

# Magneto-optical Molecular Device: Interplay of Spin Crossover, Luminescence, Photomagnetism and Photochromism.

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Dedication ((optional))

**Abstract:** A *bis*-pyrazolylpyridyl ligand, L, containing a central photochromic dithienylethene spacer predictably forms a ferrous [Fe<sub>2</sub>L<sub>3</sub>]<sup>4+</sup> helicate exhibiting spin crossover (SCO). In solution, the compound [Fe<sub>2</sub>L<sub>3</sub>](ClO<sub>4</sub>)<sub>4</sub> (**1**) preserves the magnetic properties and is fluorescent. The structure of **1** is photo-switchable following the reversible ring closure/opening of the central dithienylethene *via* irradiation with UV/visible light. This photo-isomerization switches on and off some emission bands of **1** and provides a means of externally manipulating the magnetic properties of the assembly.

The goal of nanoscience is to implement technological applications with nanodevices made of single-molecule components with specific functionalities.<sup>[1-8]</sup> In this context, the area of spintronics is bound to facilitate a technological revolution.<sup>[9-10]</sup> This field aims at controlling the electronic spin and the charge within functional devices, which will necessitate molecular switches.<sup>[11-15]</sup> The latter are molecules that can reversibly toggle between two (or more) states by means of external stimuli, with concomitant changes to relevant physicochemical properties.<sup>[16-17]</sup> A variety of mechanisms have been used as triggers, such as the redox potential,<sup>[18-22]</sup> the pH,<sup>[22-25]</sup> electromagnetic radiation,<sup>[11, 13, 25-29]</sup> or the temperature.<sup>[13, 29-30]</sup> Of particular interest is to exploit the versatility of multifunctional molecular switches. These can be molecules responsive to more than one external stimulus, such as optical and thermal,<sup>[29, 31]</sup> pressure and thermal,<sup>[32]</sup> pH and light irradiation,<sup>[33]</sup> etc. However, multitasking is most commonly manifested with the display or switching of more than one property as a response to one trigger. Examples of the latter are photochromic molecules, which modify

reversibly their structure through the action of light, leading in turn to (reversible) changes in behavior from a variety of points of view; electrical, optical, chemical, etc.<sup>[34]</sup> One of the most promising switching molecular materials are these exhibiting spin crossover (SCO).<sup>[30, 35]</sup> This property arises usually from transition metal ions exhibiting two most stable electronic configurations, and thus, magnetic states, very close in energy, conferring very different magnetic, spectroscopic or electrical properties to the carrier material, and often distinct structural features.<sup>[36-37]</sup> The perturbations that switch these materials between both states are changes to the temperature, the pressure or the chemical environment. It can be done also by light irradiation at low temperature, leading to light induced excited spin state trapping (LIESST).<sup>[31, 38]</sup> By far, the most studied SCO metal ion is Fe(II). It interconverts between the *S* = 0 (low spin, LS) and the *S* = 2 (high spin, HS) spin states, while the transition is accompanied by dramatic changes to the optical properties and to changes in bond distances to the metal center.<sup>[39-40]</sup> The effect of the SCO on spectroscopic properties translates typically into dramatically different electronic absorption profiles<sup>[41-42]</sup> or distinct Raman<sup>[43-46]</sup> or Mössbauer<sup>[47]</sup> spectra. Multifunctionality in such systems can be achieved by incorporating an additional optical probe into the molecular switch. For example, the luminescence of chromophores connected to the spin active species have served to read indirectly the spin state of SCO systems.<sup>[48-50]</sup> At the other end of multifunctionality, synthetic chemistry has provided SCO coordination complexes with photochromic units that switch their structure with light irradiation, and with it, the magnetic response of the carrier molecule. In some cases, the photochromic styrylpyridine moiety has been exploited, leading only to unidirectional transformations.<sup>[51-52]</sup> However, the switching has been carried out reversibly by incorporating a diarylethene unit to an Fe(II) complex. This has been achieved in the solid state<sup>[53]</sup> and in solution,<sup>[54-55]</sup> and significantly, at room temperature. We report here a SCO photo-switchable dinuclear coordination complex of Fe(II) with a higher degree of sophistication; it engages a photochromic ligand conceived to confer fluorescence. The latter can be turned on and off with light irradiation, while the spin state is tunable thermally, through the LIESST effect at low temperature or by room-temperature photo-isomerization. To engineer this device, we have exploited the notions to prepare dinuclear Fe(II) supramolecular helicates with SCO behavior.<sup>[56-58]</sup> Previous reports have shown that such architectures can be made with the ability to encapsulate guests and thereby modify the magnetic properties.<sup>[59-60]</sup> We have now incorporated into one such functional ligand a dithienylethene photochromic switch (Scheme 1). This unit belongs to the family of diarylethenes, which constitute excellent fluorophores and present very attractive switching properties;<sup>[4]</sup> a) they are amenable to

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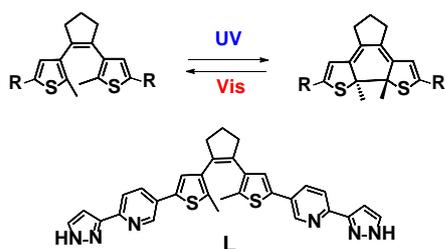
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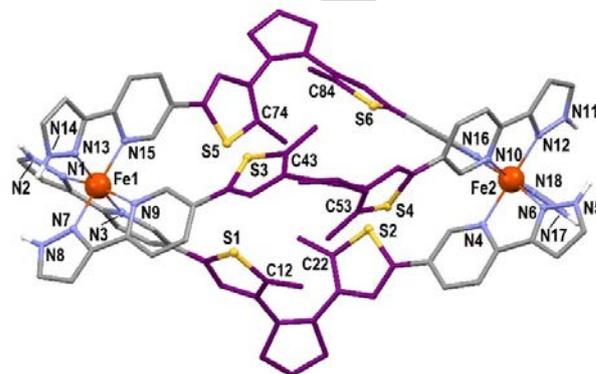
extensive chemical functionalization, *b*) they switch reversibly with light of different quality for each direction, following a closing/opening of a carbon atoms ring, *c*) both isomers are usually thermally stable, *d*) the photochromic process is highly fatigue resistant and fast. Thus, the ligand 1,2-bis-(5-(2-(pyrazol-3-yl)-pyridin-5-yl)-2-methyl-thiophen-3-yl)-cyclopentene (L, Scheme 1), was prepared first by attaching two acetylpyridine groups to a bis-chloro substituted dithiophenylethene moiety, following a Suzuki crosscoupling.<sup>[61]</sup> The structure of the resulting bis-acetyl molecule was determined (ML, Fig. S1, Table S1). This intermediate was converted into L, first by coupling the ketone distal groups to *N,N'*-dimethylformamide dimethylacetal, followed by the ring closure of both ends using N<sub>2</sub>H<sub>4</sub> (SI, Fig.S2).



**Scheme 1.** Reversible photocyclisation of a dithienylethene (top) and structure of L (bottom).

The electronic absorption spectrum of L is dominated by three bands at 202, 295 and 335 nm (Fig. S3), attributed to  $\pi \cdots \pi^*$  transitions. The latter two peaks merge at 307 nm upon irradiation with UV light ( $\lambda < 425$  nm) while a broad and intense band centered at 550 nm, responsible for the development of a dark purple color, grows rapidly. This is the result of the photocyclization of the dithienylethene unit, which is reversed by irradiating with visible light ( $\lambda > 430$  nm).<sup>[4]</sup> All the absorption lines recorded during these conversions cross at isosbestic points. These experiments reveal that L is reversibly photoconvertible. Ligand L reacts with Fe(CIO<sub>4</sub>)<sub>2</sub> in either methanol or acetone to produce orange crystals of the supramolecular helicate [Fe<sub>2</sub>L<sub>3</sub>](CIO<sub>4</sub>)<sub>4</sub> (**1**) by diffusion of toluene. The structures from both, methanol (**1a**) and acetone (**1b**) were determined, revealing two solvatomorphs of the same compound (Tables S1-S3). Disordered solvent areas and their partial loss/exchange with air moist explain the systematic poor diffraction of crystals of **1a/1b**, especially for the former. In both cases, a diffuse solvent area was analyzed and taken into account with PLATON/SQUEEZE (see SI).<sup>[62]</sup> As a result, we refrain from analyzing the structural data in too much details, in particular with respect to intermolecular interactions, and describe the molecular structure of **1b**. It is found in the monoclinic space group C2/c, exhibiting in the asymmetric moiety one formula unit of the complex salt together with five lattice molecules of acetone, two of water and two of toluene. Of the latter, one was only resolved as diffuse electron density (see SI). The unit cell encloses eight such ensembles. The complex cation [Fe<sub>2</sub>L<sub>3</sub>]<sup>4+</sup> features two distorted octahedral Fe(II) anions, each chelated by three pyrazolylpyridyl moieties from three ligands, L, that also link both metals, forming a triple-stranded

helicate (Fig. 1). The ensemble exhibits three helical domains; of these, the chirality of the metals is opposite to that featured by the twisting of the central dithienylethene units. The crystals contain in equal amounts both possible enantiomers, with  $\Delta\Delta\Delta$  and  $\Lambda\Lambda\Lambda$  configurations respectively, and are therefore racemic. At 100K the average Fe–N bond distances are 1.97(2) and 1.97(3) Å, for Fe1 and Fe2, respectively, showing that both ions are in the LS state at this temperature (see below).

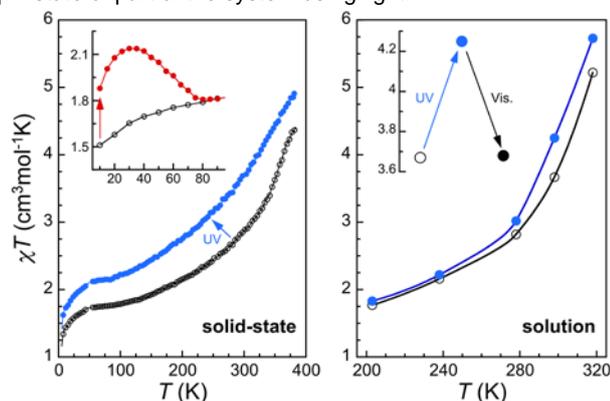


**Figure 1.** Structure of the cation [Fe<sub>2</sub>L<sub>3</sub>]<sup>4+</sup> of **1b**, with heteroatoms and selected carbon atoms labelled. Only H atoms from the N–H groups are shown (in white)

The configuration of the methyl groups in the dithienylethene units fulfill the structural requirement to expect their photocyclization,<sup>[63]</sup> *i.e.* they are antiparallel with their carrier carbon atoms within each unit separated by  $<4$  Å (3.464, 3.454 and 3.442 Å, respectively). Irradiation of crystals of **1a** with UV light ( $\lambda < 425$  nm) led immediately to a color change from orange to dark brown (Fig. S4). The reverse process was not observed even after long exposures to visible light. Possibly, the accommodation within the lattice of modifications associated with the ring closure prevents the structural changes necessary for the re-opening the cycle, as noticed before in some solids.<sup>[64]</sup> The molecules in **1a** are only weakly connected within the lattice; only pairs of C–H $\cdots$  $\pi$  interactions were detected (Fig. S5). Otherwise, the packing is ensured by interactions involving solvent molecules and anions. Solid-state magnetic susceptibility measurements on **1a** yield a reproducible  $\chi T$  vs.  $T$  plot ( $\chi$  is the molar paramagnetic susceptibility, Fig 2 left) where the  $\chi T$  value at 300K is 2.83 cm<sup>3</sup>Kmol<sup>-1</sup>, indicating that near half of the Fe(II) centers lie in the HS state (47% if  $g = 2$ ). Upon cooling, a gradual decrease occurs before reaching a plateau at near 1.7 cm<sup>3</sup>Kmol<sup>-1</sup> (29% of HS Fe(II)) below 90 K. A sharper decrease is then observed below 40 K due to the zero-field splitting (ZFS) of the residual Fe(II) centers in the HS state. The plot recorded on increasing the temperature is superimposable to the cooling branch (Fig. S6) and continues to raise beyond room temperature to reach a value of 4.41 cm<sup>3</sup>Kmol<sup>-1</sup> at 385 K (74% of HS Fe(II)) where it is still growing. *Ex situ* irradiation with UV light at room temperature affects significantly this gradual and incomplete SCO; while the overall shape of the  $\chi T$  vs.  $T$  plot is conserved, it causes an increase of the residual HS fraction at low temperature and lowers the temperature of the transition. Consistent with the above described color changes upon irradiation, the effects of UV light on the

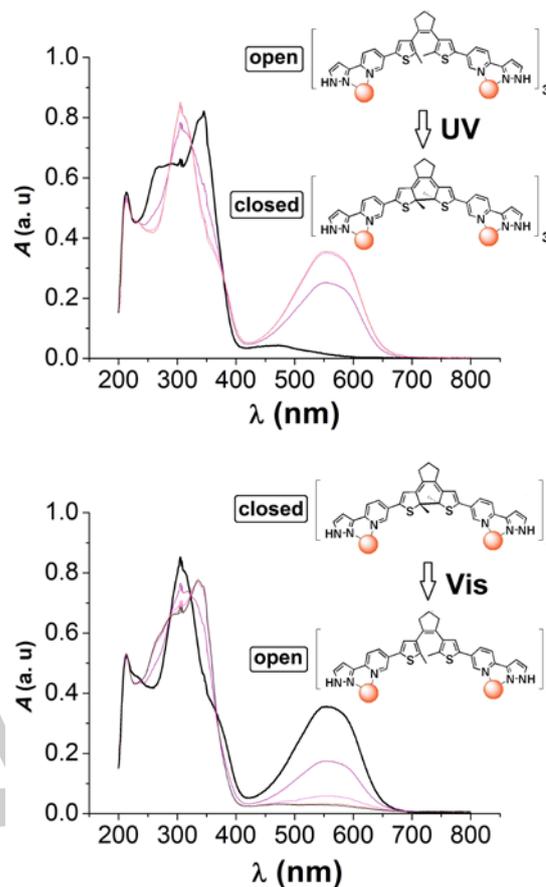
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magnetism are not reversible in the solid; continued irradiation with visible light causes no changes to the  $\chi T$  vs  $T$  curve (Fig. S6). Fresh crystals of **1a** were irradiated at 10 K with either red ( $\lambda = 800$ -900 nm), green ( $\lambda = 500$ -650 nm) or white ( $\lambda = 400$ -900 nm) light. In all cases, an increase of the susceptibility was observed, yielding  $\chi T$  of at most  $1.9 \text{ cm}^3\text{Kmol}^{-1}$  at the stationary state, thus indicative of partial photo-excitation from the LS to the HS state through the LIESST effect (Fig. 2, inset). Because similar stationary states are reached using either a small amount of polycrystalline powder or a thin pellet (Fig. S7), the limited efficiency of the LIESST effect in **1a** is, for the most part, likely due to fast relaxation of the photo-induced metastable HS state. Indeed, once in obscurity, the relaxation is already active at 10 K and is complete at ca. 80 K. The ZFS of the HS centers explains the increase of  $\chi T$  that first takes place upon heating, up to a maximum of  $2.14 \text{ cm}^3\text{Kmol}^{-1}$  at 30 K. Thus, approximately 7 % of all the Fe(II) centers of **1a** are converted to a metastable HS state by this mechanism, as an alternative method of manipulating the spin state of part of the system using light.



**Figure 2.** Plots of  $\chi T$  vs  $T$  per mole of  $[\text{Fe}_2\text{L}_3](\text{ClO}_4)_4$  (**1a**) in the solid-state (left) and in solution (right), before (empty black symbols) and after irradiation with UV light (full blue symbols,  $\lambda < 425 \text{ nm}$ ). The insets show the partial LIESST effect upon irradiation at 10 K with red light ( $800 \text{ nm} < \lambda < 900 \text{ nm}$ , full red symbols) and the reversible transformation in solution upon irradiation at 298 K with UV light and then with visible light ( $\lambda > 430 \text{ nm}$ , full black symbol).

The photochromic performance of **1** was investigated in solution through UV-Vis spectroscopy. The absorption spectrum of **1** in methanol (Fig. 3) exhibits strong bands at 213, 289 (with a shoulder) and 342 nm attributed to  $\pi$ - $\pi^*$  transitions, and a much weaker band near 470 nm ascribed to a MLCT process. Upon UV irradiation, the 264 and 354 nm bands decrease rapidly and merge into an intense signal at 307 nm, while a very broad band grows around 552 nm, which is linked to a transition within the polyenic moiety contained within the photoconverted dithienylethene unit.<sup>[4]</sup> These changes are accompanied by a color change from light yellow to dark purple. This process can be reversed completely through illumination with visible light. In both directions, the intermediate stages exhibit the same isosbestic points suggesting zero order transitions and the stability of **1** in solution throughout the photo-conversions.



**Figure 3.** Electronic absorption spectrum of **1** –bold line– in  $8 \times 10^{-6} \text{ M}$  methanol solution and its evolution during irradiation with UV light ( $\lambda < 425 \text{ nm}$ ) over 2 min. Bottom: Evolution of the absorption spectrum of the above photo-converted product –bold line– upon irradiation with visible light ( $\lambda > 430 \text{ nm}$ ) over 4 min.

NMR spectroscopy was used to investigate the effect of the reversible photo-switching of **1** in solution on its magnetic properties. The 400MHz  $^1\text{H}$ -NMR spectrum of **1** in methanol (Fig. S8) features ten paramagnetically broadened signals consistent with the idealized symmetry of the  $[\text{Fe}_2\text{L}_3]^{4+}$  helicate ( $D_3$ ). Of these, four are significantly shifted because of their proximity to Fe(II), two are at positions expected for aromatic protons and four are unique aliphatic resonances. Only the peak from N-H is missing, presumably broadened beyond detection because of the proximity to the metal and the fact that it is exchangeable with  $\text{H}_2\text{O}$ . These features confirm the presence of a percentage of HS centres. The modified Evans method<sup>[65-67]</sup> was exploited to determine the value of  $\chi$  of **1** in solution and its temperature dependence between 318 and 203K. It was implemented using a coaxial NMR tube containing a solution of **1** with 1% TMS at the outer tube and the solute with the reference at the insert tube. The difference in chemical shift between both TMS signals is proportional to  $\chi$  (SI). This furnished a  $\chi T$  value at 318 K of  $5.22 \text{ cm}^3\text{Kmol}^{-1}$ , for 87 % of Fe(II) ions in the HS state (if  $g = 2$ ) that decrease down to 30 % (with  $\chi T = 1.77 \text{ cm}^3\text{Kmol}^{-1}$ ) at 203 K, unveiling a process of SCO in solution (Fig. 2, right). This is also

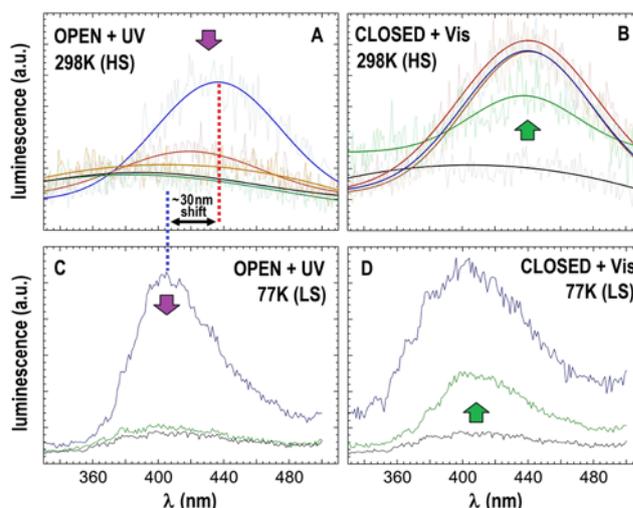
evident from dramatic reductions of the paramagnetic shifts of the various spectral features of **1** upon cooling (Fig. S9).

Irradiation of the solution with UV light causes a reduction of the SCO temperature (Fig. 2), which translates for example into an increase of the HS/LS ratio of nearly 10% of the total Fe centers (if  $g = 2$ ) at room temperature. Remarkably, upon illumination with visible light, the original  $\chi T$  vs  $T$  plot is restored completely (Fig. 2 and S10), consistent with the observations from electronic spectroscopy. These results confirm that the molecular magnetic response of **1** can be reversibly and externally manipulated with light. Remarkably, the SCO in solution is more abrupt than that observed in the solid state. This represents a rare case of anti-cooperative SCO in the solid state, leading to transitions that are more gradual than expected from the Boltzmann equilibrium.<sup>[68-69]</sup> The current one is among the very few examples corroborated by comparison with the behavior in solution.<sup>[70]</sup> As in cooperative phenomena, this occurrence is related to the effect of intermolecular interactions on the distortions related to the SCO. In the first case, these interactions propagate the distortions through the lattice, which are mainly related to volume changes. In anti-cooperative systems, the intermolecular interactions affect distortions that do not propagate, such as changes to the coordination geometry. This is consistent with the lack of strong intermolecular interactions connecting the  $[\text{Fe}_2\text{L}_3]^{4+}$  units.

Some dithienylethene molecules are capable to switch *on* and *off* a luminescence response *via* reversible photocyclization.<sup>[28, 71]</sup> The possible fluorescence of **1** was explored in methanolic solution, using as excitation wavelength the maxima observed on its electronic absorption spectrum (Fig. 3). In all cases, broad fluorescence responses were obtained between 400 and 500 nm. However, it was observed that the excitation near 350 nm affects the state of the photochromic unit itself, thus distorting the function of the switch. Instead, if light of 290 nm is used for the excitation, a broad fluorescence band near 440 nm is generated at room temperature that is almost completely quenched by irradiation of the solution with UV light after 4 min. (Fig. 4). The original fluorescence response is fully restored when the sample is irradiated with visible light. Therefore, the luminescence that follows the excitation of **1** with 290 nm light can be toggled *on* and *off* *via* the photochromism of the assembly. From a different perspective, the cyclization state of this compound may be sensed by examining its fluorescence. This behavior is consistent with the results obtained through absorption and NMR spectroscopy (see above). These experiments were also performed at 77 K. The response was above one order of magnitude more intense than at room temperature, with a much better signal-to-noise ratio (SNR), and was also reversible by using alternatively UV and visible light (Fig. 4). Interestingly, the fluorescence band exhibits upon cooling a hypsochromic shift of more than 30 nm. This shift is not associated to the thermal SCO of **1** since it was also observed on the fluorescence of the ligand L (Fig. S11).

In summary, ligand L was designed to link two Fe(II) ions in form of the molecular triple stranded helicate  $[\text{Fe}_2\text{L}_3]^{4+}$  (cation of **1**), which exhibits SCO in the solid state and in solution. In the solid state, the system can be addressed by irradiation at low temperature through the LIESST effect, resulting in the photogeneration of  $\approx 7\%$  metastable HS Fe(II) centers that relax thermally to the LS upon warming. Irradiation of solid **1** with UV

light produces a sizable change to the magnetic response of the material that is not reversible. In solution, the reversible full photo-conversion of the complex occurs thanks to the photo-cyclable moieties incorporated into L, as can be probed through absorption and  $^1\text{H-NMR}$  spectroscopy. The Evans method unveils the comparatively more abrupt thermal SCO of **1** in solution, a rare case of solid-state anti-cooperativity, and its dependence on the cyclization state, which can be manipulated externally through light irradiation. The fluorescence response of **1** in solution is also reversibly photo-switchable. The functional properties in solution are of molecular origin and therefore, this assembly is a prototype of an externally addressable molecular device for spintronics.



**Figure 4.** Fluorescence band of **1** in methanolic solution, using 264 nm light for the excitation: (A) on a fresh sample at 298 K and upon exposure to UV irradiation, (B) after subsequent exposure to visible light, and (C, D) the same at 77K. Purple and green arrows show the evolution of the spectra upon irradiation with UV and visible light, respectively. Smooth continuous lines of the top panels are fits to guide the eye.

## Acknowledgements

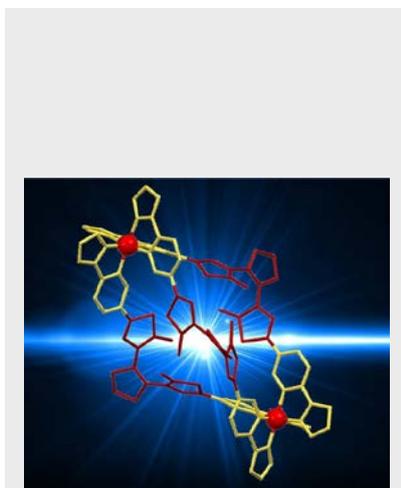
G.A. thanks the Generalitat de Catalunya for the prize ICREA Academia 2008 and 2013 and the ERC for a Starting Grant (258060 FuncMolQIP). The authors thank the Spanish MINECO for grants MAT2014-53961-R (OR), CTQ2015-68370-P (GA) and a Juan de la Cierva Program Fellowship (ME) and the ERC for a Predoctoral (JSU) and Posdoctoral (LB) Fellowship under Grant 258060 FuncMolQIP. This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC0205CH11231.

**Keywords:** dithienylethene • photo-switching • spin crossover • fluorescence • molecular devices

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A spin-crossover molecule incorporates a photoswitchable unit that allows tuning reversibly its magnetic properties and its fluorescent response using light.



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