Supporting information

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

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Refinement of hydrides

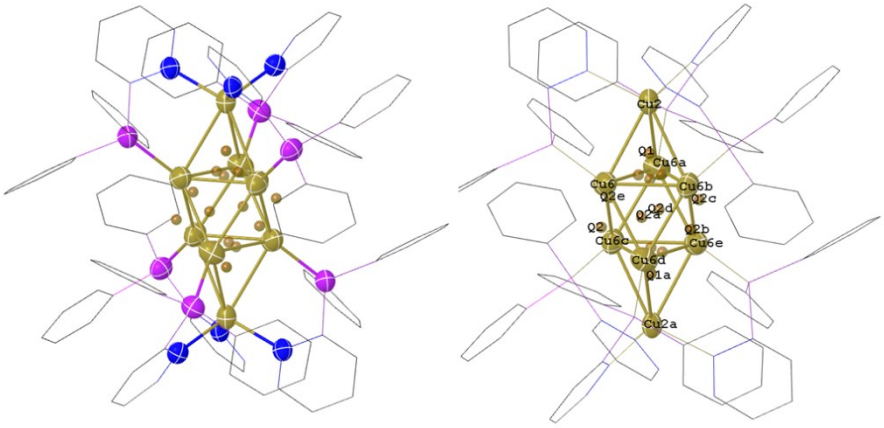
In each case, the positions of the hydrides were detected from the difference electron density map, and their positions were allowed to refine freely, or with restraints of the Cu–H distances of the hydride to be equal (via SADI).

The positions of six the hydrides in $[Cu_8H_6L_6]^{2+}$ were determined by high quality crystallography diffraction data and corroborated by DFT calculations. There are two independent $[Cu_8H_6L_6]^{2+}$ clusters per unit cell. In type A $[Cu_8H_6L_6]^{2+}$ (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 $[Cu_8H_6L_6]^{2+}$, 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.

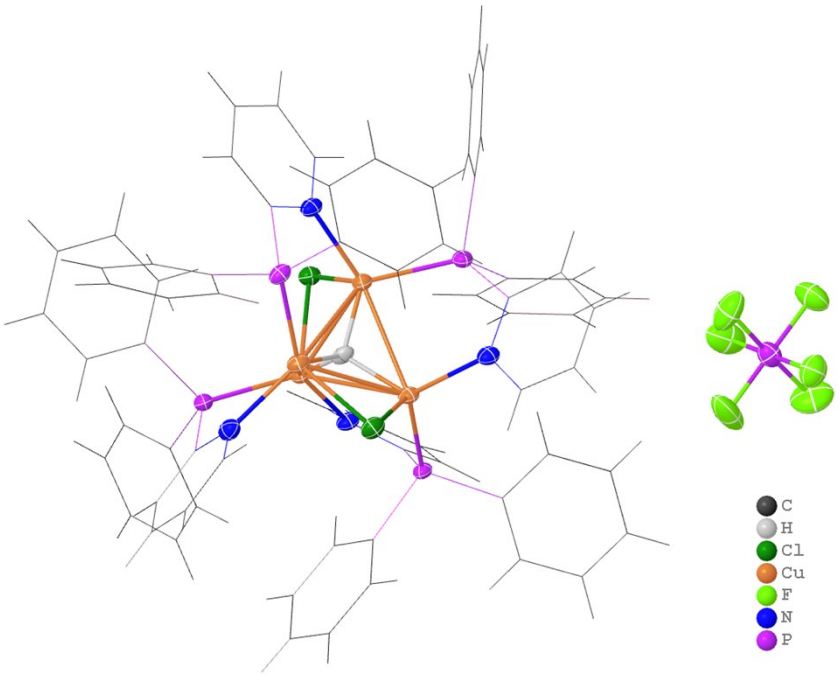
In the final stage of crystallographic data refinement, 6 hydrides position could be located by residual electron density: The max peak (Q1 = 1.98) was located at center of copper tetrahedron and the Q2 = 1.33 was found at triply-bridge triangle copper face. These two Q peaks were refined as 2 μ_4 hydrides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

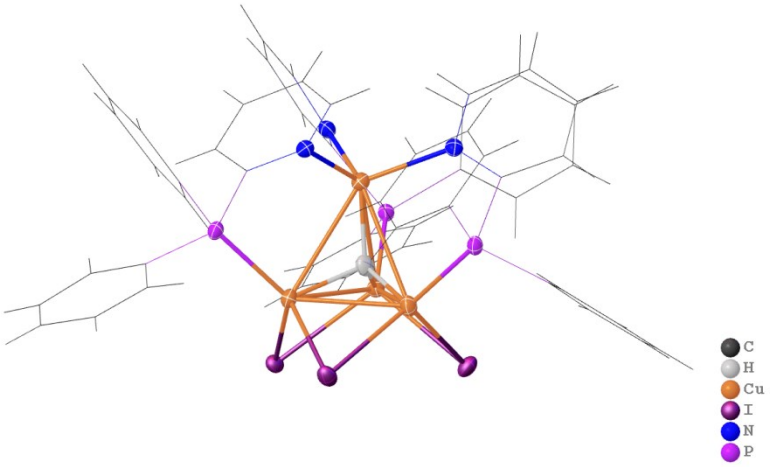
The anisotropic refinement of μ_4 hydride has been performed in series **2** and **3**.[1]

Figure S1 a: Refinement of hydrides: residual peaks Q1 and Q2 e·A^{-3} in $[Cu_8H_6L_6]^{2+}$ and the anisotropic refinement of μ_4 hydride in 2 and 3 clusters.



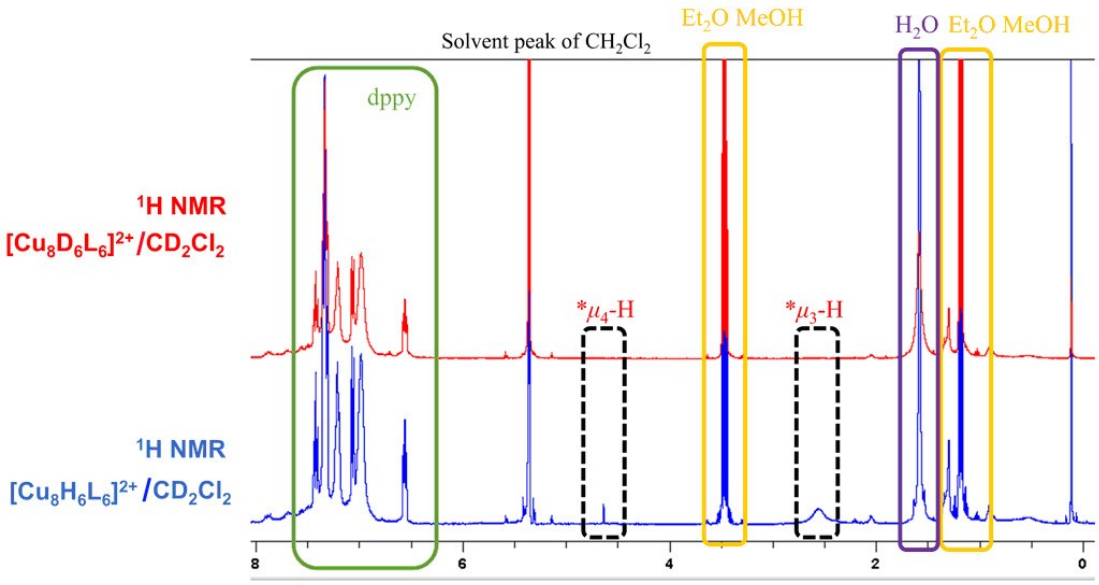
Q1 = 1.98 2 μ-4
Q2 = 1.33 6 μ-3



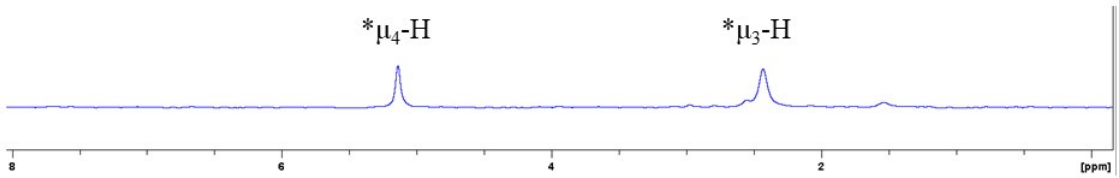


NMR

Figure S2 a: $[Cu_8D_6L_6]^{2+}$ ^{1}H NMR and $[Cu_8H_6L_6]^{2+}$ ^{1}H NMR and $[Cu_8D_6L_6]^{2+}$ ^{2}H NMR.



^{2}H NMR of $[Cu_8D_6L_6]^{2+}$ / CH_2Cl_2



^{1}H NMR proves that there are two types of hydrides in $[Cu_8H_6L_6]^{2+}$(single peak at 4.6 ppm is attributed as μ_4-H and peak at 2.6 ppm is attributed as μ_3-H). The broad peak of ^{1}H 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]

^{2}H NMR of $[Cu_8D_6L_6]^{2+}$ in CH_2Cl_2 indicates that there are two types of deuterides in $[Cu_8D_6L_6]^{2+}$ (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: ^{1}H NMR of 2c, 2e, 3b, 3c in CD_2Cl_2.

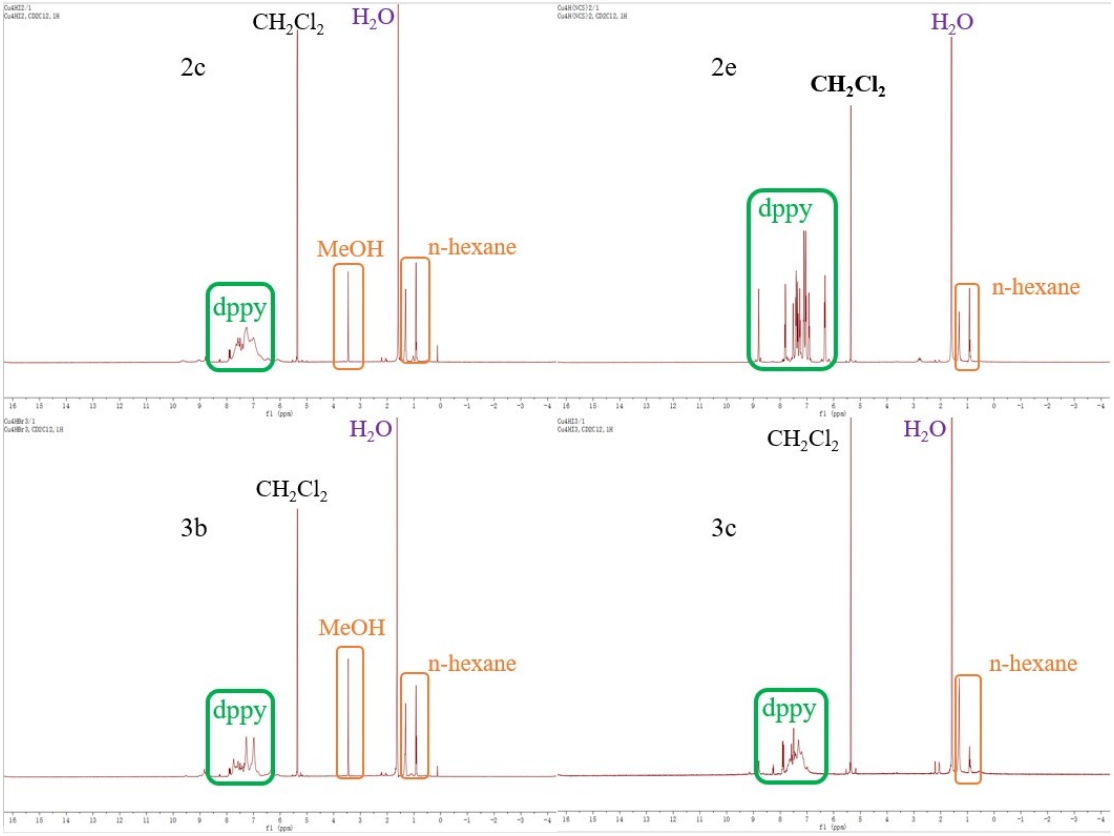
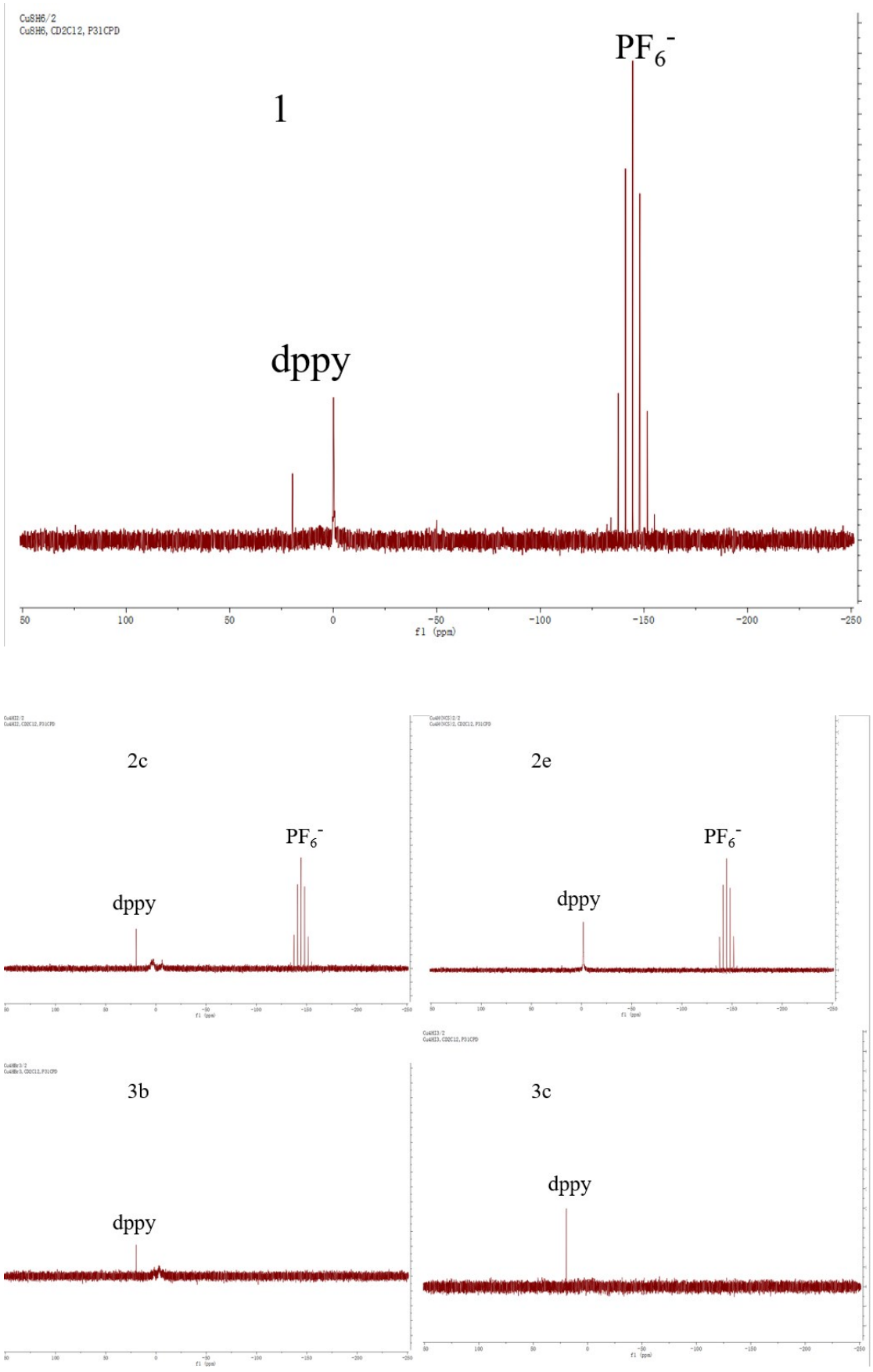
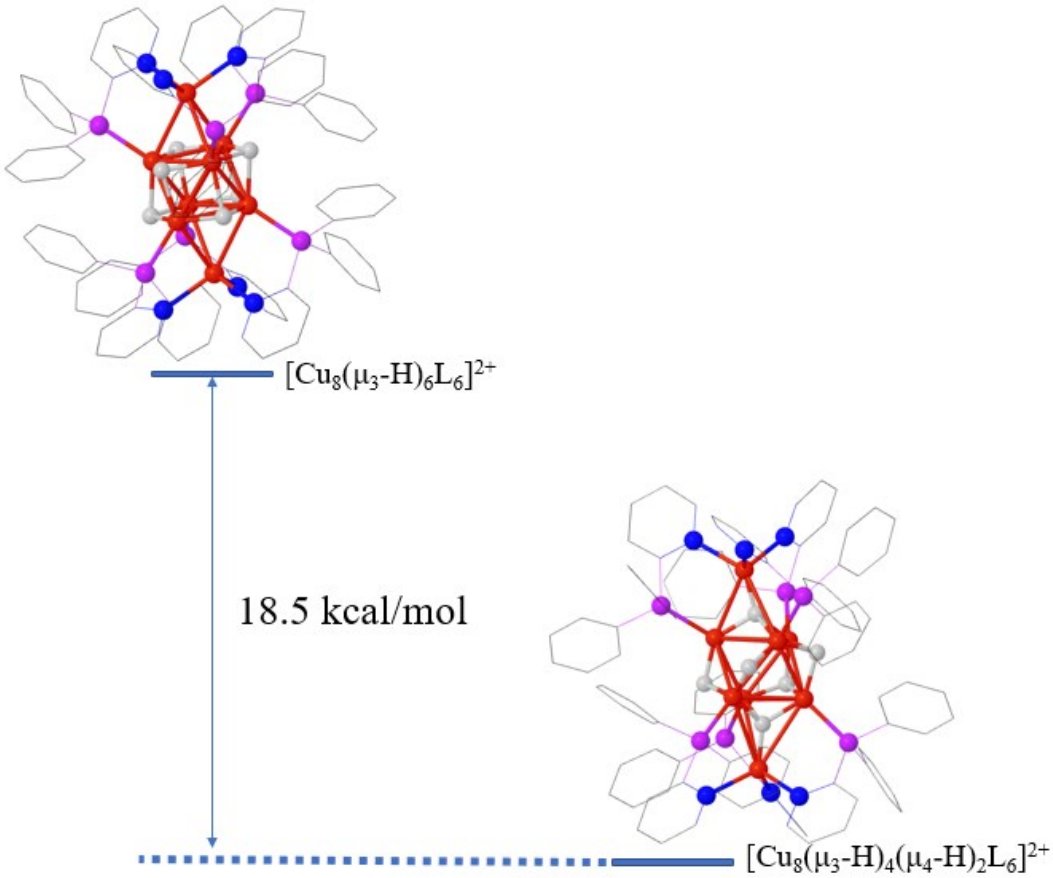


Figure S2 c: ^{31}P NMR of 1, 2c, 2e, 3b, 3c in CD_2Cl_2.



DFT calculation

Figure S3: Density functional theory (DFT) calculations of $[Cu_8H_6L_6]^{2+}$.



Coordinate of $[Cu_8(\mu_3\text{-}H)_6L_6]^{2+}$

Cu	-0.946102	-2.995137	0.606225	C	3.257826	-5.681147	0.043885
Cu	1.036295	-1.434753	-0.372287	H	2.956087	-6.217707	-0.851272
H	1.911368	0.207912	-0.892642	C	-0.207553	-6.253774	-3.036204
P	1.984841	-3.365750	-1.035510	H	-0.097300	-6.947125	-3.864484
N	-0.488312	-4.455031	-0.921167	C	3.299855	-3.649965	1.369219
C	-1.492977	-5.274911	-1.270244	H	3.003586	-2.614234	1.500442
H	-2.406666	-5.173420	-0.695648	C	3.983932	-6.339718	1.036093
C	0.673132	-4.526835	-1.608255	H	4.248238	-7.385506	0.909386
C	-1.398024	-6.189347	-2.315445	C	4.342980	-3.704407	-2.614539
H	-2.248028	-6.812945	-2.566546	H	4.753565	-4.309152	-1.811826
C	0.842420	-5.409091	-2.677601	C	4.378756	-5.651481	2.188086
H	1.782564	-5.423975	-3.217986	H	4.949842	-6.166330	2.955270
C	3.047822	-3.183780	-2.507605	C	2.526246	-2.396579	-3.551773
C	2.919118	-4.328652	0.202122	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
H	-1.907356	-3.347176	5.769302
C	1.230298	-5.174140	4.472813
H	1.759018	-5.664054	5.284840
C	-3.369126	-1.075174	3.685116
H	-3.114046	-0.404876	2.870661
C	-4.005645	-2.867555	5.733554
H	-4.255137	-3.565468	6.527446
C	-0.215668	-0.477417	6.263751
H	-1.236631	-0.746108	6.516703
C	-5.006926	-2.087647	5.145543
H	-6.034291	-2.182797	5.485027
C	1.624682	-0.439430	4.682419
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
H	3.442430	0.475552	5.368655
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
H	-1.228587	1.123679	-1.312240
P	-3.433125	-1.704047	-1.287385
N	-3.072018	-3.266313	0.891018
C	-3.431565	-4.001167	1.955931
H	-2.618636	-4.445999	2.518599
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C	-4.756546	-4.175222	2.345579
H	-4.987862	-4.763053	3.226113
C	-5.391566	-2.792126	0.489915
H	-6.138900	-2.287396	-0.112422
C	-4.790961	-0.523855	-1.593506
C	-3.429730	-2.905927	-2.661136
C	-4.452180	-3.841453	-2.881061
H	-5.304347	-3.886032	-2.208693
C	-5.755766	-3.553844	1.599755
H	-6.800489	-3.657411	1.876828
C	-2.325835	-2.868323	-3.525893
H	-1.521576	-2.167041	-3.327987
C	-4.376967	-4.715902	-3.965098
H	-5.171747	-5.436206	-4.135623
C	-5.646699	-0.574309	-2.700377
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H	-3.232796	-5.336911	-5.683057
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H	-7.490080	2.225641	-2.098453
C	-6.612784	0.419903	-2.881074
H	-7.274372	0.376627	-3.741300
Cu	0.945700	2.994736	-0.606230
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
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H	-1.782991	5.424189	3.217511
C	-3.048137	3.183768	2.507509
C	-2.919664	4.327816	-0.202412
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H	-2.955343	6.217670	0.849588
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H	-3.005998	2.612277	-1.499142
C	-3.984917	6.338416	-1.036924
H	-4.248907	7.384353	-0.910788
C	-4.343486	3.704004	2.614069
H	-4.754244	4.308119	1.810971
C	-4.381090	5.649310	-2.187934
H	-4.952877	6.163648	-2.954939
C	-2.526314	2.397437	3.552209
H	-1.537684	1.956805	3.450519
C	-4.039152	4.305970	-2.352767
H	-4.341780	3.768208	-3.246198
C	-3.283959	2.162403	4.696123
H	-2.872853	1.555510	5.497204
C	-4.577479	2.684677	4.799303
H	-5.171488	2.492800	5.687762
C	-5.106014	3.448371	3.757625
H	-6.110433	3.854082	3.835812
Cu	0.412740	0.564196	-1.669059
H	-0.150327	-1.287071	-1.677571
P	0.660963	1.579164	-3.663626
N	0.112925	3.899111	-2.385251
C	-0.372366	5.142596	-2.238749
H	-0.225184	5.595275	-1.264709
C	-0.050194	3.277240	-3.574075
C	-1.046265	5.818673	-3.251956
H	-1.434975	6.814024	-3.071379
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H	-0.853784	3.345992	-5.568239
C	-0.300858	0.797132	-5.002807
C	2.357365	1.838368	-4.285316
C	2.683911	2.743619	-5.306459
H	1.907993	3.347650	-5.768396

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H	-1.758401	5.663887	-5.285284
C	3.369475	1.075588	-3.684063
H	3.114174	0.404884	-2.870008
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
C	-1.623957	0.438491	-4.682501
H	-2.011016	0.647323	-3.688228
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H	5.463657	0.590750	-3.657620
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H	-3.441346	-0.477121	-5.368853
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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	C	5.883604	-1.510739	0.850293
H	3.232178	5.337705	5.682626	H	5.965352	-2.324231	0.135736
C	4.906200	-0.535178	0.674543	C	6.737626	-1.455445	1.956696
H	4.212909	-0.598800	-0.160497	H	7.493565	-2.221964	2.098260
C	2.259992	3.735966	4.615985	C	6.614292	-0.417368	2.881294
H	1.408326	3.690339	5.287977	H	7.275801	-0.373587	3.741556

Coordinate of $[Cu_8(\mu_3\text{-}H)_4(\mu_4\text{-}H)_2L_6]^{2+}$

Cu	12.791103	22.096706	10.573643	C	14.653192	15.224383	8.710593
Cu	12.841877	20.816497	8.185956	H	15.318238	14.444946	9.070607
H	12.887793	20.306790	6.574168	Cu	13.573021	23.418765	8.007247
P	13.803168	19.209771	9.510094	H	12.847175	22.370746	5.025009
N	12.635343	20.215873	11.701006	P	14.414195	24.807460	9.618544
C	12.088631	20.216704	12.925478	N	14.662828	22.805250	11.404092
H	11.801311	21.187658	13.315428	C	15.268984	22.050550	12.333321
C	13.003807	19.034846	11.160121	H	14.709136	21.191806	12.683332
C	11.880392	19.055641	13.666055	C	15.327004	23.880375	10.918501
H	11.438408	19.113562	14.655124	C	16.548761	22.314571	12.814236
C	12.801860	17.823078	11.823438	H	16.994234	21.658005	13.552826
H	13.087886	16.892225	11.347801	C	16.612012	24.212836	11.350127
C	13.845357	17.510098	8.827863	H	17.110060	25.081418	10.934692
C	15.528928	19.616249	9.960928	C	15.662814	25.971282	8.950052
C	16.207264	19.007985	11.027730	C	13.272401	25.838115	10.607836
H	15.692905	18.300390	11.672067	C	13.630149	26.381650	11.851116
C	12.237880	17.834148	13.098857	H	14.608463	26.172461	12.275055
H	12.081435	16.904934	13.638485	C	17.233748	23.417604	12.312156
C	16.190086	20.570505	9.174822	H	18.233982	23.656481	12.660727
H	15.661409	21.075714	8.373775	C	12.000728	26.100958	10.078542
C	17.542651	19.322549	11.278227	H	11.718159	25.654852	9.130340
H	18.065720	18.842836	12.100540	C	12.735191	27.196324	12.544670
C	14.699981	16.495090	9.284635	H	13.021844	27.622628	13.501762
H	15.416183	16.699112	10.073227	C	15.860737	27.271948	9.433911
C	18.203083	20.258174	10.477274	H	15.257341	27.644698	10.254733
H	19.243065	20.501219	10.674437	C	11.474529	27.466302	12.005758
C	12.963635	17.237383	7.770958	H	10.779662	28.103046	12.545398
H	12.331997	18.032896	7.390806	C	16.436784	25.513414	7.869176
C	17.522994	20.887212	9.433032	H	16.265386	24.514138	7.478509
H	18.026069	21.623077	8.813263	C	11.107813	26.914508	10.776522
C	12.914740	15.964631	7.200950	H	10.125550	27.116930	10.359353
H	12.230756	15.768207	6.381497	C	17.405654	26.338128	7.298755
C	13.757620	14.956285	7.671696	H	18.002066	25.970985	6.468810
H	13.723672	13.966024	7.227379	C	17.600860	27.632243	7.788729

H	**18.351098**	**28.277102**	**7.340909**
C	**16.826537**	**28.097378**	**8.853698**
H	**16.972655**	**29.104115**	**9.234060**
Cu	**11.091326**	**22.972744**	**7.847302**
H	**10.520621**	**22.578061**	**6.265157**
P	**9.588847**	**22.507082**	**9.473355**
N	**11.184697**	**23.169004**	**11.563138**
C	**11.515506**	**23.789274**	**12.705255**
H	**12.558293**	**23.714111**	**12.996804**
C	**9.907035**	**23.257210**	**11.125077**
C	**10.604439**	**24.509534**	**13.473449**
H	**10.930196**	**24.999778**	**14.383782**
C	**8.934266**	**23.962545**	**11.838236**
H	**7.919683**	**24.013822**	**11.461080**
C	**7.833500**	**22.856526**	**9.107835**
C	**9.626716**	**20.704563**	**9.786117**
C	**9.385994**	**20.134766**	**11.041796**
H	**9.210949**	**20.772411**	**11.903212**
C	**9.286262**	**24.591272**	**13.032120**
H	**8.543254**	**25.141276**	**13.601697**
C	**9.859065**	**19.866960**	**8.683140**
H	**10.026681**	**20.302762**	**7.704224**
C	**9.376956**	**18.747389**	**11.192359**
H	**9.191563**	**18.313511**	**12.169853**
C	**6.766328**	**22.209197**	**9.747348**
H	**6.963683**	**21.470916**	**10.518698**
C	**9.604875**	**17.919202**	**10.091388**
H	**9.591100**	**16.839931**	**10.210960**
C	**7.569160**	**23.778979**	**8.084109**
H	**8.400203**	**24.254387**	**7.568800**
C	**9.839992**	**18.481398**	**8.834893**
H	**9.997591**	**17.845403**	**7.970456**
C	**6.253048**	**24.064482**	**7.717543**
H	**6.054510**	**24.780755**	**6.925549**
C	**5.194299**	**23.424262**	**8.366202**
H	**4.169930**	**23.643106**	**8.080023**
C	**5.452072**	**22.496035**	**9.379641**
H	**4.628868**	**21.992575**	**9.877777**
Cu	**12.782040**	**22.076267**	**3.408415**
Cu	**12.167697**	**23.767158**	**5.801813**
H	**12.178017**	**24.390069**	**7.432970**
P	**12.116381**	**25.315380**	**4.159863**
N	**13.595824**	**23.820986**	**2.425538**

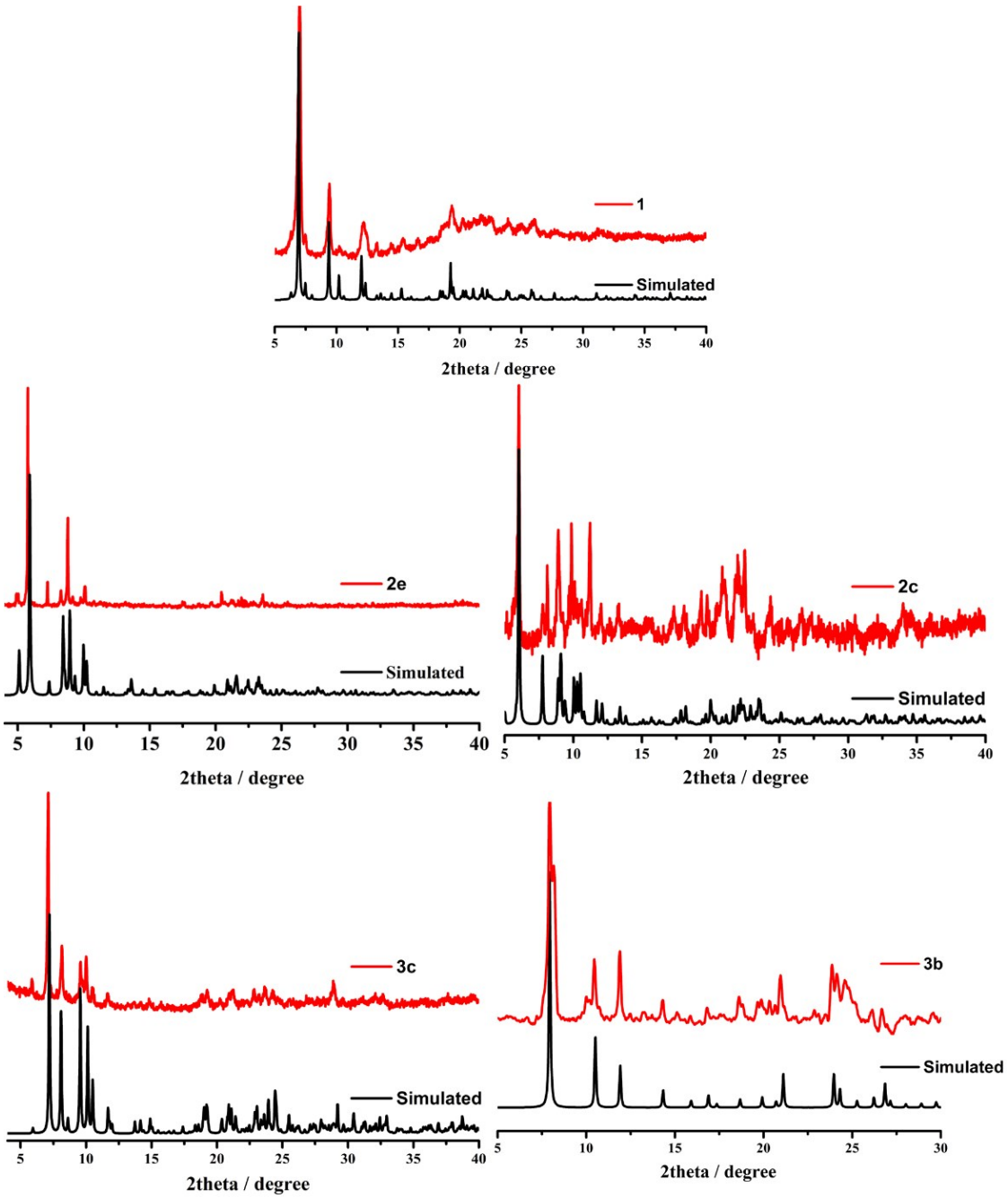
C	**14.504014**	**23.595882**	**1.462472**
H	**14.663790**	**22.555939**	**1.198143**
C	**13.372716**	**25.094360**	**2.819662**
C	**15.223182**	**24.613397**	**0.842409**
H	**15.952053**	**24.372976**	**0.076771**
C	**14.061325**	**26.169750**	**2.251545**
H	**13.866442**	**27.177560**	**2.599811**
C	**12.490252**	**26.989437**	**4.785981**
C	**10.543227**	**25.394372**	**3.233047**
C	**10.400031**	**26.058810**	**2.006235**
H	**11.255072**	**26.548376**	**1.548655**
C	**14.993687**	**25.927157**	**1.244154**
H	**15.535500**	**26.750024**	**0.787634**
C	**9.437669**	**24.738139**	**3.796884**
H	**9.562905**	**24.186926**	**4.725422**
C	**9.159886**	**26.091938**	**1.367534**
H	**9.052237**	**26.616672**	**0.422707**
C	**11.910515**	**28.171255**	**4.307471**
H	**11.160188**	**28.132892**	**3.524047**
C	**8.058447**	**25.454491**	**1.944287**
H	**7.094004**	**25.483640**	**1.445801**
C	**13.441096**	**27.051842**	**5.820486**
H	**13.855989**	**26.134635**	**6.229260**
C	**8.199884**	**24.773050**	**3.155393**
H	**7.349547**	**24.260696**	**3.596217**
C	**13.830697**	**28.283308**	**6.343560**
H	**14.571221**	**28.319062**	**7.136047**
C	**13.254561**	**29.459940**	**5.855710**
H	**13.548810**	**30.420343**	**6.268515**
C	**12.291267**	**29.402330**	**4.846542**
H	**11.834978**	**30.315874**	**4.476934**
Cu	**11.611100**	**21.285641**	**5.867893**
H	**12.445479**	**22.284727**	**8.943639**
P	**10.380071**	**20.064628**	**4.420692**
N	**10.891216**	**21.818952**	**2.432525**
C	**10.635562**	**22.561437**	**1.343866**
H	**11.449356**	**23.190806**	**1.000358**
C	**9.908692**	**21.031848**	**2.924493**
C	**9.402912**	**22.557261**	**0.696700**
H	**9.245161**	**23.187913**	**-0.170405**
C	**8.643220**	**20.978029**	**2.337362**
H	**7.876509**	**20.344629**	**2.769542**
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**

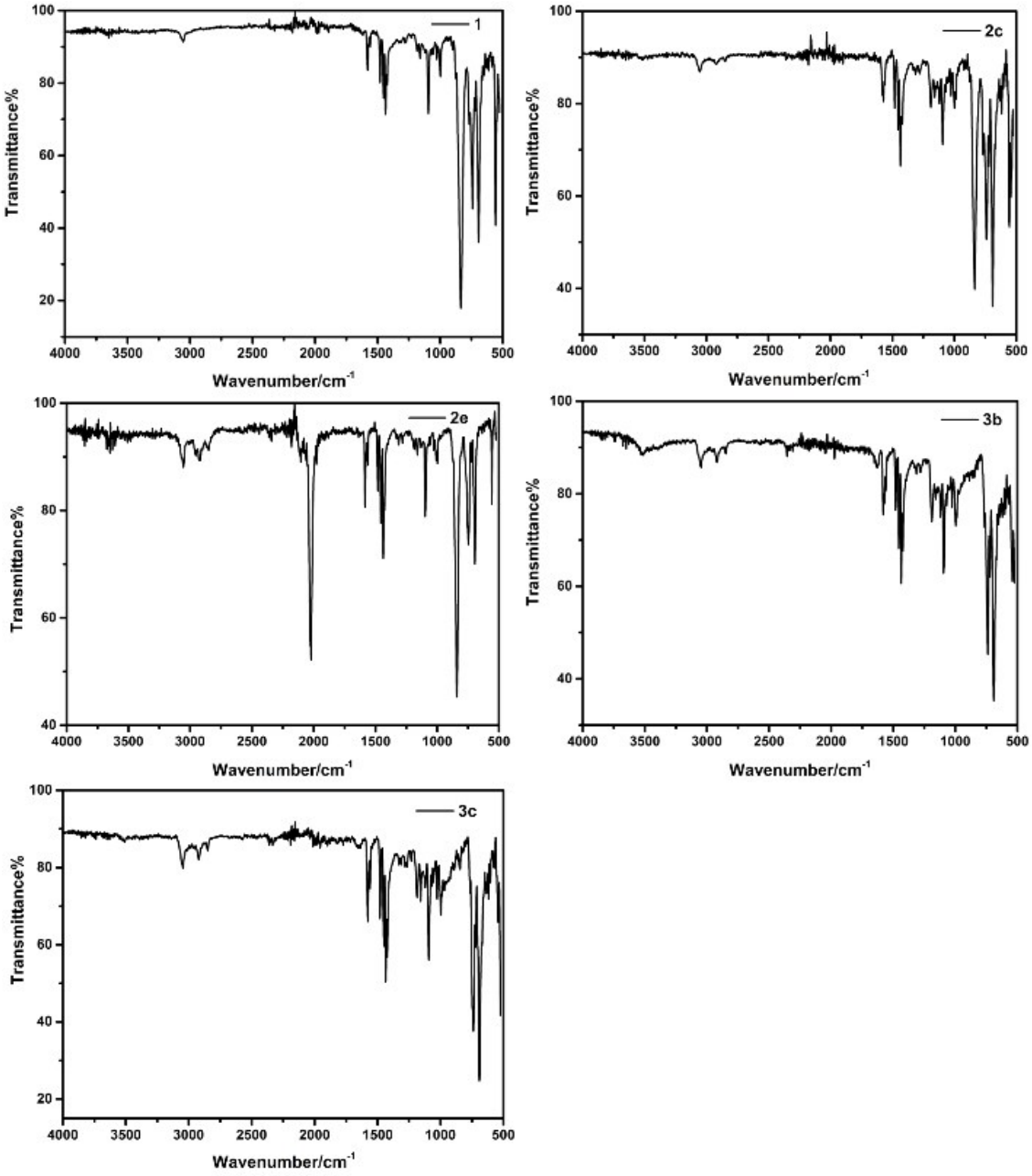
PXRD

Figure S4: Experimental and simulated PXRD patterns.



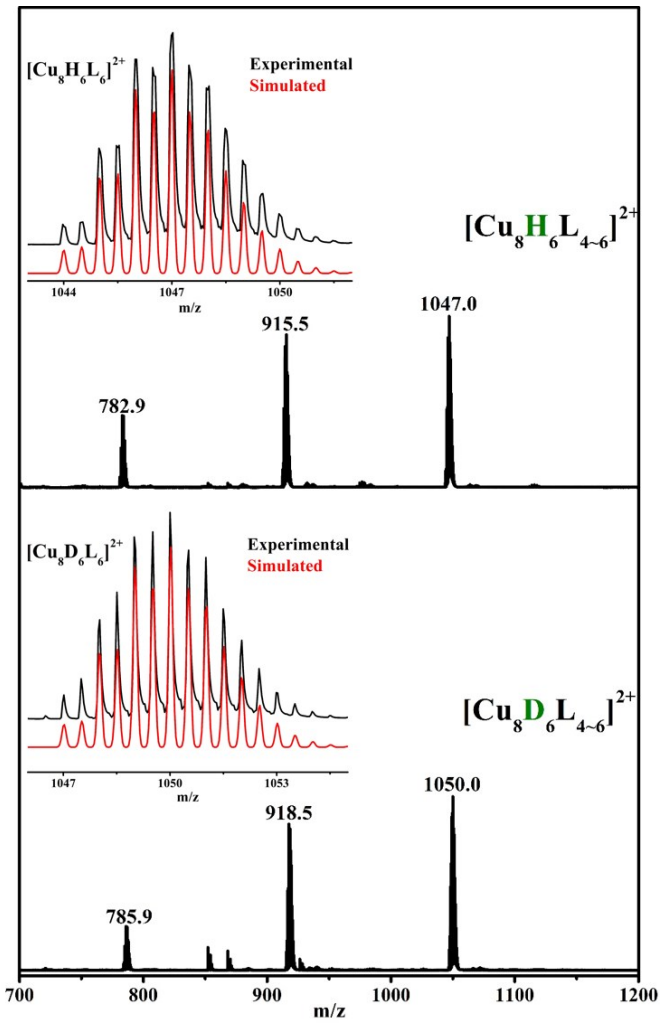
IR

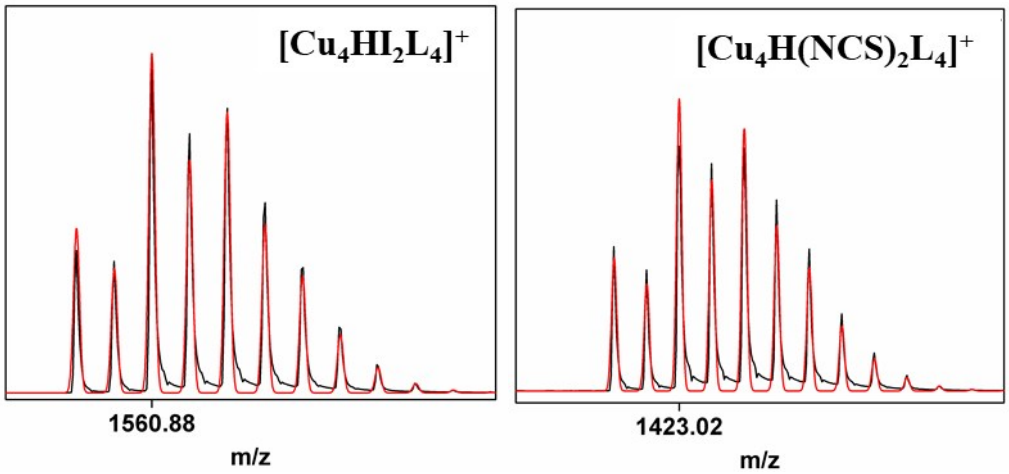
Figure S5: The IR spectra.



MS

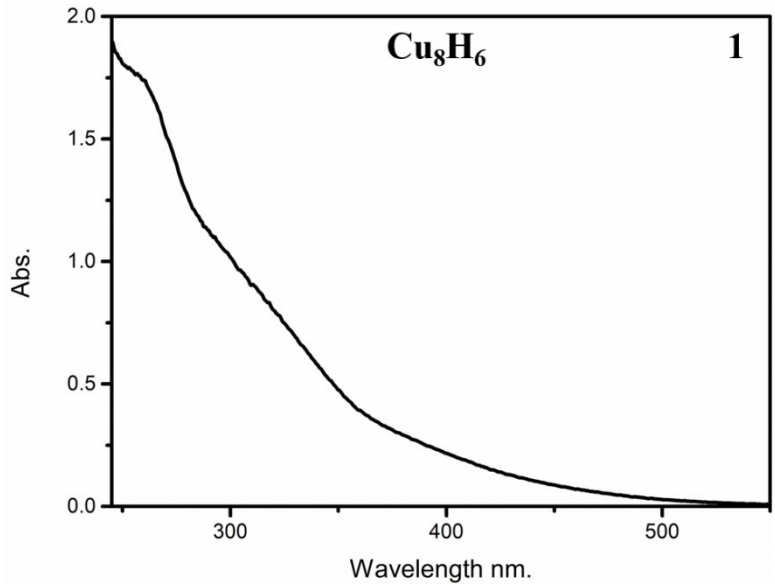
Figure S6: ESI–TOF–MS of $[Cu_8H_6L_6]^{2+}$, $[Cu_8D_6L_6]^{2+}$, $[Cu_4HI_2L_4]^{+}$ and $[Cu_4H(NCS)_2L_4]^{+}$.

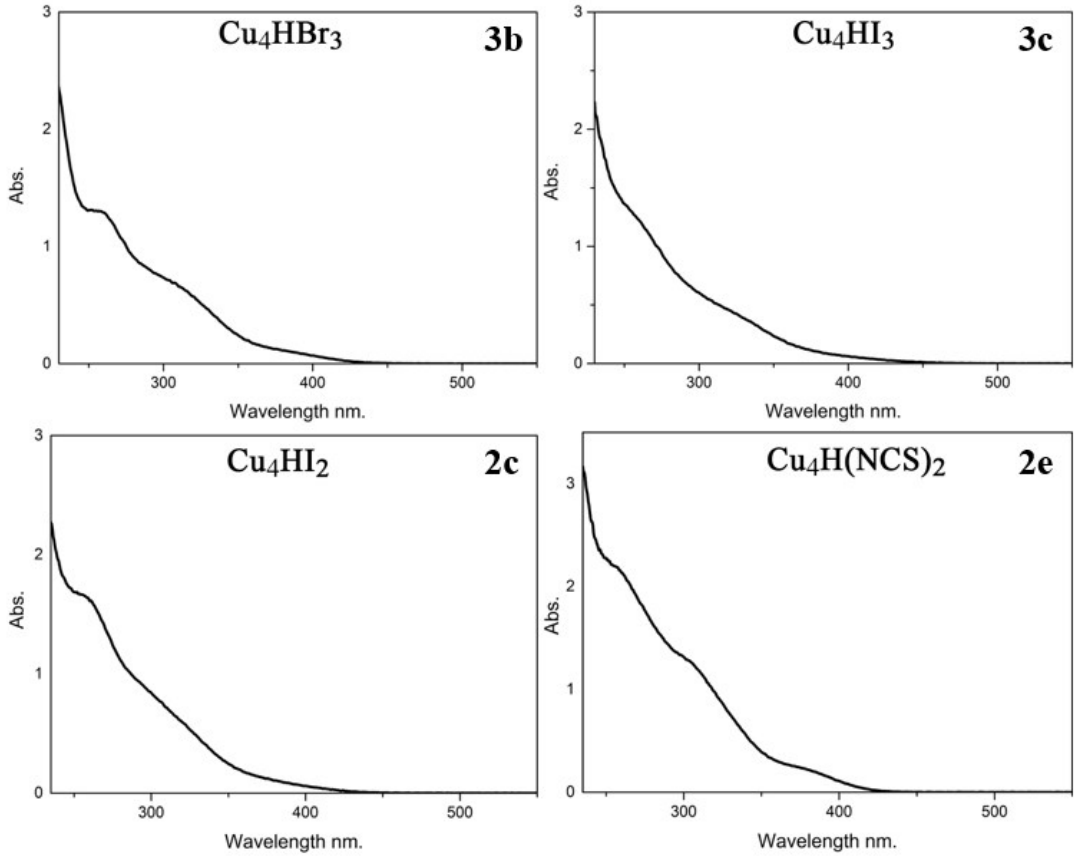




UV/Vis

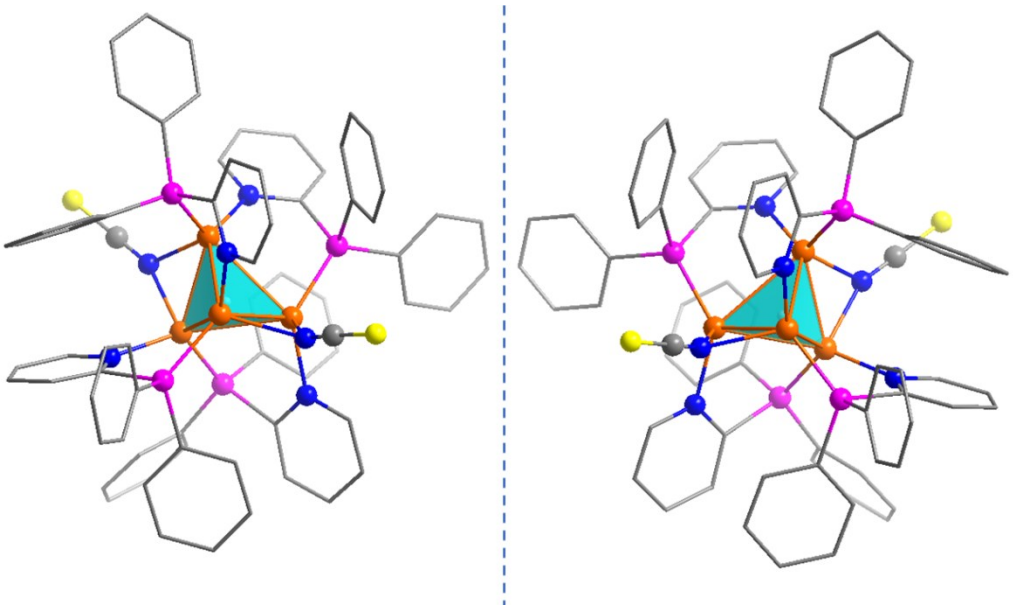
Figure S7: UV/Vis absorption spectra of 1, 3b, 3c, 2c and 2e in dichloromethane solution.



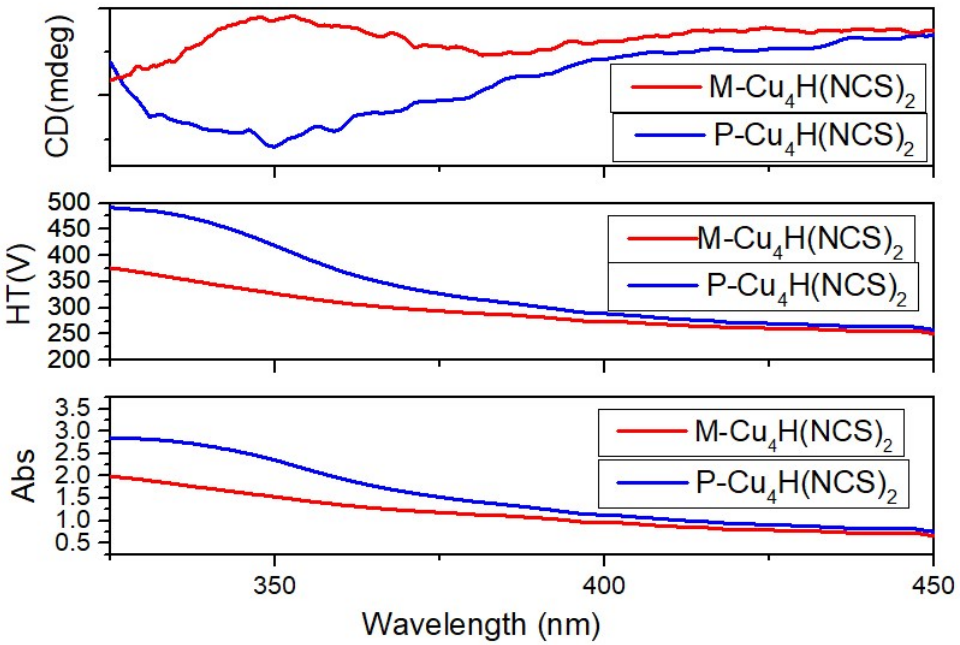


CD

Figure S8: CD of *M*-[$Cu_4H(NCS)_2$][PF_6] and *P*-[$Cu_4H(NCS)_2$][PF_6] enantiomers (From top to bottom are CD, voltage and absorption *vs.* wavelength (nm), respectively).



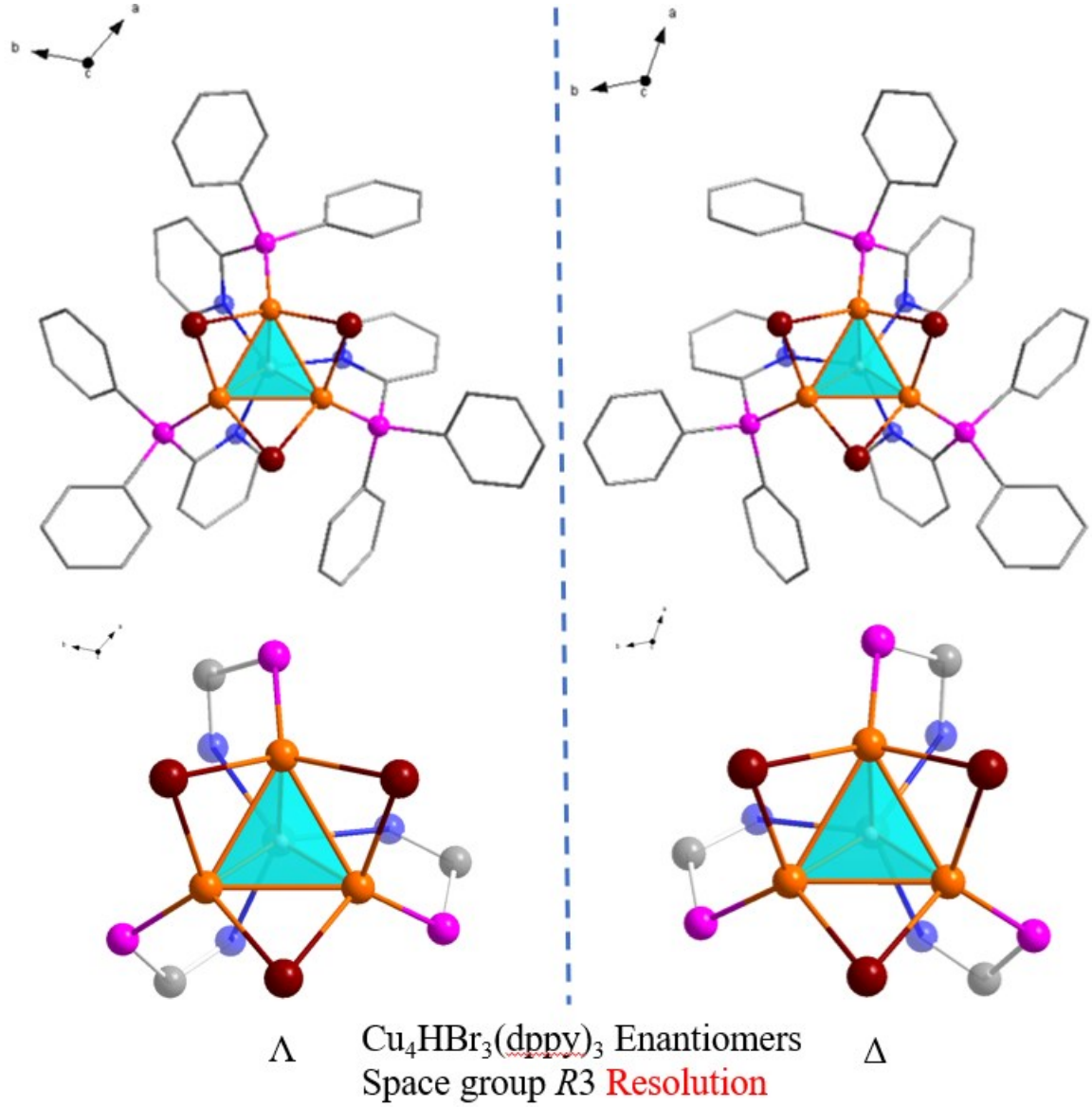
Enantiomers of $[Cu_4H(NCS)_2]^+$ left: *M*, right: *P*.



Yellow crystals of *M* and *P* enantiomers of $[Cu_4H(NCS)_2L_4][PF_6]$were prepared as KBr pellets (m_s : m_{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 [Cu_4HBr_3] (3b). Left: Λ Right: Δ.



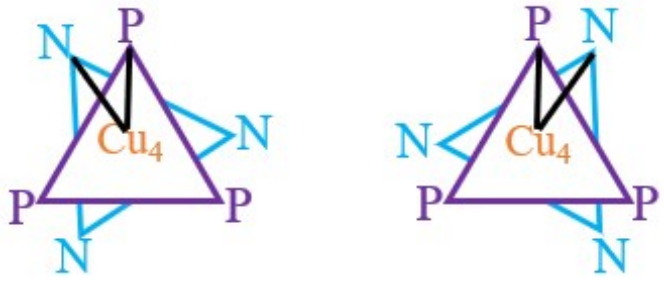
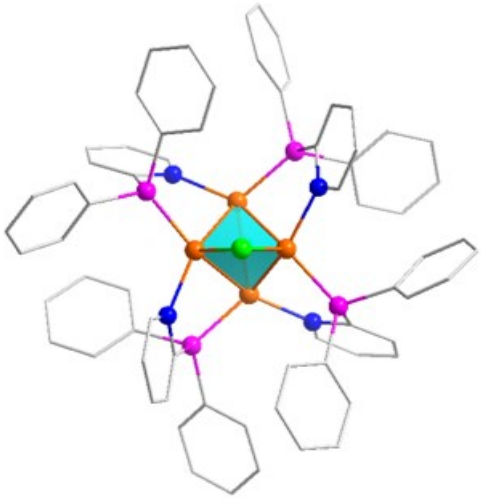
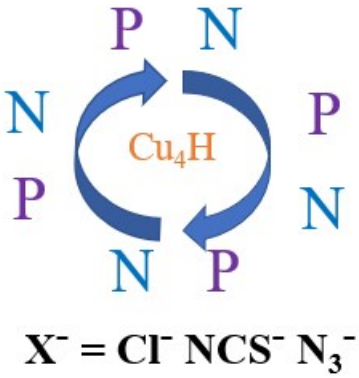
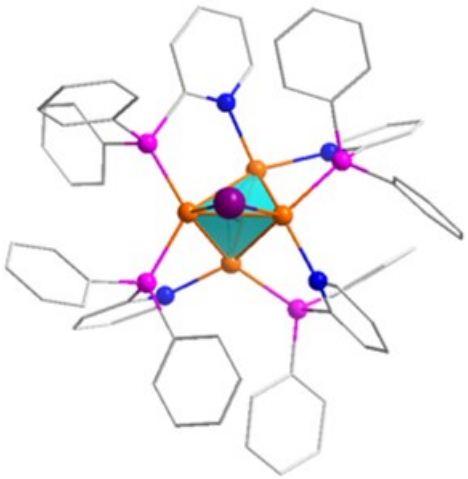


Figure S10: Different coordination mode of $[Cu_4HX_2L_4]^+$ clusters ($X^- = Cl^-$, Br^-, I^-, N_3^-, NCS^-).







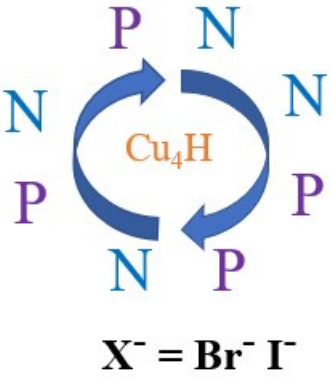


Figure S11: Packing of $[Cu_4HBr_3]$ Δ and Λ (3b) crystals.

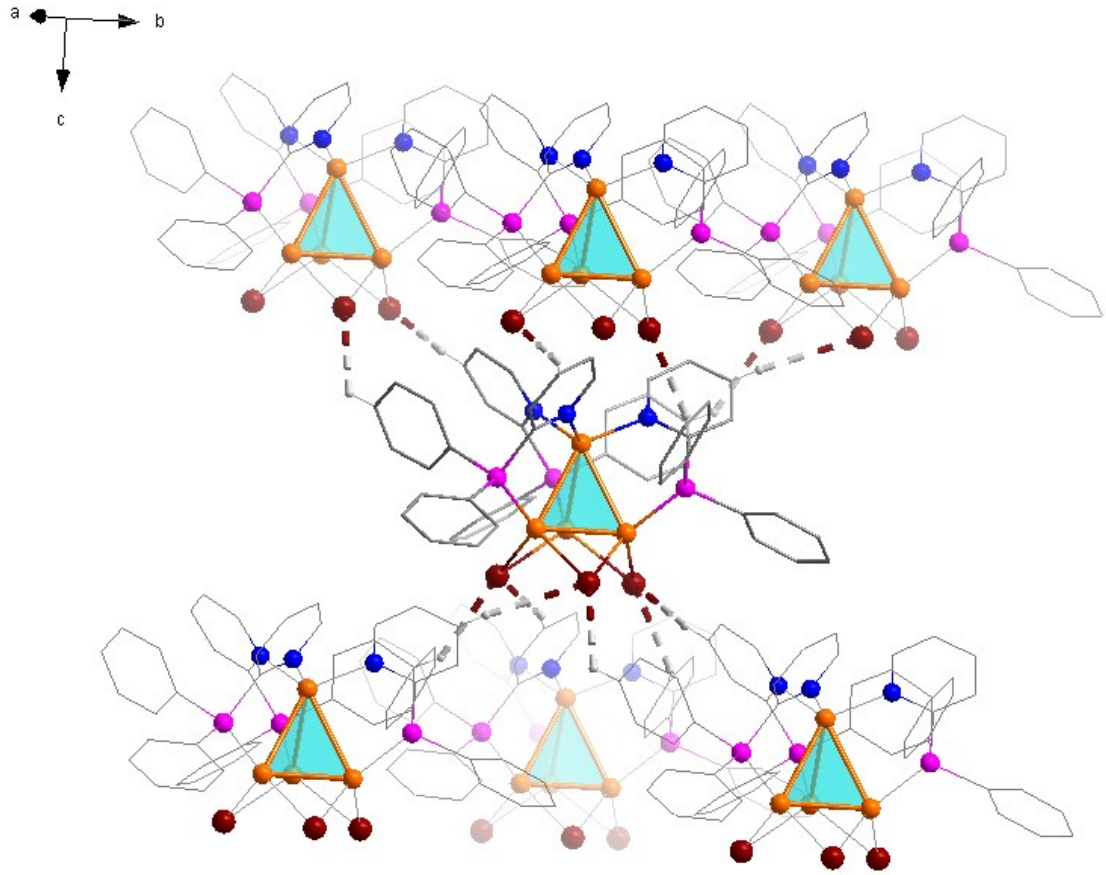
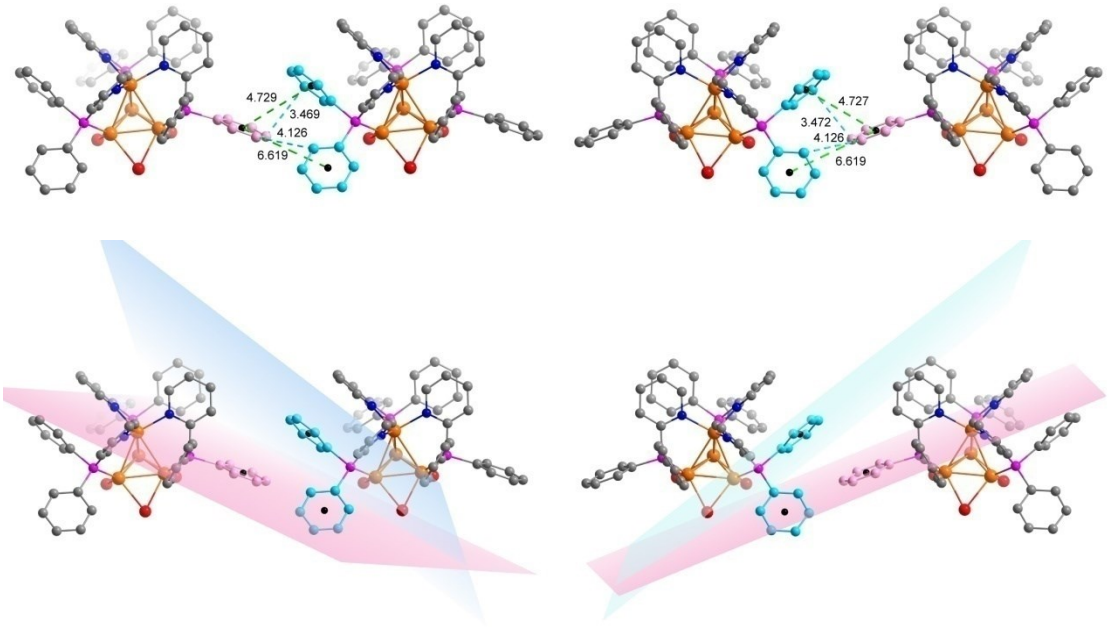
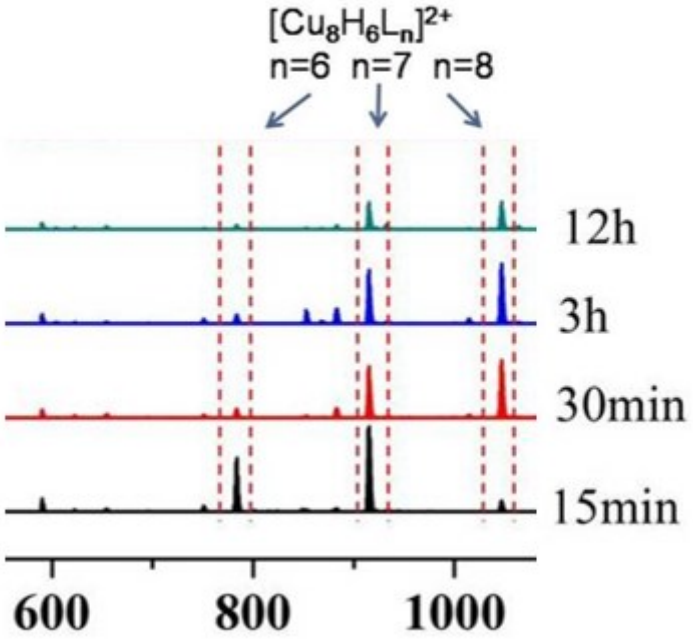


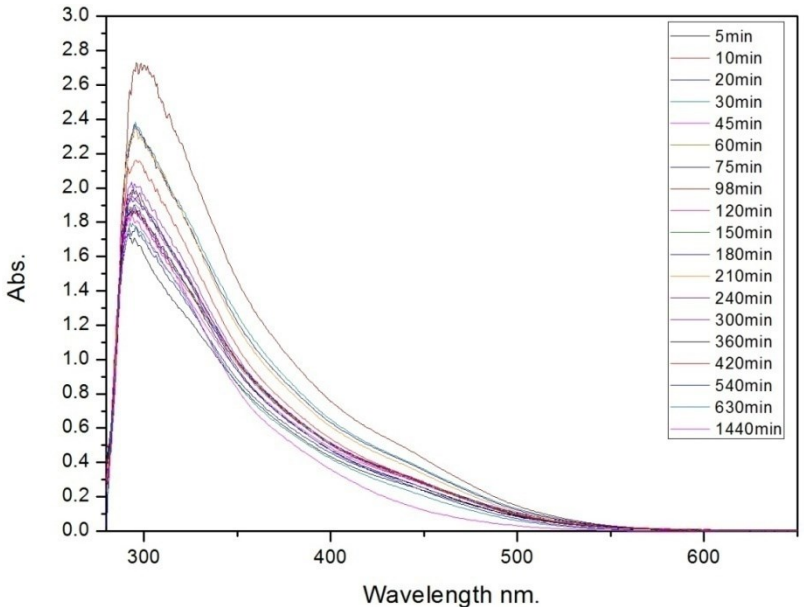
Figure S12: Short contacts in "key-and-lock" shape recognition in $[Cu_4HBr_3]$ Δ and Λ (3b) crystals.



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	**$[Cu_8H_6L_6]^{2+}$ 1**	**$[Cu_4HCl_2L_4]^{+}$ 2a**	**$[Cu_4HI_2L_4]^{+}$ 2c**
CCDC	2039341	2039342	2039343
Moieties	$[Cu_8H_6L_6][PF_6]_2$ $\cdot 2CH_2Cl_2$	$[Cu_4HCl_2L_4][PF_6]$ $\cdot 2CH_2Cl_2$	$[Cu_4HI_2L_4][PF_6]$ $\cdot CH_2Cl_2$
Empirical formula	$C_{104}H_{94}Cu_8N_6P_8F_{12}Cl_4$	$C_{70}H_{61}Cu_4N_4P_5F_6Cl_6$	$C_{69}H_{59}Cl_2Cu_4I_2N_4P_5F_6$
Formula weight	2553.73	1693.93	1791.91
T (K)	100(10)	100(10)	100(10)
Crystal system	$P\bar{3}$	$P2_1/c$	$P2_1/n$
Space group	Trigonal	Monoclinic	Monoclinic
a (Å)	25.4756(5)	13.7032(1)	16.4263(1)
b (Å)	25.4756(5)	26.1636(2)	12.0316(1)
c (Å)	13.9849(4)	20.0973(2)	35.2262(3)
α (°)	90	90	90
β (°)	90	96.232(1)	92.5280(10)
γ (°)	120	90	90
V (Å^3)	7860.3(4)	7162.8(1)	6955.14(9)
Z	3	4	4
ρ_{calcd} (g/cm^{-3})	1.617	1.571	1.711
μ (mm^{-1})	4.434	4.955	10.644
F(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
θ limits (°)	3.160 to 66.739	3.658 to 78.166	2.921 to 75.941
Limiting indices	$-27 \le h \le 29$	$-17 \le h \le 16$	$-20 \le h \le 20$
	$-29 \le k \le 30$	$-32 \le k \le 32$	$-14 \le k \le 14$
	$-16 \le l \le 16$	$-25 \le l \le 25$	$-43 \le l \le 43$
Reflections / unique	22580 / 8942	53516 / 14837	51048 / 13832
R_{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
R_1, wR_2 [$I > 2\sigma(I)$]	0.0771, 0.2070	0.0375, 0.0929	0.0315, 0.0783
R_1, wR_2 (all data)	0.1232, 0.2365	0.0488, 0.1019	0.0363, 0.0817
$\Delta\rho$ (e·A^{-3})	1.553, –0.786	0.699, –0.818	1.010, –1.028

Continued Table S1: Crystal data. (1)

Name	**$[Cu_4H(N_3)_2L_4]^+$ 2d**	**$[Cu_4H(NCS)_2L_4]^+$ 2e (*M*)**	**$[Cu_4H(NCS)_2L_4]^+$ 2e (*P*)**
CCDC	2039344	2039345	2039346
Moieties	$[Cu_4H(N_3)_2L_4][PF_6]$ $\cdot 2CH_2Cl_2$	$[Cu_4H(NCS)_2L_4]$ $[PF_6]\cdot 1.25CH_2Cl_2$	$[Cu_4H(NCS)_2L_4]$ $[PF_6]\cdot 1.25CH_2Cl_2$
Empirical formula	$C_{70}H_{61}Cu_4N_{10}P_5F_6Cl_4$	$C_{71.25}H_{59.5}Cl_{2.5}Cu_4$ $S_2N_6P_5F_6$	$C_{71.25}H_{59.5}Cl_{2.5}Cu_4S_2$ $N_6P_5F_6$
Formula weight	1707.09	1675.50	1675.50
T (K)	100(10)	100(10)	100(10)
Crystal system	*Cc*	$P2_12_12_1$	$P2_12_12_1$
Space group	Monoclinic	Orthorhombic	Orthorhombic
a (Å)	30.2978(2)	13.1572(2)	13.1571(2)
b (Å)	18.41230(10)	16.6001(2)	16.5948(2)
c (Å)	15.20620(10)	34.5546(5)	34.5954(4)
α (°)	90	90	90
β (°)	121.0420(10)	90	90
γ (°)	90	90	90
V (Å^3)	7267.98(10)	7547.10(18)	7553.54(17)
Z	4	4	4
ρ_{calcd} (g/cm^{-3})	1.560	1.475	1.473
μ (mm^{-1})	4.254	4.096	4.093
F(000)	3456	3394	3394
Radiation (Å)	CuKα (λ = 1.54184)	CuKα (λ= 1.54184)	CuKα (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	$-37 \le h \le 38$	$-16 \le h \le 16$	$-15 \le h \le 15$
	$-23 \le k \le 22$	$-21 \le k \le 21$	$-20 \le k \le 17$
	$-18 \le l \le 19$	$-42 \le l \le 43$	$-38 \le l \le 43$
Reflections / unique	95245 / 14260	43431 / 15466	46360 / 15033
R_{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)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0409, 0.1089	0.0557, 0.1481	0.0387, 0.1005
R_1, wR_2 (all data)	0.0424, 0.1100	0.0642, 0.1595	0.0428, 0.1039
$\Delta\rho$ (e·A^{-3})	1.09, –0.53	1.063, –1.204	1.120, –0.854

Continued Table S1: Crystal data. (2)

Name	**$[Cu_4HBr_3L_3]$ 3b (Δ)DBM**	**$[Cu_4HBr_3L_3]$ 3b (Δ)DCM**
CCDC	2039347	2039348
Moieties	$[Cu_4HBr_3L_3]\cdot 2CH_2Br_2$	$[Cu_4HBr_3L_3]\cdot 2CH_2Cl_2$
Empirical formula	$C_{53}H_{47}Br_7Cu_4N_3P_3$	$C_{53}H_{47}Br_3Cl_4Cu_4N_3P_3$
Formula weight	1632.37	1454.53
T (K)	100(10)	100(10)
Crystal system	$R3$	$R3$
Space group	Trigonal	Trigonal
a (Å)	14.9752(2)	14.8018(2)
b (Å)	14.9752(2)	14.8018(2)
c (Å)	22.1086(2)	22.1489(3)
α (°)	90	90
β (°)	90	90
γ (°)	120	120
V (Å^3)	4193.75(14)	4202.54(13)
Z	3	3
ρ_{calcd} (g/cm^{-3})	1.894	1.724
μ (mm^{-1})	8.484	7.081
F(000)	2376	2160
Radiation (Å)	CuKα (λ = 1.54184)	CuKα (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	$-18 \le h \le 18$	$-17 \le h \le 17$
	$-18 \le k \le 17$	$-18 \le k \le 17$
	$-27 \le l \le 27$	$-26 \le l \le 26$
Reflections / unique	34214 / 4056	9131 / 3463
R_{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)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0348, 0.0841	0.0259, 0.0624
R_1, wR_2 (all data)	0.0363, 0.0851	0.0272, 0.0631
$\Delta\rho$ (e·A^{-3})	0.920, –0.590	0.606, –0.837

Continued Table S1: Crystal data. (3)

Name	**$[Cu_4HBr_3L_3]$ 3b (Λ)DBM**	**$[Cu_4HBr_3L_3]$ 3b (Λ)DCM**	**$[Cu_4HI_3L_3]$ 3c**
	2039349	2039350	2039351
Moieties	$[Cu_4HBr_3L_3]$ $\cdot 2CH_2Br_2$	$[Cu_4HBr_3L_3]$ $\cdot 2CH_2Cl_2$	$[Cu_4HI_3L_3]$ $\cdot 1.5CH_2Cl_2$
Empirical formula	$C_{53}H_{47}Br_7Cu_4N_3P_3$	$C_{53}H_{47}Br_3Cl_4Cu_4N_3P_3$	$C_{52.5}H_{46}Cl_3Cu_4I_3N_3P_3$
Formula weight	1632.37	1454.53	1553.04
T (K)	203(2)	100(10)	100(10)
Crystal system	*R*3	*R*3	*Fdd*2
Space group	Trigonal	Trigonal	Orthorhombic
a (Å)	14.9436(8)	14.7989(2)	49.0830(4)
b (Å)	14.9436(8)	14.7989(2)	37.3456(3)
c (Å)	22.1101(11)	22.1361(3)	11.73950(10)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	120	120	90
V (Å^3)	4275.9(5)	4198.46(13)	21518.9(3)
Z	3	3	16
ρ_{calcd} (g/cm^{-3})	1.902	1.726	1.917
μ (mm^{-1})	6.500	7.088	17.816
F(000)	2376	2160	12048
Radiation (Å)	MoKα (λ=0.71073)	CuKα (λ = 1.54184)	CuKα (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	$-20 \le h \le 19$	$-17 \le h \le 18$	$-60 \le h \le 34$
	$-20 \le k \le 19$	$-18 \le k \le 15$	$-46 \le k \le 47$
	$-28 \le l \le 29$	$-27 \le l \le 27$	$-12 \le l \le 14$
Reflections / unique	12357 / 4511	10098 /3703	25721 /9639
R_{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)	\
R_1, wR_2 [$I > 2\sigma(I)$]	0.0302, 0.0597	0.0283, 0.0654	0.0214, 0.0563
R_1, wR_2 (all data)	0.0390, 0.0612	0.0309, 0.0679	0.0232, 0.0568
$\Delta\rho$ (e·A^{-3})	0.506, –0.304	0.608, –0.918	0.490, –0.670

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

$[Cu_8H_6L_6][PF_6]_2$ **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.

$[Cu_4HI_2L_4][PF_6]$ **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)

$[Cu_4H(N_3)_2L_4][PF_6]$ **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

$[Cu_4H(NCS)_2L_4][PF_6]$ (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

$[Cu_4H(NCS)_2L_4][PF_6]$ (*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

$[Cu_4HBr_3L_3]\cdot CH_2Br_2$ (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)

$[Cu_4HBr_3L_3]\cdot CH_2Cl_2$ (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.

$[Cu_4HBr_3L_3]\cdot CH_2Br_2$ (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

$[Cu_4HBr_3L_3]\cdot CH_2Cl_2$ (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

$[Cu_4HI_3L_3]$ **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 Cu_4H clusters.

	Space group	Z	Cell volume/Å^3	Racemic /Enantiomic
$[Cu_4HCl_2L_4]^+$	$P2_1/c$	4	7162.80	Racemic crystal
$[Cu_4HBr_2L_4]^+$	P-1	2	3667.0	Racemic crystal
$[Cu_4HI_2L_4]^+$	$P2_1/n$	4	6955.14	Racemic crystal
$[Cu_4H(N_3)_2L_4]^+$	Cc	4	7267.98	Racemic crystal
$[Cu_4H(NCS)_2L_4]^+$ *M*	$P2_12_12_1$	4	7574.10	Enantiomic crystals
$[Cu_4H(NCS)_2L_4]^+$ *P*	$P2_12_12_1$	4	7553.54	Enantiomic crystals
$[Cu_4HBr_3L_3]$ Δ	$R3$	3	4202.54	Enantiomic crystals
$[Cu_4HBr_3L_3]$ Λ	$R3$	3	4198.46	Enantiomic crystals
$[Cu_4HI_3L_3]$	$Fdd2$	16	21518.9	Racemic crystal

* $[Cu_4HBr_2L_4]^+$ was determined at 203 K. The other data were determined at 100 K.

Table S4: Neighboring clusters' hydrogen bonds of Cu_4 clusters (Å, °).

2a $[Cu_4HCl_2L_4]^+$ ($P2_1/c$)

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 $[Cu_4HBr_2L_4]^+$ (P–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 $[Cu_4HI_2L_4]^+$ ($P2_1/n$)

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 Cu_4 clusters (Å, °). (1)

2e $[Cu_4H(NCS)_2L_4]^+$ (*M*) ($P2_12_12_1$)

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 $[Cu_4H(NCS)_2L_4]^+$ (*P*) ($P2_12_12_1$)

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 $[Cu_4HBr_3L_3]$ (*R*3)(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 $[Cu_4HBr_3L_3]$ (*R*3)(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 $[Cu_4HI_3L_3]$ (*Fdd*2)

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 °.

	$[Cu_4HBr_3L_3]$ Δ	$[Cu_4HBr_3L_3]$ 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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