Electronic Supplementary Material (ESI) for Dalton Transactions.

Chiral Copper-Hydride Nanoclusters: Synthesis, Structure, and Assembly

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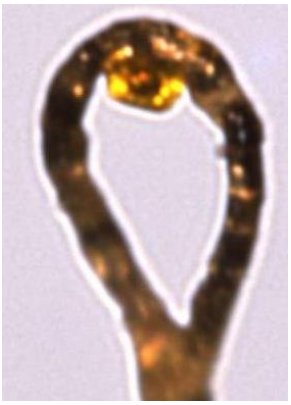


Figure S1. Digital photographs Cu_{14} crystals.

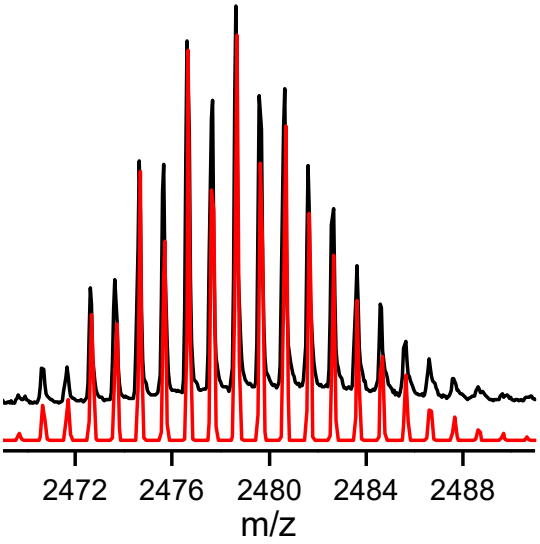


Figure S2. The comparison between simulated and experimental isotopic patterns of $[Cu_{14}(^{t}BuS)_3(PPh_3)_5H_{10}]^+$.

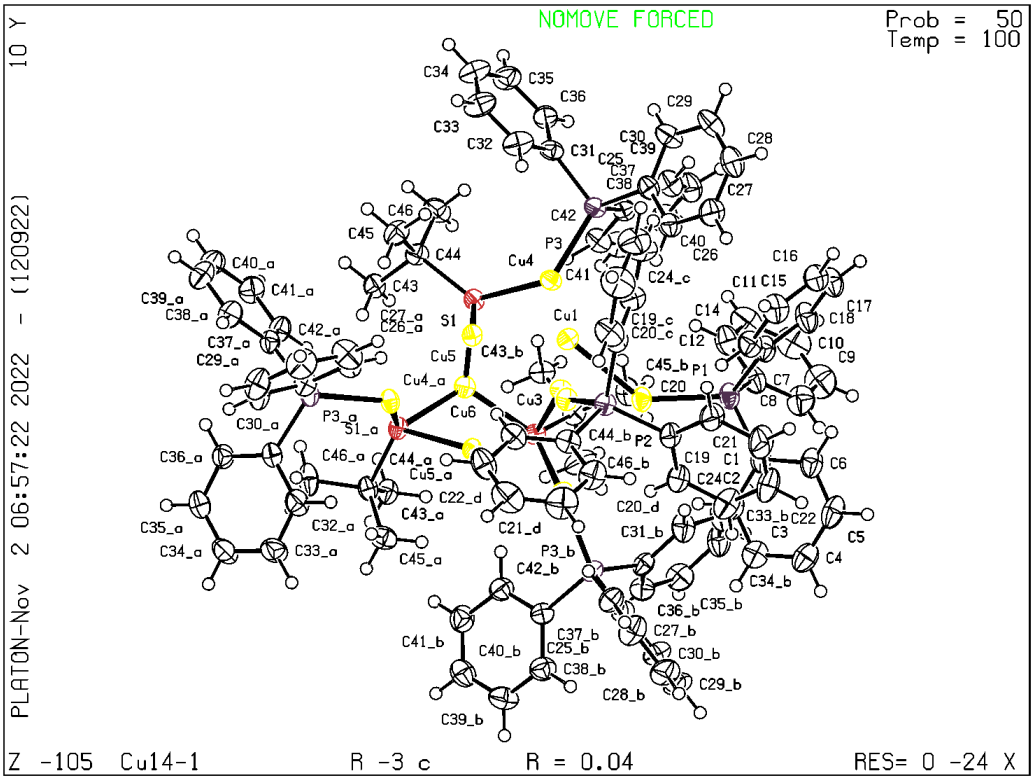


Figure S3. The thermal ellipsoids of the ORTEP diagram of Cu_{14}.

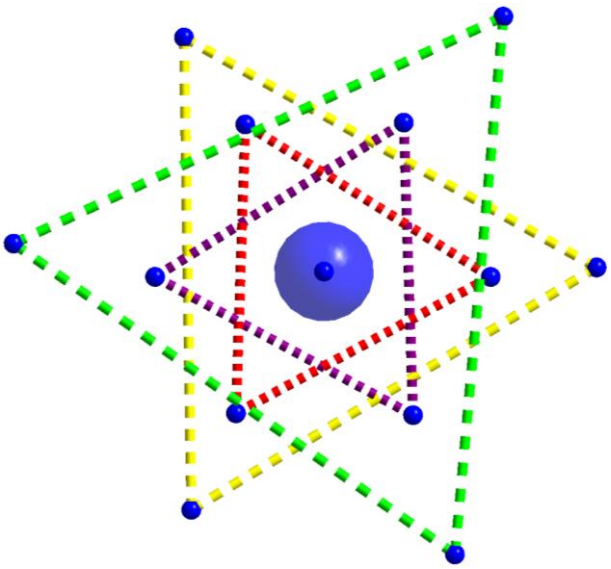


Figure S4. Layer-by-layer anatomy of metal framework of the Cu_{14} cluster in the top view.

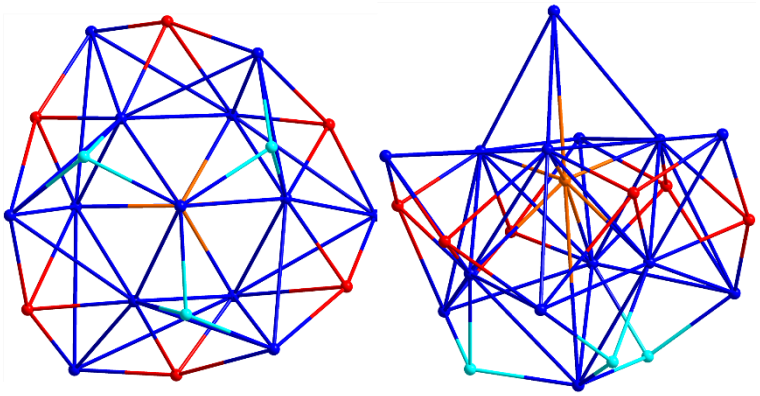


Figure S5. Metal framework of Cu_{14} cluster with hydride positions proposed in different views. Colour codes for atoms: blue spheres, Cu; red, orange, and turquoise spheres, H.

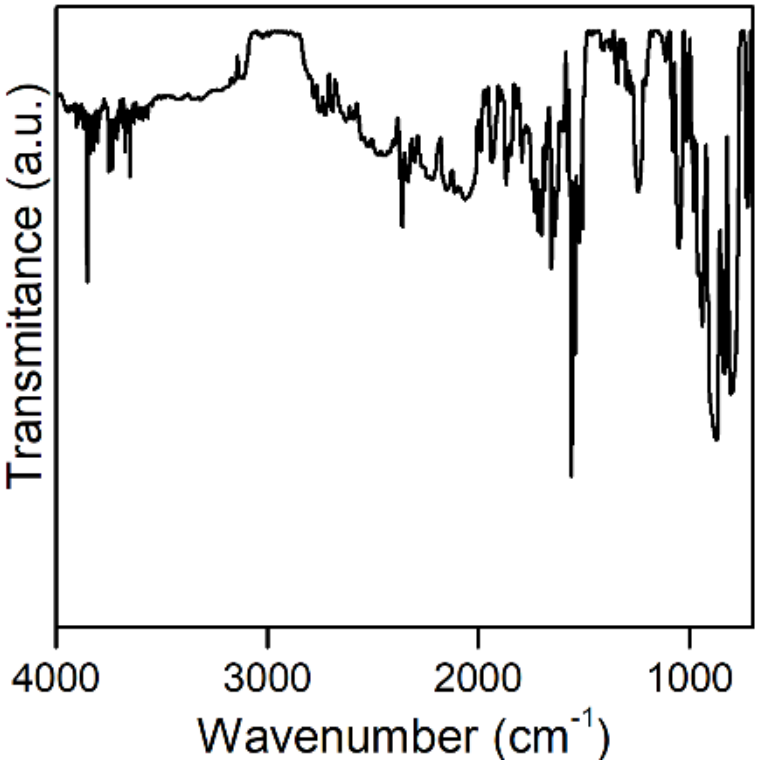


Figure S6. IR spectrum of Cu_{14} cluster.

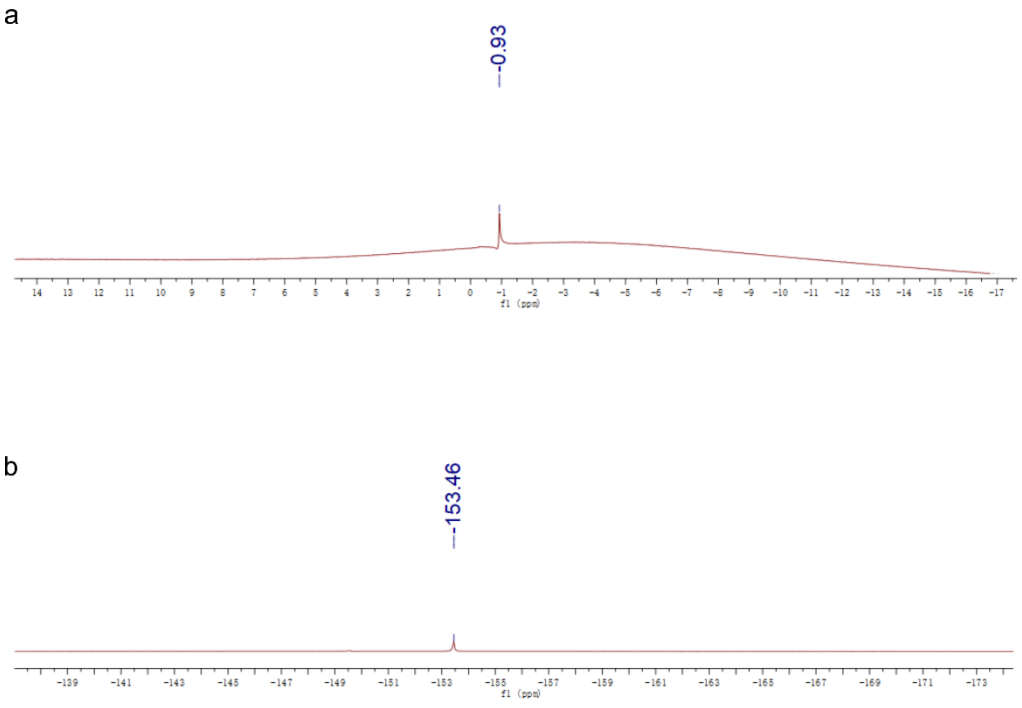


Figure S7. ^{11}B (a) and ^{19}F (b) NMR of Cu_{14} in $CDCl_3$ showing the presence of BF_4^- in the cluster.

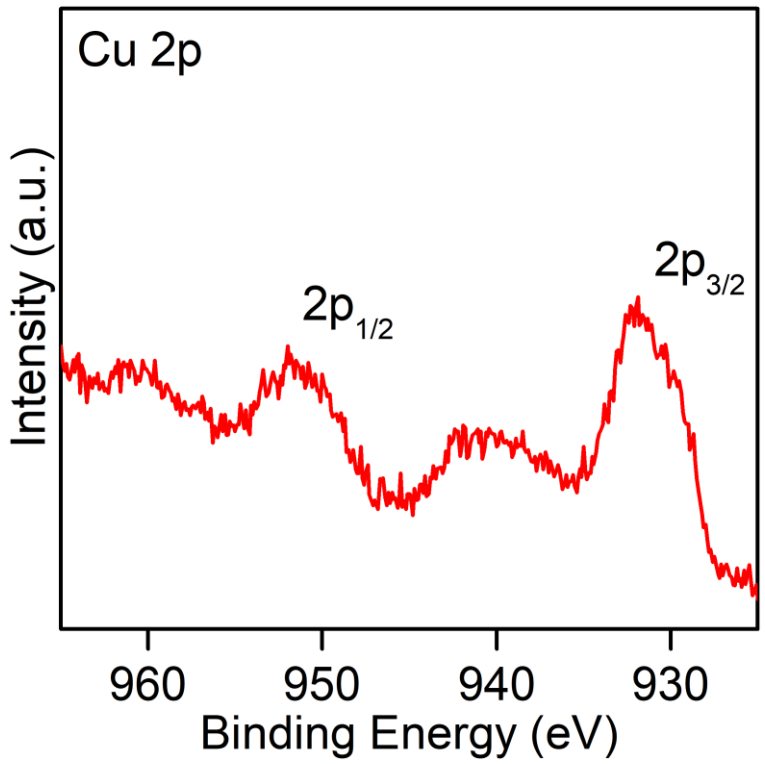


Figure S8. High-resolution XPS spectra of Cu 2p of Cu_{14} cluster.

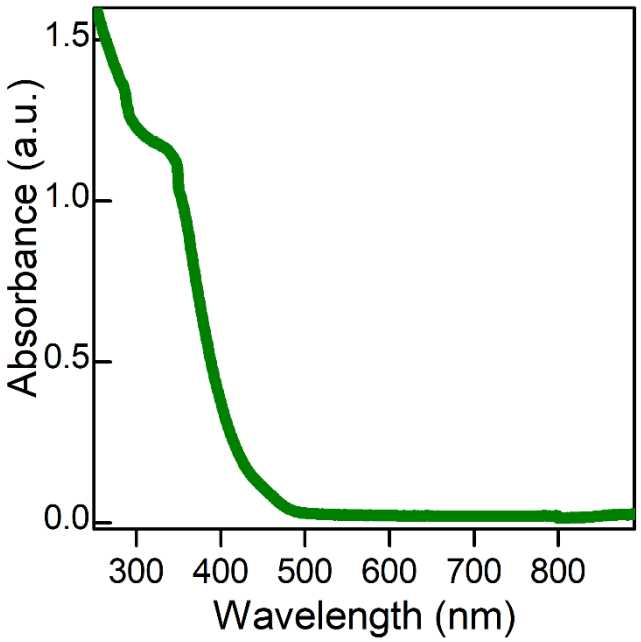


Figure S9. UV-Vis spectrum of Cu_{14} cluster in dichloromethane.

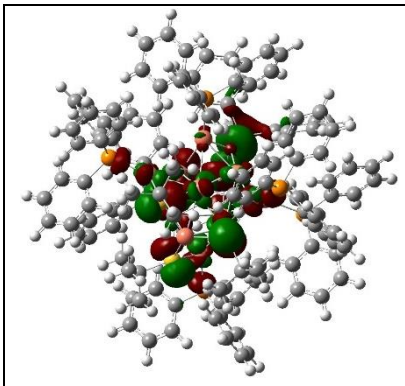
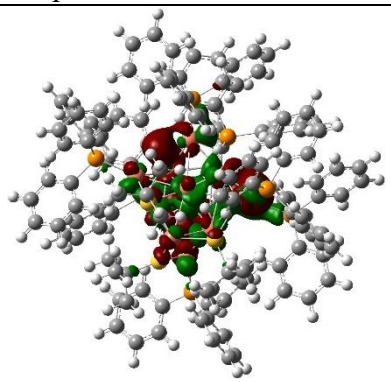
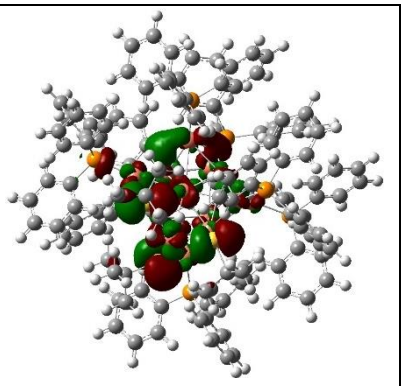
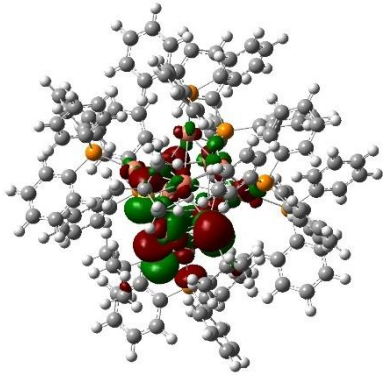
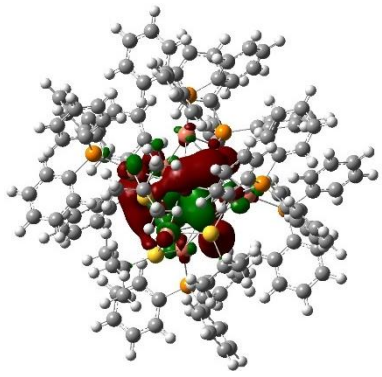
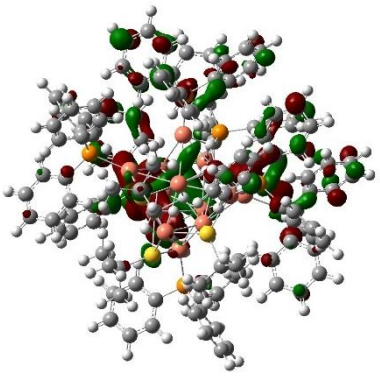
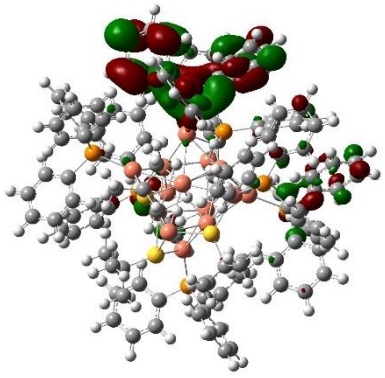
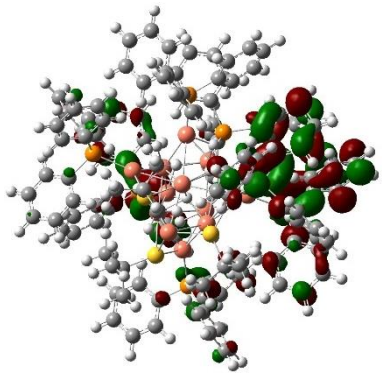
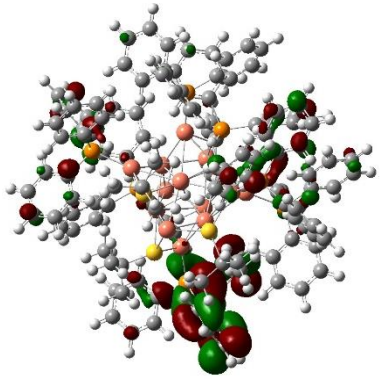
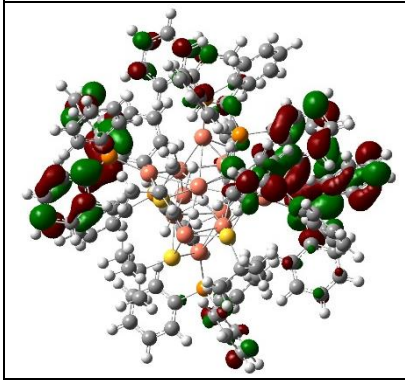
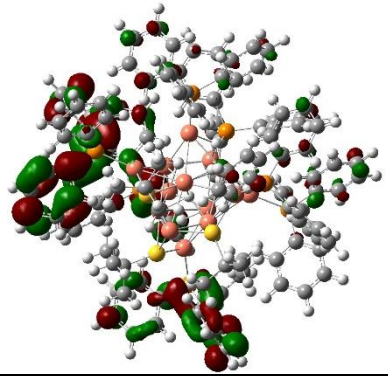
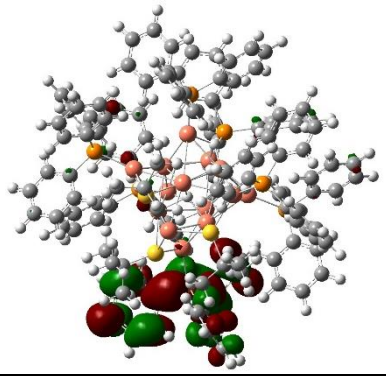
Table S1. Crystallographic data of Cu_{14}.

CCDC No.	2216936
Formula	$C_{147.50}H_{152}Cu_{14}O_{5.50}P_7S_3$
Formula weight	3205.13
Temperature/K	99.89(9)
Crystal system	trigonal
Space group	R-3c
a (Å)	17.6260(3)
b (Å)	17.6260(3)
c (Å)	154.6133(19)
α (˚)	90
β (˚)	90
γ (˚)	120
V ($Å^3$)	41599.2(15)
Z	12
D_c / (g ċcm^{-3})	1.535
Radiation	Cu Kα (λ= 1.54184 Å)
Theta (˚) range	2.9420 to 65.4930
Index ranges	$-20 \le h \le 20$, $-20 \le k \le 14$, $-178 \le l \le 182$
Refls. Total	8043
Restraints	0
Parameters	490
R_{int}	0.0602
R_1/wR_2 [I>2σ(I)]	0.0358 0.0966
R_1/wR_2 (all data)	0.0396 0.0993
GoF	1.093

Table S2. Selected bond lengths (Å) for compound Cu_{14}.

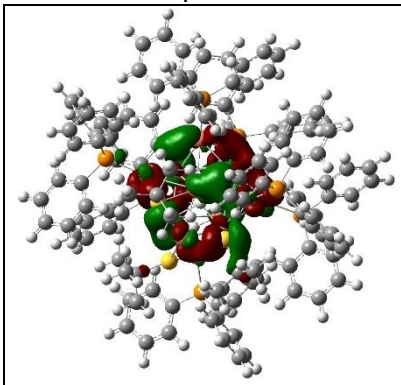
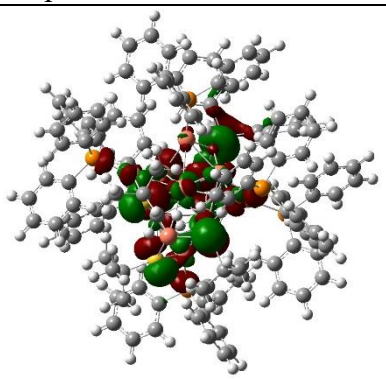
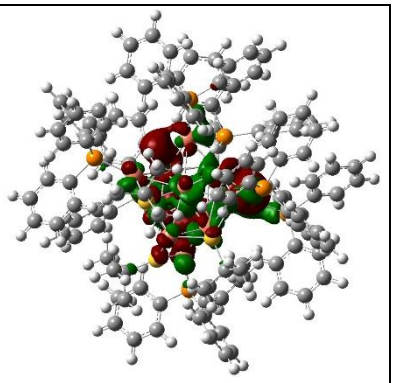
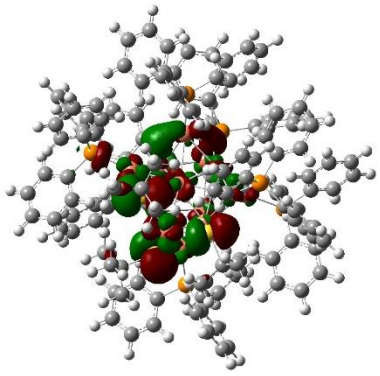
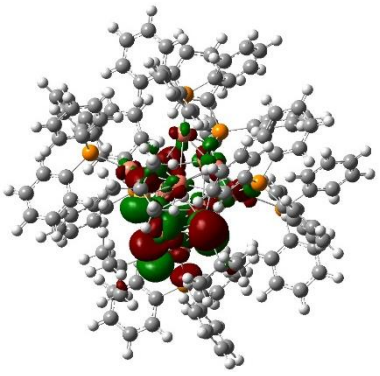
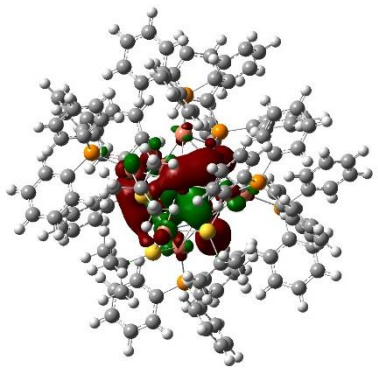
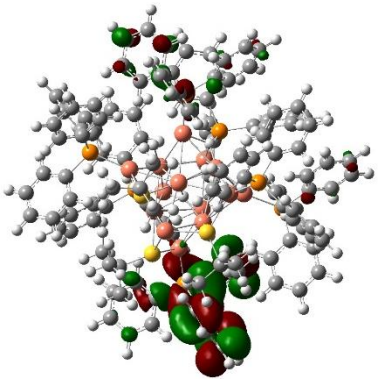
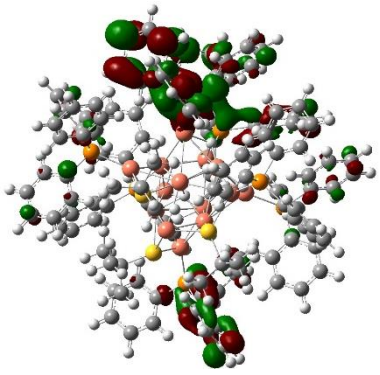
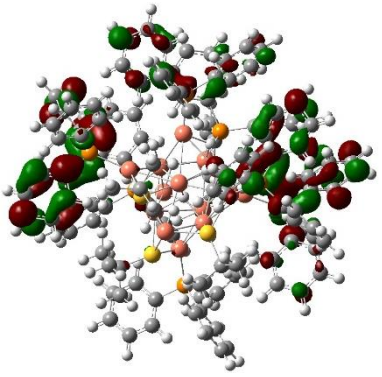
Parameter	value	Parameter	value
Cu1-Cu1	2.9288(7)	Cu4-S1	2.3142(7)
Cu1-Cu3	2.5426(6)	Cu4-P3	2.2236(8)
Cu1-Cu4	2.4491(5)	Cu6-Cu5	2.7350(6)
Cu1-Cu5	2.4823(5)	Cu6-S1	2.2392(7)
Cu1-Cu5	2.6050(5)	Cu5-Cu5	2.8920(7)
Cu1-Cu2	2.4894(6)	Cu5-Cu2	2.7365(6)
Cu3-Cu2	3.0170(5)	Cu5-S1	2.2827(7)
Cu3-P2	2.2507(12)	Cu2- P1	2.2355(9)
Cu4-Cu5	2.7996(6)		

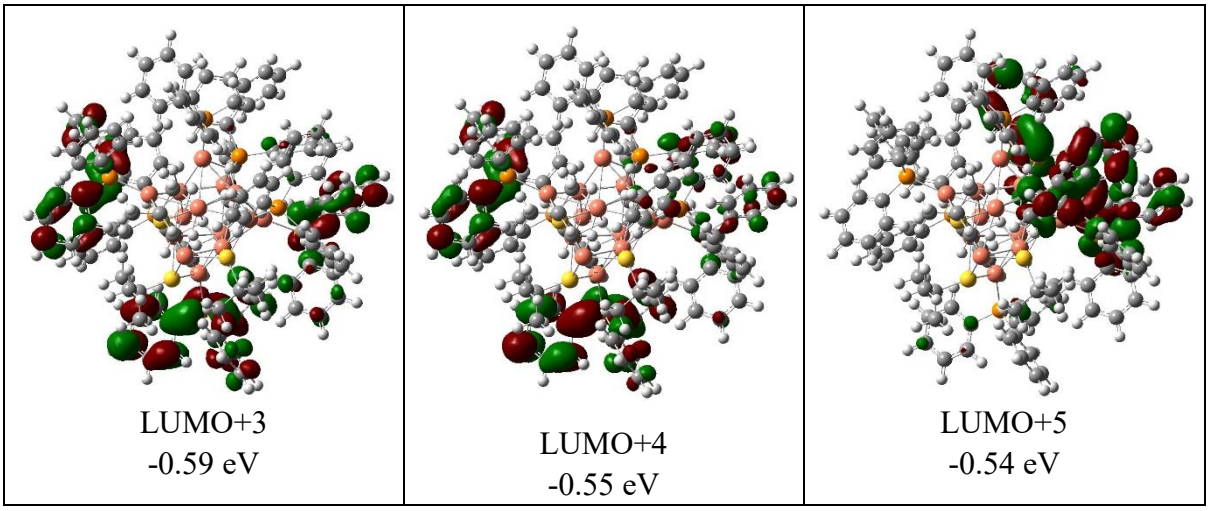
Table S3. α frontier orbitals. Gap=0.28 eV.

 HOMO-5 -4.80 eV	 HOMO-4 -4.49 eV	 HOMO-3 -4.44 eV
 HOMO-2 -4.41 eV	 HOMO-1 -4.12 eV	 HOMO -1.09 eV
 LUMO -0.81 eV	 LUMO+1 -0.75 eV	 LUMO+2 -0.72 eV
		

LUMO+3 -0.66 eV	LUMO+4 -0.65 eV	LUMO+5 -0.63 eV

Table S4. β frontier orbitals. Gap=3.27 eV.

 HOMO-5 -4.89 eV	 HOMO-4 -4.80 eV	 HOMO-3 -4.48 eV
 HOMO-2 -4.43 eV	 HOMO-1 -4.41 eV	 HOMO -4.11 eV
 LUMO -0.84 eV	 LUMO+1 -0.66 eV	 LUMO+2 -0.59 eV



LUMO+3
-0.59 eV

LUMO+4
-0.55 eV

LUMO+5
-0.54 eV

Table S5. Optimized Fractional Atomic Coordinates.

Tag	Atom	x	y	z	Tag	Atom	x	y	z
1	Cu	-1.8616	-0.1594	0.3590	153	C	2.3322	-6.9732	-4.9957
2	Cu	1.1350	-1.5796	0.3255	154	H	1.9484	-7.6682	-5.7378
3	Cu	0.8895	1.7902	0.3932	155	C	0.0567	-4.5611	3.9444
4	Cu	0.1233	0.0110	2.1561	156	H	-0.1315	-3.4934	3.9182
5	Cu	-3.1215	-1.1111	-1.5595	157	C	-3.2141	-2.2968	5.2105
6	Cu	2.5088	-2.1297	-1.6601	158	H	-4.1348	-2.4967	4.6714
7	Cu	0.5087	3.2390	-1.5466	159	C	-0.2784	-6.7773	3.0423
8	Cu	-0.0651	-0.0138	-3.8787	160	H	-0.7351	-7.4475	2.3236
9	Cu	-0.3174	-1.6287	-1.7191	161	C	-3.6170	-5.7663	3.5291
10	Cu	-1.4801	2.2896	1.0830	162	H	-2.8663	-6.5146	3.7656
11	S	-1.7993	-1.5714	-3.5473	163	C	-5.8441	-4.8676	3.8405
12	P	-5.3957	-1.4563	-1.7268	164	H	-6.8177	-4.9114	4.3218
13	Cu	1.4811	0.5499	-1.7358	165	C	6.2606	-2.3632	-1.9786
14	Cu	-1.1697	-2.4939	1.0085	166	H	5.7108	-1.7065	-1.3074
15	S	2.1425	-0.7297	-3.5892	167	C	-0.8014	-1.8509	6.5416
16	P	3.9390	-3.9109	-1.8591	168	H	0.1408	-1.6955	7.0587
17	Cu	-1.2330	1.0612	-1.7145	169	C	-0.7439	-5.9397	-0.5298
18	Cu	2.8213	0.1855	0.9918	170	H	0.0543	-5.2053	-0.4828
19	S	-0.5025	2.2815	-3.5856	171	C	8.2751	-2.8754	-3.2130
20	P	1.2999	5.4124	-1.8287	172	H	9.2908	-2.6238	-3.5073
21	P	0.1583	-0.0266	4.5350	173	C	4.3124	1.0336	-3.8159
22	P	-3.1168	3.7034	1.8706	174	H	3.7004	1.8093	-3.3462
23	C	-1.7970	-3.1501	-4.6063	175	H	5.0804	1.5217	-4.4330
24	C	-5.9338	-3.1135	-2.3508	176	H	4.8207	0.4809	-3.0213
25	C	-6.1809	-0.2796	-2.9159	177	C	1.1289	-6.4624	4.9898
26	C	-6.4040	-1.2329	-0.1925	178	H	1.7720	-6.8722	5.7642

27	C	-0.6433	-3.0256	-5.6062	179	C	5.4428	-6.4434	1.0794
28	H	-0.7524	-2.1332	-6.2329	180	H	6.3240	-7.0608	1.2367
29	H	-0.6294	-3.9065	-6.2647	181	C	2.9880	-7.4490	-3.8580
30	H	0.3168	-2.9630	-5.0858	182	H	3.1201	-8.5181	-3.7107
31	C	0.2263	2.7606	4.6115	183	C	7.5658	-2.0377	-2.3499
32	H	0.6496	2.6523	3.6158	184	H	8.0186	-1.1282	-1.9662
33	C	-6.9603	-3.2813	-3.2937	185	C	3.3047	-5.5998	1.8296
34	H	-7.4602	-2.4102	-3.7084	186	H	2.5110	-5.5629	2.5689
35	C	-4.2834	4.3955	0.5954	187	C	0.5504	-7.3030	4.0378
36	C	-5.4563	0.0569	-4.0755	188	H	0.7366	-8.3733	4.0691
37	H	-4.4629	-0.3569	-4.2256	189	C	-2.8152	-6.8461	0.3241
38	C	-2.4968	5.2303	2.7106	190	H	-3.6183	-6.8395	1.0534
39	C	-0.1709	1.6167	5.3282	191	C	4.4262	-6.4145	2.0372
40	C	-7.4336	0.3155	-2.7032	192	H	4.5073	-7.0110	2.9418
41	H	-8.0047	0.0749	-1.8116	193	C	0.8768	-5.0881	4.9405
42	C	-5.9864	0.9458	-5.0095	194	H	1.3293	-4.4206	5.6678
43	H	-5.4128	1.1969	-5.8974	195	C	-4.8702	-5.8223	4.1420
44	C	-1.2841	5.7862	2.2633	196	H	-5.0832	-6.6113	4.8591
45	H	-0.7282	5.2929	1.4713	197	C	-0.7427	-6.8922	-1.5492
46	C	-7.6316	-1.8809	0.0187	198	H	0.0636	-6.8959	-2.2778
47	H	-8.0078	-2.5852	-0.7175	199	C	-2.9522	-2.9495	6.4164
48	C	-3.1398	-3.2301	-5.3511	200	H	-3.6822	-3.6424	6.8254
49	H	-3.9816	-3.3411	-4.6606	201	C	-1.7440	-2.7277	7.0803
50	H	-3.1443	-4.1023	-6.0204	202	H	-1.5281	-3.2455	8.0113
51	H	-3.3088	-2.3386	-5.9660	203	C	-1.7753	-7.8311	-1.6303
52	C	-4.3021	2.9821	3.0840	204	H	-1.7746	-8.5761	-2.4217
53	C	-0.7767	6.9516	2.8328	205	C	-2.8136	-7.8020	-0.6959
54	H	0.1504	7.3700	2.4538	206	H	-3.6200	-8.5295	-0.7519
55	C	-5.9399	-0.3245	0.7722	207	H	1.8931	2.0528	-1.0598
56	H	-4.9917	0.1868	0.6239	208	H	0.2561	-1.7409	1.7330
57	C	-7.3378	-4.5586	-3.7119	209	H	2.7994	-1.2070	-0.0051
58	H	-8.1291	-4.6706	-4.4484	210	P	4.9555	0.8510	1.6213
59	C	-7.2425	1.5237	-4.7956	211	C	-1.9070	3.0188	-4.6295
60	H	-7.6531	2.2207	-5.5215	212	C	0.0346	6.6406	-2.3812
61	C	-3.8278	1.9874	3.9554	213	C	2.6354	5.5838	-3.0939
62	H	-2.8139	1.6177	3.8403	214	C	2.0377	6.2011	-0.3302
63	C	0.0537	4.0343	5.1551	215	C	-2.2821	1.9964	-5.7142
64	H	0.3419	4.9079	4.5782	216	H	-1.4327	1.7688	-6.3687
65	C	-5.6212	3.4440	3.2456	217	H	-3.0897	2.4041	-6.3405
66	H	-6.0184	4.2039	2.5799	218	H	-2.6315	1.0575	-5.2731
67	C	-3.1624	5.8542	3.7797	219	C	2.5577	-1.4783	4.5961
68	H	-4.0952	5.4447	4.1554	220	H	2.2086	-1.8702	3.6453
69	C	-1.4550	7.5700	3.8952	221	C	0.3300	7.6997	-3.2552

70	H	-1.0573	8.4746	4.3480	222	H	1.3355	7.8162	-3.6487
71	C	-5.2902	-4.2544	-1.8420	223	C	5.9926	1.5757	0.2671
72	H	-4.4828	-4.1469	-1.1220	224	C	2.5998	4.7188	-4.2009
73	C	-0.7809	1.7826	6.5827	225	H	1.8169	3.9689	-4.2704
74	H	-1.1137	0.9151	7.1438	226	C	6.0090	-0.4730	2.3413
75	C	-4.7694	3.5286	-0.3978	227	C	1.7765	-0.5352	5.2860
76	H	-4.4110	2.5032	-0.4447	228	C	3.6697	6.5270	-2.9977
77	C	-6.7013	-5.6858	-3.1895	229	H	3.7098	7.1980	-2.1456
78	H	-6.9956	-6.6795	-3.5174	230	C	3.5759	4.8050	-5.1941
79	C	-1.5809	-4.3835	-3.7247	231	H	3.5404	4.1252	-6.0411
80	H	-0.6306	-4.3234	-3.1846	232	C	5.7921	-1.8010	1.9399
81	H	-1.5608	-5.2883	-4.3498	233	H	4.9965	-2.0246	1.2345
82	H	-2.3829	-4.5003	-2.9909	234	C	2.0151	7.5830	-0.0956
83	C	-5.9533	1.9381	5.1162	235	H	1.5283	8.2444	-0.8065
84	H	-6.5890	1.5400	5.9029	236	C	-1.4003	4.3168	-5.2707
85	C	-8.3781	-1.6231	1.1718	237	H	-1.1464	5.0674	-4.5160
86	H	-9.3280	-2.1306	1.3213	238	H	-2.1879	4.7415	-5.9097
87	C	-7.9601	1.2108	-3.6395	239	H	-0.5173	4.1380	-5.8941
88	H	-8.9346	1.6590	-3.4626	240	C	5.0288	2.1776	2.9236
89	C	-5.6784	-5.5316	-2.2507	241	C	6.6054	-2.8266	2.4244
90	H	-5.1651	-6.3986	-1.8461	242	H	6.4371	-3.8437	2.0889
91	C	-6.6929	-0.0577	1.9176	243	C	2.6358	5.3588	0.6196
92	H	-6.3230	0.6530	2.6482	244	H	2.6128	4.2830	0.4706
93	C	-6.4376	2.9213	4.2502	245	C	-0.6674	8.5927	-3.6470
94	H	-7.4567	3.2861	4.3549	246	H	-0.4268	9.3986	-4.3356
95	C	-4.7405	5.7228	0.6141	247	C	4.6036	5.7463	-5.0913
96	H	-4.3774	6.4090	1.3725	248	H	5.3651	5.8083	-5.8645
97	C	-7.9121	-0.7090	2.1193	249	C	3.9963	2.2228	3.8716
98	H	-8.4982	-0.5009	3.0110	250	H	3.1576	1.5400	3.7834
99	C	-4.6440	1.4695	4.9630	251	C	3.7882	-1.8925	5.1124
100	H	-4.2576	0.6967	5.6197	252	H	4.3962	-2.5934	4.5487
101	C	-2.6403	7.0107	4.3666	253	C	6.0784	3.1066	3.0211
102	H	-3.1738	7.4747	5.1932	254	H	6.8846	3.0949	2.2939
103	C	-5.7094	3.9695	-1.3316	255	C	7.0310	-0.1972	3.2688
104	H	-6.0822	3.2778	-2.0820	256	H	7.1962	0.8215	3.6068
105	C	-0.5401	4.1875	6.4088	257	C	7.6208	-2.5423	3.3455
106	H	-0.6942	5.1826	6.8176	258	H	8.2482	-3.3435	3.7277
107	C	-0.9632	3.0610	7.1197	259	C	-1.2800	6.4983	-1.9054
108	H	-1.4416	3.1749	8.0892	260	H	-1.5322	5.6719	-1.2470
109	C	-6.1620	5.2912	-1.3009	261	C	2.2547	-0.0232	6.5042
110	H	-6.8924	5.6359	-2.0285	262	H	1.6702	0.7152	7.0447
111	C	-5.6724	6.1669	-0.3293	263	C	5.3689	2.4097	-0.6751
112	H	-6.0251	7.1951	-0.2930	264	H	4.2936	2.5596	-0.6324

113	H	0.8656	-2.6584	-1.0792	265	C	-1.9700	8.4432	-3.1689
114	H	-1.4940	0.6837	1.7658	266	H	-2.7473	9.1358	-3.4814
115	H	-2.4552	-1.7762	0.1276	267	C	-3.1143	3.3121	-3.7371
116	P	-1.6913	-4.6267	1.7554	268	H	-3.4708	2.4036	-3.2443
117	C	3.4570	0.1078	-4.6778	269	H	-3.9379	3.7238	-4.3386
118	C	5.6509	-3.5350	-2.4536	270	H	-2.8625	4.0409	-2.9628
119	C	3.3315	-5.1705	-3.0763	271	C	5.0797	4.0632	5.0106
120	C	4.2038	-4.8814	-0.3193	272	H	5.0959	4.7936	5.8157
121	C	2.7355	0.8866	-5.7825	273	C	2.6127	8.1153	1.0512
122	H	2.1340	0.2153	-6.4069	274	H	2.5952	9.1893	1.2185
123	H	3.4809	1.3737	-6.4290	275	C	4.6494	6.6066	-3.9918
124	H	2.0719	1.6534	-5.3723	276	H	5.4461	7.3408	-3.9041
125	C	-2.2686	-1.4220	4.6682	277	C	-2.2743	7.3987	-2.2935
126	H	-2.4589	-0.9498	3.7086	278	H	-3.2846	7.2661	-1.9207
127	C	6.3702	-4.3651	-3.3245	279	C	3.2107	5.8879	1.7766
128	H	5.9082	-5.2654	-3.7176	280	H	3.6455	5.2224	2.5155
129	C	-1.7746	-5.9124	0.4224	281	C	6.1068	4.0381	4.0638
130	C	2.6602	-4.7040	-4.2189	282	H	6.9311	4.7435	4.1317
131	H	2.5108	-3.6353	-4.3517	283	C	7.3726	1.3345	0.1453
132	C	-3.3252	-4.7520	2.5993	284	H	7.8708	0.6761	0.8500
133	C	-1.0569	-1.1775	5.3354	285	C	3.2108	7.2687	1.9867
134	C	3.4827	-6.5559	-2.9039	286	H	3.6635	7.6830	2.8842
135	H	3.9922	-6.9396	-2.0264	287	C	4.0228	3.1558	4.9101
136	C	2.1677	-5.5961	-5.1701	288	H	3.2071	3.1812	5.6266
137	H	1.6503	-5.2130	-6.0455	289	C	7.8245	-1.2300	3.7731
138	C	-4.3069	-3.7888	2.3107	290	H	8.6062	-1.0028	4.4939
139	H	-4.0737	-2.9730	1.6303	291	C	6.1112	3.0249	-1.6842
140	C	5.3400	-5.6784	-0.0834	292	H	5.6110	3.6732	-2.3982
141	H	6.1457	-5.7050	-0.8110	293	C	4.2538	-1.3768	6.3221
142	C	4.3187	-1.0103	-5.2882	294	H	5.2178	-1.6924	6.7125
143	H	4.8503	-1.5751	-4.5159	295	C	3.4819	-0.4435	7.0219
144	H	5.0672	-0.5752	-5.9656	296	H	3.8413	-0.0308	7.9610
145	H	3.7093	-1.7142	-5.8652	297	C	7.4846	2.7880	-1.7906
146	C	-0.5330	-5.3947	2.9783	298	H	8.0599	3.2582	-2.5836
147	C	-5.5603	-3.8504	2.9229	299	C	8.1096	1.9301	-0.8820
148	H	-6.3070	-3.0966	2.6906	300	H	9.1757	1.7310	-0.9630
149	C	3.1978	-4.8438	0.6651	301	H	-2.7053	0.5740	-1.0320
150	H	2.3259	-4.2138	0.5125	302	H	1.5338	1.0547	1.7722
151	C	7.6719	-4.0362	-3.7020	303	H	-0.2695	3.0570	0.1718
152	H	8.2162	-4.6882	-4.3805	304	H	-0.0135	-0.0291	-1.0018

Table S6. Optimized Bond Lengths.

Tag	Atoms	Length/Å	Tag	Atoms	Length/Å
1-2	Cu-Cu	3.316373	153-154	C-H	1.086732
1-3	Cu-Cu	3.372056	146-155	C-C	1.405671
3-4	Cu-Cu	2.619229	155-156	C-H	1.084475
1-5	Cu-Cu	2.484735	125-157	C-C	1.397625
2-6	Cu-Cu	2.476303	157-158	C-H	1.085497
3-7	Cu-Cu	2.450907	146-159	C-C	1.407217
5-8	Cu-Cu	3.990536	159-160	C-H	1.0837
2-9	Cu-Cu	2.50841	132-161	C-C	1.406687
3-10	Cu-Cu	2.518008	161-162	C-H	1.085982
9-11	Cu-S	2.354091	147-163	C-C	1.399053
5-12	Cu-P	2.306274	163-164	C-H	1.086963
3-13	Cu-Cu	2.533872	118-165	C-C	1.403811
1-14	Cu-Cu	2.520052	165-166	C-H	1.088111
8-15	Cu-S	2.338736	133-167	C-C	1.404855
6-16	Cu-P	2.292979	167-168	C-H	1.085995
1-17	Cu-Cu	2.486928	129-169	C-C	1.403536
2-18	Cu-Cu	2.530423	168-170	C-H	1.085696
17-19	Cu-S	2.350249	151-171	C-C	1.396554
7-20	Cu-P	2.330111	171-172	C-H	1.087051
4-21	Cu-P	2.379433	117-173	C-C	1.527022
10-22	Cu-P	2.301673	173-174	C-H	1.094086
11-23	S-C	1.900995	173-175	C-H	1.099487
12-24	P-Cu	1.850714	173-176	C-H	1.093219
12-25	P-Cu	1.848027	155-177	C-C	2.420172
12-26	P-Cu	1.849543	177-178	C-H	1.086826
23-27	C-C	1.531736	140-179	C-C	1.395646
27-28	C-H	1.095901	179-180	C-H	1.087443
27-29	C-H	1.099915	153-181	C-C	1.396783
27-30	C-H	1.093806	181-182	C-H	1.087287
21-31	P-C	2.789051	165-183	C-C	1.395475
31-32	C-H	1.087311	183-184	C-H	1.08598
24-33	Cu-C	1.403907	149-185	C-C	1.392526
33-34	C-H	1.086562	185-186	C-H	1.085303
22-35	P-C	1.86175	177-187	C-C	1.395632
25-36	Cu-C	1.408194	187-188	C-H	1.086819
36-37	C-H	1.086571	129-189	C-C	1.4015
22-38	P-C	1.849685	189-190	C-H	1.084838
31-39	C-C	1.407075	179-191	C-C	1.396992
25-40	Cu-C	1.403072	191-192	C-H	1.086643
40-41	C-H	1.085745	155-193	C-C	1.393754
36-42	C-C	1.394137	193-194	C-H	1.085883

42-43	C-H	1.08642	161-195	C-C	1.396204
38-44	C-C	1.407031	195-196	C-H	1.087329
44-45	C-H	1.08613	169-197	C-C	1.395197
26-46	Cu-C	1.40407	197-198	C-H	1.086708
46-47	C-H	1.086081	157-199	C-C	1.395968
23-48	C-C	1.5376	199-200	C-H	1.086406
48-49	C-H	1.094393	167-201	C-C	1.39557
48-50	C-H	1.099436	201-202	C-H	1.086982
48-51	C-H	1.096151	197-203	C-C	1.397935
22-52	P-C	1.843215	203-204	C-H	1.0869
44-53	C-C	1.392826	203-205	C-C	1.397201
53-54	C-H	1.085511	205-206	C-H	1.087447
26-55	Cu-C	1.404018	13-207	Cu-H	1.69858
55-56	C-H	1.087414	2-208	Cu-H	1.667271
33-57	C-C	1.395963	18-209	Cu-H	1.712653
57-58	C-H	1.086886	18-210	Cu-P	2.322511
42-59	C-C	1.399151	19-211	S-C	1.89896
59-60	C-H	1.086848	20-212	P-C	1.847893
52-61	C-C	1.404855	20-213	P-C	1.847596
61-62	C-H	1.085293	20-214	P-C	1.847144
31-63	C-C	1.39561	211-215	C-C	1.536994
63-64	C-H	1.085752	215-216	C-H	1.096199
52-65	C-C	1.407028	215-217	C-H	1.100282
65-66	C-H	1.085499	215-218	C-H	1.094645
38-67	C-C	1.405405	21-219	P-C	2.80502
67-68	C-H	1.085787	219-220	C-H	1.086059
53-69	C-C	1.403943	212-221	C-C	1.404499
69-70	C-H	1.086962	221-222	C-H	1.086039
24-71	Cu-C	1.405263	210-223	P-C	1.853283
71-72	C-H	1.087101	213-224	C-C	1.405339
39-73	C-C	1.404806	224-225	C-H	1.086339
73-74	C-H	1.085454	210-226	P-C	1.838869
35-75	C-C	1.405054	219-227	C-C	1.405505
75-76	C-H	1.087231	213-228	C-C	1.403114
57-77	C-C	1.39595	228-229	C-H	1.085423
77-78	C-H	1.086955	224-230	C-C	1.395302
23-79	C-C	1.531424	230-231	C-H	1.086657
79-80	C-H	1.094732	226-232	C-C	1.404165
79-81	C-H	1.09984	232-233	C-H	1.086533
79-82	C-H	1.093353	214-234	C-C	1.40178
61-83	C-C	2.422275	234-235	C-H	1.086274
83-84	C-H	1.087024	211-236	C-C	1.533874
46-85	C-C	1.39762	236-237	C-H	1.094198

85-86	C-H	1.08728	236-238	C-H	1.099537
69-87	C-C	1.396299	236-239	C-H	1.095643
87-88	C-H	1.087051	210-240	P-C	1.860458
71-89	C-C	1.396088	232-241	C-C	1.395786
89-90	C-H	1.085726	241-242	C-H	1.084122
55-91	C-C	1.396479	214-243	C-C	1.403359
91-92	C-H	1.084293	243-244	C-H	1.086258
65-93	C-C	1.396023	221-245	C-C	1.394881
93-94	C-H	1.08737	245-246	C-H	1.087013
35-95	C-C	1.403926	230-247	C-C	1.397355
95-96	C-H	1.085323	247-248	C-H	1.086951
85-97	C-C	1.396594	240-249	C-C	1.402453
97-98	C-H	1.087102	249-250	C-H	1.085081
61-99	C-C	1.396361	219-251	C-C	1.397284
99-100	C-H	1.085225	251-252	C-H	1.085648
69-101	C-C	1.392858	240-253	C-C	1.405045
101-102	C-H	1.087751	253-254	C-H	1.085842
75-103	C-C	1.396415	226-255	C-C	1.407398
103-104	C-H	1.086558	255-256	C-H	1.086017
63-105	C-C	1.395718	241-257	C-C	1.400107
105-106	C-H	1.086812	257-258	C-H	1.087004
105-107	C-C	1.397612	212-259	C-C	1.405277
107-108	C-H	1.087054	259-260	C-H	1.086323
103-109	C-C	1.39736	227-261	C-C	1.405261
109-110	C-H	1.087042	261-262	C-H	1.085871
109-111	C-C	1.396628	223-263	C-C	1.404362
111-112	C-H	1.087686	263-264	C-H	1.086586
9-113	Cu-H	1.693872	245-265	C-C	1.395675
1-114	Cu-H	1.680752	265-266	C-H	1.086976
14-115	Cu-H	1.715713	211-267	C-C	1.529726
14-116	Cu-P	2.319224	267-268	C-H	1.093314
15-117	S-C	1.901153	267-269	C-H	1.099825
16-118	P-C	1.850683	267-270	C-H	1.092722
16-119	P-C	1.853988	249-271	C-C	2.420371
16-120	P-C	1.8393	271-272	C-H	1.087158
117-121	C-C	1.532146	234-273	C-C	1.398458
121-122	C-H	1.096482	273-274	C-H	1.087107
121-123	C-H	1.100331	247-275	C-C	1.396879
121-124	C-H	1.093903	275-276	C-H	1.086977
21-125	P-C	2.802595	259-277	C-C	1.396365
125-126	C-H	1.086268	277-278	C-H	1.084997
118-127	C-C	1.401772	243-279	C-C	1.396108
127-128	C-H	1.085614	279-280	C-H	1.085328

116-129	P-C	1.853836	271-281	C-C	1.3971
119-130	C-C	1.404917	281-282	C-H	1.087103
130-131	C-H	1.087192	223-283	C-C	1.406203
116-132	P-C	1.843239	283-284	C-H	1.085502
125-133	C-C	1.404703	283-285	C-C	1.396261
119-134	C-C	1.404279	285-286	C-H	1.087258
134-135	C-H	1.084856	249-287	C-C	1.396221
130-136	C-C	1.393998	287-288	C-H	1.086017
136-137	C-H	1.086672	257-289	C-C	1.395203
132-138	C-C	1.405289	289-290	C-H	1.087278
138-139	C-H	1.087572	263-291	C-C	1.395574
120-140	C-C	1.407683	291-292	C-H	1.086464
140-141	C-H	1.085988	251-293	C-C	1.39505
117-142	C-C	1.537988	293-294	C-H	1.086897
142-143	C-H	1.094532	261-295	C-C	1.396695
142-144	C-H	1.099261	295-296	C-H	1.086854
142-145	C-H	1.095351	291-297	C-C	1.397702
116-146	P-C	1.851239	297-298	C-H	1.086748
138-147	C-C	1.396331	297-299	C-C	1.397244
147-148	C-H	1.086079	299-300	C-H	1.087521
120-149	C-C	1.408072	17-301	Cu-H	1.694418
149-150	C-H	1.086475	3-302	Cu-H	1.690473
127-151	C-C	1.394624	10-303	Cu-H	1.698452
151-152	C-H	1.087096	13-304	Cu-H	1.762934
136-153	C-C	1.397828			

Table S7. Comparison of Optimized and Experimental Bond Lengths for Cu_{14}.

Atom	**Atom**	**Optimized average length/ Å**	**Atom**	**Atom**	**Experimental average length/ Å**
Cu	Cu	2.754	Cu	Cu	2.430
Cu	S	2.348	Cu	S	2.115
Cu	P	2.180	Cu	P	2.115
Cu	H	1.701	Cu	H	1.440
C	C	1.439	C	C	1.242
C	S	1.900	C	S	1.584
C	P	2.008	C	P	1.683
C	H	1.088	C	H	0.972