A Simple and Robust Reversible Redox-Fluorescence Molecular Switch Based on a 1,4-Disubstituted Azine with Ferrocene and Pyrene units.

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Preparation of 1-pyrenecarboxaldehyde (diethoxyphosphinyl) hydrazone 1. - To a mixture of diethyl phosphorohydrazidate1 (0.183 g, 1.08 mmol) and anhydrous Na2SO4 (20 g) in dry CH2Cl2 (25 ml), 1-pyrenecarboxaldehyde (0.250 g, 1.08 mmol) was added dropwise. The resulting solution was stirred at room temperature for 6 h and then filtered. From the filtrate the solvent was removed under vacuum to give the corresponding diethoxyphosphinyl hydrazone in almost quantitative yield, as a coloured oil, which was used in the next step, without further purification. 1H NMR (CDCl3): δ 1.36 (t, 6H, J = 7.05 Hz), 4.28-4.36 (m, 4H), 7.61 (d, 1H, 2JH-P = 27.40 Hz), 8.03-8.12 (m, 3H), 8.15-8.22 (m, 4H), 8.46 (d, 1H, J = 8.07 Hz), 8.67 (d, 1H, J = 9.26 Hz), 8.77 (s, 1H). 13C NMR (CDCl3): δ 16.29 (d, 2xCH3, J = 13.40 Hz), 63.64 (d, 2xCH2O, J = 21.84 Hz), 82.46 (CH), 124.68 (q), 124.92 (q), 124.99 (CH), 125.05 (CH), 125.49 (CH), 125.81 (CH), 126.17 (CH), 126.89 (q), 127.42 (CH), 128.18 (CH), 128.48 (CH), 128.64 (q), 130.63 (q), 131.34 (q), 132.08 (q), 143.37 (d, CH=N, J = 73.60 Hz). EIMS, m/z (%): 380 (M+, 22), 227 (100).

Preparation of 2,3-diaza-1-ferrocenyl-4-pyrenyl-1,3-butadiene 2. - To a solution of 1 (0.410 g, 1.08 mmol) in dry THF (20 ml), at –78°C and under nitrogen atmosphere, n-butyllithium 1.6 M in hexane (0.70 ml) was dropped. Then, a solution of ferrocenecarboxaldehyde (0.231 g, 1.08 mmol) in dry THF (10 ml) was added dropwise and the mixture was stirred for 30 min. The reaction mixture was allowed to reach the room temperature and then it was stirred overnight. The solvent was evaporated under reduced pressure and the resulting solid was slurried with diethyl ether (25 ml) to give 2 as a crude product which was recrystallized from dichloromethane/diethyl ether (1/10). Yield: 60%. Mp: 168-170°C.

1 A. Zwierzak, A. Sulewska, Synthesis, 1976, 835.
**Figure S1.** Cyclic Voltammogram of 2 in acetonitrile using nBu$_4$NPF$_6$ 0.1M, as supporting electrolyte, AgCl/Ag, as the reference electrode, and platinium wires, as counter and working electrodes at 150mV/s scanning until 2.0V to observe the irreversible oxidation of the pyrene subunit

**Figure S2.** Emission spectra of 2 in acetonitrile (2.5x10$^{-5}$M) in the presence of different amounts of copper (II) triflate. Arrows indicate bands that increase or decrease during the experiment.
Figure S3. (a) Fluorescence emission spectra of 2 recorded after the addition of one equivalent of Cu(ClO₄)₂. Spectra were recorded at the beginning every hour until 28 hours. (b) Evolution of the fluorescence intensity of 2 versus time monitored at 385 nm (c = 1.10⁻⁵M in AcCN, λₜ}catch=350nm).