Electronic Supplementary Information (ESI)

Structure and modified property of an inclusion complex of self-dimerised Cu(II) complex in γ- cyclodextrines

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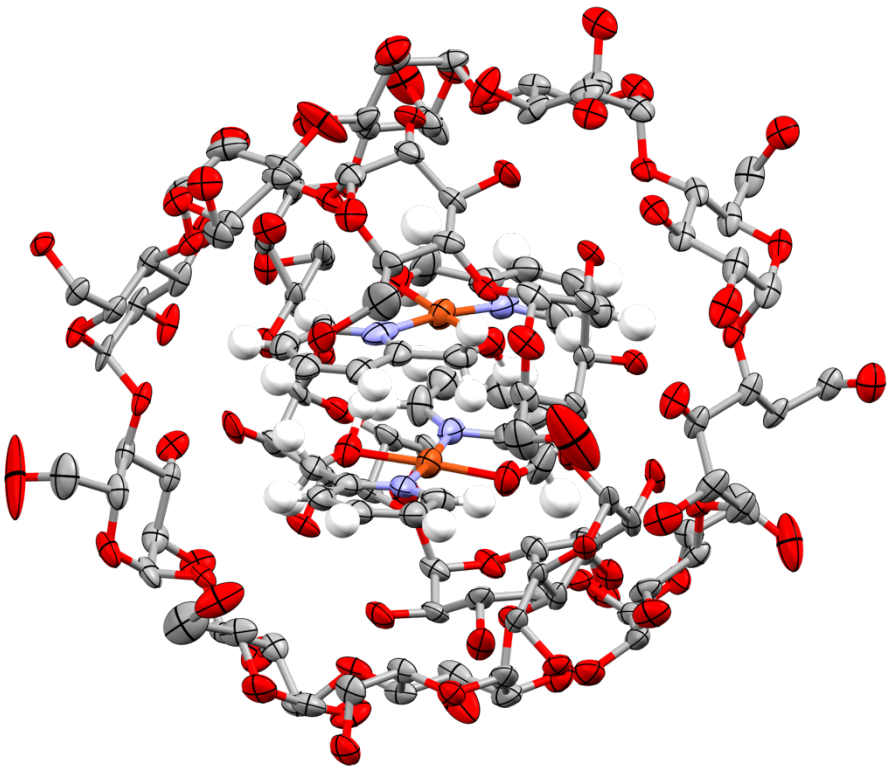


Figure S1 Crystal structure of the inclusion complex **1**·35H_2O. (orange: Cu, red: O, grey: C, blue: N, white: H) The thermal ellipsoids are drawn at the 50% probability level. Counter anions, water molecules and protons except for $[Cu(L)(HL)]^+$ are omitted for clarity.

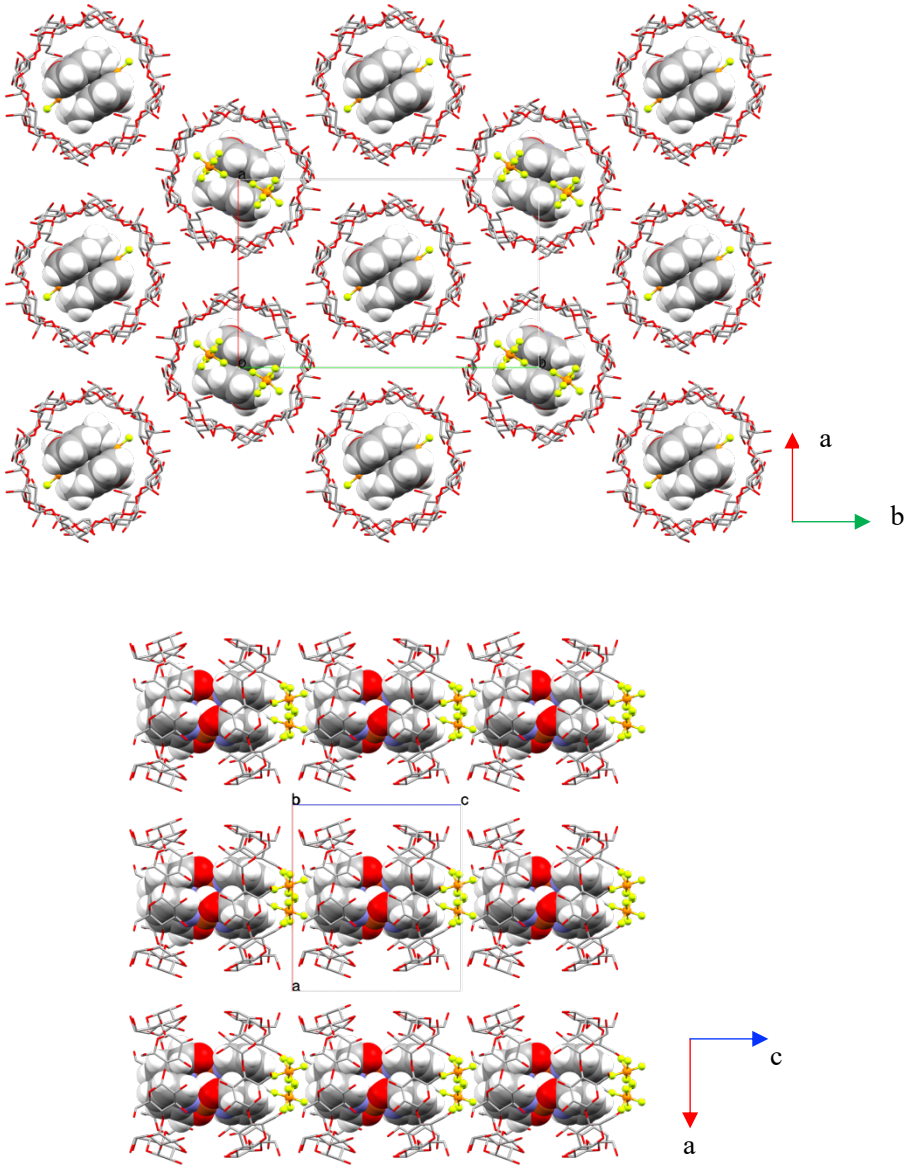


Figure S2 Molecular packing of the inclusion complex **1**·35H_2O. $[Cu(L)(HL)]^+$: CPK model; γ-CD: capped sticks model; counter anions: ball and stick model (orange: Cu, red: O, grey: C, blue: N, white: H, light orange: P, yellow: F). Water molecules and protons except for $[Cu(L)(HL)]^+$ are omitted for clarity. Top: view from the c axis direction; bottom: view from the b axis direction.

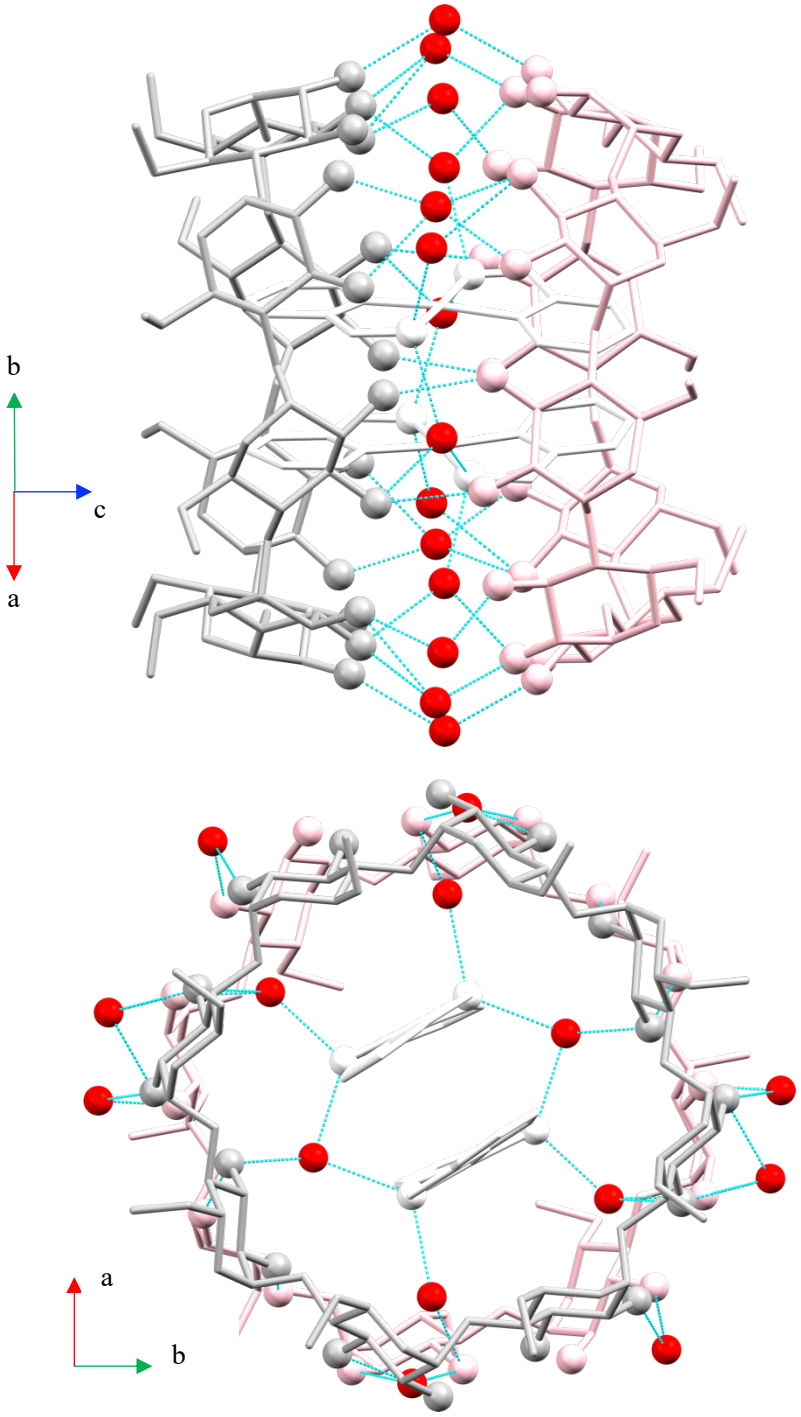


Figure S3 Intra-molecular hydrogen bonding in the inclusion complex **1**·35H_2O. Hydrogen-bonding water molecules and hydrogen-bonding oxygen atoms are represented by balls and sticks. Other atoms and bonds are represented by capped sticks. Other water molecules, counter anions and protons are omitted for clarity.

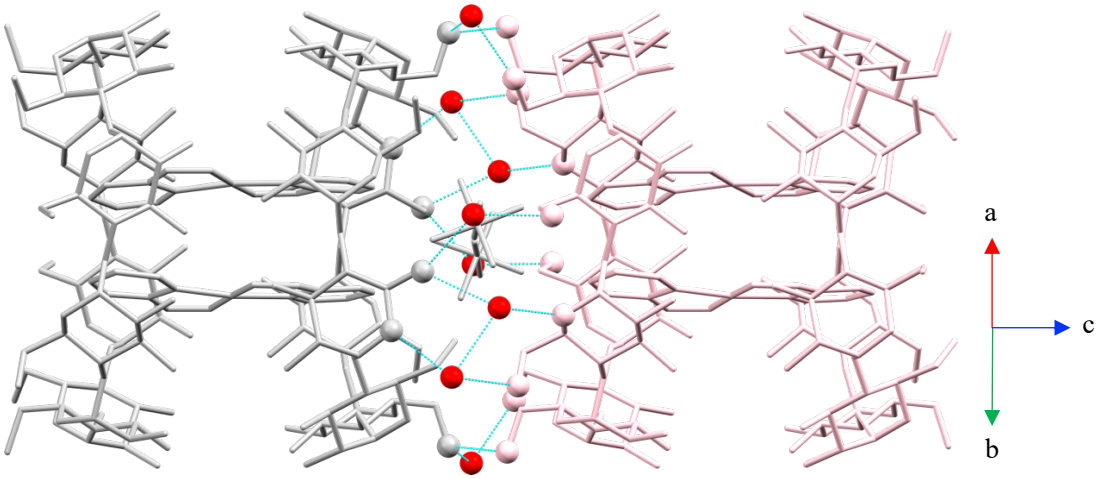


Figure S4 Inter-molecular hydrogen bonding in the inclusion complex **1**·35H_2O. Hydrogen-bonding water molecules and hydrogen-bonding oxygen atoms are represented by balls and sticks. Other atoms are represented by capped sticks. Other water molecules and protons are omitted for clarity.

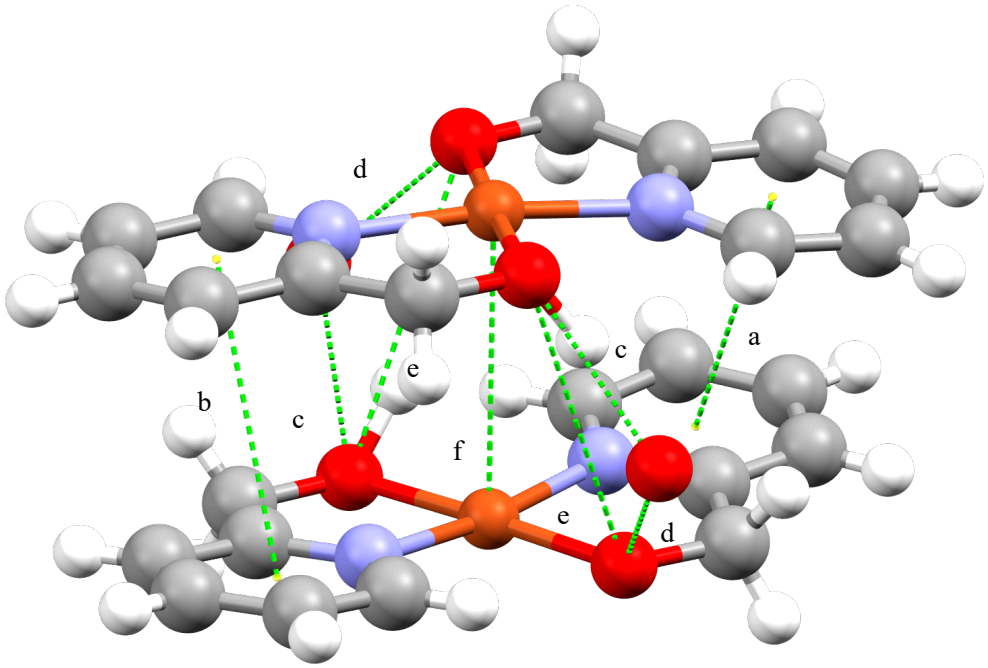


Figure S5 π–π stacking, hydrogen bonding and Cu...Cu interaction between two $[Cu(L)(HL)]^+$ fragments. The distances between the pyridyl-ring centroids (a, b) are 3.665(5) Å (for a) and 3.642(6) Å (for b). The O_{HL}...O_{water} distance (c) is 2.68(1) Å. The O_L...O_{water} distance (d) is 2.78(1) Å. The O_L...O_{HL} distance (e) is 4.09(1) Å. The Cu...Cu distance (f) is 3.755(2) Å.

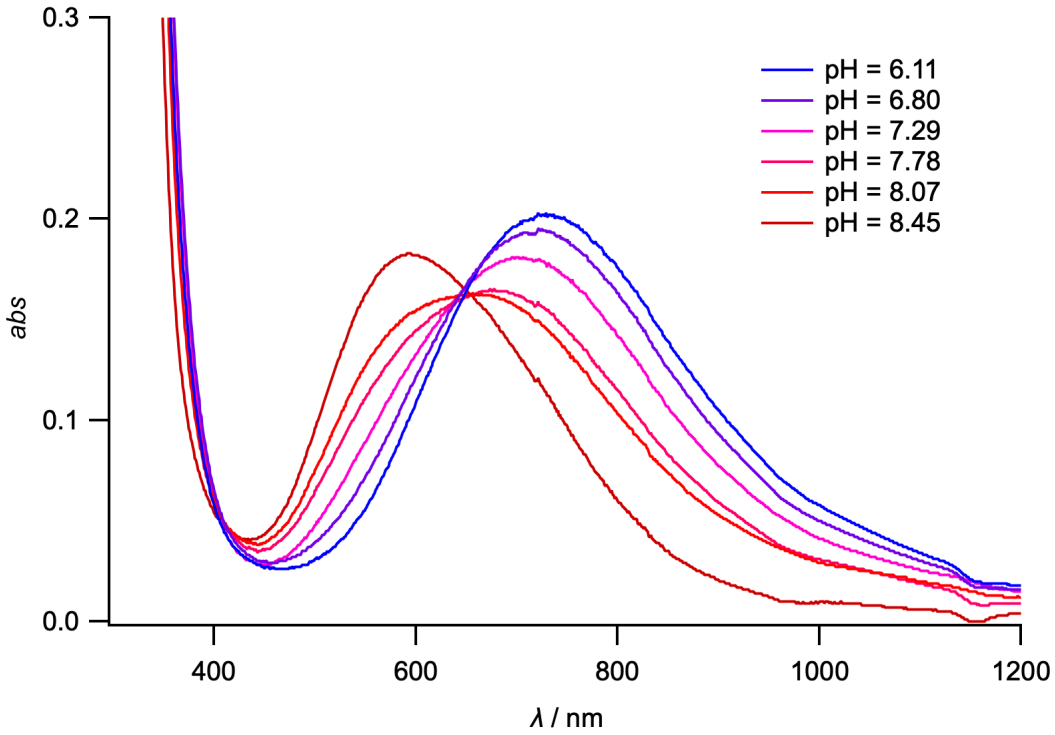


Figure S6 Titration of inclusion complex **1**. Inclusion complex **1**·31H_2O (2.50 g, 6.24×10^{-4} mol) was dissolved into 100 mL H_2O. A mixture of 4 mL of the stock solution and 6 mL of buffer solution was used to measure the absorption spectra. After the measurement, the rest of the solution was used to determine the pH. Table S1 summarises the buffer solutions used. The optical path length was 1 cm.

Table S1 Buffer solutions

entry	buffer solutions
1	NaH_2PO_4 aq. 6.00 mL and Na_2HPO_4 aq. 0.37 mL
2	NaH_2PO_4 aq. 4.00 mL and Na_2HPO_4 aq. 2.47 mL
3	NaH_2PO_4 aq. 2.00 mL and Na_2HPO_4 aq. 3.90 mL
4	NaH_2PO_4 aq. 1.00 mL and Na_2HPO_4 aq. 6.17 mL
5	NaH_2PO_4 aq. 0.50 mL and Na_2HPO_4 aq. 6.60 mL
6	water only

The concentration of all solutions was 0.1 mol dm^{-3}.

Table S2 Calculated Gibbs free energy

Gibbs free energy / kcal mol^{-1}	basis set	
	M06L	ωB97XD
$G_{(\text{monomeric } [Cu(L)(HL)]^+ \text{ fragment})}$	-1.1572×10^6	-1.1570×10^6
$G_{(\text{monomeric } [Cu(L)_2] \text{ fragment})}$	-1.1564×10^6	-1.1564×10^6
$G_{(\text{dimeric } [Cu(L)(HL)]^+ \text{ assembly})}$	-5.7859×10^5	-5.7848×10^5
$G_{(\text{dimeric } [Cu(L)_2] \text{ assembly})}$	-5.7832×10^5	-5.7820×10^5
ΔG ($G_{(\text{dimeric } [Cu(L)(HL)]^+ \text{ assembly})} - G_{(\text{monomeric } [Cu(L)(HL)]^+ \text{ fragment})}\times2$)	−12.57	−23.14
ΔG ($G_{(\text{dimeric } [Cu(L)_2] \text{ assembly})} - G_{(\text{monomeric } [Cu(L)_2] \text{ fragment})}\times2$)	240.9	−3.923

Table S3 Coordinates of the monomeric $[Cu(L)(HL)]^+$ fragment optimised by M06L

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-0.030750	-0.021162	0.043097
2	8	0	-0.418678	-1.862976	-0.006105
3	8	0	0.541995	1.991516	0.244541
4	7	0	-1.970721	0.248886	0.004206
5	7	0	1.941856	-0.235024	-0.011569
6	6	0	1.898031	2.167066	-0.203958
7	6	0	-1.773232	-2.149161	-0.021608
8	6	0	-2.646998	1.413693	-0.005092
9	6	0	2.548497	-1.431990	0.049647
10	6	0	2.677291	0.889495	-0.083660
11	6	0	-2.639186	-0.923142	-0.021870
12	6	0	-4.028234	1.454376	-0.036359
13	6	0	3.928531	-1.549330	0.037831
14	6	0	4.066068	0.846177	-0.094433
15	6	0	-4.031897	-0.948073	-0.052714
16	6	0	-4.732209	0.248682	-0.059076
17	6	0	4.698144	-0.390335	-0.033192
18	1	0	0.497718	2.216714	1.190372
19	1	0	1.825301	2.466703	-1.254881
20	1	0	-2.064396	-2.766248	0.851414
21	1	0	2.371344	2.986298	0.343739
22	1	0	-2.048460	-2.752385	-0.909184
23	1	0	-2.040731	2.315774	0.008368
24	1	0	1.878651	-2.286757	0.104913
25	1	0	-4.541531	2.411173	-0.044413
26	1	0	4.388256	-2.531526	0.089583
27	1	0	4.637329	1.769647	-0.145661
28	1	0	-4.549369	-1.904585	-0.073734
29	1	0	-5.819372	0.247744	-0.083901
30	1	0	5.783688	-0.448944	-0.035476

Table S4 Coordinates of the monomeric [Cu(L)$_2$] fragment optimised by M06L

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.000000	0.000004	-0.000001
2	8	0	0.432263	1.862183	0.000049
3	8	0	-0.432258	-1.862178	-0.000066
4	7	0	1.981069	-0.251753	0.000082
5	7	0	-1.981070	0.251754	-0.000078
6	6	0	-1.778950	-2.141083	-0.000004
7	6	0	1.778955	2.141084	0.000023
8	6	0	2.645925	-1.419837	0.000060
9	6	0	-2.645931	1.419836	-0.000065
10	6	0	-2.652255	-0.913717	-0.000021
11	6	0	2.652257	0.913715	0.000028
12	6	0	4.028540	-1.471651	-0.000002
13	6	0	-4.028546	1.471645	-0.000006
14	6	0	-4.047116	-0.932326	0.000036
15	6	0	4.047118	0.932320	-0.000033
16	6	0	4.740259	-0.269279	-0.000049
17	6	0	-4.740261	0.269271	0.000044
18	1	0	-2.081325	-2.753331	-0.877814
19	1	0	2.081316	2.753308	0.877856
20	1	0	-2.081270	-2.753249	0.877882
21	1	0	2.081294	2.753273	-0.877841
22	1	0	2.017436	-2.308154	0.000098
23	1	0	-2.017446	2.308155	-0.000104
24	1	0	4.538782	-2.430746	-0.000017
25	1	0	-4.538792	2.430738	0.000002
26	1	0	-4.572420	-1.885616	0.000080
27	1	0	4.572426	1.885608	-0.000073
28	1	0	5.828200	-0.275231	-0.000096
29	1	0	-5.828202	0.275219	0.000087

Table S5 Coordinates of the monomeric $[Cu(L)(HL)]^+$ fragment optimised by ωB97XD

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-0.029248	-0.044941	0.060588
2	8	0	-0.415001	-1.860777	0.019175
3	8	0	0.516882	1.952711	0.274537
4	7	0	-1.969770	0.248634	0.007691
5	7	0	1.949089	-0.238051	-0.013748
6	6	0	1.857766	2.167610	-0.189522
7	6	0	-1.770776	-2.155876	-0.004477
8	6	0	-2.635477	1.417540	-0.016412
9	6	0	2.570174	-1.426291	0.034537
10	6	0	2.663680	0.894300	-0.085298
11	6	0	-2.637694	-0.916113	-0.020337
12	6	0	-4.015033	1.464906	-0.064483
13	6	0	3.951335	-1.523171	0.010484
14	6	0	4.051463	0.876521	-0.109476
15	6	0	-4.029711	-0.939420	-0.068075
16	6	0	-4.722935	0.261075	-0.089525
17	6	0	4.701681	-0.351558	-0.061266
18	1	0	0.454350	2.202058	1.209714
19	1	0	1.771758	2.466076	-1.236994
20	1	0	-2.066982	-2.756884	0.872403
21	1	0	2.322271	2.983146	0.366544
22	1	0	-2.036530	-2.754874	-0.892200
23	1	0	-2.027327	2.314837	-0.001118
24	1	0	1.915978	-2.289292	0.089940
25	1	0	-4.523605	2.421068	-0.084378
26	1	0	4.426024	-2.495855	0.051924
27	1	0	4.606628	1.806496	-0.161604
28	1	0	-4.549749	-1.891101	-0.091076
29	1	0	-5.807224	0.265129	-0.129052
30	1	0	5.785490	-0.394213	-0.075359

Table S6 Coordinates of the monomeric [Cu(L)$_2$] fragment optimised by ωB97XD

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.000000	0.000000	-0.000006
2	8	0	-0.422937	-1.839683	0.000010
3	8	0	0.422937	1.839683	-0.000044
4	7	0	-1.994114	0.255371	0.000032
5	7	0	1.994115	-0.255371	-0.000033
6	6	0	1.769146	2.142383	0.000025
7	6	0	-1.769146	-2.142383	0.000044
8	6	0	-2.662353	1.419739	0.000015
9	6	0	2.662353	-1.419739	-0.000046
10	6	0	2.653794	0.909394	0.000005
11	6	0	-2.653794	-0.909394	0.000021
12	6	0	-4.044532	1.463632	-0.000016
13	6	0	4.044532	-1.463632	-0.000021
14	6	0	4.048161	0.941572	0.000031
15	6	0	-4.048161	-0.941572	-0.000006
16	6	0	-4.747604	0.256077	-0.000024
17	6	0	4.747604	-0.256077	0.000016
18	1	0	2.059469	2.746626	-0.880484
19	1	0	-2.059421	-2.746555	0.880619
20	1	0	2.059403	2.746545	0.880612
21	1	0	-2.059452	-2.746616	-0.880478
22	1	0	-2.042321	2.309952	0.000023
23	1	0	2.042321	-2.309951	-0.000073
24	1	0	-4.559564	2.417038	-0.000034
25	1	0	4.559564	-2.417038	-0.000031
26	1	0	4.565332	1.895690	0.000064
27	1	0	-4.565332	-1.895690	-0.000018
28	1	0	-5.833031	0.255109	-0.000051
29	1	0	5.833031	-0.255109	0.000038

Table S7 Coordinates of the dimeric $[Cu(L)(HL)]^+$ assembly optimised by M06L

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-0.000932	1.570705	0.019530
2	8	0	-1.830525	1.083570	0.345600
3	8	0	1.995949	1.408491	-0.417142
4	7	0	0.138083	1.723819	1.966718
5	7	0	-0.138083	1.732381	-1.940306
6	6	0	2.277390	1.603702	-1.805100
7	6	0	-2.204886	1.223614	1.686061
8	6	0	1.237561	2.036013	2.679892
9	6	0	-1.309063	1.844209	-2.594771
10	6	0	1.021028	1.705616	-2.623181
11	6	0	-1.040888	1.512849	2.588754
12	6	0	1.204393	2.133452	4.059129
13	6	0	-1.365004	1.929081	-3.974529
14	6	0	1.035032	1.791507	-4.012363
15	6	0	-1.137554	1.595748	3.975272
16	6	0	-0.005540	1.904441	4.716141
17	6	0	-0.170361	1.898950	-4.693518
18	1	0	2.085868	0.422589	-0.178984
19	1	0	2.853755	2.531498	-1.894593
20	1	0	-2.715611	0.311907	2.046259
21	1	0	2.916458	0.790582	-2.171418
22	1	0	-2.939690	2.039253	1.802239
23	1	0	2.143660	2.212903	2.104842
24	1	0	-2.195394	1.860421	-1.964827
25	1	0	2.108088	2.384674	4.605615
26	1	0	-2.325992	2.013275	-4.472519
27	1	0	1.982652	1.760314	-4.544596
28	1	0	-2.095883	1.416354	4.457425
29	1	0	-0.061945	1.966131	5.800138
30	1	0	-0.179839	1.953540	-5.779214
31	29	0	0.000932	-1.570705	0.019530

32	8	0	1.830525	-1.083570	0.345600
33	8	0	-1.995949	-1.408491	-0.417142
34	7	0	-0.138083	-1.723819	1.966718
35	7	0	0.138083	-1.732381	-1.940306
36	6	0	-2.277390	-1.603702	-1.805100
37	6	0	2.204886	-1.223614	1.686061
38	6	0	-1.237561	-2.036013	2.679892
39	6	0	1.309063	-1.844209	-2.594771
40	6	0	-1.021028	-1.705616	-2.623181
41	6	0	1.040888	-1.512849	2.588754
42	6	0	-1.204393	-2.133452	4.059129
43	6	0	1.365004	-1.929081	-3.974529
44	6	0	-1.035032	-1.791507	-4.012363
45	6	0	1.137554	-1.595748	3.975272
46	6	0	0.005540	-1.904441	4.716141
47	6	0	0.170361	-1.898950	-4.693518
48	1	0	-2.085868	-0.422589	-0.178984
49	1	0	-2.853755	-2.531498	-1.894593
50	1	0	2.715611	-0.311907	2.046259
51	1	0	-2.916458	-0.790582	-2.171418
52	1	0	2.939690	-2.039253	1.802239
53	1	0	-2.143660	-2.212903	2.104842
54	1	0	2.195394	-1.860421	-1.964827
55	1	0	-2.108088	-2.384674	4.605615
56	1	0	2.325992	-2.013275	-4.472519
57	1	0	-1.982652	-1.760314	-4.544596
58	1	0	2.095883	-1.416354	4.457425
59	1	0	0.061945	-1.966131	5.800138
60	1	0	0.179839	-1.953540	-5.779214

Table S8 Coordinates of the dimeric [Cu(L)$_2$] assembly optimised by M06L

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.002799	1.581325	0.001286
2	8	0	1.440232	0.370268	-0.004811
3	8	0	-1.527672	2.637585	-0.045421
4	7	0	0.327278	1.688502	-1.920826
5	7	0	-0.116780	1.779413	1.936206
6	6	0	-2.210553	2.629718	1.171528
7	6	0	2.137826	0.299885	-1.210437
8	6	0	-0.418105	2.375747	-2.799545
9	6	0	0.826236	1.465675	2.838389
10	6	0	-1.290756	2.331970	2.313805
11	6	0	1.401614	0.973440	-2.322940
12	6	0	-0.116780	2.366072	-4.152112
13	6	0	0.618405	1.679690	4.191043
14	6	0	-1.558071	2.561585	3.658459
15	6	0	1.749275	0.923069	-3.668988
16	6	0	0.978920	1.622732	-4.590088
17	6	0	-0.594190	2.231101	4.603600
18	1	0	-2.703922	3.604284	1.316017
19	1	0	2.350452	-0.762923	-1.440235
20	1	0	-3.016790	1.871793	1.167172
21	1	0	3.131236	0.768816	-1.087901
22	1	0	-1.255166	2.928281	-2.377919
23	1	0	1.740332	1.027995	2.442263
24	1	0	-0.732981	2.930667	-4.844589
25	1	0	1.391768	1.408155	4.903181
26	1	0	-2.504963	3.008088	3.950297
27	1	0	2.608890	0.334851	-3.980174
28	1	0	1.230888	1.588548	-5.646836
29	1	0	-0.783780	2.408368	5.659333
30	29	0	-0.002799	-1.581325	0.001286
31	8	0	-1.440232	-0.370268	-0.004811

32	8	0	1.527672	-2.637585	-0.045421
33	7	0	-0.327278	-1.688502	-1.920826
34	7	0	0.116780	-1.779413	1.936206
35	6	0	2.210553	-2.629718	1.171528
36	6	0	-2.137826	-0.299885	-1.210437
37	6	0	0.418105	-2.375747	-2.799545
38	6	0	-0.826236	-1.465675	2.838389
39	6	0	1.290756	-2.331970	2.313805
40	6	0	-1.401614	-0.973440	-2.322940
41	6	0	0.116780	-2.366072	-4.152112
42	6	0	-0.618405	-1.679690	4.191043
43	6	0	1.558071	-2.561585	3.658459
44	6	0	-1.749275	-0.923069	-3.668988
45	6	0	-0.978920	-1.622732	-4.590088
46	6	0	0.594190	-2.231101	4.603600
47	1	0	2.703922	-3.604284	1.316017
48	1	0	-2.350452	0.762923	-1.440235
49	1	0	3.016790	-1.871793	1.167172
50	1	0	-3.131236	-0.768816	-1.087901
51	1	0	1.255166	-2.928281	-2.377919
52	1	0	-1.740332	-1.027995	2.442263
53	1	0	0.732981	-2.930667	-4.844589
54	1	0	-1.391768	-1.408155	4.903181
55	1	0	2.504963	-3.008088	3.950297
56	1	0	-2.608890	-0.334851	-3.980174
57	1	0	-1.230888	-1.588548	-5.646836
58	1	0	0.783780	-2.408368	5.659333

Table S9 Coordinates of the dimeric $[Cu(L)(HL)]^+$ assembly optimised by ωB97XD

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-0.004187	1.625528	0.015407
2	8	0	-1.825136	1.162491	0.354265
3	8	0	1.936229	1.259528	-0.399493
4	7	0	0.169779	1.750903	1.956558
5	7	0	-0.141943	1.765199	-1.940702
6	6	0	2.252674	1.404980	-1.779699
7	6	0	-2.191233	1.304537	1.700167
8	6	0	1.294683	2.004562	2.648929
9	6	0	-1.294683	1.974540	-2.600035
10	6	0	1.004914	1.590788	-2.613815
11	6	0	-0.993483	1.538659	2.593086
12	6	0	1.297288	2.045435	4.029911
13	6	0	-1.340002	2.015277	-3.981153
14	6	0	1.031855	1.614360	-4.003270
15	6	0	-1.059929	1.564838	3.982387
16	6	0	0.097069	1.818344	4.705334
17	6	0	-0.154851	1.827963	-4.692063
18	1	0	1.997599	0.267531	-0.120241
19	1	0	2.892902	2.284489	-1.889457
20	1	0	-2.725359	0.411050	2.054375
21	1	0	2.815734	0.533192	-2.126010
22	1	0	-2.878561	2.153218	1.825113
23	1	0	2.190115	2.171752	2.060566
24	1	0	-2.175220	2.100752	-1.980160
25	1	0	2.218317	2.246513	4.562919
26	1	0	-2.283273	2.182130	-4.486211
27	1	0	1.968080	1.460761	-4.527942
28	1	0	-2.006266	1.382661	4.479398
29	1	0	0.068320	1.835407	5.789524
30	1	0	-0.158508	1.842786	-5.776521
31	29	0	0.004187	-1.625528	0.015407

32	8	0	1.825136	-1.162491	0.354265
33	8	0	-1.936229	-1.259528	-0.399493
34	7	0	-0.169779	-1.750903	1.956558
35	7	0	0.141943	-1.765199	-1.940702
36	6	0	-2.252674	-1.404980	-1.779699
37	6	0	2.191233	-1.304537	1.700167
38	6	0	-1.294683	-2.004562	2.648929
39	6	0	1.294683	-1.974540	-2.600035
40	6	0	-1.004914	-1.590788	-2.613815
41	6	0	0.993483	-1.538659	2.593086
42	6	0	-1.297288	-2.045435	4.029911
43	6	0	1.340002	-2.015277	-3.981153
44	6	0	-1.031855	-1.614360	-4.003270
45	6	0	1.059929	-1.564838	3.982387
46	6	0	-0.097069	-1.818344	4.705334
47	6	0	0.154851	-1.827963	-4.692063
48	1	0	-1.997599	-0.267531	-0.120241
49	1	0	-2.892902	-2.284489	-1.889457
50	1	0	2.725359	-0.411050	2.054375
51	1	0	-2.815734	-0.533192	-2.126010
52	1	0	2.878561	-2.153218	1.825113
53	1	0	-2.190115	-2.171752	2.060566
54	1	0	2.175220	-2.100752	-1.980160
55	1	0	-2.218317	-2.246513	4.562919
56	1	0	2.283273	-2.182130	-4.486211
57	1	0	-1.968080	-1.460761	-4.527942
58	1	0	2.006266	-1.382661	4.479398
59	1	0	-0.068320	-1.835407	5.789524
60	1	0	0.158508	-1.842786	-5.776521

Table S10 Coordinates of the dimeric [Cu(L)$_2$] assembly optimised by ωB97XD

Centre Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-0.076232	1.621339	-0.564141
2	8	0	-0.911463	0.494675	-1.840814
3	8	0	0.776115	2.773662	0.672872
4	7	0	-1.955938	2.099218	-0.049371
5	7	0	1.792220	1.220727	-1.178400
6	6	0	2.152381	2.818492	0.587955
7	6	0	-2.288182	0.576137	-1.884604
8	6	0	-2.338664	2.892680	0.962737
9	6	0	2.157925	0.385504	-2.162284
10	6	0	2.711823	1.891560	-0.474570
11	6	0	-2.862875	1.437414	-0.777133
12	6	0	-3.672069	3.059674	1.290623
13	6	0	3.487856	0.185216	-2.485991
14	6	0	4.071052	1.728098	-0.737156
15	6	0	-4.225443	1.557513	-0.503458
16	6	0	-4.632035	2.375226	0.539976
17	6	0	4.460866	0.867094	-1.751962
18	1	0	2.521525	3.835039	0.351320
19	1	0	-2.766937	-0.416157	-1.808714
20	1	0	2.638965	2.543622	1.542442
21	1	0	-2.649702	1.005769	-2.839105
22	1	0	-1.532685	3.380156	1.500731
23	1	0	1.341875	-0.117223	-2.669427
24	1	0	-3.954612	3.704522	2.114478
25	1	0	3.757471	-0.495469	-3.285116
26	1	0	4.802397	2.269473	-0.145750
27	1	0	-4.943896	1.003258	-1.098684
28	1	0	-5.686685	2.480815	0.773295
29	1	0	5.513894	0.720942	-1.970215
30	29	0	0.080382	-1.594255	0.538600
31	8	0	-0.784305	-0.512334	1.833911

32	8	0	0.967541	-2.676238	-0.735354
33	7	0	-1.784782	-2.170443	0.064417
34	7	0	1.938287	-1.135967	1.149107
35	6	0	2.341652	-2.717289	-0.621424
36	6	0	-2.153958	-0.666505	1.909086
37	6	0	-2.149879	-2.983097	-0.938769
38	6	0	2.280792	-0.297260	2.138437
39	6	0	2.875776	-1.788751	0.452242
40	6	0	-2.707718	-1.555582	0.813027
41	6	0	-3.480355	-3.217050	-1.237033
42	6	0	3.603770	-0.075018	2.475598
43	6	0	4.229439	-1.609089	0.733831
44	6	0	-4.068274	-1.744983	0.570602
45	6	0	-4.456641	-2.581874	-0.464493
46	6	0	4.595022	-0.744927	1.754781
47	1	0	2.709743	-3.732559	-0.376643
48	1	0	-2.685635	0.299450	1.847272
49	1	0	2.845600	-2.440763	-1.565919
50	1	0	-2.468923	-1.116377	2.870545
51	1	0	-1.333230	-3.431955	-1.493910
52	1	0	1.451213	0.189721	2.639544
53	1	0	-3.748469	-3.875641	-2.054821
54	1	0	3.853890	0.610191	3.277195
55	1	0	4.975389	-2.140632	0.151770
56	1	0	-4.800236	-1.227731	1.182462
57	1	0	-5.509640	-2.739374	-0.674883
58	1	0	5.643168	-0.586514	1.987508

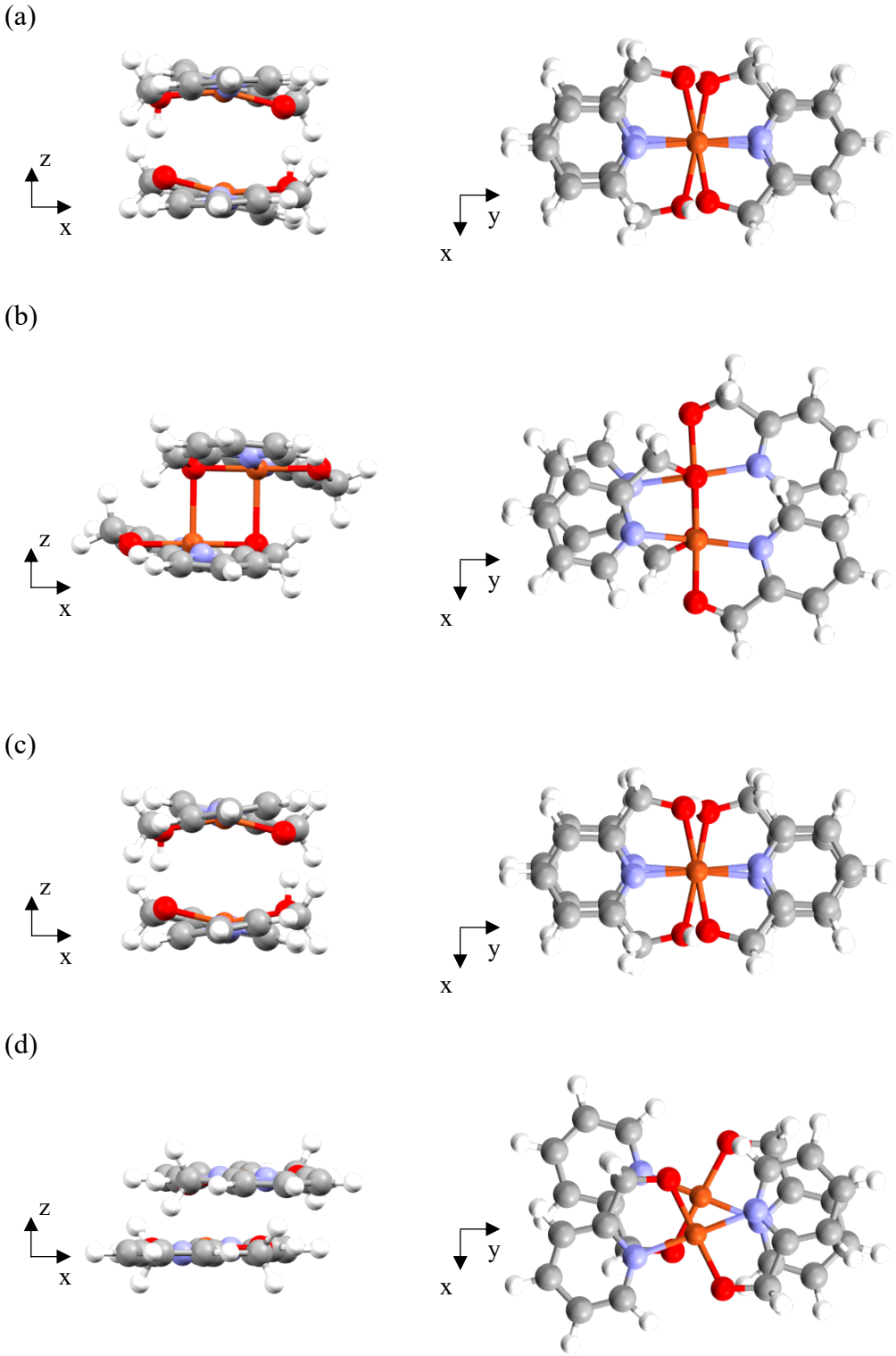
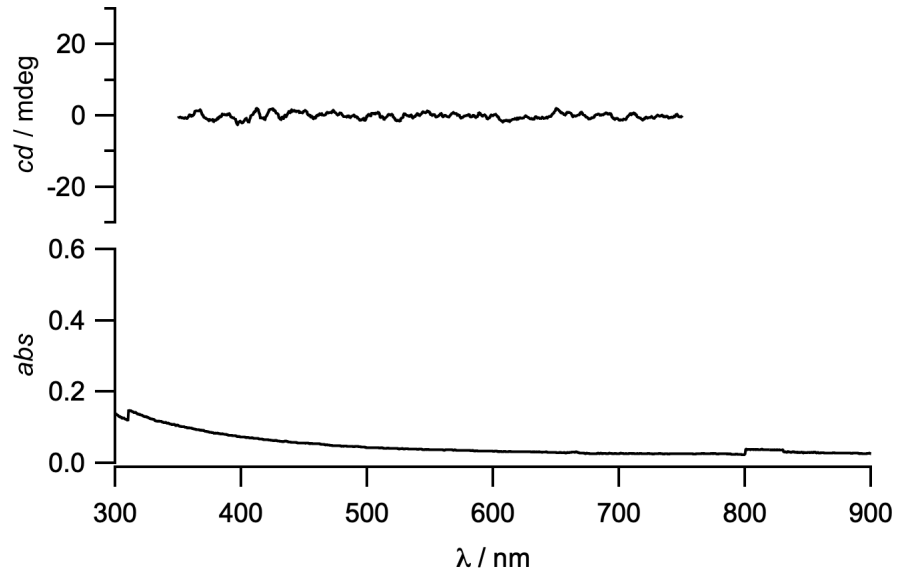


Figure S7 Optimised structures of the dimeric assembly in water: (a) dimeric $[Cu(L)(HL)]^+$ assembly by M06L; (b) dimeric $[Cu(L)_2]$ assembly by M06L; (c) dimeric $[Cu(L)(HL)]^+$ assembly by ωB97XD; (d) dimeric $[Cu(L)_2]$ assembly by ωB97XD.

(a)



(b)

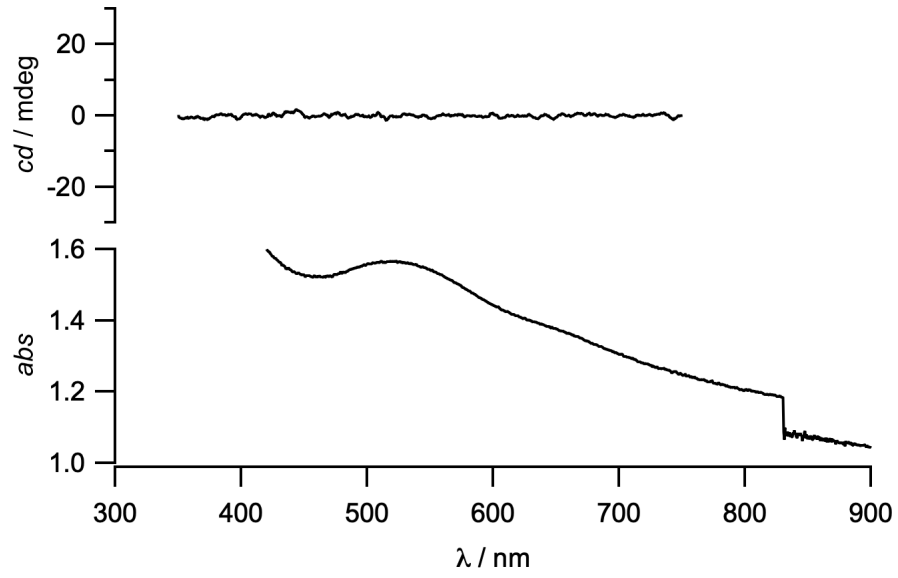


Figure S8 Circular dichroism (top) and absorption (bottom) spectra of γ-CD (a) and [Cu(L)(HL)]PF_6 (b).

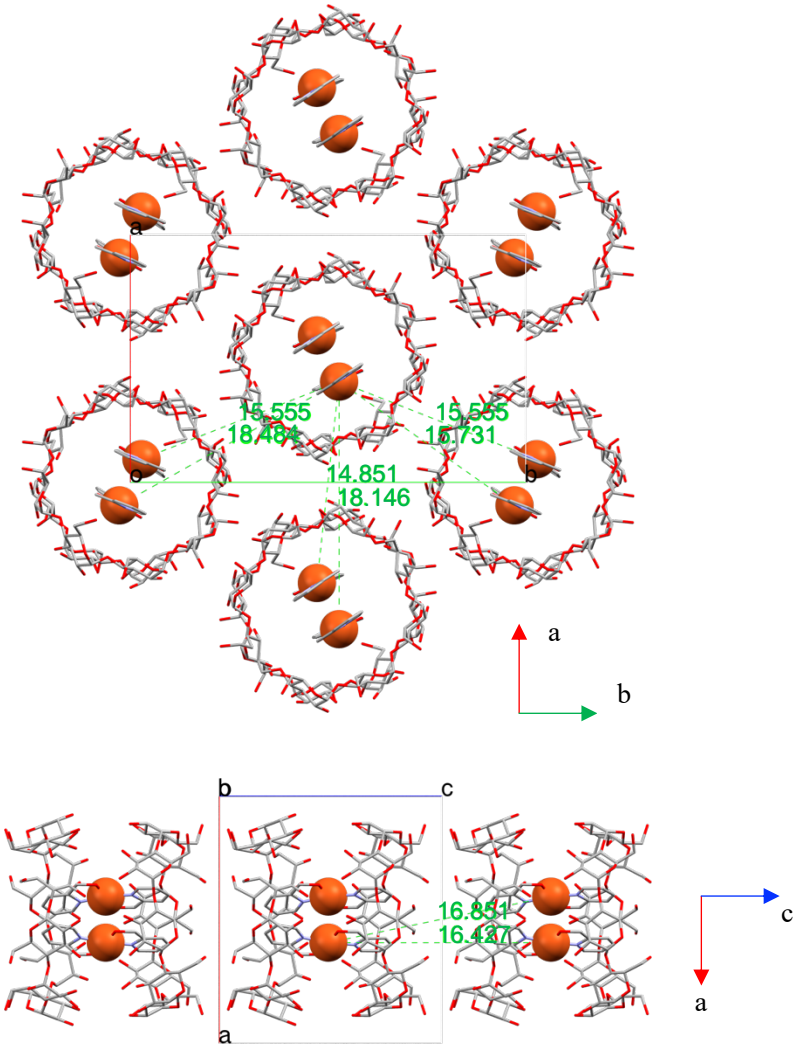


Figure S9 Inter-dimeric assembly Cu...Cu distances. Cu: CPK model; γ-CD: capped sticks model; (red: O, grey: C, blue: N). Water molecules, counter anions and protons are omitted for clarity. Top: view from the c axis direction; bottom: view from the b axis direction.

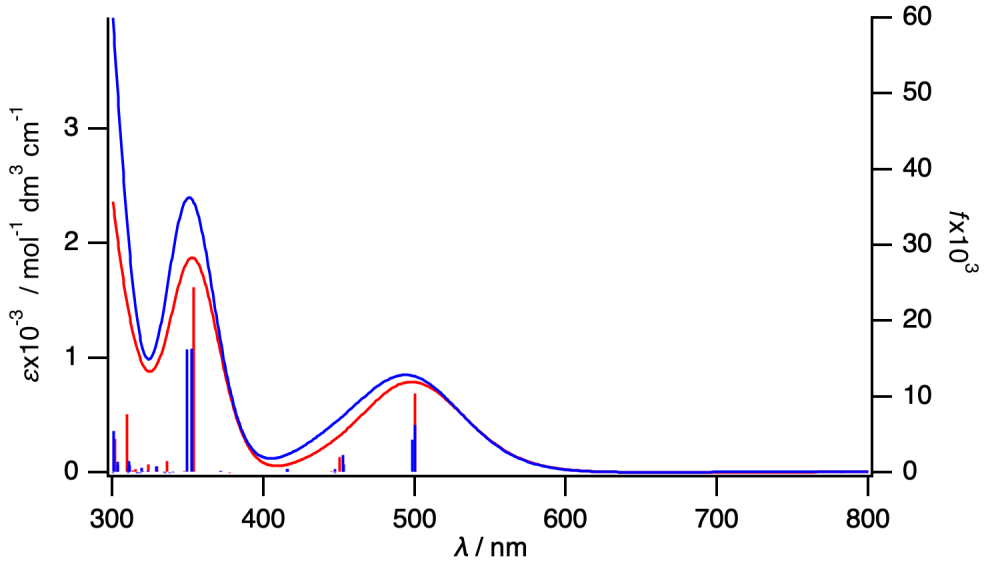


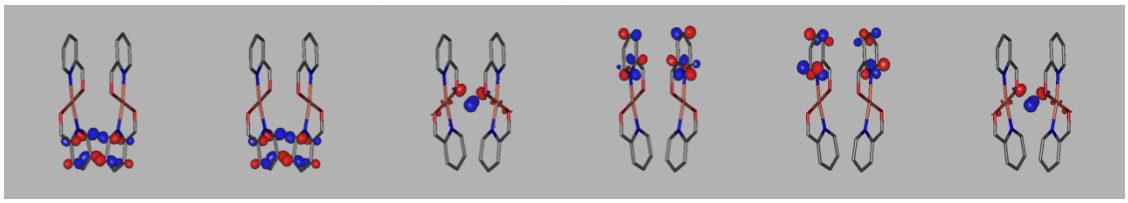
Figure S10 Simulated absorption spectra. The red and blue spectra are the simulated spectra for the monomeric $[Cu(L)(HL)]^+$ fragment and the dimeric $[Cu(L)(HL)]^+$ assembly, respectively. The solid line indicates the simulated spectra (left scale) and the vertical lines indicate the oscillator strength (right scale).

Table S11. Calculated transitions and compositions of molecular orbitals for the dimeric $[Cu(L)(HL)]^+$ assembly

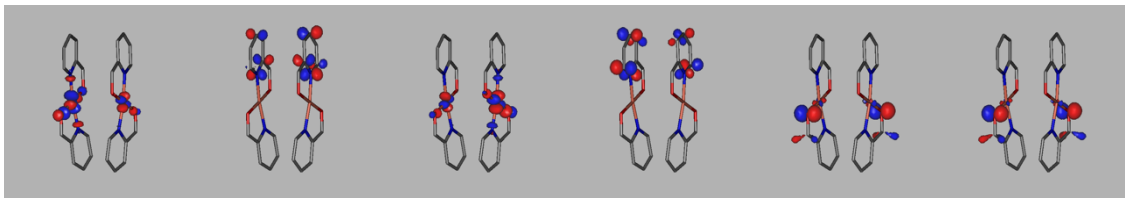
No.	energy /cm^{-1}	wavelength /nm	oscillator strength	symmetry	transition [a]
1	12779.85493	782.4814958	0.0001	3.007-A	HOMO-01(B)->LUMO(B) (18%), HOMO-01(B)->LUMO+01(B) (22%), HOMO(B)->LUMO(B) (41%)
2	12784.69425	782.185307	0	3.007-A	HOMO-01(B)->LUMO(B) (22%), HOMO-01(B)->LUMO+01(B) (18%), HOMO(B)->LUMO+01(B) (40%)
3	20000.13018	499.9967456	0.0063	3.004-A	HOMO-11(B)->LUMO+01(B) (17%), HOMO-4(B)->LUMO(B) (13%), HOMO-03(B)->LUMO+01(B) (20%)
4	20064.65453	498.3888452	0.0043	3.004-A	HOMO-11(B)->LUMO(B) (18%), HOMO-04(B)->LUMO+01(B) (13%), HOMO-03(B)->LUMO(B) (20%)
5	22083.46027	452.8275859	0.0011	3.004-A	HOMO-20(B)->LUMO+01(B) (14%), HOMO-15(B)->LUMO+01(B) (10%), HOMO-12(B)->LUMO+01(B) (10%), HOMO-11(B)->LUMO(B) (15%)
6	22092.33236	452.645734	0.0023	3.004-A	HOMO-19(B)->LUMO(B) (11%), HOMO-15(B)->LUMO(B) (10%), HOMO-12(B)->LUMO(B) (10%), HOMO-11(B)->LUMO+01(B) (15%)
7	22360.10844	447.2250226	0	3.004-A	HOMO-21(B)->LUMO+01(B) (19%), HOMO-18(B)->LUMO(B) (20%), HOMO-10(B)->LUMO+01(B) (23%), HOMO-08(B)->LUMO(B) (13%)
8	22364.14121	447.1443776	0.0004	3.004-A	HOMO-21(B)->LUMO(B) (19%), HOMO-18(B)->LUMO+01(B) (20%), HOMO-10(B)->LUMO(B) (23%), HOMO-08(B)->LUMO+01(B) (13%)
9	24028.06299	416.1800309	0.0004	3.012-A	HOMO-01(B)->LUMO+01(B) (38%), HOMO(B)->LUMO(B) (46%)
10	24054.67929	415.7195313	0.0004	3.010-A	HOMO-01(B)->LUMO(B) (39%), HOMO(B)->LUMO+01(B) (47%)
11	26896.17054	371.800141	0.0002	3.018-A	HOMO-19(B)->LUMO(B) (11%), HOMO-17(B)->LUMO(B) (14%), HOMO-16(B)->LUMO+01(B) (13%), HOMO-01(B)->LUMO(B) (13%)
12	26913.91474	371.5550152	0.0002	3.018-A	HOMO-20(B)->LUMO+01(B) (15%), HOMO-17(B)->LUMO+01(B) (14%), HOMO-16(B)->LUMO(B) (13%), HOMO-01(B)->LUMO+01(B) (13%)
13	28375.39137	352.4180467	0.0163	3.012-A	HOMO-4(B)->LUMO(B) (21%), HOMO-03(B)->LUMO+01(B) (18%)
14	28635.10189	349.2217362	0.0162	3.013-A	HOMO-04(B)->LUMO+01(B) (20%), HOMO-3(B)->LUMO(B) (20%)
15	29390.03684	340.2513598	0.0001	4.026-A	HOMO-04(A)->LUMO+09(A) (11%), HOMO-02(B)->LUMO+11(B) (10%)
16	29594.09511	337.9052464	0	3.836-A	HOMO-02(B)->LUMO+01(B) (16%)
17	29869.93672	334.7847735	0	3.161-A	HOMO-05(B)->LUMO+01(B) (15%), HOMO-2(B)->LUMO(B) (53%)
18	29890.90714	334.5499002	0.0001	3.411-A	HOMO-05(B)->LUMO(B) (12%), HOMO-2(B)->LUMO+01(B) (39%)
19	30388.55122	329.0712982	0.0008	4.054-A	HOMO(A)->LUMO+02(A) (21%), HOMO(B)->LUMO+03(B) (15%), HOMO(B)->LUMO+04(B) (31%)

20	30921.6837	323.3976551	0.0002	4.071-A	HOMO-01(B)->LUMO+03(B) (14%), HOMO(B)->LUMO+02(B) (20%)
21	31324.15436	319.242457	0.0006	4.050-A	HOMO(B)->LUMO+03(B) (15%), HOMO(B)->LUMO+04(B) (12%)
22	31383.03283	318.6435184	0	4.084-A	HOMO-01(A)->LUMO+02(A) (18%), HOMO-01(B)->LUMO+04(B) (31%)
23	31580.63867	316.6497076	0	3.014-A	HOMO-04(B)->LUMO(B) (37%), HOMO-04(B)->LUMO+01(B) (13%), HOMO-03(B)->LUMO(B) (31%), HOMO-03(B)->LUMO+01(B) (15%)
24	31604.8353	316.4072809	0	3.013-A	HOMO-04(B)->LUMO(B) (13%), HOMO-04(B)->LUMO+01(B) (41%), HOMO-03(B)->LUMO(B) (13%), HOMO-03(B)->LUMO+01(B) (30%)
25	32101.67283	311.510246	0.001	3.585-A	HOMO(B)->LUMO+2(B) (50%)
26	32130.70879	311.2287396	0.0015	3.529-A	HOMO-05(B)->LUMO(B) (17%), HOMO(B)->LUMO+03(B) (25%)
27	32194.42659	310.6127693	0.0007	3.201-A	HOMO-05(B)->LUMO(B) (43%), HOMO-02(B)->LUMO+01(B) (19%), HOMO(B)->LUMO+03(B) (13%)
28	32207.33146	310.4883127	0	3.013-A	HOMO-05(B)->LUMO+01(B) (64%), HOMO-02(B)->LUMO(B) (27%)
29	32928.39112	303.6892985	0.001	3.801-A	HOMO(A)->LUMO+01(A) (24%)
30	32931.61734	303.6595469	0.0014	3.842-A	HOMO(A)->LUMO(A) (25%)
31	33259.88499	300.6624949	0.0055	3.695-A	HOMO-02(A)->LUMO+01(A) (11%), HOMO-01(A)->LUMO(A) (12%), HOMO(A)->LUMO+01(A) (15%), HOMO(A)->LUMO+02(A) (11%)
32	33275.20952	300.5240281	0	3.879-A	HOMO-01(A)->LUMO+01(A) (13%), HOMO(A)->LUMO(A) (28%)

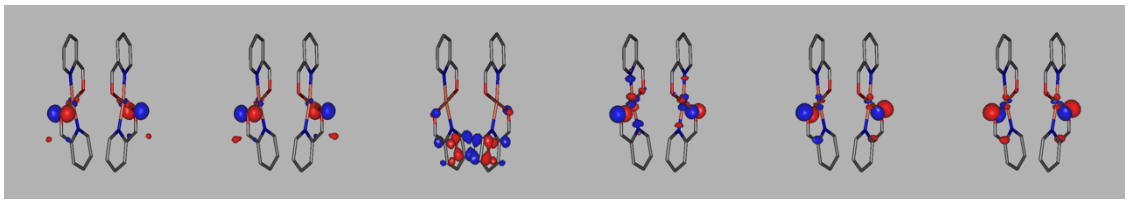
[a] Only major transitions (>10%) are shown. (A) and (B) represent the alpha and beta molecular orbitals, respectively.



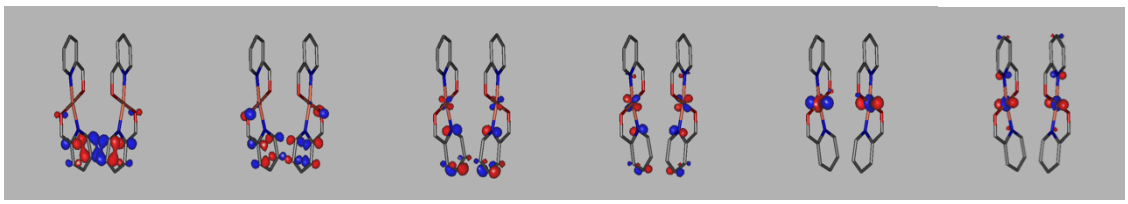
LUMO+11(B) LUMO+09(A) LUMO+04(B) LUMO+03(B) LUMO+02(B) LUMO+02(A)



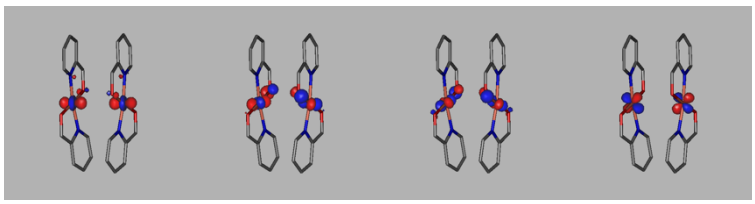
LUMO+01(B) LUMO+01(A) LUMO(B) LUMO(A) HOMO(B) HOMO(A)



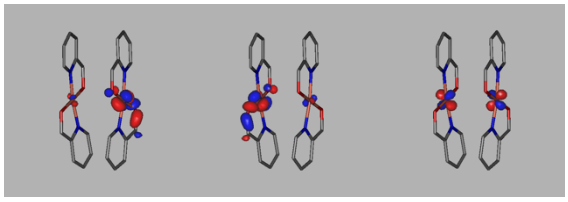
HOMO-01(B) HOMO-01(A) HOMO-02(B) HOMO-02(A) HOMO-03(B) HOMO-04(B)



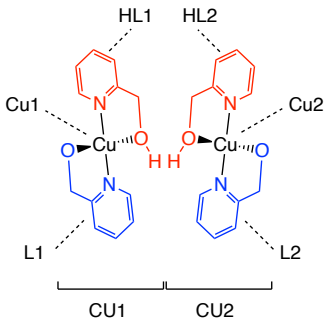
HOMO-04(A) HOMO-05(B) HOMO-08(B) HOMO-10(B) HOMO-11(B) HOMO-12(B)



HOMO-15(B) HOMO-16(B) HOMO-17(B) HOMO-18(B)



HOMO-19(B) HOMO-20(B) HOMO-21(B)



numbering

Figure S11 Calculated molecular orbitals

Table S12 Details of transitions

transition	contribution ratio of molecular part [a]															
	initial MO								final MO							
	Cu1	HL1	L1	Cu2	HL2	L2	CU1	CU2	Cu1	HL1	L1	Cu2	HL2	L2	CU1	CU2
HOMO(A)->LUMO+01(A)	0.04	0.01	0.44	0.04	0.01	0.45	0.50	0.50	0.02	0.38	0.02	0.02	0.54	0.02	0.42	0.58
HOMO(A)->LUMO+02(A)	0.04	0.01	0.44	0.04	0.01	0.45	0.50	0.50	0.04	0.36	0.10	0.04	0.36	0.10	0.50	0.50
HOMO(A)->LUMO(A)	0.04	0.01	0.44	0.04	0.01	0.45	0.50	0.50	0.01	0.56	0.01	0.01	0.41	0.00	0.58	0.42
HOMO(B)->LUMO+01(B)	0.05	0.01	0.43	0.05	0.01	0.44	0.50	0.50	0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO(B)->LUMO+02(B)	0.05	0.01	0.43	0.05	0.01	0.44	0.50	0.50	0.01	0.53	0.01	0.01	0.44	0.00	0.54	0.46
HOMO(B)->LUMO+03(B)	0.05	0.01	0.43	0.05	0.01	0.44	0.50	0.50	0.02	0.42	0.02	0.02	0.50	0.02	0.46	0.54
HOMO(B)->LUMO+04(B)	0.05	0.01	0.43	0.05	0.01	0.44	0.50	0.50	0.04	0.36	0.10	0.04	0.36	0.10	0.50	0.50
HOMO(B)->LUMO(B)	0.05	0.01	0.43	0.05	0.01	0.44	0.50	0.50	0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72
HOMO-01(A)->LUMO+01(A)	0.05	0.01	0.44	0.05	0.02	0.43	0.50	0.50	0.02	0.38	0.02	0.02	0.54	0.02	0.42	0.58
HOMO-01(A)->LUMO+02(A)	0.05	0.01	0.44	0.05	0.02	0.43	0.50	0.50	0.04	0.36	0.10	0.04	0.36	0.10	0.50	0.50
HOMO-01(A)->LUMO(A)	0.05	0.01	0.44	0.05	0.02	0.43	0.50	0.50	0.01	0.56	0.01	0.01	0.41	0.00	0.58	0.42
HOMO-01(B)->LUMO+01(B)	0.06	0.01	0.43	0.06	0.01	0.43	0.50	0.50	0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-01(B)->LUMO+03(B)	0.06	0.01	0.43	0.06	0.01	0.43	0.50	0.50	0.02	0.42	0.02	0.02	0.50	0.02	0.46	0.54
HOMO-01(B)->LUMO+04(B)	0.06	0.01	0.43	0.06	0.01	0.43	0.50	0.50	0.04	0.36	0.10	0.04	0.36	0.10	0.50	0.50
HOMO-01(B)->LUMO(B)	0.06	0.01	0.43	0.06	0.01	0.43	0.50	0.50	0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72
HOMO-02(A)->LUMO+01(A)	0.18	0.09	0.33	0.12	0.06	0.22	0.60	0.40	0.02	0.38	0.02	0.02	0.54	0.02	0.42	0.58
HOMO-02(B)->LUMO+01(B)	0.02	0.01	0.47	0.02	0.01	0.47	0.50	0.50	0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-02(B)->LUMO+11(B)	0.02	0.01	0.47	0.02	0.01	0.47	0.50	0.50	0.03	0.04	0.47	0.02	0.03	0.41	0.54	0.46
HOMO-02(B)->LUMO(B)	0.02	0.01	0.47	0.02	0.01	0.47	0.50	0.50	0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72
HOMO-03(B)->LUMO+01(B)	0.16	0.03	0.33	0.15	0.03	0.30	0.52	0.48	0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-03(B)->LUMO(B)	0.16	0.03	0.33	0.15	0.03	0.30	0.52	0.48	0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72
HOMO-04(A)->LUMO+09(A)	0.01	0.01	0.49	0.01	0.01	0.49	0.50	0.50	0.02	0.03	0.47	0.02	0.02	0.42	0.53	0.47
HOMO-04(B)->LUMO+01(B)	0.12	0.03	0.33	0.13	0.04	0.36	0.48	0.52	0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-04(B)->LUMO(B)	0.12	0.03	0.33	0.13	0.04	0.36	0.48	0.52	0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72
HOMO-05(B)->LUMO+01(B)	0.04	0.01	0.46	0.04	0.01	0.45	0.50	0.50	0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-05(B)->LUMO(B)	0.04	0.01	0.46	0.04	0.01	0.45	0.50	0.50	0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72
HOMO-08(B)->LUMO+01(B)	0.09	0.07	0.34	0.09	0.07	0.34	0.50	0.50	0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-08(B)->LUMO(B)	0.09	0.07	0.34	0.09	0.07	0.34	0.50	0.50	0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72
HOMO-10(B)->LUMO+01(B)	0.19	0.08	0.22	0.19	0.08	0.22	0.50	0.50	0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-10(B)->LUMO(B)	0.19	0.08	0.22	0.19	0.08	0.22	0.50	0.50	0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72

HOMO-11(B)->LUMO+01(B)	0.42	0.06	0.02	0.42	0.06	0.02	0.50	0.50		0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-11(B)->LUMO(B)	0.42	0.06	0.02	0.42	0.06	0.02	0.50	0.50		0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72
HOMO-12(B)->LUMO+01(B)	0.26	0.16	0.08	0.26	0.16	0.08	0.50	0.50		0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-12(B)->LUMO(B)	0.26	0.16	0.08	0.26	0.16	0.08	0.50	0.50		0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72
HOMO-15(B)->LUMO+01(B)	0.32	0.13	0.05	0.32	0.13	0.05	0.50	0.50		0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-15(B)->LUMO(B)	0.32	0.13	0.05	0.32	0.13	0.05	0.50	0.50		0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72
HOMO-16(B)->LUMO+01(B)	0.30	0.16	0.04	0.30	0.16	0.04	0.50	0.50		0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-16(B)->LUMO(B)	0.30	0.16	0.04	0.30	0.16	0.04	0.50	0.50		0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72
HOMO-17(B)->LUMO+01(B)	0.24	0.18	0.09	0.24	0.17	0.08	0.50	0.50		0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-17(B)->LUMO(B)	0.24	0.18	0.09	0.24	0.17	0.08	0.50	0.50		0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72
HOMO-18(B)->LUMO+01(B)	0.39	0.04	0.07	0.39	0.04	0.07	0.50	0.50		0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-18(B)->LUMO(B)	0.39	0.04	0.07	0.39	0.04	0.07	0.50	0.50		0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72
HOMO-19(B)->LUMO(B)	0.05	0.01	0.02	0.56	0.11	0.25	0.08	0.92		0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72
HOMO-20(B)->LUMO+01(B)	0.57	0.10	0.25	0.05	0.01	0.01	0.93	0.07		0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-21(B)->LUMO+01(B)	0.36	0.07	0.07	0.36	0.07	0.07	0.50	0.50		0.40	0.12	0.19	0.16	0.05	0.07	0.72	0.28
HOMO-21(B)->LUMO(B)	0.36	0.07	0.07	0.36	0.07	0.07	0.50	0.50		0.15	0.05	0.08	0.40	0.12	0.20	0.28	0.72

[a] CU*n* represents the contribution ratio of the monomeric $[Cu(L)(HL)]^+$ fragment and can be calculated from the sum of the contribution ratio of Cu*n*, HL*n* and L*n* (see numbering in Fig. S9).
The contribution ratio marked by red means that the ratio is larger than 0.7.

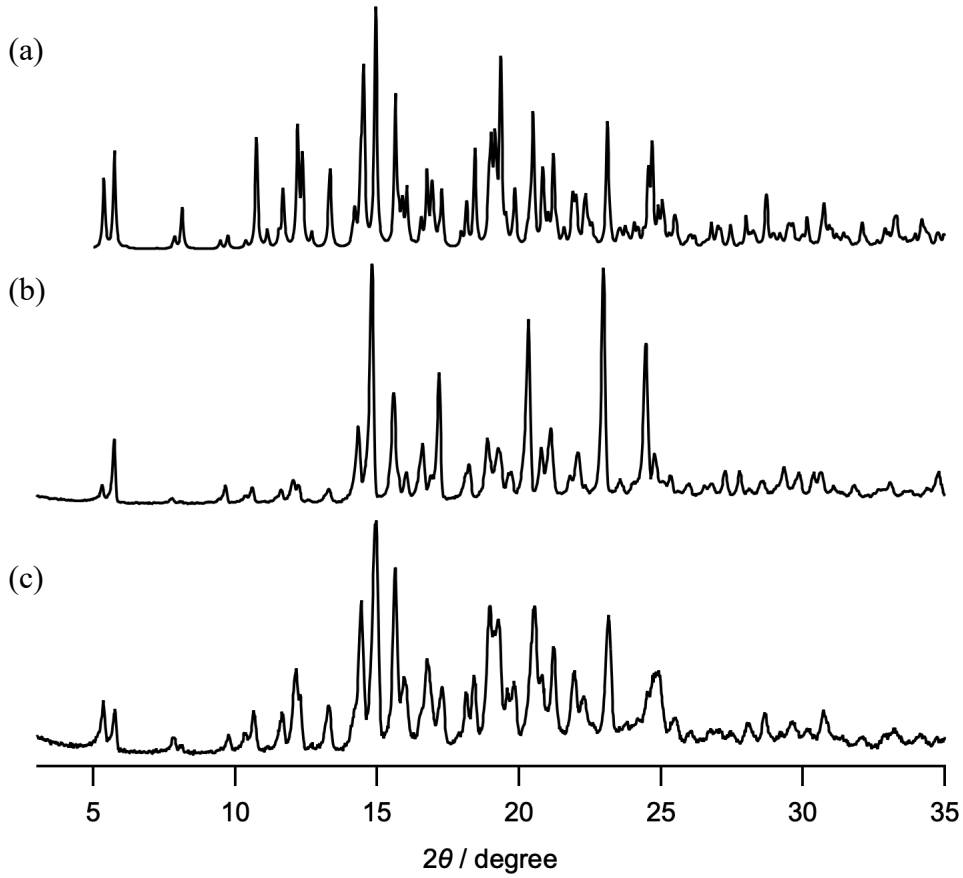


Figure S12 PXRD patterns of inclusion complex **1**. (a) Simulated pattern; (b) observed pattern of freshly prepared sample; (c) observed pattern after exposed to ambient atmosphere overnight.

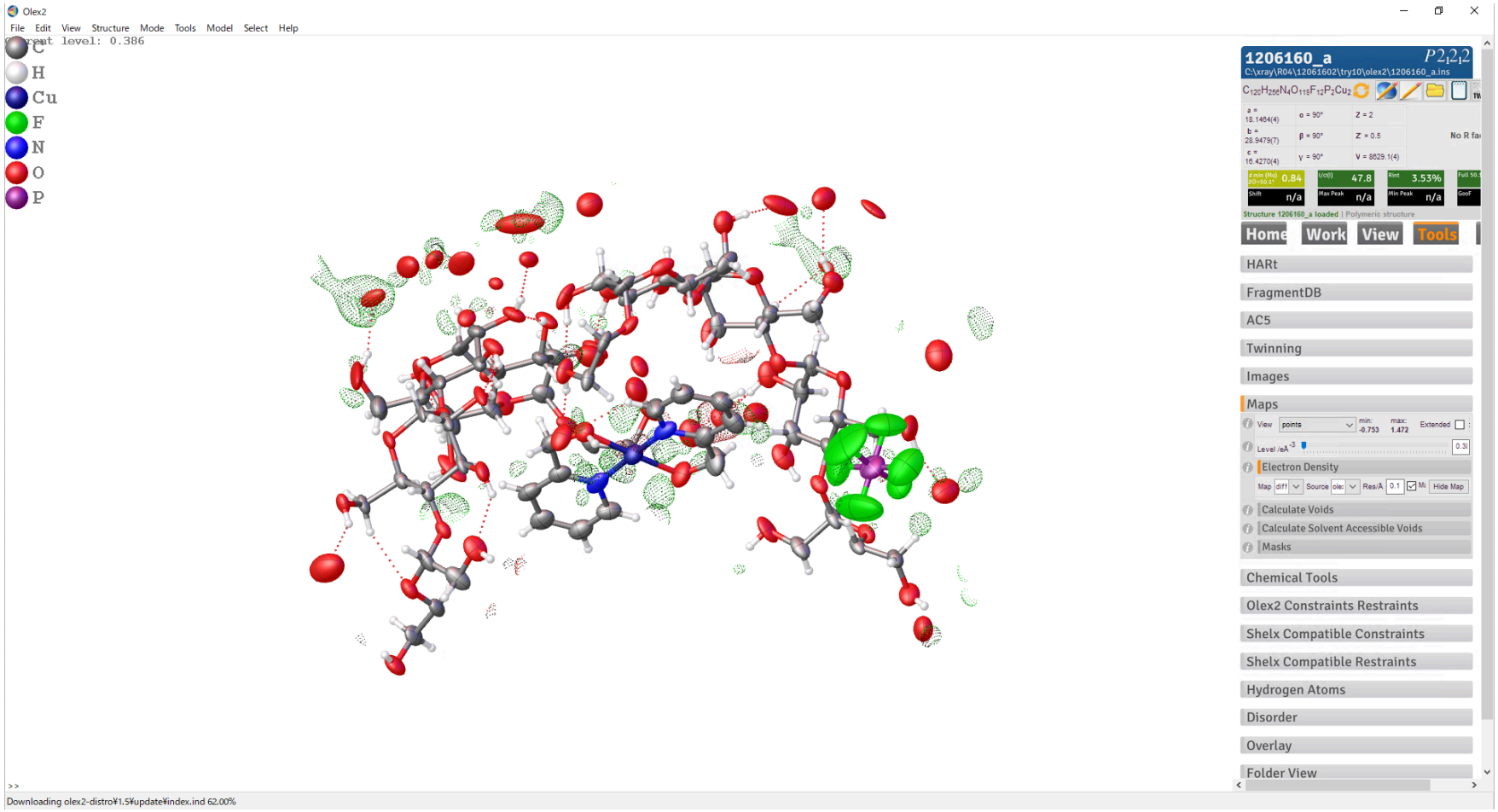


Figure S13 The residual density map