

Supporting information

Dissection of bicapped octahedral copper hydride cluster to form two chiral tetrahedral copper hydride cluster series exhibiting auto deracemization and photoluminescence

Han Xu,^a Ying-Zi Han,^a Jie OuYang,^a Zuo-Chang Chen,^a Hui-Jun Chen,^a Hong-Hong Nie,^a Zichao Tang,^a Shi-Yao Yang,^{*a} Rong-Bin Huang^a and Lan-Sun Zheng,^a Boon K. Teo^{*a}

^aState Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy materials, and College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.

Refinement of hydrides

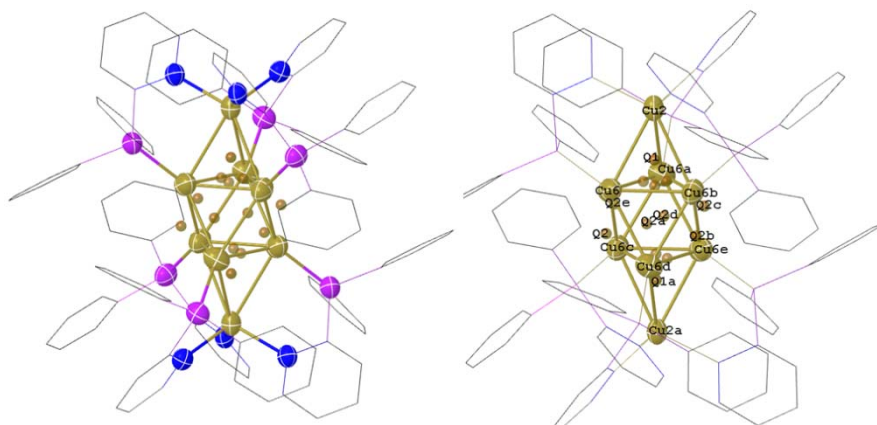
In each case, the positions of the hydrides were detected from the difference electron density map, and their positions were allowed to refine freely, or with restraints of the Cu–H distances of the hydride to be equal (via SADI).

The positions of six the hydrides in $[\text{Cu}_8\text{H}_6\text{L}_6]^{2+}$ were determined by high quality crystallography diffraction data and corroborated by DFT calculations. There are two independent $[\text{Cu}_8\text{H}_6\text{L}_6]^{2+}$ clusters per unit cell. In type A $[\text{Cu}_8\text{H}_6\text{L}_6]^{2+}$ (at the origin), two μ_4 hydrides are located in the centers of the two tetrahedra, and the four μ_3 hydrides are distributed in the six equatorial triangle faces of the central octahedron. In type B $[\text{Cu}_8\text{H}_6\text{L}_6]^{2+}$, one tetrahedron contained one μ_4 hydride in the center, while the other tetrahedron contained only 0.1 μ_4 hydride in the center, and 0.9 μ_3 hydride at the shared face of the tetrahedron and the octahedron. The situation in the six equatorial triangle faces of the octahedron was the same as that for type A.

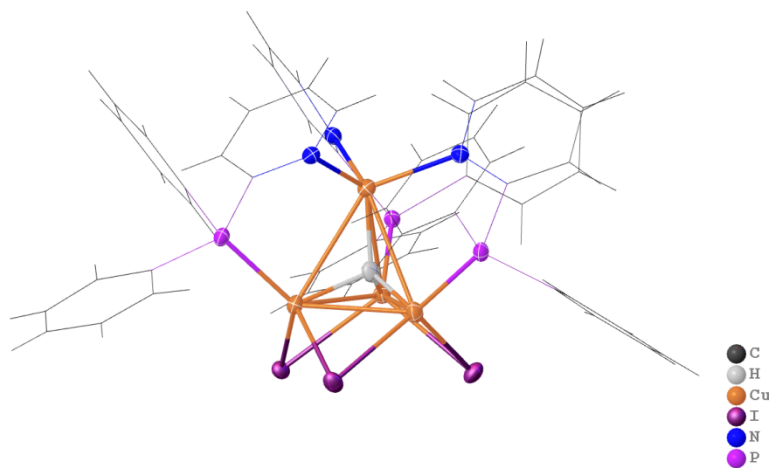
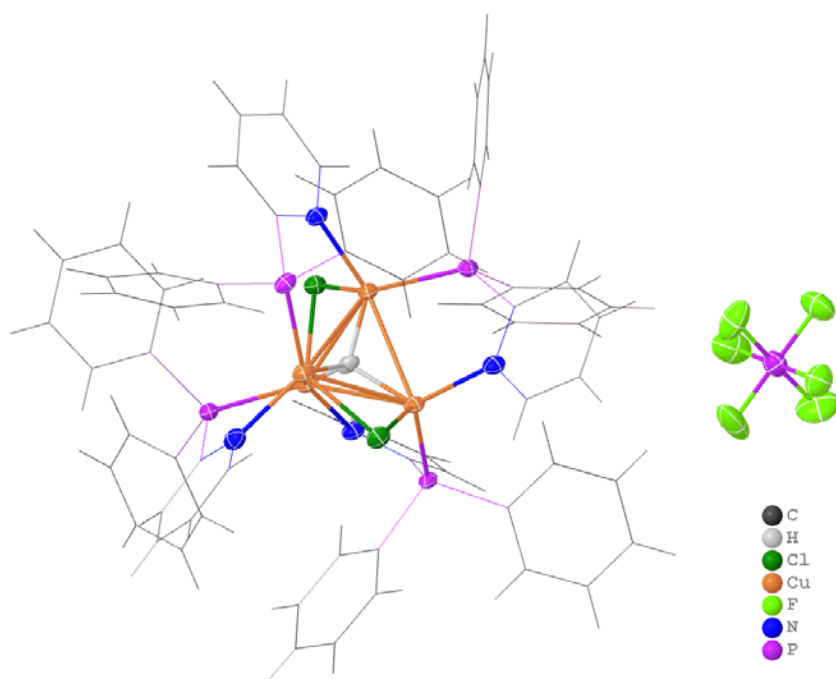
In the final stage of crystallographic data refinement, 6 hydrides position could be located by residual electron density: The max peak ($Q1 = 1.98$) was located at center of copper tetrahedron and the $Q2 = 1.33$ was found at triply-bridge triangle copper face. These two Q peaks were refined as 2 μ_4 hydrides (occupancy 1) and 6 disordered μ_3 hydrides (occupancy 2/3).

The anisotropic refinement of μ_4 hydride has been performed in series 2 and 3.¹

Figure S1 a: Refinement of hydrides: residual peaks Q1 and Q2 $\text{e}^{-}\text{\AA}^{-3}$ in $[\text{Cu}_8\text{H}_6\text{L}_6]^{2+}$ and the anisotropic refinement of μ_4 hydride in 2 and 3 clusters.

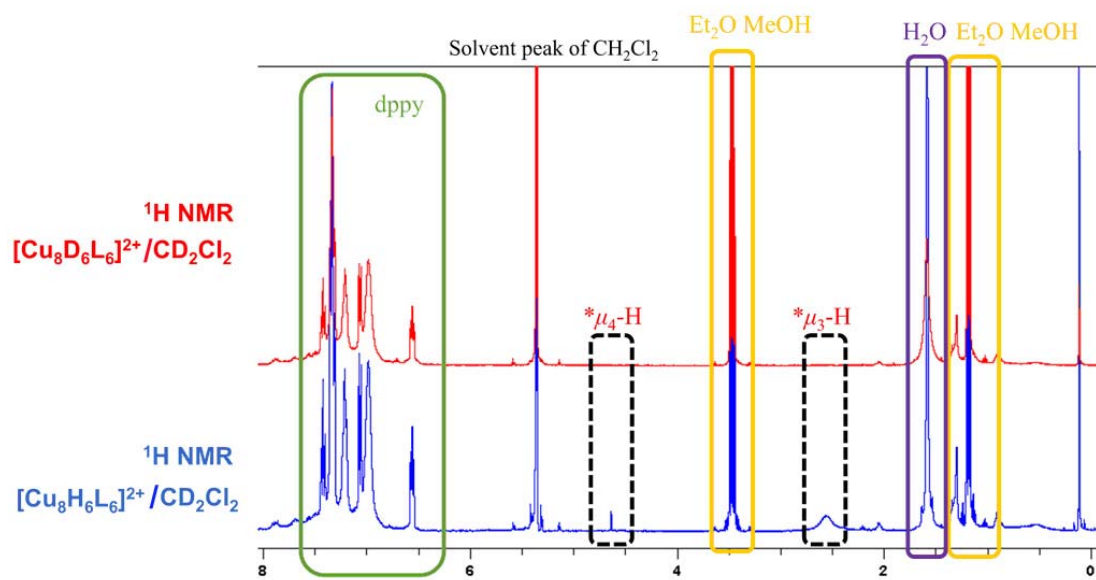


$$\begin{aligned} \text{Q1} &= 1.98 \text{ } 2 \mu\text{-4} \\ \text{Q2} &= 1.33 \text{ } 6 \mu\text{-3} \end{aligned}$$

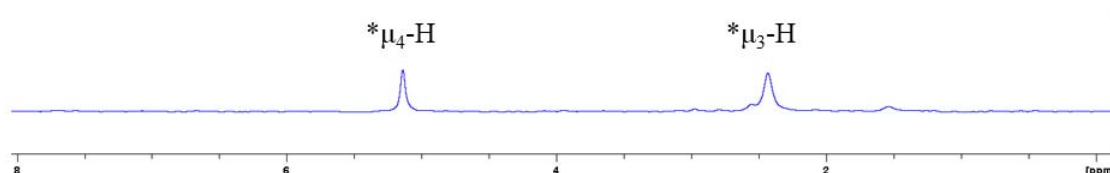


NMR

Figure S2 a: $[\text{Cu}_8\text{D}_6\text{L}_6]^{2+}$ ^1H NMR and $[\text{Cu}_8\text{H}_6\text{L}_6]^{2+}$ ^1H NMR and $[\text{Cu}_8\text{D}_6\text{L}_6]^{2+}$ ^2H NMR.



^2H NMR of $[\text{Cu}_8\text{D}_6\text{L}_6]^{2+}$ / CH_2Cl_2



^1H NMR proves that there are two types of hydrides in $[\text{Cu}_8\text{H}_6\text{L}_6]^{2+}$ (single peak at 4.6 ppm is attributed as $\mu_4\text{-H}$ and peak at 2.6 ppm is attributed as $\mu_3\text{-H}$). The broad peak of ^1H NMR at 2.6 ppm also proved the disorder of μ_3 hydrides, which was caused by fluxional hydrides has also been observed by previous work.^{2, 3}

^2H NMR of $[\text{Cu}_8\text{D}_6\text{L}_6]^{2+}$ in CH_2Cl_2 indicates that there are two types of deuterides in $[\text{Cu}_8\text{D}_6\text{L}_6]^{2+}$ (single peak at 5.1 ppm was attributed as μ_4 deuteride and peak at 2.4 ppm was attributed as μ_3 deuteride)

Figure S2 b: ^1H NMR of 2c, 2e, 3b, 3c in CD_2Cl_2 .

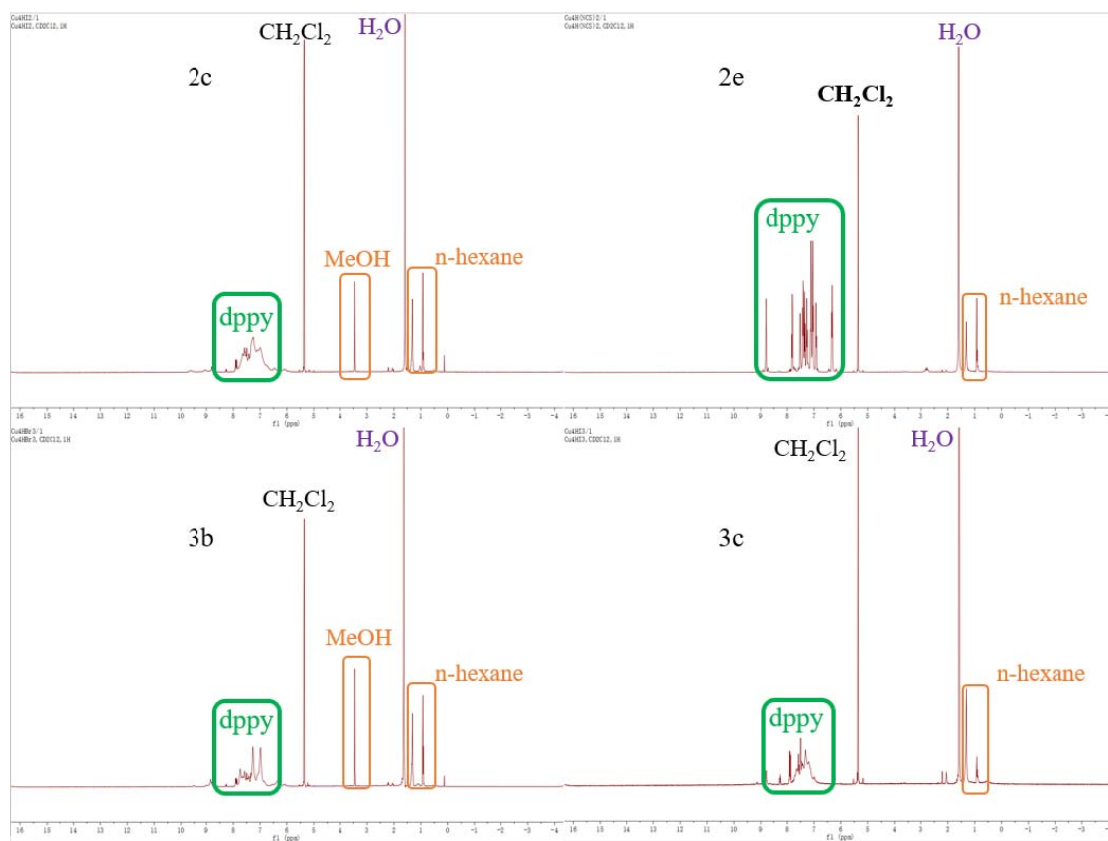
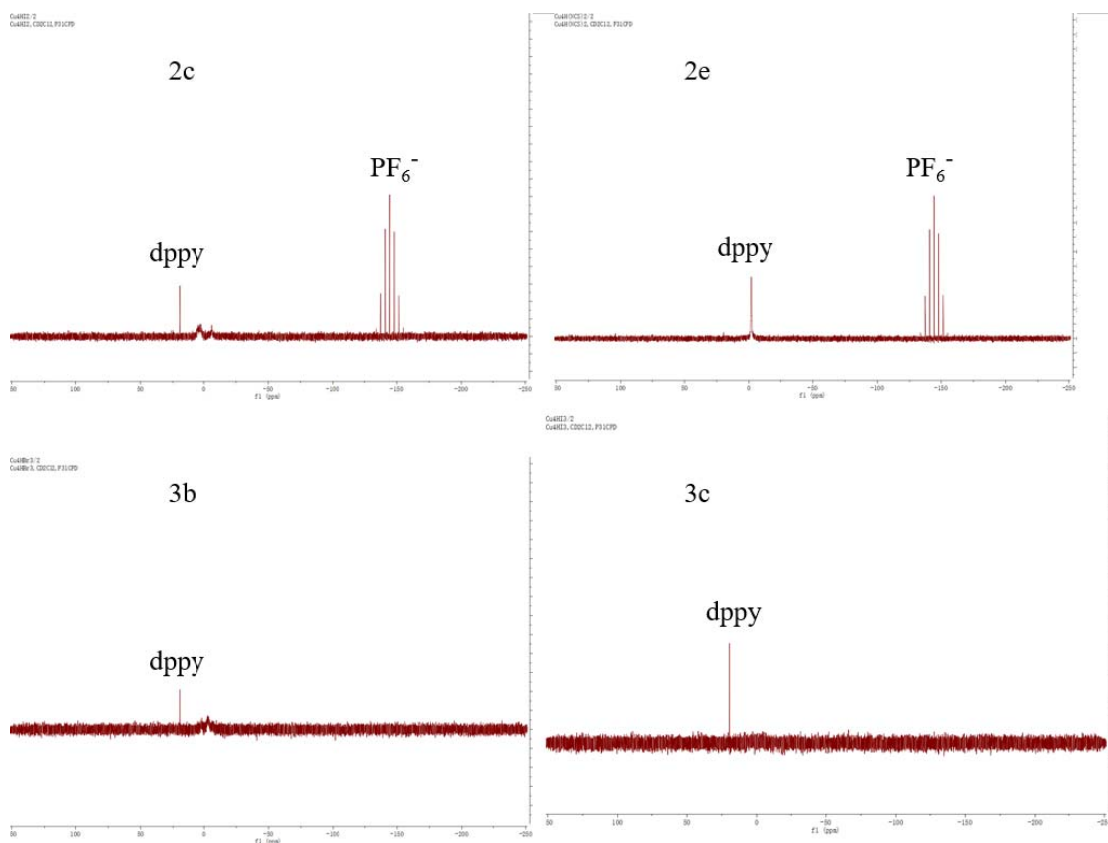
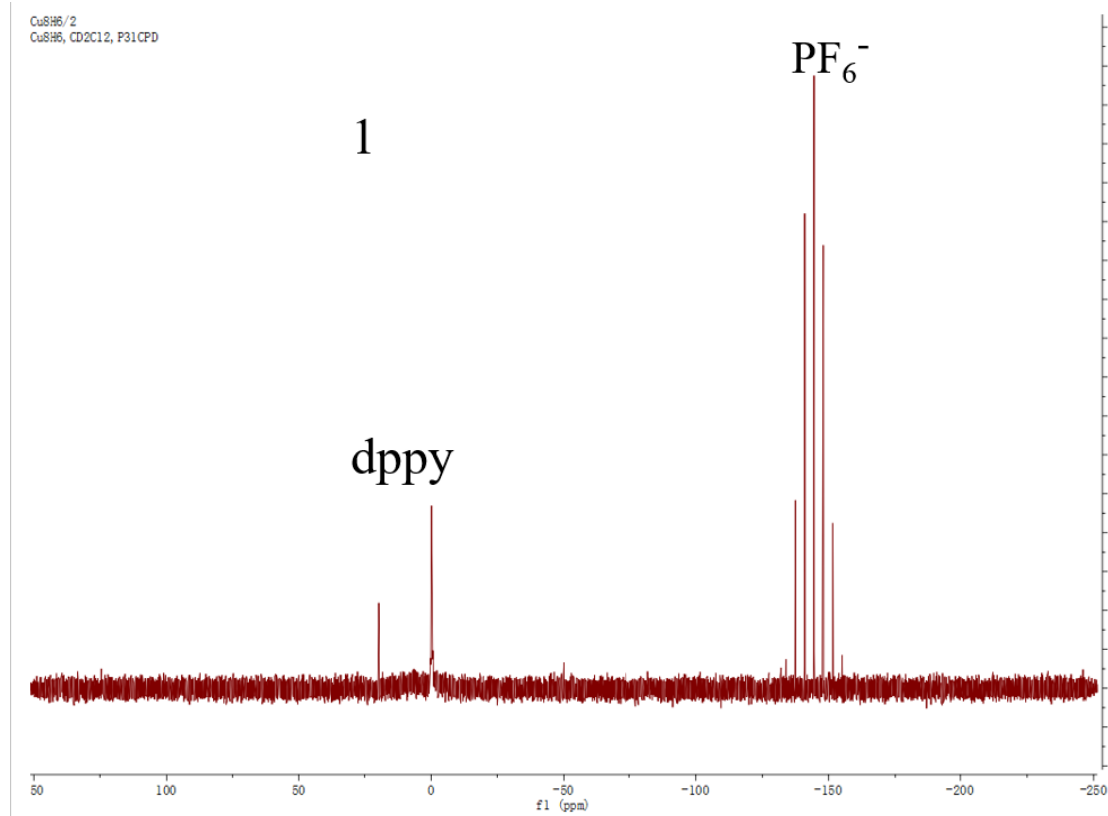
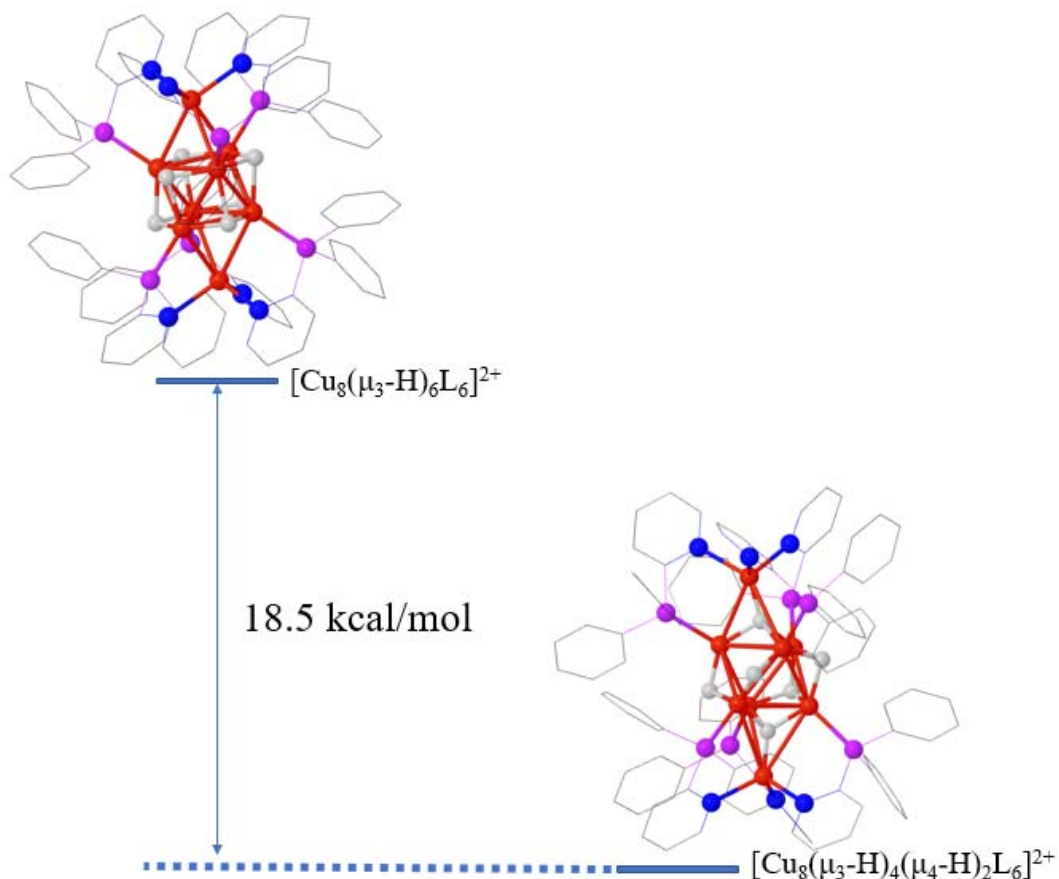


Figure S2 c: ^{31}P NMR of 1, 2c, 2e, 3b, 3c in CD_2Cl_2 .



DFT calculation

Figure S3: Density functional theory (DFT) calculations of $[\text{Cu}_8\text{H}_6\text{L}_6]^{2+}$.



Coordinate of $[\text{Cu}_8(\mu_3\text{-H})_6\text{L}_6]^{2+}$

Cu	-0.946102	-2.995137	0.606225
Cu	1.036295	-1.434753	-0.372287
H	1.911368	0.207912	-0.892642
P	1.984841	-3.365750	-1.035510
N	-0.488312	-4.455031	-0.921167
C	-1.492977	-5.274911	-1.270244
H	-2.406666	-5.173420	-0.695648
C	0.673132	-4.526835	-1.608255
C	-1.398024	-6.189347	-2.315445
H	-2.248028	-6.812945	-2.566546
C	0.842420	-5.409091	-2.677601
H	1.782564	-5.423975	-3.217986
C	3.047822	-3.183780	-2.507605
C	2.919118	-4.328652	0.202122

C	3.257826	-5.681147	0.043885
H	2.956087	-6.217707	-0.851272
C	-0.207553	-6.253774	-3.036204
H	-0.097300	-6.947125	-3.864484
C	3.299855	-3.649965	1.369219
H	3.003586	-2.614234	1.500442
C	3.983932	-6.339718	1.036093
H	4.248238	-7.385506	0.909386
C	4.342980	-3.704407	-2.614539
H	4.753565	-4.309152	-1.811826
C	4.378756	-5.651481	2.188086
H	4.949842	-6.166330	2.955270
C	2.526246	-2.396579	-3.551773
H	1.537800	-1.955620	-3.449729

C	4.036323	-4.308362	2.353683
H	4.337871	-3.771279	3.247887
C	3.283948	-2.161023	-4.695538
H	2.873041	-1.553421	-5.496185
C	4.577259	-2.683740	-4.799122
H	5.171313	-2.491490	-5.687471
C	5.105541	-3.448337	-3.757976
H	6.109811	-3.854360	-3.836464
Cu	-0.412577	-0.564406	1.669179
H	0.150494	1.286882	1.677679
P	-0.660723	-1.579359	3.663747
N	-0.113210	-3.899476	2.385239
C	0.372121	-5.142938	2.238668
H	0.224720	-5.595657	1.264682
C	0.050233	-3.277534	3.574013
C	1.046352	-5.818940	3.251705
H	1.435071	-6.814274	3.071054
C	0.725663	-3.884271	4.635209
H	0.854349	-3.346208	5.567962
C	0.301417	-0.797434	5.002750
C	-2.356988	-1.838233	4.285959
C	-2.683309	-2.743026	5.307580
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H	1.759018	-5.664054	5.284840
C	-3.369126	-1.075174	3.685116
H	-3.114046	-0.404876	2.870661
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H	2.011723	-0.648711	3.688235
C	-4.688196	-1.193402	4.122081
H	-5.463039	-0.589124	3.660083
C	2.422714	0.203861	5.624350
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C	1.902913	0.520704	6.883715
H	2.522959	1.030936	7.614630
C	0.585305	0.185256	7.198501
H	0.179750	0.431570	8.175444

Cu	-1.484501	-0.712127	-0.749377
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P	-3.433125	-1.704047	-1.287385
N	-3.072018	-3.266313	0.891018
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C	-4.452180	-3.841453	-2.881061
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C	-5.755766	-3.553844	1.599755
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C	-2.325835	-2.868323	-3.525893
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C	-5.646699	-0.574309	-2.700377
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Cu	-1.036222	1.434531	0.372418
H	-1.911192	-0.208138	0.892929
P	-1.985098	3.365459	1.035414
N	0.487898	4.454977	0.920813
C	1.492553	5.274921	1.269764
H	2.406249	5.173358	0.695191
C	-0.673535	4.526831	1.607914

C	1.397577	6.189511	2.314829
H	2.247571	6.813158	2.565842
C	-0.842854	5.409255	2.677115
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H	-3.005998	2.612277	-1.499142
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P	0.660963	1.579164	-3.663626
N	0.112925	3.899111	-2.385251
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C	-0.725341	3.884014	-4.635430
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C	2.683911	2.743619	-5.306459
H	1.907993	3.347650	-5.768396

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C	3.369475	1.075588	-3.684063
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C	4.006485	2.869001	-5.731449
H	4.256171	3.567346	-6.524899
C	0.216309	0.477599	-6.263901
H	1.237179	0.746679	-6.516812
C	5.007785	2.089506	-5.142922
H	6.035345	2.185350	-5.481619
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H	-2.011016	0.647323	-3.688228
C	4.688808	1.194737	-4.119992
H	5.463657	0.590750	-3.657620
C	-2.421768	-0.204913	-5.624543
H	-3.441346	-0.477121	-5.368853
C	-1.901908	-0.521208	-6.884020
H	-2.521776	-1.031521	-7.615028
C	-0.584448	-0.185154	-7.198780
H	-0.178829	-0.431094	-8.175792
Cu	1.484637	0.711970	0.749476
H	1.228804	-1.123872	1.312346
P	3.433128	1.704249	1.287464
N	3.071542	3.265747	-0.891408
C	3.430858	3.999633	-1.957072
H	2.617794	4.443962	-2.519949
C	4.040114	2.675813	-0.156417
C	4.755736	4.173209	-2.347289
H	4.986843	4.760216	-3.228431
C	5.391166	2.791679	-0.490603
H	6.138610	2.287201	0.111810
C	4.791573	0.524800	1.593815
C	3.429443	2.906400	2.660978
C	4.451333	3.842681	2.880299
H	5.303152	3.887765	2.207526
C	5.755122	3.552436	-1.601184
H	6.799769	3.655617	-1.878686
C	2.325999	2.868110	3.526278
H	1.522224	2.166105	3.328971
C	4.375986	4.717267	3.964220
H	5.170325	5.438174	4.134256
C	5.647247	0.575926	2.700710
H	5.561884	1.387432	3.416761

C	3.283568	4.659319	4.835909
H	3.232178	5.337705	5.682626
C	4.906200	-0.535178	0.674543
H	4.212909	-0.598800	-0.160497
C	2.259992	3.735966	4.615985
H	1.408326	3.690339	5.287977

C	5.883604	-1.510739	0.850293
H	5.965352	-2.324231	0.135736
C	6.737626	-1.455445	1.956696
H	7.493565	-2.221964	2.098260
C	6.614292	-0.417368	2.881294
H	7.275801	-0.373587	3.741556

Coordinate of $[\text{Cu}_8(\mu_3\text{-H})_4(\mu_4\text{-H})_2\text{L}_6]^{2+}$

Cu	12.791103	22.096706	10.573643
Cu	12.841877	20.816497	8.185956
H	12.887793	20.306790	6.574168
P	13.803168	19.209771	9.510094
N	12.635343	20.215873	11.701006
C	12.088631	20.216704	12.925478
H	11.801311	21.187658	13.315428
C	13.003807	19.034846	11.160121
C	11.880392	19.055641	13.666055
H	11.438408	19.113562	14.655124
C	12.801860	17.823078	11.823438
H	13.087886	16.892225	11.347801
C	13.845357	17.510098	8.827863
C	15.528928	19.616249	9.960928
C	16.207264	19.007985	11.027730
H	15.692905	18.300390	11.672067
C	12.237880	17.834148	13.098857
H	12.081435	16.904934	13.638485
C	16.190086	20.570505	9.174822
H	15.661409	21.075714	8.373775
C	17.542651	19.322549	11.278227
H	18.065720	18.842836	12.100540
C	14.699981	16.495090	9.284635
H	15.416183	16.699112	10.073227
C	18.203083	20.258174	10.477274
H	19.243065	20.501219	10.674437
C	12.963635	17.237383	7.770958
H	12.331997	18.032896	7.390806
C	17.522994	20.887212	9.433032
H	18.026069	21.623077	8.813263
C	12.914740	15.964631	7.200950
H	12.230756	15.768207	6.381497
C	13.757620	14.956285	7.671696
H	13.723672	13.966024	7.227379

C	14.653192	15.224383	8.710593
H	15.318238	14.444946	9.070607
Cu	13.573021	23.418765	8.007247
H	12.847175	22.370746	5.025009
P	14.414195	24.807460	9.618544
N	14.662828	22.805250	11.404092
C	15.268984	22.050550	12.333321
H	14.709136	21.191806	12.683332
C	15.327004	23.880375	10.918501
C	16.548761	22.314571	12.814236
H	16.994234	21.658005	13.552826
C	16.612012	24.212836	11.350127
H	17.110060	25.081418	10.934692
C	15.662814	25.971282	8.950052
C	13.272401	25.838115	10.607836
C	13.630149	26.381650	11.851116
H	14.608463	26.172461	12.275055
C	17.233748	23.417604	12.312156
H	18.233982	23.656481	12.660727
C	12.000728	26.100958	10.078542
H	11.718159	25.654852	9.130340
C	12.735191	27.196324	12.544670
H	13.021844	27.622628	13.501762
C	15.860737	27.271948	9.433911
H	15.257341	27.644698	10.254733
C	11.474529	27.466302	12.005758
H	10.779662	28.103046	12.545398
C	16.436784	25.513414	7.869176
H	16.265386	24.514138	7.478509
C	11.107813	26.914508	10.776522
H	10.125550	27.116930	10.359353
C	17.405654	26.338128	7.298755
H	18.002066	25.970985	6.468810
C	17.600860	27.632243	7.788729

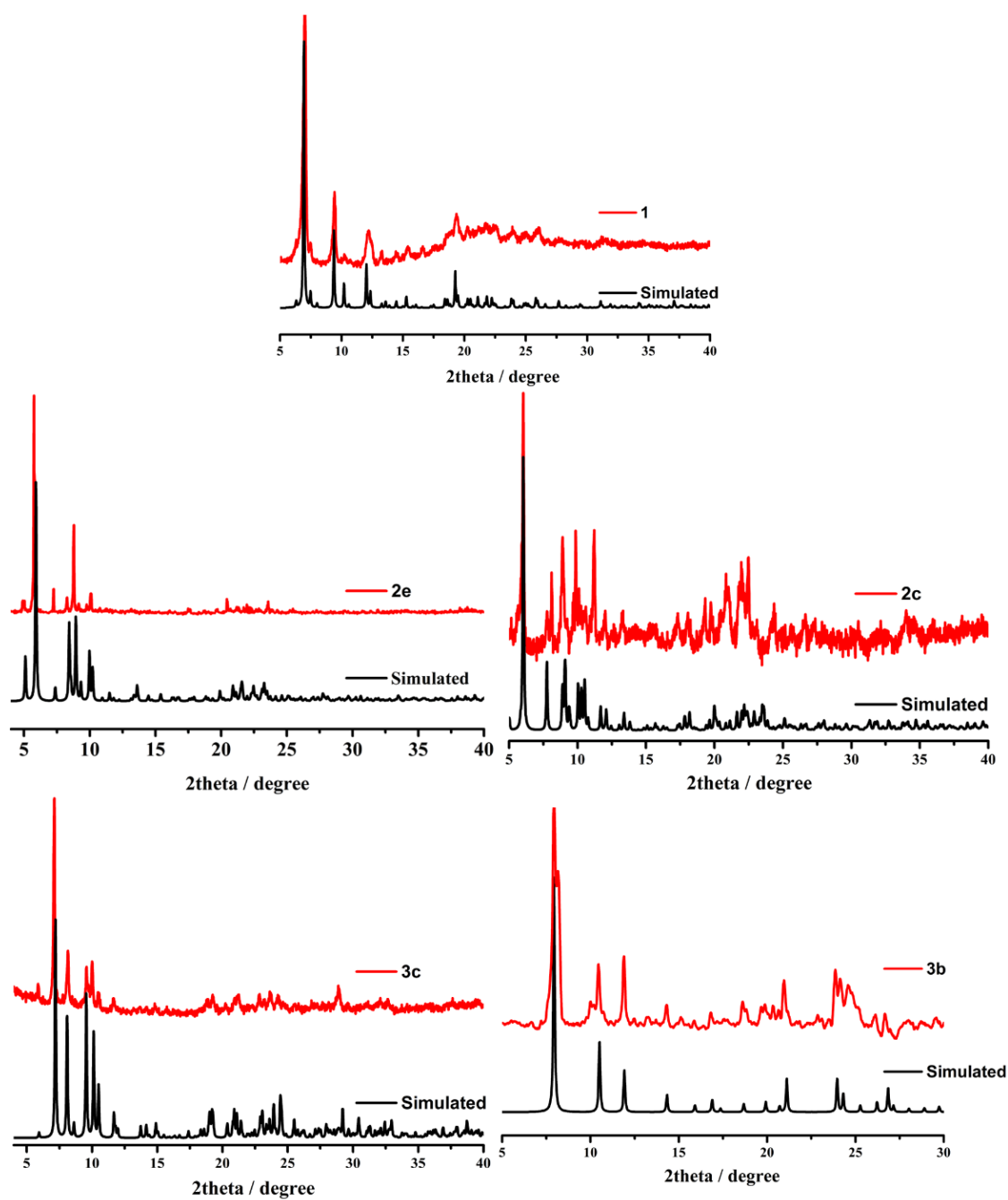
H	18.351098	28.277102	7.340909	C	14.504014	23.595882	1.462472
C	16.826537	28.097378	8.853698	H	14.663790	22.555939	1.198143
H	16.972655	29.104115	9.234060	C	13.372716	25.094360	2.819662
Cu	11.091326	22.972744	7.847302	C	15.223182	24.613397	0.842409
H	10.520621	22.578061	6.265157	H	15.952053	24.372976	0.076771
P	9.588847	22.507082	9.473355	C	14.061325	26.169750	2.251545
N	11.184697	23.169004	11.563138	H	13.866442	27.177560	2.599811
C	11.515506	23.789274	12.705255	C	12.490252	26.989437	4.785981
H	12.558293	23.714111	12.996804	C	10.543227	25.394372	3.233047
C	9.907035	23.257210	11.125077	C	10.400031	26.058810	2.006235
C	10.604439	24.509534	13.473449	H	11.255072	26.548376	1.548655
H	10.930196	24.999778	14.383782	C	14.993687	25.927157	1.244154
C	8.934266	23.962545	11.838236	H	15.535500	26.750024	0.787634
H	7.919683	24.013822	11.461080	C	9.437669	24.738139	3.796884
C	7.833500	22.856526	9.107835	H	9.562905	24.186926	4.725422
C	9.626716	20.704563	9.786117	C	9.159886	26.091938	1.367534
C	9.385994	20.134766	11.041796	H	9.052237	26.616672	0.422707
H	9.210949	20.772411	11.903212	C	11.910515	28.171255	4.307471
C	9.286262	24.591272	13.032120	H	11.160188	28.132892	3.524047
H	8.543254	25.141276	13.601697	C	8.058447	25.454491	1.944287
C	9.859065	19.866960	8.683140	H	7.094004	25.483640	1.445801
H	10.026681	20.302762	7.704224	C	13.441096	27.051842	5.820486
C	9.376956	18.747389	11.192359	H	13.855989	26.134635	6.229260
H	9.191563	18.313511	12.169853	C	8.199884	24.773050	3.155393
C	6.766328	22.209197	9.747348	H	7.349547	24.260696	3.596217
H	6.963683	21.470916	10.518698	C	13.830697	28.283308	6.343560
C	9.604875	17.919202	10.091388	H	14.571221	28.319062	7.136047
H	9.591100	16.839931	10.210960	C	13.254561	29.459940	5.855710
C	7.569160	23.778979	8.084109	H	13.548810	30.420343	6.268515
H	8.400203	24.254387	7.568800	C	12.291267	29.402330	4.846542
C	9.839992	18.481398	8.834893	H	11.834978	30.315874	4.476934
H	9.997591	17.845403	7.970456	Cu	11.611100	21.285641	5.867893
C	6.253048	24.064482	7.717543	H	12.445479	22.284727	8.943639
H	6.054510	24.780755	6.925549	P	10.380071	20.064628	4.420692
C	5.194299	23.424262	8.366202	N	10.891216	21.818952	2.432525
H	4.169930	23.643106	8.080023	C	10.635562	22.561437	1.343866
C	5.452072	22.496035	9.379641	H	11.449356	23.190806	1.000358
H	4.628868	21.992575	9.877777	C	9.908692	21.031848	2.924493
Cu	12.782040	22.076267	3.408415	C	9.402912	22.557261	0.696700
Cu	12.167697	23.767158	5.801813	H	9.245161	23.187913	-0.170405
H	12.178017	24.390069	7.432970	C	8.643220	20.978029	2.337362
P	12.116381	25.315380	4.159863	H	7.876509	20.344629	2.769542
N	13.595824	23.820986	2.425538	C	8.778997	19.590153	5.164211

C	11.109448	18.542351	3.720864
C	10.538081	17.836096	2.652006
H	9.617722	18.189822	2.195954
C	8.387404	21.749912	1.204428
H	7.410827	21.723774	0.730512
C	12.305762	18.084919	4.291969
H	12.760741	18.660058	5.092064
C	11.147097	16.675062	2.175717
H	10.698358	16.127567	1.352097
C	8.324765	18.268636	5.254409
H	8.881202	17.467662	4.778253
C	12.330030	16.214299	2.761223
H	12.800360	15.308853	2.388965
C	8.049020	20.616699	5.792445
H	8.426737	21.634764	5.770711
C	12.910147	16.921242	3.816363
H	13.835288	16.574454	4.266380
C	6.875698	20.324989	6.482465
H	6.322504	21.124628	6.964163
C	6.429931	19.002512	6.572689
H	5.522056	18.771833	7.121959
C	7.154671	17.978816	5.961801
H	6.809206	16.951410	6.030251
Cu	14.047982	21.752659	6.128450
H	14.879175	22.718500	7.214515
P	15.631118	20.952536	4.719125
N	13.964412	20.448994	2.645317
C	13.494245	19.795409	1.570839
H	12.574121	20.184452	1.147164

C	15.093547	19.996310	3.235515
C	14.118308	18.674870	1.030349
H	13.687988	18.177345	0.168570
C	15.777296	18.877404	2.753526
H	16.676827	18.539941	3.256081
C	16.826346	19.846528	5.544433
C	16.581647	22.326572	3.971694
C	17.519827	22.136669	2.946569
H	17.713061	21.138154	2.564240
C	15.285943	18.210278	1.632526
H	15.803158	17.339688	1.240511
C	16.325693	23.623843	4.442490
H	15.581366	23.768187	5.219371
C	18.211479	23.226988	2.417856
H	18.944904	23.072732	1.631802
C	18.203847	20.086902	5.611012
H	18.635042	20.930416	5.081833
C	17.960732	24.514552	2.899792
H	18.498179	25.361844	2.483936
C	16.280101	18.758939	6.249977
H	15.205478	18.593997	6.244534
C	17.013458	24.712617	3.906899
H	16.800509	25.713199	4.270966
C	17.105628	17.909283	6.981210
H	16.671779	17.071955	7.517042
C	18.480100	18.155453	7.045401
H	19.121881	17.503647	7.630357
C	19.024876	19.245240	6.366182
H	20.091966	19.440878	6.417578

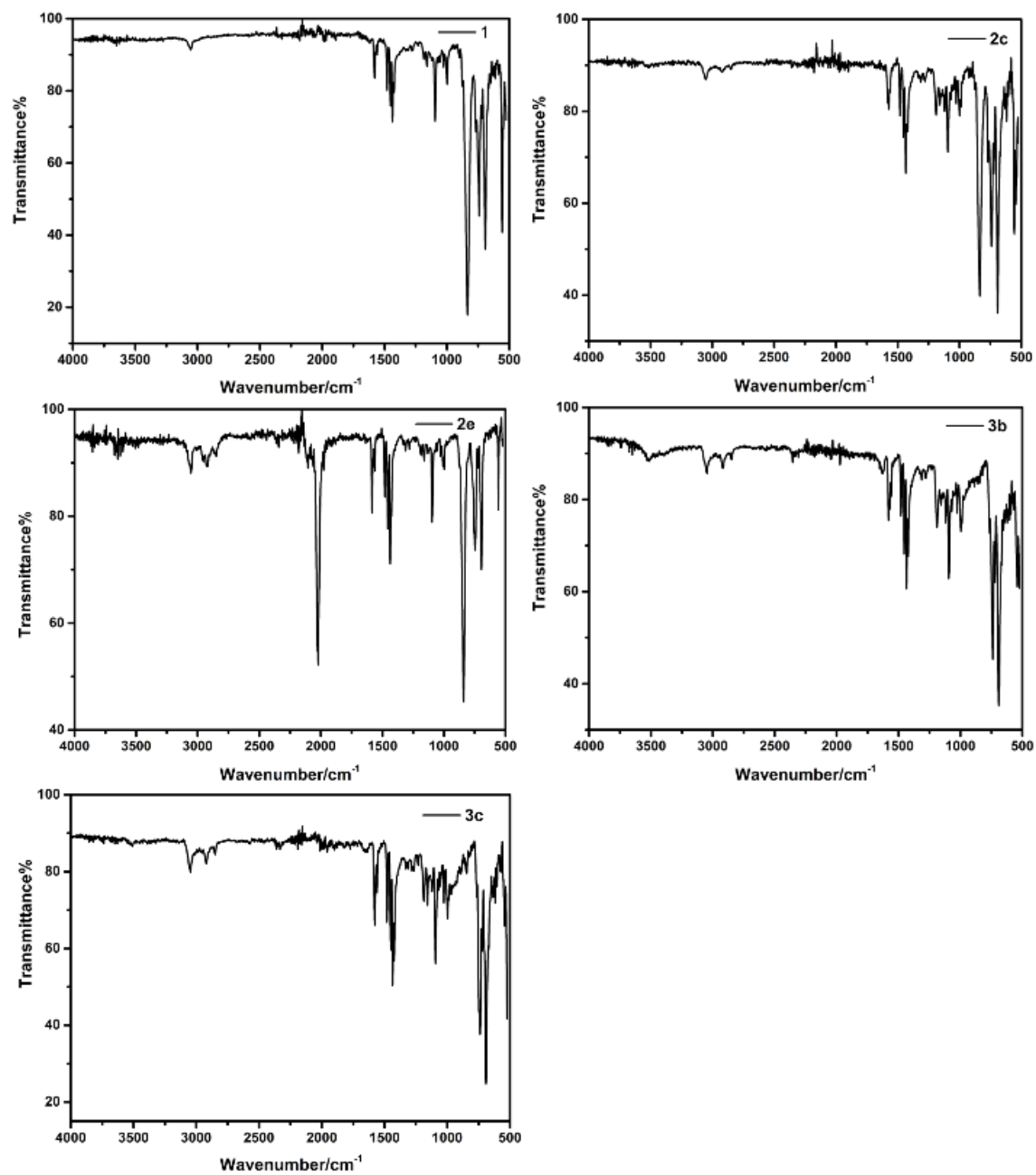
PXRD

Figure S4: Experimental and simulated PXRD patterns.



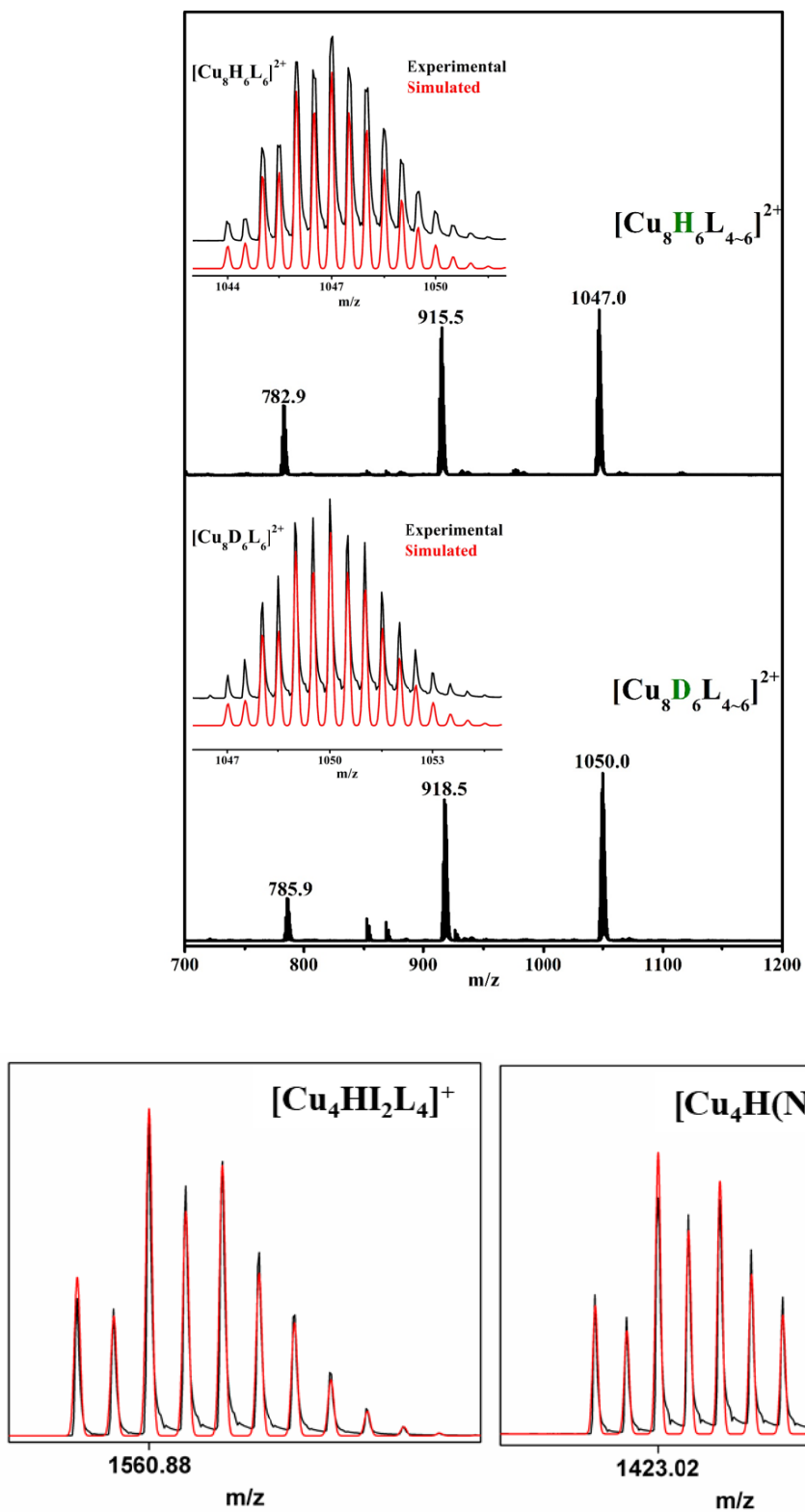
IR

Figure S5: The IR spectra.



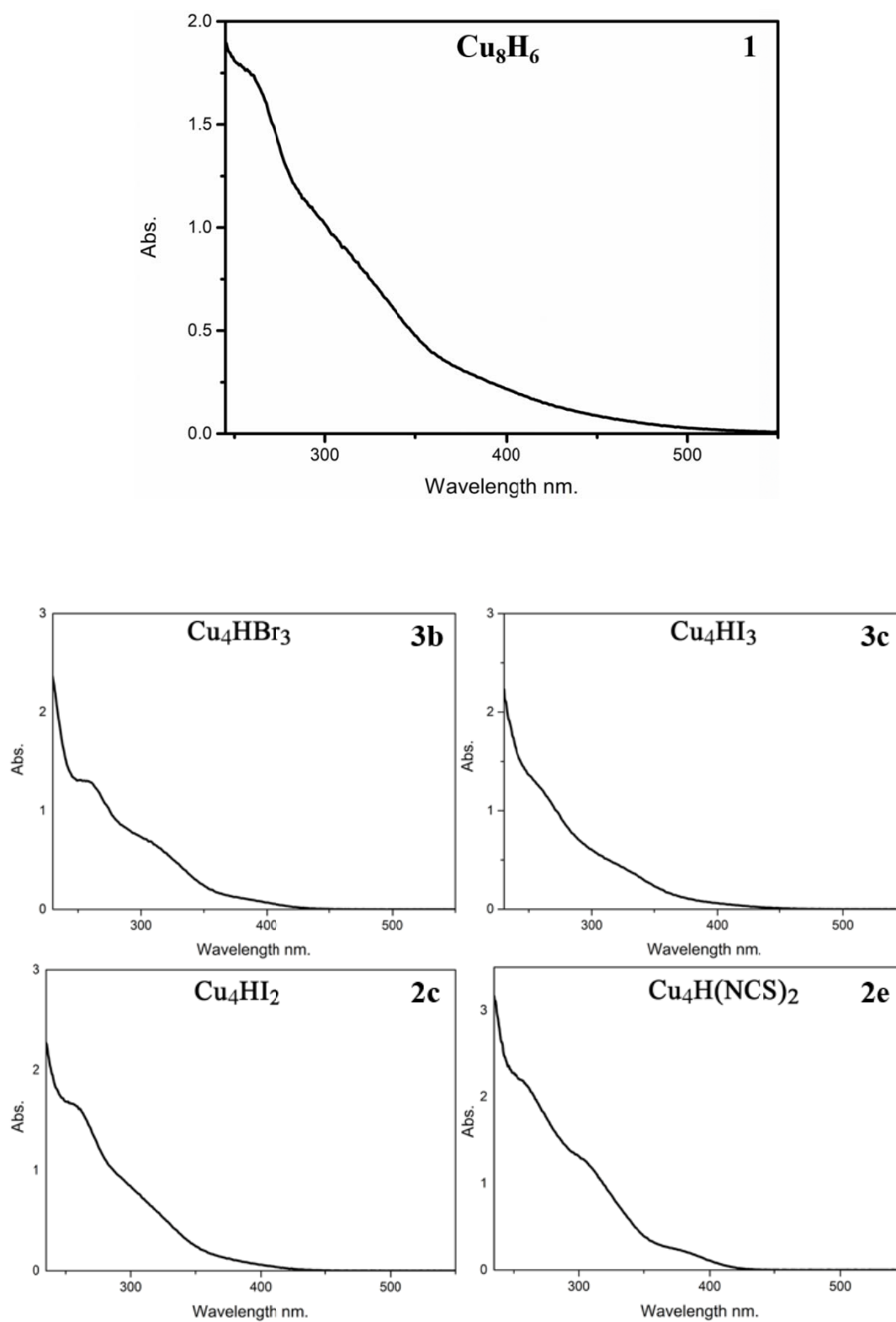
MS

Figure S6: ESI-TOF-MS of $[\text{Cu}_8\text{H}_6\text{L}_6]^{2+}$, $[\text{Cu}_8\text{D}_6\text{L}_6]^{2+}$, $[\text{Cu}_4\text{HI}_2\text{L}_4]^+$ and $[\text{Cu}_4\text{H}(\text{NCS})_2\text{L}_4]^+$.



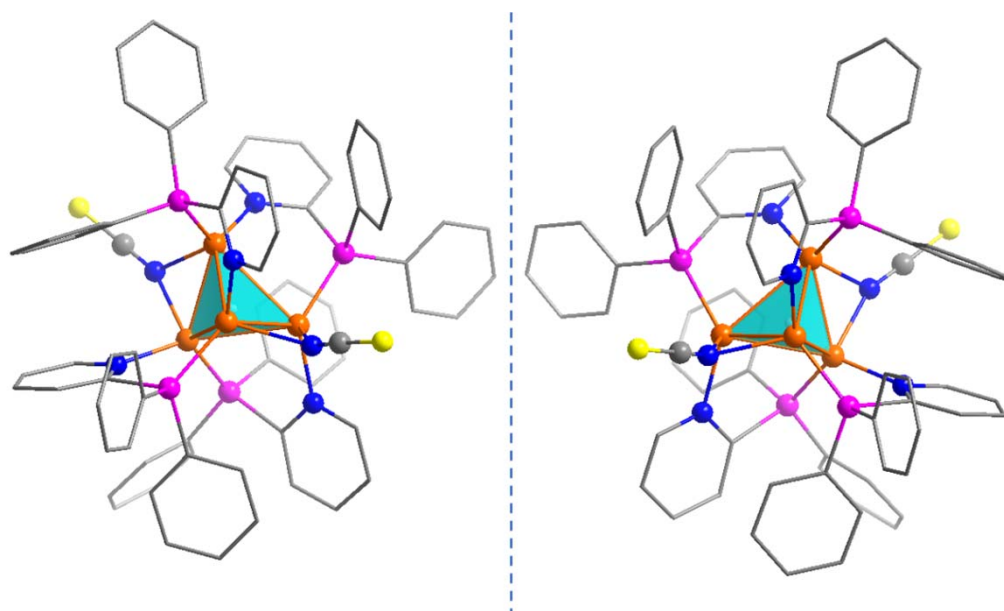
UV/Vis

Figure S7: UV/Vis absorption spectra of 1, 3b, 3c, 2c and 2e in dichloromethane solution.

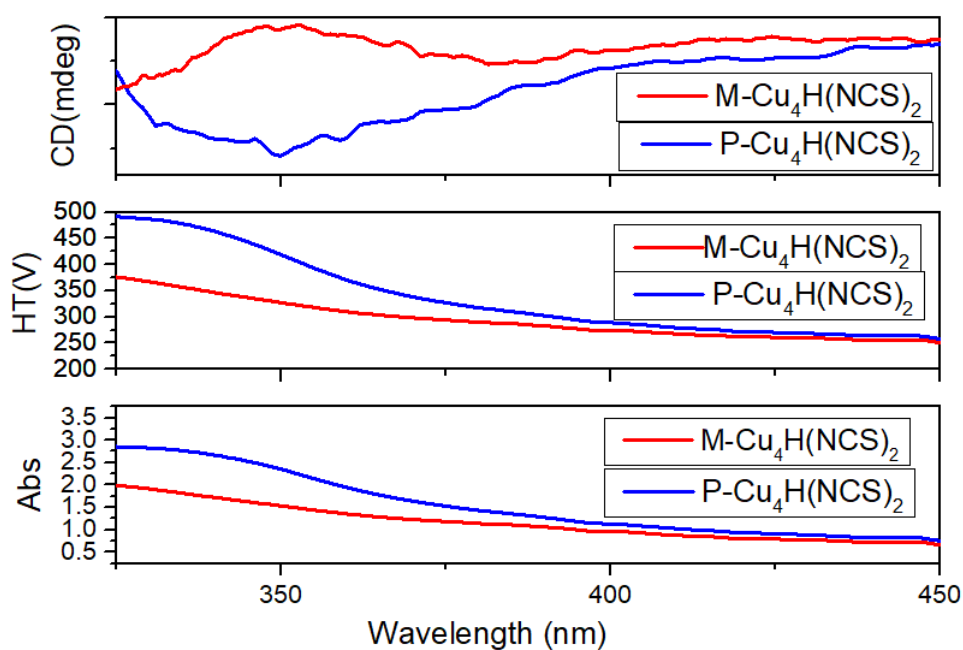


CD

Figure S8: CD of M -[Cu₄H(NCS)₂][PF₆] and P -[Cu₄H(NCS)₂][PF₆] enantiomers (From top to bottom are CD, voltage and absorption *vs.* wavelength (nm), respectively).



Enantiomers of [Cu₄H(NCS)₂]⁺ left: M , right: P .



Yellow crystals of M and P enantiomers of [Cu₄H(NCS)₂L₄][PF₆] were prepared as KBr pellets ($m_s : m_{\text{KBr}} = 1:200$) and the CD spectra were obtained in the 200-800 cm⁻¹ range using Jasco-810 spectrometer.

Structure figures

Figure S9: Enantiomers $[\text{Cu}_4\text{HBr}_3]$ (**3b**). Left: Λ Right: Δ .

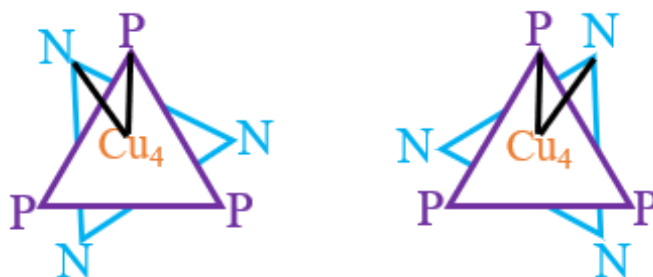
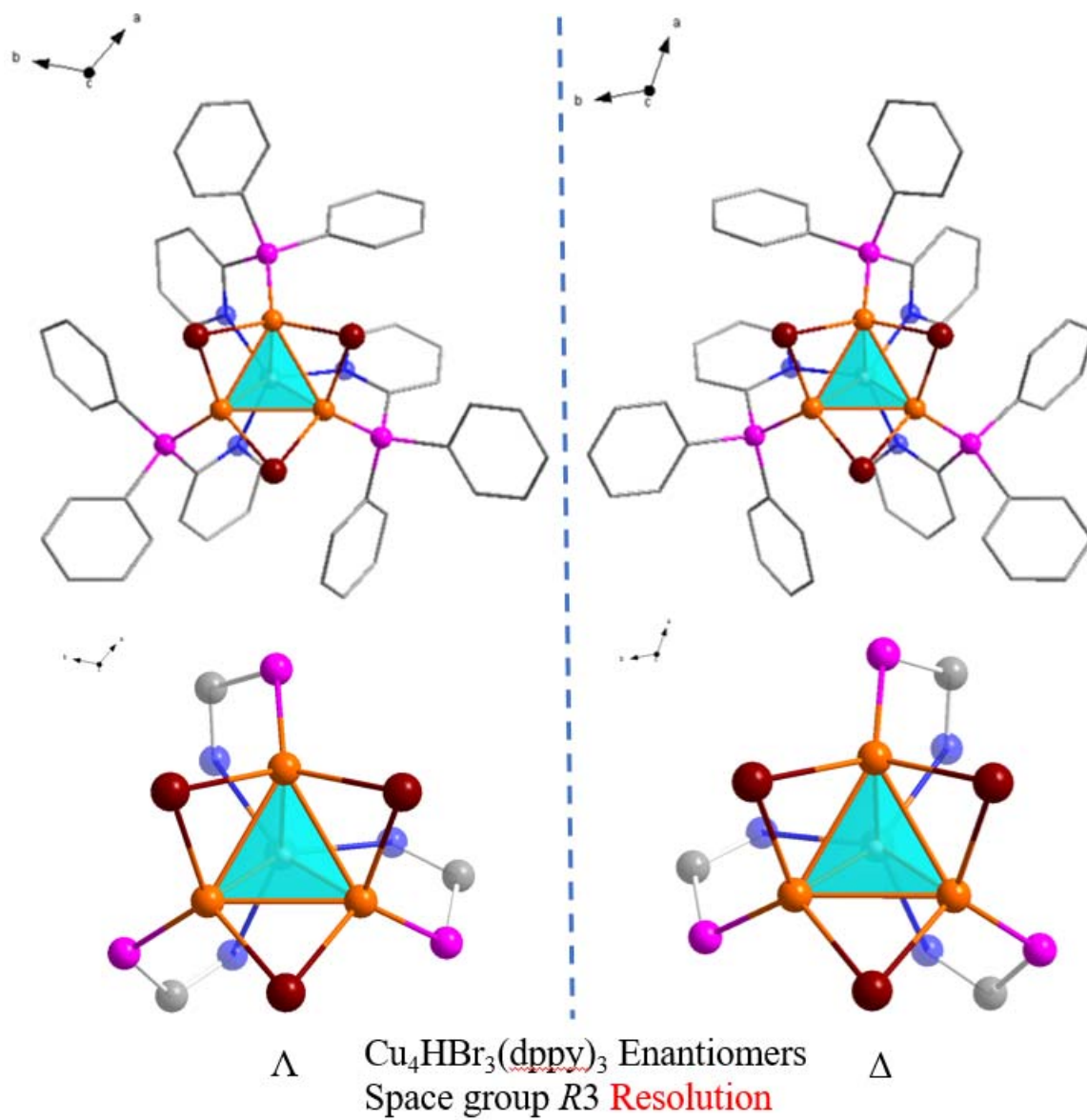


Figure S10: Different coordination mode of $[\text{Cu}_4\text{HX}_2\text{L}_4]^+$ clusters ($\text{X}^- = \text{Cl}^-$, Br^- , I^- , N_3^- , NCS^-).

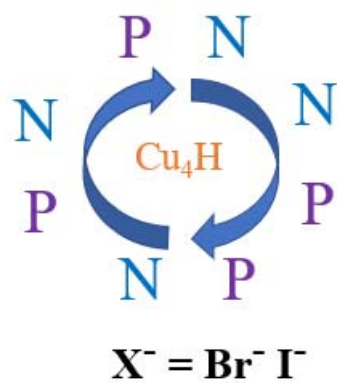
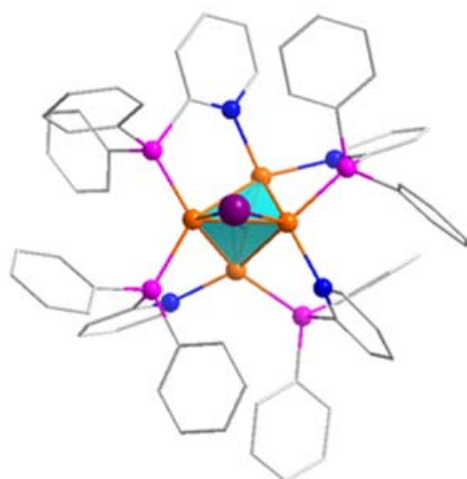
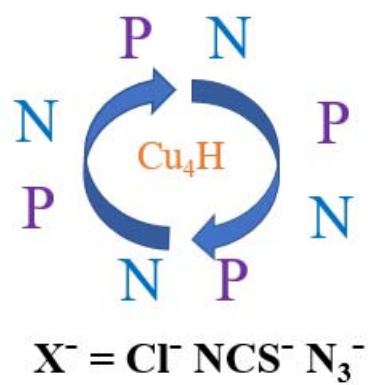
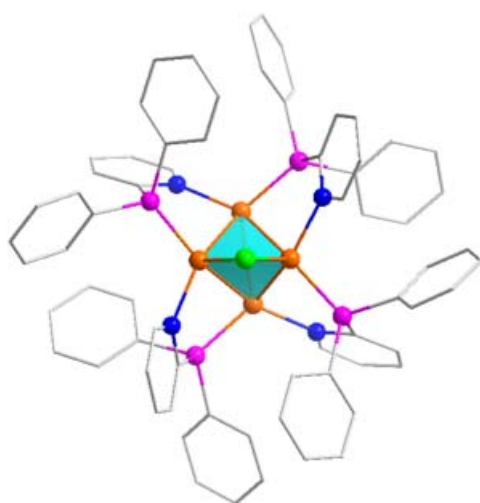


Figure S11: Packing of $[\text{Cu}_4\text{HBr}_3]$ Δ and Λ (3b**) crystals.**

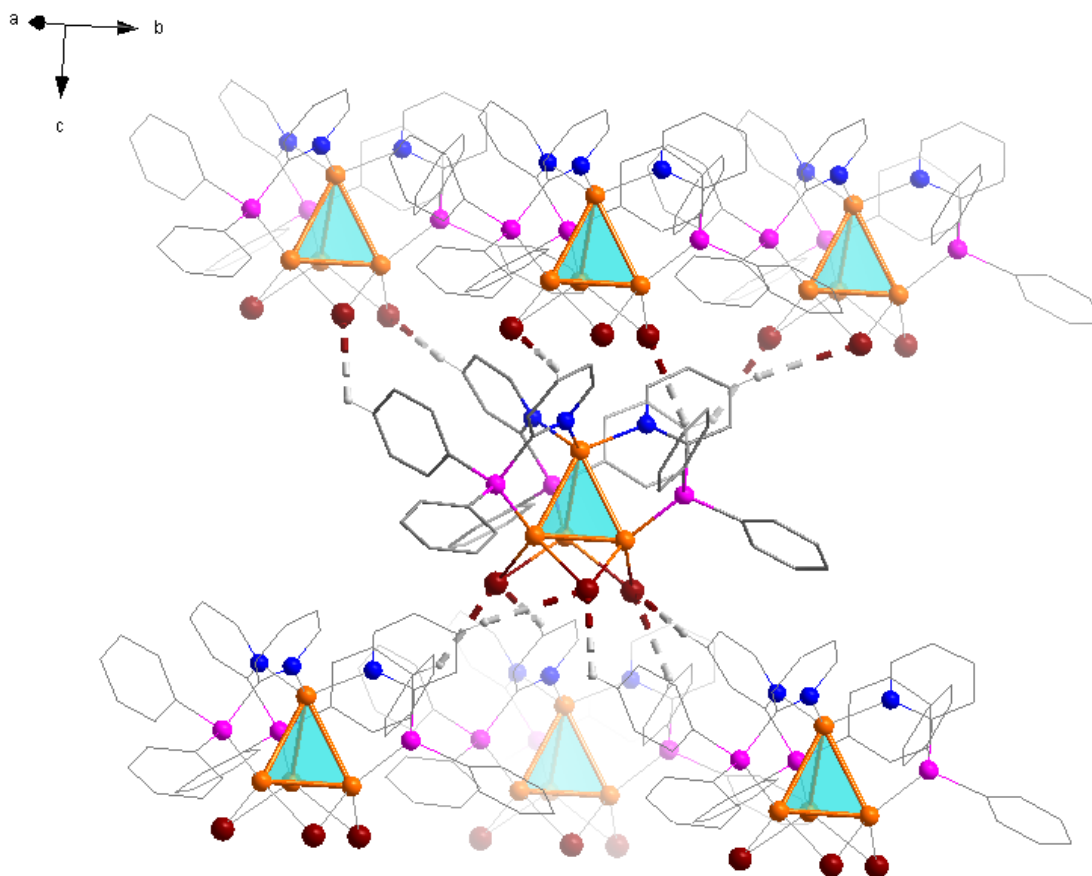
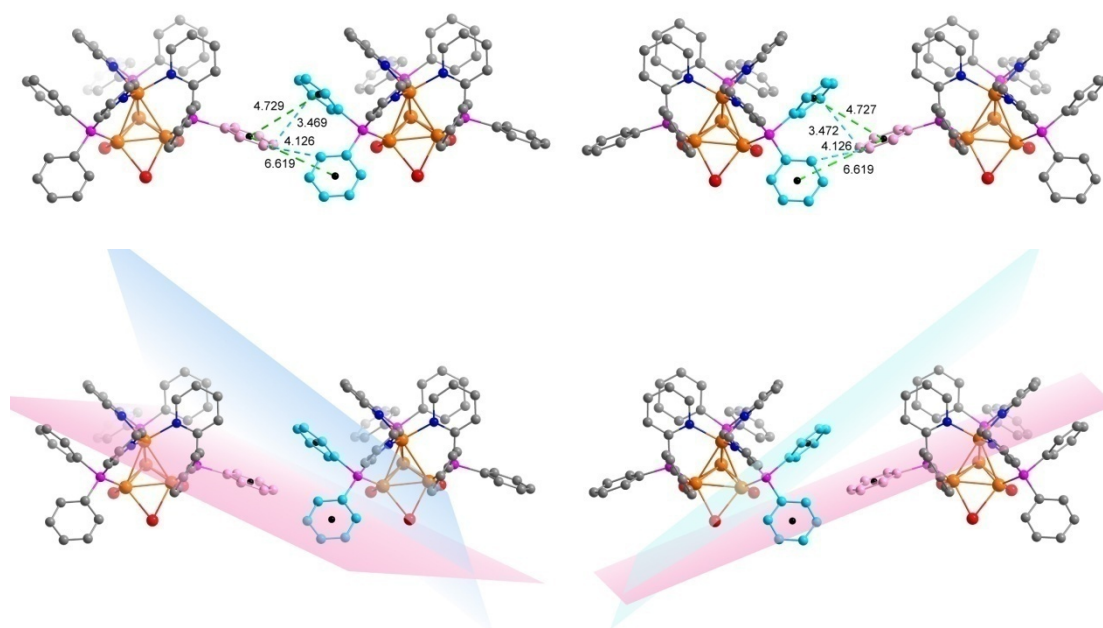
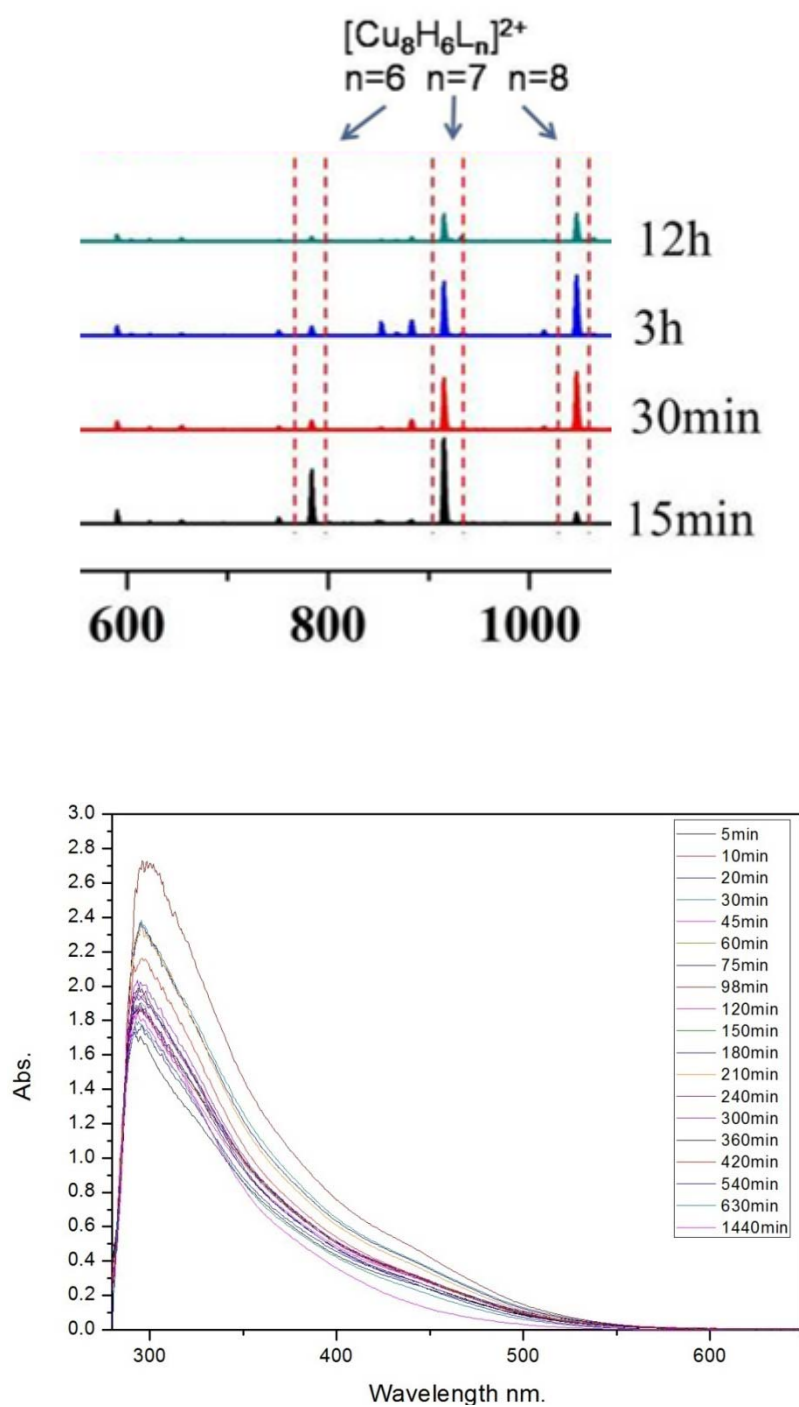


Figure S12: Short contacts in “key-and-lock” shape recognition in $[\text{Cu}_4\text{HBr}_3]$ Δ and Λ (3b**) crystals**



MS and UV-Vis of 1

Figure S13: The MS and UV-Vis of the red reaction solution of 1.



Table

Table S1: Crystal data

Name	[Cu ₈ H ₆ L ₆] ²⁺ 1	[Cu ₄ HCl ₂ L ₄] ⁺ 2a	[Cu ₄ HI ₂ L ₄] ⁺ 2c
CCDC	2039341	2039342	2039343
Moieties	[Cu ₈ H ₆ L ₆][PF ₆] ₂ ·2CH ₂ Cl ₂	[Cu ₄ HCl ₂ L ₄][PF ₆] ·2CH ₂ Cl ₂	[Cu ₄ HI ₂ L ₄][PF ₆] ·CH ₂ Cl ₂
Empirical formula	C ₁₀₄ H ₉₄ Cu ₈ N ₆ P ₈ F ₁₂ Cl ₄	C ₇₀ H ₆₁ Cu ₄ N ₄ P ₅ F ₆ Cl ₆	C ₆₉ H ₅₉ Cl ₂ Cu ₄ I ₂ N ₄ P ₅ F ₆
Formula weight	2553.73	1693.93	1791.91
<i>T</i> (K)	100(10)	100(10)	100(10)
Crystal system	<i>P</i> –3	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
Space group	Trigonal	Monoclinic	Monoclinic
<i>a</i> (Å)	25.4756(5)	13.7032(1)	16.4263(1)
<i>b</i> (Å)	25.4756(5)	26.1636(2)	12.0316(1)
<i>c</i> (Å)	13.9849(4)	20.0973(2)	35.2262(3)
<i>α</i> (°)	90	90	90
<i>β</i> (°)	90	96.232(1)	92.5280(10)
<i>γ</i> (°)	120	90	90
<i>V</i> (Å ³)	7860.3(4)	7162.8(1)	6955.14(9)
<i>Z</i>	3	4	4
<i>ρ</i> _{calcd} (g/cm ^{–3})	1.617	1.571	1.711
<i>μ</i> (mm ^{–1})	4.434	4.955	10.644
<i>F</i> (000)	3856	3424	3544
Radiation (Å)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
Crystal size (mm)	0.12×0.02×0.02	0.20×0.20×0.20	0.20×0.20×0.10
<i>θ</i> limits (°)	3.160 to 66.739	3.658 to 78.166	2.921 to 75.941
Limiting indices	–27 ≤ <i>h</i> ≤ 29 –29 ≤ <i>k</i> ≤ 30 –16 ≤ <i>l</i> ≤ 16	–17 ≤ <i>h</i> ≤ 16 –32 ≤ <i>k</i> ≤ 32 –25 ≤ <i>l</i> ≤ 25	–20 ≤ <i>h</i> ≤ 20 –14 ≤ <i>k</i> ≤ 14 –43 ≤ <i>l</i> ≤ 43
Reflections / unique	22580 / 8942	53516 / 14837	51048 / 13832
<i>R</i> _{int}	0.0734	0.0391	0.0420
Completeness (%)	96.0	99.8	95.3
Data/restraints/parameters	8942 / 518 / 758	14837 / 0 / 897	13832 / 6 / 833
GooFs	1.004	1.048	1.032
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0771, 0.2070	0.0375, 0.0929	0.0315, 0.0783
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1232, 0.2365	0.0488, 0.1019	0.0363, 0.0817
Δρ (e·Å ^{–3})	1.553, –0.786	0.699, –0.818	1.010, –1.028

Continued Table S1: Crystal data (1)

Name	[Cu ₄ H(N ₃) ₂ L ₄] ⁺ 2d	[Cu ₄ H(NCS) ₂ L ₄] ⁺ 2e (M)	[Cu ₄ H(NCS) ₂ L ₄] ⁺ 2e (P)
CCDC	2039344	2039345	2039346
Moieties	[Cu ₄ H(N ₃) ₂ L ₄][PF ₆] ·2CH ₂ Cl ₂	[Cu ₄ H(NCS) ₂ L ₄] [PF ₆]·1.25CH ₂ Cl ₂	[Cu ₄ H(NCS) ₂ L ₄] [PF ₆]·1.25CH ₂ Cl ₂
Empirical formula	C ₇₀ H ₆₁ Cu ₄ N ₁₀ P ₅ F ₆ Cl ₄	C _{71.25} H _{59.5} Cl _{2.5} Cu ₄ S ₂ N ₆ P ₅ F ₆	C _{71.25} H _{59.5} Cl _{2.5} Cu ₄ S ₂ N ₆ P ₅ F ₆
Formula weight	1707.09	1675.50	1675.50
<i>T</i> (K)	100(10)	100(10)	100(10)
Crystal system	<i>Cc</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Space group	Monoclinic	Orthorhombic	Orthorhombic
<i>a</i> (Å)	30.2978(2)	13.1572(2)	13.1571(2)
<i>b</i> (Å)	18.41230(10)	16.6001(2)	16.5948(2)
<i>c</i> (Å)	15.20620(10)	34.5546(5)	34.5954(4)
α (°)	90	90	90
β (°)	121.0420(10)	90	90
γ (°)	90	90	90
<i>V</i> (Å ³)	7267.98(10)	7547.10(18)	7553.54(17)
<i>Z</i>	4	4	4
ρ_{calcd} (g/cm ⁻³)	1.560	1.475	1.473
μ (mm ⁻¹)	4.254	4.096	4.093
<i>F</i> (000)	3456	3394	3394
Radiation (Å)	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)
Crystal size (mm)	0.30×0.20×0.10	0.20×0.20×0.10	0.30×0.20×0.10
θ limits (°)	2.935 to 76.974	2.953 to 78.032	2.554 to 76.958
Limiting indices	-37 ≤ <i>h</i> ≤ 38 -23 ≤ <i>k</i> ≤ 22 -18 ≤ <i>l</i> ≤ 19	-16 ≤ <i>h</i> ≤ 16 -21 ≤ <i>k</i> ≤ 21 -42 ≤ <i>l</i> ≤ 43	-15 ≤ <i>h</i> ≤ 15 -20 ≤ <i>k</i> ≤ 17 -38 ≤ <i>l</i> ≤ 43
Reflections / unique	95245 / 14260	43431 / 15466	46360 / 15033
<i>R</i> _{int}	0.0360	0.0506	0.0478
Completeness (%)	99.8	98.0	94.5
Data/restraints/parameters	14257 / 993 / 1003	15446 / 32 / 896	15033 / 608 / 896
GooFs	1.021	1.059	1.060
Flack parameter	0.016(12)	0.013(10)	-0.003(7)
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0409, 0.1089	0.0557, 0.1481	0.0387, 0.1005
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0424, 0.1100	0.0642, 0.1595	0.0428, 0.1039
$\Delta\rho$ (e·Å ⁻³)	1.09, -0.53	1.063, -1.204	1.120, -0.854

Continued Table S1: Crystal data (2)

Name	[Cu ₄ HBr ₃ L ₃] 3b (Δ)DBM	[Cu ₄ HBr ₃ L ₃] 3b (Δ)DCM
CCDC	2039347	2039348
Moieties	[Cu ₄ HBr ₃ L ₃]·2CH ₂ Br ₂	[Cu ₄ HBr ₃ L ₃]·2CH ₂ Cl ₂
Empirical formula	C ₅₃ H ₄₇ Br ₇ Cu ₄ N ₃ P ₃	C ₅₃ H ₄₇ Br ₃ Cl ₄ Cu ₄ N ₃ P ₃
Formula weight	1632.37	1454.53
<i>T</i> (K)	100(10)	100(10)
Crystal system	<i>R</i> 3	<i>R</i> 3
Space group	Trigonal	Trigonal
<i>a</i> (Å)	14.9752(2)	14.8018(2)
<i>b</i> (Å)	14.9752(2)	14.8018(2)
<i>c</i> (Å)	22.1086(2)	22.1489(3)
<i>α</i> (°)	90	90
<i>β</i> (°)	90	90
<i>γ</i> (°)	120	120
<i>V</i> (Å ³)	4193.75(14)	4202.54(13)
<i>Z</i>	3	3
ρ_{calcd} (g/cm ⁻³)	1.894	1.724
μ (mm ⁻¹)	8.484	7.081
<i>F</i> (000)	2376	2160
Radiation (Å)	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)
Crystal size (mm)	0.10×0.10×0.10	0.20×0.20×0.20
θ limits (°)	3.952 to 78.290	3.984 to 73.099
Limiting indices	$-18 \leq h \leq 18$ $-18 \leq k \leq 17$ $-27 \leq l \leq 27$	$-17 \leq h \leq 17$ $-18 \leq k \leq 17$ $-26 \leq l \leq 26$
Reflections / unique	34214 / 4056	9131 / 3463
<i>R</i> _{int}	0.0446	0.0233
Completeness (%)	99.6	95.7
Data/restraints/parameters	4056 / 7 / 242	3463 / 1 / 234
GooFs	1.047	1.055
Flack parameter	-0.017(10)	-0.010(9)
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0348, 0.0841	0.0259, 0.0624
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0363, 0.0851	0.0272, 0.0631
$\Delta\rho$ (e·Å ⁻³)	0.920, -0.590	0.606, -0.837

Continued Table S1: Crystal data (3)

Name	[Cu ₄ HBr ₃ L ₃] 3b (Λ)DBM	[Cu ₄ HBr ₃ L ₃] 3b (Λ)DCM	[Cu ₄ HI ₃ L ₃] 3c
	2039349	2039350	2039351
Moieties	[Cu ₄ HBr ₃ L ₃] ·2CH ₂ Br ₂	[Cu ₄ HBr ₃ L ₃] ·2CH ₂ Cl ₂	[Cu ₄ HI ₃ L ₃] ·1.5CH ₂ Cl ₂
Empirical formula	C ₅₃ H ₄₇ Br ₇ Cu ₄ N ₃ P ₃	C ₅₃ H ₄₇ Br ₃ Cl ₄ Cu ₄ N ₃ P ₃	C _{52.5} H ₄₆ Cl ₃ Cu ₄ I ₃ N ₃ P ₃
Formula weight	1632.37	1454.53	1553.04
<i>T</i> (K)	203(2)	100(10)	100(10)
Crystal system	<i>R</i> 3	<i>R</i> 3	<i>Fdd</i> 2
Space group	Trigonal	Trigonal	Orthorhombic
<i>a</i> (Å)	14.9436(8)	14.7989(2)	49.0830(4)
<i>b</i> (Å)	14.9436(8)	14.7989(2)	37.3456(3)
<i>c</i> (Å)	22.1101(11)	22.1361(3)	11.73950(10)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	120	120	90
<i>V</i> (Å ³)	4275.9(5)	4198.46(13)	21518.9(3)
<i>Z</i>	3	3	16
ρ_{calcd} (g/cm ⁻³)	1.902	1.726	1.917
μ (mm ⁻¹)	6.500	7.088	17.816
<i>F</i> (000)	2376	2160	12048
Radiation (Å)	MoK α (λ =0.71073)	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)
Crystal size (mm)	0.13×0.12×0.10	0.20×0.20×0.20	0.05×0.05×0.02
θ limits (°)	1.823 to 28.732	3.986 to 76.678	2.974 to 77.008
Limiting indices	-20 ≤ <i>h</i> ≤ 19 -20 ≤ <i>k</i> ≤ 19 -28 ≤ <i>l</i> ≤ 29	-17 ≤ <i>h</i> ≤ 18 -18 ≤ <i>k</i> ≤ 15 -27 ≤ <i>l</i> ≤ 27	-60 ≤ <i>h</i> ≤ 34 -46 ≤ <i>k</i> ≤ 47 -12 ≤ <i>l</i> ≤ 14
Reflections / unique	12357 / 4511	10098 / 3703	25721 / 9639
<i>R</i> _{int}	0.0248	0.0264	0.0294
Completeness (%)	95.0	97.0	96.6
Data/restraints/parameters	4511 / 343 / 298	3703 / 7 / 234	9639 / 1 / 622
GooFs	1.000	1.076	1.050
Flack parameter	0.013(5)	-0.031(11)	\
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0302, 0.0597	0.0283, 0.0654	0.0214, 0.0563
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0390, 0.0612	0.0309, 0.0679	0.0232, 0.0568
$\Delta\rho$ (e·Å ⁻³)	0.506, -0.304	0.608, -0.918	0.490, -0.670

Table S2: Cu–Cu and Cu–H distances of all clusters.

[Cu ₈ H ₆ L ₆][PF ₆] ₂ 1			
Cu – Cu	Length (Å)	Cu – H	Length (Å)
Cu1 – Cu4 ¹	2.7760(18)	Cu1 – HA	1.639(12)
Cu1 – Cu4	2.7760(18)	Cu2 – HA	1.640(5)
Cu1 – Cu4 ²	2.7760(18)	Cu4 – HD	1.650(12)
Cu3 – Cu5 ¹	2.8152(19)	Cu3 – HD	1.649(5)
Cu3 – Cu5	2.8152(19)	Cu2 – H	1.59(4)
Cu3 – Cu5 ²	2.8152(19)	Cu3 – H	1.59(4)
Cu4 – Cu4 ¹	2.5575(18)	Cu2 – HC	1.71(5)
Cu4 – Cu4 ²	2.5575(18)	Cu3 – HC	1.70(5)
Cu4 – Cu5 ²	2.5948(16)	Cu5 – HE	1.81(12)
Cu4 – Cu5	2.5939(15)	Cu6 – HE	1.60(5)
Cu5 – Cu5 ²	2.5416(19)	Cu6 – HF	1.63(4)
Cu5 – Cu5 ¹	2.5416(19)		
Cu2 – Cu6	2.8346(19)		
Cu2 – Cu6 ³	2.835(2)		
Cu2 – Cu6 ⁴	2.835(2)		
Cu6 – Cu6 ⁵	2.621(2)		
Cu6 – Cu6 ³	2.5564(18)		
Cu6 – Cu6 ⁴	2.5564(18)		
Cu6 – Cu6 ⁶	2.621(2)		
Average Type A	2.67	Average Type A	1.639
Average Type B	2.647	Average Type B	1.6463
¹ 1-y, +x-y, +z; ² 1+y-x, 1-x, +z; ³ 1+y-x, 2-x, +z;			
⁴ 2-y, 1+x-y, +z; ⁵ 1-y+x, +x, 1-z; ⁶ +y, 1-x+y, 1-z.			

[Cu ₄ HI ₂ L ₄][PF ₆] 2c			
Cu–Cu	Length (Å)	Cu–H	Length (Å)
Cu1 – Cu2	2.6380(6)	Cu1 – H	1.712(12)
Cu4 – Cu3	2.6772(6)	Cu2 – H	1.726(12)
Cu1 – Cu3	2.6261(6)	Cu3 – H	1.724(13)
Cu2 – Cu4	2.8309(6)	Cu4 – H	1.717(12)
Cu2 – Cu3	2.9977(6)		
Cu1 – Cu4	3.0354(6)		
Average	2.802	Average	1.7198

Continued Table S2: Cu–Cu and Cu–H distances of all clusters. (1)

[Cu₄H(N₃)₂L₄][PF₆] 2d			
Cu–Cu	Length (Å)	Cu–H	Length (Å)
Cu1 – Cu2	2.8776(10)	Cu1 – H	1.727(9)
Cu2 – Cu3	2.6423(11)	Cu2 – H	1.724(9)
Cu1 – Cu3	2.9108(10)	Cu3 – H	1.724(9)
Cu1 – Cu4	2.6356(10)	Cu4 – H	1.726(9)
Cu2 – Cu4	2.8212(10)		
Cu4 – Cu3	2.9872(11)		
Average	2.8125	Average	1.725

[Cu₄H(NCS)₂L₄][PF₆] (M) 2e			
Cu–Cu	Length (Å)	Cu–Cu	Length (Å)
Cu1 – Cu2	2.9800(13)	Cu1 – H	1.728(17)
Cu1 – Cu4	2.9229(13)	Cu2 – H	1.736(17)
Cu1 – Cu3	2.5890(13)	Cu3 – H	1.733(18)
Cu2 – Cu4	2.6871(14)	Cu4 – H	1.738(17)
Cu2 – Cu3	2.8549(14)		
Cu4 – Cu3	2.9238(14)		
Average	2.8263	Average	1.734

[Cu₄H(NCS)₂L₄][PF₆] (P) 2e			
Cu–Cu	Length (Å)	Cu–Cu	Length (Å)
Cu1 – Cu2	2.9859(9)	Cu1 – H	1.731(17)
Cu1 – Cu4	2.9170(9)	Cu2 – H	1.737(17)
Cu1 – Cu3	2.5914(9)	Cu3 – H	1.732(17)
Cu2 – Cu4	2.6876(9)	Cu4 – H	1.735(17)
Cu2 – Cu3	2.8612(9)		
Cu4 – Cu3	2.9170(9)		
Average	2.8267	Average	1.734

[Cu₄HBr₃L₃]·CH₂Br₂ (Δ) 3b			
Cu–Cu	Length (Å)	Cu–H	Length (Å)
Cu1 – Cu2 ²	2.9083(11)	Cu1 – H	1.51(16)
Cu1 – Cu2	2.9082(11)	Cu2 ² – H	1.80(9)
Cu1 – Cu2 ¹	2.9083(11)	Cu2 ¹ – H	1.80(9)
Cu2 – Cu2 ¹	2.6235(11)		
Cu2 – Cu2 ²	2.6235(11)		
Average	2.7659	Average	1.729
¹ +y-x, 1-x, +z; ² 1-y, 1+x-y, +z.			

Continued Table S2: Cu–Cu and Cu–H distances of all clusters. (2)

[Cu ₄ HBr ₃ L ₃]·CH ₂ Cl ₂ (Δ) 3b			
Cu–Cu	Length (Å)	Cu–H	Length (Å)
Cu1 – Cu2 ²	2.9083(11)	Cu1 – H	1.814(10)
Cu1 – Cu2	2.9082(11)	Cu2 ² – H	1.656(4)
Cu1 – Cu2 ¹	2.9083(11)	Cu2 ¹ – H	1.656(4)
Cu2 – Cu2 ¹	2.6235(11)		
Cu2 – Cu2 ²	2.6235(11)		
Average	2.7659	Average	1.696
¹ +y-x, 1-x, +z; ² 1-y, 1+x-y, +z.			

[Cu ₄ HBr ₃ L ₃]·CH ₂ Br ₂ (Λ) 3b			
Cu–Cu	Length (Å)	Cu–H	Length (Å)
Cu1 – Cu2 ²	2.9073(12)	Cu1 – H	1.71(5)
Cu1 – Cu2	2.9073(12)	Cu2 ² – H	1.65(11)
Cu1 – Cu2 ¹	2.9073(12)	Cu2 ¹ – H	1.65(11)
Cu2 – Cu2 ²	2.6227(12)		
Cu2 – Cu2 ¹	2.6227(13)		
Average	2.765	Average	1.665
¹ 1-y, 1+x-y, +z; ² +y-x, 1-x, +z			

[Cu ₄ HBr ₃ L ₃]·CH ₂ Cl ₂ (Λ) 3b			
Cu–Cu	Length (Å)	Cu–Cu	Length (Å)
Cu1 – Cu2 ²	2.9073(12)	Cu1 – H	1.706(17)
Cu1 – Cu2	2.9073(12)	Cu2 ² – H	1.701(8)
Cu1 – Cu2 ¹	2.9073(12)	Cu2 ¹ – H	1.701(8)
Cu2 – Cu2 ²	2.6227(12)		
Cu2 – Cu2 ¹	2.6227(13)		
Average	2.765	Average	1.702
¹ 1-y, 1+x-y, +z; ² +y-x, 1-x, +z			

[Cu ₄ HI ₃ L ₃] 3c			
Cu–Cu	Length (Å)	Cu–H	Length (Å)
Cu1 – Cu2	2.6639(10)	Cu1 – H	1.63(8)
Cu2 – Cu3	2.6231(9)	Cu2 – H	1.79(8)
Cu1 – Cu3	2.6683(10)	Cu3 – H	1.62(8)
Cu1 – Cu4	2.8842(10)	Cu4 – H	1.79(8)
Cu2 – Cu4	2.9068(10)		
Cu4 – Cu3	2.9310(10)		
Average	2.7796	Average	1.708

Table S3: Crystal information of Cu₄H clusters.

	Space group	Z	Cell volume/Å ³	Racemic /Enantiomeric
[Cu ₄ HCl ₂ L ₄] ⁺	<i>P2₁/c</i>	4	7162.80	Racemic crystal
[Cu ₄ HBr ₂ L ₄] ⁺	<i>P</i> -1	2	3667.0	Racemic crystal
[Cu ₄ HI ₂ L ₄] ⁺	<i>P2₁/n</i>	4	6955.14	Racemic crystal
[Cu ₄ H(N ₃) ₂ L ₄] ⁺	<i>Cc</i>	4	7267.98	Racemic crystal
[Cu ₄ H(NCS) ₂ L ₄] ⁺ <i>M</i>	<i>P2₁2₁2₁</i>	4	7574.10	Enantiomeric crystals
[Cu ₄ H(NCS) ₂ L ₄] ⁺ <i>P</i>	<i>P2₁2₁2₁</i>	4	7553.54	Enantiomeric crystals
[Cu ₄ HBr ₃ L ₃] Δ	<i>R3</i>	3	4202.54	Enantiomeric crystals
[Cu ₄ HBr ₃ L ₃] Λ	<i>R3</i>	3	4198.46	Enantiomeric crystals
[Cu ₄ HI ₃ L ₃]	<i>Fdd2</i>	16	21518.9	Racemic crystal

* [Cu₄HBr₂L₄]⁺ was determined at 203 K. The other data were determined at 100 K.

Table S4: Neighboring clusters' hydrogen bonds of Cu₄ clusters (Å, °)

2a [Cu₄HCl₂L₄]⁺ (<i>P2₁/c</i>)				
A...H-D	d(D-H)	d(H...A)	d(D...A)	∠ (DHA)
Cl1...H49-C49 ⁱ	0.950	2.868	3.557	130.229
Cl1...H60-C60 ⁱⁱ	0.950	3.740	4.513	140.450
Cl2...H66-C66 ⁱⁱⁱ	0.950	2.997	3.694	131.379
Cl2...H10-C10 ^{iv}	0.950	3.024	3.752	134.521

ⁱ 1-x, 1-y, 1-z; ⁱⁱ +x, 1/2-y, 1/2+z; ⁱⁱⁱ 1-x, 1-y, -z; ^{iv} +x, 1/2-y, -1/2+z.

2b [Cu₄HBr₂L₄]⁺ (<i>P</i>-1)				
A...H-D	d(D-H)	d(H...A)	d(D...A)	∠ (DHA)
Br1...H56A-C56 ⁱ	0.94	2.863	3.588	134.733
Br2...H38A-C38 ⁱⁱ	0.94	2.783	3.445	128.292

ⁱ 1-x, -y, 1-z; ⁱⁱ 1-x, 1-y, -z.

2c [Cu₄HI₂L₄]⁺ (<i>P2₁/n</i>)				
A...H-D	d(D-H)	d(H...A)	d(D...A)	∠ (DHA)
I1...H49-C49 ⁱ	0.930	3.233	3.977	138.437
I1...H60-C60 ⁱⁱ	0.930	3.273	3.713	111.290
I2...H13-C13 ⁱⁱⁱ	0.930	3.382	3.779	108.344
I2...H24-C24 ^{iv}	0.930	3.221	3.855	127.141

ⁱ +x, -1+y, +z; ⁱⁱ +x, 1/2-y, 1/2+z; ⁱⁱⁱ +x, 1+y, +z; ^{iv} -x, 1-y, 1-z.

Continued Table S4: Neighboring clusters' hydrogen bonds for Cu₄ clusters (Å, °)
(1)

2e [Cu₄H(NCS)₂L₄]⁺ (M) (P2₁2₁2₁)				
A...H-D	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
S1...H47-C47 ⁱ	0.950	3.081	3.799	133.582
S1...H32-C32 ⁱⁱ	0.950	2.854	3.629	139.561
S2...H4-C4 ⁱⁱⁱ	0.950	3.008	3.804	142.282
S2...H9-C9 ^{iv}	0.950	3.022	3.876	150.267

ⁱ 1/2+x, 3/2-y, 1-z; ⁱⁱ 1+x, +y, +z; ⁱⁱⁱ 1-x, 1/2+y, 3/2-z; ^{iv} -1+x, +y, +z.

2e [Cu₄H(NCS)₂L₄]⁺ (P) (P2₁2₁2₁)				
A...H-D	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
S1...H2-C2 ⁱ	0.950	3.010	3.792	142.743
S1...H9-C9 ⁱⁱ	0.950	3.045	3.880	150.105
S2...H32-C32 ⁱⁱⁱ	0.950	2.855	3.631	141.710
S2...H47-C47 ^{iv}	0.950	3.080	3.795	135.013

ⁱ 1-x, -1/2+y, 1/2-z; ⁱⁱ 1+x, +y, +z; ⁱⁱⁱ -1+x, +y, +z; ^{iv} -1/2+x, 3/2-y, 1-z.

3b [Cu₄HBr₃L₃] (R3)(Δ)				
A...H-D	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
Br1...H9-C9 ⁱ	0.930	2.866	3.524	128.815

ⁱ -1/3+x, -2/3+y, 1/3+z.

3b [Cu₄HBr₃L₃] (R3)(Λ)				
A...H-D	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
Br1...H15-C15 ⁱ	0.950	2.850	3.523	128.726

ⁱ 2/3+x, 1/3+y, 1/3+z.

3c [Cu₄HI₃L₃] (Fdd2)				
A...H-D	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
I1...H43-C43 ⁱ	0.930	3.095	3.839	138.248
I1...H22-C22 ⁱⁱ	0.930	3.228	3.886	129.438
I2...H50-C50 ⁱⁱⁱ	0.930	3.256	3.806	119.888
I2...H9-C9 ^{iv}	0.930	3.195	4.078	159.116
I3...H37-C37 ^v	0.930	2.945	3.713	140.899

ⁱ -1/4+x, 5/4-y, 1/4+z; ⁱⁱ 1-x, 3/2-y, 1/2+z; ⁱⁱⁱ 5/4-x, -1/4+y, -1/4+z;
^{iv} 5/4-x, -1/4+y, 3/4+z; ^v +x, +y, -1+z.

Table S5: Short contacts in Key-lock relationship, π - π distances Å, angles °

	[Cu ₄ HBr ₃ L ₃] Δ	[Cu ₄ HBr ₃ L ₃] Λ
Shortest C-C ring1-ring2	3.469	3.472
d center1-center2	4.729	4.727
d center2-plane1	3.683	3.683
θ	38.8	38.8
Dihedral angle plane1-plane2	28.4	28.2

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