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Electronic Supporting Information

High-efficiency Solution-processed Light-emitting Diode Based on a Phosphorescent Ag_3Cu_5 Cluster Complex

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Table S1. Crystal Data and Structure Refinement for Ag_3Cu_5 Cluster Complex.

	Ag_3Cu_5 Cluster
chemical formula	$C_{255}H_{239}N_9P_6Ag_3Cu_5Cl_2O_8$
formula weight	4455.57
crystal system	Triclinic
space group	$P\ \bar{1}$
T (k)	273 (2)
a (Å)	15.479 (2)
b (Å)	15.967 (2)
c (Å)	54.448 (6)
α (°)	83.158 (5)
β (°)	89.009 (4)
γ (°)	75.683 (6)
V (Å^3)	12943.32 (3)
Z	2
density (g/cm^3)	1.143
reflns collected	196725
unique reflns	47348
R_{int}	0.171
F(000)	4612
R_1[a] [I>2σ(I)]	0.082
wR_2[b] [I>2σ(I)]	0.261
GOF	1.01

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b]$wR_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table S2. Selected Interatomic Distances (Å) and Bond Angles (°) of Ag_3Cu_5 Cluster Complex.

Ag1–Cu1	2.6379(10)	Ag1–Cu2	2.6529(11)
Ag2–Cu1	2.6616(11)	Ag2–Cu3	2.6485(10)
Ag3–Cu2	2.6702(11)	Ag3–Cu3	2.6818(9)
Cu1–Cu4	2.5555(12)	Cu1–Cu5	2.5928(12)
Cu2–Cu4	2.6269(11)	Cu2–Cu5	2.5346(11)
Cu3–Cu4	2.5248(13)	Cu5–Cu3	2.5956(13)
Cu4–Cu5	2.6979(12)	Ag1–C143	2.549(7)
Ag1–P6	2.490(2)	Ag1–P1	2.5038(19)
Ag2–C171	2.510(7)	Ag3–C115	2.450(8)
Ag2–P4	2.476(2)	Ag2–P5	2.467(2)
Ag3–P2	2.4709(18)	Ag3–P3	2.447(2)
Cu1–C89	1.952(8)	Cu1–C199	1.947(8)
Cu1–N3	2.057(6)	Cu2–N1	2.063(5)
Cu2 C115	1.958(8)	Cu2–C143	1.960(8)
Cu3–C171	1.976(7)	Cu3–C227	1.962(7)
Cu3–N2	2.073(6)	Cu4–C89	2.063(8)
Cu4–C115	2.094(7)	Cu4–C171	2.074(7)
Cu5–C143	2.083(7)	Cu5–C199	2.040(7)
Cu5–C227	2.073(8)		
P6-Ag1-P1	118.04(7)	P1-Ag1-C143	92.93(16)
P6-Ag1-C143	123.28(18)	P6-Ag1-C89	89.51(17)
P1-Ag1-C89	116.81(16)	C143-Ag1-C89	118.8(2)
P5-Ag2-P4	119.78(6)	P5-Ag2-C171	118.00(18)
P4-Ag2-C171	93.50(18)	P5-Ag2-C199	91.12(17)
P4-Ag2-C199	120.80(19)	C171-Ag2-C199	116.0(2)
P3-Ag3-C115	119.0(2)	P3-Ag3-P2	120.03(7)
C115-Ag3-P2	93.05(16)	P3-Ag3-C227	93.95(18)
C115-Ag3-C227	112.7(2)	P2-Ag3-C227	120.04(18)
C199-Cu1-C89	161.3(3)	C199-Cu1-N3	98.6(3)
C89-Cu1-N3	100.0(3)	C115-Cu2-N1	97.6(3)
C115-Cu2-C143	160.9(3)	C143-Cu2-N1	101.4(3)
C227-Cu3-C171	161.1(3)	C227-Cu3-N2	97.3(3)
C171-Cu3-N2	101.4(3)	C89-Cu4-C171	111.8(3)
C89-Cu4-C115	121.5(3)	C171-Cu4-C115	115.5(3)
C199-Cu5-C227	120.1(3)	C199-Cu5-C143	114.0(3)
C227-Cu5-C143	113.2(3)		

Table S3. The Partial Molecular Orbital Compositions (%) by SCPA Approach and the Absorption Transitions in the Ground State for Ag_3Cu_5 Cluster Complex in the CH_2Cl_2 Solution Calculated by TD-DFT Method at the PBE1PBE Level

orbital	energy (eV)	MO contribution (%)			
		Cu (s/p/d)	Ag (s/p/d)	dpppy	ebzcz
LUMO+8	-1.53	47.98 (86/13/1)	22.05 (81/10/9)	19.36	10.61
LUMO+7	-1.56	43.43 (67/30/3)	33.69 (85/10/5)	20.66	2.21
LUMO+1	-1.83	22.42 (39/56/5)	43.13 (88/9/3)	19.15	15.30
LUMO	-1.94	21.01 (23/72/5)	46.82 (85/12/3)	13.97	18.20
HOMO	-5.47	35.42 (14/7/79)	7.06 (72/6/22)	6.78	50.75
HOMO-1	-5.52	32.74 (13/5/82)	4.27 (54/8/38)	8.12	54.87
HOMO-2	-5.62	13.27 (35/11/54)	3.69 (58/12/29)	1.18	81.86
HOMO-3	-5.71	9.54 (47/13/40)	6.70 (69/17/14)	1.58	82.18
HOMO-6	-5.87	34.05 (6/4/89)	4.04 (36/17/47)	7.51	54.41

state	*E*, nm (eV)	O.S.	transition (contrib.)	assignment	measured (nm)
S_1	444 (2.79)	0.0730	HOMO→LUMO (67%)	^{1}MC/^{1}LMCT/^{1}IL	435
			HOMO-1→LUMO (11%)	^{1}MC/^{1}LMCT/^{1}IL	
S_2	436 (2.85)	0.0526	HOMO-1→LUMO (48%)	^{1}MC/^{1}LMCT/^{1}IL	
			HOMO-6→LUMO (12%)	^{1}MC/^{1}LMCT/^{1}IL	
S_3	432 (2.87)	0.0664	HOMO→LUMO+1 (53%)	^{1}MC/^{1}LMCT/^{1}IL/^{1}LLCT	
			HOMO-1→LUMO+1 (13%)	^{1}MC/^{1}LMCT/^{1}IL/^{1}LLCT	
S_{16}	381 (3.25)	0.9183	HOMO-2→LUMO+1 (18%)	^{1}LMCT/^{1}LLCT/^{1}IL/^{1}MC	368
			HOMO-3→LUMO (17%)	^{1}LMCT/^{1}IL/^{1}LLCT	
S_{26}	363 (3.41)	0.3998	HOMO-1→LUMO+8 (19%)	^{1}MC/^{1}LMCT/^{1}LLCT/^{1}IL	350
			HOMO→LUMO+7 (14%)	^{1}MC/^{1}LMCT/^{1}LLCT	

Table S4. The Partial Molecular Orbital Compositions (%) by SCPA Approach and Emission Transitions in the Lowest-Energy Triplet State for Ag_3Cu_5 Cluster Complex in the CH_2Cl_2 Solution Calculated by TD-DFT Method at the PBE1PBE Level.

orbital	energy (eV)	MO Contribution (%)			
		Cu (s/p/d)	Ag (s/p/d)	dpppy	ebzcz
LUMO	-2.30	20.83 (25/67/8)	19.31 (77/12/11)	53.52	6.34
HOMO	-5.38	38.84 (16/6/78)	5.70 (70/6/24)	8.55	46.90

state	*E*, nm (eV)	O.S.	transition (contrib.)	assignment	measured (nm)
T_1	592 (2.09)	0.0000	HOMO->LUMO (74%)	^{3}LLCT/^{3}MC	590

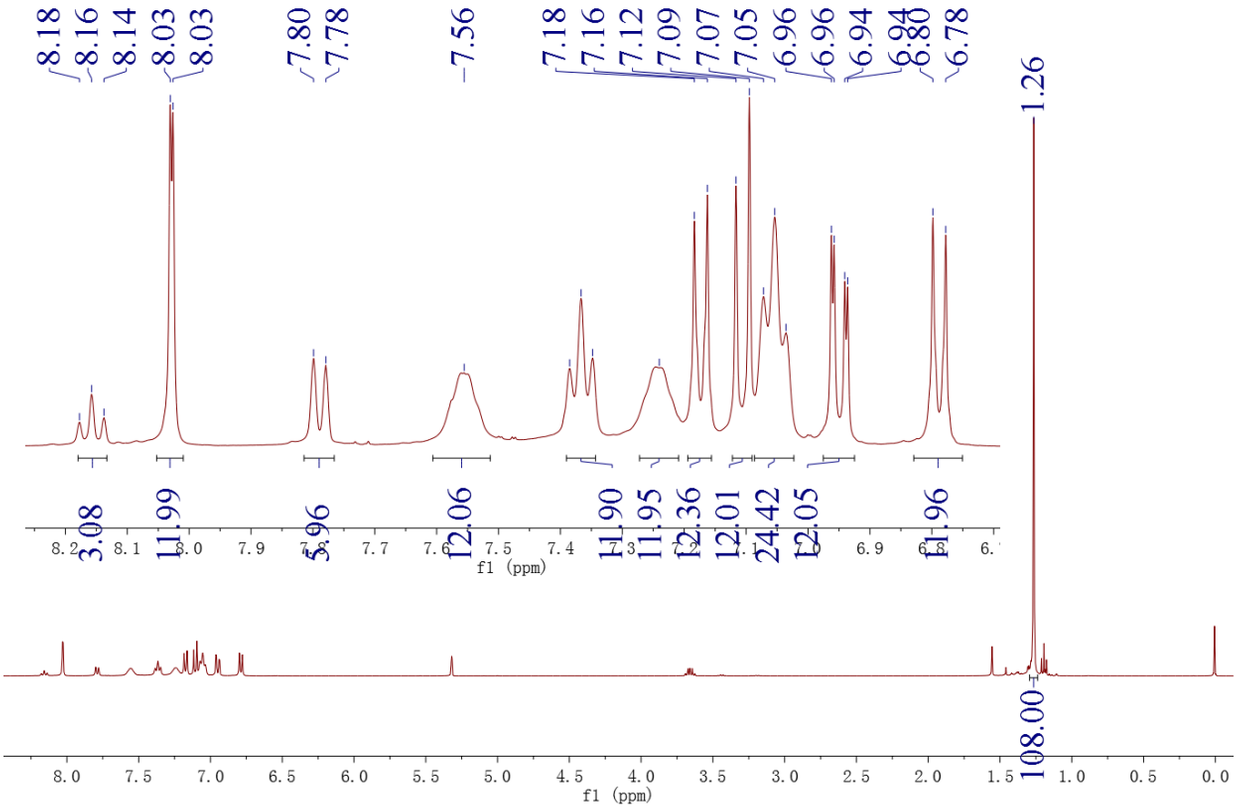


Fig. S1 The ^{1}H NMR spectrum of Ag_3Cu_5 cluster compound in CD_2Cl_2 solution at ambient temperature.

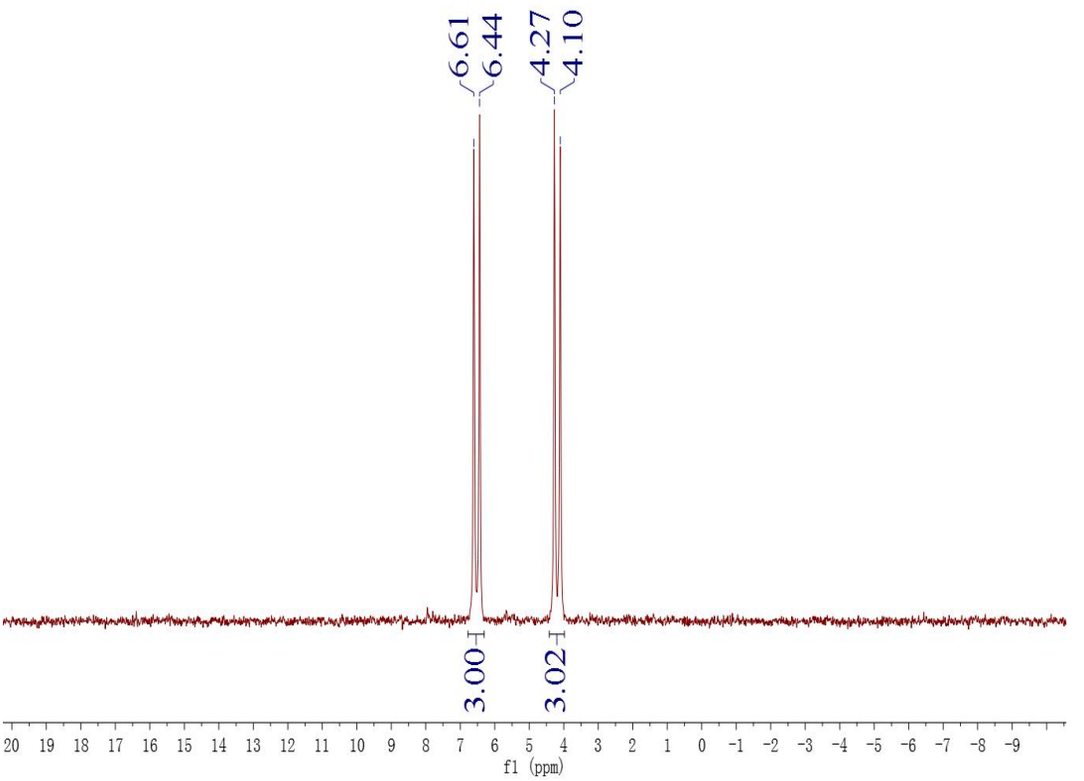


Fig. S2 The ^{31}P NMR spectrum of Ag_3Cu_5 cluster compound in CD_2Cl_2 solution at ambient temperature.

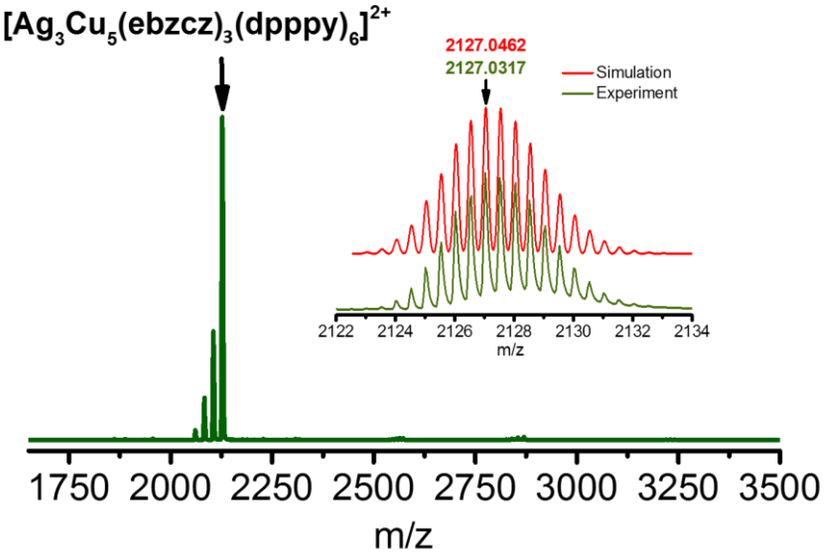


Fig. S3 The high-resolution mass spectrometry of Ag_3Cu_5 cluster compound. Inset: The measured (green) and simulated (red) isotopic patterns.

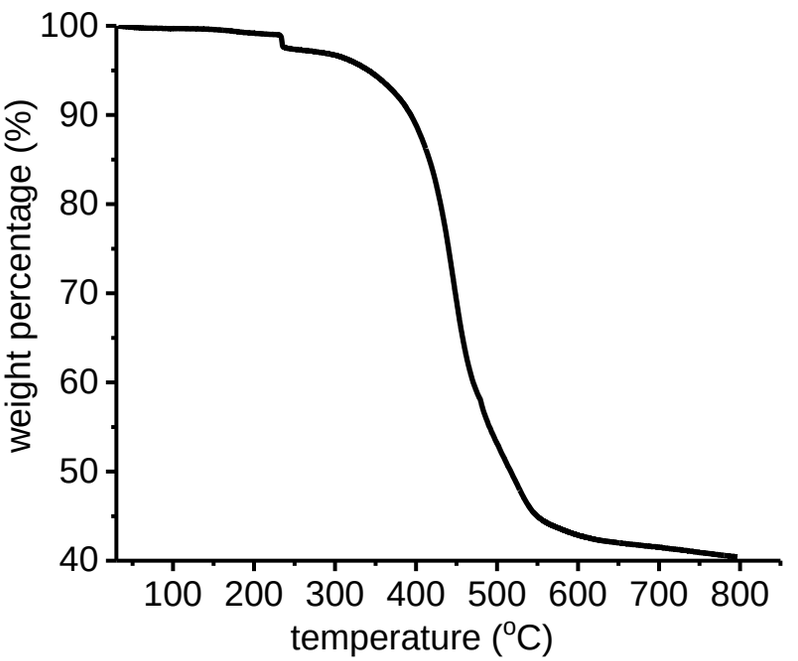


Fig. S4 The plot of thermogravimetric analysis of Ag_3Cu_5 cluster compound.

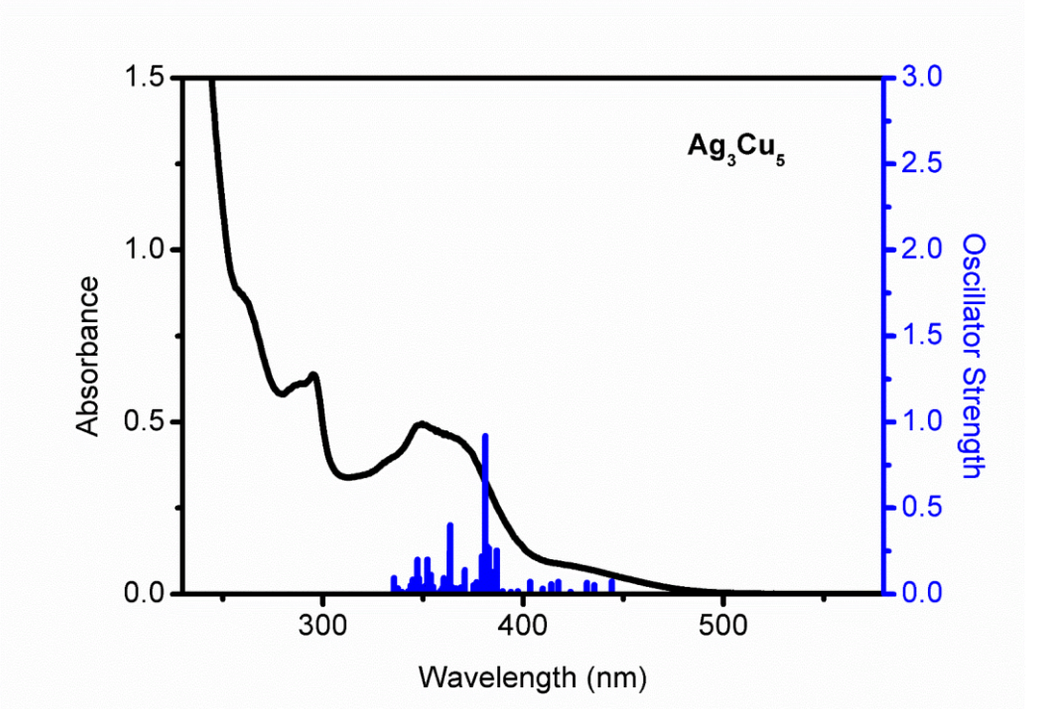


Fig. S5 The calculated (blue bars) and experimentally measured (black line) absorption spectra of Ag_3Cu_5 cluster compound in CH_2Cl_2 solution at ambient temperature, calculated by TD-DFT method at the PBE1PBE level.

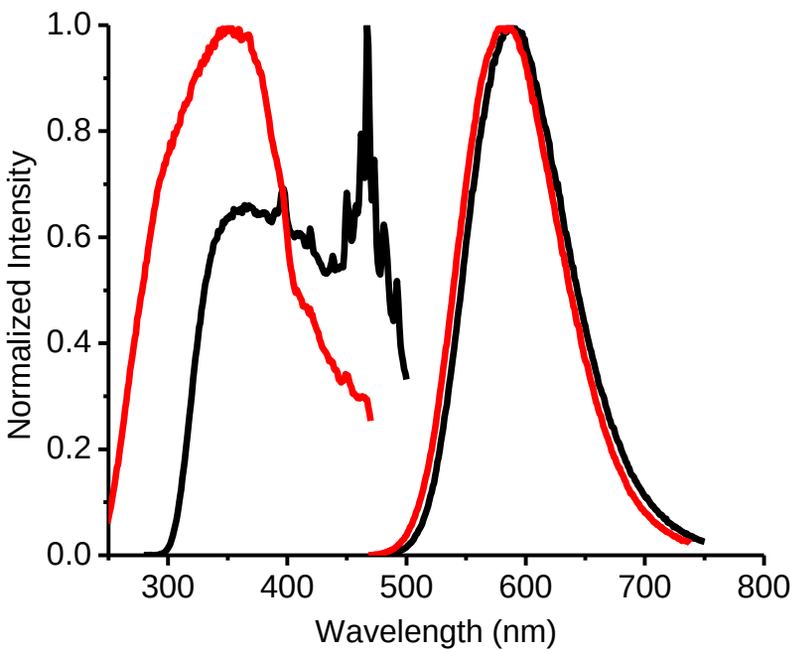


Fig. S6 The excitation and emission spectra of Ag_3Cu_5 cluster compound in solid state (black) and film (red) at room temperature.

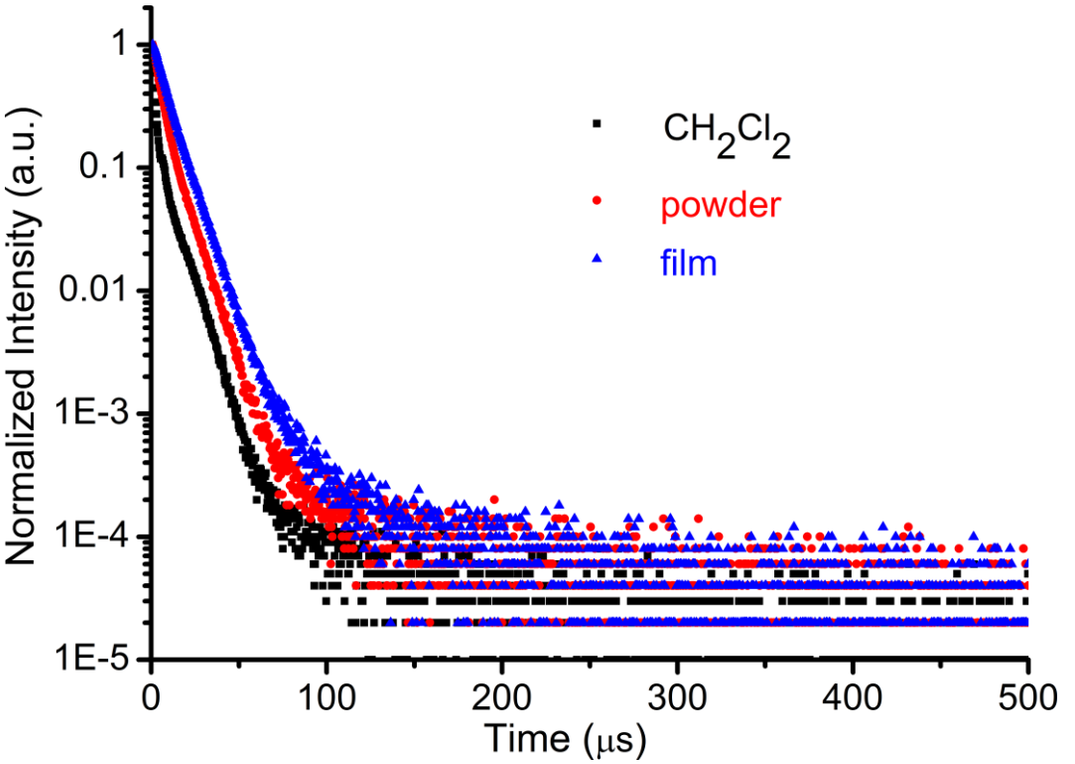
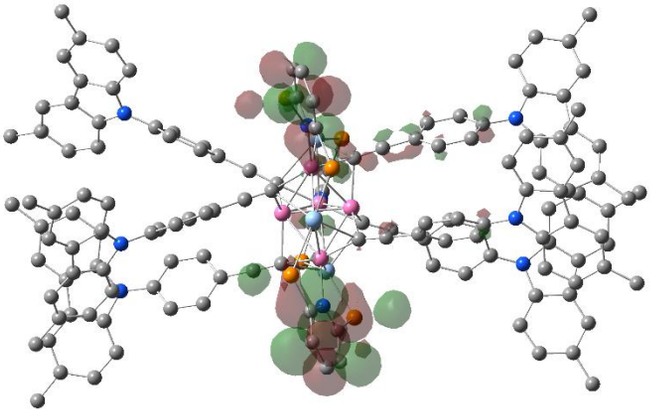
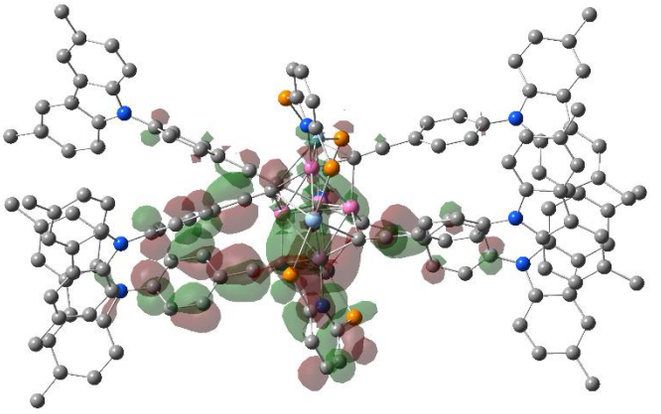


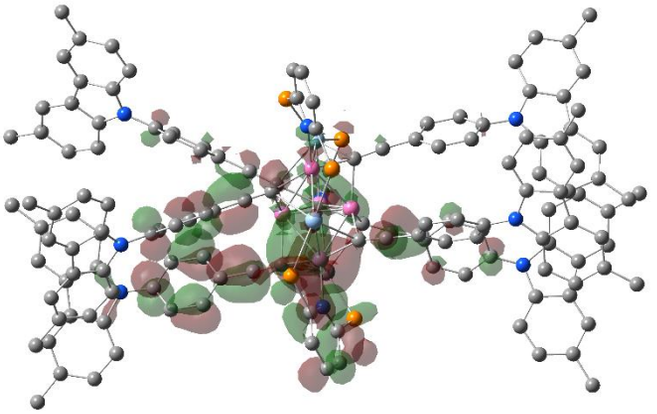
Fig. S7 The luminescent decay curves of Ag_3Cu_5 cluster compound in CH_2Cl_2, powder and film states at room temperature.



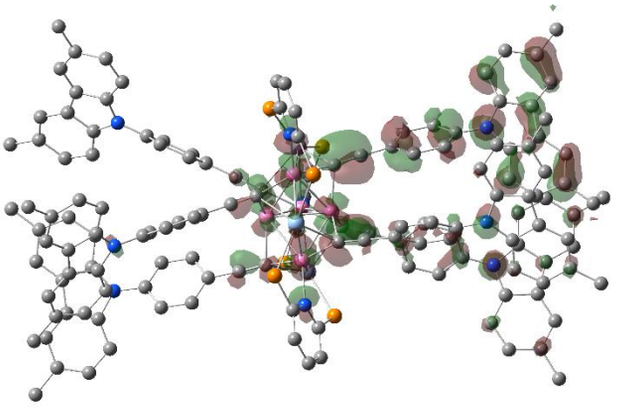
LUMO+1



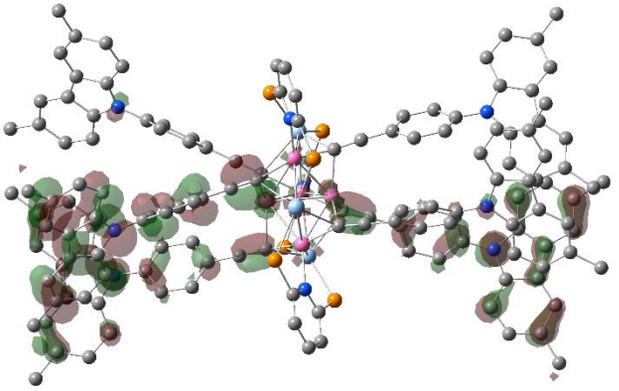
LUMO



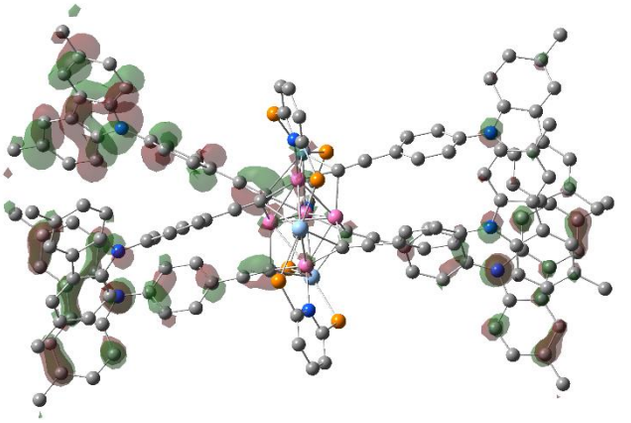
HOMO



HOMO-1



HOMO-2



HOMO-3

Fig. S8 Plots of the frontier molecular orbitals involved in the absorption transition (isovalue = 0.02) for Ag_3Cu_5 cluster compound by TD-DFT method at the PBE1PBE level.