

## Electronic supplementary information

Substituent effects on spin-crossover Fe(II)N<sub>4</sub>O<sub>2</sub> pyrenyl hydrazone complexes  
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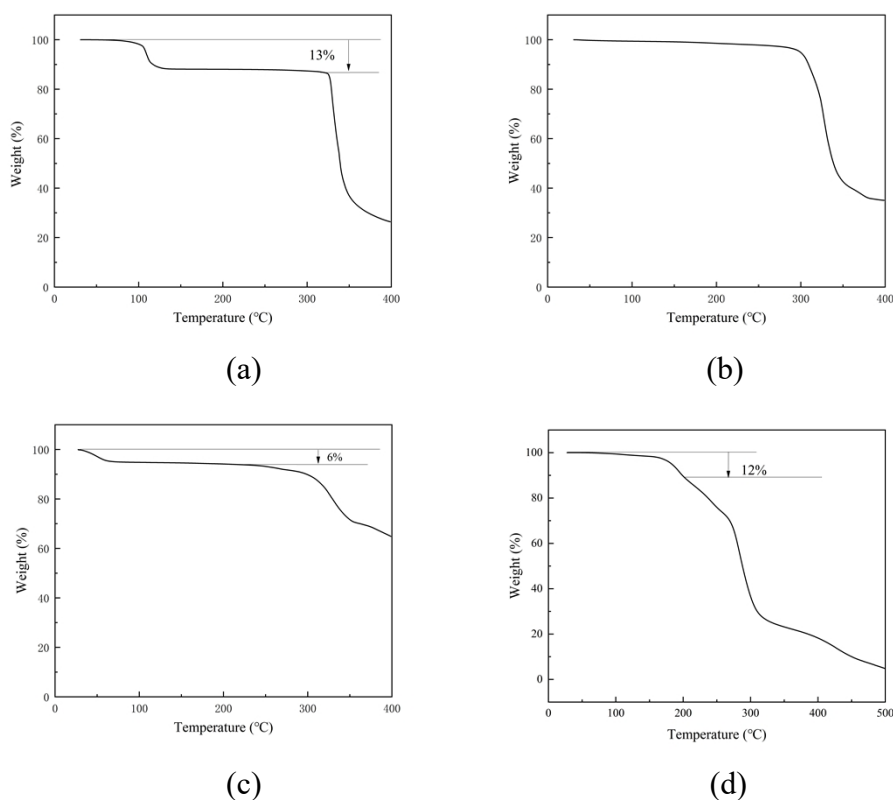
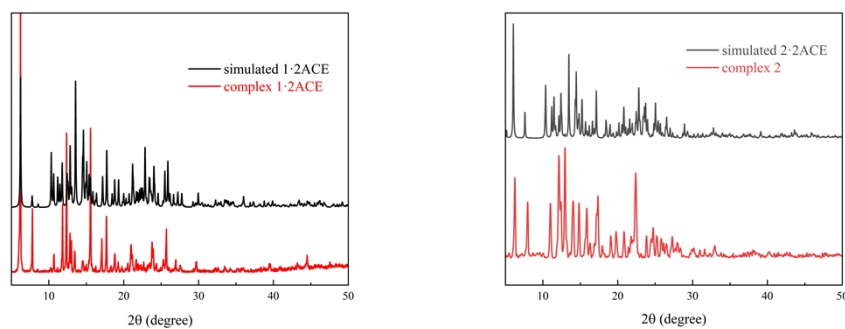


Fig. S1. The thermogravimetric analyses (TGA) for complexes **1·2ACE** (a), **2** (b), **3·ACE** (c) and **4·6H<sub>2</sub>O** (d).



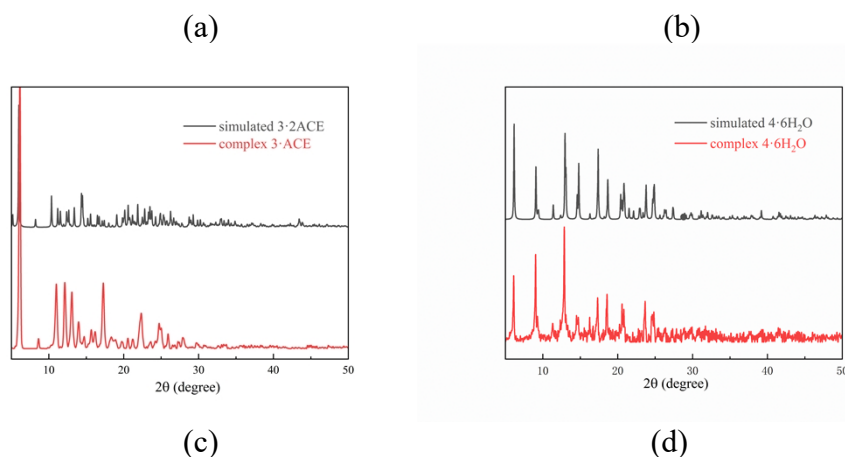


Fig. S2. The powder XRD patterns of the complexes and that simulated from crystal data.

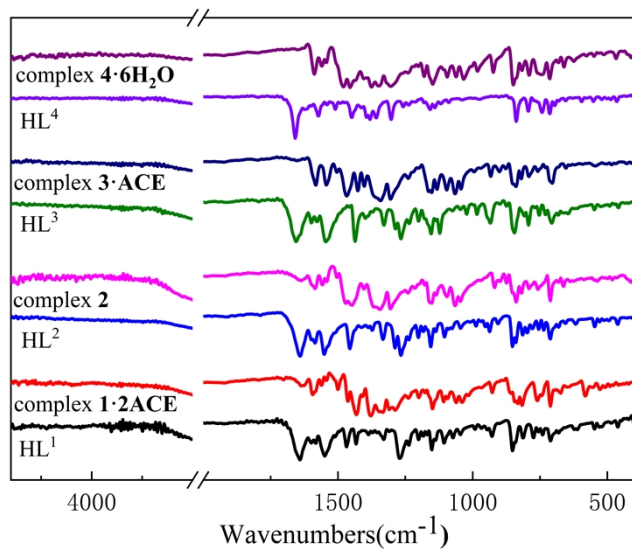
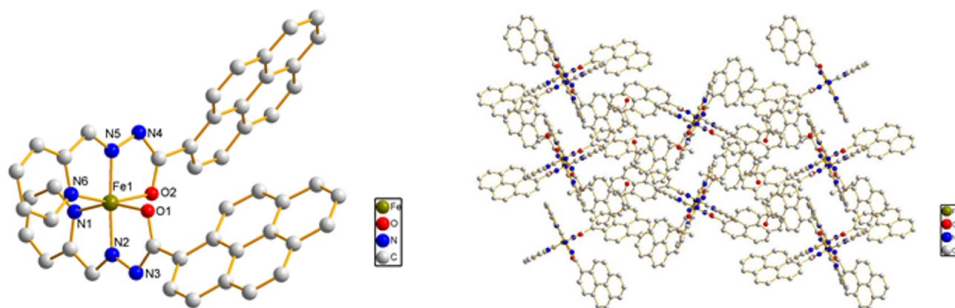


Fig. S3. The IR spectra of ligand HL<sup>1-4</sup> and the complexes.



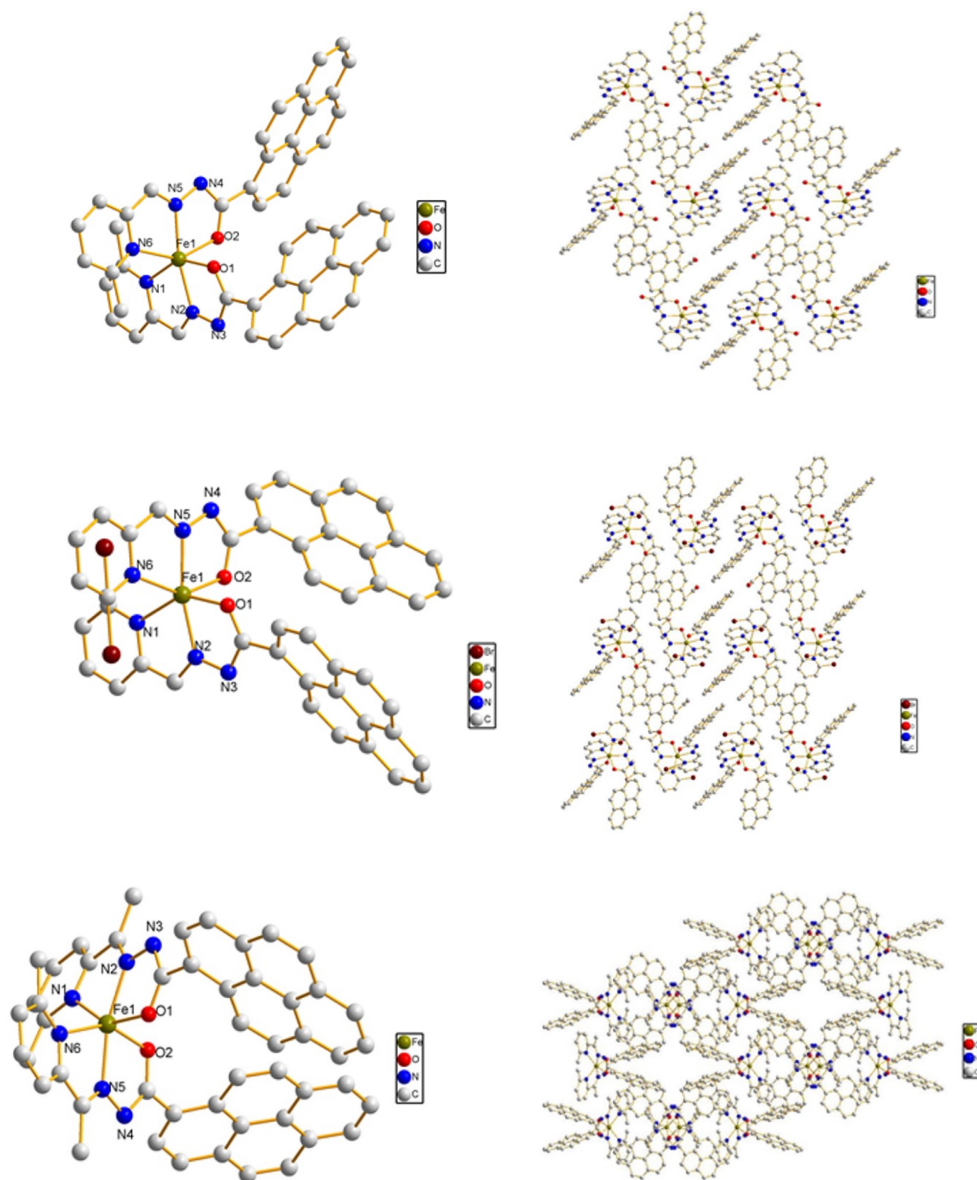


Fig. S4. Crystal structure and two-dimensional supramolecular structure of complexes  $1 \cdot 2\text{ACE} - 3 \cdot 2\text{ACE}$  and  $4 \cdot 6\text{H}_2\text{O}$ . Hydrogen atoms and acetone have been omitted for clarity.

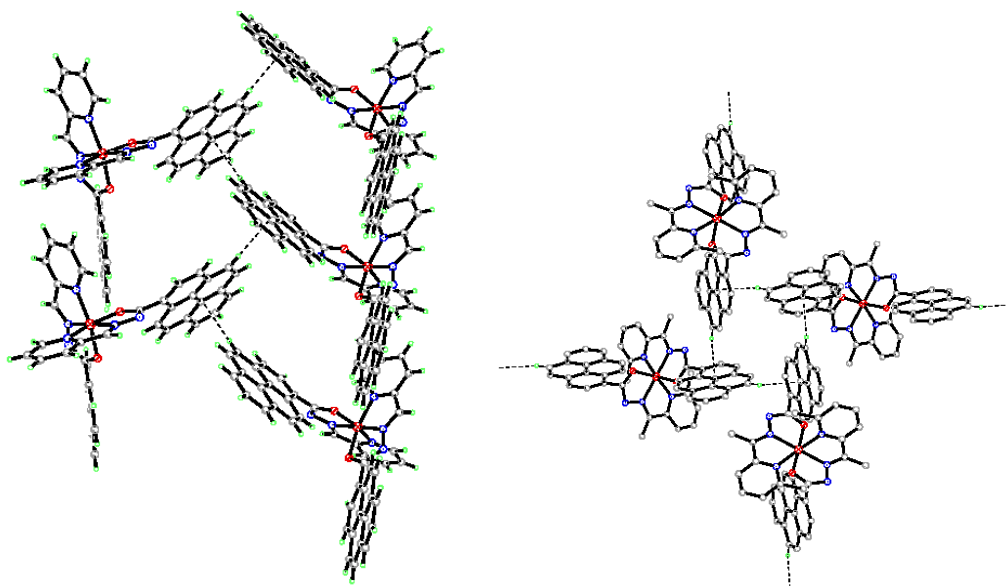


Fig. S5. Left: C-H... $\pi$  linked supramolecular 1D chain structure in complexes **1**·**2ACE** - **3**·**2ACE**. Right: C-H... $\pi$  linked supramolecular 2D structure based on the  $\text{Fe}_4$  units for complex **4**·**6H<sub>2</sub>O**.

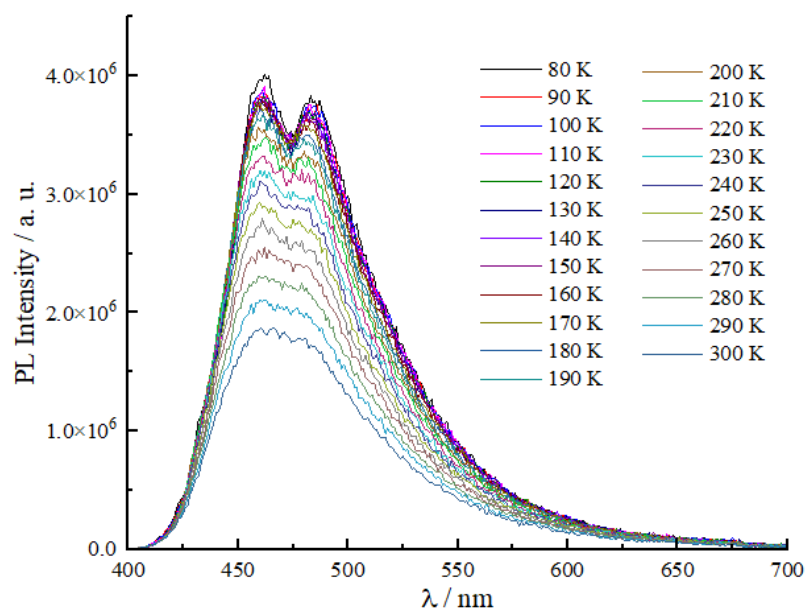


Fig. S6. Solid state temperature-dependent emission spectra of the free ligand HL<sup>4</sup> ( $\lambda_{\text{ex}} = 350 \text{ nm}$ ).