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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Extrinsic vs intrinsic luminescence and their interplay with spin crossover in 3D Hofmann-type coordination polymers

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The research of new multifunctional materials, as those undergoing spin crossover (SCO) and luminescent properties, is extremely important in the development of further optical and electronic switching devices. As a new step towards this ambitious aim, the coupling of SCO and fluorescence is presented here following two main strategies: whether the fluorescent agent is integrated as a part of the main structure of a 3D SCO coordination polymer {Fe^{II}(*bpan*)[M^I(CN)₂]₂} (*bpan* = bis(4-pyridyl)anthracene, M^I = Ag (**FebpanAg**), Au (**FebpanAu**)] or is a guest molecule inserted within the cavities of the 3D switchable framework {Fe^{II}(*bpb*)[M^I(CN)₂]₂} pyrene (*bpb* = bis(4-pyridyl)butadiyne, M^I = Ag (**FebpAg·pyr**), Au (**FebpbAu·Pyr**)]. The magnetic, calorimetric, structural, UV-Vis absorption and fluorescent characterizations were performed confirming the occurrence of a SCO-fluorescence interplay in the studied compounds. Moreover, the relevance of the intrinsic or extrinsic nature of the luminescence on the efficiency of the interplay is discussed on the basis of the available information.

Introduction

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The spin crossover (SCO) phenomena, exhaustively studied for Fe^{II} pseudo-octahedral complexes, deals with the reversible, detectable and controllable switching between the paramagnetic high-spin (HS) and the diamagnetic low-spin (LS) electronic configurations.¹⁻³ The HS \leftrightarrow LS transition can be achieved via an external perturbation (i.e. temperature or pressure change, light, an electric field or the adsorption/desorption of analytes) and is accompanied by substantial changes in optical, magnetic and structural properties. Therefore, the SCO event can be monitored by a wide range of different techniques such as magnetic susceptibility measurements, Mössbauer spectroscopy, UV-Vis-NIR absorption spectroscopy, X-ray diffraction, X-ray absorption or heat capacity measurements, among others. Due to their potential applications in electronics and/or opto-electronic devices,^{4,5} these switchable compounds have attracted much attention in the realms of materials physics and chemistry.

Modulation of luminescence by controlling the HS/LS population and/or, conversely, tracking the HS/LS population

during the SCO behavior by measuring the relative intensity of the luminescence signal are appealing features that may facilitate the integration of a SCO system into a real device. Although the approach of combining SCO and luminescence in the same material dates from two decades ago, it has been only recently that this idea has entailed a significant number of studies. They are classified according to the way by which the fluorophore is integrated in the SCO material as: i) doping agent (mechanophysical mixture);6-9 ii) decorative element of coreshell nanoparticles;¹⁰⁻¹⁴ iii) intrinsic part of the SCO structure;¹⁵⁻ ²⁵ and iv) counterion.²⁶ With the exception of reference 25 which deals with a 2D compound, the aforementioned luminescent SCO materials are based on Fe^{II} discrete mononuclear or binuclear complexes and 1D polymeric compounds derived from triazole ligand. In general, all these synthetic strategies successfully resulted in a more or less marked modulation of the luminescence triggered by the spin state change. Regarding the synergic mechanism, the spectral overlap between the luminophore (the sensitizer) and the SCO center (the acceptor) results in an emission-re-absorption process in which the latter acts as a quencher of the luminescence.²⁷ In this case, the mechanism can be easily explained by the superposition of the metal-to-ligand charge transfer (MLCT) band or spin-allowed metal-centered d-d transitions $({}^{1}A_{1} \rightarrow {}^{1}T_{1}, {}^{1}A_{1} \rightarrow {}^{1}T_{2})$ band observed in the LS state and the corresponding region of the emission fluorescent spectrum. However, if the distance between the sensitizer and the acceptor is shorter than 10 nm, as long as there is spectral overlap, non-radiative energy transfer can also be taken place.

The porous functionality offered by most of the 3D SCO Hofmann-type coordination polymers²⁸⁻³¹ represents an interesting platform, yet almost unexplored, to investigate the

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^{f.} Electronic Supplementary Information (ESI) available. CCDC 1965270-1965275. Synthesis and characterization of ligands and coordination polymers, experimental and instrumental details. See DOI: 10.1039/x0xx00000x.

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interplay between SCO and luminescence. As a first example utilizing this approach, we recently reported on the clathration of the pyrene (pyr) fluorophore in the SCO framework {Fe^{II}(*bpben*)[Au^I(CN)₂]₂} (*bpben* = 1,4-bis(4-pyridyl)benzene). This compound displays synergic thermo- and photomodulation of the pyrene guest monomer and host-guest (*bpben*-pyrene) excimer fluorescence signals that reflects the parallel thermo- and photo-induced HS \leftrightarrow LS spin state change in the host framework.³²

These interesting results encouraged us to explore new bifunctional porous $\{Fe^{II}(L)[M^{I}(CN)_{2}]_{2}\}$ (M^I = Ag, Au) 3D frameworks capable to combine SCO and luminescence in a synergistic way. As a new step in this direction, here we report on the synthesis and characterization of two unprecedented series of doubly interpenetrated Hofmann-type coordination polymers formulated as {Fe^{II}(bpb)[M^I(CN)₂]₂}·pyrene (bpb = bis(4-pyridyl)butadiyne, M^I = Ag (**FebpbAg·pyr**), Au (FebpbAu·Pyr)) and $\{Fe^{II}(bpan)[M^{I}(CN)_{2}]_{2}\}$ (bpan = bis(4pyridyl)anthracene, M^I = Ag (FebpanAg), Au (FebpanAu)) (Scheme 1). In the series based on the bpb bridging pillar ligand, luminescence is, similarly as in the aforementioned bpben system, an extrinsic property that stems from the pyrene guest molecule. In contrast, the series based on the anthracenebearing bpan bridging ligand, represents the first example of a 3D Hofmann-type SCO coordination polymer with intrinsic luminescence.



Scheme 1. Structure of the pillar ligands used in the study of synergies between SCO and luminescence in Hofmann-type coordination polymers.

Results and Discussion

Synthesis

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Single crystals of compounds {Fe^{II}(*bpan*)[M^I(CN)₂]₂} (M^I = Ag (**FebpanAg**) or Au (**FebpanAu**)) were obtained using liquid-toliquid diffusions from Fe^{II}(BF₄)₂·6H₂O, KM^I(CN)₂ (M^I = Ag or Au) and *bpan* ligand in methanol-dichloromethane solutions. Same conditions were used for the synthesis of the zinc analogue complex **ZnbpanAu** albeit using Zn^{II}(BF₄)₂·6H₂O instead of the Fe^{II} salt. Similarly, crystals of {Fe^{II}(*bpb*)[M^I(CN)₂]₂}·Pyrene (M^I = Ag (**FebpbAg·pyr**) or Au (**FebpbAu·pyr**)) were synthesized following similar liquid phase diffusion methodology but using saturated methanol solutions of the pyrene fluorophore (see experimental section). Despite considerable efforts to obtain single crystals of the *bpb* Zn^{II} complex, the desired product was not formed.

Elemental analysis and powder X-ray diffraction; (PXRD) measurements confirmed the high puPity ${}^{1}\text{O} \texttt{F} {}^{0} \overline{\texttt{F}} {}^{0} \overline{$ polycrystalline samples (see experimental section and Figure S1, respectively). Comparison of the PXRD spectra also reveals that the Au and Ag counterparts are isostructural in both series of complexes as the more intense peaks are well reproduced from one derivative to the other. Thermogravimetric analysis were for FebpbAg·pyr/FebpbAu·pyr and performed FebpanAg/FebpanAu clathrates confirming the presence of about 1 molecule of pyrene per Fe^{II} ion for the former and the absence of trapped solvent for the latter (Figure S2) in good agreement with the elemental analysis and structural data shown hereafter.

SCO properties

Magnetic and calorimetric studies. The temperature dependence of the χ_M T product (where χ_M is the molar susceptibility and T is the temperature) for compounds FebpanAg/FebpanAu and FebpbAg·pyr/FebpbAu·pyr is depicted in Figure 1. In all cases, at room temperature, the value of $\chi_M T$ is about 3.2 cm³ K mol⁻¹ indicating that practically all the Fe^{II} centers are in the HS state (S = 2). Upon cooling, the $\chi_M T$ value of FebpanAu/FebpanAg remains almost constant until dropping abruptly at $T_{1/2}\downarrow^1 = 242/222$ K ($T_{1/2} =$ temperature at which the population of the HS and LS Fe^{II} ions is equal to 50%) reaching a value ca. 0.70/1.09 cm³ K mol⁻¹ at 205 K. For **FebpanAu**, this χ_M T value remains almost constant upon cooling defining a plateau 65 K wide before undergoing a second small drop at $T_{1/2} \downarrow^2$ = 143 K reaching a value of 0.34 cm³ K mol⁻¹ at 50 K. Considering these variations of χ_M T, ca. 80% and 10% of the Fe^{II} ions are involved in the spin state change in the first and the second step, respectively, whereas about 10% of the Fe^{II} centers remain as residual HS species at low temperature. In the heating mode, the $\chi_M T$ vs T curve for **FebpanAu** does not match $(T_{1/2}\uparrow^2 = 163 \text{ K and } T_{1/2}\uparrow^1 = 252 \text{ K})$ with the cooling mode, thereby defining a hysteresis 10 K (first step) and 20 K (second step) wide.



Figure 1. $\chi_M T$ vs T plots of compounds FebpbAu-pyr, FebpbAg-pyr, FebpanAu and FebpanAg (blue and red plots correspond to the cooling and heating modes, respectively).



Figure 2. Thermal dependence of single crystal absorption spectra during the thermal transition for FebpbAg·pyr (a) and FebpaAau (b), and the corresponding HS fraction (γ_{HS}) vs T curves obtained from the optical density difference at 533 and 800 nm for FebpbAg·pyr and between 550 and 716 nm for FebpaAau (c).

Below 215 K, the magnetic behavior of **FebpanAg** slightly differs from that of the homologous Au derivative. After the first abrupt transition in the cooling mode, the $\chi_M T$ decreases gradually reaching a value of 0.6 cm³ K mol⁻¹ at 50 K. Whereas in the heating mode, a slight increase in the $\chi_M T$ increase is observed above 85 K and stabilized at 130 K ($\Delta \chi_M T = 0.2 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$) defining an asymmetric hysteresis loop. At higher temperatures, an abrupt increase in $\chi_M T$ ($T_{1/2} \uparrow^1 = 228$ K) is observed resulting in a hysteresis loop 6 K wide.

Compound **FebpbAu-pyr** presents a gradual and incomplete spin transition without hysteresis centered at $T_{1/2} \approx 100$ K with a remaining HS fraction of 72 % at 50 K. Unlikely, the analogous compound **FebpbAg-pyr** displays a gradual decrease of the $\chi_{M}T$ value with two steps associated with HS-to-LS transitions involving ca. 31% (from 180 to 150 K) and 15% (from 150 to 125 K) of the Fe^{II} ions, respectively. At 50 K, the value of $\chi_{M}T$ is 1.56 cm³ K mol⁻¹ showing that about 52% of the Fe^{II} ions remain in the HS state. The heating and cooling mode curves do not match thereby defining two hysteresis loops 4 K ($T_{1/2}\downarrow^1 = 156$ K, $T_{1/2}\uparrow^1$ = 160 K) and 7 K ($T_{1/2}\downarrow^2 = 136$ K, $T_{1/2}\uparrow^2 = 143$ K) wide. Repeating cycles on this sample shows very reproducible results (Figure S3).

The thermodynamic parameters associated with the SCO have been obtained from the differential scanning calorimetry (DSC) measurements for all samples except for FebpbAu·pyr since its characteristic $T_{1/2}$ is out the temperature window of our calorimeter. The thermal dependence of the anomalous heat capacity variation (ΔCp) for FebpanAu, FebpanAg and FebpbAg·pyr is displayed in Figure S4. The average enthalpy (ΔH) and entropy $(\Delta S = \Delta H/T_i)$ variations as well as the average temperatures (T_i) of the maxima/minima of the Δ Cp vs T plots are gathered in Table 1. The average T_i temperatures of the observed anomalies are consistent with those obtained from the magnetic measurements for the SCO. For FebpanAu and **FebpanAg**, the overall ΔH and ΔS values associated with the SCO are consistent with those reported for related 3D SCO Hofmann-type coordination polymers with cooperative SCO. For **FebpbAg·pyr**, extrapolation of the HS↔LS transformation to 100% affords Δ H and Δ S values (ca. 8 kJ / mol and 54 J / K mol) consistent with the gradual character of the thermal spin transition.

Table 1. Thermodynamic parameters obtained from DSC measurements

		$T_{1/2}^{av}(K)$	∆Hav (kJ/mol)	∆Sav (J/Kmol)
FebpanAu	1st step	250.0	19.22	76.9
	2nd step	152.1	0.19	1.3
	Overall		19.41	78.2
FebpanAg	1st step	236.5	18.3	80.7
	2nd step	150.0ª	0.6	4.2
	Overall		18.9	84.9
FebpbAg·pyr	1st step	160.0	2.3 ^b	16.3 ^b
	2nd step	140.0	1.8 ^b	10.5 ^b
	Overall		4.1	26.8

^aOnly heating mode; ^b Evaluated for the 50% incomplete SCO

Single crystal optical absorption spectroscopy. Figures 2a and 2b display the thermal evolution of the optical absorption spectra for a single crystal of FebpbAg·pyr and of FebpanAu, respectively, in the heating mode recorded at 5 K min⁻¹ (see Figure S5 for the cooling mode). The thickness of both crystals was approximately 100 μ m. In both cases, the tail of the very intense metal-ligand-charge-transfer (MLCT) band is observed between 450 and 800 nm at room temperature. Below 450 nm, the MLCT band saturates due to its high extinction coefficient. When both crystals are cooled down below the spin transition temperature, the ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ d-d transition band ($\epsilon_{530-550nm} \approx 50$ M⁻¹·cm⁻¹) characteristic for the LS state of Fe^{II}, reaches a maximum at 10 K. The difference in optical density at 533/800 nm as well as 550/716 nm has been used for the silver and gold derivatives, respectively, to establish the thermal dependence of the HS molar fraction (γ_{HS}) through Vegard's law as stated elsewhere.³³ The γ_{HS} vs T curves obtained for **FebpbAg·pyr** or FebpanAu (Figure 2c) match very well the SCO behaviors found via magnetic studies albeit higher spin transition temperatures have been observed ($T_{1/2}\downarrow^1$ = 158 K, $T_{1/2}\downarrow^2$ = 136 K and $T_{1/2}\uparrow^1$ = 161 K, $T_{1/2}$ [↑]² = 140 K for **FebpbAg·pyr**; $T_{1/2}$ = 242 K and $T_{1/2}$ [↑] = 275 K for FebpanAu). The subtle difference in the SCO temperature may be attributed to the faster temperature scan rate employed for the single crystal optical absorption

measurements (5 K min⁻¹ vs 1 K min⁻¹), that is, the real temperature of the sample may be lower than the nominal one during heating. In the case of **FebpbAg·pyr**, the values of the HS fraction have been corrected by using the residual HS fraction obtained at low temperatures extracted from the χ T vs T curve. The size of the **FebpbAu·pyr** and **FebpanAg** crystals was too small to record their absorption spectra individually. Therefore, dilution of the grinded crystals in KBr pellets and dispersion in mineral oil have been tried out but, as shown in Figure S6, the quality of the optical absorption spectra is poor due to sample inhomogeneity.

Crystal structures

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Structural data of **FebpanAu** were successfully recorded at 280, 200, and 120 K allowing to identify the structures at the different steps defined by the SCO curve. However, despite numerous attempts, we were not able to get good single crystals of the isostructural **FebpanAg** and **ZnbpanAu** thus preventing a complete analysis of their structures. The structures of complexes **FebpbAu·pyr** and **FebpbAg·pyr** were determined at 120 and 250/100 K, respectively. Tables S1 and S2 show the main crystallographic parameters obtained from the single crystal X-ray data of all studied compounds.

Structure of FebpanAu. At 280 K, the structure of FebpanAu shows the monoclinic P2/c space group. It is constituted of two crystallographically non-equivalent pseudoctahedral [Fe^{II}N₆] environments. The equatorial positions of the octahedrons are coordinated by four [Au(CN)₂]⁻ groups which connect nonequivalent adjacent Fe^{II} centers (Fe1-Fe2-Fe1- ...) building up 2D infinite ${Fe_4[Au(CN)_2]_4}_{\infty}$ sheets. The apical positions are occupied by two crystallographically distinct ditopic bpan ligands acting as pillars between adjacent sheets, thereby defining a 3D framework with primitive cubic unit (pcu) topology (Figure 3). Each type of axial bpan ligand bridges one type of inequivalent Fe centers (Fe1 or Fe2) (Figure 3). Although the NC-Au-CN moieties are essentially linear, the coordination bonds between the NC-Au-CN groups and the Fe^{II} ions form an angle strongly deviated from 180° (Fe1-N3-C15 = 165.78°; Fe1-N8-C34 = 158.97°; Fe2-N6-C32 = 163.69°; Fe2-N7-C33 = 164.78°), thereby conferring to the $\{Fe_4[Au(CN)_2]_4\}_{\infty}$ layers a corrugated shape. Indeed, if we consider the four NC-Au-CN groups radiating from Fe2, the four connected Fe1 sites are 1.029 Å below the equatorial plane Fe2N6N7N6N7. Consequently, the {Fe₄[Au(CN)₂]₄} rhomboidal windows, whose Fe…Fe diagonals make 11.584 and 17.007 Å long, are slightly folded with respect to the short diagonal deviating 14.38° from planarity. The angles of the rhomboid are 68.099° and 110.579°. At 280 K, the Fe-N average distances, Fe1-N = 2.148 Å and Fe2-N = 2.157 Å, are typical of the Fe^{II} ions in the HS state in agreement with the magnetic data. The sum of the deviation from 90° of the twelve cis N-Fe-N bond angles (Σ) are 20.17° and 22.49° for Fe1 and Fe2 respectively.

The open nature of the framework favors the interpenetration of a second equivalent 3D structure, in such a way that each *bpan* ligand of one network passes exactly through the center of the $Fe_4[Au(CN)_2]_4$ rhomboids of the other.

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Figure 3. a) Representative fragment of the framework with the asymmetric unit cell numbering for FebpanAu at 280 K and b) View of a single 3D network. Yellow and orange octahedrons correspond to Fe1 and Fe2, respectively.

The interpenetration is stabilized by aurophilic interactions (Au1…Au2 = 3.428 Å) (Figure 4a and 4b). The anthracene moieties of the two independent bpan ligands display different orientations with respect to the plane defined by the atoms N1N2N3N3'(bpan1) around Fe1 and N4N5N6N6'(bpan2) around Fe2, being respectively 26.37° and 19.41°. The planes containing the pyridine rings asymmetrically bisect the equatorial angles N3Fe1N8 [pyridine containing N1 (51.41°) and N2 (67.66°)] and N6Fe2N7 [pyridine containing N4 (62.42°) and N5 (73.79°)]. Furthermore, the pyridine moieties are nearly orthogonal with respect to the anthracene fragment [bpan1: $pyridine(N1) = 77.76^\circ$, $pyridine(N2) = 94.03^\circ$; bpan2: pyridine(N4) = 93.20° and pyridine(N5) = 81.84°] (see Figure 3). This arrangement is adopted to minimize the inter- and intranetwork repulsion between the hydrogen atoms of the anthracene groups. In addition, anthracene moieties from different networks display very weak $\pi {\cdots} \pi$ interactions with C…C contacts well above 4.1 Å (centroid-centroid distances of ca. 5.4 Å).

When cooling down to 200 K, the crystal color changes from pale-yellow to red indicating the occurrence of the spin transition, consistently with the magnetic and optical absorption measurements. Furthermore, the SCO is

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accompanied by a change of the space group from monoclinic P2/c to orthorhombic *Cmma*.



Figure 4. Perspective views of the interpenetrated frameworks down to a) [010] and b) [100] directions for FebpanAu at 280 K

As a consequence of the symmetry breaking, the asymmetric unit now contains a unique octahedral Fe^{II} center, which is coordinated equatorially to four identical $[Au(CN)_2]^-$ groups and axially to only one crystallographically distinct bpan ligand. The average Fe-N bond length, equal to 1.954 Å, is 0.204 Å shorter than at 280 K, confirming that the HS \leftrightarrow LS transition is almost complete. Consistently, the angular distortion of the octahedron, Σ , decreases significantly to a value of 9.87° while the Fe-N-C(Au) angle increases up to 171.12° making the framework less distorted than in the monoclinic HS phase. Consequently, the two pyridine moieties are now practically coplanar and their planes bisect the N3-Fe-N3' angles into two identical portions of 46.01°. In contrast, the anthracene group is disordered in two crystallographically equivalent orientations forming an angle of 31.42° to each other (Figure S7a). However, the average orientation is strictly orthogonal with respect to the pyridine groups. Furthermore, the constraining of the grid during the SCO process occurs in an anisotropic manner since the long Fe…Fe diagonal of the {Fe₄[Au(CN)₂]₄} rhomboid decreases by 1.133 Å until 15.874 (1) Å, while the short one increases by 0.736 Å up to 12.320(1) Å.³⁴ The Au-Au interactions between the two equivalent interpenetrated nets show a distance of 3.273 Å, 0.155 Å shorter with respect to the distance at 280 K.

When further cooling to 120 K, the structure undergoes a second crystallographic phase transition displaying the monoclinic P2/n space group. The structure is very similar to that at 200 K but it shows some important differences: i) the

average orientation of the anthracene groups, which rate still disordered at 50% in two non-equivalent: orientations (Mow rotated with respect to each other by 22.57°, Figure S7b), is no longer orthogonal to the pyridine rings defining angles of 73.28° (pyridineN1) and 77.17° (pyridineN2); ii) the plane containing the two pyridine rings bisects the N3-Fe-N4 angles forming an angle of 54.56° with respect to the N1N3N2N3' plane; iii) the Fe-N average distance of 1.944 Å is slightly shorter (ca. 0.010 Å) than that at 200 K and reflects on the additional lowtemperature step observed in the magnetic measurements; iv) the aurophilic interactions are also stronger after this second phase transition showing a Au-Au distance value of 3.260 Å; and v) the long/short Fe…Fe diagonal of the {Fe4[Au(CN)₂]₄} rhomboid slightly increases/decreases upon additional conversion to reach values of 15.914 and 12.298 Å, respectively.

Structure of FebpbM·pyr (M = Ag, Au). *FebpbM·pyr* (M = Ag, Au) are isostructural. Therefore, we will delineate in detail the structure of the Ag derivative at 250 and 100 K. The structure of the Au derivative was measured at 120 K where it remains in the HS state and is comparable with that of the Ag analogue at 250 K (see SI Table S2).

FebpbAg·pyr displays the triclinic P-1 space group at 250 and 100 K. Topologically, the structure of FebpbAg·pyr is essentially the same as for FebpanAu discussed above. The most significant difference is that the corresponding {Fe₄[Ag(CN)₂]₄}_∞ layers are pillared by the longer and much less bulky bpb bridging ligand forming a much open **pcu** framework (Figure 5). The average Fe-N bond length and octahedral angular distortion Σ of the crystallographically unique Fe^{II} center are respectively, 2.180 Å and 18.37° at 250 K and 2.073 Å and 17.67° at 100 K. The equatorial Fe-N-C(Ag) bond angles, found in the range of 7.09°-13.5° (250 K) and 6.66°-10.61° (100 K), slightly deviate from the linearity. The moderate variation, 0.107 Å, of the average Fe-N bond length corresponds to the occurrence of a HS-to-LS conversion of 53.5%, which is in perfect agreement with the magnetic and optical data. The crystals change from yellow (HS)-to-dark orange (LS) when cooling from 250 K to 100 K.



Figure 5. Fragment of the FebpbM·pyr (M = Ag, Au) framework emphasizing the atom numbering of the asymmetric unit.

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(a) (b)

Figure 6. a) Side and b) top views of a fragment of the FebpbM.pvr (M = Ag, Au) structure showing the interpenetration of the two frameworks (blue/orange) and intercalation of the two crystallographycally distinct pyrene molecules marked in color green (pyr1) and salmon (pyr2).

As a consequence of its high void volume, this network is interpenetrated with a second equivalent structure as observed in Figure 6a. Unlike the *bpan* pillar ligand in **FebpanAu**, the *bpb* ligands of one network passes slightly shifted from the center of the $\{Fe_4(Ag(CN)_2)_4\}$ rhomboids of the other network (Figure 6b) thereby leaving wide channels for the intercalation of two crystallographically independent pyrene guest molecules within the generated pores. The two trapped pyrene guests are positioned face-to-face with respect to the pyridine coordinating groups of the *bpb* ligands, establishing a large number of $\pi \cdots \pi$ interactions (Figure S8). In one of the pyrene molecules, the $\pi \cdots \pi$ interactions are modified as a consequence of the spin state change (Table S3).

Coupling between luminescence and SCO

The interplay between the two concurrent properties, i.e. luminescence and SCO, has been investigated for the dicyanoargentate derivatives FebpbAg·pyr and FebpanAg. This choice was based on the fact that the dicyanoargentate counterpart of the bpb derivative displays a more complete SCO which takes place at higher temperature. Therefore, among FebpanAg and FebpanAu, the former was studied for comparison with FebpbAg·pyr. The thermal evolution of the luminescence spectra has been followed for an ensemble of single crystals of the selected compounds. In the case of

FebpbAg·pyr, a very similar behavior to that described for the analogous compound {Fe^{II}(bpben)[(Au(CN)2)2]}@pyrene@54Aas been found even though in the present case the transition is much more incomplete. As observed in Figure 7a, two main contributions are present in the luminescence spectra at room temperature upon irradiation at 345 nm (see corresponding excitation spectra in Figure S9a). In the interval 350-450 nm, a multicomponent band, split into two main peaks, associated with the monomer form of pyrene is observed. From 450 to 700 nm a much broader and less defined band appears. This contribution is associated with the emission arising from the heterodimeric excimer formed by the pyrene molecules and the *bpb* bridging ligand due to strong $\pi \cdots \pi$ interactions established between them.³⁵ Upon cooling from room temperature, the intensity of the monomer and excimer signals increases due to reduction of thermal quenching, that is, in the configurational coordinate model, the probability of finding a crossing point between the potential energy surfaces of the ground state and the higher energy excited states, populated at high temperatures, increases leading to non-radiative transitions.²⁷ However, at ca. 200 K, the intensity of the excimer signal is stabilized and, upon further cooling, it decreases abruptly whereas the intensity of the monomer band keeps on increasing. At 10 K, where $\gamma_{HS} \approx \gamma_{LS} \approx 0.5$, the monomer signal intensity reaches to a maximum in intensity and displays a highly defined doublet due to the reduction of vibrational degrees of freedom at such low temperatures, whereas the excimer signal is significantly quenched. This observation can be attributed to the overlap of the optical absorption spectra in the LS state and the excimer emission.

Figure 7b shows the fluorescence emision of FebpanAg as a function of temperature (see corresponding excitation spectra in Figure S9b). At room temperature, irradiation at 345 nm induces the observation of two main contributions: a more resolved signal in the wave-length range 350-490 nm from the monomer and a broader and less defined band in the interval 490-700 nm from the excimer.³⁶⁻³⁸ The fluorescence behavior of the anthracene excimer is usually characterized by a very short lifetime and makes difficult to detect it at room temperature albeit high pressure conditions in the crystalline state lead to its observation.³⁶ In the present case, the crystallinity of the sample and the rigidity of the lattice may contribute to the observation of the excimer signal from anthracene. Nonetheless, these interactions are less significant than in FebpbAg·pyr, what would explain the lower intensity of the excimer signal in FebpanAg with respect to FebpbAg·pyr. Upon cooling, both monomer and excimer signals increase in intensity. However, below 230 K, in correlation with the thermal spin transition of the complex, the excimer band undergoes some modifications in shape and seems to disappear upon further cooling whereas the intensity of the monomer signal increases giving rise to well-structured bands. As in the previous case, this behavior may be ascribed to the high optical absorption of the LS species within the range of the excimer emission.



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Figure 7. Thermal evolution of the fluorescence of an ensemble of crystals of (a) FebpbAg·pyr and (b) FebpanAg during cooling at 5 K/min.

In order to analyze in more detail the thermal dependence of the fluorescence for compound **FebpbAg·pyr**, the intensities of the excimer and monomer signal were extracted

from the corresponding spectra during cooling (Figure 7a) and heating (FigureS10a) and plotted as a function of temperature (Figure 8a and S10b). The HS fraction, γ_{HS} , was calculated as the ratio between both signals and its thermal evolution is depicted in Figure 8b. The resulting profile is consistent with the SCO observed from single crystal optical absorption spectroscopy although the thermal hysteresis is wider and the spin transition temperature is shifted towards lower temperatures. These discrepancies are likely related to differences in the temperature scanning rate used for each measurement method. Hence, previously as observed in ${Fe^{II}(bpben)[(Au(CN)_2)_2]}@pyrene,^{32}$ the modification of the luminescence behavior of pyrene has been demonstrated to be a sensitive technique to monitoring the SCO for compound FebpbAg·pyr. In both cases, for the bpben- and bpb-containing compounds, the SCO observed through the thermal variation of the magnetic susceptibility can be accurately reproduced by the luminescence measurements (Figure S11).

Similarly, the thermal SCO of the intrinsically luminescent compound **FebpanAg** was also obtained by calculating γ_{HS} as the ratio of the excimer and the monomer signal. However, in this case the monomer signal was calculated as the average of the maximum intensity of the different observed peaks (see



Figure 8. (a) Thermal dependence of the monomer and excimer emission intensity of **FebpbAg-pyr** in the cooling mode. (b) Comparison of the HS fraction, $\gamma_{\rm HS}$, obtained from the ratio of the monomer emission over the excimer emission (filled diamonds) and from single crystal absorption spectroscopy (filled circles) in the heating and cooling modes at 5 K/min.

peaks from [1] to [5] in Figure 9a (and Figure S10c) and the intensity vs T plots for the cooling and heating modes in Figure 10b and S10d, respectively). Although the resulting thermal dependence of the luminescence partially agrees with that obtained by magnetic susceptibility measurements (even the multi-step feature), the former displays a more gradual shape (Figure 9c). These small differences can be ascribed to the faster temperature scan rates used for recording the thermal dependence of luminescence and the fact of exciting an ensemble of crystals. On the other hand, it is worth mentioning that the emission spectra of FebpanAg was obtained from exciting in the different structured-excitation bands with the origin of the different vibrational contributions between the ground and excited electronic states S₀ and S₁ (see excitation spectrum in Figure S12a)^{39,40} However, if one excites into the π - π^* band of anthracene at approximately 260 nm, the emission is slightly different and in fact, when following the thermal evolution of the emission spectra the intensities of all peaks equally increase upon cooling, but the relative intensity of all the vibrational bands stays constant and the excimer signal is not present (see Figures S12b and S12c for comparison). Interestingly, other studies point to the same relative intensities and shape of the emission spectrum of anthracene regardless of whether the excitation is carried out at 280 or 360 nm.⁴¹

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Figure 9. Compound **FebpanAg**. Thermal evolution of: the monomer and excimer emission spectra (a); the different intensity maxima 1-6 (b); and the HS fraction (γ_{HS}) obtained from the ratio of the monomer emission over the excimer emission during the heating and cooling modes at 5 K/min (the results are compared with the thermal transition obtained by magnetism).

In order to verify whether the flurescence-SCO synergy observed for **FebpbAg·pyr** and **FebpanAg** also takes place in the corresponding **FebpbAu·pyr** and **FebpanAu** analogues, their fluorescence spectra have been recorded at 300 K and at 80 K (see Figure S13 containing a full characterization of the absorption, excitation and fluorescence spectra). Whereas at 300 K the 100% of the Fe^{II} ions exhibit the HS state, at 80 K **FebpbAu·pyr** and **FebpanAu** display 70%/30% and 0%/100% HS/LS state, respectively. Indeed, in the LS state, the intensities of the monomer signal increase significantly with respect to the excimer one, which exhibits once again a quench due to the strong optical absorption of the samples in the excimer region. Consistenly, the excimer quenching is complete for the *bpan* Page 8 of 12

derivative whereas it is partial for **FebpbAu-pyr** confirming the incomple character of its spin transition. Finally, the thermal dependence of the fluorescence spectra of the isostructural analogue **ZnbpanAu** has been recorded in the heating mode and, as expected, both monomer and excimer intensities increase at low temperatures since the Zn counterpart is not SCO-active (Figure S14).

Light Induced Spin State Trappping (LIESST) experiments

First, LIESST effect studies were carried out for compounds FebpbAg·pyr and FebpanAu via single crystal optical absorption since, as mentioned above, these are the samples from which big enough single crystals are obtained for absorption spectroscopy studies. The irradiation with a 532 nm laser for 10 minutes at 10 K revealed a LS-to-HS photoconversion of 100% for FebpbAg·pyr and 80% for FebpanAu (Figure S15a and S15d, respectively). The temperature at which 50% of the photogenerated HS centers have relaxed to the LS state at a heating rate of 0.3 K/min is T_{LIESST} ≈ 43 and 40 K for pyrene- and anthracene-containing SCO compounds, respectively (Figure S15b and S15e). These results have been confirmed by magnetic measurements (Figure S16). The photoswitching experiments were also followed by fluorescence spectroscopy for FebpbAg·pyr and FebpanAu. In the case of FebpbAg·pyr, as long as the temperature is not modified, the monomer signal remains stable upon irradiation whereas the excimer signal increases significantly evidencing the LS to HS conversion due to light stimulus (Figure S15c). In the case of FebpanAu no significant change occurs upon excitation at 532 nm and the excimer signal is not formed probably because the efficiency of LIESST effect is slightly lower than we previously observed by absorption spectroscopy (Figure S15f). Besides, we evidenced during the thermal transition, that the excimer signal is observed only when γ_{HS} approaches 1.

Concluding remarks

This work has been undertaken as a new step in the study of the interplay between SCO and luminescence in 3D Hofmanntype coordination polymers. We have proposed two different approaches, one of them takes advantage of the porous nature of the framework to include a fluorescent guest, as recently reported for {Fe^{II}(bpben)[Au^I(CN)₂]₂}·pyr, in which luminescence is an extrinsec property of the framework. The other approach, for the first time, includes luminescence as an intrisinc function of the SCO framework using a fluorescent bridging pillar ligand. In the first case we have chosen the bridging ligand bpb previously used in the synthesis of the coordination polymers ${Fe^{(bpb)}[M^{(CN)}]} \cdot G$ (M[∥] Ni, Pt) = Pd, and {Fe^{II}(*bpb*)[Ag^I(CN)₂]₂}.^{42,43} The tetracyanometallate derivatives exhibit cooperative one- or two-step SCO behavior when two molecules of naphthalene or nitrobenzene (G) are docked inside the pores. However, the much longer dicyanoargentate ligand, facilitates a singular four-fold interpenetration of identical open frameworks, with pcu topology, even in presence of high concentrations of naphthalene or nitrobenzene guests. The inter-framework packing is so tight that does not leave

Published on 19 December 2019. Downloaded on 1/2/2020 11:28:41 PM

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room for guest molecules, thereby favoring strong elastic frustration⁴⁴ and, consequently, the occurrence of an incomplete SCO centered at ca. 130 K. In contrast, selfassembling of Fe^{II}, *bpb* and $[M^{I}(CN)_{2}]^{-}$ (M^I = Ag, Au) in presence of the much larger pyrene guest molecule favors the formation of a supramolecular isomer consisting of two-fold interpenetrated frameworks while the pyrene molecules are docked in the available spaces in a similar fashion as described for the bpben derivative. Despite the probable decongestion of the crystal packing in FebpbM·pyr (M = Ag, Au), elastic frustration seems to remain since the SCO in both compounds is very incomplete and occurs at very low temperatures. Apparently, the interpenetration of the frameworks and the large number of host-guest $\pi \cdots \pi$ short-range interactions strongly influence the SCO behavior of this system. The lower SCO temperature observed for FebpbAu·pyr compared to FebpbAg·pyr is usually expected in Hofman-type coordination polymers and is attributed to the slightly weaker ligand field induced by [Au(CN)2]-.29

Concerning the system FebpanM (M = Ag, Au), a reverse situation is observed with respect to the average critical temperatures above mentioned for the bpb derivatives. Both bpan derivatives undergo rather complete hysteretic SCO behaviors but, unexpectedly, the critical average temperature of the main transition is ca. 15 K lower for the Ag derivative. This suggests that, despite their isostructural nature, subtle effects of the crystal packing contribute to the effective ligand field experienced by the Fe^{II} center with a slightly larger destabilization of the LS state in case of the Ag derivative. Interestingly, both SCO behaviors can be classified as two-step transitions with very asymmetric steps. For example, compound FebpanAu presents a first step at high temperatures involving ca. 80% of the Fe^{II} centers and, separated by a large plateau ca. 70 K wide, and a second step occurs at lower temperatures involving ca. 10% of Fe^{II} centers. This behavior is associated with two consecutive symmetry breaking transformations. In addition to the expected structural changes associated with the coordination environment of Fe^{II}, the rotational freedom of the bulky anthracene group situated between the two coordinating pyridines of the bpan ligand seems to be in the origin of this singular behavior. Indeed, there is a clear correlation between the change in orientation of the anthracene groups, the change in crystallographic phase and the stabilization of the distinct HS/LS Fe^{II} fractions. In the HS state (280 K) the anthracene groups of the two crystallographically distinct bpan ligands are ordered. However, at 200 K after the first phase transition where ca. 80% of the Fe^{II} are LS, the structure features a unique bpan ligand but the anthracene displays positional disorder with two anthracene moieties distributed at 50% separated by 31.42°. One of the orientations practically matches that of the HS structure but the other is rotated 32.14° for the framework containing the Fe1 and 47.78° for the framework containing the Fe2 (see Figure S7a). At 120 K, the positional disorder remains but the angle between the two orientations is 22.57°. When comparing the position of the average planes of the two orientations defined by each anthracene at 120 and 200 K a subsequent rotation of 17.59° and 26.44° occurs (see Figure

S7b). The latter reorientation is responsible for the additional symmetry breaking and small hysteretic spin state charge at low temperature. Thus, throughout the HS \leftrightarrow LS transition, while the network shrinks, the anthracene moieties rotate most likely to minimize the interatomic repulsions. The SCO behavior of the isostructural silver derivative is perfectly comparable with that of the Au counterpart, although, the low temperature hysteretic spin transition is less pronounced in the Ag derivative, particularly in the cooling branch. This different behavior may be related to the higher flexibility of the [Ag(CN)₂]-bridge, and hence, to the larger adaptability to the steric constraints progressively generated by the anthracene groups while lowering the temperature.

As far as the SCO-fluorescence synergy is concerned, the excimer signal of FebpbAg·pyr is strongly quenched upon cooling due to the strong absorption of the $\mathrm{Fe}^{\scriptscriptstyle \parallel}$ in the LS state whereas it is maximum at room temperature when the HS state is fully populated. Besides, the relatively short-distances between pyrene molecule and Fe centers may favor nonradiative energy transfer between both species. Similar behavior has been recently reported for FebpbenAu·pyr.³² In the case of FebpanAg, radiative energy transfer occurs due to spectral overlap between the Fe^{II} and the anthracene molecules being minimum at room temperature when the excimer signal is observed due to the lower oscillator strength of the optical absorption transtion of the Fe^{II} in the HS state. However, due to the longer distance between anthracene moiety and Fe^{II} atom in FebpanAg with respect to the distance between pyrene guest and Fe^{II} atom in FebpbAg·pyr, non-radiative energy transfer is rather attributable to the latter compound resulting in a more obvious synergy. Besides, the $\pi \cdots \pi$ interactions operating between anthracene moieties in FebpanAg are much weaker than the frontal $\pi \cdots \pi$ interactions between pyrene and *bpb* bridging ligand in FebpbAg·pyr giving rise to a weaker fluorescence signal of the excimer. This might be the reason why the synergy between the spin state and the luminescence is much more significant for FebpbAg·pyr than for FebpanAg. Moreover, a third aspect to take into account is that the excimer signal in both FebpbAg·pyr and FebpanAg could be partially affected by self-concentration quenching. However, the large Stokes shift between the monomer absorption and excimer emission signals make it rather unlikely.

Likewise, in the case of **FebpbAg·pyr** the relative intensity of the excimer signal increases very significantly, with respect to that of the monomer, upon photoexcitation at low temperature (LIESST effect, $\lambda^{irr} = 532$ nm) due to the LS to HS photoconversion. This was previously observed for **FebpbenAu·pyr**.³² Hence, further experiments will be carried out in the future in this respect to study the thermal dependence of the HS to LS relaxation after LIESST probed by fluorescence measurements. Comparison with analogous results obtained by absorption spectroscopy would provide a different approach to study the SCO-luminescence synergy.

The differences in the SCO-fluorescence coupling when considering either an intrinsic or an extrinsic luminescent 3D Hofmann-type compound is difficult to rationalize because even if the quantum yield of the luminophores are similar (0.36 and

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0.32 for anthracene and pyrene respectively in cyclohexane)⁴⁵ and the oscillator strength of the acceptors are comparable, the synergy strongly depends on the geometry of the whole arrengement. In this sense, the extrinsic luminescence obtained throught the insertion of different guest fluorescent molecules such as pyrene seems very promising due to the capacity of controling the geometry and, in consequence, the guest-guest, guest-ligand and guest-Fe^{II} distances. Nonetheless, the nature of the energy transfer processes ocurring based on the location of the luminophore and SCO centres within the structure plays a key role in the deep understanding of the parameters governing the SCO-luminescence synergy. In this sense, the change of the luminescence lifetimes and quantum yields of the luminophore depend upon incorporation into the Fe^{II} SCO 3D network. In addition, the comparison of results with the equivalent non-switchable material based on Zn^{II} would give an idea of the extent of non-radiative energy transfer involved in the synergy and of the importance of the lattice rigidity in the quantum yield values. In principle, stiffness is expected to prevent non-radiative decays hence leading to higher quantum yield.^{27,46} Thus, further studies will be directed towards analysing the luminescence lifetime and the quantum yield of the studied compounds as a function of the spin fraction.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support from the Spanish Ministerio de Economía y Competitividad (MINECO) and FEDER funds (CTQ2016-78341-P and Unidad de Excelencia María de Maeztu MDM-2015-0538), the Generalitat Valenciana (PROMETEO/2016/147) and the Swiss National Science Foundation (Grant No 200020_152780). M. M.-S. thanks MINECO for a predoctoral FPI grant.

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Graphical abstract

View Article Online DOI: 10.1039/C9TC06422B

Two unprecedented series of coordination polymers have been synthesized to exhibit extrinsic or intrinsic luminescence modulated by spin crossover behavior. This study provides further insight into the features governing the synergy between these two properties.

