Supplementary Information of Effect of Back Skeleton Ligand On Ultrafast Excited-state Dynamics of Cu(I) Cyano Substituted Bipyridine Complexes

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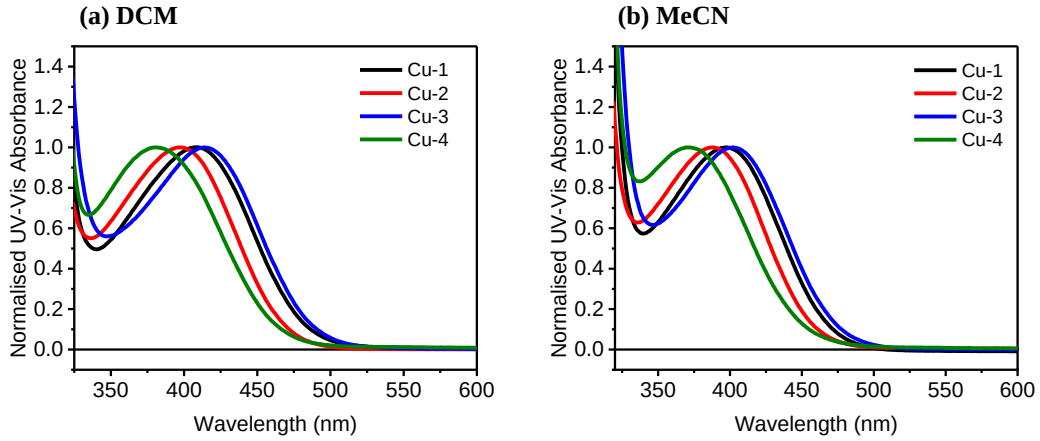

Fig.S1: UV-Vis absorption spectra of Cu(I) complexes (Cu-1, 2, 3, and 4) in a). DCM, b). MeCN

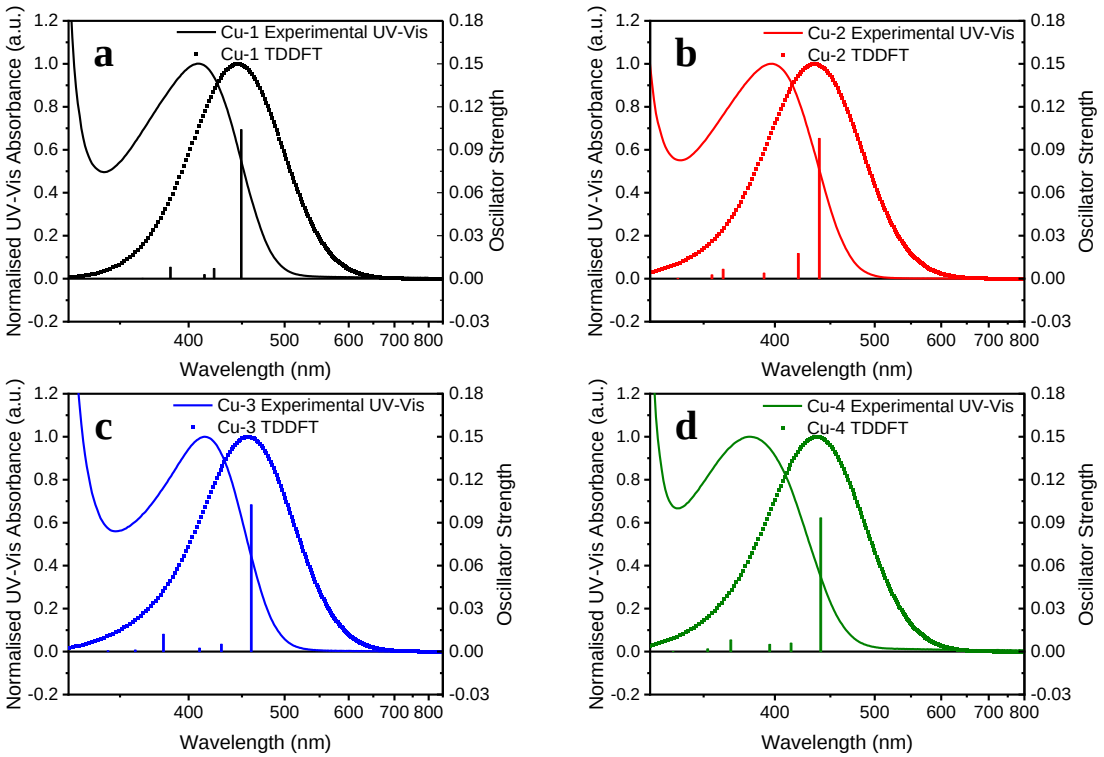

Fig.S2: Experimental UV-Vis absorption spectra in glass cuvette (solid line) and UV-Vis absorption spectra in DCM given by TD-DFT with FWHM 0.3333 eV (dots) of a). **Cu-1**, b). **Cu-2**, c). **Cu-3** and d). **Cu-4** with corresponding oscillator strength of singlet states calculated out by TD-DFT. Corresponding oscillator strength of singlet excited states of each complex are summarised in **Table.S2**.

Table.S1: UV-Vis absorption spectra peak of Cu(I) complexes in DCM collected by UV-Vis absorption spectrometer in glass cuvette and Calculated by TD-DFT method

Compound	**Compound Number**	**λ_{max} DCM/nm**	**$\lambda_{maxTDDFT}$ DCM/nm**
CuXANT(cBpy)	Cu-1	410	444
CuXANT(Me2cBpy)	Cu-2	396	433.6
CuPOP(cBpy)	Cu-3	414	456
Cu(PPh3)2(cBpy)	Cu-4	380	436

Table.S2: Summary of oscillator Strength of Cu(I) complexes in DCM calculated by TD-DFT method

Excited States	**Cu-1** Oscillator Strength	**Cu-2** Oscillator Strength	**Cu-3** Oscillator Strength	**Cu-4** Oscillator Strength
S1	0.10406	0.09796	0.10251	0.09338
S2	0.00715	0.01762	0.00521	0.00598
S3	0.00285	0.00394	0.00245	0.00504
S4	0.00806	0.00661	0.01215	0.00814
S5	2.51E-04	0.0027	0.00116	0.00189
S6	1.27E-04	2.71E-04	6.29E-04	7.04E-05

Based on the oscillator strength given in **Table.S2**, it could be deduced that the absorption peak in UV-Vis region is dominated by S0→S1 state transition absorption. The peak energy of UV-Vis spectra given by TD-DFT is around 0.3-0.4 eV lower than experimental UV-Vis (summarised in **Table.S1**) could be attributed to the relatively low Hartree-Fock contribution of the PBE0 functional used in TD-DFT calculation of these complexes.[1]

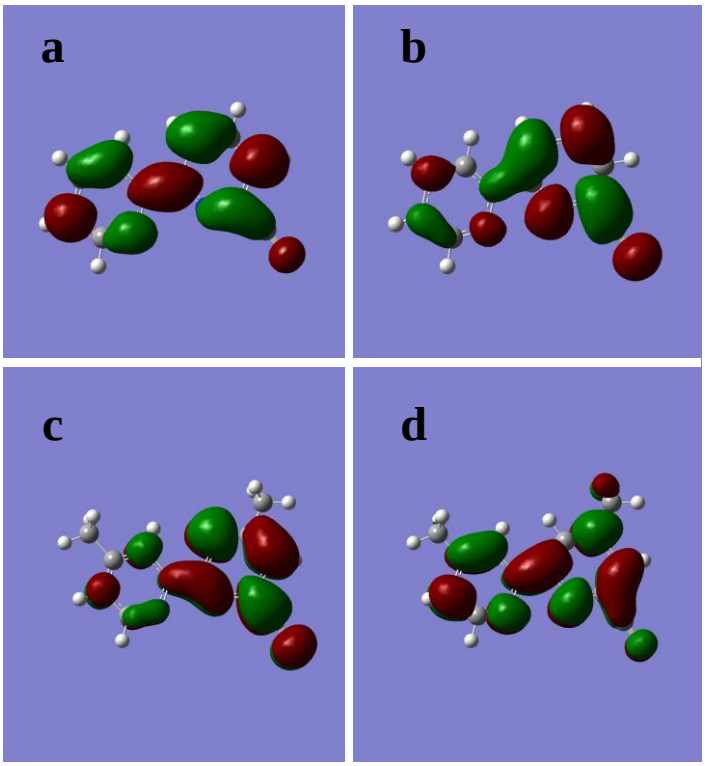

Fig.S3: a). LUMO (-1.8083 eV) and b). LUMO+1 (-1.7631 eV) of 6-cyano-2,2′-bipyridine (cBpy) molecule together with c). LUMO (-1.7289 eV) and d). LUMO+1 (-1.6207 eV) of 4,4′-dimethyl-6-cyano-2,2′-bipyridine (Me_2cBpy) molecule modelled by TD-DFT method.

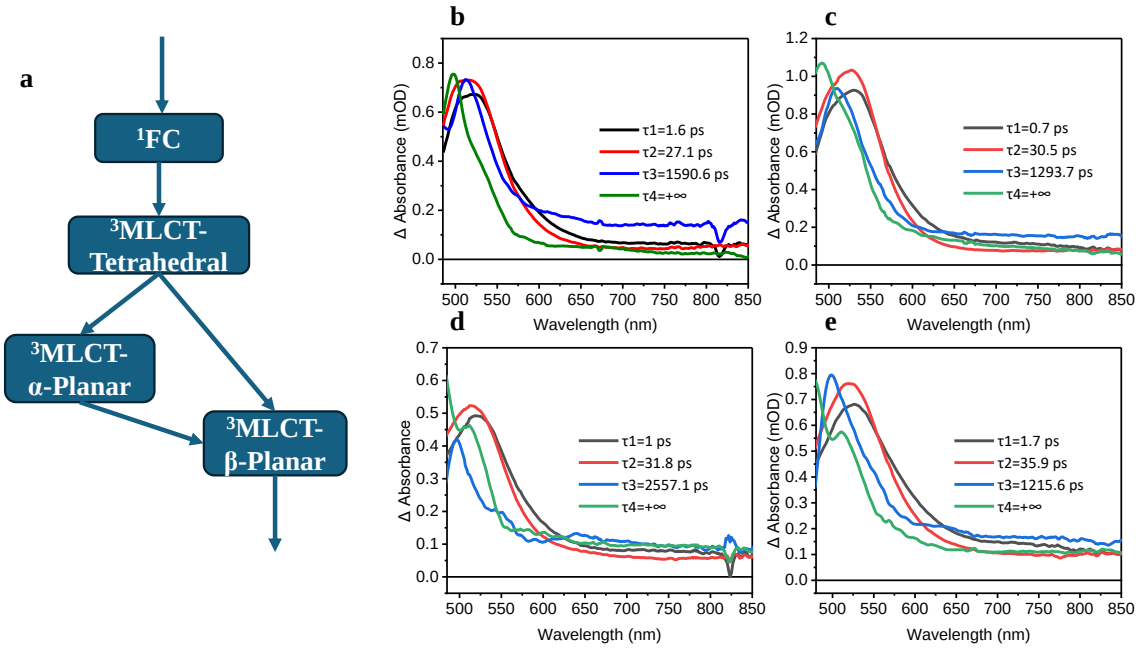

Fig.S4: a). the model used for global analysis, and the SAS together with corresponding lifetimes extracted for TA of b). **Cu-1**, c). **Cu-2**, d). **Cu-3** and e). **Cu-4** in DCM.

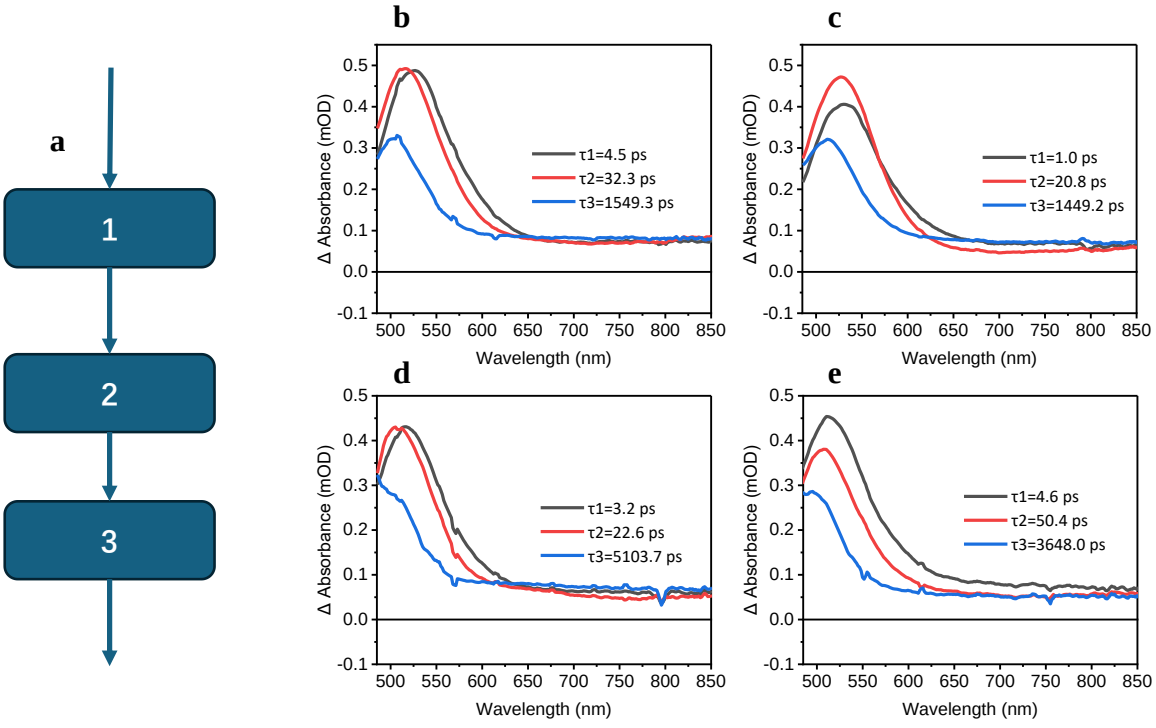

Fig.S5: a). Sequential model used in global analysis here and EAS extracted from Cu(I) complexes TA spectra of b). **Cu-1**, c). **Cu-2**, d). **Cu-3** and e). **Cu-4** based on sequential model.

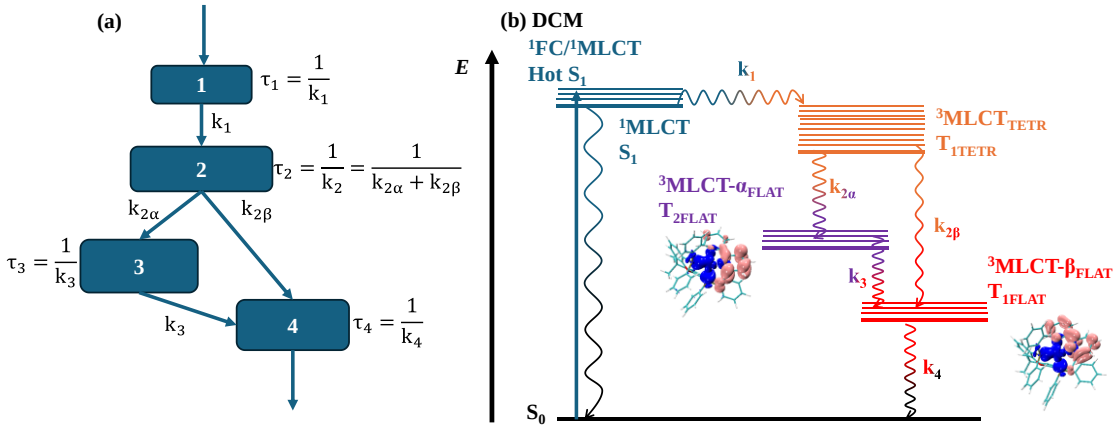

Fig.S6: a). Kinetic model used for global analysis of TA of Cu(I) complexes in DCM and b). energy level diagram suggested for Cu(I) complexes in DCM. In which each the nature of each excited states suggested by TD-DFT is given and the energy calculated by TD-DFT for each complex are summarised in **Table.S3**. Here the TD-DFT calculation of S_1 and T_{1TETR} are done under optimized S_0 geometry and T_{1FLAT} and T_{2FLAT} are done under optimized T_1 geometry

Table.S3: Summary of energy of excited states calculated by TD-DFT and corresponding assignments of each Cu(I) complexes investigated in DCM. Here S_1 and T_{1TETR} are calculated under optimized S_0 geometry and T_{1FLAT} and T_{2FLAT} are calculated under optimized T_1 geometry. Fragment analysis of these states are given in **Table.S5-S12**.

Excited States TDDFT	Assignment	**Cu-1** Energy TDDFT/eV	**Cu-2** Energy TDDFT/eV	**Cu-3** Energy TDDFT/eV	**Cu-4** Energy TDDFT/eV
S_1	^{1}MLCT	2.760	2.824	2.695	2.815
T_{1TETR}	^{3}MLCT$_{TETR}$	2.442	2.508	2.394	2.502
T_{2FLAT}	^{3}MLCT-α_{FLAT}	2.109	2.169	2.071	2.121
T_{1FLAT}	^{3}MLCT-β_{FLAT}	1.238	1.297	1.196	1.229

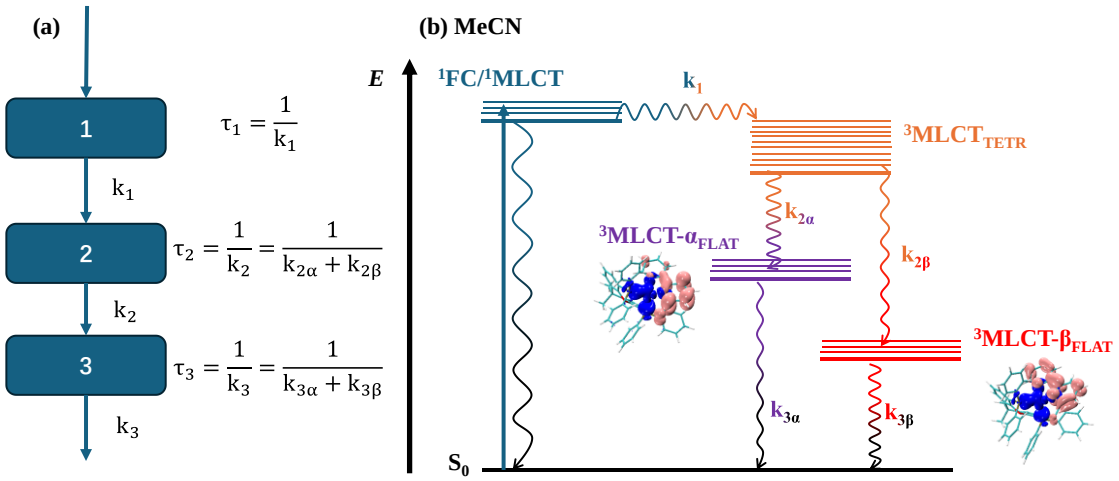

Fig.S7: a). Kinetic model used for global analysis of TA of Cu(I) complexes in MeCN and b). energy level diagram suggested for Cu(I) complexes in MeCN.

For Cu(I) complexes in dichloromethane (DCM) investigated in this research, the kinetic model used for extracting species associated spectra (SAS) from its corresponding TA is shown in **Fig.S6a**. Here the global analysis extracted lifetimes for each state (τ_n) which relationship between lifetime and corresponding rate coefficient (k) is also shown in **Fig.S6a**. In which the first excited state decays into the second excited state with lifetime $\tau_1 = \frac{1}{k_1}$, second excited populated branch decays into two different excited states with lifetime $\tau_2 = \frac{1}{k_2} = \frac{1}{k_{2\alpha}+k_{2\beta}}$ and then the third state decays into the forth state with lifetime $\tau_3 = \frac{1}{k_3}$ and the forth state decays into ground state with lifetime $\tau_4 = \frac{1}{k_4}$. Here the $k_{2\alpha}$ is rate of decay process from 2 to 3 so it is ^{3}MLCT$_{TETR}$ to ^{3}MLCT-α$_{FLAT}$ shown in the energy level diagram in **Fig.S6b** and $k_{2\beta}$ is rate of decay process from 2 to 4 so ^{3}MLCT$_{TETR}$ to ^{3}MLCT-β$_{FLAT}$。

For Cu(I) complexes in acetonitrile (MeCN), a sequential model (shown in **Fig.S7a**) is used for global analysis. Similar to the condition in DCM, the decay of the second excited state with lifetime $\tau_2 = \frac{1}{k_2}$ is also actually branches into two states with kinetic rate coefficient $k_2 = k_{2\alpha} + k_{2\beta}$, here $k_{2\alpha}$ is the rate coefficient for ^{3}MLCT$_{TETR}$ to ^{3}MLCT-α$_{FLAT}$ and $k_{2\beta}$ is the rate coefficient for ^{3}MLCT$_{TETR}$ to ^{3}MLCT-β$_{FLAT}$. In this model, ^{3}MLCT-α$_{FLAT}$ and ^{3}MLCT-β$_{FLAT}$ are treated as one state 3 because they are populated and decay together and cannot be distinguished so the lifetime of the state 3 in model $\tau_3 = \frac{1}{k_3}$ is also with $k_3 = k_{3\alpha} + k_{3\beta}$ and the $k_{3\alpha}$ represents decay from ^{3}MLCT-α$_{FLAT}$ to ground state, $k_{3\beta}$ represents decay from ^{3}MLCT-β$_{FLAT}$ to ground state.

Table.S4: Summary of Lifetimes of corresponding SAS extracted from TA spectra of Cu(I) complexes in DCM and MeCN investigated in this research.

Compound	Number	Solvent	τ_1/ps	τ_2/ps	τ_3/ps	τ_4/ps
Cu(cBPY)(XANT)	**Cu-1**	DCM	1.6	27.1	1590.6	$+\infty$
		MeCN	4.5	32.3	1549.3	-
Cu(Me$_2$cBPY)(XANT)	**Cu-2**	DCM	0.7	30.5	1293.7	$+\infty$
		MeCN	1	20.8	1449.2	-
Cu(cBpy)(POP)	**Cu-3**	DCM	1	31.8	2557.1	$+\infty$
		MeCN	3.2	22.6	5103.7	-
Cu(cBpy)(PPh$_3$)$_2$	**Cu-4**	DCM	1.7	35.9	1215.6	$+\infty$
		MeCN	4.6	50.4	3648	-

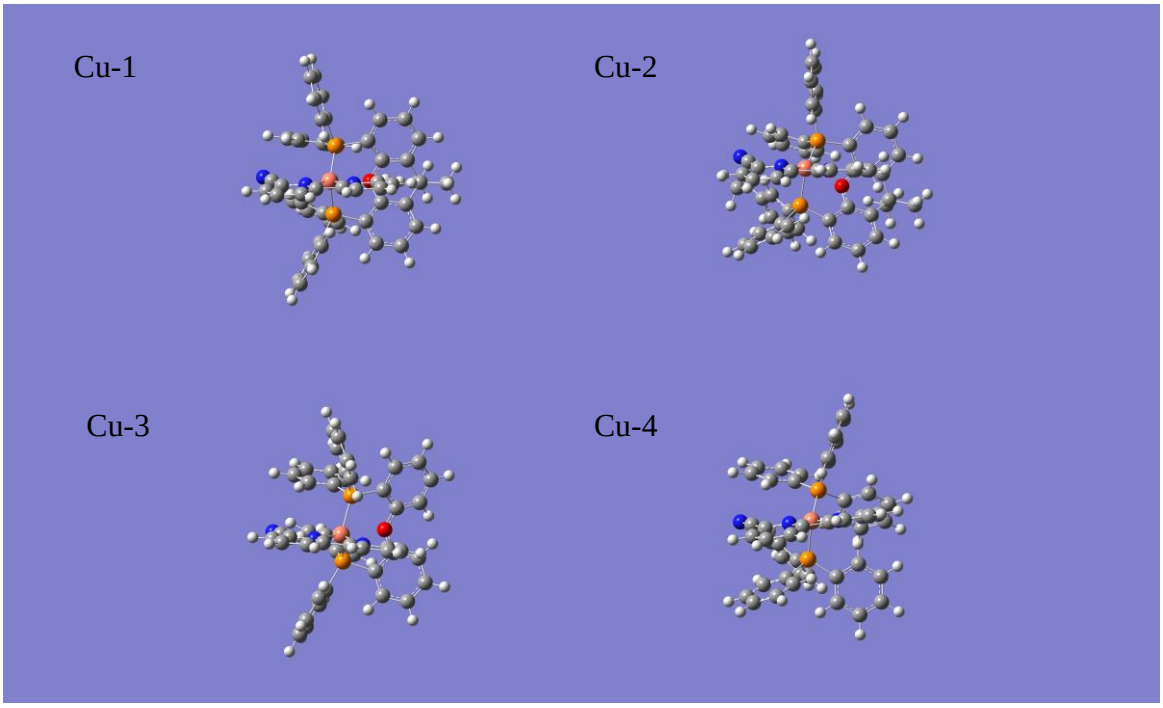

Fig.S8: Ground State Geometries of **Cu-1**, **2**, **3** and **4** suggested by DFT calculation.

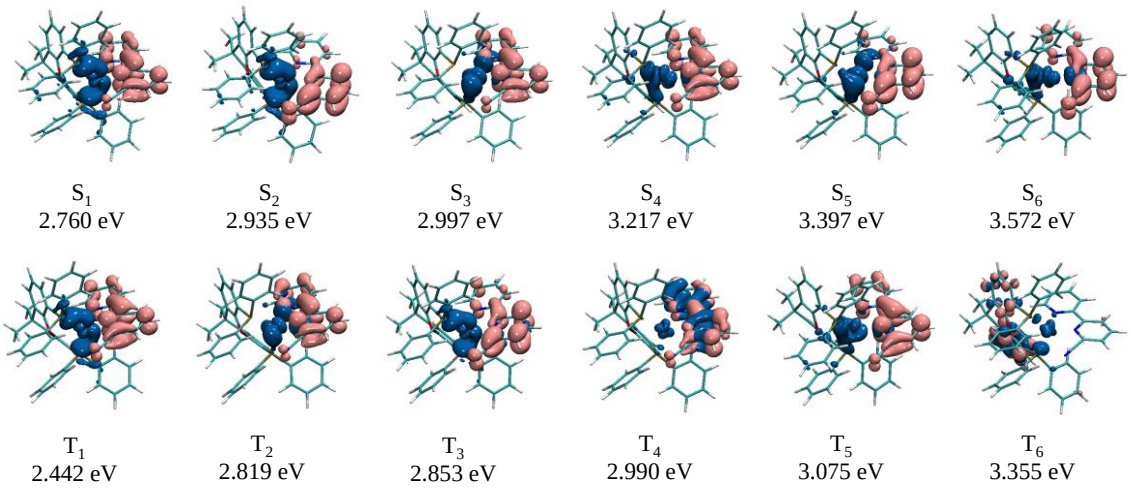

Fig.S9: Electron-Hole density analysis result of **Cu-1** in DCM

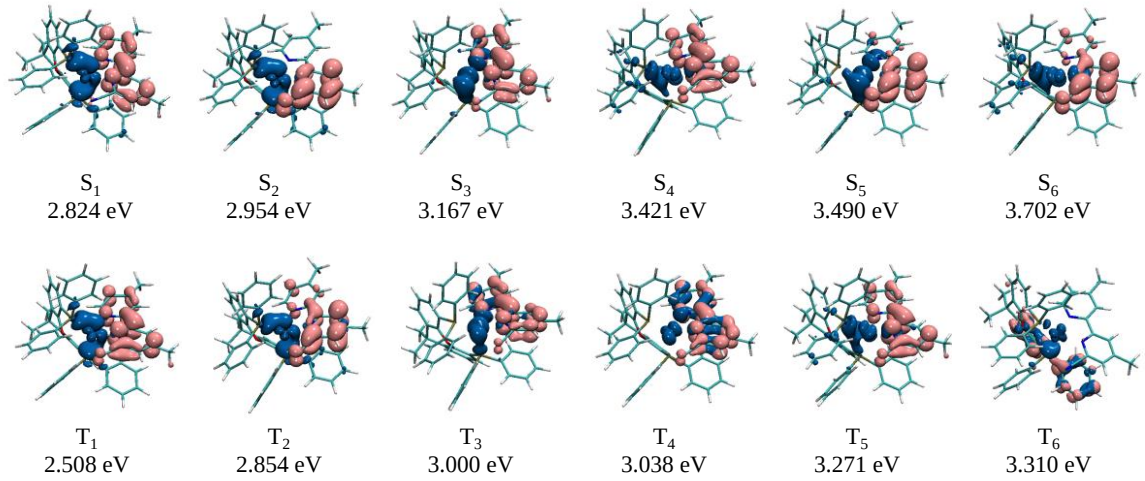

Fig.S10: Electron-Hole density analysis result of **Cu-2** in DCM

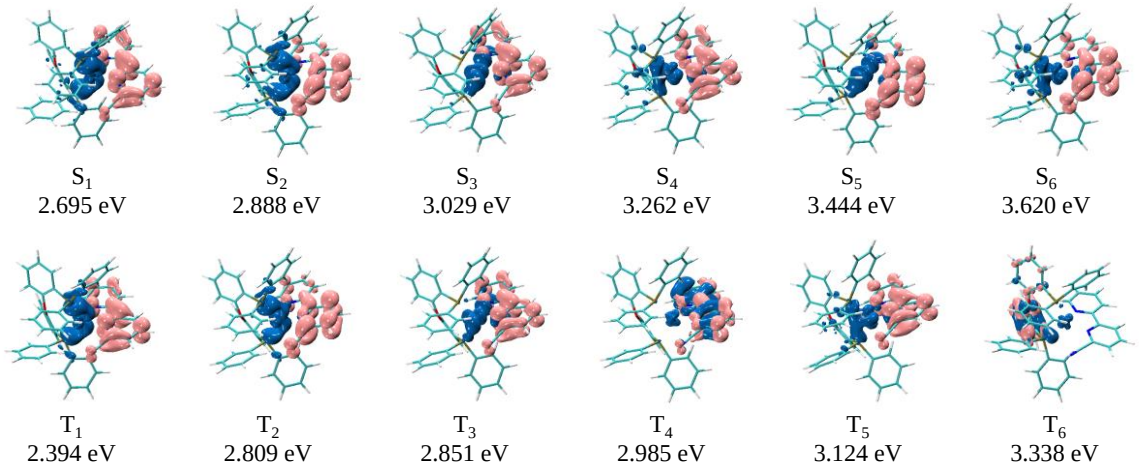

Fig.S11: Electron-Hole density analysis result of **Cu-3** in DCM

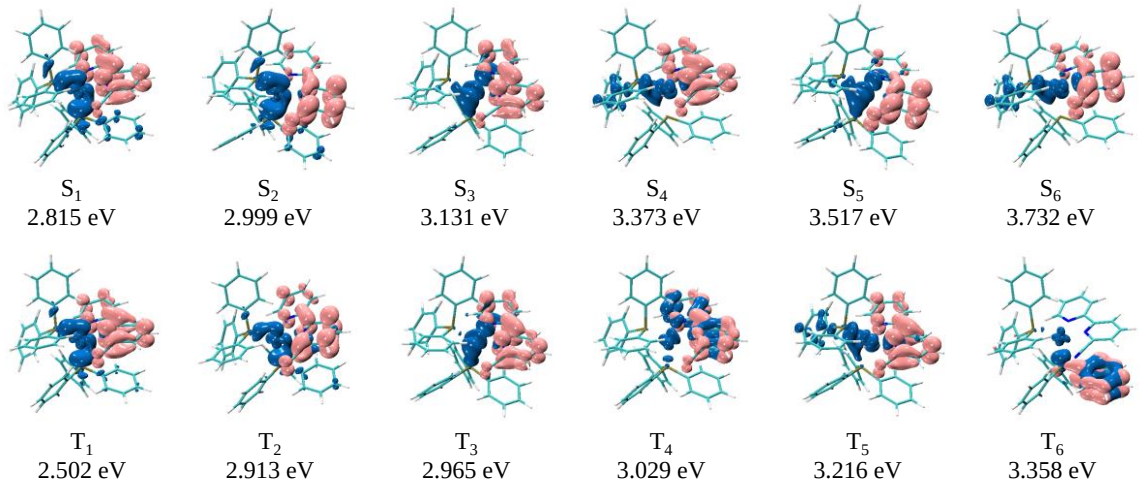

Fig.S12: Electron-Hole density analysis result of **Cu-4** in DCM

Fragment Electron-Hole Analysis

To present the electron-hole distribution in excited states of Cu(I) complexes investigated here, fragment analysis was done by using the Multiwfn software.[2] The results of fragment analysis is given in **Table.S5-S8** for **Cu-1** to **Cu-4** based on TD-DFT results under their S_0 geometry and in **Table.S9-S12** is based on TD-DFT results under their T_1 geometry, in the scheme where negative value indicates loss of electron density (or in another word "hole") compared with ground state and positive value indicates gain of electron density compared with ground state. The fragment is separated based on each Cu(I) complex nature, for **Cu-1**, it is Cu center, Py ring with CN substituent (Py-CN) and Py ring without CN substituent (Py) and XANT ligand. The rest complexes' fragments can also be told from the name used. From this analysis, it is more obvious that the difference between T_1 and T_2 state is for T_1 electron density donated from Cu(I) center (and also amount from P^P) ligand distributed more equally on both pyridine rings and for T_2 electron density is majorly on CN substituted pyridine ring.

Table.S5: Fragment analysis result of **Cu-1** based on TD-DFT result under optimized S_0 geometry of **Cu-1** complex in DCM suggested by Multiwfn here negative value indicates loss of electron density in excited state compared with ground state and positive value indicates gain of electron density in excited state. Cu for Cu(I) center, Py for pyridine ring without CN substituent, Py-CN for pyridine ring with CN substituent. XANT stands for P^P ligand XANT

Cu-1 Fragment Analysis										
Singlet State						Triplet State				
S1	2.760 eV	449.2 nm				T1	2.442 eV	507.7 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-35.52	2.33	9.09	-33.20		1 (Cu)	-41.32	3.00	11.14	-38.32
2 (Py)	-2.57	34.28	9.38	31.71		2 (Py)	-3.28	28.93	9.73	25.65
3 (Py-CN)	-3.16	60.48	13.83	57.32		3 (Py-CN)	-7.55	65.19	22.19	57.64
4 (XANT)	-58.75	2.91	13.08	-55.84		4 (XANT)	-47.85	2.88	11.75	-44.96
S2	2.935 eV	422.4 nm				T2	2.819 eV	439.8 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-35.77	0.38	3.70	-35.38		1 (Cu)	-60.62	2.85	13.14	-57.77
2 (Py)	-2.49	12.00	5.47	9.51		2 (Py)	-21.44	37.22	28.25	15.78
3 (Py-CN)	-3.16	87.18	16.60	84.02		3 (Py-CN)	-11.06	57.23	25.16	46.17
4 (XANT)	-58.58	0.44	5.06	-58.14		4 (XANT)	-6.88	2.70	4.31	-4.18
S3	2.997 eV	413.7 nm				T3	2.853 eV	434.6 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-62.13	2.61	12.73	-59.52		1 (Cu)	-31.35	0.25	2.82	-31.10
2 (Py)	-20.00	35.48	26.64	15.49		2 (Py)	-5.95	20.70	11.10	14.75
3 (Py-CN)	-6.24	59.22	19.23	52.98		3 (Py-CN)	-14.65	78.47	33.91	63.82
4 (XANT)	-11.63	2.69	5.59	-8.95		4 (XANT)	-48.05	0.58	5.26	-47.47
S4	3.217 eV	385.4 nm				T4	2.990 eV	414.7 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-54.85	2.62	11.99	-52.23		1 (Cu)	-8.2	0.68	2.36	-7.52
2 (Py)	-0.28	29.84	2.89	29.56		2 (Py)	-42.34	39.96	41.13	-2.38
3 (Py-CN)	-11.68	64.79	27.51	53.11		3 (Py-CN)	-39.54	58.35	48.03	18.81
4 (XANT)	-33.19	2.74	9.54	-30.45		4 (XANT)	-9.92	1.01	3.17	-8.91
S5	3.397 eV	365.0 nm				T5	3.075 eV	403.2 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-57.57	0.36	4.54	-57.22		1 (Cu)	-51.73	2.69	11.81	-49.03
2 (Py)	-18.46	13.59	15.84	-4.86		2 (Py)	-2.09	28.96	7.78	26.87
3 (Py-CN)	-4.54	85.68	19.73	81.14		3 (Py-CN)	-11.49	65.43	27.42	53.95
4 (XANT)	-19.43	0.37	2.68	-19.06		4 (XANT)	-34.69	2.91	10.04	-31.79
S6	3.572 eV	347.1 nm				T6	3.355 eV	369.6 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-50.46	0.31	3.95	-50.15		1 (Cu)	-9.13	1.31	3.45	-7.83
2 (Py)	-0.93	17.28	4.01	16.35		2 (Py)	-1.24	0.87	1.04	-0.37
3 (Py-CN)	-14.54	82.02	34.54	67.47		3 (Py-CN)	-0.52	5.95	1.75	5.43
4 (XANT)	-34.07	0.40	3.68	-33.68		4 (XANT)	-89.11	91.88	90.49	2.77

Table.S6: Fragment analysis result of **Cu-2** based on TD-DFT result under optimized S_0 geometry of **Cu-2** complex in DCM suggested by Multiwfn here negative value indicates loss of electron density in excited state compared with ground state and positive value indicates gain of electron density in excited state. Cu for Cu(I) center, Me-Py for methylpyridine ring without CN substituent, Me-Py-CN for methylpyridine ring with CN substituent. XANT stands for P^P ligand XANT

Cu-2 Fragment Analysis									
Singlet State						Triplet State				
S1	2.824 eV	439.0 nm				T1	2.508 eV	494.4 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-37.71	1.83	8.31	-35.88		1 (Cu)	-41.8	2.73	10.67	-39.08
2 (Me-Py)	-3.12	40.50	11.24	37.38		2 (Me-Py)	-3.96	29.70	10.84	25.75
3 (Me-Py-CN)	-5.15	55.00	16.84	49.85		3 (Me-Py-CN)	-10.62	64.92	26.26	54.30
4 (XANT)	-54.02	2.67	12.01	-51.35		4 (XANT)	-43.61	2.65	10.74	-40.97
S2	2.954 eV	419.7 nm				T2	2.854 eV	434.4 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-36.88	0.77	5.33	-36.11		1 (Cu)	-34.12	0.36	3.53	-33.75
2 (Me-Py)	-2.74	5.01	3.71	2.27		2 (Me-Py)	-4.64	17.46	9.00	12.82
3 (Me-Py-CN)	-4.84	92.80	21.19	87.96		3 (Me-Py-CN)	-13.03	80.69	32.43	67.66
4 (XANT)	-55.54	1.42	8.88	-54.12		4 (XANT)	-48.22	1.48	8.46	-46.73
S3	3.167 eV	391.5 nm				T3	3.000 eV	413.3 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-59.26	2.32	11.72	-56.94		1 (Cu)	-40.22	1.93	8.81	-38.28
2 (Me-Py)	-19.79	38.89	27.57	18.60		2 (Me-Py)	-29.25	39.56	34.02	10.31
3 (Me-Py-CN)	-4.3	56.70	15.62	52.40		3 (Me-Py-CN)	-16.48	55.63	30.28	39.16
4 (XANT)	-16.64	2.58	6.56	-14.06		4 (XANT)	-14.05	2.87	6.36	-11.18
S4	3.421 eV	362.4 nm				T4	3.038 eV	408.1 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-55.3	2.41	11.54	-52.89		1 (Cu)	-26.07	1.40	6.04	-24.67
2 (Me-Py)	-0.6	32.72	4.44	32.11		2 (Me-Py)	-32.54	36.44	34.44	3.91
3 (Me-Py-CN)	-12.12	62.30	27.48	50.18		3 (Me-Py-CN)	-34.31	60.31	45.49	25.99
4 (XANT)	-31.98	2.57	9.07	-29.41		4 (XANT)	-7.08	1.85	3.62	-5.23
S5	3.490 eV	355.3 nm				T5	3.271 eV	379.0 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-56.33	0.54	5.50	-55.79		1 (Cu)	-51.16	2.53	11.38	-48.63
2 (Me-Py)	-17.07	9.64	12.83	-7.43		2 (Me-Py)	-1.9	29.24	7.46	27.34
3 (Me-Py-CN)	-3.43	88.71	17.45	85.28		3 (Me-Py-CN)	-13.95	64.36	29.96	50.42
4 (XANT)	-23.16	1.11	5.08	-22.05		4 (XANT)	-32.99	3.87	11.29	-29.12
S6	3.702 eV	334.9 nm				T6	3.310 eV	374.6 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-52.41	0.42	4.70	-51.99		1 (Cu)	-10.79	1.78	4.38	-9.01
2 (Me-Py)	-1.49	12.84	4.38	11.35		2 (Me-Py)	-0.81	2.06	1.29	1.25
3 (Me-Py-CN)	-14.76	85.58	35.54	70.82		3 (Me-Py-CN)	-1.68	2.34	1.98	0.66
4 (XANT)	-31.33	1.16	6.02	-30.17		4 (XANT)	-86.72	93.82	90.20	7.10

Table.S7: Fragment analysis result of **Cu-3** based on TD-DFT result under optimized S_0 geometry of **Cu-3** complex in DCM suggested by Multiwfn here negative value indicates loss of electron density in excited state compared with ground state and positive value indicates gain of electron density in excited state. Cu for Cu(I) center, Py for pyridine ring without CN substituent, Py-CN for pyridine ring with CN substituent. POP stands for P^P ligand POP.

Cu-3 Fragment Analysis									
Singlet State						Triplet State				
S1	2.695 eV	460.1 nm				T1	2.394 eV	517.9 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-35.85	2.47	9.40	-33.38		1 (Cu)	-41.16	3.04	11.19	-38.11
2 (Py)	-2.98	32.89	9.89	29.91		2 (Py)	-3.74	29.97	10.59	26.23
3 (Py-CN)	-2.94	61.86	13.49	58.91		3 (Py-CN)	-6.10	64.14	19.78	58.04
4 (POP)	-58.23	2.79	12.74	-55.45		4 (POP)	-49.00	2.85	11.82	-46.15
S2	2.888 eV	439.3 nm				T2	2.809 eV	441.4 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-35.72	0.31	3.35	-35.40		1 (Cu)	-35.34	0.51	4.24	-34.83
2 (Py)	-2.76	14.16	6.26	11.40		2 (Py)	-7.04	20.95	12.14	13.92
3 (Py-CN)	-2.87	84.98	15.61	82.11		3 (Py-CN)	-12.86	77.74	31.62	64.88
4 (POP)	-58.65	0.55	5.66	-58.11		4 (POP)	-44.76	0.80	5.98	-43.96
S3	3.029 eV	409.3 nm				T3	2.851 eV	434.9 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-62.74	2.70	13.02	-60.03		1 (Cu)	-58.07	2.57	12.22	-55.49
2 (Py)	-19.49	35.46	26.29	15.97		2 (Py)	-18.24	35.30	25.37	17.07
3 (Py-CN)	-7.09	59.27	20.51	52.18		3 (Py-CN)	-11.37	59.77	26.07	48.40
4 (POP)	-10.68	2.56	5.23	-8.12		4 (POP)	-12.32	2.35	5.39	-9.97
S4	3.262 eV	380.1 nm				T4	2.985 eV	415.4 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-53.25	2.68	11.94	-50.57		1 (Cu)	-6.8	0.76	2.27	-6.05
2 (Py)	-0.7	30.28	4.60	29.58		2 (Py)	-44.19	42.05	43.11	-2.15
3 (Py-CN)	-10.26	64.41	25.71	54.14		3 (Py-CN)	-41.11	55.84	47.91	14.73
4 (POP)	-35.79	2.64	9.72	-33.15		4 (POP)	-7.89	1.36	3.28	-6.53
S5	3.444 eV	360.0 nm				T5	3.124 eV	396.9 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-58.73	0.34	4.49	-58.39		1 (Cu)	-50.43	2.74	11.77	-47.69
2 (Py)	-18.67	14.20	16.28	-4.47		2 (Py)	-2.58	29.40	8.71	26.81
3 (Py-CN)	-5.64	84.94	21.88	79.31		3 (Py-CN)	-10.6	64.74	26.19	54.14
4 (POP)	-16.96	0.52	2.96	-16.45		4 (POP)	-36.39	3.12	10.66	-33.26
S6	3.620 eV	342.5 nm				T6	3.338 eV	371.4 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-48.36	0.27	3.61	-48.09		1 (Cu)	-6.37	2.08	3.64	-4.28
2 (Py)	-0.85	17.19	3.82	16.34		2 (Py)	-0.57	0.43	0.49	-0.14
3 (Py-CN)	-13.03	82.04	32.70	69.01		3 (Py-CN)	-0.53	0.62	0.57	0.09
4 (POP)	-37.76	0.50	4.34	-37.26		4 (POP)	-92.54	96.86	94.68	4.33

Table.S8: Fragment analysis result of **Cu-4** based on TD-DFT result under optimized S_0 geometry of **Cu-4** complex in DCM suggested by Multiwfn here negative value indicates loss of electron density in excited state compared with ground state and positive value indicates gain of electron density in excited state. Cu for Cu(I) center, Py for pyridine ring without CN substituent, Py-CN for pyridine ring with CN substituent. PPh3-I and PPh3-II indicates the two different PPh_3 ligand in **Cu-4**.

Cu-4 Fragment Analysis										
Singlet State						Triplet State				
S1	2.815 eV	440.4 nm				T1	2.502 eV	495.5 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-36.51	2.19	8.94	-34.32		1 (Cu)	-42.14	2.83	10.92	-39.31
2 (Py)	-2.33	32.91	8.75	30.58		2 (Py)	-3.22	27.40	9.40	24.18
3 (Py-CN)	-4.67	61.93	17.00	57.27		3 (Py-CN)	-9.56	66.89	25.29	57.33
4 (PPh3-I)	-17.71	1.01	4.22	-16.71		4 (PPh3-I)	-15.94	1.10	4.18	-14.84
5 (PPh3-II)	-38.78	1.96	8.73	-36.82		5 (PPh3-II)	-29.13	1.78	7.19	-27.36
S2	2.999 eV	413.4 nm				T2	2.913 eV	425.6 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-36.16	0.35	3.55	-35.18		1 (Cu)	-29.74	0.36	3.25	-29.39
2 (Py)	-2.38	13.17	5.60	10.79		2 (Py)	-9.69	25.58	15.74	15.89
3 (Py-CN)	-4.4	85.59	19.41	81.19		3 (Py-CN)	-18.17	72.96	36.41	54.79
4 (PPh3-I)	-17.74	0.18	1.78	-17.56		4 (PPh3-I)	-13.46	0.32	2.08	-13.14
5 (PPh3-II)	-39.32	0.71	5.28	-38.61		5 (PPh3-II)	-28.94	0.79	4.77	-28.16
S3	3.131 eV	396.0 nm				T3	2.965 eV	418.2 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-59.87	2.49	12.22	-57.38		1 (Cu)	-52.17	2.35	11.08	-49.82
2 (Py)	-19.99	35.84	26.77	15.85		2 (Py)	-22.32	36.61	28.59	14.28
3 (Py-CN)	-4.22	58.95	15.77	54.74		3 (Py-CN)	-7.3	58.31	20.63	51.01
4 (PPh3-I)	-6.25	1.06	2.58	-5.19		4 (PPh3-I)	-4.65	0.98	2.14	-3.67
5 (PPh3-II)	-9.66	1.65	3.99	-8.01		5 (PPh3-II)	-13.55	1.75	4.87	-11.80
S4	3.373 eV	367.6 nm				T4	3.029 eV	409.3 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-53.93	2.53	11.69	-51.40		1 (Cu)	-17.93	0.92	4.07	-17.01
2 (Py)	-0.69	29.83	4.53	29.14		2 (Py)	-35.22	36.77	35.99	1.54
3 (Py-CN)	-12.16	64.92	28.09	52.77		3 (Py-CN)	-36.79	60.83	47.31	24.04
4 (PPh3-I)	-28.94	1.07	5.55	-27.87		4 (PPh3-I)	-2.55	0.47	1.10	-2.08
5 (PPh3-II)	-4.28	1.65	2.66	-2.64		5 (PPh3-II)	-7.51	1.00	2.75	-6.51
S5	3.517 eV	352.5 nm				T5	3.216 eV	385.5 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-55.12	0.36	4.46	-54.76		1 (Cu)	-49.68	2.67	11.53	-47.01
2 (Py)	-17.83	14.00	15.80	-3.83		2 (Py)	-1.56	27.46	6.54	25.90
3 (Py-CN)	-2.91	84.85	15.72	81.94		3 (Py-CN)	-14.47	66.75	31.08	52.28
4 (PPh3-I)	-11.55	0.17	1.40	-11.38		4 (PPh3-I)	-28.01	1.39	6.23	-26.63
5 (PPh3-II)	-12.59	0.61	2.78	-11.97		5 (PPh3-II)	-6.28	1.73	3.30	-4.55
S6	3.732 eV	332.2 nm				T6	3.358 eV	369.2 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%		Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-52.11	0.26	3.71	-51.84		1 (Cu)	-8.03	2.27	4.27	-5.77
2 (Py)	-1.99	16.81	5.78	14.82		2 (Py)	-1.04	0.99	1.01	-0.05
3 (Py-CN)	-15.2	82.18	35.34	66.98		3 (Py-CN)	-1.49	1.96	1.71	0.47
4 (PPh3-I)	-26.91	0.16	2.10	-26.74		4 (PPh3-I)	-8.22	6.16	7.12	-2.06
5 (PPh3-II)	-3.8	0.58	1.49	-3.22		5 (PPh3-II)	-81.22	88.62	84.84	7.40

Table.S9: Fragment analysis result of **Cu-1** based on TD-DFT result of **Cu-1** under T_1 geometry in DCM suggested by Multiwfn here negative value indicates loss of electron density in excited state compared with ground state and positive value indicates gain of electron density in excited state. Cu for Cu(I) center, Py for pyridine ring without CN substituent, Py-CN for pyridine ring with CN substituent. XANT indicates XANT ligand in **Cu-1**.

T1	1.238 eV	1001.5 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-45.85	5.10	15.29	-40.75
2 (Py)	-9.57	33.54	17.92	23.96
3 (Py-CN)	-11.62	56.96	25.73	45.34
4 (XANT)	-32.96	4.40	12.04	-28.56
T2	2.109 eV	587.9 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-40.52	0.60	4.92	-39.92
2 (Py)	-7.74	13.46	10.21	5.72
3 (Py-CN)	-11.17	84.55	30.73	73.39
4 (XANT)	-40.58	1.39	7.52	-39.18
T3	2.568 eV	482.8 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-55.77	4.58	15.97	-51.20
2 (Py)	-14.14	38.05	23.19	23.91
3 (Py-CN)	-3.88	52.70	14.31	48.82
4 (XANT)	-26.20	4.68	11.07	-21.53
T4	2.599 eV	477.0 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-18.56	2.66	7.03	-15.90
2 (Py)	-35.88	40.97	38.34	5.08
3 (Py-CN)	-39.86	52.54	45.76	12.68
4 (XANT)	-5.69	3.83	4.67	-1.86
T5	2.868 eV	432.3 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-44.92	3.90	13.24	-41.02
2 (Py)	-8.08	44.31	18.92	36.23
3 (Py-CN)	-11.66	34.91	20.18	23.25
4 (XANT)	-35.34	16.87	24.42	-18.46
T6	2.975 eV	416.8 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-36.30	3.71	11.61	-32.59
2 (Py)	-12.47	27.92	18.66	15.46
3 (Py-CN)	-11.47	28.51	18.08	17.04
4 (XANT)	-39.76	39.86	39.81	0.10

Table.S10: Fragment analysis result of **Cu-2** based on TD-DFT result of **Cu-2** under T_1 geometry in DCM suggested by Multiwfn here negative value indicates loss of electron density in excited state compared with ground state and positive value indicates gain of electron density in excited state. Cu for Cu(I) center, Py for pyridine ring without CN substituent, Py-CN for pyridine ring with CN substituent. XANT indicates the XANT ligand in **Cu-2**.

T1	1.297 eV	955.9 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-45.93	4.61	14.55	-41.32
2 (Me-Py)	-10.14	37.75	19.57	27.60
3 (Me-Py-CN)	-11.36	53.57	24.67	42.21
4 (XANT)	-32.57	4.08	11.53	-28.49
T2	2.169 eV	571.6 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-41.42	0.87	6.01	-40.54
2 (Me-Py)	-7.67	9.47	8.52	1.79
3 (Me-Py-CN)	-11.41	87.63	31.61	76.22
4 (XANT)	-39.5	2.03	8.95	-37.47
T3	2.566 eV	483.2 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-18.03	2.52	6.74	-15.51
2 (Me-Py)	-39.81	46.24	42.90	6.43
3 (Me-Py-CN)	-34.93	48.00	40.94	13.07
4 (XANT)	-7.23	3.24	4.84	-3.99
T4	2.616 eV	473.9 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-52.33	3.93	14.33	-48.40
2 (Me-Py)	-15.78	40.09	25.15	24.30
3 (Me-Py-CN)	-10.53	51.88	23.38	41.35
4 (XANT)	-21.36	4.10	9.36	-17.25
T5	2.910 eV	426.1 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-42.21	4.22	13.35	-37.99
2 (Me-Py)	-6.37	27.48	13.23	21.11
3 (Me-Py-CN)	-9.53	22.74	14.72	13.21
4 (XANT)	-41.89	45.56	43.68	3.67
T6	2.978 eV	416.3 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-41.83	3.64	12.34	-38.19
2 (Me-Py)	-8.9	25.06	14.93	16.16
3 (Me-Py-CN)	-10.92	34.27	19.34	23.35
4 (XANT)	-38.35	37.03	37.68	-1.32

Table.S11: Fragment analysis result of **Cu-3** based on TD-DFT result of **Cu-3** under T_1 geometry in DCM suggested by Multiwfn here negative value indicates loss of electron density in excited state compared with ground state and positive value indicates gain of electron density in excited state. Cu for Cu(I) center, Py for pyridine ring without CN substituent, Py-CN for pyridine ring with CN substituent. POP indicates the POP ligand in **Cu-3**.

T1	1.196 eV	1036.7 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-44.68	5.18	15.22	-39.50
2 (Py)	-9.70	34.14	18.20	24.43
3 (Py-CN)	-11.23	56.18	25.12	44.95
4 (POP)	-34.38	4.50	12.44	-29.88
T2	2.071 eV	598.7 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-39.40	0.63	5.00	-38.77
2 (Py)	-7.66	12.47	9.78	4.81
3 (Py-CN)	-10.92	85.32	30.52	74.41
4 (POP)	-42.02	1.57	8.13	-40.45
T3	2.531 eV	489.9 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-54.05	4.66	15.87	-49.39
2 (Py)	-14.11	38.29	23.24	24.18
3 (Py-CN)	-4.67	52.26	15.62	47.59
4 (POP)	-27.17	4.79	11.41	-22.38
T4	2.594 eV	478.0 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-18.81	2.69	7.12	-16.12
2 (Py)	-36.74	42.88	39.69	6.14
3 (Py-CN)	-37.16	50.47	43.30	13.31
4 (POP)	-7.29	3.96	5.37	-3.33
T5	2.829 eV	438.3 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-42.33	3.32	11.85	-39.01
2 (Py)	-8.20	50.32	20.31	42.12
3 (Py-CN)	-10.18	23.00	15.30	12.82
4 (POP)	-39.29	23.36	30.29	-15.93
T6	2.951 eV	420.1 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-37.89	3.80	12.00	-34.10
2 (Py)	-13.75	33.58	21.49	19.83
3 (Py-CN)	-14.20	42.09	24.45	27.89
4 (POP)	-34.15	20.53	26.48	-13.62

Table.S12: Fragment analysis result of **Cu-4** based on TD-DFT result of **Cu-4** under T_1 geometry in DCM suggested by Multiwfn here negative value indicates loss of electron density in excited state compared with ground state and positive value indicates gain of electron density in excited state. Cu for Cu(I) center, Py for pyridine ring without CN substituent, Py-CN for pyridine ring with CN substituent. PPh3-I and PPh3-II indicates the two different PPh_3 ligands in **Cu-4**.

T1	1.229 eV	1008.8 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-45.82	5.24	15.49	-40.58
2 (Py)	-9.52	33.34	17.82	23.82
3 (Py-CN)	-11.91	56.69	25.99	44.78
4 (PPh3-I)	-15.53	1.65	5.07	-13.88
5 (PPh3-II)	-17.21	3.08	7.28	-14.14
T2	2.121 eV	584.6 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-40.87	0.53	4.65	-40.34
2 (Py)	-7.73	14.00	10.40	6.27
3 (Py-CN)	-11.59	83.83	31.17	72.25
4 (PPh3-I)	-18.31	0.19	1.85	-18.13
5 (PPh3-II)	-21.50	1.45	5.58	-20.05
T3	2.615 eV	474.1 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-45.77	4.40	14.19	-41.37
2 (Py)	-22.23	40.99	30.19	18.75
3 (Py-CN)	-8.99	49.75	21.15	40.76
4 (PPh3-I)	-1.38	1.55	1.46	0.17
5 (PPh3-II)	-21.62	3.32	8.47	-18.31
T4	2.633 eV	470.9 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-24.90	2.93	8.55	-21.97
2 (Py)	-32.66	39.78	36.05	7.12
3 (Py-CN)	-35.92	53.70	43.92	17.78
4 (PPh3-I)	-1.23	1.22	1.23	-0.01
5 (PPh3-II)	-5.29	2.36	3.53	-2.92
T5	2.902 eV	427.2 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-41.09	5.10	14.48	-35.98
2 (Py)	-9.15	48.13	20.99	38.97
3 (Py-CN)	-10.16	17.63	13.38	7.47
4 (PPh3-I)	-23.17	20.37	21.73	-2.80
5 (PPh3-II)	-16.43	8.77	12.00	-7.66
T6	3.078 eV	402.8 nm		
Fragment	Hole/%	Electron/%	Overlap/%	Diff/%
1 (Cu)	-41.65	5.93	15.71	-35.72
2 (Py)	-6.35	18.46	10.83	12.11
3 (Py-CN)	-9.37	17.22	12.70	7.84
4 (PPh3-I)	-28.13	49.50	37.31	21.37
5 (PPh3-II)	-14.50	8.90	11.36	-5.60

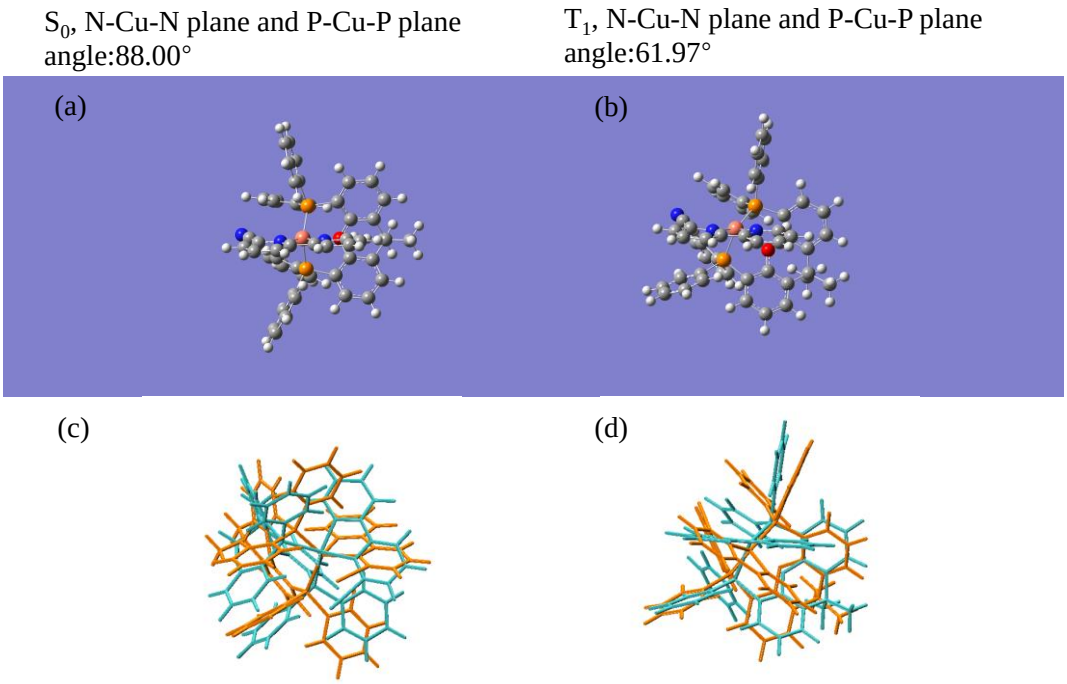

Fig.S13: Optimized ground state (S_0) geometry (a) and the first triplet excited state (T_1) geometry (b) of **Cu-1** cation in DCM optimized by Gaussian Calculation together with comparison of S_0 (orange) and T_1 (cyan) geometry (c, d).

Cartesian Co-ordinates (XYZ format) of S_0 state of **Cu-1**.

C	0.960556	-3.65344	-1.23425
C	0.295461	-4.383	-2.21883
C	-1.02941	-4.09325	-2.54768
C	-1.72517	-3.07461	-1.89065
C	-1.03004	-2.35908	-0.91522
C	0.30169	-2.61405	-0.57255
C	-3.19181	-2.71627	-2.11015
C	-3.30011	-1.1994	-1.98124
C	-2.51884	-0.57699	-1.00437
O	-1.64144	-1.32166	-0.26695
C	-4.14651	-0.38323	-2.73534
C	-4.20803	0.991056	-2.50305
C	-3.41321	1.582849	-1.52365
C	-2.54114	0.800917	-0.75906
P	1.072256	-1.46676	0.624347
P	-1.29655	1.488153	0.398498
C	-3.70846	-3.21462	-3.45469
C	-4.01589	-3.35631	-0.97303
Cu	0.729081	0.641277	-0.15455
N	1.023961	0.669685	-2.23626
C	2.13054	1.324371	-2.62716

C	2.472462	1.434296	-3.97721
C	1.647504	0.849134	-4.9323
C	0.504972	0.173107	-4.51511
C	2.949807	1.910587	-1.53968
N	2.448578	1.796328	-0.30212
C	3.136558	2.302807	0.729663
C	4.366833	2.9427	0.5902
C	4.893577	3.056414	-0.69356
C	4.18078	2.540245	-1.76665
H	2.000513	-3.87847	-0.98851
H	0.816534	-5.18954	-2.73868
H	-1.52699	-4.67849	-3.32227
H	-4.77269	-0.82187	-3.51334
H	-4.88035	1.610564	-3.09999
H	-3.45155	2.662388	-1.3666
H	-4.77139	-2.96513	-3.57851
H	-3.6328	-4.30902	-3.51632
H	-3.14728	-2.7782	-4.29437
H	-3.66282	-3.02232	0.013693
H	-5.07654	-3.08065	-1.07213
H	-3.93075	-4.4526	-1.01523
H	3.366942	1.972595	-4.28858
H	1.89723	0.924363	-5.99232
H	-0.17205	-0.30102	-5.22692
H	4.886849	3.33461	1.464383
H	5.855601	3.545329	-0.85432
H	4.585108	2.621142	-2.77467
C	2.804682	-2.03432	0.705568
C	3.290209	-2.85519	1.728823
C	3.677701	-1.59562	-0.30055
C	4.632783	-3.23338	1.742266
H	2.61782	-3.19647	2.519258
C	5.014526	-1.98402	-0.29027
H	3.302935	-0.95118	-1.10023
C	5.494643	-2.80131	0.734743
H	5.00662	-3.87155	2.546335
H	5.686272	-1.64133	-1.0807
H	6.545555	-3.09951	0.749118
C	0.341234	-1.95773	2.220849
C	-0.3216	-3.17898	2.390709
C	0.45764	-1.07665	3.302738
C	-0.85814	-3.51549	3.63247
H	-0.42059	-3.86993	1.550194
C	-0.06824	-1.42379	4.544495

H	0.954519	-0.11195	3.177641
C	-0.72867	-2.64082	4.711
H	-1.37842	-4.46812	3.757203
H	0.024682	-0.72943	5.381858
H	-1.15088	-2.9055	5.683355
C	-1.95693	1.149392	2.067272
C	-1.39749	1.847253	3.14689
C	-2.95173	0.19663	2.30584
C	-1.84555	1.609244	4.442526
H	-0.60447	2.57939	2.97642
C	-3.3852	-0.05039	3.608017
H	-3.39939	-0.35379	1.476564
C	-2.83917	0.657858	4.676499
H	-1.40731	2.16338	5.275857
H	-4.16007	-0.79987	3.78478
H	-3.18402	0.464679	5.69496
C	-1.49598	3.291281	0.204759
C	-2.53145	4.008216	0.818619
C	-0.58187	3.963396	-0.61539
C	-2.64905	5.380204	0.607971
H	-3.24444	3.491271	1.465528
C	-0.70541	5.335253	-0.82903
H	0.231513	3.40269	-1.08386
C	-1.73836	6.043997	-0.21634
H	-3.45689	5.935658	1.089972
H	0.011837	5.852952	-1.46997
H	-1.83284	7.120484	-0.37733
C	0.233403	0.111933	-3.1522
H	-0.65611	-0.40439	-2.78538
C	2.538156	2.161733	2.029398
N	2.074477	2.062075	3.086231
C50H39CuN3OP2(1+)			

Cartesian Co-ordinates (XYZ format) of T_1 state of **Cu-1**.

C	1.429345	-2.35846	-2.69227
C	0.819476	-2.69865	-3.89796
C	-0.56054	-2.56924	-4.06361
C	-1.37091	-2.1107	-3.02179
C	-0.72699	-1.7642	-1.83496
C	0.653111	-1.86425	-1.63967
C	-2.89646	-2.04563	-3.04965
C	-3.31601	-0.84807	-2.2029
C	-2.56221	-0.565	-1.06517
O	-1.44775	-1.29385	-0.77509

C	-4.42192	-0.02799	-2.44133
C	-4.74971	1.014715	-1.57152
C	-3.96283	1.285918	-0.45446
C	-2.83894	0.4941	-0.1979
P	1.283334	-1.31585	-0.01554
P	-1.56302	0.879069	1.039334
C	-3.43957	-1.95576	-4.47132
C	-3.43352	-3.32163	-2.36661
Cu	0.567402	0.973988	0.103233
N	0.324688	2.1923	-1.47821
C	1.506869	2.778762	-1.85748
C	1.575194	3.485742	-3.07975
C	0.459634	3.585546	-3.8807
C	-0.7454	2.975416	-3.47051
C	2.599872	2.604391	-0.94878
N	2.333868	1.79922	0.14136
C	3.288649	1.668034	1.10785
C	4.545224	2.223245	1.008834
C	4.853989	2.985267	-0.14331
C	3.873607	3.181398	-1.09687
H	2.508063	-2.46967	-2.57203
H	1.428234	-3.07622	-4.72169
H	-1.00958	-2.84754	-5.01799
H	-5.04583	-0.20216	-3.319
H	-5.62386	1.634652	-1.77897
H	-4.19889	2.129085	0.197301
H	-4.53805	-1.9357	-4.46608
H	-3.14584	-2.83869	-5.05536
H	-3.07491	-1.05638	-4.98908
H	-3.05377	-3.41438	-1.33801
H	-4.53286	-3.29692	-2.3277
H	-3.11981	-4.21289	-2.93039
H	2.514969	3.943845	-3.38887
H	0.510797	4.130898	-4.82528
H	-1.65304	3.03221	-4.07166
H	5.267756	2.078902	1.811936
H	5.841707	3.43182	-0.26069
H	4.083132	3.800176	-1.9702
C	3.093758	-1.41325	-0.16279
C	3.868295	-2.17267	0.720075
C	3.724643	-0.62644	-1.13933
C	5.259575	-2.13863	0.630406
H	3.388202	-2.78873	1.482751
C	5.111988	-0.60475	-1.22952

H	3.132447	-0.02246	-1.83095
C	5.882407	-1.35548	-0.33952
H	5.858377	-2.73107	1.325649
H	5.593819	0.011583	-1.99141
H	6.972555	-1.32916	-0.40392
C	0.776192	-2.6312	1.133263
C	0.240579	-3.83652	0.661556
C	0.951079	-2.43822	2.5097
C	-0.11086	-4.84044	1.560947
H	0.101595	-3.99741	-0.40938
C	0.613088	-3.45422	3.399908
H	1.3607	-1.50022	2.890549
C	0.079806	-4.65341	2.929532
H	-0.52993	-5.77726	1.186775
H	0.757515	-3.2994	4.470848
H	-0.19259	-5.44395	3.632582
C	-1.78145	-0.27615	2.422028
C	-1.13819	0.02041	3.632032
C	-2.56602	-1.42819	2.310944
C	-1.30663	-0.81704	4.729837
H	-0.51144	0.91143	3.721008
C	-2.71796	-2.26931	3.411377
H	-3.07021	-1.6662	1.372365
C	-2.098	-1.96101	4.621111
H	-0.81082	-0.57809	5.673129
H	-3.33016	-3.16915	3.321721
H	-2.2252	-2.62039	5.482616
C	-2.03102	2.503397	1.709302
C	-3.05169	2.618267	2.664021
C	-1.38018	3.652023	1.241714
C	-3.41907	3.874756	3.137422
H	-3.55617	1.724638	3.039214
C	-1.75244	4.906582	1.72149
H	-0.58174	3.566729	0.50052
C	-2.77059	5.018253	2.66708
H	-4.21527	3.961885	3.880001
H	-1.23991	5.799228	1.356649
H	-3.05902	6.001932	3.044667
C	-0.75572	2.295114	-2.27108
H	-1.66701	1.811259	-1.9154
C	2.912729	0.938708	2.279151
N	2.584752	0.376978	3.24127

C50H39CuN3OP2(1+)

S_0, N-Cu-N plane and P-Cu-P plane angle: 81.93°

T_1, N-Cu-N plane and P-Cu-P plane angle:61.75°

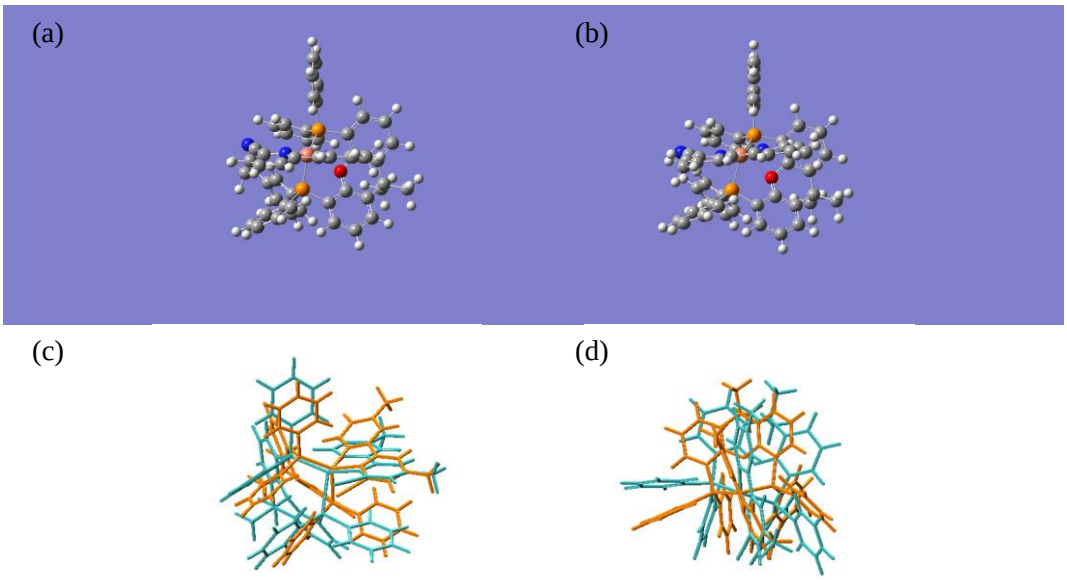

Fig.S14: Optimized ground state (S_0) geometry (a) and the first triplet excited state (T_1) geometry (b) of **Cu-2** cation in DCM optimized by Gaussian Calculation together with comparison of S_0 (orange) and T_1 (cyan) geometry (c, d).

Cartesian Co-ordinates (XYZ format) of S_0 state of **Cu-2.**

C	-0.67082	-0.98726	3.735538
C	-0.08804	-0.42181	4.868586
C	1.15952	0.199015	4.792867
C	1.861477	0.254427	3.585879
C	1.250052	-0.31496	2.468404
C	-0.00877	-0.92565	2.506398
C	3.264999	0.823483	3.40359
C	3.305187	1.479109	2.026379
C	2.620501	0.843418	0.987103
O	1.876049	-0.27082	1.253425
C	4.009984	2.642617	1.709091
C	4.034436	3.130384	0.402371
C	3.342642	2.473995	-0.61308
C	2.610378	1.315745	-0.33162
P	-0.67221	-1.48679	0.90074
P	1.48961	0.50353	-1.53458
C	3.636391	1.799525	4.513832
C	4.260878	-0.35586	3.401255
Cu	-0.5193	0.270095	-0.55142
N	-1.10236	2.023704	0.440131
C	-2.37238	2.389099	0.202279

C	-2.90419	3.571095	0.718816
C	-2.11579	4.405184	1.515434
C	-0.79884	3.995115	1.755671
C	-3.16281	1.447167	-0.62542
N	-2.45699	0.512794	-1.27304
C	-3.12185	-0.39909	-1.99636
C	-4.50814	-0.44563	-2.08885
C	-5.263	0.517507	-1.4069
C	-4.56026	1.48126	-0.68573
H	-1.65041	-1.46519	3.800852
H	-0.612	-0.46595	5.825565
H	1.593955	0.634442	5.693862
H	4.554261	3.177242	2.488667
H	4.59595	4.038628	0.174406
H	3.34956	2.876164	-1.62782
H	4.659384	2.175596	4.373981
H	3.617512	1.29825	5.49135
H	2.949607	2.658302	4.548495
H	4.018403	-1.08246	2.611829
H	5.283782	0.012025	3.230061
H	4.231016	-0.8779	4.36954
H	-3.93103	3.859278	0.491401
H	-0.12669	4.597822	2.369582
H	-4.98753	-1.22669	-2.68059
H	-5.1115	2.241421	-0.13158
C	-2.40373	-1.96026	1.223908
C	-2.89878	-3.23128	0.912264
C	-3.29565	-0.9586	1.638811
C	-4.26571	-3.49388	1.011298
H	-2.21534	-4.01712	0.582739
C	-4.65664	-1.22756	1.744887
H	-2.92009	0.039938	1.878418
C	-5.14628	-2.49559	1.424667
H	-4.64288	-4.48857	0.762371
H	-5.3407	-0.44018	2.070124
H	-6.21616	-2.70395	1.498676
C	0.212621	-3.05121	0.597192
C	0.789723	-3.78318	1.642591
C	0.315499	-3.52169	-0.71702
C	1.460359	-4.9742	1.372984
H	0.718638	-3.41833	2.670051
C	0.975923	-4.72015	-0.97982
H	-0.11907	-2.95183	-1.54073
C	1.551899	-5.4451	0.062561

H	1.91334	-5.5382	2.191802
H	1.052443	-5.07851	-2.00821
H	2.079311	-6.3789	-0.14667
C	2.369692	-1.00518	-2.06479
C	1.869456	-1.69149	-3.18064
C	3.474872	-1.51715	-1.37947
C	2.482413	-2.86283	-3.61412
H	0.991319	-1.31272	-3.71032
C	4.074805	-2.70152	-1.80738
H	3.87614	-0.99152	-0.51065
C	3.584939	-3.37236	-2.92598
H	2.088836	-3.38763	-4.4878
H	4.935354	-3.09735	-1.26308
H	4.059449	-4.29774	-3.26074
C	1.573436	1.595214	-2.99338
C	2.644404	1.567309	-3.8961
C	0.52594	2.503222	-3.1895
C	2.666992	2.445353	-4.97736
H	3.460176	0.854147	-3.75362
C	0.554494	3.384516	-4.26912
H	-0.31686	2.510015	-2.49197
C	1.624598	3.355456	-5.16304
H	3.502981	2.419358	-5.68022
H	-0.26604	4.090282	-4.41735
H	1.644697	4.041307	-6.01331
C	-0.33815	2.810136	1.199801
H	0.68941	2.479608	1.369196
C	-2.31492	-1.36165	-2.6975
N	-1.67288	-2.13671	-3.27147
C	-6.75583	0.479139	-1.42826
H	-7.13338	0.352189	-2.45314
H	-7.11351	-0.38212	-0.84121
H	-7.1909	1.390793	-0.99933
C	-2.65526	5.672162	2.097111
H	-3.6233	5.941861	1.655155
H	-2.79559	5.560481	3.184227
H	-1.9526	6.504801	1.947112

C52H43CuN3OP2(1+)

Cartesian Co-ordinates (XYZ format) of T_1 state of **Cu-2.**

C	-0.78754	1.0282	-3.59769
C	-0.22817	0.495417	-4.7572
C	1.036888	-0.09425	-4.73552
C	1.783848	-0.15268	-3.55626

C	1.188094	0.374546	-2.41133
C	-0.08253	0.955739	-2.39252
C	3.220233	-0.65887	-3.44426
C	3.372291	-1.29588	-2.06664
C	2.683111	-0.71296	-1.00444
O	1.849357	0.343725	-1.21722
C	4.179523	-2.39502	-1.76194
C	4.288611	-2.87146	-0.45346
C	3.567991	-2.28156	0.582439
C	2.73679	-1.19116	0.306663
P	-0.67861	1.547691	-0.77077
P	1.526792	-0.49639	1.471976
C	3.572476	-1.63293	-4.56293
C	4.156208	0.566938	-3.50874
Cu	-0.62488	-0.43309	0.593139
N	-0.90471	-2.29731	-0.07296
C	-2.2403	-2.60494	-0.18473
C	-2.6312	-3.78784	-0.8565
C	-1.69399	-4.64242	-1.40063
C	-0.32338	-4.2903	-1.26323
C	-3.13866	-1.66205	0.401255
N	-2.54195	-0.54414	0.946544
C	-3.32394	0.35266	1.603214
C	-4.69313	0.257816	1.677344
C	-5.34508	-0.84251	1.045559
C	-4.54437	-1.79061	0.440283
H	-1.77396	1.493467	-3.6277
H	-0.78409	0.54501	-5.69538
H	1.450713	-0.49915	-5.66009
H	4.739271	-2.89229	-2.55529
H	4.933194	-3.72701	-0.24355
H	3.622805	-2.6856	1.595029
H	4.617279	-1.96144	-4.47567
H	3.478249	-1.14734	-5.54381
H	2.923219	-2.52071	-4.54761
H	3.922719	1.290299	-2.71329
H	5.203693	0.251283	-3.39147
H	4.046954	1.075066	-4.47857
H	-3.69251	-4.0235	-0.94931
H	0.465859	-4.92588	-1.66753
H	-5.26085	1.016821	2.216446
H	-5.00854	-2.66361	-0.02173
C	-2.39946	2.060166	-1.06779
C	-2.85579	3.344458	-0.754

C	-3.30782	1.095405	-1.53111
C	-4.20785	3.656256	-0.89498
H	-2.15855	4.103309	-0.39381
C	-4.65288	1.415422	-1.67818
H	-2.96732	0.085084	-1.77018
C	-5.10694	2.695009	-1.35302
H	-4.55769	4.660065	-0.64408
H	-5.35224	0.656874	-2.03605
H	-6.16576	2.94229	-1.45823
C	0.279874	3.063365	-0.46512
C	1.091738	3.620092	-1.46176
C	0.185243	3.688914	0.784788
C	1.797035	4.794415	-1.20939
H	1.17194	3.141404	-2.43977
C	0.880244	4.872098	1.022128
H	-0.43649	3.260973	1.574026
C	1.6885	5.424669	0.029714
H	2.429983	5.221717	-1.99046
H	0.797679	5.356662	1.996916
H	2.239736	6.347644	0.223878
C	2.173695	1.094956	2.056202
C	1.555152	1.68083	3.169766
C	3.253627	1.732905	1.438912
C	2.040493	2.880091	3.680441
H	0.696913	1.197181	3.643309
C	3.723764	2.942228	1.947434
H	3.738108	1.283695	0.569753
C	3.126346	3.510206	3.071416
H	1.561754	3.329213	4.553258
H	4.566879	3.439677	1.463409
H	3.502831	4.454769	3.470424
C	1.592568	-1.5911	2.922305
C	2.607228	-1.45545	3.880454
C	0.632444	-2.6014	3.060061
C	2.660528	-2.33121	4.961411
H	3.352796	-0.66287	3.782549
C	0.692054	-3.47392	4.145294
H	-0.16317	-2.70606	2.318277
C	1.704518	-3.33997	5.094227
H	3.452519	-2.2243	5.705929
H	-0.06035	-4.25844	4.250566
H	1.747813	-4.02252	5.946094
C	0.008027	-3.12838	-0.60526
H	1.054258	-2.83979	-0.48595

C	-2.64147	1.425384	2.264962
N	-2.07473	2.270038	2.823804
C	-6.83626	-0.93594	1.060764
H	-7.22593	-0.91051	2.09099
H	-7.28344	-0.07858	0.530745
H	-7.18895	-1.85815	0.580021
C	-2.08281	-5.89772	-2.11369
H	-3.17236	-6.0325	-2.13845
H	-1.7099	-5.88816	-3.15043
H	-1.63487	-6.77763	-1.62462

C52H43CuN3OP2(1+)

S_0, N-Cu-N plane and P-Cu-P plane angle: 88.45°

T_1, N-Cu-N plane and P-Cu-P plane angle: 63.87°

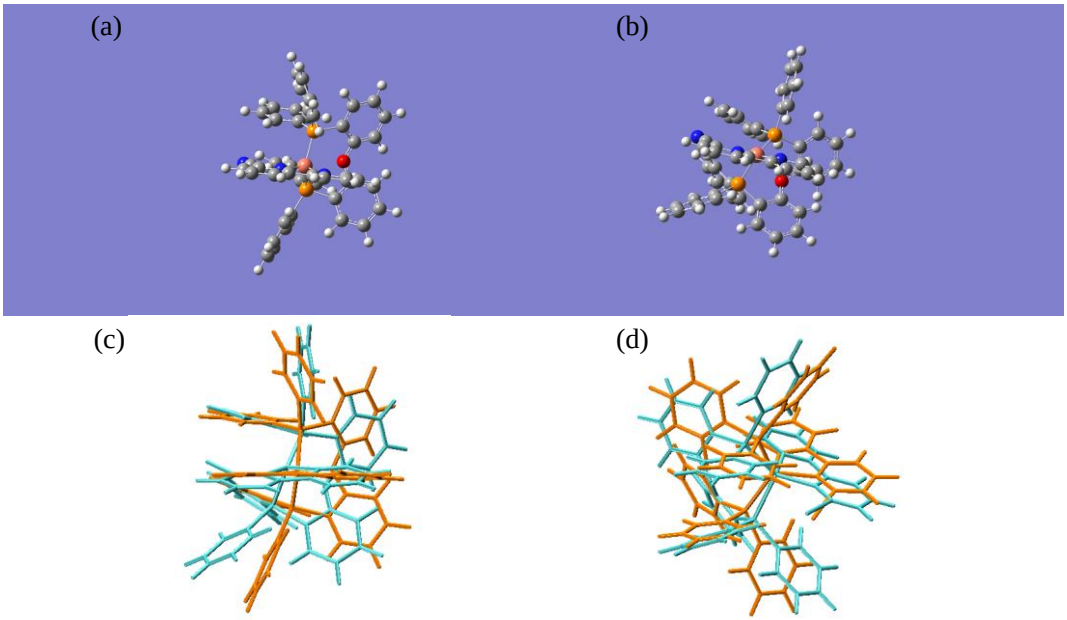

Fig.S15: Optimized ground state (S_0) geometry (a) and the first triplet excited state (T_1) geometry (b) of **Cu-3** cation in DCM optimized by Gaussian Calculation together with comparison of S_0 (orange) and T_1 (cyan) geometry (c, d).

Cartesian Co-ordinates (XYZ format) of S_0 state of **Cu-3.**

C	0.868833	4.825518	-1.20306
C	0.677195	4.928888	-2.57302
C	0.234218	3.814998	-3.28051
C	0.019546	2.636966	-2.56677
N	0.224923	2.52505	-1.24704
C	0.629206	3.603324	-0.5609
C	0.777424	3.426218	0.902642
N	0.412448	2.226143	1.384836
C	0.48766	1.995475	2.695338
C	0.9446	2.948897	3.599548
Cu	0.029828	0.790464	-0.10131
C	3.369807	-2.0491	1.725766
C	3.603388	-2.88241	2.816755
C	2.528043	-3.37677	3.55233
C	1.225413	-3.00764	3.225068
C	1.003566	-2.12345	2.169045
C	2.069935	-1.66501	1.376457
O	-0.2555	-1.75341	1.786262
C	-1.16203	-1.12146	2.589134
C	-1.12391	-1.10029	3.982532

C	-2.12053	-0.41868	4.68321
C	-3.14988	0.230607	4.007615
C	-3.17023	0.221811	2.613461
C	-2.17627	-0.43995	1.889011
P	1.725776	-0.71778	-0.15837
P	-1.97041	-0.25711	0.082109
C	-0.47211	1.472505	-3.25175
N	-0.88212	0.560719	-3.83628
C	-3.44655	0.68868	-0.42562
C	-3.34044	2.08392	-0.49187
C	-4.44207	2.856268	-0.85434
C	-5.65319	2.237628	-1.16552
C	-5.762	0.8474	-1.10922
C	-4.66415	0.072865	-0.73888
C	-2.00921	-2.11755	-1.97245
C	-2.22921	-3.3665	-2.54688
C	-2.25138	-1.9221	-0.60674
C	-2.6758	-4.43101	-1.76368
C	-2.9095	-4.24157	-0.40217
C	-2.70326	-2.98968	0.176051
C	3.666917	1.250883	-0.05616
C	3.361089	-0.01391	-0.57692
C	4.898733	1.843709	-0.32214
C	5.831661	1.182914	-1.1222
C	5.531184	-0.07341	-1.64868
C	4.302309	-0.67354	-1.37649
C	1.486208	-2.04721	-1.39143
C	1.325406	-3.39075	-1.03914
C	1.106385	-4.35105	-2.02634
C	1.05593	-3.98107	-3.36851
C	1.213458	-2.64102	-3.7249
C	1.417842	-1.67813	-2.74186
C	1.344929	4.18829	3.109473
C	1.258709	4.433306	1.742933
H	1.193864	5.695632	-0.63464
H	0.860008	5.873658	-3.08721
H	0.051139	3.849246	-4.35451
H	0.16708	1.009487	3.037988
H	0.986148	2.714186	4.663951
H	4.210863	-1.69619	1.125487
H	4.625534	-3.16614	3.074912
H	2.697537	-4.06469	4.383462
H	0.379454	-3.42546	3.770876
H	-0.32256	-1.59336	4.529624

H	-2.08368	-0.40391	5.774692
H	-3.9319	0.753094	4.561789
H	-3.95773	0.753649	2.075218
H	-2.38561	2.562149	-0.25658
H	-4.35224	3.943928	-0.90236
H	-6.51559	2.841125	-1.45831
H	-6.7091	0.362059	-1.35617
H	-4.75114	-1.01557	-0.69686
H	-1.64641	-1.29435	-2.59213
H	-2.03637	-3.5107	-3.61187
H	-2.83842	-5.41264	-2.21511
H	-3.25927	-5.07198	0.215812
H	-2.89783	-2.84436	1.241166
H	2.934383	1.771434	0.565124
H	5.127569	2.828934	0.090694
H	6.795279	1.649982	-1.33861
H	6.259618	-0.59308	-2.27546
H	4.073653	-1.65832	-1.79007
H	1.373468	-3.69661	0.007527
H	0.975274	-5.39701	-1.74014
H	0.88592	-4.73645	-4.13919
H	1.165812	-2.34027	-4.77394
H	1.531334	-0.63063	-3.02978
H	1.72016	4.961531	3.782478
H	1.568492	5.398487	1.343927
C47H35CuN3OP2(1+)			

Cartesian Co-ordinates (XYZ format) of T_1 state of **Cu-3.**

C	-3.29348	3.429845	-1.4952
C	-3.96257	2.857331	-2.55883
C	-3.51646	1.609347	-3.05801
C	-2.44857	1.000631	-2.43656
N	-1.80195	1.537686	-1.3623
C	-2.19579	2.780265	-0.9009
C	-1.41674	3.30703	0.179206
N	-0.32392	2.557863	0.536454
C	0.464911	2.955342	1.548758
C	0.234382	4.108587	2.267838
Cu	-0.30486	0.78034	-0.37155
C	4.202718	0.708159	1.196835
C	4.906482	0.579177	2.391617
C	4.305188	-0.03267	3.490988
C	2.989907	-0.48886	3.419088
C	2.277048	-0.31241	2.235865

C	2.883302	0.254057	1.104944
O	0.99675	-0.75484	2.060556
C	-0.07174	-0.38066	2.823845
C	0.010561	0.25082	4.0612
C	-1.16386	0.527961	4.760377
C	-2.40498	0.167565	4.241283
C	-2.47999	-0.42749	2.984492
C	-1.31936	-0.68555	2.247963
P	1.94482	0.259613	-0.45455
P	-1.33141	-1.18792	0.492736
C	-1.96615	-0.26116	-2.91089
N	-1.55931	-1.27656	-3.29994
C	-3.09482	-1.33547	0.05975
C	-3.90272	-0.18851	0.112558
C	-5.24208	-0.25682	-0.2568
C	-5.7871	-1.46525	-0.69262
C	-4.9906	-2.60791	-0.74224
C	-3.65	-2.5481	-0.36481
C	-0.46421	-3.44366	-0.86347
C	0.026446	-4.74274	-0.96099
C	-0.64165	-2.86152	0.398975
C	0.361349	-5.45583	0.18996
C	0.1971	-4.87129	1.445406
C	-0.30936	-3.57813	1.554091
C	2.35109	2.754022	-1.63845
C	2.818674	1.437383	-1.5359
C	3.026854	3.672752	-2.43909
C	4.165476	3.28264	-3.14278
C	4.6296	1.969749	-3.04918
C	3.959283	1.045832	-2.25168
C	2.274179	-1.36027	-1.20733
C	2.990762	-2.36548	-0.55172
C	3.256795	-3.56453	-1.21088
C	2.817324	-3.75881	-2.5193
C	2.088335	-2.76128	-3.16827
C	1.80766	-1.56704	-2.51306
C	-0.88337	4.898225	1.917673
C	-1.69989	4.500557	0.8825
H	-3.60797	4.402962	-1.11622
H	-4.81079	3.363967	-3.02004
H	-3.99614	1.127837	-3.90996
H	1.323781	2.317815	1.774493
H	0.906902	4.39183	3.077611
H	4.680861	1.162455	0.326764

H	5.934283	0.940538	2.45752
H	4.865814	-0.16537	4.418635
H	2.529697	-0.99477	4.268134
H	0.973588	0.534237	4.482699
H	-1.09748	1.025068	5.730487
H	-3.31842	0.362852	4.805691
H	-3.4534	-0.68153	2.562768
H	-3.48724	0.765302	0.443494
H	-5.85937	0.643001	-0.21256
H	-6.83627	-1.5157	-0.99256
H	-5.41325	-3.55813	-1.076
H	-3.03699	-3.44994	-0.40467
H	-0.71747	-2.88707	-1.76925
H	0.157439	-5.19557	-1.94558
H	0.754391	-6.47185	0.108085
H	0.45721	-5.42739	2.3489
H	-0.45278	-3.13028	2.539618
H	1.453853	3.060745	-1.09724
H	2.655808	4.696919	-2.5171
H	4.691484	4.003198	-3.77319
H	5.518646	1.660867	-3.60337
H	4.321405	0.017169	-2.18833
H	3.353674	-2.21255	0.46661
H	3.81598	-4.34952	-0.69738
H	3.034706	-4.69764	-3.03368
H	1.727395	-2.91625	-4.18723
H	1.226822	-0.79272	-3.02133
H	-1.10241	5.81785	2.46404
H	-2.57127	5.097105	0.611048
C47H35CuN3OP2(1+)			

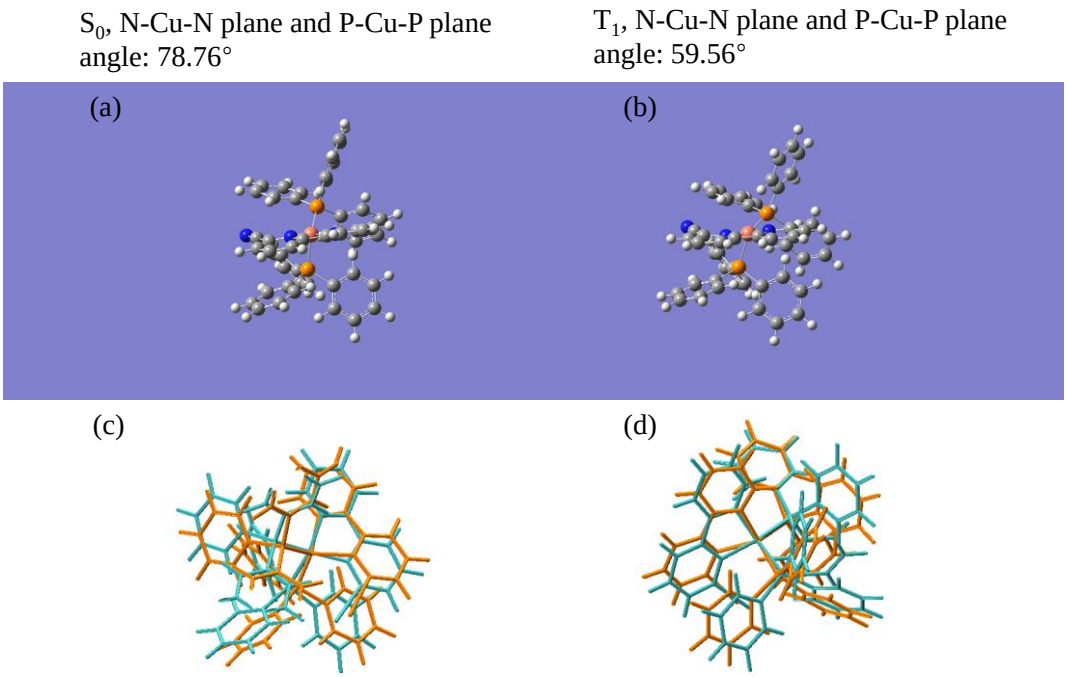

Fig.S16: Optimized ground state (S_0) geometry (a) and the first triplet excited state (T_1) geometry (b) of **Cu-4** cation in DCM optimized by Gaussian Calculation together with comparison of S_0 (orange) and T_1 (cyan) geometry (c, d).

Cartesian Co-ordinates (XYZ format) of S_0 state of **Cu-4.**

C	1.710354	-4.41191	1.087101
C	1.102721	-4.69806	2.305056
C	0.223773	-3.77	2.855673
C	-0.01961	-2.59344	2.155338
C	1.41767	-3.20299	0.451098
C	2.030448	-2.80723	-0.83828
C	2.018271	-1.33007	-2.60818
C	3.138287	-1.91566	-3.19604
C	3.711306	-3.00816	-2.55283
C	3.152423	-3.45982	-1.36631
Cu	0.155636	-0.66645	-0.23226
P	-2.07674	-0.28476	-0.32391
C	-3.1262	-1.77922	-0.41926
C	-4.52255	-1.70577	-0.32028
C	-5.28939	-2.86429	-0.40017
C	-4.67027	-4.10342	-0.58398
C	-3.28325	-4.18174	-0.69047
C	-2.51244	-3.02155	-0.60916
C	-2.80672	0.832869	-1.5723
C	-3.84154	1.732363	-1.2884

C	-4.34792	2.554168	-2.29388
C	-3.83182	2.481491	-3.58787
C	-2.81034	1.576915	-3.87874
C	-2.30032	0.757202	-2.87507
C	-2.50864	0.470508	1.286576
C	-2.95106	-0.31743	2.357585
C	-3.1056	0.242804	3.626315
C	-2.83112	1.593677	3.836182
C	-2.40355	2.386285	2.77031
C	-2.23702	1.830186	1.504958
C	3.047256	1.082457	-0.4543
P	1.417823	1.137463	0.36753
C	3.400319	1.9601	-1.48359
C	4.600751	1.783202	-2.17343
C	5.456736	0.736073	-1.8384
C	5.112351	-0.13876	-0.80526
C	3.912759	0.028082	-0.12126
C	0.697274	2.766987	-0.02686
C	-2E-05	2.89754	-1.23616
C	-0.67573	4.078001	-1.53517
C	-0.66776	5.134977	-0.62412
C	0.032168	5.013508	0.576986
C	0.715432	3.835624	0.876925
C	1.79975	1.223467	2.148613
C	0.80937	0.806991	3.047627
C	1.028142	0.884451	4.421053
C	2.243432	1.367221	4.906653
C	3.235569	1.779796	4.016098
C	3.016114	1.712735	2.641227
C	1.396318	-0.20424	-3.24962
N	0.916528	0.694214	-3.80162
H	2.391292	-5.13197	0.634315
H	1.313608	-5.63962	2.815679
H	-0.27324	-3.94965	3.809814
H	-0.70934	-1.84296	2.547753
H	3.542544	-1.51647	-4.1261
H	4.593228	-3.49606	-2.97052
H	3.601391	-4.30045	-0.8386
H	-5.01285	-0.73901	-0.18027
H	-6.3772	-2.80196	-0.32157
H	-5.27557	-5.01076	-0.64758
H	-2.79658	-5.14838	-0.83877
H	-1.42445	-3.07583	-0.69592
H	-4.24815	1.805393	-0.27751

H	-5.15022	3.258585	-2.0624
H	-4.22628	3.132735	-4.37138
H	-2.3972	1.516259	-4.88806
H	-1.48819	0.064348	-3.10336
H	-3.18201	-1.3739	2.20149
H	-3.44937	-0.3824	4.453599
H	-2.95261	2.02987	4.830208
H	-2.18531	3.445564	2.923406
H	-1.88621	2.459604	0.684876
H	2.733427	2.781143	-1.75576
H	4.865986	2.47267	-2.97818
H	6.395069	0.600252	-2.38096
H	5.779702	-0.96066	-0.53591
H	3.646307	-0.66507	0.681604
H	-0.03266	2.067316	-1.94433
H	-1.22796	4.158556	-2.47428
H	-1.21215	6.0552	-0.84857
H	0.040838	5.839716	1.291744
H	1.244605	3.740706	1.82749
H	-0.14557	0.436514	2.668645
H	0.245214	0.563412	5.111882
H	2.419245	1.42216	5.983552
H	4.187083	2.160784	4.394261
H	3.794362	2.04145	1.948572
N	0.557493	-2.32019	0.985153
N	1.473521	-1.75922	-1.46061

C47H37CuN3P2(1+)

Cartesian Co-ordinates (XYZ format) of T_1 state of **Cu-4.**

C	-1.4563	4.58447	0.903743
C	-0.54357	5.007086	1.84383
C	0.612479	4.232804	2.086274
C	0.776237	3.070161	1.3654
C	-1.23169	3.385498	0.189446
C	-2.10307	2.850026	-0.81305
C	-2.44905	1.107076	-2.36681
C	-3.58543	1.702918	-2.86884
C	-4.02144	2.918462	-2.29265
C	-3.26516	3.484687	-1.28461
Cu	-0.18716	0.836703	-0.41044
P	2.048475	0.143172	-0.36943
C	3.181033	1.465557	-0.90474
C	4.568002	1.265222	-0.8426
C	5.432031	2.251906	-1.3061

C	4.920208	3.435756	-1.84277
C	3.542957	3.631303	-1.91855
C	2.671275	2.648194	-1.45098
C	2.376267	-1.21395	-1.53621
C	3.293787	-2.23845	-1.27576
C	3.525783	-3.21893	-2.23786
C	2.854978	-3.17822	-3.46034
C	1.952525	-2.14884	-3.72759
C	1.71431	-1.16871	-2.76885
C	2.629459	-0.40701	1.261664
C	3.31382	0.464372	2.119827
C	3.605636	0.071463	3.425129
C	3.224929	-1.19014	3.88094
C	2.556699	-2.06582	3.025041
C	2.256508	-1.67741	1.723447
C	-3.08646	-1.06735	-0.05014
P	-1.33674	-1.06892	0.452601
C	-3.63534	-2.06791	-0.85697
C	-4.96005	-1.96752	-1.28149
C	-5.7379	-0.87508	-0.90258
C	-5.1945	0.11948	-0.08652
C	-3.87393	0.027632	0.337444
C	-0.71935	-2.76452	0.22732
C	-0.37332	-3.18428	-1.06499
C	0.153732	-4.458	-1.26497
C	0.348308	-5.31374	-0.18116
C	0.00105	-4.90001	1.105371
C	-0.53431	-3.63081	1.313238
C	-1.41233	-0.78008	2.250914
C	-0.43405	0.003111	2.872684
C	-0.47242	0.217397	4.248832
C	-1.49017	-0.35116	5.012008
C	-2.47278	-1.13074	4.397815
C	-2.44021	-1.34286	3.022535
C	-1.96427	-0.09813	-2.96321
N	-1.55414	-1.05957	-3.46984
H	-2.35636	5.168638	0.711709
H	-0.71522	5.932807	2.396633
H	1.363173	4.533347	2.817301
H	1.65525	2.442069	1.521795
H	-4.11978	1.236799	-3.69655
H	-4.92346	3.410628	-2.65707
H	-3.5634	4.441757	-0.85488
H	4.974536	0.337156	-0.43259

H	6.511575	2.095149	-1.25258
H	5.602031	4.207693	-2.20682
H	3.140301	4.553749	-2.34224
H	1.592172	2.806963	-1.50781
H	3.826267	-2.27928	-0.32374
H	4.236789	-4.02112	-2.02867
H	3.036741	-3.95324	-4.20841
H	1.418423	-2.11281	-4.67921
H	0.996833	-0.37313	-2.98143
H	3.633298	1.448808	1.770525
H	4.13905	0.757116	4.086928
H	3.453376	-1.4932	4.905043
H	2.258049	-3.05754	3.371796
H	1.7239	-2.36787	1.068306
H	-3.0316	-2.92508	-1.16089
H	-5.38394	-2.75123	-1.91315
H	-6.77377	-0.79844	-1.24077
H	-5.80102	0.975881	0.215605
H	-3.45289	0.812104	0.9716
H	-0.51629	-2.52055	-1.9201
H	0.42425	-4.77455	-2.27422
H	0.773477	-6.30757	-0.33871
H	0.150293	-5.56813	1.956486
H	-0.78837	-3.30839	2.324725
H	0.369559	0.447648	2.285628
H	0.297322	0.831962	4.720119
H	-1.52303	-0.18383	6.091008
H	-3.27311	-1.57419	4.994296
H	-3.21743	-1.94478	2.545867
N	-0.10597	2.645727	0.445868
N	-1.72773	1.623426	-1.32684

C47H37CuN3P2(1+)

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2 T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.