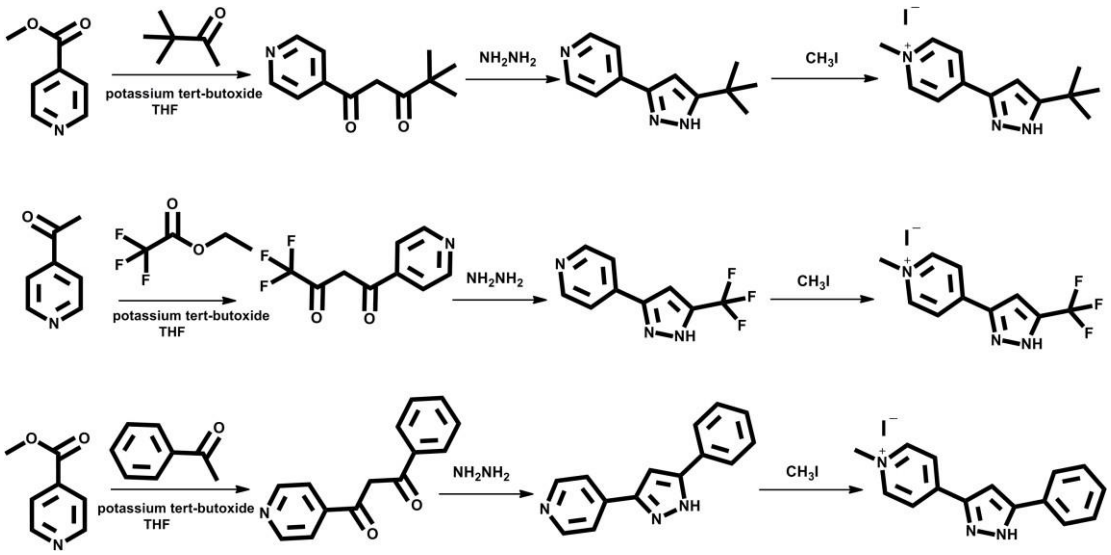
Substituent regulated photoluminescent thermochromism in a rare type of octahedral Cu_4I_4 clusters

*Ya-Dong Yu, Ling-Bin Meng, Qiu-Cheng Chen, Guang-Hui Chen and Xiao-Chun Huang**

Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province, Shantou University, Shantou, 515063, China.

Supporting Information

Contents



Scheme S1 Three-step syntheses of the ligands.

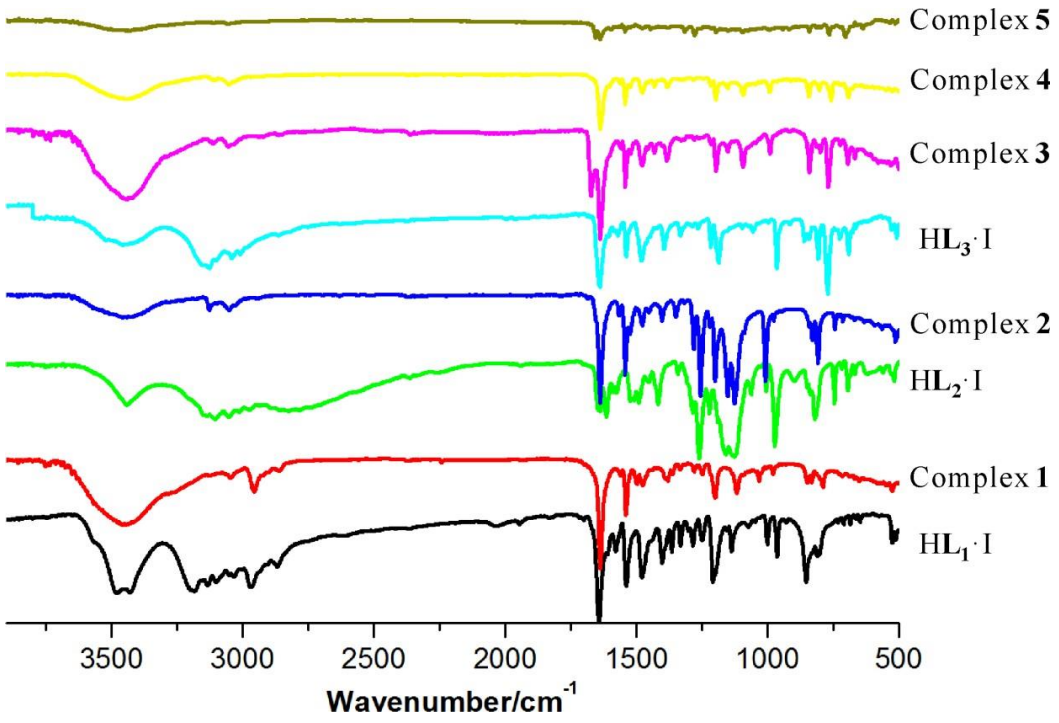


Fig. S1 IR spectra of the five copper iodide clusters and the three proligands.

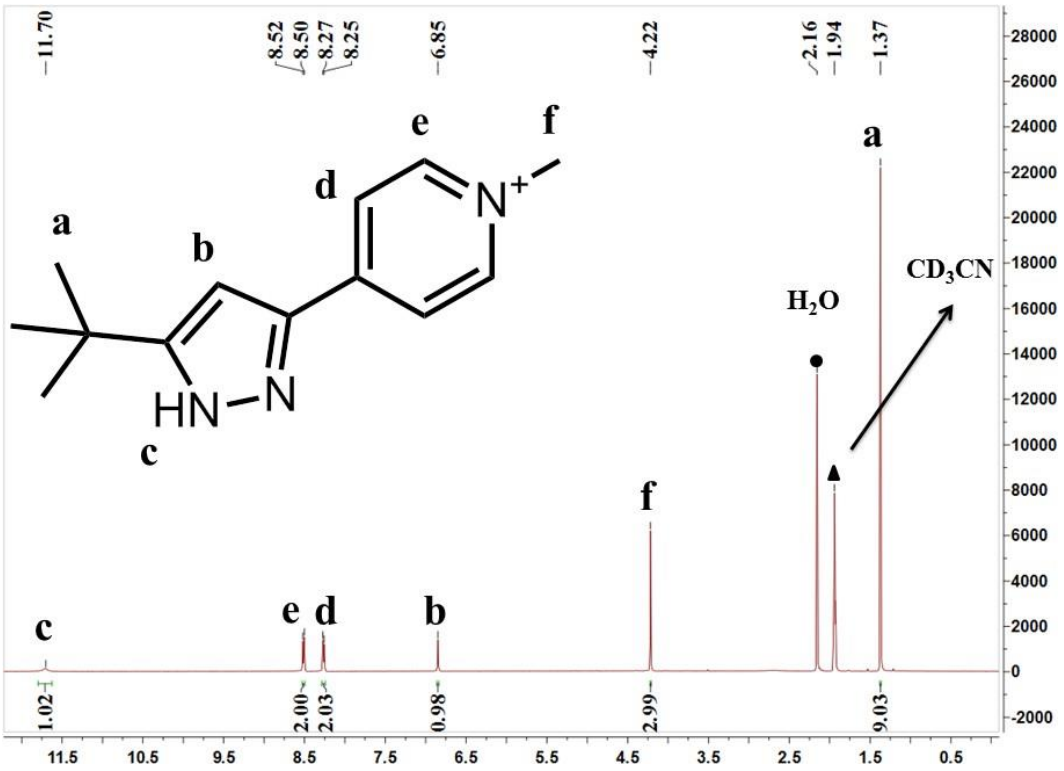


Fig. S2 ^{1}H NMR spectrum (400 MHz, CD_3CN) of proligand H**L$_1$**·I.The black circle shape and triangle shape denote the solvent residual signals of H_2O and CD_3CN, respectively.

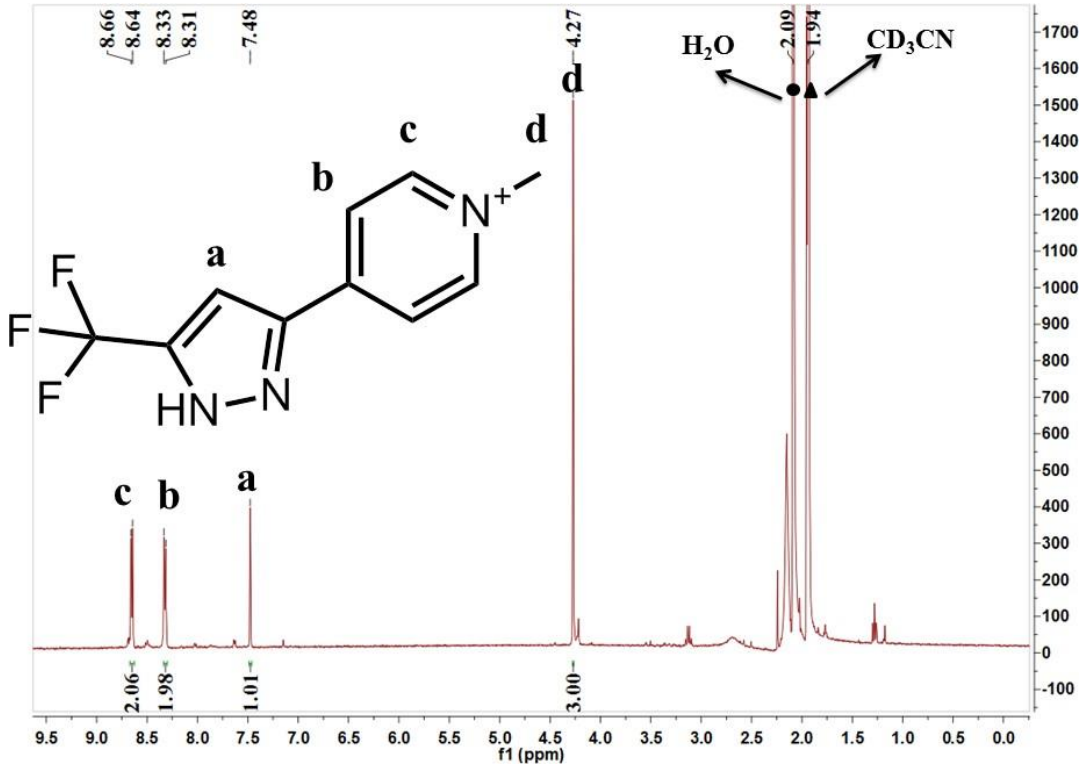


Fig. S3 ^{1}H NMR spectrum (400 MHz, CD_3CN) of proligand H**L$_2$**·I. The black circle shape and triangle shape denote the solvent residual signals of H_2O and CD_3CN, respectively.

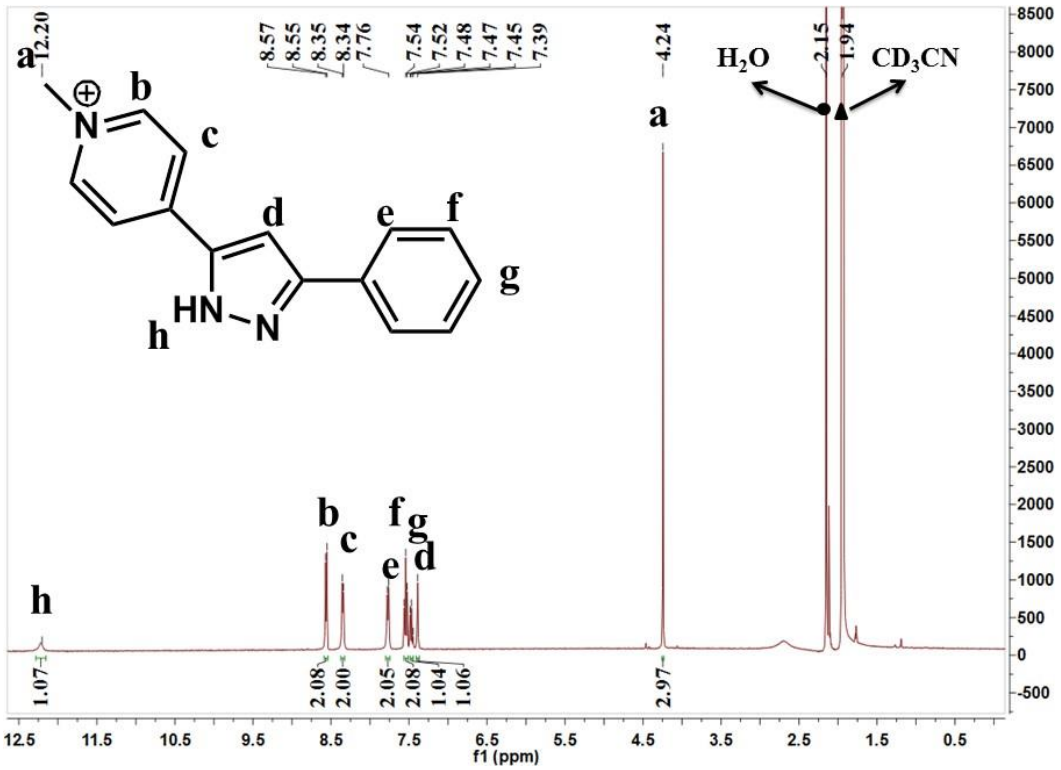


Fig. S4 ^{1}H NMR spectrum (400 MHz, CD_3CN) of proligand H**L**$_3$·I. The black circle shape and triangle shape denote the solvent residual signals of H_2O and CD_3CN, respectively.

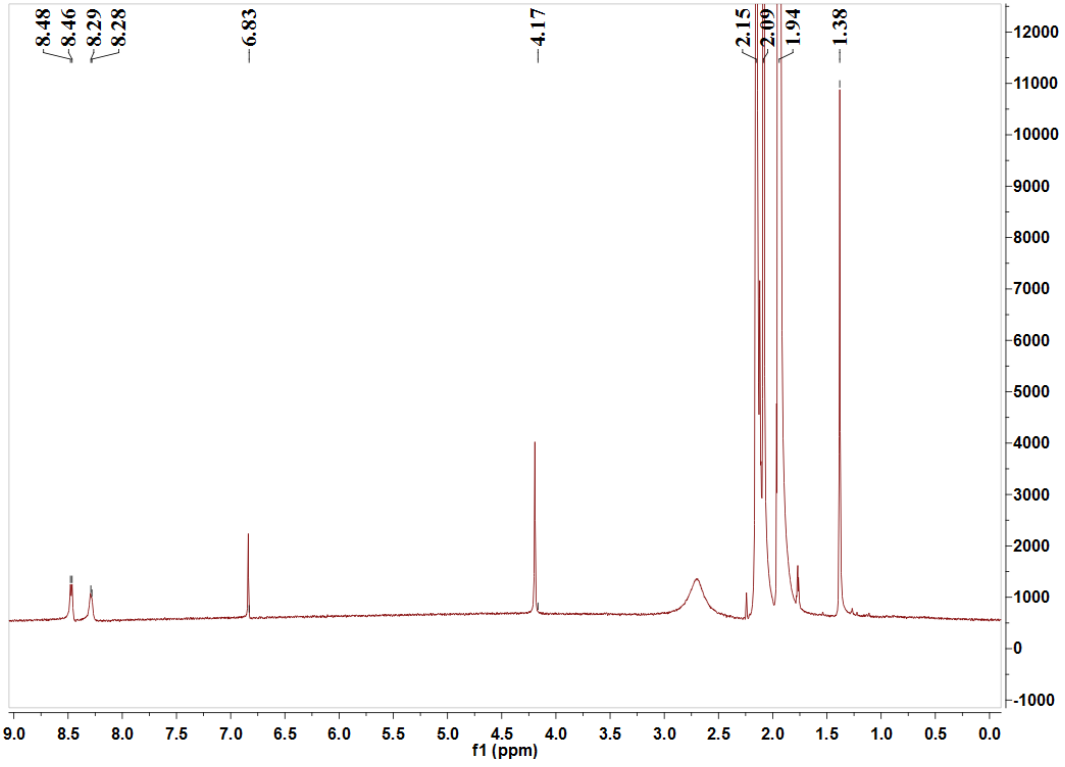


Fig. S5 ^{1}H NMR spectrum (400 MHz, CD_3CN) of the complex **1**. The signals at 2.15, 2.09 and 1.94 ppm are the solvent residual signals of H_2O, acetone and CD_3CN, respectively.

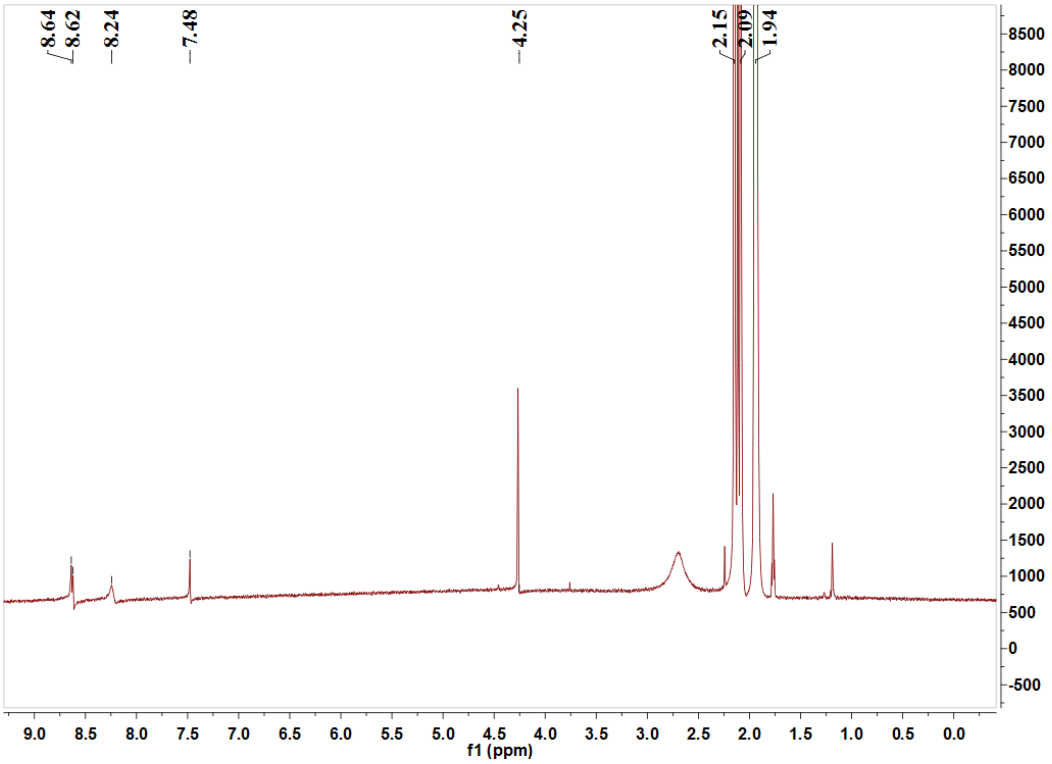


Fig. S6 ^{1}H NMR spectrum (400 MHz, CD_3CN) of the complex **2**. The signals at 2.15, 2.09 and 1.94 ppm are the solvent residual signals of H_2O, acetone and CD_3CN, respectively.

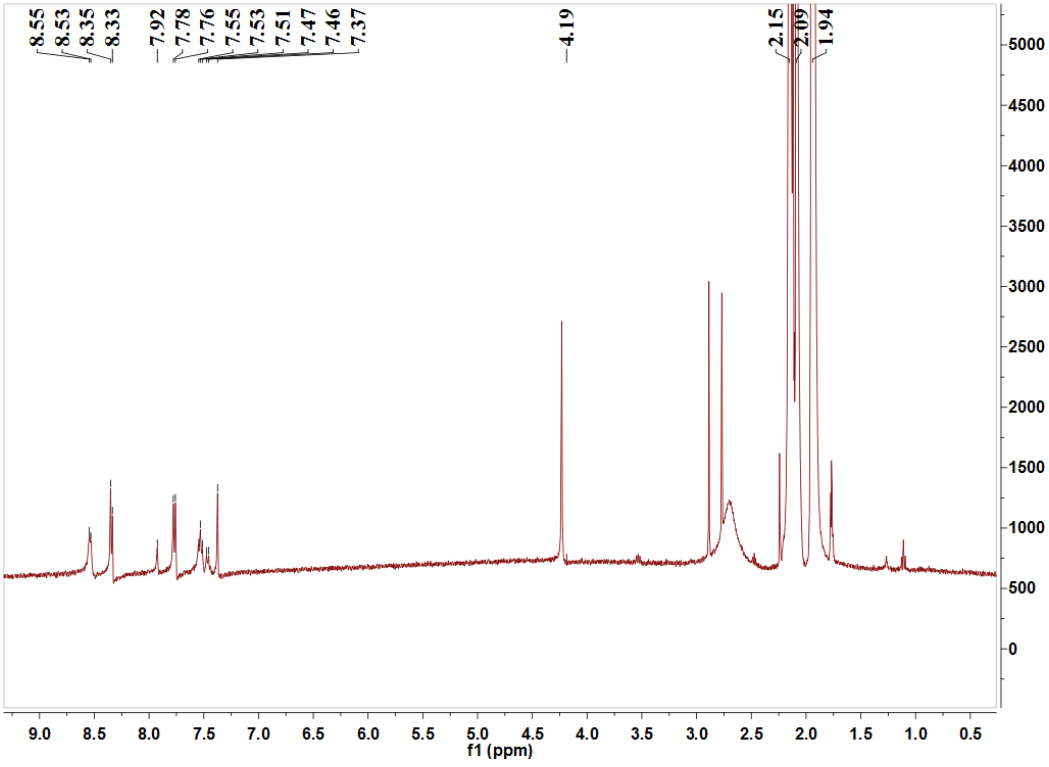


Fig. S7 ^{1}H NMR spectrum (400 MHz, CD_3CN) of the complex **3**. The signals at 2.15, 2.09 and 1.94 ppm are the solvent residual signals of H_2O, acetone and CD_3CN, respectively.

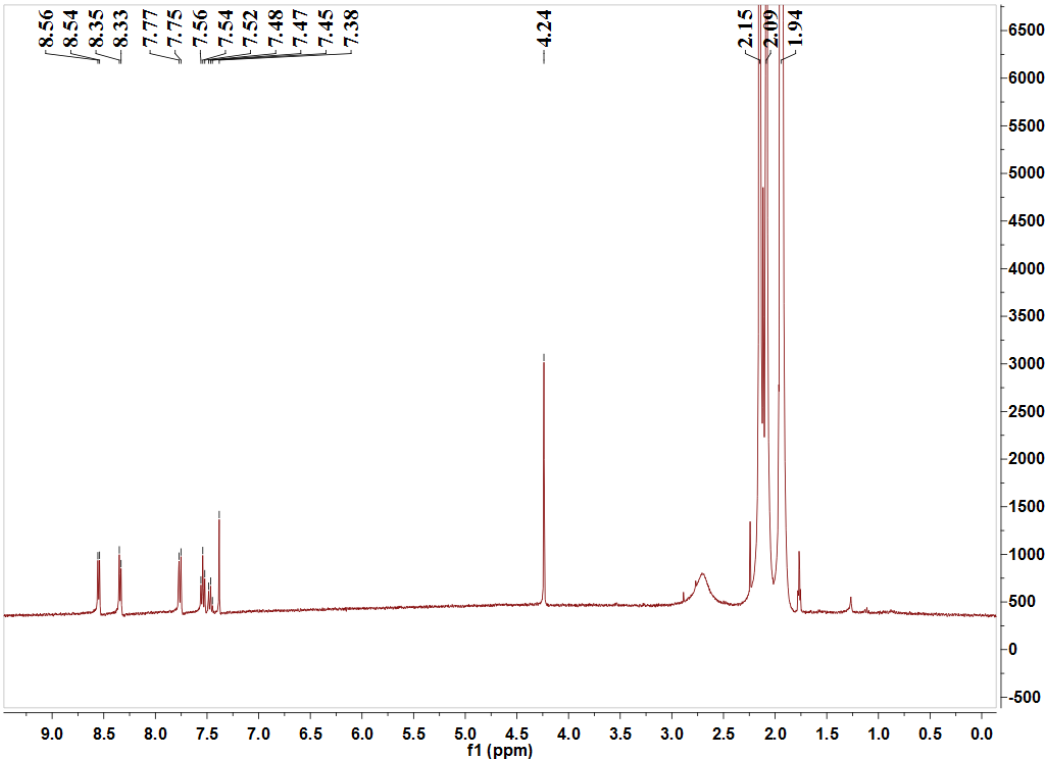


Fig. S8 ^{1}H NMR spectrum (400 MHz, CD_3CN) of the complex **4**. The signals at 2.15, 2.09 and 1.94 ppm are the solvent residual signals of H_2O, acetone and CD_3CN, respectively.

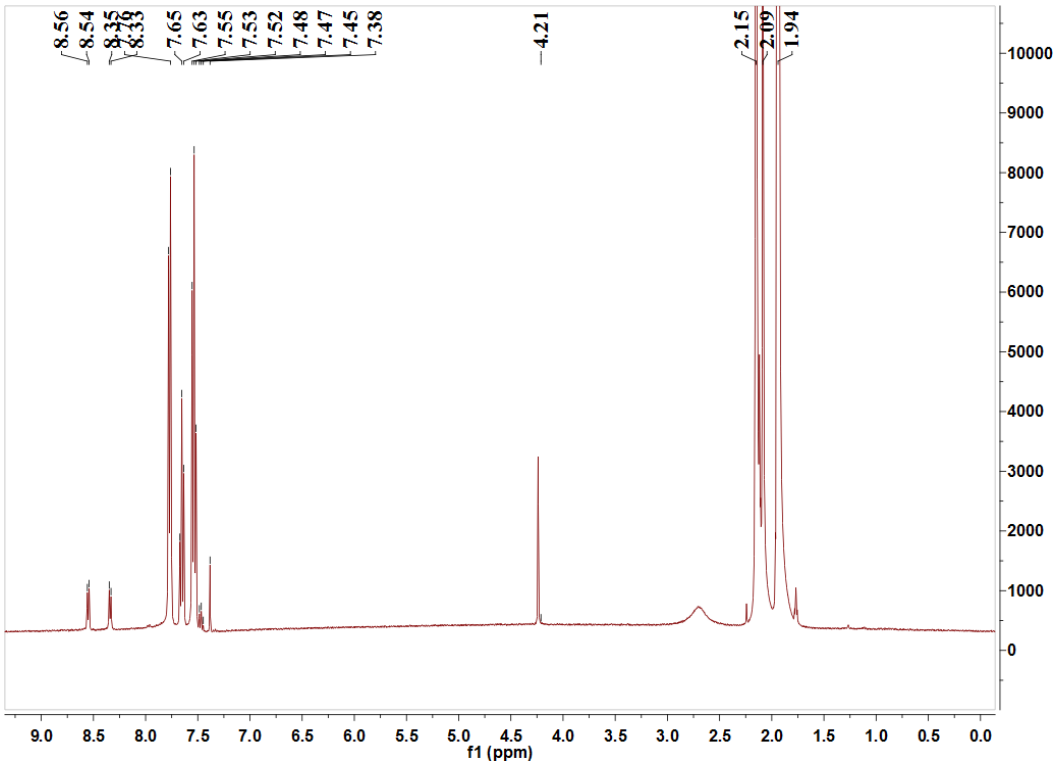


Fig. S9 ^{1}H NMR spectrum (400 MHz, CD_3CN) of the complex **5**. The signals at 2.15, 2.09 and 1.94 ppm are the solvent residual signals of H_2O, acetone and CD_3CN, respectively.

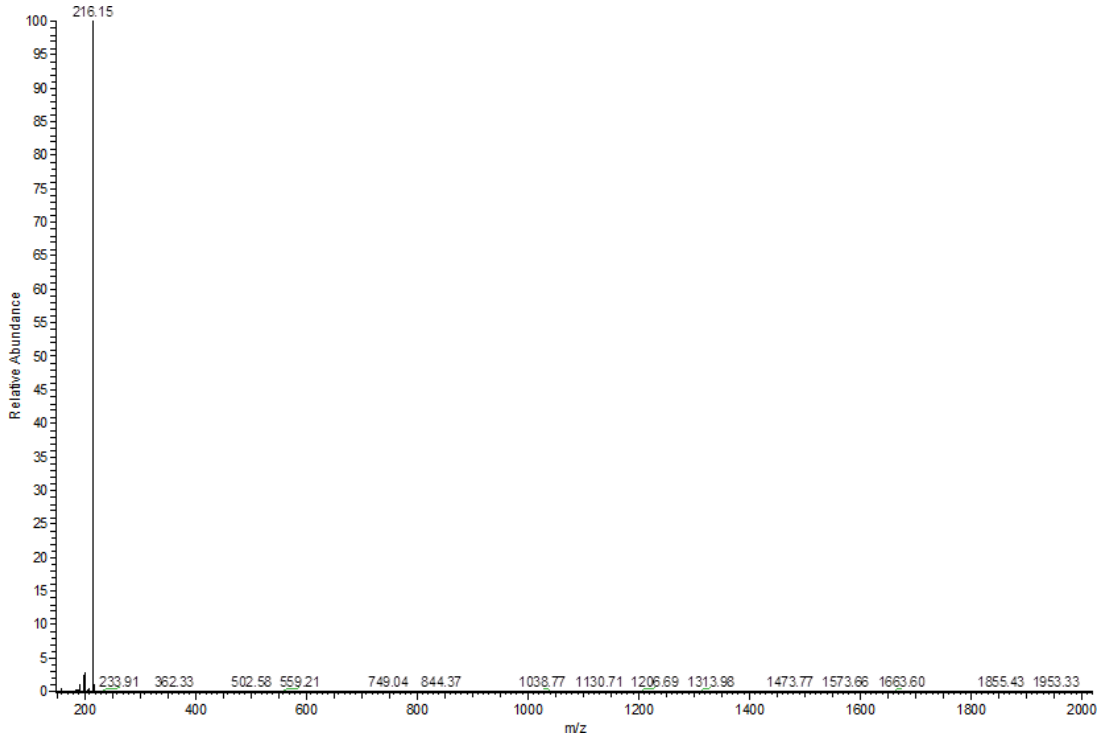


Fig. S10 ESI-MS for complex **1** in acetonitrile at positive mode.

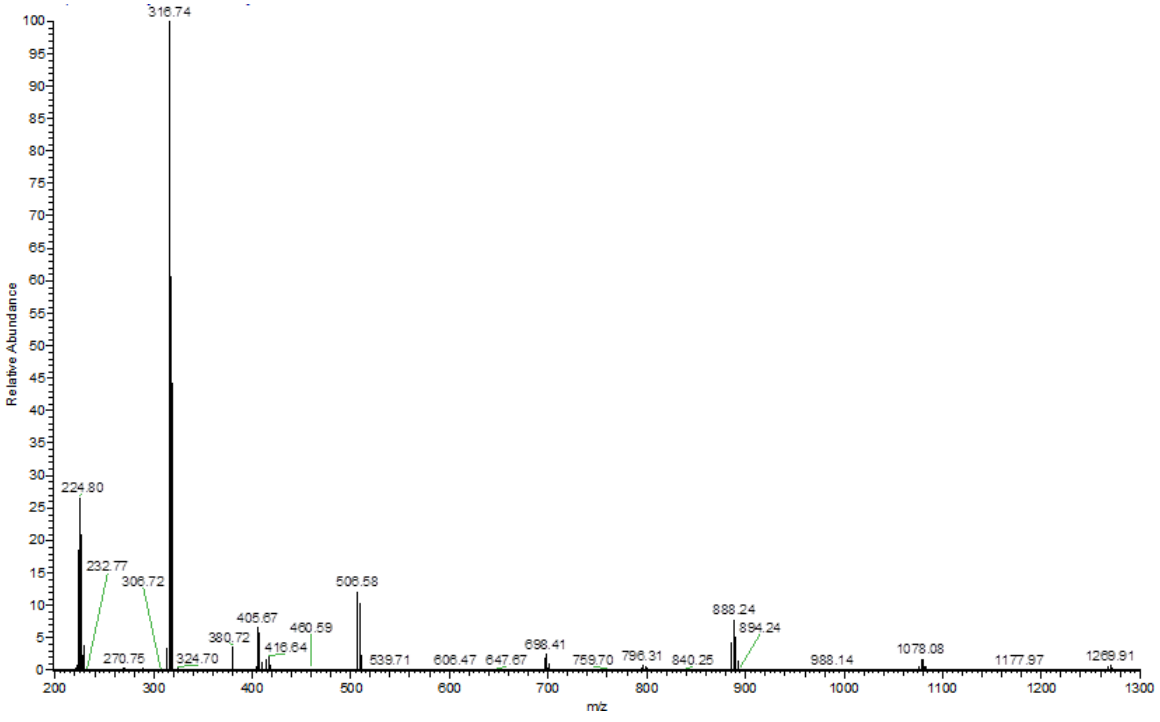


Fig. S11 ESI-MS for complex **1** in acetonitrile at negative mode.

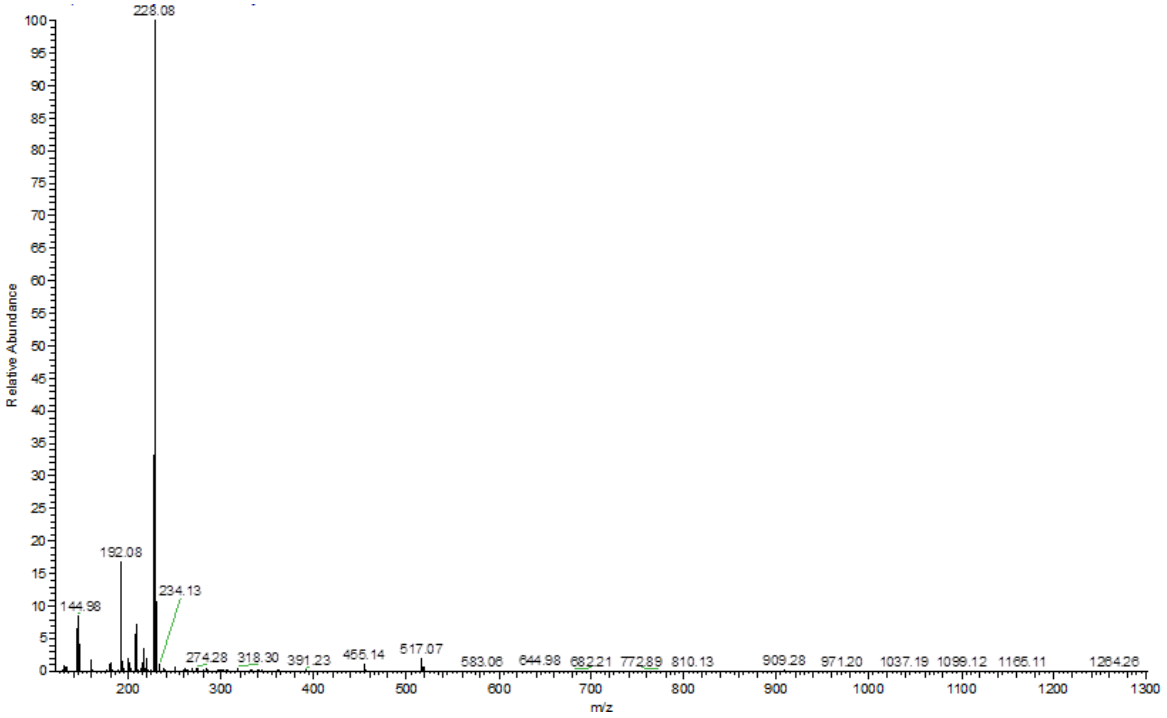


Fig. S12 ESI-MS for complex **2** in acetonitrile at positive mode.

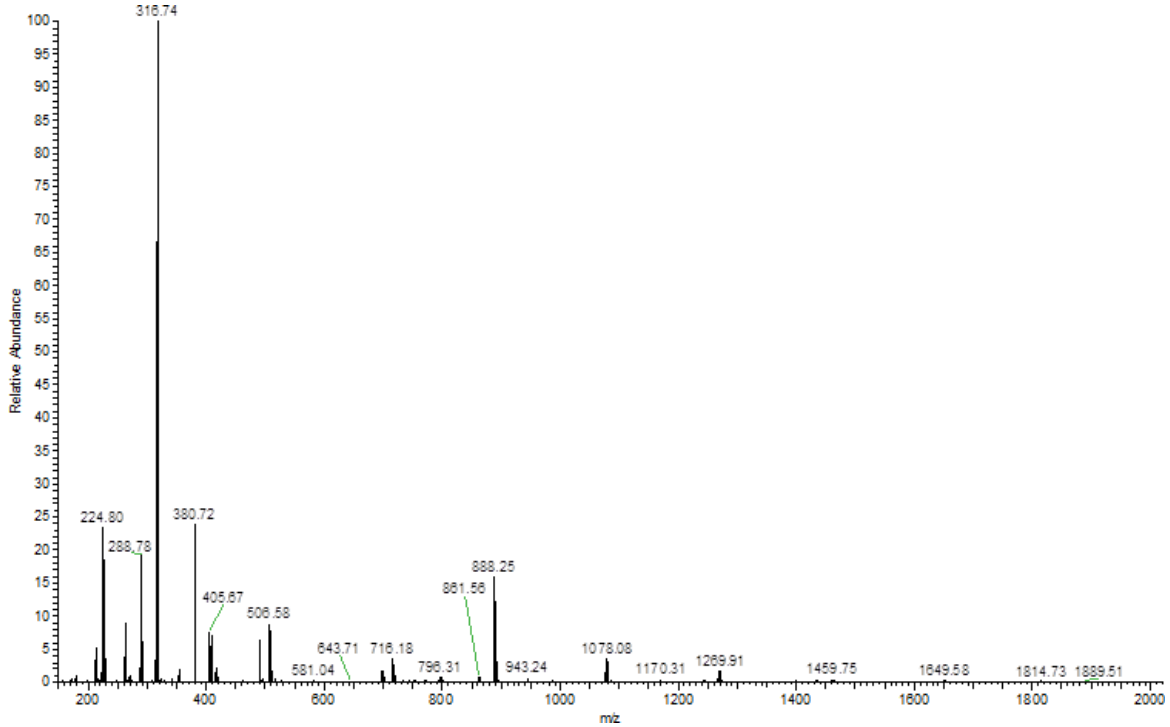


Fig. S13 ESI-MS for complex **2** in acetonitrile at negative mode.

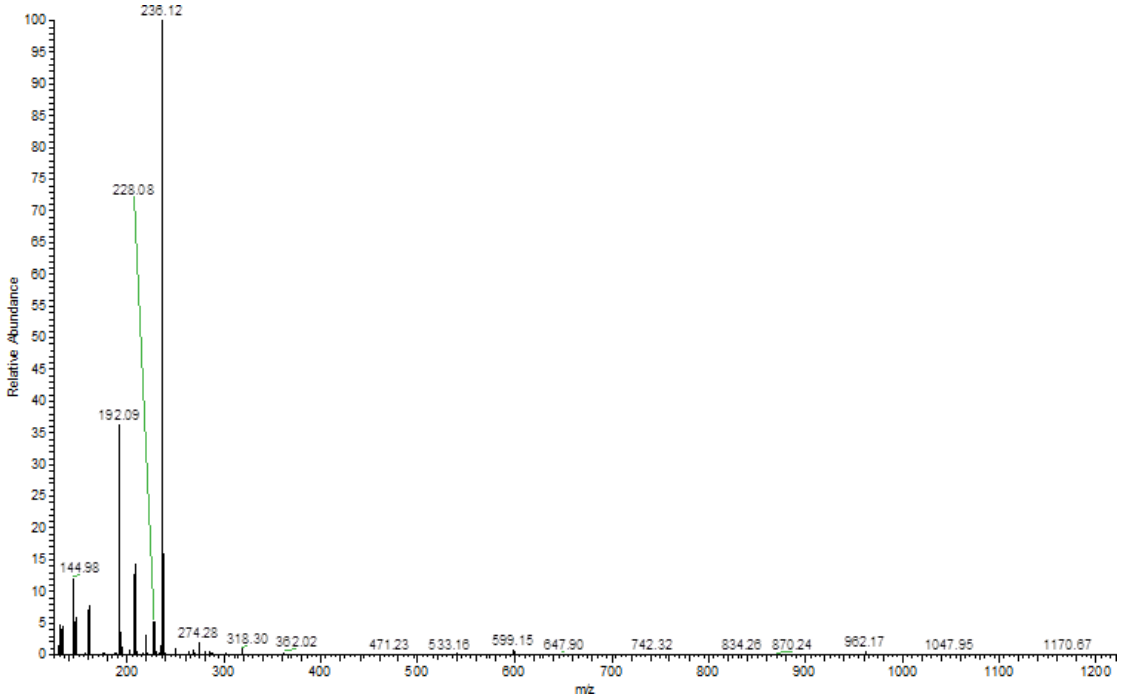


Fig. S14 ESI-MS for complex **3** in acetonitrile at positive mode.

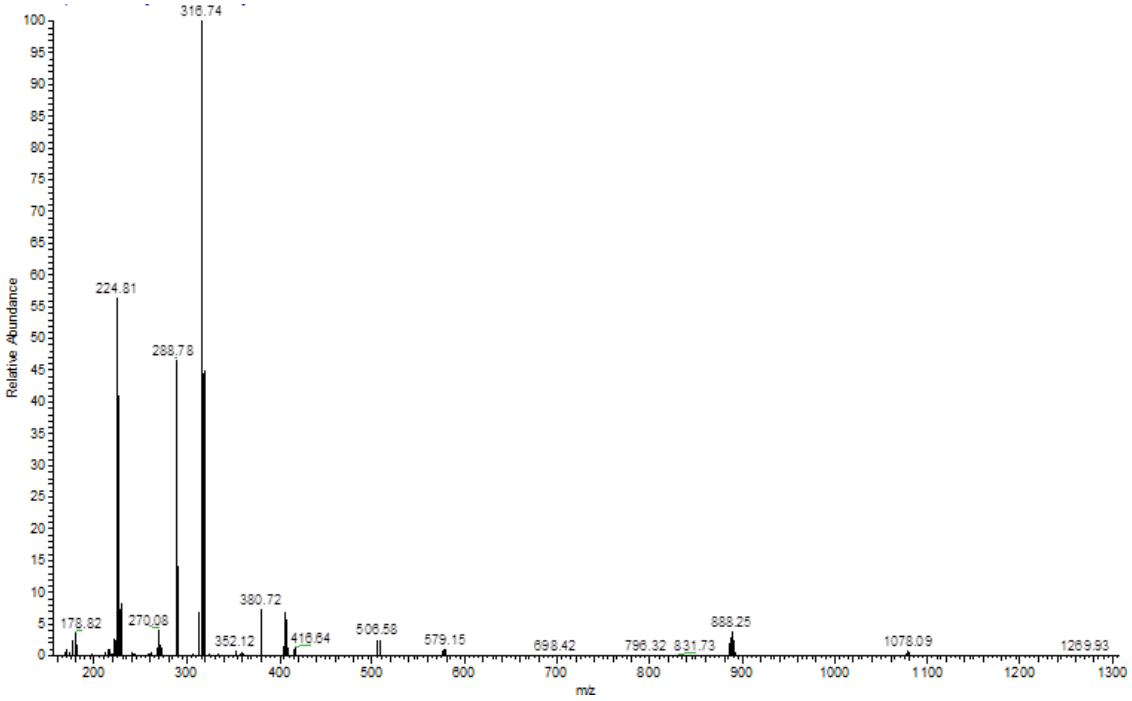


Fig. S15 ESI-MS for complex **3** in acetonitrile at negative mode.

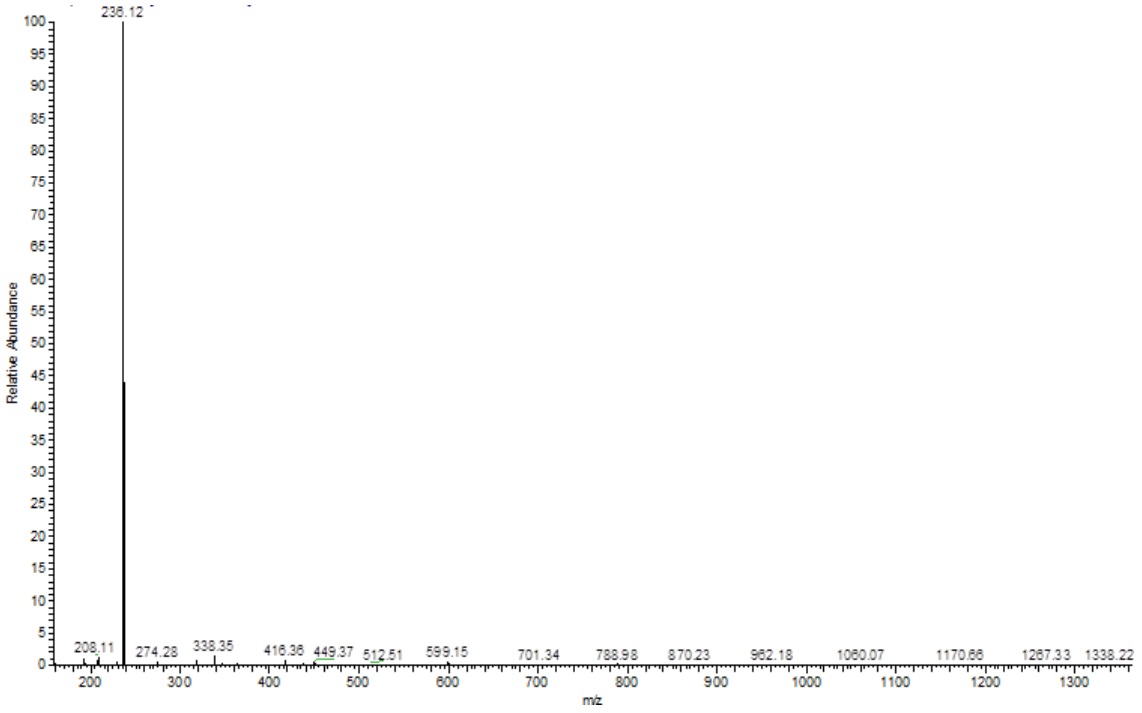


Fig. S16 ESI-MS for complex **4** in acetonitrile at positive mode.

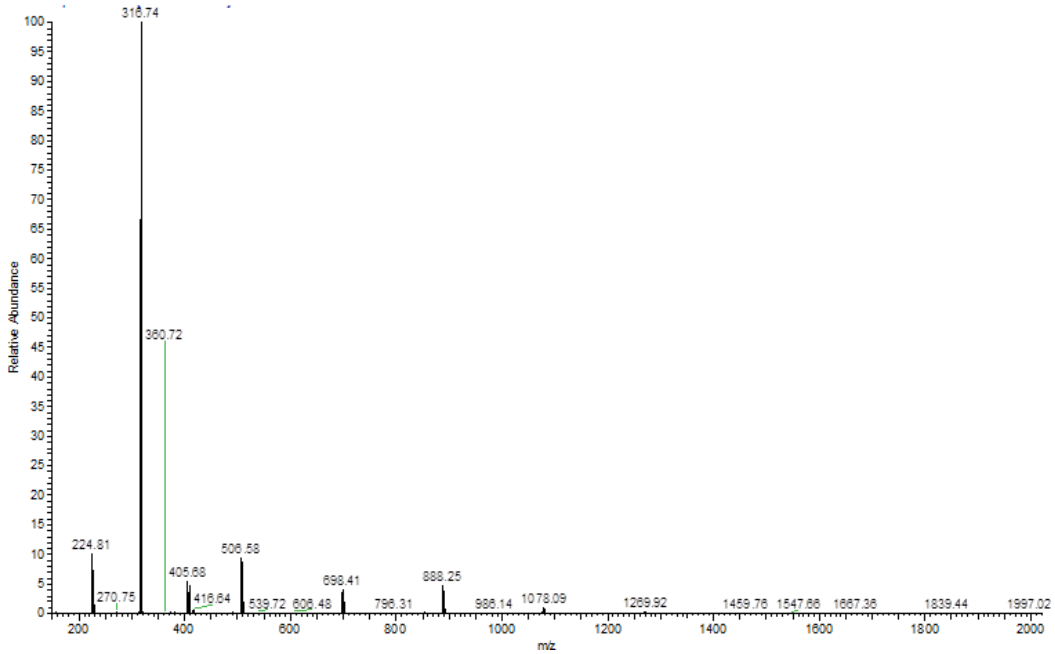


Fig. S17 ESI-MS for complex **4** in acetonitrile at negative mode.

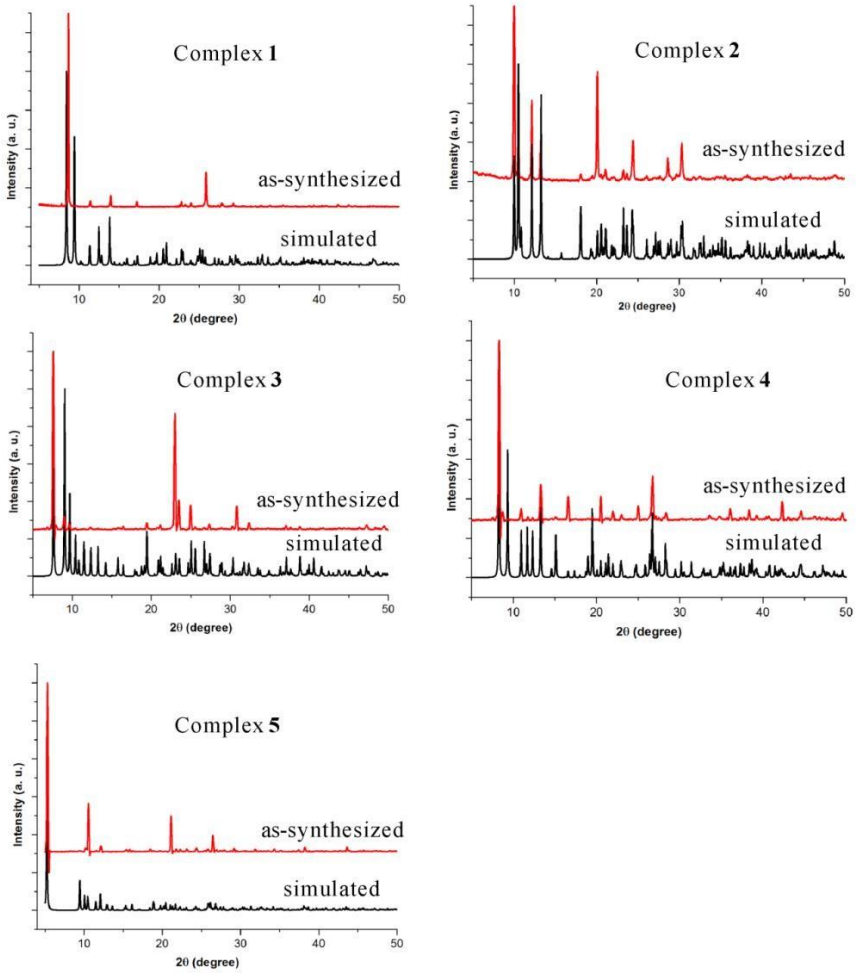


Fig. S18 Comparison of the experimental PXRD patterns of complex **1**–**5** with the simulated patterns.

Table S1. X-ray Crystallographic Data for of Complex **1**–**5**

	1 (293 K)	**2** (293 K)	**2** (100 K)
formula	$C_{28}H_{37}Cu_4I_4N_7$	$C_{20}H_{16}Cu_4F_6I_4N_6$	$C_{20}H_{16}Cu_4F_6I_4N_6$
fw	1233.41	1216.15	1216.15
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a /Å	15.6308(10)	9.3659(3)	9.2037(7)
b /Å	11.7536(8)	9.8423(2)	9.8345(5)
c /Å	21.0207(14)	16.7265(4)	16.6471(9)
α/deg	90.00	90.00	90.00
β/deg	92.486(6)	102.865(3)	103.656(6)
γ/deg	90.00	90.00	90.00
V/ Å^3	3858.3(4)	1503.18(7)	1464.20(15)
Z	4	2	2
D_{cal}/g·cm^{-3}	2.123	2.687	2.758
reflns collected	20677	10017	7418
unique reflns	6787	2634	2557
GOF	1.055	1.036	1.041

R_{int}	0.0833	0.0292	0.0541
R_1[a] [I > 2sigma(I)]	0.0981	0.0256	0.0369
wR_2[b](all data)	0.2960	0.0551	0.0793

	3 (293 K)	**3** (100 K)	**4** (293 K)	**4** (100 K)	**5** (293 K)	**5** (100 K)
formula	$C_{30}H_{26}Cu_4I_4N_6$	$C_{30}H_{26}Cu_4I_4N_6$	$C_{30}H_{26}Cu_4I_4N_6$	$C_{30}H_{26}Cu_4I_4N_6$	$C_{56}H_{46}Cu_4I_4N_6O_2$	$C_{56}H_{46}Cu_4I_4N_6O_2$
fw	1232.33	1232.33	1232.33	1232.33	1596.75	1596.75
cryst syst	orthorhombic	orthorhombic	triclinic	triclinic	triclinic	triclinic
space group	*Pnma*	*Pnma*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	23.146(3)	22.6213(6)	8.3998(6)	8.2740(4)	8.5250(4)	8.3723(2)
b /Å	18.2397(18)	18.2046(5)	9.9053(5)	9.8472(4)	9.6093(4)	9.5464(2)
c /Å	9.1304(10)	9.0203(2)	10.7689(6)	10.7436(5)	17.1221(7)	16.9481(4)
α/deg	90.00	90.00	96.490(5)	96.543(2)	98.411(3)	98.4350(10)
β/deg	90.00	90.00	91.848(5)	91.051(2)	92.127(4)	92.2940(10)
γ/deg	90.00	90.00	105.378(6)	105.758(2)	99.493(3)	98.6550(10)
V/ Å^3	3854.6(8)	3714.67(16)	856.57(9)	835.84(7)	1365.84(10)	1322.00(5)
Z	4	4	1	1	1	1
D_{cal}/g·cm^{-3}	2.123	2.204	2.389	2.448	1.941	2.006
reflns collected	14303	37092	7094	12416	9674	20972
unique reflns	3499	3519	2999	3030	4803	4816
GOF	1.009	1.015	1.007	1.041	1.032	1.042
R_{int}	0.1123	0.0580	0.0321	0.0428	0.0328	0.0389
R_1[a] [I > 2sigma(I)]	0.0749	0.0372	0.0316	0.0301	0.0458	0.0298
wR_2[b] (all data)	0.2097	0.0945	0.0596	0.0997	0.1349	0.0842

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{[\sum w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$ for all data.

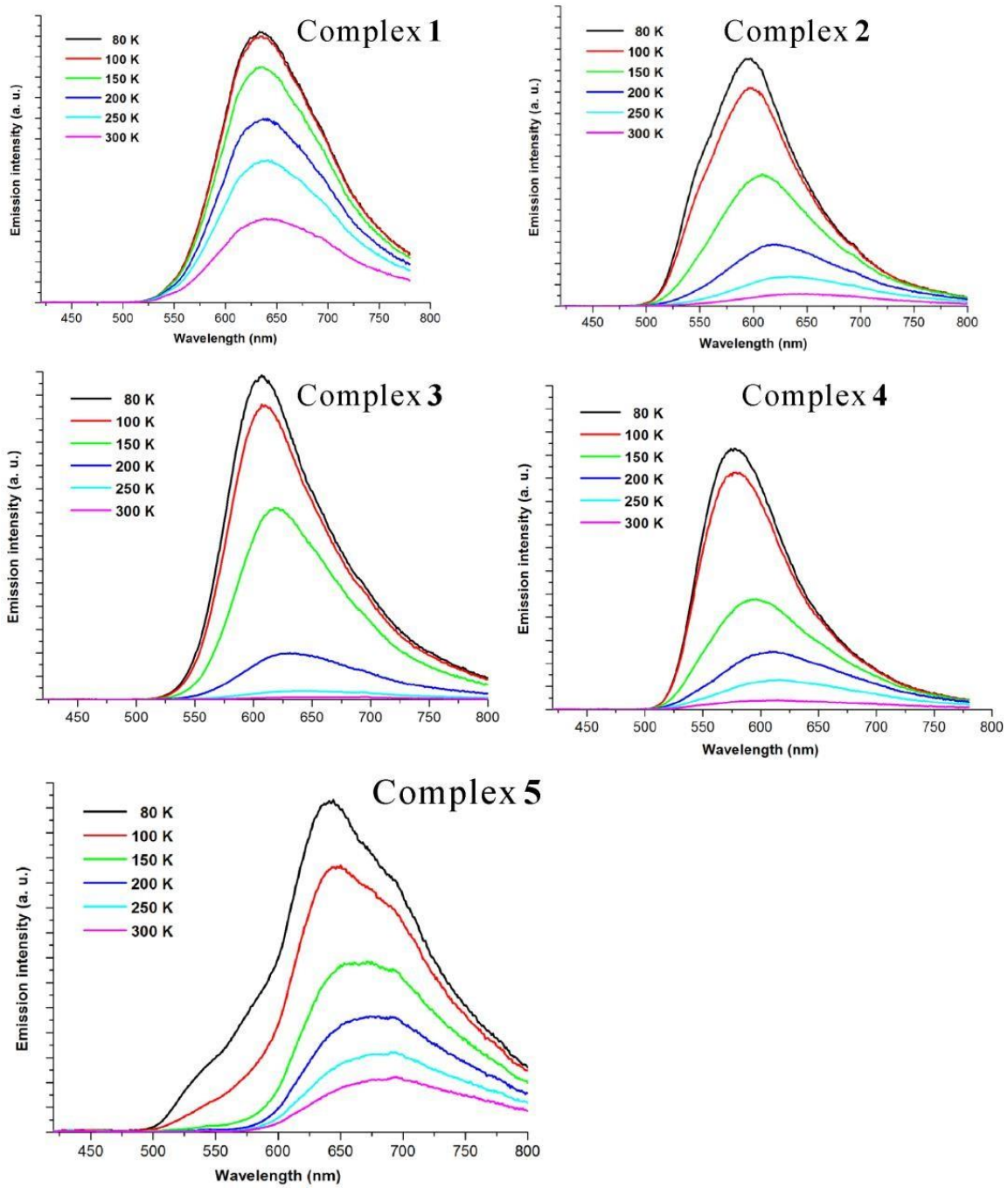


Fig. S19 Temperature dependence of solid-state luminescence spectra of cluster **1**–**5** from 300 to 80 K at λ_{ex} = 330 nm for **1** and λ_{ex} = 340 nm for **2**–**5**.

Table S2. Photoluminescence CIE Coordinates, Peak Emission Wavelength (λ_{em}), and Lifetime (τ) for Clusters **1**–**5** in the Solid State

compound	CIE[a]		λ_{em} (nm)		τ (μs)[b]	
	80 K	300 K	80 K	300 K	80 K	300 K
1	(0.62, 0.37)	(0.61, 0.38)	633	640	5.0	4.8
2	(0.52, 0.46)	(0.58, 0.40)	597	650	14.6	5.1
3	(0.59, 0.39)	(0.60, 0.36)	607	655	7.4	4.9
4	(0.51, 0.48)	(0.54, 0.43)	577	615	7.9	4.8
5	(0.58, 0.40)	(0.62, 0.31)	644	695	8.4	4.7

[a]CIE represents the Commission International d'Eclairage coordinates. [b]For lifetime measurements, the pulsed excitation source of 337 nm generated from a nitrogen laser was used throughout.

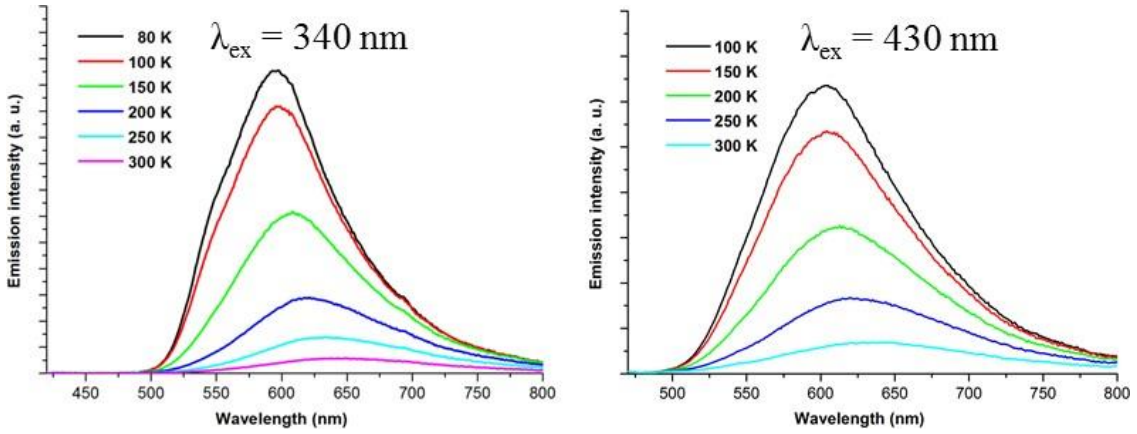


Fig. S20 Temperature dependence of solid-state luminescence spectra of cluster **2** at λ_{ex} = 340 nm (left) and λ_{ex} = 430 nm (right).

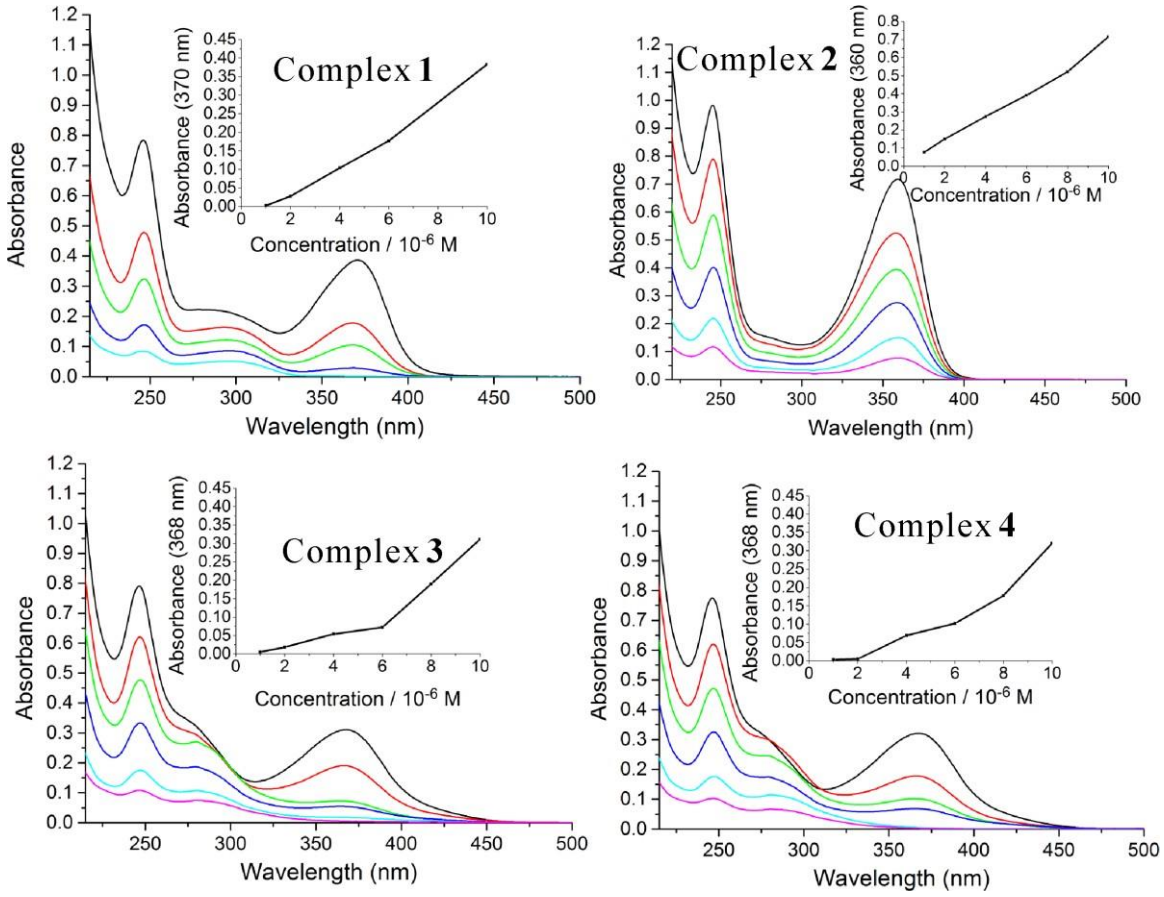


Fig. S21 UV–vis absorption spectra of **1**–**4** in acetonitrile at different concentrations. The inset shows the apparent absorbance as a function of the concentration (1–10 μM) of **1** (λ_{abs} = 370 nm), **2** (λ_{abs} = 360 nm), **3** (λ_{abs} = 368 nm), **4** (λ_{abs} = 368 nm) in CH_3CN at 298 K.

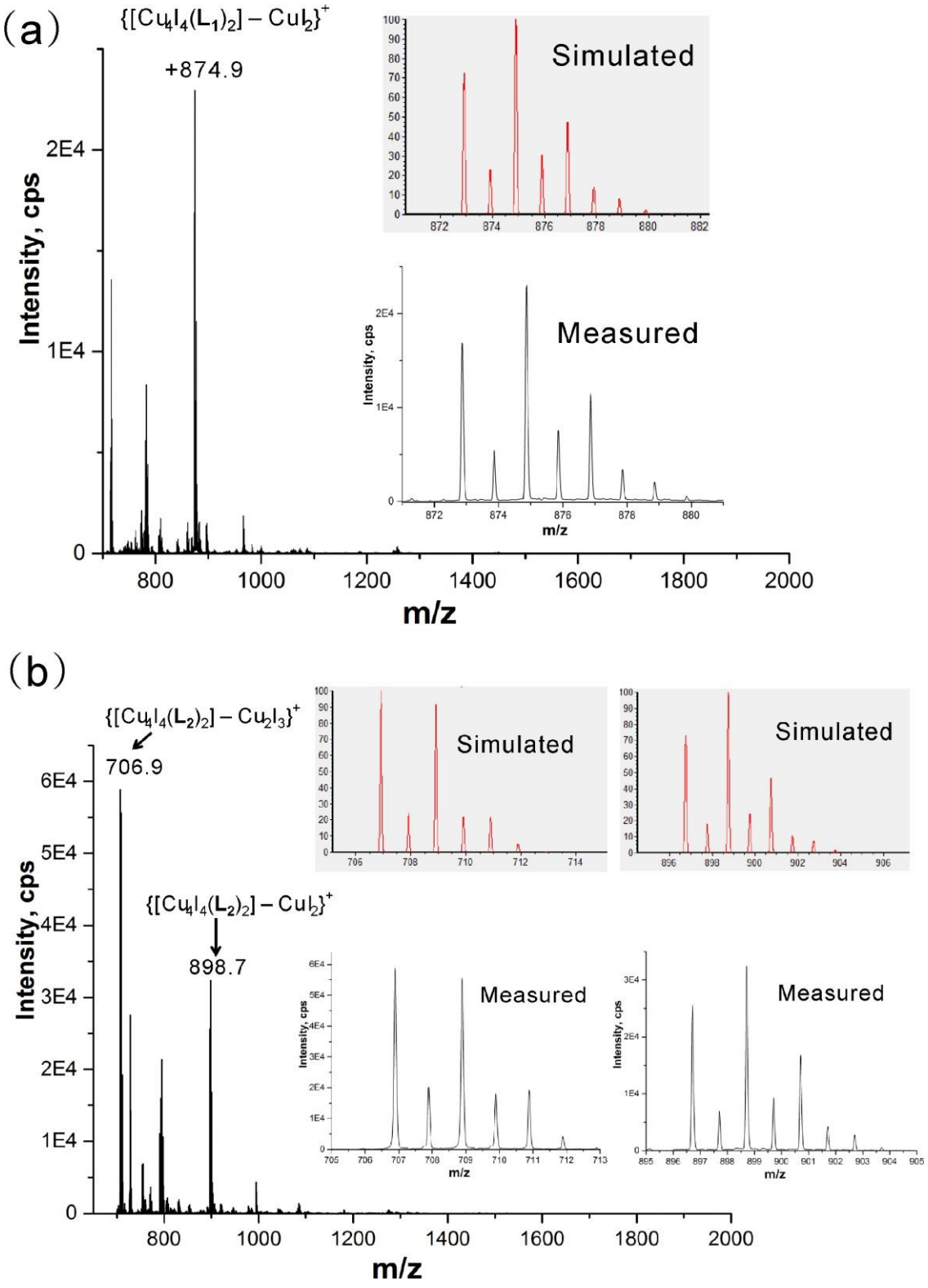


Fig. S22 (a) MALDI-TOF mass spectrum of complex **1** and (b) of complex **2** in acetonitrile solution with experimental isotopic distribution pattern (black, inset) and simulated isotopic distribution pattern (red, inset).

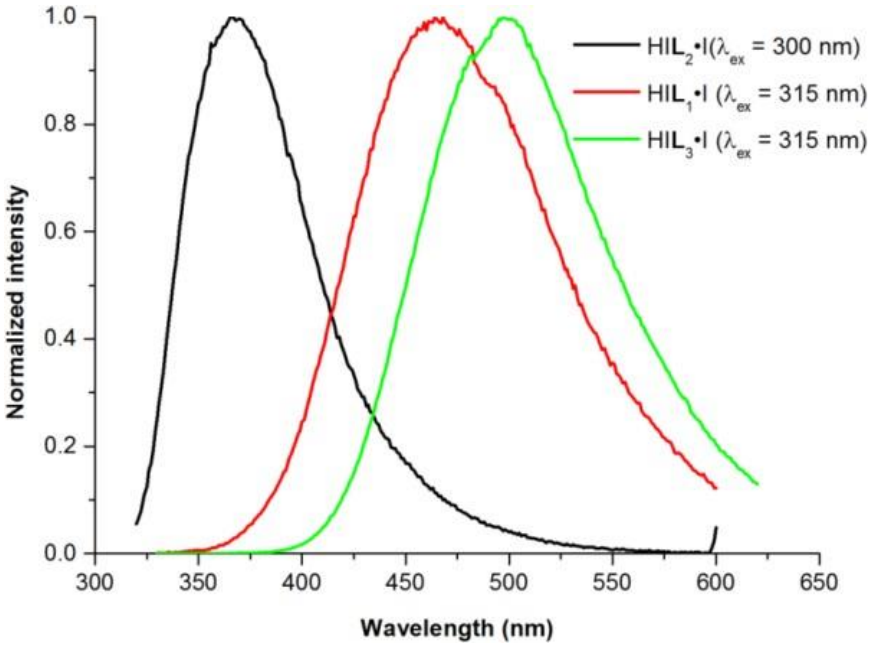


Fig. S23 Normalized emission spectra of the proligands in acetonitrile solution at room temperature.

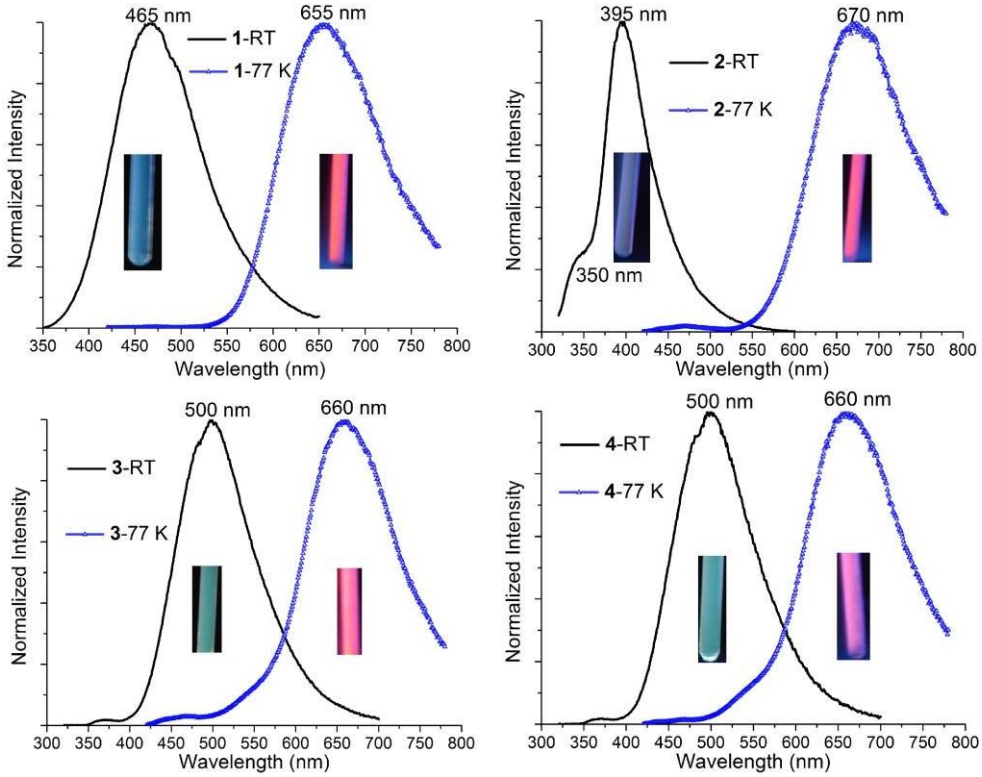


Fig. S24 Luminescence spectra of clusters **1**–**4** in dry acetonitrile solution (1 x 10^{-4} M) at RT (λ_{ex} = 320 nm for **1**, at 307 nm for **2**, at 315 nm for **3**, and at 310 nm for **4**) and 77 K (λ_{ex} = 330 nm for **1**–**4**). Corresponding photos under UV irradiation at 254 nm (UV lamp) for RT and at 365 nm for 77 K are showed in the inset.

Table S3. Emission Wavelengths λ_{em} for **2** Based on T_1 Optimized Geometry in Gas Phase Calculated with Various Functionals Employing Time-Dependent Density Functional Theory and the 6-31G(d) Basis Set

	λ_{em} (nm)
PBE0	4055.5
M06-2X	902.4
ωB97X-D	761.30

Table S4. Relevant Computed Data for **1**–**4**

/ Å	**1**			**2**				**3**				**4**		
	exp	S_0	T_1^{UDFT}	exp	S_0	T_1^{UDFT}	T_1^{TDDFT}	exp	S_0	T_1^{UDFT}	T_1^{TDDFT}	exp	S_0	T_1^{UDFT}
Cu–Cu	2.544–2.891	2.657–2.932	2.552–2.828	2.520–2.918	2.669–3.017	2.779–3.151	2.689–3.250	2.466–2.852	2.660–2.870	2.635–3.045	2.704–3.190	2.572–2.906	2.663–2.940	2.786–3.112
Cu–I	2.473–3.739	2.596–3.897	2.485–3.738	2.514–3.262	2.591–3.994	2.560–3.449	2.568–3.626	2.540–3.242	2.646–2.985	2.598–2.950	2.597–3.628	2.528–3.207	2.604–3.946	2.568–3.494
Cu–N	1,896–2.028	1.997–2.089	1.945–2.035	1.947–1.980	1.996–2.012	1.965–2.041	1.946–2.123	1.947–1.993	2.034–2.048	1.978–2.014	1.965–2.108	1.949–1.978	2.002–2.092	1.966–2.026

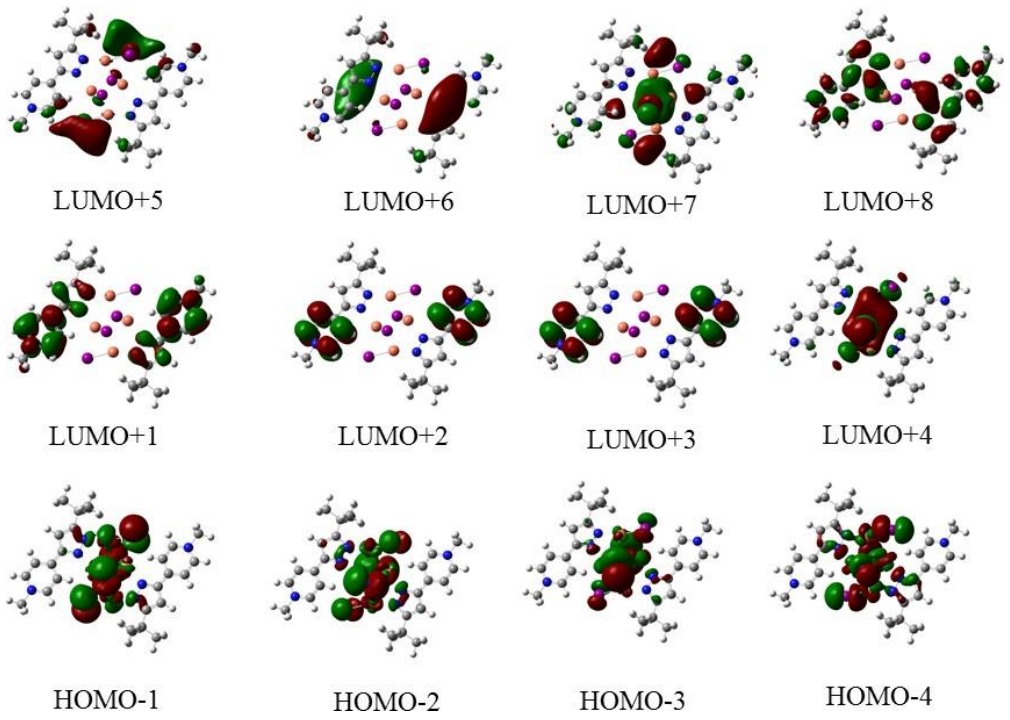


Fig. S25 Isodensity surface plots of some molecular orbitals of complex **1** calculated for the singlet ground state at the S_0 optimized geometry.

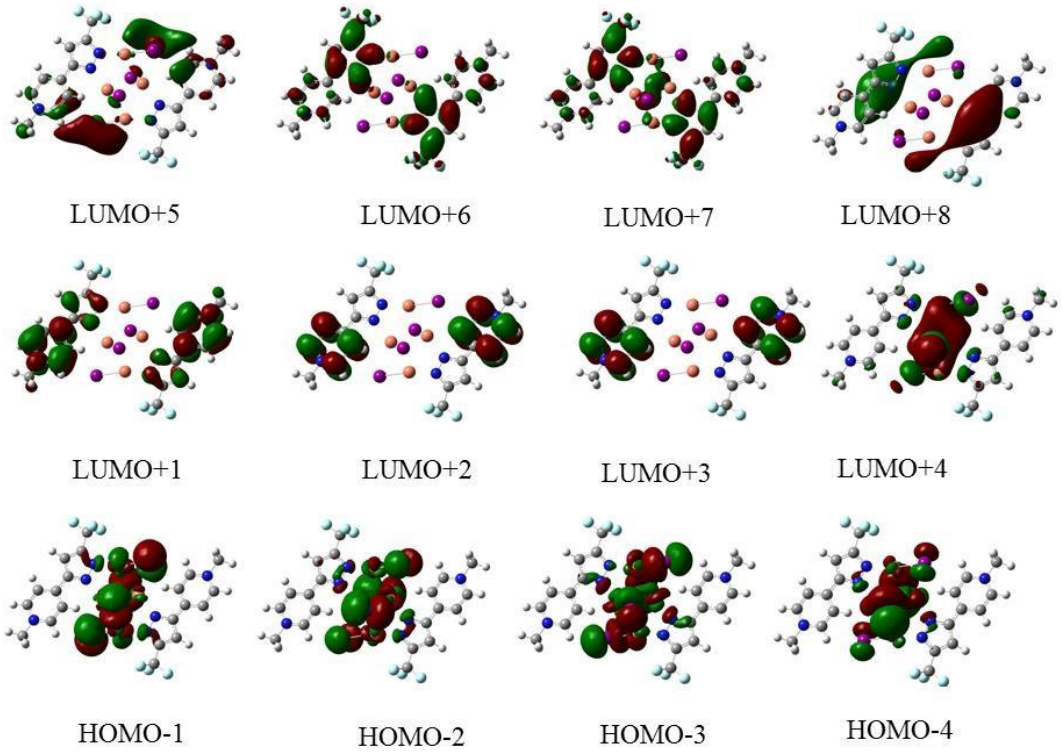


Fig. S26 Isodensity surface plots of some molecular orbitals of complex **2** calculated for the singlet ground state at the S_0 optimized geometry.

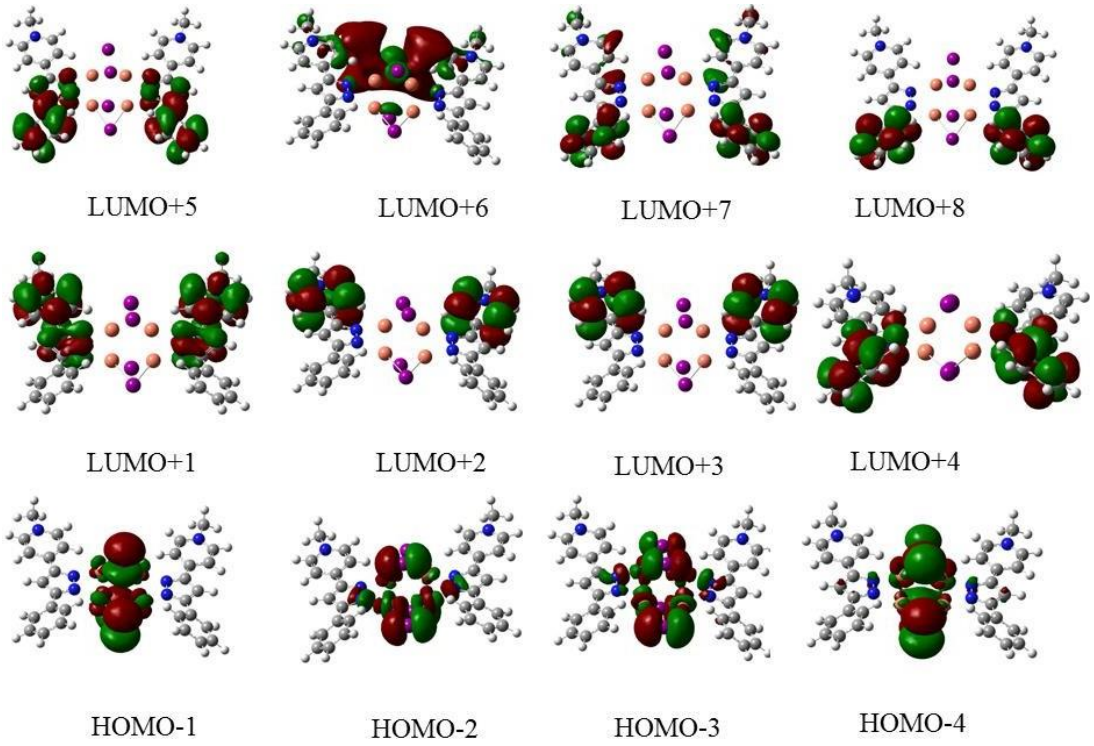


Fig. S27 Isodensity surface plots of some molecular orbitals of complex **3** calculated for the singlet ground state at the S_0 optimized geometry.

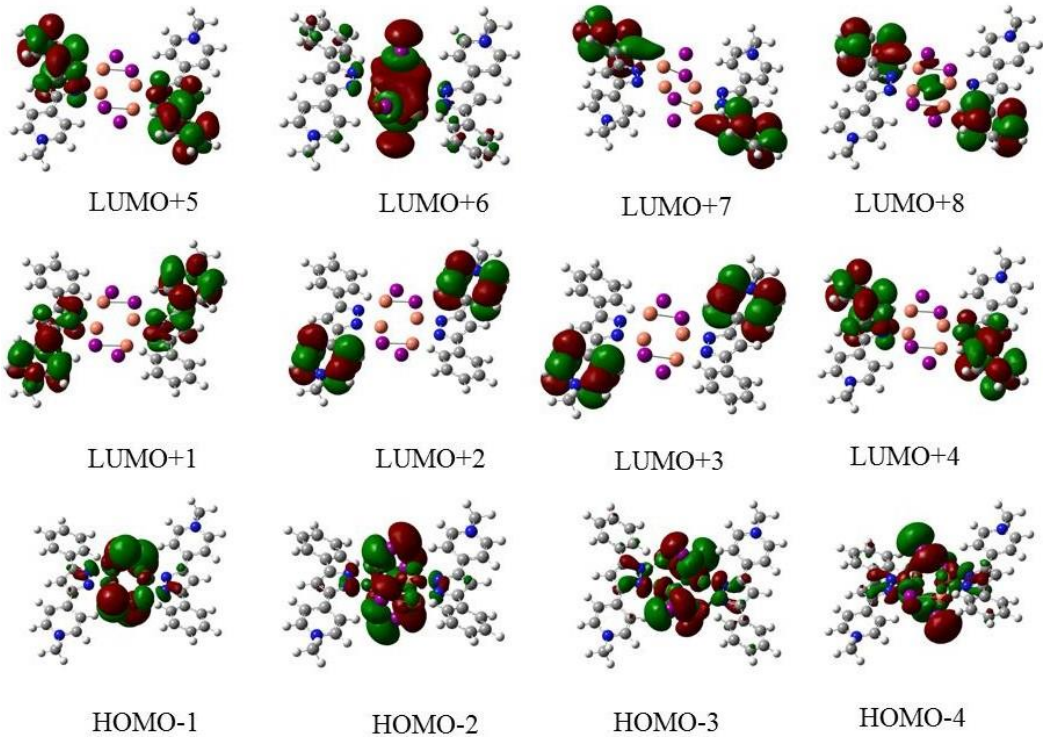
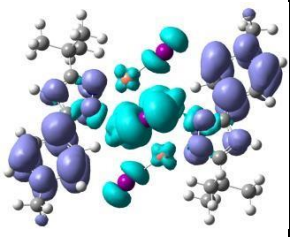
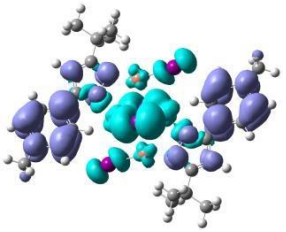
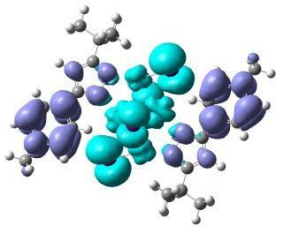
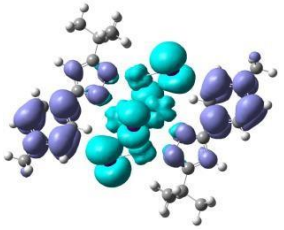
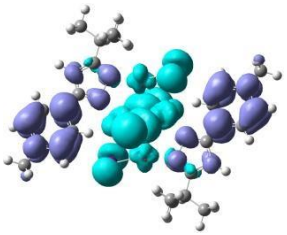
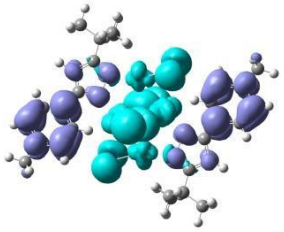
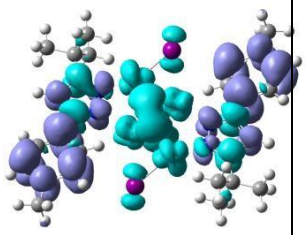
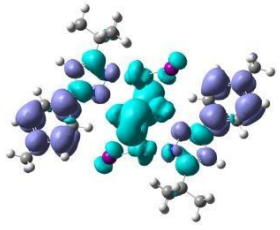
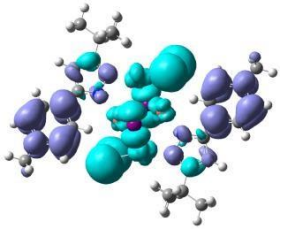
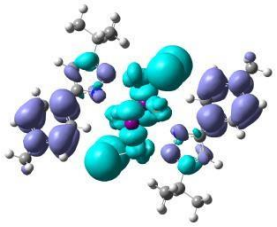
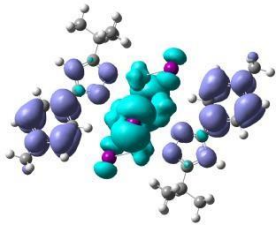
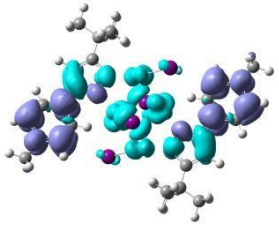
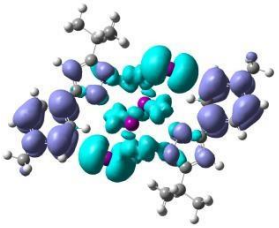
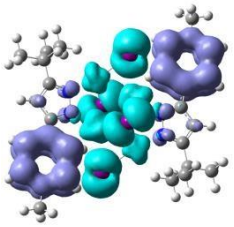
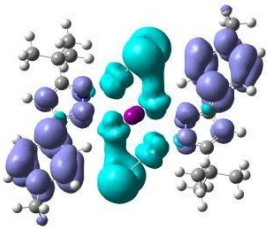
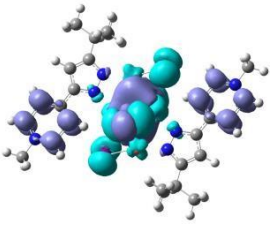


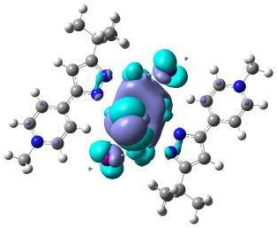
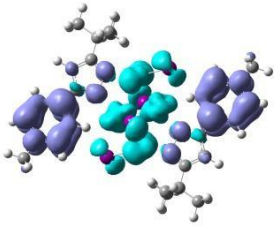
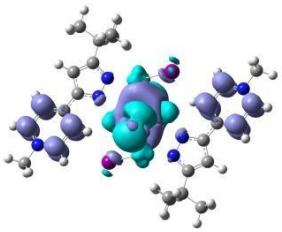
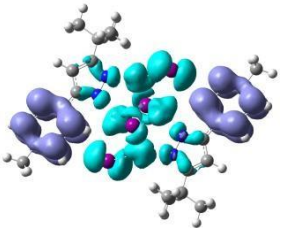
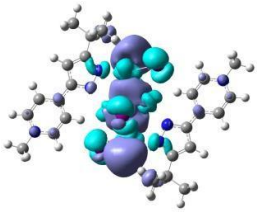
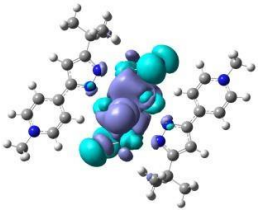
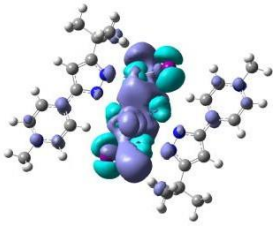
Fig. S28 Isodensity surface plots of some molecular orbitals of complex **4** calculated for the singlet ground state at the S_0 optimized geometry.

Table S5. Calculated TDDFT Singlet-Singlet Excitation Energies, Oscillator Strengths (*f*), Transition Assignments in Terms of Electronic Density Difference (EDD) Maps for the First 10 and Most Intense ($f > 0.03$) Transitions of Complex **1** at the S_0 Optimized Geometry in the Gas State[a]

Excited states	λ (nm)	Energy (eV)	*f*	EDD	Assignment[b]
$S_0 \rightarrow S_1$	423.1	2.929	0.0015		^{1}(X + M)LCT
$S_0 \rightarrow S_2$	422.6	2.933	0.0000		^{1}(X + M)LCT

$S_0 \rightarrow S_3$	401.4	3.088	0.0000		^{1}(X + M)LCT
$S_0 \rightarrow S_4$	400.2	3.097	0.0202		^{1}(X + M)LCT
$S_0 \rightarrow S_5$	381.4	3.250	0.0188		^{1}(X + M)LCT
$S_0 \rightarrow S_6$	380.3	3.259	0.0000		^{1}(X + M)LCT
$S_0 \rightarrow S_7$	370.5	3.346	0.4219		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_8$	370.4	3.346	0.0000		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_9$	357.0	3.472	f=0.0000		^{1}(X + M)LCT

$S_0 \rightarrow S_{10}$	356.1	3.481	0.0224		^{1}(X + M)LCT
$S_0 \rightarrow S_{14}$	338.0	3.667	0.0889		^{1}(X + M)LCT
$S_0 \rightarrow S_{16}$	325.4	3.810	0.3983		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{17}$	318.0	3.898	0.0793		^{1}(X + M)LCT
$S_0 \rightarrow S_{28}$	283.4	4.374	0.0562		^{1}(X + M)LCT
$S_0 \rightarrow S_{31}$	274.3	4.518	0.0349		^{1}(X + M)LCT
$S_0 \rightarrow S_{37}$	265.7	4.665	0.0510		^{1}CC/^{1}(X + M)LCT

$S_0 \rightarrow S_{45}$	254.8	4.865	0.0801		^{1}CC
$S_0 \rightarrow S_{51}$	249.3	4.971	0.0429		^{1}(X + M)LCT
$S_0 \rightarrow S_{59}$	242.2	5.117	0.1242		^{1}CC/^{1}(X + M)LCT
$S_0 \rightarrow S_{71}$	232.3	5.336	0.0411		^{1}(X + M)LCT
$S_0 \rightarrow S_{74}$	229.6	5.398	0.0418		^{1}CC
$S_0 \rightarrow S_{81}$	225.57	5.4965	0.0376		^{1}CC
$S_0 \rightarrow S_{95}$	215.9	5.742	0.0727		^{1}CC

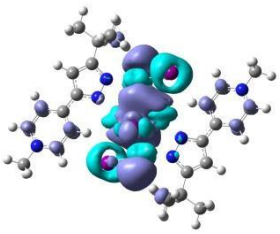
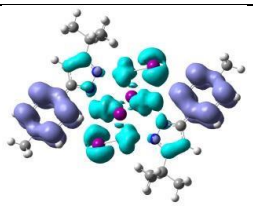
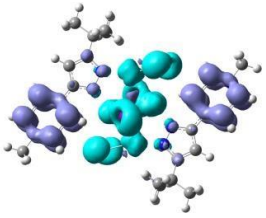
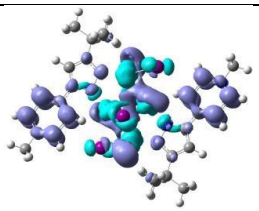
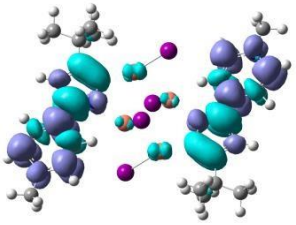
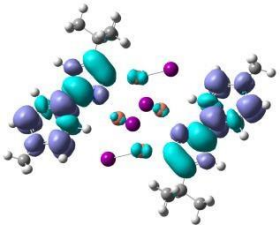
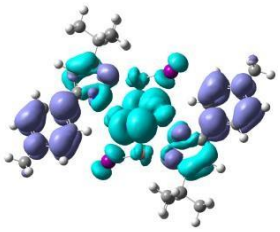
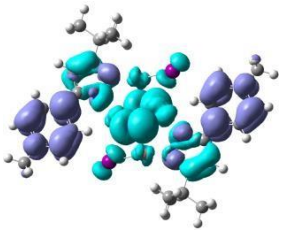
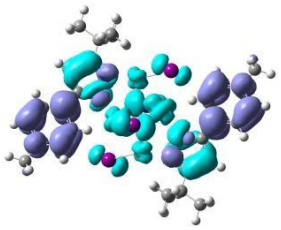
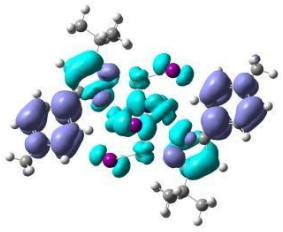
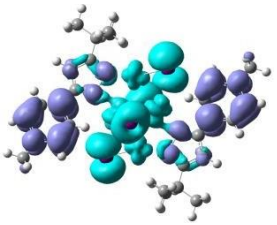
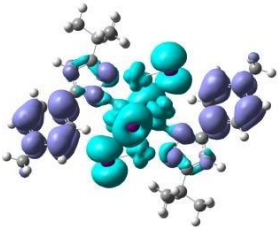
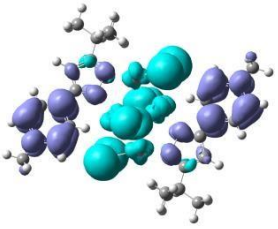
$S_0 \rightarrow S_{99}$	214.4	5.780	0.0567		^{1}CC
$S_0 \rightarrow S_{103}$	213.3	5.812	0.0884		^{1}(X + M)LCT
$S_0 \rightarrow S_{118}$	205.2	6.041	0.0382		^{1}(X + M)LCT
$S_0 \rightarrow S_{121}$	204.2	6.069	0.0309		^{1}CC/^{1}(X + M)LCT
[a]In the EDD maps (isovalue 0.005), Blue and purple represent zones of depletion and augmentation of electron density. Transitions with $f > 0.1$ are marked in orange (the same below). [b]CC (cluster centered) is a combination of a halide-to-metal charge transfer (XMCT) and copper-centered transitions.					

Table S6. Calculated TDDFT Singlet-Triplet Excitation Energies and Transition Assignments in Terms of Electronic Density Difference (EDD) Maps for the First 10 Transitions of Complex **1** at the S_0 Optimized Geometry in the Gas State

Excited states	λ (nm)	Energy (eV)	EDD	Assignment
$S_0 \rightarrow T_1$	524.9	2.361		^{3}ILCT
$S_0 \rightarrow T_2$	524.9	2.361		^{3}ILCT

$S_0 \rightarrow T_3$	434.0	2.856		^{3}(X + M)LCT/^{3}ILCT
$S_0 \rightarrow T_4$	432.9	2.863		^{3}(X + M)LCT/^{3}ILCT
$S_0 \rightarrow T_5$	428.5	2.893		^{3}(X + M)LCT/^{3}ILCT
$S_0 \rightarrow T_6$	428.2	2.895		^{3}(X + M)LCT/^{3}ILCT
$S_0 \rightarrow T_7$	400.8	3.093		^{3}(X + M)LCT
$S_0 \rightarrow T_8$	400.1	3.098		^{3}(X + M)LCT
$S_0 \rightarrow T_9$	375.4	3.301		^{3}(X + M)LCT

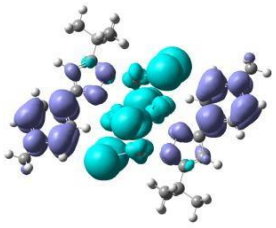
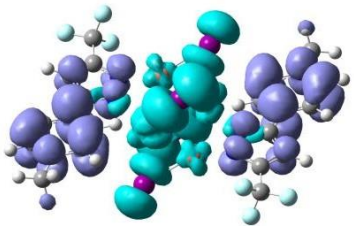
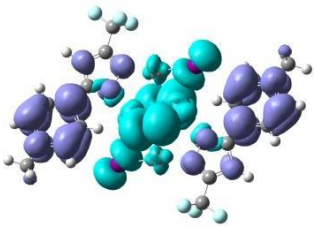
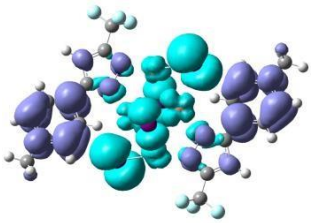
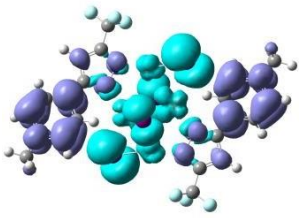
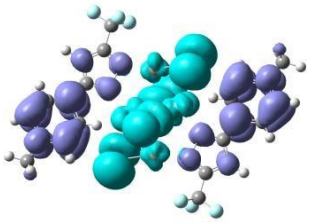
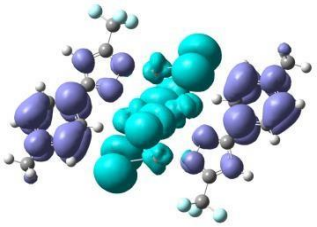
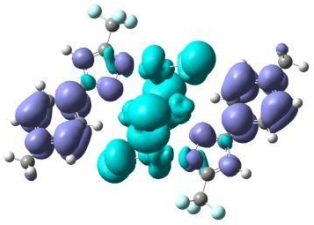
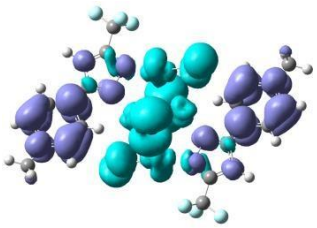
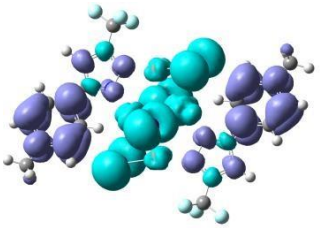
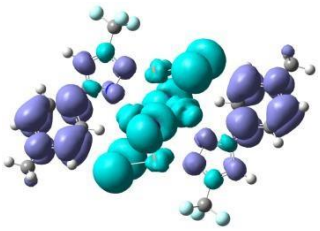
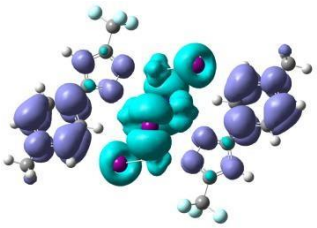
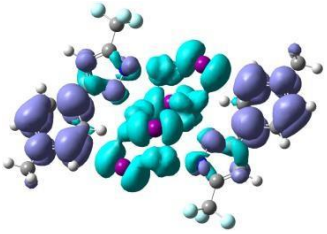
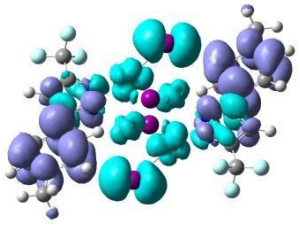
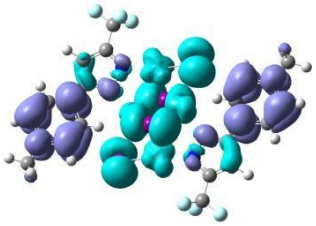
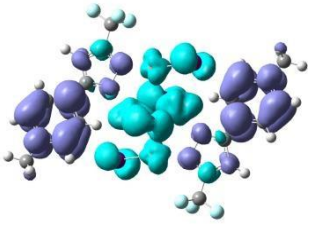
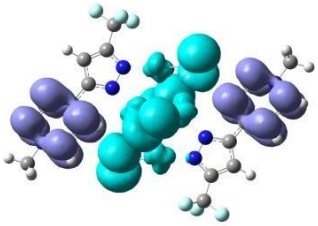
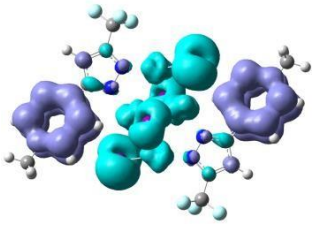
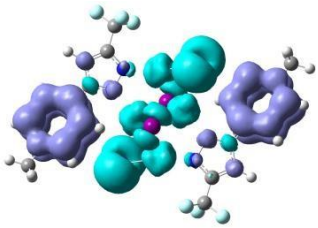
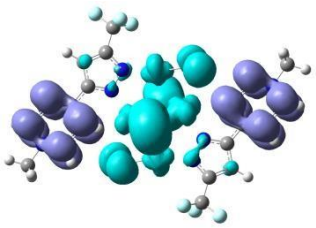
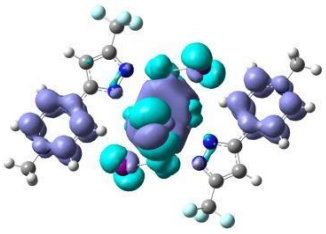
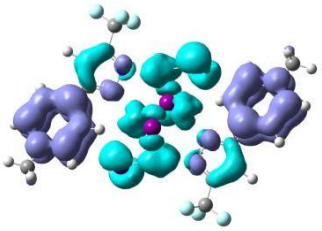
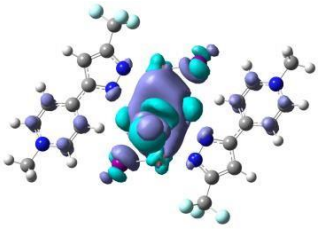
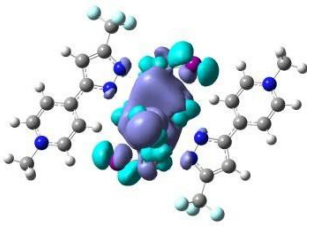
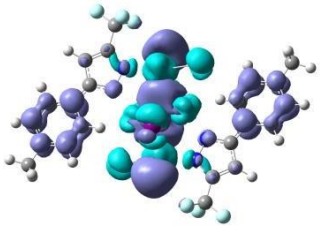
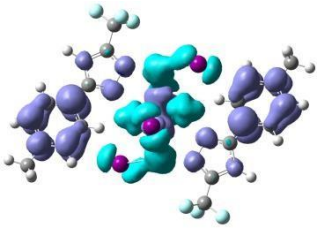
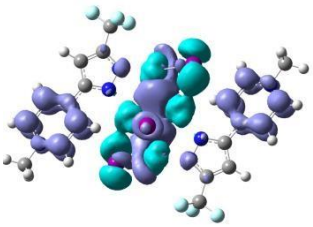
$S_0 \rightarrow T_{10}$	374.5	3.310		^{3}(X + M)LCT

Table S7. Calculated TDDFT Singlet-Singlet Excitation Energies, Oscillator Strengths (*f*), Transition Assignments in Terms of Electronic Density Difference (EDD) Maps for the First 10 and Most Intense ($f > 0.03$) Transitions of Complex **2** at the S_0 Optimized Geometry in the Gas State

Excited states	λ (nm)	Energy (eV)	*f*	EDD	Assignment
$S_0 \rightarrow S_1$	436.9	2.837	0.0020		^{1}(X + M)LCT
$S_0 \rightarrow S_2$	435.9	2.843	0.0000		^{1}(X + M)LCT
$S_0 \rightarrow S_3$	417.1	2.972	0.0000		^{1}(X + M)LCT
$S_0 \rightarrow S_4$	415.6	2.982	0.0232		^{1}(X + M)LCT
$S_0 \rightarrow S_5$	393.5	3.150	0.0079		^{1}(X + M)LCT

$S_0 \rightarrow S_6$	392.5	3.158	0.0000		^{1}(X + M)LCT
$S_0 \rightarrow S_7$	373.7	3.317	0.0000		^{1}(X + M)LCT
$S_0 \rightarrow S_8$	372.5	3.327	0.1132		^{1}(X + M)LCT
$S_0 \rightarrow S_9$	362.6	3.419	0.0000		^{1}(X + M)LCT
$S_0 \rightarrow S_{10}$	362.2	3.422	0.0595		^{1}(X + M)LCT
$S_0 \rightarrow S_{14}$	345.0	3.593	0.0435		^{1}(X + M)LCT
$S_0 \rightarrow S_{16}$	325.4	3.809	0.0995		^{1}(X + M)LCT

$S_0 \rightarrow S_{17}$	322.6	3.842	0.3446		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{20}$	310.0	3.999	0.0806		^{1}(X + M)LCT
$S_0 \rightarrow S_{21}$	308.8	4.014	0.0563		^{1}(X + M)LCT
$S_0 \rightarrow S_{23}$	296.7	4.177	0.0603		^{1}(X + M)LCT
$S_0 \rightarrow S_{32}$	277.2	4.472	0.0440		^{1}(X + M)LCT
$S_0 \rightarrow S_{33}$	276.3	4.486	0.0840		^{1}(X + M)LCT
$S_0 \rightarrow S_{45}$	258.1	4.802	0.03040		^{1}(X + M)LCT

$S_0 \rightarrow S_{53}$	251.7	4.924	0.0322		^{1}CC/^{1}(X + M)LCT
$S_0 \rightarrow S_{56}$	249.4	4.969	0.0683		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{63}$	241.5	5.133	0.1302		^{1}CC
$S_0 \rightarrow S_{75}$	231.1	5.364	0.0515		^{1}CC
$S_0 \rightarrow S_{81}$	227.0	5.460	0.0309		^{1}CC
$S_0 \rightarrow S_{93}$	220.1	5.631	0.0391		^{1}(X + M)LCT/^{1}CC
$S_0 \rightarrow S_{100}$	214.9	5.767	0.0449		^{1}CC/^{1}(X + M)LCT

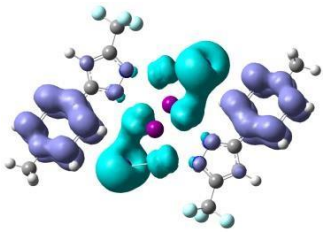
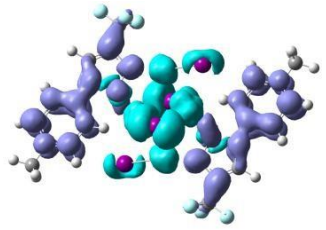
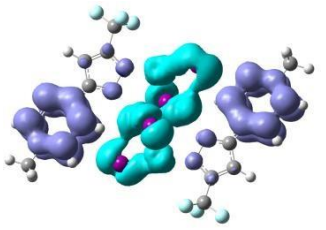
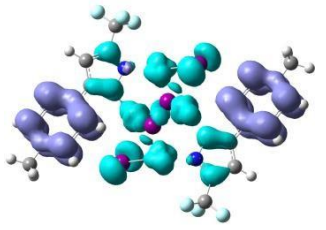
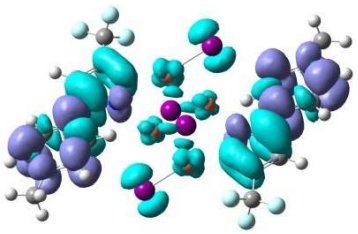
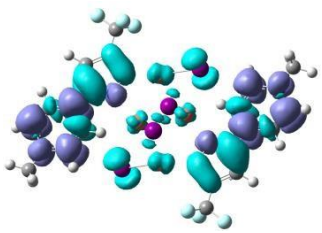
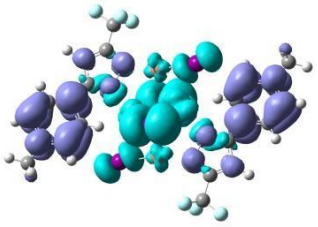
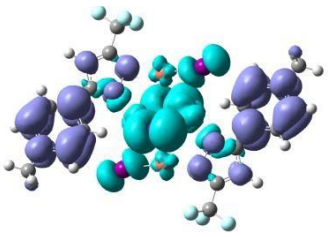
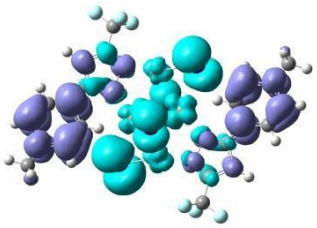
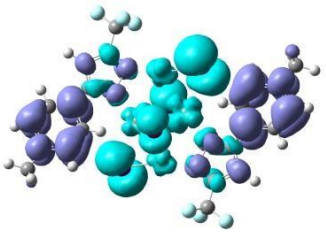
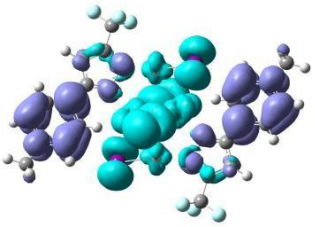
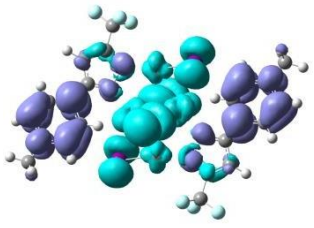
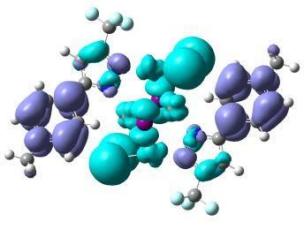
$S_0 \rightarrow S_{105}$	213.8	5.796	0.0527		^{1}(X + M)LCT
$S_0 \rightarrow S_{111}$	210.4	5.892	0.0335		^{1}(X + M)LCT
$S_0 \rightarrow S_{116}$	208.5	5.946	0.0328		^{1}(X + M)LCT
$S_0 \rightarrow S_{119}$	207.3	5.979	0.0923		^{1}(X + M)LCT/^{1}ILCT

Table S8. Calculated TDDFT Singlet-Triplet Excitation Energies and Transition Assignments in Terms of Electronic Density Difference (EDD) Maps for the First 10 Transitions of Complex **2** at the S_0 Optimized Geometry in the Gas State

Excited states	λ (nm)	Energy (eV)	EDD	Assignment
$S_0 \rightarrow T_1$	470.6	2.634		^{3}ILCT/^{3}(X + M)LCT
$S_0 \rightarrow T_2$	470.3	2.636		^{3}ILCT/^{3}(X + M)LCT

$S_0 \rightarrow T_3$	441.9	2.805		^{3}(X + M)LCT
$S_0 \rightarrow T_4$	440.6	2.813		^{3}(X + M)LCT
$S_0 \rightarrow T_5$	423.0	2.930		^{3}(X + M)LCT
$S_0 \rightarrow T_6$	422.8	2.931		^{3}(X + M)LCT
$S_0 \rightarrow T_7$	398.9	3.107		^{3}(X + M)LCT
$S_0 \rightarrow T_8$	398.1	3.113		^{3}(X + M)LCT
$S_0 \rightarrow T_9$	385.0	3.219		^{3}(X + M)LCT

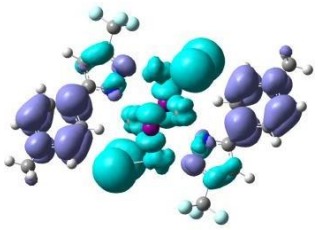
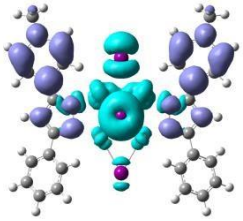
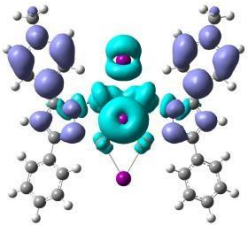
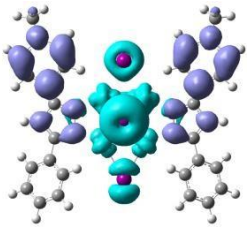
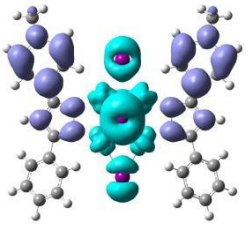
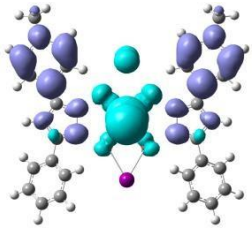
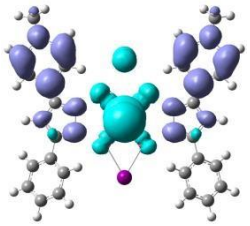
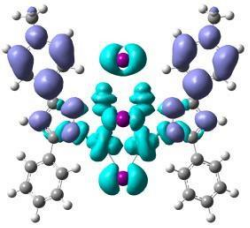
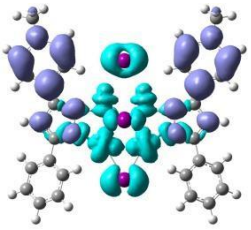
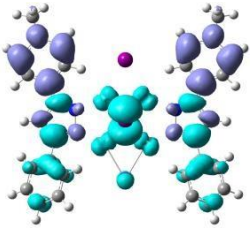
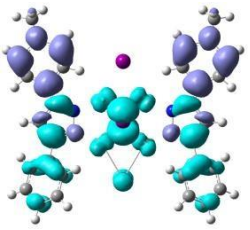
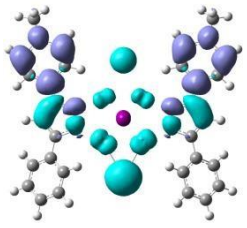
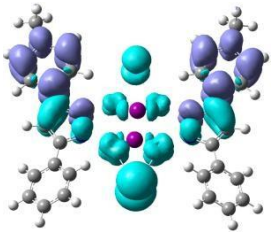
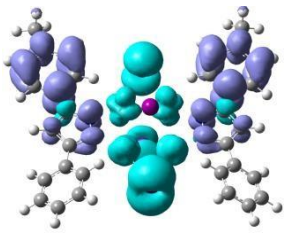
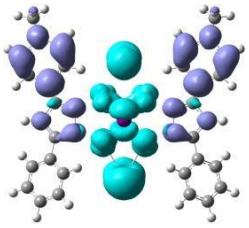
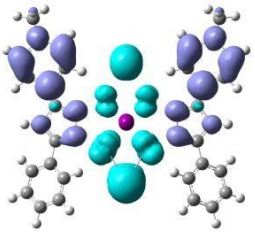
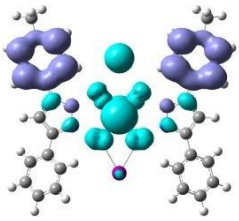
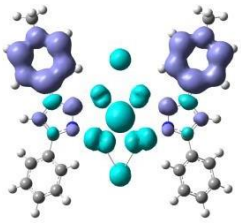
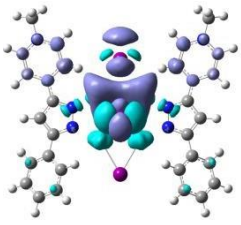
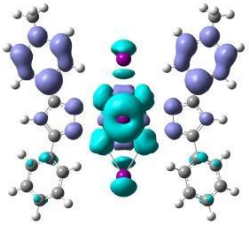
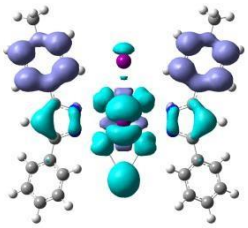
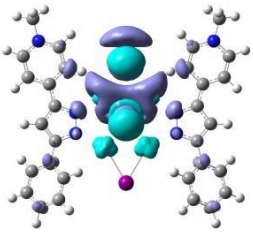
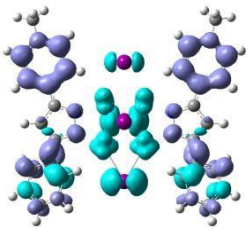
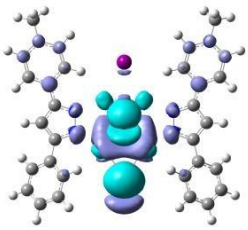
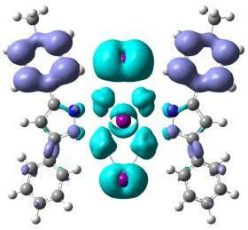
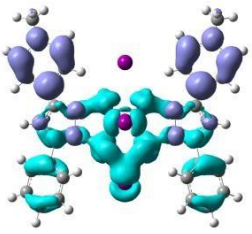
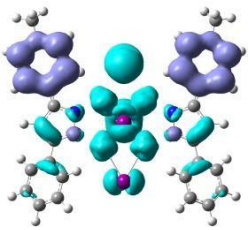
$S_0 \rightarrow T_{10}$	384.3	3.225		^{3}(X + M)LCT

Table S9. Calculated TDDFT Singlet-Singlet Excitation Energies, Oscillator Strengths (*f*), Transition Assignments in Terms of Electronic Density Difference (EDD) Maps for the First 10 and Most Intense ($f > 0.03$) Transitions of Complex **3** at the S_0 Optimized Geometry in the Gas State

Excited states	λ (nm)	Energy (eV)	*f*	EDD	Assignment
$S_0 \rightarrow S_1$	450.2	2.753	0.0000		^{1}(X + M)LCT
$S_0 \rightarrow S_2$	449.7	2.757	0.0008		^{1}(X + M)LCT
$S_0 \rightarrow S_3$	433.4	2.860	0.0029		^{1}(X + M)LCT
$S_0 \rightarrow S_4$	432.2	2.868	0.0039		^{1}(X + M)LCT
$S_0 \rightarrow S_5$	426.0	2.910	0.0192		^{1}(X + M)LCT

$S_0 \rightarrow S_6$	423.1	2.930	0.0099		^{1}(X + M)LCT
$S_0 \rightarrow S_7$	416.0	2.980	0.0003		^{1}(X + M)LCT
$S_0 \rightarrow S_8$	414.3	2.992	0.0002		^{1}(X + M)LCT
$S_0 \rightarrow S_9$	391.4	3.167	0.1587		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{10}$	385.4	3.216	0.3375		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{15}$	348.0	3.563	0.0353		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{16}$	344.0	3.605	0.4853		^{1}(X + M)LCT/^{1}ILCT

$S_0 \rightarrow S_{26}$	298.0	4.160	0.1426		^{1}(X + M)LCT
$S_0 \rightarrow S_{27}$	296.3	4.185	0.0830		^{1}(X + M)LCT
$S_0 \rightarrow S_{31}$	285.3	4.345	0.0576		^{1}(X + M)LCT
$S_0 \rightarrow S_{44}$	273.0	4.541	0.0510		^{1}(X + M)LCT
$S_0 \rightarrow S_{45}$	271.8	4.561	0.0621		^{1}(X + M)LCT
$S_0 \rightarrow S_{55}$	251.1	4.937	0.0494		^{1}CC
$S_0 \rightarrow S_{62}$	246.5	5.030	0.0423		^{1}(X + M)LCT/^{1}CC

$S_0 \rightarrow S_{65}$	244.4	5.073	0.2277		^{1}(X + M)LCT/^{1}CC/^{1}ILCT
$S_0 \rightarrow S_{74}$	235.6	5.263	0.0583		^{1}CC
$S_0 \rightarrow S_{79}$	233.0	5.321	0.0802		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{81}$	231.9	5.347	0.0638		^{1}CC
$S_0 \rightarrow S_{86}$	228.7	5.422	0.0927		^{1}(X + M)LCT
$S_0 \rightarrow S_{90}$	228.2	5.433	0.1045		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{93}$	225.4	5.501	0.0488		^{1}(X + M)LCT/^{1}ILCT

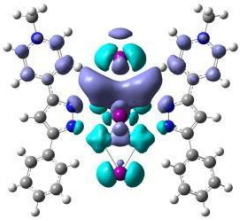
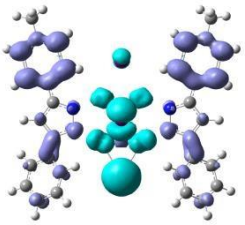
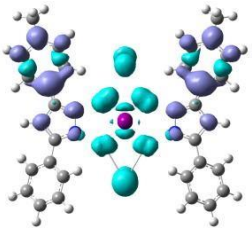
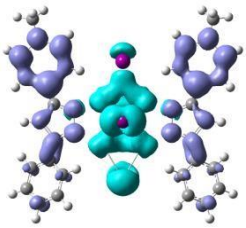
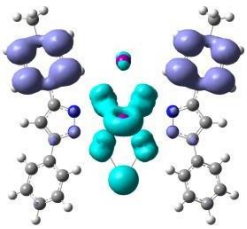
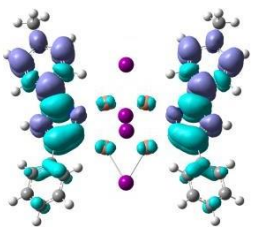
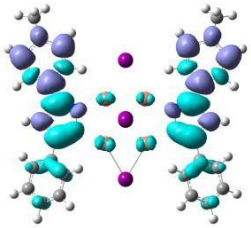
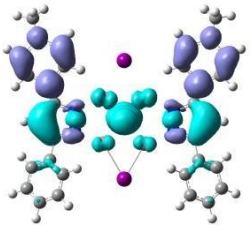
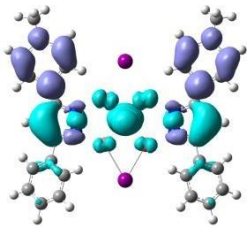
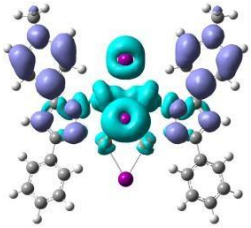
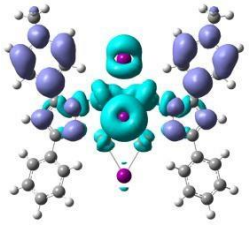
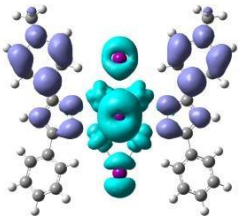
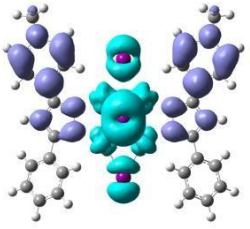
$S_0 \rightarrow S_{98}$	222.1	5.581	0.0848		^{1}CC
$S_0 \rightarrow S_{105}$	219.0	5.661	0.0357		^{1}(X + M)LCT
$S_0 \rightarrow S_{117}$	213.6	5.804	0.1404		^{1}(X + M)LCT
$S_0 \rightarrow S_{118}$	213.5	5.807	0.0309		^{1}(X + M)LCT
$S_0 \rightarrow S_{146}$	204.1	6.075	0.0416		^{1}(X + M)LCT

Table S10. Calculated TDDFT Singlet-Triplet Excitation Energies and Transition Assignments in Terms of Electronic Density Difference (EDD) Maps for the First 10 Transitions of Complex **3** at the S_0 Optimized Geometry in the Gas State

Excited states	λ (nm)	Energy (eV)	EDD	Assignment
$S_0 \rightarrow T_1$	566.1	2.190		^{3}ILCT

$S_0 \rightarrow T_2$	566.1	2.190		^{3}ILCT
$S_0 \rightarrow T_3$	474.5	2.613		^{3}(X + M)LCT/^{3}ILCT
$S_0 \rightarrow T_4$	474.0	2.616		^{3}(X + M)LCT/^{3}ILCT
$S_0 \rightarrow T_5$	458.5	2.704		^{3}(X + M)LCT
$S_0 \rightarrow T_6$	457.9	2.708		^{3}(X + M)LCT
$S_0 \rightarrow T_7$	435.5	2.847		^{3}(X + M)LCT
$S_0 \rightarrow T_8$	434.4	2.854		^{3}(X + M)LCT

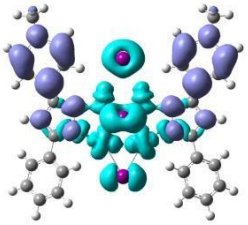
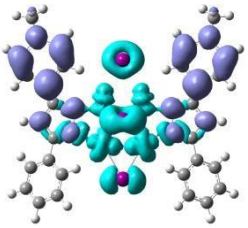
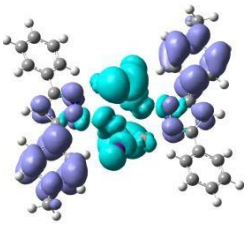
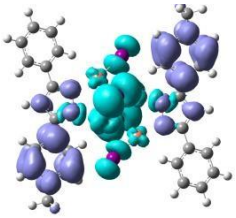
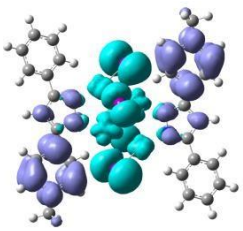
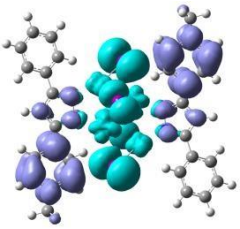
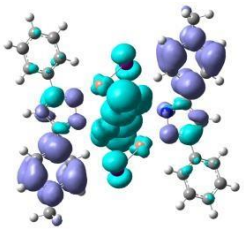
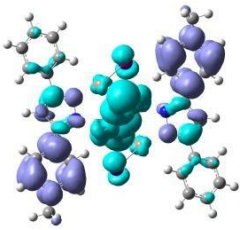
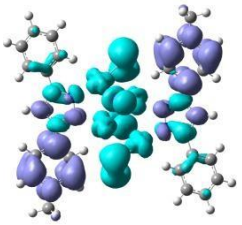
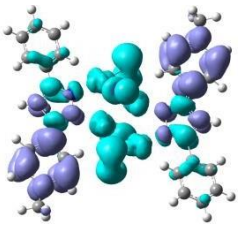
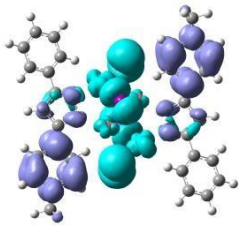
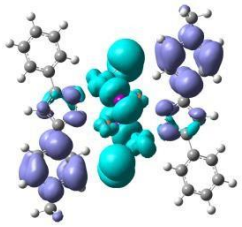
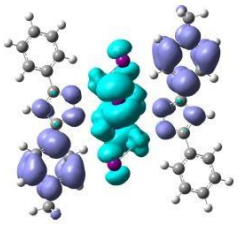
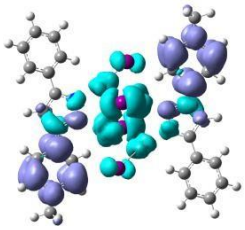
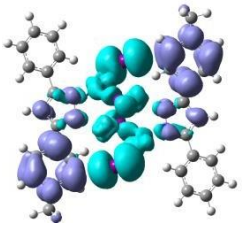
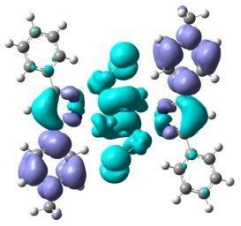
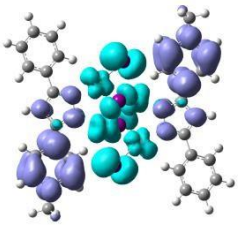
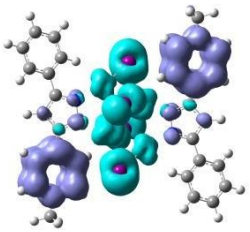
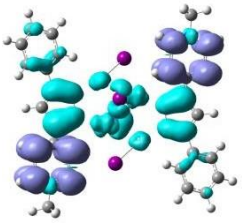
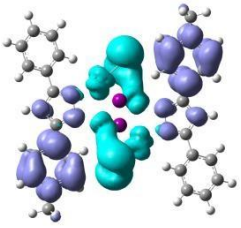
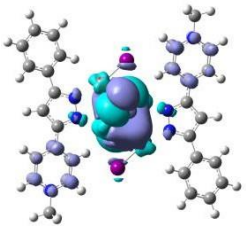
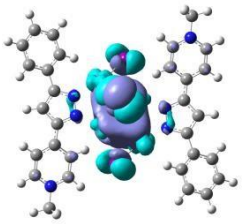
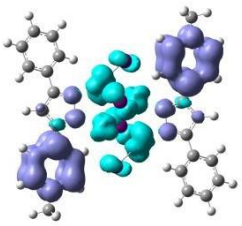
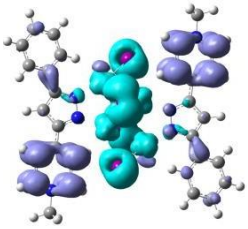
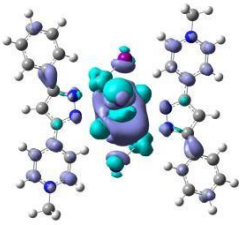
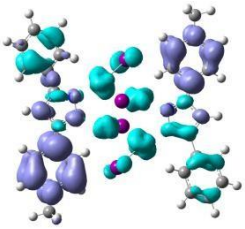
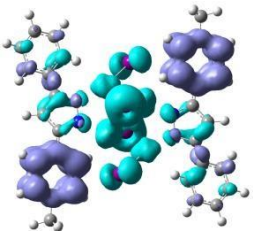
$S_0 \rightarrow T_9$	425.2	2.916		^{3}(X + M)LCT
$S_0 \rightarrow T_{10}$	423.5	2.927		^{3}(X + M)LCT

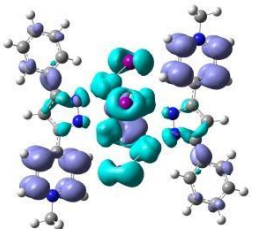
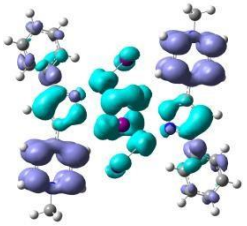
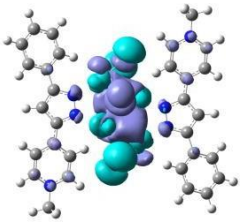
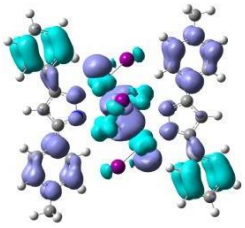
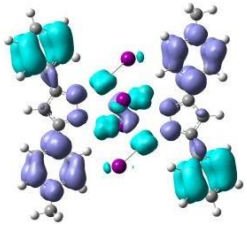
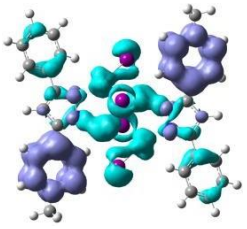
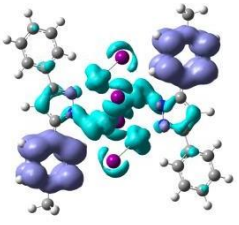
Table S11. Calculated TDDFT Singlet-Singlet Excitation Energies, Oscillator Strengths (*f*), Transition Assignments in Terms of Electronic Density Difference (EDD) Maps for the First 10 and Most Intense ($f > 0.03$) Transitions of Complex **4** at the S_0 Optimized Geometry in the Gas State

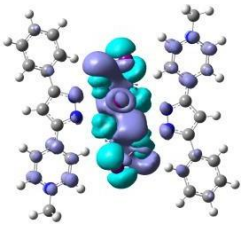
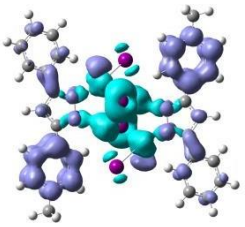
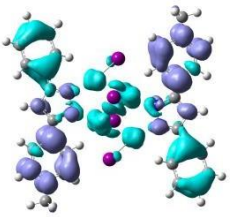
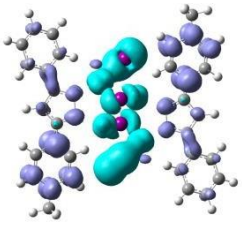
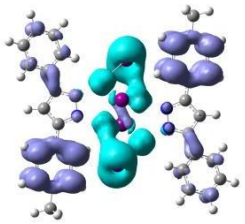
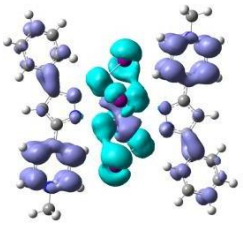
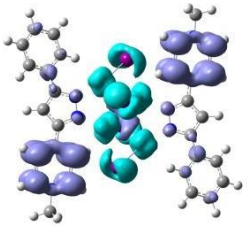
Excited states	λ (nm)	Energy (eV)	*f*	EDD	Assignment
$S_0 \rightarrow S_1$	424.2	2.923	0.0009		^{1}(X + M)LCT
$S_0 \rightarrow S_2$	423.7	2.926	0.0000		^{1}(X + M)LCT
$S_0 \rightarrow S_3$	403.7	3.071	0.0000		^{1}(X + M)LCT
$S_0 \rightarrow S_4$	402.4	3.081	0.0255		^{1}(X + M)LCT

$S_0 \rightarrow S_5$	383.4	3.234	0.1647		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_6$	381.9	3.246	0.0000		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_7$	379.5	3.267	0.0000		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_8$	378.4	3.276	0.3081		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_9$	361.5	3.430	0.0000		^{1}(X + M)LCT
$S_0 \rightarrow S_{10}$	360.5	3.440	0.0084		^{1}(X + M)LCT
$S_0 \rightarrow S_{14}$	339.9	3.648	0.0552		^{1}(X + M)LCT

$S_0 \rightarrow S_{16}$	324.5	3.821	0.2890		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{17}$	321.4	3.858	0.0916		^{1}(X + M)LCT
$S_0 \rightarrow S_{20}$	316.9	3.912	0.1112		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{21}$	305.8	4.055	0.0516		^{1}(X + M)LCT
$S_0 \rightarrow S_{28}$	285.7	4.341	0.0579		^{1}(X + M)LCT
$S_0 \rightarrow S_{32}$	276.3	4.488	0.0403		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{33}$	275.6	4.498	0.0371		^{1}(X + M)LCT

$S_0 \rightarrow S_{39}$	266.0	4.661	0.0438		^{1}CC
$S_0 \rightarrow S_{45}$	255.3	4.857	0.0812		^{1}CC
$S_0 \rightarrow S_{51}$	251.9	4.922	0.1280		^{1}(X + M)LCT
$S_0 \rightarrow S_{60}$	244.6	5.069	0.1193		^{1}(X + M)LCT
$S_0 \rightarrow S_{63}$	241.8	5.127	0.1273		^{1}CC
$S_0 \rightarrow S_{69}$	237.6	5.217	0.0317		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{72}$	235.6	5.263	0.1066		^{1}(X + M)LCT/^{1}ILCT

$S_0 \rightarrow S_{78}$	232.5	5.333	0.2441		^{1}(X + M)LCT
$S_0 \rightarrow S_{80}$	231.4	5.357	0.1094		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{87}$	226.8	5.466	0.0341		^{1}CC
$S_0 \rightarrow S_{88}$	226.2	5.480	0.1239		^{1}CC /^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{90}$	224.5	5.523	0.0574		^{1}ILCT /^{1}CC /^{1}(X + M)LCT
$S_0 \rightarrow S_{105}$	217.4	5.702	0.0384		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{107}$	216.8	5.719	0.0413		^{1}(X + M)LCT/^{1}ILCT

$S_0 \rightarrow S_{109}$	216.2	5.734	0.1040		^{1}CC
$S_0 \rightarrow S_{118}$	212.4	5.836	0.0688		^{1}(X + M)LCT/^{1}CC
$S_0 \rightarrow S_{119}$	212.1	5.845	0.1212		^{1}(X + M)LCT/^{1}ILCT
$S_0 \rightarrow S_{122}$	210.6	5.886	0.0455		^{1}(X + M)LCT
$S_0 \rightarrow S_{126}$	208.5	5.945	0.0405		^{1}(X + M)LCT
$S_0 \rightarrow S_{128}$	208.1	5.958	0.0643		^{1}(X + M)LCT/^{1}CC
$S_0 \rightarrow S_{133}$	206.4	6.007	0.0927		^{1}(X + M)LCT/^{1}CC

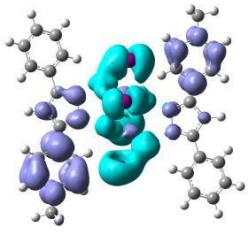
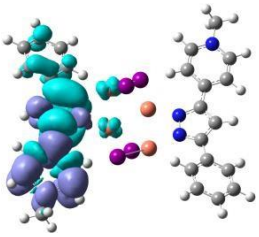
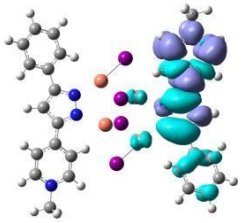
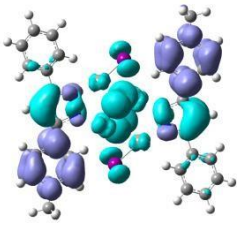
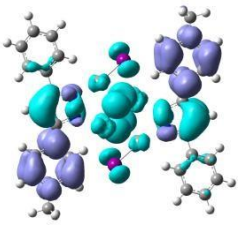
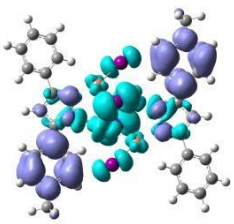
$S_0 \rightarrow S_{140}$	203.9	6.081	0.0562		^{1}(X + M)LCT/^{1}CC

Table S12. Calculated TDDFT Singlet-Triplet Excitation Energies and Transition Assignments in Terms of Electronic Density Difference (EDD) Maps for the First 10 Transitions of Complex **4** at the S_0 Optimized Geometry in the Gas State

Excited states	λ (nm)	Energy (eV)	EDD	Assignment
$S_0 \rightarrow T_1$	519.1	2.388		^{3}ILCT
$S_0 \rightarrow T_2$	519.1	2.388		^{3}ILCT
$S_0 \rightarrow T_3$	437.1	2.835		^{3}(X + M)LCT/^{3}ILCT
$S_0 \rightarrow T_4$	437.1	2.835		^{3}(X + M)LCT/^{3}ILCT
$S_0 \rightarrow T_5$	436.3	2.841		^{3}(X + M)LCT

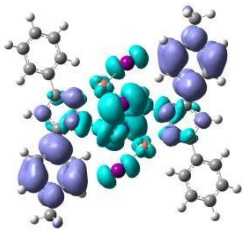
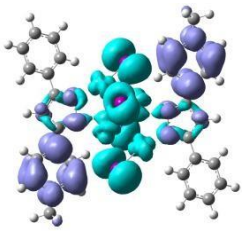
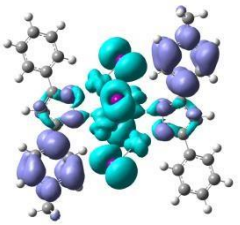
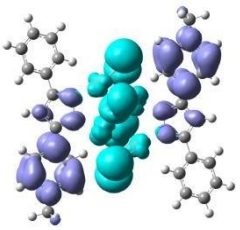
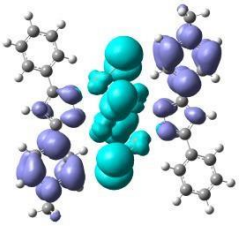
$S_0 \rightarrow T_6$	430.6	2.878		^{3}(X + M)LCT
$S_0 \rightarrow T_7$	430.1	2.882		^{3}(X + M)LCT
$S_0 \rightarrow T_8$	402.5	3.080		^{3}(X + M)LCT
$S_0 \rightarrow T_9$	401.8	3.085		^{3}(X + M)LCT
$S_0 \rightarrow T_{10}$	379.3	3.268		^{3}(X + M)LCT

Table S13. Calculated TDDFT Singlet-Singlet Excitation Wavelengths and Transition Assignments for the Most Intense (f > 0.1) Transitions of Complex **1**–**4** at the S_0 Optimized Geometry in the Gas State

	f	λ (nm)	Assignment
1	0.4219	370.5	^{1}(X + M)LCT/^{1}ILCT
	0.3983	325.4	^{1}(X + M)LCT/^{1}ILCT
	0.1242	242.2	^{1}CC/^{1}(X + M)LCT
2	0.1132	372.5	^{1}(X + M)LCT
	0.3446	322.6	^{1}(X + M)LCT/^{1}ILCT

	0.1302	241.5	^{1}CC
3	0.1587	391.4	^{1}(X + M)LCT/^{1}ILCT
	0.3375	385.4	^{1}(X + M)LCT/^{1}ILCT
	0.4853	344.0	^{1}(X + M)LCT/^{1}ILCT
	0.1426	298.0	^{1}(X + M)LCT/^{1}ILCT
	0.2277	244.4	^{1}(X + M)LCT/^{1}CC/^{1}ILCT
4	0.1647	383.4	^{1}(X + M)LCT/^{1}ILCT
	0.3081	378.4	^{1}(X + M)LCT/^{1}ILCT
	0.2890	324.5	^{1}(X + M)LCT/^{1}ILCT
	0.1112	316.9	^{1}(X + M)LCT/^{1}ILCT
	0.1280	251.9	^{1}(X + M)LCT
	0.1193	244.6	^{1}(X + M)LCT
	0.1273	241.8	^{1}CC

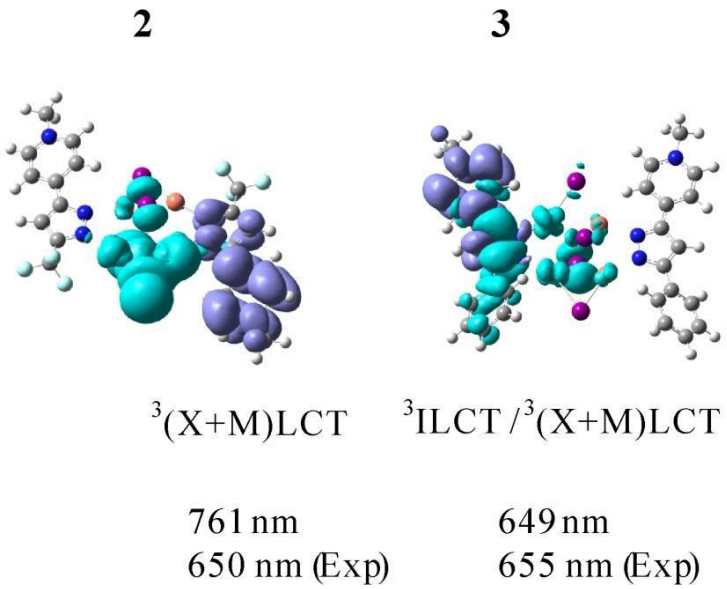


Fig. S29 The density difference plots (isovalue 0.0005) for the lowest triplet excitation of complex **2** and **3** in vacuo, calculated at the TDDFT optimized T_1 geometry. Blue and purple represent zones of depletion and augmentation of electron density in the T_1 excited state versus the S_0 ground state. The calculated emission wavelengths together with the experimental ones at 300 K are also listed for the sake of comparison.

Table S14. Coordinates of geometry optimized structures

(1) XYZ coordinates of S_0 optimized geometry for complex **1**

Cu	-1.37745500	-0.27037100	-0.39713800
Cu	-0.13535800	2.37744300	-0.17963700
Cu	0.13535600	-2.37743500	0.17962900
Cu	1.37745100	0.27037100	0.39714600
I	2.03095900	2.90943300	1.14893600
I	0.43389700	0.64056800	-2.26780100
I	-0.43388800	-0.64057500	2.26781000
I	-2.03097300	-2.90942500	-1.14892600
N	-2.70655100	1.30665100	-0.05895800
N	-2.12981800	2.49012200	-0.16127500
N	-6.62417000	-1.80411600	0.50525500
C	-5.30085100	-1.90963400	0.79449400
C	-7.12589700	-0.61386300	0.09115200
C	-7.47342000	-2.98825900	0.57471900
C	-4.04985700	1.50046800	0.00291400
C	-3.07061500	3.47497300	-0.16751200
C	-4.45612800	-0.84448700	0.66663800
C	-1.88654000	5.29466600	1.03857300
C	-2.67319400	4.92974900	-0.23042900
C	-6.32376600	0.48377900	-0.06237200
C	-4.93423800	0.40015500	0.19361900
C	-4.31867900	2.88306300	-0.08382500
C	-1.79053000	5.16905200	-1.46474500
C	-3.92325000	5.80695100	-0.32502100
N	2.12981500	-2.49011600	0.16125700
N	2.70655500	-1.30664600	0.05896200
C	3.07060700	-3.47497300	0.16747200
C	4.04986100	-1.50046900	-0.00291500
C	4.31867300	-2.88307000	0.08377000
C	2.67317700	-4.92974800	0.23036100
C	4.93424900	-0.40015600	-0.19359500
C	1.88650700	-5.29462900	-1.03864100
C	1.79052600	-5.16907700	1.46468100
C	3.92322900	-5.80695900	0.32491700
C	6.32377800	-0.48379400	0.06239100
C	4.45614900	0.84449600	-0.66659700
C	7.12591700	0.61384400	-0.09111600
C	5.30087900	1.90964000	-0.79443600
N	6.62419700	1.80410800	-0.50520000

C	7.47345600	2.98824600	-0.57464600
H	-4.95131700	-2.88271700	1.11953900
H	-8.18837100	-0.59281300	-0.12151300
H	-7.33175900	-3.60744300	-0.31529800
H	-8.51778400	-2.68287100	0.64196600
H	-7.21771400	-3.56831900	1.46281500
H	-3.41233200	-0.96599200	0.93607300
H	-2.49773100	5.14501400	1.93466100
H	-1.57814300	6.34583400	1.00334500
H	-0.98703500	4.67799100	1.13640700
H	-6.76513800	1.40891400	-0.41421900
H	-5.27885900	3.37610900	-0.03902700
H	-1.49100500	6.22197800	-1.51507700
H	-2.32308300	4.91483700	-2.38694800
H	-0.88063700	4.56019200	-1.42470000
H	-4.56595300	5.68174900	0.55325000
H	-4.51042700	5.57065800	-1.21919600
H	-3.63651400	6.86214600	-0.37966200
H	5.27884800	-3.37612100	0.03894300
H	2.49768800	-5.14495700	-1.93473300
H	1.57810400	-6.34579500	-1.00343500
H	0.98700400	-4.67794600	-1.13644800
H	1.49099900	-6.22200400	1.51499200
H	2.32308900	-4.91488500	2.38688400
H	0.88063300	-4.56021500	1.42466000
H	4.56592300	-5.68174000	-0.55335900
H	4.51041800	-5.57069000	1.21909100
H	3.63648800	-6.86215300	0.37953700
H	6.76514500	-1.40893900	0.41422100
H	3.41235400	0.96601100	-0.93603300
H	8.18839000	0.59278300	0.12154600
H	4.95135100	2.88273000	-1.11946700
H	7.33180100	3.60741700	0.31538200
H	8.51781800	2.68285300	-0.64190000
H	7.21775200	3.56832300	-1.46273200

(2) XYZ coordinates of UDFT optimized T_1 geometry for complex **1**

Cu	-1.44834900	-0.42802900	-0.27263700
Cu	-0.36688700	2.18065400	-0.10519700
Cu	0.36738900	-2.18467200	0.10399200
Cu	1.44868500	0.42654100	0.27200900
I	0.45643500	0.74362800	-2.21764200
I	-0.45430700	-0.74915500	2.21683700

I	-1.52825200	-2.91844600	-1.32645100
I	1.52331900	2.91596100	1.33303600
N	-2.86878600	1.02582400	-0.16496800
N	-2.30120000	2.25450300	-0.31995800
N	-6.91450400	-1.98414600	0.41339200
C	-5.57654300	-2.27795000	0.21155300
C	-7.35805100	-0.72356800	0.47936400
C	-7.90664700	-3.10693000	0.62953700
C	-4.18900100	1.20624600	-0.07045900
C	-3.26400300	3.20340800	-0.33078300
C	-4.68363000	-1.23598800	0.14811500
C	-2.36536900	5.10326000	0.92823700
C	-2.94805100	4.67782600	-0.37974300
C	-6.50363700	0.32980000	0.38099900
C	-5.13185800	0.08316100	0.15800500
C	-4.48203100	2.58327200	-0.17905700
C	-1.92202100	4.93062400	-1.47991700
C	-4.20419900	5.43947800	-0.70479400
N	2.29946400	-2.25221900	0.31805800
N	2.86654900	-1.02324500	0.16338000
C	3.26355800	-3.19897700	0.32911800
C	4.18716700	-1.19931600	0.06812500
C	4.48048700	-2.57625400	0.17672000
C	2.95035200	-4.67388600	0.37853800
C	5.13102200	-0.07544000	-0.16068300
C	2.36825400	-5.10098500	-0.92919600
C	1.92498800	-4.92818300	1.47898200
C	4.20807500	-5.43293500	0.70354400
C	6.50362000	-0.32399100	-0.38386800
C	4.68432900	1.24444700	-0.15085200
C	7.35930100	0.72759500	-0.48240700
C	5.57788300	2.28576200	-0.21442200
N	6.91723300	1.99001300	-0.41663600
C	7.91052600	3.11113700	-0.63322000
H	-5.28177700	-3.24883000	0.10868700
H	-8.35743800	-0.55973000	0.60556900
H	-8.36324500	-3.33513200	-0.26883500
H	-8.61262800	-2.80121800	1.31642900
H	-7.40331300	-3.93423700	0.98469200
H	-3.68549000	-1.43611800	0.09212700
H	-3.11692600	5.39237400	1.57824800
H	-1.72505300	5.90234000	0.78983400
H	-1.83643300	4.32688100	1.35818000
H	-6.85125700	1.28461700	0.46838000

H	-5.40332200	3.02083400	-0.15257900
H	-1.17411100	5.54942700	-1.13027000
H	-2.37355700	5.37456600	-2.29536100
H	-1.49473200	4.03940200	-1.78406900
H	-4.94028600	5.19724300	-0.01908000
H	-4.53422500	5.17618900	-1.64897600
H	-4.01612200	6.45026100	-0.66900100
H	5.40231600	-3.01251900	0.14996000
H	3.12018300	-5.38890100	-1.57925300
H	1.72952800	-5.90125900	-0.79031100
H	1.83778400	-4.32580300	-1.35942400
H	1.17820600	-5.54856200	1.12966400
H	2.37739600	-5.37092000	2.29454600
H	1.49610500	-4.03761600	1.78298500
H	4.94355700	-5.18953700	0.01761600
H	4.53781100	-5.16870000	1.64754200
H	4.02190300	-6.44407100	0.66810400
H	6.85020100	-1.27919800	-0.47122000
H	3.68660600	1.44617300	-0.09480900
H	8.35836400	0.56201700	-0.60866100
H	5.28384100	3.25678100	-0.11160600
H	8.36777000	3.33927100	0.26490500
H	8.61608200	2.80445800	-1.32018800
H	7.40823800	3.93904800	-0.98856000

(3) XYZ coordinates of S_0 optimized geometry for complex **2**

Cu	-1.34762600	-0.23351400	-0.37981300
Cu	-0.01567700	2.46511200	-0.15658800
Cu	0.01584400	-2.46468600	0.15548200
Cu	1.34739200	0.23365400	0.38051000
I	0.43194900	0.68002900	-2.26932300
I	-2.18371200	-2.78661800	-1.17623400
I	-0.43174100	-0.68100700	2.26976600
I	2.18293300	2.78701300	1.17672500
N	-2.61803800	1.39976400	-0.00689700
N	-2.00926900	2.56373400	-0.11897100
N	-6.54048500	-1.67562900	0.52859200
N	2.00937100	-2.56336100	0.11809800
N	2.61833100	-1.39939500	0.00708500
C	-7.38222800	-2.86811300	0.59099400
C	-7.02937400	-0.50911500	0.04231100
C	-5.23907100	-1.75977000	0.89844800
C	-3.95725000	1.62252800	0.04137800

C	-2.93686100	3.54546000	-0.14925700
C	-6.22689200	0.59158100	-0.10579400
C	-4.85851200	0.52566900	0.23284700
C	-4.39442800	-0.69009200	0.77791600
C	-4.20473800	3.00346200	-0.06550000
C	-2.52362600	4.97350900	-0.20360500
C	2.93679600	-3.54528300	0.14757600
C	3.95750600	-1.62236100	-0.04134900
C	4.20475700	-3.00343600	0.06432400
C	2.52330500	-4.97329600	0.20072500
C	4.85898700	-0.52555100	-0.23201000
F	1.49737200	-5.15771600	1.04654700
F	3.54407500	-5.74526900	0.60881200
F	2.13015300	-5.43254400	-0.99748400
F	-1.49735900	5.15731800	-1.04915700
F	-3.54435200	5.74491300	-0.61287200
F	-2.13107600	5.43401200	0.99432300
C	6.22738000	-0.59201800	0.10647100
C	4.39513000	0.69071900	-0.77614000
C	7.03010600	0.50859600	-0.04093300
C	5.23999900	1.76028900	-0.89597100
N	6.54144100	1.67557200	-0.52631800
C	7.38346600	2.86788900	-0.58813600
H	5.14674600	-3.53088700	0.04043600
H	-7.18922300	-3.40097300	1.52317900
H	-7.16224900	-3.52389000	-0.25538100
H	-8.43120000	-2.57376900	0.56171800
H	-8.07707600	-0.50821300	-0.23397600
H	-4.90236900	-2.71774300	1.27690400
H	-6.65221900	1.49799800	-0.52087800
H	-3.36475600	-0.78978400	1.10756100
H	-5.14681100	3.53078100	-0.04203900
H	6.65253700	-1.49883200	0.52086400
H	3.36544500	0.79087500	-1.10557500
H	8.07783600	0.50724500	0.23524600
H	4.90347300	2.71862000	-1.27368200
H	7.19115400	3.40085500	-1.52040800
H	7.16311400	3.52365100	0.25815200
H	8.43235500	2.57332300	-0.55821900

(4) XYZ coordinates of UDFT optimized T_1 geometry for complex **2**

Cu	1.71040800	0.41968700	-0.20987700
Cu	0.25217800	-2.36987900	-0.05854300

Cu	-0.25220100	2.36998300	0.05878600
Cu	-1.71043400	-0.41962400	0.20991100
I	-0.18213500	-0.38940700	-2.09283900
I	2.12137800	3.04025300	-0.63036100
I	0.18213100	0.38930000	2.09288800
I	-2.12143900	-3.04016600	0.63046500
N	2.89237900	-1.22935800	0.02010400
N	2.21809300	-2.37530200	-0.04948900
N	7.18342300	1.51856600	0.34577000
N	-2.21811300	2.37536500	0.04964000
N	-2.89236100	1.22940600	-0.02010200
C	8.15912500	2.59221200	0.34267700
C	7.50178800	0.28700200	-0.16506300
C	5.89718500	1.75499500	0.75799100
C	4.21980500	-1.51090800	0.01724100
C	3.09505700	-3.39064800	-0.11079300
C	6.56710500	-0.70262500	-0.26931100
C	5.22569600	-0.48597300	0.13351100
C	4.93544100	0.79128300	0.67286800
C	4.38970200	-2.90322700	-0.07849400
C	2.61847300	-4.79895400	-0.13352300
C	-3.09511600	3.39068200	0.11086400
C	-4.21979300	1.51091100	-0.01736500
C	-4.38974500	2.90322000	0.07840800
C	-2.61857800	4.79900200	0.13368800
C	-5.22561600	0.48592900	-0.13378300
F	-1.51260600	4.93041000	0.89045400
F	-3.55991100	5.61478600	0.62924100
F	-2.30290100	5.25010100	-1.09164000
F	1.51239500	-4.93034300	-0.89013900
F	3.55971800	-5.61477900	-0.62917700
F	2.30294400	-5.25000900	1.09185900
C	-6.56708200	0.70248700	0.26890000
C	-4.93521400	-0.79130100	-0.67312600
C	-7.50169200	-0.28719500	0.16452100
C	-5.89689000	-1.75507100	-0.75838100
N	-7.18319100	-1.51873000	-0.34630400
C	-8.15882700	-2.59243500	-0.34333600
H	-5.30713800	3.47216300	0.08537700
H	7.96884100	3.26146900	1.18396700
H	8.10998800	3.16864400	-0.58813300
H	9.16245800	2.17614900	0.45178600
H	8.52999200	0.15625300	-0.48058100
H	5.69575000	2.74190500	1.15712800

H	6.86847600	-1.65496800	-0.69119100
H	3.94117300	1.02076100	1.03811900
H	5.30707400	-3.47220100	-0.08553900
H	-6.86855700	1.65480100	0.69077200
H	-3.94088400	-1.02071100	-1.03825400
H	-8.52994000	-0.15651900	0.47992700
H	-5.69534800	-2.74196300	-1.15751100
H	-7.96837600	-3.26169600	-1.18458500
H	-8.10979200	-3.16884900	0.58749200
H	-9.16217000	-2.17643800	-0.45260100

(5) XYZ coordinates of S_0 optimized geometry for complex **3**

Cu	1.33051100	-1.69447600	-0.04864900
Cu	-1.33018300	-1.69484100	-0.04857700
Cu	1.26721500	1.17350400	0.03955600
Cu	-1.26736300	1.17334900	0.03952100
I	-0.00038200	3.65611000	0.09753800
I	0.00045600	-3.98204200	-0.10981400
I	0.00003800	-0.18707500	2.15782100
I	0.00009000	-0.08881400	-2.14169000
C	5.87433200	6.39780700	-0.00298000
N	3.18092500	-0.85277400	0.02800600
N	3.18883600	0.46441500	0.01924700
N	5.52465000	4.98316100	-0.05064000
H	6.87068000	6.53988600	-0.42236900
H	5.86075100	6.76089500	1.02867700
H	5.15933100	6.96919800	-0.59691400
C	6.48948000	4.02987800	-0.09006900
C	6.18160600	2.69834700	-0.08178900
H	7.51158900	4.38833400	-0.13093100
C	4.83187500	2.26460600	-0.02635000
H	6.99180800	1.98056700	-0.12383000
C	3.85550800	3.28975800	0.01770500
C	4.48598400	0.88586900	-0.01826400
C	4.21928600	4.60393000	0.00520000
H	2.79629000	3.05416700	0.05800800
H	3.48266000	5.39919800	0.03725600
C	5.32769700	-0.24442600	-0.03421100
C	4.46468400	-1.32509800	-0.00068400
H	6.40747900	-0.27732200	-0.03000200
C	4.77851500	-2.75513900	0.01843300
C	3.93581900	-3.67013000	0.66003400
C	5.94594600	-3.22590700	-0.59661400

C	4.25075700	-5.02428300	0.67653200
H	3.02982500	-3.32039600	1.14633400
C	5.41532200	-5.48279300	0.06664900
H	3.57804500	-5.72018200	1.16889600
C	6.26360300	-4.57827700	-0.56918300
H	5.65879800	-6.54136600	0.08082400
H	7.16881900	-4.92958100	-1.05671400
H	6.59327400	-2.52735600	-1.12035200
H	-3.02910500	-3.32080800	1.14686500
N	-3.18066600	-0.85332300	0.02807800
N	-3.18887200	0.46386900	0.01918400
H	-2.79711500	3.05391600	0.05741100
C	-3.93499000	-3.67078700	0.66053500
C	-4.46431400	-1.32594800	-0.00051500
C	-4.48613200	0.88502000	-0.01832000
C	-3.85641200	3.28914700	0.01719200
C	-4.77783000	-2.75605500	0.01875700
C	-4.24963800	-5.02500700	0.67718900
C	-5.32757400	-0.24547700	-0.03404200
C	-4.83244000	2.26366500	-0.02658800
C	-4.22062100	4.60319700	0.00454100
C	-5.94511800	-3.22716100	-0.59630800
H	-3.57680700	-5.72068900	1.16969900
C	-5.41405900	-5.48385200	0.06728600
H	-6.40734800	-0.27861300	-0.02973500
C	-6.18231900	2.69695800	-0.08193200
H	-3.48424800	5.39870800	0.03639700
N	-5.52611500	4.98199200	-0.05119800
C	-6.26248500	-4.57959500	-0.56872500
H	-6.59256500	-2.52883100	-1.12019300
H	-5.65731100	-6.54247400	0.08158300
C	-6.49063500	4.02838700	-0.09037400
H	-6.99229100	1.97890800	-0.12376400
C	-5.87625600	6.39653000	-0.00369900
H	-7.16759200	-4.93115100	-1.05627600
H	-7.51286700	4.38650000	-0.13116600
H	-6.87270200	6.53822300	-0.42298400
H	-5.86266600	6.75977100	1.02790500
H	-5.16151500	6.96806900	-0.59780200

(6) XYZ coordinates of UDFT optimized T_1 geometry for complex **3**

Cu	1.45057500	-1.74862100	-0.02438000
Cu	-1.45050700	-1.74863100	-0.02439200

Cu	1.31763700	1.29226100	0.08910900
Cu	-1.31770200	1.29228100	0.08906600
I	-0.00003700	3.60243200	0.29028300
I	0.00005100	-3.89821200	-0.19206500
I	-0.00000300	-0.43388200	2.08649900
I	0.00001300	-0.21751200	-2.01136100
C	6.09917600	6.42611100	-0.13225800
N	3.17766800	-0.78619700	0.05347800
N	3.18887400	0.54827800	0.03169700
N	5.67488400	5.04156400	-0.18735300
H	6.97855500	6.56586600	-0.76429500
H	6.34600600	6.72816500	0.89246700
H	5.30005000	7.06859700	-0.50742300
C	6.59299900	4.03554400	-0.34699600
C	6.22369900	2.72283200	-0.31367300
H	7.61694600	4.35050900	-0.50994000
C	4.87255100	2.34019800	-0.10200700
H	6.99174100	1.97346700	-0.46605100
C	3.95424500	3.40695800	0.07113400
C	4.48046200	0.95714700	-0.06722300
C	4.36197700	4.70656300	0.02988600
H	2.90136700	3.21010700	0.23872300
H	3.67253500	5.53254200	0.16012900
C	5.31025600	-0.17832400	-0.11287400
C	4.44280800	-1.25868400	-0.02540500
H	6.38902300	-0.21783900	-0.14855200
C	4.73041300	-2.69447900	0.00520300
C	3.96444500	-3.55915500	0.79790800
C	5.77998700	-3.22708500	-0.75330900
C	4.22830200	-4.92490200	0.81315500
H	3.17512400	-3.15230500	1.42599900
C	5.27203100	-5.44482000	0.05245300
H	3.62146900	-5.58113800	1.43035000
C	6.04989200	-4.59032500	-0.72685500
H	5.48017800	-6.51075700	0.06749500
H	6.86346900	-4.99002100	-1.32579000
H	6.36888000	-2.56545800	-1.38269400
H	-3.17497600	-3.15230000	1.42614200
N	-3.17763100	-0.78626100	0.05346800
N	-3.18888900	0.54821200	0.03162400
H	-2.90143500	3.21008000	0.23825800
C	-3.96429400	-3.55921000	0.79808500
C	-4.44275700	-1.25880000	-0.02533900
C	-4.48049600	0.95703000	-0.06726500

C	-3.95434400	3.40687600	0.07079800
C	-4.73031000	-2.69460300	0.00535100
C	-4.22810200	-4.92496700	0.81340900
C	-5.31024800	-0.17847500	-0.11283100
C	-4.87263600	2.34006500	-0.10211600
C	-4.36212900	4.70646100	0.02949300
C	-5.77988400	-3.22728600	-0.75310600
H	-3.62123200	-5.58114800	1.43062600
C	-5.27183000	-5.44496100	0.05275900
H	-6.38901400	-0.21803400	-0.14848300
C	-6.22382700	2.72263300	-0.31362900
H	-3.67269800	5.53247700	0.15956700
N	-5.67507900	5.04139700	-0.18759300
C	-6.04974100	-4.59053400	-0.72657500
H	-6.36881600	-2.56571300	-1.38251100
H	-5.47994000	-6.51090400	0.06786200
C	-6.59318000	4.03532900	-0.34701800
H	-6.99186700	1.97322900	-0.46582500
C	-6.09941600	6.42593200	-0.13255300
H	-6.86331900	-4.99029000	-1.32546900
H	-7.61716100	4.35024100	-0.50984500
H	-6.97887400	6.56560700	-0.76449800
H	-6.34613600	6.72805600	0.89217700
H	-5.30035800	7.06841800	-0.50786200

(7) XYZ coordinates of S_0 optimized geometry for complex **4**

Cu	-1.03788400	-0.91677400	0.38843000
Cu	1.03792500	0.91665900	-0.38841400
Cu	1.33515800	-1.99879100	-0.15435100
Cu	-1.33499500	1.99883900	0.15459900
I	-0.29344700	-3.50607500	1.20978500
I	0.29353500	3.50590200	-1.20992200
I	0.00337800	-0.81564600	-2.26718800
I	-0.00335500	0.81548400	2.26729900
N	3.10512600	-1.06483600	-0.07596200
N	-2.97965000	-0.24573900	-0.00821300
C	-4.74899500	-6.41049600	-0.62274100
N	-4.65816000	-4.95532900	-0.55851600
H	-5.79710300	-6.70754800	-0.66133800
H	-4.27606400	-6.85595200	0.25660200
H	-4.24721200	-6.76740600	-1.52351200
C	-5.71099500	-4.21299100	-0.13500500

C	-5.61223300	-2.85584700	0.01252900
H	-6.61946800	-4.75898400	0.09058400
C	-4.39384700	-2.19193800	-0.26008600
H	-6.47247600	-2.30449900	0.37386200
C	-3.33263800	-2.99191600	-0.74138200
C	-4.22506800	-0.78691100	-0.07543400
C	-3.48463800	-4.34430100	-0.86345300
H	-2.38676500	-2.54085700	-1.02334100
H	-2.67583700	-4.98499300	-1.19487300
C	-5.17922300	0.24497900	-0.00823300
C	-4.42452300	1.40719100	0.06643200
H	-6.25380500	0.16704700	-0.09179000
N	-3.10497300	1.06484200	0.07614000
C	-4.86537300	2.80300200	0.11157100
C	-6.10281100	3.13478500	0.67784600
C	-4.06928200	3.82758100	-0.41717300
C	-6.53414600	4.45550900	0.71492700
H	-6.71806400	2.35088500	1.11142700
C	-5.73307100	5.46860000	0.19240800
H	-7.49452900	4.69616500	1.16250000
C	-4.49999000	5.14887800	-0.37069500
H	-6.06840000	6.50137600	0.22495000
H	-3.86972000	5.92951300	-0.78726000
H	-3.11489000	3.58495700	-0.87868300
H	3.11507200	-3.58493000	0.87841900
N	2.97970300	0.24574000	0.00833500
C	4.42470800	-1.40706200	-0.06641200
H	2.38677700	2.54045000	1.02402800
C	4.06956400	-3.82747700	0.41707600
C	4.22508200	0.78701500	0.07538600
C	5.17932300	-0.24478500	0.00819500
C	4.86566900	-2.80283300	-0.11151800
C	3.33241300	2.99177700	0.74167400
C	4.50036800	-5.14874400	0.37063400
C	4.39364000	2.19208200	0.25995800
H	6.25390100	-0.16673600	0.09168900
C	6.10321100	-3.13452400	-0.67762400
C	3.48412500	4.34420700	0.86366200
C	5.73355500	-5.46837300	-0.19228600
H	3.87007500	-5.92942700	0.78707400
C	5.61176600	2.85626600	-0.01309700
H	6.71848000	-2.35058000	-1.11110100
C	6.53464000	-4.45521600	-0.71466500
H	2.67530200	4.98471600	1.19537600

N	4.65737100	4.95551600	0.55824000
H	6.06895700	-6.50112600	-0.22480600
C	5.71023900	4.21344300	0.13435400
H	6.47201100	2.30511200	-0.37472300
H	7.49510700	-4.69579600	-1.16209800
C	4.74783900	6.41071300	0.62235300
H	6.61848300	4.75966500	-0.09160000
H	5.79588400	6.70805300	0.66041800
H	4.27435000	6.85598700	-0.25678100
H	4.24639900	6.76753000	1.52335300

(8) XYZ coordinates of UDFT optimized T_1 geometry for complex **4**

Cu	1.57735800	0.75358400	0.19465800
Cu	-1.57734400	-0.75368500	-0.19465600
Cu	-0.76954800	2.24482500	0.01052800
Cu	0.76961100	-2.24495300	-0.01051800
I	1.42008000	3.40012200	0.69597500
I	-1.42001200	-3.40025200	-0.69601400
I	0.05475000	0.46589900	-2.09659600
I	-0.05471800	-0.46601800	2.09660000
N	-2.69677000	1.85669900	0.04781100
N	3.07682700	-0.57807100	-0.09928300
C	7.28980100	4.38330000	-0.41518500
N	6.59739500	3.10949400	-0.41916800
H	8.36434600	4.21718100	-0.51413800
H	7.09779600	4.93698100	0.51123600
H	6.95390800	4.98485300	-1.26224100
C	7.19266700	1.99096500	0.10612400
C	6.51682100	0.81019800	0.21349000
H	8.22011200	2.10919300	0.42922200
C	5.16447900	0.69971300	-0.19901200
H	7.02945900	-0.04204600	0.64553400
C	4.58657400	1.86941000	-0.75300100
C	4.43205500	-0.53350600	-0.08256700
C	5.29404600	3.03197400	-0.84113500
H	3.56986900	1.85356400	-1.12814600
H	4.86894600	3.94069200	-1.25024200
C	4.92456500	-1.84536700	0.00586600
C	3.78985400	-2.65110800	0.01055900
H	5.95456500	-2.17057100	-0.01932000
N	2.69683100	-1.85676200	-0.04782300
C	3.69179900	-4.11278900	0.05128800
C	4.62816200	-4.86145400	0.77522100

C	2.67437600	-4.78962300	-0.63352600
C	4.54460800	-6.24830900	0.81982600
H	5.41149100	-4.34448400	1.32277900
C	3.52038200	-6.91125100	0.14682100
H	5.27590300	-6.81363400	1.39089500
C	2.58556100	-6.17658600	-0.57808400
H	3.45272900	-7.99467400	0.18612600
H	1.78825600	-6.68321000	-1.11447300
H	1.96022500	-4.22605800	-1.22904600
H	-1.95955500	4.22596200	1.22798400
N	-3.07682400	0.57802500	0.09930400
C	-3.78972800	2.65110500	-0.01080700
H	-3.57048700	-1.85340100	1.12907700
C	-2.67380900	4.78955100	0.63260900
C	-4.43207800	0.53356500	0.08266400
C	-4.92449900	1.84547200	-0.00566900
C	-3.69151400	4.11276100	-0.05182500
C	-4.58710800	-1.86916800	0.75371400
C	-2.58481600	6.17649400	0.57692500
C	-5.16469000	-0.69952800	0.19928200
H	-5.95446500	2.17077100	0.01969100
C	-4.62793700	4.86143600	-0.77567200
C	-5.29481800	-3.03156800	0.84208800
C	-3.51971800	6.91117500	-0.14786100
H	-1.78729200	6.68308900	1.11301300
C	-6.51703100	-0.80984600	-0.21326800
H	-5.41146800	4.34448800	-1.32296100
C	-4.54420200	6.24827200	-0.82051500
H	-4.86994700	-3.94024600	1.25152600
N	-6.59812500	-3.10895500	0.41998400
H	-3.45191400	7.99458100	-0.18736500
C	-7.19311800	-1.99045500	-0.10567100
H	-7.02947200	0.04239100	-0.64555800
H	-5.27555300	6.81360900	-1.39150000
C	-7.29078500	-4.38262500	0.41628700
H	-8.22055900	-2.10856400	-0.42883000
H	-8.36530900	-4.21626600	0.51507500
H	-7.09878600	-4.93660200	-0.50995800
H	-6.95510400	-4.98400600	1.26354900