Electronic Supplementary Material

Controllable dimensions copper cyanide polymers modulated by rigid and flexible bis-(imidazole) ligands: synthesis, crystal structure and fluorescence properties

Hui Xu,[ab] Bo-Yu Zhou,[c] Kai Yu,[b] Zhan-Hua Su,[b] Bai-Bin Zhou,*[b] and Zhong-Min Su*[a]

[a]*College of Chemistry, Jilin University, Changchun, 130012, PR China;*

[b]*Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, Harbin Normal University, Harbin 150025, People's Republic of China;*

[c]*Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900, Sichuan, China;*

1. Structural figures

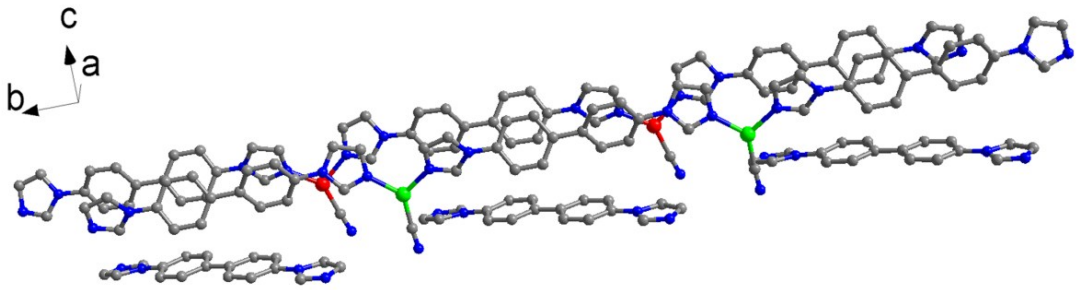


Fig. S1 The 1D parallel chains of polymer **1** along crystallographic *a*-axis. (All H atoms were omitted for clarity).

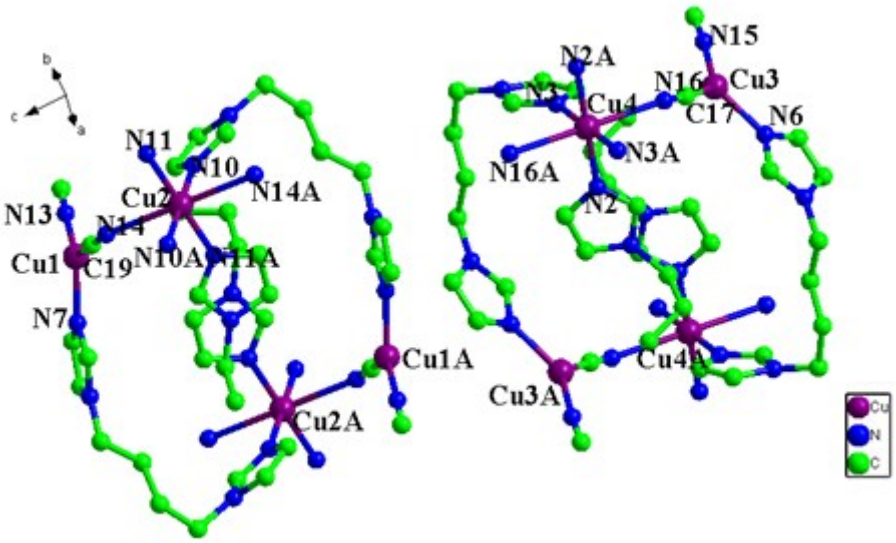


Fig. S2 View of the coordination environments of Cu atoms in polymer **2**.

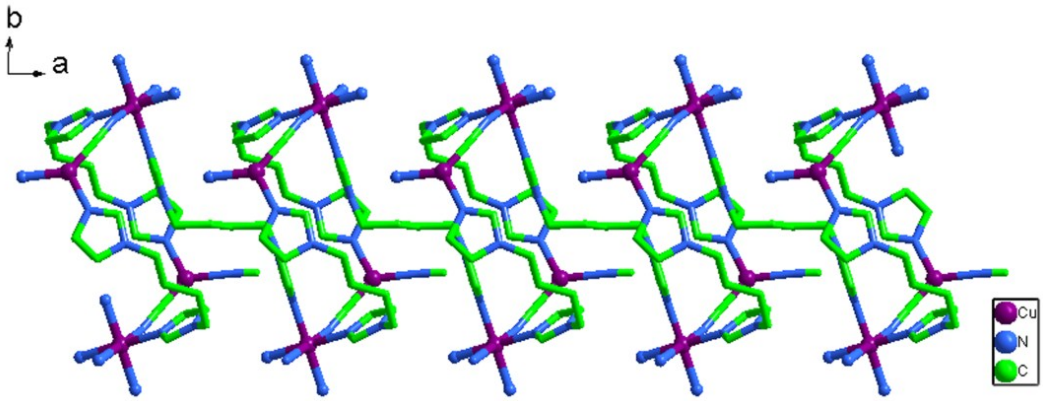


Fig. S3 The 1D chain shown from *a* direction in polymer **2**.

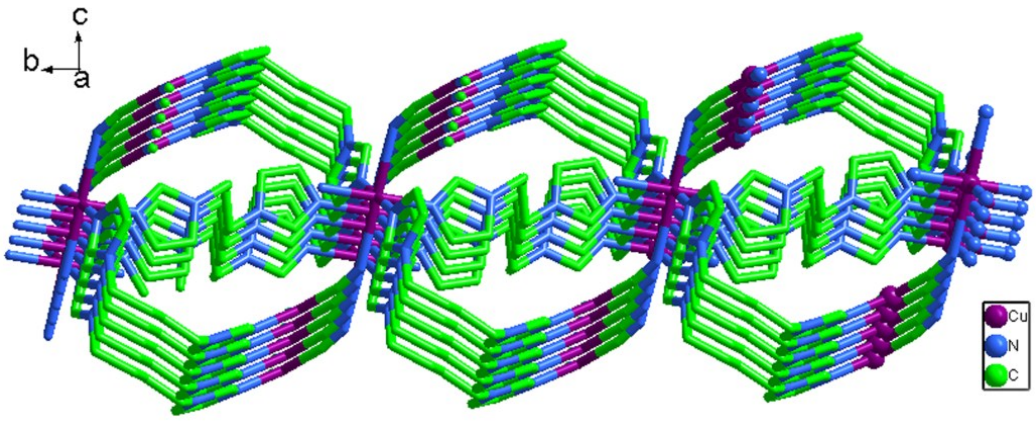


Fig. S4 View of 2D layer structures of polymer **2** along the crystallographic *a* axis.

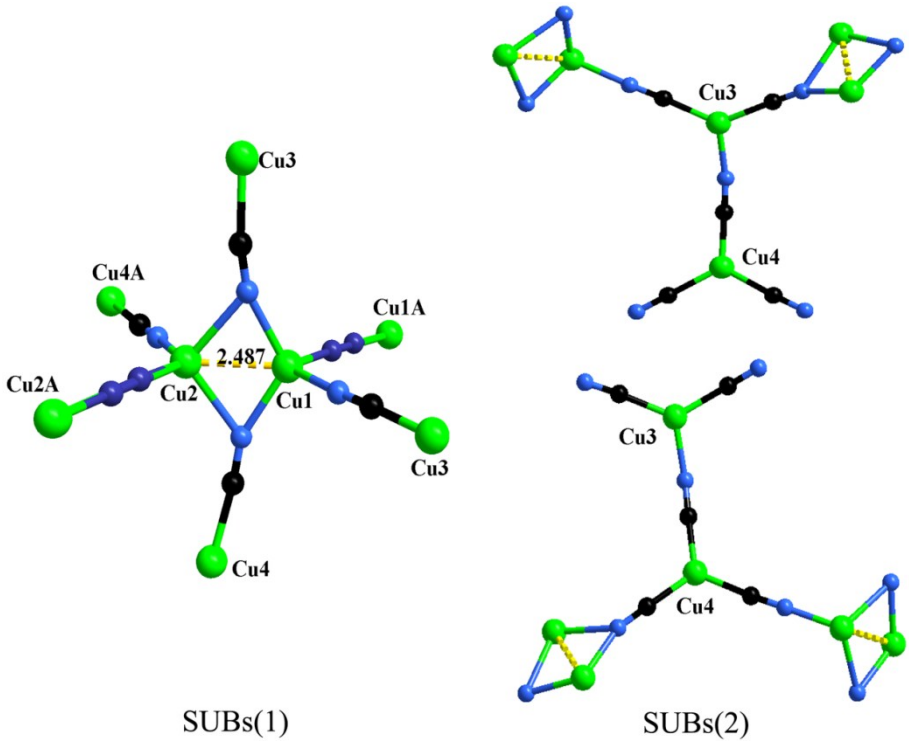


Fig. S5 Two kinds of secondary building units in polymer **3**.

2. Physical characterization

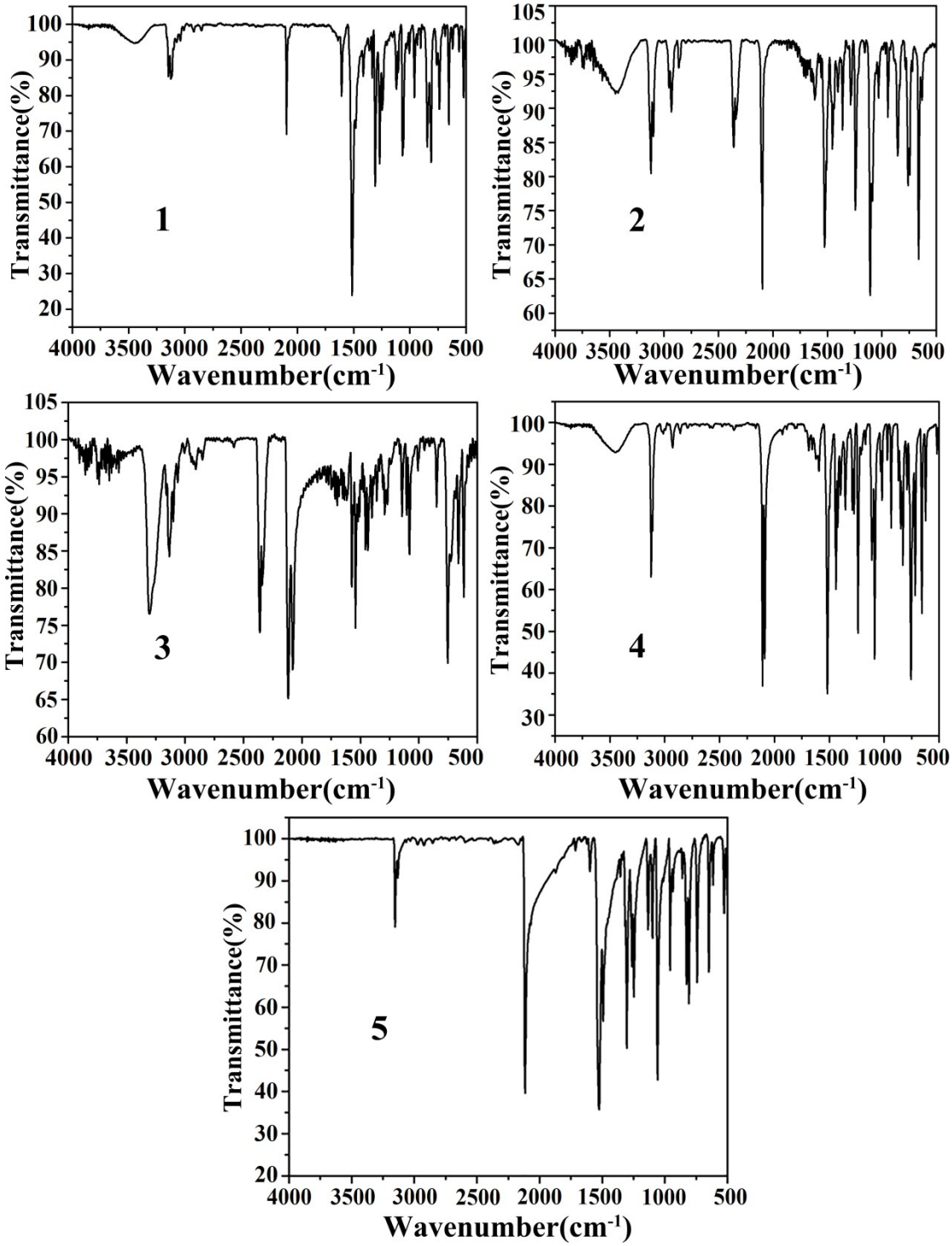


Fig. S6 IR spectra of **1-5**.

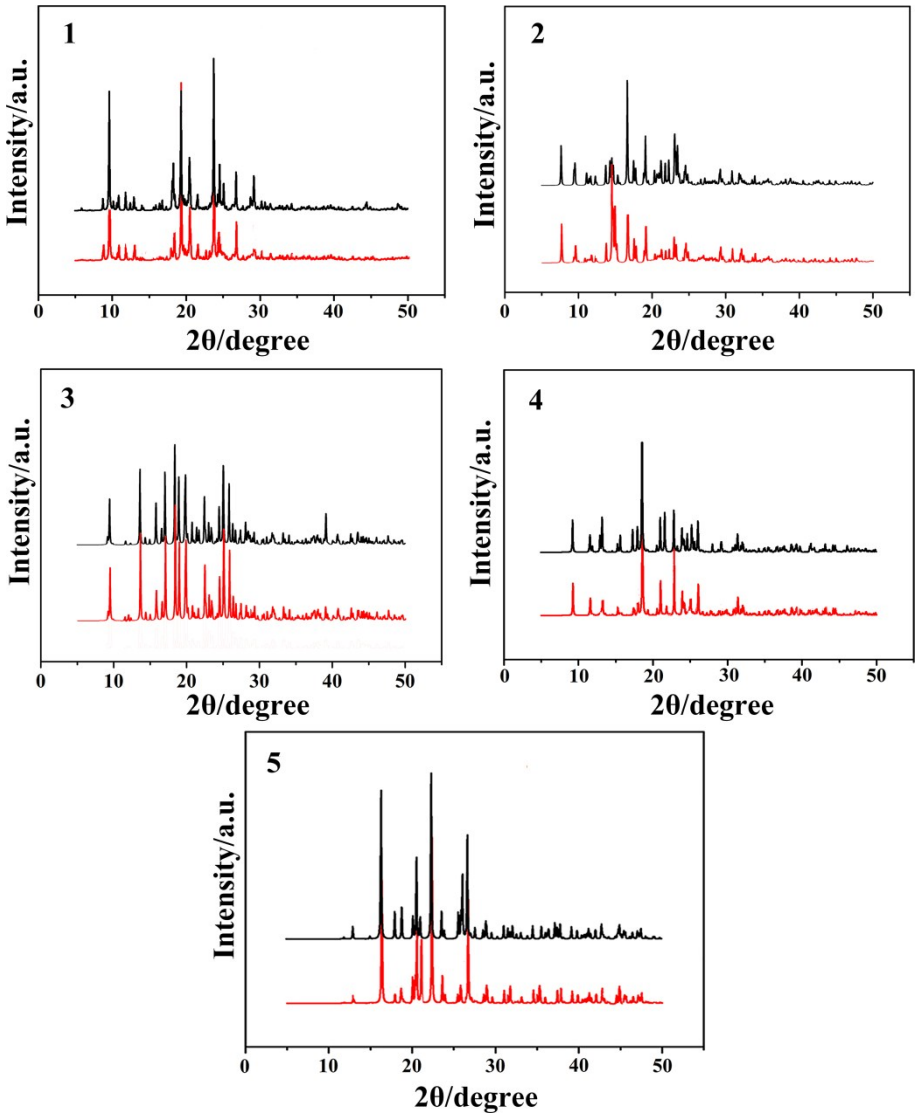


Fig. S7 PXRD contrast curves of **1-5**.

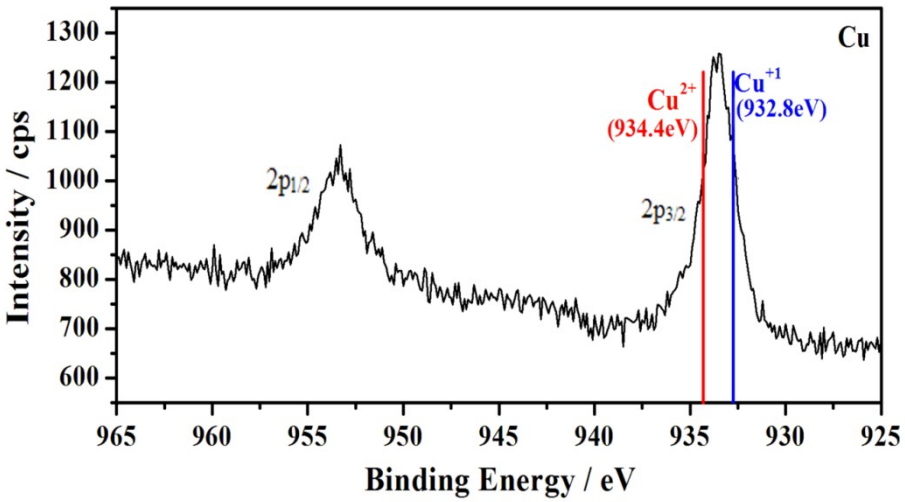


Fig. S8 The XPS spectra of polymer **2**.

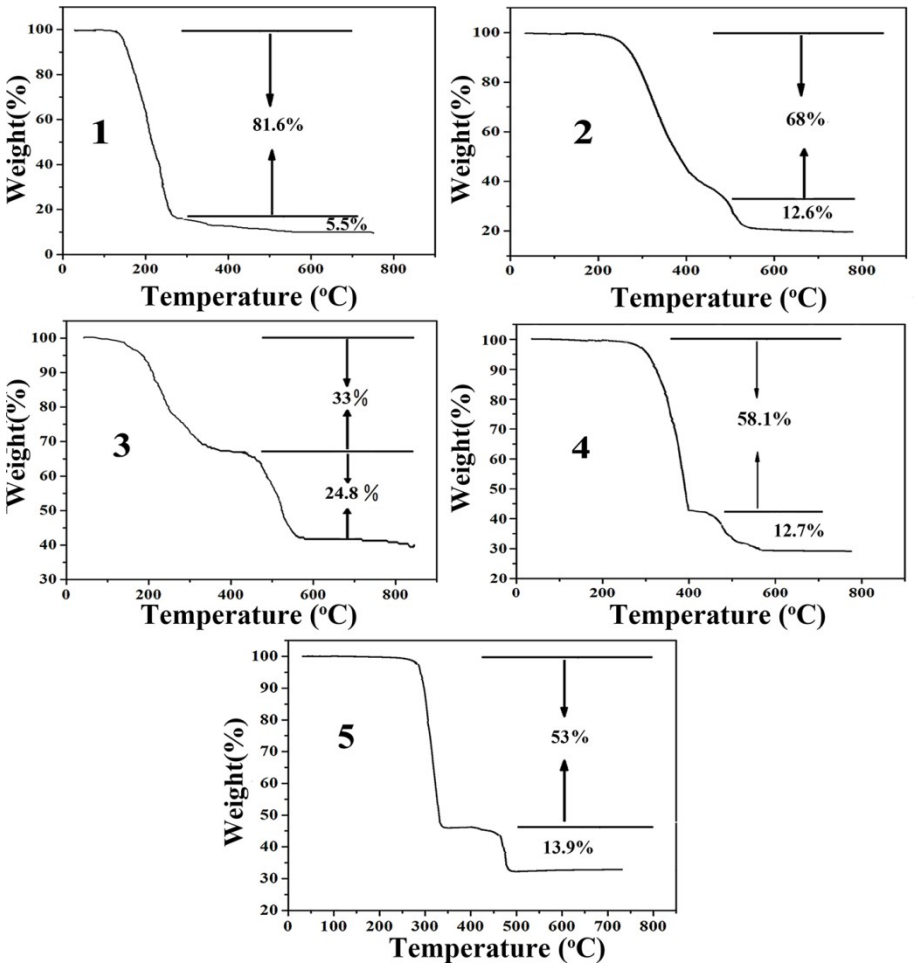


Fig. S9 TG curves of polymers **1-5**.

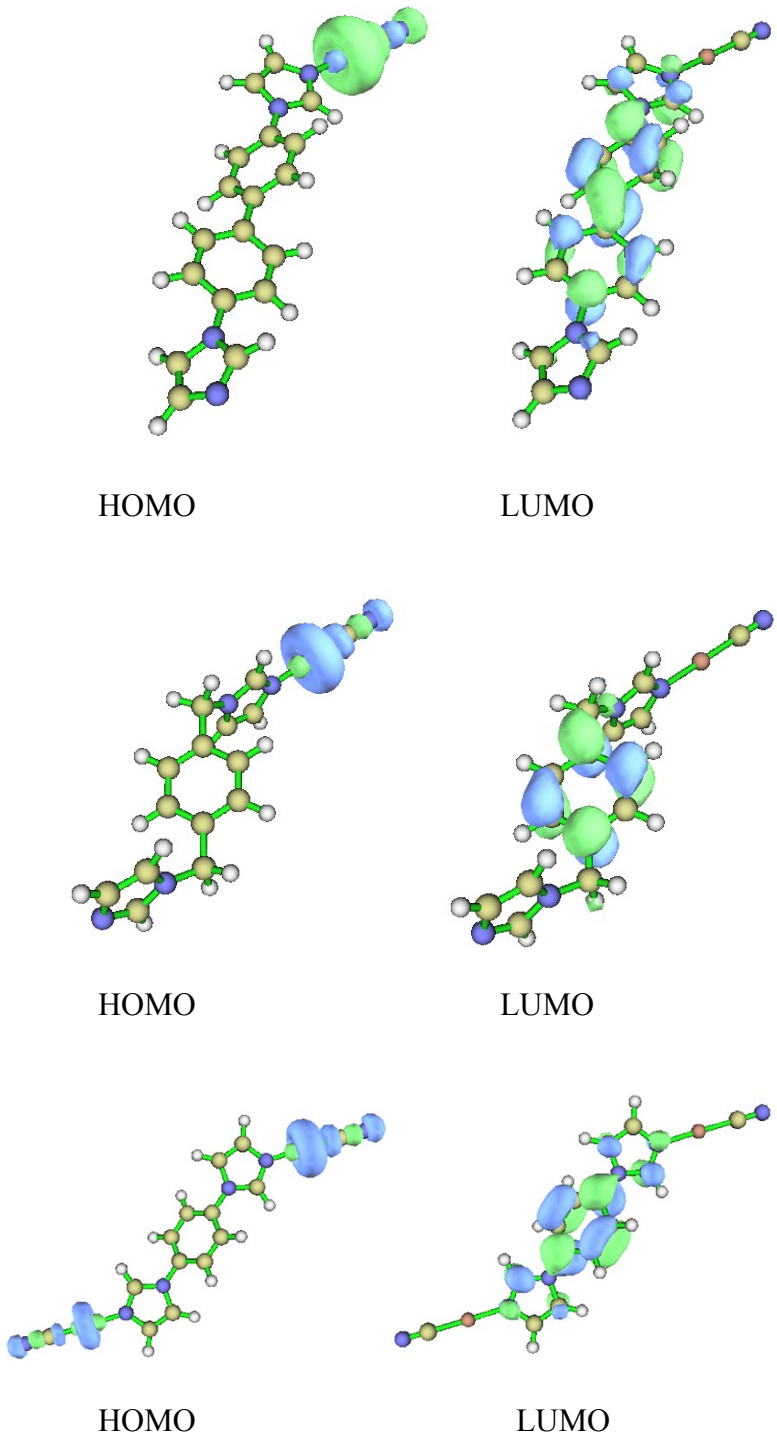


Fig. S10 Electron-density distribution of the lowest unoccupied and highest occupied orbitals calculated for **1** (top), **4** (middle) and **5** (bottom).

Table S1. Crystal data for polymers **1-5**

Polymer	**1**	**2**	**3**	**4**	**5**
Chemical formula	$C_{56}H_{42}Cu_2N_{14}$	$C_{34}H_{42}Cu_3N_{16}$	$C_{16.62}H_{18}Cu_4N_{10.38}$	$C_{16}H_{14}Cu_2N_6$	$C_7H_5CuN_3$
Formula weight	1038.14	865.49	617.37	417.43	194.69
Crystal. size, mm^3	0.29 x 0.26 x 0.18	0.280x0.260 x 0.180	0.240 x 0.220 x 0.220	0.36 x 0.28 x 0.30	0.28 x0.25 x0.19
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$	P-1	$P2_12_12$	$P2_1$/n	$C\ 2/C$
a, Å	15.071(3)	8.0872(5)	13.0156(6)	8.8138(18)	11.089(7)
b, Å	17.319(4)	10.2331(6)	14.3792(7)	15.406	8.790(5)
c, Å	18.468(4)	23.4179(13)	12.3581(6)	12.203	15.236(9)
α	90	88.4500(10)	90	90	90
β, deg	96.99(3)	80.9560(10)	90	94.92(3)	102.882(11)
γ	90	86.5680	90	90	90
V ($Å^3$)	4784.6(18)	1910.17(19)	2312.87(19)	1650.9(6)	1447.6(15)
Z	4	2	4	4	8
D_{calc}/Mg m^{-3}	1.441	1.505	1.773	1.679	1.786
μ(MoKα), mm^{-1}	0.945	1.704	3.654	2.585	2.941
F(000), e	2580	1032	688	1071	776.0
θ range, deg/°	1.36- 27.24	2.17- 28.37	2.17 - 28.34	2.64-27.41	2.74-28.23
Reflections collected/unique/ R_{int}	27259/10716/ 0.0398	17744 /9557/ 0.0272	14112 / 5788/ 0.0272	9446 / 3769 / 0.0220	4389 / 1758/ 0.0283
Data/restraints/ parameters	10505 / 0 / 649	9251 / 0 / 481	5758 / 0 / 281	3722 / 0 / 217	1758/0/ 101
R_1/ wR_2 $[I \geq 2\sigma(I)]$[a]	0.0458 / 0.1051	0.0447 / 0.0970	0.0372/ 0.0793	0.0295/0.0754	0.0291/0.0765
GOF on F^2	1.015	1.012	1.015	1.060	1.059
$\Delta\rho$fin(max/min),e$Å^{-3}$	0.488/ -0.346	0.536/ -0.376	0.575/ -0.391	0.442/-0.502	0.460/-0.288

[a] $R_1 = \sum||F_0|-|F_C||/\sum|F_0|$; $wR_2 = \sum[w(F_0^2-F_C^2)^2]/\sum[w(F_0^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å) and bond angles (°) for polymers **1-5**

Polymer **1**

Cu(1)-C(38)	1.883(3)	Cu(2)-C(1)	1.879(3)
Cu(1)-N(7)	1.971(2)	Cu(2)-N(2)	2.002(2)
Cu(1)-N(8)	2.059(2)	Cu(2)-N(3)	2.012(2)
C(38)-Cu(1)-N(7)	140.88(11)	C(1)-Cu(2)-N(3)	124.82(12)
C(38)-Cu(1)-N(8)	115.02(11)	C(1)-Cu(2)-N(2)	129.78(12)
N(7)-Cu(1)-N(8)	104.04(10)	N(2)-Cu(2)-N(3)	105.26(10)

Polymer **2**

Cu(1)-C(19)	1.924(3)	Cu(3)-N(6)	2.056(3)
Cu(1)-N(7)	2.024(3)	Cu(3)-N(15)	1.998(4)
Cu(1)-N(13)	2.024(4)	Cu(3)-C(17)	1.929(4)
Cu(2)-N(11)#1	2.022(2)	Cu(4)-N(3)	2.025(2)
Cu(2)-N(11)	2.022(2)	Cu(4)-N(3)#2	2.025(2)
Cu(2)-N(10)	2.027(2)	Cu(4)-N(2)	2.026(2)
Cu(2)-N(10)#1	2.027(2)	Cu(4)-N(2)#2	2.026(2)
Cu(2)-N(14)	2.552	Cu(4)-N(16)	2.528
C(19)-Cu(1)-N(7)	114.82(11)	C(17)-Cu(3)-N(15)	131.72(12)
C(19)-Cu(1)-N(13)	131.25(12)	C(17)-Cu(3)-N(6)	110.59(11)
N(7)-Cu(1)-N(13)	113.53(11)	N(15)-Cu(3)-N(6)	117.65(12)
N(11)-Cu(2)-N(11)#1	180.00(14)	N(3)#2-Cu(4)-N(3)	180.0
N(11)-Cu(2)-N(10)	88.26(9)	N(3)#2-Cu(4)-N(2)	91.38(9)
N(11)#1-Cu(2)-N(10)	91.74(9)	N(3)-Cu(4)-N(2)	88.62(9)
N(11)-Cu(2)-N(10)#1	91.74(9)	N(3)#2-Cu(4)-N(2)#2	88.62(9)
N(11)#1-Cu(2)-N(10)#1	88.26(9)	N(3)-Cu(4)-N(2)#2	91.38(9)
N(10)-Cu(2)-N(10)#1	180.00(12)	N(2)-Cu(4)-N(2)#2	180.00(14)

Polymer **3**

Cu(1)-N(8)	1.971(4)	Cu(2)-N(5)	2.294(5)
Cu(1)-N(7)	2.006(4)	Cu(3)-C(14)#1	1.881(4)
Cu(1)-N(5)	2.031(5)	Cu(3)-N(11)	1.947(5)
Cu(1)-N(6)	2.047(5)	Cu(3)-C(13)	1.904(4)
Cu(2)-N(10)	1.925(4)	Cu(4)-C(15)#2	1.904(4)
Cu(2)-N(9)	1.934(5)	Cu(4)-C(16)	1.909(4)
Cu(2)-N(6)	2.225(4)	Cu(4)-C(12)	1.878(5)
N(8)-Cu(1)-N(7)	107.13(16)	N(10)-Cu(2)-N(5)	101.48(17)
N(8)-Cu(1)-N(5)	109.30(16)	N(9)-Cu(2)-N(5)	109.27(15)
N(7)-Cu(1)-N(5)	108.95(16)	N(6)-Cu(2)-N(5)	100.95(17)
N(8)-Cu(1)-N(6)	107.83(17)	C(14)#1-Cu(3)-C(13)	129.19(17)
N(7)-Cu(1)-N(6)	105.72(15)	C(14)#1-Cu(3)-N(11)	120.91(18)
N(5)-Cu(1)-N(6)	117.43(17)	C(13)-Cu(3)-N(11)	109.84(17)
N(10)-Cu(2)-N(9)	124. 60(17)	C(15)#2-Cu(4)-C(16)	119.03(17)
N(10)-Cu(2)-N(6)	104.72(17)	C(15)#2-Cu(4)-C(12)	119.79(19)
N(9)-Cu(2)-N(6)	112.85(16)	C(16)-Cu(4)-C(12)	121.16(18)

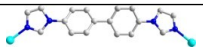
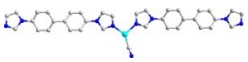
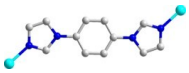
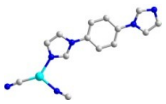
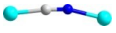
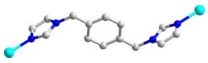
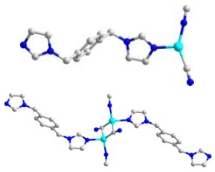
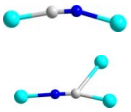
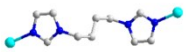
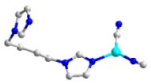
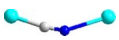
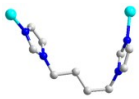
Polymer **4**			
Cu(1)-C(8)	1.924(2)	Cu(1)-Cu(1)#2	2.5766(8)
Cu(1)-N(8)	2.007(2)	Cu(2)-C(9)	1.896(2)
Cu(1)-N(1)	2.0458(19)	Cu(2)-N(7)	1.916(2)
Cu(1)-C(8)#2	2.476(3)	Cu(2)-N(3)	2.058(2)
C(8)-Cu(1)-N(8)	121.28(9)	N(8)-Cu(1)-Cu(1)#2	128.61(7)
C(8)-Cu(1)-N(1)	123.45(9)	N(1)-Cu(1)-Cu(1)#2	119.54(6)
N(8)-Cu(1)-N(1)	99.08(8)	C(8)#2-Cu(1)-Cu(1)#2	44.71(5)
C(8)-Cu(1)-C(8)#2	109.59(7)	C(9)-Cu(2)-N(7)	143.74(9)
N(8)-Cu(1)-C(8)#2	104.24(9)	C(9)-Cu(2)-N(3)	111.92(9)
N(1)-Cu(1)-C(8)#2	94.86(8)	N(7)-Cu(2)-N(3)	104.32(8)
C(8)-Cu(1)-Cu(1)#2	64.87(7)		

Polymer **5**			
C(7)-Cu(1)	1.860(2)	N(3)-Cu(1)-N(2)	98.22(9)
N(3)-Cu(1)	1.980(2)	C(7)#2-N(3)-Cu(1)	164.12(18)
Cu(1)-N(2)	1.993(19)	C(7)-Cu(1)-N(3)	125.16(9)
N(3)#1-C(7)-Cu(1)	174.63(19)	C(7)-Cu(1)-N(2)	136.61(8)

Table S3. Bond-valence sum calculations values in polymer **2**

Bond type	Bond distance/Å	Bond valence I	Bond valence II	Bond valance sum
Cu(1)-N(7)	2.024(3)	0.297		1.068 for Cu1
Cu(1)-N(13)	2.024(4)	0.297		
Cu(1)-C(19)	1.924(3)	0.474		
Cu(3)-N(6)	2.056(3)	0.272		1.058 for Cu3
Cu(3)-N(15)	1.998(4)	0.318		
Cu(3)-C(17)	1.929(4)	0.468		
Cu(2)-N(11)	2.022(2)		0.298	1.338 for Cu2
Cu(2)-N(10)	2.027(2)		0.294	
Cu(2)-N(14)	2.552		0.077	
Cu(4)-N(3)	2.025(2)		0.296	1.334 for Cu4
Cu(4)-N(2)	2.026(2)		0.295	
Cu(4)-N(16)	2.528		0.076	

Table S4. The summary of the dimension, conformation of ligands, coordinated numbers of Cu and bridging modes of CN^- anions in **1–5**

	Compound	Ligands	Coordinated number of Cu	Dimension	Conformation of ligands	Schematic diagram of Cu and ligands	Bridging modes of CN^- anion
Rigid ligand	1	bbi	3	1D			
	5	bib	3	2D			
	4	bix	3,6	3D			
Flexible ligand	2	bimb	3,6	2D			
							
	3	dip	3,6	3D