Supplementary Information for:

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

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

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

(1, \( n=4, m=2 \); 2, \( n=2, m=1 \); 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.
**Fig. S7** Frontier molecular orbitals of 1-4 for the ground state geometry in the gas phase.