Sensors and Switches from Supramolecular Chemistry

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1 Molecular Recognition and Sensors

Molecular recognition is one of the corner stones of supramolecular chemistry.[1] Given any substrate (molecule, cation, or anion), the supramolecular approach is that an appropriate receptor, possessing structural and chemical features suitable for substrate recognition, can be designed. The keyword is shape. This concept is illustrated in Figure 1.

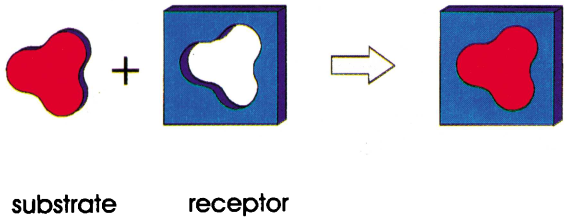


Figure 1 The basic principle of *molecular recognition*: for any given substrate, a receptor possessing geometrical and bonding features for specific interaction can be designed.

Synthetic chemists have addressed the challenge of designing and building concave receptors having shapes and dimensions suitable for hosting any kind of substrate and the ability of establishing with the substrate interactions of a sufficient energy (*e.g.* hydrogen bonds or π-interactions for a molecule; coordinative interactions for a metal ion; electrostatic interactions for an anion). However, even the most sophisticated and specific host system is useless, in a practical sense, if it is not able to communicate to the external operator that receptor–substrate interaction is taking place and recognition has occurred. To make this possible, one has to append to the receptor framework a molecular subunit displaying a well-defined and perceptible property. In particular, such a property, or, to be more precise, the quantity expressing the property, should change drastically, following the receptor–substrate interaction. Such a situation is illustrated in Figure 2.

The assembly of a specific receptor with a subunit capable of signalling the occurrence of receptor–substrate interaction constitutes a *sensor*. Sensor efficiency is related to a comparable extent (i) to the selectivity of the binding tendencies and (ii) to ease and simplicity of detecting and measuring the displayed signal.

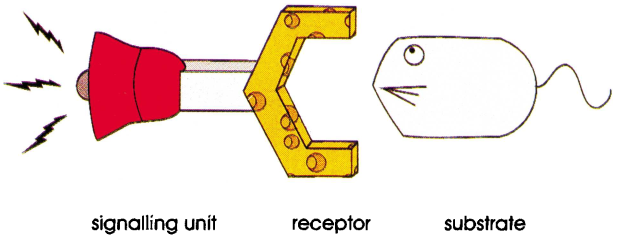
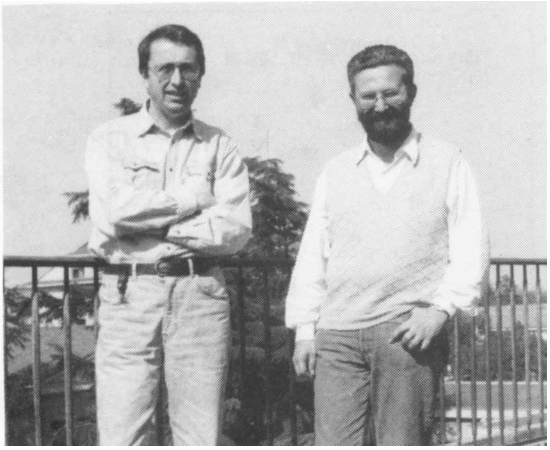


Figure 2 Designing a receptor for which the substrate has a specific affinity may not suffice; something should signal to the operator that recognition has occurred. Assembling a *receptor* and a *signalling unit* makes a *sensor*.

2 Fluorescent Sensors for Metal Ions

A property detectable and measurable in real time, using instrumentation that is not too expensive, often at very low concentration levels of the envisaged analyte ($\leq 10^{-7}$ M), is *fluorescence*. Fluorescent sensors for metal ions have been developed by several groups during the past decade.[2] A number of these sensing supramolecules contain anthracene as a fluorescent subunit (or fluorophore) for its strong and well characterized emission and its chemical stability. An anthracene-based sensor for *s* block metal ions, developed by de Silva,[3] is depicted in Figure 3. The receptor is an 18-membered macrocycle containing five ethereal oxygen atoms and an amine nitrogen atom as donors. Thus, by analogy with the classical ligand 18-crown-6, it is suitable for a selective interaction with the K^+ ion. Before metal incorporation, the supramolecular system (1) is not fluorescent. In particular, the typical anthracene fluorescence is quenched *via* an electron-transfer process from the fairly reducing tertiary amine group of the macrocyclic ring (*i.e.* from the



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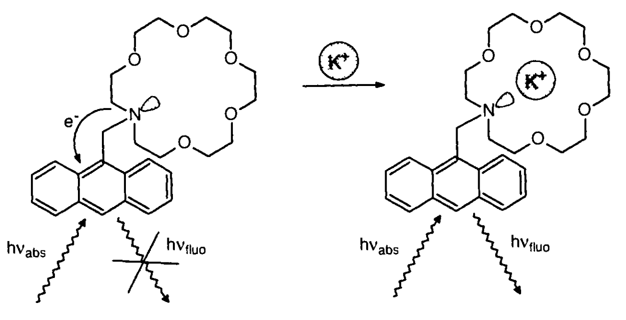
Luigi Fabbrizzi was born in Florence in 1946. He graduated from the University of Florence, where he did post-doctoral work on the thermochemistry of metal polyamine complexes with P. Paoletti and, from 1972, he was lecturer of Inorganic Chemistry. In 1980 he was appointed as a Professor of Chemistry at the University of Pavia, where he is presently Head of the Department of General Chemistry. His main research interest covers the design of supramolecular systems that contain transition metal centres and profit from their redox activity and electron-transfer properties.

Antonio Poggi was born and educated in Florence, where he graduated in 1979. After a two-year appointment as a post-doctoral fellow at York University, Downsview (Ontario), Canada, with A. B. P. Lever, in 1983 he joined the Department of General Chemistry at the University of Pavia (Italy) as a Research Associate. In 1987 he was appointed as an Associate Professor in the same Department. His current research interests are centred on the redox chemistry of macrocyclic transition metal complexes and the kinetic study of fast reactions.



(1)

Figure 3 A PET sensor for K$^+$. Metal coordination stops the electron-transfer process from the tertiary amine group to the photo-excited anthracene fragment and restores fluorescence.

amine lone-pair) to the photo-excited fluorophore. Following metal coordination, the oxidation potential of the amine group is substantially lowered (as the lone pair is involved in coordination) and the electron-transfer process is prevented on a purely thermodynamic basis. As a consequence, fluorescence is restored. Therefore, the interaction between the receptor and the K$^+$ ion is communicated to the outside by the appearance of the intense emission spectrum of anthracene. Sensors of type of (1), which work through a Photo-induced Electron Transfer mechanism (PET), should contain, besides the receptor and the fluorophore, an internal device providing the electron release: in this case, the tertiary amine nitrogen atom.

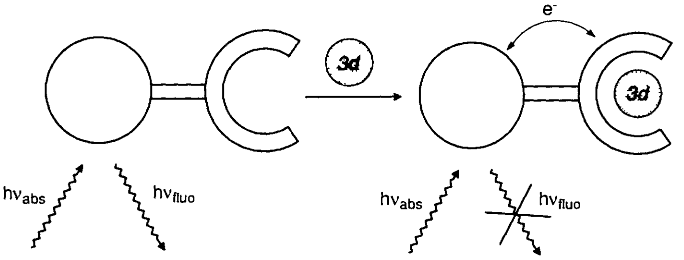
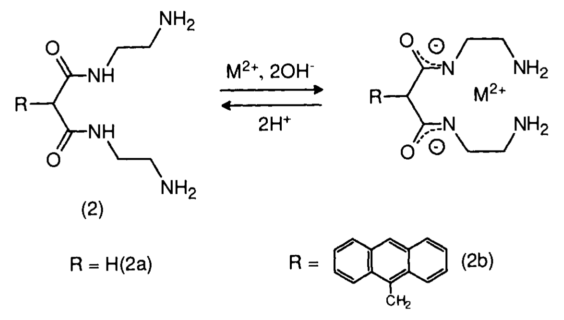


Figure 4 Design of a PET sensor for a transition metal. The redox-active metal ion itself provides the electron release to the excited fluorophore (or uptake therefrom).

In our laboratory, there has been a recent interest in the development of PET sensors for transition metal ions.[4] It should be possible in this case (following the supramolecular approach) to assemble a fluorescent fragment and a selective receptor. However, the 'internal device providing electron release' may be unnecessary: *d* block metals are *per se* inclined towards easy and reversible electron-transfer processes and have access to different and consecutive oxidation states. Such an access can be typically controlled by varying the coordinative environment around the metal. Thus, when designing a PET sensor, one should choose as a receptor a ligand capable of stabilizing an adjacent oxidation state of the envisaged cation. Figure 4 outlines a supramolecular sensor in which the metal–receptor interaction is signalled through fluorescence quenching. Quenching can be induced from the transfer of an electron to the excited state of the fluorophore directly from the metal centre, or, alternatively, through an electron-transfer process from the photo-excited fragment to the metal centre. The following example concerns the design of a PET sensor for the copper(II) ion, based on a metal-to-fluorophore electron transfer.

Coordination chemistry studies have shown that the diamine–diamide quadridentate ligand (2a) reported in Scheme 1 chelates the Cu^{II} ion, with simultaneous deprotonation of the two amide groups.[5] Such a coordinative environment favours the access to the otherwise elusive Cu^{III} state.[6] The Cu^{II}/Cu^{III} redox change takes place at a moderately positive potential. Thus, we considered the diamine–diamide chelating fragment (2a) suitable for promoting an electron-transfer process from the bound Cu^{II} centre to a luminescent subunit and we attached it to the anthracene moiety, through a $-CH_2-$ bridge, to give the supramolecular system (2b).



Scheme 1 Complexation of a 3*d* metal ion M^{II} (M = Cu, Ni) by a diamide–diamine chelating agent with simultaneous deprotonation of the two amide groups. The process is pH controlled.

Titration experiments carried out in a spectrofluorimetric cuvette showed that (2b) displays the typical emission spectrum of anthracene, without any alteration, over the 2—12 pH range, in an acetonitrile–water mixture (4:1 v/v).

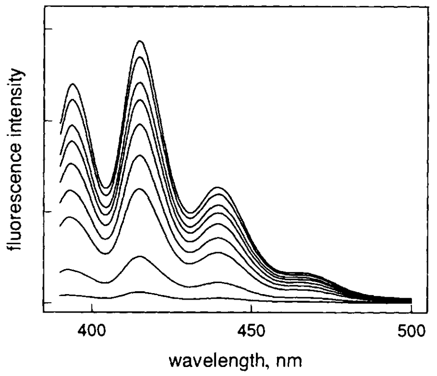


Figure 5 Emission spectra of a solution containing equivalent amounts of (2b), Cu^{II}, and excess strong acid, during the titration with standard base.

However, if 1 equivalent of Cu^{II} is added to a solution of (2b) containing excess strong acid, and titration with standard NaOH is carried out, a progressive decrease of the fluorescent emission is observed from pH = 5 onwards (as shown in Figure 5), until quenching is complete at pH $\geq$ 7. A typical sigmoidal profile of the fluorescence intensity *vs.* pH plot is observed, as shown in Figure 6.

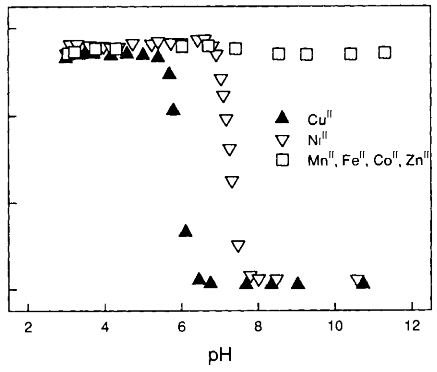
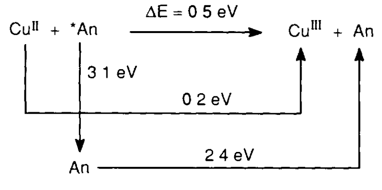


Figure 6 Fluorescence intensity of the uncomplexed sensor (2b) does not change over the 2—12 pH range. Fluorescence decreases and is then quenched in the presence of 1 equivalent of Cu^{II} (pH = 5.5—6.5) and of Ni^{II} (pH = 7—8). Other 3*d* metals (Mn^{II}, Fe^{II}, Co^{II}, Zn^{II}) do not alter (2b) fluorescence.

Quenching of the fluorescence of the supramolecular system (2b) is associated with the complexation of the Cu^{II} ion by the chelating fragment, as shown in Scheme 1, and has to be ascribed to the transfer of an electron from the divalent metal centre (which reaches the Cu^{III} state) to the photo-excited state of anthracene, *An.



Scheme 2 Thermodynamic cycle for the electron-transfer process from Cu^{II} to *An in the complexed supramolecular system (2b). The E_{*An} potential corresponding to E_{00} zero spectroscopic energy has been calculated from the energy of the emission band of uncomplexed (2b)

The ET process responsible for fluorescence quenching, reported in Scheme 2, is thermodynamically favoured, being characterized by a distinctly positive change of potential, $\Delta E_{ET} = 0.5$ eV. This value has been calculated from the combination of the appropriate photochemical and electrochemical quantities ($\Delta E_{ET} = E_{*An} - E^\circ_{Cu^{III}/Cu^{II}} - E^\circ_{An/An^-}$), according to the cycle outlined in Scheme 2.[7]

A sigmoidal decrease of fluorescence intensity is also observed, in the 7—9 pH range, when a similar titration experiment is carried out in the presence of 1 equivalent of Ni^{II} (see Figure 6). In this case, fluorescence quenching is associated with the complexation of the 3*d* ion and the subsequent electron-transfer process from the metal centre to the proximate photo-excited subunit. The electron transfer from Ni^{II} to *An is thermodynamically allowed ($\Delta E_{ET} = 0.35$ V) and reflects the easy access to the Ni^{III} state in a square coordinative environment containing two amine and two deprotonated amide groups.[9] However, if the spectrofluorimetric titration is carried out in presence of equivalent amounts of other divalent transition metal ions (Mn^{II}, Fe^{II}, Co^{II}, Zn^{II}) the fluorescence of the anthracene fragment remains unchanged over the complete pH range (see Figure 6). Such behaviour can be accounted for when it is considered that the complexation equilibrium in Scheme 1 involves the strongly endothermic deprotonation of the two amide groups. This very unfavourable contribution is compensated only by the coordination of Cu^{II} and Ni^{II} ions – late in the 3*d* series and very much profiting from the Ligand Field Stabilization Energy. The endothermic effect is not overcome, and metal complexation does not take place, for ions earlier in the 3*d* series (Mn^{II}, Fe^{II}, Co^{II}), which do not profit too much from LFSE effects. Zn^{II} has a d^{10} electronic configuration and cannot profit at all from such stabilization. Thus, receptor selectivity is not strictly related to geometrical features (shape and size of the hosting concavity relative to the shape and dimensions of the substrate), as typically observed with spherical ions of Groups I and II, but is associated with the host's capability of establishing more or less intense coordinative interactions with the metal centre. In short, the receptor, looking in the solution for its metal partner, does not recognize the radius of the metal, but its position in the Periodic Table.

The further task is to discriminate between Cu^{II} and Ni^{II}. This is possible if one operates at the proper pH value. In fact, titration experiments have shown that sensor (2b) binds Cu^{II} about two pH units before Ni^{II} (see Figure 6). Such a behaviour reflects the generally observed greater solution stability of Cu^{II} complexes with poly-aza ligands compared to those of Ni^{II}. In particular, fluorescence intensity *vs* pH profiles displayed in Figure 6 indicate that at pH7 the Cu^{II} complex has been formed, whereas complexation of Ni^{II} has yet to begin. Thus, when sensor (2b) was dissolved in an aqueous acetonitrile solution buffered at pH7 and the solution was titrated in the spectrofluorimetric cuvette with a solution of Ni^{II}, fluorescence emission was not altered, even after the addition of more than 1 equivalent of Ni^{II} (see Figure 7). But when the same solution was titrated with Cu^{II}, a linear decrease of fluorescence emission was observed, which was completely quenched after the addition of 1 equivalent of Cu^{II}. At pH7, therefore, sensor (2b) recognizes Cu^{II} but not Ni^{II}.

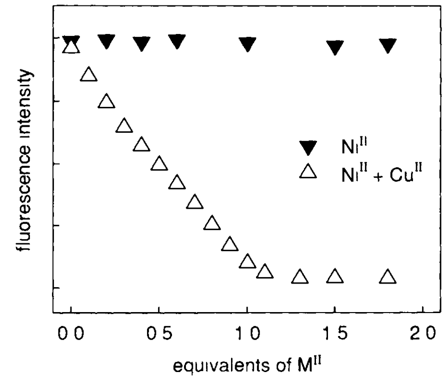


Figure 7 Fluorescence intensity of a solution of (2b) buffered at pH = 7 when titrated first with Ni^{II} and then with Cu^{II}. (2b) recognizes Cu^{II}, but not Ni^{II}

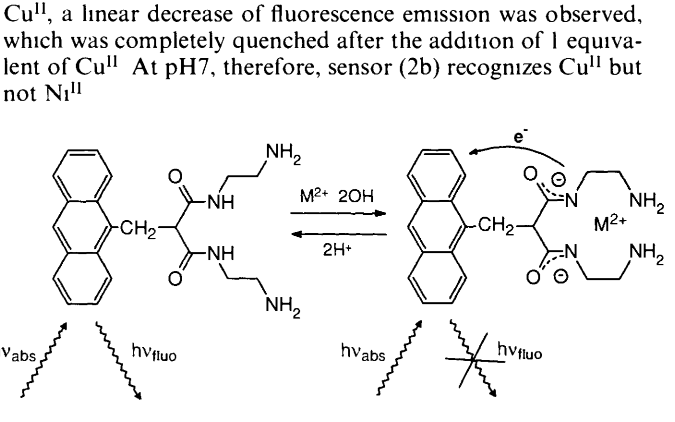


Figure 8 A PET sensor for Cu^{II} and Ni^{II} metal ions. On coordination, an electron is transferred from the metal to the photo-excited anthracene fragment and quenches fluorescence

Recall that in the sensing of *s* block cations (typically non-redox-active), the uncomplexed system (1) was non-fluorescent and recognition was signalled through a revival of fluorescence (as illustrated in Figure 3). For the redox-active transition metal ions Cu^{II} and Ni^{II} the opposite behaviour is observed: the uncomplexed sensor (2b) is fluorescent and recognition is signalled through fluorescence quenching (as illustrated in Figure 8).

3 Molecular Switches Operating *via* a pH or a pM Change

In a more general sense, the fluorescent sensors described above can be defined as molecular systems in which a distinctive property, fluorescence, is varied at will from the outside. From the point of view of the supramolecular design, such systems must be constituted by two well-defined components, as illustrated in Figure 9.

One of the components, the *active unit*, exhibits a well detectable property. The active unit is linked, through a *spacer*,

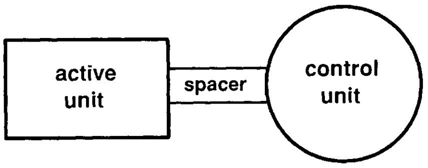


Figure 9 A two-component supramolecular system for the control of a given property. The *active unit* displays the property, which is modified by the state of the bistable *control unit*

to the *control unit* This latter component can exist in two different states of comparable stability (a *bistable* system) and the reversible access to each state can be controlled through the variation of an external (or *bulk*) parameter Most significantly, each state affects to a different extent the property displayed by the proximate active unit one enhances, the other depresses the property In conclusion, one can modify at will the property of the active unit by varying a bulk parameter of the solution In some cases, a fine variation of the bulk parameter causes a sharp change of the envisaged property, as though moving from an ON state to an OFF state or *vice versa* (see Figure 10)

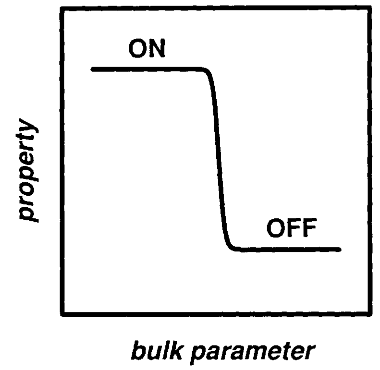
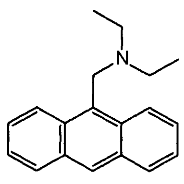


Figure 10 The origin of the switch metaphor The fine variation of a *bulk* parameter of the solution (*e g* pH), through the mediation of the control unit, switches on/off the property displayed by the active unit (*e g* fluorescence)

This state of affairs and the marked inclination of supramolecular chemistry to borrow words from everyday language has resulted in the control unit being referred to as a *switch* [1,10,11] The switch metaphor is especially appropriate when the active unit is a light-emitting fragment (switching a light bulb on/off)

As an example, by varying the bulk parameter pH, one can



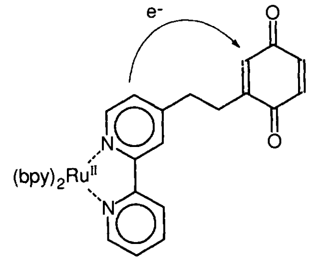
(3)

switch on/off the fluorescence of an anthracene fragment linked through a $-CH_2-$ bridge to a tertiary amine group, which works as a switch [12] In particular, if a solution of (3) containing excess strong acid is titrated with standard base, a fluorescence intensity *vs* pH sigmoidal profile is obtained, which is similar to that displayed in Figure 10 In acidic solution, the intense fluorescence of anthracene is observed, subsequently, with pH approaching the pK_A value of the anthrylammonium acid, fluorescence decreases and is completely quenched in definitely basic solution The ON/OFF mechanism is again associated with a PET process In solutions of $pH \geq (pK_A + 1)$, the dominating species is the amine form and an electron is spontaneously transferred from the lone pair of the amine nitrogen atom to the photo-excited fluorophore, quenching fluorescence At $pH \leq (pK_A - 1)$, the amine group of (3) is protonated and the electron transfer is thermodynamically prevented The pH switchable fluorescent system (3) can be considered also as a sensor for H^+, the receptor (the amine group) working as a switch

In a similar way, sensors (1) and (2b) also can be considered as switchable systems which are operated through a variation of the concentration of K^+ and Cu^{2+}, respectively (or by a pM change, if the bulk parameter is expressed on the logarithmic scale)

4 Redox Switchable Fluorescent Systems

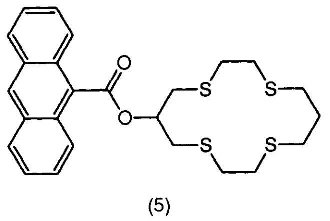
Besides pH (and pM), there exists another convenient bulk parameter that can be varied at will by the operator the redox potential, E In order to modify a property through a change of the redox potential, the control unit must be a redox-active fragment, whose forms, oxidized and reduced, should exhibit comparable solution stabilities In addition, the two forms should affect the property displayed by the active unit (*e g* fluorescence) to different extents A redox switch (or electroswitch) for fluorescence has been recently described by Lehn [13]



(4)

Figure 11 A redox switchable luminescent system [13] The quinone subunit promotes an electron transfer from the photo-excited $[Ru^{II}(bpy)_3]^{2+}$ fragment, and quenches fluorescence On reduction to the hydroquinone form, any electron-transfer process is prevented and fluorescence is awakened

In the supramolecular system (4) the classical inorganic fluorophore $[Ru^{II}(bpy)_3]^{2+}$, which absorbs and emits light in the visible region, is linked through a $-CH_2CH_2-$ spacer to a quinone subunit The $[Ru^{II}(bpy)_3]^{2+}$ fragment in (4) does not fluoresce, as the appended quinone subunit, oxidizing in nature, takes an electron from the proximate photo-excited fragment, quenching fluorescence However, if the quinone fragment, in an acidic aqueous acetonitrile solution, is reduced to the hydroquinone form ($O{=}R{=}O + 2e^- + 2H^+ = HO{-}R{-}OH$), the electron-transfer process is prevented and the fluorescence of the $[Ru^{II}(bpy)_3]^{2+}$ fragment is awakened Consecutive additions of reducing and oxidizing agents ($S_2O_4^{2-}$ and Ce^{IV}) switch the fluorescence on/off



(5)

We have more recently developed a further redox-switchable fluorescent system Reversing Lehn's approach, which was to assemble a metal-centred fluorophore and an organic switch, we looked at an organic fluorescent fragment (anthracene again) and at a metal-centred switch (the Cu^{II}/Cu^{I} couple) In this connection, we synthesized the two-component system (5), in which the anthracene subunit has been linked through an estereal bridge to a 14-membered macrocycle, which contains four thia-ethereal sulfur donor atoms (thiacyclam) [14] Thiacyclam was chosen as it forms fairly stable complexes with both Cu^{II} and Cu^{I},[15,16] thus providing a bistable redox system The reversible Cu^{II}/Cu^{I} couple behaves as an efficient switch of anthracene fluorescence in system (5) In fact, an acetonitrile solution of $[Cu^{II}(5)]^{2+}$, bright blue in colour, does not display any fluorescence However, if the experiment of controlled potential electrolysis is carried out on this solution and, in particular, the potential of the working electrode (a platinum gauze) is set at 200 mV *vs* SCE, the solution decolorizes, due to the Cu^{II}-to-Cu^{I} change, and fluoresces The emission spectrum of the electrolysed solution is shown in Figure 12

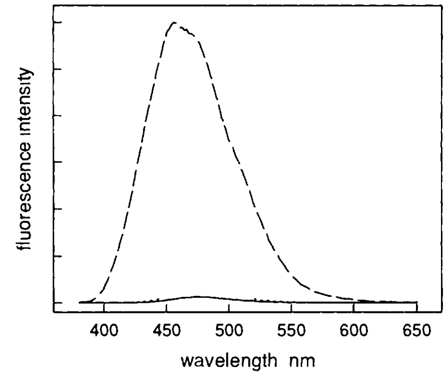


Figure 12 Emission spectra of a solution of $[Cu^{II}(5)]^{2+}$ in acetonitrile during a controlled potential electrolysis experiment (——) before electrolysis (-----) the potential of the working electrode has been set at 200 mV *vs* SCE $[Cu^{II}(5)]^{2+}$ is reduced to $[Cu^{I}(5)]^{+}$ and the fluorescence is revived, ( ) the potential of the working electrode has been set at 800 mV *vs* SCE $[Cu^{I}(5)]^{+}$ is oxidized back to $[Cu^{II}(5)]^{2+}$ and fluorescence is quenched

If then the potential of the platinum gauze is set at 800 mV, the solution takes again the blue colour of the $[Cu^{II}(5)]^{2+}$ species and fluorescence is killed One can go back and forth, switching on and off the fluorescence at will, by simply adjusting the working electrode potential to 200 and 800 mV, consecutively

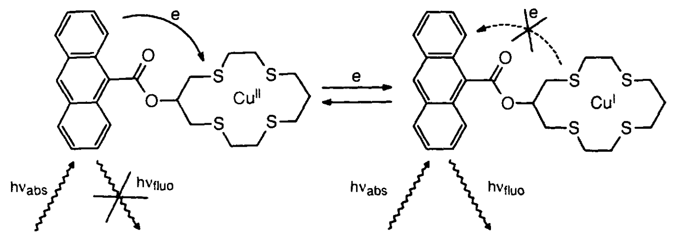


Figure 13 Redox switching of anthracene fluorescence through the Cu^{II}/Cu^{I} couple The oxidized metal centre Cu^{II} induces an electron transfer process from the excited fluorophore and quenches fluorescence On reduction to Cu^{I}, no electron transfer takes place and fluorescence revives

The behaviour described above, illustrated in Figure 13, deserves some comments First, the emission spectrum of the $[Cu^{I}(5)]^{+}$ form, as displayed in Figure 12, is distinctly different from that typically observed for anthracene derivatives (an example is shown in Figure 5) it is about one order of magnitude less intense, it is displaced towards higher wavelengths, it does not present a well-defined vibrational structure A similar emission spectrum is observed for esters of the anthracenoic acid,[17] and corresponds to a charge-transfer excited state, $^{*}An_{CT}$ The second and most important point is that such an excited state is deactivated by the proximate metal centre, when the latter is in its oxidized form (Cu^{II}), but not when it is in its reduced form (Cu^{I}) The mechanism of the non-radiative decay in the $[Cu^{II}(5)]^{2+}$ state involves an electron transfer from the photo-excited fragment $^{*}An_{CT}$ to the Cu^{II} centre, as described by the following equation

$$Cu^{II} + {}^{*}An_{CT} = Cu^{I} + An^{+} \qquad (1)$$

The change of potential associated with the electron transfer process (equation 1), obtained through a cycle similar to that reported in Scheme 2, is extremely favourable $\Delta E_{ET} = E^{*}_{AnCT} + E^{\circ}_{Cu^{II}\ Cu^{I}} - E^{\circ}_{An\ \ An} = 2\ 0$ V and accounts for the observed neat fluorescence quenching The question is now why an electron-transfer process does not take place from the Cu^{I} centre to the charge-transfer excited state $^{*}An_{CT}$, as described by equation 2

$$Cu^{I} + {}^{*}An_{CT} = Cu^{II} + An \qquad (2)$$

In this connection, it should be noted that the ET process shown in equation 2 is much less favoured from a thermodynamic point of view In particular, the associate potential change is only slightly positive ($\Delta E_{ET} = E^{*}_{An_{CT}} + E^{\circ}_{Cu^{II}\ Cu^{I}} - E^{\circ}_{An\ An} = 0\ 1$ V) and such a weakly exo-ergonic contribution does not ensure an electron transfer fast enough to compete with the radiative decay of the $^{*}An_{CT}$ state

The previous discussion has demonstrated the possibility of assembling a redox-switchable fluorescent system using off-the-shelf components the fluorophore, Fl, and the redox couple, M^{+}/M, to be used as a switch However, the choice of components should be made carefully, taking into account the relevant photophysical and electrochemical parameters (E_{*Fl}, $E^{\circ}_{Fl\ \ Fl}$, $E^{\circ}_{Fl\ Fl}$, $E^{\circ}_{M\ \ M}$) In fact, four combinations of components can be generated, two favourable and two unfavourable, as illustrated in Table 1

Table 1 Assembling of a fluorophore Fl and a redox couple M^{+}/M Four combinations are possible, depending upon the values of E_{*Fl} (excited fluorophore potential, corresponding to E_{00}, zero spectroscopic energy, which is obtained from the energy of the emission band), and $E^{\circ}_{Fl\ \ Fl}$, $E^{\circ}_{Fl\ Fl}$, $E^{\circ}_{M\ \ M}$ (electrode potentials of the corresponding redox couples, from voltammetry studies on the supramolecule or on the separate components) Only combinations (a) and (b) generate a switching situation

	Thermodynamic balance	State
(a)	$E_{*Fl} > [E^{\circ}_{Fl\ \ Fl} - E^{\circ}_{M\ \ M}]$	OFF
	$E_{*Fl} < [E^{\circ}_{M\ \ M} - E^{\circ}_{Fl\ Fl}\ ]$	ON
(b)	$E_{*Fl} < [E^{\circ}_{Fl\ \ Fl} - E^{\circ}_{M\ \ M}]$	ON
	$E_{*Fl} > [E^{\circ}_{M\ \ M} - E^{\circ}_{Fl\ Fl}\ ]$	OFF
(c)	$E_{*Fl} > [E^{\circ}_{Fl\ \ Fl} - E^{\circ}_{M\ \ M}]$	OFF
	$E_{*Fl} > [E^{\circ}_{M\ \ M} - E^{\circ}_{Fl\ Fl}\ ]$	OFF
(d)	$E_{*Fl} < [E^{\circ}_{Fl\ \ Fl} - E^{\circ}_{M\ \ M}]$	ON
	$E_{*Fl} < [E^{\circ}_{M\ \ M} - E^{\circ}_{Fl\ Fl}\ ]$	ON

System (5) should correspond to situation (a), in which the energy of the photo-excited state is high enough to promote the electron transfer from *Fl to the oxidized form of the control unit, M^{+}, but not enough to induce the electron transfer from the reduced form M to *Fl [18] Combination (b), too, generates a switchable situation, from the opposite thermodynamic argument in this case, the quenching act is provided by the electron transfer from M to *Fl Combinations (c) and (d) do not generate a switchable situation and should be avoided In combination (c), a photoexcited state too rich in energy favours both electron-transfer pathways, and generates an OFF/OFF situation If the photo-excited state is too low in energy, neither of the electron transfer pathways is activated, as illustrated in combination (d), and the ON state is always maintained, whatever the oxidation state of the control unit It should be noted that the inequalities of Table 1 are to some degree approximations and may not apply too strictly [20] Moreover, as the rate of an ET process is related to the magnitude of ΔE_{ET}, it may happen that an electron-transfer process is slightly favoured from a thermodynamic point of view, but is too slow to compete with the radiative decay of the excited state [22] Other effects are related to the lifetime of the excited state of the fluorophore, to the length and nature of the spacer, and to the rigidity of the whole supramolecular system

5 Conclusions

One of the aims of the previous discussion was to demonstrate that, in the vocabulary of supramolecular chemistry, the terms *sensor* and *switchable system* can be used to indicate the same object – they simply point to a difference in application and use.

When using the term *sensor*, attention is focused on the receptor–substrate specific interaction: the active unit plays an ancillary role and is expected only to communicate the occurrence of the recognition, by activating/deactivating a given property. In the previous sections we have presented selected examples of supramolecular sensors for *s* and *d* block metal ions, for protons (and for electrons too, if one is inclined to consider the redox-active component a receptor).

The term *switchable system* is used from a different point of view. The attention is now directed towards the signal, on its generation and control. Figure 14 sums up the switch metaphor. The light-bulb is switched on/off through a switch, which is in turn operated by a finger: in the molecular world, the action of the finger is to vary the pH, pM, or redox potential.

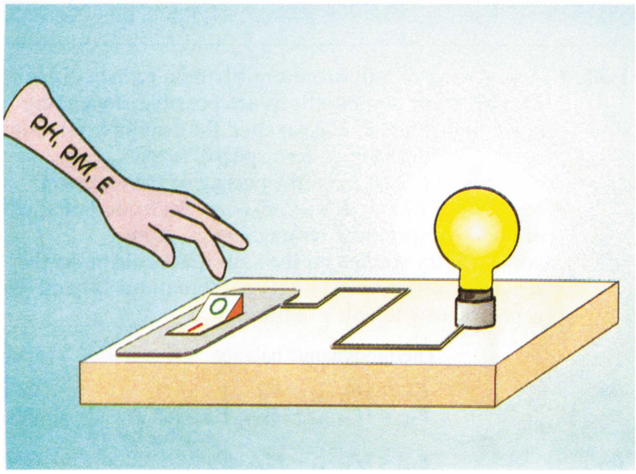


Figure 14 Completion of the switch metaphor. The operator, varying a bulk parameter of the solution (pH, pM, E), switches on/off, through the control unit, a property of the active unit. The metaphor seems especially appropriate when the active unit is a light-emitting fragment.

The analogy seems good. The only arguable element is the electrical wire (the spacer, in the supramolecular system). In the examples discussed above, very short spacers have been used (1—2 methylene groups) and the active unit and the control unit are quite close together. As though the electrician placed the switch near the chandelier, on the ceiling! Another questionable point is that the spacers used in the above examples are not permeable to electrons: in fact, the electron transfer between control unit and active unit occurs through space. Notice that in the design of a sensor, the length of the spacer is not relevant at all. On the contrary, length and nature of the spacer may be very significant as far as generation, remote control, and processing of signals at a molecular level is concerned. Using a conjugated polyolefinic chain as a spacer can allow the switch to trigger the signal at a distance of tens of Å, for instance from one side to the other of a membrane.[23] The insertion of molecular wires of an appropriate length between control unit and active unit appears as a natural and stimulating development of the chemistry of switchable systems.

6 References and Notes

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