

## Supporting Information

### **Intrinsic Fluorescence–Spin Crossover Synergy in a 3D Fe(II) Hofmann-Type Framework Built from 1,6-dipyridylpyrene and $[M^I(CN)_2]^-$ ( $M^I = Ag, Au$ ) bridging ligands**

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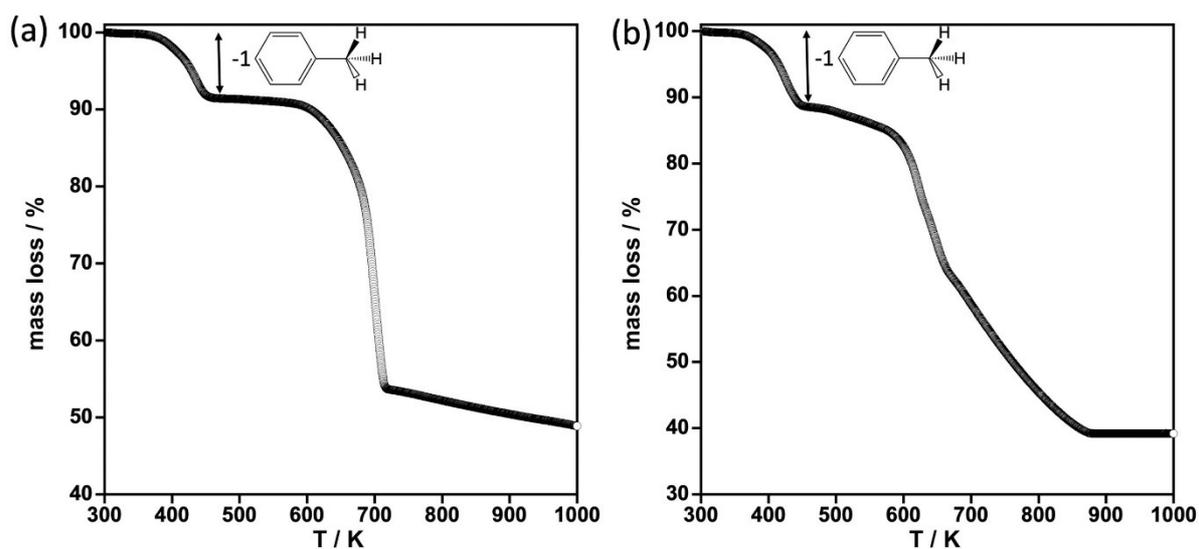
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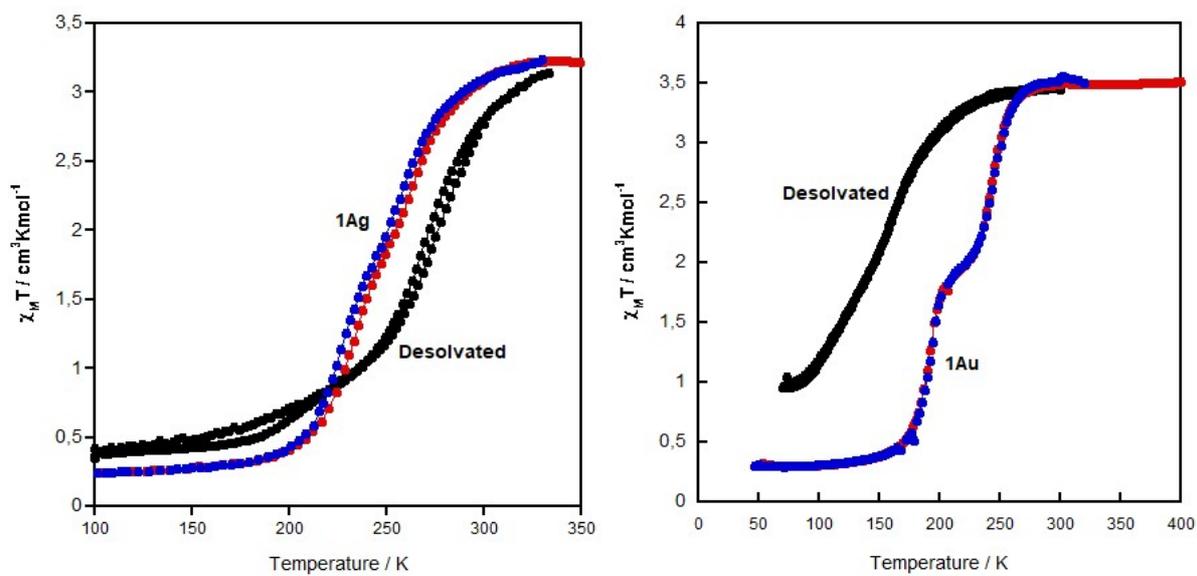
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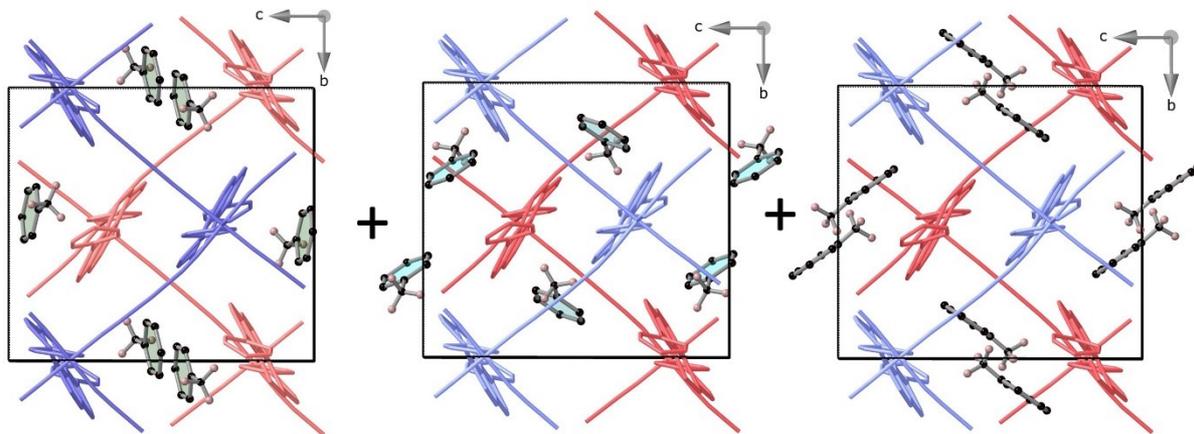
Table S1. Relevant crystallographic data of **1Au**.

	300 K	220 K	120 K
Empirical formula	C <sub>37</sub> H <sub>20</sub> N <sub>6</sub> Au <sub>2</sub> Fe	C <sub>37</sub> H <sub>22.50</sub> N <sub>6</sub> Au <sub>2</sub> Fe	C <sub>37</sub> H <sub>24</sub> N <sub>6</sub> Au <sub>2</sub> Fe
<i>Mr</i>	998.37	1000.89	1002.40
Crystal system	monoclinic		
Space group	P2 <sub>1</sub> /c		
<i>a</i> (Å)	18.4123(3)	18.2575(3)	18.1084(3)
<i>b</i> (Å)	13.3795(2)	13.3689(2)	13.3261(2)
<i>c</i> (Å)	15.9755(2)	15.6321(3)	15.2744(2)
$\beta$ (°)	106.323(2)	105.192(2)	104.445(2)
<i>V</i> (Å <sup>3</sup> )	3776.89(10)	3682.18(11)	3569.41(10)
<i>Z</i>	4		
Crystal color	yellow	orange	red
<i>D<sub>c</sub></i> (mg cm <sup>-3</sup> )	1.756	1.805	1.865
<i>F</i> (000)	1872	1882	1888
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	17.599	18.052	18.623
Crystal size (mm)	0.02x0.02x0.10		
No. of total reflection	7637	7484	7257
No. of reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	5688	5330	5998
<i>R</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0426	0.0501	0.0507
<i>wR</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.1224	0.1291	0.1330
<i>S</i>	1.026	1.039	1.049

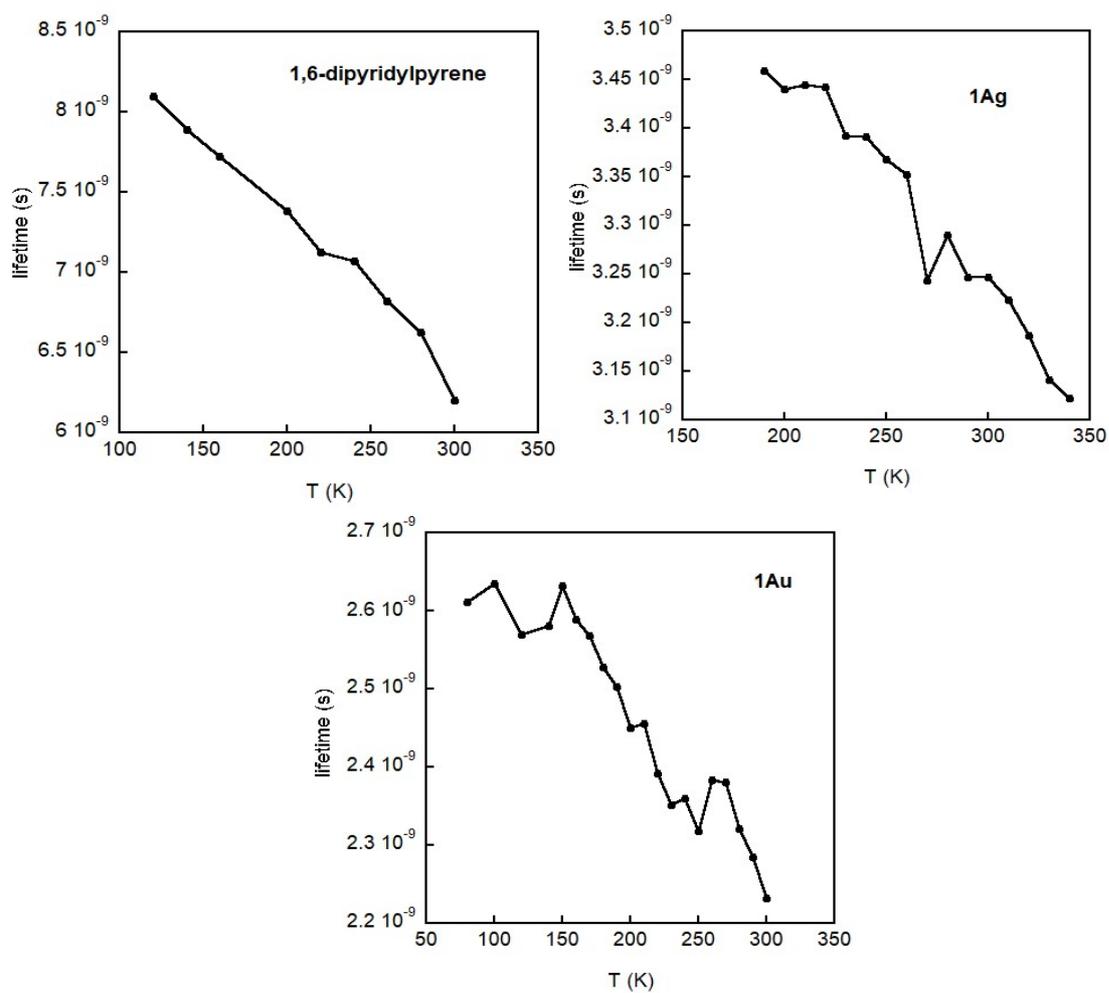
Figure S1. Thermogravimetric analysis of **1Au** (a) and **1Ag** (b).



**Figure S2.**  $\chi_M T$  vs. T plots for **1Ag** and **1Au**, before and after toluene release.



**Figure S3.** Positional disorder of the toluene molecule resolved in three separated snapshots.



**Figure S4.** Intensity average lifetime as a function of temperature for the free ligand 1,6-dipyridylpyrene, and the compounds **1Ag** and **1Au**.