2 fragment, according to an EET mechanism, as shown in Scheme 1. The excited fluorophore Fl_2 deactivates by emitting light at 480 nm.

Formation of a 1:1 adduct between $[Zn^{II}(\mathbf{L1})]^{2+}$ and coumarin 343 is also demonstrated by the titration profiles shown in Fig. 2 (plots of the intensity of the band at 424 nm, λ_1, decreasing, and of the band at 480 nm, λ_2, increasing, vs. the added equivalents of coumarin 343). Non-linear least-squares treatment of the profiles gave the following $\log K$ value for the adduct formation equilibrium: 5.98 ± 0.04 ($\lambda = 424$ nm) and 6.01 ± 0.03 ($\lambda = 480$).

Zn^{II} is the essential structural component of the supramolecular assembly. Its central role is also demonstrated by a titration experiment in which a standard solution of zinc(II) triflate is added to a solution containing equimolar amounts of **L1** and coumarin 343 and irradiated at 330 nm. On Zn^{II} addition, the band at 480 nm (λ_2) forms and develops, to reach a plateau after the addition of 1 equivalent of Zn^{II} (see Fig. 3).

The hexamine **L2** has been designed to incorporate two Zn^{II} cation. It consists of two triamine fragments, linked by two anthracenyl spacers. The spacers also play the role of the Fl_1 fluorophore (anthracene: absorption band centred at 372 nm; emission band centred at 426 nm). Each Zn^{II} ion in its triamine compartment is expected to assume four-or five-coordination, according to a tetrhaedral or trigonal bipyramidal stereochemistry, respectively, the remaining coordinative positions being occupied by solvent molecules.

A solution of the dinuclear complex $[Zn^{II}_2(\mathbf{L2})]^{4+}$, when irradiated at 356 nm, shows the typically structured emission spectrum of the anthracene fragment. On titration with a standard solution of coumarin 343, the intensity of the anthracene emission band decreases, while a new band forms and develops, with a maximum at 490 nm (see Fig. 4): this is the band of the coumarin 343 fluorophore (Fl_2), which demonstrates the occurrence of an EET process from an excited anthracene subunit of the complex. It is suggested that the carboxylic group of coumarin 343 deprotonates and bridges the two Zn^{II} centres with the two oxygen atoms of the carboxylate

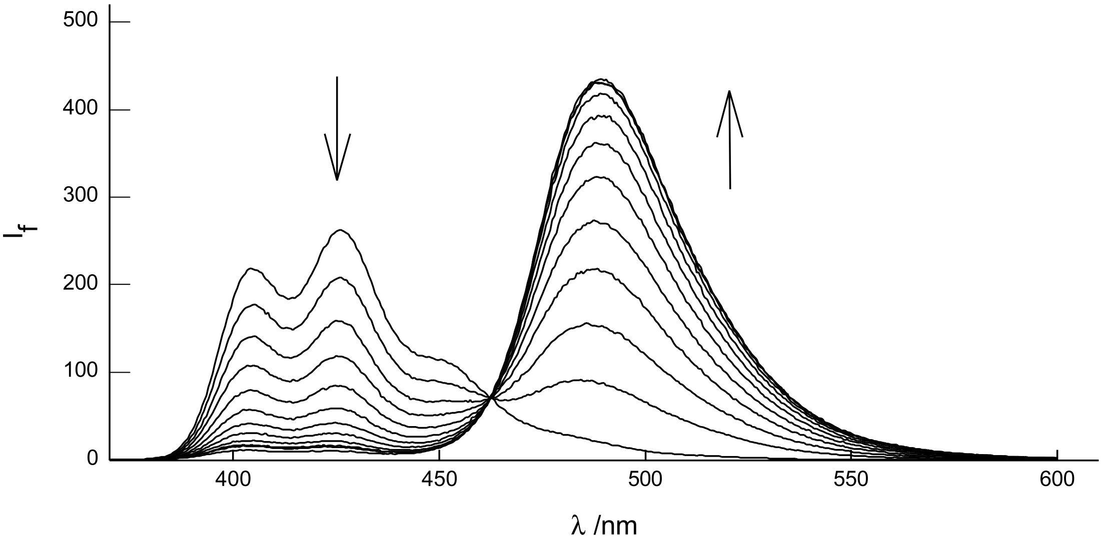


FIGURE 4 Selected emission spectra obtained in the spectrofluorimetric titration of $[Zn^{II}_2(\mathbf{L2})]^{4+}$ (10^{-5} M in MeOH) with coumarin 343.

group, displacing coordinated solvent molecules and forming a 1:1 adduct.

Titration profiles, based on the intensity of the bands centred at 405 nm (decreasing) and at 490 nm (increasing) support the 1:1 stoichiometry (see Fig. 5), while non-linear least-squares treatment provides the binding constant of coumarin 343 to $[Zn^{II}_2(\mathbf{L2})]^{4+}$: 6.38 ± 0.05 from the band at 405 nm and 6.16 ± 0.05 from the band at 490 nm.

Formation of a 1:1 adduct is also demonstrated by a titration experiment in which a standard solution of Zn^{II} triflate is added stepwise to a solution containing equimolar amounts of the hexamine **L2** and of coumarin 343, which is irradiated at 356 nm. Addition of Zn^{II} up to 1 equivalent does not cause any serious development of an emission band in the 470–500 nm interval. With subsequent addition, the band of coumarin 343 begins to develop and reaches its maximum intensity after the addition of two equivalents of Zn^{II} (see Fig. 6). This behaviour can be explained considering that binding of the carboxylate group of coumarin 343, which involves the bridging of the two metal centres, can take place only when two Zn^{II} ions are positioned in the two triamine compartments of **L2**.

Scheme 2 shows the hypothesised geometrical aspects on which the intra-molecular EET process is based.

CONCLUSIONS

This work has demonstrated that the metal–ligand interactions can be profitably utilised to generate supramolecular systems suitable for the occurrence of intra-molecular EET processes from Fl_1 to Fl_2. In the examples considered before, the Fl_1 fragment is a part of a Zn^{II} containing polyamine platform, while Fl_2 is the coumarin 343 fluorophore. Binding of coumarin carboxylate to Zn^{II} centre(s) brings Fl_1 and Fl_2 close enough to ensure the occurrence of double

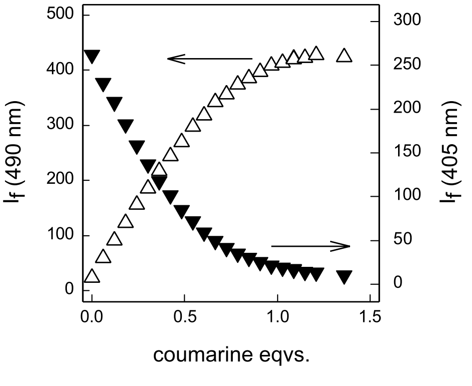


FIGURE 5 Titration profiles obtained adding coumarin 343 to a 10^{-5} M solution of $[Zn^{II}_2(\mathbf{L2})]^{4+}$ in MeOH.

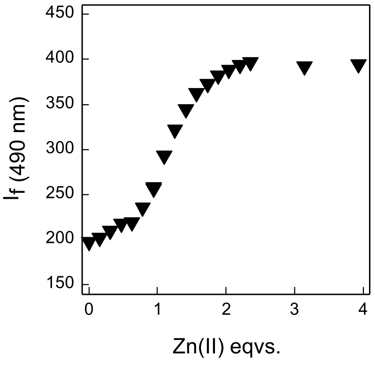
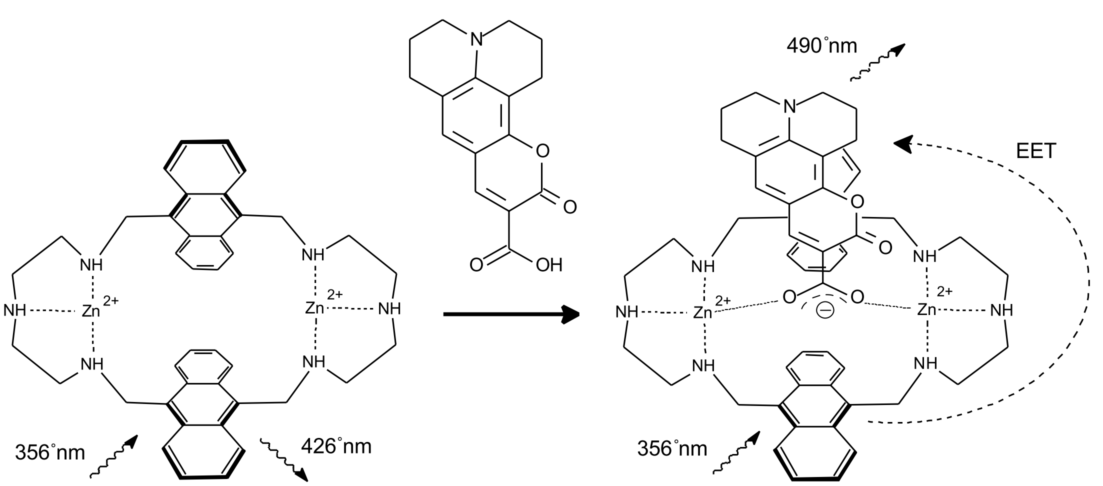


FIGURE 6 The titration profile obtained adding Zn(II) to a solution containing equimolar quantities (10^{-5} M in MeOH) of ligand **L2** and coumarin 343.



SCHEME 2: Hypothesized mechanism for the intramolecular electronic energy transfer (EET) involving **L2**.

electron exchange in a fast and efficient way. The Zn^{II} ion is unique in its role, due to its coordinative versatility, to its photophysical inactivity, and to its lability, which provides fast and reversible interaction with the energy acceptor fragment, coumarin 343.

MATERIALS AND METHODS

General

All reagents (Aldrich) were used without any further purifications. Fluorescence measurements were carried out in a Perkin–Elmer LS-50B fluorimeter. Mass spectra were obtained with a Finnigan TQS 700 mass spectrometer.

Spectrofluorimetric titrations: Spectrofluorimetric titrations were performed in methanol solutions (10^{-5} M) of the ligands. Standard solutions of $Zn(CF_3SO_3)_2$ in methanol were used for ligand titrations and to prepare *in situ* the corresponding Zn(II) complex, which were titrated with standard solutions (MeOH) of coumarin 343.

Association Constants Determination

The association constants were determined by analysing the fluorescence intensity changes obtained following the addition of a known concentration of coumarin 343. The values were calculated at two emission wavelengths by using the Hyperquad software [15].

Synthesis

Preparation and characterisation of ligand **L1** have been reported elsewhere [14]. Ligand **L2** was synthesised as follows: 9,10-anthracenedicarboxaldehyde (1.7 mmol, 0.4 g) in 200 ml of a MeCN/MeOH (10:1) mixture was heated under reflux until complete solubilisation. The solution was cooled under room temperature and was added dropwise over 4 h to 1.7 mmol (185 μl) of diethylenetriamine in MeCN (70 ml) under magnetic stirring. The reaction was achieved by heating at 50°C for 72 h. The precipitate formed was filtered off and dissolved in a solution of hot methanol (100 ml) to which 0.3 g of $NaBH_4$ was added carefully. The solvent was removed under reduced pressure after the reaction mixture was kept at 50°C overnight. The resulting solid was suspended in 100 ml of mixture H_2O/CH_2Cl_2 (5:1) and the aqueous phase was extracted with three portions of CH_2Cl_2. The organic phases were collected and dried with $MgSO_4$. The ligand **L2** was obtained, after removing the organic phase, as an orange–brown powder, which was washed with several portions of diethyl ether. Yield: 47%. (Found: C 77.95, H 7.34, N 13.53; calcd: C 78.65, H 7.59, N 13.76). ESI MS m/z (%): 611 (100) MH^+.

Acknowledgements

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