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**ARTICLE TYPE**

# Spin-crossover complex based on 2,6-bis(pyrazol-1-yl)pyridine (1-bpp) ligand functionalized with a carboxylate group

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**Combining Fe(II) with the carboxylate-functionalized 2,6-bis(pyrazol-1-yl)pyridine (bppCOOH) ligand results in the spin-crossover compound [Fe(bppCOOH)₂](ClO₄)₂ that**
10 **shows an abrupt spin transition with $T_{1/2}$ of ca. 380 K and a $T_{LIESST}$ of 60 K thanks to the presence of a hydrogen-bonded linear network of complexes.**

Spin crossover (SCO) complexes constitute one of the most spectacular examples of molecular bistability. In these systems
15 low-spin (LS) to high-spin (HS) transitions can be triggered through a variety of external stimuli (temperature, pressure or electromagnetic radiation). Besides the interesting fundamental aspects of this phenomenon, it is of growing interest in the area of functional materials due to possible applications in sensors,
20 memories or switching devices.[1] The most studied SCO systems are based on iron(II) complexes that undergo spin crossover between their diamagnetic LS (S = 0) and paramagnetic HS (S = 2) configurations.[2] The change of electronic configuration is accompanied by drastic changes in the optical and magnetic
25 properties of these compounds.[3] Thus, under given experimental conditions, the same material can be found in two states showing different optical and magnetic behaviour. Abrupt transformations with hysteretic behaviour are expected for systems with strong intermolecular interactions.
30 An interesting family of spin crossover compounds are bis-chelated iron(II) complexes of the tridentate ligands of the 2,6-bis(pyrazol-1-yl)pyridine (1-bpp) family, which can be functionalized at its periphery with a variety of substituents.[4] The spin change in these materials is usually very abrupt and takes
35 place with thermal hysteresis close to room temperature.[5] In addition, [Fe(1-bpp)₂]²⁺ salts have the advantage of exhibiting spin-crossover induced by irradiation: Light-Induced Excited Spin State Trapping effect (LIESST)[6] at high temperatures with relatively long lifetimes of the photoinduced metastable states.[7]
40 Substitution in the pyridine ring allows functional groups to be included at the periphery of the [Fe(1-bpp)₂]²⁺ centre without significantly perturbing the iron(II) centre.[8] This approach has afforded spin-crossover compounds with a variety of different pendant functionalities, coordination polymers or complexes for
45 deposition on surfaces.[9-14] In an attempt to improve these results, we have added a carboxylate group to this ligand (bppCOOH, see Scheme 1). The well-known coordination capability of the carboxylate ligand could enable the binding to metal ions or the grafting on metal oxide surfaces, which is an essential step for the
50 preparation of devices based on the spin-crossover phenomenon.[15] As a first step in this direction, herein we present the synthesis, the structural and magnetic characterization of the [Fe^II(bppCOOH)₂](ClO₄)₂ compound.
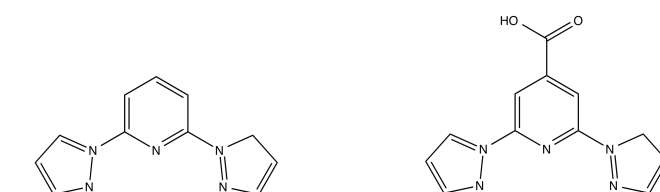


55 Scheme 1. Molecular structure of 1-bpp (left) and bppCOOH (right) ligands.

Slow diffusion of diethyl ether on the mixture solution of Fe(ClO₄)₂·xH₂O and bppCOOH in a 1:2 molar ratio in acetone yielded crystals of compound [Fe(bppCOOH)₂](ClO₄)₂.



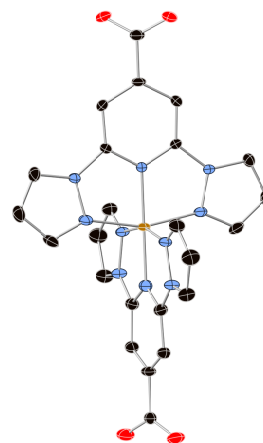60 **Fig.1** X-ray structure of the complex [Fe^II(bppCOOH)₂]²⁺ (C(black), N(blue), O(red) and Fe(yellow)) (hydrogen atoms omitted for clarity).

The structure of the compound was revealed by single crystal X-ray diffraction at 120 K and confirmed by the powder X-ray diffraction pattern (Fig. S1, ESI†). It crystallizes in monoclinic
65 crystal system with centrosymmetric *C*2/c space group. The

asymmetric unit is composed by half $[Fe(bppCOOH)_2]^{2+}$ cation (Fig. 1) and one perchlorate anion. The central iron(II) ion of the complex is coordinated by six nitrogen atoms from two tridentate bppCOOH ligands with a distorted octahedral coordination geometry close to the ideal $D_{2d}$ symmetry associated to a $[Fe(1\text{-}bpp)_2]^{2+}$ centre (*trans*-N(pyridyl)-Fe-N(pyridyl) angle ($\phi$) of 180º and dihedral angle between the least squares planes of the two ligands ($\theta$) of 87º). Fe-N bond lengths are in the range 1.888(4)-1.981(2) Å, typical of LS Fe-N lenghts for this type of ligand.[9] Neighbouring $[Fe(bppCOOH)_2]^{2+}$ cations are linked through hydrogen bonds between the carboxylate groups ($d_{O1\cdots O3}$ = 2.671 Å, Fig. 2), forming a chain that runs along the *b* axis. These chains are linked through intermolecular interactions that involve the pyrazole groups and the carboxylate groups of neighbouring molecules giving rise to layers of complexes on the *bc* plane separated by layers of perchlorate anions (Fig. S2, ESI†). Finally, $[Fe(bppCOOH)_2]^{2+}$ complexes of neighbouring layers present short contacts involving CH groups of the pyrazole rings (Fig. S2, ESI†). The presence of the carboxylate groups causes then a different packing to that found in many salts of $[Fe(1\text{-}bpp)_2]^{2+}$ and derivatives. This is the so called "terpyridine embrace" crystal packing motif, a four-fold layer formed by π-π and edge-to-face C-X···π interactions between pyrazole groups of neighbouring molecules, which leads to a face-to-face configuration of the pyrazole groups with intermolecular distances comprised between 3.4 and 3.6 Å.[16] In contrast to this, in our compound the shortest intermolecular contacts of the pyrazole groups are with the carboxylate oxygen atoms of a complex belonging to a neighbouring chain (Fig. S2, ESI†).
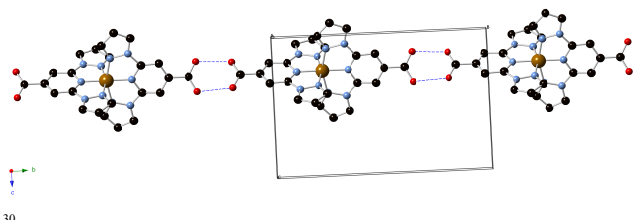


**Fig. 2** Supramolecular 1D hydrogen-bonded chain structure of the complex $[Fe^{II}(bppCOOH)_2](ClO_4)_2$. The counter ions and hydrogen atoms are omitted for clarity.

The temperature dependence of the magnetic susceptibility of the compound was studied in heating and cooling modes. In the temperature range 2-370 K, the product of the molar magnetic susceptibility times the temperature, $\chi_M T$, (Fig. 3) shows a value close to 0, typical of diamagnetic LS state (S=0). Above this temperature, there is a sharp increase to a saturated HS value of 3.3 cm³.K.mol⁻¹, which corresponds to 100 % of Fe$^{II}$ in the HS state (S = 2). This is consistent with the structure solved at 120 K which shows typical distances of LS Fe(II). The same behaviour is observed in heating and cooling modes with a small thermal hysteresis of 3 K ($T_{1/2}\uparrow$ = 384 K and $T_{1/2}\downarrow$ = 381 K, with $T_{1/2}$ = temperature of 50 % HS→LS conversion). The presence of a thermal hysteresis loop clearly demonstrates the existence of a significant level of cooperativity probably due to the presence of intermolecular interactions mediated by the hydrogen-bonds between neighbouring $[Fe(bppCOOH)_2]^{2+}$ complexes. A similar cooperative behaviour has been observed for $[Fe^{II}(\mathbf{L})_2H](ClO_4)_3$·MeOH ($\mathbf{L}$ = 4′-(4‴-pyridyl)-1,2′:6′1″-

bis(pyrazolyl)pyridine), which also contains hydrogen-bonded chains of complexes.[17] Finally, it is worth mentioning that the $T_{1/2}$ of this complex is noticeably higher than that of the unsubstituted 1-bpp Fe(II) complex (260 K)[18] but similar to that of other 1-bpp Fe(II) complexes with substituents in the fourth position of the pyridine ring[5,9,13,19,20] or 2,6-bis(pyrazol-3-yl)pyridine (3-bpp) Fe(II) complexes.[21]
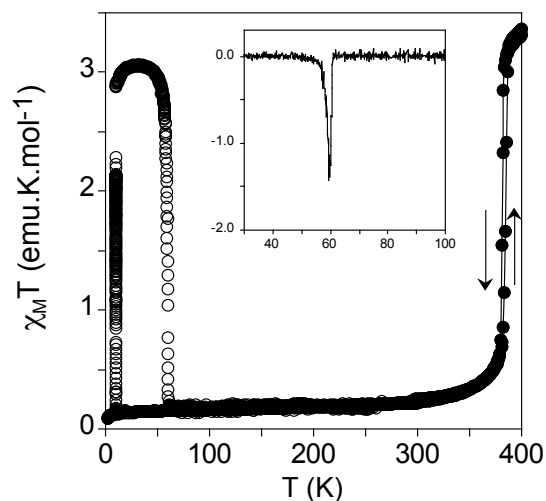


**Fig. 3** Thermal variation of $\chi_M T$ for $[Fe^{II}(bppCOOH)_2](ClO_4)_2$. Full circles: data recorded in the cooling and warming modes without irradiation; empty circles: data recorded after irradiation at 10 K. The inset graph shows the temperature dependence of the first derivative of $\chi_M T$ with respect to the temperature.

The differential scanning calorimetry (DSC) measurement exhibits in the heating mode an endothermic peak centred at 383 K that corresponds to the LS to HS transition. Upon cooling a exothermic peak centred at 381 K is observed assigned to the HS to LS transition, in good agreement with magnetic measurements (Fig. S3 and table S2, ESI†).

For photomagnetic measurements the compound was irradiated with green light ($\lambda$ = 532 nm, optical power 3.4 mW cm⁻²) at 10 K in the SQUID. A drastic increase of the magnetic signal was observed. After about two hours, the irradiation was switched off. The temperature was then increased at a rate of 0.3 K min⁻¹ and the magnetic susceptibility recorded. The $\chi_M T$ value after irradiation is higher than the value recorded in the dark at temperatures below 60 K (see empty circles Fig. 3). The fraction of Fe$^{II}$ photoconverted after irradiation is calculated to be 90 %. The LIESST temperature ($T_{LIESST}$), defined as the minimum of the derivate of $\chi_M T$ with temperature, is 60 K. This value may be compared with those previously obtained for other 1-bpp compounds. Létard et al. have shown that a linear correlation between the thermal spin crossover temperature and $T_{LIESST}$ holds generally for iron (II) complexes. In particular, for the Fe(1-bpp)$_2$ family, the two physical quantities may be related by the formula: $T_{LIESST} = T_0 - 0.3\ T_{1/2}$, with $T_0$ = 150 K.[7b,16] Taking $T_{1/2}$ = 382 K as the mean value of $T_{1/2}\uparrow$ and $T_{1/2}\downarrow$, a $T_{LIESST}$ of 35.4 K is expected (well below the observed one of 60 K). Interestingly,

the other Fe(1-bpp)$_2$ derivative with a high $T_{1/2}$ showing LIESST effect is the [Fe(L)$_2$](BF$_4$)$_2$ complex (L=2,6-bis(4iodopyrazol-1-yl)pyridine) with a reported $T_{1/2} > 360$ K and an experimental $T$(LIESST) of 54 K.[16] Therefore, there is a reasonable agreement between the data of the two compounds. More studies needed to understand the photomagnetic behaviour of this compound (structure and relaxation kinetics of the photoinduced metastable state) are in progress.

In conclusion, we have demonstrated that the functionalization of the 1-bpp ligand with a carboxylate group is a suitable strategy for the preparation of new spin-crossover complexes. The presence of a carboxylate group linked to this spin-crossover complex makes it a useful synthon for the preparation of polynuclear metal complexes, polymers (metal-organic frameworks MOFs) or for the anchoring to metal-oxide surfaces/nanostructures. Preliminary results obtained by us show that some of these goals are possible. Thus, reaction of [Fe(bppCOOH)$_2$]$^{2+}$ complex with Fe$^{3+}$ ions and water molecules gives rise to a nonanuclear cluster formed by an iron trimer coordinated to six partially deprotonated [Fe(bppCOOH)$_2$]$^{2+}$ units. On the other hand, X-ray photoelectron spectroscopy (XPS) measurements of a glass substrate covered with Al$_2$O$_3$ that has been immersed into an acetonitrile solution of [Fe(bppCOOH)$_2$](ClO$_4$)$_2$ confirm the deposition of the complex.

## Notes and references

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† Electronic Supplementary Information (ESI) available: [ESI contains the experimental information about the synthesis and structural and physical characterisation. X ray powder diffraction pattern of Fe$^{II}$(bppCOOH)$_2$](ClO$_4$)$_2$ at 300 K, DSC curves and calculations and structural views of the structure.]. See DOI: 10.1039/b000000x/

‡ CCDC 977453 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data centre via www.ccdc.cam.ac.uk/data_request/cif.

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