## **Supporting information**

# Extrinsic vs intrinsic luminescence and their interplay with spin crossover in 3D Hofmann-type Coordination Polymers

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#### **Experimental section**

#### Synthetic procedures

*Bpb* ligand was prepared according to the synthesis described in the literature.<sup>1</sup>

Synthesis of 1,4-bis(4-pyridyl)anthracene (bpan). To a mixture of 4-pyridylboronic acid (2.2 g, 18 mmol), 9,10-dibromoanthracene (1.7 g, 5 mmol) and palladium tetrakis(triphenylphosphine) (381.6 mg, 0.33 mmol) in dioxane (40 mL) purged with Ar was added dropwise a solution of  $K_2CO_3$  (2.6 g, 18.8 mmol) in H<sub>2</sub>O (20 mL). After being stirred at 100 °C for 18 h, the mixture was cooled to room temperature and removed the aqueous phase. The dioxane layer was filtered and removed under reduced pressure. The product was dissolved in dichloromethane (100 mL), filtrated and washed twice with 5 g of Na<sub>2</sub>CO<sub>3</sub> in 25 mL of water. The dichloromethane solution was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure getting 1.2 g (72%) of yellow product.

*Synthesis of FebpanAu, FebpanAg and ZnbpanAu*. Single crystals of FebpanAu/FebpanAg were grown by slow liquid-to-liquid diffusion methods using a layering tube. The bottom was filled with a mixture of  $Fe(BF_4)_2$ ·  $6H_2O$  (27.8 mg, 0.1 mmol) in 1 mL of methanol and bpan (33.2 mg, 0.1 mmol) in 2 mL of dichloromethane. The middle was filled with an interphase of 5 mL of methanol-dichloromethane (1:1). The top was filled with a solution of potassium dicyanoaurate/dicyanoargentate (57.6/39.8 mg, 0.2 mmol). Similar diffusion conditions were used for obtaining the **ZnbpanAu** derivative but using Zn(BF<sub>4</sub>)<sub>2</sub>·  $6H_2O$  (34.6 mg, 0.1 mmol) instead of the Fe<sup>II</sup> salt. Afterwards, the tube was closed and light-yellow rhomboid crystals (almost colorless for the Zn counterpart) were formed within two days with relative high yield (c.a. 45%). *Elemental Analysis*: Calculated for FebpanAu [C<sub>28</sub>H<sub>16</sub>Au<sub>2</sub>FeN<sub>6</sub> (886.3) (%)]: C 37.95; H 1.82; N 9.48. Found (%): C 38.09; H 1.71; N 9.13. Calculated for FebpanAg [C<sub>28</sub>H<sub>16</sub>Ag<sub>2</sub>FeN<sub>6</sub> (707.9) (%)]: C 47.50; H 2.28; N 11.87. Found (%): C 47.89; H 2.16; N 11.46. Calculated for ZnbpanAu [C<sub>28</sub>H<sub>16</sub>Au<sub>2</sub>ZnN<sub>6</sub> (895.8) (%)]: C 37.54; H 1.80; N 9.38. Found (%): C 37.92; H 1.92; N 9.63.

*Synthesis of FebpbAu-pyr* and *FebpbAg-pyr*. Single crystals of **FebpbAu-pyr/FebpbAg-pyr** were obtained through liquid-to-liquid diffusion methods using a modified H-shape tube with 3 arms. The peripheral arms were filled 2 mL methanol solutions containing 0.1 mmol (33.7 mg) of Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.2 mmol of K[Au<sup>1</sup>(CN)<sub>2</sub>]/K[Ag<sup>I</sup>(CN)<sub>2</sub>] (57.6/39.8 mg) respectively, and the center arm was filled with a 2 mL methanol solution of 0.1 mmol (20 mg) of the bpb ligand. Afterwards, the rest of the tube was carefully filled with a methanolic solution saturated with pyrene and sealed with parafilm. After two weeks, orange **FebpbAu-pyr/FebpbAg-pyr** blocks suitable for single crystal X-ray analysis appeared within the H tube. *Elemental Analysis*: Calculated for **FebpbAu-pyr** [C<sub>34</sub>H<sub>18</sub>Au<sub>2</sub>FeN<sub>6</sub> (960.3) (%)]: C 42.52; H 1.89; N 8.75. Found (%): C 42.23; H 1.86; N 8.91. Calculated for **FebpbAg-pyr** [C<sub>34</sub>H<sub>18</sub>Ag<sub>2</sub>FeN<sub>6</sub> (782.2) (%): C 52.21; H 2.32; N 10.75. Found (%): C 52.81; H 2.48; N 10.44.

#### Physical characterization.

Elemental analyses (C, H, and N) were performed with a CE Instruments EA 1110 CHNS Elemental analyzer. Magnetic measurements were performed with a Quantum Design MPMS-XL-5 SQUID magnetometer in the 2 to 400 K temperature range with an applied magnetic field of 0.1 T. Experimental susceptibilities were corrected for diamagnetism of the constituent atoms by the use of Pascal's constants. Photomagnetic measurements were performed irradiating with a Diode Pumped Solid State Laser DPSS-532-20 from Chylas and a coupled via an optical fiber to the cavity of the SQUID magnetometer. The optical power at the sample surface was adjusted to  $\sim 3 \text{ mW} \cdot \text{cm}^{-2}$ , and it was verified that it resulted in no significant change in magnetic response due to heating of the sample. The photomagnetic samples consisted of a thin layer of compound whose weight was corrected by comparison of a thermal spin crossover curve with that of a more accurately weighted sample of the same compound. Calorimetric measurements were performed using a differential scanning calorimeter Mettler Toledo DSC 821e. Low temperatures were obtained with an aluminium block attached to the sample holder, refrigerated with a flow of liquid nitrogen and stabilized at a temperature of 110 K. The sample holder was kept in a dry box under a flow of dry nitrogen gas to avoid water condensation. The measurements were carried out using around 15 mg of polycrystalline samples sealed in aluminium pans with a mechanical crimp. Temperature and heat flow calibrations were made with standard samples of indium by using its melting transition (429.6 K, 28.45 J g<sup>-1</sup>). An overall accuracy of  $\pm 0.2$  K in temperature and  $\pm 2\%$  in the heat capacity is estimated. The uncertainty increases for the determination of the anomalous enthalpy and entropy due to the subtraction of an unknown baseline. Powder X-ray measurements where performed on a PANalytical Empyrean X-ray powder diffractometer (monochromatic CuKa radiation).

*Single crystal absorption spectroscopy*. Single crystals of **FebpbAg·pyr** and **FebpanAu** were mounted on a copper plate with a previously drilled hole. One crystal was deposited in the middle of the hole and fixed with silver paste nanoparticles (Agar Scientific Ltd.) to ensure a good thermal conductivity. The sample was then introduced into a closed cycle cryostat (Janis-Sumimoto SHI-4.5), which operates between 4 and 300 K and it is equipped with a programmable temperature controller (Lakeshore Model 331). The cryostat was introduced into a double beam spectrometer (Varian Cary 5000). The irradiation for the photoinduced experiments (LIESST) was performed with a HeNe laser at 532 nm with a power of 2 mW/ mm<sup>2</sup>.

*Photoluminescence spectroscopy.* The excitation and luminescence spectra of **FebpbAg·pyr**, **FebpbAu·pyr**, **FebpanAg** and **FebpanAu** were recorded on a Fluorolog 3-22 (Horiba Jobin Yvon), equipped with a watercooled photo multiplier tube (PMT). A calibration function was applied to account for the wavelengthdependent sensitivity of the photomultiplier tube, the wavelength dependent sensitivity of the photomultiplier tube, the throughput of the analyzing monochromator and the power fluctuation of the xenon lamp. For the ambient temperature and 80 K measurements a quartz capillary was filled with 20 mg of the crystals and was introduced in a liquid nitrogen dewar made of quartz which was filled with liquid nitrogen for the 80 K measurements until the high-spin to low-spin conversion was observed by the color change from yellow to red respectively. For the temperature dependence measurements an ensemble of **FebpbAg·pyr** or **FebpanAg** crystal are deposited in a cooper plate and fixed with silver paste nanoparticles to ensure a good thermal conductivity. The sample was then introduced into the above described cryostat, that was in turn aligned in the Fluorolog.

Single crystal X-ray measurements. Single crystals were mounted on a glass fiber using a viscous hydrocarbon oil to coat the crystal and then transferred directly to the cold nitrogen stream for data collection. X-ray data were collected on a Supernova diffractometer equipped with a graphite-monochromated Enhance (Mo) X-ray Source ( $\lambda = 0.71073$  Å). The program CrysAlisPro, Oxford Diffraction Ltd., was used for unit cell determinations and data reduction. Empirical absorption correction was performed using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structures of were solved with the ShelXT structure solution program<sup>2</sup> and refined with the SHELXL-2013 program,<sup>3</sup> using Olex2.<sup>4</sup> Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters.

**Figure S1.** Experimental (black lines) and simulated (grey lines) powder X-ray diffraction patterns of the studied compounds.





**Figure S2.** Thermogravimetric analysis of a) **FebpbAg·pyr**, b) **FebpbAu·pyr**, c) **FebpanAg** and **FebpanAu**.

**Figure S3.**  $\chi_M$ T vs T curves obtained for compound **FebpbAg·pyr** registered within two successive cooling and heating cycles.



**Figure S4.** DSC curves for compounds a) **FebpanAg**, b) **FebpanAu** and c) **FebpbAg·pyr**. The blue and red lines represent the cooling and heating modes, respectively. Magnetic curves are also represented for comparison. Inset: DSC regions of interest enlarged.



**Figure S5.** Thermal dependence of the single crystal absorption spectra during the thermal transition in the cooling mode for a) **FebpbAg·pyr** and b) **FebpanAu**.



**Figure S6.** Absorption spectra at 300 and 10 K of grinded crystals of *FebpanAg* a) diluted and pressed in a KBr pellet and b) dispersed in a mineral oil. In both cases the sample is strongly affected by the preparition and the MLCT and d-d bands of  $Fe^{II}$  observed for *FebpanAu and FebpbAg·pyr* are not observed. Instead, the relatively week band observed at around 220 nm could be tentatively assigned to the absorption band of anthracene.





**Figure S7.** Side and top perspectives for a representative fragment of the **FebpanAu** framework upon successive crystallographic transformations (a)  $280 \text{ K} \rightarrow 200 \text{ K}$  and b)  $200 \text{ K} \rightarrow 120 \text{ K}$ ) involving the rotation of the anthracene moiety.



**Figure S8.** Intermolecular short C···C  $\pi$ -contacts smaller than the sum of the Van der Waals radii (c.a. 3.7 Å) for the two types of pyrene molecules.





**Figure S9.** Excitation spectrum of an ensemble of crystals of a) *FebpbAg·pyr* and b) *FebpanAg* measured at 525 nm in a quartz capillary.

**Figure S10.** Thermal evolution of the fluorescence of an ensemble of crystals of **FebpbAg·pyr** (a) and **FebpanAg** (c) during heating at 5 K/min and extracted normalized evolution of the excimer and monomer intensity for **FebpbAg·pyr** (b) and **FebpanAg** (d).



**Figure S11.** Thermal evolution of the excimer signal for a)  $\{Fe^{II}(bpb)[(Ag(CN)_2)_2]\}$ @pyrene and b)  $\{Fe^{II}(bpben)(Au(CN)_2)_2\}$  during heating at 5 K/min. Two similar ligands give rise to two clearly different thermal spin transitions, which can be followed by fluorescence.







**Figure S13.** Single crystal absorption spectra of a) *FebpbAu·pyr* and b) *FebpanAu* at 300 and 10 K in the HS and LS state respectively; room temperature excitation spectra of an ensemble of crystals of c) *FebpbAu·pyr* and d) *FebpanAu* measured at 525 nm, and corresponding fluorescence spectra of an ensemble of crystals of e) *FebpbAu·pyr* and f) *FebpanAu* after excitation at 345 nm at 300 and 80 K in the HS and LS state, respectively.



**Figure S14.** Fluorescence spectra of an ensemble of crystals of *ZnbpanAu* after excitation at 345 nm during heating from 10 K to 300 K at 5 K/min.



**Figure S15.** Photo-induced LS to HS transition at 10 K and subsequent HS to LS relaxation while heating at 0.3 K/min up to 60 K for a) **FebpbAg·pyr** and d) **FebpanAu**. Evolution of the HS fraction during the thermal HS to LS relaxation with the corresponding  $T_{\text{LIESST}}$  indicated in the figure for b) **FebpbAg·pyr** and e) **FebpanAu**. Fluorescence spectra of the sample at room temperature and at 10 K before LIESST and 10 K after LIESST for c) **FebpbAg·pyr** and f) **FebpanAu**.



**Figure S16.** Cooling mode thermal transition at 1 K/min (blue diamonds), photo-induced LS to HS transition at 10 K upon irradiation at 632 nm (green triangles), HS to LS relaxation while heating at 0.3 K/min (orange triangles) and subsequent heating mode thermal transition (red diamonds) obtained by magnetic susceptibility measurement on a multicrystalline sample of a) *FebpanAu* and b) *FebpbAg·Pyr*. The percentage of LS fraction photoconverted through LIESST and the T<sub>LIESST</sub> are in agreement with the data obtained by single crystal absorption spectroscopy upon irradiation at 532 nm.



Sample	FebpanAu				
<i>T</i> (K)	280	200	120		
Empirical formula	$C_{56}H_{32}Au_4Fe_2N_{12}$	C22H12Au2FeN6	C <sub>28</sub> H <sub>16</sub> Au <sub>2</sub> Fe N <sub>6</sub>		
Mr	1772.50	810.16	886.25		
Crystal system	Monoclinic	Orthorhombic	Monoclinic		
Space group	P2/c	стта	P2/n		
a (Å)	11.6053(5)	12.3200(8)	10.0487(11)		
$b(\dot{A})$	15.8026(5)	15.8744(10)	15.414(2)		
c (Å)	16.9870(5)	15.3989(12)	10.0635(13)		
α	90	90	90		
β	90.113(3)	90	104.609(3)		
γ	90	90	90		
$V(Å^3)$	3115.3 (2)	3011.6(4)	1508.3(3)		
Z	2	4	2		
F(000)	1640	1480	820		
$D_{\rm c} ({\rm mg}{\rm cm}^{-3})$	1.890	1.787	1.951		
$\mu$ (Mo-K <sub>a</sub> )(mm <sup>-1</sup> )	9.879	10.210	10.202		
No. of total reflections	16766	18353	17833		
$[I > 2\sigma(I)]$					
$R[I>2\sigma(I)]$	0.0612	0.0688	0.0685		
$wR[I>2\sigma(I)]$	0.0793	0.1867	0.1700		
Goodness-of-fit on F2	1.032	1.050	1.000		

**Table S1.** Selected crystallographic parameters for **FebpanAu** at 280, 200 and 120 K.

 Table S2. Selected crystallographic parameters for FebpbAg·pyr and FebpbAu·pyr.

Sample	FebpbAg·pyr		FebpbAu·pyr				
<i>T</i> (K)	250	100	120				
Empirical formula	$\begin{array}{c} C_{42}H_{23}Ag_2Fe\\ N_6 \end{array}$	C42H23Ag2FeN6	$C_{42}H_{23}Au_2FeN_6$				
Mr	883.25	883.25	1061.45				
Crystal system		Triclinic					
Space group	<i>P</i> -1						
a (Å)	10.6198(6)	10.4725(5)	10.4750(9)				
$b(\mathbf{A})$	10.6201(6)	10.4766(5)	10.4803(10)				
<i>c</i> (Å)	16.6476(9)	16.4736(8)	16.5967(16)				
α	101.223(5)	93.637(4)	93.218(8)				
β	93.765(5)	100.867(4)	100.823(8)				
γ	96.999(5)	97.191(4)	97.269(8)				
$V(\text{\AA}^3)$	1820.22(18)	1754.01(15)	1769.2(3)				
Ζ	2	2	2				
<i>F</i> (000)	874.0	874.0	1002.0				
$D_{\rm c} ({\rm mg}~{\rm cm}^{-3})$	1.612	1.672	1.992				
$\mu$ (Mo-K <sub><math>\alpha</math></sub> )(mm <sup>-1</sup> )	1.497	1.554	8.716				
No. of total reflections	13228	19947	17844				
$[I > 2\sigma(I)]$							
$R[I>2\sigma(I)]$	0.0666	0.0703	0.0857				
$wR[I > 2\sigma(I)]$	0.1660	0.1805	0.1690				
Goodness-of-fit on F2	1.039	1.038	1.061				

Pyrene1 <sup>a</sup>	T = 100 K	T = 250 K	Pyrene2 <sup>♭</sup>	T = 100 K	T = 250 K
C8…C26	3.28(2)	3.29(1)	C4…C36	3.34(2)	3.58(1)
C8…C25	3.37(2)	3.39(1)	C7…C41	3.35(2)	3.69(1)
C7…C26	3.38(2)	3.41(1)	C2…C35	3.38(2)	3.37(1)
C7…C25	3.38(2)	3.42(1)	C6…C38	3.40(2)	3.46(1)
C10···C28	3.41(2)	3.45(1)	C2…C40	3.40(2)	3.46(1)
C9…C27	3.44(2)	3.49(1)	C1…C35	3.43(2)	3.38(1)
C13···C31	3.44(2)	3.54(1)	C8…C42	3.48(2)	3.57(1)
C13···C30	3.47(2)	3.63(1)	C3…C36	3.50(2)	3.61(1)
C14…C23	3.51(2)	3.61(1)	C5…C36	3.53(2)	3.60(1)
C11C34	3.52(2)	3.55(1)	C4…C37	3.54(2)	3.55(1)
C11C29	3.53(2)	3.55(1)	C3…C37	3.55(2)	3.55(1)
C9…C28	3.54(2)	3.59(1)	C8···C41	3.57(2)	
C9…C26	3.56(2)	3.56(1)	C3…C35	3.58(2)	
C14…C22	3.56(2)	3.64(1)	C7…C38	3.60(2)	
C10···C29	3.58(2)	3.68(1)	C6…C39	3.61(2)	3.66(1)
C14…C31	3.58(2)		C6…C41	3.62(2)	
C8C27	3.63(2)	3.67(1)	C6…C37	3.67(2)	
$C10\cdots C22$	3.67(2)	3.69(1)	C7…C42	3.68(2)	3.56(1)
C12C34	3.68(2)		C3C38	3.68(2)	3.64(1)
			C8…C40	3.68(2)	3.67(1)
			C2…C36		3.69(1)

**Table S3**. Intermolecular  $\pi$ - $\pi$  distances smaller than the sum of the C···C Vander Waals distance (c.a. 3.7 Å) between pyrene and the pyridine moieties of the brigding ligand bpb for FebpbAg·pyr.

<sup>a</sup>Color code: salmon; <sup>b</sup>Color code Green in Figure S7

### REFERENCES

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