

Supporting Information

Facilely controllable synthesis of copper-benzothiadiazole complexes via solvothermal reactions: exploring the customized synthetic approach by experiments

Chen Hu,^{†,‡} Yingnan Zhao,^{†,‡} Xiao Han,[‡] Jiaqi Song,[†] Jie Ding,^{*,†} Hongwei Hou^{*,†}

[†]Green Catalysis Center, College of Chemistry, Zhengzhou University, Henan 450001, China.

[‡]College of Chemical Engineering & Material, Handan University, Hebei, 056005, China.

E-mail: jieding@zzu.edu.cn; E-mail: [houhongw@zzu.edu.cn](mailto:huhongw@zzu.edu.cn).

Experimental Details

Materials. All chemical reagents were purchased from commercial suppliers without further purification.), the synthetic procedure of **L1** is according to the literature.¹

Physical Measurements. The FT-IR spectra were recorded in the range of 400–4000 cm^{-1} on a Bruker Tensor 27 spectrophotometer from KBr pellets. The elemental analyses were performed with FLASH EA 1112 elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded on Cu $K\alpha_1$ radiation on a PANalyticalX'Pert PRO diffractometer. Thermal analyses were carried out on a Netzsch STA 449C thermal analyzer at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ in air. UV-Vis absorption spectra were obtained from a JASCO FP-8300 UV/Vis Spectrophotometer at room temperature. The measurements of steady-state emission spectra were conducted on a JASCO FP-8300 fluorescence spectrophotometer at room temperature. The emission lifetime were detected with a photoluminescence quantum yield measurement system (Edinburgh Instruments Ltd FLS980 Fluorescence Spectrometer, the fluorescence lifetime measurement range is 100 ps ~ 50 μs .) at room temperature. The results from the PXRD patterns are in close agreement with that calculated from the single-crystal structure determination. Due to the TGA result, there was no solvent molecules in **C2** and **C3**. Hence, N_2 gas sorption experiments of coordination polymers **C2** and **C3** were tested without the solvent-removing treatments, which were collected on a Micromeritics 3Flex surface area and pore size analyzer under ultrahigh vacuum in a clean system, with a diaphragm and turbo pumping system. Ultrahigh-purity-grade (> 99.999%) N_2 gas was applied in all adsorption

measurements. The experimental temperature was maintained by liquid nitrogen (77 K).

Crystal structure of **C1-C5** determination by X-ray diffraction was performed on Bruker D8 VENTURE with the X-ray source (Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$) at temperature of 295 K. Absorption corrections were implemented by SADABS-2016/2 (Bruker, 2016/2). An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares and difference Fourier techniques, based on F^2 , using ShelXL. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically and refined using a riding model. All the hydrogen atoms were included in the final refinement. The final formulas were determined by combining element analyses and XPS. Crystallographic crystal data and structure processing parameters for **C1-C5** are listed in Table S1-S2. Hydrogen bonding geometry, selected bond lengths and bond angles for **C1-C5** are listed in Table S3-S5 of the Supporting Information. Crystallographic data for **C1-C5** have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference numbers CCDC 2031789-2031793.

Table S1. Crystal data and structure refinement data of complexes **C1-C5**.

compound	C1	C2	C3	C4	C5
Formula	C ₁₈ H ₁₅ CuIN ₇ S	C ₁₆ H ₁₂ BrCu N ₆ S	C ₃₂ H ₂₀ Br ₃ Cu ₃ N 12S ₂	C ₁₆ H ₈ ClCu N ₆ S	C ₁₆ H ₈ ClCu _{0.5} N ₆ S
Fw	551.87	463.83	1067.07	415.33	383.56
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
space group	P-1	P2 ₁ /c	C2/c	P-1	C2/c
<i>a</i> (Å)	7.8851(8)	7.8338(3)	14.745(5)	7.9536(13)	13.1118(6)
<i>b</i> (Å)	9.4706(8)	17.9378(6)	11.282(4)	7.9780(17)	12.8370(6)
<i>c</i> (Å)	14.9633(13)	11.5775(4)	21.686(7)	12.239(2)	18.0339(8)
α (°)	92.531(3)	90.000	90	98.887(8)	90.000
β (°)	102.966(3)	93.2380(10)	107.907(12)	99.985(5)	102.238(2)
γ (°)	113.898(3)	90.000	90	94.096(7)	90.000
<i>V</i> (Å ³)	984.06(16)	1624.29(10)	3432.8(19)	751.8(2)	2966.4(2)
<i>Z</i>	2	4	4	2	8
<i>D_c</i> (g·cm ⁻³)	1.862	1.897	2.065	1.835	1.718
μ (mm ⁻¹)	2.804	3.945	5.502	1.781	1.107
2 θ range (°)	5.652 to 55.224	5.682 to 55.168	4.672 to 54.99	5.718 to 55.136	4.492 to 64.934
<i>F</i> (000)	540.0	1632	2080.0	416.0	1548.0
Data / restraints / parameters	4556/0/254	3751/0/234	3911/0/240	3453/0/229	5323/1/231
Reflections collected	15213	34292	18021	34289	44105
Goodness of fit on F ²	1.058	1.035	1.036	1.048	1.031
Final R indices [<i>I</i> > 2sigma (<i>I</i>)]	R ₁ = 0.0250, wR ₂ = 0.0567	R ₁ = 0.0228, wR ₂ = 0.0488	R ₁ = 0.0232, wR ₂ = 0.0518	R ₁ = 0.0262, wR ₂ = 0.0694	R ₁ = 0.0403, wR ₂ = 0.0945
Final R indices [all data]	R ₁ = 0.0321, wR ₂ = 0.0592	R ₁ = 0.0334, wR ₂ = 0.0521	R ₁ = 0.0315, wR ₂ = 0.0544	R ₁ = 0.0299, wR ₂ = 0.0715	R ₁ = 0.0708, wR ₂ = 0.1052

Largest peak and hole/ $e\text{\AA}^{-3}$	diff. and	0.42/-0.81	0.32/-0.39	0.40/-0.38	0.45/-0.32	0.51/-0.92
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Table S2. Hydrogen bonding geometry (Å, °) for **C1-C5**.

C1				
D–H...A	D–H	H...A	D...A	<D–H...A
N3–H3...I1	0.86	2.75	3.6134(19)	176.8
N5–H5...N2	0.86	2.38	2.794(3)	110.4
C8–H8...N6	0.93	2.36	2.950(3)	121.4
C15–H15...I1 ^{#2}	0.93	3.16	4.089(2)	177.2
C18–H18A...I1 ^{#3}	0.96	3.18	4.039(3)	150.4
C2				
D–H...A	D–H	H...A	D...A	<D–H...A
N5–H5...Br1 ^{#3}	0.75(2)	2.85(2)	3.4865(19)	145(2)
C1–H1...Br1	0.93	2.83	3.518(2)	131.5
C11–H11...Br1 ^{#4}	0.93	3.13	3.9012(19)	141.6
C16–H16...Br1 ^{#2}	0.93	2.77	3.452(2)	130.9
C16–H16...N1 ^{#4}	0.93	2.68	3.378(3)	132.9
C3				
D–H...A	D–H	H...A	D...A	<D–H...A
N5–H5...Br2 ^{#1}	0.79(3)	2.93(3)	3.533(2)	136(2)
C1–H1...Br1 ^{#3}	0.93	3.05	3.769(3)	135.2
C2–H2...Br1 ^{#4}	0.93	3.13	3.829(3)	133.7
C4–H4...Br2	0.93	3.08	3.548(2)	113.3
C13–H13...Br1 ^{#3}	0.93	2.99	3.581(3)	123.1
C16–H16...Br1 ^{#1}	0.93	3.02	3.663(3)	127.4
C4				
D–H...A	D–H	H...A	D...A	<D–H...A
C16–H16...Cl1 ^{#3}	0.93	2.89	3.631(2)	138.0
C4–H4...N1 ^{#1}	0.93	2.57	3.442(2)	156.6
C13–H13...N5 ^{#4}	0.93	2.59	3.422(3)	149.0
C5				
D–H...A	D–H	H...A	D...A	<D–H...A
C4–H4...N1 ^{#1}	0.93	2.66	3.584(2)	169.9
C13–H13...Cl1 ^{#2}	0.93	2.88	3.712(19)	150.0
C1–H1...Cl1 ^{#3}	0.95(2)	2.73(2)	3.461(17)	134.1(17)
C16–H16...Cl1 ^{#3}	0.88(3)	2.91(3)	3.601(2)	137(2)

Symmetry codes:

C1: #1 = 2-x, 2-y, 2-z; #2 = x-1, y, z-1, z-1/2; #3 = -x+2, -y+1, -z+2;**C2:** #1 = 2-x, 1-y, 2-z; #2 = 1-x, 1-y, 1-z; #3 = x-1, y, z-1; #4 = x, y, z-1;**C3:** #1 = 3/2-x, 3/2-y, 1-z; #2 = 1-x, +y, 1/2-z; #3 = -x+1, -y+1, -z+1, #4 = x-1/2, y+1/2, z;**C4:** #1 = 1-x, -y, 1-z; #2 = 2-x, 1-y, 2-z; #3 = -x+1, -y+1, -z+1; #4 = -x+2, -y+2, -z+1;**C5:** #1 = -x+1/2, -y+3/2, -z+1; #2 = x+1/2, -y+3/2, z-1/2; #3 = -x+1, -y+1, -z+1;

Table S3. Selected Bond Lengths (Å) for **C1 – C5**.

C1					
I1–Cu1	2.6081(5)	Cu1–N7	2.036(2)	N4–C5	1.346(3)
I1–Cu1 ^{#1}	2.7102(4)	S1–N2	1.6150(19)	N5–C9	1.379(3)
N1–S1	1.611(2)	C1–N4	1.347(3)	N5–C12	1.392(3)
N1–C11	1.347(3)	N2–C10	1.343(3)	N6–C12	1.332(3)
Cu1–Cu1 ^{#1}	2.9964(7)	N3–C5	1.364(3)	N6–C16	1.351(3)
Cu1–N4	2.0791(19)	N3–C6	1.412(3)	N7–C17	1.124(3)
C2					
Br1–Cu1	2.6091(3)	N1–C8	1.349(2)	N5–C10	1.387(2)
Br1–Cu1 ^{#1}	2.6561(3)	N2–C9	1.344(2)	N5–C12	1.393(2)
Cu1–N4	2.0069(16)	N3–C5	1.370(3)	N6–C12	1.342(2)
Cu1–N6 ^{#2}	2.0128(15)	N3–C7	1.410(2)	N6–C16	1.348(2)
S1–N1	1.6123(18)	N4–C1	1.349(3)		
S1–N2	1.6191(17)	N4–C5	1.348(2)		
C3					
Br1–Cu1	2.4764(8)	S1–N2	1.626(2)	N4–C1	1.379(3)
Br1–Cu2	2.4253(6)	N1–C8	1.345(3)	N4–C5	1.399(3)
Br2–Cu2	2.3682(9)	N2–C9	1.341(3)	N4–C6	1.385(3)
Cu1–Cu2	2.7964(8)	N3–C5	1.346(3)	N5–C10	1.388(3)
Cu1–N3	1.9609(18)	N3–C7	1.385(3)	N5–C12	1.404(3)
Cu1–N6 ^{#1}	2.0078(18)	N6–C12	1.345(3)		
S1–N1	1.625(2)	N6–C16	1.350(3)		
C4					
Cu1–N3 ^{#1}	1.8765(13)	N4–C6	1.401(2)	N3–C5	1.339(2)
Cu1–N3	1.8765(13)	N4–C1	1.386(2)	N5–C10	1.363(2)
Cu2–Cl1 ^{#2}	2.1134(7)	N6–C11	1.3948(19)	N5–C12	1.327(2)
Cu2–Cl1	2.1134(7)	N6–C12	1.412(2)	N1–C8	1.341(2)
S1–N1	1.6328(16)	N6–C16	1.385(2)	N2–C9	1.343(2)
S1–N2	1.6256(16)	N3–C7	1.378(2)	N4–C5	1.4004(19)
C5					
Cu1–Cl1	2.2813(5)	N1–C8	1.334(2)	N4–C6	1.394(2)
Cu1–Cl1 ^{#1}	2.2814(5)	S1–N2	1.6178(16)	N5–C10	1.364(2)
Cu1–N3 ^{#1}	1.9593(12)	N2–C9	1.339(2)	N5–C12	1.325(2)
Cu1–N3	1.9594(12)	N3–C5	1.335(2)	N6–C11	1.3944(18)
C1–N4	1.380(2)	N3–C7	1.3650(18)	N6–C12	1.405(2)
N1–S1	1.6251(15)	N4–C5	1.3981(18)	N6–C16	1.376(2)

Symmetry codes:

C1: #1 = 2-x, 2-y, 2-z; #2 = x-1, y, z-1, z-1/2; #3 = -x+2, -y+1, -z+2;**C2:** #1 = 2-x, 1-y, 2-z; #2 = 1-x, 1-y, 1-z; #3 = x-1, y, z-1; #4 = x, y, z-1;**C3:** #1 = 3/2-x, 3/2-y, 1-z; #2 = 1-x, +y, 1/2-z; #3 = -x+1, -y+1, -z+1, #4 = x-1/2, y+1/2, z;**C4:** #1 = 1-x, -y, 1-z; #2 = 2-x, 1-y, 2-z; #3 = -x+1, -y+1, -z+1; #4 = -x+2, -y+2, -z+1;

C5: #1 = -x+1/2, -y+3/2, -z+1; #2 = x+1/2, -y+3/2, z-1/2; #3 = -x+1, -y+1, -z+1;

Table S4. Selected Bond Angles (degree) for **C1 – C5**.

C1			
Cu1–I1–Cu1 ^{#1}	68.554(13)	N7–Cu1–I1	111.72(7)
I1–Cu1–I1 ^{#1}	111.446(13)	N7–Cu1–I1 ^{#1}	100.53(7)
I1–Cu1–Cu1 ^{#1}	57.337(12)	N7–Cu1–Cu1 ^{#1}	119.17(6)
I1 ^{#1} –Cu1–Cu1 ^{#1}	54.109(12)	N7–Cu1–N4	105.61(8)
N4–Cu1–I1	120.57(5)	C5–N3–C6	125.70(19)
N4–Cu1–I1 ^{#1}	104.90(5)	C9–N5–C12	130.83(19)
N4–Cu1–Cu1 ^{#1}	132.47(5)		
C2			
Cu1–Br1–Cu1 ^{#1}	76.886(11)	N6 ^{#2} –Cu1–Br1	101.45(5)
Br1–Cu1–Br1 ^{#1}	103.116(11)	N6 ^{#2} –Cu1–Br1 ^{#1}	96.29(5)
N4–Cu1–Br1 ^{#1}	100.03(5)	C5–N3–C7	128.02(18)
N4–Cu1–Br1	101.74(5)	C10–N5–C12	125.14(18)
N4–Cu1–N6 ^{#2}	147.68(7)		
C3			
Cu2–Br1–Cu1	69.56(2)	Br1 ^{#2} –Cu2–Cu1	160.160(17)
Br1–Cu1–Cu2	54.360(12)	Br2–Cu2–Br1 ^{#2}	125.858(15)
N3–Cu1–Br1	117.42(5)	Br2–Cu2–Br1	125.857(15)
N3–Cu1–Cu2	124.30(6)	Br2–Cu2–Cu1 ^{#2}	70.937(13)
N3–Cu1–N6 ^{#1}	133.22(7)	Br2–Cu2–Cu1	70.937(13)
N6 ^{#1} –Cu1–Br1	107.30(5)	Cu1 ^{#2} –Cu2–Cu1	141.87(3)
N6 ^{#1} –Cu1–Cu2	92.19(6)	C5–N3–Cu1	127.03(15)
Br1 ^{#2} –Cu2–Br1	108.29(3)	C5–N3–C7	105.13(17)
Br1–Cu2–Cu1 ^{#2}	160.161(17)	C7–N3–Cu1	125.91(14)
Br1–Cu2–Cu1	56.08(2)	C10–N5–C12	123.8(2)
Br1 ^{#2} –Cu2–Cu1 ^{#2}	56.08(2)		
C4			
N3 ^{#1} –Cu1–N3	180	C16–N6–C11	133.48(15)
Cl1 ^{#2} –Cu2–Cl1	180	C16–N6–C12	120.26(14)
C5–N4–C6	107.27(12)	C7–N3–Cu1	124.85(11)
C1–N4–C5	119.70(14)	C5–N3–Cu1	128.80(11)
C1–N4–C6	132.88(14)	C5–N3–C7	105.70(13)
C11–N6–C12	106.10(13)	C12–N5–C10	104.59(14)
C5			
Cl1–Cu1–Cl1 ^{#1}	180	C1–N4–C5	118.61(14)
N3 ^{#1} –Cu1–Cl1	89.78(4)	C1–N4–C6	134.27(13)
N3 ^{#1} –Cu1–Cl1 ^{#1}	90.22(4)	C6–N4–C5	107.12(12)
N3–Cu1–Cl1 ^{#1}	89.78(4)	C12–N5–C10	104.48(14)
N3–Cu1–Cl1	90.22(4)	C11–N6–C12	106.03(14)
N3 ^{#1} –Cu1–N3	180.00(6)	C16–N6–C11	133.64(15)

C5–N3–Cu1	125.56(10)	C16–N6–C12	120.33(15)
C5–N3–C7	106.21(13)	C7–N3–Cu1	128.15(11)

Symmetry codes:

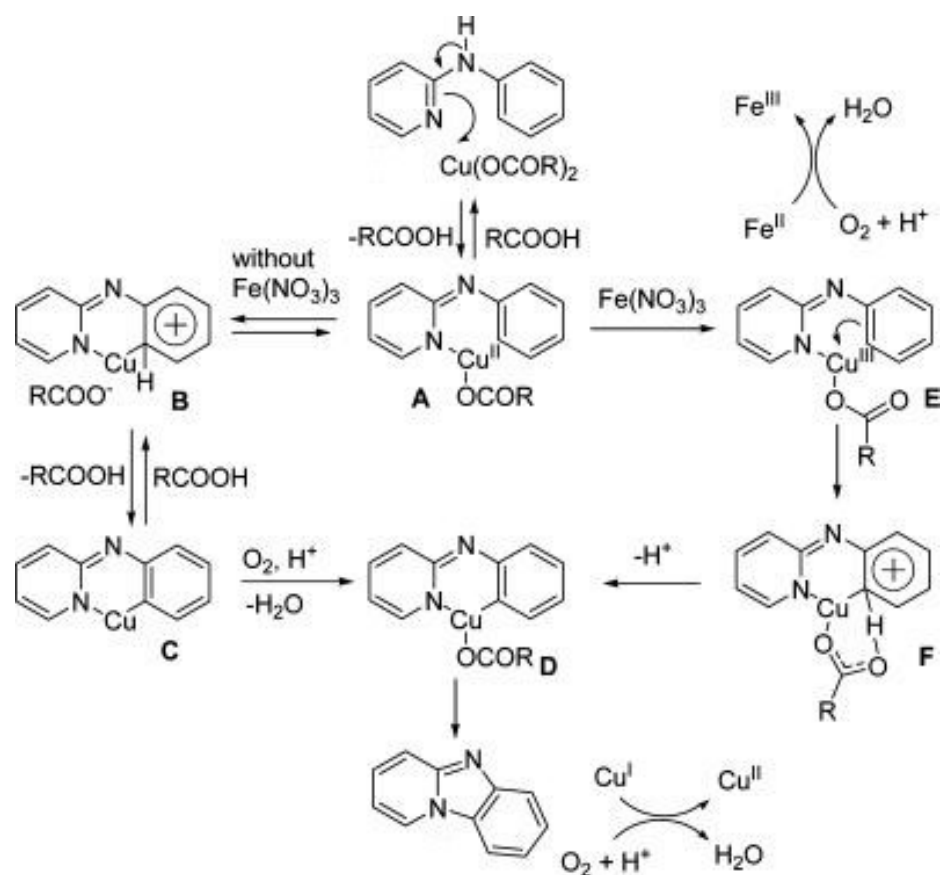
C1: #1 = 2-x, 2-y, 2-z; #2 = x-1, y, z-1, z-1/2; #3 = -x+2, -y+1, -z+2;

C2: #1 = 2-x, 1-y, 2-z; #2 = 1-x, 1-y, 1-z; #3 = x-1, y, z-1; #4 = x, y, z-1;

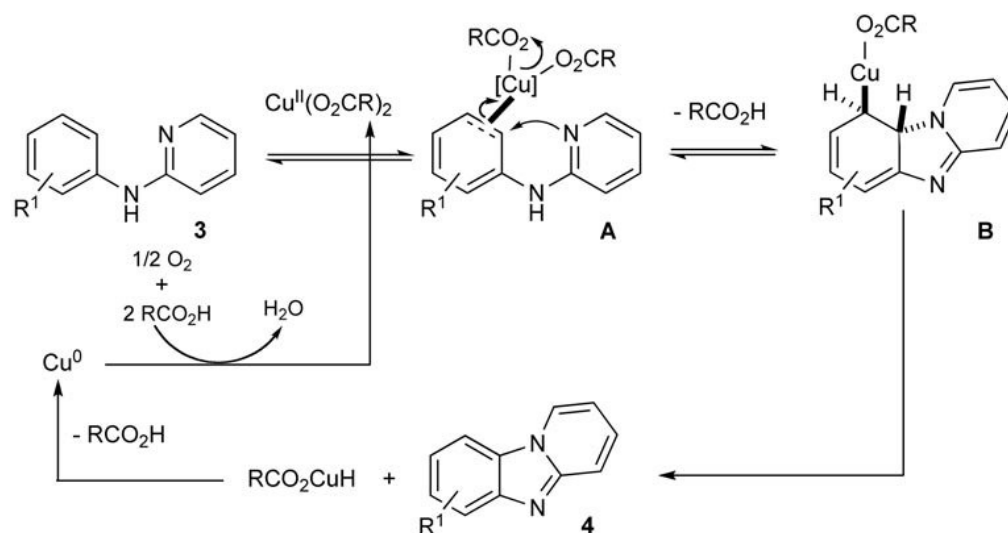
C3: #1 = 3/2-x, 3/2-y, 1-z; #2 = 1-x, +y, 1/2-z; #3 = -x+1, -y+1, -z+1, #4 = x-1/2, y+1/2, z;

C4: #1 = 1-x, -y, 1-z; #2 = 2-x, 1-y, 2-z; #3 = -x+1, -y+1, -z+1; #4 = -x+2, -y+2, -z+1;

C5: #1 = -x+1/2, -y+3/2, -z+1; #2 = x+1/2, -y+3/2, z-1/2; #3 = -x+1, -y+1, -z+1;



Scheme S1. Proposed mechanism for the intramolecular C–H amination with and without iron salt reported by Zhu and co-workers².



Scheme S2. Proposed mechanism for the intramolecular C–H amination reported by Maes and co-workers³.

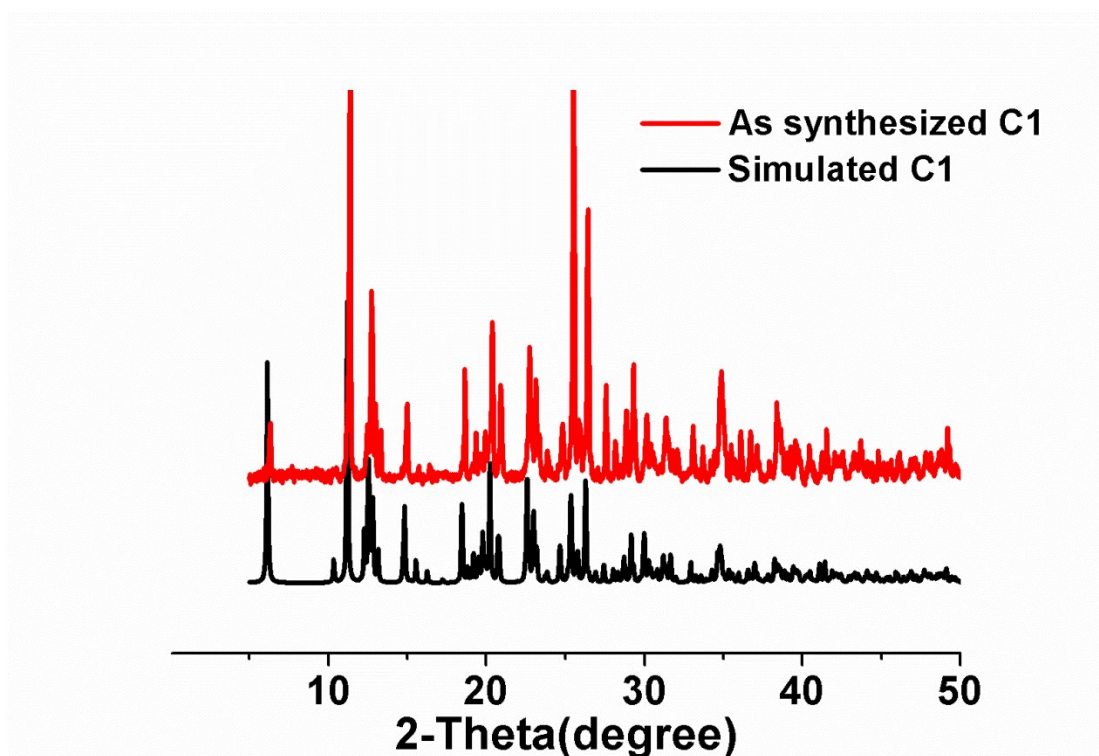


Figure S1. The simulated (black) and experimental (red) PXR D patterns for complex C1.

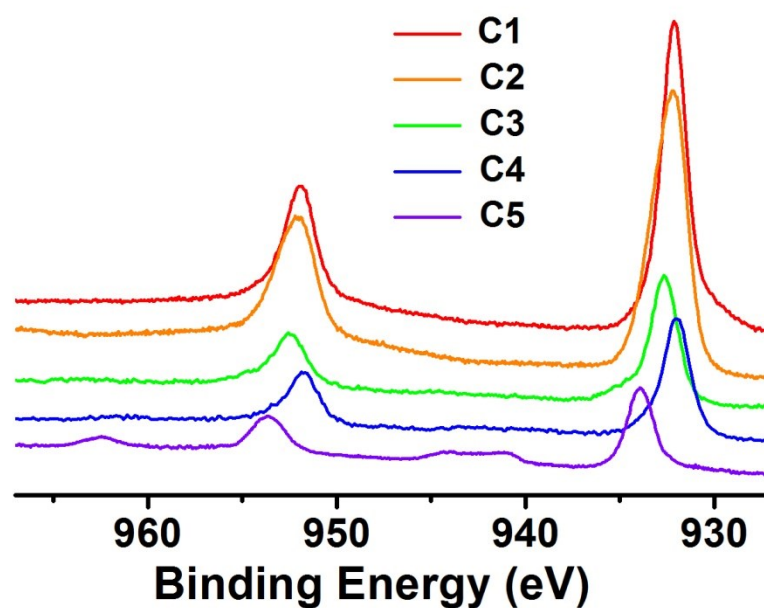


Figure S2. X-ray photoelectron spectra (XPS) of complexes C1 (red), C2 (orange), C3 (green), C4 (blue) and C5 (violet) recorded in the Cu 2p region.

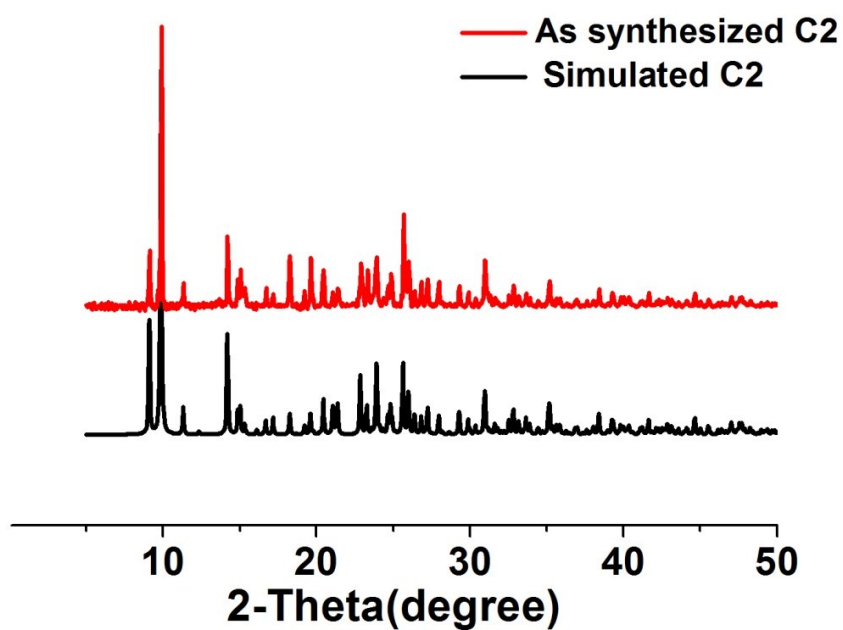


Figure S3. The simulated (black) and experimental (red) PXRD patterns for complex C2.

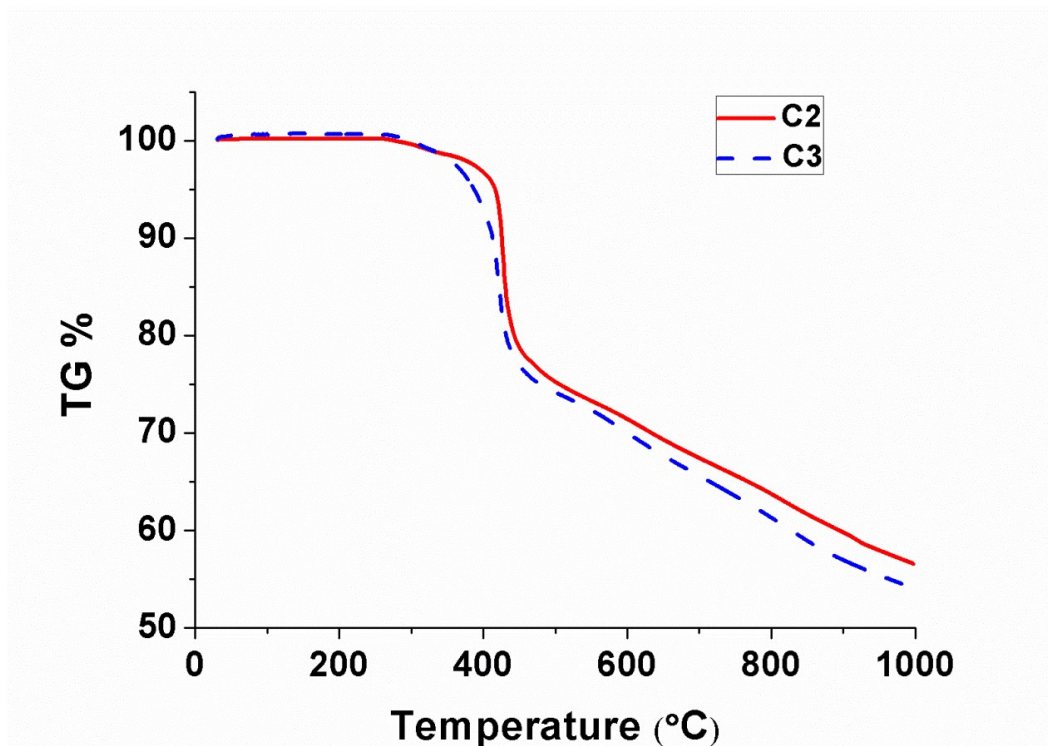


Figure S4. TGA curves of C2 (red solid line) and C3 (blue dot line).

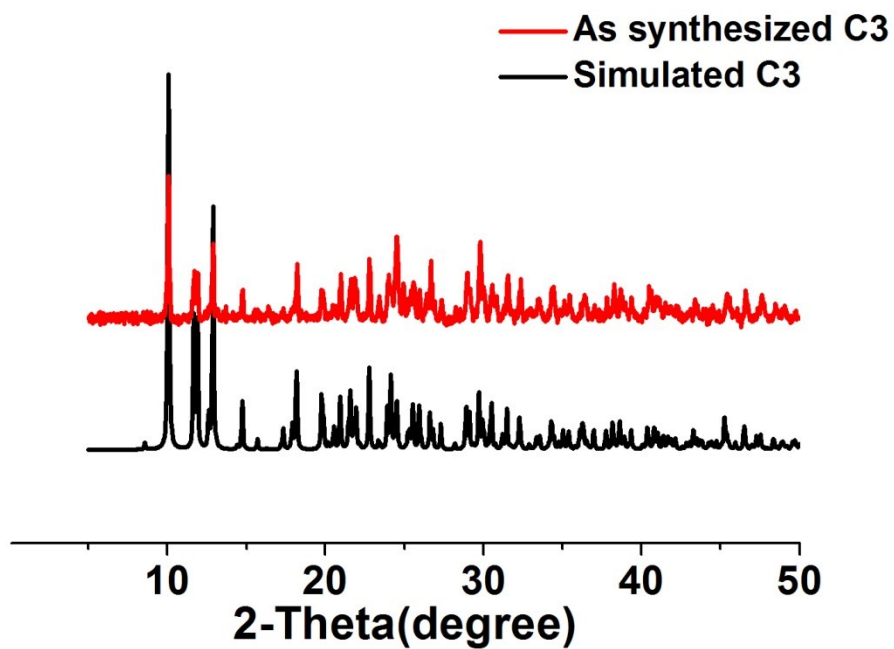


Figure S5. The simulated (black) and experimental (red) PXRD patterns for complex C3.

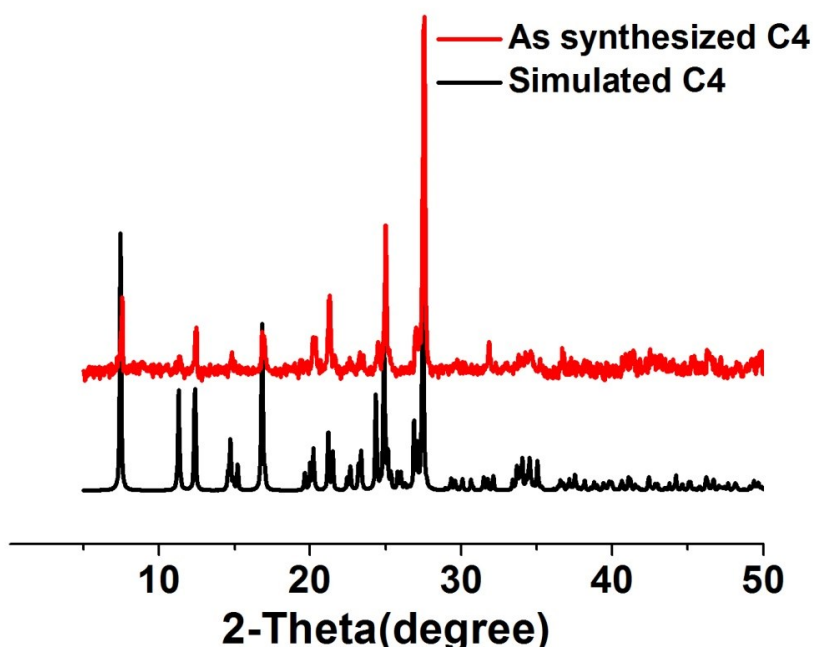


Figure S6. The simulated (black) and experimental (red) PXRD patterns for complex C4.

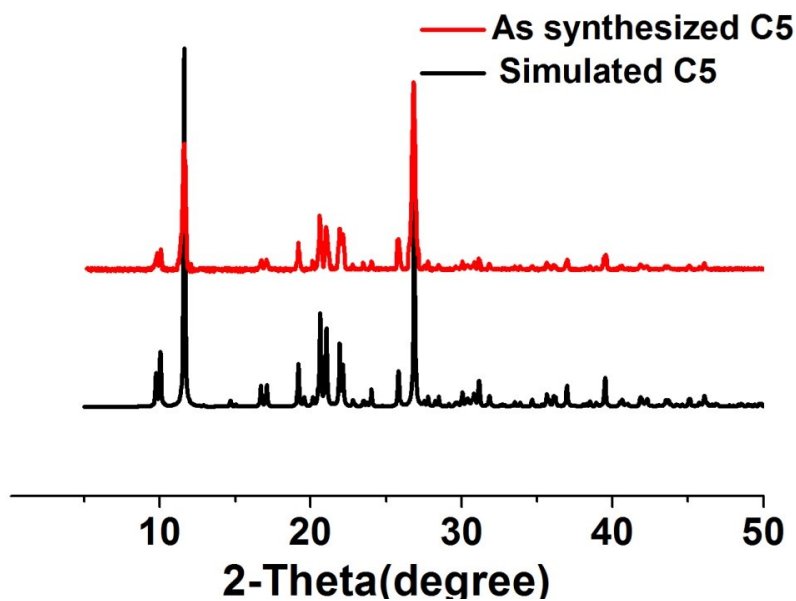


Figure S7. The simulated (black) and experimental (red) PXRD patterns for complex C5.

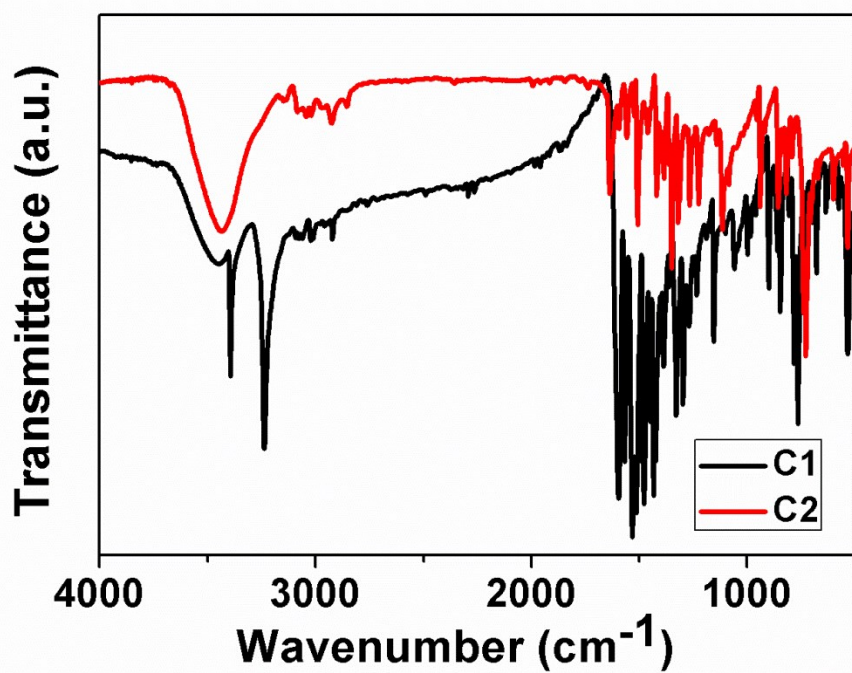


Figure S10. IR spectra for complexes C1 (black), C2 (red).

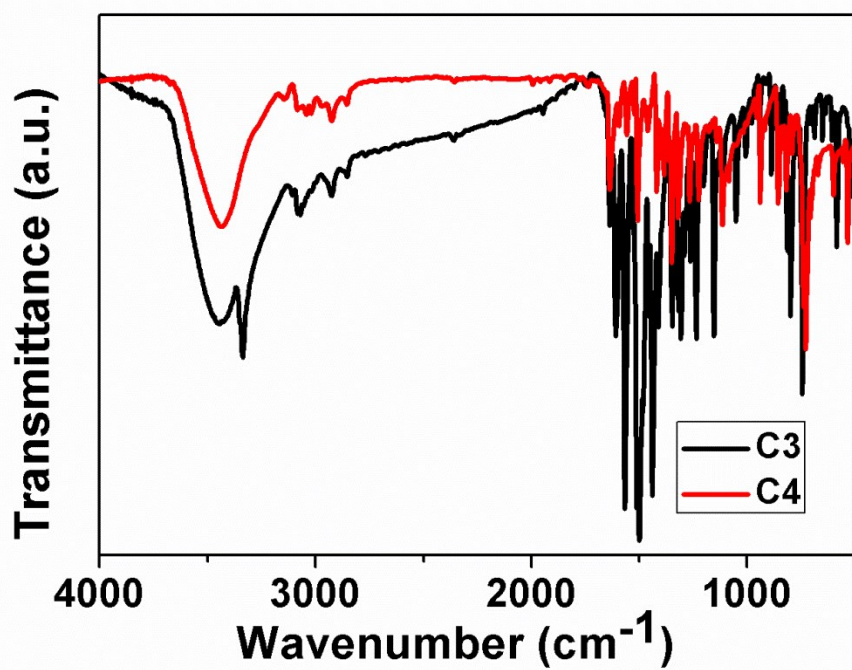


Figure S11. IR spectra for complexes C3 (black), C4 (red).

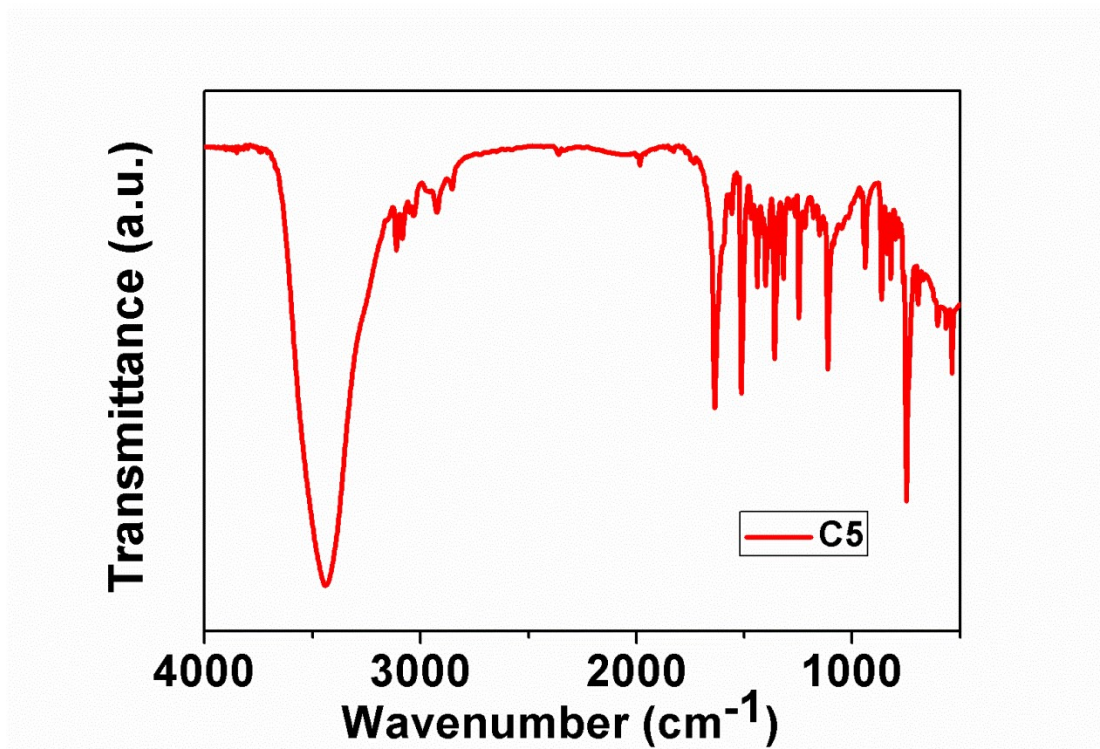


Figure S12. IR spectra for complexes C5 (red).

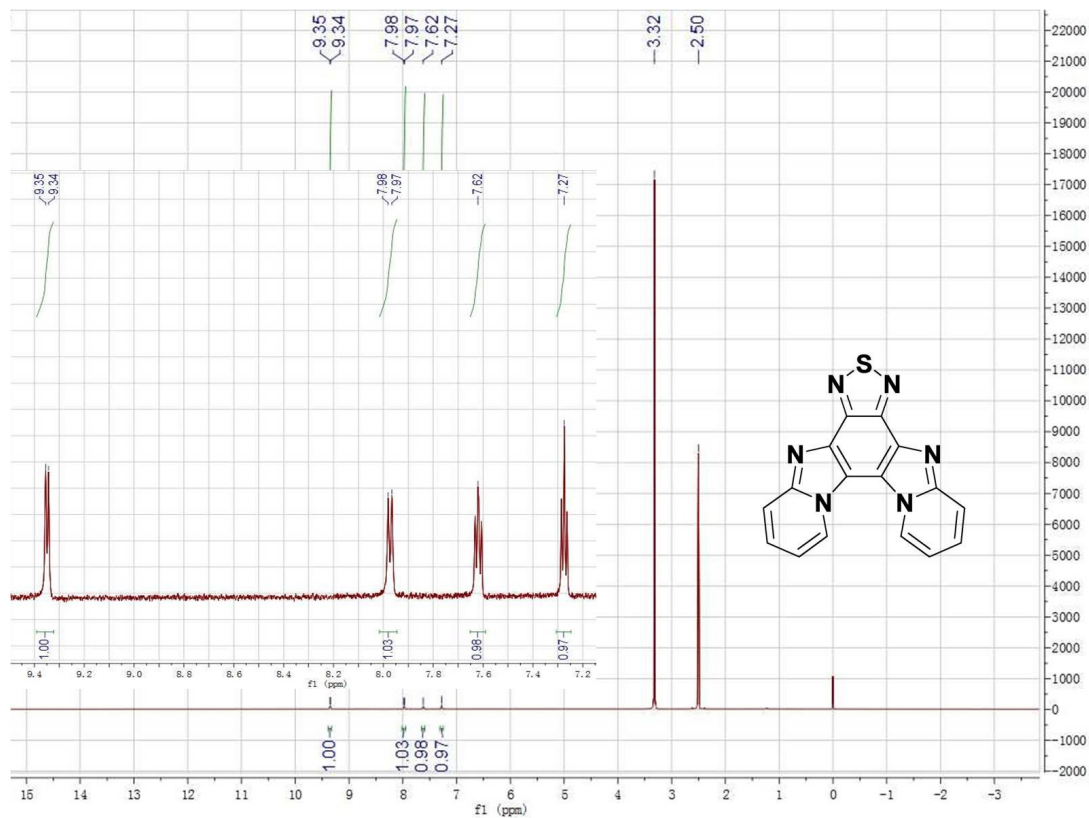


Figure S13. ¹H-NMR spectrum of L3.