Supplementary Information for:

Charge-transfer metal-organic frameworks based on CuCN architecture units: crystal structures, luminescence properties and theoretical investigations

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$$Cu^{2+} + [Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + Cu^{+}$$

$$nCu^{+} + nCN^{-} + mL \rightarrow [(CuCN)_nL_m] \text{ (L =bix, bmimb, bimb)}$$

(**1**, $n = 4$, $m = 2$; **2**, **3**, $n=2$, $m = 1$; **4**, $n=3$, $m = 1$)

Scheme S1. A reasonable mechanism under the solvothermal condition

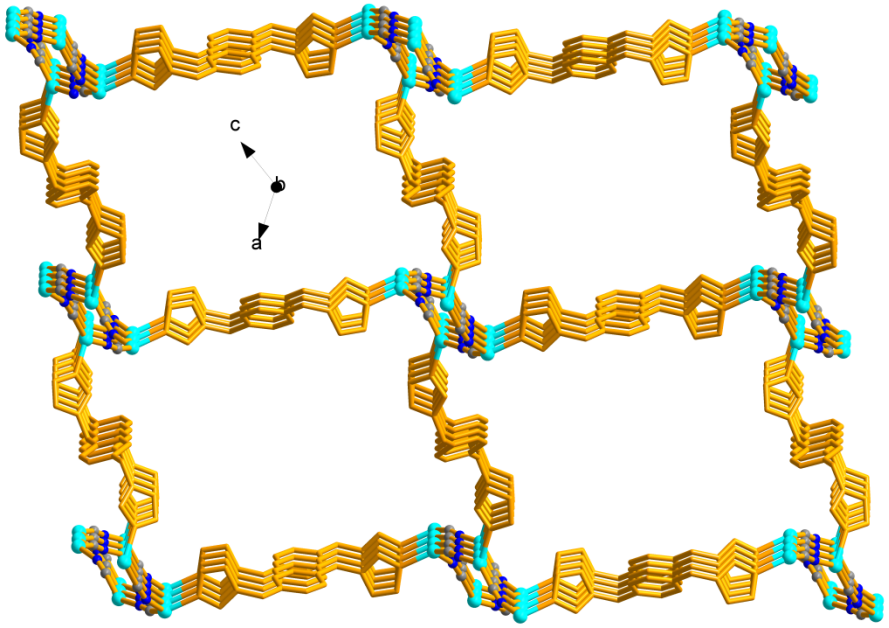


Fig. S1 View of the 3D framework of complex **1** along the *b*-axis, H-atoms have been omitted for clarity.

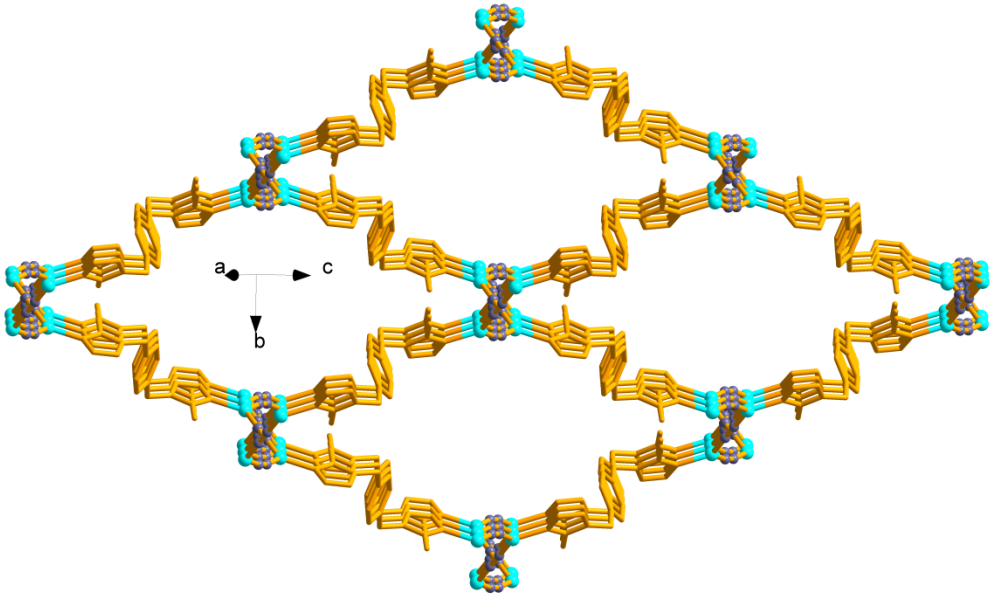


Fig. S2 View of the 3D framework of complex **2** along the [101] direction, H-atoms have been omitted for clarity.

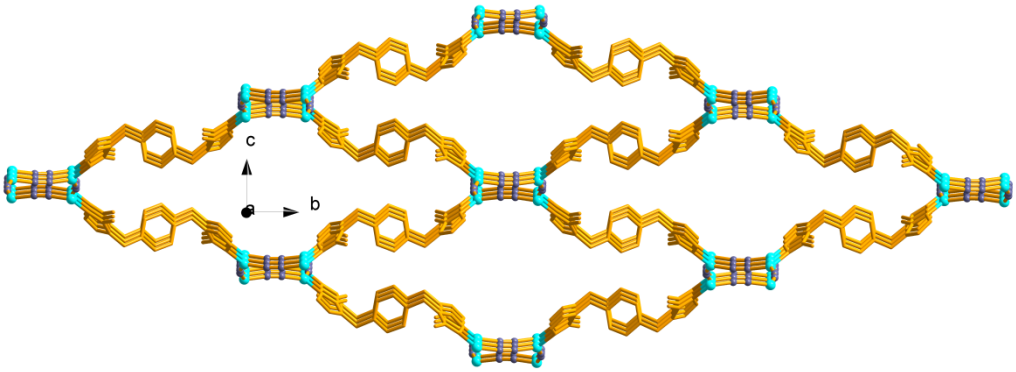


Fig. S3 View of the 3D framework of complex **3** along the *a*-axis, H-atoms have been omitted for clarity.

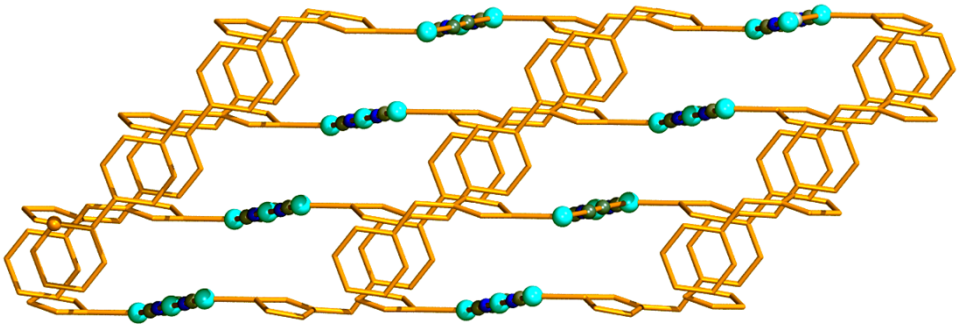


Fig. S4 View of the 3D supramolecular framework of complex **4** along the [110] direction, H-atoms have been omitted for clarity.

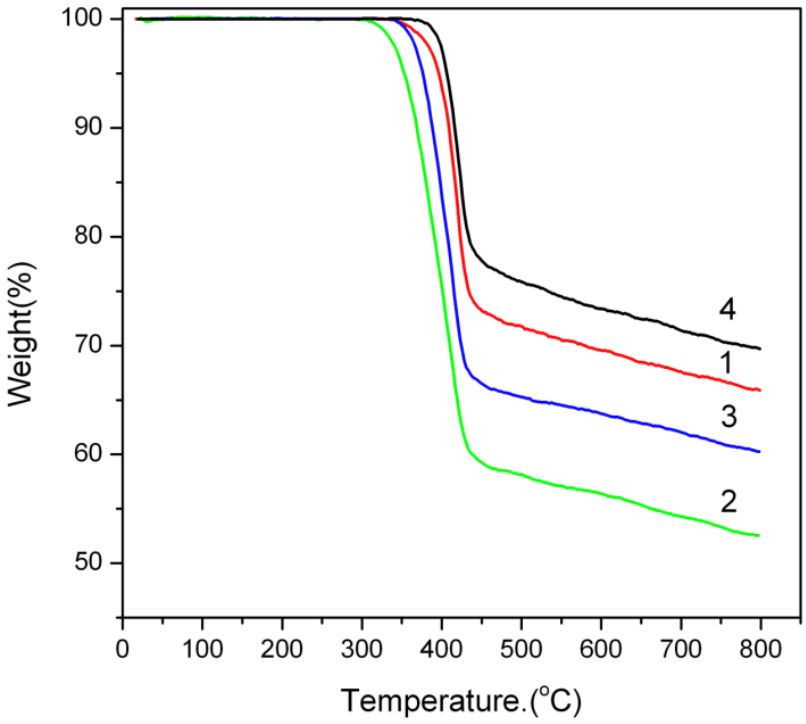


Fig. S5 Thermogravimetry curves for **1-4**

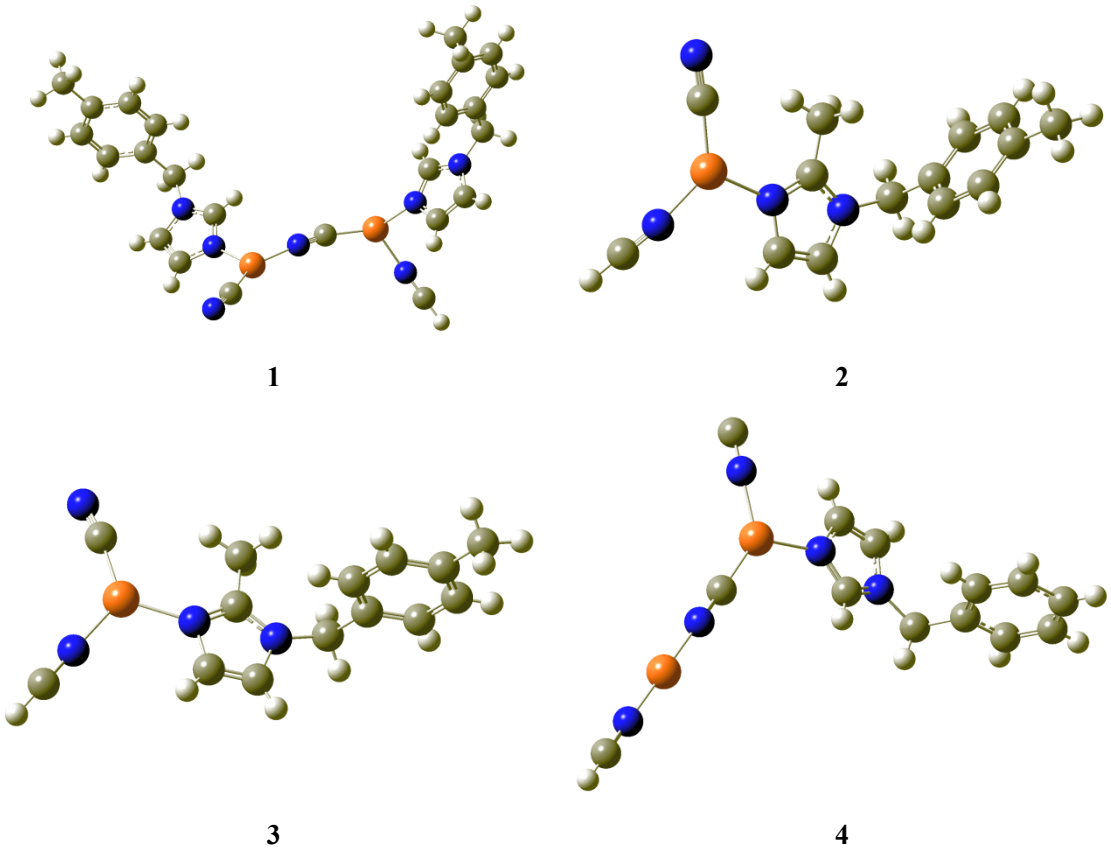
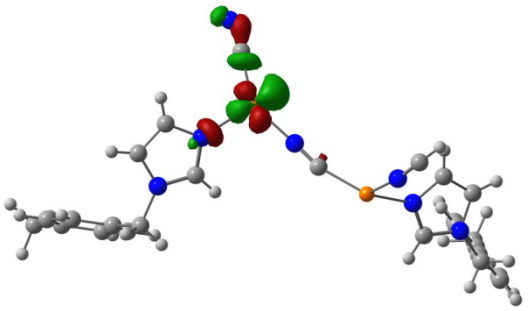
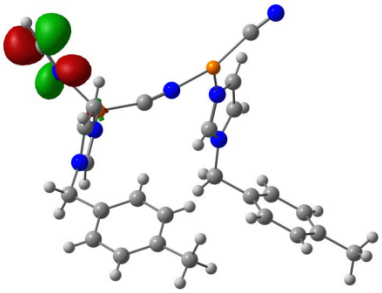


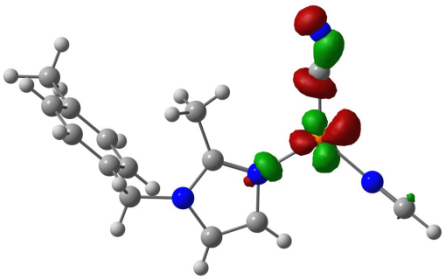
Fig. S6 Calculation models of **1-4.**

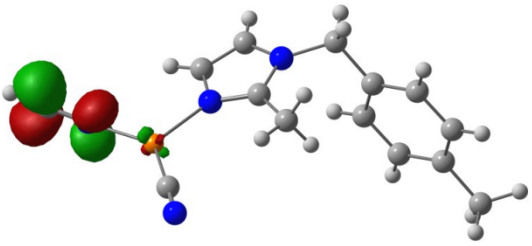




HOMO **LUMO**

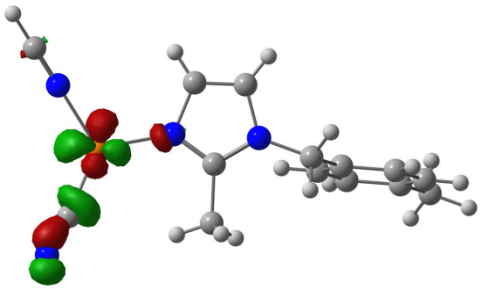
1

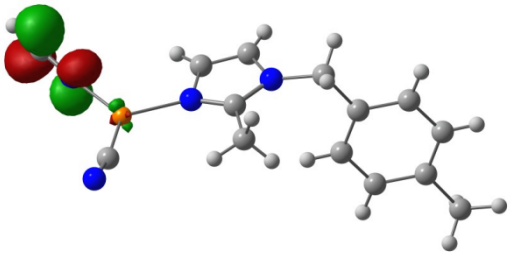




HOMO **LUMO**

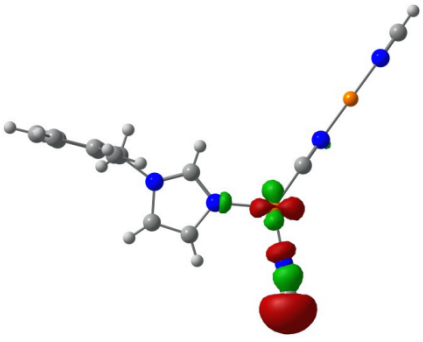
2

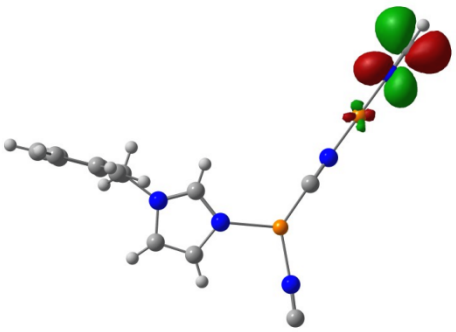




HOMO **LUMO**

3





HOMO **LUMO+1**

4

Fig. S7 Frontier molecular orbitals of **1-4** for the ground state geometry in the gas phase.