

# A simple and robust reversible redox–fluorescence molecular switch based on a 1,4-disubstituted azine with ferrocene and pyrene units†

Rosario Martínez,<sup>a</sup> Imma Ratera,<sup>b</sup> Alberto Tárraga,<sup>a</sup> Pedro Molina\*<sup>a</sup> and Jaume Veciana\*<sup>b</sup>

Received (in Cambridge, UK) 12th June 2006, Accepted 10th July 2006

First published as an Advance Article on the web 2nd August 2006

DOI: 10.1039/b608264e

Taking advantage of the properties of the ferrocene as a redox and electron donor active unit and the pyrene as a fluorescent unit, dyad **2** shows a fast and reversible redox-switchable fluorescence emission.

There is considerable optimism that bistable switchable molecules will eventually play a key role in the design and operation of future nanoscale electronic devices.<sup>1</sup> What these specific roles will be, however, is currently an open question that must be addressed by a variety of different approaches. Efficient molecular switching materials are targets of increasing interest for electronics and optical memory devices.<sup>2</sup> Such materials can be obtained by connecting, through a proper bridge, an electro- (or photo-) switchable subunit with a subunit responsible for the signal output that must possess a given physical property to be modulated by an external stimulus, like electrons or light. Among all the possible signal outputs of switching materials, fluorescence emission is considered to be one of the most attractive owing to it being a high sensitivity, easy detection and low-cost procedure.<sup>3</sup> In addition, designing fluorescent redox- (or photo-) switchable materials is essential to provide a non-destructive readout capability. On the other hand, the development of signal-controlling redox functionalities in molecular systems attracts substantial research efforts directed to the design of information storage and processing systems and the development of new electronic materials.<sup>4</sup> Such materials might also find use as probes for redox processes and in studies of electron and energy transfer mechanisms.<sup>5</sup>

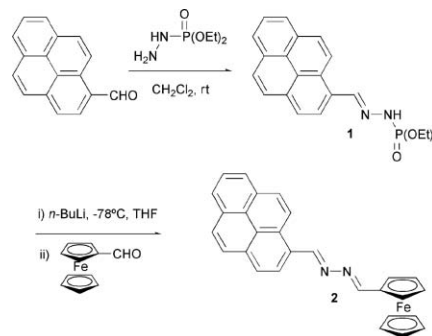
Our strategy for designing fluorescence redox-switchable molecular systems is to incorporate, as a signal-controlling redox unit, a ferrocenyl group because of its ability to be reversibly oxidized and several other additional advantages.<sup>6,7</sup> To prepare ferrocene-based fluorescence switches also requires a rational selection of the fluorescent subunit as well as of the bridge connecting both subunits. For such a purpose, it should be taken into account that the fluorescence spectrum of the fluorophore unit should not overlap largely with the absorption spectrum of the corresponding oxidized ferricinium unit. Otherwise, intramolecular energy transfer would occur under oxidation and in this case the expected fluorescence enhancement would not be

observed.<sup>8</sup> For this work we have chosen the well-characterized pyrene<sup>9</sup> as a fluorophore probe connecting it to a ferrocene unit through a 2,3-diaza-1,3-butadiene bridge. Pyrene has often been used as an effective fluorescence probe because of its high detection sensibility.<sup>10</sup> The formation of self-assembled complexes results in a remarkable change in the fluorescence emission intensities of the pyrene excimer and monomer. As far as we know, no examples of ferrocene-based dyads with a pyrene group linked by a simple bridge have been described up to now.

Herein we report the synthesis, and spectral and electrochemical studies of the new dyad **2** showing that this simple molecule acts as a robust and reversible fluorescence–redox switchable bistable molecular system whose fluorescence emission intensity depends on the oxidation state of the ferrocene unit. In this way we demonstrate that dyad **2** offers a great potential as a new class of material for fluorescence switching devices.

Preparation of dyad **2** was carried out by a modification of the Zwiernak's synthesis of unsymmetrical azines.<sup>11</sup> The method started from compound **1** (Scheme 1), which was prepared on the basis of a condensation reaction between the amino group of diethyl phosphorohydrazidate and 1-pyrenecarboxaldehyde in CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 6 hours. Metallation of compound **1** with butyllithium in THF at –78 °C under nitrogen followed by reaction with ferrocenecarboxaldehyde leads to the novel dyad **2**, in an overall yield of 60% after recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O† (for more details see ESI†).

A cyclic voltammogram of **2** was recorded in an acetonitrile solution containing 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>. As shown in Fig. 1 and Fig. S1†, one reversible oxidation wave at  $E_{1/2} = +0.770$  V (vs. decamethylferrocene; DMFc) and one irreversible oxidation wave around +1.492 V (vs. DMFc) were observed. The oxidation wave at the lower potential corresponds to the oxidation of the



**Scheme 1** Synthesis of 1-ferrocenyl-4-pyrenyl-2,3-diaza-1,3-butadiene (**2**): (i) anhydrous Na<sub>2</sub>SO<sub>4</sub>, 1-pyrenecarboxaldehyde, CH<sub>2</sub>Cl<sub>2</sub>, rt, 6 h; (ii) THF, –78 °C and then ferrocenecarboxaldehyde, 12 h, rt.

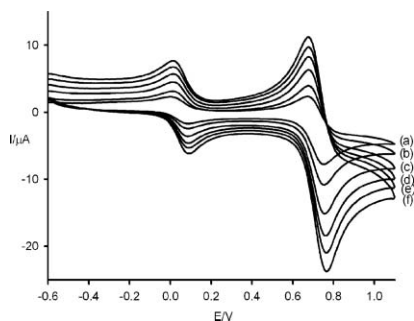
<sup>a</sup>Departamento de Química Orgánica, Facultad de Química Universidad de Murcia, Campus de Espinardo, 30100 Murcia, Spain.

E-mail: pmolina@um.es; Fax: +34 968 364149; Tel: +34 968 367496

<sup>b</sup>Institut de Ciència de Materials de Barcelona (CSIC), Campus Universitari, 08193 Bellaterra, Catalonia, Spain.

E-mail: veciana@icmab.es; Fax: +34 93 5805729; Tel: +34 93 580 1853

† Electronic supplementary information (ESI) available: Experimental details for compounds **1** and **2**; CV and fluorescence measurements of compound **2**. See DOI: 10.1039/b608264e



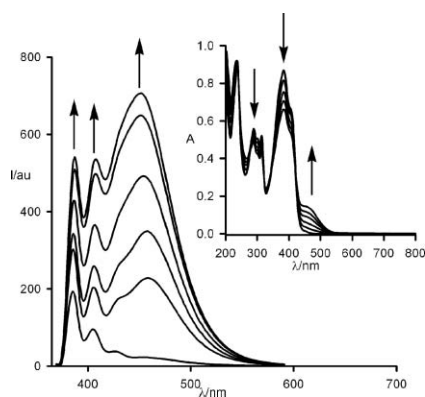
**Fig. 1** Cyclic voltammogram of **2** in acetonitrile using *n*-Bu<sub>4</sub>NPF<sub>6</sub> 0.1 M as the supporting electrolyte, AgCl/Ag, as the reference electrode, and platinum wires, as the counter and working electrodes in the presence of DMFc, as the internal standard. Different scanning rates were used to check the reversibility of the system: (a) 0.05 V s<sup>-1</sup>; (b) 0.10 V s<sup>-1</sup>; (c) 0.20 V s<sup>-1</sup>; (d) 0.30 V s<sup>-1</sup>; (e) 0.40 V s<sup>-1</sup>; (f) 0.50 V s<sup>-1</sup>.

ferrocenyl subunit while the irreversible oxidation peak is attributed to the oxidation of the pyrenyl subunit. Different scanning rates were used to check the complete electrochemical reversibility of the Fe<sup>II</sup>/Fe<sup>III</sup> redox couple of dyad **2** at potentials lower than +1.0 V (see ESI†).

The UV–visible spectrum of dyad **2** in acetonitrile shows a broad and structured absorption band in the visible range between 320 and 430 nm with a main absorption maximum centred at 382 nm, which is ascribable to the pyrenyl chromophore<sup>12</sup> (Fig. 2, inset). The remaining absorption bands observed in the UV region are due to the other chromophores of neutral **2**.

Addition of a chemical oxidant, like copper(II) triflate (trifluoromethanesulfonate)<sup>13</sup> to an acetonitrile solution of **2** caused notable changes in the absorption spectrum upon addition of an increasing amount of Cu<sup>2+</sup> ion. A marked bathochromic shift in its λ<sub>max</sub> was apparent. The absorption maximum at 382 nm in the visible region decreased in intensity and was accompanied by the formation of a new weak absorption band at 457 nm (Δλ<sub>max</sub> = 75 nm). The latter band is characteristic of oxidized ferrocenyl derivatives and is assigned to a Cp→Fe<sup>III</sup> ligand-to-metal charge transfer transition.<sup>14</sup>

As expected, neutral dyad **2** shows a weak fluorescence. The emission spectrum in acetonitrile displays typical monomer



**Fig. 2** Emission spectra (acetonitrile–water 7 : 3; *c* = 2.5 × 10<sup>-5</sup> M) and absorption spectra (acetonitrile; *c* = 2.5 × 10<sup>-5</sup> M) of **2** in the presence of different amounts of copper(II) triflate. Arrows indicate bands that increase during the experiment.

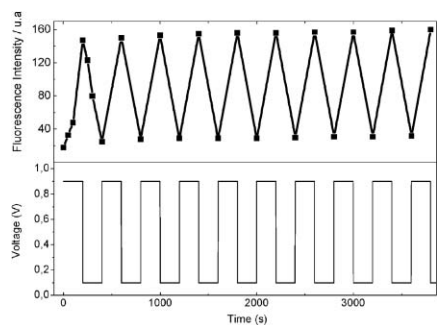
emission bands at 385, 405 and 425 nm (λ<sub>exc</sub> = 350 nm) with well-resolved vibronic features,<sup>15</sup> with rather low quantum yield (Φ = 0.0035)<sup>16</sup> that is similar to those exhibited by pyrene derivatives in which the fluorescence emission is quenched.<sup>17</sup> However, the addition of copper(II) triflate to an acetonitrile solution of **2** yields an evident enhancement of fluorescence emission (see ESI†).

Thus, the fluorescence intensity grew with increasing amounts of Cu(II) ions added to the solution and an intensity maximum is reached at [2]/[Cu<sup>2+</sup>] = 1 with a quantum yield of Φ = 0.0174 that represents a 5-fold increase compared to that of neutral **2**. The emission spectrum of dyad **2** in acetonitrile–water (7 : 3) (Fig. 2), also shows weak fluorescence with two emission bands at 385 and 405 nm (monomer emission) with a rather low quantum yield (Φ = 0.0056). However, addition of only small amounts of Cu<sup>2+</sup> to the solution induced a dramatic increase of the excimer emission band at 451 nm. The final fluorescence enhancement factor (FEF) was 700, the ratio I<sub>E</sub>/I<sub>M</sub> = 1.3 and the quantum yield was 10-fold (Φ = 0.059).

Such interesting results may be explained by quenching of the fluorescence of the pyrene subunit in the neutral dyad **2** by the ferrocene subunit. Thus, only a weak emission band is observed. Quenching by the ferrocene subunit may occur *via* either electron transfer or energy transfer from the ferrocenyl group that acts as an electron donor, to the excited state of the pyrenyl group, acting as an electron acceptor unit.<sup>17</sup> After oxidation of neutral dyad **2**, the electron-donating ability of the ferrocene subunit is reduced and, as a result, the electron transfer is arrested leading to a fluorescence enhancement. Now, the spectral overlap between the absorption spectrum of the ferrocinium unit and the fluorescent spectrum of the pyrene unit is small. Consequently, the resonance energy transfer from the excited state of pyrene to the ferrocinium unit cannot take place efficiently.

As the ferrocene/ferrocinium pair transformation in **2** can be reversibly carried out, the possibility of obtaining a redox–fluorescence switch based on dyad **2** was opened. In order to explore this possibility, spectroelectrochemical studies were performed.<sup>18</sup>

Applying a high voltage potential step of +0.9 V (*vs.* Ag/AgCl) to an acetonitrile solution of dyad **2**, containing *n*-Bu<sub>4</sub>NPF<sub>6</sub> 0.1 M as the supporting electrolyte, for 200 s, led to a fast oxidation of the neutral species of **2** into the pyrene–ferrocinium species **2**<sup>+</sup>, and as expected to a fast enhancement of the fluorescence emission. Interestingly, a subsequent application of a reduction potential for 200 s of +0.1 V (*vs.* Ag/AgCl) to the same solution resulted in a fast decrease of the fluorescence intensity of the solution. After the electrochemical reduction was completed, the initial low fluorescence intensity of the solution (before applying an oxidation potential) was completely recovered in a short time. Such a fluorescence change can be understood as follows: by reference to the cyclic voltammogram of dyad **2**, the ferrocinium subunit generated during the oxidation process is reduced to the neutral ferrocene by applying a potential of +0.1 V. Consequently, the electron transfer reaction from the ferrocene subunit to the pyrene unit occurs efficiently again, leading to a decrease in fluorescence. Oxidation of dyad **2** and its subsequent reduction were carried out over several cycles in a chronoamperometric experiment (Fig. 3). The fluorescence intensity was recovered after each step and found to be rapidly and fully recovered on completion of the step; thus,



**Fig. 3** Stepwise oxidation and reduction cycles carried out in acetonitrile with dyad **2** ( $c = 10^{-4}$  M) by chronoamperometric analysis, which uses fixed potentials at +0.9 V (for oxidation) and +0.1 V (for reduction) changed every 200 s, following the changes by the evolution of the fluorescence intensity at 385 nm ( $\lambda_{\text{exc}} = 350$  nm).

demonstrating the reversibility of the switching process. As a result, a fast and robust redox–fluorescence switch can be established on the basis of dyad **2** by taking advantage of the properties of the ferrocene electron donor and the pyrene as a fluorescent read-out unit.

In summary, the synthesis, and spectroscopic and spectroelectrochemical studies of a novel, simple, robust and fast redox–fluorescent molecular switch based on a ferrocene–pyrene disubstituted azine are presented. Depending of the oxidation state of the ferrocene, the emission fluorescence intensity of this bistable dyad in solution can be reversibly modulated. Such behaviour can be attributed to the properties of the redox-active ferrocene unit linked to the pyrene acceptor unit which fluoresces efficiently.

This work was supported by the Dirección General de Investigación (Spain) (projects MAT2003-04699 and CTQ2004-02201), Generalitat de Catalunya (2005 SGR-00591). R.M. and I.R. are grateful to Ministerio Educación y Ciencia for a predoctoral grant and a “Juan de la Cierva” contract, respectively.

## Notes and references

† Relevant data of compound **2**: mp: 168–170 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.30 (s, 5H), 4.54 (t, 2H,  $J = 1.80$  Hz), 4.82 (t, 2H,  $J = 1.80$  Hz), 8.04 (t, 1H,  $J = 7.52$  Hz), 8.09 (d, 1H,  $J = 8.71$  Hz), 8.16 (d, 1H,  $J = 9.02$  Hz), 8.21–8.26 (m, 4H), 8.72 (d, 1H,  $J = 8.10$  Hz), 8.78 (s, 1H), 8.90 (d, 1H,  $J = 9.32$  Hz), 9.66 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  68.99 (2  $\times$  CH, Cp), 69.50 (5  $\times$  CH, Cp), 71.33 (2  $\times$  CH, Cp), 77.83 (q, Cp), 122.83 (CH), 124.64 (q), 125 (q), 125.06 (CH), 125.77 (CH), 125.90 (CH), 125.97 (CH), 126.21 (CH), 127.07 (q), 127.49 (CH), 128.70 (CH), 128.73 (CH), 130.28 (q), 130.67 (q), 131.30 (q), 133.09 (q), 158.78 (CH=N), 163.84 (CH=N). EIMS (70 eV)  $m/z$  (%): 440 ( $\text{M}^+$ , 72), 375 (18), 228 (36), 227 (100), 211 (27), 121 (49), 56 (15); found: C: 76.52; H: 4.36; N: 6.48. Calc. for  $\text{C}_{28}\text{H}_{20}\text{N}_2\text{Fe}$ : C, 76.38; H, 4.58; N, 6.36%.

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- Excited-state quenching by energy transfer requires good overlap between the emission spectrum of the excited molecule and the absorption spectrum of the quencher. In fact, the absorption band of ferrocene overlaps with the pyrene emission band, making energy transfer a favorable process. See: D. Albagli, G. C. Bazan, R. R. Schrock and M. S. Wrighton, *J. Phys. Chem.*, 1993, **97**, 10211.
- Spectroelectrochemical experiments were performed in a quartz cell. A thin platinum wire was used as the working electrode, while an Ag wire acted as the reference electrode. A 0.1 M  $n\text{-Bu}_4\text{NPF}_6$  acetonitrile solution was employed as the solvent and the supporting electrolyte respectively. The fluorescence spectra were recorded with a Varian spectrophotometer (model Cary Elipse). The potential was applied with a potentiostat Galvanostat 263 A of EG&PAR.
- In the case that the fluorescence emission is not activated and deactivated every 200 s but only activated once by the oxidation of the ferrocene, the fluorescence intensity of the solution after the first fast increase keeps increasing gradually with the time (see Figure S3†). In this case the resulting ferricinium species behaves as an electron acceptor, and a reverse electron transfer from the pyrene to the ferricinium unit should not be ruled out as a potential relaxation path of the excited pyrenyl\* subunit (see: S. Leroy-Lhez, J. Baffreau, L. Perrin, E. Levillain, M. Allain, M. J. Blesa and P. Hudhomme, *J. Org. Chem.*, 2005, **70**, 6313). Such a kinetic process should be less efficient because the fluorescence emission of the pyrene subunit is slowly restored.