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A Zinc(II)-Driven Intramolecular Photoinduced Electron Transfer

**Luigi Fabbrizzi,* Maurizio Licchelli,
Piersandro Pallavicini, and Angelo Taglietti**

Dipartimento di Chimica Generale, Università di Pavia,
via Taramelli 12, I-27100 Pavia, Italy

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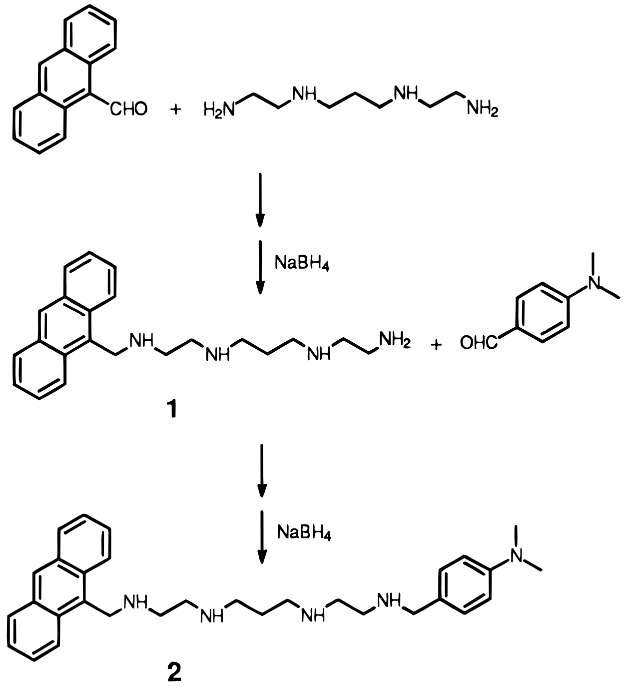
Two-component supramolecules in which a donor (D) and an acceptor (A) fragment are covalently linked represent an ideal system for investigating a primary chemical event: *electron transfer*. If D (or A) is fluorescent, any photoinduced electron transfer may be conveniently followed through the quenching of the fluorescence emission.[1] The spacer connecting D and A plays a crucial role: when it is rigid, the intramolecular electron transfer process takes place *via* a through-bond interaction, which may be efficient over distances as large as 20 Å.[2] When the spacer is flexible (*e.g.* an aliphatic chain), the two-component system may occasionally fold and bring the interacting fragments into direct contact, according to a statistically controlled process, allowing the electron transfer process to take place. However, folding can be favored and properly addressed by making use of a template. The template is a chemical entity (a molecule, an ion) able to interact through noncovalent (and reversible) interactions with the D−A system. If the interaction possesses some elements of selectivity, the D−A system can be viewed as a sensor for the template species, signalling the occurrence of the receptor-substrate binding through fluorescence quenching.[3]

In this work we wished to investigate the role of *3d* metal ions as templates for D−A systems and we used as a spacer an aliphatic polyamine, *i.e.* a flexible fragment which can coordinate transition metals. The chosen donor fragment was dimethylaniline (dma, $E^\circ_{\mathrm{dma}^+/\mathrm{dma}} = 0.78$ V *vs* SCE, in MeCN solution), whereas the acceptor and fluorescent subunit was anthracene (an, $E^\circ_{\mathrm{an}/\mathrm{an}^-} = -1.93$ V *vs* SCE, in MeCN solution). The energy of the photoexcited state *an ($E_{0-0} = 3.1$ eV) is large enough to exceed the $e[E^\circ_{\mathrm{an}/\mathrm{an}^-} - E^\circ_{\mathrm{dma}^+/\mathrm{dma}}]$ energy difference and to guarantee the occurrence of the photoinduced electron transfer (PET) process on a thermodynamic basis ($\Delta G^\circ_{\mathrm{ET}} = -E_{0-0} + e(E^\circ_{\mathrm{an}/\mathrm{an}^-} - E^\circ_{\mathrm{dma}^+/\mathrm{dma}}) = -0.4$ eV). The an and dma fragments were linked by the tetraamine bridge $-CH_2NH(CH_2)_2NH(CH_2)_3NH(CH_2)_2NHCH_2-$, according to the synthetic pathway outlined in Scheme 1. The method involves the following: (i) the Schiff base condensation between 9-anthracenealdehyde and the appropriate linear tetraamine, present in a 5-fold excess, in order to minimize disubstitution, followed by hydrogenation of the C=N double bond with sodium borohydride; (ii) Schiff base condensation at the opposite $-NH_2$ group of 4-(dimethylamino)benzaldehyde, according to a 1:1 stoichiometry, and subsequent hydrogenation, to give the D−A system **2**. The procedure appears particularly convenient and can be generally used to connect any couple of subunits of varying nature, provided the corresponding aldehyde derivatives are available. The spacer considered corresponds to the quadridentate ligand 2.3.2-tet, whose coordinating tendencies toward 3d metal ions are well documented.[4,5] The intermediate **1** was also investigated, for comparative purposes. As a templating agent, we examined first the Zn^{II} ion, which is non-redox-active and should not quench *an by an electron transfer process.

Scheme 1



The photophysical behavior of **1** and **2** in solution (MeCN/water 80:20, v/v) was investigated by carrying out spectrofluorimetric investigations at varying pH. The reference system **1** was considered first and a solution of **1**, containing excess acid, was titrated with standard base. Under acidic conditions (pH < 3), the strong and characteristically structured emission band of anthracene was observed. Fluorescence intensity decreased until complete quenching during the addition of the second and third equivalent of base (after the excess acid had been neutralized). This would indicate that, in the course of the deprotonation of the tetraammonium fragment, the second and third proton are released from the two ammonium groups closest to the anthracene subunit. In fact, following deprotonation, the lone pair on the nitrogen atom is available for an electron transfer process to the proximate photoexcited fluorophore *an, which causes a nonradiative decay and induces fluorescence quenching. Photoinduced electron transfer in derivatives of anthrylamines is a well-characterized phenomenon and constitutes the basis of pH switching of fluorescence.[6] The most efficient quenching effect should be provided by the secondary amine group adjacent to the anthracene moiety. Figure 1 illustrates the pH dependence of the fluorescence intensity, I_F, obtained from the titration experiment. From the I_F vs pH plot, a pK_A value of 3.9 is assigned to the more acidic photoactive ammonium group and a pK_A value of 7.8 to the less acidic photoactive ammonium group. Noticeably, such values correspond to the pK_{A2} and pK_{A3} values obtained for **1**

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[1] Kavarnos, G. J. *Fundamentals of Photoinduced Electron Transfer*; VCH Publishers Inc.: New York, 1993.

[2] Winkler, J. R.; Gray, H. B. *Chem. Rev.* **1992**, *92*, 369.

[3] Valeur, B.; Bourson, J.; Pouget, J. In *Fluorescent Chemosensors for Ion and Molecule Recognition*; Czarnik, A. W., Ed.; ACS Symposium Series 538; American Chemical Society: Washington, DC, 1993.

[4] Weatherburn, D. C.; Billo, E. J.; Jones, J. P.; Margerum, D. W. *Inorg. Chem.* **1970**, *9*, 1557.

[5] Fabbrizzi, L.; Barbucci, R.; Paoletti, J. *J. Chem. Soc., Dalton. Trans.* **1972**, 1529.

[6] Bissell, R. A.; de Silva, A. P.; Guranatne, H. Q. N.; Lynch, P. L. M.; Maguire, G. E. M.; McCoy, C. P.; Sundanayake, K. R. A. S. *Top. Curr. Chem.* **1993**, *168*, 223.

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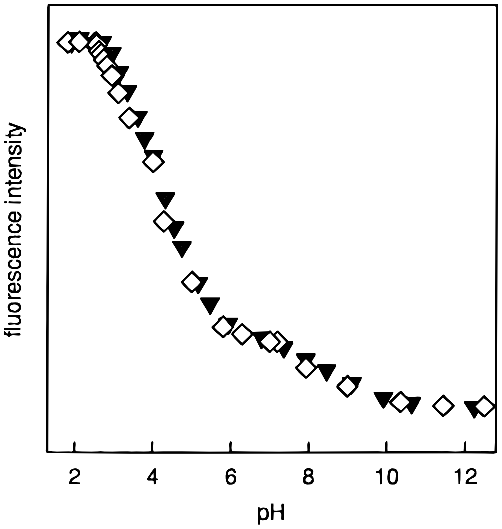

Figure 1. pH dependence of the fluorescence intensity of **1** (triangles) and **2** (diamonds) in an MeCN/H_2O (80:20 v/v) solution.

through independent potentiometric titration experiments. A further spectrofluorimetric titration experiment was carried out on a solution as before, but which contained also 1 equiv of Zn^{II}. Figure 2 shows the corresponding titration profile. Noticeably, a fluorescence intensity decrease was observed also in the present case, whose profile superimposed on that of the metal-free solution. However, at pH = 4.5, I_F stopped decreasing, then increased to reach almost the original value. The first part of the profile reflects the deprotonation of the polyammonium fragment, with the consequent electron transfer from one of the proximate amine groups to the photoexcited anthracene fragment of **2**. The following fluorescence increase should be ascribed to the fact that, at pH = 4.5, the polyamine spacer begins to coordinate the Zn^{II} ion, completing metal complexation at pH ≥ 6. With complexation, the amine lone pairs are coordinated to the metal center, making their electrons unavailable for any electron transfer process, which restores fluorescence. Anthracene fluorescence enhancement following Zn^{II}-amine interaction has been previously observed with a series of anthracenyl-substituted polyaza macrocycles.[7]

Titration of a metal-free solution of the D−A system **2** gave results similar to those for **1**. In particular, the I_F *vs* pH profile is nearly coincident with that observed for system **1** (see Figure 1). It should be noted that, in strongly acidic conditions, electrostatic repulsions between ammonium groups would stretch the spacer such that the an and dma subunits are well separated. A distance of 20.6 Å from the aniline nitrogen atom to the C(9) atom of the anthracene moiety, i.e. that linked to the spacer, was estimated using MM+ modeling. The spacer should probably remain extended also in the course of the deprotonation of the second and third ammonium group, thus preventing the molecular folding and a through-space interaction between the *an and dma fragments. Thus, the quenching mechanism observed with a metal-free solution of **2** should be the same as for the reference system **1** and should involve an electron transfer from the proximate secondary amine groups to the fluorophore.

Conversely, titration of **2** in presence of equimolar Zn^{II} produced a quite different profile than for **1**. In particular, *I_F did not stop decreasing,* as for reference system **1**, *but constantly diminished until complete quenching* (see Figure 2).

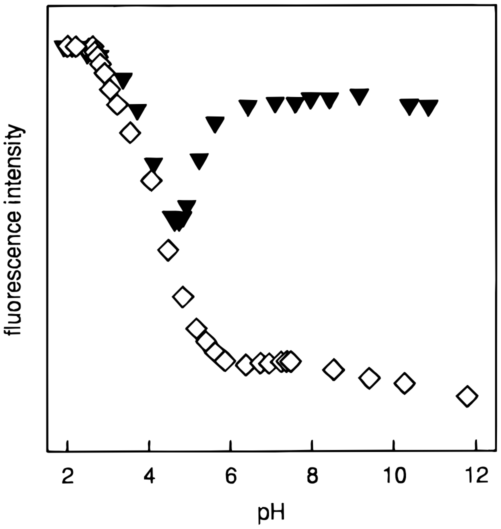

Figure 2. pH dependence of the fluorescence intensity of **1** (triangles) and **2** (diamonds), in presence of equimolar Zn^{II}, in an MeCN/H_2O (80:20 v/v) solution. In the case of the reference system **1**, Zn^{II} coordination (pH ≥ 5) prevents the electron transfer from the proximate amine groups of the spacer and restores fluorescence of the anthracene subunit. In the case of **2**, Zn^{II} coordination brings the dma and *an fragments close enough to allow electron transfer, which quenches the fluorescence.

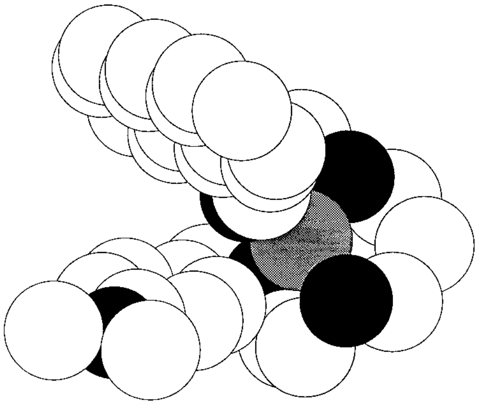

Figure 3. CPK model of the $[Zn^{II}(\mathbf{2})]^{2+}$ adduct, as obtained through MM+. The distance between the C(9) atom of the anthracene subunit and the nitrogen atom of the dimethylaniline fragment is 5.1 Å, to be compared with the 20.6 Å distance observed in the extended molecule **2**.

Such a behavior has to be associated to the coordination of the tetraamine bridge around the Zn^{II} center, which makes the D-to-A intramolecular electron transfer process feasible from a structural point of view. Such a statement is based on the following points: (i) as the metal−ligand interaction prevents any electron release from the proximate amine groups, quenching has to be attributed to the transfer of an electron from dma to *an; (ii) Zn^{II} tetraamine complexes usually adopt a tetrahedral coordination; (iii) molecular modeling shows that wrapping of **2** around the metal center, when a tetrahedral mode of coordination of the tetraamine spacer is imposed, brings the D and A moieties close enough to interact. Figure 3 shows the structure of the $[Zn^{II}(\mathbf{2})]^{2+}$ adduct, as obtained through MM+ modeling. The distance between the aniline nitrogen atom and the C(9) atom of anthracene is 5.1 Å (compared to 20.6 Å in the extended metal-free system **2**). Shorter distances and more favorable orientations of the two aromatic moieties of **2** are obtained by rotating the σ bonds connecting the terminal nitrogen atoms of the tetra-amine spacer with the carbon atoms of the $-CH_2-$ groups linked to the an and dma subunits. Thus, the Zn^{II} ion favors the electron transfer process responsible for

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(7) Akkaya, E. U.; Huston, M. E.; Czarnik, A. W. *J. Am. Chem. Soc.* **1990**, *112*, 3590.

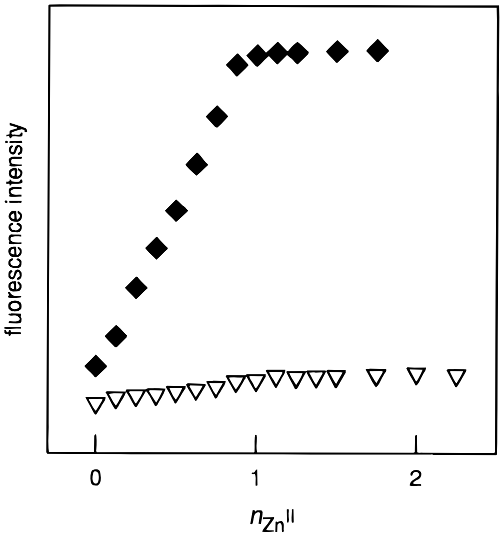
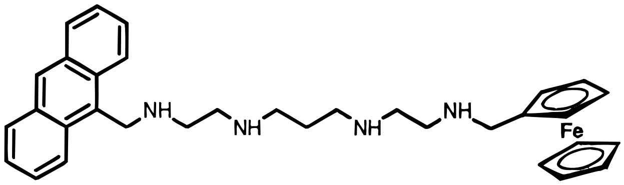


Figure 4. Titration of an MeCN/H_2O (80:20) solution of either **1** (diamonds) or **2** (triangles), buffered at pH = 8.1, with Zn^{II}.

quenching, by imposing a favorable stereochemical arrangement to the D−A system **2**.

It may be of some interest to verify the sensing properties of **1** and **2** toward the Zn^{II} ion. In this connection, an MeCN/H_2O solution of **1**, adjusted to pH = 8.1 with morpholine buffer, was titrated with a standard Zn^{II} solution. Following metal addition, the fluorescence was progressively restored, to reach a *plateau* value at 1 equivalent (see Figure 4). In this sense, the anthracene substituted tetra-amine **1** represents a further efficient chemosensor for Zn^{II} of the series introduced by Czarnik.[8] On the other hand, titration with Zn^{II} of a buffered solution of **2** produced only a slight increase of the fluorescence intensity and a very modest constant value was obtained after the addition of 1 equivalent of metal (see Figure 4), discouraging any use of **2** as a Zn^{II} sensor. However, the equivalence point is interesting, as it exactly indicates a *switching* of the mechanism of fluorescence quenching: from amine-to-anthracene electron transfer to dimethylaniline-to-anthracene electron transfer.

The above template approach seems quite general and should work with any D/A couple, provided that the PET process is thermodynamically allowed. In this connection, we considered the D−A system **3**, in which the organic donor fragment dma had been replaced by ferrocene (Fc). Spectrofluorimetric titration experiments on an MeCN/H_2O solution of **3**, in the absence and presence of equimolar Zn^{II}, gave analogous results as for **2**. In particular, the fluorescence of the Zn^{II} containing acidic solution of **3** was fully quenched with base addition. This behavior is not surprising, if one considers that Fc is a better donor than dma ($E°_{Fc^+/Fc}$ = 0.10 V vs SCE in MeCN), which makes the Fc-to-*an electron transfer process more favorable ($\Delta G°_{ET} = -1.1$ eV). Thus, also in the present case, Zn^{II} coordination by the tetra-amine spacer brings the organometallic donor subunit close enough to the anthracene fragment to permit electron transfer.



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Finally, we wished to investigate other transition metal ions as further templates for addressing intramolecular electron transfer in D−A systems like **2**. In particular, 3d metals would appear as versatile candidates because of their capability of imposing many different stereochemical arrangements, depending upon their electronic configuration. Spectrofluorimetric titration of a solution of either **1** or **2** in aqueous MeCN, in presence of an equimolar amount of Cu^{II}, caused a sharp fluorescence quenching in the pH range 2.5-3.5. At these pH values, the Cu^{II} tetraamine complexes form, which are remarkably more stable than the corresponding Zn^{II} complexes of **1** and **2**. The fact that fluorescence quenching takes place also with the reference system **1** would indicate that the nonradiative deactivation of *an occurs *via* a direct interaction between the fluorophore and the metal center. Quenching of *an can take place through either an *energy transfer* or an *electron transfer* mechanism. On one side, Cu^{II} possesses a half-filled *3d* level of low energy ($x^2 - y^2$), which can be involved in an energy transfer process of the Dexter type (double electron exchange).[9,10] On the other hand, the *an-to-Cu^{II} electron transfer process is favored from a thermodynamic point of view ($\Delta E_{ET} = -1.1$ eV). In any case, the proximate transition metal center deactivates *an through a very fast and efficient mechanism, which, in system **2**, precludes the slower intramolecular D-to-A electron transfer process. Ni^{II} has the same effect as Cu^{II}, quenching fluorescence of both **1** and **2** in the 4−6 pH range.

Experimental Section

General Methods. Emission spectra were taken on a Perkin-Elmer LS-50 luminescence spectrometer (excitation wavelength 364 nm; maximum emission intensities at 415 nm) and were all uncorrected for instrumental response. Spectrofluorimetric titrations were performed on acetonitrile/water (4:1) solutions (50 mL, 5×10^{-4} M), using standard $HClO_4$, NaOH, and $M^{II}(ClO_4)_2$ solutions.[11] The pH scale was calibrated prior to each titration experiment in aqueous acetonitrile, through the Gran method.[12] Mass spectra were obtained with a Finnigan TSQ700 instrument.

Materials. Anthracene-9-carbaldehyde (Fluka), ferrocene-1-aldehyde (Aldrich) and 4-(dimethylamino)benzaldehyde (Aldrich) were used without further purification. *N,N′*-Bis(2-aminoethyl)propane-1,3-diamine (2.3.2-tet) was prepared as described for the analogous tetraamine 3.2.3-tet,[13] distilled at reduced pressure (125 °C; 5×10^{-2} torr) and stored over NaOH in the refrigerator.

***N*-(2-Aminoethyl)-*N′*-{2-[(anthracen-9-ylmethyl)amino]ethyl}-propane-1,3-diamine, 1.** 2.3.2-tet (3.2 g, 20 mmol) and anthracene-9-carbaldehyde (0.81 g, 4 mmol) were dissolved in ethanol (50 mL) and allowed to react for 36 h at room temperature. Then $NaBH_4$ (1.7 g, 45 mmol) was added portionwise and the resulting solution warmed at 50 °C for 4 h. Ethanol was distilled off under reduced pressure, the residue was treated with water (40 mL) and extracted with dichloromethane (3 × 30 mL). After the extract was dried over $MgSO_4$ and solvent removed at the rotary evaporator, a semisolid residue formed, which was characterized as its tetrahydrobromide salt.

1·4HBr. **1** (0.5 g, 1.43 mmol) was dissolved in ethanol and treated with excess aqueous 48% HBr. A yellowish precipitate formed, which was recrystallized from ethanol and dried under *vacuum*. Yield: 73%. Anal. Calcd for $C_{22}H_{34}N_4Br_4$ (M_R 674.15): C, 39.20; H, 5.08; N, 8.31. Found: C 39.53; H, 4.95; N, 8.12.

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(8) Huston, M. E.; Haider, K. W.; Czarnik, A. W. *J. Am. Chem. Soc.* **1988**, *110*, 4460.

(9) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: Chichester, England, 1991.

(10) Suppan, P. *Chemistry and Light*, Royal Society of Chemistry: Cambridge, U.K., 1994; p 66.

(11) Fabbrizzi, L.; Licchelli, M.; Pallavicini, P.; Perotti, A.; Sacchi, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1975.

(12) Gran, G. *Analyst* **1952**, *77*, 661.

(13) Barefield, E. K.; Wagner, F.; Herlinger, A. W; Dahl, A. R. *Inorg. Synth.* **1975**, *16*, 220.

***N*-{2-[(Anthracen-9-ylmethyl)amino]ethyl}-*N′*-[2-(((4-dimethylamino)-benzyl)amino)ethyl]propane-1,3-diamine, 2.** **1** (0.5 g, 1.43 mmol) and 4-(dimethylamino)benzaldehyde (0.213 g, 1.43 mmol) were allowed to react in ethanolic solution (30 mL) for 36 h at room temperature. $NaBH_4$ (0.57 g. 15 mmol) was added portionwise and the resulting solution warmed at 50 °C for 4 h. After ethanol was distilled off, under reduced pressure, the residue was treated with water (30 mL) and extracted with dichloromethane (3 × 30 mL). The solution was dried over $MgSO_4$ and the solvent was removed at the rotary evaporator, to give a semisolid residue. MS (ESI): *m/z* (%): 484 (100%) $[M + H^+]$.

***N*-{2-[(Anthracen-9-yl-methyl)amino]ethyl}-*N′*-[2-((ferrocenylmethyl)amino)ethyl]propane-1,3-diamine, 3.** The two-component system **3** was obtained as a semisolid product through Schiff-base condensation of **1** with ferrocene-1-aldehyde and reduction with $NaBH_4$, following the same procedure as for **2**. MS (ESI): *m/z* (%): 549 (100%) $[M + H^+]$.

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