Supporting Information

Exohedral Cuprofullerene: Sequentially Expanding Metal Olefin Up to a $C_{60}@Cu_{24}$ Rhombicuboctahedron

Shun-Ze Zhan,*[†§] Guo-Hui Zhang,[†] Jing-Hong Li,[†] Jia-Li Liu,[†] Si-Hui Zhu,[†]

Weigang Lu,[‡] Ji Zheng,[‡] Seik Weng Ng[⊥], Dan Li*[‡]

[†] Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province, Shantou University, Shantou 515063, P. R. China

[‡] College of Chemistry and Materials Science, Jinan University, Guangzhou 510632, P. R. China

[§] Chemistry and Chemical Engineering Guangdong Laboratory, Shantou 515031, P. R. China

[⊥] UCSI University, 1 Jalan Puncak Menara Gading, UCSI Heights, 56000 Cheras, Kuala Lumpur, Malaysia

*Email: szzhan@stu.edu.cn (S.Z.Z.).
*Email: danli@jnu.edu.cn (D.L.).

Content

Section 1: Experimental Section

1.1 Materials and Physical Measurements

Commercially available chemicals were purchased and used without further purification. C_{60} (99.5%) were purchased from Xiamen Funano New Material Technology Company LTD. 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. 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. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q50 Thermogravimetric Analyzer under a nitrogen flow of 40 $mL \cdot min^{-1}$ at a heating rate of 10 $°C \cdot min^{-1}$. The diffuse reflectance solid-state UV-Vis spectra of the complexes were obtained on a Lambda950 UV/Vis/NIR spectrophotometer of Perkin Elmer using pure powder sample and pure $BaSO_4$ as background. The UV-Vis absorption of C_{60} in toluene solution (10^{-4} $mol \cdot L^{-1}$) was also obtained on the Lambda950 UV/Vis/NIR spectrophotometer of Perkin Elmer.

In all cases, the pure crystalline sample was selected mechanically under a microscope with 40-time amplification and used for measurements.

1.2 Synthesis

Complex 1 $[Cu_3(C_3F_7COO)_3(H_2O)_3]_2[(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2)_2\text{-}C_{60}]$: A mixture of Cu_2O (10.0 mg, 0.07 mmol), heptafluorobutyric acid (C_3F_7COOH, 15.0 mg, 0.07 mmol) and C_{60}-saturated chlorobenzene solution (1.0 mL, 7.0 mg/mL, 0.0097 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 $°C \cdot h^{-1}$. Black block crystals were separated mechanically, washed with a little chlorobenzene to remove the residual C_{60} solid, and dried in air. Yield: 8.4 mg, 34.7% based on C_{60}. IR data (KBr, cm^{-1}): 3406 vs, 1638 vs, 1407 m, 1336 m, 1221 s, 1159 m, 1119 m, 1084 w, 968 w, 938 w, 818 w, 716 w, 632 s, 521 s.

Complex 2 {[$Cu_3(C_3F_7COO)_3(H_2O)$](μ_2-H_2O)[$Cu_3(C_3F_7COO)_3(H_2O)(C_3F_7COOH)$]}$_2$[($\mu_3$-$\eta^2$:$\eta^2$:$\eta^2$)$_4$-$C_{60}$)]·[$Cu(C_3F_7COO)_2(H_2O)_4$]·($C_6H_5Cl$)}

A mixture of Cu_2O (10.0 mg, 0.07 mmol), heptafluorobutyric acid (C_3F_7COOH, 30.0 mg, 0.14 mmol) and C_{60}-saturated chlorobenzene solution (1.0 mL, 7.0 mg/mL, 0.0097 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}. Dark-red needle crystals were separated mechanically, washed with a little chlorobenzene to remove the residual C_{60} solid, and dried in air. Yield: 19.9 mg, 38.0% based on C_{60}. IR data (KBr, cm^{-1}): 3402 vs, 1678 vs, 1638 vs, 1412 w, 1336 m, 1279 m, 1222 s, 1159 m, 1119 m, 1084 w, 974 w, 938 w, 818 w, 742 s, 720 s, 632 w, 526 m.

Complex 3 [$Cu_{24}(C_5F_6O_4)_{12}(\mu_2$-$H_2O)_{12}$][($\mu_3$-$\eta^2$:$\eta^2$:$\eta^2$)$_8$-$C_{60}$]·($H_2O$)$_{18}$·($C_7H_8$)$_4$}

A mixture of Cu_2O (10.0 mg, 0.07 mmol), hexafluoroglutaric acid ($HOOCC_3F_6COOH$, 16.8 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, washed with a little toluene to remove the residual C_{60} solid, and dried in N_2. Yield: 3.2 mg, 12.8% based on C_{60}. IR data (KBr, cm^{-1}): 3522 s, 1689 vs, 1400 s, 1273 w, 1255 w, 1155 vs, 1046 w, 945 m, 823 m, 744 w, 516 w.

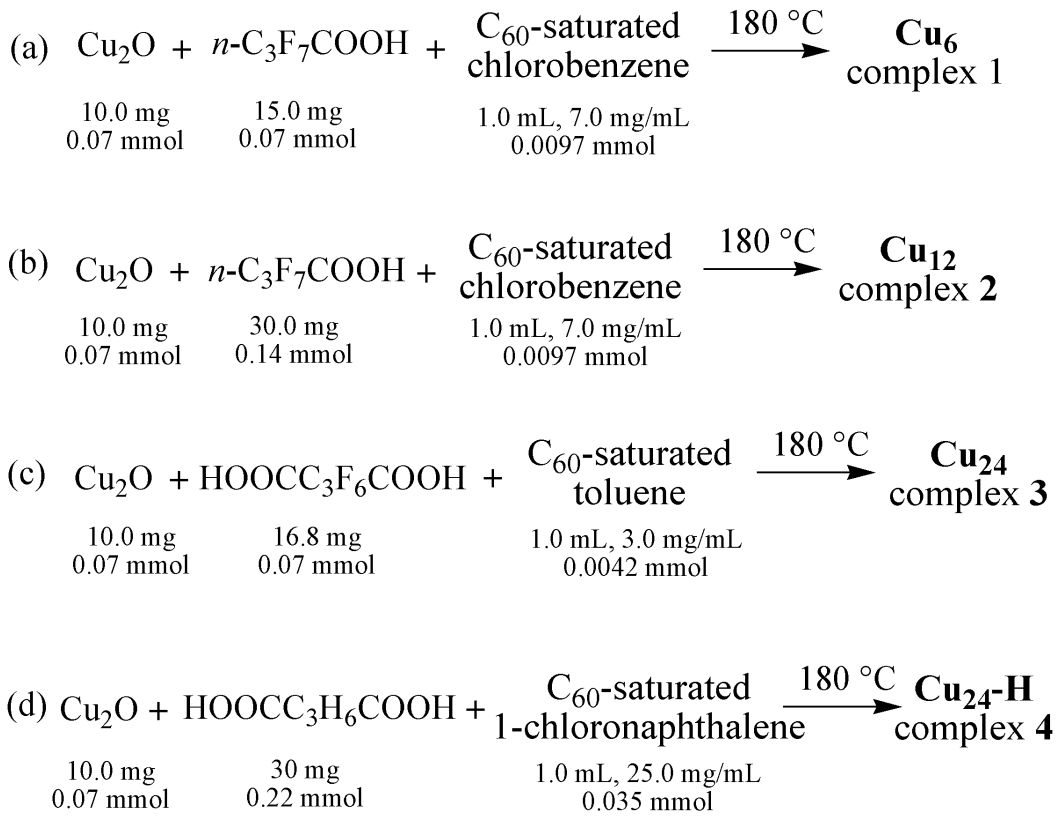
Complex 4 [$Cu_{24}(C_5H_6O_4)_{12}(HOOCC_3H_6COOH)_6$][($\mu_3$-$\eta^2$:$\eta^2$:$\eta^2$)$_8$-$C_{60}$]·($C_{10}H_7Cl$)$_6$

A mixture of Cu_2O (10.0 mg, 0.07 mmol), glutaric acid ($HOOCC_3H_6COOH$, 30 mg, 0.22 mmol) and C_{60} solution of 1-chloronaphthalene (1.0 mL, 25.0 mg/mL, 0.035 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, washed with a little toluene to remove the residual C_{60} solid, and dried

in N_2. Yield: 2.0 mg, 1% based on C_{60}. IR data (KBr, cm^{-1}): 3441 vs, 2932 s, 1673 w, 1563 vs, 1412 vs, 1346 w, 1310 m, 1058 m, 570 w, 526 w.

Note that: The red crystal samples of the complex **3** and **4** will turn into dark-red and even dark color after tens of minutes in air, losing their crystalline. So immediate measurements are necessary to ensure their crystalline purity.

Caution! In the solvothermal synthesis, the reaction solution should not exceed half the volume of the glass tube to avoid overloading. Be careful to avoid burning and cutting yourself when flame-sealing and opening the glass tubes.



Scheme S1. Synthesis reactions of the cuprofullerene complexes **1**-**4**.

Section 2: Crystal Data and Additional Structural Description

2.1 Crystal Structural Determination

Data were processed with the CrysAlisPro 1.171.39.7e (Rigaku Oxford Diffraction, 2015). Structures were solved by direct methods (SHELXTL-97) and refined on F^2 using full-matrix last-squares (SHELXTL-97).[1] 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. Crystal data and structure refinement for the adduct are given in Table S1. Selected bond lengths and angles are summarized in Tables S2. CCDC nos. 1967677−1967680 contain the supplementary crystallographic data for this paper.

2.1 Crystal Data

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

	1	**2**	**3**	**4**
Chemical formula	$C_{84}H_{12}Cu_6F_{42}O_{18}$	$C_{137}H_{32}Cl_2Cu_{13}F_{113}O_{42}$	$C_{148}H_{92}Cu_{24}F_{72}O_{78}$	$C_{210}H_{162}Cl_6Cu_{24}O_{72}$
Formula weight	2488.18	5393.54	6011.17	5575.05
Crystal system	trigonal	triclinic	triclinic	trigonal
Space group	R-3m	P-1	P-1	R-3
a (Å)	14.2233(4)	13.5207(2)	17.7170(3)	25.6664(6)
b (Å)	14.2233(4)	18.2853(3)	17.7627(6)	25.6664(6)
c (Å)	37.3147(2)	18.8367(2)	17.8073(4)	24.6267(9)
α (deg)	90	107.6850(10)	63.110(3)	90
β (deg)	90	108.6850(10)	88.8395(17)	90
γ (deg)	120	95.6440(10)	86.946(2)	120
V ($Å^3$)	6537.54(8)	4103.09(11)	4990.9(2)	14049.7(8)
Z	3	1	1	3
D_{calc} (gcm^{-3})	1.896	2.183	2.000	1.977
μ (mm^{-1})	3.064	4.021	4.092	4.475
Reflections collected	17729	45555	59746	15603
Unique reflections	1675	16148	19675	6122
R_{int}	0.0290	0.0414	0.0333	0.0337
GOF	1.115	1.046	1.055	1.070
R_1 [a] [$I > 2\sigma(I)$]	0.1171	0.0898	0.0554	0.0547
wR_2 [b] [$I > 2\sigma(I)$]	0.3200	0.2558	0.1647	0.1495
R_1 [a] [all refl.]	0.1183	0.0957	0.0623	0.0598
wR_2 [b] [all refl.]	0.3211	0.2628	0.1700	0.1539

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond lengths (Å) and bond angles (°) of the coordination bonds and CC bond lengths (Å) of C_{60} moiety for the complex **1** measured at 100 K.

bond lengths			
Cu-O(carboxylate)		Cu-O(water)	
Cu1-O1	1.9976(1)	Cu1-O1W	2.1642(9)
Cu-C			
Cu1-C1		2.0180(2)	
Cu-Cu			
Cu-Cu		3.3526(1)	
C-C (coordinated hexagons)			
C=C (6, 6)		C-C (6, 5)	
C1-C1#1	1.4310(8)	C1-C1#2	1.4835(5)
C-C (other)			
(6, 6)			
C2-C3	1.3943(3)	C4-C5	1.3903(1)
C6-C6#3	1.3721(1)		
(6, 5)			
C1-C2	1.4643(5)	C2-C4	1.4468(5)
C3-C3#1	1.4448(7)	C5-C6#2	1.4525(8)
C3-C6#3	1.4536(1)	C5-C6	1.4528(7)
bond angles			
O1#1-Cu1-O1	94.7(3)	O1-Cu1-C1	151.7(2)
O1-Cu1-O1W	91.9(2)	C1-Cu1-O1W	98.6(2)
O1-Cu1-C1#1	111.1(2)	C1-Cu1-C1#1	41.5(3)
Symmetry codes			
#1 1-y, 1-x, +z #2 +x, +x-y, +z #3 1/3-y+x, 2/3-y, 2/3-z			

Table S3. Selected bond lengths (Å) and bond angles (°) of the coordination bonds and CC bond lengths (Å) of C_{60} moiety for the complex **2** measured at 100 K.

bond lengths			
Cu-O(carboxylate)			
Cu1-O1	1.9805(2)	Cu4-O7	1.9853(2)
Cu1-O2	1.9254(2)	Cu4-O12	1.9639(2)
Cu2-O3	2.0126(2)	Cu5-O8	2.0050(2)
Cu2-O4	1.9917(2)	Cu5-O9	1.9734(2)
Cu3-O5	1.9790(2)	Cu6-O10	1.9696(2)
Cu3-O6	1.9754(2)	Cu6-O11	1.9708(2)

Cu-O(water)			
Cu2-O1W	2.2152(2)	Cu4-O2W	2.2498(2)
Cu3-O2W	2.2198(2)	Cu5-O3W	2.2115(2)
Cu-O(carboxylic acid)		Cu6-O13	2.2939(2)
Cu-C			
Cu1-C1	1.9931(2)	Cu4-C7	2.0004(2)
Cu1-C2	2.0404(2)	Cu4-C8	2.0304(2)
Cu2-C3	1.9908(2)	Cu5-C9	2.0148(2)
Cu2-C4	2.0478(2)	Cu5-C10	2.0267(2)
Cu3-C5	2.0229(2)	Cu6-C11	2.0196(2)
Cu3-C6	2.0185(2)	Cu6-C12	1.9813(2)
Cu-Cu (intra Cu_3 units)			
Cu1-Cu2	3.3134(3)	Cu4-Cu5	3.2737(3)
Cu1-Cu3	3.2560(3)	Cu5-Cu6	3.4079(4)
Cu2-Cu3	3.3748(3)	Cu4-Cu6	3.2165(3)
Cu-Cu (inter Cu_3 units)			
Cu3-Cu4	3.5020(4)		
C-C (coordinated hexagons)			
(6,6)			
C1-C2	1.4427(1)	C3-C4	1.4361(1)
C5-C6	1.4480(1)	C7-C8	1.4467(1)
C9-C10	1.4363(1)	C10-C11	1.4897(1)
(6,5)			
C1-C6	1.4868(1)	C2-C3	1.4885(1)
C4-C5	1.4945(1)	C7-C12	1.4942(1)
C8-C9	1.4754(1)	C11-C12	1.4389(1)
C-C (other)			
(6,6)			
C13-C20#1	1.3921(1)	C19-C28#1	1.3821(1)
C14-C23#1	1.3980(1)	C21-C22	1.3876(1)
C15-C16	1.3878(1)	C25-C26	1.3960(1)
C17-C24#1	1.3930(1)	C29-C30	1.3871(1)
C18-C27#1	1.3969(1)		
(6,5)			
C1-C13	1.4549(1)	C14-C15	1.4350(1)
C2-C28	1.4456(1)	C16-C17	1.4443(1)
C3-C26	1.4625(1)	C17-C18	1.4345(1)
C5-C8	1.4504(1)	C19-C20	1.4457(1)
C4-C29	1.4588(1)	C20-C21	1.4459(7)

C6-C15	1.4627(1)	C22-C23	1.4366(1)
C7-C16	1.4629(1)	C22-C30	1.4519(1)
C9-C29	1.4549(1)	C23-C24	1.4380(1)
C10-C21	1.4594(1)	C24-C25	1.4447(1)
C11-C19	1.4575(1)	C25-C30	1.4509(1)
C12-C18	1.4554(1)	C26-C27	1.4229(1)
C13-C14	1.4362(1)	C27-C28	1.4571(1)
bond angles			
O2-Cu1-O1	102.4(2)	O7-Cu4-C7	152.83(19)
O2-Cu1-C2	108.9(2)	O12-Cu4-O2W	91.67(19)
O2-Cu1-C1	150.7(2)	O12-Cu4-O7	93.27(18)
O1-Cu1-C2	148.4(2)	O12-Cu4-C8	154.3(2)
O1-Cu1-C1	106.5(2)	O12-Cu4-C7	112.4(2)
C1-Cu1-C2	41.9(2)	C8-Cu4-O2W	95.44(19)
O3-Cu2-O1W	94.84(16)	C7-Cu4-O2W	100.40(19)
O3-Cu2-C4	148.37(19)	C7-Cu4-C8	42.06(19)
O4-Cu2-O3	92.00(18)	O8-Cu5-O3W	90.15(17)
O4-Cu2-O1W	87.43(18)	O8-Cu5-C9	103.34(19)
O4-Cu2-C4	116.39(19)	O8-Cu5-C10	144.97(19)
C3-Cu2-O3	107.34(19)	O9-Cu5-O8	95.49(18)
C3-Cu2-O1W	105.62(19)	O9-Cu5-O3W	93.88(18)
C3-Cu2-O4	155.28(19)	O9-Cu5-C9	152.90(19)
C3-Cu2-C4	41.6(2)	O9-Cu5-C10	117.12(19)
C4-Cu2-O1W	99.81(18)	C9-Cu5-O3W	105.25(18)
O5-Cu3-O2W	89.05(18)	C9-Cu5-C10	41.6(2)
O5-Cu3-C6	154.6(2)	C10-Cu5-O3W	99.47(19)
O5-Cu3-C5	114.64(19)	O10-Cu6-O11	92.7(2)
O6-Cu3-O2W	91.79(19)	O10-Cu6-O13	87.69(19)
O6-Cu3-O5	91.90(19)	O10-Cu6-C11	114.5(2)
O6-Cu3-C6	110.3(2)	O10-Cu6-C12	155.0(2)
O6-Cu3-C5	152.2(2)	O11-Cu6-O13	87.6(2)
C6-Cu3-O2W	101.95(19)	O11-Cu6-C11	151.2(2)
C6-Cu3-C5	42.0(2)	O11-Cu6-C12	109.3(2)
C5-Cu3-O2W	96.5(2)	C11-Cu6-O13	102.1(2)
O7-Cu4-O2W	87.2(2)	C12-Cu6-O13	104.4(2)
O7-Cu4-C8	111.6(2)	C12-Cu6-C11	42.2(2)
Symmetry codes			
#1 2-x, 1-y, 1-z; #2 -1-x, 1-y, -z			

Table S4. Selected bond lengths (Å) and bond angles (°) of the coordination bonds and CC bond lengths (Å) of C_{60} moiety for the complexes **3** measured at 100 K.

bond lengths			
Cu-O(carboxylate)			
Cu1-O1	1.9520(5)	Cu7-O16	1.9657(5)
Cu1-O19#1	1.9819(5)	Cu7-O4#1	1.9813(5)
Cu2-O2	1.9561(5)	Cu8-O12	1.9858(5)
Cu2-O5	1.9439(5)	Cu8-O17	1.9716(5)
Cu3-O7	1.9878(5)	Cu9-O11	1.9717(4)
Cu3-O9	1.9610(5)	Cu9-O21	1.9629(5)
Cu4-O8	1.9761(5)	Cu10-O18	1.9680(5)
Cu4-O13	1.9696(5)	Cu10-O22	1.9578(5)
Cu5-O10	1.9736(5)	Cu11-O6#1	1.9941(5)
Cu5-O14	1.9613(5)	Cu11-O20	1.9450(5)
Cu6-O15	1.9605(5)	Cu12-O3	1.9492(5)
Cu6-O24#1	1.9817(5)	Cu12-O23	1.9772(5)
Cu-O(water)			
Cu1-O4W#1	2.2469(6)	Cu7-O4W	2.2332(5)
Cu2-O1W	2.3103(6)	Cu8-O3W	2.2070(5)
Cu3-O1W	2.2707(6)	Cu9-O5W	2.2530(6)
Cu4-O2W	2.2237(5)	Cu10-O6W	2.2554(6)
Cu5-O3W	2.2398(6)	Cu11-O6W	2.2381(5)
Cu6-O2W	2.2330(5)	Cu12-O5W	2.2383(5)
Cu-C			
Cu1-C1	1.9821(5)	Cu7-C13	2.0051(5)
Cu1-C2	2.0547(5)	Cu7-C14	2.0346(5)
Cu2-C3	1.9882(5)	Cu8-C15	2.0246(5)
Cu2-C4	2.0375(5)	Cu8-C16	2.0304(5)
Cu3-C5	1.9994(5)	Cu9-C17	2.0103(5)
Cu3-C6	2.0239(5)	Cu9-C18	2.0379(5)
Cu4-C7	2.0231(5)	Cu10-C19	2.0135(5)
Cu4-C8	2.0157(5)	Cu10-C20	2.0116(5)
Cu5-C9	2.0011(5)	Cu11-C21	2.0588(5)
Cu5-C10	2.0244(5)	Cu11-C22	1.9938(5)
Cu6-C11	2.0080(5)	Cu12-C23	2.0222(5)
Cu6-C12	2.0283(5)	Cu12-C24	1.9991(5)

Cu-Cu (intra Cu_3 units)			
Cu1-Cu11	3.3346(8)	Cu3-Cu5	3.3905(9)
Cu2-Cu1	3.3383(8)	Cu5-Cu4	3.3256(8)
Cu2-Cu11	3.2809(8)	Cu3-Cu4	3.3102(8)
Cu8-Cu9	3.2930(8)	Cu7-Cu12	3.3060(8)
Cu8-Cu10	3.3436(8)	Cu12-Cu6	3.2870(8)
Cu9-Cu10	3.3758(9)	Cu7-Cu6	3.4031(9)
Cu-Cu (inter Cu_3 units)			
Cu5-Cu8	3.3973(9)	Cu4-Cu6	3.3807(9)
Cu12-Cu9	3.4192(9)	Cu7-Cu1	3.4019(9)
Cu2-Cu3	3.4305(9)	Cu10-Cu11	3.4359(9)
C-C(in coordinated hexagons)			
(6, 6)			
C1-C2	1.4363(3)	C3-C4	1.4315(3)
C5-C6	1.4297(3)	C7-C8	1.4297(3)
C9-C10	1.4323(3)	C11-C12	1.4379(3)
C13-C14	1.4276(3)	C15-C16	1.4249(3)
C17-C18	1.4375(3)	C19-C20	1.4406(3)
C21-C22	1.4318(3)	C23-C24	1.4320(3)
(6, 5)			
C1-C21#1	1.4714(3)	C2-C3	1.4782(3)
C4-C22#1	1.4778(3)	C5-C7	1.4811(3)
C6-C10	1.4840(3)	C8-C9	1.4782(3)
C11-C24#1	1.4753(3)	C12-C14	1.4744(3)
C13-C23#1	1.4841(3)	C15-C17	1.4738(3)
C16-C20	1.4799(3)	C18-C19	1.4774(3)
C-C(in other)			
(6, 6)			
C25-C26	1.3807(3)	C29-C30	1.3782(3)
C27-C28	1.3803(3)		
(6, 5)			
C23-C25	1.4550(3)	C3-C25	1.4530(3)
C17-C26	1.4539(3)	C6-C26	1.4558(3)
C14-C27	1.4531(3)	C9-C27	1.4524(3)
C16-C28	1.4600(3)	C1-C28#1	1.4549(3)
C22-C29	1.4497(3)	C7-C29#1	1.4541(3)

C19-C30	1.4506(3)	C11-C30#1	1.4589(3)
C10-C15	1.4737(3)	C8-C12	1.4731(3)
C2-C13#1	1.4598(3)	C20-C21	1.4595(3)
C4-C5	1.4597(3)	C18-C24	1.4670(3)
bond angles			
O1-Cu1-O4W#1	88.60(14)	O4#1-Cu7-O4W	88.64(14)
O1-Cu1-O19#1	101.57(16)	O4#1-Cu7-C13	106.22(16)
O1-Cu1-C1	152.71(17)	O4#1-Cu7-C14	147.41(16)
O1-Cu1-C2	112.23(16)	O16-Cu7-O4#1	99.90(15)
O19#1-Cu1-O4W#1	93.24(14)	O16-Cu7-O4W	93.50(14)
O19#1-Cu1-C1	103.29(17)	O16-Cu7-C13	151.16(16)
O19#1-Cu1-C2	144.69(17)	O16-Cu7-C14	111.16(16)
C1-Cu1-O4W#1	101.02(15)	C13-Cu7-O4W	99.06(15)
C1-Cu1-C2	41.63(17)	C13-Cu7-C14	41.38(16)
C2-Cu1-O4W#1	97.39(15)	C14-Cu7-O4W	98.77(15)
O2-Cu2-O1W	93.49(14)	O12-Cu8-O3W	86.73(14)
O2-Cu2-C3	103.52(17)	O12-Cu8-C15	107.34(16)
O2-Cu2-C4	144.81(17)	O12-Cu8-C16	148.16(17)
O5-Cu2-O1W	87.13(15)	O17-Cu8-O3W	91.57(15)
O5-Cu2-O2	101.29(17)	O17-Cu8-O12	102.45(16)
O5-Cu2-C3	153.13(17)	O17-Cu8-C15	148.78(17)
O5-Cu2-C4	112.34(16)	O17-Cu8-C16	108.12(17)
C3-Cu2-O1W	101.43(15)	C15-Cu8-O3W	99.18(15)
C3-Cu2-C4	41.63(16)	C15-Cu8-C16	41.15(17)
C4-Cu2-O1W	98.10(15)	C16-Cu8-O3W	100.92(15)
O7-Cu3-O1W	86.49(13)	O11-Cu9-O5W	88.82(15)
O7-Cu3-C5	107.94(16)	O11-Cu9-C17	104.53(17)
O7-Cu3-C6	149.29(16)	O11-Cu9-C18	146.12(17)
O9-Cu3-O1W	90.43(14)	O21-Cu9-O5W	86.14(14)
O9-Cu3-O7	101.31(15)	O21-Cu9-O11	104.19(16)
O9-Cu3-C5	149.32(17)	O21-Cu9-C17	150.04(16)
O9-Cu3-C6	108.25(16)	O21-Cu9-C18	109.29(16)
C5-Cu3-O1W	100.24(15)	C17-Cu9-O5W	102.78(15)
C5-Cu3-C6	41.62(17)	C17-Cu9-C18	41.59(16)

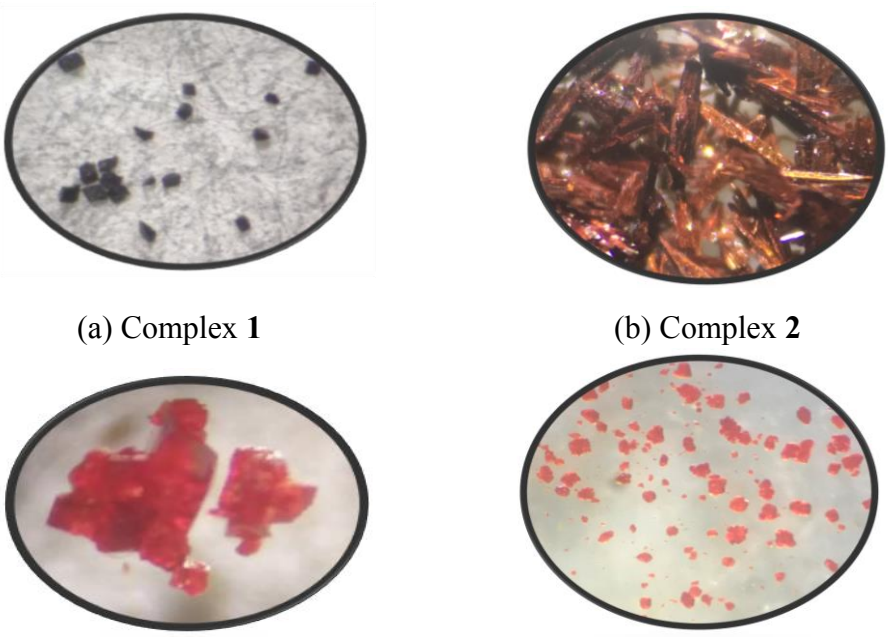
C6-Cu3-O1W	101.17(14)	C18-Cu9-O5W	98.27(15)
O8-Cu4-O2W	88.74(13)	O18-Cu10-O6W	85.02(15)
O8-Cu4-C7	107.19(16)	O18-Cu10-C19	147.76(17)
O8-Cu4-C8	148.49(16)	O18-Cu10-C20	105.97(17)
O13-Cu4-O2W	89.16(14)	O22-Cu10-O6W	91.99(15)
O13-Cu4-O8	101.89(15)	O22-Cu10-O18	103.85(18)
O13-Cu4-C7	149.48(16)	O22-Cu10-C19	107.52(18)
O13-Cu4-C8	108.65(16)	O22-Cu10-C20	148.95(18)
C7-Cu4-O2W	100.41(15)	C19-Cu10-O6W	101.01(15)
C8-Cu4-O2W	99.14(14)	C20-Cu10-O6W	98.97(15)
C8-Cu4-C7	41.47(17)	C20-Cu10-C19	41.94(16)
O10-Cu5-O3W	87.87(15)	O6#1-Cu11-O6W	91.68(14)
O10-Cu5-C9	150.09(17)	O6#1-Cu11-C21	144.54(17)
O10-Cu5-C10	109.64(16)	O20-Cu11-O6#1	102.23(17)
O14-Cu5-O3W	90.18(14)	O20-Cu11-O6W	89.27(15)
O14-Cu5-O10	103.64(16)	O20-Cu11-C21	111.99(16)
O14-Cu5-C9	104.10(17)	O20-Cu11-C22	152.01(17)
O14-Cu5-C10	145.73(17)	C21-Cu11-O6W	97.62(15)
C9-Cu5-O3W	102.99(15)	C22-Cu11-O6#1	103.31(17)
C9-Cu5-C10	41.68(17)	C22-Cu11-O6W	101.20(15)
C10-Cu5-O3W	98.84(15)	C22-Cu11-C21	41.34(16)
O15-Cu6-O2W	87.84(14)	O3-Cu12-O5W	90.56(14)
O15-Cu6-O24#1	98.55(16)	O3-Cu12-O23	99.74(15)
O15-Cu6-C11	148.37(17)	O3-Cu12-C23	110.48(17)
O15-Cu6-C12	107.20(17)	O3-Cu12-C24	151.73(17)
O24#1-Cu6-O2W	91.45(14)	O23-Cu12-O5W	84.39(13)
O24#1-Cu6-C11	111.29(17)	O23-Cu12-C23	149.09(16)
O24#1-Cu6-C12	152.47(17)	O23-Cu12-C24	107.49(16)
C11-Cu6-O2W	101.23(15)	C23-Cu12-O5W	101.24(14)
C11-Cu6-C12	41.75(17)	C24-Cu12-O5W	99.37(14)
C12-Cu6-O2W	98.97(14)	C24-Cu12-C23	41.72(17)
Symmetry codes			
#1 1-x,1-y,1-z			

Table S5. Selected bond lengths (Å) and bond angles (°) of the coordination bonds and CC bond lengths (Å) of C_{60} moiety for the complexes **4** measured at 100 K.

bond lengths			
Cu-O(carboxylate)			
Cu1-O1	1.9459(5)	Cu3-O10	1.9254(5)
Cu1-O2#1	1.9813(5)	Cu3-O12#2	1.9505(5)
Cu2-O3	1.9495(5)	Cu4-O4#3	1.9972(5)
Cu2-O9	1.9498(5)	Cu4-O11	1.9336(5)
Cu-O(carboxylic acid)			
Cu1-O5	2.3285(6)	Cu3-O7#2	2.4093(6)
Cu2-O5	2.3979(6)	Cu4-O7#2	2.3495(6)
Cu-C			
Cu1-C1	2.0026(5)	Cu3-C5	2.0044(5)
Cu1-C2	2.0288(5)	Cu3-C6	2.0171(5)
Cu2-C3	2.0193(5)	Cu4-C7	2.0423(5)
Cu2-C4	2.0013(5)	Cu4-C8	2.0186(5)
Cu-Cu (intra Cu_3 units)			
Cu1-Cu1#1	3.2162(8)	Cu2-Cu3	3.2272(8)
Cu2-Cu4	3.2414(8)	Cu3-Cu4	3.2511(8)
Cu-Cu (inter Cu_3 units)			
Cu2-Cu1	3.5430(9)	Cu3-Cu4	3.5098(9)
C-C (coordinated hexagons)			
C=C(6, 6)		C-C(6, 6)	
C1-C2	1.4333(3)	C1-C2#1	1.4811(4)
C3-C4	1.4310(3)	C3-C8#2	1.4772(4)
C5-C6	1.4336(3)	C4-C6	1.4781(4)
C7-C8	1.4324(3)	C5-C7#2	1.4850(4)
C-C(other)			
(6, 6)			
C9-C10		1.3787(3)	
(6, 5)			
C4-C9	1.4569(4)	C5-C9#2	1.4463(3)
C1-C10	1.4528(3)	C8-C10#2	1.4595(4)
C2-C3	1.4735(4)	C6-C7	1.4666(4)

angles			
O1-Cu1-O2#1	97.87(14)	O10-Cu3-O7#2	92.78(15)
O1-Cu1-O5	88.88(12)	O10-Cu3-O12#2	97.73(17)
O1-Cu1-C1	153.90(14)	O10-Cu3-C5	153.34(16)
O1-Cu1-C2	112.40(14)	O10-Cu3-C6	111.74(16)
O2#1-Cu1-O5	90.28(13)	O12#2-Cu3-O7#2	89.64(12)
O2#1-Cu1-C1	107.66(15)	O12#2-Cu3-C5	108.33(16)
O2#1-Cu1-C2	149.05(15)	O12#2-Cu3-C6	149.84(16)
C1-Cu1-O5	96.20(13)	C5-Cu3-O7#2	92.93(13)
C1-Cu1-C2	41.65(15)	C5-Cu3-C6	41.77(15)
C2-Cu1-O5	96.42(14)	C6-Cu3-O7#2	95.02(13)
O3-Cu2-O5	88.87(12)	O4#3-Cu4-O7#2	88.39(12)
O3-Cu2-O9	99.19(14)	O4#3-Cu4-C7	147.68(15)
O3-Cu2-C3	111.26(15)	O4#3-Cu4-C8	106.57(15)
O3-Cu2-C4	152.82(15)	O11-Cu4-O4#3	101.1(2)
O9-Cu2-O5	91.05(13)	O11-Cu4-O7#2	94.12(14)
O9-Cu2-C3	148.92(15)	O11-Cu4-C7	110.46(19)
O9-Cu2-C4	107.47(14)	O11-Cu4-C8	151.49(19)
C3-Cu2-O5	95.47(13)	C7-Cu4-O7#2	95.73(13)
C4-Cu2-O5	95.72(13)	C8-Cu4-O7#2	93.24(13)
C4-Cu2-C3	41.70(15)	C8-Cu4-C7	41.30(15)
Symmetry codes			
#1 1+y-x, 1-x, +z; #2 1/3-y+x, -1/3+x, 2/3-z; #3 1/3+y, 2/3-x+y, 2/3-z			

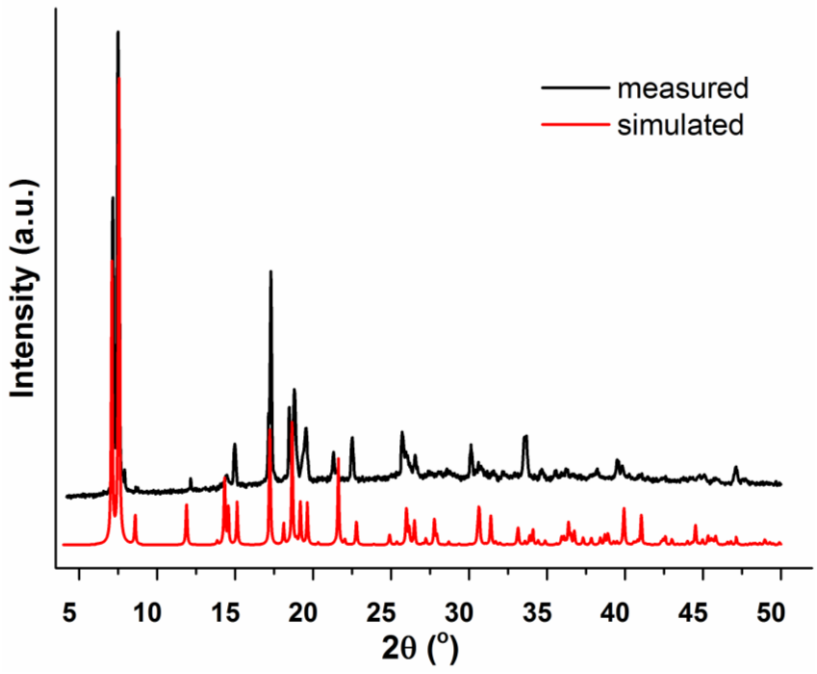
2.3 Additional Structural Description



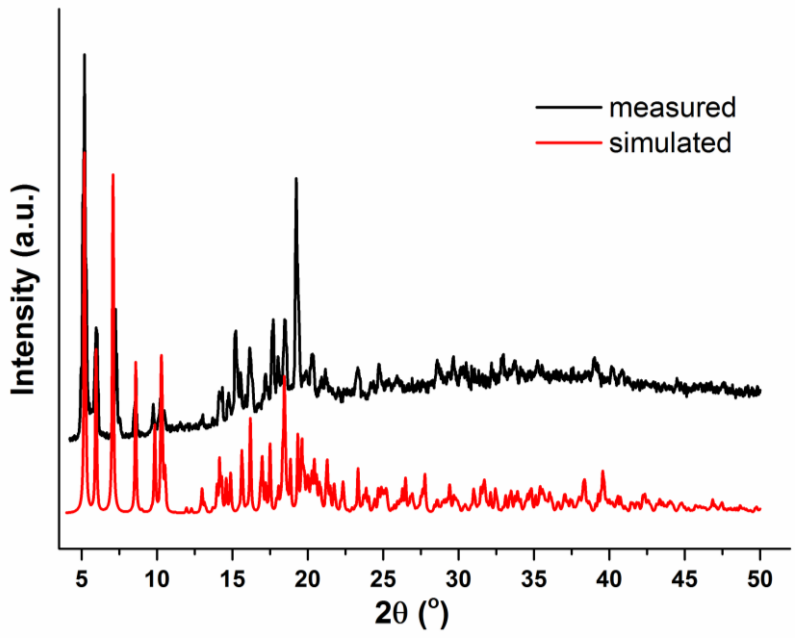
(a) Complex **1** (b) Complex **2**

(c) Complex **3** (d) Complex **4**

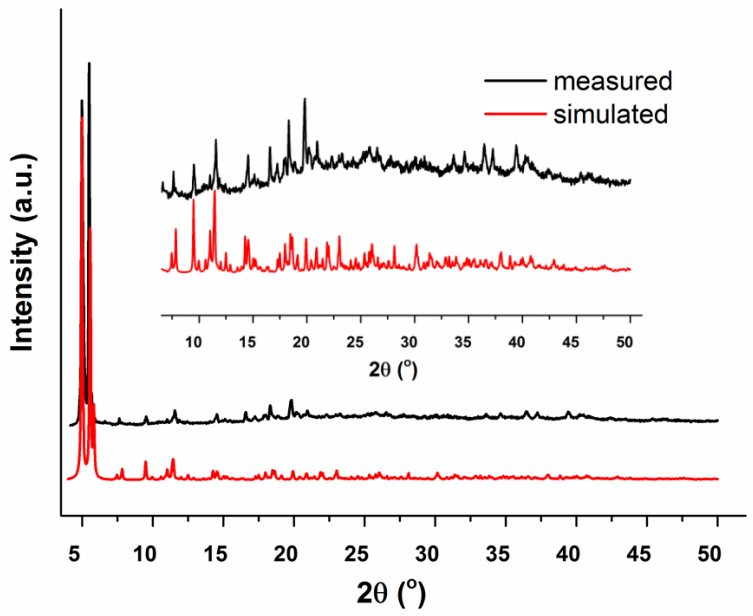
Figure S1. Photographs of the crystal samples for the complexes **1**-**4** amplified 40 times by microscope under natural night



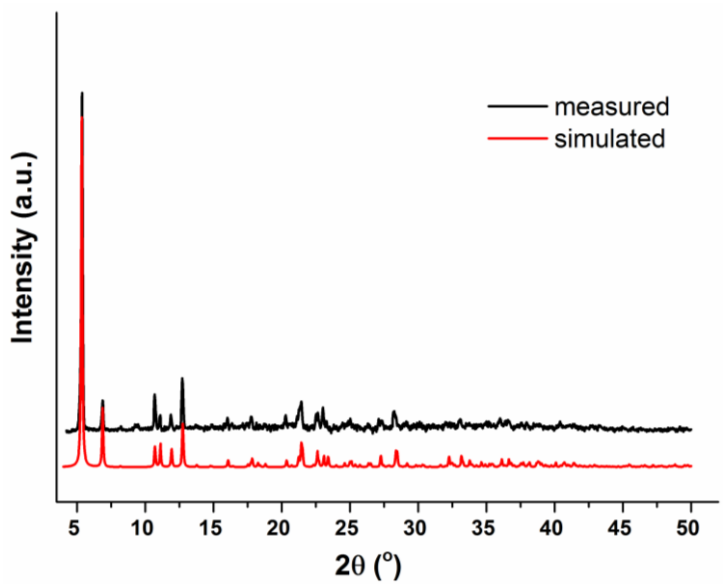
(a) Complex **1**



(b) Complex **2**

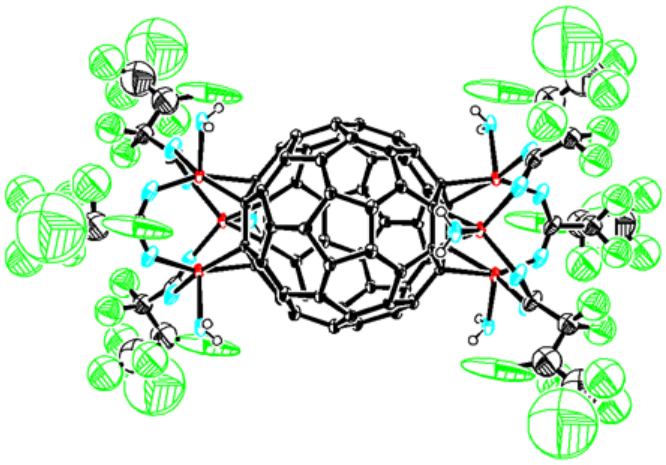


(c) Complex **3**

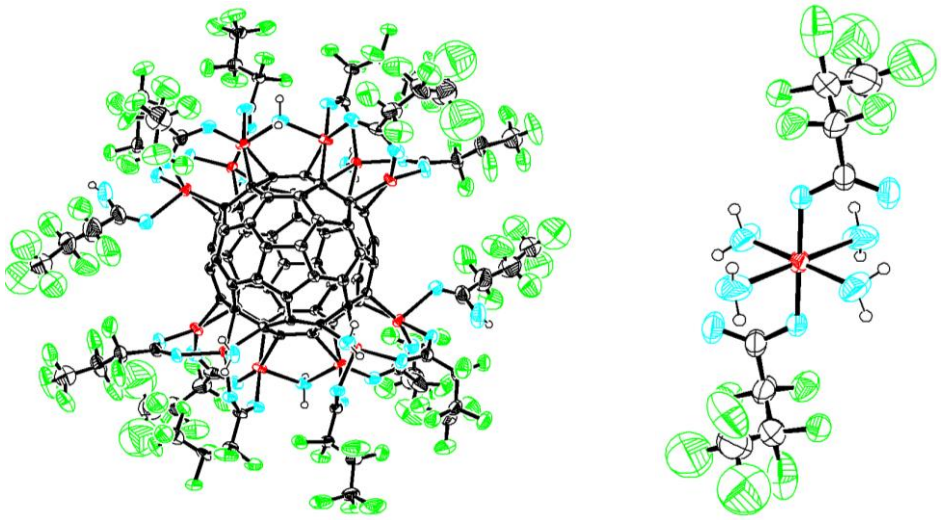


(d) Complex **4**

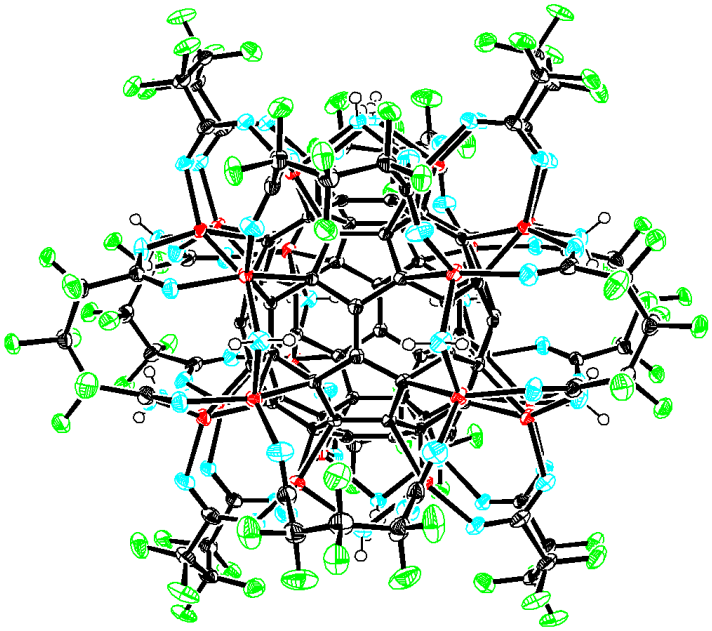
Figure S2. Comparison of the simulated and measured X-ray powder diffraction patterns of the complexes **1**-**4**.



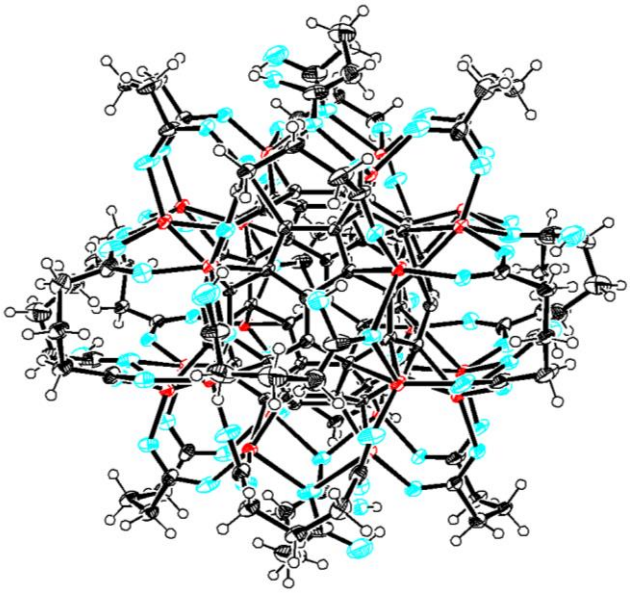
(a) Complex **1**



(b) Complex **2**

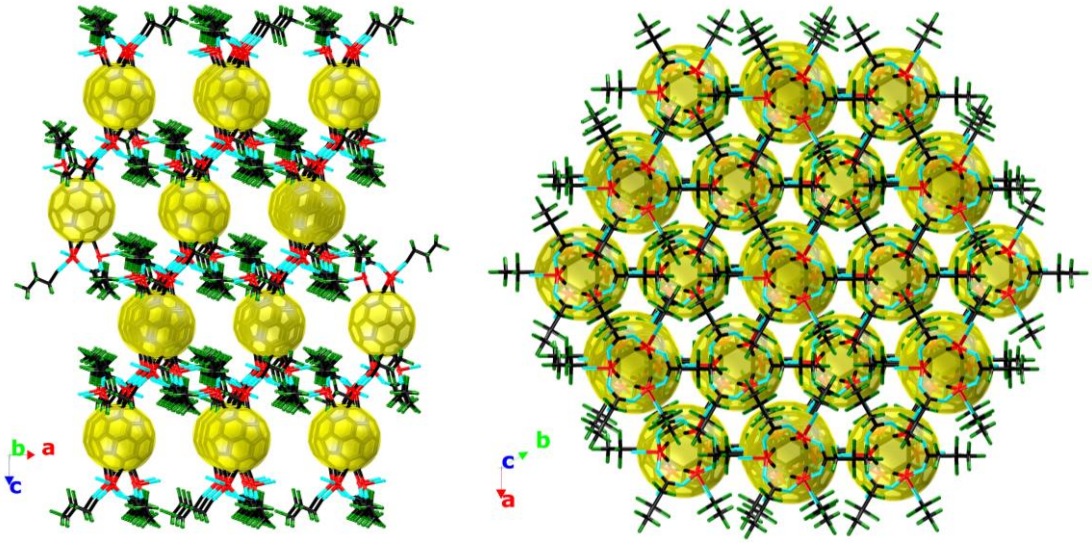


(c) Complex **3**



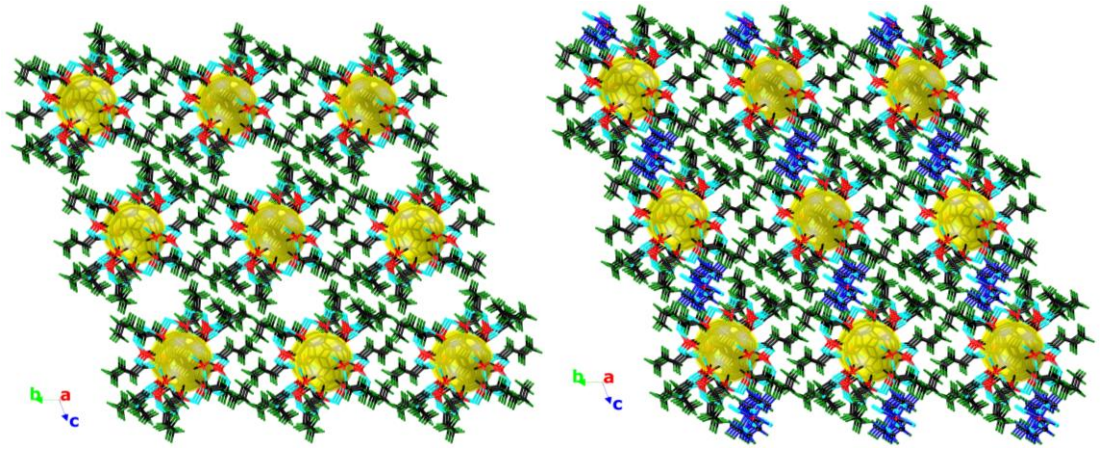
(d) Complex **4**

Figure S3. Molecular structures of the complexes **1**-**4** with 50% thermal ellipsoid. (Color codes: red, Cu; cyan, N; black, C; white cycle, H. The crystallized solvent molecules are omitted for clarity.)



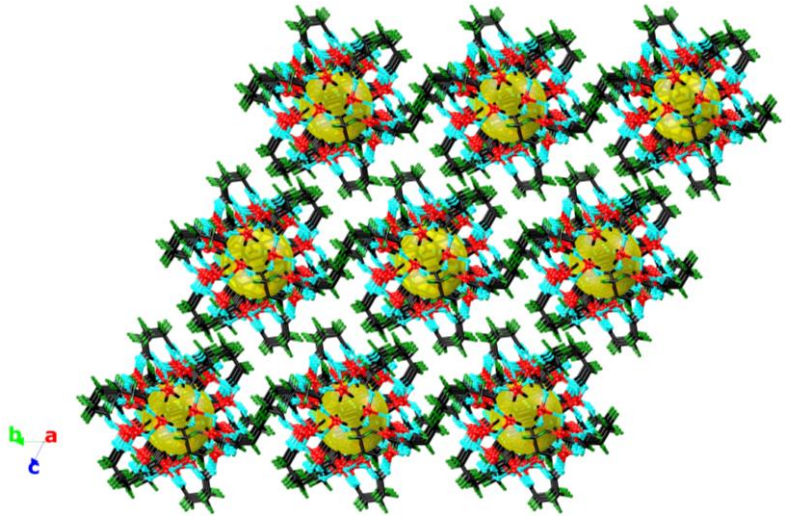
(a) (b)

Figure S4. Packing structures of the complex **1** along *b* (a) and *c* (b) axis.

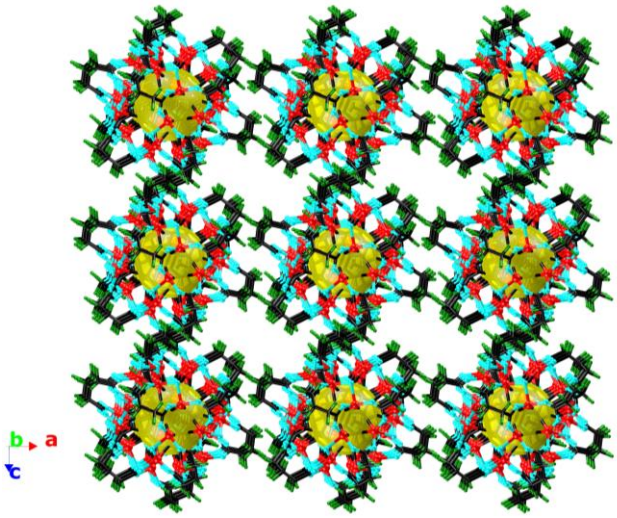


(a) (b)

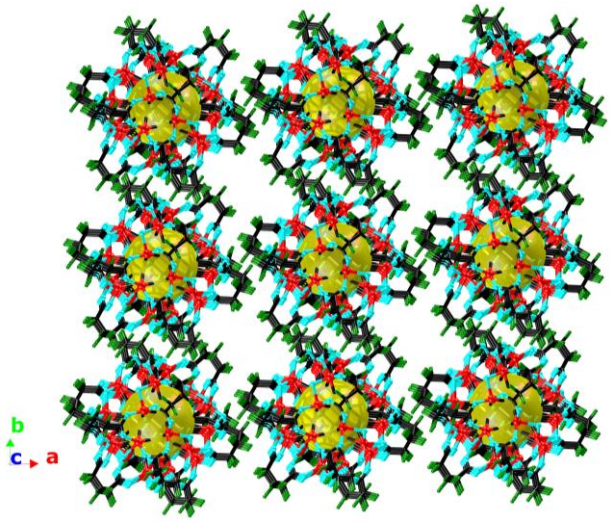
Figure S5. Packing structures of the complex **2** along *a* axis showing the co-crystallized $Cu(H_2O)_4(C_3F_7COO)_2$ fragments (blue in b) occupied the channel (a) between the cuprofullerene molecules.



(a)

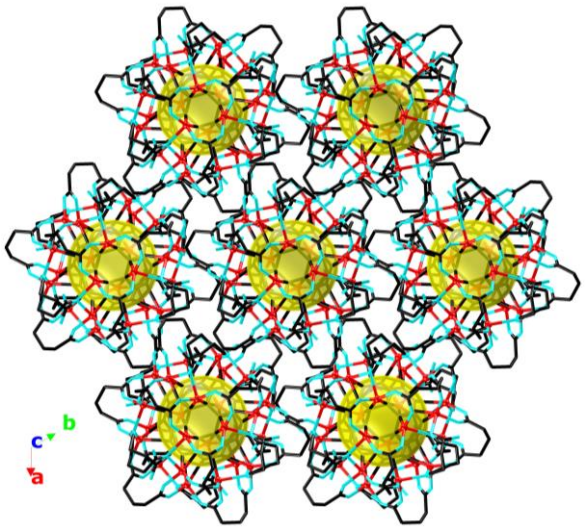


(b)

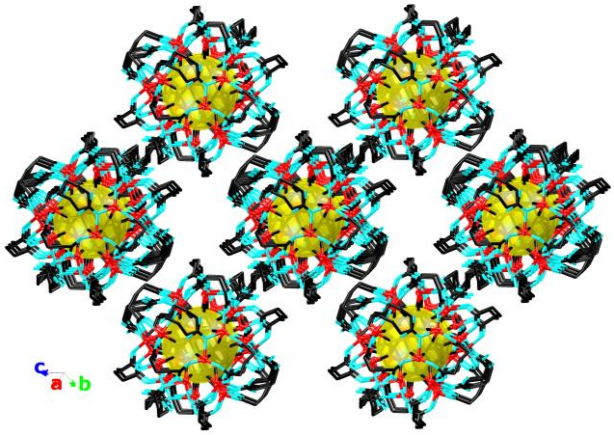


(c)

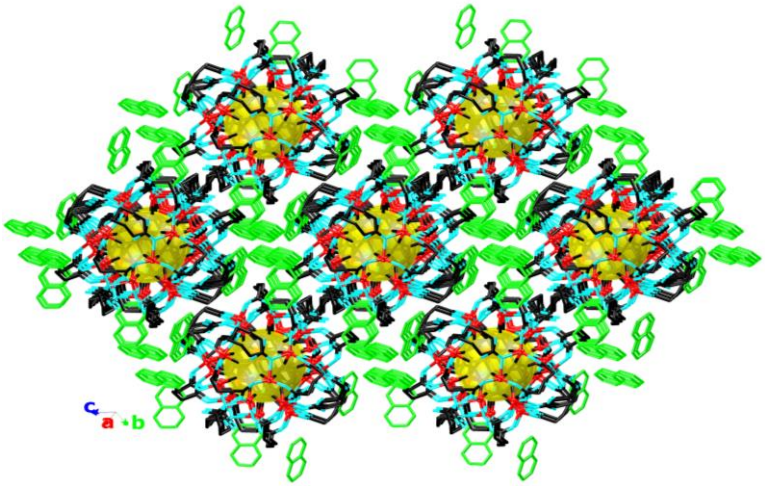
Figure S6. Packing structures of the complex **3** along *a* (a), *b* (b), and *c* (c) axis respectively. The crystallized solvent molecules are omitted for clarity.



(a)



(b)

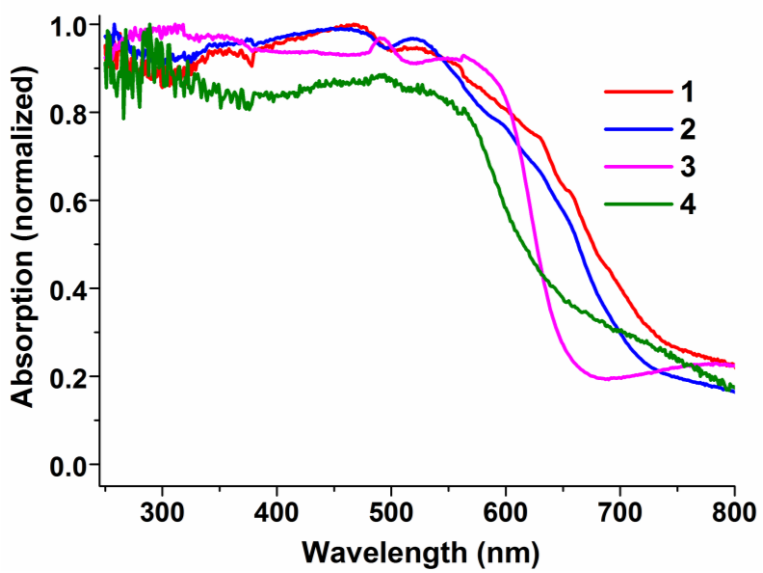


(c)

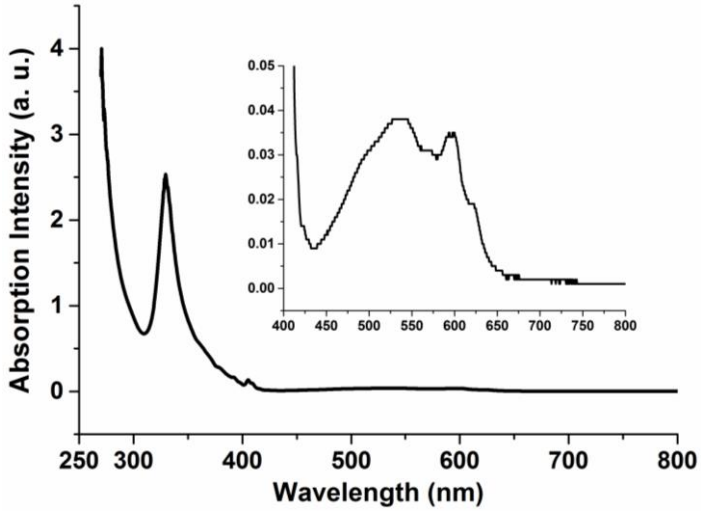
Figure S7. Packing structures of the complex **4**. The crystallized 1-chloronaphthalene molecules are omitted in (a) and (b) and shown in green in (c). The Cl atoms are omitted in 1-chloronaphthalene for their disordered position.

Section 3: Properties

3.1 UV-Vis Absorption Spectra



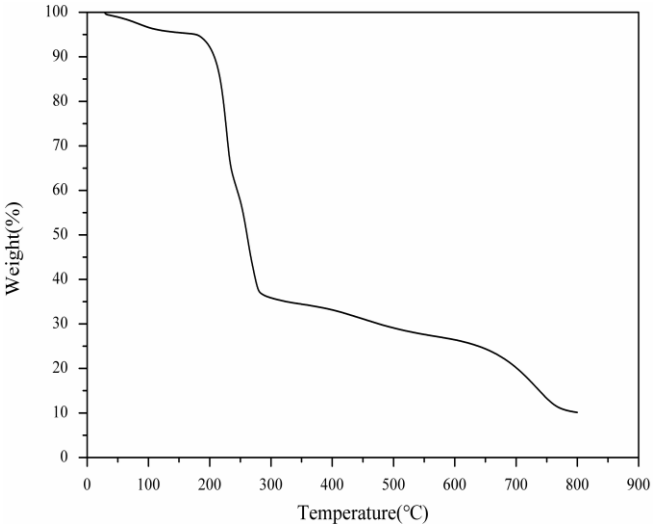
(a)



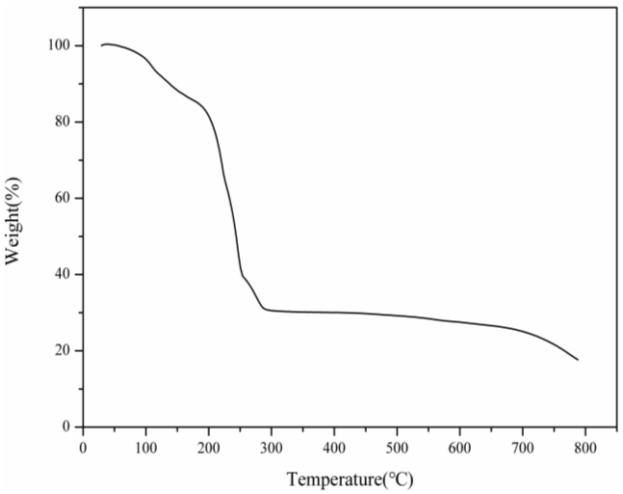
(b)

Figure S8 Comparison of the UV-Vis diffuse reflectance spectra of the complexes **1**-**4** (a) and the absorption of C_{60} in toluene solution (10^{-4} mol·L^{-1}) (b).

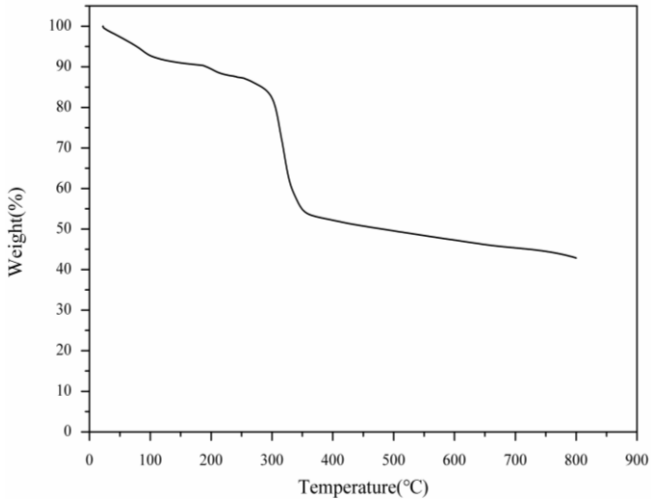
3.2 Thermal Stability



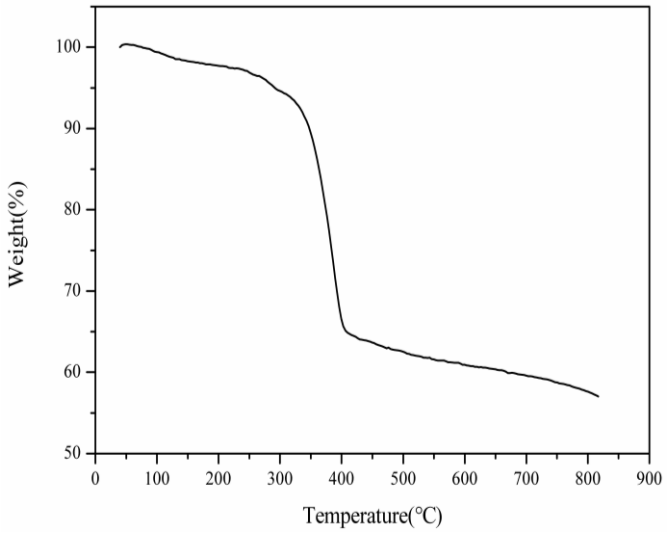
(a) Complex **1**



(b) Complex **2**



(c) Complex **3**



(d) Complex **4**

Figure S9 Thermogravimetric analysis (TGA) plots of the complexes **1**-**4**.

Section 4. Theoretical Calculation Details

4.1 Time Dependent Density Functional Theory (TD-DFT) Calculation

All the calculations were carried out with Gaussian 09 software package.[2] The exact-exchange-incorporated PBE0 hybrid functional[3-5] was employed throughout with LANDL2DZ basis set[6] for Cu atoms and 6-31G** basis set[7] for C, O, F, H atoms. The models of the complexes were generated from the crystal data without any optimization, and only the Cu_{12} fragment in the complex **2** was used for calculation. To perform wavefunction analysis, some of the out files were used as input files of Multiwfn software packages.[8] Electron density difference (EDD) maps could be obtained to provide accurate assignments of excited states by calculating singlet-singlet spin-allowed transitions. Orbit contributions for the selected excited states and orbital composition analysis with Hirshfeld method were all analyzed by Multiwfn software packages.[9]

4.2 Calculation Results

Table S6 The calculated first 20 singlet-singlet spin-allowed transitions based on complexes of **Cu_6**, **Cu_{12}**, **Cu_{24}**, **Cu_{24}**-H and **C_{60}**

Cu_6			
No.	E/eV	λ/nm	*f*
1	1.9914	622.59	0.0000
2	2.0039	618.72	0.0000
3	2.0040	618.68	0.0000
4	2.2457	552.09	0.0000
5	2.2603	548.53	0.0000
6	2.2603	548.52	0.0000
7	2.3359	530.78	0.0000
8	2.3361	530.72	0.0000
9	2.4078	514.94	0.0000
10	2.4078	514.93	0.0000
11	**2.4111**	**514.22**	**0.0054**
12	**2.4112**	**514.20**	**0.0054**
13	2.4353	509.11	0.0000
14	2.4634	503.31	0.0000
15	2.5289	490.27	0.0000
16	2.5320	489.68	0.0000
17	2.5418	487.78	0.0000
18	2.5419	487.77	0.0000
19	**2.6086**	**475.29**	**0.0199**
20	**2.6086**	**475.28**	**0.0199**
Cu_{12}			
No.	E/eV	λ/nm	*f*
1	1.9394	639.30	0.0000
2	2.0738	597.87	0.0000
3	2.1632	573.16	0.0000
4	2.2269	556.76	0.0000

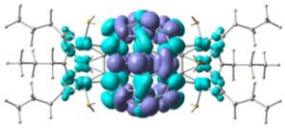
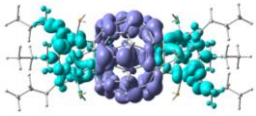
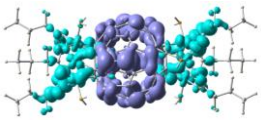
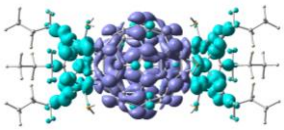
5	2.2564	549.47	0.0000
6	2.2724	545.62	0.0000
7	2.3414	529.52	0.0000
8	2.4251	511.25	0.0000
9	**2.4427**	**507.58**	**0.1263**
10	2.4564	504.74	0.0000
11	2.5000	495.93	0.0000
12	2.5305	489.96	0.0000
13	**2.5396**	**488.21**	**0.0520**
14	**2.5539**	**485.46**	**0.0172**
15	2.5561	485.05	0.0000
16	2.6054	475.87	0.0000
17	**2.6180**	**473.59**	**0.0075**
18	**2.6223**	**472.80**	**0.0024**
19	2.6271	471.94	0.0000
20	2.6384	469.92	0.0000
Cu_{24}			
No.	E/eV	λ/nm	*f*
1	2.2678	546.71	0.0000
2	2.2774	544.41	0.0000
3	2.2954	540.14	0.0000
4	2.3413	529.56	0.0000
5	2.3523	527.07	0.0000
6	2.3574	525.93	0.0000
7	2.4864	498.65	0.0000
8	2.4882	498.29	0.0000
9	2.5075	494.45	0.0000
10	2.5312	489.82	0.0000
11	**2.5398**	**488.16**	**0.0022**
12	**2.5577**	**484.75**	**0.0039**
13	2.5580	484.69	0.0000
14	**2.5672**	**482.95**	**0.0027**

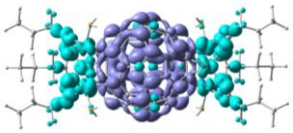
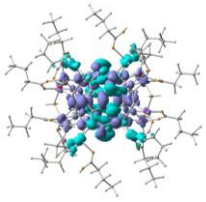
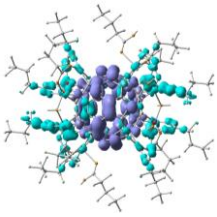
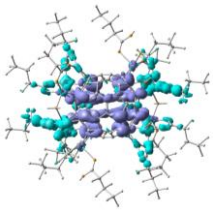
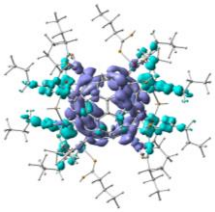
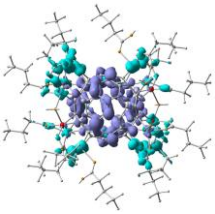
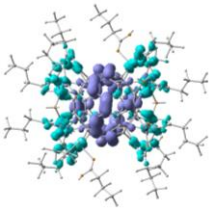
15	**2.5756**	**481.39**	**0.0052**
16	2.5763	481.25	0.0000
17	2.5813	480.33	0.0000
18	**2.5824**	**480.12**	**0.0010**
19	2.5947	477.84	0.0000
20	**2.5964**	**477.53**	**0.0008**
Cu_{24}-H			
No.	E/eV	λ/nm	*f*
1	2.3646	524.33	0.0000
2	2.3651	524.21	0.0000
3	2.3652	524.19	0.0000
4	2.4042	515.70	0.0000
5	2.4345	509.28	0.0000
6	2.4345	509.27	0.0000
7	2.5096	494.04	0.0000
8	2.5096	494.04	0.0000
9	2.5150	492.97	0.0000
10	2.5566	484.95	0.0000
11	**2.5861**	**479.42**	**0.0029**
12	**2.5906**	**478.59**	**0.0066**
13	**2.5907**	**478.57**	**0.0067**
14	2.5989	477.06	0.0000
15	2.6011	476.67	0.0000
16	2.6012	476.65	0.0000
17	**2.6107**	**474.90**	**0.0182**
18	2.6221	472.84	0.0000
19	2.6222	472.82	0.0000
20	**2.6378**	**470.02**	**0.0327**
C_{60}			
No.	E/eV	λ/nm	*f*
1	2.3235	533.62	0.0000
2	2.3235	533.61	0.0000

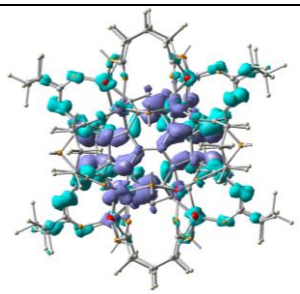
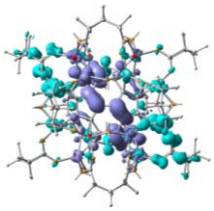
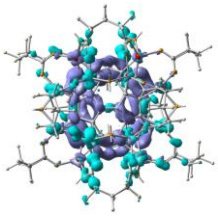
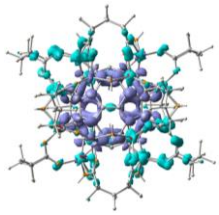
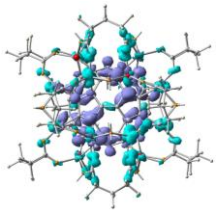
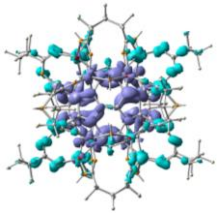
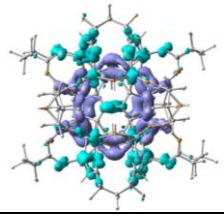
3	2.3235	533.61	0.0000
4	2.3236	533.59	0.0000
5	2.3254	533.17	0.0000
6	2.3255	533.16	0.0000
7	2.3255	533.15	0.0000
8	2.3286	532.44	0.0000
9	2.3287	532.43	0.0000
10	2.3287	532.42	0.0000
11	2.5136	493.26	0.0000
12	2.5136	493.26	0.0000
13	2.5136	493.25	0.0000
14	2.5137	493.24	0.0000
15	2.5137	493.24	0.0000
16	3.4364	360.79	0.0000
17	3.4365	360.79	0.0000
18	3.4365	360.78	0.0000
19	3.4587	358.47	0.0000
20	3.4587	358.47	0.0000
21	3.4588	358.46	0.0000
22	3.4588	358.46	0.0000
23	3.4588	358.46	0.0000
24	3.5363	350.60	0.0000
25	3.5363	350.60	0.0000
26	3.5364	350.60	0.0000
27	3.5364	350.59	0.0000
28	3.6955	335.50	0.0000
29	3.6955	335.50	0.0000
30	3.6955	335.50	0.0000
31	3.6956	335.50	0.0000
32	3.7267	332.69	0.0000
33	3.7268	332.68	0.0000
34	3.7268	332.68	0.0000

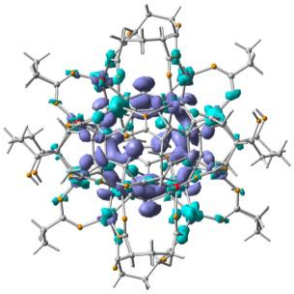
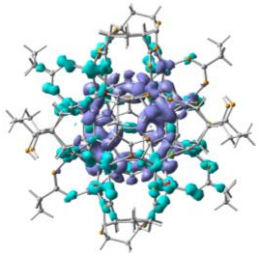
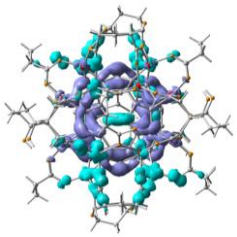
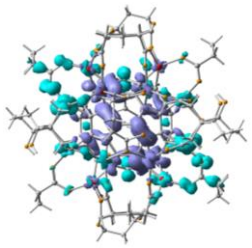
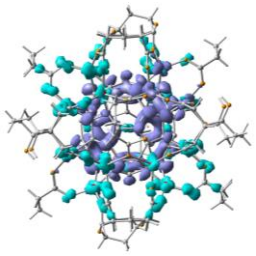
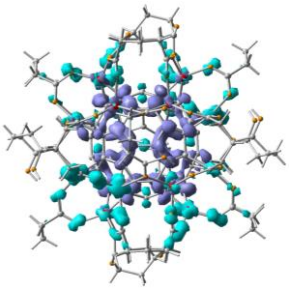
35	3.7268	332.68	0.0000
36	3.7269	332.67	0.0000
37	**3.7694**	**328.92**	**0.0145**
38	**3.7694**	**328.92**	**0.0145**
39	**3.7694**	**328.92**	**0.0145**
40	3.7962	326.60	0.0000
41	3.7963	326.60	0.0000
42	3.7963	326.59	0.0000
43	3.7963	326.59	0.0000
44	3.7964	326.59	0.0000
45	3.8196	324.60	0.0000
46	3.8196	324.60	0.0000
47	3.8197	324.59	0.0000
48	3.8197	324.59	0.0000
49	3.8468	322.30	0.0000
50	3.8468	322.30	0.0000

Table S7 The calculated absorption data, the electron density difference (EDD) maps (isovalue = 0.0004 a.u.) and the orbital transitions of the selected vertical singlet excited states for complexes **Cu_6**, **Cu_{12}**, **Cu_{24}** and **Cu_{24}**-H and C_{60}.

Cu_6					
No.	E(eV)	λ(nm)	*f*	EDD	Major transitions and contributions (H = HOMO, L = LUMO)
1	1.9914	622.59	0.0000		H → L (98.04%)
11	2.4111	514.22	0.0054		H-3 → L (97.42%)
12	2.4112	514.20	0.0054		H-4 → L (97.42%)
19	2.6086	475.29	0.0199		H-4 → L+2 (41.44%) H-3 → L+1 (41.17%) H-4 → L+1 (5.42%) H-3 → L+2 (5.38%)

20	2.6086	475.28	0.0199		H-4 → L+1 (41.31%) H-3 → L+2 (41.30%) H-4 → L+2 (5.43%) H-3 → L+1 (5.37%)
Cu_{12}					
No.	E(eV)	λ(nm)	*f*	EDD	Major transitions and contributions (H = HOMO, L = LUMO)
1	1.9394	639.30	0.0000		H → L (97.52%)
9	2.4427	507.58	0.1263		H-3 → L (92.23%)
13	2.5396	488.21	0.0520		H-3 → L+1 (74.08%) H-3 → L+2 (13.65%)
14	2.5539	485.46	0.0172		H-3 → L+2 (72.58%) H-3 → L+1 (16.26%)
17	2.6180	473.59	0.0075		H-6 → L (54.28%) H-7 → L (14.82%) H-6 → L+1 (9.07%) H-3 → L+2 (8.05%) H-7 → L+1 (6.72%)
18	2.6223	472.80	0.0024		H-7 → L (63.60%) H-6 → L (18.99%) H-6 → L+2 (5.59%)

Cu_{24}					
No.	E(eV)	λ(nm)	*f*	EDD	Major transitions and contributions (H = HOMO, L = LUMO)
1	2.2678	546.71	0.0000		H → L (57.53%) H → L+1 (29.02%)
11	2.5398	488.16	0.0022		H-3 → L (68.40%) H-4 → L (9.57%) H-3 → L+2 (7.88%)
12	2.5577	484.75	0.0039		H-4 → L (41.51%) H-3 → L (14.69%) H-3 → L+1 (14.35%) H-8 → L (6.03%)
14	2.5672	482.95	0.0027		H-3 → L+2 (33.28%) H-4 → L+1 (28.13%) H-8 → L (12.59%) H-4 → L (8.51%)
15	2.5756	481.39	0.0052		H-3 → L+1 (32.55%) H-4 → L+1 (16.48%) H-7 → L+2 (11.41%) H-7 → L+1 (7.51%) H-3 → L+2 (6.60%) H-9 → L+2 (5.64%)
18	2.5824	480.12	0.0010		H-3 → L+1 (21.90%) H-7 → L+1 (21.32%) H-4 → L+1 (16.43%) H-4 → L (8.70%) H-3 → L+2 (5.90%) H-7 → L+2 (5.52%)
20	2.5964	477.53	0.0008		H-4 → L+2 (64.11%) H-7 → L (9.44%) H-8 → L (7.40%) H-4 → L+1 (5.14%)

Cu_{24}-H					
No.	E(eV)	λ(nm)	*f*	EDD	Major transitions and contributions (H = HOMO, L = LUMO)
1	2.3646	524.33	0.0000		H-1 → L (41.14%) H → L+1 (35.55%) H-2 → L (6.41%) H-3 → L+1 (6.25%) H → L (6.04%)
11	2.5861	479.42	0.0029		H-5 → L (33.87%) H-4 → L+1 (33.70%) H-4 → L (15.11%) H-5 → L+1 (14.38%)
12	2.5906	478.59	0.0066		H-4 → L+2 (61.52%) H-5 → L+1 (11.45%) H-4 → L (11.21%)
13	2.5907	478.57	0.0067		H-5 → L+2 (61.56%) H-4 → L+1 (11.68%) H-5 → L (10.97%)
17	2.6107	474.90	0.0182		H-4 → L (30.42%) H-5→ L+1 (30.38%) H-5 → L (13.41%) H-4 → L+1 (13.31%) H-7 → L+2 (6.28%)
20	2.6378	470.02	0.0327		H-4 → L+2 (25.13%) H-5 → L+1 (23.23%) H-4 → L (22.85%) H-8 → L (5.16%)

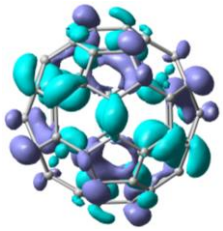
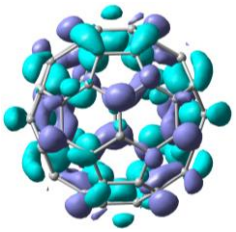
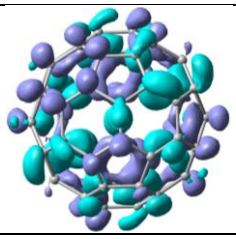
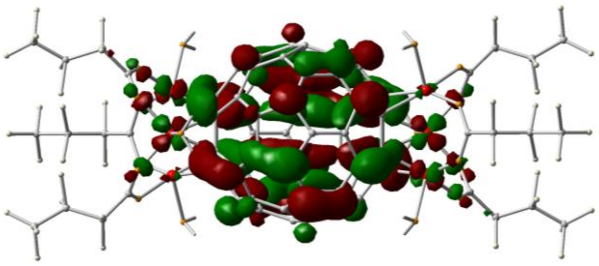
C_{60}					
No.	E(eV)	λ(nm)	*f*	EDD	Major transitions and contributions (H = HOMO, L = LUMO)
37	3.7694	328.92	0.0145		H-1 → L+3 (17.54%) H → L+4 (16.02%) H-3 → L+5 (9.65%) H-2 → L+5 (8.77%) H-2 → L+3 (8.42%) H → L+5 (7.01%) H-1 → L+4 (5.13%) H-8 → L (5.06%)
38	3.7694	328.92	0.0145		H → L+3 (18.65%) H-4 → L+5 (13.87%) H-4 → L+4 (13.20%) H-2 → L+4 (11.09%) H-3 → L+4 (5.42%) H → L+5 (5.25%) H-3 → L+5 (5.21%)
39	3.7694	328.92	0.0145		H-1 → L+5 (22.02%) H-3 → L+3 (20.50%) H-2 → L+4 (13.37%) H-4 → L+4 (10.78%)

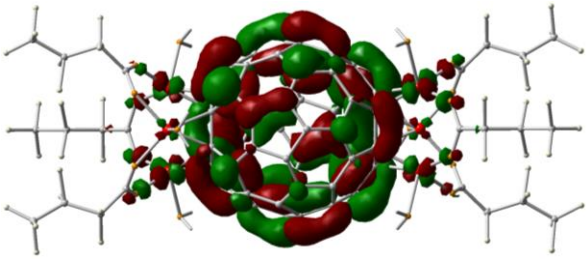
Table S8 The calculated atom contributions (%) for the orbitals of the complexes of Cu_6, Cu_{12}, Cu_{24} and Cu_{24}-H.

complexes	No.	atom contributions				
		Cu	C(fullerene)	O	C(carboxylate)	F
Cu_6	572 (H-4)	31.71	28.64	26.46	9.64	3.28
	573 (H-3)	31.71	28.64	26.46	9.64	3.28
	576 (H)	14.93	71.96	10.71	1.26	0.51
	577 (L)	1.20	97.54	0.61	0.10	0.02
	578 (L+1)	13.41	81.83	3.29	0.95	0.19
	579 (L+2)	13.41	81.83	3.29	0.95	0.19
Cu_{12}	1039 (H-7)	34.79	30.86	22.33	8.70	3.20
	1040 (H-6)	31.05	30.34	23.61	10.53	4.38
	1043 (H-3)	34.61	33.31	20.28	8.62	3.04
	1046 (H)	17.48	70.27	8.11	3.02	1.04
	1047 (L)	12.11	83.70	2.95	0.88	0.21
	1048 (L+1)	17.56	76.59	4.12	1.25	0.28
	1049 (L+2)	22.65	69.90	5.29	1.68	0.37

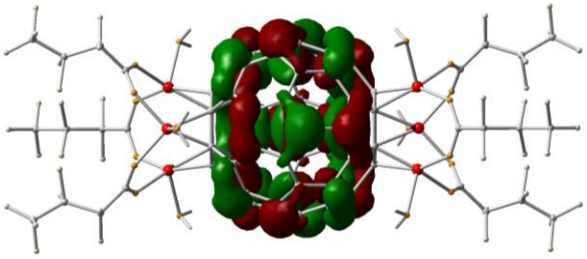
C_{24}	1155 (H-9)	34.74	20.85	27.26	11.92	5.16
	1156 (H-8)	35.42	21.24	26.66	11.52	5.07
	1157 (H-7)	35.21	21.16	27.00	11.48	5.06
	1160 (H-4)	37.25	26.93	23.22	8.95	3.43
	1161 (H-3)	37.16	27.06	23.20	8.92	3.44
	1164 (H)	33.68	32.93	21.20	8.48	3.59
	1165 (L)	28.88	61.17	7.12	2.16	0.44
	1166 (L+1)	28.81	61.28	7.10	2.15	0.44
	1167 (L+2)	28.74	61.24	7.17	2.18	0.45
Cu_{24}-H	1018 (H-8)	40.70	25.10	24.47	8.21	
	1019 (H-7)	41.10	22.28	26.16	9.08	
	1021 (H-5)	38.27	28.55	23.03	8.63	
	1022 (H-4)	38.27	28.55	23.04	8.63	
	1026 (H)	37.87	37.26	18.50	5.68	
	1027 (L)	29.03	61.37	7.03	2.21	
	1028 (L+1)	29.03	61.37	7.03	2.20	
	1029 (L+2)	28.68	61.98	6.84	2.12	



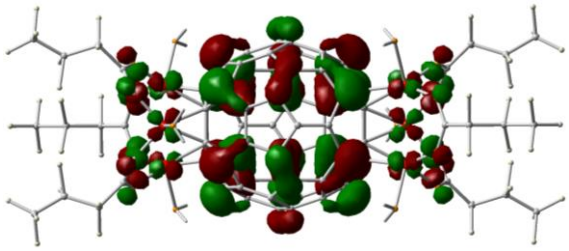
(a) LUMO+2



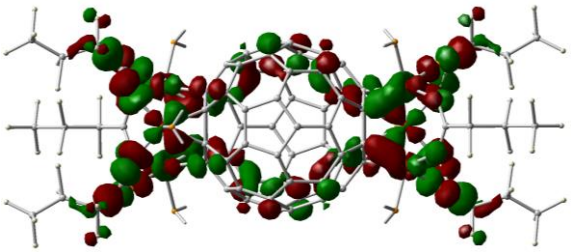
(b) LUMO+1



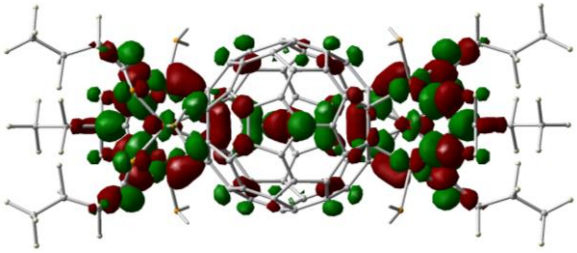
(c) LUMO



(d) HOMO

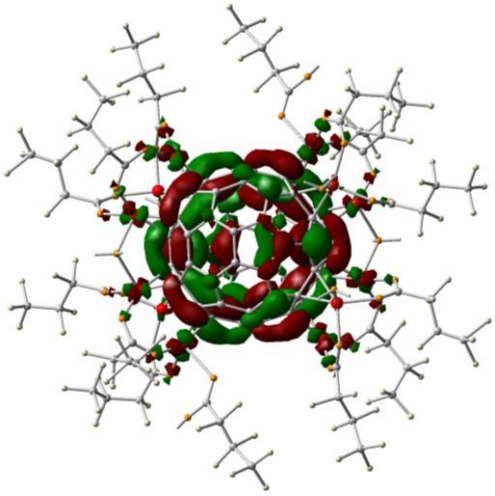


(e) HOMO-3

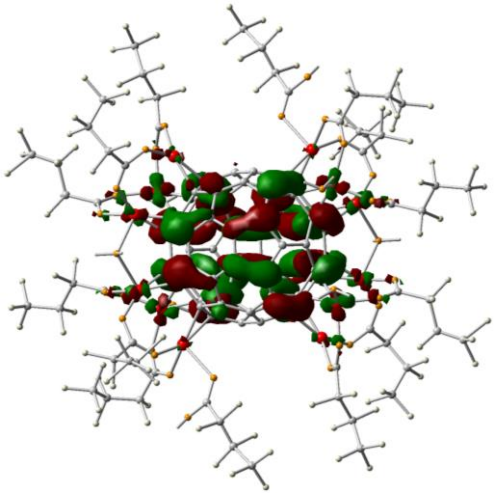


(f) HOMO-4

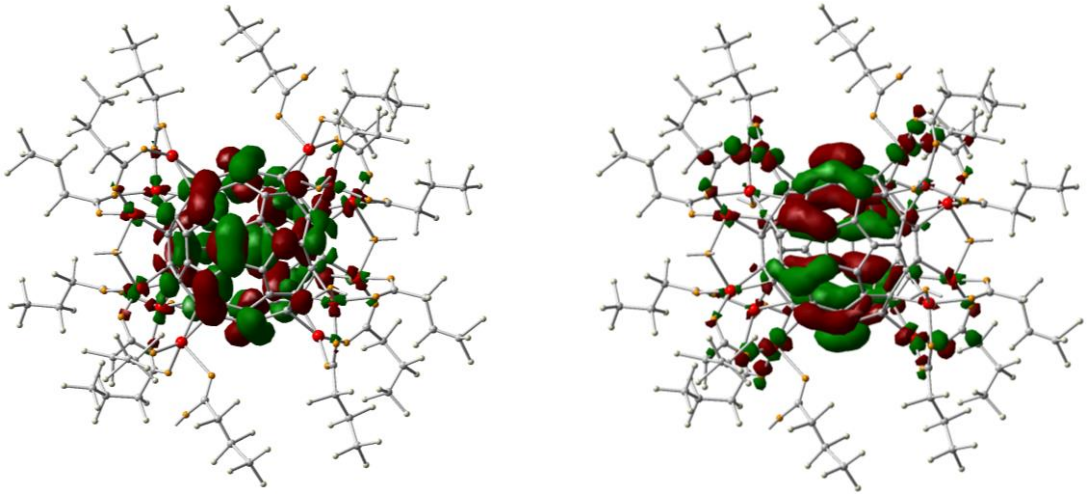
Figure S10. The contour of the frontier molecular orbitals for the cuprofullerene **Cu_6** molecule in the complex **1** (isovalue = 0.02).



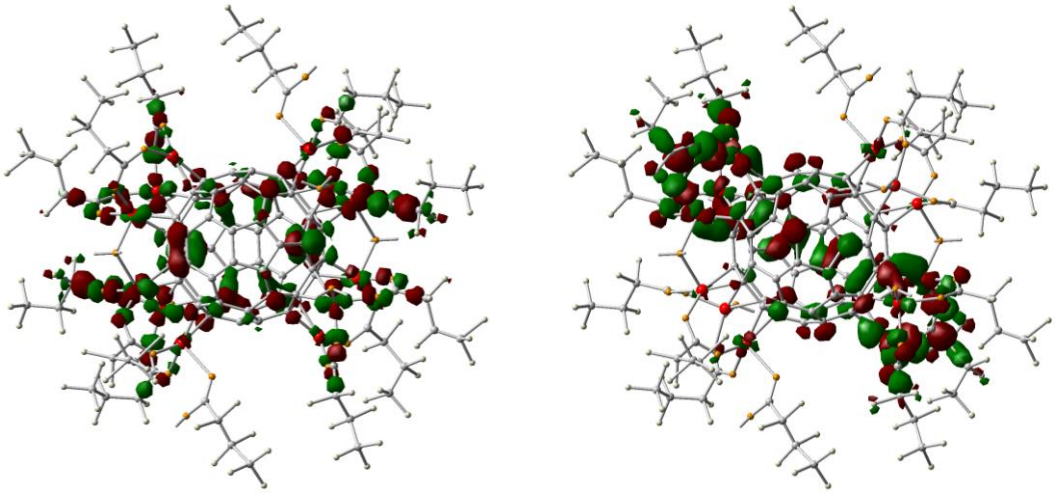
(a) LUMO+2



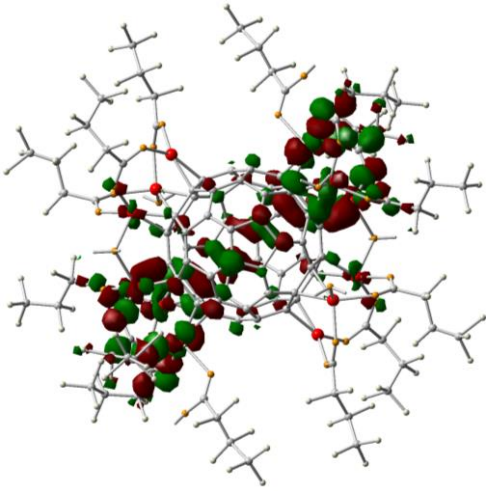
(b) LUMO+1



(c) LUMO (d) HOMO

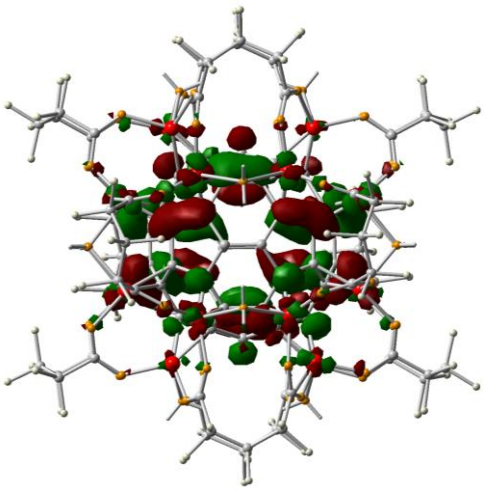


(e) HOMO-3 (f) HOMO-6

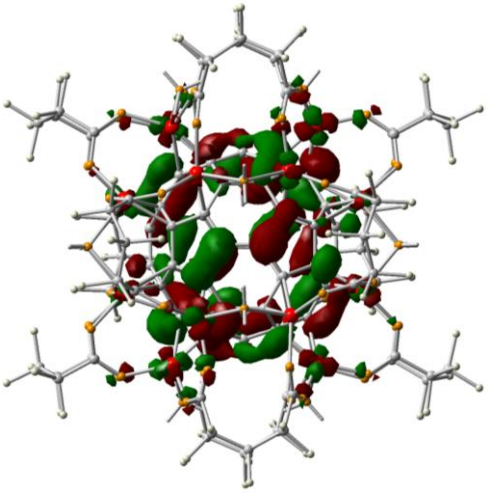


(g) HOMO-7

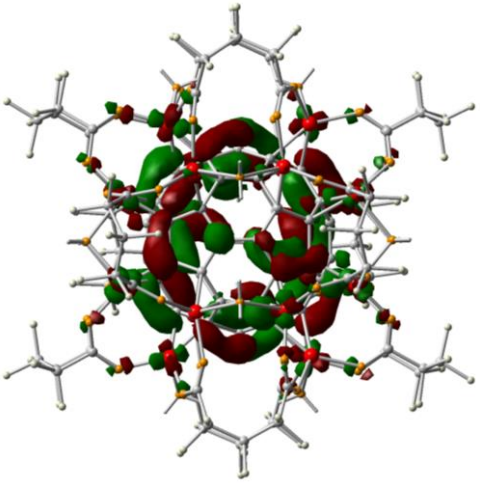
Figure S11. The contour of the frontier molecular orbitals for the cuprofullerene **Cu_{12}** molecule in the complex **2** (isovalue = 0.02).



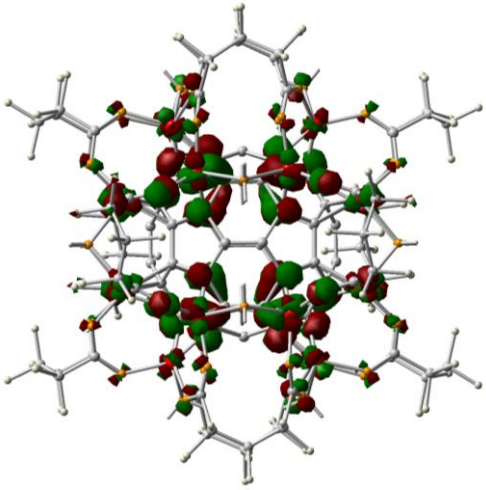
(a) LUMO+2



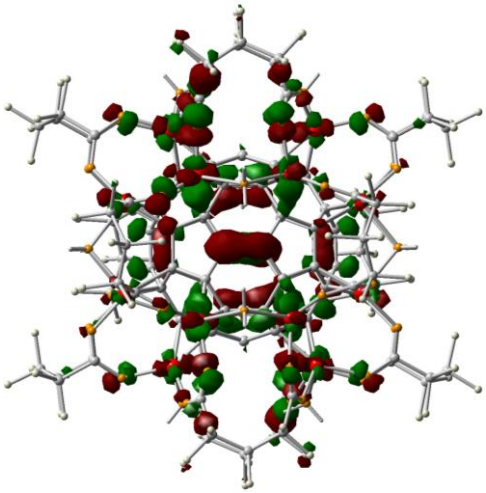
(b) LUMO+1



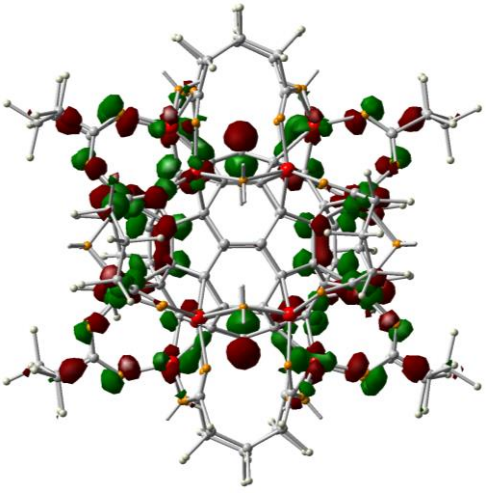
(c) LUMO



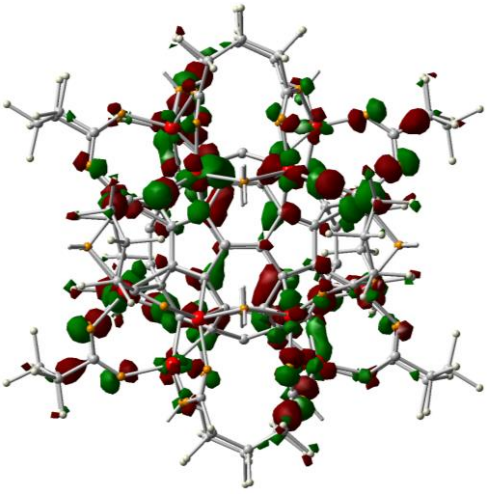
(d) HOMO



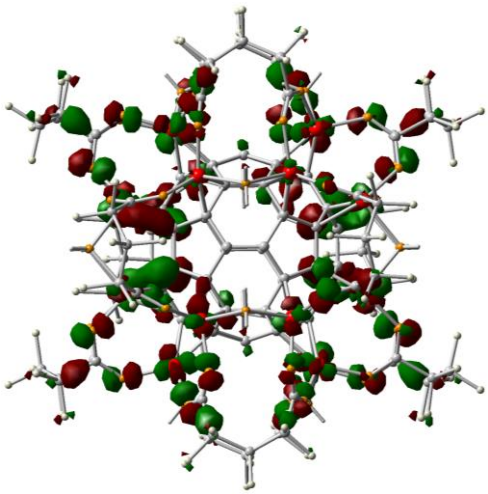
(e) HOMO-3



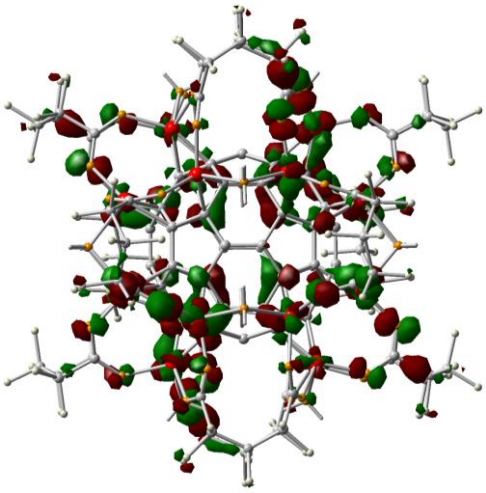
(f) HOMO-4



(g) HOMO-7

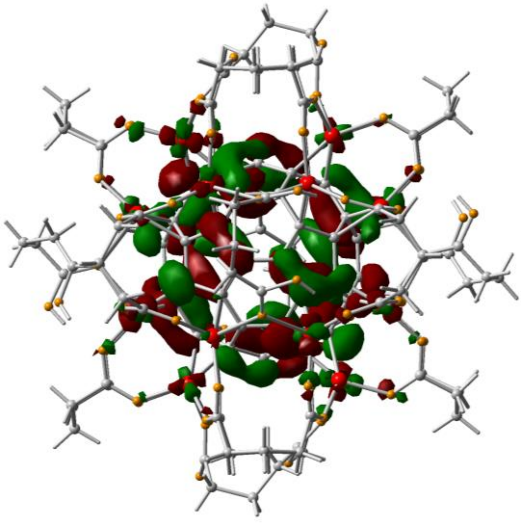


(h) HOMO-8

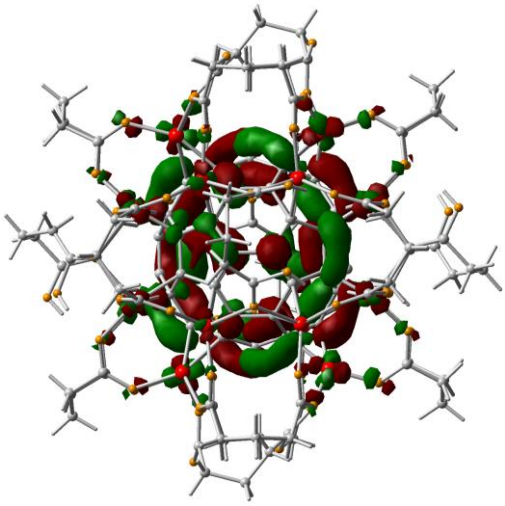


(i) HOMO-9

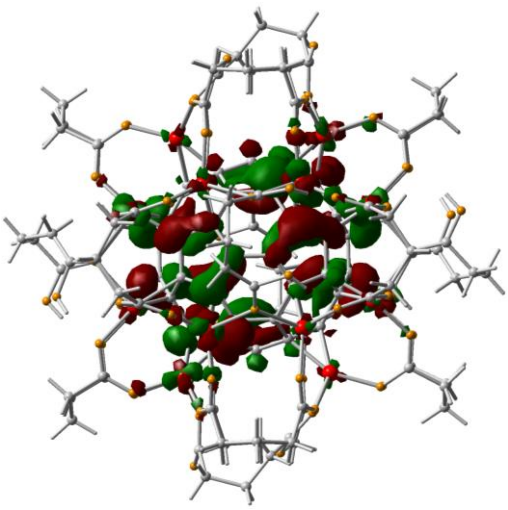
Figure S12. The contour of the frontier molecular orbitals for the cuprofullerene **Cu_{24}** molecule in the complex **3** (isovalue = 0.02).



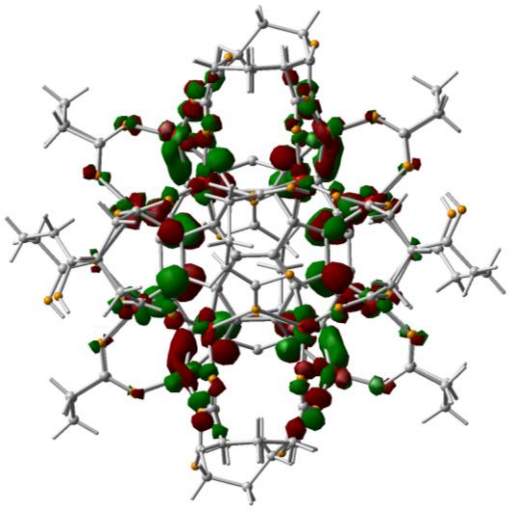
(a) LUMO+2



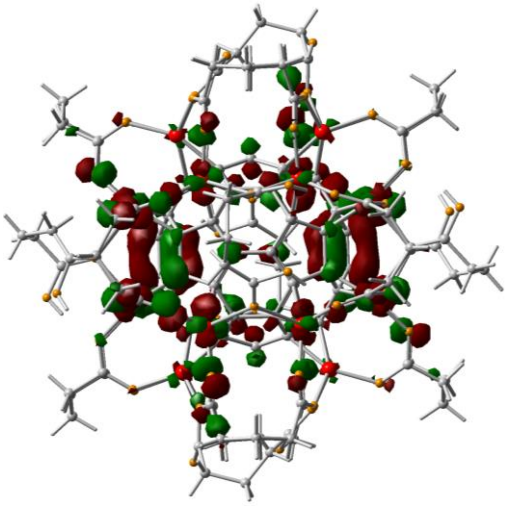
(b) LUMO+1



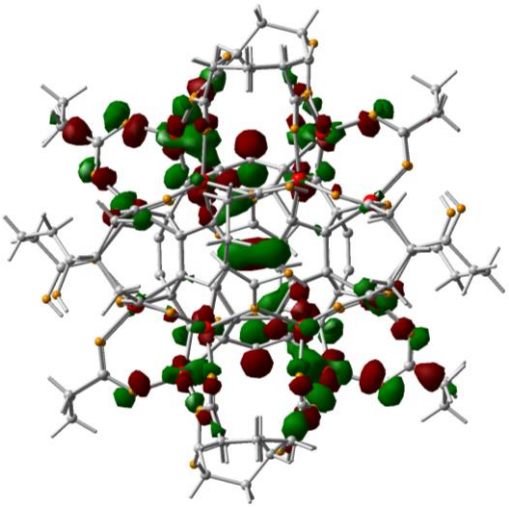
(c) LUMO



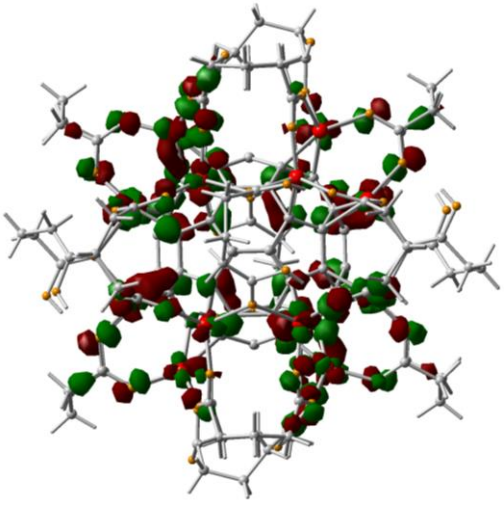
(d) HOMO



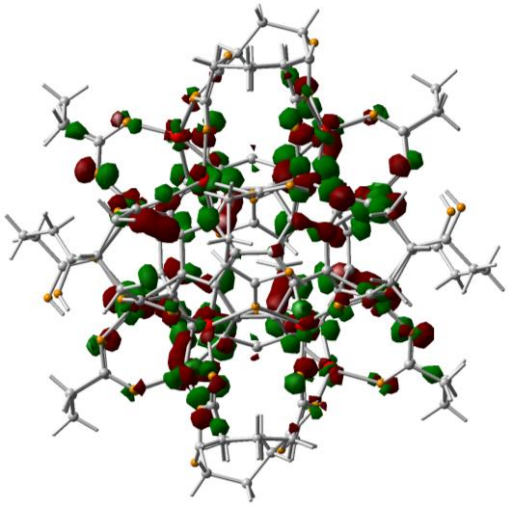
(e) HOMO-4



(f) HOMO-5

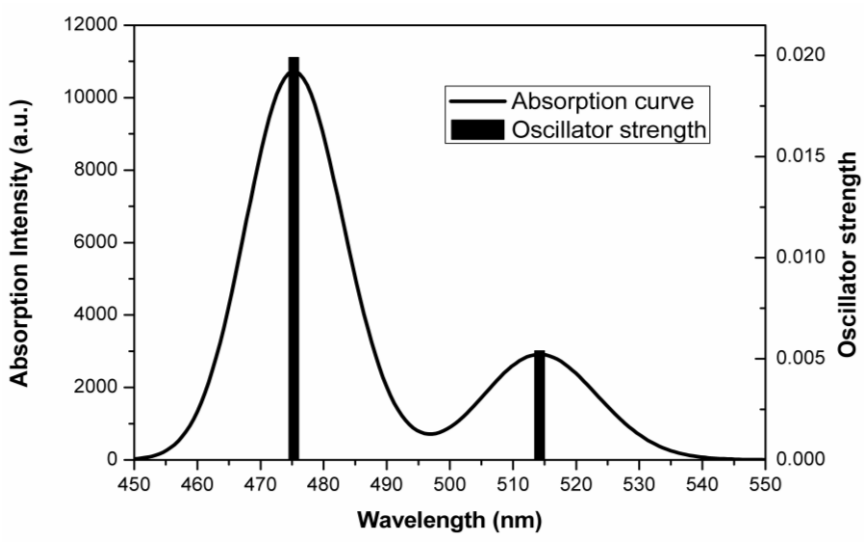


(g) HOMO-7

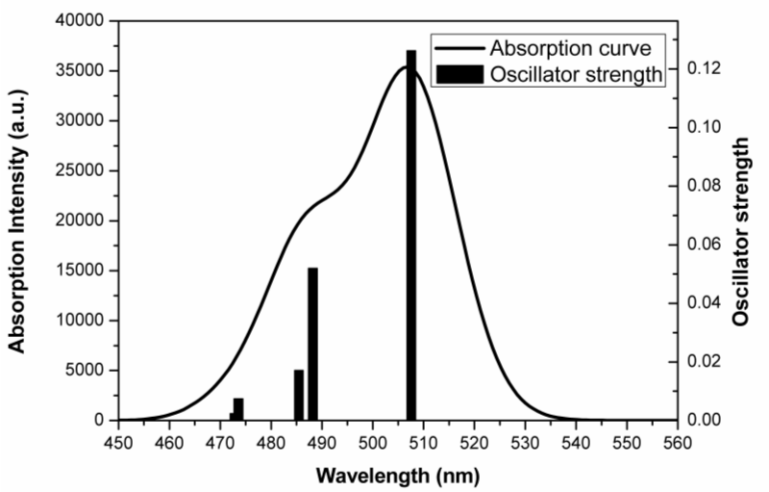


(h) HOMO-8

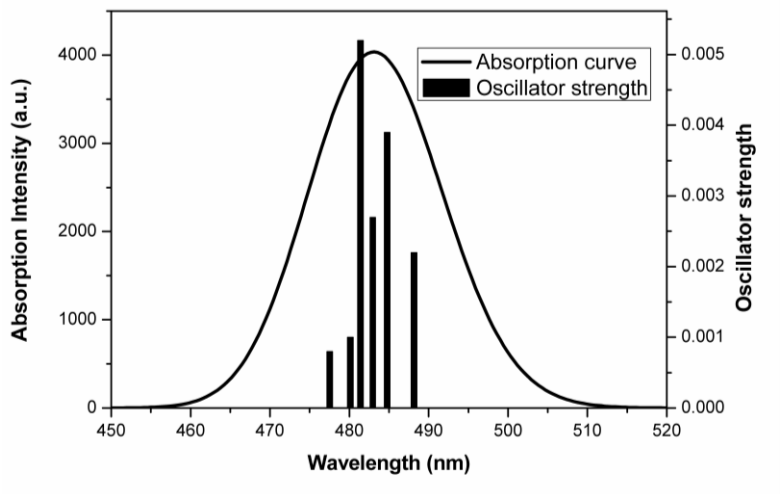
Figure S13. The contours of the frontier molecular orbitals for the cuprofullerene **Cu_{24}-H** molecule in the complex **4** (isovalue = 0.02).



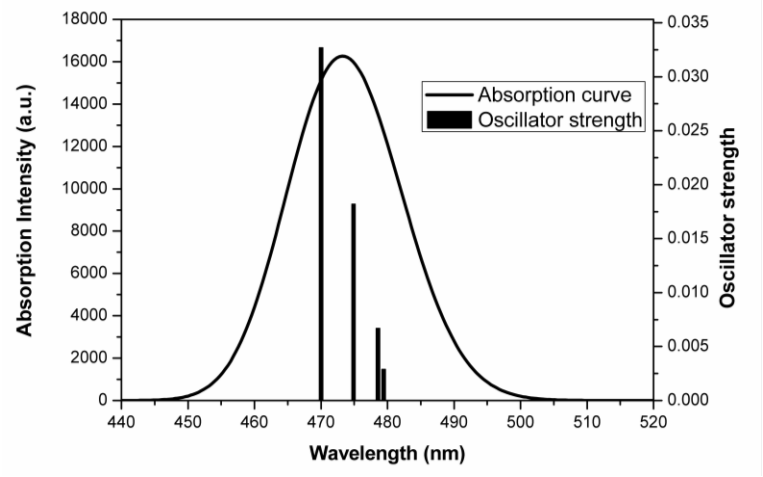
(a) **Cu_6**



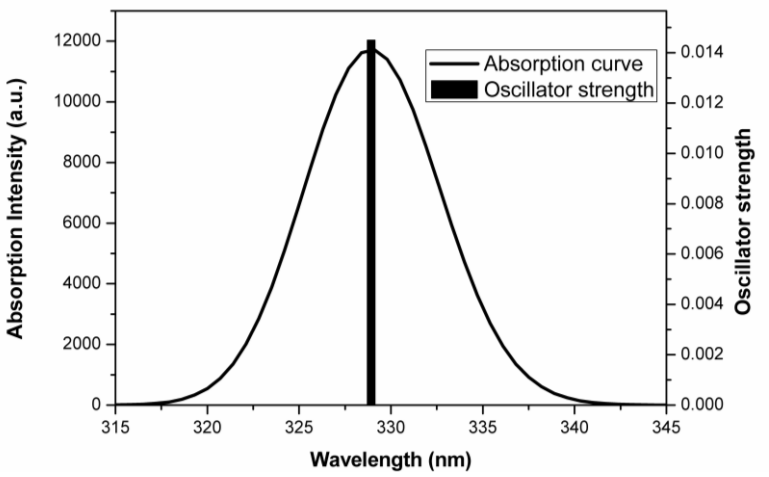
(b) **Cu_{12}**



(c) **Cu_{24}**



(d) **Cu$_{24}$**-H



(e) C_{60}

Figure S14. Calculated UV-Vis absorption spectra based on (a) **Cu$_6$**, (b) **Cu$_{12}$**, (c) **Cu$_{24}$**, (d) **Cu$_{24}$**-H and (e) C_{60}.

Reference

1. Sheldrick, G. M. *Acta Crystallogr. A* 2008, **64**, 112.
2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr. J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; J. Burant, C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision A.01, Gaussian, Inc., Wallingford, CT, 2009.

3. Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, 77, 3865.
4. Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, 78, 1396.
5. Adamo, C.; Barone, V. *Theor. Chem. Acc.* **2000**, 105(2), 169-172.
6. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, 82, 270-283.
7. Del Bene, J. E. *Chem. Phys. Lett.* **1983**, 94(2), 213-217.
8. Lu, T.; Chen, F. W. *J. Comp. Chem*. **2012**, 33, 580-592.
9. Multiwfn manual, version 3.6(dev), http://multiwfn.codeplex.com/.