Supporting Information

Chemoselective mechanochemical route toward a bright TADF-emitting CuI–coordination polymer

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§1. X-Ray crystallography

Table S1. Data collection and selected refinement parameters for **1**–**3**.

	1	**2**	**3**
CCDC number	1866163	1866162	1585528
Chemical formula	$C_{16}H_{22}Cu_2I_2N_2S_2$	$C_{16}H_{22}Cu_3I_3N_2S_2$	$C_{16}H_{22}Cu_3I_3N_2S_2$
M_r	687.35	877.79	877.79
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2/n$	Monoclinic, $C2/c$
a, b, c (Å)	8.7276 (4), 14.4775 (7), 9.7601 (5)	9.9190 (5), 9.0927 (6), 13.9818 (8)	9.6005 (6), 17.2685 (15), 15.6571 (10)
β (°)	112.665 (2)	95.811 (2)	107.090 (2)
V (Å^3)	1137.99 (10)	1254.55 (13)	2481.1 (3)
Z	2	2	4
μ (mm^{-1})	4.77	6.38	6.45
Crystal size (mm)	0.70 × 0.42 × 0.15	0.9 × 0.8 × 0.3	0.90 × 0.20 × 0.06
T_{min}, T_{max}	0.509, 0.928	0.581, 0.746	0.431, 0.862
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15030, 2545, 2221	23069, 2651, 2130	21846, 2845, 2492
R_{int}	0.042	0.033	0.052
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650	0.633	0.649
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.087, 1.04	0.025, 0.052, 1.08	0.035, 0.098, 1.08
No. of reflections	2545	2651	2845
No. of parameters	111	121	137
No. of restraints	0	0	4
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	2.01, -1.49	0.71, -0.64	1.03, -1.66

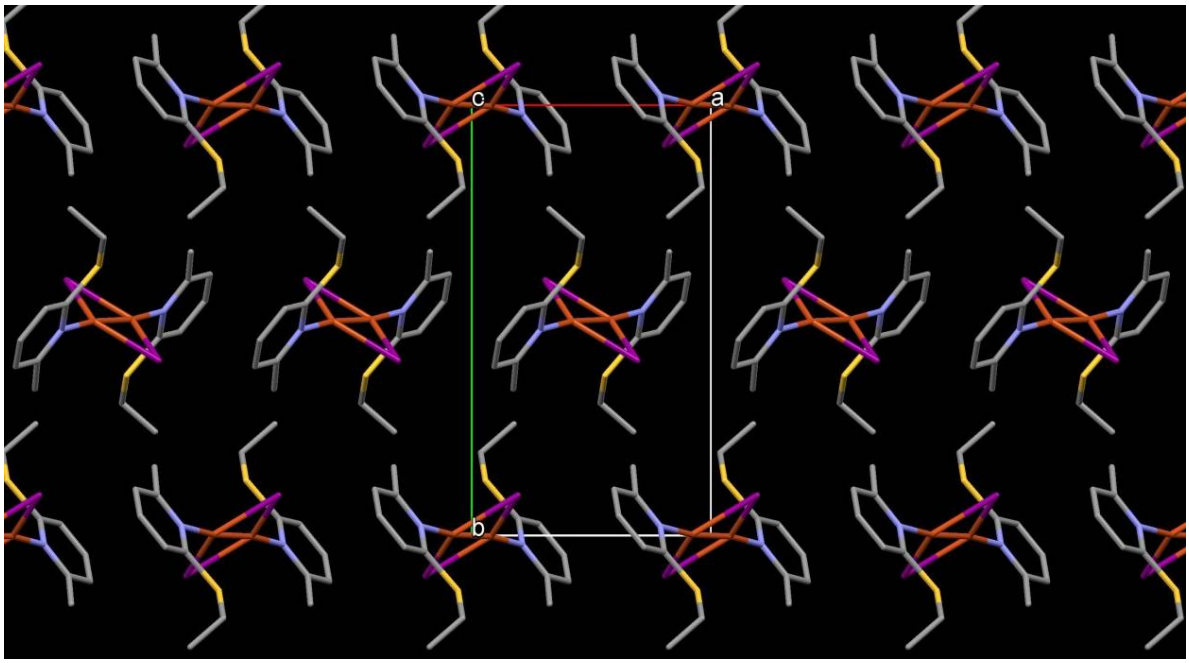


Figure S1. Perspective view of crystal packing of **1** along *c* axis (the H atoms are omitted).

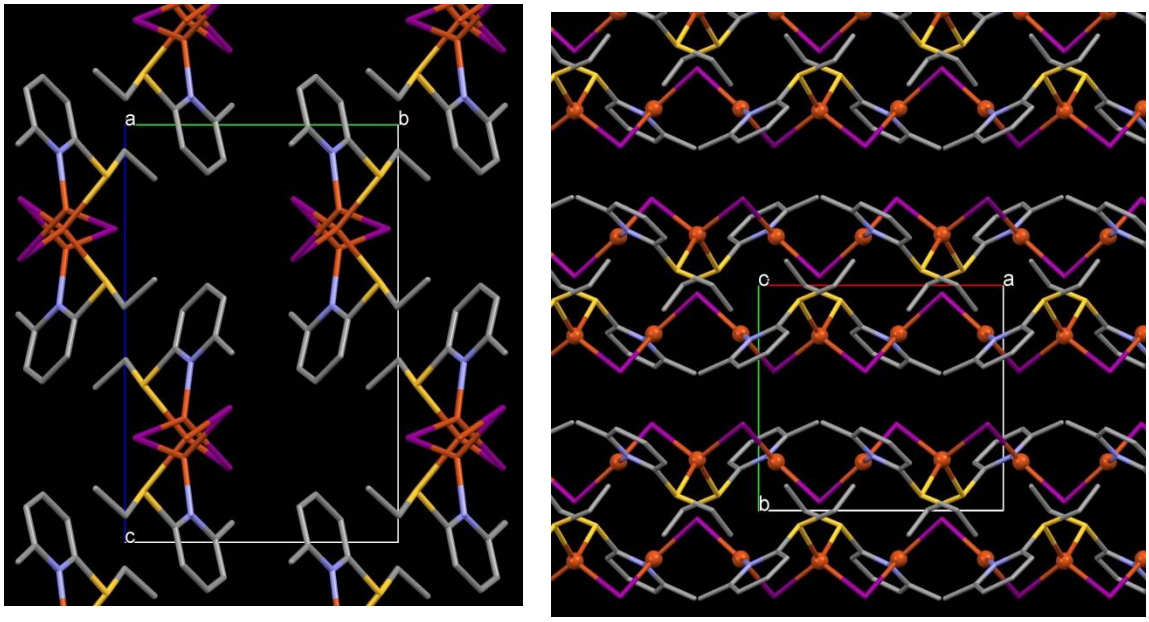


Figure S2. Perspective views of crystal packing of CP **2** along *a* (*left*) and *c* (*right*) axes (the H atoms are omitted).

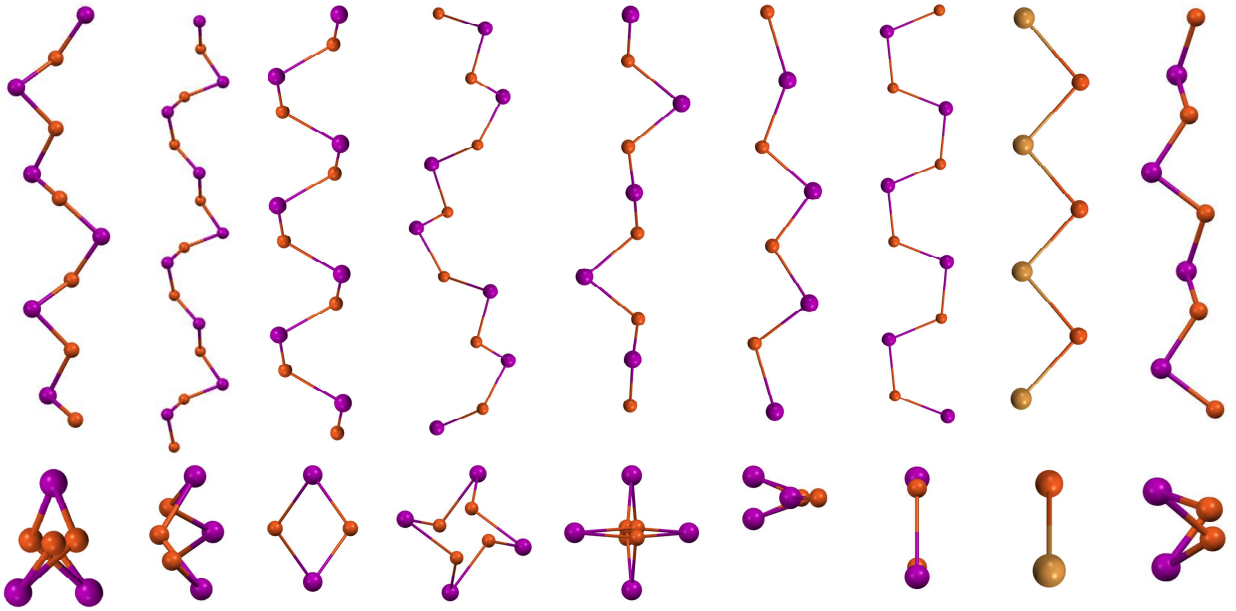


Figure S3. Side and end-on views of $(–Cu–Hal–)_n$ chains in CPs **2** and **3** compared with those in known CPs. Iodine atoms are violet, and bromine atoms are brownish-colored ones.

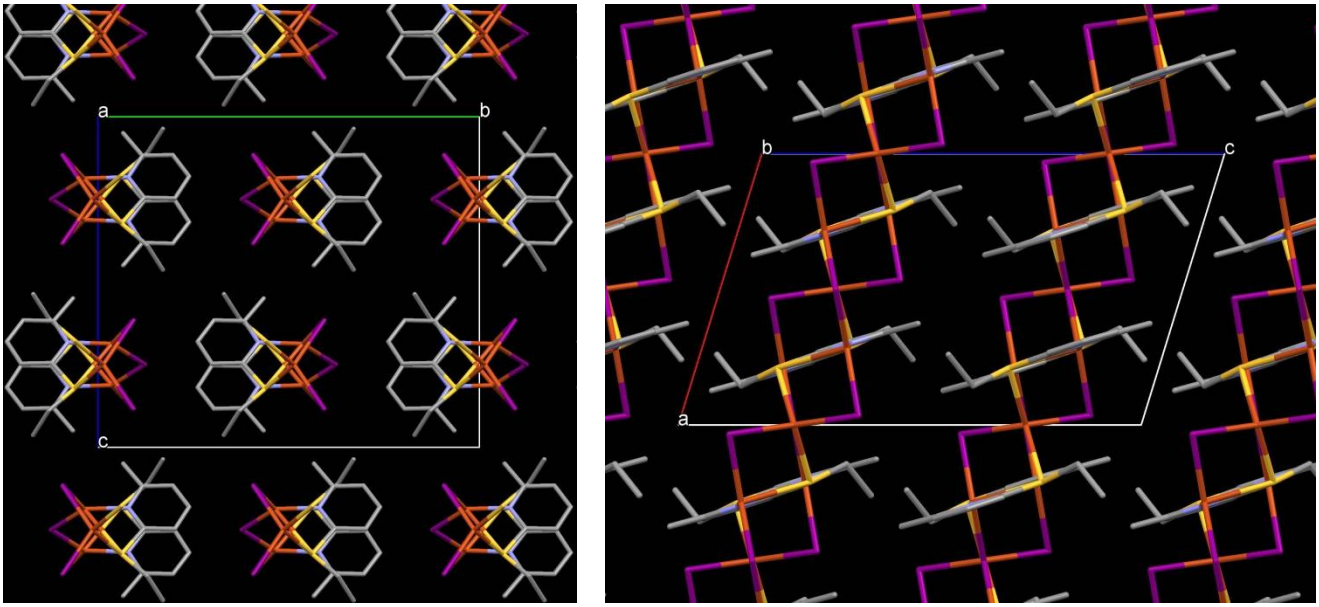


Figure S4. Perspective views of crystal packing of CP **3** along *a* (*left*) and *b* (*right*) axes (the H atoms are omitted).

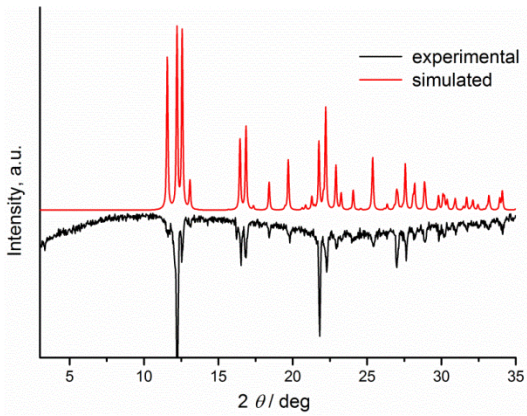


Figure S5. Experimental and simulated XRPD patters of complex **1**.

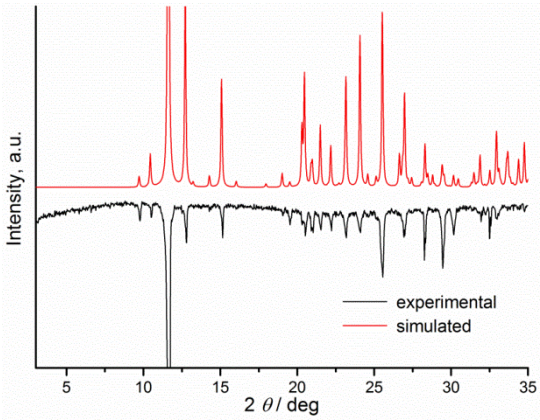


Figure S6. Experimental and simulated XRPD patters of CP **2**.

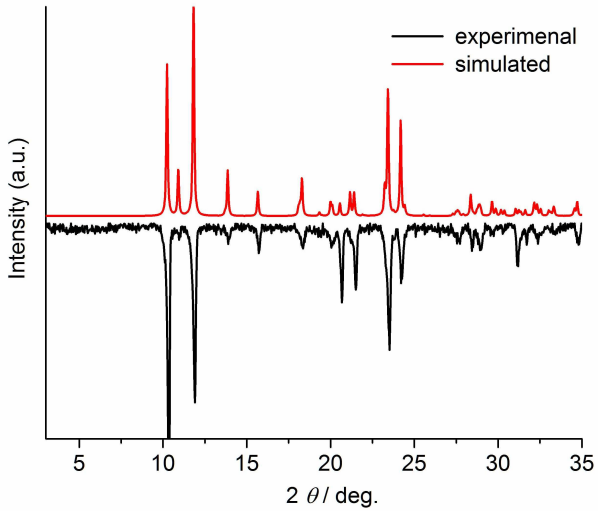


Figure S7. Experimental and simulated XRPD patters of CP **3**.

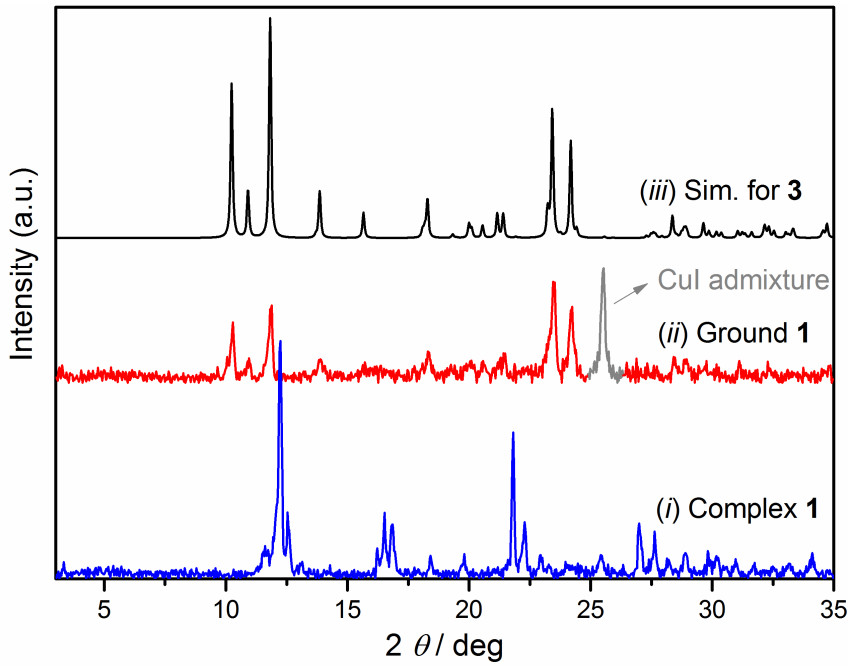


Figure S8. PXRD patterns of: (*i*) crystalline complex **1**; (*ii*) ground powder of **1** (with several drops of MeCN). The simulated PXRD pattern for CP **3** is in the top of the picture.

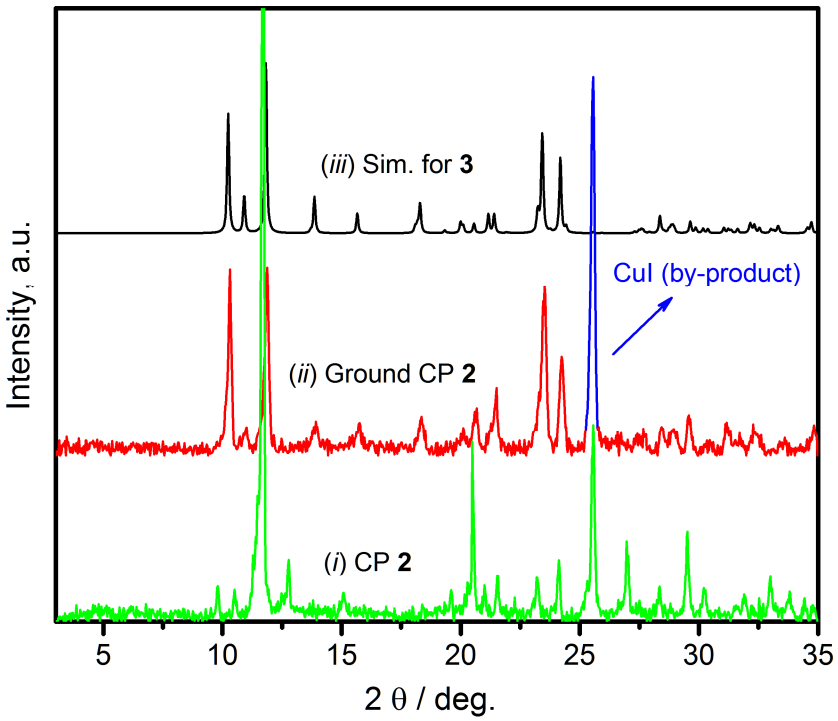


Figure S9. PXRD patterns of: (*i*) crystalline CP **2**; (*ii*) ground powder of CP **2** (with several drops of MeCN). The simulated PXRD pattern for CP **3** is in the top of the picture.

§2. FT-IR spectra

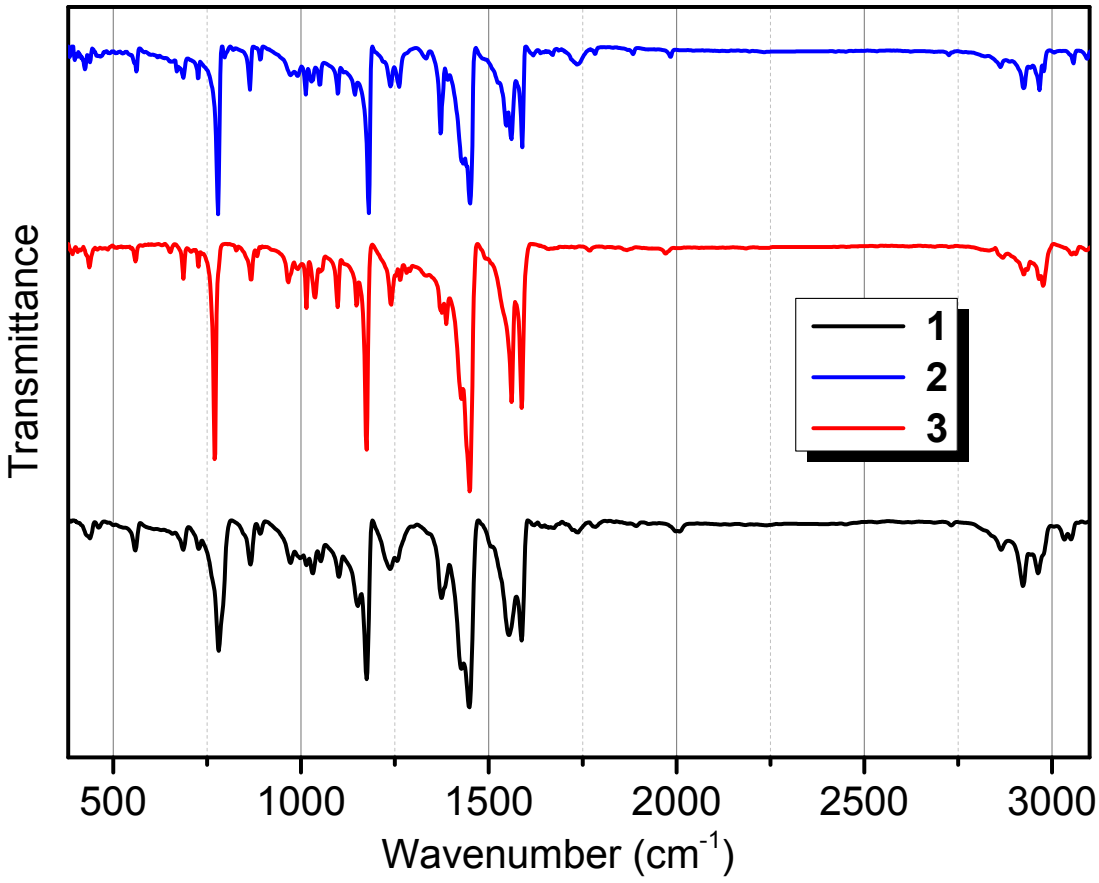
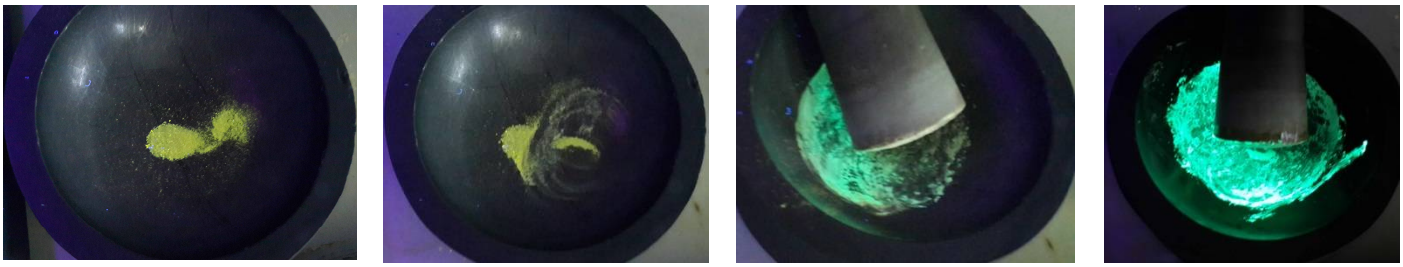


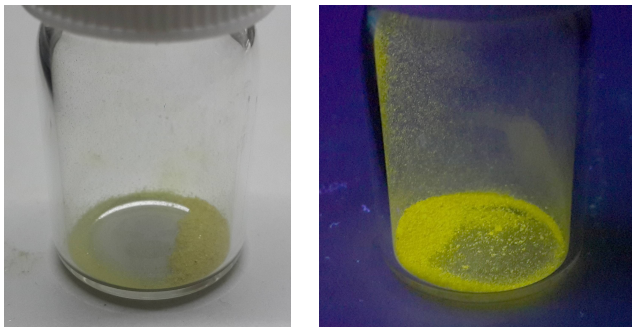
Figure S10. FT-IR spectra of **1**–**3** in the 400–3100 cm^{-1} range.

§3. Photophysical data



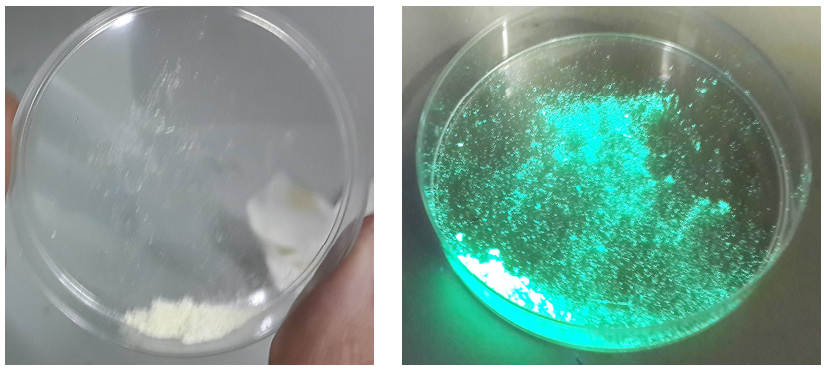
(***a***) (***b***) (***c***) (***d***)

Figure S11. An enhancement of the photoluminescence associated with **2**→**3** isomerisation under solvent-assistant mechanochemical conditions (views under UV-lamp): (*a*) crystalline **2**; (*b*) ground **2**; (*c*–*d*) ground **2** with several drops of MeCN.



(***a***) (***b***)

Figure S12. Photographs of the powder of CP **2** under ambient light (*left*) and UV-light (*right*).



(***a***) (***b***)

Figure S13. Photographs of the powder of CP **3** under ambient light (*left*) and UV-light (*right*).

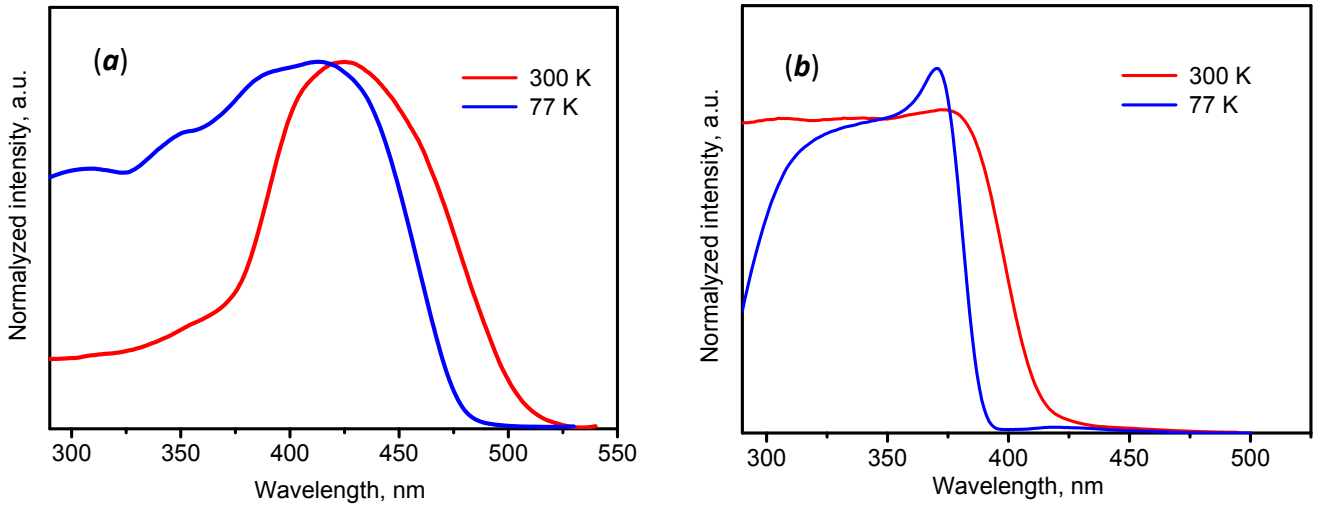


Figure S14. (***a***) Solid-state PLE spectra of CP **2** at 77 and 300 K (λ_{em} = 545 nm); (***b***) Solid-state PLE spectra of CP **3** at 77 and 300 K (λ_{em} = 515 nm).

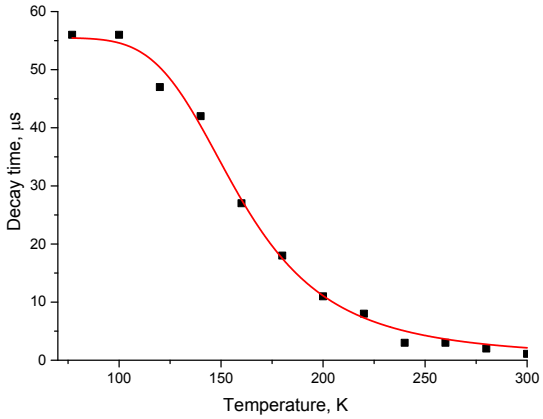
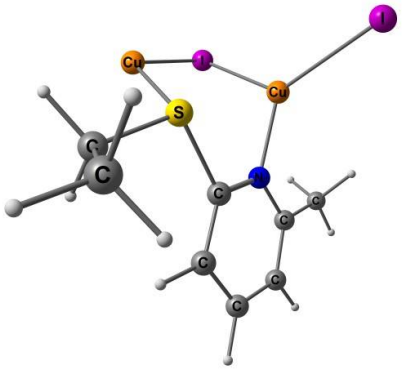
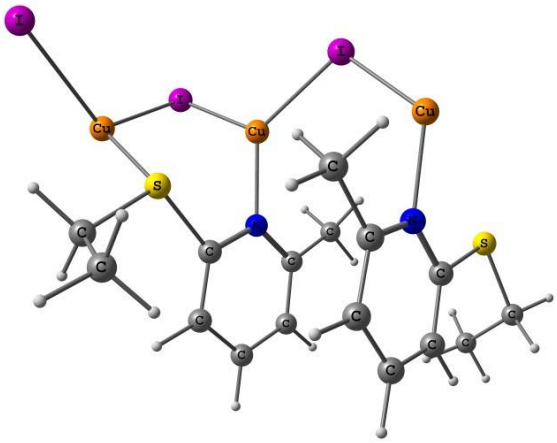


Figure S15. Temperature dependence of emission lifetime for CP **2** (λ_{ex} = 420 nm and λ_{det} = 545 nm).

§4. Computational details



$[Cu_2I_2L]$ (3a)



$[Cu_3I_3L_2]$ (3b)

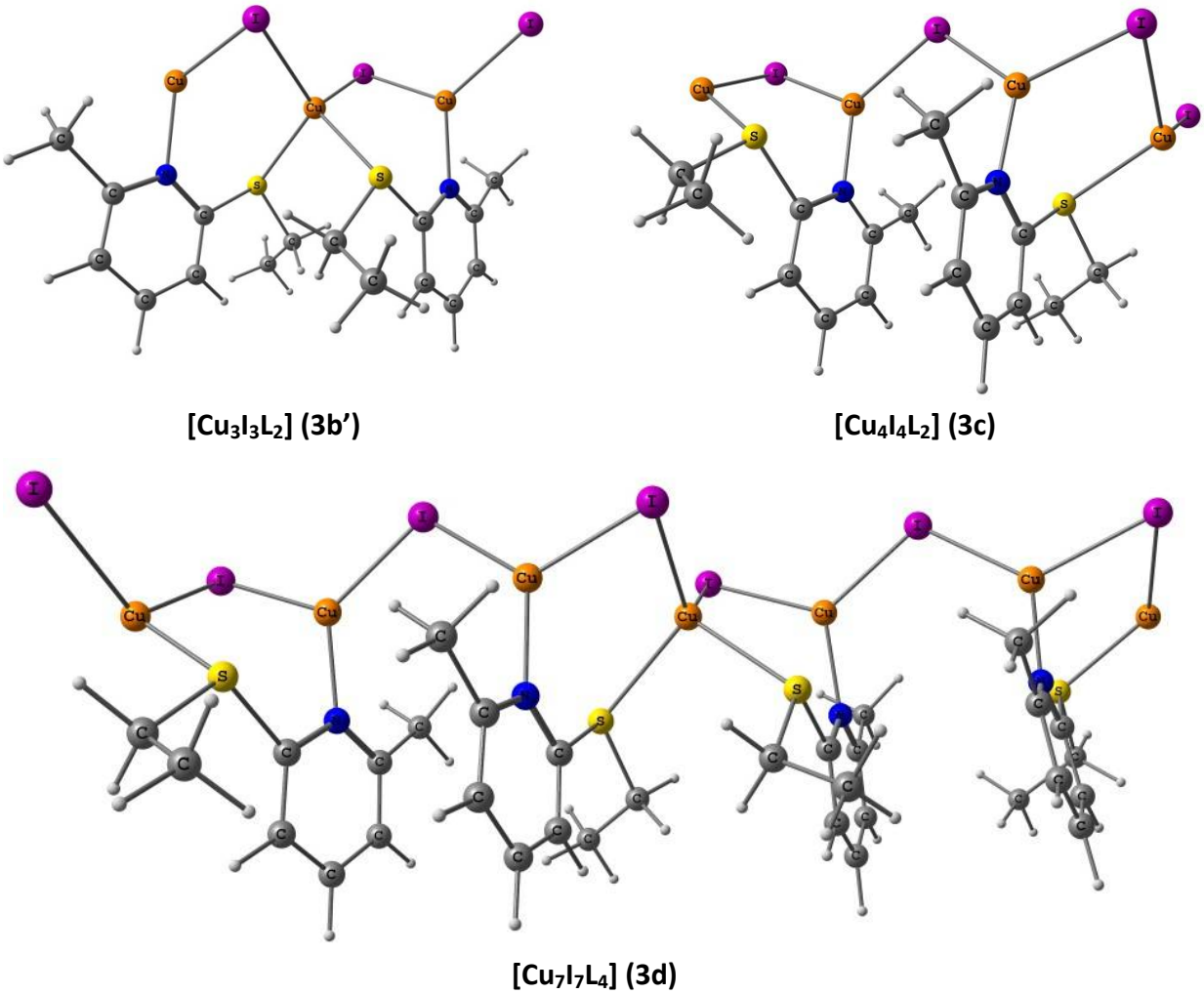


Figure S16. Perspective view of the B3LYP/def2-TZVPP optimized molecular fragments **3a-d** of the polymeric structure $[Cu_3I_3L_2]_n$ (**3**).

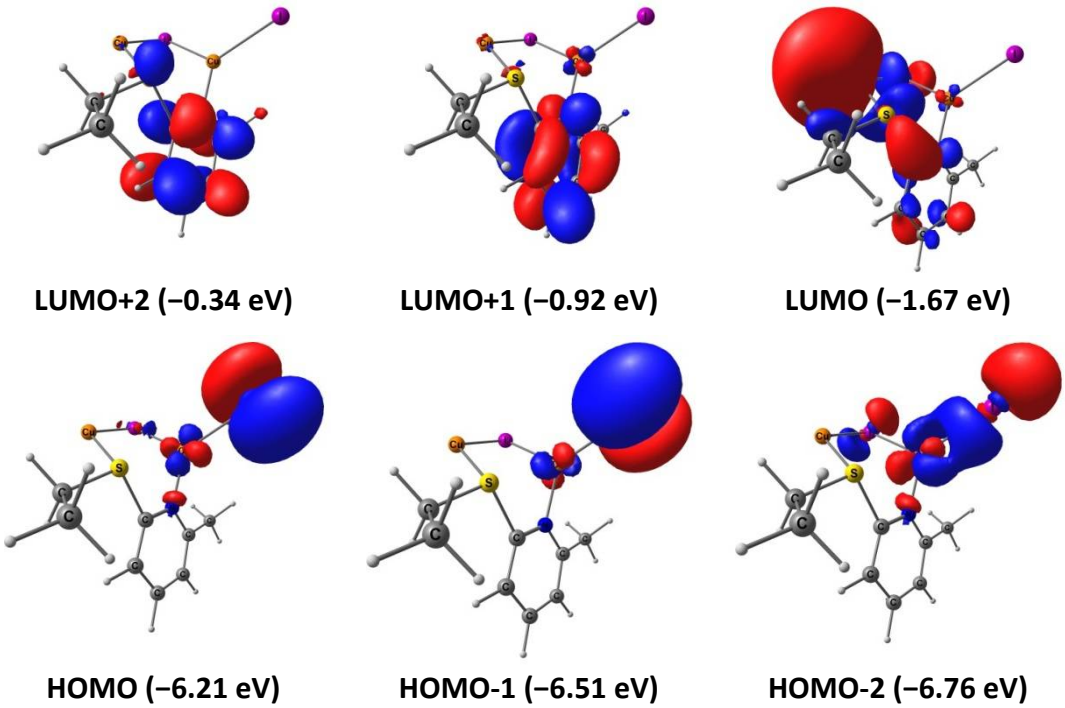


Figure S17. 3D images of CAM-B3LYP/def2-TZVPP MOs of the model fragment $[Cu_2I_2L]$ (**3a**).

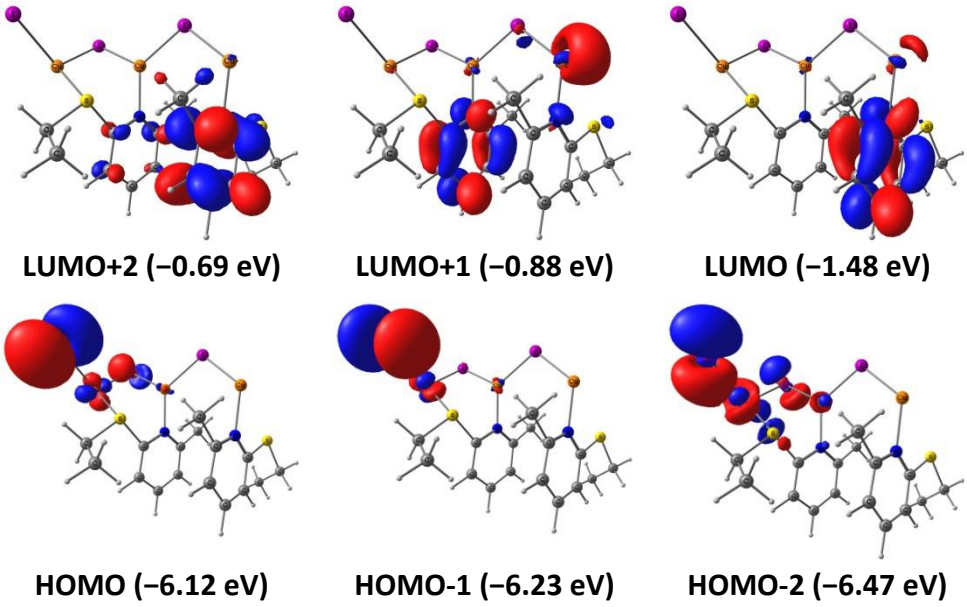


Figure S18. 3D images of CAM-B3LYP/def2-TZVPP MOs of the model fragment $[Cu_3I_3L_2]$ (**3b**).

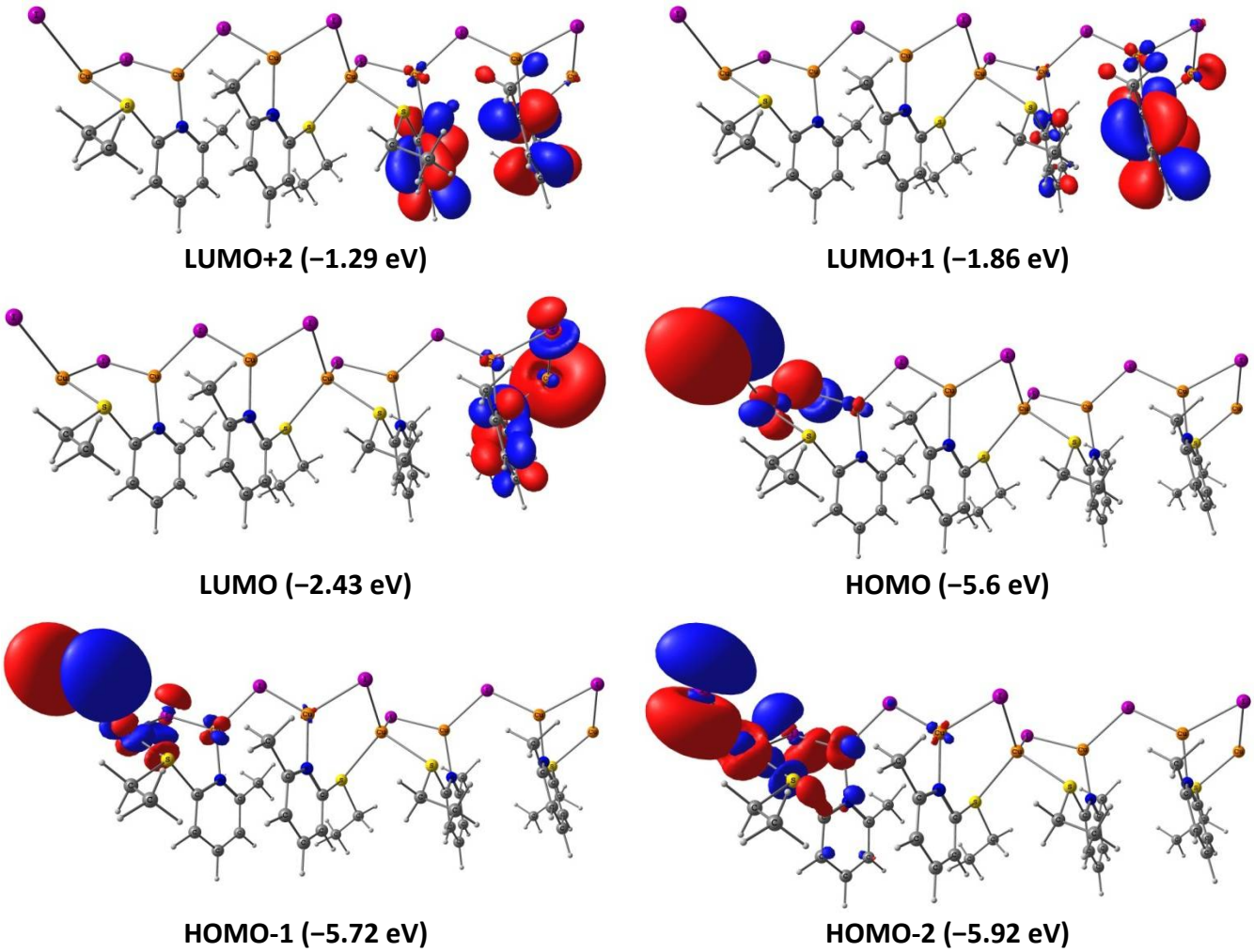


Figure S19. 3D images of CAM-B3LYP/def2-TZVPP MOs of the model fragment $[Cu_7I_7L_4]$ (**3d**).

Table S2. The most significant singlet-singlet electronic transitions (wavelength, λ, and oscillator strength, *f*, *f* > 0.02) in the absorption spectra of the **3a-c**.

	method	**λ (nm)**	***f***
3a	B3LYP/def2-TZVPP	457/366/324/295	0.053/0.021/0.022/0.021
	CAM-B3LYP/def2-TZVPP	356/342/326	0.040/0.031/0.026
	LC-wPBE/def2-TZVPP	336/309/283	0.030/0.030/0.044
3b	B3LYP/def2-TZVPP	403/378/361/322	0.023/0.023/0.072/0.022
	CAM-B3LYP/def2-TZVPP	363/343/328/323/317/314	0.026/0.029/0.043/0.058/0.020/0.031
	LC-wPBE/def2-TZVPP	312/311/280	0.068/0.050/0.057
3c	B3LYP/LANL2DZ	424/400	0.029/0.036
	B3LYP/def2-TZVPP	419/393	0.025/0.027
	CAM-B3LYP/LANL2DZ	324/319/295	0.073/0.022/0.025
	CAM-B3LYP/def2-TZVPP	353/326/324	0.028/0.051/0.029
	LC-wPBE/LANL2DZ	299/295/287	0.046/0.037/0.043
	LC-wPBE/def2-TZVPP	317/303/302	0.052/0.022/0.048

Cartesian coordinates of the optimized [Cu_2I_2L] (3a) molecular fragment

Cu	-0.05013274286577	0.03822450961300	0.06718619454815
I	2.53319998879460	0.00000000365462	0.00000000210932
I	-1.27465299908827	2.15540636264373	-0.00000001034849
Cu	1.94431808458256	-1.20214914621577	-2.22611348616516
N	-0.87234294807430	-1.79865512757134	0.09929625221813
C	-1.01889377509920	-2.50506383728887	-1.02718093629166
C	-1.64258968676766	-3.74132841093728	-1.08223988339880
C	-2.15118257832232	-4.25460751364894	0.10358367922865
C	-2.01261483795663	-3.52969720739793	1.27559533316602
C	-1.36297269001245	-2.29833447842180	1.25366105125729
S	-0.33173372431604	-1.63423957517211	-2.44359848231444
C	-0.49023014841441	-2.83563455254285	-3.76902761090098
C	-1.86533989184824	-2.86596397335996	-4.43313858283640
H	0.25793523530807	-2.52684177500413	-4.49943768903525
H	-0.18021649532987	-3.81473523640142	-3.40645071034758
H	-1.86831328780281	-3.59439052880025	-5.24556284527177
H	-2.11181677084189	-1.89050990712352	-4.85030404250643
H	-2.65575302575139	-3.13565603633764	-3.73478270972337
H	-1.74047218921395	-4.29226147774200	-2.00239451549695
H	-2.65122299079539	-5.21361931335800	0.10574645448076
H	-2.40292958101163	-3.90810737686122	2.20910679325744
C	-1.17860767956817	-1.47359990416915	2.48688593619166
H	-1.64591617343246	-1.94375062550280	3.34970017733241
H	-0.11609686143856	-1.33523344669581	2.69590899947729
H	-1.60574562681480	-0.47878524827670	2.34119998816227

Cartesian coordinates of the optimized [$Cu_4I_4L_2$] (3c) molecular fragment

Cu	-0.03260089799062	0.02639373928809	0.07501791711328
I	2.53319998958146	0.00000001753800	-0.00000001755495
I	-1.27465295700959	2.15540629200973	0.00000003784846
Cu	1.94431812330943	-1.20214917264442	-2.22611349453988
Cu	-3.70471213612340	1.55237565721168	-0.04103083462467
I	-5.48184864719261	3.35741476359778	-0.01418144746493
Cu	-5.94891500034109	2.03857400374491	2.17443318518761
I	-5.36017835981544	3.24058939783804	4.40065741495039
N	-0.87234318292404	-1.79865500886436	0.09929625302681
C	-1.01889352535138	-2.50506394480338	-1.02718094903137
C	-1.55840041029930	-3.78053476473129	-1.06393831799662
C	-1.95065014437608	-4.34408768449426	0.14265107720847
C	-1.77676473395000	-3.63322584515582	1.31776317529764
C	-1.22971875079176	-2.35366344558392	1.27644030990382
S	-0.36104160057204	-1.62273360048547	-2.45016008962272
C	-0.49023022319337	-2.83563452237566	-3.76902759676158
C	-1.86564656144943	-2.92975667573282	-4.42439365395596
H	0.23976375399363	-2.50109996936629	-4.50674999701548
H	-0.13778909150572	-3.79839598303228	-3.40182287607618
H	-1.83960054701860	-3.66704732537459	-5.22815653846226
H	-2.15461961167268	-1.97137166211260	-4.85312044066070
H	-2.63948312968008	-3.22660587599839	-3.71857381607409
H	-1.66959213509808	-4.32877980767516	-1.98408239556539
H	-2.37783240733110	-5.33751927781843	0.15938773163673
H	-2.05540043359612	-4.06122471137771	2.26950668238606
C	-0.97910869887448	-1.55262994208261	2.51380245532830
H	-1.33097858644129	-2.07533871764682	3.39993197808855
H	0.09029087435961	-1.36185315300494	2.62510220844209
H	-1.47887779829541	-0.58457058111896	2.45532506866374
N	-4.39906745478495	-0.34892302154418	-0.22221440987864
C	-4.78558734127126	-0.95616482550429	0.91160991705726
C	-5.38224490403862	-2.21976514947131	0.89326923883530
C	-5.60174451336505	-2.82947273976776	-0.32909808090736

C	-5.23129203753318	-2.17811698848531	-1.49897607245892
C	-4.62612249466791	-0.92983066348403	-1.41474715491849
S	-4.60004625167088	0.06237885618214	2.33650405527780
C	-5.42058011764853	-0.88081346682682	3.64978298819129
C	-4.57472188448344	-1.96003384868644	4.31404960859602
H	-5.66063290978568	-0.09495830198706	4.36775142779948
H	-6.36555001185813	-1.26321975991127	3.26692181375481
H	-3.67227619105486	-1.52801087213644	4.74471517751445
H	-4.27941401340131	-2.74668473248294	3.61924252711491
H	-5.14214365395199	-2.42354377297679	5.12329784896537
H	-5.68394301399494	-2.70804521355910	1.80506171430546
H	-6.07559595951258	-3.80166111582067	-0.36995045200423
H	-5.42456643082849	-2.61830450776124	-2.46677821322431
C	-4.24512687793548	-0.14292238152995	-2.63106821765068
H	-3.19921360321657	0.16358155098880	-2.58401962803548
H	-4.41289251001554	-0.71537535412854	-3.54170648388144
H	-4.83951704656892	0.77202445791526	-2.67897717333769

Cartesian coordinates of the optimized $[Cu_7I_7L_4]$ (3d) molecular fragment

Cu	0.04173683799466	-0.01124511678274	-0.07966754538227
I	2.50409997121847	0.00000000929062	0.00000000282215
I	-1.28946566947447	2.18045423779052	-0.00000001524622
Cu	-2.02446021393174	1.06164793670473	2.22611351216684
Cu	3.22200485518724	-2.39863418762317	0.04103077818828
I	5.68030348659382	-3.00949352414910	0.01418145873624
Cu	4.78285927724890	-4.08284598677863	-2.17443320445327
I	5.51781250137405	-2.96423289024331	-4.40065740883152
Cu	6.80714700111141	-5.14476467951107	-4.40057443477796
I	9.31124690728792	-5.14491530291520	-4.40069660195558
Cu	10.02900970695111	-7.54359003815021	-4.35954042602638
I	12.48727003727140	-8.15459895834674	-4.38646876701367
Cu	11.58965437194204	-9.22804389863064	-6.57496775049969
I	12.32456641548977	-8.10962395482790	-8.80130273947426
N	-1.10414946825679	-1.66643201323255	-0.09930085692254
C	-1.37134232590542	-2.28837508016643	-1.26432511393901
C	-2.32168716769833	-3.30372838563573	-1.32938203691932
C	-3.02843833086105	-3.65370823809356	-0.19240396529248
C	-2.77133851234816	-2.99131535529137	0.99977449511371
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S	-1.29038393644066	-1.08918954710583	2.45074241687449
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