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## Spacer type mediated tunable spin crossover (SCO) characteristics of pyrene decorated 2,6-bis(pyrazol-1-yl)pyridine (bpp) based Fe(II) molecular spintronic modules†

Kuppusamy Senthil Kumar,<sup>a</sup> Ivan Šalitroš,<sup>b</sup> Eufemio Moreno-Pineda<sup>c</sup> and Mario Ruben<sup>†a,c</sup>

A simple “isomer-like” variation of the spacer group in a set of Fe(II) spin crossover (SCO) complexes designed to probe spin state dependence of electrical conductivity in graphene-based molecular spintronic junctions led to the observation of remarkable variations in the thermal- and light-induced magnetic characteristics, paving a simple route for the design of functional SCO complexes with different temperature switching regimes based on a 2,6-bis(pyrazol-1-yl)pyridine ligand skeleton.

In the emerging area of molecular spintronics, individual magnetic molecules are placed and probed in three terminal nano-devices such as spin transistors, wherein the magnetic molecule is connected between the source and drain, and a gate electrode is used to tune the spin state of the molecule through electron injection or electric field, enabling the spin state dependent conductivity measurement at the single-molecule level.<sup>1</sup> Such devices are advantageous for the building of nanoscale memory and switching elements due to their use of both the charge and spin state of an electron.<sup>2</sup> Fe(II) based spin crossover (SCO) complexes are candidates for the realization of spintronic modules due to their bistable nature originating from their reversible inter-conversion between the low spin (LS) and high spin (HS) states.<sup>3</sup> In order to study the spin state dependence of the electrical conductivity modulations of a single SCO complex in a spintronic junction, the SCO complex should be coupled with electrodes through suitable

anchoring groups. In this regard, SCO complexes with thiol,<sup>4</sup> pyridine,<sup>5</sup> thiocyanido<sup>6</sup> and pyrene<sup>7</sup> anchoring groups for the surface functionalization of the noble metal and graphite/graphene electrodes have been reported. The advent of graphene based electrodes<sup>8</sup> for conductance measurement of individual molecules in an electrode–molecule–electrode junction provided an opportunity to form molecular spintronic junctions based on supramolecular  $\pi$ – $\pi$  interactions between the electrode and a SCO molecule tailored with polycyclic aromatic anchoring groups such as pyrene. In this direction, an SCO active Fe(II) complex based on a pyrene decorated 2,6-di(1*H*-pyrazol-1-yl)pyridine (bpp) based ligand has previously been reported.<sup>7</sup> To further build on in this direction and to understand the role of the spacer type in tuning the SCO characteristics, a set of isomerically pyrene decorated ligands of varying spacer type, bpp-COOR (R =  $-(\text{CH}_2)_n$ -pyrene,  $n = 4$ , **L**<sup>1</sup>) and bpp-CH<sub>2</sub>OR (R =  $-\text{OC}(\text{CH}_2)_n$ -pyrene,  $n = 3$ , **L**<sup>2</sup>), have been designed and synthesized as shown in Scheme 1.

This simple variation in the substitution pattern led to remarkable modulation of SCO characteristics of the corresponding pyrene tethered Fe(II) complexes as described below.

The syntheses of ligands **L**<sup>1</sup> and **L**<sup>2</sup> were carried out *via* *N,N*-dicyclohexylcarbodiimide (DCC) coupling reactions between the corresponding pyrene and bpp derivatives as shown in Scheme 2.

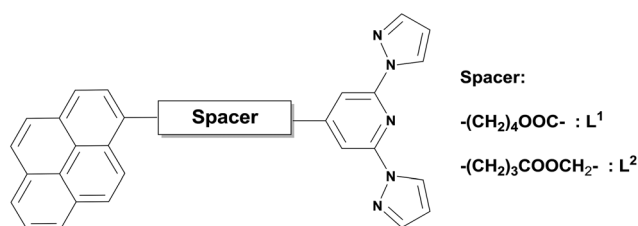
The target Fe(II) complexes [Fe(**L**<sup>x</sup>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, **x** = 1–2 were synthesized by performing complexation reactions in a CH<sub>2</sub>Cl<sub>2</sub>/

<sup>a</sup>Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), CNRS-Université de Strasbourg, 23, rue du Loess, BP 43, 67034 Strasbourg cedex 2, France. E-mail: mario.ruben@kit.edu

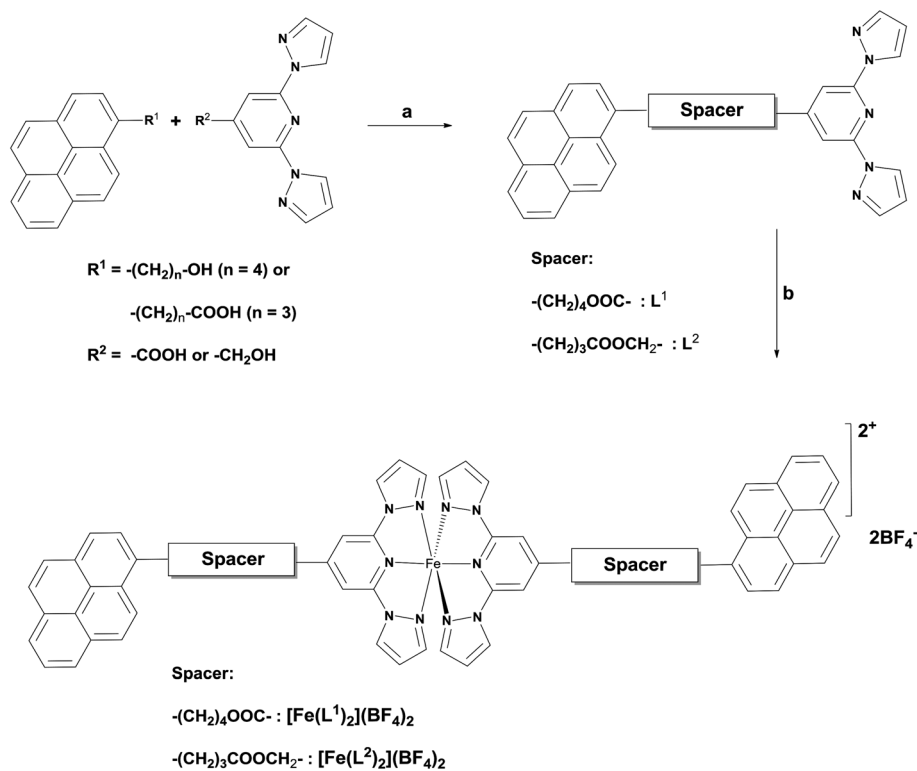
<sup>b</sup>Institute of Inorganic Chemistry, Technology and Materials, Faculty of Chemical and Food Technology, Slovak University of Technology, Bratislava, 81237, Slovak Republic

<sup>c</sup>Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

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Scheme 1 Chemical representation of the structures of ligands **L**<sup>1</sup> and **L**<sup>2</sup>.



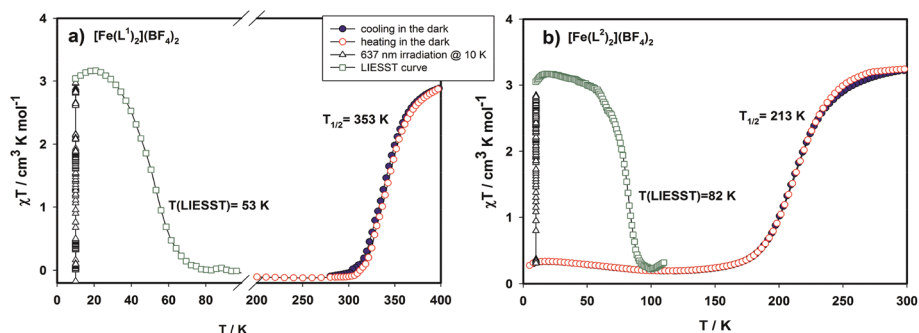
**Scheme 2** Synthetic scheme of pyrene decorated SCO modules. Key: (a) DCC/DMAP, DCM, RT, Ar, 24 h, yield: 69% for  $\text{L}^1$  and 69% for  $\text{L}^2$  and (b)  $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , RT, Ar, 4 h, yield: 49% for  $[\text{Fe}(\text{L}^1)_2](\text{BF}_4)_2$  and 53% for  $[\text{Fe}(\text{L}^2)_2](\text{BF}_4)_2$ .

MeOH solvent mixture; see Schemes 1 and 2 of the ESI† for further details. Our attempts to grow single crystals of the complexes described in this work were not successful. However, the complexes  $[\text{Fe}(\text{L}^1)_2](\text{BF}_4)_2$  and  $[\text{Fe}(\text{L}^2)_2](\text{BF}_4)_2$  are thoroughly characterized employing suitable analytical methods as shown in the ESI†. Single crystals of  $\text{L}^1$  could be obtained upon slow evaporation of a saturated dichloromethane (DCM) solution of it, see Fig. S1 and Table S1† for the structure and related parameters. Electronic absorption (UV-vis) spectral characteristics of the ligands and complexes in solution and the solid state (see the ESI† for experimental details) showed the expected pyrene centred electronic transitions in the UV region as depicted in Fig. S2 and S4.†<sup>7</sup> A broad metal to ligand charge transfer (<sup>1</sup>MLCT) transition centred around *ca.* 464 nm was observed for  $[\text{Fe}(\text{L}^1)_2](\text{BF}_4)_2$  indicating the LS state of the complex in solution. Such a broad feature is not evident in  $[\text{Fe}(\text{L}^2)_2](\text{BF}_4)_2$  and the relatively sharp feature at *ca.* 425 nm is tentatively attributed to the metal centred d-d transitions indicating the HS state of the complex in solution. Photoluminescence (PL) studies of the ligands and complexes in solution showed the pyrene based emission features with a fine structure (*cf.* Fig. S3 and S5†), whereas PL studies of ligands and complexes in the solid state showed broad and featureless emission bands manifestation of strong intermolecular interactions. Note the remarkable quenching of the pyrene centred PL of the Fe(II) complexes relative to their ligand counterparts in the solid state; a detailed analysis of this observation is a subject of future investigation.

Temperature dependent SQUID magnetic studies of the complex  $[\text{Fe}(\text{L}^1)_2](\text{BF}_4)_2$  featured above room temperature SCO characteristics analogous to its parent carboxylic acid substituted bpp complex (bpp-COOH) reported by Abhervé *et al.*<sup>9</sup> The complex showed nearly complete SCO as depicted in Fig. 1a. At 400 K, the  $\chi_m T$  product function reaches *ca.*  $3 \text{ cm}^3 \text{ K mol}^{-1}$  which is comparable to the expected spin only value for the HS Fe(II) mononuclear system ( $3.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ,  $g = 2.0$ ,  $S = 2$ ); a small and reproducible hysteresis loop of *ca.* 2 K accompanied the SCO features, indicating a cooperative nature of the switching mechanism. The observation of SCO with a  $T_{1/2}$  value of 353 K and the LS nature of the  $[\text{Fe}(\text{L}^1)_2](\text{BF}_4)_2$  complex at RT hint the requirement of significant thermal energy to effect SCO and a reasonably symmetric coordination environment around the Fe(II) metal centre,<sup>3k</sup> respectively.

Red light irradiation ( $\lambda = 637 \text{ nm}$ ;  $10 \text{ mW cm}^{-2}$ ) of the  $[\text{Fe}(\text{L}^1)_2](\text{BF}_4)_2$  complex in the low temperature region effected photoinduced SCO, namely the light induced excited spin state trapping (LIESST) effect, with  $T_{(\text{LIESST})} = 53 \text{ K}$  as depicted by the green squares in Fig. 1a. Heating of the metastable HS compound led to a small increase in the  $\chi_m T$  value tentatively attributed to the zero field splitting effect,<sup>10</sup> followed by an abrupt and cooperative thermally induced relaxation back to the LS state as depicted in Fig. 1a (green squares).

Interestingly, the  $[\text{Fe}(\text{L}^2)_2](\text{BF}_4)_2$  complex showed altogether different  $\chi_m T$  vs.  $T$  characteristics in comparison with its  $[\text{Fe}(\text{L}^1)_2](\text{BF}_4)_2$  counterpart. The complex  $[\text{Fe}(\text{L}^2)_2](\text{BF}_4)_2$  showed complete SCO with a  $T_{1/2}$  value of 213 K without apparent



**Fig. 1**  $\chi_m T$  vs.  $T$  and LIESST plots of ground microcrystalline samples of (a)  $[\text{Fe}(\text{L}^1)_2](\text{BF}_4)_2$  and (b)  $[\text{Fe}(\text{L}^2)_2](\text{BF}_4)_2$  complexes. The magnetic data are scan rate independent and similar  $\chi_m T$  vs.  $T$  plots were obtained on repeated scanning.

hysteresis upon repeated cycling from 300 to 5 K and *vice versa* (cf. Fig. 1b); notably, as in the case of  $[\text{Fe}(\text{L}^1)_2](\text{BF}_4)_2$ , its SCO characteristics are more reminiscent of those of the parent hydroxy-methyl substituted bpp complex (bpp-CH<sub>2</sub>OH) extensively studied by Halcrow and co-workers.<sup>11</sup> Compound  $[\text{Fe}(\text{L}^2)_2](\text{BF}_4)_2$  showed quantitative LS  $\rightarrow$  HS photoconversion upon red light irradiation ( $\lambda = 637 \text{ nm}$ ;  $10 \text{ mW cm}^{-2}$ ) with  $T_{\text{LIESST}} = 82 \text{ K}$ . The photomagnetic characteristics of the complexes showed, in agreement with the inverse energy gap law,<sup>12</sup> a decrease of  $T_{\text{LIESST}}$  from 82 K for  $[\text{Fe}(\text{L}^2)_2](\text{BF}_4)_2$  to 53 K for  $[\text{Fe}(\text{L}^1)_2](\text{BF}_4)_2$ .

The remarkable difference in the  $T_{1/2}$  values obtained for complexes  $[\text{Fe}(\text{L}^1)_2](\text{BF}_4)_2$  and  $[\text{Fe}(\text{L}^2)_2](\text{BF}_4)_2$  could be attributed to the varying ligand field strengths of  $\text{L}^1$  and  $\text{L}^2$ . The ligand  $\text{L}^1$  bearing the electron withdrawing carboxylic ester moiety at the 4-position of the pyridine ring of the bpp skeleton exerts a significantly stronger ligand field due to the lowering of the bpp based  $\pi^*$  molecular orbitals and strengthening of Fe-bpp  $\pi$ -back bonding. Such stabilization of the  $\pi^*$  MOs is ruled out for the ligand  $\text{L}^2$  directly substituted with the  $-\text{CH}_2-$  group at the bpp skeleton leading to relatively reduced ligand field strength and hence lowering of the  $T_{1/2}$  value for the complex  $[\text{Fe}(\text{L}^2)_2](\text{BF}_4)_2$  in comparison with  $[\text{Fe}(\text{L}^1)_2](\text{BF}_4)_2$ . These conclusions are in line with the recent report from Halcrow and co-workers detailing the relationship between ligand substituents and spin states in Fe(II) complexes featuring bpp ligand systems substituted with electron-withdrawing and donating groups.<sup>13</sup> This observation and validation of prevailing electronic effects over steric effects in pyrene decorated SCO complexes studied in this work bode well for the realization of single molecule spintronic devices based on functional Fe(II) SCO complexes. The lack of the crystal structure of the complexes in the present communication is justified in view of the single molecule experiments proposed, wherein intramolecular interactions among SCO entities are summarily absent.

In essence, a set of Fe(II)-bpp based complex systems tailored with pyrene anchoring groups are reported to show tunable SCO characteristics. The observation of spacer group mediated modulation of SCO characteristics is quite exciting in terms of design and realization of functional SCO com-

plexes with pre-defined switching properties<sup>3k</sup> based on the same coordinating, bpp in this case, motif/ligand skeleton. The two examples,  $[\text{Fe}(\text{L}^1)_2](\text{BF}_4)_2$  and  $[\text{Fe}(\text{L}^2)_2](\text{BF}_4)_2$ , detailed in this study could enable the temperature programmable supramolecular SCO-graphene hybrids.

## Conflict of interest

There are no conflicts of interest to declare.

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