

Cite this: *Chem. Commun.*, 2011, **47**, 6846–6848

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COMMUNICATION

Complete solid state photoisomerization of bis(dipyrazolylstyrylpyridine)iron(II) to change magnetic properties†

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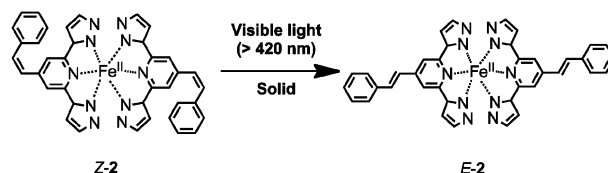
Received 1st April 2011, Accepted 18th April 2011

DOI: 10.1039/c1cc11850a

Iron(II) complexes of *Z*- and *E*-2,6-di(1*H*-pyrazol-1-yl)-4-styrylpyridine (*Z*-2 and *E*-2, respectively) exhibited visible light photoisomerization from *Z*-2 to *E*-2, both in solution and in solid phases. *Z*-2 occupied the high-spin state over the full temperature range examined, whereas *E*-2 displayed a spin crossover phenomenon between 100 K and 300 K.

Photomagnetic effects, which are magnetic effects produced by photoinduction, have attracted attention for the development of light-responsive single molecule devices.¹ The creation of photomagnetic systems that operate in ambient environments requires that photomagnetic effects be accessible at room temperature. Nevertheless, many of these materials exhibit magnetic bistability upon illumination at cryogenic temperatures due to the absence of an activation barrier between the magnetic states.² Bistability may be ameliorated by leveraging the hysteretic properties of these materials³ or by introducing photoisomerizable molecules that exhibit bistability at room temperature.⁴

Iron(II) complexed with 2,6-di(1*H*-pyrazol-1-yl)pyridine exhibits spin crossover (SC) between the electronic high-spin (HS) and low-spin (LS) states.⁵ Coupling this iron(II) complex to a stilbene moiety, which can act as an active photoisomerizable component in solution and solid states,⁶ may produce photomagnetic effects under ambient conditions as a result of the ligand-driven light-induced spin change (LD-LISC) phenomenon, which was first proposed by Zarembowitch *et al.* in 1994⁷ and has been observed mostly in solution⁸ and in thin polymer films.⁹ However, in spite of current great efforts, a quantitative change in magnetic susceptibility before and after photoirradiation in crystalline solid state has not been reported. It should be noted that solid state photoisomerization of the iron styrylpyridine complex was reported by Boillot *et al.*,¹⁰ while the magnetic properties have not been indicated. In the present study of iron(II) complexes with *Z*- or *E*-2,6-di(1*H*-pyrazol-1-yl)-4-styrylpyridine (denoted *Z*-1 or *E*-1, respectively), we investigated the visible



Scheme 1 Photoisomerization of *Z*-2 to *E*-2 by visible light (>420 nm) irradiation. Counter anions are omitted.

light one-way photoisomerization of [Fe(*Z*-1)₂](BF₄)₂ (*Z*-2), both in solid and in solution, and identified significant photomagnetic effects in the solid state (Scheme 1). The novel tridentate ligands *Z*-1 and *E*-1 were synthesized from 2,6-di(1*H*-pyrazol-1-yl)isonicotinaldehyde as the starting material (for details, see the ESI†). The reaction of *Z*-1 with Fe(BF₄)₂·6H₂O in acetone, *Z*-2 was obtained as yellow microcrystals, and following recrystallization from nitromethane/diethyl ether afforded single crystals. Likewise, the reaction of *E*-1 with Fe(BF₄)₂·6H₂O in acetone, followed by recrystallization from propylene carbonate (PC)/ethyl acetate/diethyl ether, afforded single crystals of [Fe(*E*-1)₂](BF₄)₂·2PC (*E*-2·2PC). The complexes were characterized by elemental analysis and X-ray crystallography.

An ORTEP diagram of *Z*-2 is shown in Fig. 1. The torsion angles around the alkenyl moieties, C6–C12–C13–C14 (7.55°) and C25–C31–C32–C33 (−7.73°), assured the *Z*-configurations of the ligands.^{6c} At a low temperature of 90 K, the average Fe–L bond distance (2.170 Å) and the Σ parameter (172.42°), which is the sum of the 12 bite angles around the coordination

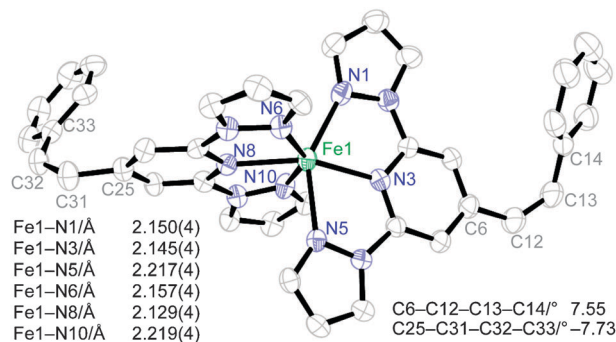


Fig. 1 ORTEP diagram showing 50% probability and the pertinent bonding properties of the cation molecule in *Z*-2 at 90 K. Hydrogen atoms are omitted for clarity.

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† Electronic supplementary information (ESI) available. CCDC 811070–811071. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc11850a

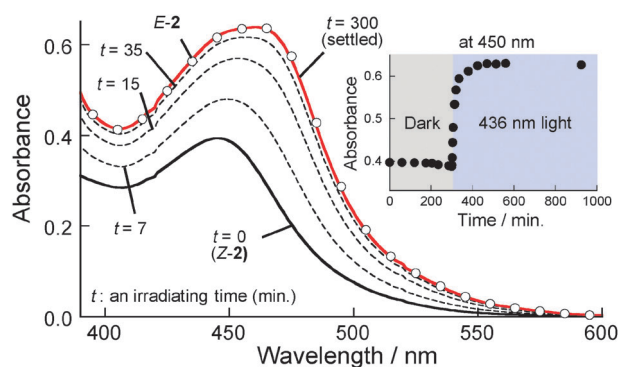


Fig. 2 UV-vis spectral changes of Z-2 in acetone (0.106 mM) upon irradiation with 436 nm light, and the spectrum of E-2 in acetone (circles, 0.106 mM). Inset: time-course changes in absorbance of Z-2 at 450 nm.

sphere, suggested that the iron(II) center was in the HS state.^{5,11} In contrast, the average Fe–L bond distance (1.935 Å) and the Σ parameter (84.64°) for the E-2 complex at 113 K (see the ESI†) suggested that the iron(II) center was in the LS state.^{5,11} The different spin states of the Z-2 and E-2 compounds indicated that the spin state may be tuned *via* a Z-to-E photoisomerization in the alkenyl moieties.

Photoisomerization of Z-2 in acetone upon photoirradiation with 436 nm light, which corresponded to the energy of the metal-to-ligand charge transfer (MLCT) band, was examined by UV-vis spectroscopy (Fig. 2). In this experiment, 1.0 equivalent Z-1, which did not absorb light at this wavelength, was added to the solution to avoid formation of dissociated complexes (see the ESI†). The intensity of the MLCT absorption band was observed to increase upon photoirradiation. The spectral changes equilibrated to a spectrum consistent with that of E-2, indicating a photo-induced Z-to-E one-way isomerization of Z-2. On the other hand, photoirradiation with 436 nm for E-2 in acetone caused no photoreaction. It should be noted that the spectral changes were absent in the dark, confirming that isomerization occurred not by thermal activation, but by photoabsorption.

The one-way isomerization was thought to be derived from the formal reduction of stilbene to stilbazole in the MLCT excited state of Z-2, because electrochemically reduced stilbene¹² and some MLCT-excited ruthenium(II) complexes¹³ have demonstrated the same photoisomerization behaviours. The uniqueness of the one-way photoisomerization behaviours of the iron(II) complex was evident by comparison of its wavelength-dependent photoisomerization with the properties of the ligands and corresponding zinc(II) complexes (see the ESI†).

We found that the visible light one-way photoisomerization of Z-2 was active also in the solid phase. Irradiation of Z-2 in a KBr pellet with 436 nm light produced gradual changes in colour and in the IR spectrum (Fig. 3). A peak at 976 cm⁻¹ in the IR spectrum of Z-2, attributed to a C–H out-of-plane bending mode of the alkenyl moieties,¹⁴ was shifted to 970 cm⁻¹ upon photoirradiation. This energy decrease corresponded to the difference in the peak positions of the non-substituted Z-stilbene (966 cm⁻¹) and the E-stilbene (960 cm⁻¹), suggesting the occurrence of Z-to-E photoisomerization.¹² These changes

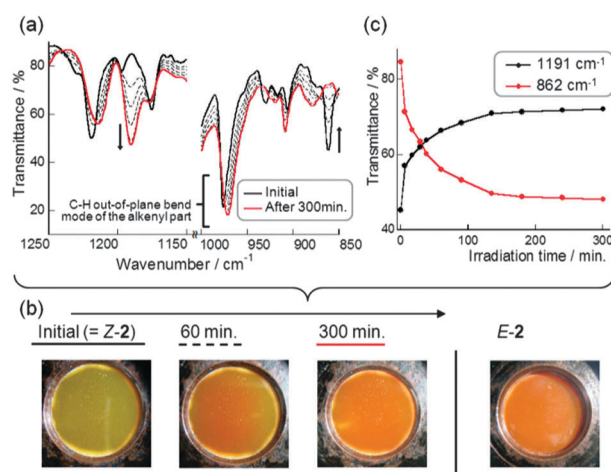


Fig. 3 Time-course changes in (a) the IR spectrum, (b) colour, and (c) transmittance at characteristic peaks of Z-2 pelletized with KBr upon irradiation with 436 nm light.

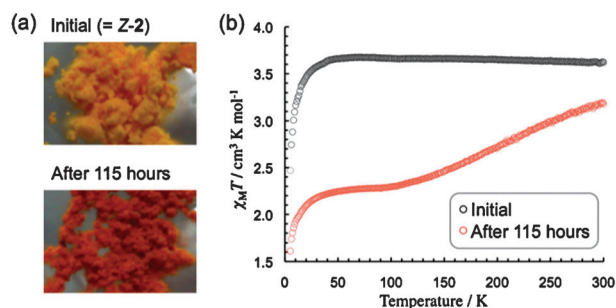


Fig. 4 (a) Photographs and (b) temperature dependence of $\chi_M T$ for Z-2 before and after visible light (>420 nm) irradiation for 115 hours.

equilibrated within 300 min to afford colour and IR spectrum (see the ESI†) that were identical to those of E-2.

Photographs of the bulk microcrystalline compounds and the temperature-dependence of $\chi_M T$ for Z-2 are shown in Fig. 4. Bulk crystalline samples of Z-2 exhibited a $\chi_M T$ of 3.6 cm³ K mol⁻¹ at 300 K, which was typical for iron(II) complexes in the HS state.¹¹ This value did not change significantly as the temperature was decreased to 30 K. Below 30 K, $\chi_M T$ suddenly dropped due to zero-field splitting of the HS iron(II) complex in a distorted octahedral environment. Thus, Z-2 occupied a HS state over the entire temperature range measured.

In contrast, the product of Z-2 obtained after sufficient visible light irradiation (>420 nm) for 115 hours displayed thermal spin crossover. The irradiated sample exhibited a $\chi_M T$ of 3.1 cm³ K mol⁻¹ at 300 K, which was smaller than the value for Z-2 at the same temperature. $\chi_M T$ gradually decreased to 2.2 cm³ K mol⁻¹ at 100 K due to thermal spin crossover. $\chi_M T$ did not change significantly upon cooling to 30 K. Below 30 K, $\chi_M T$ suddenly dropped due to zero-field splitting. IR and UV-vis spectra of the irradiated sample indicate that nearly all of the Z-2 species in the solid state were isomerized (see the ESI†) as well as in the solution or in a KBr pellet. Therefore HS signatures observed in the magnetic susceptibility measurements after photoirradiation shown in Fig. 4 were derived from E-2.

In conclusion, we successfully demonstrated the photochemical conversion of the magnetic properties of **Z-2** using visible light in both solution and solid states. Further efforts toward identifying derivatives of **Z-2** that exhibit more intense photomagnetic conversions at room temperature are now underway in our group.

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