Electronic Supplementary Material (ESI) for Dalton Transactions.

Cationic copper(I) iodide cluster MOF exhibiting unusual ligand assisted thermochromism

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Supporting Information

Experimental Section

General Remarks:

All manipulations involving phosphorus halides were performed under dry atmosphere in standard Schlenk-glassware. CuI and 3-aminoquinoline were purchased from Aldrich and used as received. The $PSCl_3$ was purchased locally (SPECTROCHEM, India) and used as received. NMR spectra were recorded on a 400 MHz Jeol FT spectrometer (^{1}H-NMR: 400.13 MHz, $^{13}C\{^1H\}$-NMR: 100.62 MHz, $^{31}P\{^1H\}$-NMR: 161.97 MHz) at room temperature using $SiMe_4$ (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P) as external standards. The powder X-ray diffraction data were obtained from a Bruker-D8 Advance diffractometer. Thermal analysis data has been obtained from a Perkin-Elmer STA-6000 thermogravimetric analyser. Elemental analyses were performed on a Vario-EL cube elemental analyser. FT-IR spectra were taken on a Perkin-Elmer spectrophotometer. The absorption and emission studies were done by a Perkin-Elmer Lambda 45 UV-Visible spectrophotometer and SPEX Flurolog HORIBA JOBIN VYON fluorescence spectrophotometer with a double-grating 0.22 m SPEX 1680 monochromator and a 450W Xe lamp as the excitation source. The excitation and emission spectra of the complexes were corrected at instrumental function. The photoluminescence lifetime measurements were carried out using a SPEX Flurolog HORIBA JOBIN VYON 1934 D phosphorimeter.

Synthesis:

L^1: To a stirred solution of 3-aminoquinoline (2.492 g, 0.0172 mol) and triethylamine (2.75 mL, 1.995 g, 0.019mol) in toluene (150 mL) at 0 ^{0}C, $PSCl_3$ (0.5 mL, 0.835 g, 0.00492 mol) was added drop wise over a period of 10 minutes. The resulting mixture was refluxed for 4 h at 110 ^{0}C to yield a yellow precipitate. The precipitate was collected by filtration and washed with water and 0.5% aqueous NaOH solution to remove the amine hydrochloride by-product. The resulting powder was washed three times with water and dissolved in methanol/chloroform mixture. This solution was dried with $MgSO_4$, filtered and evaporated to yield **L^1**. Yellow crystals of $L^1 \cdot H_2O$ suitable for X-ray analysis were obtained from its solution in $MeOH/CHCl_3$ after 3 days. Yield: 2.86 g (85%). M.P. 230-233, ^{1}H-NMR (400 MHz, $(CD_3)_2SO$: δ 7.44 (dd, 3H, C*H*), 7.49 (td, 3H, C*H*), 7.76 (td, 3H, C*H*), 8.06 (d, 3H, C*H*), 8.85 (d, 3H, C*H*), 9.05 (d, 3H, C*H*). $^{13}C\{^1H\}$-NMR (100 MHz, $\{(CD_3)_2SO\}$): δ 120.41, 127.44, 128.45, 128.97, 135.40, 143.62, 145.31, 145.60. ^{31}P-NMR (161 MHz, $\{(CD_3)_2SO\}$): δ 39.89. FT-IR data in powdered sample (cm^{-1}): 3352, 3058, 2359, 1593, 1459, 1334, 1181, 1128, 985, 925, 876, 737, 645. Anal. calcd. for $C_{27}H_{21}N_6PS$: C, 65.84; H, 4.30; N, 17.06; S, 6.51. Found: C, 65.74; H, 4.57; N, 16.98; S, 6.31.

1: To a stirred solution of L^1 (49mg, 0.1mmol) in dichloromethane (5ml) and MeOH (2ml), CuI (57mg, 0.3mmol) in CH_3CN (15ml) was added leading to an immediate formation of a yellow precipitate. To this mixture, 2 mL of DMF containing few drops of water was added and the mixture was further stirred for 4 h at which point most of the precipitate were dissolved. The solution was then filtered through a thick pad of celite and left for crystallization.[25] Yellow crystals of 1 suitable for X-ray diffraction were obtained after 10 days. Yield: 49 mg (43% based on Cu). FT-IR data in KBr pellet (cm^{-1}): 3521, 3453, 2921, 2852, 1656, 1457, 1344, 1209, 931, 744, 659. Anal. calcd. for $C_{66}H_{76}Cu_6I_5N_{15}O_7P_2S_2$: C, 33.97; H, 3.28; N, 9.00; S, 2.75. Found: C, 34.28; H, 3.40; N, 9.06; S, 2.92.

Crystallography:

Reflections were collected on a Bruker Smart Apex Duo diffractometer at 100 K using MoKα radiation (λ = 0.71073 Å) (Table S1, supporting information). Structures were refined by full-matrix least-squares against F^2 using all data (SHELX97).[1] All non-hydrogen atoms were refined aniostropically if not stated otherwise. Hydrogen atoms were constrained in geometric positions to

their parent atoms. Crystals of **1** diffracted weakly at higher angles and hence a 2θ = 50 ° cut-off was applied. The solvated DMF molecule in **1** was disordered and refined over two positions with SIMU/SAME restraints.

Lifetime and Quantum Yield:

The luminescent lifetime of L^1, **1** were measured by Time Correlated Single Photon Counting (TCSPC) method at 298K using a Nano-LED laser of wavelength 370 nm and 1.5 ns pulse. The 77K phosphorescence decay was measured using a pulsed tungsten lamp at the corresponding sample excitation wavelengths. The 298K luminescence decay profiles were fitted to tri-exponential curves. Similarly, the 77K phosphorescence decay profiles were fitted to mono-exponential equations. The lifetimes were fitted by using the software DAS-6, Data-station provided by Horiba Yvon Jobin. The quality factor χ^2 in all instances has been found to be closer to unity.

Fluorescence quantum yields in solution were determined by using the equation $\varphi_s = \varphi_r(F_sA_r/F_rA_s)(n_r/n_s)$.[2] In this equation, φ is the fluorescent quantum yield, F is the area of the emission, n is the refractive index of the solvent, and A is the absorbance of the solution at the exciting wavelength. The subscripts r and s denote the reference and sample, respectively. Quinine sulfate was employed as the standard.

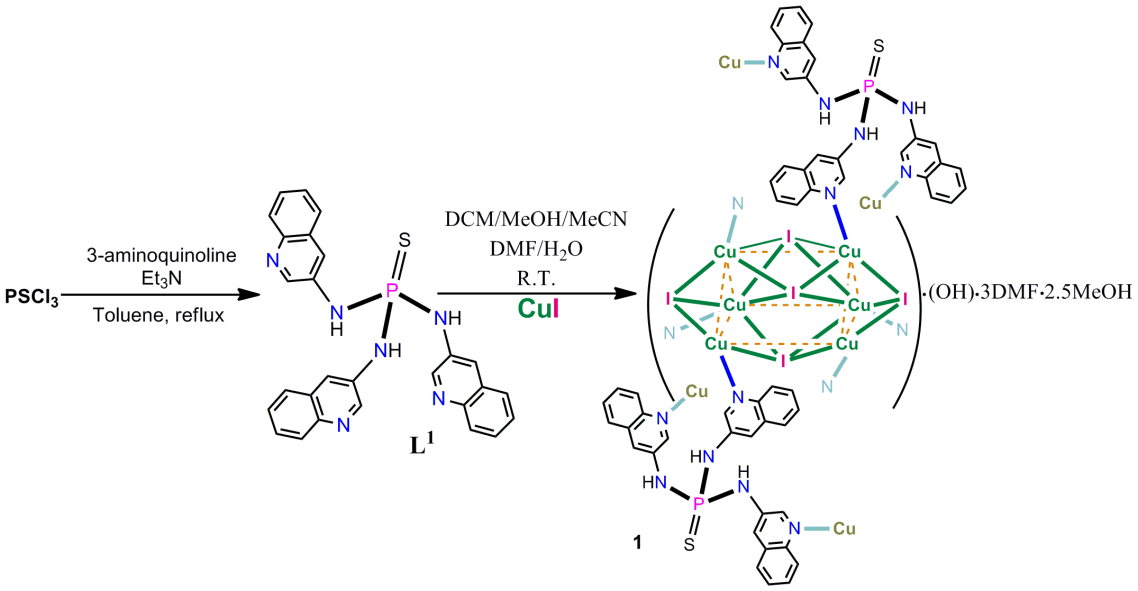
Computational Details:

The density functional theory (DFT) calculations have been performed by using Gaussian 03 program package. The B3LYP exchange-correlation functional was used throughout for all calculations. The 6-31g(d,p) basis set was used for geometry optimization and time-dependant (TDDFT) calculation for ligand L^1.[3,4] A combination of basis sets i.e., 6-31g(d) for C, H, N, P and S, and LANL2DZ for Cu and I atoms, respectively, were used for the bare $[Cu_6I_5]^+$ cluster as well as on discrete model compounds $\{Cu_6I_5[(AQNH)H_2P{=}S]_6\}$ (**1a**) to obtain the geometry optimization and TDDFT calculations for the excitation energies. The calculated absorption spectra and related MO contributions were obtained from the TDDFT output file and *gausssum2.2.6.1*.[5] The theoretical emission wavelengths of L^1 and **1a** were derived by single point energy calculations on the optimized triplets as the energy difference between the lowest energy triplet state and its corresponding singlet state.

Table S1: Crystal Data.

Compound	**L^1.H_2O**	**1**	**1 at RT**
Chemical formula	$C_{27}H_{23}N_6OPS$	$C_{67}H_{77}Cu_6I_5N_{15}O_{6.50}P_2S_2$	$C_{54}H_{36}Cu_6I_5N_{12}P_2S_2$
Formula weight	510.54	2338.24	1994.75
Temperature	100(2)K	100(2) K	298(2)
Crystal system	Monoclinic	Trigonal	Hexagonal
Space group	P2(1)/n	P-3	P6(3)/m
a (Å); α (°)	12.5293(9); 90	14.304(4); 90	14.306(4); 90
b (Å); β(°)	13.0003(9); 97.7630(10)	14.304(4); 90	14.306(4); 90
c (Å); γ (°)	16.0504(11); 90	24.223(7); 120	25.130(7); 120
V ($Å^3$); Z	2590.4(3); 4	4292.0(19); 2	4454(2); 2
ρ (calc.) mg m^{-3}	1.309	1.809	1.487
μ(Mo K_α) mm^{-1}	0.219	3.399	3.255
$2\theta_{max}$ (°)	56	50	50
R(int)	0.0582	0.1581	0.0935
Completeness to θ	99.4 %	98.9 %	99.5 %
Data / param.	6497 / 333	5002 / 313	2679 / 125
GOF	1.021	1.003	0.991
R1 [F>4σ(F)]	0.0391	0.0755	0.0549
wR2 (all data)	0.0994	0.2207	0.1684
max. peak/hole (e.$Å^{-3}$)	0.438/-0.584	1.36 /-0.900	1.109/-0.986

The crystal structure of **1** at room-temperature was solved in the hexagonal space group P6(3)/m. Due to the diffuse nature of the solvated molecules, the atom positions of the DMF, methanol and hydroxide ion could not be located precisely. Hence, the electron densities due to these groups were removed by the SQUEEZE/PLATON routine. Except the space group difference, the packing diagram of **1** at 298K was exactly matching with that of the 100K structure. The room temperature data was obtained only to compare the Cu...Cu and Cu...I bond differences between the RT and the 100K data as discussed in the main text.



Scheme S1

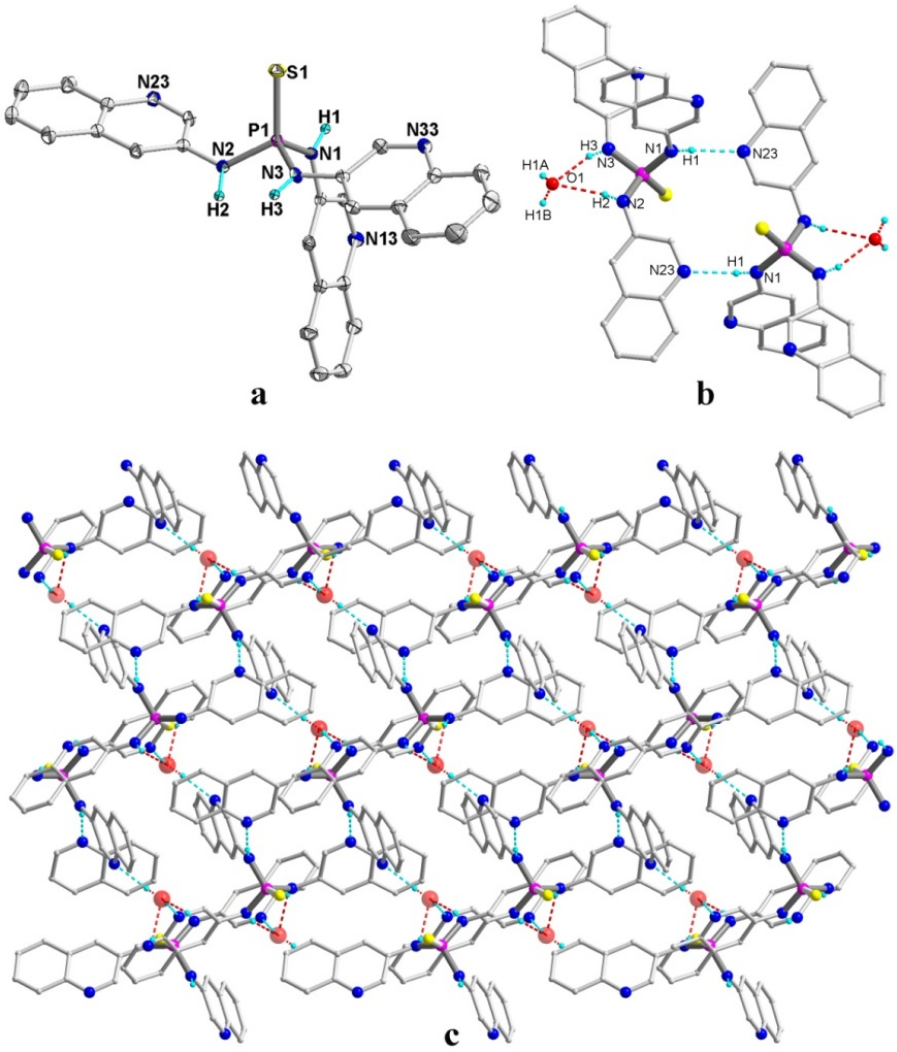


Figure S1: (a) Ortep plot at 50% ellipsoid probability for L^1 (a) dimer formation in L^1 by using N-H hydrogen bonding (c) 3-dimensional network via N-H…O and O-H…N hydrogen bonding interactions.

The thiophosphoramide ligand L^1 was synthesized from the reaction of $PSCl_3$ with 3-aminoquinoline in refluxing toluene solutions. The ligand was characterized by ^{31}P-NMR, mass spectra and by single crystal X-ray diffraction. Crystals of L^1 was obtained by slow evaporation of its solution in methanol and solved as its solvated adduct as $L^1 \cdot H_2O$ (Figure S1). The crystal structure of $L^1 \cdot H_2O$ was obtained in the monoclinic space group $P2_1/n$. It consists of three un-symmetrically arranged aminoquinolyl moieties consisting of two chelating N-H moieties and one non-chelating N-H site. Thus, two of the three N-H groups are H-bonded to the solvated oxygen through a chelating interaction, while the third one is H-bonded to one of the ring N-atom (N23). The remaining ring N-sites are involved in H-bonding interactions with the water hydrogens and leads to the formation of a 3D-supramolecular network.

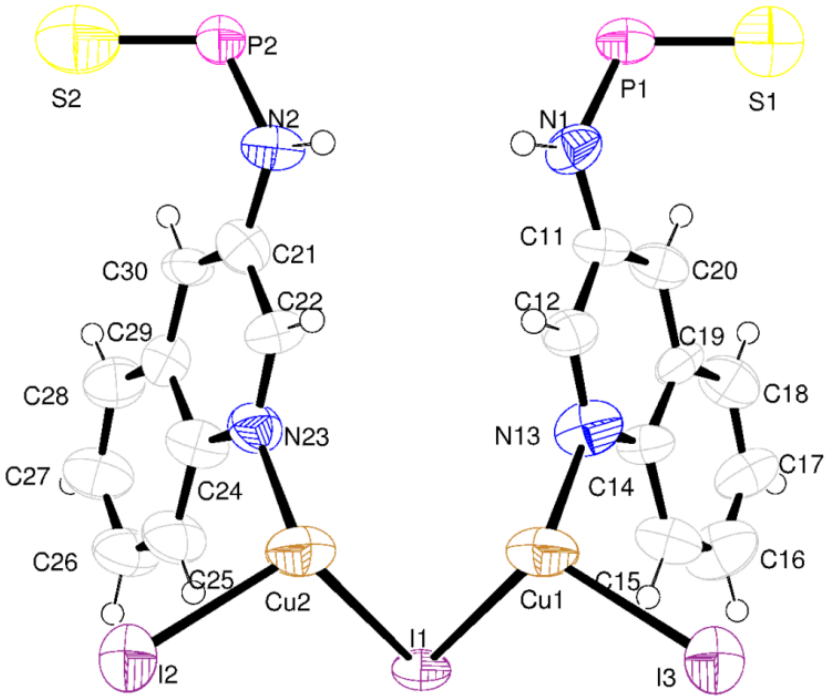


Figure S2: Ortep plot at 50% ellipsoid probability for the cationic segment of **1.**

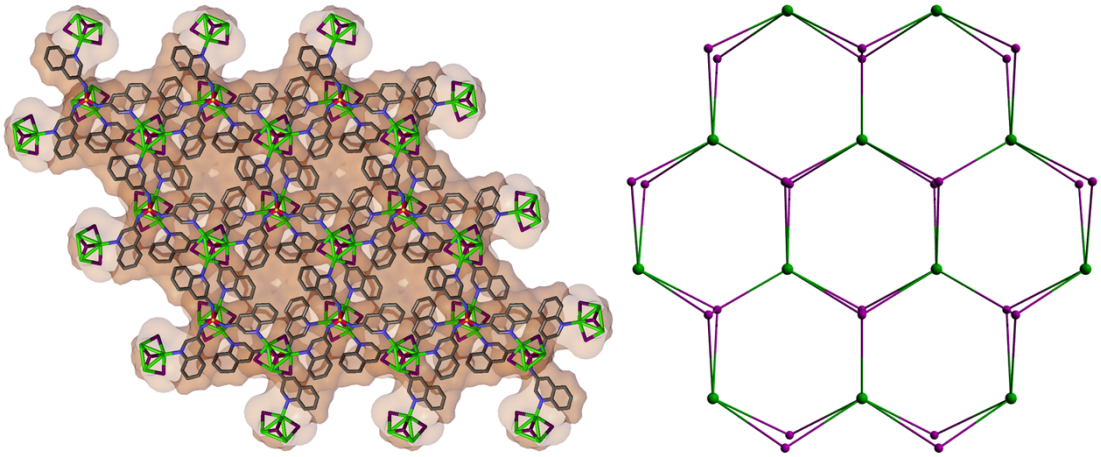


Figure S3: Packing structure of **1** along the c-axis (left) and its topological view showing the binodal $(3c)_2$,6c-net as that of MoS_2 (3c for the ligand and 6c for the cluster) represented by the Schläfli symbol $(4^3)_2$ $(4^3.6^{12})$.

A survey of the literature reveals cationic clusters such as $[Cu_4I_2]^{2+}$, $[Cu_4I_3]^{+}$, $[Cu_6I_2]^{4+}$, $[Cu_6I_4]^{2+}$, $[Cu_6I_5]^{+}$, $[Cu_7I_4]^{3+}$, $[Cu_8I_6]^{2+}$, $[Cu_{10}I_4]^{6+}$ and $[Cu_{24}I_{10}]^{14+}$ are scarcely reported.[6] In most of the instances these cationic clusters were found to possess a triangular plane of three Cu-atoms. Hence the C_3-symmetric ligation[7] of L^1 provides an ideal platform for stabilizing rugby-ball shaped cationic clusters in **1**. Although there was one previous report for the $[Cu_6I_5]^{+}$ cluster along with $[Cu_4I_3]^{+}$,[6h] no clear photo-physical characterization of this compound was undertaken.

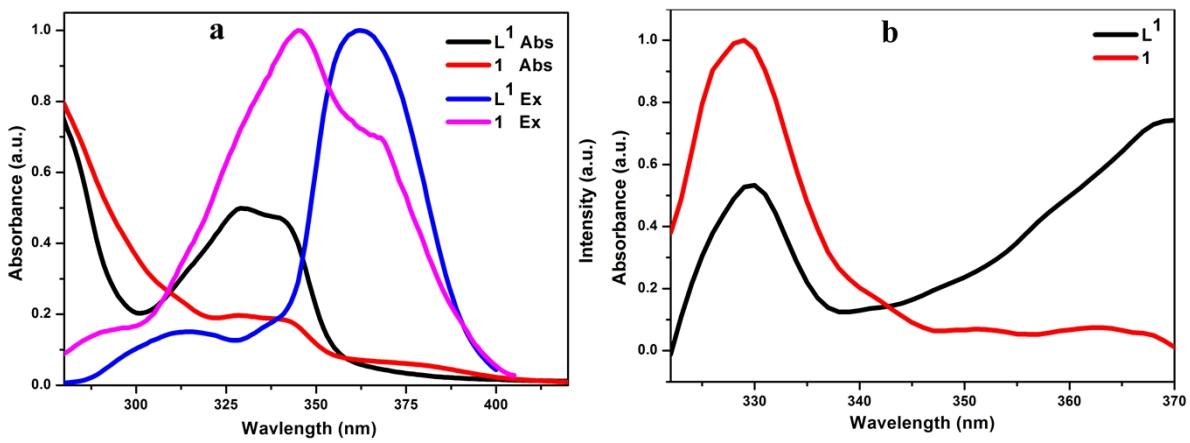


Figure S4: (a) Absorbance and Excitation spectra of L^1 and **1**in DMF. (b) Solid-state diffuse reflectance spectra of L^1 and **1**

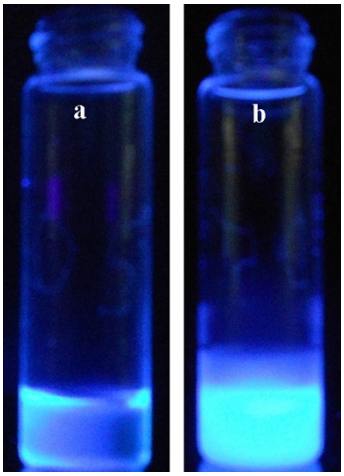


Figure S5: Emission colours under the UV-lamp (λ = 365 nm) for L^1 (a) at 298K and (b) at 77K

Table S2: Photo physical Data.

Compound	**λ_{abs} (nm)**	**λ_{ex}(nm)**	**λ_{em} (nm)**	**τ_1**	**τ_2**	**τ_3**	**φ**
L^1(DMF)	330	360 360	408(298K) 532(77K)	1.747(ns) 0.986 (μs)	4.0091(ns)		0.84
L^1(Solid)	330	360	411 (298K) 518 (77K)	0.9(ns) 0.986 (μs)	0.053(ns)	4.139(ns)	
1(DMF)	345 385	345 345 360 360	370(298K) 614(77K) 420(298K) 614(77K)	 0.670(ns) 467.93(μs)	 3.606(ns)		0.36
1 (Solid)	330 370	360	419 (298K) 594 (298K)	0.077(ns) 236.96(μs)	0.076(ns)	4.775(ns)	

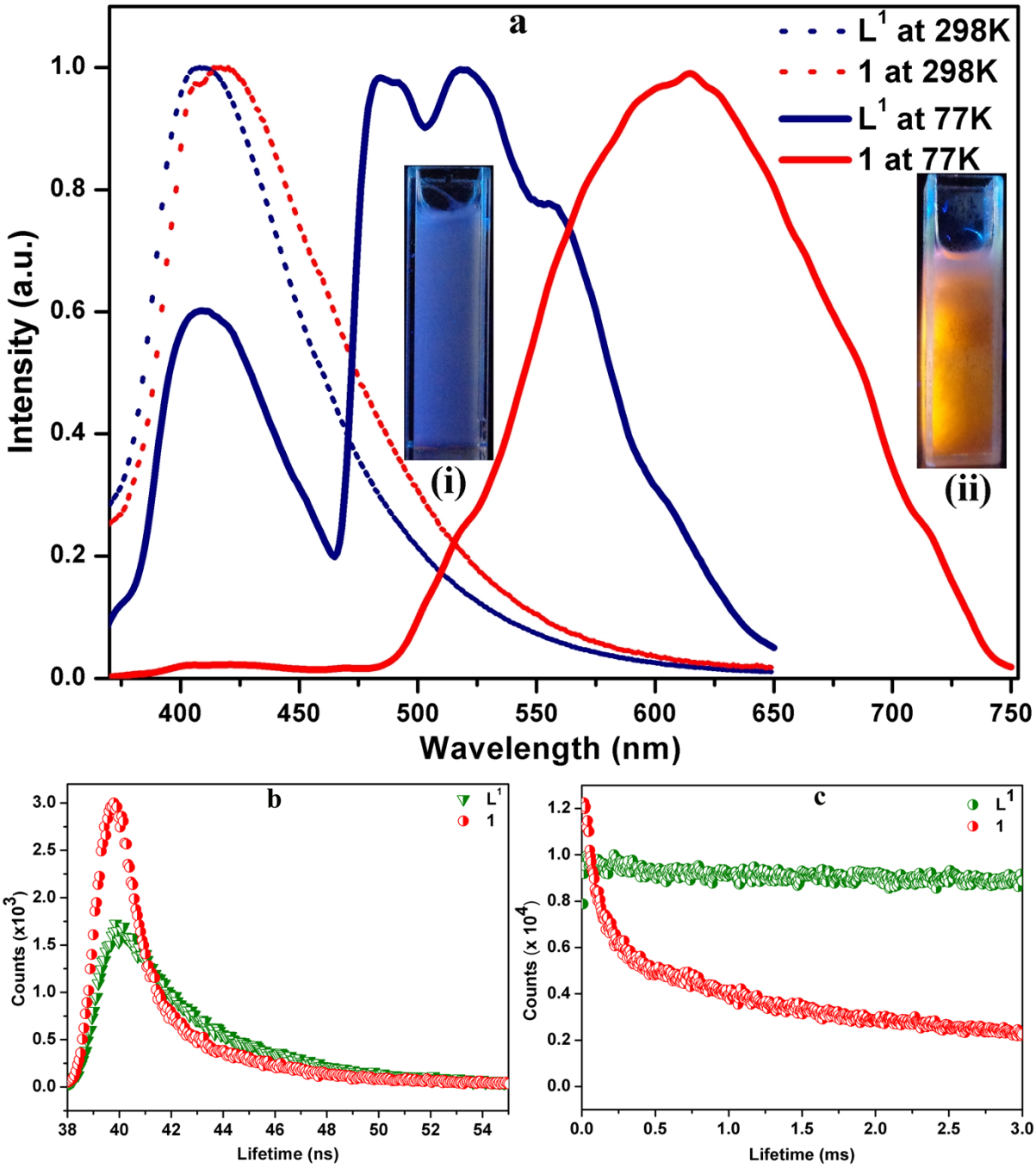


Figure S6: (a) Normalized emission spectra for L^1 and **1** in DMF (λ_{ex} = 360 nm); inset: the emission colour of 1 at (i) 298K and (ii) 77K under the UV-lamp (λ = 365 nm). (b) TCSPC decay profiles of the 298K fluorescence in L^1 and **1** in DMF and (c) the 77K phosphorescence measured using the tungsten-lamp in L^1 and **1** in DMF.

The emission spectra of **1** in DMF suspension shows the same trend for the observed HE and LE peaks of **1** in the solid-state confirming the stability of **1** in DMF suspensions. Similarly the life time values of L^1 and 1 in DMF also similarly correlates to that of the solid-samples.

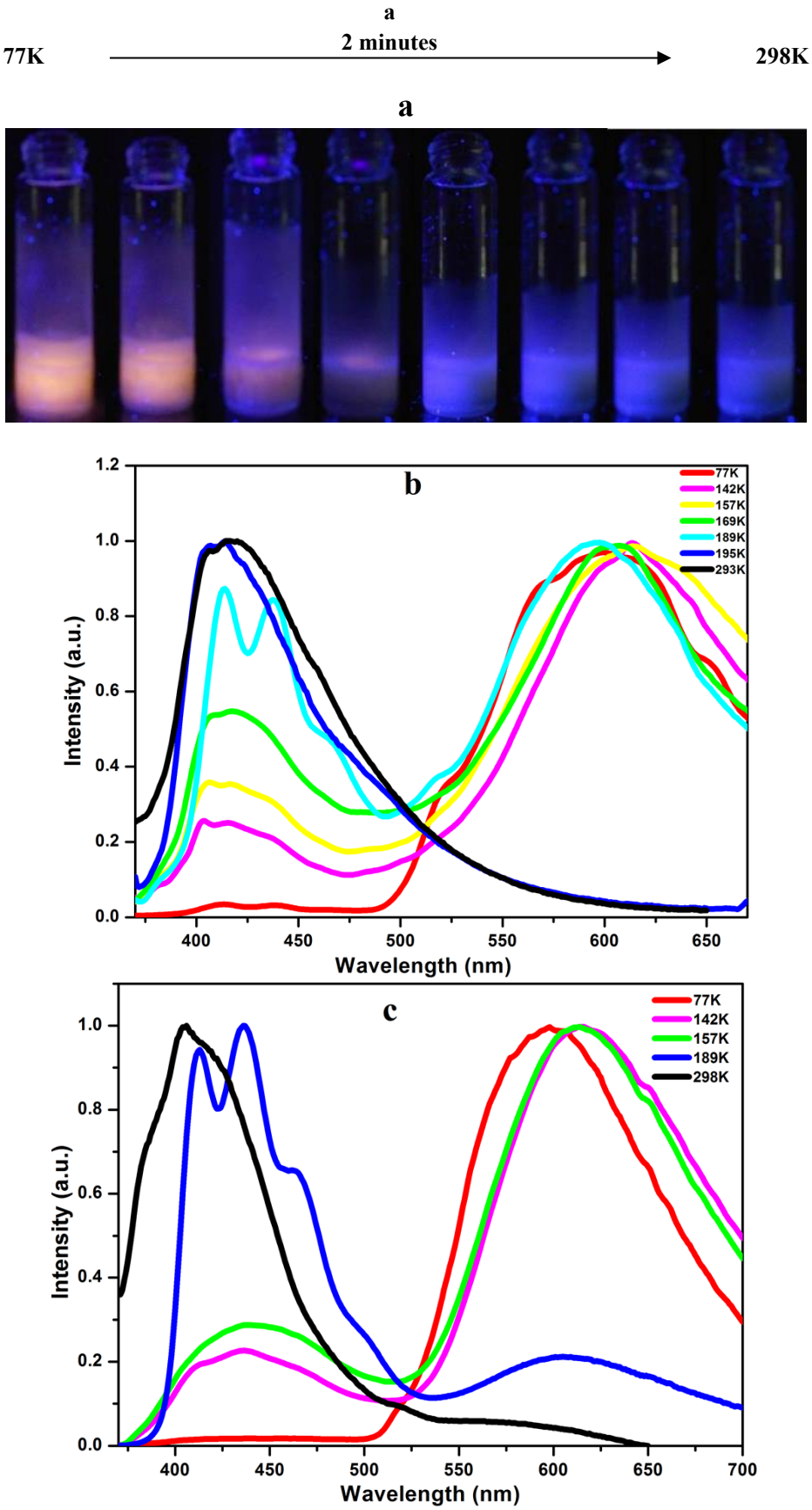


Figure S7: (a) Change in emission colours in **1** in DMF suspensions upon allowing the sample to warm up from 77K to 298K; phosphorescence emission spectra of **1** at various temperatures (b) in DMF suspension and (c) in DCM suspension (λ_{em} = 406 nm at 298K and 600 nm at 77K).

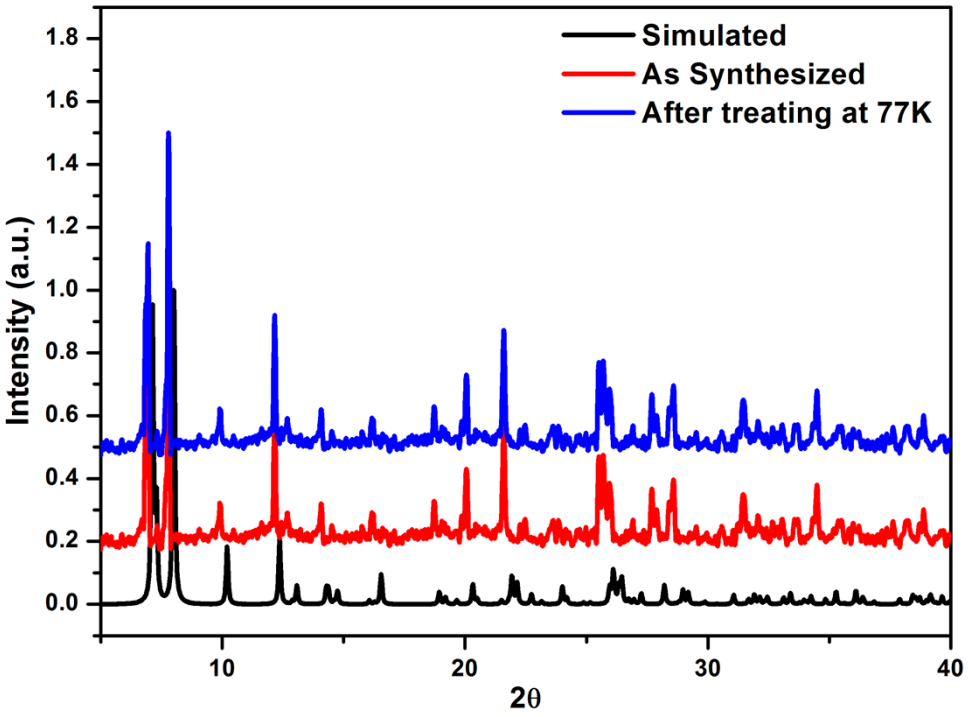


Figure S8: Powder X-Ray diffraction data for **1** before and after photo-physical measurements in DMF suspensions

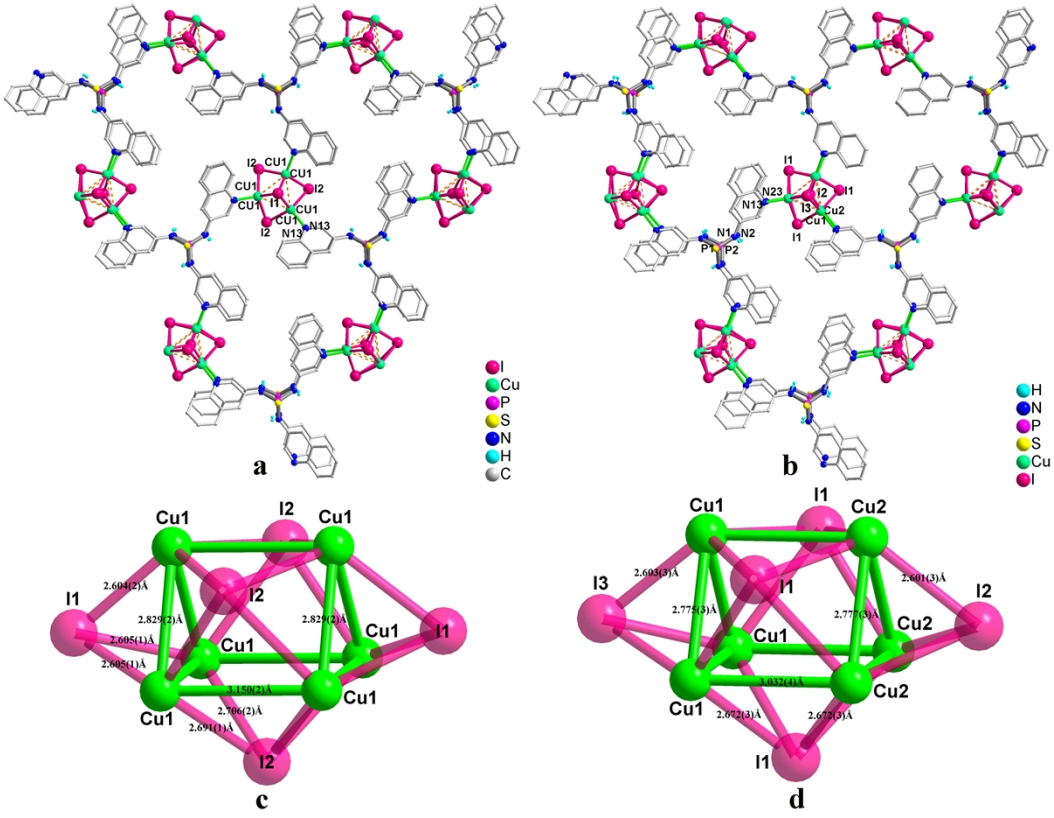


Figure S9: Molecular structure of **1** at (a) at 298K and (b) at 100K. Bond distance in $[Cu_6I_5]^+$cluster core in **1**, (c) at 298K and (d) at 100K

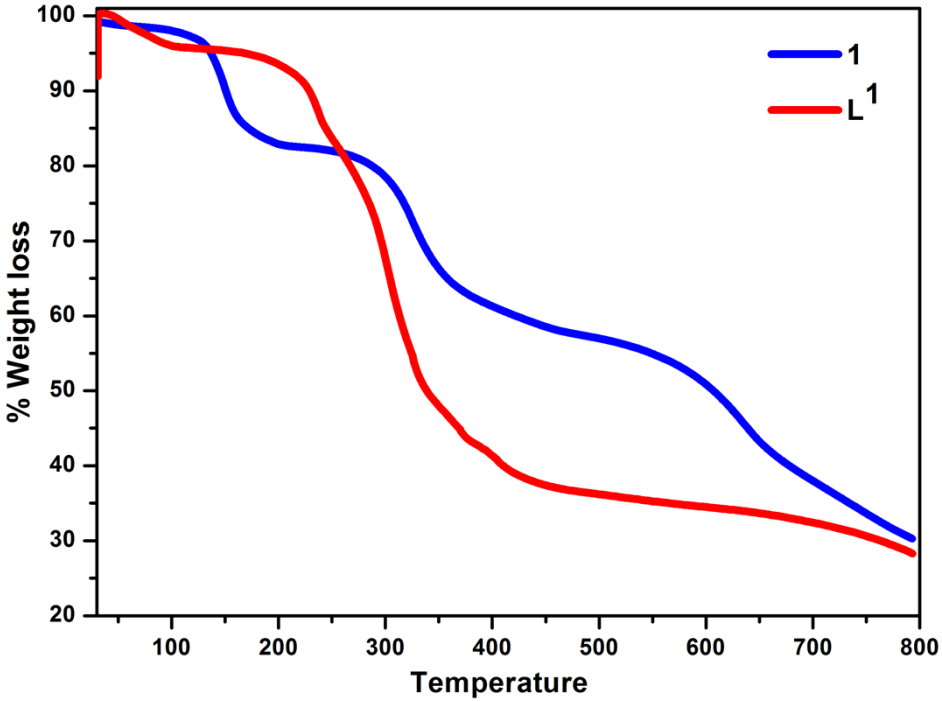


Figure S10: Thermogravimetric Plots

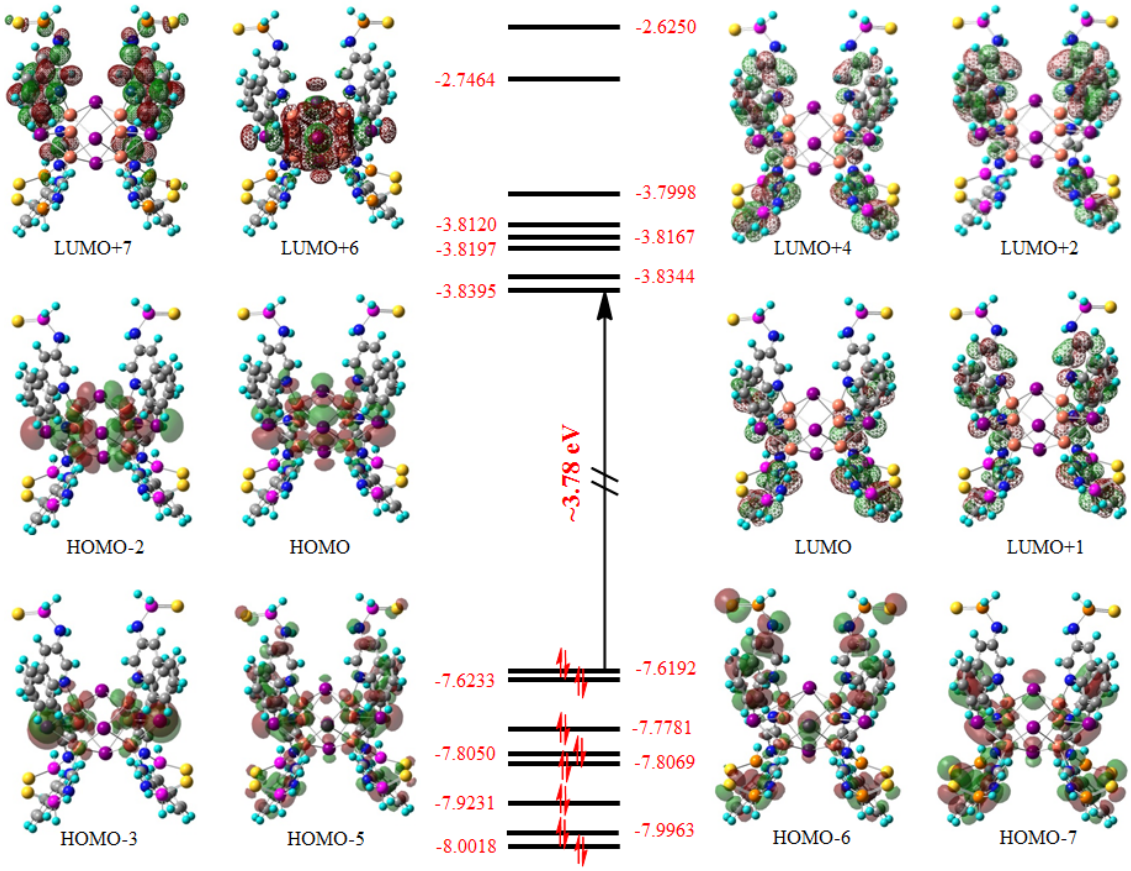


Figure S11. DFT derived surface diagrams and energies (in eV) of some relevant molecular orbitals calculated for singlet ground state at the S_0 optimized geometry for **1a**. Similar data for L^1 and the bare cluster are available in the ESI (Figure S10-S11).

Table S3. TDDFT computed transition wavelengths (λ), oscillator strengths (*f*), and major orbital contributions (%) for singlet-singlet transitions of **1a**. (H and L denotes HOMO and LUMO, respectively).

λ (nm)	(*f*)	**Orbitals involved** (%)
413.29	0.0023	H-4 →L (16%), H-3 →L+1 (12%), H-1 →L+3 (37%), H →L+4 (27%)
390.76	0.0124	H-2 →L+3 (93%)
390.68	0.0124	H-2 →L+4 (93%)
380.46	0.0023	H-4 →L (33%), H-3 →L+1 (29%), H-1 →L+3 (17%), H →L+4 (15%)
374.48	0.0029	H-4 →L+1 (32%), H-3 →L (35%), H-1 →L+4 (14%), H →L+3 (15%)
363.96	0.005	H-4 →L+4 (17%), H-3 →L+3 (12%), H-3 →L+5 (48%)
363.9	0.005	H-4 →L+3 (12%), H-4 →L+5 (52%), H-3 →L+4 (14%)
353.92	0.0962	H-5 →L (42%)
353.9	0.0963	H-5 →L+1 (42%)
352.6	0.0013	H-7 →L (16%), H-7 →L+1 (16%), H-6 →L (16%), H-6 →L+1 (16%)
351.58	0.0027	H-6 →L+2 (16%), H-5 →L (27%)
351.54	0.0026	H-7 →L+2 (16%), H-5 →L+1 (27%)
350.03	0.0048	H-5 →L+2 (62%)
343.63	0.003	H-5 →L+3 (32%)
343.59	0.0026	H-6 →L+5 (11%), H-5 →L+4 (32%)
343.4	0.0085	H-7 →L (11%), H-7 →L+1 (10%), H-6 →L (12%), H-6 →L+1 (10%), H-5 →L+2 (23%)
343.18	0.0618	H-7 →L+3 (20%), H-6 →L+4 (19%)

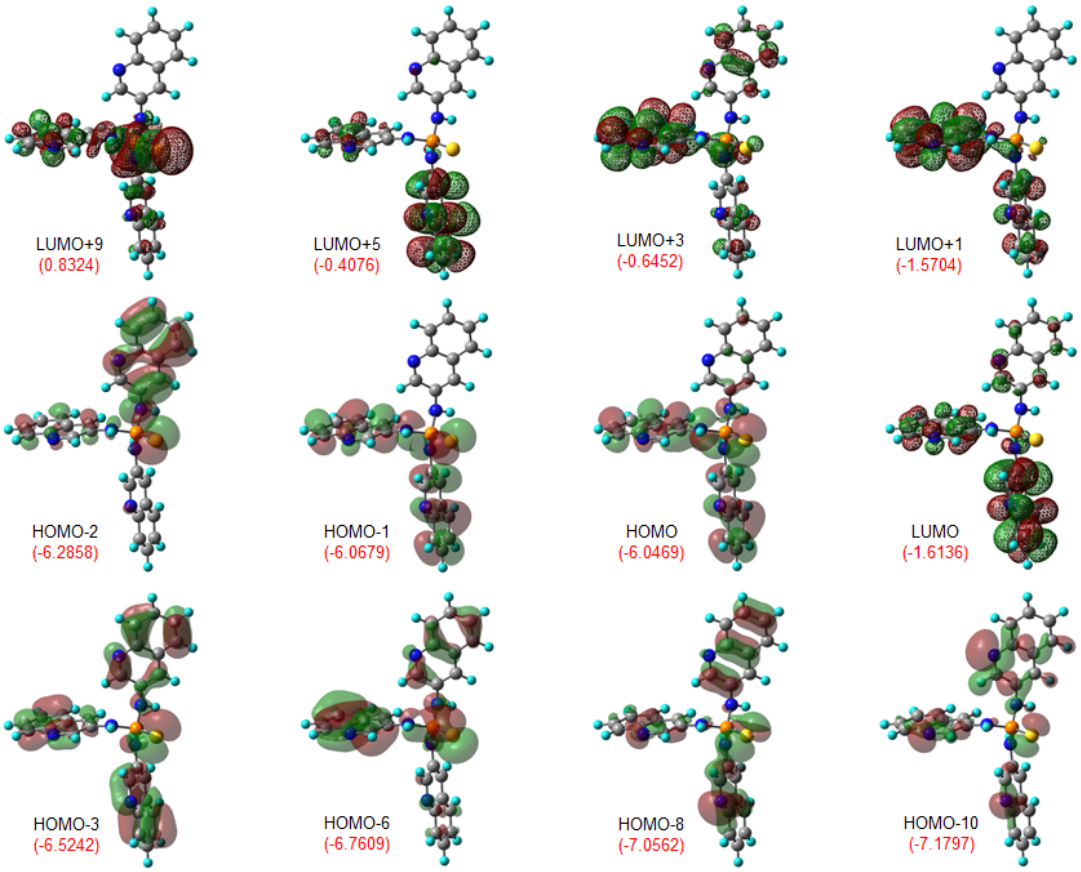


Figure S12: DFT derived surface diagrams and energies (in eV) of some relevant MOs calculated for singlet ground state at the S_0 optimized geometry for L^1.

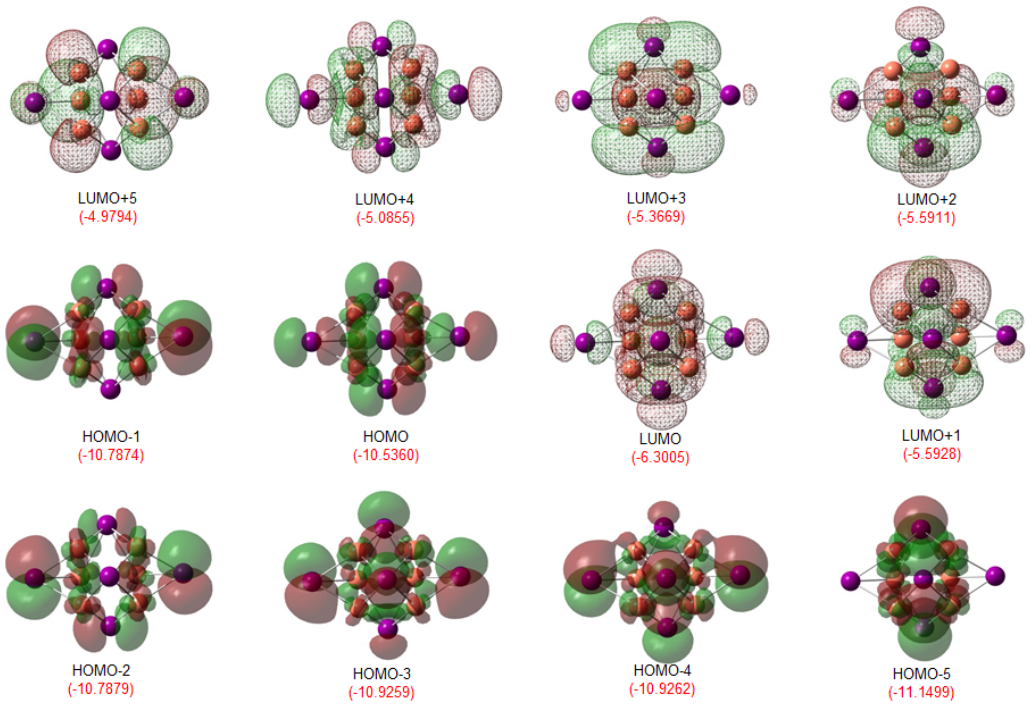


Figure S13: DFT derived surface diagrams and energies (in eV) of some relevant MOs calculated for ground state at the S_0 optimized geometry for Bare $[Cu_6I_5]^+$ cluster.

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Results of Topology analysis for 1

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############################
Compound 1
############################
Topology for P1
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Atom P1 links by bridge ligands and has
Common vertex with                    R(A-A)        f
X  1    1.3333    0.6667    0.7500   ( 1 0 0)    8.714A      1
X  1    0.3333   -0.3333    0.7500   ( 0-1 0)    8.714A      1
```

X 1 0.3333 0.6667 0.7500 (0 0 0) 8.714A 1

Topology for X1 (X1 is the centroid dummy atom of the $[Cu_6I_5]^+$ cluster)

Atom X1 links by bridge ligands and has

Common vertex with					R(A-A)	f
P	1	0.6667	1.3333	0.6395 (0 1 0)	8.714A	1
P	1	0.6667	0.3333	0.8605 (0 0 1)	8.714A	1
P	1	-0.3333	0.3333	0.8605 (-1 0 1)	8.714A	1
P	1	0.6667	1.3333	0.8605 (0 1 1)	8.714A	1
P	1	0.6667	0.3333	0.6395 (0 0 0)	8.714A	1
P	1	-0.3333	0.3333	0.6395 (-1 0 0)	8.714A	1

Structural group analysis

Structural group No 1

Structure consists of layers (0 0 1) with XS2P2N6

Coordination sequences

P1: 1 2 3 4 5 6 7 8 9 10
Num 3 13 9 24 15 36 21 48 27 60
Cum 4 17 26 50 65 101 122 170 197 257
Rad 8.7(0.0) 14.1(2.6) 20.3(2.6) 27.0(2.0) 33.0(2.9) 39.7(2.4) 46.0(3.2) 52.6(2.9) 58.9(3.6) 65.6(3.4)
Cmp X3 P13 X9 P24 X15 P36 X21 P48 X27 P60

X1: 1 2 3 4 5 6 7 8 9 10
Num 6 6 18 12 30 18 42 24 54 30
Cum 7 13 31 43 73 91 133 157 211 241
Rad 8.7(0.0) 14.3(0.0) 20.3(2.6) 26.7(2.0) 33.0(2.8) 39.5(2.5) 46.0(3.2) 52.5(2.9) 58.9(3.6) 65.5(3.4)
Cmp P6 X6 P18 X12 P30 X18 P42 X24 P54 X30

TD10=251

Vertex symbols for selected sublattice

P1 Point symbol:{4^3}
Extended point symbol:[4.4.4]

X1 Point symbol:{4^3.6^12}
Extended point symbol:[4(2).4(2).4(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2)]

Point symbol for net: {4^3.6^12}{4^3}2
3,6-c net with stoichiometry (3-c)2(6-c); 2-nodal net

Topological type: 3,6L66 (1D_2D.ttd) {4^3.6^12}{4^3}2 - VS [4.4.4]
[4(2).4(2).4(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2)] (76188 types in 11 databases)
Elapsed time: 22.03 sec.

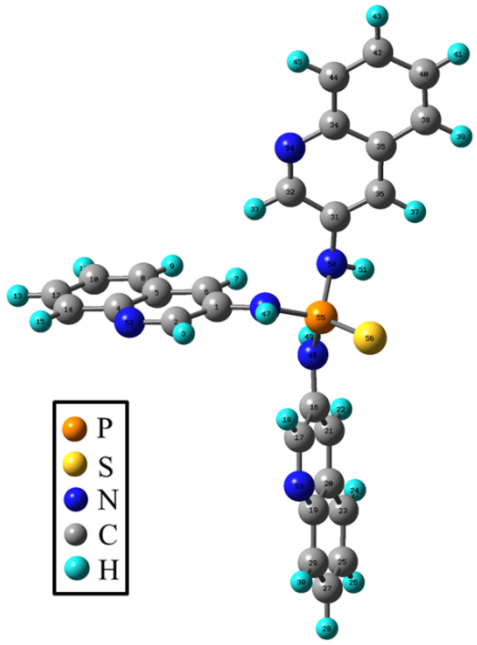

Figure S14: Optimized singlet geometry of L^1.

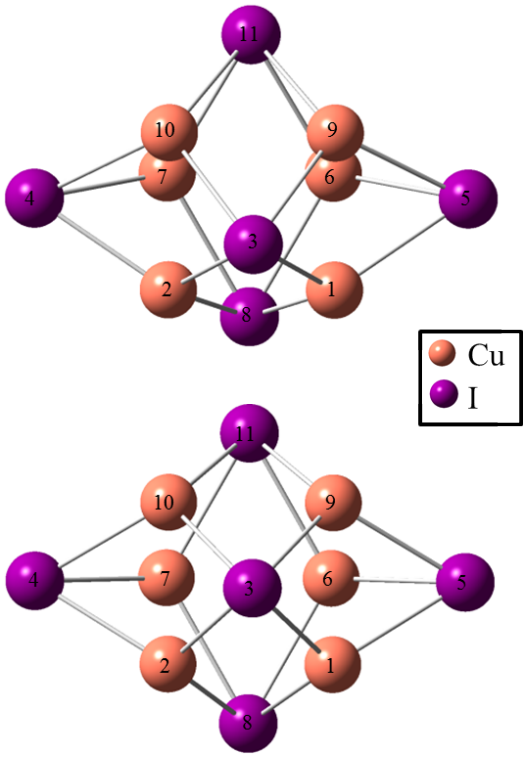

Figure S15: Optimized singlet geometry of Bare $[Cu_6I_5]^+$ cluster.

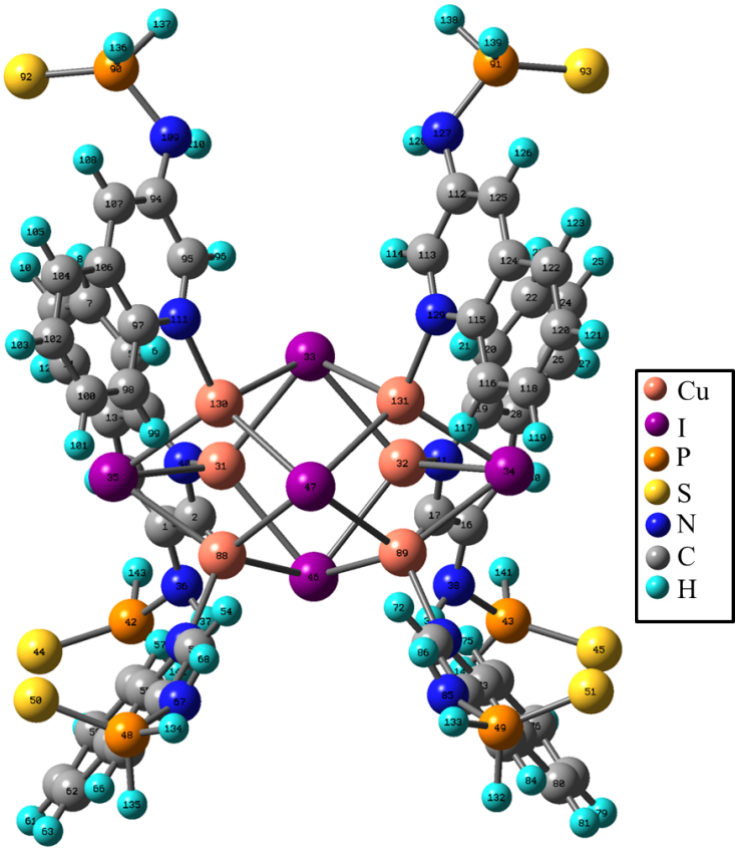

Figure S16: Optimized singlet geometry of **1a.**

Table S4. Averaged Cu...Cu, Cu-I and Cu-N bond lengths from computed data of **1a**.

Parameters	Average Bond Lengths in Å	
	S_0	T
Cu...Cu within Cu_3-triangles	3.0101	3.0350
Cu...Cu along the three rims	3.5750	3.5511
Cu-I distances for μ_4-iodides	2.8645	2.8667
Cu-I distances for μ_3-iodides	2.7439	2.7437
Cu-N distances	2.1055	2.0945

Table S5. Relevant bond angles from computed data of **1a**.

Atomic centers involved	S_0	T
Cu(31)-I(33)-Cu(32)	77.31	75.9
Cu(31)-I(33)-Cu(130)	63.23	63.14
Cu(31)-I(33)-Cu(131)	109.37	106.62
Cu(32)-I(33)-Cu(130)	109.33	110.02
Cu(32)-I(33)-Cu(131)	63.26	64.44
Cu(130)-I(33)-Cu(131)	77.44	75.92
Cu(32)-I(34)-Cu(89)	66.62	71.77
Cu(32)-I(34)-Cu(131)	66.36	67.97
Cu(89)-I(34)-Cu(131)	66.66	66.83
Cu(31)-I(35)-Cu(88)	66.58	63.92
Cu(31)-I(35)-Cu(130)	66.37	66.09
Cu(88)-I(35)-Cu(130)	66.56	66.48
Cu(31)-I(46)-Cu(32)	77.59	75.13
Cu(31)-I(46)-Cu(88)	63.45	60.78
Cu(31)-I(46)-Cu(89)	109.36	109.38
Cu(32)-I(46)-Cu(88)	109.29	109.51
Cu(32)-I(46)-Cu(89)	63.47	68.2
Cu(88)-I(46)-Cu(89)	76.72	77.81
Cu(88)-I(47)-Cu(89)	77.06	77.31
Cu(88)-I(47)-Cu(130)	63.44	63.52
Cu(88)-I(47)-Cu(131)	109.27	107.66
Cu(89)-I(47)-Cu(130)	109.34	111.25
Cu(89)-I(47)-Cu(131)	63.49	63.54
Cu(130)-I(47)-Cu(131)	77.21	77.2

Table S6. TDDFT computed transition wavelengths, oscillator strengths, and major orbital contributions for Singlet-Singlet Transitions of L^1. (H and L denotes HOMO and LUMO, respectively)

Transition λ, (nm)	Oscillator Strength (*f*)	Nature of the Transition (% contribution)
315.37	0.0429	H→L (90%)
309.82	0.0068	H→L+1 (85%)
305.09	0.0267	H→L+2 (80%)
301.46	0.0535	H-2→L (30%), H-2→L+1 (13%)
299.27	0.0473	H-1→L (69%)
293.34	0.0675	H-1→L+1 (59%), H-1→L+2 (12%)
291.97	0.0038	H-9→L+2 (30%), H-7→L+2 (26%)
290.05	0.0075	H-10→L (40%), H-10→L+1 (12%)
289.36	0.0186	H-1→L+1 (16%), H-1→L+2 (53%)
286.42	0.0104	H-8→L+1 (19%), H-2→L+1 (34%)
278.33	0.0321	H-3→L (33%), H-3→L+1 (22%)
276	0.017	H-4→L (44%), H-4→L+1 (13%)

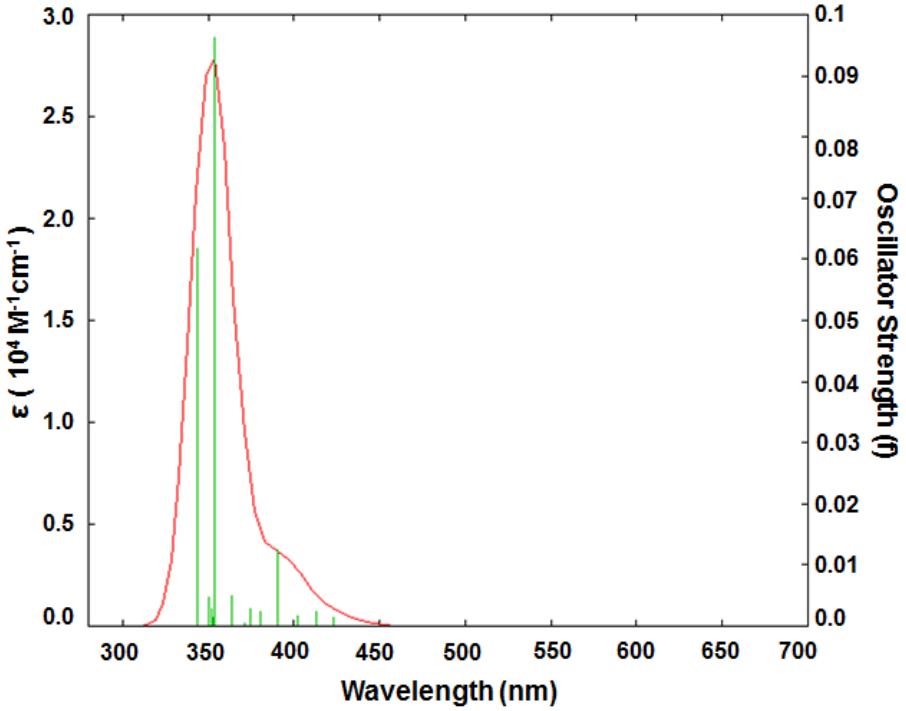

Figure S17: TDDFT Calculated transitions (in green) and corresponding absorption spectrum (in red) of **1a**.

Computational Details

Table S7: Coordinates from singlet optimized structure 1a

No.	Atom	X	Y	Z
1	C	4.517288	-3.618155	-3.023277
2	C	3.488776	-2.848483	-2.418036
3	H	2.748613	-3.345501	-1.79335
4	C	4.25449	-0.860603	-3.342623
5	C	4.125297	0.538599	-3.522486
6	H	3.303415	1.051786	-3.035032
7	C	5.02249	1.22248	-4.312758
8	H	4.913672	2.29399	-4.452562
9	C	6.084816	0.53943	-4.955073
10	H	6.780143	1.093844	-5.57826
11	C	6.233456	-0.819012	-4.797718
12	H	7.04261	-1.349685	-5.292194
13	C	5.324549	-1.555021	-3.990402
14	C	5.434991	-2.953065	-3.814251
15	H	6.23867	-3.479706	-4.319922
16	C	4.425662	-3.79941	2.922673
17	C	3.429129	-2.987516	2.318836
18	H	2.698449	-3.445652	1.654555
19	C	4.201799	-1.051845	3.342513
20	C	4.091892	0.341457	3.572179

21	H	3.29564	0.887861	3.07835
22	C	4.976107	0.977749	4.415146
23	H	4.882582	2.045136	4.592789
24	C	6.005556	0.250304	5.062471
25	H	6.690748	0.767036	5.727831
26	C	6.135042	-1.103665	4.856899
27	H	6.919477	-1.667681	5.354197
28	C	5.238858	-1.791052	3.994393
29	C	5.329613	-3.18317	3.767123
30	H	6.107713	-3.744204	4.275762
31	Cu	1.598912	-0.649962	-1.813075
32	Cu	1.580682	-0.740698	1.768454
33	I	2.030631	1.499723	0.036138
34	I	-0.03278	-0.105414	3.89747
35	I	0.007296	0.091346	-3.921904
36	N	4.55686	-5.001313	-2.76143
37	H	3.713441	-5.346926	-2.312302
38	N	4.448586	-5.171823	2.605602
39	H	3.611271	-5.480892	2.119438
40	N	3.350507	-1.542433	-2.562836
41	N	3.309074	-1.686034	2.511455
42	P	5.272315	-6.170091	-3.810732
43	P	5.100357	-6.396471	3.632893
44	S	4.647043	-6.410724	-5.636114
45	S	4.381579	-6.716195	5.411047
46	I	0.295131	-2.508234	-0.073357
47	I	-2.315533	1.00961	0.002973
48	P	-8.033646	-1.214659	-3.744273
49	P	-8.069321	-1.368297	3.625607
50	S	-7.925889	-0.403737	-5.508476
51	S	-7.984137	-0.679905	5.442111
52	C	-5.45303	-1.93582	-3.017152
53	C	-4.25884	-1.472611	-2.404162
54	H	-4.300717	-0.61526	-1.734851
55	C	-2.951422	-3.09535	-3.428037
56	C	-1.684763	-3.690655	-3.647148
57	H	-0.819856	-3.272977	-3.14278
58	C	-1.563272	-4.770756	-4.493186
59	H	-0.588671	-5.219286	-4.661835
60	C	-2.699099	-5.300451	-5.154288
61	H	-2.583947	-6.149133	-5.821896
62	C	-3.94102	-4.742314	-4.958292
63	H	-4.815103	-5.141884	-5.465435
64	C	-4.101698	-3.627213	-4.092014
65	C	-5.358643	-3.021062	-3.867439
66	H	-6.228843	-3.419766	-4.38009

67	N	-6.660844	-1.284736	-2.6999
68	H	-6.523004	-0.420563	-2.183306
69	N	-3.066889	-2.010935	-2.591342
70	C	-5.484591	-2.050615	2.874796
71	C	-4.285327	-1.566892	2.287748
72	H	-4.31837	-0.673453	1.666906
73	C	-2.995124	-3.258245	3.217753
74	C	-1.734468	-3.876118	3.405414
75	H	-0.865097	-3.438172	2.926657
76	C	-1.623939	-5.002505	4.190483
77	H	-0.653487	-5.467639	4.337007
78	C	-2.766158	-5.558437	4.81838
79	H	-2.660175	-6.444124	5.43768
80	C	-4.002643	-4.979206	4.651536
81	H	-4.881294	-5.399212	5.133568
82	C	-4.151566	-3.81562	3.849316
83	C	-5.402035	-3.184353	3.66063
84	H	-6.275725	-3.602965	4.150944
85	N	-6.684147	-1.36713	2.595079
86	H	-6.532084	-0.464343	2.153798
87	N	-3.099218	-2.127478	2.443105
88	Cu	-1.394575	-0.987724	-1.823478
89	Cu	-1.414004	-1.078472	1.737912
90	P	2.893319	7.704794	-3.521498
91	P	2.907118	7.459779	3.975992
92	S	3.509702	7.261745	-5.311831
93	S	3.509999	6.876524	5.730371
94	C	0.995538	5.803839	-2.822665
95	C	0.815534	4.514491	-2.255769
96	H	1.592667	4.100099	-1.616363
97	C	-1.260082	4.223614	-3.255546
98	C	-2.40893	3.427817	-3.487553
99	H	-2.466166	2.44992	-3.021714
100	C	-3.421015	3.890306	-4.29924
101	H	-4.295624	3.272221	-4.479533
102	C	-3.329263	5.165244	-4.910808
103	H	-4.134799	5.512413	-5.550965
104	C	-2.225569	5.959025	-4.701457
105	H	-2.147671	6.935882	-5.171081
106	C	-1.162913	5.511745	-3.870607
107	C	-0.008958	6.293249	-3.635603
108	H	0.066634	7.267188	-4.109627
109	N	2.166304	6.517519	-2.500467
110	H	2.856975	5.950315	-2.016741
111	N	-0.246893	3.754218	-2.453649
112	C	0.994151	5.640182	3.123415

113	C	0.809165	4.389328	2.477033
114	H	1.590604	4.006155	1.823508
115	C	-1.280869	4.058289	3.433523
116	C	-2.437461	3.258921	3.606798
117	H	-2.495826	2.309913	3.08469
118	C	-3.455226	3.681035	4.433327
119	H	-4.335985	3.060126	4.568725
120	C	-3.361431	4.917913	5.118479
121	H	-4.171422	5.233571	5.769239
122	C	-2.249913	5.713988	4.967422
123	H	-2.170688	6.661311	5.493816
124	C	-1.18085	5.307263	4.124125
125	C	-0.016728	6.089832	3.951247
126	H	0.061779	7.031945	4.485298
127	N	2.178497	6.358033	2.864029
128	H	2.869718	5.811403	2.357717
129	N	-0.26162	3.628208	2.617147
130	Cu	-0.182023	1.768398	-1.758726
131	Cu	-0.199199	1.679083	1.819897
132	H	-8.470049	-2.714441	3.490264
133	H	-8.929899	-0.708316	2.721239
134	H	-8.904309	-0.617537	-2.806342
135	H	-8.438289	-2.565998	-3.708258
136	H	1.925805	8.72832	-3.435981
137	H	3.861952	8.131505	-2.58673
138	H	3.884664	7.950701	3.083029
139	H	1.94626	8.492811	3.962285
140	H	5.003604	-7.447265	2.694595
141	H	6.469943	-6.063207	3.567812
142	H	5.140232	-7.264057	-2.927578
143	H	6.633757	-5.829422	-3.662986

Table S8: Coordinates from triplet optimized structure 1a

No.	Atom	X	Y	Z
1	C	-6.018761	-2.379506	0.703512
2	C	-4.704367	-1.863521	0.569654
3	H	-4.52403	-0.807898	0.762807
4	C	-3.826266	-3.919589	-0.054128
5	C	-2.719165	-4.71214	-0.445
6	H	-1.746001	-4.239965	-0.524006
7	C	-2.887583	-6.050573	-0.724353
8	H	-2.036467	-6.651152	-1.031196
9	C	-4.165704	-6.654034	-0.622541
10	H	-4.27988	-7.709684	-0.849619
11	C	-5.257741	-5.908618	-0.242826

12	H	-6.241015	-6.364562	-0.165333
13	C	-5.119385	-4.524586	0.049168
14	C	-6.214406	-3.721463	0.440915
15	H	-7.195918	-4.17728	0.533486
16	C	-3.053645	-0.911689	5.766273
17	C	-2.374097	-0.638281	4.550619
18	H	-2.876841	-0.064381	3.774436
19	C	-0.450728	-1.748956	5.229282
20	C	0.87472	-2.176583	4.969323
21	H	1.324528	-1.92505	4.014969
22	C	1.57372	-2.886735	5.920164
23	H	2.591613	-3.205796	5.716675
24	C	0.979418	-3.200479	7.167905
25	H	1.546512	-3.758594	7.906857
26	C	-0.305961	-2.797694	7.44652
27	H	-0.766266	-3.032139	8.402509
28	C	-1.054237	-2.061454	6.488576
29	C	-2.376997	-1.628956	6.733679
30	H	-2.84077	-1.873064	7.68477
31	Cu	-1.89328	-1.531039	-0.31395
32	Cu	-0.237896	-0.324628	2.525855
33	I	0.619438	-2.364018	0.734904
34	I	1.767935	1.425685	3.117874
35	I	-1.900682	-1.50593	-3.070106
36	N	-7.05753	-1.511337	1.11711
37	H	-6.71633	-0.573349	1.316637
38	N	-4.385464	-0.467246	5.917032
39	H	-4.718008	0.047285	5.105271
40	N	-3.653122	-2.582429	0.2142
41	N	-1.142044	-1.033362	4.280685
42	P	-8.587328	-1.4491	0.312204
43	P	-4.999262	0.210111	7.385436
44	S	-8.719962	-0.980492	-1.573675
45	S	-4.225485	1.818529	8.15891
46	I	-2.139304	1.069526	0.909502
47	I	1.464398	1.289257	-1.568453
48	P	-0.842496	5.955393	-6.448845
49	P	4.490908	7.594054	-0.292299
50	S	-0.792694	4.834639	-8.037849
51	S	5.889227	6.877127	0.855238
52	C	-1.786987	4.388816	-4.366916
53	C	-1.382289	3.344111	-3.495675
54	H	-0.327296	3.228739	-3.255549
55	C	-3.552666	2.566724	-3.21304
56	C	-4.461343	1.646111	-2.635081
57	H	-4.070081	0.87075	-1.985724

58	C	-5.808455	1.729986	-2.911336
59	H	-6.500413	1.015777	-2.473622
60	C	-6.303198	2.738956	-3.77516
61	H	-7.367537	2.788153	-3.984718
62	C	-5.444323	3.646465	-4.350225
63	H	-5.817463	4.419512	-5.016614
64	C	-4.049083	3.585538	-4.086889
65	C	-3.133041	4.497866	-4.657366
66	H	-3.510153	5.272598	-5.318279
67	N	-0.804547	5.272578	-4.862322
68	H	0.137211	5.000715	-4.592163
69	N	-2.208105	2.474375	-2.940066
70	C	2.149406	6.162604	0.166326
71	C	1.60437	4.902925	0.029722
72	H	1.96059	4.23305	-0.747933
73	C	0.137236	5.224115	1.862012
74	C	-0.877764	4.763579	2.68864
75	H	-1.275318	3.767576	2.522699
76	C	-1.405017	5.568461	3.750231
77	H	-2.190511	5.162639	4.379728
78	C	-0.911249	6.834557	3.963133
79	H	-1.297007	7.456242	4.764738
80	C	0.114847	7.330813	3.125485
81	H	0.510168	8.329643	3.289572
82	C	0.656549	6.553771	2.072383
83	C	1.673852	7.034133	1.231157
84	H	2.049164	8.043648	1.342636
85	N	3.112343	6.623281	-0.728332
86	H	3.349885	5.935607	-1.441703
87	N	0.634309	4.401413	0.85
88	Cu	-1.370818	0.886306	-1.845631
89	Cu	0.42321	2.371524	0.90624
90	P	3.061801	-7.629826	-3.394986
91	P	7.320747	-4.578769	1.951081
92	S	1.455188	-8.349667	-4.221209
93	S	7.4795	-4.344841	3.875433
94	C	2.777982	-4.871613	-3.319447
95	C	2.136644	-3.829152	-2.60064
96	H	1.85662	-3.992215	-1.56161
97	C	2.156972	-2.38663	-4.419158
98	C	1.835065	-1.1322	-4.993457
99	H	1.33535	-0.390916	-4.37935
100	C	2.145105	-0.871608	-6.309894
101	H	1.889943	0.090082	-6.744933
102	C	2.788852	-1.850678	-7.106786
103	H	3.022951	-1.629281	-8.143759

104	C	3.111649	-3.077502	-6.574855
105	H	3.600303	-3.834444	-7.182329
106	C	2.803975	-3.379922	-5.22076
107	C	3.10925	-4.631571	-4.638986
108	H	3.597483	-5.385431	-5.249191
109	N	3.067139	-6.074433	-2.639926
110	H	2.649356	-6.108067	-1.713262
111	N	1.836381	-2.646682	-3.10778
112	C	5.910508	-2.395032	0.987734
113	C	4.596651	-1.869516	0.879809
114	H	3.748282	-2.551144	0.876735
115	C	5.344635	0.328028	0.794692
116	C	5.071282	1.715586	0.706829
117	H	4.038276	2.03795	0.636414
118	C	6.101234	2.630295	0.728424
119	H	5.886846	3.693855	0.673411
120	C	7.446355	2.196587	0.834664
121	H	8.24521	2.931824	0.853266
122	C	7.741137	0.855968	0.920253
123	H	8.770282	0.517876	1.006256
124	C	6.701697	-0.113031	0.905151
125	C	6.961568	-1.498821	0.999421
126	H	7.991454	-1.832409	1.084303
127	N	6.073241	-3.795042	1.048188
128	H	5.18803	-4.289734	1.120333
129	N	4.313343	-0.581648	0.785481
130	Cu	0.602307	-1.374229	-1.965287
131	Cu	2.293759	-0.010094	0.838111
132	H	3.842637	8.762098	0.15292
133	H	4.858783	7.935863	-1.6107
134	H	0.232369	6.850529	-6.255705
135	H	-1.960531	6.806402	-6.324483
136	H	4.187757	-7.49722	-4.234413
137	H	3.594915	-8.334763	-2.29393
138	H	7.055007	-5.881762	1.476235
139	H	8.447632	-4.209673	1.186824
140	H	-6.347661	0.275982	6.97153
141	H	-4.99843	-0.935828	8.207673
142	H	-9.220684	-0.589181	1.235183
143	H	-9.111155	-2.708441	0.668148

Table S9: Coordinates from singlet optimized structure of Bare $\{Cu_6I_5\}^+$ cluster

No.	Atom	X	Y	Z
1	Cu	-1.375951	-1.544013	0.24468
2	Cu	1.375964	-1.544001	0.244584

3	I	-0.000042	-1.766836	-2.179866
4	I	3.593301	0.000814	0.000292
5	I	-3.593186	0.00081	0.000296
6	Cu	-1.374854	0.984143	1.21444
7	Cu	1.374859	0.98405	1.214477
8	I	-0.000041	-1.005347	2.61904
9	Cu	-1.375319	0.559497	-1.458721
10	Cu	1.375316	0.55957	-1.458657
11	I	-0.000041	2.770971	-0.440201

Table S10: Coordinates from singlet optimized structure of L^1

No.	Atom	X	Y	Z
1	C	0.116249	1.67101	0.999593
2	C	-0.17652	2.553852	2.084569
3	H	-0.13143	2.163378	3.102975
4	C	-0.57161	4.333841	0.686446
5	C	-0.29828	3.53992	-0.47108
6	C	0.061782	2.181951	-0.28134
7	H	0.306745	1.567747	-1.14112
8	C	-0.38446	4.144306	-1.75275
9	H	-0.1709	3.5447	-2.63384
10	C	-0.73081	5.471442	-1.87637
11	H	-0.79384	5.924836	-2.86117
12	C	-1.00595	6.254395	-0.7284
13	H	-1.27804	7.298965	-0.84533
14	C	-0.92739	5.697116	0.528443
15	H	-1.13028	6.272177	1.425807
16	C	-2.51156	-1.18968	-0.22826
17	C	-2.99826	-1.09559	1.110087
18	H	-2.31681	-0.80196	1.904886
19	C	-5.1315	-1.69737	0.486829
20	C	-4.75318	-1.80294	-0.88883
21	C	-3.40165	-1.54408	-1.21965
22	H	-3.07495	-1.62994	-2.2538
23	C	-5.73413	-2.17045	-1.84742
24	H	-5.44616	-2.25295	-2.89232
25	C	-7.03017	-2.42076	-1.45605
26	H	-7.77419	-2.70249	-2.19528
27	C	-7.4047	-2.31358	-0.09361
28	H	-8.43182	-2.51389	0.196037
29	C	-6.47541	-1.95855	0.858261
30	H	-6.73365	-1.86882	1.908184
31	C	2.739864	-0.88384	-0.61787
32	C	3.316759	0.354519	-0.21356

33	H	2.674879	1.223951	-0.09777
34	C	5.436375	-0.54128	-0.14656
35	C	4.962319	-1.82561	-0.56246
36	C	3.571043	-1.96973	-0.78447
37	H	3.16937	-2.93629	-1.07954
38	C	5.889932	-2.88873	-0.71914
39	H	5.526244	-3.86448	-1.03015
40	C	7.229191	-2.68399	-0.47479
41	H	7.933505	-3.50171	-0.59469
42	C	7.699044	-1.41116	-0.06575
43	H	8.758959	-1.26823	0.122044
44	C	6.822821	-0.36134	0.094835
45	H	7.156047	0.622734	0.407173
46	N	0.4541	0.339565	1.311412
47	H	0.614214	0.148144	2.293137
48	N	-1.17075	-0.88175	-0.54068
49	H	-0.9988	-0.58329	-1.4919
50	N	1.335089	-0.96038	-0.88935
51	H	1.146123	-1.73335	-1.52526
52	N	-0.49638	3.816973	1.949323
53	N	-4.2394	-1.34384	1.457787
54	N	4.598853	0.52484	0.01966
55	P	0.211497	-1.07496	0.416056
56	S	0.287053	-2.63218	1.584982

Table S11: Coordinates from triplet optimized structure of L^1

No.	Atom	X	Y	Z
1	C	-0.11822	1.448777	1.112075
2	C	-0.67263	2.212821	2.184322
3	H	-0.66556	1.786799	3.189132
4	C	-1.23027	3.963062	0.803275
5	C	-0.70261	3.28573	-0.34043
6	C	-0.12968	2.002675	-0.15178
7	H	0.310599	1.481383	-0.99549
8	C	-0.76143	3.927424	-1.60533
9	H	-0.3541	3.417833	-2.47476
10	C	-1.3237	5.178671	-1.72708
11	H	-1.36359	5.661832	-2.69884
12	C	-1.85147	5.844864	-0.59387
13	H	-2.29188	6.830526	-0.70924
14	C	-1.80508	5.249662	0.647122
15	H	-2.19869	5.736424	1.533221
16	C	-2.29336	-1.49395	-0.1592
17	C	-2.73824	-1.84548	1.098496
18	H	-2.04496	-1.94306	1.926906

19	C	-4.96592	-2.01522	0.379416
20	C	-4.60981	-1.65427	-0.97859
21	C	-3.26484	-1.39149	-1.24597
22	H	-2.93357	-1.13181	-2.24763
23	C	-5.63232	-1.58636	-1.95957
24	H	-5.36632	-1.31317	-2.97724
25	C	-6.99212	-1.86581	-1.63326
26	H	-7.74966	-1.80418	-2.40789
27	C	-7.32364	-2.2075	-0.34965
28	H	-8.35302	-2.42361	-0.08133
29	C	-6.30402	-2.2838	0.667701
30	H	-6.55916	-2.55446	1.686391
31	C	2.901321	-0.65739	-0.574
32	C	3.336118	0.571781	0.001336
33	H	2.597767	1.325666	0.260824
34	C	5.551627	-0.04558	-0.11215
35	C	5.223571	-1.3044	-0.70797
36	C	3.853323	-1.59083	-0.92035
37	H	3.563282	-2.54657	-1.35087
38	C	6.268392	-2.20501	-1.0433
39	H	6.016293	-3.16258	-1.49118
40	C	7.580636	-1.86871	-0.79827
41	H	8.375203	-2.56276	-1.05526
42	C	7.905694	-0.62079	-0.21065
43	H	8.946444	-0.37275	-0.02527
44	C	6.913583	0.272773	0.125397
45	H	7.134816	1.234247	0.576597
46	N	0.422545	0.180963	1.414867
47	H	0.519595	-0.02546	2.402206
48	N	-0.96657	-1.22222	-0.50398
49	H	-0.85166	-0.74377	-1.38995
50	N	1.509659	-0.87464	-0.82952
51	H	1.393266	-1.60646	-1.52858
52	N	-1.19475	3.407001	2.051194
53	N	-4.04112	-2.10246	1.384999
54	N	4.595735	0.867765	0.230525
55	P	0.431569	-1.22172	0.472252
56	S	0.764583	-2.79268	1.568215

Table S12: Selected bond-lengths and angles for L^1 and **1**

Compound	Bond length	Bond angle
L^1	P(1)-S(1) : 1.9297(6) P(1)-N(1) : 1.6511(13) P(1)-N(2) : 1.6634(13) P(1)-N(3) : 1.6590(14)	N(1)-P(1)-N(2) : 109.20(7) N(1)-P(1)-N(3) : 106.42(7) N(3)-P(1)-N(2) : 96.62(7) N(1)-P(1)-S(1) : 107.93(5) N(2)-P(1)-S(1) : 116.67(5)

		N(3)-P(1)-S(1) : 119.13(5)
1	P(1)-S(1) : 1.872(14) P(2)-S(2) : 1.875(15) P(1)-N(1) : 1.660(13) P(1)-N(1)#1 : 1.660(13) P(1)-N(1)#2 : 1.660(13) P(2)-N(2) : 1.668(13) P(2)-N(2)#1 : 1.668(13) P(2)-N(2)#2 : 1.668(13) Cu(1)-N(13) : 2.071(13) Cu(1)-I(3) : 2.603(3) Cu(1)-I(1)#3 : 2.672(2) Cu(1)-I(1) : 2.672(2) Cu(1)-Cu(1)#4 : 2.775(3) Cu(1)-Cu(1)#3 : 2.775(3) Cu(1)-Cu(2) : 3.032(4) Cu(2)-N(23) : 2.061(13) Cu(2)-I(2) : 2.601(3) Cu(2)-I(1)#3 : 2.672(2) Cu(2)-I(1) : 2.672(2) Cu(2)-Cu(2)#4 : 2.777(3) Cu(2)-Cu(2)#3 : 2.777(3) I(1)-Cu(2)#4 : 2.671(2) I(1)-Cu(1)#4 : 2.672(2) I(2)-Cu(2)#3 : 2.601(3) I(2)-Cu(2)#4 : 2.601(3) I(3)-Cu(1)#3 : 2.603(3) I(3)-Cu(1)#4 : 2.603(3)	N(1)#1-P(1)-N(1)#2 : 103.4(7) N(1)#1-P(1)-N(1) : 103.4(7) N(1)#2-P(1)-N(1) : 103.4(7) N(1)#1-P(1)-S(1) : 115.0(6) N(1)#2-P(1)-S(1) : 115.0(5) N(1)-P(1)-S(1) : 115.0(6) N(2)-P(2)-N(2)#1 : 102.9(7) N(2)-P(2)-N(2)#2 : 102.9(7) N(2)#1-P(2)-N(2)#2 : 102.9(7) N(2)-P(2)-S(2) : 115.4(6) N(2)#1-P(2)-S(2) : 115.4(6) N(2)#2-P(2)-S(2) : 115.4(6) N(13)-Cu(1)-I(3) : 109.8(5) N(13)-Cu(1)-I(1)#3 : 107.5(4) I(3)-Cu(1)-I(1)#3 : 111.54(8) N(13)-Cu(1)-I(1) : 107.6(4) I(3)-Cu(1)-I(1) : 111.53(7) I(1)#3-Cu(1)-I(1) : 108.78(10) N(13)-Cu(1)-Cu(1)#4 : 145.4(4) I(3)-Cu(1)-Cu(1)#4 : 57.79(5) I(1)#3-Cu(1)-Cu(1)#4 : 107.08(6) I(1)-Cu(1)-Cu(1)#4 : 58.70(7) N(13)-Cu(1)-Cu(1)#3 : 145.3(4) I(3)-Cu(1)-Cu(1)#3 : 57.79(5) I(1)#3-Cu(1)-Cu(1)#3 : 58.72(8) I(1)-Cu(1)-Cu(1)#3 : 107.07(6) Cu(1)#4-Cu(1)-Cu(1)#3 : 60.000(1) N(13)-Cu(1)-Cu(2) : 108.2(4) I(3)-Cu(1)-Cu(2) : 142.03(9) I(1)#3-Cu(1)-Cu(2) : 55.43(7) I(1)-Cu(1)-Cu(2) : 55.43(7) Cu(1)#4-Cu(1)-Cu(2) : 90.02(5) Cu(1)#3-Cu(1)-Cu(2) : 90.02(5) N(23)-Cu(2)-I(2) : 109.5(4) N(23)-Cu(2)-I(1)#3 : 107.8(4) I(2)-Cu(2)-I(1)#3 : 111.48(8) N(23)-Cu(2)-I(1) : 107.7(4) I(2)-Cu(2)-I(1) : 111.47(7) I(1)#3-Cu(2)-I(1) : 108.79(10) N(23)-Cu(2)-Cu(2)#4 : 145.1(4) I(2)-Cu(2)-Cu(2)#4 : 57.74(5) I(1)#3-Cu(2)-Cu(2)#4 : 107.06(6) I(1)-Cu(2)-Cu(2)#4 : 58.68(7) N(23)-Cu(2)-Cu(2)#3 : 145.3(4) I(2)-Cu(2)-Cu(2)#3 : 57.74(5) I(1)#3-Cu(2)-Cu(2)#3 : 58.69(8) I(1)-Cu(2)-Cu(2)#3 : 107.05(6) Cu(2)#4-Cu(2)-Cu(2)#3 : 59.999(1) N(23)-Cu(2)-Cu(1) : 108.6(4) I(2)-Cu(2)-Cu(1) : 141.93(9) I(1)#3-Cu(2)-Cu(1) : 55.43(7)

		I(1)-Cu(2)-Cu(1) : 55.44(7) Cu(2)#4-Cu(2)-Cu(1) : 89.98(5) Cu(2)#3-Cu(2)-Cu(1) : 89.98(5) Cu(2)#4-I(1)-Cu(1)#4 : 69.14(8) Cu(2)#4-I(1)-Cu(2) : 62.63(9) Cu(1)#4-I(1)-Cu(2) : 100.59(7) Cu(2)#4-I(1)-Cu(1) : 100.58(7) Cu(1)#4-I(1)-Cu(1) : 62.58(9) Cu(2)-I(1)-Cu(1) : 69.13(7) Cu(2)-I(2)-Cu(2)#3 : 64.53(9) Cu(2)-I(2)-Cu(2)#4 : 64.53(9) Cu(2)#3-I(2)-Cu(2)#4 : 64.53(9) Cu(1)-I(3)-Cu(1)#3 : 64.42(9) Cu(1)-I(3)-Cu(1)#4 : 64.42(9) Cu(1)#3-I(3)-Cu(1)#4 : 64.42(9)

Table S13: H-bonding table for L^1 and **1**

Compound	**D-H...A**	**d(H...A)Å**	**d(D...A)Å**	**<(DHA)°**
L^1	N(1)-H(1)...N(23)#1	2.05	2.9177(18)	168.2
	N(2)-H(2)...O(1)#2	2.12	2.8278(18)	137.1
	N(3)-H(3)...O(1)#2	1.95	2.8039(17)	164.1
	O(1)-H(1A)...N(33)	1.81(3)	2.7072(18)	170(2)
	O(1)-H(1B)...N(13)#3	1.97(3)	2.8067(19)	169(3)
	#1 -x+2,-y+1,-z #2 -x+3/2,y+1/2,-z+1/2 #3 -x+1,-y+1,-z			
1	N(1)-H(1)...O(1)#7	1.98	2.83(3)	163.8
	N(1)-H(1)...O(1')#7	2.14	3.01(5)	171.9
	N(2)-H(2)...O(1')#7	1.84	2.69(5)	163.3
	N(2)-H(2)...O(1)#7	2.06	2.93(3)	168.2
	#1 -y+2,x-y+2,z #2 -x+y,-x+2,z #3 -y+1,x-y+1,z #4 -x+y,-x+1,z #5 -x+1,-y+2,-z+1 #6 -x+1,-y+2,-z+2 #7 x,y+1,z			