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Molecular switches of fluorescence operating through metal centred redox couples

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Contents

Abstract

Three-component molecular systems (redox active subunit)-spacer-(light-emitting fragment) can operate as fluorescence switches, following the alternate addition of an oxidizing agent and a reducing agent (or the adjustment of the potential of the working electrode in an electrolysis experiment). The redox active subunit typically consists of a metal centred redox couple ($M^{(n+1)+}/M^{n+}$), encircled by a macrocyclic receptor, and switching efficiency requires that one of the two oxidation states quenches the proximate fluorophore and the other does not. Four ON/OFF systems, based on either the Cu^{II}/Cu^{I} or Ni^{III}/Ni^{II} couple, will be discussed. The nature of the quenching process responsible for the OFF state, either electron transfer or energy transfer, is related to the length and to the flexibility-rigidity of the spacer. © 1998 Elsevier Science S.A.

Keywords: Molecular switches; Fluorescence; Energy transfer; Electron transfer; Macrocyclic complexes

1. Introduction

There is a widespread tendency in modern chemistry to use words taken from everyday life when giving molecules names inspired either by their shape or properties

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or the function they perform[1]. Amongst these words one of the most frequently used is: *switch* [1–5]. It is said that a molecular property is switched ON/OFF when it is made to vary (it is enhanced/reduced) by several orders of magnitude. To take a classical example, the addition of a few drops of standard base to an aqueous solution containing phenolphthalein induces the appearance of an intense red colour (an absorption band centred at 556 nm forms and develops to 1.47×10^4 $M^{-1}\,cm^{-1}$), which is associated with a molecular rearrangement following the release of a proton. The red colour of the solution can be created/destroyed at will by an external operator through the fine variation of a parameter, in this case pH. We usually say that the colour is switched ON/OFF through a fine variation of the pH. One could hardly liken phenolphthalein to a switch from everyday life, however. Even in the molecular world, a switch is a device consisting of several independent components, which have to be properly connected and, if necessary, replaced.

In the most general sense, a molecular switch can be constructed by assembling three main components: (1) an active subunit, displaying the property to be killed/resurrected (switched ON/OFF); (2) a control subunit, which is sensitive to the external stimulus and affects the property of the active subunit accordingly; and (3) a spacer connecting the two subunits and allowing proper communication between them.

In the following sections, we will consider the design of three-component systems capable of switching luminescence on and off. Luminescence is an ideal property for such switching, displaying the following useful features: in most cases it is visible to the naked eye, it can be measured by relatively unsophisticated equipment, it can be detected even in extremely dilute solutions and, most interestingly for signalling purposes, it can be quenched *via* two well defined mechanisms (electron transfer, eT, and energy transfer, ET). Moreover, the appropriate subunit can be chosen from a large number of light-emitting fragments with diverse photophysical properties. The control subunit, on the other hand, should exist in two different states of comparable stability (a *bistable* system) and each state should affect the active unit and modify its luminescence to a substantially different extent. For instance, the control subunit can exist in an oxidized and in a reduced form, C_{ox} and C_{red}, separated by a reversible redox-change and behaves such that C_{ox} quenches the proximate fluorophore Fl and C_{red} does not. This situation is sketched in Fig. 1. Thus, in turn, one can switch light emission ON/OFF at will, by the alternate addition to the solution of a reducing agent and an oxidizing agent.

Fig. 2 illustrates the mode of interaction of the control unit C with the proximate fluorophore Fl, within a three-component system $C \sim Fl$. ON/OFF activity results when one of the two forms of the bistable couple C quenches the excited fluorophore through either an ET or eT mechanism and the other does not.

Control subunits that contain transition metal centres are especially convenient as they undergo fast and kinetically uncomplicated one-electron redox changes. Moreover, transition metals tend to participate in luminescence quenching of both

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[1] Most of the currently used trivial names, from barrels to wires, have been reviewed.

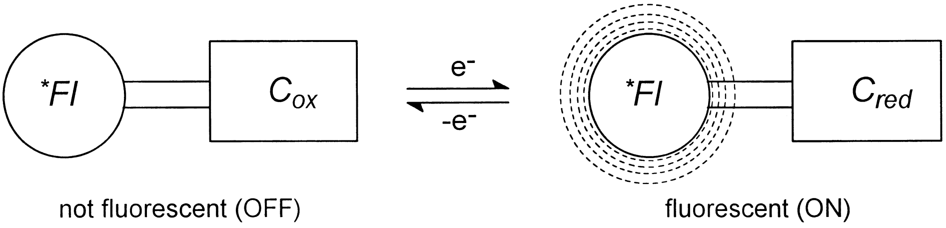


Fig. 1. The multicomponent approach to the design of a redox switch of fluorescence. Switch efficiency requires that the control unit C in its oxidized form, C_{ox}, quenches the proximate photo-excited fluorophore Fl* and the reduced form C_{red} does not (OFF/ON switch). The other favourable ON/OFF situation can be obtained when C_{red} quenches Fl* and C_{ox} does not.

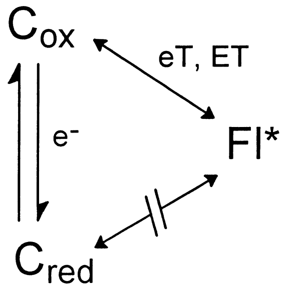


Fig. 2. The basis of an OFF/ON redox switch of fluorescence. Either an energy transfer (ET) or an electron transfer (eT) mechanism can be responsible for the quenching of the light emitting fragment Fl*, in a multicomponent redox unit-spacer-fluorophore system C ~ Fl.

the eT and ET varieties. Finally, the potential of the metal centred redox couple can be modulated by varying the nature of the hosting coordinative environment.

It may be useful to classify fluorescence switches according to the mode of communication between the control subunit and the photo-excited light-emitting fragment (the signal transduction mechanism), that is eT and ET. The nature of the spacer may play an important role in determining which mechanism is important for signal transduction.

This review will describe some three-component molecular switches of fluorescence whose control subunit contains a transition metal and will try to define the photophysical and electrochemical parameters as well as the geometrical features that determine the switching efficiency.

2. Fluorescence switches operating through the energy transfer (ET) mechanism

A metal ion can quench an excited fluorophore via an ET mechanism, either by a bimolecular or an intramolecular process, if it possesses empty or half-filled d orbitals of appropriate energy. The mechanism is illustrated by the orbital scheme in Fig. 3.

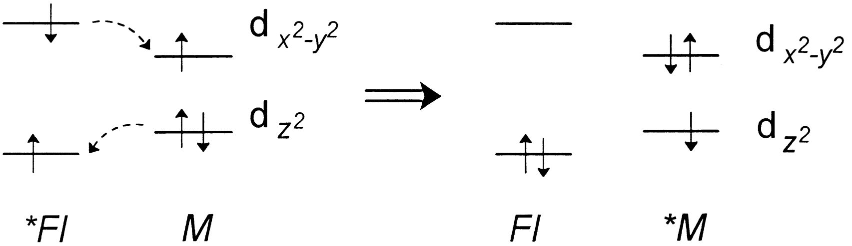
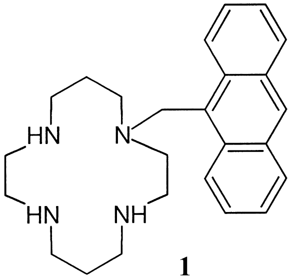


Fig. 3. Details of an energy transfer process (double-electron exchange mechanism) involving an excited fluorophore and a d^9 metal ion in an elongated-octahedral coordinative arrangement.

In particular, the case of a d^9 cation in an elongated-octahedral environment is sketched in the figure. The excited fluorophore is deactivated through a double electron exchange (ET process of the Dexter type) [6] involving the highest occupied d orbitals of the metal centre M, d_{z^2} and $d_{x^2-y^2}$. The excited state M* which results from the ET process then undergoes rapid non-radiative decay.



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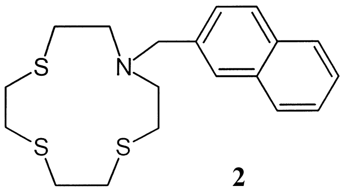
An intramolecular ET process of this type has been observed in three-component systems of type **1**, in which a metal centre M can be hosted by a *cyclam* ring and the macrocyclic subunit is linked to an anthracene fragment by a -CH_2- spacer [7]. In particular, full quenching of the anthracene emission has been observed for $M = Ni^{II}$, d^8, and Cu^{II}, d^9. On the other hand, when $M = Zn^{II}$, d^{10}, the multicomponent system **1** displays typical anthracene fluorescence. In the latter case, the complete filling of the 3d levels prevents electron circulation and quenching via Energy Transfer from taking place. The above evidence teaches us that a redox couple d^9/d^{10}, when hosted in the cyclam receptor of system **1**, would give rise to a redox-switchable luminescent device. The most obvious and convenient redox couple corresponding to the d^9/d^{10} configuration is Cu^{II}/Cu^{I}. However, the tetramine ring of cyclam is not the perfect host for such a couple, as it stabilizes very much the Cu^{II} state, and, conversely, forms a poorly stable Cu^{I} species. In particular, $[Cu^{I}(cyclam)]^+$ is obtained through cathodic reduction of the $[Cu^{II}(cyclam)]^{2+}$ complex at a very negative potential and lasts in an MeCN solution only on the time scale of a cyclic voltammetry experiment [8]. In order to better balance the stability of the two states, donor atoms that stabilize Cu^{I} should be put in the coordinating set of the receptor subunit. In particular, the soft thioethereal sulphur atom displays a special affinity towards the soft Cu^{I} centre, the extra-stability deriving from metal-to-ligand π-bonding interaction. Thus, the three-component system **2** was considered, in which an NS_3 macrocycle is linked by a $-CH_2-$ group to a naphthalene fluorophore, through the nitrogen atom (R. Bergonzi et al., unpublished results).



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System **2** gives a much better bistable system, the blue $[Cu^{II}(\mathbf{2})]^{2+}$ complex, in an MeCN solution, undergoing quasi-reversible one-electron reduction at a moderately negative potential (-0.14 V versus Fc^{+}/Fc). An MeCN solution of $[Cu^{II}(\mathbf{2})]^{2+}$ form is not fluorescent. On addition of the reducing agent 2,5-di-tert-butylhydrochinone, the blue solution decolorizes, due to the formation of the $[Cu^{I}(\mathbf{2})]^{+}$ species, and the naphthalene emission is revived. Addition of an oxidizing agent, $NOBF_4$, restores the blue colour and quenches the fluorescence almost completely. Thus, the $[Cu^{II,I}(\mathbf{2})]^{2+}$ system represents an example of molecular switch of fluorescence, whose OFF situation is generated by an ET process involving the fluorophore and the Cu^{II} centre. The switching mechanism is pictorially illustrated in Fig. 4.

A double-electron exchange ET process in the $[Cu^{II}(\mathbf{2})]^{2+}$ system is thermodynamically favoured, as indicated by the distinctly negative value of the free energy change: $\Delta G^{\circ}_{ET} = -E^{0-0}(\text{naphth}) + E^{0-0}\{[Cu^{II}(NS_3)]^{2+}\} = -3.8 + 3.3\ \text{eV} = -0.5\ \text{eV}$. Notice that in the present case $E^{0-0}([Cu^{II}(NS_3)]^{2+})$ refers to the intense absorption band centred at 375 nm ($\epsilon = 1.8 \times 10^3\ M^{-1}\ cm^{-1}$), which has a LMCT character. However, the occurrence of an intramolecular ET process in the $[Cu^{II}(\mathbf{2})]^{2+}$ form has to be demonstrated, since fluorescence quenching could be due to an intramolecular electron transfer (eT) mechanism, e.g. from the excited fluorophore to the metal centre, instead. Discrimination between ET and eT mechanisms can be achieved through spectrofluorimetric investigations on solutions vitrified at 77 K. In this

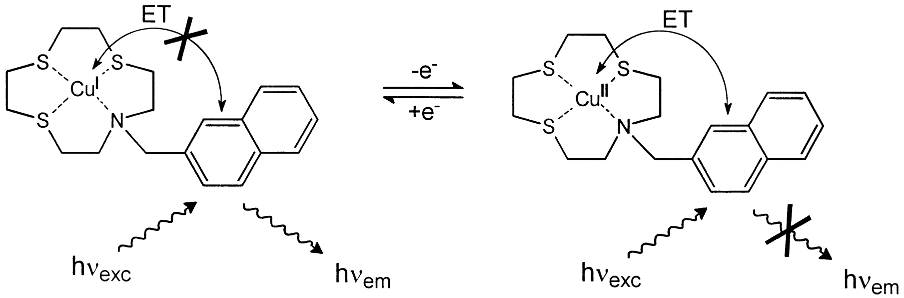


Fig. 4. Sketch of the fluorescence switching activity of the $[Cu^{II,I}(2)]^{2+,+}$ system. The Cu^{II} centre promotes an ET process causing fluorescence quenching. Reduction to the photophysically inactive Cu^{I} species makes fluorescence revive.

connection, it should be noted that the occurrence of an eT process leads to an effective electrical charge redistribution. As an example, Fig. 5 sketches the eT process from the excited fluorophore Fl* to the Cu^{II} centre (which makes available its half-filled x^2-y^2 level).

The redistribution of electrical charge following the eT process (from $Fl^* \sim Cu^{2+}$ to $Fl^+ \sim Cu^+$) induces a drastic rearrangement of solvating molecules. Solvent immobilization prevents such a rearrangement and inhibits the occurrence of the eT process. Thus, a system whose lack of fluorescence in a liquid solution at room temperature is due to the operation of an eT mechanism, should fluoresce when the solution is frozen at liquid nitrogen temperature. On the other hand, the ET process, as illustrated in Fig. 3, involves a simple circulation of electrons, does not induce any net charge creation or redistribution, and does not cause any reorientation of the solvating molecules. As a consequence, an ET process is equally efficient both in a liquid and in an immobilized solution. Thus, fluorescence quenched *via* an ET mechanism should not be restored when the solution is frozen.

Interestingly, a solution of $[Cu^{II}(\mathbf{2})]^{2+}$ frozen at 77 K in the glass forming solvent butyronitrile (BuCN), does not fluoresce, unequivocally demonstrating the ET nature of the quenching process.

Switches that operate through an ET process are rare and confined to a limited number of redox couples. The d^9/d^{10} case does not seem to extend much further than the Cu^{II}/Cu^{I} change. Anther couple which could involve a favourable change of the electronic configuration is d^0/d^1. The Ti^{IV}/Ti^{III} fits the electronic requirement, but the design of the appropriate hosting subunit is not straightforward.

3. Fluorescence switches operating through the electron transfer (eT) mechanism

The choice of a metal centred redox couple for a molecular switch operating through an eT mechanism is not related to a particular change of the electronic configuration, but can, in principle, range over the entire *d* block of the Periodic Table. The only requirement is that one of the oxidation states induces an intramolecular electron transfer process from/to the proximate excited fluorophore and the other oxidation state does not. Such switching is thermodynamically determined

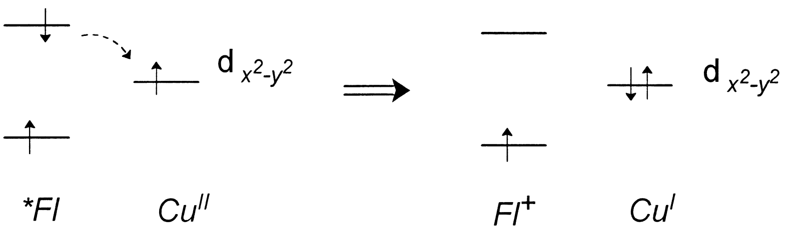


Fig. 5. Details of an electron transfer process (double-electron exchange mechanism) involving an excited fluorophore and a d^9 metal ion in an octahedrally elongated coordinative arrangement.

and, in particular, the occurrence of each eT process can be predicted by taking into account the relevant photophysical and electrochemical parameters.

Fig. 6 describes the eT processes: (a) from the photoexcited fluorophore Fl* to the oxidized metal M^+; and (b) from the reduced metal M to the photoexcited fluorophore Fl*. The corresponding free energy changes ΔG°_{eT} can be calculated through the thermodynamic cycles illustrated in the figure, where E^{0-0} represents the photophysical energy of the fluorophore and can be measured from its emission spectrum and E° values are the normal reduction potentials, which can be obtained from voltammetry studies either on the whole system under investigation or its individual components.

A switching situation is obtained when: (1) ΔG°_{eT}(oxidized)<0 (fluorescence OFF) and ΔG°_{eT}(reduced)>0 (fluorescence ON); (2) ΔG°_{eT}(ox)>0 (ON) and ΔG°_{eT}(red)<0 (OFF). Undesirable non-switching situations are obtained for: (3) ΔG°_{eT}(ox)<0 (OFF) and ΔG°_{eT}(red)<0 (OFF); (4) ΔG°_{eT}(ox)>0 (ON) and ΔG°_{eT}(red)>0 (ON).

An OFF/ON switch based on the eT mechanism is given by the three-component system **3** [9]. The fluorophore is a dansyl subunit and the switch is the Ni^{III}/Ni^{II} couple within an *azacyclam* receptor. The Ni^{II} form, in an MeCN solution, displays the typical dansylamide fluorescence in the visible region, which originates from a

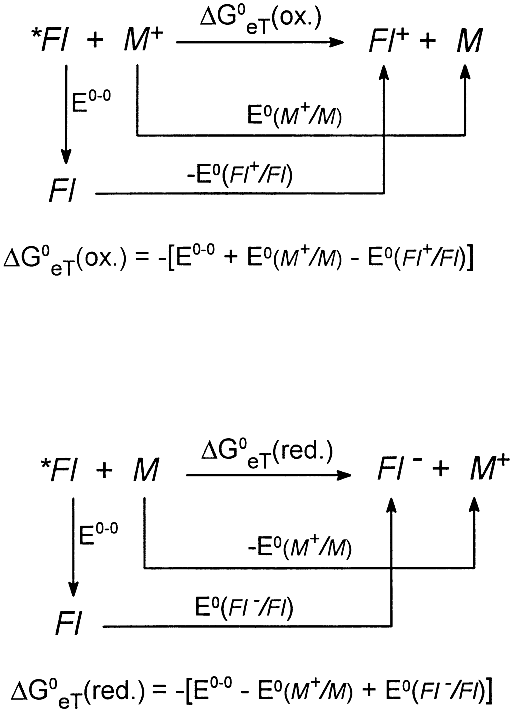
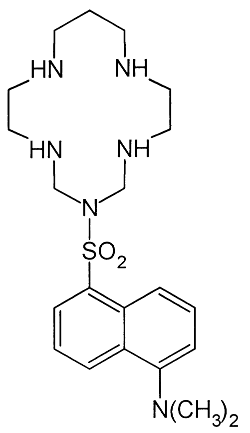


Fig. 6. Thermodynamic aspects of photo-induced electron transfer processes involving a fluorophore Fl and a metal centred redox couple M^+/M.



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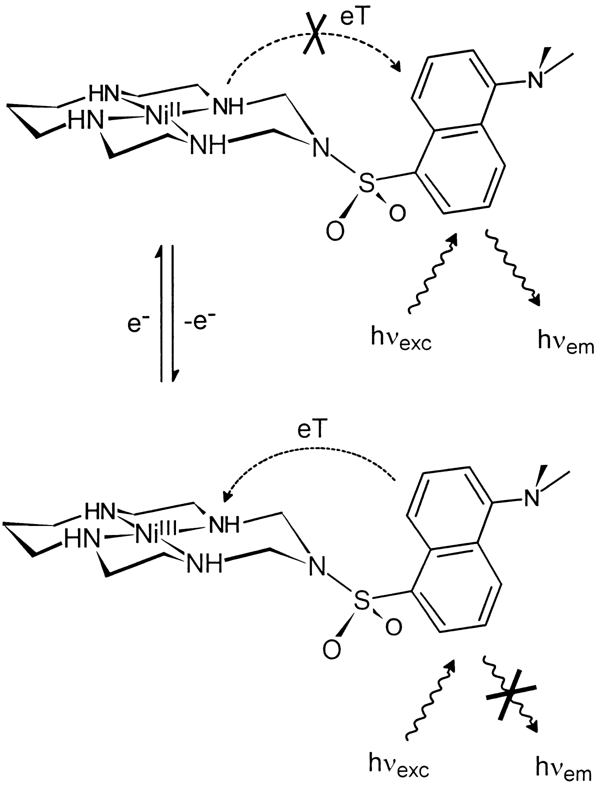
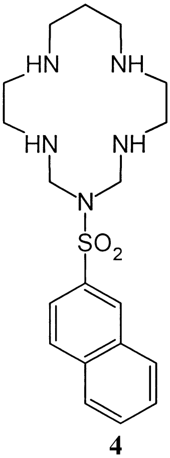


Fig. 7. Sketch of the fluorescence switching activity of the $[Ni^{III,II}(\mathbf{3})]^{3+,2+}$ system. The Ni^{III} centre promotes a fluorophore-to-metal electron transfer and quenches dansyl fluorescence. The Ni^{II}-to-dansyl electron transfer process is thermodynamically disfavoured. Thus, the Ni^{III}-to-Ni^{II} reduction restores fluorescence.

charge-transfer excited state. On anodic oxidation, in a controlled potential electrolysis experiment (working electrode potential: 0.23 V versus Fc^+/Fc), the fluorescent emission is completely quenched. Then, if the potential is set at −0.07 V, the emission is revived. The fluorescence can be switched ON/OFF at will, by adjusting the potential of the working electrode. Fluorescence quenching/enhancement can be realized chemically in an ethanolic solution using sodium peroxydisulphate as an oxidizing agent and sodium nitrite as a reducing agent. Interestingly, freezing of the ethanolic solution of the Ni^{III} form makes fluorescence revive, which indicates that room temperature quenching is due to a genuine eT mechanism (from the excited fluorophore to the metal). Notice that the occurrence of an intramolecular eT process in the $[Ni^{III}(\mathbf{3})]^{3+}$ system is accounted for by a very negative ΔG°_{eT} value: −1.93 eV. Relevant parameters from which ΔG°_{eT} has been calculated are reported in Table 1.

On the other hand, non-occurrence of an eT process in the $[Ni^{II}(\mathbf{3})]^{2+}$ form is rationalized by the distinctly positive value of ΔG°_{eT}: ≥ 0.7 eV (see Table 1 for contributing photophysical and photochemical quantities).

The functional behaviour of the switching system **3** is pictorially illustrated in Fig. 7. Stereochemical sketches are based upon the molecular structure of the $[Ni^{II}(\mathbf{3})](ClO_4)_2$ compound which has been determined through X-ray diffraction analysis.



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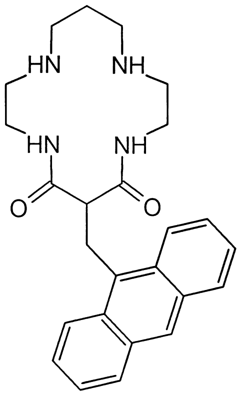

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Replacing the fluorophore does not alter the functionality of the device. In fact, system **4**, in which the same nickel–azacyclam subunit is linked to the 2-sulfonilnaphthalene fluorescent fragment, also displays OFF/ON behaviour: the oxidized form extinguishes naphthalene fluorescence, the reduced form brings it back [9]. The intramolecular eT process in the the $[Ni^{III}(\mathbf{4})]^{3+}$, whose nature has been demonstrated by spectrofluorimetric studies on a vitrified ethanolic solution, is thermodynamically favoured ($\Delta G^\circ_{eT} = -2.27$ eV, see Table 1). On the other hand, the Ni^{II}-to-fluorophore eT process, although slightly favoured ($\Delta G^\circ_{eT} = -0.22$ eV, see Table 1), is not fast enough to compete with the radiative deactivation.

Table 1
Relevant photophysical and electrochemical quantities for systems related to **1**–**6**

	E^{0-0} [a]	$E^0(\mathrm{Cu^{II}/Cu^{I}})$ [b]	$E^0(\mathrm{Ni^{III}/Ni^{II}})$ [c]	$E^0(\mathrm{Fl^{+}/Fl})$ [b]	$E^0(\mathrm{Fl/Fl^{-}})$ [b]	$\Delta G^0_{\mathrm{eT}}(\mathrm{ox})$	$\Delta G^0_{\mathrm{eT}}(\mathrm{red})$	Switching	Operating mechanism [d]
$[\mathrm{Ni^{III/II}}(\mathbf{1})]^{3+/2+}$	3.1	—	0.20	0.84	−2.40	−2.46	−0.50	OFF/OFF	ET
$[\mathrm{Cu^{II/I}}(\mathbf{2})]^{2+/+}$	3.8	−0.14	—	1.20	−2.95	−2.46	−0.99	OFF/ON	ET
$[\mathrm{Ni^{III/II}}(\mathbf{3})]^{3+/2+}$	2.4	—	0.08	0.55	≤ −3.0	−1.93	≥0.7	OFF/ON	eT
$[\mathrm{Ni^{III/II}}(\mathbf{4})]^{3+/2+}$	3.3	—	0.18	1.21	−2.90	−2.27	−0.22	OFF/ON	eT
$[\mathrm{Ni^{III/II}}(\mathbf{5})]^{+/0}$	3.1	—	0.30	0.84	−2.40	−2.56	−0.40	OFF/OFF	eT
$[\mathrm{Cu^{II/I}}(\mathbf{6})]^{2+/+}$	2.7	0.25	—	1.08	−2.46	−1.87	0.01	OFF/ON	eT

[a] eV; determined from emission spectra.

[b] V versus Fc^+/Fc, 0.1 M Bu_4NClO_4 in MeCN at 25 °C.

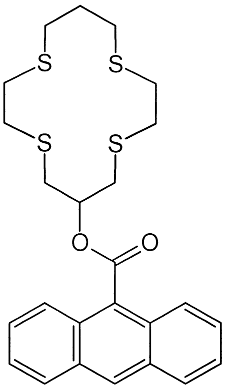
[c] V versus Fc^+/Fc, 0.1 M Bu_3BzNCl in MeCN at 25 °C.

[d] Ascertained from spectrofluorimetric investigations on solutions frozen at 77 K.

Control subunits based on the Ni^{III}/Ni^{II} redox couple do not necessarily lead to efficient OFF/ON switching systems. In the three-component system **5**, the fluorophore is anthracene and the host for the redox couple is dioxocyclamato(2−) [7]. The doubly deprotonated diamide–diamine macrocycle typically favours the access to high oxidation states of the encircled metal, including Ni^{III}, and thus makes the electrode potential of the Ni^{III}/Ni^{II} especially low (0.3 V versus Fc^+/Fc). Neither the oxidized or reduced forms of **5** fluoresce at room temperature in a BuCN solution, but both them fluoresce when frozen at liquid nitrogen temperature. Thus, the complex acts as an OFF/OFF "switch", based on an eT mechanism. Inspection of the relevant parameters in Table 1 indicates that occurrence of the eT process in the $[Ni^{II}(\mathbf{5})]^{2+}$ form is mainly related to the ease of oxidation of the metal centre within the dioxocyclamato(2−) ring. On the other hand, the occurrence of an eT process in the oxidized form $[Ni^{III}(\mathbf{5})]^{3+}$ is favoured by the facile oxidation of the anthracene fragment, An, to anthracenium, An^+.

4. ET versus eT mechanisms

From the examples illustrated in the two previous sections we can derive some very simple general principles: an ET switch has to be based on the Cu^{II}/Cu^{I} couple and synthetic efforts must be aimed towards a receptor subunit for which both oxidation states are stable (e.g. by putting some thioethereal sulphur atoms in the donor set). The design of an eT based switch is not guided by such strict limitations, making it less predictable, but also more versatile: one has only to choose the redox couple and the fluorophore whose E^{0-0} and $E°$ values combine appropriately to give either an ON/OFF or an OFF/ON situation (the reported successful examples **3** and **4** were both of the OFF/ON type). However, things are not always so simple, since the two mechanisms may compete in certain circumstances and the factors determining the prevalence of the one or of the other have yet to be elucidated.



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A puzzling example is given by system **6** [10]. Here, the most classical of organic fluorophores, anthracene, is connected through an estereal group to a 14-membered tetra-thiaethereal macrocycle (thiacyclam). Thiacyclam is the perfect host for both Cu^{I} and Cu^{II} cations. Stable $[Cu^{I}(thiacyclam)]^{+}$ and $[Cu^{II}(thiacyclam)]^{2+}$ complexes have been isolated and their stereochemistry determined through X-ray diffraction studies: Cu^{I}, tetrahedral [11]; Cu^{II}, square [12]. The moderately positive $E°(Cu^{II}/Cu^{I})$, 0.10 V versus Fc^{+}/Fc in MeCN, ensures bistability in solution. On these premises, $[Cu^{II,I}(\mathbf{6})]^{2+,+}$, which displays a similar redox behaviour ($E°=$ 0.25 V), ought to act as the typical fluorescence switch that operates through an ET mechanism. Indeed, an MeCN solution of the $[Cu^{II}(\mathbf{6})]^{2+}$ form, bright blue in colour, does not fluoresce. On electrochemical reduction (working electrode potential: -0.05 V versus Fc^{+}/Fc) the colourless species $[Cu^{I}(\mathbf{6})]^{+}$ forms and the solution fluoresces. Noticeably, the emission band is not that usually observed for anthracene at 400 nm and with the typical vibrational structure, but a less intense non-structured band, centred at 460 nm. Such an emission arises from a charge-transfer excited state An(CT)*. Is is superimposable with that measured for **6** in absence of any metal and is very similar to that observed with the ethyl ester of 9-anthracenoic acid [13]. This indicates that orbital interactions responsible for the An(CT)* state are restricted to anthracene and the estereal group and do not involve the sulphur atoms of the macrocycle. On setting the working platinum gauze electrode to 0.55 V (oxidation) and -0.05 V (reduction), alternately, in a controlled potential electrolysis experiment, the CT emission at 460 nm was successively killed and resurrected, demonstrating an ideal switching behaviour. However, freezing the solution of the $[Cu^{II}(\mathbf{6})]^{2+}$ form at 77 K made the emission revive sharply, indicating that the switch operated through an eT process rather than the expected ET mechanism. Such behaviour is fully supported on a thermodynamic basis: in fact, the An(CT)* to Cu^{II} eT process is strongly favoured, $\Delta G°_{eT} = -1.87$ eV (see Table 1 for photophysical and electrochemical contributions). On the other hand, the Cu^{I} to An(CT)* eT process is characterized by a positive $\Delta G°_{eT}$ value (0.01 eV). Systems **2** and **6** are very similar. The question is why in $[Cu^{II}(\mathbf{6})]^{2+}$ the eT mechanism operates, whereas in $[Cu^{II}(\mathbf{2})]^{2+}$ fluorescence quenching is induced by an ET process.

Another paradox comes from the $[Ni^{III,II}(\mathbf{1})]^{3+/2+}$ system, in which both the oxidized and reduced forms do not display the anthracene fluorescence (a useless OFF/OFF device). The lack of emission even in a vitrified medium indicates the occurrence of ET processes both in Ni^{III} and Ni^{II} derivatives. It should be noted that, on a thermodynamic basis, fluorescence quenching in both oxidized and reduced forms could also be induced by the eT mechanism, as indicated by the distinctly negative values of ΔG_{eT}: Ni^{III}, -2.46 eV; Ni^{II}, -0.50 eV (see Table 1). Notice also that the $[Ni^{III,II}(\mathbf{1})]^{3+/2+}$ is structurally similar to the $[Ni^{III,II}(\mathbf{3})]^{3+/2+}$ and $[Ni^{III,II}(\mathbf{4})]^{3+/2+}$ systems described above, but that these last two systems behave as OFF/ON switches, with fluorescence quenching in the Ni^{III} derivatives ensured by an eT mechanism.

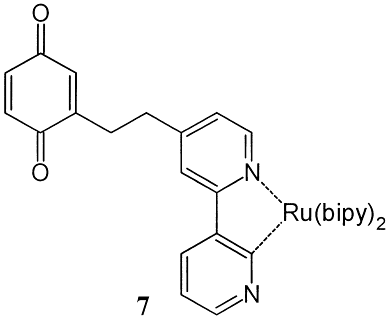
The limited number of systems investigated does not allow us to clearly define the principles directing whether an ET or an eT mechanism will prevail. However, some empirical guidelines can be tentatively suggested. All of the systems investigated consist of a macrocycle (the receptor of the redox couple) and of an aromatic fluorophore connected by a spacer. The ET mechanism operates in those systems

(**1**,**2**) in which the spacer is a simple -CH_2- group, bound to an amine nitrogen atom of the macrocycle. On the other hand, the eT process takes place in systems (**3**–**6**) in which the spacer is linked to a carbon atom (**5**,**6**) of the ring or to a nitrogen atom not involved in the coordination process. Thus, the ET mechanism is observed in systems in which the distance between the metal centre and the fluorescent fragment is especially low (M–C = 4.5 Å for **1**, 4.4 Å for **2**, as calculated by molecular modelling, using semi-empirical methods; C is the closest carbon atom of the fluorophore, i.e. that bound to the spacer). M–C distances are considerably larger in eT systems: **3**, 5.9 Å (which coincides nicely with the distance observed in the crystal structure [9]); **4**, 6.0 Å; **5**, 6.1 Å; **6**, 6.9 Å. It has been demonstrated for an homogeneous series of covalently linked donor–acceptor systems that at the shorter distances the ET mechanism dominates, whereas over longer distances the eT mechanism prevails [14]. Thus, the metal–fluorophore distance is an important factor in determining the predominance of an ET or an eT mechanism. Secondly, the N-bound -CH_2- spacer imparts flexibility to systems **1** and **2**. Thus, in these systems it is possible for the fluorophore and the metal to come into occasional contact. Van der Waals contact is a pre-requisite for the occurrence of ET processes of the Dexter type. On the other hand, the eT systems possess quite rigid bridges: the sulphonamide group (**3** and **4**), and estereal group (**6**). In system **5**, the spacer is a -CH_2- group, but it is linked to a rigid portion of the macrocycle. Moreover, systems **3**–**6**, which contain largely delocalized π-orbitals, are rather permeable to electrons. Thus, even if rigidity prevents Van der Waals contacts, electrons can easily and quickly travel along the bridge from the excited fluorophore to the metal (or vice versa).

It should be noted that the "choice" of the ET mechanism by system **2** is favourable for switching purposes since the occurrence of an eT mechanism would generate a frustrating OFF/OFF switch (see Table 1).

5. A luminescence switch based on a purely organic redox couple

All the described fluorescence switches operating through an eT mechanism contain a redox active metal centre in their control unit. However, the first reported redox switch of luminescence, by Lehn, **7**, was based on a purely organic couple: quinone/hydroquinone [15].

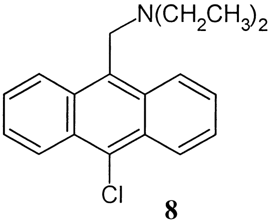


7

The luminescent fragment was the most popular amongst lumophore: $[Ru^{II}(bpy)_3]^{2+}$. System **7** behaves as an efficient OFF/ON switch and operates via the eT mechanism. In its oxidized form, the quinone subunit, RO_2, a classical electron acceptor, quenches $[Ru^{II}(bpy)_3]^{2+}$ luminescence through a lumophore-to-control unit eT process. On the other hand, a control unit-to-lumophore eT process does not take place when **7** is in its reduced form, hydroquinone, $R(OH)_2$, and so the $[Ru^{II}(bpy)_3]^{2+}$ fragment displays its typical emission centred at 608 nm. Luminescence switching with **7** can be carried out electrochemically at a platinum working electrode in aqueous MeCN. It should be noted that system **7** does not fit the one-electron stoichiometry of the triangular scheme of Fig. 2, as the quinone/hydroquinone redox change involves two electrons (and two protons): $RO_2 + 2e^- + 2H^+ = R(OH)_2$. In any case, the eT process responsible of luminescence quenching: $[Ru^{II}(bpy)_3]^{2+} + RO_2 \rightarrow [Ru^{III}(bpy)_3]^{3+} + RO_2^{\bullet -}$ is characterized by a negative ΔG°_{eT} value (~ -0.3 eV), whereas the ΔG°_{eT} value for the $Ru^{II}(bpy)_3]^{2+} + R(OH)_2 \rightarrow [Ru^{II}(bpy)_2(bp\dot{y}^-)]^+ + R(OH)_2^{+}$ is unfavourable (~ 0.2 eV)[16].

6. Varying the input that activates a luminescence switch

In everyday life, the input which turns ON/OFF the light of a bulb is typically given by the pressure of a finger on the switch. In the molecular world, as we tried to illustrate in the previous Sections, the input can be an *electron*, either supplied or removed by a reducing agent or an oxidizing agent, respectively. Another small particle that can act as a finger is the *proton*. In this case the control unit of the multicomponent system has to be a fragment displaying acid–base tendencies, e.g. $L + H^+ = LH^+$. In order to get successful fluorescence switching, only one of the two forms of the bistable couple L/LH^+ should be able to quench the proximate fluorophore. Some multicomponent fluorescence switches have been recently reported by de Silva [17,18].



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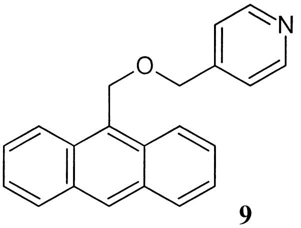

9

In system **8** [17], L is a tertiary amine group ($pK_A = 7.7$), and in **9** [18], L is a pyridine fragment ($pK_A = 5.1$). The unprotonated form of **8** is non-fluorescent, due to the occurrence of a thermodynamically favoured transfer of an electron from the lone pair of the amine group to the photoexcited anthracene fragment. On protonation, the electron lone pair is involved in covalent binding and the LH^+-to-Fl* eT process is inhibited. As a consequence, anthracene fluorescence is fully restored.

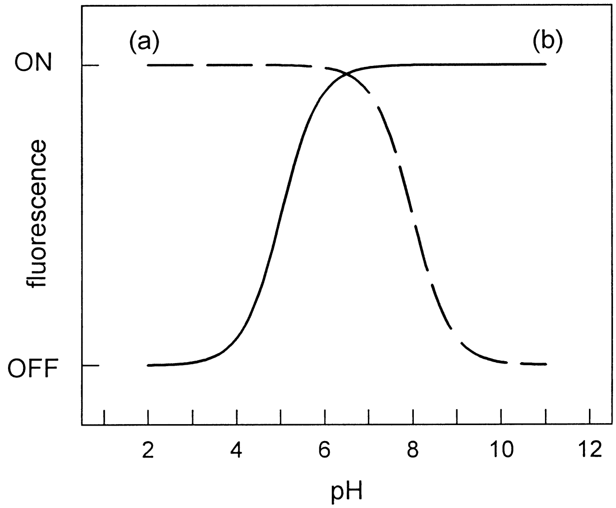

Fig. 8. Calculated fluorescence versus pH sigmoidal profiles for multicomponent system (acid/base fragment-spacer-fluorophore) of type **8** (*a*: ON/OFF response, $pK_A = 5$) and of type **9** (*b*: OFF/ON response, $pK_A = 8$).

Fig. 8, curve (a), shows the variation of the fluorescence intensity, I_F, of a system of type **8** upon pH variation, calculated for a $pK_A = 8$. The sigmoidal profile clearly illustrates the switch metaphor: a subtle variation of an external stimulus, pH (over the $pK_A \pm 1$ range) induces a drastic change of the property, I_F, which can be reversibly switched ON/OFF. System **9** displays the opposite behaviour (OFF/ON), as the protonated form, containing the pyridinium fragment pyH^+, quenches fluorescence and the L form, containing pyridine, does not. Quenching has to be ascribed to an eT process from the photoexcited fluorophore to the pyridinium fragment: $Fl^* + pyH^+ \rightarrow Fl^+ + pyH^\cdot$. On the other hand, the py-to-Fl* eT process is disfavoured. The OFF/ON I_F versus pH profile for a system of type **9**, with a $pK_A = 5$, is illustrated in Fig. 8, curve (b). Very interestingly, linking of the two acid–base functionalities, amine and pyridine, to the same fluorophore (anthracene) gives rise to a system dispaying an I_F versus pH profile which is the sum of profiles (a) and (b) of Fig. 8 and which is therefore capable of indicating a “pH window”, rather than a simple pH variation as indicators usually do [18].

As well as electrons and protons, the input activating a luminescence switch may also be given by metal ions. In this case, the active subunit has to be a receptor for a given cation. A combination of selectivity in the metal–receptor interaction (i.e. recognition) and signal transduction produces a molecular sensor (or chemosensor) [19]. Fluorescent chemosensors for metal ions are useful tools in chemical analysis and there exists a growing interest for their application in biology and medicine [20]. The design of multicomponent luminescent sensors for cations is a fastly expanding area in modern synthetic chemistry and has to be based upon the concepts of coordination chemistry.

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