Supporting Information

Nanostructures of Tetranuclear Copper(I) Complexes with Short Cu(I)···Cu(I) Contacts: Crystallization Induced Emission Enhancement

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Experimental Section

All starting materials were purchased from commercial sources and used as received. The solvents used for synthesis were of analytical grade unless stated otherwise. The solvents used for nanostructure preparations and photophysical measurements were of HPLC grade. The ligand N,N'-bis(5,7-dimethyl-1,8-naphthyridine-2-yl)-amine, [1] was prepared in accordance with literature methods.

Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan MAT 95 mass spectrometer using 3-nitrobenzyl alcohol as matrix. ^{1}H and ^{31}P NMR spectra were recorded with Avance 400 FT-NMR spectrometers. Elemental analyses were performed by Beijing Institute of Chemistry, Chinese Academy of Sciences. UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis spectrophotometer. Steady-state emission spectra were obtained on a SPEX 1681 Fluorolog-2 series F111AI fluorescence spectrophotometer. Emission lifetime measurements were performed with a Quanta Ray DCR-3 pulsed Nd:YAG laser system (pulse output 355 nm, 8 ns). Luminescent quantum yields were referenced to degassed $[Ru(bpy)_3](ClO_4)_2$ in acetonitrile ($\Phi_r = 0.062$) with estimated error of ±15%.

TEM and SAED were performed on a Philips Tecnai G2 20 S-TWIN transmission electron microscope with an accelerating voltage of 200 kV. The TEM images and SAED patterns were taken by Gatan MultiScan Camera Model 794. TEM samples were prepared by depositing a few drops of suspensions on the formvar-coated copper grids and the excess solvent was removed by a piece of filter paper. The SEM images were taken on a Hitachi S-4800 field emission scanning electron microscope operating at 5.0 kV. SEM samples were prepared by drop-casting suspensions onto silicon wafers. Gold sputtering was applied before SEM

1 Y. Chen, W. F. Fu, J. L. Li, X. J. Zhao, X. M. Ou, *New J. Chem.* **2007**, 1785–1788.

observations. AFM images were recorded on a NanoScope IIIa Scanning Probe Microscope (Digital Instruments, USA) in the tapping mode with a standard etched silicon probe. The AFM images were analyzed with the free software Gwyddion (http://gwyddion.net/).

The powder XRD patterns were recorded on a Bruker D8 Powder X-ray Diffractometer operating with graphite monochromatized CuK_α radiation (λ = 1.54056 Å) and a nickel filter. The scanning rate was 0.5° min^{-1} in the 2θ range from 3 to 50°.

Single crystals of **1**–**3** suitable for x-ray structure analysis were obtained by vapor diffusion of diethyl ether into CH_2Cl_2 solutions over the period of several days. The diffraction data were collected at room temperature on a Bruker Smart CCD area detector with graphite monochromatized MoK_α radiation (λ = 0.71073 Å).

Synthesis and Characterization

A mixture of $[Cu(CH_3CN)_4]BF_4$ (0.315 g, 1.0 mmol) and N,N'-bis(1,8-naphthyridine-2-yl)amine (0.165 g, 0.5 mmol) in CH_2Cl_2 (50 mL) was stirred for 4 hours at room temperature under N_2 atmosphere, and then dcpm (0.5 mmol), dppm (0.5 mmol) or PPh_3 (1.0 mmol) was added. The resulted solution was stirred another 6 hours and then filtered. Slow diffusion of diethyl ether into the filtrate afforded crystals suitable for X-ray structural analysis.

$[Cu_4(L)_2(dcpm)_2](2BF_4)$ (1). Yield 0.31 g (65%). MS (+FAB): *m/z* 1816 [M–BF_4], 1729 [M–2BF_4]. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.21 (d, 4H, J = 8.9 Hz), 7.19 (s, 4H), 7.09 (d, 4H, J = 9.0 Hz), 3.11 (s, 12H), 2.65 (s, 12H), 1.78–1.58 (m, 28H), 1.31–1.13 (m, 32H), 0.85–0.63 (m, 20H), 0.52–0.44 (m, 8H), 0.11 (br s, 4H); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 14.65 (J_{PP} =

131.9 Hz), 9.60 (J_{PP} = 133.1 Hz). Elemental analysis Calcd for $C_{90}H_{128}B_2Cu_4F_8N_{10}P_4$ (1901.76): C, 56.84; H, 6.78; N, 7.37; found: C, 56.66; H, 7.26; N, 7.27.

$[Cu_4(L)_2(dppm)_2](2BF_4)$ (2). Yield 0.27 g (58%). MS (+FAB): *m/z* 1767 [M–BF_4], 1680 [M–$2BF_4$]. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.91 (d, 4H, J = 9.0 Hz), 7.23–7.14 (m, 12H), 7.11 (s, 4H), 7.06 (t, 8H, J = 7.4 Hz), 6.94 (d, 4H, J = 9.0 Hz), 6.84 (t, 4H, J = 7.3 Hz), 6.74 (t, 8H, J = 7.7 Hz), 6.57 (t, 8H, J = 7.2 Hz), 3.03 (t, 4H, J = 9.3 Hz), 2.85 (s, 12H), 2.58 (s, 12H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = –9.26 (J_{PP} = 149.8 Hz), –10.79 (J_{PP} = 151.6 Hz). Elemental analysis Calcd for $C_{90}H_{80}B_2Cu_4F_8N_{10}P_4$ (1853.38): C, 58.33; H, 4.35; N, 7.56; found: C, 57.66; H, 4.70; N, 7.33.

$[Cu(HL)PPh_3](BF_4)$ (3) Yield 0.19 g (51%). MS (+FAB): *m/z* 655 [M–BF_4]. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.39 (s, 1H, NH), 8.65 (d, 2H, J = 8.9 Hz), 7.51 (d, 2H, J = 8.9 Hz), 7.38 (t, 3H, J = 7.0 Hz), 7.27 (m, 12H), 7.16 (s, 2H), 2.65(s, 6H), 1.93 (s, 6H); ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6): δ = 5.06. Elemental analysis Calcd for $C_{38}H_{34}BCuF_4N_5P$ (742.02): C, 61.51; H, 4.62; N, 9.44; found: C, 61.65; H, 4.83; N, 9.21.

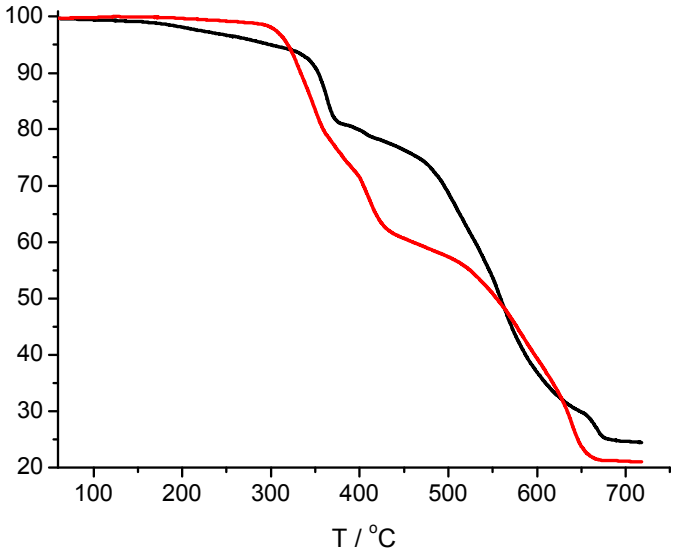


Fig. S1 TG analysis for complexes **1** (red line) and **2** (black line) under a nitrogen atmosphere.

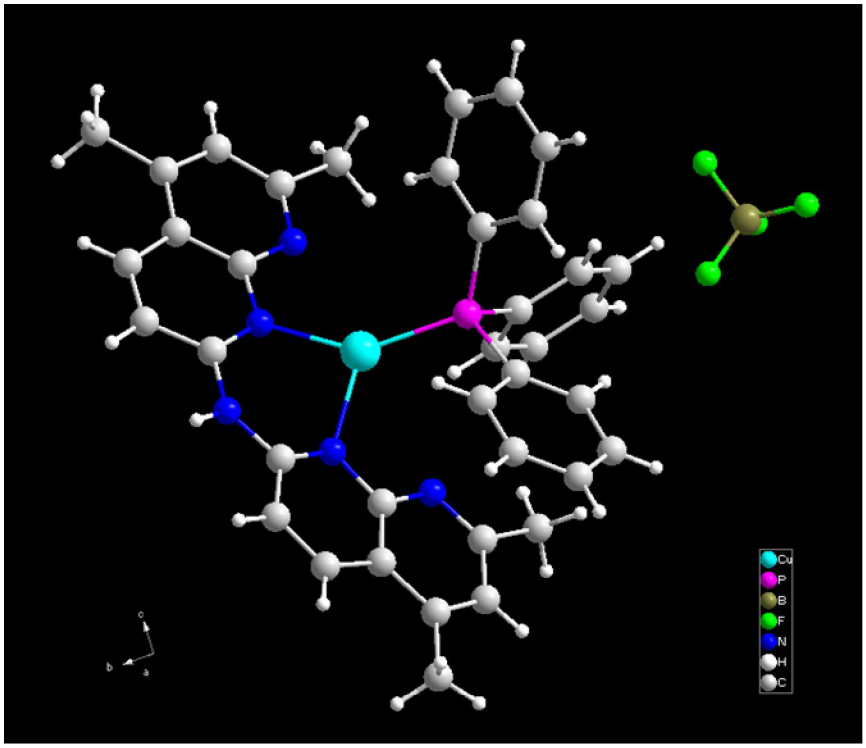


Fig. S2 Crystal structure of **3**.

Table S1 Selected Bond Lengths (Å) and Angles (°) for **1**–**3**.

	Bond Lengths /Å		Angles /°	
1	Cu(1)-Cu(2)	2.6116(5)	N(1)-Cu(1)-N(4)#1	110.19(6)
	Cu(1)-N(1)	1.9949(1)	N(2)-Cu(2)-N(5)#1	110.24(6)
	Cu(1)-N(4)#1	2.0631(1)	N(1)-Cu(1)-P(1)	130.40(5)
	Cu(2)-N(5)#1	2.0338(1)	N(4)#1-Cu(1)-P(1)	119.30(4)
	Cu(2)-N(2)	2.0608(1)	N(2)-Cu(2)-P(2)	116.13(4)
	Cu(1)-P(1)	2.2040(7)	N(5)#1-Cu(2)-P(2)	133.61(4)
	Cu(2)-P(2)	2.2215(7)		
2	Cu(1)-Cu(2)	2.6107(9)	N(1)-Cu(1)-N(5)#1	118.15(2)
	Cu(2)-Cu(2)#1	2.8223(1)	N(3)-Cu(2)-N(4)#1	118.58(2)
	Cu(1)-N(1)	2.029(4)	N(1)-Cu(1)-P(1)	107.44(1)
	Cu(1)-N(5)	2.009(4)	N(5)-Cu(1)-P(1)	134.34(1)
	Cu(2)-N(4)	1.985(4)	N(3)-Cu(2)-P(2)	108.51(1)
	Cu(2)-N(3)	2.027(4)	N(4)-Cu(2)-P(2)	132.44(1)
	Cu(1)-P(1)	2.2152(2)		
	Cu(2)-P(2)	2.1953(2)		
3	Cu(1)-N(3)	2.003(4)	N(3)-Cu(1)-N(5)	89.83(2)
	Cu(1)-N(5)	2.075(4)	N(3)-Cu(1)-P(1)	144.62(1)
	Cu(1)-P(1)	2.1776(1)	N(5)-Cu(1)-P(1)	120.92(1)

Symmetry code of **1**: #1 -x+1/2, -y+3/2, -z+1;
Symmetry code of **2**: #1 -x+1, -y+1, -z+1.

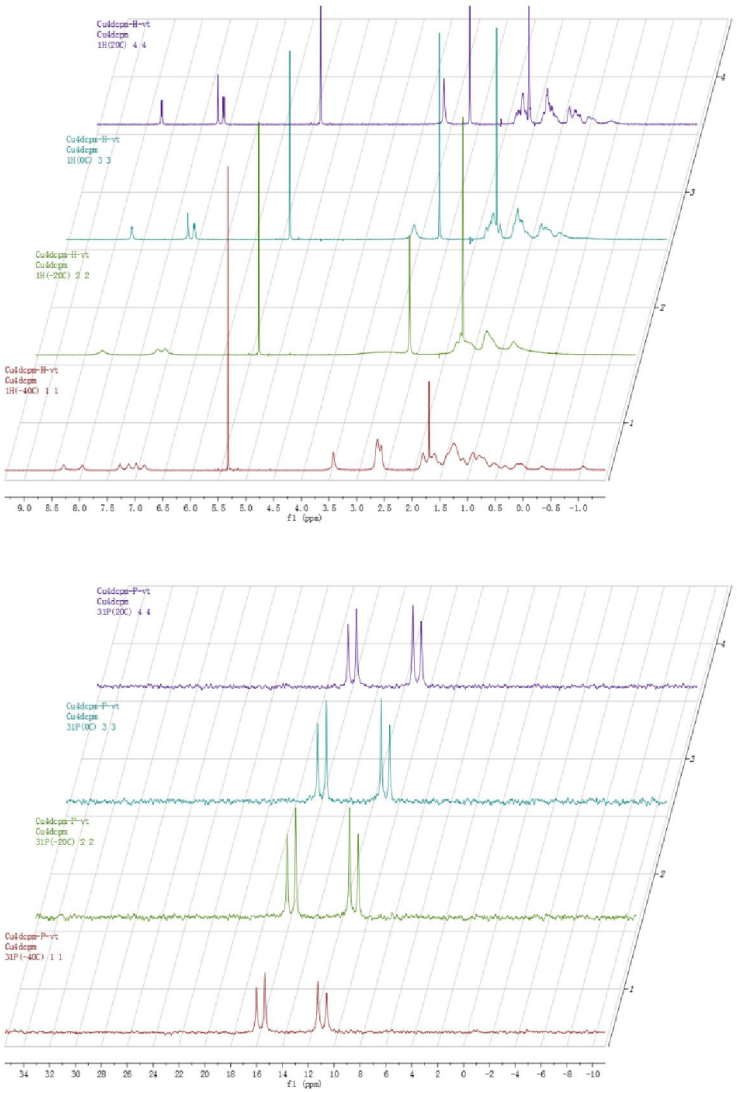
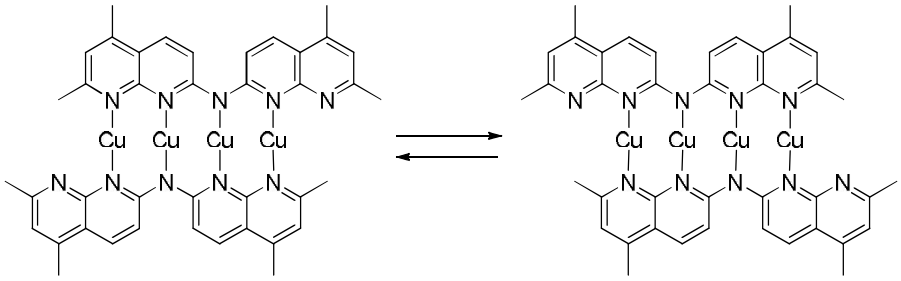


Fig. S3 Variable-temperature ^{1}H (top) and ^{31}P (bottom) NMR spectra of **1** in CD_2Cl_2 solution at 20, 0, –20 and –40 ^{o}C.



Scheme S1 Fluxional structures of complex **1** in the NMR time scale at room temperature.

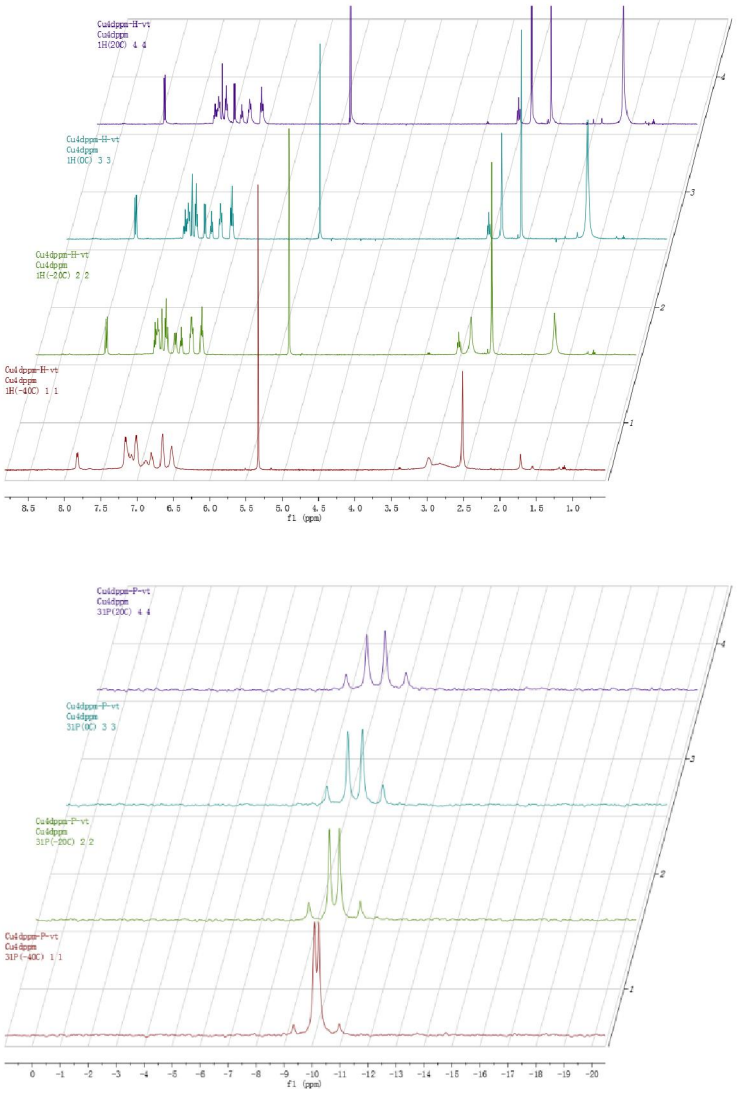


Fig. S4 Variable-temperature ^{1}H (top) and ^{31}P (bottom) NMR spectra of **2** in CD_2Cl_2 solution at 20, 0, –20 and –40 ^{o}C.

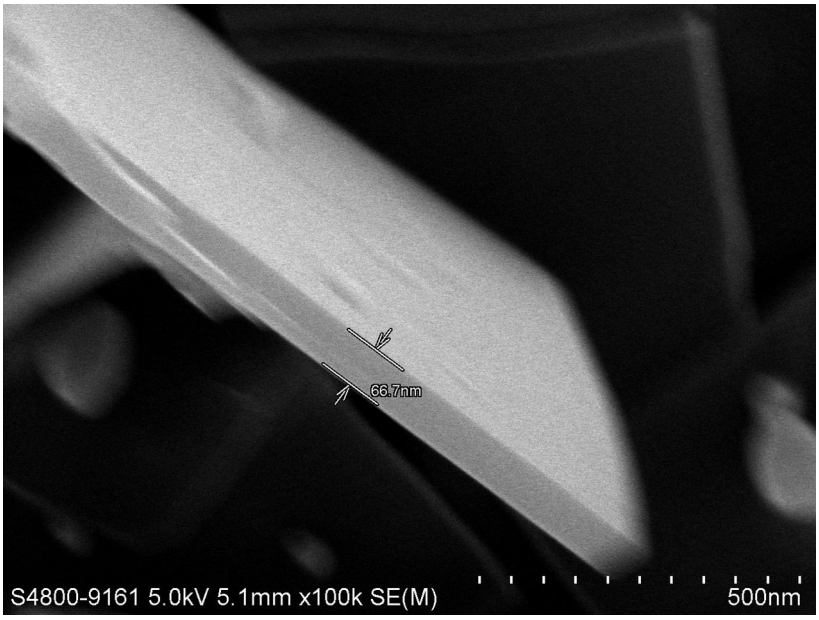


Fig. S5 Determination of the thickness of a nanosheet of **2** by measuring the dimensions of the cross-section under scanning electron microscope.

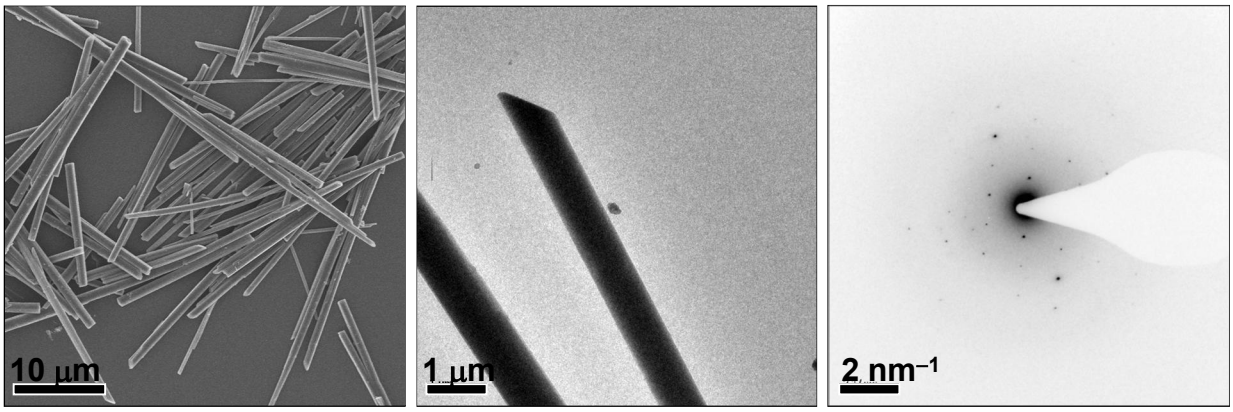


Fig. S6 Characterizations of microrods of **3**: (from left to right) SEM image, TEM image and its corresponding SAED pattern.

Table S2 Spectroscopic and Photophysical Properties of **1**–**3**.

	medium (T / K)	λ_{abs} / nm (ε / $mol^{-1}dm^3cm^{-1}$)	λ_{em} / nm (τ / μs)	φ
1	CH_2Cl_2 (298)	456 (31770) 371 (18600) 334 (24000) 298 (37970) 254 (51460)	602 (0.11)	0.01
	CH_3OH/CH_3CH_2OH (1/4)(77)		588 (155.1)	
	solid (298)		565 (0.25)	
	solid (77)		570 (60.4)	
2	CH_2Cl_2 (298)	454 (37030) 379 (16960) 366 (18080) 309 (38370)	613 (0.32)	0.02
	CH_3OH/CH_3CH_2OH (1/4)(77)		583 (267.2)	
	solid (298)		609 (0.35)	
	solid (77)		612 (112.8)	
3	CH_2Cl_2 (298)	375 (13910) 359 (18420) 329 (12880) 257 (37160)		

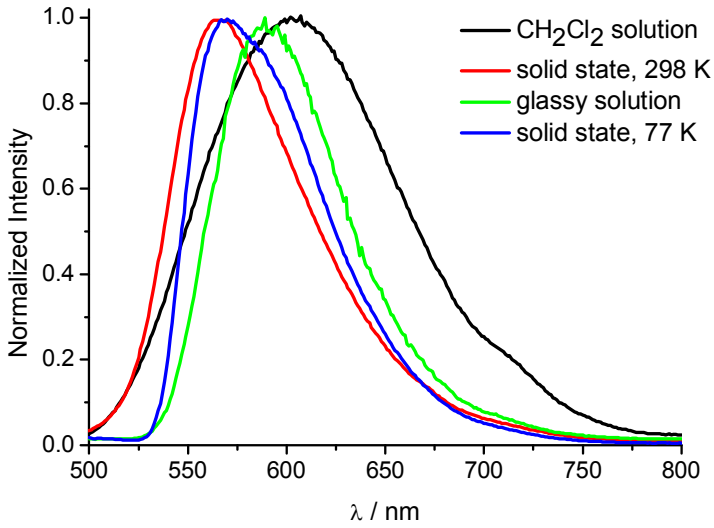


Fig. S7 Emission spectra of **1**.

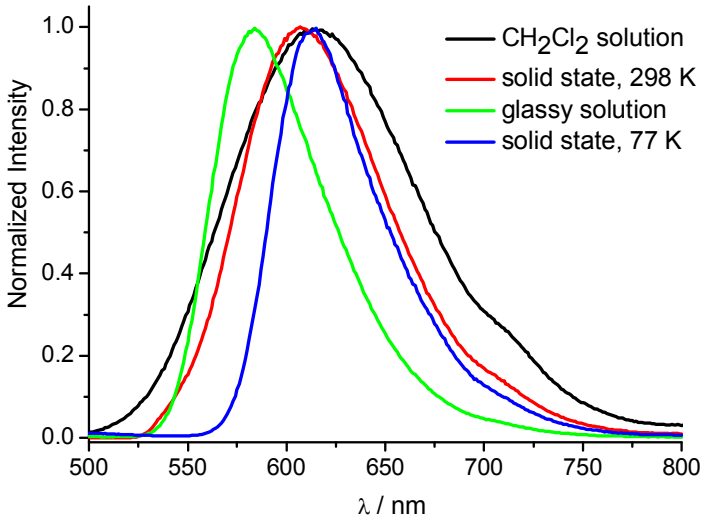


Fig. S8 Emission spectra of **2**.

Computational Details

Density Functional Theory (DFT) was employed for geometry optimizations of the ground state (S_0) and the lowest triplet excited state (T_1) of $[Cu_4(NpNNp)_2X_2]^{2+}$ (X = dcpm (**1**) or dppm (**2**)) using the density functional M05.[1] The 6-31G*[2] basis set was applied to all atoms except Cu, where the Stuttgart relativistic pseudopotential and its accompanying basis set was used instead.[3] Singlet and triplet excited state energies and their nature at both the optimized S_0 and T_1 states were then obtained using the Time-Dependent DFT (TDDFT) approach using the same density functional, M05 but with the basis set, LANL2DZ implemented in Gaussian 03.[4] All calculations were performed using the G03 suite of programs.[4]

In the present study, we have not optimized higher-lying triplet excited states (e.g. $T_{7/8}$). The emission energy from $T_{7/8}$ states was estimated by noting that the energy difference between the $T_{3/4}$ and $T_{7/8}$ states are ~1270 cm^{-1} at the optimized S_0 geometry of complex **1**. Assuming that the energy gap between the two emissive states is similar at the triplet excited state relaxed geometries, the emission energy of the higher-lying triplet excited state was estimated to be ~550 nm.

Table S3 Cartesian coordinates of complex **1** at S_0 optimized geometry.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	1.485663	0.664397	0.204517
2	29	0	3.778750	-0.473671	-0.499403
3	15	0	2.371938	2.581211	1.004164
4	15	0	5.036573	0.853143	0.860366
5	7	0	0.905791	-1.138321	1.103634
6	7	0	2.817031	-2.190782	0.307205
7	7	0	4.792737	-3.080922	-0.434110
8	7	0	-1.147587	-0.467451	1.919989
9	7	0	-3.233583	0.285021	2.590264
10	6	0	1.666527	-2.259157	0.992976
11	6	0	1.231980	-3.516985	1.538951
12	1	0	0.287281	-3.565565	2.067967
13	6	0	1.988909	-4.638314	1.375629
14	1	0	1.642911	-5.585356	1.778762
15	6	0	3.228998	-4.567983	0.688085
16	6	0	3.604778	-3.296412	0.178202
17	6	0	5.628884	-4.103864	-0.567094
18	6	0	5.314942	-5.407064	-0.121995
19	1	0	6.035696	-6.205298	-0.268102
20	6	0	4.115974	-5.663043	0.511077
21	6	0	6.949092	-3.848765	-1.232011
22	1	0	6.860320	-3.976236	-2.317208
23	1	0	7.713541	-4.547001	-0.884207
24	1	0	7.290677	-2.829397	-1.042391
25	6	0	3.776419	-7.034220	1.009893
26	1	0	2.845987	-7.401969	0.565203
27	1	0	3.640825	-7.039509	2.096374
28	1	0	4.565681	-7.748052	0.770317
29	6	0	0.062734	-0.986343	2.172118
30	6	0	0.467308	-1.289993	3.510323
31	1	0	1.451803	-1.707530	3.687718
32	6	0	-0.374229	-1.005439	4.544701
33	1	0	-0.064207	-1.206088	5.564882
34	6	0	-1.650063	-0.436161	4.295705
35	6	0	-2.005308	-0.197544	2.938091
36	6	0	-4.096212	0.578402	3.566410
37	6	0	-3.784603	0.413838	4.931445
38	1	0	-4.527394	0.688071	5.672794
39	6	0	-2.570512	-0.103991	5.324915
40	6	0	-5.456194	1.072438	3.192943
41	1	0	-5.426277	1.631384	2.257188
42	1	0	-5.871473	1.710469	3.976647
43	1	0	-6.139982	0.224551	3.069902
44	6	0	-2.238070	-0.298131	6.771639
45	1	0	-3.068137	0.005194	7.410994
46	1	0	-1.360957	0.292509	7.057525
47	1	0	-2.010450	-1.345832	6.993231
48	6	0	1.559222	3.304274	2.533479
49	1	0	2.099004	4.229404	2.772428
50	6	0	0.090695	3.659859	2.247804
51	1	0	-0.452220	2.750343	1.955322
52	1	0	0.008757	4.353626	1.405829
53	6	0	-0.587673	4.280920	3.468767
54	1	0	-0.119115	5.248732	3.690134
55	1	0	-1.636188	4.491893	3.230227
56	6	0	-0.491303	3.377673	4.692262

57	1	0	-1.082773	2.469128	4.516105
58	1	0	-0.930720	3.871870	5.564944
59	6	0	0.956714	2.995626	4.978697
60	1	0	1.008659	2.287705	5.813897
61	1	0	1.511434	3.887538	5.297629
62	6	0	1.647656	2.384420	3.757736
63	1	0	2.691426	2.176138	4.014875
64	1	0	1.184303	1.418840	3.524091
65	6	0	2.330875	4.025271	-0.198386
66	1	0	1.253468	4.199682	-0.309765
67	6	0	2.862222	3.643897	-1.586689
68	1	0	2.359980	2.743025	-1.944615
69	1	0	3.926274	3.395037	-1.523976
70	6	0	2.686087	4.779131	-2.595449
71	1	0	1.614671	4.944144	-2.777837
72	1	0	3.118642	4.482102	-3.557009
73	6	0	3.314587	6.077858	-2.104387
74	1	0	4.404476	5.955434	-2.047124
75	1	0	3.133324	6.884749	-2.821538
76	6	0	2.776549	6.460744	-0.730526
77	1	0	1.707519	6.699986	-0.811517
78	1	0	3.267977	7.368089	-0.365068
79	6	0	2.960359	5.336549	0.291883
80	1	0	2.526069	5.645981	1.247186
81	1	0	4.034795	5.197521	0.467482
82	6	0	4.169107	2.395532	1.476895
83	1	0	4.727130	3.270572	1.136983
84	1	0	4.231893	2.409846	2.567086
85	6	0	6.675847	1.513485	0.227999
86	1	0	7.097417	2.124406	1.036242
87	6	0	7.657016	0.370284	-0.071886
88	1	0	7.838647	-0.228488	0.825888
89	1	0	7.207018	-0.306022	-0.809788
90	6	0	8.992582	0.887581	-0.608540
91	1	0	9.505786	1.449348	0.182626
92	1	0	9.638908	0.037303	-0.850177
93	6	0	8.810941	1.784227	-1.827936
94	1	0	8.421655	1.189212	-2.665640
95	1	0	9.777817	2.178490	-2.155790
96	6	0	7.849863	2.926680	-1.526706
97	1	0	7.679669	3.532556	-2.422885
98	1	0	8.301961	3.595974	-0.783437
99	6	0	6.507760	2.421439	-0.996832
100	1	0	5.883328	3.285380	-0.749179
101	1	0	5.982024	1.873282	-1.789964
102	6	0	5.523524	-0.052437	2.433039
103	1	0	6.081448	-0.916701	2.047752
104	6	0	4.295869	-0.609734	3.165323
105	1	0	3.699352	-1.207984	2.474058
106	1	0	3.655172	0.215119	3.499767
107	6	0	4.690783	-1.449743	4.379675
108	1	0	3.787366	-1.791336	4.899294
109	1	0	5.210526	-2.354989	4.039111
110	6	0	5.591391	-0.676925	5.336293
111	1	0	5.027146	0.157694	5.774136
112	1	0	5.897986	-1.314433	6.171604
113	6	0	6.817041	-0.133004	4.611631
114	1	0	7.446483	-0.970276	4.283338
115	1	0	7.431461	0.464469	5.292991
116	6	0	6.439403	0.715423	3.395628
117	1	0	7.354026	1.038855	2.890642
118	1	0	5.936172	1.627599	3.742623

119	29	0	-1.485634	-0.664014	-0.203396
120	29	0	-3.780817	0.471473	0.499296
121	15	0	-2.370606	-2.580703	-1.002524
122	15	0	-5.035482	-0.853206	-0.866965
123	7	0	-0.907520	1.139854	-1.099519
124	7	0	-2.819662	2.191306	-0.303551
125	7	0	-4.796010	3.080399	0.437147
126	7	0	1.144940	0.467986	-1.917979
127	7	0	3.228577	-0.288441	-2.591395
128	6	0	-1.668226	2.260707	-0.987627
129	6	0	-1.232879	3.519383	-1.531030
130	1	0	-0.287141	3.568866	-2.058102
131	6	0	-1.990151	4.640437	-1.367182
132	1	0	-1.643604	5.588113	-1.768397
133	6	0	-3.231218	4.569023	-0.681520
134	6	0	-3.607512	3.296738	-0.173797
135	6	0	-5.632223	4.103147	0.570885
136	6	0	-5.317940	5.406967	0.127784
137	1	0	-6.038875	6.204960	0.274275
138	6	0	-4.118424	5.663817	-0.503920
139	6	0	-6.952821	3.847139	1.234678
140	1	0	-6.864867	3.974453	2.319981
141	1	0	-7.717350	4.545088	0.886515
142	1	0	-7.293728	2.827663	1.044571
143	6	0	-3.778533	7.035665	-1.000663
144	1	0	-2.848710	7.403095	-0.554432
145	1	0	-3.641661	7.042292	-2.086974
146	1	0	-4.568223	7.749046	-0.761150
147	6	0	-0.064987	0.988711	-2.168607
148	6	0	-0.470128	1.294698	-3.506095
149	1	0	-1.453935	1.714309	-3.682172
150	6	0	0.369880	1.009763	-4.541580
151	1	0	0.059282	1.212124	-5.561249
152	6	0	1.644707	0.437547	-4.294406
153	6	0	2.001030	0.197244	-2.937350
154	6	0	4.089121	-0.583480	-3.568820
155	6	0	3.776299	-0.417301	-4.933388
156	1	0	4.517434	-0.693131	-5.675808
157	6	0	2.563135	0.104019	-5.324993
158	6	0	5.448283	-1.081361	-3.197593
159	1	0	5.418974	-1.637402	-2.260141
160	1	0	5.859177	-1.723065	-3.980635
161	1	0	6.135349	-0.235493	-3.078978
162	6	0	2.229550	0.300284	-6.771172
163	1	0	3.058129	-0.004595	-7.411712
164	1	0	1.350606	-0.287796	-7.056663
165	1	0	2.004405	1.348772	-6.991560
166	6	0	-1.552612	-3.306090	-2.527822
167	1	0	-2.093026	-4.230354	-2.768744
168	6	0	-0.086025	-3.664003	-2.235224
169	1	0	0.456906	-2.754935	-1.941415
170	1	0	-0.008845	-4.357071	-1.392215
171	6	0	0.596951	-4.287189	-3.452486
172	1	0	0.127544	-5.254171	-3.675646
173	1	0	1.643898	-4.500088	-3.208762
174	6	0	0.508277	-3.384277	-4.676747
175	1	0	1.100603	-2.476786	-4.498033
176	1	0	0.950999	-3.879587	-5.547127
177	6	0	-0.937659	-2.999708	-4.970291
178	1	0	-0.984317	-2.292138	-5.806101
179	1	0	-1.492399	-3.890798	-5.291459
180	6	0	-1.633464	-2.386637	-3.752967

181	1	0	-2.675576	-2.176394	-4.015268
182	1	0	-1.169456	-1.421839	-3.517468
183	6	0	-2.332674	-4.021946	0.203077
184	1	0	-1.255334	-4.192356	0.321056
185	6	0	-2.873200	-3.640013	1.587656
186	1	0	-2.378405	-2.735328	1.946202
187	1	0	-3.938448	-3.398265	1.518863
188	6	0	-2.695506	-4.772063	2.599679
189	1	0	-1.624024	-4.931487	2.786578
190	1	0	-3.133325	-4.475140	3.558886
191	6	0	-3.316155	-6.074632	2.108808
192	1	0	-4.406377	-5.957239	2.047378
193	1	0	-3.133903	-6.879372	2.828137
194	6	0	-2.771441	-6.457922	0.737635
195	1	0	-1.701862	-6.693094	0.823196
196	1	0	-3.258076	-7.367763	0.371953
197	6	0	-2.955067	-5.336336	-0.287717
198	1	0	-2.515328	-5.645928	-1.240464
199	1	0	-4.029189	-5.201240	-0.468401
200	6	0	-4.165883	-2.395205	-1.481933
201	1	0	-4.725292	-3.271043	-1.146195
202	1	0	-4.223566	-2.407366	-2.572412
203	6	0	-6.677186	-1.513336	-0.240449
204	1	0	-7.096166	-2.123528	-1.050552
205	6	0	-7.658689	-0.369601	0.056406
206	1	0	-7.836922	0.229266	-0.841987
207	1	0	-7.210767	0.306479	0.795835
208	6	0	-8.996382	-0.886090	0.588474
209	1	0	-9.507448	-1.447148	-0.204597
210	1	0	-9.642831	-0.035379	0.828271
211	6	0	-8.819528	-1.783317	1.808122
212	1	0	-8.432480	-1.188978	2.647346
213	1	0	-9.787797	-2.176896	2.132613
214	6	0	-7.858448	-2.926448	1.509514
215	1	0	-7.691791	-3.532935	2.405932
216	1	0	-8.308697	-3.594978	0.764443
217	6	0	-6.514140	-2.422226	0.984314
218	1	0	-5.890019	-3.286724	0.737882
219	1	0	-5.990226	-1.875385	1.779564
220	6	0	-5.518319	0.052617	-2.440907
221	1	0	-6.079517	0.915405	-2.057116
222	6	0	-4.289319	0.613069	-3.168446
223	1	0	-3.697087	1.212482	-2.474593
224	1	0	-3.645308	-0.210110	-3.500793
225	6	0	-4.681657	1.452863	-4.383808
226	1	0	-3.777128	1.797016	-4.899794
227	1	0	-5.204858	2.356648	-4.044652
228	6	0	-5.576897	0.678632	-5.344289
229	1	0	-5.009216	-0.154591	-5.780339
230	1	0	-5.881708	1.315898	-6.180431
231	6	0	-6.804014	0.131881	-4.624348
232	1	0	-7.436351	0.967681	-4.297897
233	1	0	-7.414784	-0.466522	-5.308152
234	6	0	-6.429059	-0.716412	-3.407431
235	1	0	-7.345008	-1.042044	-2.906353
236	1	0	-5.922607	-1.627277	-3.753142

Table S4 Cartesian coordinates of complex **2** at the optimized S_0 geometry

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-3.630654	-0.489266	0.524835
2	29	0	-1.278285	0.616843	0.084731
3	15	0	-4.767296	1.122149	-0.606763
4	15	0	-2.026594	2.557034	-0.771666
5	7	0	-2.915475	-2.055186	-0.678457
6	7	0	-4.759534	-3.147284	0.151717
7	7	0	-1.050492	-0.875345	-1.384433
8	7	0	1.000760	-0.117179	-2.075930
9	7	0	3.128924	0.628616	-2.585377
10	6	0	-3.710568	-3.165181	-0.702023
11	6	0	-5.582542	-4.191085	0.161847
12	6	0	-5.397618	-5.317076	-0.667870
13	1	0	-6.101743	-6.140734	-0.611438
14	6	0	-4.335501	-5.372434	-1.548232
15	6	0	-3.458897	-4.257197	-1.576665
16	6	0	-2.333702	-4.149193	-2.434571
17	1	0	-2.083350	-4.964000	-3.105989
18	6	0	-1.553191	-3.033007	-2.407481
19	1	0	-0.675547	-2.963610	-3.038958
20	6	0	-1.861812	-1.959633	-1.503303
21	6	0	-6.744024	-4.147526	1.111385
22	1	0	-7.277840	-3.196214	1.031529
23	1	0	-6.395024	-4.236782	2.145599
24	1	0	-7.451419	-4.957348	0.926046
25	6	0	-4.125669	-6.556930	-2.440752
26	1	0	-4.890195	-7.317304	-2.274331
27	1	0	-3.149252	-7.020233	-2.265292
28	1	0	-4.164382	-6.270665	-3.496820
29	6	0	1.862024	0.361500	-3.008120
30	6	0	4.021052	1.057135	-3.483623
31	6	0	3.674480	1.308446	-4.825493
32	1	0	4.435550	1.685817	-5.499971
33	6	0	2.397452	1.068064	-5.288452
34	6	0	1.462094	0.542240	-4.360292
35	6	0	0.136153	0.167604	-4.703327
36	1	0	-0.212680	0.298163	-5.722196
37	6	0	-0.701440	-0.357141	-3.762161
38	1	0	-1.716397	-0.649475	-4.008112
39	6	0	-0.245420	-0.478819	-2.414996
40	6	0	5.432232	1.243889	-3.029236
41	1	0	5.900348	0.268110	-2.853004
42	1	0	6.028997	1.770789	-3.776029
43	1	0	5.457329	1.802756	-2.091339
44	6	0	2.020662	1.346883	-6.709837
45	1	0	2.865436	1.746510	-7.272226
46	1	0	1.677815	0.441654	-7.220830
47	1	0	1.205932	2.077183	-6.758965
48	6	0	-3.626085	2.189423	-1.622417
49	1	0	-3.362454	1.582505	-2.495246
50	1	0	-4.133370	3.097349	-1.962917
51	6	0	-5.919288	0.454730	-1.868971
52	6	0	-6.652917	-0.692092	-1.533357
53	1	0	-6.492831	-1.175569	-0.574066
54	6	0	-7.573757	-1.231107	-2.427367
55	1	0	-8.135999	-2.118202	-2.151035

56	6	0	-7.768794	-0.639403	-3.673506
57	1	0	-8.485728	-1.060504	-4.371524
58	6	0	-7.039077	0.494564	-4.022086
59	1	0	-7.187064	0.961120	-4.991385
60	6	0	-6.122102	1.040561	-3.126231
61	1	0	-5.574380	1.931619	-3.417955
62	6	0	-5.784615	2.325296	0.335012
63	6	0	-5.502423	2.536929	1.691111
64	1	0	-4.703427	1.977998	2.171250
65	6	0	-6.233255	3.466959	2.427883
66	1	0	-5.999811	3.628687	3.475911
67	6	0	-7.264385	4.180905	1.822631
68	1	0	-7.841013	4.897837	2.398606
69	6	0	-7.562351	3.965928	0.477918
70	1	0	-8.373220	4.511585	0.005241
71	6	0	-6.827539	3.045367	-0.263528
72	1	0	-7.082936	2.877406	-1.305320
73	6	0	-2.387687	3.971685	0.333801
74	6	0	-2.222084	3.815619	1.715201
75	1	0	-1.878346	2.863214	2.110266
76	6	0	-2.506911	4.869118	2.582708
77	1	0	-2.378085	4.739072	3.653397
78	6	0	-2.959505	6.084554	2.076386
79	1	0	-3.184209	6.905183	2.750614
80	6	0	-3.120246	6.250923	0.700482
81	1	0	-3.467629	7.200024	0.304030
82	6	0	-2.832462	5.202566	-0.167163
83	1	0	-2.943138	5.350920	-1.238004
84	6	0	-0.956167	3.273822	-2.078194
85	6	0	0.376486	3.539402	-1.724640
86	1	0	0.721862	3.343246	-0.713695
87	6	0	1.271605	4.050170	-2.658572
88	1	0	2.297429	4.250137	-2.361028
89	6	0	0.852302	4.297165	-3.966127
90	1	0	1.549343	4.698092	-4.696270
91	6	0	-0.466339	4.034403	-4.328987
92	1	0	-0.804817	4.238187	-5.340842
93	6	0	-1.367256	3.526939	-3.391916
94	1	0	-2.391346	3.338917	-3.699563
95	29	0	3.630666	0.489326	-0.524630
96	29	0	1.278313	-0.616912	-0.084590
97	7	0	2.915382	2.055173	0.678719
98	7	0	4.759323	3.147448	-0.151496
99	7	0	1.050475	0.875243	1.384716
100	7	0	-1.000875	0.117267	2.076202
101	7	0	-3.128964	-0.628792	2.585599
102	15	0	4.767561	-1.122083	0.606880
103	15	0	2.026894	-2.557021	0.771439
104	6	0	3.710349	3.165262	0.702239
105	6	0	5.582173	4.191376	-0.161735
106	6	0	5.397067	5.317421	0.667859
107	1	0	6.101062	6.141186	0.611343
108	6	0	4.334967	5.372676	1.548252
109	6	0	3.458565	4.257288	1.576837
110	6	0	2.333472	4.149137	2.434864
111	1	0	2.083082	4.963911	3.106306
112	6	0	1.553111	3.032847	2.407864
113	1	0	0.675531	2.963322	3.039418
114	6	0	1.861747	1.959542	1.503613
115	6	0	6.743665	4.147918	-1.111267
116	1	0	6.394742	4.238631	-2.145388
117	1	0	7.451666	4.957013	-0.925045

118	1	0	7.276735	3.196111	-1.032473
119	6	0	4.124978	6.557212	2.440680
120	1	0	4.889346	7.317716	2.274129
121	1	0	3.148457	7.020312	2.265264
122	1	0	4.163837	6.271044	3.496769
123	6	0	-1.862091	-0.361587	3.008355
124	6	0	-4.021016	-1.057606	3.483775
125	6	0	-3.674433	-1.308917	4.825647
126	1	0	-4.435452	-1.686466	5.500083
127	6	0	-2.397469	-1.068314	5.288654
128	6	0	-1.462141	-0.542396	4.360511
129	6	0	-0.136228	-0.167683	4.703572
130	1	0	0.212625	-0.298298	5.722426
131	6	0	0.701368	0.357049	3.762406
132	1	0	1.716339	0.649357	4.008342
133	6	0	0.245333	0.478775	2.415254
134	6	0	-5.432133	-1.244747	3.029328
135	1	0	-5.900735	-0.269100	2.853698
136	1	0	-6.028614	-1.772362	3.775843
137	1	0	-5.457012	-1.803084	2.091108
138	6	0	-2.020708	-1.347015	6.710073
139	1	0	-2.865471	-1.746669	7.272461
140	1	0	-1.677948	-0.441733	7.221024
141	1	0	-1.205921	-2.077245	6.759282
142	6	0	3.626302	-2.189528	1.622325
143	1	0	3.362661	-1.582637	2.495165
144	1	0	4.133536	-3.097482	1.962824
145	6	0	5.919375	-0.454917	1.869355
146	6	0	6.652360	0.692528	1.534461
147	1	0	6.491901	1.176609	0.575538
148	6	0	7.573071	1.231356	2.428728
149	1	0	8.134825	2.118927	2.152945
150	6	0	7.768588	0.638848	3.674407
151	1	0	8.485412	1.059799	4.372629
152	6	0	7.039496	-0.495747	4.022276
153	1	0	7.187855	-0.962918	4.991221
154	6	0	6.122682	-1.041566	3.126160
155	1	0	5.575445	-1.933112	3.417308
156	6	0	5.784878	-2.325013	-0.335151
157	6	0	5.501424	-2.537635	-1.690834
158	1	0	4.701649	-1.979413	-2.170513
159	6	0	6.232030	-3.467700	-2.427779
160	1	0	5.997582	-3.630219	-3.475461
161	6	0	7.264205	-4.180671	-1.823151
162	1	0	7.840643	-4.897638	-2.399275
163	6	0	7.563463	-3.964649	-0.478896
164	1	0	8.375146	-4.509529	-0.006716
165	6	0	6.828866	-3.044074	0.262752
166	1	0	7.085212	-2.875364	1.304185
167	6	0	2.388149	-3.971417	-0.334308
168	6	0	2.221100	-3.815593	-1.715559
169	1	0	1.876381	-2.863443	-2.110387
170	6	0	2.505921	-4.868936	-2.583260
171	1	0	2.375963	-4.739072	-3.653835
172	6	0	2.959995	-6.083959	-2.077285
173	1	0	3.184704	-6.904460	-2.751666
174	6	0	3.122260	-6.250070	-0.701528
175	1	0	3.470808	-7.198859	-0.305338
176	6	0	2.834466	-5.201879	0.166312
177	1	0	2.946355	-5.350071	1.237049
178	6	0	0.956321	-3.274043	2.077730
179	6	0	-0.376123	-3.540187	1.723818

180	1	0	-0.721213	-3.344558	0.712669
181	6	0	-1.271437	-4.050765	2.657660
182	1	0	-2.297089	-4.251166	2.359831
183	6	0	-0.852497	-4.297218	3.965435
184	1	0	-1.549676	-4.698096	4.695476
185	6	0	0.465936	-4.033924	4.328639
186	1	0	0.804166	-4.237277	5.340667
187	6	0	1.366995	-3.526422	3.391720
188	1	0	2.390897	-3.337927	3.699701

Table S5 Cartesian coordinates of complex **1** at the optimized T_1 geometry

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-1.490525	0.586583	-0.156346
2	29	0	-3.824735	-0.319353	0.625126
3	15	0	-2.266521	2.419887	-1.258976
4	15	0	-4.995507	0.826491	-0.963365
5	7	0	-0.932887	-1.345920	-0.906946
6	7	0	-2.922802	-2.181629	-0.043339
7	7	0	-4.966149	-2.853552	0.742123
8	7	0	1.091549	-0.767267	-1.832941
9	7	0	3.142785	-0.028053	-2.621454
10	6	0	-1.773189	-2.403146	-0.687656
11	6	0	-1.409771	-3.736946	-1.077412
12	1	0	-0.464307	-3.903862	-1.580286
13	6	0	-2.243428	-4.783209	-0.810311
14	1	0	-1.956436	-5.789895	-1.098405
15	6	0	-3.487312	-4.554976	-0.169923
16	6	0	-3.785933	-3.212659	0.187200
17	6	0	-5.869905	-3.798666	0.970955
18	6	0	-5.636894	-5.161491	0.677435
19	1	0	-6.410743	-5.890409	0.895356
20	6	0	-4.448791	-5.564557	0.104646
21	6	0	-7.175489	-3.382725	1.579665
22	1	0	-7.064456	-3.258990	2.662859
23	1	0	-7.955988	-4.127041	1.411050
24	1	0	-7.506112	-2.424583	1.172803
25	6	0	-4.191818	-7.001638	-0.230771
26	1	0	-3.293961	-7.374062	0.272768
27	1	0	-4.041431	-7.138276	-1.306776
28	1	0	-5.029183	-7.632779	0.070165
29	6	0	-0.116649	-1.339949	-1.993912
30	6	0	-0.512838	-1.838147	-3.278191
31	1	0	-1.488151	-2.296115	-3.395165
32	6	0	0.320722	-1.685135	-4.344205
33	1	0	0.012605	-2.034467	-5.324139
34	6	0	1.582623	-1.049173	-4.190973
35	6	0	1.935580	-0.608884	-2.884778
36	6	0	3.980571	0.174649	-3.643897
37	6	0	3.672382	-0.201014	-4.964806
38	1	0	4.395073	0.003419	-5.747560
39	6	0	2.482280	-0.829224	-5.265331
40	6	0	5.306976	0.806364	-3.368061
41	1	0	5.265627	1.444554	-2.484161
42	1	0	5.638369	1.403558	-4.221308
43	1	0	6.064974	0.032014	-3.201962
44	6	0	2.151140	-1.238996	-6.666462
45	1	0	2.962671	-0.992009	-7.351969

46	1	0	1.247092	-0.732593	-7.020976
47	1	0	1.969111	-2.315953	-6.736555
48	6	0	-1.405030	2.943597	-2.844430
49	1	0	-1.952767	3.813944	-3.227281
50	6	0	0.047416	3.366988	-2.573446
51	1	0	0.595384	2.518740	-2.139608
52	1	0	0.090838	4.175634	-1.837668
53	6	0	0.751070	3.821701	-3.852174
54	1	0	0.275156	4.739911	-4.220105
55	1	0	1.789463	4.084433	-3.619831
56	6	0	0.705101	2.753577	-4.938187
57	1	0	1.313302	1.895561	-4.623796
58	1	0	1.154951	3.132422	-5.861867
59	6	0	-0.724678	2.293875	-5.201989
60	1	0	-0.732830	1.466152	-5.920862
61	1	0	-1.288576	3.110690	-5.670656
62	6	0	-1.440288	1.855033	-3.923558
63	1	0	-2.471202	1.585757	-4.174859
64	1	0	-0.968144	0.946152	-3.534249
65	6	0	-2.221315	3.999369	-0.236141
66	1	0	-1.143961	4.180893	-0.136179
67	6	0	-2.768521	3.798084	1.183296
68	1	0	-2.258314	2.961629	1.666056
69	1	0	-3.826790	3.522376	1.140047
70	6	0	-2.619479	5.058990	2.036451
71	1	0	-1.552469	5.252051	2.218973
72	1	0	-3.070627	4.886365	3.019485
73	6	0	-3.237753	6.282315	1.369801
74	1	0	-4.326145	6.151541	1.304559
75	1	0	-3.070974	7.174486	1.981487
76	6	0	-2.669286	6.486873	-0.028904
77	1	0	-1.602013	6.737150	0.042702
78	1	0	-3.152520	7.338013	-0.519776
79	6	0	-2.834883	5.240000	-0.900168
80	1	0	-2.382794	5.425761	-1.879313
81	1	0	-3.906258	5.082697	-1.076008
82	6	0	-4.051576	2.228074	-1.770502
83	1	0	-4.585154	3.162862	-1.586893
84	1	0	-4.074839	2.078758	-2.851867
85	6	0	-6.616044	1.634690	-0.468454
86	1	0	-6.996655	2.134588	-1.367850
87	6	0	-7.643565	0.575838	-0.036633
88	1	0	-7.821925	-0.144341	-0.841150
89	1	0	-7.236476	0.004448	0.806241
90	6	0	-8.975211	1.203418	0.375603
91	1	0	-9.448291	1.659336	-0.503759
92	1	0	-9.655873	0.416142	0.716442
93	6	0	-8.795637	2.259783	1.458032
94	1	0	-8.447340	1.781698	2.383749
95	1	0	-9.756449	2.726932	1.695108
96	6	0	-7.789582	3.319225	1.022600
97	1	0	-7.626819	4.047830	1.823802
98	1	0	-8.201111	3.880436	0.173755
99	6	0	-6.448325	2.706414	0.615299
100	1	0	-5.790108	3.505891	0.259723
101	1	0	-5.960501	2.270444	1.496363
102	6	0	-5.514076	-0.259961	-2.408604
103	1	0	-6.086329	-1.052395	-1.907284
104	6	0	-4.315917	-0.941318	-3.082533
105	1	0	-3.711692	-1.449561	-2.329218
106	1	0	-3.670427	-0.185880	-3.547693
107	6	0	-4.761529	-1.934284	-4.157420

108	1	0	-3.879886	-2.372781	-4.640581
109	1	0	-5.295512	-2.765797	-3.678211
110	6	0	-5.665778	-1.282156	-5.197190
111	1	0	-5.089710	-0.541258	-5.768042
112	1	0	-6.014116	-2.026489	-5.920345
113	6	0	-6.853804	-0.596706	-4.534015
114	1	0	-7.503847	-1.354915	-4.078150
115	1	0	-7.462985	-0.079181	-5.281898
116	6	0	-6.419433	0.399260	-3.456964
117	1	0	-7.313720	0.827069	-2.996723
118	1	0	-5.887392	1.231739	-3.937252
119	29	0	1.446497	-0.612382	0.239247
120	29	0	3.765487	0.381659	-0.599437
121	15	0	2.386229	-2.464566	1.230239
122	15	0	5.068940	-0.811757	0.837616
123	7	0	1.002929	1.160107	1.067787
124	7	0	2.867660	2.162986	0.127368
125	7	0	4.861639	2.979083	-0.638565
126	7	0	-1.106483	0.619990	1.903123
127	7	0	-3.252890	0.099052	2.612385
128	6	0	1.721591	2.295855	0.835916
129	6	0	1.273846	3.576657	1.276279
130	1	0	0.322447	3.657580	1.786605
131	6	0	2.034917	4.688236	1.025068
132	1	0	1.680628	5.667198	1.329657
133	6	0	3.294932	4.550625	0.387920
134	6	0	3.670966	3.241794	-0.046080
135	6	0	5.708678	3.983725	-0.819976
136	6	0	5.400587	5.314851	-0.446712
137	1	0	6.131892	6.095773	-0.630653
138	6	0	4.199484	5.623789	0.159113
139	6	0	7.055980	3.679925	-1.400838
140	1	0	7.043166	2.756379	-1.980069
141	1	0	7.413110	4.494320	-2.035656
142	1	0	7.788412	3.555413	-0.594274
143	6	0	3.866769	7.023743	0.572278
144	1	0	2.956303	7.379230	0.078541
145	1	0	3.696462	7.089615	1.651917
146	1	0	4.673756	7.712566	0.319273
147	6	0	0.127167	1.147731	2.158771
148	6	0	0.535929	1.564844	3.422720
149	1	0	1.538029	1.951962	3.570283
150	6	0	-0.337333	1.402731	4.496225
151	1	0	-0.027806	1.680214	5.496326
152	6	0	-1.634069	0.881191	4.270539
153	6	0	-2.005335	0.528220	2.922009
154	6	0	-4.154939	-0.056927	3.619137
155	6	0	-3.832092	0.201723	4.948002
156	1	0	-4.586836	0.040209	5.711292
157	6	0	-2.576998	0.681338	5.309534
158	6	0	-5.541182	-0.487198	3.263260
159	1	0	-5.532195	-1.208617	2.444477
160	1	0	-6.045369	-0.937471	4.121869
161	1	0	-6.144017	0.373470	2.948914
162	6	0	-2.231119	0.972413	6.735644
163	1	0	-3.063629	0.735908	7.400567
164	1	0	-1.364094	0.386087	7.063307
165	1	0	-1.976710	2.028406	6.883009
166	6	0	1.611897	-2.988199	2.855268
167	1	0	2.141741	-3.897605	3.165258
168	6	0	0.125671	-3.333919	2.661682
169	1	0	-0.411098	-2.447359	2.297537

170	1	0	-0.001694	-4.110865	1.901076
171	6	0	-0.511287	-3.805796	3.969364
172	1	0	-0.057635	-4.759562	4.269555
173	1	0	-1.574082	-4.008111	3.797833
174	6	0	-0.338357	-2.784150	5.086624
175	1	0	-0.915518	-1.882883	4.844406
176	1	0	-0.749740	-3.175148	6.022990
177	6	0	1.128734	-2.414532	5.274304
178	1	0	1.229554	-1.622654	6.024694
179	1	0	1.676898	-3.282228	5.663880
180	6	0	1.779611	-1.950733	3.970195
181	1	0	2.839957	-1.755195	4.159740
182	1	0	1.330910	-1.001123	3.659710
183	6	0	2.245807	-4.017257	0.182849
184	1	0	1.160468	-4.113755	0.056942
185	6	0	2.852553	-3.846295	-1.215327
186	1	0	2.444771	-2.956276	-1.698236
187	1	0	3.931713	-3.684009	-1.131715
188	6	0	2.613430	-5.074410	-2.095214
189	1	0	1.538745	-5.170223	-2.303909
190	1	0	3.101247	-4.926120	-3.064874
191	6	0	3.113875	-6.353884	-1.434453
192	1	0	4.208119	-6.316000	-1.351337
193	1	0	2.882391	-7.221841	-2.059967
194	6	0	2.507603	-6.526310	-0.047677
195	1	0	1.425297	-6.690141	-0.139544
196	1	0	2.913260	-7.418477	0.439827
197	6	0	2.751984	-5.307429	0.844778
198	1	0	2.263147	-5.471944	1.808946
199	1	0	3.827956	-5.228184	1.047981
200	6	0	4.211539	-2.294754	1.592177
201	1	0	4.719794	-3.199475	1.250358
202	1	0	4.347608	-2.264278	2.675709
203	6	0	6.689090	-1.505622	0.192927
204	1	0	7.144839	-2.057834	1.024479
205	6	0	7.642882	-0.369300	-0.210982
206	1	0	7.849558	0.285618	0.640443
207	1	0	7.157425	0.255844	-0.970773
208	6	0	8.966507	-0.900457	-0.761870
209	1	0	9.514382	-1.407556	0.042888
210	1	0	9.591550	-0.057577	-1.074922
211	6	0	8.756193	-1.870561	-1.917427
212	1	0	8.324319	-1.334628	-2.773993
213	1	0	9.716807	-2.269062	-2.258255
214	6	0	7.828102	-3.007990	-1.509577
215	1	0	7.638850	-3.674348	-2.357557
216	1	0	8.319416	-3.618025	-0.740993
217	6	0	6.495028	-2.491716	-0.965664
218	1	0	5.894677	-3.347294	-0.640984
219	1	0	5.932938	-2.004395	-1.773575
220	6	0	5.613720	0.224349	2.306663
221	1	0	6.134803	1.057736	1.815865
222	6	0	4.424694	0.832265	3.060659
223	1	0	3.762853	1.341695	2.358708
224	1	0	3.834487	0.036093	3.527668
225	6	0	4.884093	1.803838	4.147816
226	1	0	4.010889	2.188981	4.687114
227	1	0	5.364547	2.671848	3.676631
228	6	0	5.858741	1.147289	5.118661
229	1	0	5.335025	0.366359	5.686269
230	1	0	6.215422	1.876357	5.852998
231	6	0	7.038153	0.528685	4.377185

232	1	0	7.640004	1.325417	3.920737
233	1	0	7.698700	0.006893	5.076806
234	6	0	6.589583	-0.444163	3.284097
235	1	0	7.473552	-0.823555	2.764102
236	1	0	6.109174	-1.311077	3.757130

Table S6 Cartesian coordinates of complex **2** at the optimized T_1 geometry

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	3.816380	-0.537437	-0.577626
2	29	0	1.432191	0.403388	0.072094
3	15	0	4.934426	0.990888	0.645085
4	15	0	2.163224	2.033733	1.462309
5	7	0	2.863447	-2.198693	0.462337
6	7	0	4.991874	-2.778440	-0.089267
7	7	0	0.775874	-1.409519	1.074847
8	7	0	-1.199933	-0.610602	1.910368
9	7	0	-3.185167	0.374556	2.597537
10	6	0	3.809105	-3.178419	0.427432
11	6	0	6.004354	-3.634555	-0.081500
12	6	0	5.863430	-4.961447	0.392143
13	1	0	6.722833	-5.624054	0.365201
14	6	0	4.658743	-5.414766	0.888384
15	6	0	3.582319	-4.484735	0.928155
16	6	0	2.286821	-4.750608	1.440720
17	1	0	2.032858	-5.746193	1.790504
18	6	0	1.352126	-3.754722	1.495105
19	1	0	0.352621	-3.954577	1.864709
20	6	0	1.679665	-2.438748	1.028270
21	6	0	7.325347	-3.160400	-0.604438
22	1	0	7.409366	-3.369531	-1.677289
23	1	0	8.155197	-3.668666	-0.108247
24	1	0	7.432570	-2.083615	-0.461542
25	6	0	4.496068	-6.817705	1.386698
26	1	0	5.421501	-7.385056	1.279097
27	1	0	3.712457	-7.346407	0.834029
28	1	0	4.213709	-6.833965	2.444507
29	6	0	-2.032920	-0.272992	2.928962
30	6	0	-4.006033	0.757988	3.585649
31	6	0	-3.720550	0.515264	4.938973
32	1	0	-4.417604	0.865627	5.692564
33	6	0	-2.578246	-0.167122	5.312771
34	6	0	-1.711317	-0.589736	4.277641
35	6	0	-0.502494	-1.303188	4.510990
36	1	0	-0.219667	-1.558787	5.526570
37	6	0	0.311275	-1.649795	3.477591
38	1	0	1.243915	-2.172248	3.653286
39	6	0	-0.036756	-1.256194	2.143579
40	6	0	-5.275808	1.456465	3.215159
41	1	0	-5.991299	0.750435	2.776689
42	1	0	-5.749565	1.908600	4.088210
43	1	0	-5.092128	2.227107	2.463955
44	6	0	-2.264508	-0.419188	6.754486
45	1	0	-3.063692	-0.057550	7.402833
46	1	0	-2.124010	-1.485132	6.958076
47	1	0	-1.339449	0.092188	7.042364
48	6	0	3.872349	1.617756	2.038647

49	1	0	3.775154	0.777363	2.732540
50	1	0	4.340832	2.449941	2.572474
51	6	0	6.394097	0.310523	1.523984
52	6	0	7.700113	0.729977	1.241347
53	1	0	7.875742	1.541978	0.543609
54	6	0	8.787979	0.108548	1.854275
55	1	0	9.794300	0.446530	1.627037
56	6	0	8.587084	-0.932667	2.755951
57	1	0	9.435697	-1.410019	3.236057
58	6	0	7.290162	-1.361254	3.039078
59	1	0	7.125914	-2.175295	3.738726
60	6	0	6.203370	-0.752657	2.420362
61	1	0	5.202161	-1.125642	2.623349
62	6	0	5.538683	2.501410	-0.192087
63	6	0	5.518644	2.546453	-1.592122
64	1	0	5.123063	1.706680	-2.155292
65	6	0	5.982346	3.672301	-2.271237
66	1	0	5.965529	3.691487	-3.356593
67	6	0	6.461456	4.767733	-1.558336
68	1	0	6.820925	5.646107	-2.085345
69	6	0	6.484275	4.734569	-0.163789
70	1	0	6.860931	5.585442	0.395154
71	6	0	6.032018	3.607850	0.515521
72	1	0	6.076086	3.594508	1.600920
73	6	0	2.332872	3.713474	0.742618
74	6	0	2.356541	3.861173	-0.649653
75	1	0	2.238745	2.990558	-1.288435
76	6	0	2.551520	5.117428	-1.221019
77	1	0	2.587131	5.217985	-2.301862
78	6	0	2.709567	6.237474	-0.408288
79	1	0	2.859667	7.216477	-0.853614
80	6	0	2.673042	6.101153	0.979069
81	1	0	2.790162	6.972542	1.615825
82	6	0	2.488090	4.847082	1.553231
83	1	0	2.457218	4.754924	2.635275
84	6	0	1.211245	2.343325	2.999676
85	6	0	-0.132587	2.725882	2.855616
86	1	0	-0.572058	2.813495	1.864318
87	6	0	-0.912107	3.007494	3.972281
88	1	0	-1.945759	3.314999	3.841603
89	6	0	-0.371502	2.890987	5.253374
90	1	0	-0.978851	3.117795	6.124797
91	6	0	0.954239	2.495946	5.408370
92	1	0	1.387790	2.413256	6.400730
93	6	0	1.743669	2.228011	4.288922
94	1	0	2.780295	1.944305	4.438957
95	29	0	-3.782260	0.575635	0.563323
96	29	0	-1.350428	-0.350366	-0.116756
97	7	0	-2.883313	2.165740	-0.520134
98	7	0	-4.962093	2.870961	0.074095
99	7	0	-0.884990	1.231767	-1.209880
100	7	0	1.180403	0.478293	-1.958540
101	7	0	3.256636	-0.349639	-2.584808
102	15	0	-4.979897	-0.963622	-0.579488
103	15	0	-2.217958	-2.052583	-1.403400
104	6	0	-3.790358	3.178446	-0.523142
105	6	0	-5.937990	3.771965	0.047699
106	6	0	-5.762699	5.051212	-0.527556
107	1	0	-6.589333	5.754035	-0.511219
108	6	0	-4.562294	5.413634	-1.110684
109	6	0	-3.530801	4.436377	-1.133374
110	6	0	-2.251054	4.611004	-1.723668

111	1	0	-1.971485	5.570362	-2.145451
112	6	0	-1.369326	3.565515	-1.772517
113	1	0	-0.391303	3.680847	-2.222523
114	6	0	-1.723709	2.311632	-1.185958
115	6	0	-7.250622	3.383577	0.655826
116	1	0	-7.188515	3.400974	1.749661
117	1	0	-8.051699	4.062471	0.358941
118	1	0	-7.519197	2.366613	0.356885
119	6	0	-4.363646	6.770027	-1.712592
120	1	0	-5.260367	7.382766	-1.611865
121	1	0	-3.538476	7.300943	-1.226118
122	1	0	-4.121488	6.702373	-2.778223
123	6	0	2.067502	0.189385	-2.947458
124	6	0	4.151373	-0.685676	-3.559144
125	6	0	3.878055	-0.486092	-4.907925
126	1	0	4.623602	-0.775836	-5.641530
127	6	0	2.676324	0.076652	-5.331830
128	6	0	1.737869	0.441893	-4.332027
129	6	0	0.485520	1.021128	-4.631137
130	1	0	0.199582	1.202212	-5.659513
131	6	0	-0.394182	1.336317	-3.596756
132	1	0	-1.373961	1.749976	-3.807619
133	6	0	-0.023296	1.057410	-2.285378
134	6	0	5.449027	-1.296805	-3.136869
135	1	0	5.974945	-0.669230	-2.408372
136	1	0	6.109756	-1.445460	-3.992983
137	1	0	5.285265	-2.264439	-2.653168
138	6	0	2.376378	0.281346	-6.782979
139	1	0	3.210131	-0.041303	-7.409469
140	1	0	2.176067	1.334722	-7.011462
141	1	0	1.487415	-0.283985	-7.089842
142	6	0	-3.926186	-1.620284	-1.963597
143	1	0	-3.822312	-0.792530	-2.671413
144	1	0	-4.402662	-2.454343	-2.487320
145	6	0	-6.424899	-0.263427	-1.464980
146	6	0	-7.736209	-0.664653	-1.180489
147	1	0	-7.923672	-1.467318	-0.475017
148	6	0	-8.814603	-0.037631	-1.804048
149	1	0	-9.825534	-0.361064	-1.576361
150	6	0	-8.598246	0.989788	-2.718009
151	1	0	-9.439631	1.471341	-3.206447
152	6	0	-7.295647	1.398533	-3.003945
153	1	0	-7.119656	2.200389	-3.714573
154	6	0	-6.217608	0.784927	-2.374939
155	1	0	-5.211822	1.140665	-2.585307
156	6	0	-5.616069	-2.450671	0.274930
157	6	0	-5.681470	-2.445328	1.674186
158	1	0	-5.335492	-1.577843	2.228235
159	6	0	-6.174035	-3.550415	2.366329
160	1	0	-6.225026	-3.530209	3.450634
161	6	0	-6.598019	-4.676857	1.666620
162	1	0	-6.979220	-5.540015	2.203142
163	6	0	-6.539681	-4.693001	0.273076
164	1	0	-6.874960	-5.567177	-0.276126
165	6	0	-6.059619	-3.585826	-0.419363
166	1	0	-6.041027	-3.613409	-1.504840
167	6	0	-2.383565	-3.701712	-0.623646
168	6	0	-2.509546	-3.807454	0.767542
169	1	0	-2.469787	-2.916486	1.386432
170	6	0	-2.706988	-5.051786	1.362433
171	1	0	-2.820452	-5.121374	2.440183
172	6	0	-2.765485	-6.200936	0.576859

173	1	0	-2.916207	-7.170786	1.041395
174	6	0	-2.628714	-6.105113	-0.807124
175	1	0	-2.668021	-6.998716	-1.422587
176	6	0	-2.439514	-4.863401	-1.406796
177	1	0	-2.327573	-4.801999	-2.485142
178	6	0	-1.264595	-2.370413	-2.926477
179	6	0	0.088962	-2.716340	-2.775801
180	1	0	0.532598	-2.779196	-1.785512
181	6	0	0.876170	-2.976358	-3.891695
182	1	0	1.922172	-3.237019	-3.761223
183	6	0	0.330558	-2.882604	-5.172015
184	1	0	0.947505	-3.086049	-6.041924
185	6	0	-1.006284	-2.527355	-5.331490
186	1	0	-1.438589	-2.456658	-6.324906
187	6	0	-1.802563	-2.271847	-4.215867
188	1	0	-2.844583	-2.009346	-4.367413

Table S7 TDDFT results at the optimized S_0 geometry of complex **1** with $\lambda > 420$ nm.

	λ / nm	E / cm^{-1}	F	Nature	CI coefficients
T1	501	19977		H-6 → L+1 H-4 → L+1 H-3 → L+1 H-2 → L H-1 → L H → L+1	0.10146 0.10954 -0.16278 0.14206 0.52025 0.37166
T2	500	20012		H-6 → L H-4 → L H-3 → L H-2 → L+1 H-1 → L+1 H → L	0.10323 0.11098 -0.16700 0.14008 0.42219 0.47804
T3	463	21609		H-35 → L+1 H-29 → L H-26 → L+1 H-10 → L H-3 → L H-1 → L+1 H → L	0.11056 0.12317 0.13750 0.10284 0.16043 -0.38952 0.39555
T4	462			H-35 → L H-29 → L+1 H-26 → L H-11 → L H-3 → L+1 H-2 → L H-1 → L H → L+1	0.11225 0.13547 0.14707 -0.12046 0.10424 0.13705 -0.31457 0.45083
S1	445	22489	0.1236	H → L	0.67880

S2	443	22595	0.0000	H-1 → L H → L+1	0.52484 0.42994
T5	435	22993		H-19 → L+3 H-18 → L+2 H-11 → L+3 H-7 → L+2 H-4 → L H-3 → L+2 H-2 → L+3 H-1 → L+2 H-1 → L+3 H → L+2	0.16127 0.16361 0.13124 0.11533 -0.16212 -0.18661 -0.16168 -0.12759 -0.31576 0.32965
T6	434	23015		H-19 → L+2 H-18 → L+3 H-17 → L+2 H-11 → L+2 H-10 → L+3 H-7 → L+3 H-4 → L+1 H-3 → L+3 H-2 → L+2 H-2 → L+3 H-1 → L+2 H-1 → L+3 H → L+3	0.16932 0.18378 0.10413 0.12550 -0.10114 0.11740 0.12783 -0.14922 -0.13322 0.12934 -0.31498 0.12491 0.33325
S3	434	23026	0.0000	H-4 → L+1 H-1 → L H → L+1	-0.10479 -0.42937 0.52873
T7	428	23360		H-19 → L+1 H-19 → L+3 H-18 → L H-18 → L+2 H-17 → L+1 H-17 → L+3 H-9 → L H-4 → L H-2 → L+1 H-1 → L+4 H → L H → L+5	0.12632 -0.17308 -0.16872 -0.18783 0.10127 -0.12707 -0.13983 -0.14852 -0.24728 -0.16006 0.19611 -0.15007
T8	427	23428		H-19 → L H-19 → L+2 H-18 → L+1 H-18 → L+3 H-17 → L H-17 → L+2	-0.11888 -0.15217 0.14434 -0.18237 -0.10966 -0.11132

				H-9 → L+1 H-4 → L+1 H-3 → L H-2 → L H-1 → L+2 H-1 → L+5 H → L+1 H → L+4	0.12703 0.16051 0.10924 0.27333 -0.10550 0.13830 -0.24015 0.13994
S4	421	23758	0.1907	H → L+1	0.67490

Table S8 TDDFT results at the optimized S_0 geometry of complex **2** at $\lambda > 420$ nm.

	λ / nm	E / cm^{-1}	f	Nature	CI coefficients
T1	504	19855		H-3 → L H-2 → L+1 H-1 → L+1 H → L	0.10316 0.11952 -0.37394 0.56060
T2	501	19945		H-4 → L+1 H-3 → L+1 H-2 → L H-1 → L H → L+1	0.10089 -0.11655 -0.11773 0.50993 -0.43516
T3	463	21580		H-42 → L+1 H-41 → L H-5 → L+1 H-4 → L H-3 → L H-2 → L+1 H-1 → L+1 H → L	0.22025 -0.18879 0.14260 0.13630 -0.20133 0.11053 0.41318 0.27625
T4	462	21625		H-42 → L H-41 → L+1 H-5 → L H-3 → L+1 H-2 → L H-1 → L H → L+1 H → L+4	.21564 -0.19158 0.17987 -0.14806 0.17197 0.31604 0.38236 -0.10718
S1	449	22271	0.0000	H-1 → L+1 H → L	-0.15577 0.66609
T5	432	23123		H-31 → L+2 H-26 → L+3 H-25 → L+2 H-24 → L+3 H-21 → L+2	0.12924 0.14645 0.15748 -0.14010 -0.12673

				H-18 → L+3 H-11 → L+2 H-10 → L+3 H-7 → L+3 H-3 → L+2 H-2 → L+3 H-1 → L+3 H → L+2	-0.11812 -0.12186 0.10507 -0.10983 0.17444 -0.16216 0.31467 0.27899
T6	432	23126		H-31 → L+3 H-26 → L+2 H-25 → L+3 H-24 → L+2 H-21 → L+3 H-18 → L+2 H-11 → L+3 H-10 → L+2 H-7 → L+2 H-4 → L+3 H-3 → L+3 H-2 → L+2 H-1 → L+2 H → L+3	0.12805 0.14055 0.15735 -0.13479 -0.12657 -0.11326 -0.12470 0.10155 -0.10320 -0.10399 0.17643 -0.15959 0.31011 0.28796
S2	430	23265	0.3241	H-1 → L H → L+1	0.62968 -0.24748
T7	424	23569		H-42 → L H-25 → L+3 H-10 → L H-5 → L H-4 → L+1 H-4 → L+3 H-3 → L+1 H-1 → L H-1 → L+2 H-1 → L+5 H → L+1 H → L+3 H → L+4	0.11915 -0.11238 0.10387 0.18707 -0.12840 -0.11521 -0.18035 -0.18067 0.25582 0.12999 -0.23451 0.19879 -0.10618
S3	424	23605	0.0736	H-1 → L H → L+1	0.26257 0.63547
T8	424	23610		H-42 → L H-26 → L+3 H-25 → L+2 H-5 → L+1 H-4 → L H-4 → L+2 H-3 → L	-0.10344 -0.10266 -0.11582 -0.15072 0.22966 -0.13025 0.19408

				H-1 → L+1 H-1 → L+3 H-1 → L+4 H → L H → L+2	0.15340 0.26030 -0.12887 0.16569 0.23317
S4	420	23786	0.0000	H-1 → L+1 H → L	0.66032 0.16195

Table S9 TDDFT results at the optimized T_1 geometry of complex **1**.

	λ / nm	E / cm^{-1}	f	Nature	CI coefficients
T1	594	16841		H-5 → L H-2 → L H → L	-0.12541 0.13847 0.67554
S1	526	19024	0.0860	H → L	0.68068
T2	519	19256		H-35 → L H-30 → L H-28 → L H-11 → L H-3 → L H-1 → L	-0.17517 -0.13559 0.12128 0.14479 0.23784 0.55799
T3	500	19991		H-7 → L+1 H-3 → L H-3 → L+1 H-2 → L+1 H-1 → L+1 H -> L+1	-0.10911 0.11114 -0.19565 -0.11751 .55968 0.27695
T4	482	20766		H-3 → L+1 H-1 → L+1 H → L+1	-0.10425 -0.26850 0.54506
S2	478	20923	0.0103	H-1 → L H → L+1	0.67259 -0.10510
T5	470	21282		H-35 → L H-30 → L H-6 → L H-5 → L H-4 → L H-4 → L+3 H-3 → L H-2 → L H-1 → L H-1 → L+1 H → L+2 H → L+3	-0.10226 -0.12196 -.17653 0.23998 0.10972 0.10137 0.22080 -0.12058 -0.25797 -0.10395 0.16255 0.36477
S3	459	21796	0.0205	H-1 → L	0.10500

				H → L+1	0.67290

Table S10 TDDFT results at the optimized T_1 geometry of complex **2**.

	λ / nm	E / cm^{-1}	f	Nature	CI coefficients
T1	626	15980		H-3 → L H-1 → L H → L	-0.10252 -0.15102 0.68210
S1	546	18331	0.0707	H → L	0.68085
T2	526	19013		H-44 → L H-43 → L H-28 → L H-11 → L H-5 → L H-4 → L H-3 → L H-1 → L H-1 → L+1 H → L H → L+1	-0.20808 0.11006 -0.13539 0.13599 0.11734 -0.13353 0.17065 0.50458 -0.10212 0.15009 -0.17216
T3	512	19534		H-3 → L H-1 → L H-1 → L+1 H → L+1	0.10019 0.10404 0.35905 0.52745
T4	481	20774		H-42 → L+1 H-5 → L+1 H-3 → L+1 H-1 → L H-1 → L+1 H → L+1 H → L+2	-0.11001 0.10480 -0.21426 -0.12319 0.46137 -0.32629 -0.10703
T5	469	21338		H-44 → L H-5 → L H-4 → L H-4 → L+2 H-3 → L H-3 → L+2 H-2 → L H-1 → L H-1 → L+1 H-1 → L+2 H → L+2	0.10991 -0.19614 0.29557 -0.10019 0.19246 -0.14562 0.10054 0.22190 0.11674 -0.16350 0.36668
S2	468	21381	0.0846	H-1 → L H → L+1	-0.24659 0.63488
S3	463	21596	0.0456	H-3 → L	0.10433

				H-1 → L H → L+1	0.62934 0.25771

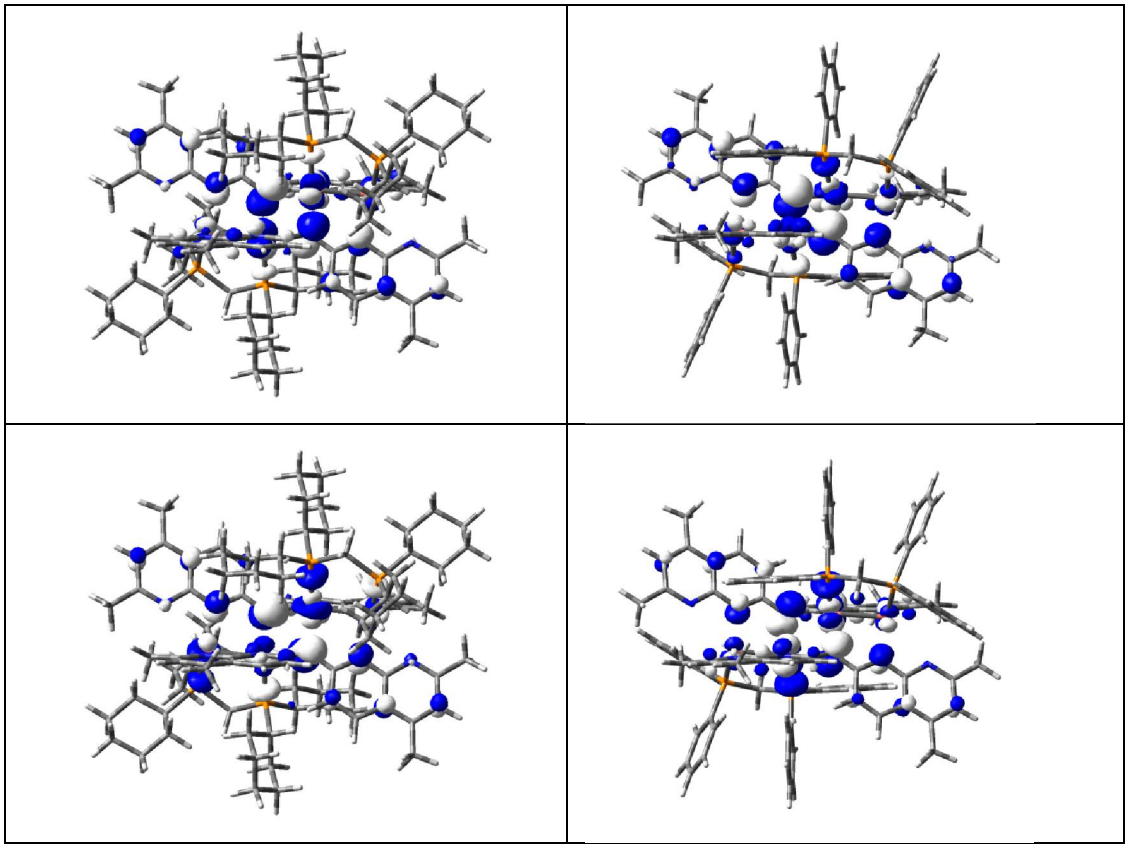


Fig. S9 H-1 (top) and HOMO (bottom) MO surfaces of complex **1** (left) and complex **2** (right) at their respective optimized S_0 geometries.

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