Electronic Supplementary Information (ESI)

Regioisomeric Core-shell Cuprofullerene $C_{60}@Cu_{24}$

You-Shi Guo,[a] Shun-Ze Zhan,*[ab] Jia-Jing Zhong,[a] Weigang Lu[b] , Seik Weng Ng[c] and and Dan Li*[b]

[a] *Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province, Shantou University, Shantou 515063, P. R. China *Email: szzhan@stu.edu.cn*

[b] *College of Chemistry and Materials Science, and Guangdong Provincial Key Laboratory of Functional Supramolecular Coordination Materials and Applications, Jinan University, Guangzhou 510632, P. R. China *Email: danli@jnu.edu.cn*

[c.] *UCSI University, Cheras, Kuala Lumpur, Malaysia*

Content

1 Experimental Procedures

1.1 Materials and Physical Measurements

Commercially available starting materials and solvents were used without further purification. C_{60} (99.5%) was purchased from Xiamen Funano New Material Technology Company LTD without purifications. Single crystal X-ray data collection for the material was performed on a Rigaku OD (Enhance Cu X-ray Source, Kα, λ = 1.54184 Å) with CCD Plate (XtaLAB Pro: Kappa single) under 100 K. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q50 Thermogravimetric Analyzer under a nitrogen flow of 40 mL·min^{-1} at a heating rate of 20 °C·min^{-1}. Powder X-ray diffraction (PXRD) experiment was performed on a MiniFlex 600 X-ray diffractometer of Riguku Corporation. Infrared spectrum (IR) was obtained in KBr pellet on a Nicolet Avatar 360 FTIR spectrometer in the range of 4000–500 cm^{-1}; abbreviations used for the IR bands are: w = weak, m = medium, s = strong, vs = very strong. The diffuse reflectance solid-state UV-Vis spectra of these complexes were obtained on a Lambda950 UV/Vis/NIR spectrophotometer of Perkin Elmer using pure powder sample and pure $BaSO_4$ as background.

1.2 Synthesis

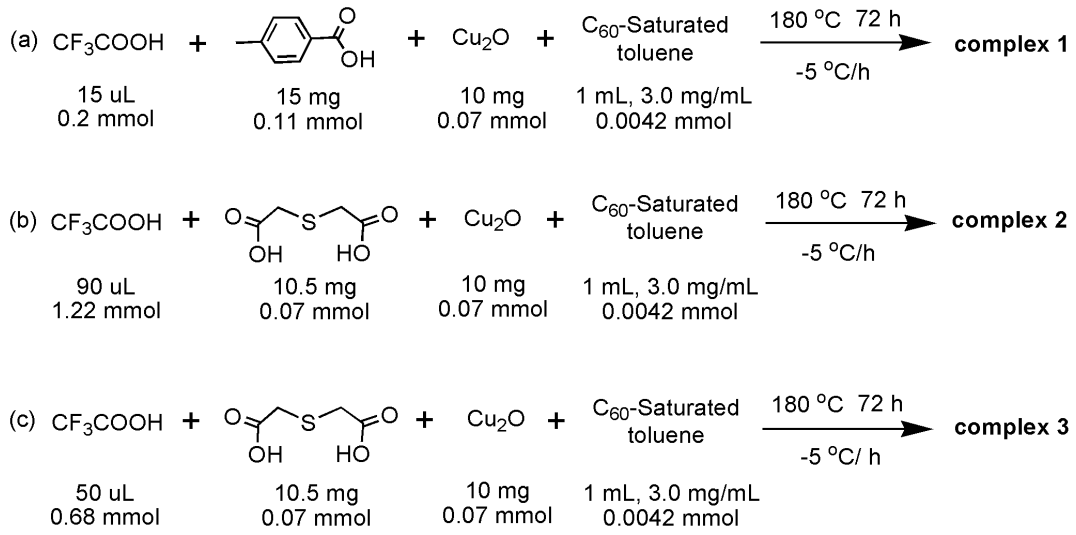
Complex **1**: A mixture of Cu_2O (10.0 mg, 0.07 mmol), trifluoroacetic acid (CF_3COOH, 15 μL, 0.20 mmol), 4-methylbenzoic acid (15 mg, 0.11 mmol) and C_{60}-saturated toluene solution (1.0 mL, 3.0 mg/mL, 0.0042 mmol) was sealed in a Pyrex tube with an 8.0 mm inner diameter (6.0 mL volume). Then the tube was heated at 180 °C in a programmable oven for 72 h and cooled to room temperature at the rate of –5 °C·h^{-1}. Red block crystals were separated mechanically. Yield: 18.4 mg, 67.2% (based on C_{60}). IR data (KBr, cm^{-1}): 1681 vs, 1612 s, 1542 m, 1430 m, 1290 m, 1203 vs, 1141 s, 1022 w, 842 m, 727 s, 526 m.

Complex **2**: A mixture of Cu_2O (10.0 mg, 0.07 mmol), trifluoroacetic acid (CF_3COOH, 90 μL, 1.22 mmol), thiodiglycolic acid (10.5 mg, 0.07 mmol) and C_{60}-saturated toluene solution (1.0 mL, 3.0 mg/mL, 0.0042 mmol) was sealed in a Pyrex

tube with an 8.0 mm inner diameter (6.0 mL volume). Then the tube was heated at 180 °C in a programmable oven for 72 h and cooled to room temperature at the rate of –5 °C·h $^{-1}$. Red block crystals were separated mechanically. Yield: 2.1 mg, 7.9% based on C_{60}. IR data (KBr, cm^{-1}): 3423 s, 1673 s, 1650 s, 1589 s, 1374 s, 1205 s, 1141 s, 933 s, 848 m, 790 w, 725 s, 659 w, 514 m.

Complex **3**: A mixture of Cu_2O (10.0 mg, 0.07 mmol), trifluoroacetic acid (CF_3COOH, 50 μL, 0.68 mmol), thiodiglycolic acid (10.5 mg, 0.07 mmol) and C_{60}-saturated toluene solution (1.0 mL, 3.0 mg/mL, 0.0042 mmol) was sealed in a Pyrex tube with an 8.0 mm inner diameter (6.0 mL volume). Then the tube was heated at 180 °C in a programmable oven for 72 h and cooled to room temperature at the rate of –5 °C·h $^{-1}$. Red block crystals were separated mechanically. Yield: 1.5 mg, 6.0% based on C_{60}. IR data (KBr, cm^{-1}): 3446 s, 1681 s, 1644 s, 1598 vs, 1560 vs, 1407 s, 1199 s, 1141 s, 931 w, 840 w, 790 w, 707 m, 570 w, 516 m.

Note that: The red crystal samples of the complexes **1**, **2** and **3** will turn into dark color after tens of minutes in air, losing their crystalline. So immediate measurements are necessary to ensure their crystalline purity.



Scheme S1 Synthesis reactions of the cuprofullerene complexes **1, 2** and **3.**

1.3 Crystal Structural Determination

Data collection for the adduct was performed on a Rigaku OD (Enhance Cu X-ray Source, Kα, λ = 1.54184 Å) with CCD Plate (XtaLAB Pro: Kappa single) under 100 K. Data were processed with the CrysAlisPro 1.171.39.28b (Rigaku Oxford Diffraction, 2015).

Structures were solved by direct methods by ShelXS[1] in Olex2 1.2[2] and refined on F^2 using full-matrix least-squares (SHELXL-2017/1[1] in Olex2 1.2[2]). All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. SQUEEZE program[3] was used to remove the contributions of disordered guest molecules. Crystal data and structure refinement for the complex were summarized in Table S1. Selected bond lengths and angles were given in Table S2 and Table S3.

Note that:

Complex **1**: $Cu_{24}(C_{60})_2(C_8H_8O_2)_{12}(C_2F_3O_2)_{24}$

The C_{60} sphere lies on a site of -3 Wyckoff symmetry. The acid hydrogen atom of the *p*-toluic acid was located and refined with a distance restraint of O–H 0.84±0.01 Å.

Complex **2**: $[Cu_{34}(H_2O)_2(C_{60})(C_2F_3O_2)_8(C_4H_4O_4S)_{14}]\cdot 2C_7H_8\cdot 2C_2F_3O_2H\cdot 2C_4H_6O_4S$

The C_{60} sphere lies on a site of -1 Wyckoff symmetry. The acid hydrogen atom of the free CF_3CO_2H was located and refined with a distance restraint of of O–H 0.84±0.01 Å. The H-atoms of the coordinated water molecule were generated geometrically; only one of the two forms a hydrogen bond to an acceptor O atom.

One of the $C_4H_4O_4S^{2-}$ units is disordered over two positions. The occupancy of each component was set to 0.5, and pairs of bond distances were restrained to within 0.01 Å of each other; the anisotropic displacement parameters of the unprimed and primed atoms were made to be identical.

The refinement initially converged at an *R* of 0.064, but the difference Fourier map had excess electron density (181 electron counts) in a 509 $Å^3$ void centered at (0,0,0). The electron density was assumed as two thiodiglycolic acid molecules ($C_4H_6O_4S$ has

78 electrons). The molecular volume of thiodiglycolic acid itself when calculated from its estimated 1.352 g/cm^3 is approximately 184 Å^3. The diffraction measurements are of a sufficiently high quality for the electrons to be squeezed out, and the refinement converged to a slightly lower value of 0.052.

The entity is unlikely to be toluene (64 electrons); the molecular volume of the two phases of toluene is much smaller, at about 140 Å^3 only [M. Anderson, Bosio, J. Bruneaux-Poulle and R. Fourme, *J Chim. Phys.* 74, 68-73 (1977); J. Bruneaux-Poulle and L. Bosio, *J. Mol. Struct.* 81, 253-259 (1982)]. The possibility of trifluoroacetic acid is also excluded as its molecular volume of 91 Å^3 is too small [I. Nahringbauer, J.-O. Lundgren and E. K. Andersen, *Acta Cryst.* B35, 508-510 (1979)].

Complex **3**: $[Cu_{32}(C_{60})(C_2F_3O_2)_{12}(C_4H_4O_4S)_{10}(C_4H_6O_4S)_2]\cdot C_7H_8$

The C_{60} sphere lies on a site of -1 Wyckoff symmetry. For one of the six independent thiodiglycolate groups, one $-CO_2$ end (C–O 1.23, 1.30 Å) is within hydrogen-bonding range of another thiodiglycolate (that has delocalized C–O bonds of 1.25, 1.25 Å). An acid hydrogen is placed on this end of the thiodiglycolate group. Its other $-CO_2$ end (C–O 1.21, 1.31 Å) has its presumably singly-bonded O atom within hydrogen bonding range of a presumably singly-bonded O atom of a trifluoroacetate group (C–O 1.24, 1.29 Å). Because the acid hydrogen cannot be assigned to either the thiodiglycolate or the trifluoroacetate group, this atom is arbitrarily placed mid-way between these two singly-bonded O ends. Consequently, the formula can also be represented as $[Cu_{32}(C_{60})(C_2F_3O_2)_{10}(C_2F_3O_2H)_2(C_4H_4O_4S)_{10}(C_4H_5O_4S)_2]\cdot C_7H_8$.

2 Results and Discussion

2.1 Crystal Data

Table S1 Crystal data and structure refinements for the complexes measured at 100 K

Complexes	**1**	**2**	**3**
CCDC	2109671	2090423	2090424
Chemical formula	$C_{204}H_{96}Cu_{24}F_{72}O_{72}$	$C_{150}H_{78}Cu_{34}F_{30}O_{78}S_{14}$	$C_{139}H_{60}Cu_{32}F_{36}O_{72}S_{12}$
Formula weight	6592.01	6307.67	5984.19
Crystal system	trigonal	triclinic	monoclinic
Space group	*R-3*	*P-1*	*P2₁/n*
a (Å)	32.3438(3)	17.0534(3)	17.0045(3)
b (Å)	32.3438(3)	17.7446(4)	19.5007(4)
c (Å)	18.0340(2)	18.0961(4)	24.9159(6)
α (deg)	90	64.831(2)	90
β (deg)	90	74.884(2)	91.855(2)
γ (deg)	120	74.914(2)	90
V (Å^3)	16338.2(4)	4714.17(19)	8257.8(3)
Z	3	1	2
D_{calc} (g.cm^{-3})	2.010	2.222	2.407
μ (mm^{-1})	3.809	6.528	6.952
Reflections collected	16363	49253	46534
Unique	7079	15798	16308
R_{int}	0.0201	0.0491	0.0512
GOF	1.040	1.052	1.056
R_1[a] [I >2σ(I)]	0.0411	0.0517	0.0643
wR_2[b] [I > 2σ(I)]	0.1210	0.1357	0.1822
R_1[a] [all refl.]	0.0445	0.0659	0.0752
wR_2[b] [all refl.]	0.1237	0.1445	0.1926

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table S2 Comparison of the selected bond lengths (Å) in the complexes **1**, **2** and **3**.

Bond lengths (Å)					
1		**2**		**3**	
Cu-O(**L**$_F$)					
Cu1-O1	1.956(2)	Cu1-O2#1	2.279(4)	Cu1-O2#1	2.254(4)
Cu1-O6	1.960(2)	Cu2-O7	2.264(4)	Cu2-O7	2.285(4)
Cu2-O2	1.974(2)	Cu4-O7	2.270(4)	Cu4-O7	2.251(5)
Cu2-O3	1.997(2)	Cu4-O9	1.955(4)	Cu4-O9	1.951(5)
Cu3-O4	1.968(2)	Cu5-O10	1.987(4)	Cu5-O10	1.995(5)
Cu3-O5	1.978(2)	Cu7-O21#1	2.304(4)	Cu7-O21#1	2.225(4)
Cu4-O11	1.930(2)	Cu8-O17#1	2.035(5)	Cu8-O17	1.950(5)
Cu4-O12#2	1.964(2)	Cu9-O18	1.945(4)	Cu9-O18	1.966(5)
		Cu9-O19	1.980(4)	Cu9-O19#1	2.001(4)
		Cu9-O24	2.319(4)	Cu9-O24#1	2.328(4)
		Cu13-O14	2.291(4)	Cu13-O14	2.280(4)
		Cu14-O23	1.895(4)	Cu14-O23	1.908(5)
		Cu16-O22	1.930(4)	Cu16-O22	2.005(5)
				Cu5-O35#1	2.308(5)
				Cu10-O33	2.029(5)
				Cu11-O34	1.948(5)
				Cu12-O35	2.122(6)
average	1.966	average	2.112	average	2.106
Cu-O(*H*$\mathbf{L}_{mb}$)		Cu-O (**L**$_S$)			
Cu1-O9#1	2.272(2)	Cu1-O1	1.945(4)	Cu1-O1	1.949(4)
Cu2-O7	2.202(2)	Cu1-O6	1.969(4)	Cu1-O6	1.958(4)
Cu3-O9#1	2.243(2)	Cu2-O2	1.958(4)	Cu2-O2	1.960(4)
Cu4-O7#3	2.351(2)	Cu2-O3	1.964(4)	Cu2-O3	1.970(4)
		Cu3-O4	1.992(4)	Cu3-O4	1.985(4)

		Cu3-O5	1.977(4)	Cu3-O5	1.967(4)
		Cu3-O25	2.245(4)	Cu3-O25	2.296(5)
		Cu4-O14	1.966(4)	Cu4-O14	1.975(4)
		Cu5-O11	1.937(4)	Cu5-O11	1.947(5)
		Cu6-O12	1.967(4)	Cu6-O12	1.954(4)
		Cu6-O13	1.957(4)	Cu6-O13	1.957(4)
		Cu6-O24	2.353(4)	Cu6-O24	2.404(5)
		Cu7-O15#1	1.981(4)	Cu7-O15#1	1.995(4)
		Cu7-O20	1.929(4)	Cu7-O20	1.952(4)
		Cu8-O16	1.982(4)	Cu8-O16	1.994(5)
		Cu8-O31#1	2.020(5)	Cu8-O31#1	2.222(5)
		Cu10-O24	2.359(4)	Cu10-O24#1	2.292(4)
		Cu10-O25	2.352(4)	Cu10-O25#1	2.342(4)
		Cu11-O25	2.452(4)	Cu11-O25#1	2.402(4)
		Cu11-O27	2.001(4)	Cu11-O27#1	2.001(4)
		Cu12-O28	1.926(4)	Cu12-O28	1.904(5)
		Cu12-O29	2.030(3)	Cu12-O29	2.061(6)
		Cu13-O3	2.510(4)	Cu13-O3	2.437(5)
		Cu13-O8	1.919(4)	Cu13-O8	1.911(5)
		Cu14-O19	2.290(4)	Cu14-O19	2.271(4)
		Cu15-O26	1.903(4)	Cu15-O26	1.905(5)
		Cu15-O27	2.219(4)	Cu15-O27	2.265(4)
		Cu16-O15	2.249(4)	Cu16-O15	2.267(4)
		Cu17-O30A	1.860(3)		
		Cu17-O30B	2.130(3)		
		Cu17-O32A	1.990(4)		
		Cu17-O32B	1.910(3)		

		Cu10-O33	1.986(4)		
		Cu11-O34	1.967(4)		
		Cu17-O34	2.352(4)		
		Cu17-O35	1.992(5)		
average	2.267	average	2.071	average	2.091
		Cu-O (H_2O)			
		Cu5-O37#1	2.299(4)		
		Cu12-O37	2.288(4)		
		average	2.294		
		Cu-S			
		Cu10-S4	2.312(2)	Cu10-S4#1	2.321(2)
		Cu13-S2	2.188(2)	Cu13-S2	2.184(2)
		Cu14-S3	2.175(2)	Cu14-S3	2.186 (2)
		Cu15-S5	2.171(2)	Cu15-S5	2.173(2)
		Cu16-S1	2.196(2)	Cu16-S1	2.225(2)
		Cu17-S6A	2.530(2)	Cu16-S6#3	2.333(2)
		Cu17-S6B	2.540(2)		
		Cu17-S7	2.341(2)		
		average	2.307	average	2.237
Cu-Cu (canopying)					
Cu1-Cu2	3.278(2)	Cu1-Cu2	3.260(7)	Cu1-Cu2	3.222(6)
Cu1-Cu3	3.317(2)	Cu1-Cu3	3.160(7)	Cu1-Cu3	3.160(6)
Cu2-Cu3	3.365(2)	Cu1-Cu7	3.453(8)	Cu1-Cu7	3.437(7)
Cu2-Cu4	3.460(2)	Cu2-Cu3	3.204(7)	Cu2-Cu3	3.202(6)
		Cu2-Cu4	3.425(8)	Cu2-Cu4	3.389(7)
		Cu3-Cu10	3.516(8)	Cu3-Cu10	3.506(7)
		Cu3-Cu11	3.480(8)	Cu3-Cu11	3.457(7)

		Cu4-Cu5	3.255(7)	Cu4-Cu5	3.291(6)
		Cu4-Cu6	3.261(7)	Cu4-Cu6	3.261(6)
		Cu5-Cu12	3.438(8)	Cu5-Cu12	3.506(7)
		Cu6-Cu9	3.416(8)	Cu6-Cu9	3.450(7)
		Cu6-Cu10	3.592(8)	Cu6-Cu10	3.605(7)
		Cu7-Cu8	3.283(8)	Cu7-Cu8	3.274(6)
		Cu7-Cu9	3.250(7)	Cu7-Cu9	3.255(6)
		Cu8-Cu9	3.417(8)	Cu8-Cu9	3.296(6)
		Cu9-Cu10	3.440(8)	Cu9-Cu10	3.488(7)
		Cu10-Cu11	3.304(8)	Cu10-Cu11	3.267(6)
		Cu11-Cu12	3.240(7)	Cu11-Cu12	3.217(6)
average	3.355	average	3.355	average	3.349
		Cu-Cu (standing)			
		Cu2-Cu13	3.751(9)	Cu2-Cu13	3.714(7)
		Cu3-Cu15	3.753(9)	Cu3-Cu15	3.868(8)
		Cu4-Cu13	3.521(8)	Cu4-Cu13	3.482(7)
		Cu6-Cu14	3.773(9)	Cu6-Cu14	3.721(7)
		Cu7-Cu16	3.500(8)	Cu7-Cu16	3.632(7)
		Cu9-Cu14	3.557(8)	Cu9-Cu14	3.549(7)
		Cu11-Cu15	3.542(8)	Cu11-Cu15	3.610(7)
		Cu11-Cu17	3.484(8)		
		average	3.610	average	3.654
Cu-C					
Cu1-C1	2.016(3)	Cu1-C1#1	2.015(5)	Cu1-C1#1	2.017(6)
Cu1-C2	2.016(3)	Cu1-C2#1	2.019(5)	Cu1-C2#1	2.007(5)
Cu2-C3#2	2.015(3)	Cu2-C3	2.008(5)	Cu2-C3	2.017(5)
Cu2-C4#2	2.016(3)	Cu2-C4	2.015(5)	Cu2-C4	2.018(6)

Cu3-C5	2.010(3)	Cu3-C5	2.027(5)	Cu3-C5#1	2.033(5)
Cu3-C6	2.014(3)	Cu3-C6	2.028(5)	Cu3-C6#1	2.038(5)
Cu4-C7	2.031(3)	Cu4-C7	2.009(6)	Cu4-C7	1.997(5)
Cu4-C8	1.990(3)	Cu4-C8	2.006(5)	Cu4-C8	2.026(6)
		Cu5-C9	1.996(6)	Cu5-C9	2.019(6)
		Cu5-C10	2.031(5)	Cu5-C10	2.044(6)
		Cu6-C11#1	2.004(5)	Cu6-C11	2.008(6)
		Cu6-C12#1	2.020(6)	Cu6-C12	2.013(6)
		Cu7-C13	2.039(5)	Cu7-C13#1	2.034(6)
		Cu7-C14	1.983(5)	Cu7-C14#1	2.012(6)
		Cu8-C15	2.027(5)	Cu8-C15	2.013(6)
		Cu8-C16	2.050(6)	Cu8-C16	2.015(6)
		Cu9-C17#1	2.043(6)	Cu9-C17#1	2.072(6)
		Cu9-C18#1	1.974(5)	Cu9-C18#1	2.006(6)
		Cu10-C19	1.972(5)	Cu10-C19	1.974(6)
		Cu10-C20	2.052(5)	Cu10-C20	2.086(6)
		Cu11-C21#1	2.052(5)	Cu11-C21	2.062(5)
		Cu11-C22#1	1.998(5)	Cu11-C22	1.995(6)
		Cu12-C23#1	1.987(5)	Cu12-C23#1	2.038(6)
		Cu12-C24#1	1.988(5)	Cu12-C24#1	2.050(5)
average	2.014	average	2.014	average	2.025
C-C (coordinated C=C)					
C1-C2	1.445(4)	C1-C2	1.427(8)	C1-C2	1.419(8)
C3-C4	1.433(4)	C3-C4	1.417(8)	C3-C4	1.439(8)
C5-C6	1.442(4)	C5-C6	1.416(8)	C5-C6	1.435(8)
C7-C8	1.432(4)	C7-C8	1.435(7)	C7-C8	1.425(8)
		C9-C10	1.424(8)	C9-C10	1.426(9)

		C11-C12	1.4277)	C11-C12	1.443(8)
		C13-C14	1.433(8)	C13-C14	1.426(8)
		C15-C16	1.435(7)	C15-C16	1.445(8)
		C17-C18	1.409(7)	C17-C18	1.423(8)
		C19-C20	1.435(7)	C19-C20	1.423(8)
		C21-C22	1.424(7)	C21-C22	1.439(8)
		C23-C24	1.424(7)	C23-C24	1.422(8)
average	1.438	average	1.425	average	1.430
C-C (uncoordinated C=C)					
C9-C10	1.378(4)	C25-C26	1.373(8)	C25-C26	1.384(8)
		C27-C28	1.380(8)	C27-C28	1.384(8)
		C29-C30	1.374(8)	C29-C30	1.390(8)
average	1.378	average	1.376	average	1.386
Symmetry codes					
#1: -1/3+y, 1/3-x+y ,4/3-z #2: +y-x, 1-x, +z		#1: 1-x, 1-y, 1-z		#1: 1-x, 1-y, 1-z #2: 1/2+x, 3/2-y, -1/2+z #3: 3/2-x, -1/2+y, 3/2-z	

Table S5 Comparison of the selected bond angles (º) in the complexes **3** and **4**.

Bond angles (º)					
1		**2**		**3**	
O1-Cu1-O6	90.99(11)	O1-Cu1-O6	93.14(17)	O1-Cu1-O6	94.30(19)
O1-Cu1-O9#1	90.55(9)	O1-Cu1-O21	95.05(17)	O1-Cu1-O21	95.50(18)
O1-Cu1-C1	113.87(11)	O1-Cu1-C1#1	152.70(13)	O1-Cu1-C1#1	153.67(12)
O1-Cu1-C2	155.00(11)	O1-Cu1-C2#1	111.80(12)	O1-Cu1-C2#1	113.06(12)
O6-Cu1-O9#1	93.09(9)	O6-Cu1-O21	88.33(16)	O6-Cu1-O21	87.85(17)
O6-Cu1-C1	152.67(11)	O6-Cu1-C1#1	113.20(12)	O6-Cu1-C1#1	111.27(12)
O6-Cu1-C2	111.60(11)	O6-Cu1-C2#1	154.60(15)	O6-Cu1-C2#1	152.57(2)
C1-Cu1-O9#1	97.62(9)	C1#1-Cu1-O2#1	92.81(19)	C1#1-Cu1-O2#1	92.25(2)
C1-Cu1-C2	41.99(10)	C1#1-Cu1-C2#1	41.41(13)	C2#1-Cu1-O2#1	92.88(19)
C2-Cu1-O9#1	98.45(9)	C2#1-Cu1-O21	94.05(18)	C2#1-Cu1-C1#1	41.36(2)
O2-Cu2-O3	90.25(11)	O2-Cu2-O3	95.15(17)	O2-Cu2-O3	96.87(19)
O2-Cu2-O7	91.41(9)	O2-Cu2-O7	91.61(16)	O2-Cu2-O7	88.99(18)
O2-Cu2-C3#2	113.22(11)	O2-Cu2-C3	112.82(12)	O2-Cu2-C3	110.87(2)
O2-Cu2-C4#2	153.95(10)	O2-Cu2-C4	153.51(11)	O2-Cu2-C4	152.45(2)
O3-Cu2-O7	91.12(9)	O3-Cu2-O7	91.64(15)	O3-Cu2-O7	91.42(17)
O3-Cu2-C3#2	151.60(10)	O3-Cu2-C3	151.53(12)	O3-Cu2-C3	152.04(2)
O3-Cu2-C4#2	112.19(10)	O3-Cu2-C4	110.31(12)	O3-Cu2-C4	110.25(2)
C3#2-Cu2-O7	103.47(9)	C3-Cu2-O7	93.21(18)	C3-Cu2-O7	93.21(19)
C3#2-Cu2-C42	41.66(10)	C3-Cu2-C4	41.22(13)	C3-Cu2-C4	41.88(12)
C4#2-Cu2-O7	100.81(9)	C4-Cu2-O7	94.76(18)	C4-Cu2-O7	95.24(12)
O4-Cu3-O5	90.90(11)	O4-Cu3-O25	86.87(15)	O4-Cu3-O25	87.08(17)
O4-Cu3-O9	91.80(9)	O4-Cu3-C5	110.59(19)	O4-Cu3-C5#1	109.53(2)
O4-Cu3-C5	113.42(11)	O4-Cu3-C6	151.32(19)	O4-Cu3-C6#1	150.75(2)
O4-Cu3-C6	154.51(11)	O5-Cu3-O4	95.06(16)	O5-Cu3-O4	94.01(19)
O5-Cu3-O9	89.06(9)	O5-Cu3-O25	88.45(15)	O5-Cu3-O25	89.88(17)
O5-Cu3-C5	152.99(11)	O5-Cu3-C5	153.81(12)	O5-Cu3-C5#1	155.21(2)
O5-Cu3-C6	112.01(11)	O5-Cu3-C6	113.12(19)	O5-Cu3-C6#1	114.67(2)
C5-Cu3-O9	101.16(9)	C5-Cu3-O25	98.08(18)	C5#1-Cu3-O25	98.96(2)
C5-Cu3-C6	42.00(10)	C5-Cu3-C6	40.90(12)	C5#1-Cu3-C6#1	41.38(2)
C6-Cu3-O9	99.31(9)	C6-Cu3-O25	98.62(19)	C6#1-Cu3-O25	98.47(12)
O11-Cu4-O7#3	85.95(9)	O9-Cu4-O7	87.99(16)	O9-Cu4-O7	87.29(19)

O11-Cu4-O12#2	95.32(11)	O9-Cu4-O14	97.81(17)	O9-Cu4-O14	94.83(12)
O11-Cu4-C7	112.80(11)	O9-Cu4-C7	151.94(19)	O9-Cu4-C7	155.05(2)
O11-Cu4-C8	153.61(11)	O9-Cu4-C8	110.17(19)	O9-Cu4-C8	113.79(2)
O12#2-Cu4-O7#3	94.17(9)	O14-Cu4-O7	94.54(15)	O14-Cu4-O7	96.56(17)
O12#2-Cu4-C7	150.32(11)	O14-Cu4-C7	109.68(19)	O14-Cu4-C7	109.27(2)
O12#2-Cu4-C8	108.97(11)	O14-Cu4-C8	151.11(19)	O14-Cu4-C8	150.07(2)
C7-Cu4-O7#3	96.99(9)	C7-Cu4-O7	95.18(18)	C7-Cu4-O7	96.77(2)
C8-Cu4-O7#3	101.94(9)	C8-Cu4-O7	93.52(19)	C7-Cu4-C8	41.55(2)
C8-Cu4-C7	41.72(10)	C8-Cu4-C7	41.91(12)	C8-Cu4-O7	93.91(2)
		O10-Cu5-O37#1	82.81(16)	O10-Cu5-O35#1	79.45(2)
		O10-Cu5-C9	109.31(13)	O10-Cu5-C9	113.35(2)
		O10-Cu5-C10	150.41(12)	O10-Cu5-C10	152.04(2)
		O11-Cu5-O10	100.19(17)	O11-Cu5-O10	95.04(2)
		O11-Cu5-O37#1	88.35(16)	O11-Cu5-O35#1	98.78(2)
		O11-Cu5-C9	150.10(2)	O11-Cu5-C9	150.23(2)
		O11-Cu5-C10	108.80(2)	O11-Cu5-C10	109.24(2)
		C9-Cu5-O37#1	99.78(18)	C9-Cu5-O35#1	95.65(2)
		C9-Cu5-C10	41.40(2)	C9-Cu5-C10	41.17(2)
		C10-Cu5-O37#1	103.74(18)	C10-Cu5-O35#1	109.46(2)
		O12-Cu6-O24	90.47(15)	O12-Cu6-O13	95.26(19)
		O12-Cu6-C11#1	112.18(19)	O12-Cu6-O24	92.69(17)
		O12-Cu6-C12#1	153.37(19)	O12-Cu6-C11	114.17(2)
		O13-Cu6-O12	97.17(17)	O12-Cu6-C12	155.75(2)
		O13-Cu6-O24	87.59(15)	O13-Cu6-O24	85.89(17)
		O13-Cu6-C11#1	150.32(12)	O13-Cu6-C11	150.46(2)
		O13-Cu6-C12#1	108.80(19)	O13-Cu6-C12	108.44(2)
		C11#1-Cu6-O24	96.53(17)	C11-Cu6-O24	95.53(2)
		C11#1-Cu6-C12#1	41.50(2)	C11-Cu6-C12	42.17(2)
		C12#1-Cu6-O24	96.30(19)	C12-Cu6-O24	94.63(2)
		O15#1-Cu7-O21#1	93.49(15)	O15#1-Cu7-O21#1	91.82(16)
		O15#1-Cu7-C13	150.22(12)	O15#1-Cu7-C13#1	150.67(2)
		O15#1-Cu7-C14	108.71(12)	O15#1-Cu7-C14#1	109.59(2)
		O20-Cu7-O15#1	96.95(17)	O20-Cu7-O15#1	97.59(19)
		O20-Cu7-O21#1	87.87(16)	O20-Cu7-O21#1	88.85(17)
		O20-Cu7-C13	112.41(13)	O20-Cu7-C13#1	111.35(2)

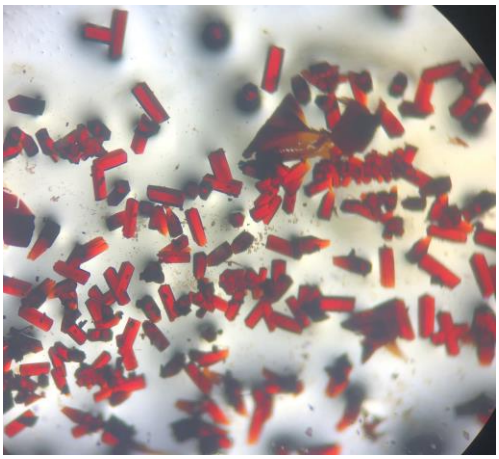
		O20-Cu7-C14	154.14(12)	O20-Cu7-C14#1	152.5(2)
		C13-Cu7-O21#1	92.13(18)	C13#1-Cu7-O21#1	93.97(19)
		C14-Cu7-O21#1	94.35(18)	C14#1-Cu7-O21#1	94.56(2)
		C14-Cu7-C13	41.73(12)	C14#1-Cu7-C13#1	41.38(2)
		O16-Cu8-O17#1	91.84(13)	O16-Cu8-O31#1	88.33(2)
		O16-Cu8-O31A#1	93.41(12)	O16-Cu8-C15	108.25(2)
		O16-Cu8-O31B#1	88.40(13)	O16-Cu8-C16	149.94(2)
		O16-Cu8-C15	104.64(19)	O17-Cu8-O16	92.93(3)
		O16-Cu8-C16	145.81(19)	O17-Cu8-O31#1	84.97(2)
		O17#1-Cu8-O31A#1	95.70(14)	O17-Cu8-C15	154.67(2)
		O17#1-Cu8-C16	117.11(12)	O17-Cu8-C16	115.02(2)
		O31B#1-Cu8-O17#1	81.61(14)	C15-Cu8-O31#1	109.02(2)
		O31B#1-Cu8-O31A#1	15.10(15)	C15-Cu8-C16	42.02(2)
		O31B#1-Cu8-C15	125.91(14)	C16-Cu8-O31#1	104.72(2)
		O31B#1-Cu8-C16	112.35(14)	O18-Cu9-O19#1	95.39(2)
		C15-Cu8-O17#1	147.54(12)	O18-Cu9-O241#	92.16(18)
		C15-Cu8-O31A#1	110.83(14)	O18-Cu9-C17#1	118.67(2)
		C15-Cu8-C16	41.26(12)	O18-Cu9-C18#1	157.76(2)
		C16-Cu8-O31A#1	100.98(14)	O19#1-Cu9-O24#1	93.22(16)
		O18-Cu9-O19	94.66(19)	O19#1-Cu9-C17#1	145.17(2)
		O18-Cu9-O24	88.46(16)	O19#1-Cu9-C18#1	104.40(2)
		O18-Cu9-C17#1	116.24(12)	C17#1-Cu9-O24#1	93.84(18)
		O18-Cu9-C18#1	156.57(13)	C18#1-Cu9-O24#1	97.17(19)
		O19-Cu9-O24	92.38(15)	C18#1-Cu9-C17#1	40.80(2)
		O19-Cu9-C17#1	147.89(19)	S4#1-Cu10-O25#1	77.54(11)
		C17#1-Cu9-O24	96.97(18)	O24#1-Cu10-S41#	79.60(11)
		C18#1-Cu9-O19	107.23(12)	O24#1-Cu10-O25#1	156.75(15)
		C18#1-Cu9-O24	98.85(18)	O33-Cu10-S41#	99.12(14)
		C18#1-Cu9-C17#1	41.07(12)	O33-Cu10-O24#1	94.22(18)
		S4-Cu10-O24	78.02(10)	O33-Cu10-O25#1	85.34(17)
		S4-Cu10-O25	78.31(10)	O33-Cu10-C20	145.46(2)
		O25-Cu10-O24	156.15(13)	C19-Cu10-S4#1	156.10(19)
		O33-Cu10-S4	97.08(13)	C19-Cu10-O24#1	97.67(19)
		O33-Cu10-O24	93.18(15)	C19-Cu10-O25#1	104.94(2)
		O33-Cu10-O25	86.88(15)	C19-Cu10-O33	104.84(2)

		O33-Cu10-C20	147.00(19)	C19-Cu10-C20	40.96(2)
		C19-Cu10-S4	157.41(17)	C20-Cu10-S4#1	115.30(16)
		C19-Cu10-O24	98.69(18)	C20-Cu10-O24#1	94.82(19)
		C19-Cu10-O25	104.28(18)	C20-Cu10-O25#1	98.65(19)
		C19-Cu10-O33	105.53(12)	O27#1-Cu11-O25#1	86.19(16)
		C19-Cu10-C20	41.76(12)	O27#1-Cu11-C21	146.17(12)
		C20-Cu10-S4	115.87(15)	O34-Cu11-O25#1	87.99(18)
		C20-Cu10-O24	95.32(18)	O34-Cu11-O27#1	106.17(12)
		C20-Cu10-O25	97.54(17)	O34-Cu11-C21	107.27(13)
		O27-Cu11-C21#1	148.21(12)	O34-Cu11-C22	148.68(16)
		O34-Cu11-O27	102.64(16)	C21-Cu11-O25#1	100.77(19)
		O34-Cu11-C21#1	108.87(19)	C22-Cu11-O25#1	99.31(19)
		O34-Cu11-C22#1	149.97(2)	C22-Cu11-O27#1	104.89(14)
		C22#1-Cu11-O27	107.45(2)	C22-Cu11-C21	41.50(16)
		C22#1-Cu11-C21#1	41.23(2)	O28-Cu12-O29	96.94(14)
		O28-Cu12-O29A	109.27(6)	O28-Cu12-O35	92.74(12)
		O28-Cu12-O29B	99.98(6)	O28-Cu12-C23#1	112.44(14)
		O28-Cu12-O37	85.95(16)	O28-Cu12-C24#1	153.18(12)
		O28-Cu12-C23#1	108.24(2)	O29-Cu12-O35	115.76(13)
		O28-Cu12-C24#1	150.21(12)	C23#1-Cu12-O29	121.36(15)
		O29A-Cu12-O37	96.28(5)	C23#1-Cu12-O35	112.69(13)
		O29A-Cu12-C24#1	99.07(6)	C23#1-Cu12-C24#1	40.76(18)
		O29B-Cu12-O37	87.76(4)	C24#1-Cu12-O29	99.17(14)
		C23#1-Cu12-O29B	149.57(6)	C24#1-Cu12-O35	99.67(13)
		C23#1-Cu12-O37	105.55(12)	S2-Cu13-O3	84.73(12)
		C23#1-Cu12-C24#1	42.05(12)	S2-Cu13-O14	85.64(12)
		C24#1-Cu12-O29B	109.23(6)	O8-Cu13-S2	163.42(15)
		C24#1-Cu12-O37	100.99(19)	O8-Cu13-O3	98.91(18)
		S2-Cu13-O14	85.97(11)	O8-Cu13-O14	110.91(18)
		O8-Cu13-S2	164.95(13)	O14-Cu13-O3	79.60(16)
		O8-Cu13-O14	109.05(16)	S3-Cu14-Cu15#2	95.88(6)
		S3-Cu14-O19	85.49(11)	S3-Cu14-O19	85.74(11)
		O23-Cu14-S3	162.97(14)	O19-Cu14-Cu15#2	139.36(12)
		O23-Cu14-O19	111.53(17)	O23-Cu14-Cu15#2	71.95(14)
		S5-Cu15-O27	88.61(11)	O23-Cu14-S3	162.88(16)

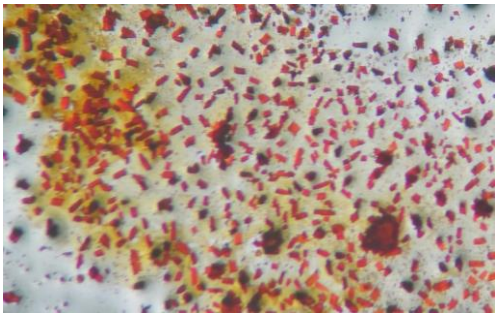
		O26-Cu15-S5	157.88(13)	O23-Cu14-O19	89.36(18)
		O26-Cu15-O27	113.37(16)	S5-Cu15-Cu14#3	84.50(5)
		S1-Cu16-O15	86.81(11)	S5-Cu15-O27	86.45(12)
		O22-Cu16-S1	160.12(14)	O26-Cu15-Cu14#3	92.92(14)
		O22-Cu16-O15	112.42(16)	O26-Cu15-S5	160.79(14)
		S7-Cu17-S6A	114.76(3)	O26-Cu15-O27	111.97(17)
		S7-Cu17-S6B	110.87(3)	O27-Cu15-Cu14#3	112.43(12)
		S7-Cu17-O34	77.63(11)	S1-Cu16-S6#4	109.63(8)
		O30A-Cu17-S6A	82.47(8)	S1-Cu16-O15	85.38(12)
		O30A-Cu17-S7	162.95(8)	O15-Cu16-S6#4	105.67(13)
		O30A-Cu17-O32A	89.25(15)	O22-Cu16-S1	144.90(14)
		O30A-Cu17-O34	85.53(8)	O22-Cu16-S6#4	99.08(15)
		O30A-Cu17-O35	91.63(10)	O22-Cu16-O15	106.28(17)
		O30B-Cu17-S6B	85.34(8)		
		O30B-Cu17-S7	163.47(7)		
		O30B-Cu17-O34	87.97(7)		
		O32A-Cu17-S6A	90.77(8)		
		O32A-Cu17-S7	91.28(9)		
		O32A-Cu17-O34	81.81(9)		
		O32A-Cu17-O35	171.33(8)		
		O32B-Cu17-S6B	79.51(9)		
		O32B-Cu17-S7	100.34(9)		
		O32B-Cu17-O30B	86.34(14)		
		O32B-Cu17-O34	84.77(9)		
		O32B-Cu17-O35	170.83(12)		
		O34-Cu17-S6A	165.80(3)		
		O34-Cu17-S6B	163.17(3)		
		O35-Cu17-S6A	98.05(3)		
		O35-Cu17-S6B	105.35(3)		
		O35-Cu17-S7	85.49(15)		
		O35-Cu17-O30B	86.36(9)		
		O35-Cu17-O34	89.64(18)		
Symmetry codes					
#1: -1/3+y, 1/3-x+y, 4/3-z #2: +y-x, 1-x, +z		#1: 1-x, 1-y, 1-z		#1: 1-x, 1-y, 1-z; #2: 1/2+x, 3/2-y, -1/2+z; #3: 3/2-x, -1/2+y, 3/2-z;	

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

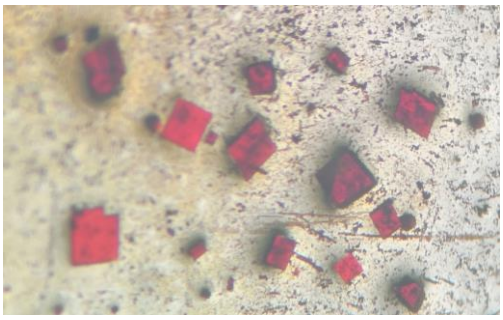
2.2 Additional Structural Description



(a) Complex **1**

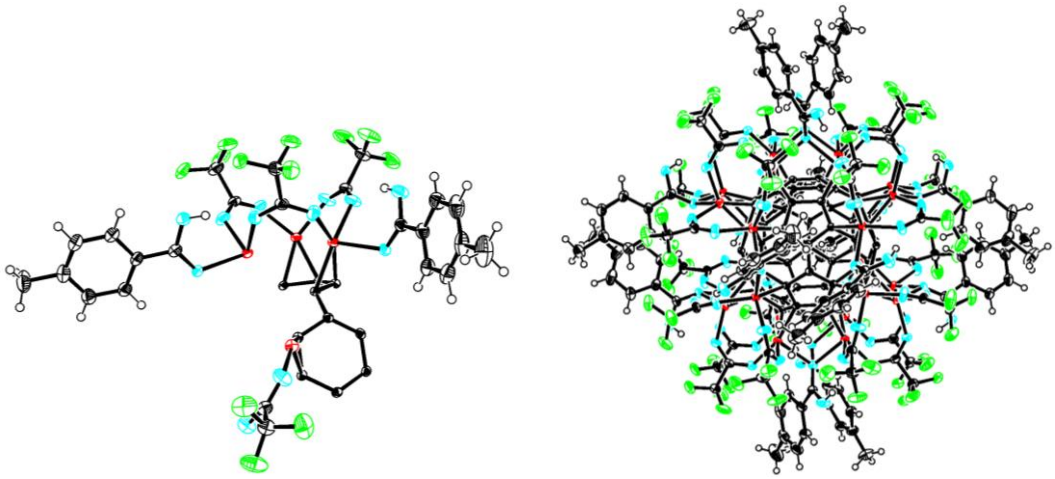


(b) Complex **2**

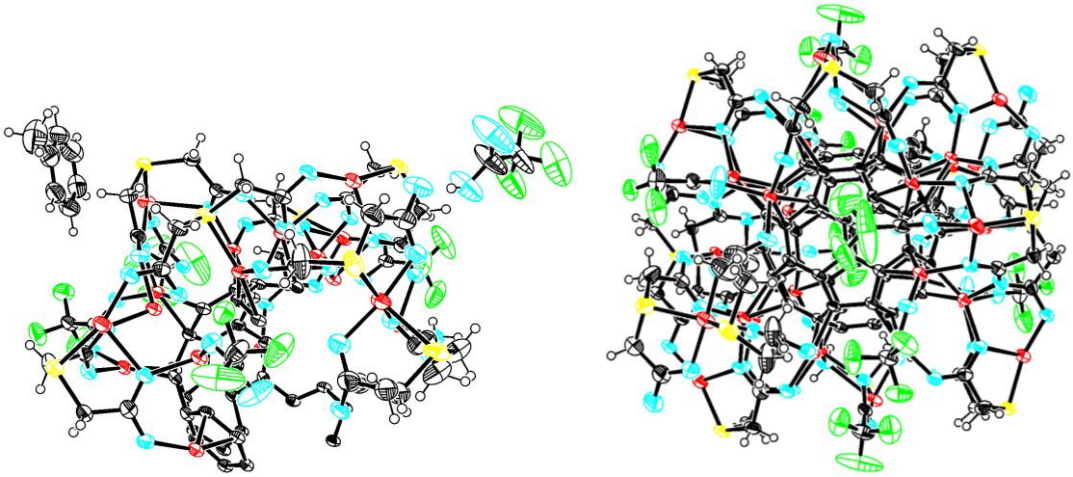


(c) Complex **3**

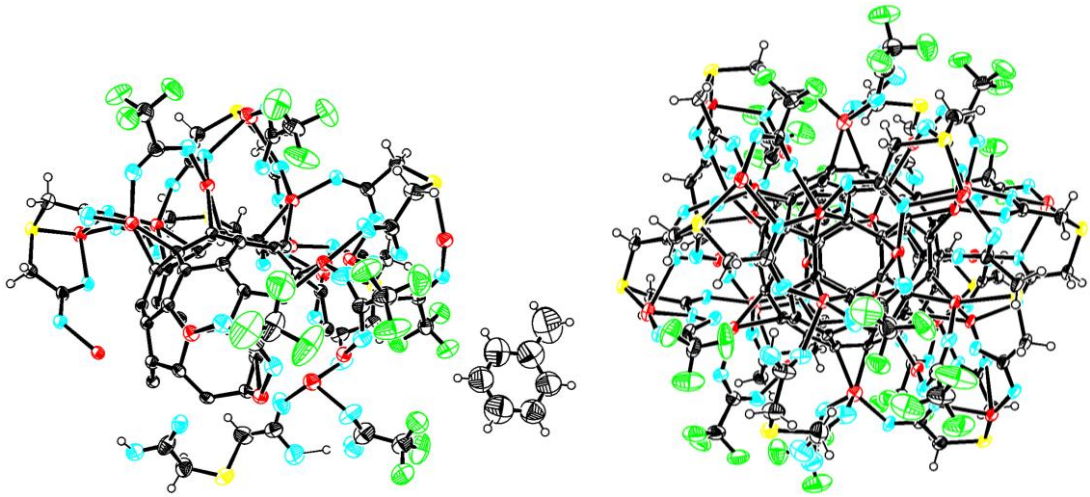
Fig. S1 Crystal images of these cuprofullerene complexes amplified 40 times under a microscope.



(a) Complex **1**

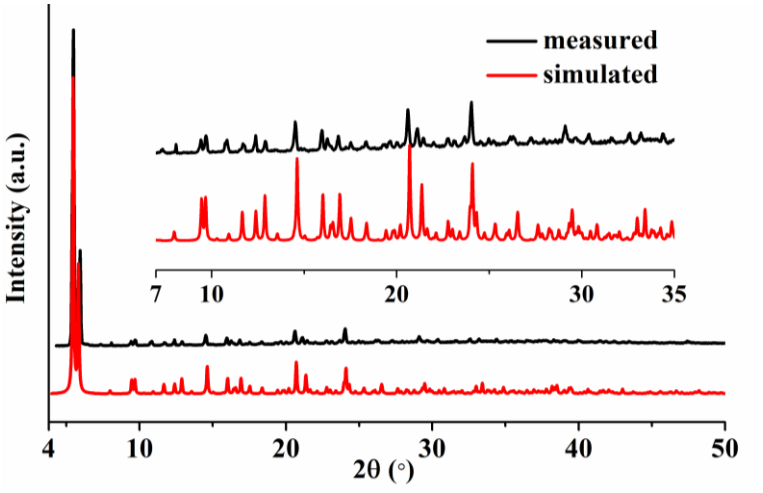


(a) Complex **2**

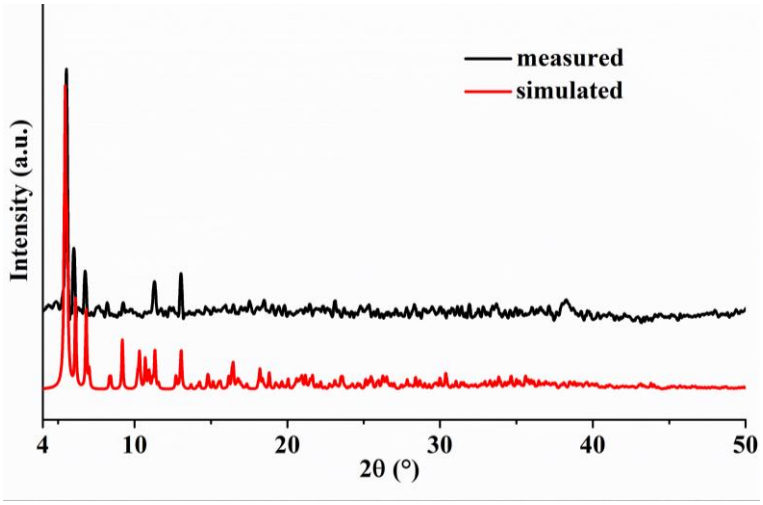


(a) Complex **3**

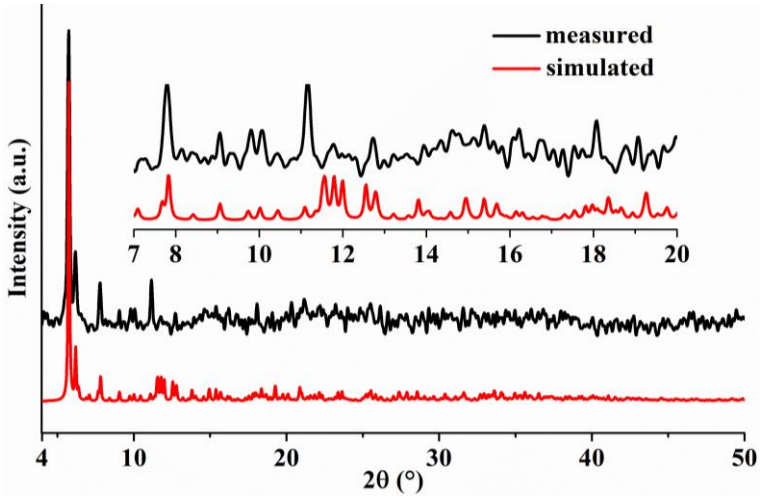
Fig. S2 Asymmetrical units (left) and molecular structures (right) of the complexes **1**-**3** with 50% thermal ellipsoid. (Color codes: red, Cu; cyan, O; yellow, S; black, C; green, F; white cycle, H.)



(a) Complex **1**

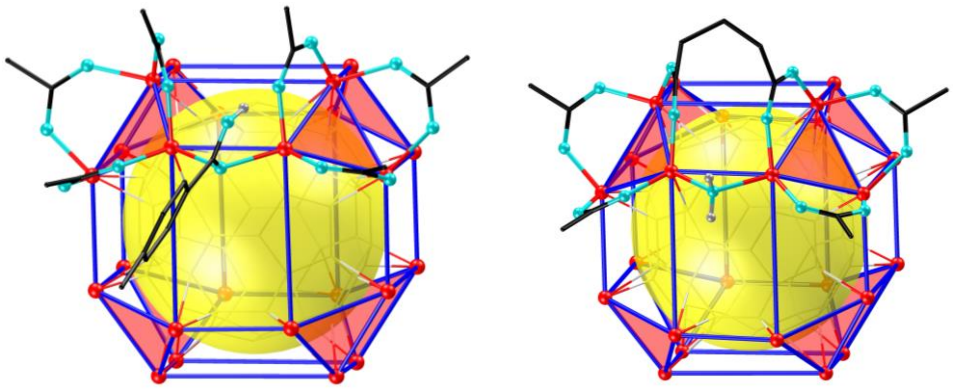


(a) Complex **2**



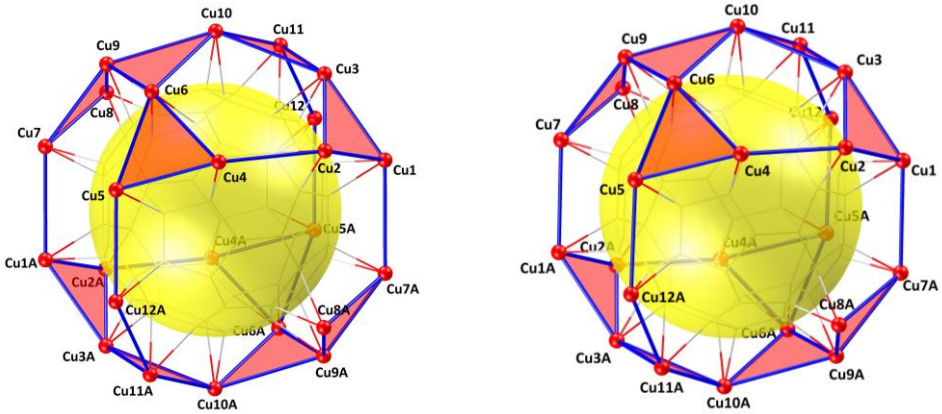
(a) Complex **3**

Fig. S3 Comparison of the simulated and measured X-ray powder diffraction patterns of the complexes **1**, **2** and **3**.

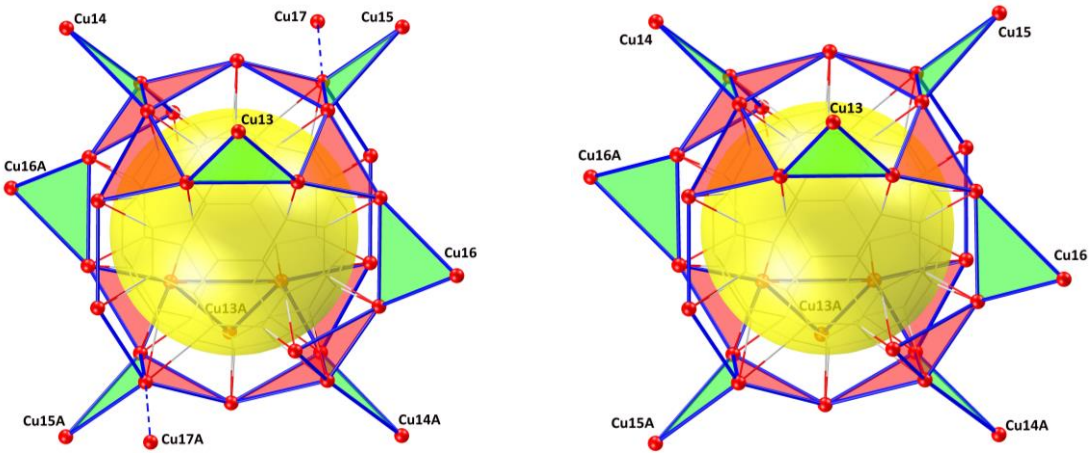


(a) (b)

Fig. S4 Comparison of the rhombicuboctahedral $C_{60}@Cu^{I}_{24}$ core-shell cuprofullerene structures in complex **1** (a) and the reported cuprofullerene glutarate previously (b). Note that all F atoms are omitted and only one whole glutarate chain is shown for clarity in right figure. Color code: red, Cu; cyan, O; black, C; gray, H.

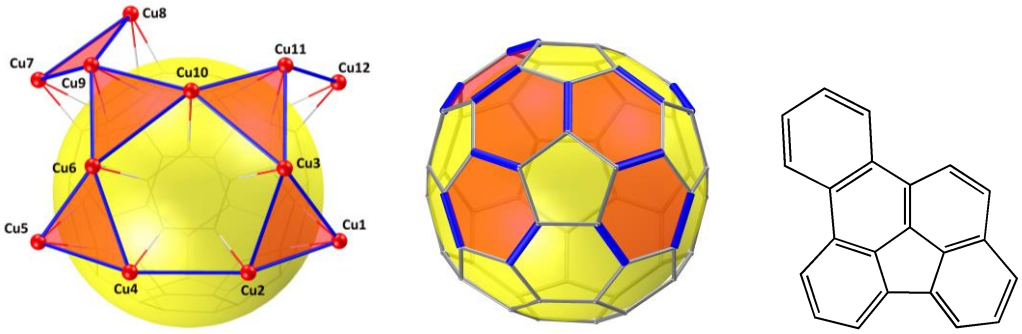


(a) $C_{60}@Cu^{I}_{24}$ structures showing two group of penta-Cu_3 trigons canopying on C_{60} surface and two Cu_{10} big rings (Cu10Cu11Cu12Cu5ACu6ACu10ACu11ACu12ACu5Cu6 and Cu10Cu3Cu1Cu7ACu9ACu10ACu3ACu1ACu7Cu9) around the C_{60} ball.



(b) triplet $C_{60}@Cu^{I}_{24}@Cu^{I}_{8}$ core-shell structures showing the canopying (red) and standing (green) Cu_3 trigons. The Cu(II) atoms (Cu17 and Cu17A) in the complex **2** are shown in left.

Fig. S5 Comparison of the core-shell cuprofullerene structures in complexes **2** and **3**.



(a) (b) (c)

Fig. S6 Penta-Cu_3 trigons (a) canopying on an indeno[1, 2, 3, 4-defg]chrysene (c) fragment of C_{60} surface (b, c).

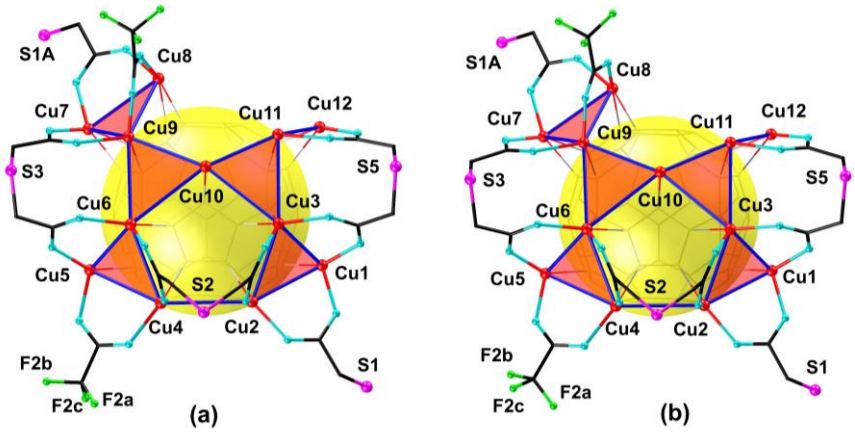
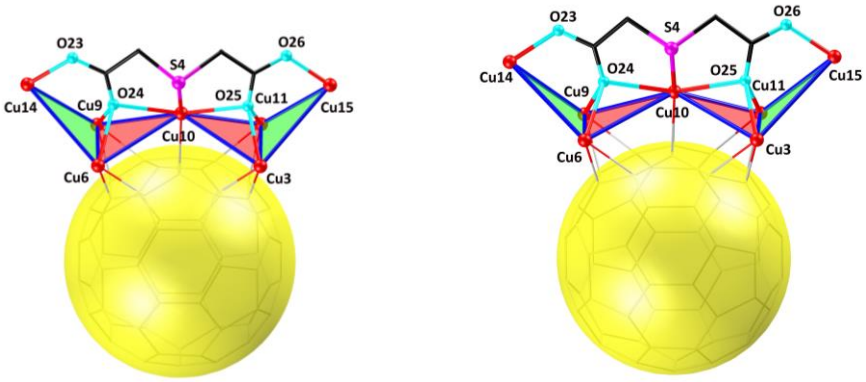
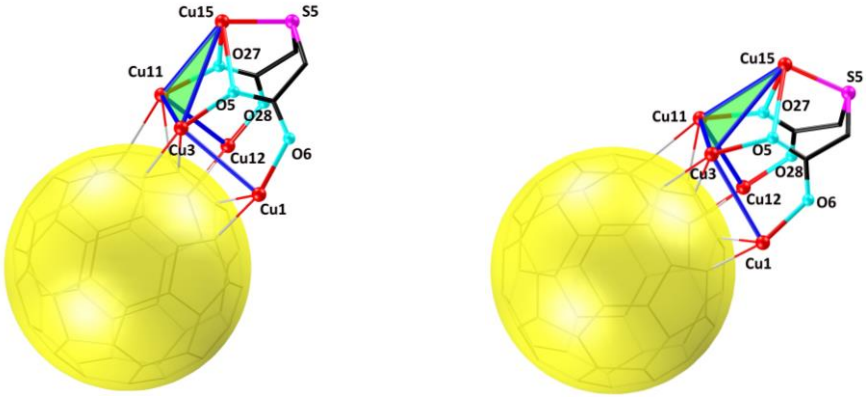


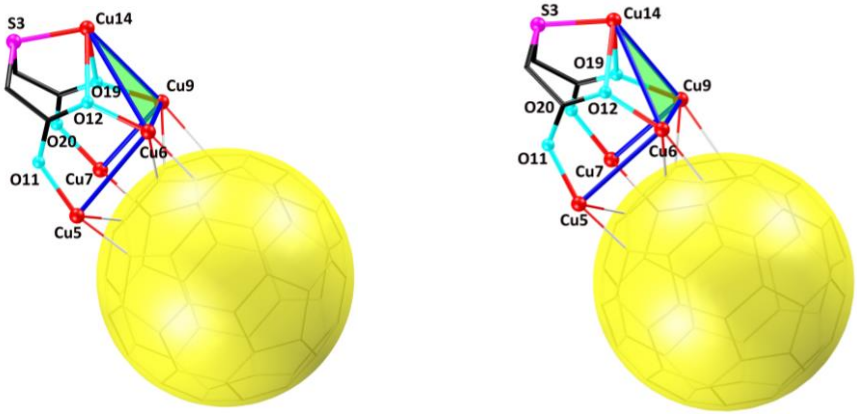
Fig. S7 The outer three Cu_3 trigons supported by three (μ_2-κ^1:κ^1)-carboxylates from **L**$_S$/**L**$_F$ in complex **2** (a) and complex **3** (b), showing Cu1Cu2Cu3 trigon is edge-bridged by three (μ_2-κ^1:κ^1)-carboxylates from three **L**$_S$ (S1, S2, and S5), Cu4Cu5Cu6 and Cu7Cu8Cu9 trigons are by three (μ_2-κ^1:κ^1)-carboxylates from two **L**$_S$ (S2, S3, and S3, S1A) and one **L**$_F$, respectively.



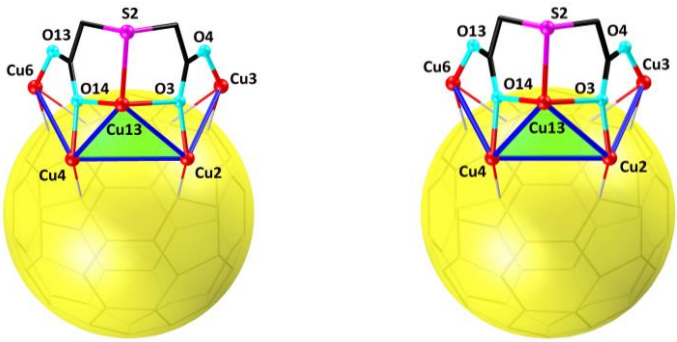
(a) similar local coordination environments of μ_7-**L**$_S$(S4) to support the canopying (red) and standing (green) Cu^I_3 trigons.



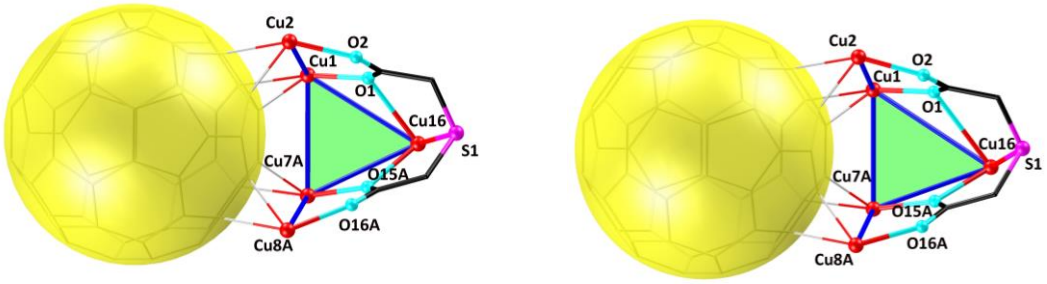
(b) similar local coordination environments of μ_5-**L**$_S$(S5) to support the standing Cu^I_3 trigons (green).



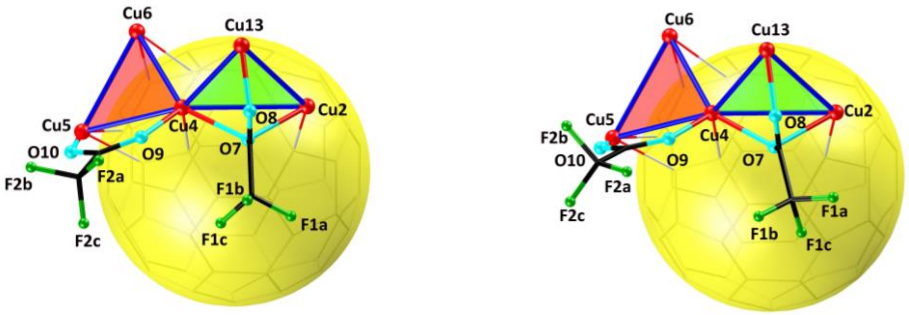
(c) similar local coordination environments of μ_5-**L**$_S$(S3) to support the standing Cu^I_3 trigons (green).



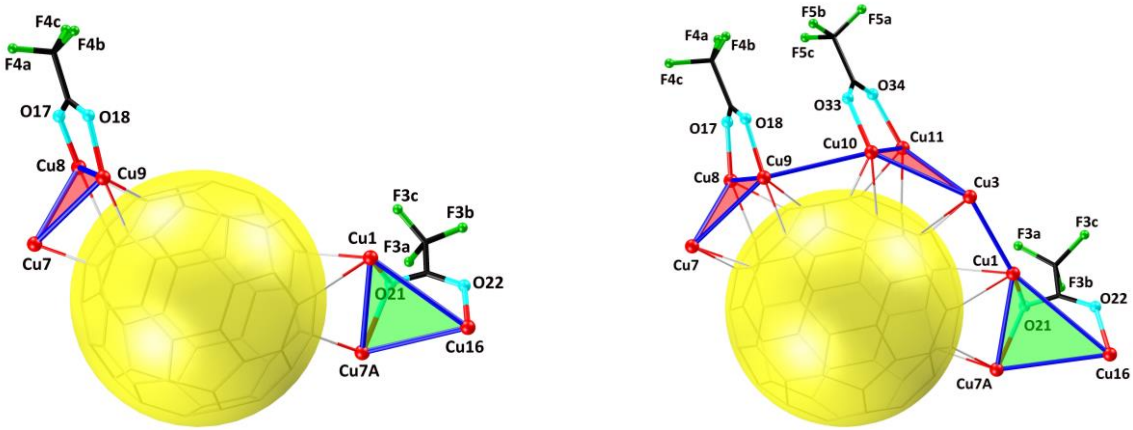
(d) similar local coordination environments of μ_5-**L**$_S$(S2) to support the standing Cu^I_3 trigons (green).



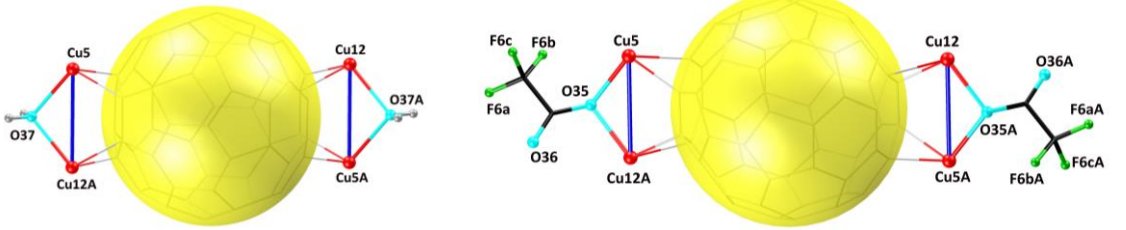
(e) similar local coordination environments of μ_5-$\mathbf{L_S}$(S1) to support the standing Cu^I_3 trigon (green) on C_{60} surface as a pillar.



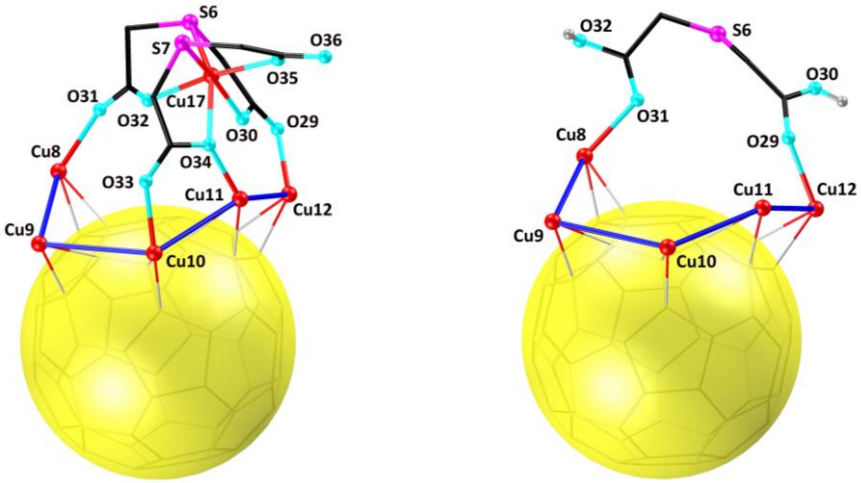
(f) similar local coordination environments of μ_2-(κ^1:κ^1)-$\mathbf{L_F}$(F2) and μ_3-(κ^1:κ^2)-$\mathbf{L_F}$(F1) to support the canopying (red) and standing (green) Cu^I_3 trigons.



(g) local coordination environments of μ_2-(κ^1:κ^1)-$\mathbf{L_F}$(F4), μ_2-(κ^1:κ^1)-$\mathbf{L_F}$(F5) (right) and μ_3-(κ^1:κ^2)-$\mathbf{L_F}$(F3) to support the canopying (red) and standing (green) Cu^I_3 trigons.

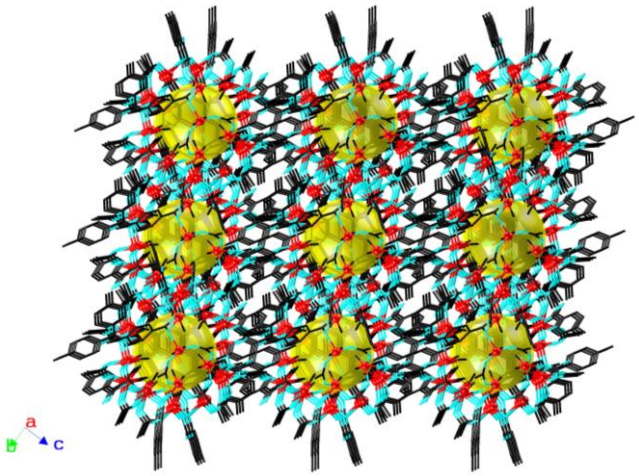


(h) local coordination environments of the pillar Cu12Cu5A and Cu5Cu12A bridged by μ_2-O from H_2O (O37 and O37A, left) and $\mathbf{L_F}$ (O35 and O35A, right).

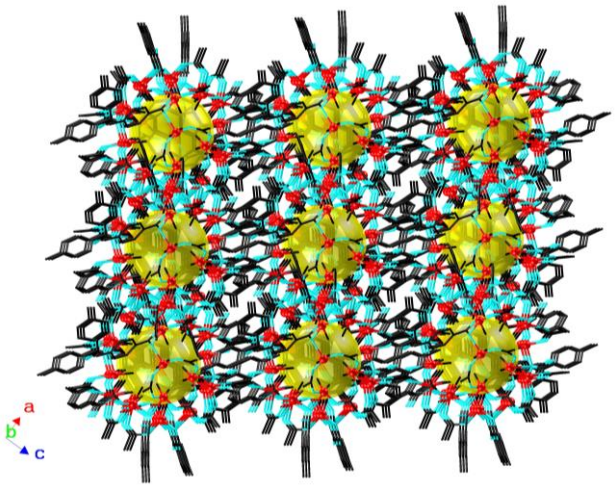


(i) local coordination environments of $\mathbf{L_S}$(S6 and S7, left) and $H_2\mathbf{L_S}$ (S6, right) showing the differences between the complex **2** and **3**. Note that Cu17 is Cu(II) atom showing Jahn-Teller coordination geometry with S6-Cu17 and O34-Cu17 longer than others. O35-Cu17, 1.992(5) Å; O32-Cu17, 1.990(4)/1.910(3) Å; O30-Cu17, 1.860(3)/2.130(3) Å; S7-Cu17, 2.341(2) Å; S6-Cu17, 2.530(2) Å; O34-Cu17 2.352(4) Å.

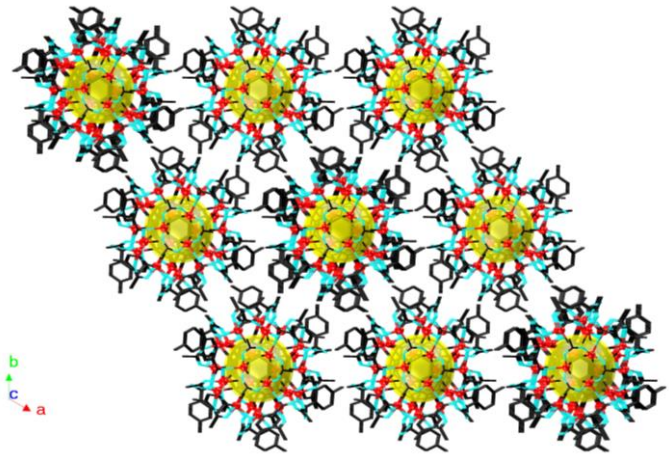
Fig. S8 Comparison of coordination environments and molecular structures between complexes **2** (left) and **3** (right) showing their similarities and differences.



(a)

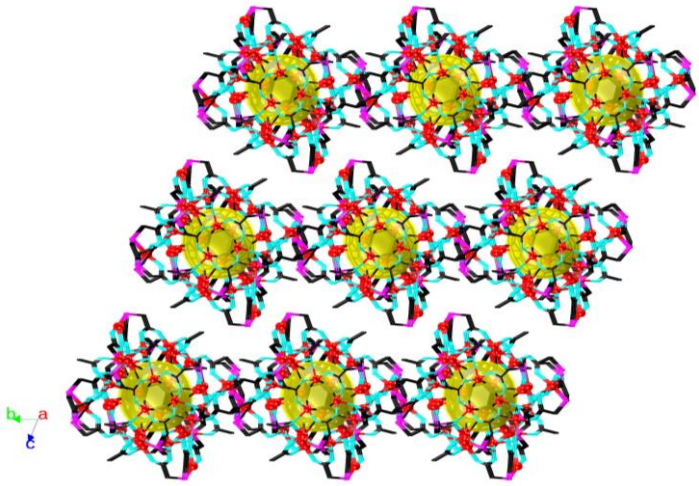


(b)

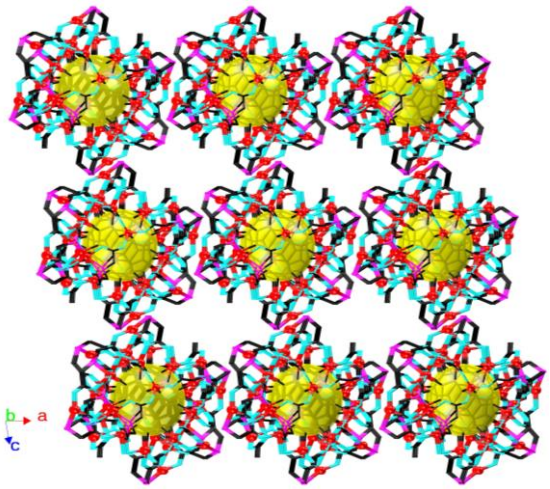


(c)

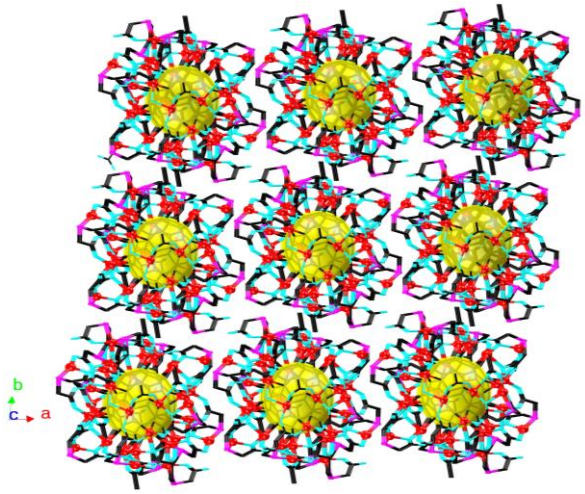
Fig. S9 Packing structures of the complex **1** along *a* (a), *b* (b) and *c* (c) axis. (The crystallized solvent molecules, F atoms and H atoms are omitted for clarity. Color codes: red, Cu; cyan, O; black, C)



(a)

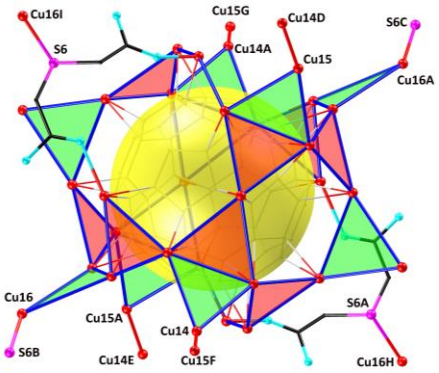


(b)

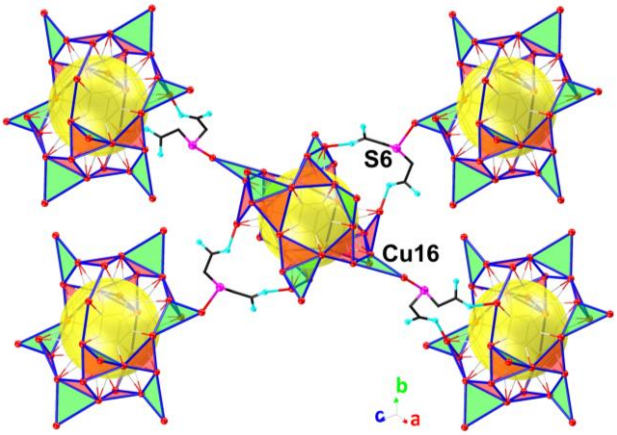


(c)

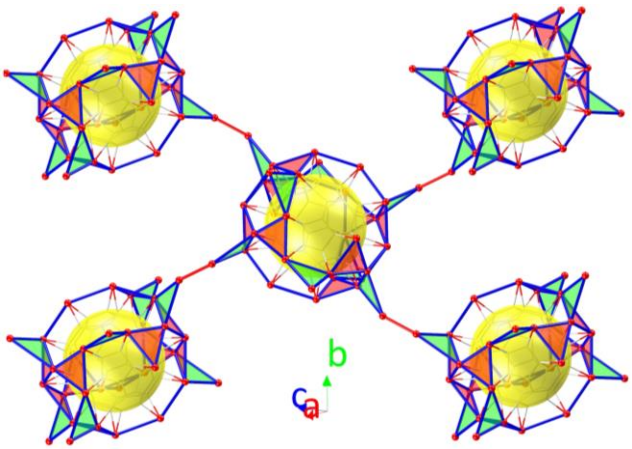
Fig. S10 Packing structures of the complex **2** along *a* (a), *b* (b) and *c* (c) axis. (The crystallized solvent molecules, F atoms and H atoms are omitted for clarity. Color codes: red, Cu; cyan, O; pink, S; black, C)



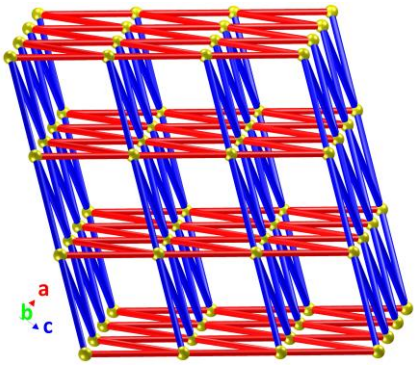
(a) 8-connected cuprofullerene unit through 4 Cu-Cu (Cu15-Cu14D, Cu14-Cu15F, Cu15A-Cu14E, Cu14A-Cu15G) and 4 Cu-S (S6-Cu16I, Cu16-S6B, S6A-Cu16H, Cu16A-S6C) interactions. (symmetry codes: A -x, -y, -z; B 0.5-x, -0.5+y, -0.5-z; C -0.5+x, 0.5-y, 0.5+z; D -0.5-x, 0.5+y, -0.5-z; E 0.5+x, -0.5-y, 0.5+z; F -0.5-x, -0.5+y, -0.5-z; G 0.5+x, 0.5-y, 0.5+z; H -0.5+x, -0.5-y, 0.5+z; I 0.5-x, 0.5+y, -0.5-z)



(b) intercuprofullerene Cu-S interactions showing a planar 4-connected sheet.

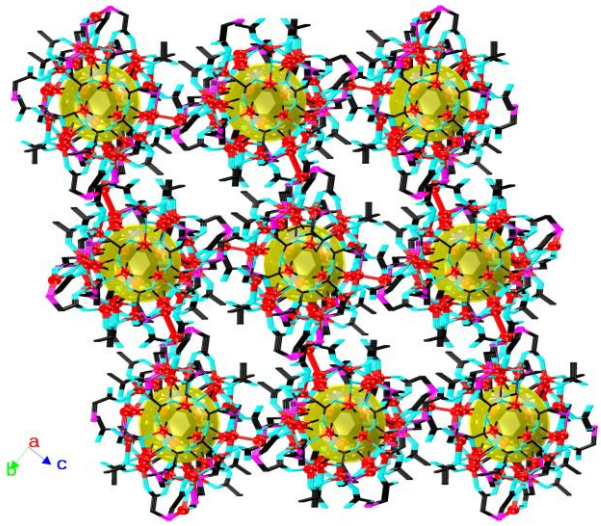


(c) intercuprofullerene Cu-Cu interactions showing a planar 4-connected sheet.

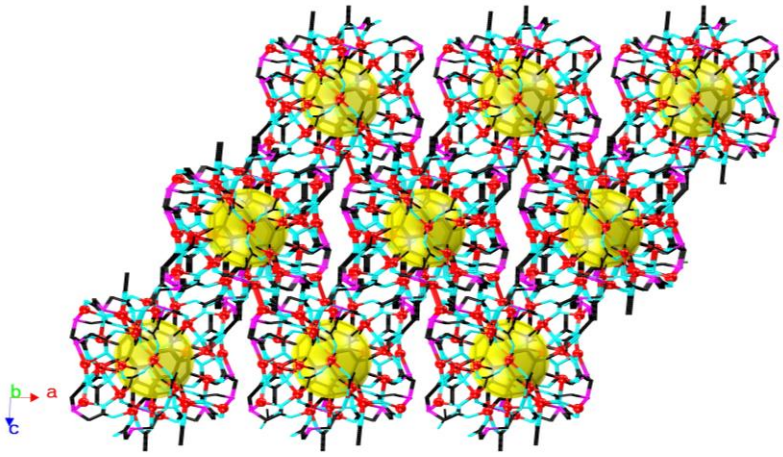


(d) simplified **bcu** (CsCl) topological network. Yellow ball represents the cuprofullerene molecule, red and blue bond represent Cu-Cu and Cu-S interactions, respectively.

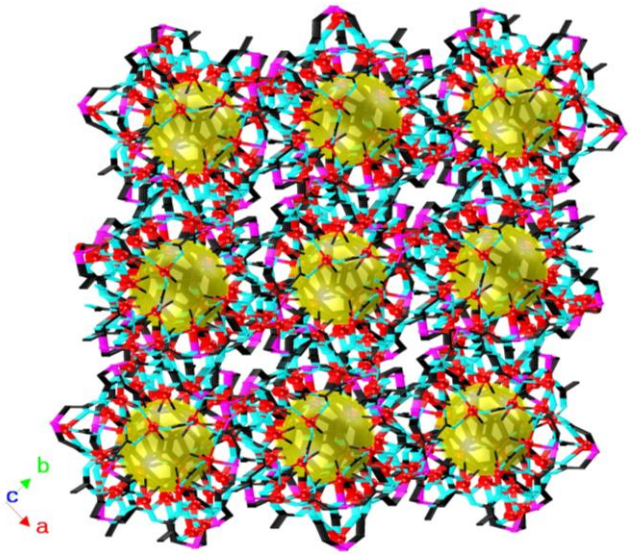
Fig. S11 Illustration of the 3-D structures of the complex **3** supported by intercuprofullerene Cu-Cu (red) and Cu-S (blue) interactions. (some atoms and fragments are omitted for clarity).



(a)



(b)



(c)

Fig. S12 Packing structures of the complex **3** along *a* (a), *b* (b) and *c* (c) axis. (The crystallized solvent molecules, F atoms and H atoms are omitted for clarity. Color codes: red, Cu; cyan, O; pink, S; black, C)

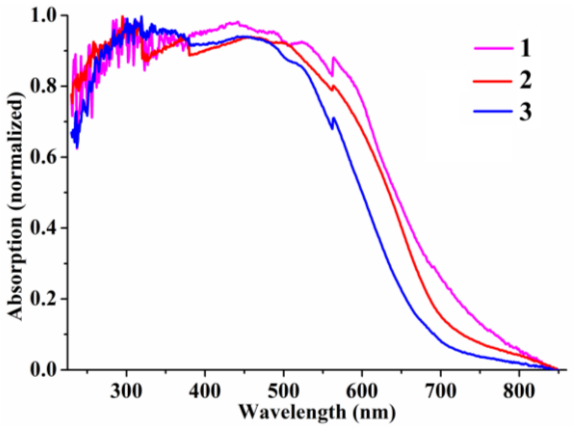
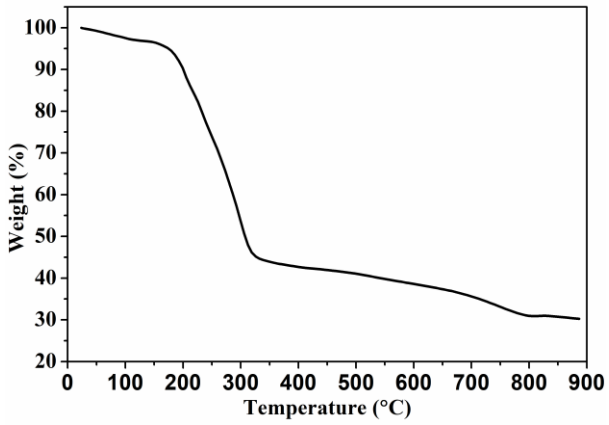
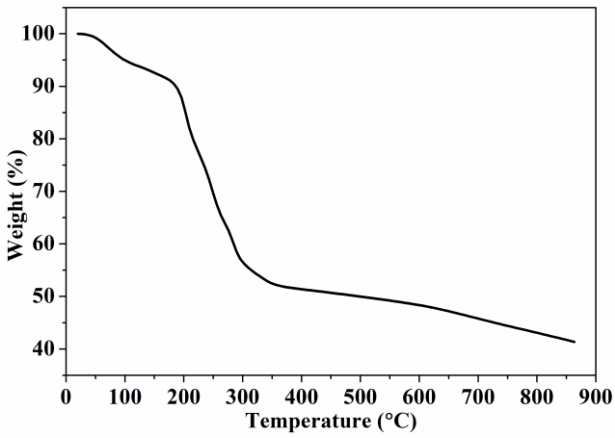


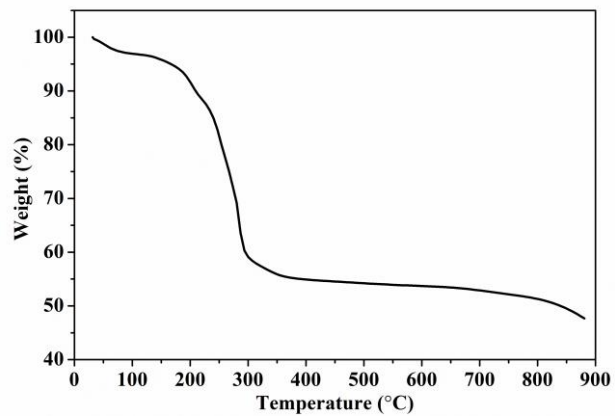
Fig. S13 Comparison of the diffuse reflectance solid-state UV-Vis spectra of the complexes **1**-**3**.



(a) Complex **1**



(b) Complex **2**



(c) Complex **3**

Fig. S14 Thermogravimetric analysis (TGA) plots of the complexes **1-3**.

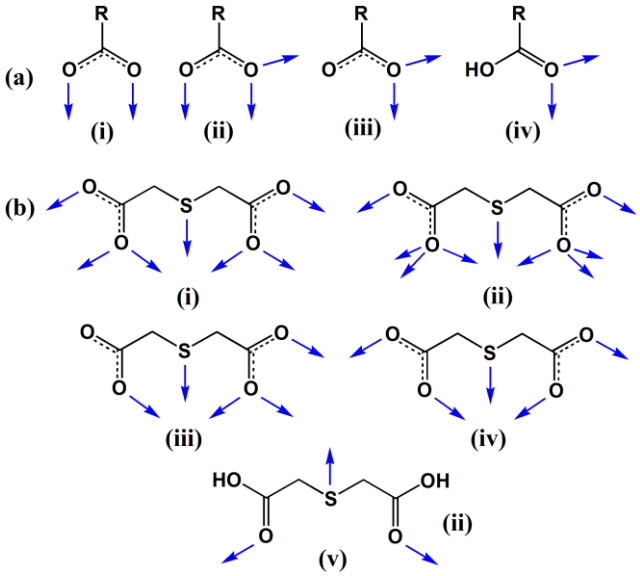


Fig. S15 Coordination modes of $\mathbf{L_F}$, $H\mathbf{L_{mb}}$ (a) and $\mathbf{L_S}$/$H_2\mathbf{L_S}$ (b) in this work. (a) (i) (μ_2-κ^1:κ^1)-COO, (ii) (μ_3-κ^1:κ^2)-COO, (iii) μ_2(O)-COO, (iv) μ_2(O)-COOH (b) (i) (μ_5-$\kappa^1{}_2$(O):$\kappa^2{}_2$(O):κ^1(S)-**Ls**, (ii) (μ_7-$\kappa^1{}_2$(O):$\kappa^3{}_2$(O):κ^1(S):)-**Ls**, (iii) (μ_3-κ^1(O):κ^2(O):κ^1(S):)-**Ls**, (iv) (μ_3-$\kappa^1{}_4$(O):κ^1(S):)-**Ls**, (v) (μ_3-$\kappa^1{}_2$(O):κ^1(S))-H_2**Ls**.

3 References

[1] G. M. Sheldrick, A short history of SHELX. *Acta Cryst.*, **2008**, *A64*: 112–122.

[2] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.*, **2009**, *42*, 339–341.

[3] A. L. Spek, *Acta Cryst.*, 2015, C71, 9–18.