Electronic Supplementary Information (ESI)

2D Coordination Sheets Based on Tetranuclear Cuprofullerene Pentafluorobenzoate and Their Electronic Properties

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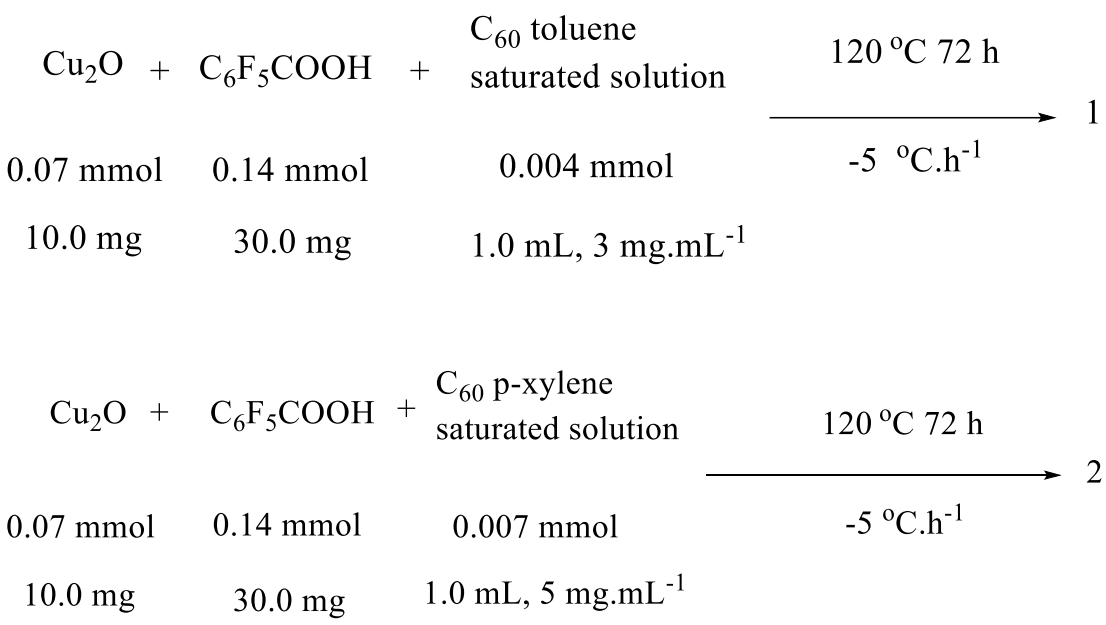


Scheme S1 Schematic illustration of preparing the two 2D polymers.

Table S1 Comparison of the selected bond lengths (Å) in the complexes **1** and **2**.

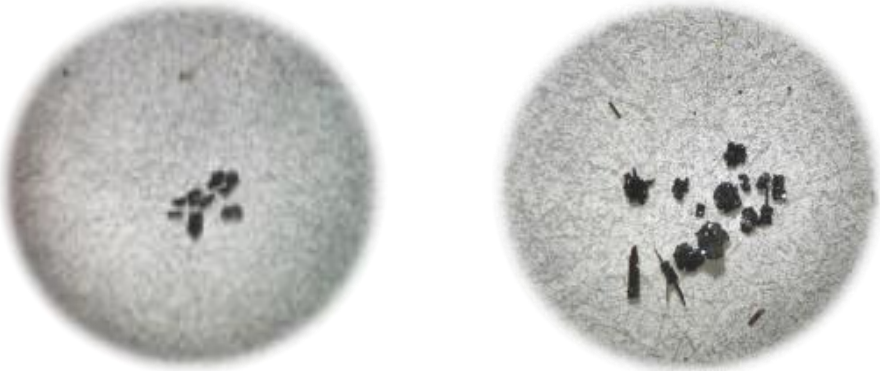
bond lengths (Å)			
1		**2**	
Cu-Cu			
Cu1-Cu2	3.052(1)	Cu1-Cu2	3.004(1)
Cu-O			
Cu1-O1	2.114(2)	Cu1-O1	2.076(3)
Cu1-O4	1.956(2)	Cu1-O4	2.034(3)
Cu2-O2	2.035(2)	Cu2-O2	1.952(3)
Cu2-O3	2.052(2)	Cu2-O3	2.047(2)
Cu1-O3#1	2.158(2)	Cu3-O3	2.148(2)
Cu2-O1#2	2.115(2)	Cu3-O5	1.964(3)
		Cu3-O8	1.936(3)
		Cu1-O1#1	2.147(2)
		Cu2-O6#2	2.206(2)
		Cu3-O6#2	2.022(2)
		Cu3-O7#2	1.942(3)
Cu-C			
Cu1-C1	2.039(2)	Cu1-C1	2.069(4)
Cu1-C2	2.028(2)	Cu1-C2	2.054(4)

Cu2-C3	2.028(2)	Cu2-C3	2.011(4)
Cu2-C4	2.077(2)	Cu2-C4	2.038(4)
coordinated C=C			
C1-C2	1.423(3)	C1-C2	1.418(7)
C3-C4	1.420(4)	C3-C4	1.419(6)
Symmetry codes			
#1 +x, 3/2−y, −1/2+z #2 +x, 3/2−y, 1/2+z		#1 1−x, 1−y, −z #2 1−x, 1−y, 1−z	

Table S2 Comparison of the selected bond angles (º) in the complexes **1** and **2**.

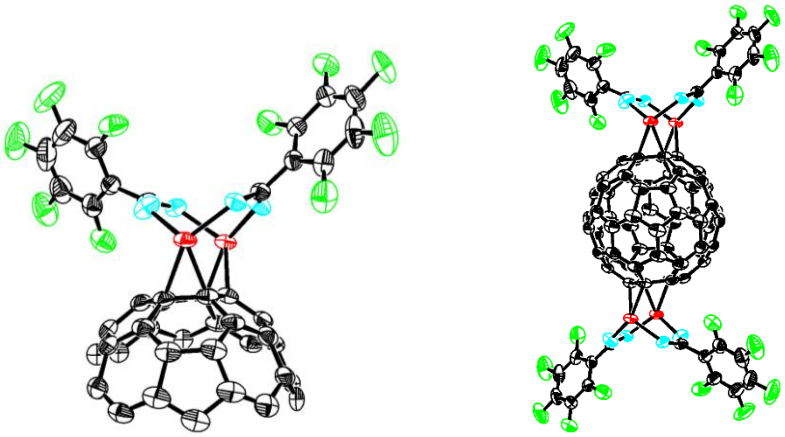
1		**2**	
O-Cu-Cu			
O1-Cu1-Cu2	79.79(4)	O1#1-Cu1-Cu2	155.76(6)
O3#1-Cu1-Cu2	156.77(4)	O1-Cu1-Cu2	79.74(6)
O4-Cu1-Cu2	76.47(5)	O4-Cu1-Cu2	74.96(8)
O1#2-Cu2-Cu1	158.79(5)	O2-Cu2-Cu1	77.83(8)
O2-Cu2-Cu1	77.16(5)	O3-Cu2-Cu1	82.89(6)
O3-Cu2-Cu1	79.62(4)	O6#2-Cu2-Cu1	159.72(7)
		O3-Cu3-Cu3#2	164.95(7)
		O5-Cu3-Cu3#2	84.87(7)
		O6#2-Cu3-Cu3#2	83.36(6)
		O7#2-Cu3-Cu3#2	83.97(8)
		O8-Cu3-Cu3#2	84.15(9)
O-Cu-O			
O1-Cu1-O4	102.03(8)	O1-Cu1-O4	98.83(1)
O2-Cu2-O3	106.68(8)	O2-Cu2-O3	105.49(2)
O4-Cu1-O3#1	98.94(7)	O1-Cu1-O1#1	79.43(2)
O2-Cu2-O1#2	99.59(7)	O4-Cu1-O1#1	96.19(1)
O3-Cu2-O1#2	81.35(6)	O5-Cu3-O3	110.18(1)
O1-Cu1-O3#1	78.97(6)	O8-Cu3-O3	95.79(1)
		O8-Cu3-O5	90.20(3)
		O2-Cu2-O6#2	96.96(1)
		O3-Cu2-O6#2	79.64(9)
		O5-Cu3-O6#2	168.22(9)

		O6#2-Cu3-O3	81.59(9)
		O7#2-Cu3-O3	95.03(1)
		O7#2-Cu3-O5	91.24(3)
		O7#2-Cu3-O6#2	87.90(1)
		O8-Cu3-O6#2	88.24(2)
		O8-Cu3-O7#2	167.86(2)
O-Cu-C			
O4-Cu1-C1	148.32(9)	O3-Cu1-C1	108.02(2)
O4-Cu1-C2	107.40(9)	O4-Cu1-C2	129.41(1)
O2-Cu2-C4	99.12(10)	O2-Cu2-C3	103.60(2)
O3-Cu2-C4	147.14(9)	O2-Cu2-C4	144.38(2)
C-Cu-Cu			
C1-Cu1-Cu2	88.05(7)	C1-Cu1-Cu2	87.38(1)
C2-Cu1-Cu2	67.30(7)	C2-Cu1-Cu2	67.40(2)
C3-Cu2-Cu1	67.56(7)	C3-Cu2-Cu1	69.10(1)
C4-Cu2-Cu1	86.82(7)	C4-Cu2-Cu1	88.98(2)
C-Cu-O			
C1-Cu1-O1	102.16(9)	C1-Cu1-O1	146.01(2)
C1-Cu1-O3#1	105.52(8)	C2-Cu1-O1	106.12(2)
C2-Cu1-O1	128.17(9)	C3-Cu2-O3	133.77(2)
C2-Cu1-O3#1	134.67(8)	C4-Cu2-O3	105.47(2)
C3-Cu2-O1#2	127.68(8)		
C3-Cu2-O2	124.91(9)		
C3-Cu2-O3	106.85(9)		
C4-Cu2-O1#2	114.35(8)		
C-Cu-C			
C2-Cu1-C1	40.95(10)	C2-Cu1-C1	40.22(2)
C3-Cu2-C4	40.44(10)	C3-Cu2-C4	41.05(2)
Symmetry codes			
#1+x, 3/2-y, -1/2+z #2+x, 3/2-y, 1/2+z		#1 1-x, 1-y, -z # 2 1-x, 1-y, 1-z	

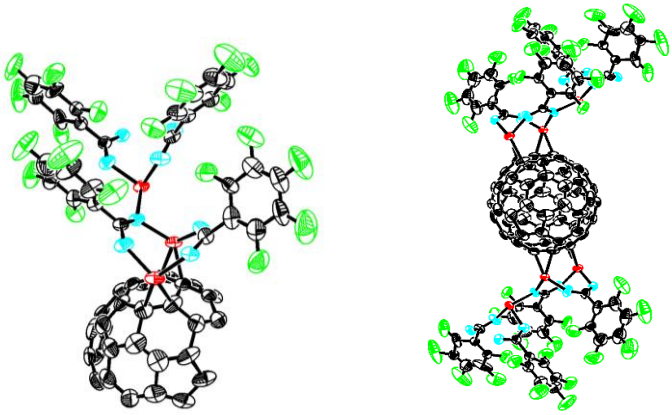


(a) complex **1** (b) complex **2**

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

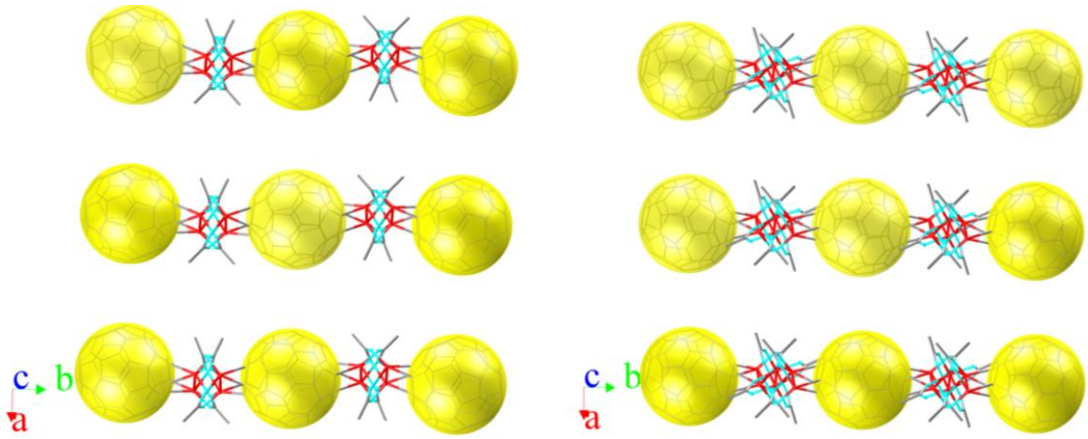


(a) complex **1**



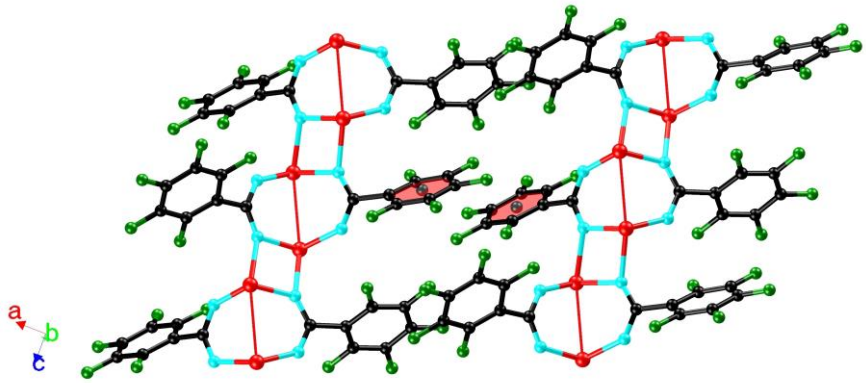
(b) complex **2**

Fig. S2 Asymmetric units (left) and molecular structures (right) of the complexes **1** (a) and **2** (b) with 50% thermal ellipsoid. (Color codes: red, Cu; cyan, O; green, F; black, C.)

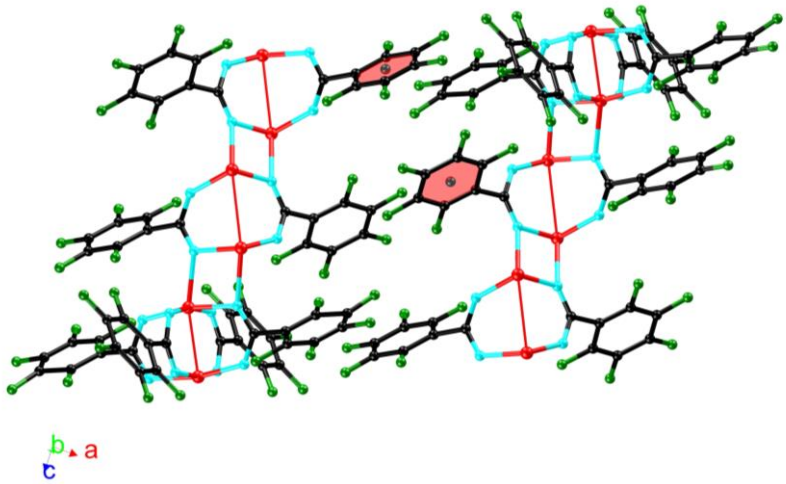


(a) complex **1** (b) complex **2**

Fig. S3 Packing structures of complexes **1** (a) and **2** (b). (-C_5F_5 were omitted for clarity; Color codes: red, Cu; cyan, O; grey, C.).

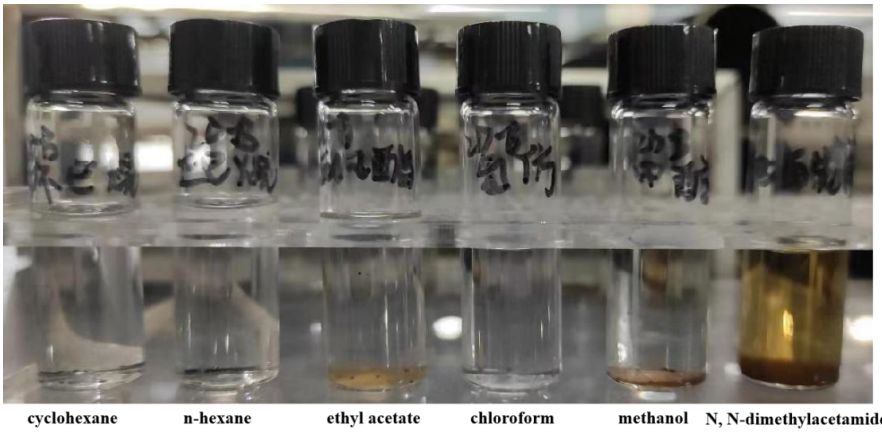


(a) complex **1**

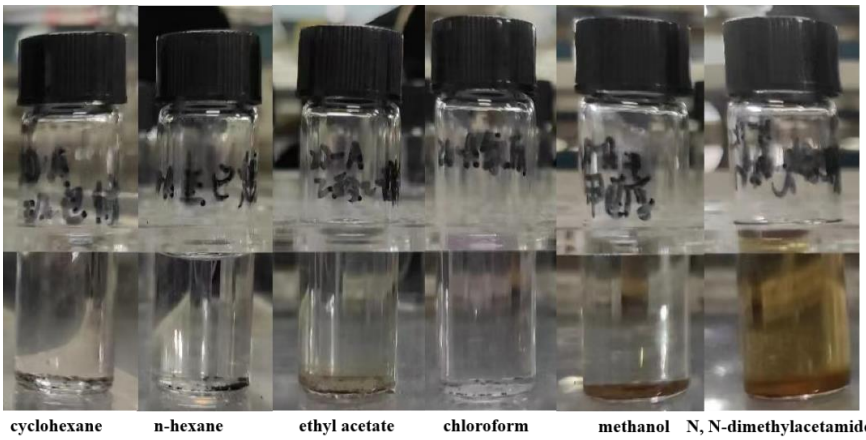


(b) complex **2**

Fig. S4 Weak interactions between these copper pentafluorobenzoate chains in complexes **1** (a) and **2** (b) to illustrate the interactions between the adjacent polymeric sheets. The shortest distances between the pentafluorophenyl centers are 5.561(7) Å in **1** and 5.029(1) Å in **2**. (Color codes: red, Cu; cyan, O; green, F; black, C.).



(a) complex **1**



(b) complex **2**

Fig. S5 Crystal samples of complexes **1** (a) and **2** (b) soaked in common solvents (cyclohexane, *n*-hexane, ethyl acetate, chloroform, methanol, N, N-dimethylacetamide).

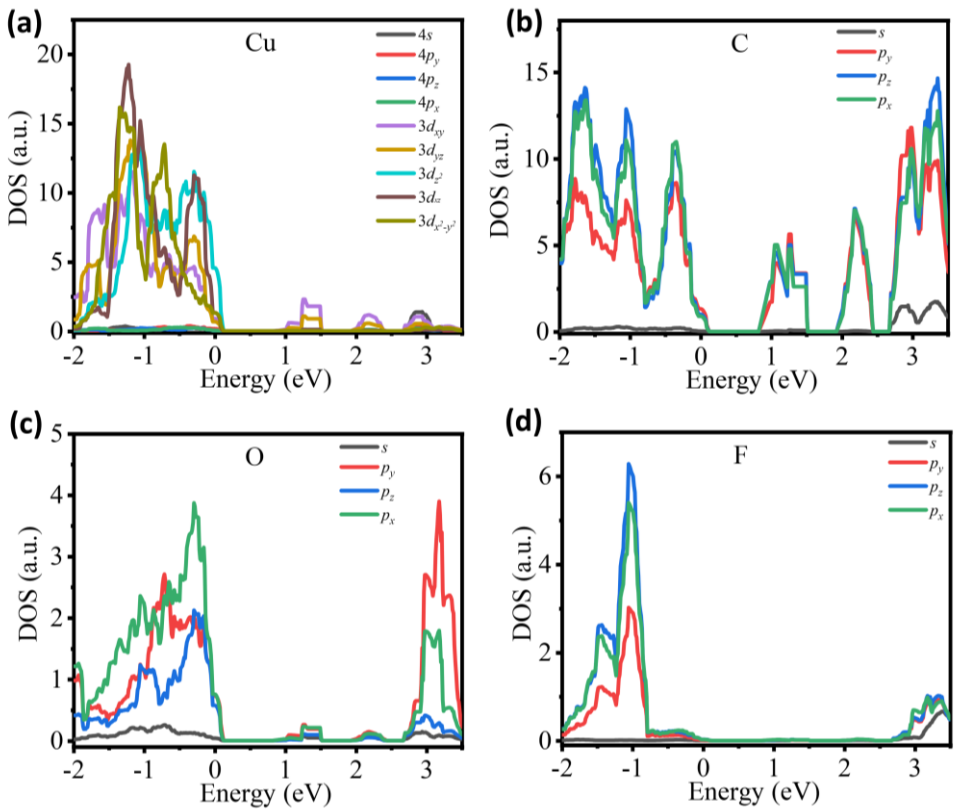


Fig. S6 Density of states of the complex **1** for Cu, C, O and F.

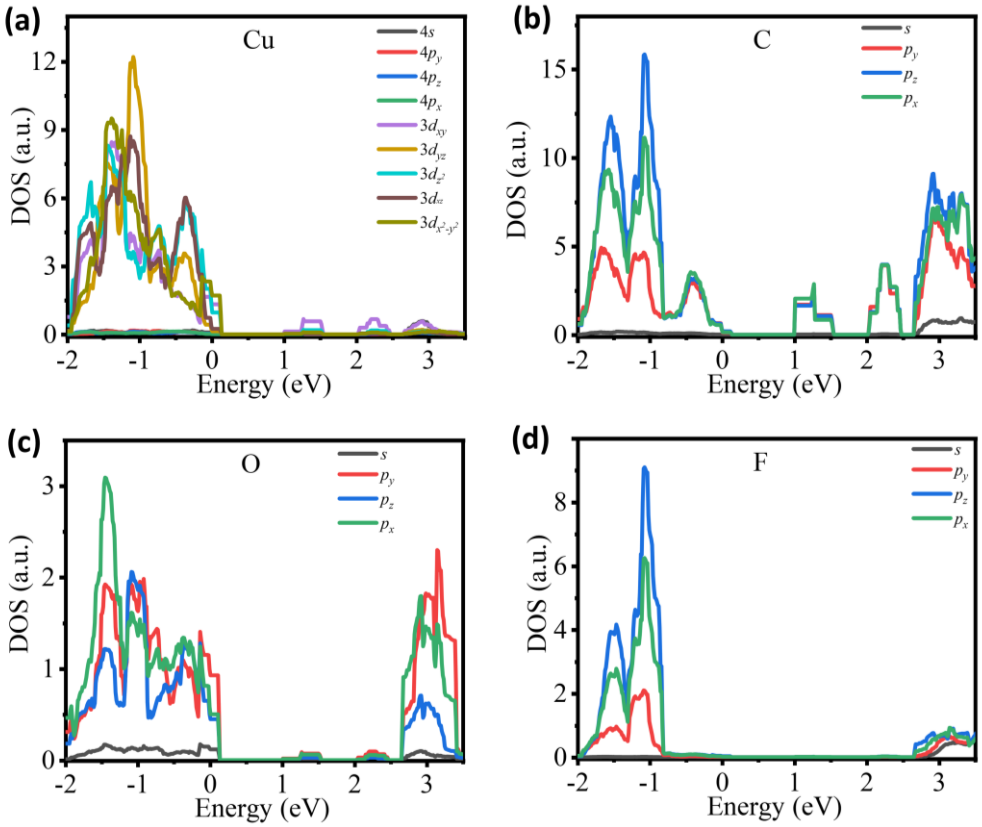
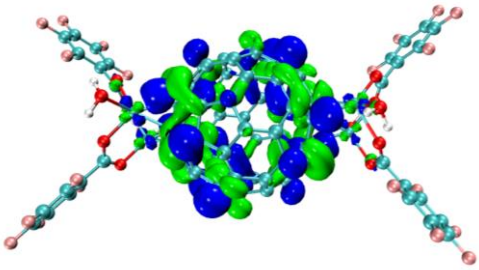


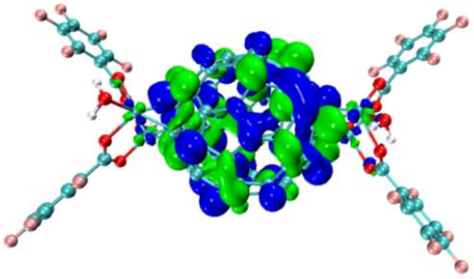
Fig. S7 Density of states of the complex **2** for Cu, C, O and F.

Table S3 The Hirshfeld compositions (%) of selected MOs in the ground state at the PBE0 level of theory for the tetranuclear cuprofullerene model.

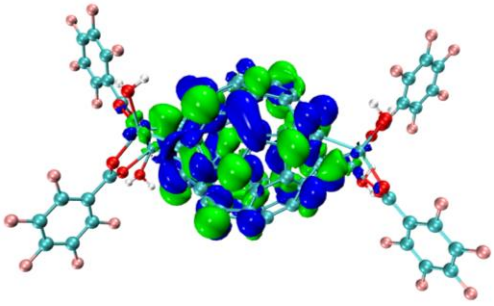
NO.	Atom contributions		
	Cu	O	C_{60}
435 (H-9)	2.93	2.06	1.13
436 (H-8)	1.22	1.12	0.60
437 (H-7)	1.27	0.97	0.55
438 (H-6)	33.91	25.02	16.30
439 (H-5)	36.83	21.24	31.02
440 (H-4)	17.21	7.76	71.79
441 (H-3)	11.12	4.26	79.60
442 (H-2)	0.14	0.08	99.60
443 (H-1)	12.12	3.74	82.02
444 (H)	12.34	5.25	78.84
445 (L)	0.74	0.25	94.79
446 (L+1)	8.43	1.75	88.70
447 (L+2)	8.71	1.79	88.39
448 (L+3)	9.24	1.86	85.28
449 (L+4)	5.11	0.85	92.64
450 (L+5)	1.78	0.44	97.28
451 (L+6)	7.76	1.26	89.24
452 (L+7)	6.29	1.11	90.28
453 (L+8)	6.33	1.38	88.66
454 (L+9)	7.03	1.61	86.96



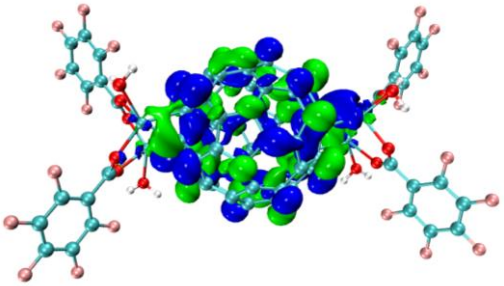
LUMO+9



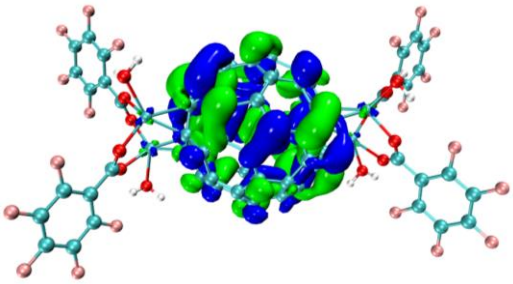
LUMO+8



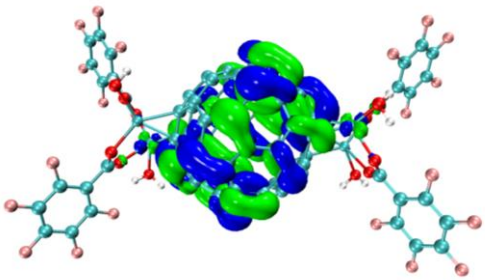
LUMO+7



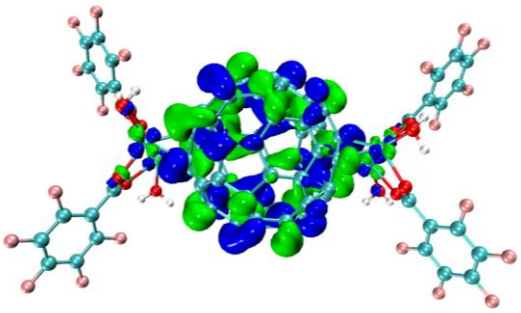
LUMO+6



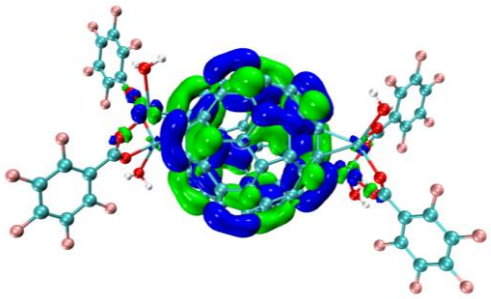
LUMO+5



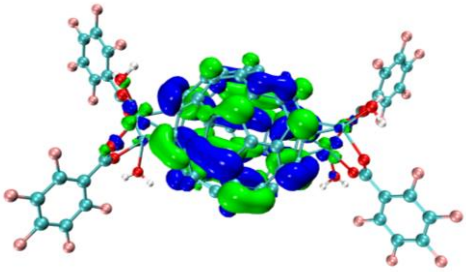
LUMO+4



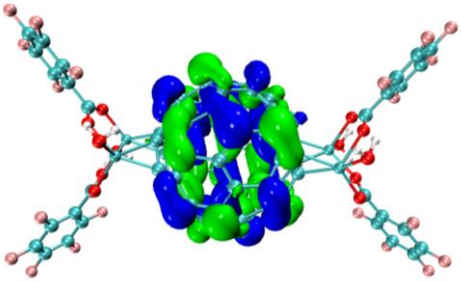
LUMO+3



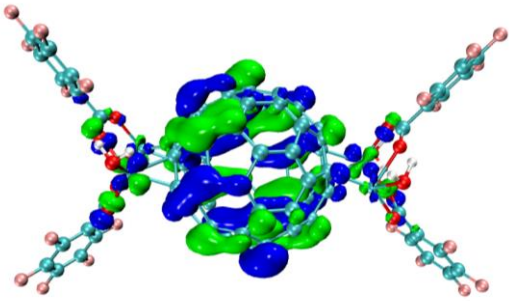
LUMO+2



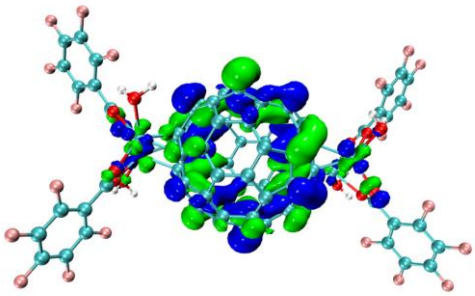
LUMO+1



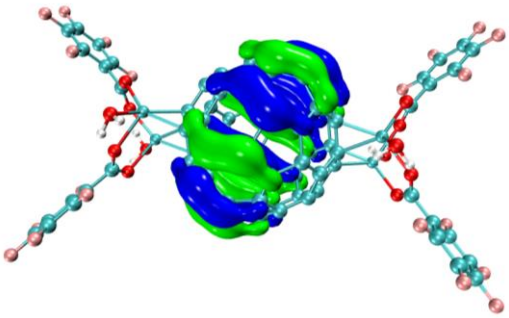
LUMO



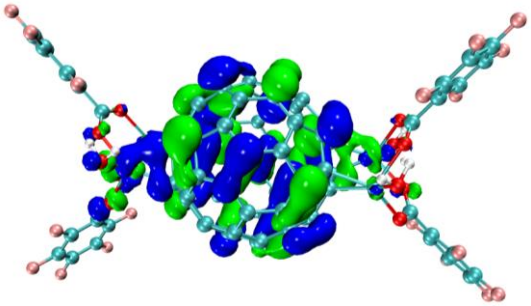
HOMO



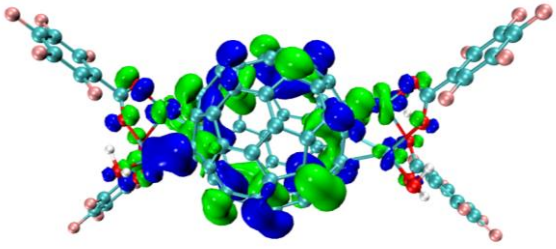
HOMO-1



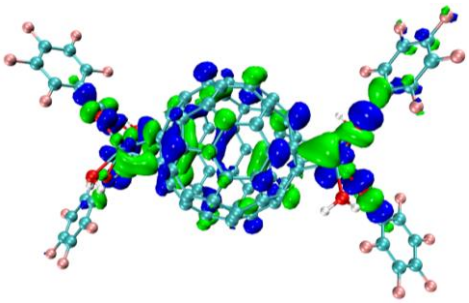
HOMO-2



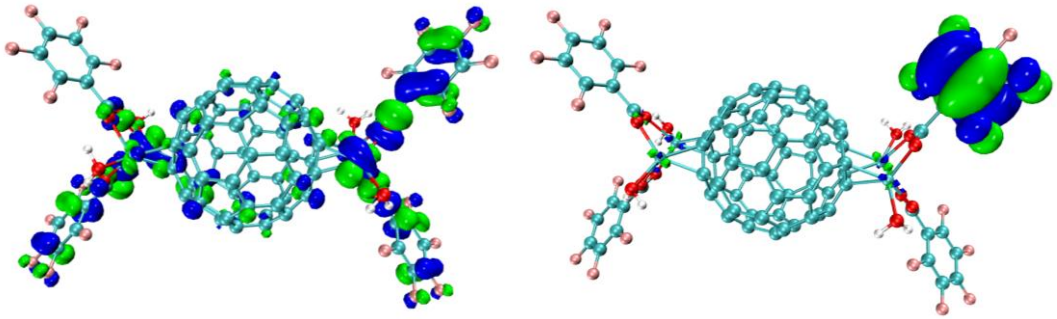
HOMO-3



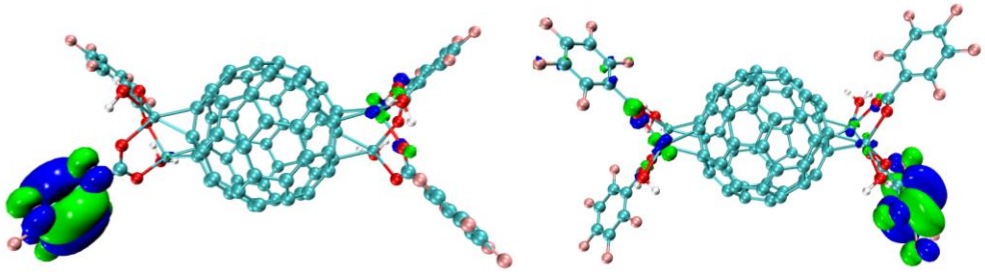
HOMO-4



HOMO-5



HOMO-6 HOMO-7



HOMO-8 HOMO-9

Fig. S8 The contour of frontier molecular orbitals from HOMO-9 to LUMO+9 at the PBE0 level of theory for the tetranuclear cuprofullerene model (isovalue = 0.02).