Supplementary Information

Title: Structures and photophysical properties of Copper(I) complexes bearing diphenylphenanthroline and bis(diphenylphosphino)alkane. The effect of phenyl groups on the phenanthroline ligand

Authors: Taro Tsubomura, Kaoru Kimura, Michihiro Nishikawa, and Toshiaki Tsukuda

Table S1 Crystallographic data for the three copper(I) complexes.

complex	$[Cu(dmpp)(dppe)]PF_6 \cdot 3(CH_2Cl_2)$	$[Cu(dmpp)(dppp)]PF_6 \cdot CH_2Cl_2 \cdot (C_2H_5)_2O$	$[Cu_2(dmpp)_2(dppb)_2](PF_6)_2 \cdot 5(CH_2Cl_2)$
empirical formula	$C_{55}H_{50}Cl_6CuF_6N_2P_3$	$C_{58}H_{58}Cl_2CuF_6N_2OP_3$	$C_{113}H_{106}Cl_{10}Cu_2F_{12}N_4P_6$
formula weight	1222.13	1140.47	2415.42
crystal system	monoclinic	monoclinic	triclinic
temperature / K	93	123	123
space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$\bar{P}_1$ (#2)
a / Å	14.1782(5)	15.0944(5)	13.540 (6)
b / Å	14.2519(5)	14.0094(5)	15.710 (6)
c / Å	27.4340(11)	27.2965(11)	15.917 (7)
α / °	90	90	73.22 (2)
β / °	98.5460(5)	93.5035(7)	69.57 (2)
γ / °	90	90	67.50 (2)
Vol / $Å^3$	5481.9(4)	5761.4(4)	2884 (2)
Z	4	4	1
D_{calcd} / g cm^{-3}	1.481	1.315	1.391
μ / mm^{-1}	0.838	0.614	0.751
data / param.	12281 / 835	13003 / 651	12271/ 676
R (I>2σ(I))	0.0547	0.0795	0.0942
wR (all)	0.1352	0.3021	0.2448
GOF	1.118	1.201	1.091
$\Delta\rho_{max}$ / $e^-Å^{-3}$	1.30	0.93	1.76
$\Delta\rho_{min}$ / $e^-Å^{-3}$	-1.14	-0.87	-1.39

Table S2 (in the following pages)

In the tables, TDDFT results were analyzed by Multifwn software (T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.)

TD-DFT calculations consider many combinations of the K-S orbitals to calculate the oscillator strength of transitions. The software calculates the transition dipole moments of many combinations of the orbitals, and then the net transition moments were calculated by summation of each moment. Gaussian 09 TDDFT outputs only a part of the results with the coefficients > 0.1 in the default calculations. In this study, combination with coefficients > 0.0001 have been printed out, and the results were analyzed by the Multifwn software. The results are shown in the following table in the order of the "norm" of the transition moments. In the left half of the table, the transition moment and norm for each combination of K-S orbitals are shown. In the right columns, the summation of the transition moments were shown, for example, No3 result is calculated by summation of the three transition moments, No.1, 2, and 3. We can see that the calculations using all components (>0.0001) well reproduce the TDDFT results which Gaussian outputs. We want know the role of diphenyl groups of dmpp ligands, so this analyses were performed. It was found that 1) HOMO->LUMO combination is dominate in the lowest-energy transitions of all complexes, 2) Almost all components are necessary to reproduce the experimental oscillator strength. However, no clear effects of the diphenyl groups were observed.

Table S2-1a Analysis of TDDFT components for **1a**, [Cu(dmp)(dppe)]+ calculated by Multiwfn software. Transition dipole moments are shown in the atomic unit.

1a					transition dipole moments				summation of transition dipole moments (from No1 to n)				
No.	MO#		MO#	Coefficient	X	Y	Z	norm	X	Y	Z	norm	
1	174	->	175	0.70024	0.15214	-1.64187	0.27503	1.67168	0.15214	-1.64187	0.27503	1.67168	
2	168	->	176	0.03895	-0.00754	0.06940	-0.01349	0.07110	0.14460	-1.57247	0.26154	1.60061	
3	174	<-	175	-0.01956	-0.00425	0.04586	-0.00768	0.04670	0.14035	-1.52660	0.25386	1.55392	
4	162	->	176	-0.01583	-0.00499	0.04462	-0.00782	0.04558	0.13536	-1.48198	0.24604	1.50835	
5	157	->	175	0.01178	-0.00197	0.02095	-0.00535	0.02171	0.13339	-1.46103	0.24069	1.48672	
6	168	<-	176	0.00993	-0.00192	0.01769	-0.00344	0.01813	0.13147	-1.44334	0.23725	1.46861	
7	162	<-	176	-0.00493	-0.00155	0.01390	-0.00243	0.01419	0.12991	-1.42944	0.23482	1.45442	
8	173	->	189	0.01112	0.00124	-0.01309	0.00180	0.01327	0.13115	-1.44254	0.23661	1.46768	
9	173	->	180	0.01324	0.00085	-0.01260	0.00113	0.01268	0.13201	-1.45514	0.23774	1.48033	
10	161	->	175	0.02187	0.00016	-0.00829	0.00575	0.01010	0.13217	-1.46343	0.24350	1.48943	
11	172	->	177	-0.01432	-0.00397	-0.00720	0.00577	0.01004	0.12820	-1.47063	0.24927	1.49711	
12	172	->	187	0.00883	0.00065	-0.00979	0.00210	0.01003	0.12885	-1.48043	0.25136	1.50713	
13	173	->	175	0.05397	0.00016	0.00981	-0.00166	0.00995	0.12900	-1.47062	0.24970	1.49723	
14	167	->	176	-0.01269	-0.00152	0.00925	-0.00303	0.00985	0.12749	-1.46137	0.24667	1.48752	
15	158	<-	186	0.00412	-0.00110	0.00941	-0.00207	0.00970	0.12639	-1.45196	0.24460	1.47784	
16	163	->	182	-0.00926	0.00092	-0.00879	0.00235	0.00914	0.12731	-1.46075	0.24695	1.48693	
17	171	->	175	-0.00678	0.00101	-0.00867	0.00155	0.00886	0.12832	-1.46941	0.24851	1.49579	
18	157	->	179	-0.00810	-0.00052	0.00707	-0.00430	0.00829	0.12779	-1.46235	0.24421	1.48809	
19	158	->	186	0.00352	-0.00094	0.00804	-0.00177	0.00828	0.12686	-1.45431	0.24244	1.47982	
20	163	->	187	-0.01485	0.00074	-0.00802	0.00132	0.00816	0.12760	-1.46233	0.24375	1.48798	
21	168	->	186	0.01270	-0.00080	0.00790	-0.00103	0.00801	0.12680	-1.45442	0.24272	1.47998	
22	161	->	178	-0.00824	0.00582	0.00301	-0.00100	0.00663	0.13262	-1.45142	0.24172	1.47737	
23	145	->	175	-0.00714	-0.00068	0.00610	-0.00110	0.00624	0.13194	-1.44531	0.24062	1.47114	
24	173	->	179	-0.01413	0.00110	-0.00590	0.00132	0.00614	0.13304	-1.45121	0.24194	1.47724	
25	170	->	185	0.00523	0.00037	0.00577	-0.00176	0.00605	0.13342	-1.44544	0.24019	1.47132	
26	173	->	178	0.01111	0.00060	-0.00590	-0.00088	0.00599	0.13402	-1.45133	0.23931	1.47702	
27	172	->	178	0.00361	0.00356	-0.00112	-0.00452	0.00586	0.13758	-1.45245	0.23479	1.47773	
28	170	->	177	-0.00666	-0.00036	-0.00406	-0.00407	0.00576	0.13722	-1.45651	0.23072	1.48104	
29	164	->	178	-0.00294	-0.00001	0.00573	-0.00024	0.00574	0.13721	-1.45078	0.23048	1.47537	
30	157	->	180	-0.00640	-0.00074	0.00511	-0.00247	0.00572	0.13647	-1.44568	0.22801	1.46989	oscillator
……	……	……	……	……	……	……	……	……	……	……	……	……	strength
13561	62	->	186	0.00000	0.00000	0.00000	0.00000	0.00000	0.09759	-1.13423	0.18748	1.15376	0.08952
							results of Gaussian09		0.09800	-1.11870	0.18360		0.08710

Table S2-1b Analysis of TDDFT components for **1b**, [Cu(dmpp)(dppe)]+ calculated by Multiwfn software. Transition dipole moments are shown in the atomic unit.

1b					transition dipole moments				summation of the components from No.1 to n				
No.	MO#		MO#	Coefficient	X	Y	Z	norm	X	Y	Z	norm	
1	214	->	215	0.69895	-1.99038	-0.05792	0.08677	1.99311	-1.99038	-0.05792	0.08677	1.99311	
2	210	->	216	-0.02823	0.08250	0.00189	-0.00155	0.08254	-1.90788	-0.05603	0.08521	1.91060	
3	214	<-	215	-0.01829	0.05208	0.00152	-0.00227	0.05216	-1.85579	-0.05452	0.08294	1.85845	
4	198	->	216	0.01822	0.04118	0.00121	-0.00351	0.04135	-1.81461	-0.05330	0.07943	1.81713	
5	210	<-	216	-0.00845	0.02469	0.00057	-0.00047	0.02470	-1.78992	-0.05274	0.07897	1.79243	
6	193	->	215	0.01284	0.02081	0.00073	-0.00144	0.02087	-1.76911	-0.05201	0.07753	1.77157	
7	204	->	216	0.01715	0.00375	-0.01736	-0.00117	0.01780	-1.76535	-0.06937	0.07636	1.76837	
8	213	->	233	0.01338	-0.01644	0.00023	0.00103	0.01647	-1.78179	-0.06914	0.07738	1.78481	
9	213	->	220	0.01757	-0.01629	0.00167	0.00099	0.01641	-1.79808	-0.06748	0.07838	1.80106	
10	205	->	216	-0.02319	0.00499	0.01464	-0.00060	0.01548	-1.79309	-0.05283	0.07777	1.79556	
11	213	->	215	0.05668	0.01488	-0.00363	-0.00145	0.01539	-1.77821	-0.05646	0.07632	1.78074	
12	213	->	219	0.01798	-0.01251	-0.00037	0.00029	0.01252	-1.79072	-0.05683	0.07661	1.79326	
13	211	->	215	0.00712	0.01220	0.00014	0.00218	0.01240	-1.77852	-0.05669	0.07879	1.78116	
14	198	<-	216	0.00498	0.01126	0.00033	-0.00096	0.01130	-1.76726	-0.05636	0.07783	1.76987	
15	203	->	216	0.01775	0.00933	0.00437	-0.00080	0.01033	-1.75793	-0.05199	0.07703	1.76039	
16	200	->	218	0.00384	0.00893	0.00182	-0.00006	0.00911	-1.74900	-0.05016	0.07697	1.75141	
17	199	->	217	0.00572	0.00869	-0.00140	-0.00171	0.00897	-1.74031	-0.05156	0.07526	1.74270	
18	211	->	229	-0.00544	-0.00815	-0.00004	0.00003	0.00815	-1.74847	-0.05160	0.07529	1.75085	
19	212	->	230	0.00806	-0.00695	0.00012	0.00279	0.00749	-1.75542	-0.05148	0.07808	1.75791	
20	199	->	216	-0.01014	0.00690	-0.00098	-0.00074	0.00701	-1.74852	-0.05246	0.07734	1.75101	
21	207	->	227	0.00296	-0.00689	-0.00083	-0.00085	0.00699	-1.75540	-0.05329	0.07650	1.75788	
22	212	->	217	-0.01284	-0.00589	0.00303	-0.00184	0.00688	-1.76130	-0.05026	0.07466	1.76359	
23	214	->	216	-0.00263	-0.00016	0.00658	-0.00028	0.00659	-1.76145	-0.04368	0.07438	1.76356	
24	196	->	215	-0.01939	-0.00622	-0.00124	0.00146	0.00651	-1.76767	-0.04492	0.07584	1.76987	
25	209	->	226	0.00549	0.00640	0.00044	0.00030	0.00643	-1.76127	-0.04448	0.07614	1.76347	
26	208	->	228	0.00259	-0.00605	0.00036	-0.00199	0.00638	-1.76731	-0.04413	0.07415	1.76942	
27	194	->	231	-0.00370	0.00615	0.00014	0.00002	0.00616	-1.76116	-0.04398	0.07417	1.76327	
28	194	<-	231	-0.00359	0.00597	0.00014	0.00002	0.00597	-1.75519	-0.04385	0.07419	1.75730	
29	206	->	224	-0.00254	0.00591	0.00026	-0.00048	0.00594	-1.74928	-0.04359	0.07371	1.75137	
30	199	->	230	-0.01109	-0.00539	0.00157	0.00143	0.00579	-1.75467	-0.04203	0.07514	1.75678	oscillator
……	……	…..	……	……	……	……	……	……	……	……	……	……	strength
18711	75	->	215	-0.00035	0.00000	0.00000	0.00000	0.00000	-1.50831	-0.04057	0.07895	1.51092	0.15564
							results of Gaussian		-1.48850	-0.04010	0.07660		0.15160

Table S2-2a continued. Analysis of TDDFT components for **2a**, [Cu(dmp)(dppp)]+ calculated by Multiwfn software. Transition dipole moments are shown in the atomic unit.

2a					transition dipole moments				summation of the components from No.1 to n				
No.	MO#		MO#	Coefficient	X	Y	Z	norm	X	Y	Z	norm	
1	178	->	179	0.70209	-0.00010	-1.36660	-0.84373	1.60607	-0.00010	-1.36660	-0.84373	1.60607	
2	166	->	180	0.01880	0.00000	0.04599	0.02756	0.05361	-0.00010	-1.32061	-0.81617	1.55247	
3	172	->	180	0.03116	0.00000	0.04595	0.01606	0.04868	-0.00010	-1.27466	-0.80012	1.50498	
4	164	->	179	0.02506	0.00002	0.01882	-0.04417	0.04802	-0.00008	-1.25584	-0.84429	1.51326	
5	178	<-	179	-0.01773	0.00000	0.03451	0.02131	0.04056	-0.00008	-1.22133	-0.82299	1.47274	
6	177	->	184	0.02174	-0.00006	-0.02864	0.00423	0.02895	-0.00014	-1.24997	-0.81876	1.49426	
7	160	->	179	0.01198	0.00000	0.01531	0.01510	0.02151	-0.00014	-1.23466	-0.80366	1.47318	
8	171	->	180	0.02041	-0.00001	0.00918	0.01799	0.02020	-0.00015	-1.22549	-0.78567	1.45571	
9	166	->	179	0.00559	0.00000	-0.01250	0.01586	0.02020	-0.00015	-1.23799	-0.76980	1.45781	
10	168	->	180	0.01756	0.00001	0.00747	0.01514	0.01689	-0.00015	-1.23052	-0.75466	1.44349	
11	160	->	181	0.01093	0.00000	0.00730	0.01354	0.01539	-0.00015	-1.22321	-0.74112	1.43021	
12	166	<-	180	0.00539	0.00000	0.01319	0.00790	0.01537	-0.00015	-1.21003	-0.73322	1.41484	
13	178	->	180	-0.00695	0.00001	0.00800	-0.01096	0.01357	-0.00014	-1.20203	-0.74418	1.41374	
14	174	->	183	-0.00525	-0.00040	0.00818	-0.00961	0.01262	-0.00055	-1.19385	-0.75379	1.41190	
15	172	->	185	-0.00835	-0.00001	0.01247	-0.00004	0.01247	-0.00056	-1.18138	-0.75383	1.40139	
16	178	->	185	-0.00799	-0.00003	-0.00663	0.01036	0.01230	-0.00058	-1.18800	-0.74347	1.40146	
17	176	->	191	0.01077	0.00000	-0.00761	-0.00953	0.01220	-0.00058	-1.19561	-0.75300	1.41298	
18	172	<-	180	0.00763	0.00000	0.01125	0.00393	0.01192	-0.00058	-1.18436	-0.74907	1.40136	
19	173	->	181	-0.00420	-0.00021	0.01048	0.00546	0.01182	-0.00079	-1.17388	-0.74361	1.38959	
20	167	->	186	-0.00946	0.00001	-0.00097	-0.01117	0.01122	-0.00078	-1.17485	-0.75478	1.39641	
21	173	->	180	0.00305	0.00008	0.00651	-0.00825	0.01051	-0.00070	-1.16834	-0.76303	1.39543	
22	169	->	186	0.00727	-0.00001	-0.00686	0.00734	0.01005	-0.00070	-1.17520	-0.75569	1.39720	
23	169	->	183	0.00443	-0.00025	0.00872	0.00450	0.00982	-0.00095	-1.16648	-0.75119	1.38743	
24	172	->	179	0.00910	-0.00001	-0.00361	0.00909	0.00978	-0.00096	-1.17009	-0.74210	1.38558	
25	166	<-	179	-0.00256	0.00000	0.00573	-0.00727	0.00925	-0.00095	-1.16437	-0.74936	1.38467	
26	164	<-	179	-0.00474	0.00000	-0.00356	0.00836	0.00908	-0.00096	-1.16793	-0.74101	1.38317	
27	175	->	179	0.01108	0.00000	-0.00801	-0.00425	0.00907	-0.00096	-1.17594	-0.74526	1.39221	
28	171	->	185	-0.00402	0.00001	-0.00884	-0.00086	0.00888	-0.00095	-1.18478	-0.74612	1.40014	
29	165	->	184	-0.00541	-0.00003	-0.00070	0.00840	0.00843	-0.00098	-1.18548	-0.73772	1.39628	
30	176	->	183	-0.01374	-0.00142	-0.00721	-0.00253	0.00777	-0.00240	-1.19269	-0.74025	1.40374	oscillator
..	.....	..	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	strength
12560	177	<-	581	-0.00010	0.00010	0.00000	0.00000	0.00000	0.00010	-0.88576	-0.54015	1.03747	0.07386
							results of Gaussian		0.00000	-0.87600	-0.53540		0.07230

Table S2-2b Analysis of TDDFT components for **2b**, [Cu(dmpp)(dppp)]+ calculated by Multiwfn software. Transition dipole moments are shown in the atomic unit.

2b					transition dipole moments				summation of the components from No.1 to n				
No.	MO		MO	Coefficient	X	Y	Z	norm	X	Y	Z	norm	
1	218	->	219	0.70070	1.94375	-0.25027	0.05452	1.96055	1.94375	-0.25027	0.05452	1.96055	
2	214	->	220	-0.02931	-0.08445	0.01677	-0.00206	0.08612	1.85930	-0.23350	0.05246	1.87464	
3	202	->	220	-0.02360	-0.05850	0.00598	-0.00530	0.05904	1.80081	-0.22752	0.04716	1.81573	
4	218	<-	219	-0.01690	-0.04688	0.00604	-0.00132	0.04729	1.75392	-0.22148	0.04585	1.76845	
5	218	->	220	0.01735	-0.00812	-0.04344	0.00057	0.04420	1.74581	-0.26493	0.04641	1.76640	
6	217	->	224	0.02503	0.02675	0.01064	0.00165	0.02884	1.77256	-0.25429	0.04806	1.79135	
7	215	->	219	0.01285	-0.02789	0.00270	0.00066	0.02802	1.74467	-0.25159	0.04872	1.76339	
8	214	<-	220	-0.00849	-0.02446	0.00486	-0.00060	0.02494	1.72021	-0.24673	0.04813	1.73848	
9	200	->	219	0.02299	0.00558	-0.01471	0.00132	0.01579	1.72579	-0.26144	0.04944	1.74618	
10	198	->	219	0.01006	-0.01511	0.00316	-0.00126	0.01549	1.71068	-0.25828	0.04818	1.73074	
11	205	->	220	-0.01304	-0.00610	-0.01412	-0.00022	0.01538	1.70458	-0.27240	0.04796	1.72688	
12	202	<-	220	-0.00603	-0.01495	0.00153	-0.00136	0.01508	1.68964	-0.27087	0.04661	1.71185	
13	216	->	234	0.01234	0.01266	-0.00667	0.00108	0.01435	1.70230	-0.27754	0.04769	1.72543	
14	215	->	233	-0.00724	0.01275	-0.00385	-0.00091	0.01335	1.71505	-0.28139	0.04678	1.73861	
15	218	->	225	0.00828	0.00124	0.01097	0.00079	0.01107	1.71629	-0.27042	0.04757	1.73811	
16	202	->	219	-0.00267	-0.00209	-0.00999	0.00021	0.01021	1.71420	-0.28041	0.04777	1.73764	
17	208	->	227	0.00852	0.00386	0.00858	0.00299	0.00988	1.71806	-0.27183	0.05077	1.74017	
18	217	->	236	0.01076	0.00981	-0.00058	0.00052	0.00984	1.72787	-0.27241	0.05128	1.74996	
19	200	->	222	-0.00729	-0.00153	0.00014	-0.00964	0.00977	1.72634	-0.27227	0.04164	1.74817	
20	218	->	230	0.00640	0.00729	0.00508	0.00102	0.00894	1.73363	-0.26719	0.04265	1.75461	
21	216	->	222	-0.01117	0.00544	0.00196	-0.00667	0.00883	1.73907	-0.26523	0.03598	1.75954	
22	214	->	226	0.00457	0.00847	-0.00163	-0.00162	0.00878	1.74754	-0.26686	0.03436	1.76813	
23	203	->	227	-0.00551	0.00149	-0.00798	-0.00016	0.00812	1.74902	-0.27484	0.03420	1.77082	
24	204	->	219	0.00895	-0.00081	0.00799	-0.00023	0.00803	1.74821	-0.26685	0.03397	1.76879	
25	198	->	221	0.00837	-0.00780	-0.00050	-0.00081	0.00786	1.74041	-0.26735	0.03316	1.76114	
26	213	->	221	-0.00631	-0.00499	-0.00571	-0.00027	0.00758	1.73543	-0.27305	0.03289	1.75708	
27	201	->	224	-0.00452	-0.00224	0.00710	0.00095	0.00750	1.73318	-0.26596	0.03384	1.75380	
28	209	->	225	-0.00373	-0.00623	-0.00409	0.00008	0.00745	1.72695	-0.27004	0.03392	1.74826	
29	212	->	223	-0.00400	-0.00205	-0.00640	0.00316	0.00743	1.72490	-0.27644	0.03708	1.74731	
30	215	->	220	-0.00189	-0.00123	-0.00731	0.00014	0.00741	1.72367	-0.28375	0.03722	1.74727	oscillator
.....	....	....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	strength
20403	78	<-	320	-0.00014	0.00014	0.00000	0.0000	-0.00000	1.38924	-0.20997	0.05008	1.40591	0.13700
							results of Gaussian09		1.37030	-0.21070	0.04930		0.13400

Table S2-3a Analysis of TDDFT components for **3a**, [Cu(dmp)(dppb)]+ calculated by Multiwfn software. Transition dipole moments are shown in the atomic unit.

					transition dipole moments				summation of the components from No.1 to n				
No.	MO#		MO#	Coefficient	X	Y	Z	norm	X	Y	Z	norm	
1	364	->	365	-0.25259	-0.32170	0.40912	-0.08547	0.52742	-0.32170	0.40912	-0.08547	0.52742	
2	363	->	366	-0.25236	-0.31966	0.40812	-0.08212	0.52487	-0.64136	0.81724	-0.16759	1.05229	
3	362	->	366	0.37078	0.04070	-0.06774	0.14621	0.16620	-0.60066	0.74950	-0.02138	0.96072	
4	361	->	365	0.41553	0.03779	-0.07296	0.11523	0.14153	-0.56287	0.67653	0.09385	0.88506	
5	360	->	366	-0.20938	-0.00919	0.00147	-0.07080	0.07141	-0.57206	0.67800	0.02305	0.88740	
6	359	->	365	-0.09444	-0.00403	0.00727	-0.04000	0.04086	-0.57609	0.68527	-0.01695	0.89541	
7	364	->	367	-0.01582	-0.02240	-0.02003	0.00511	0.03048	-0.59849	0.66524	-0.01184	0.89491	
8	363	->	368	-0.01463	-0.02073	-0.01867	0.00467	0.02829	-0.61922	0.64656	-0.00717	0.89528	
9	337	->	366	0.01535	-0.01990	-0.01617	0.00333	0.02586	-0.63912	0.63039	-0.00384	0.89771	
10	338	->	365	0.01480	-0.01532	-0.01182	0.00255	0.01952	-0.65444	0.61857	-0.00129	0.90052	
11	347	->	366	-0.01372	0.01409	0.00979	-0.00278	0.01738	-0.64036	0.62836	-0.00407	0.89717	
12	348	->	365	-0.01575	0.01427	0.00921	-0.00280	0.01721	-0.62609	0.63757	-0.00686	0.89360	
13	339	->	366	0.00585	0.01062	0.01186	-0.00274	0.01615	-0.61547	0.64943	-0.00960	0.89479	
14	340	->	367	0.00613	0.00819	-0.01272	0.00075	0.01514	-0.60728	0.63672	-0.00886	0.87993	
15	357	->	368	0.00377	-0.00884	-0.01101	0.00236	0.01432	-0.61612	0.62570	-0.00650	0.87815	
16	358	->	367	0.00354	-0.00837	-0.01014	0.00218	0.01333	-0.62450	0.61556	-0.00432	0.87689	
17	344	->	365	-0.00731	-0.00865	-0.00907	0.00284	0.01285	-0.63314	0.60649	-0.00148	0.87676	
18	340	->	365	-0.00415	0.00864	0.00914	-0.00210	0.01275	-0.62450	0.61563	-0.00358	0.87693	
19	339	->	368	-0.00551	0.00656	-0.01033	0.00067	0.01226	-0.61794	0.60529	-0.00292	0.86501	
20	347	->	368	0.00774	0.00440	-0.01112	0.00174	0.01209	-0.61354	0.59417	-0.00118	0.85409	
21	360	->	369	0.00796	-0.00858	-0.00528	0.00276	0.01044	-0.62212	0.58889	0.00158	0.85664	
22	348	->	367	0.00721	0.00347	-0.00939	0.00149	0.01012	-0.61865	0.57950	0.00306	0.84768	
23	343	->	366	0.00625	-0.00618	-0.00678	0.00228	0.00945	-0.62483	0.57272	0.00534	0.84761	
24	363	<-	366	0.00431	0.00546	-0.00697	0.00140	0.00896	-0.61937	0.56575	0.00675	0.83889	
25	354	->	366	-0.01125	-0.00749	-0.00481	0.00105	0.00896	-0.62686	0.56094	0.00779	0.84123	
26	364	<-	365	0.00428	0.00545	-0.00693	0.00145	0.00894	-0.62141	0.55401	0.00924	0.83256	
27	361	->	370	-0.00917	-0.00153	0.00843	-0.00130	0.00867	-0.62294	0.56244	0.00794	0.83932	
28	346	->	366	0.00744	-0.00496	-0.00636	0.00138	0.00818	-0.62790	0.55608	0.00932	0.83879	
29	361	->	367	0.03280	0.00377	0.00495	-0.00519	0.00810	-0.62413	0.56103	0.00413	0.83923	
30	362	->	369	-0.00688	0.00157	0.00770	-0.00187	0.00808	-0.62256	0.56873	0.00226	0.84323	oscillator
……	……	….	……	……	……	……	……	……	……	……	……	……	strength
12876	364	<-	1568	0.00011	0.00011	0.00000	0.00000	0.00000	-0.45709	0.40300	-0.01309	0.60952	0.02751
							results of Gaussian		-0.42760	0.35980	-0.01260		0.02310

Table S2-3b Analysis of TDDFT components for **3b**, [Cu(dmpp)(dppb)]+ calculated by Multiwfn software. Transition dipole moments are shown in the atomic unit.

3b					transition dipole moments				summation of the components from No.1 to n				
No.	MO#		MO#	Coefficient	X	Y	Z	norm	X	Y	Z	norm	
1	444	->	445	-0.25226	0.13756	-0.48819	0.52770	0.73193	0.13756	-0.48819	0.52770	0.73193	
2	443	->	446	-0.25093	0.13384	-0.48697	0.52394	0.72771	0.27140	-0.97516	1.05163	1.45963	
3	442	->	446	0.42095	-0.11151	0.07998	-0.13703	0.19393	0.15989	-0.89518	0.91460	1.28973	
4	441	->	445	0.42304	-0.10083	0.08185	-0.13580	0.18791	0.05906	-0.81332	0.77880	1.12762	
5	444	->	447	-0.02797	-0.02082	-0.05575	-0.05489	0.08096	0.03824	-0.86907	0.72392	1.13172	
6	443	->	448	-0.02658	-0.01982	-0.05281	-0.05270	0.07719	0.01842	-0.92188	0.67122	1.14050	
7	437	->	446	-0.01745	-0.00178	0.01653	-0.02829	0.03281	0.01664	-0.90536	0.64293	1.11054	
8	438	->	445	-0.01699	-0.00155	0.01551	-0.02775	0.03183	0.01509	-0.88985	0.61517	1.08190	
9	436	->	447	0.01189	-0.00333	0.01990	-0.02384	0.03124	0.01177	-0.86995	0.59133	1.05196	
10	435	->	448	0.01176	-0.00328	0.01985	-0.02364	0.03104	0.00848	-0.85010	0.56769	1.02226	
11	418	->	445	-0.00886	-0.00723	-0.01632	-0.01888	0.02599	0.00125	-0.86642	0.54881	1.02562	
12	440	->	446	0.04175	0.01967	-0.00526	0.00544	0.02108	0.02092	-0.87169	0.55425	1.03318	
13	419	->	446	0.00963	0.00533	0.01246	0.01561	0.02067	0.02625	-0.85923	0.56986	1.03136	
14	417	->	446	-0.00930	-0.00546	-0.01202	-0.01394	0.01919	0.02079	-0.87124	0.55593	1.03371	
15	441	->	447	0.05620	0.01305	0.00257	0.01340	0.01888	0.03384	-0.86867	0.56932	1.03917	
16	442	->	448	0.05270	0.01209	0.00426	0.01375	0.01879	0.04593	-0.86442	0.58307	1.04369	
17	420	->	445	-0.01230	0.00457	0.01094	0.01327	0.01780	0.05050	-0.85348	0.59634	1.04240	
18	436	->	445	0.01301	0.00054	-0.01413	0.01028	0.01748	0.05104	-0.86761	0.60662	1.05988	
19	435	->	446	0.01304	0.00054	-0.01401	0.01008	0.01727	0.05158	-0.88162	0.61670	1.07714	
20	419	->	448	-0.00897	-0.00370	0.00877	-0.01297	0.01609	0.04787	-0.87286	0.60372	1.06238	
21	418	->	447	-0.00695	-0.00197	0.00972	-0.01001	0.01409	0.04591	-0.86314	0.59372	1.04862	
22	443	<-	446	0.00448	-0.00239	0.00869	-0.00935	0.01299	0.04352	-0.85444	0.58436	1.03607	
23	444	<-	445	0.00446	-0.00243	0.00863	-0.00933	0.01294	0.04108	-0.84581	0.57503	1.02359	
24	423	->	447	-0.00851	-0.00181	0.00199	-0.00965	0.01002	0.03927	-0.84382	0.56538	1.01648	
25	439	->	447	0.01376	-0.00042	-0.00723	-0.00638	0.00965	0.03885	-0.85105	0.55900	1.01896	
26	440	->	448	0.01687	0.00019	-0.00706	-0.00627	0.00944	0.03904	-0.85811	0.55273	1.02146	
27	439	->	445	0.01637	0.00784	-0.00226	0.00378	0.00900	0.04689	-0.86037	0.55652	1.02574	
28	420	->	447	0.00648	-0.00214	0.00418	-0.00670	0.00818	0.04474	-0.85620	0.54982	1.01851	
29	422	->	446	0.00623	0.00201	0.00397	0.00519	0.00684	0.04676	-0.85223	0.55501	1.01809	
30	440	->	449	0.00450	-0.00235	-0.00371	-0.00514	0.00676	0.04441	-0.85594	0.54987	1.01831	oscillator
……	……	……	……	……	……	……	……	……	……	……	……	……	strength
14316	405	<-	615	-0.00010	0.00010	0.00000	0.00000	0.00000	0.05832	-0.72221	0.45501	0.85558	0.05439
							results of Gaussian		0.05040	-0.68960	0.40640		0.04780

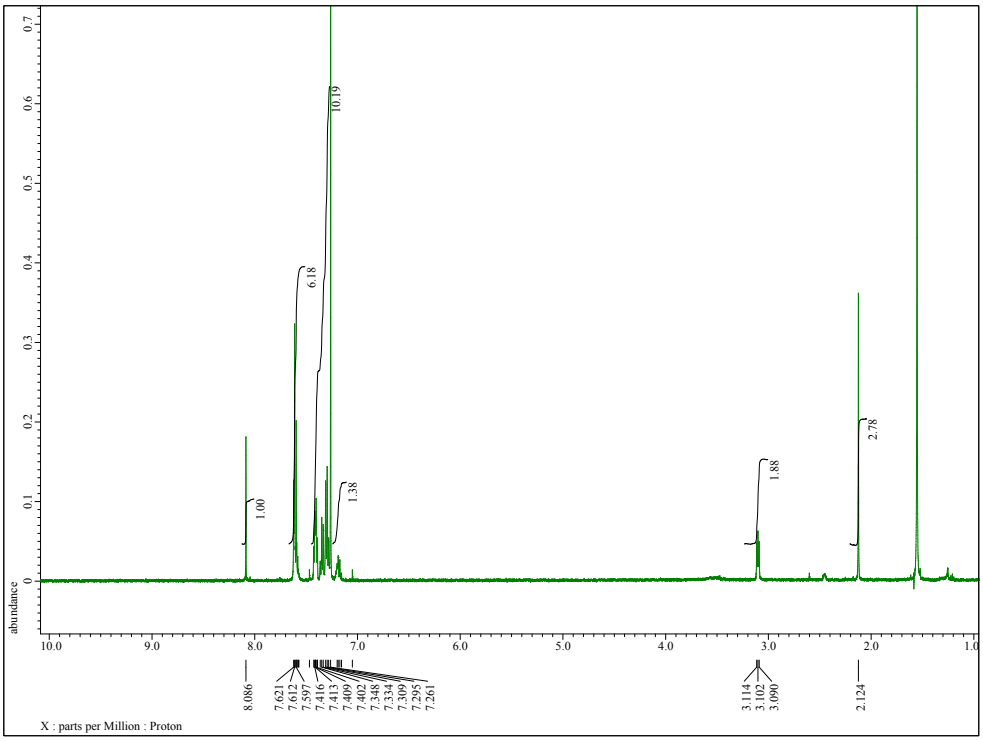


Figure S1. ^{1}H NMR spectrum in $CDCl_3$ with low concentration of **1b** at room temperature measured under the air immediately after dissolving the solid sample.

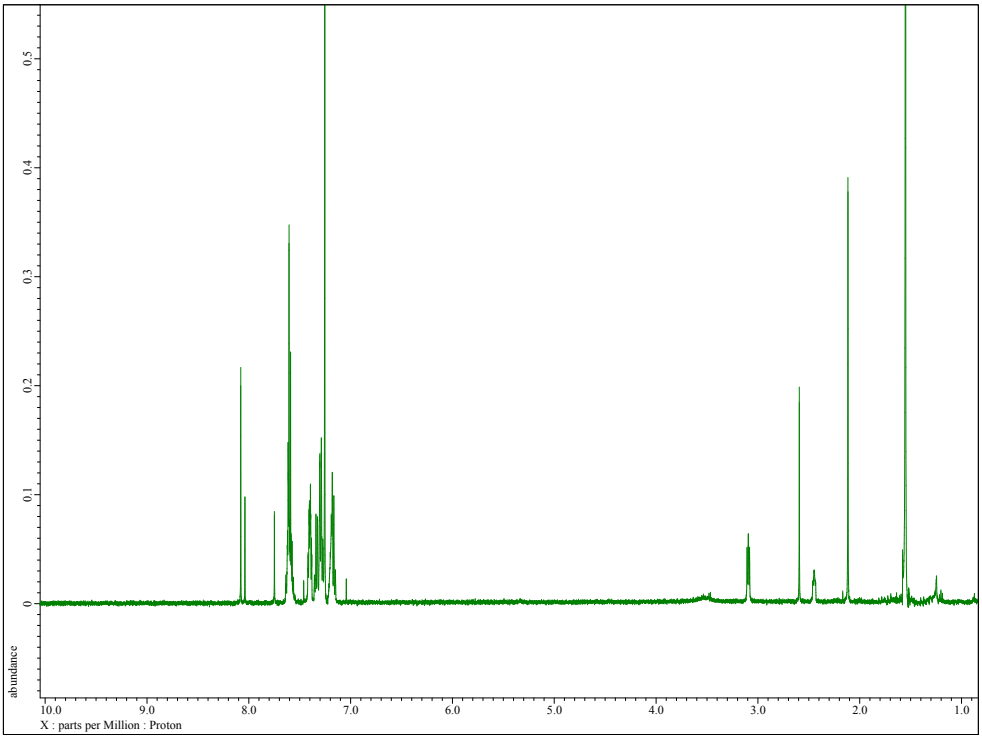


Figure S2. ^{1}H NMR spectrum in $CDCl_3$ with low concentration of **1b** at room temperature under air kept for 4 days after dissolving the solid sample in the dark.

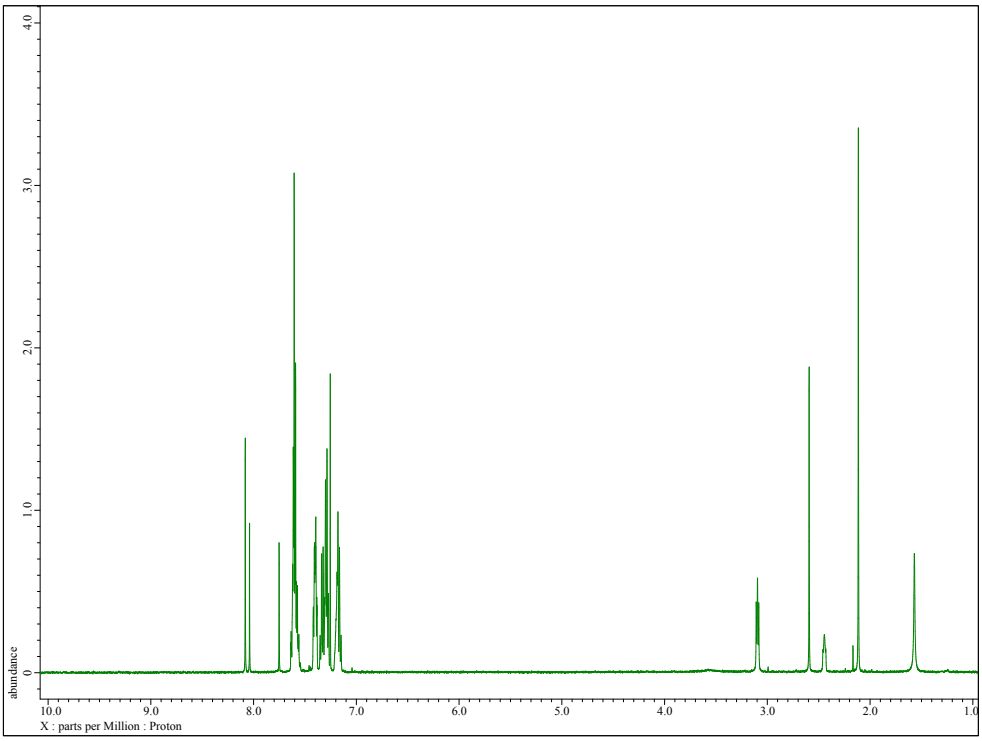


Figure S3. ^{1}H NMR spectrum in $CDCl_3$ with high concentration of **1b** at room temperature measured under the air immediately after dissolving the solid sample.

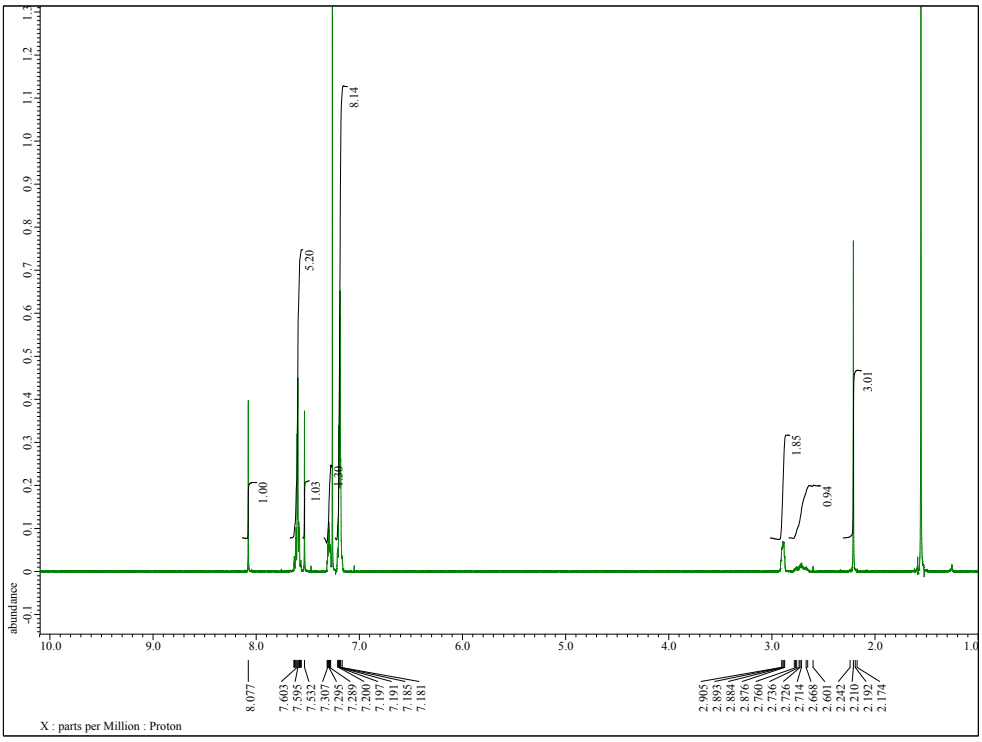


Figure S4. ^{1}H NMR spectrum a in $CDCl_3$ with low concentration of **2b** at room temperature measured under the air immediately after dissolving the solid sample.

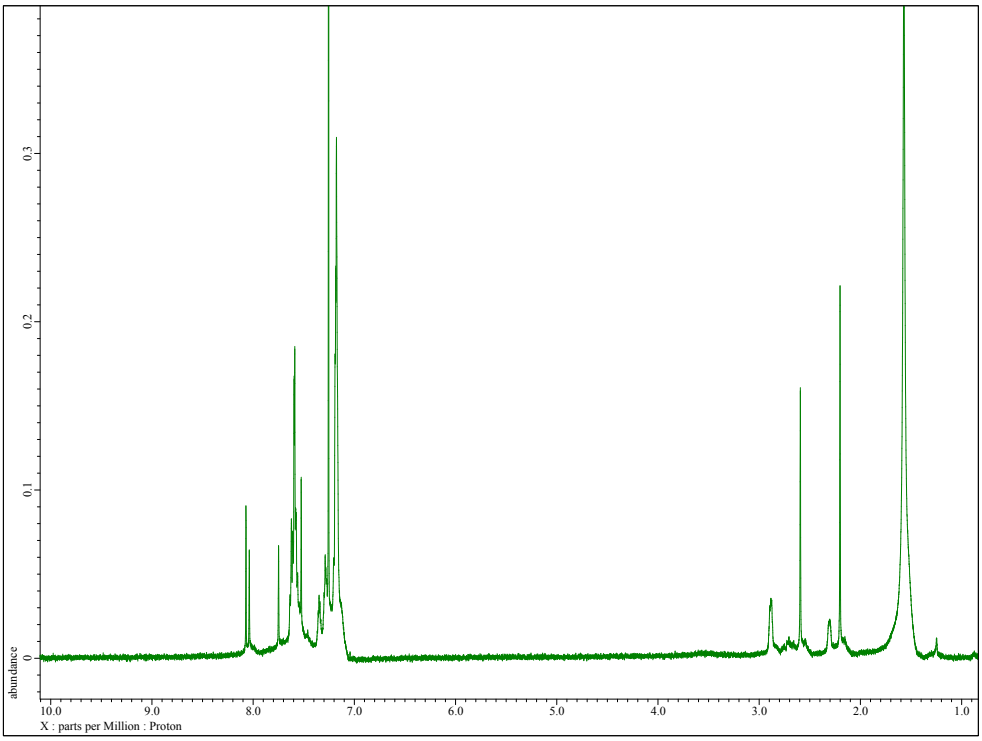


Figure S5. ^{1}H NMR spectrum in $CDCl_3$ with low concentration of **2b** at room temperature under the air kept for 4 days after dissolving the solid sample in the dark.

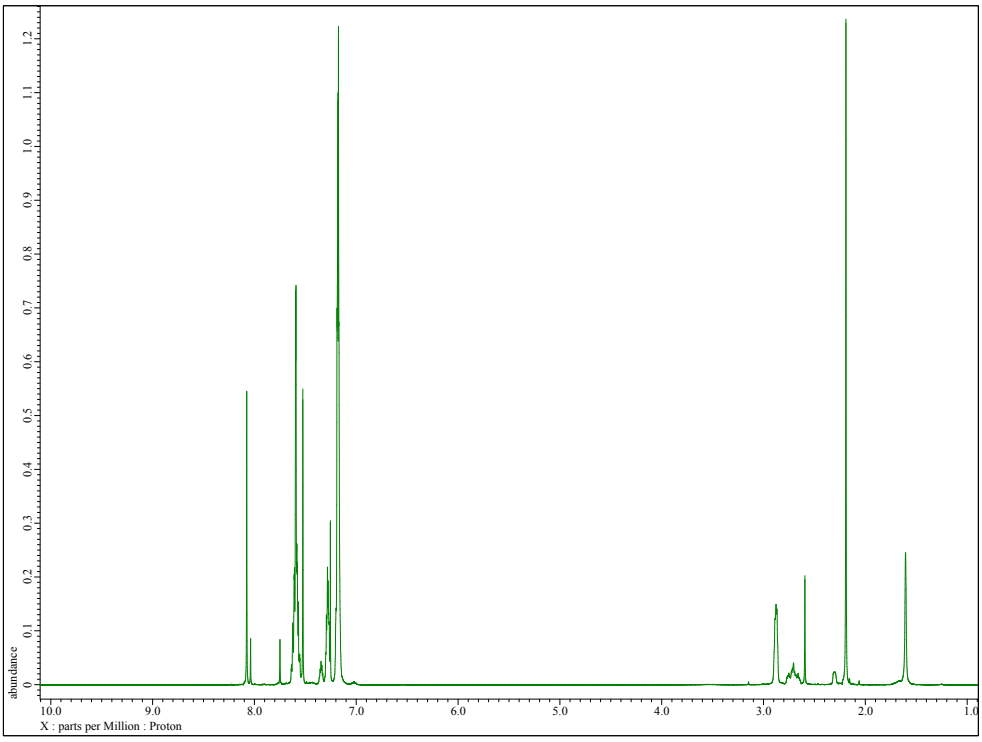


Figure S6. ^{1}H NMR spectrum in $CDCl_3$ with high concentration of **2b** at room temperature measured under the air immediately after dissolving the solid sample.

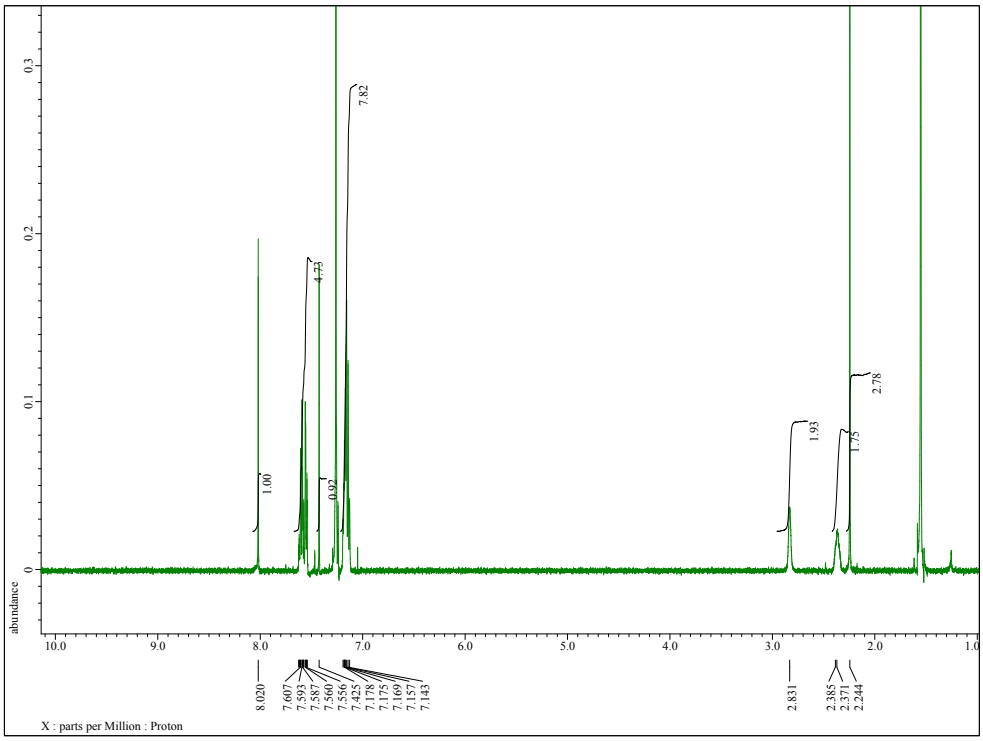


Figure S7. ^{1}H NMR spectrum in $CDCl_3$ with low concentration of **3b** at room temperature measured under the air immediately after dissolving the solid sample.

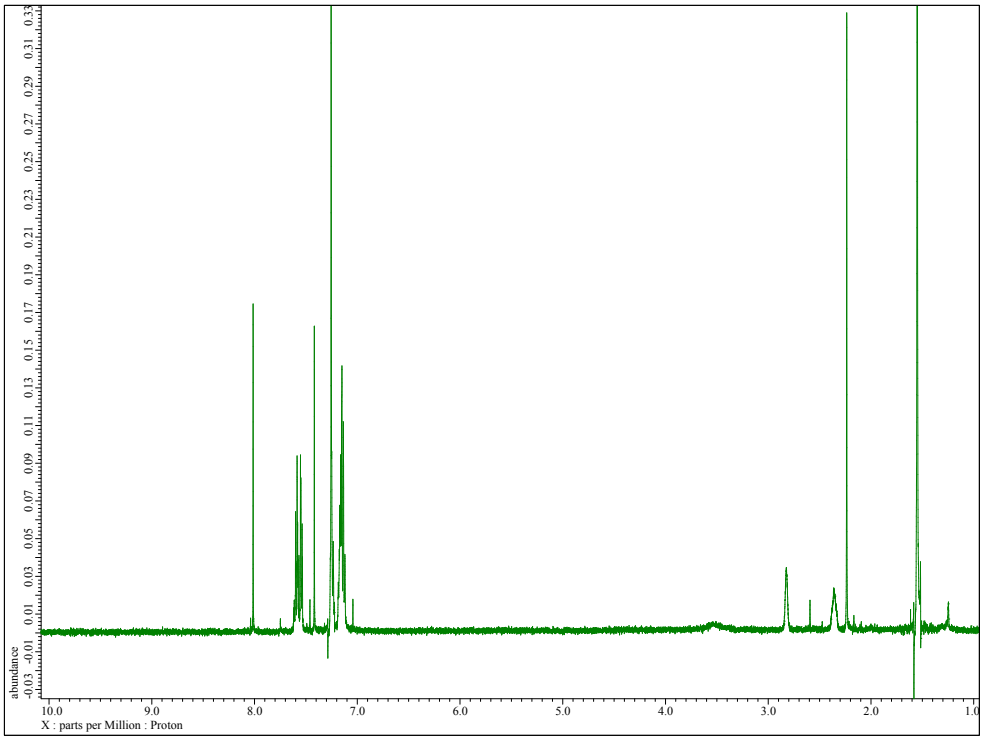


Figure S8. ^{1}H NMR spectrum in $CDCl_3$ with low concentration of **3b** at room temperature under the air kept for 4 days after dissolving the solid sample in the dark.

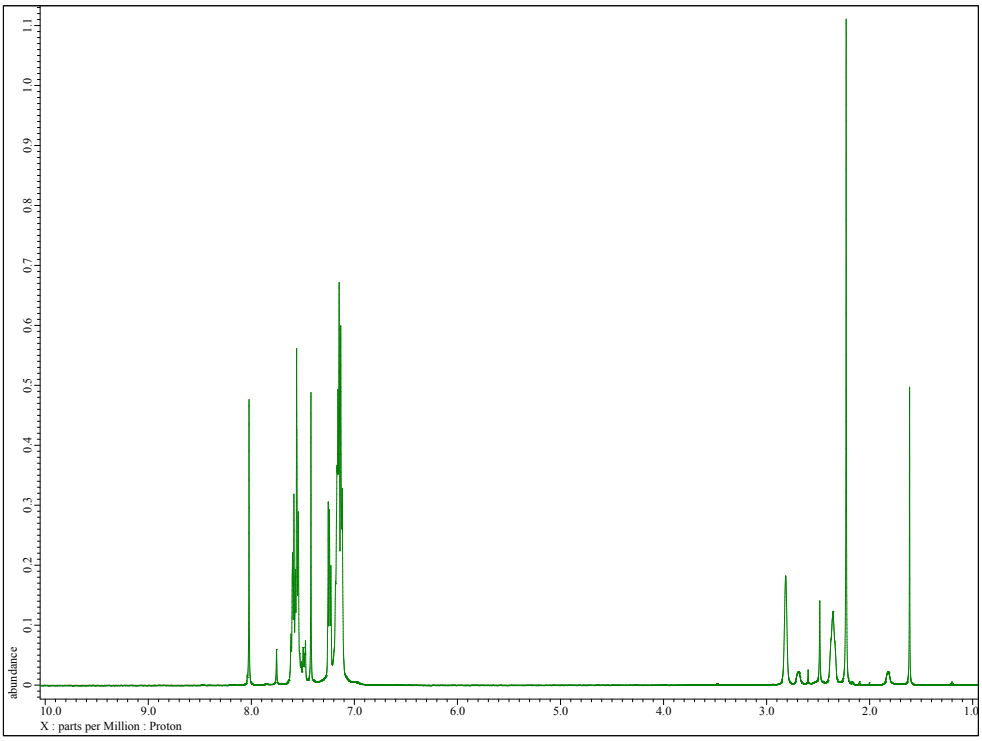


Figure S9. ^{1}H NMR spectrum of **3b** with high concentration in $CDCl_3$ at room temperature measured under the air immediately after dissolving the solid sample.

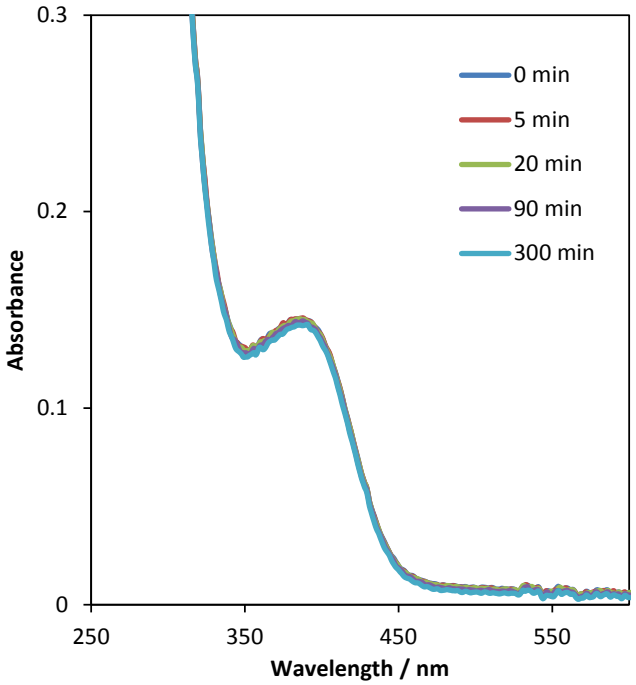
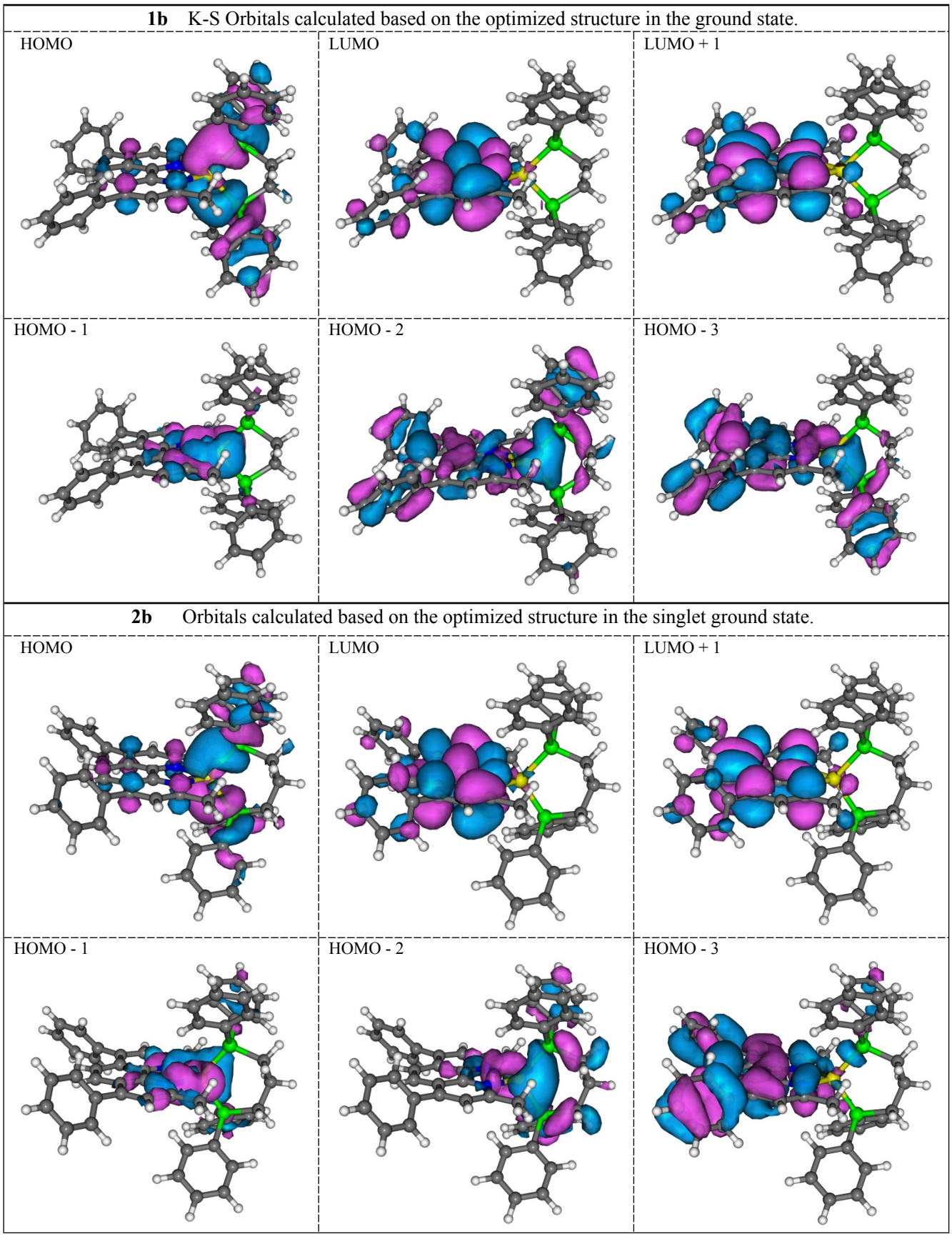


Figure S10. Time course of absorption spectra of **3b** in degassed dichloromethane at room temperature after dissolving the solid sample in the dark.

Figure S11. Kohn-Sham orbitals of **1b**, **2b**, and **3b**.



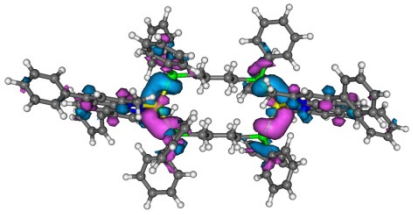
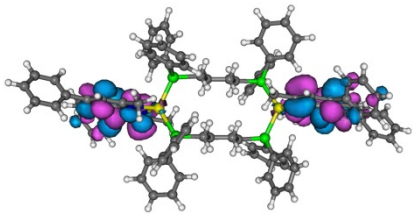
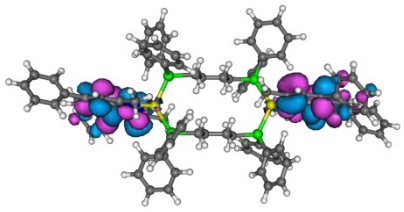
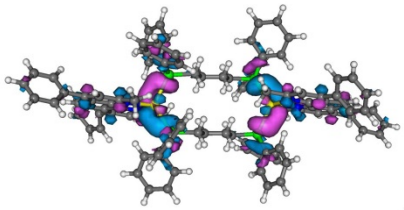
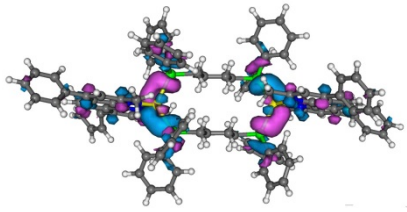
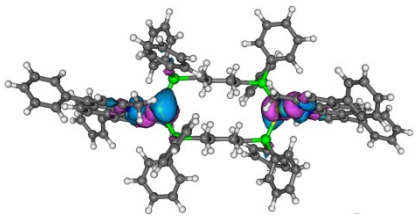
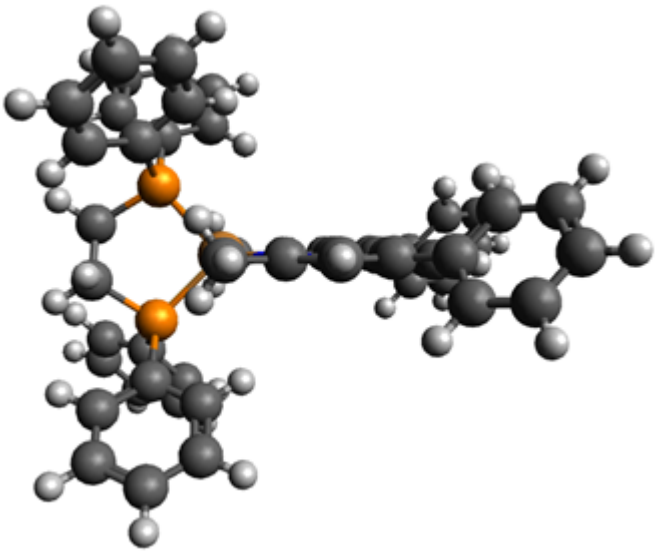
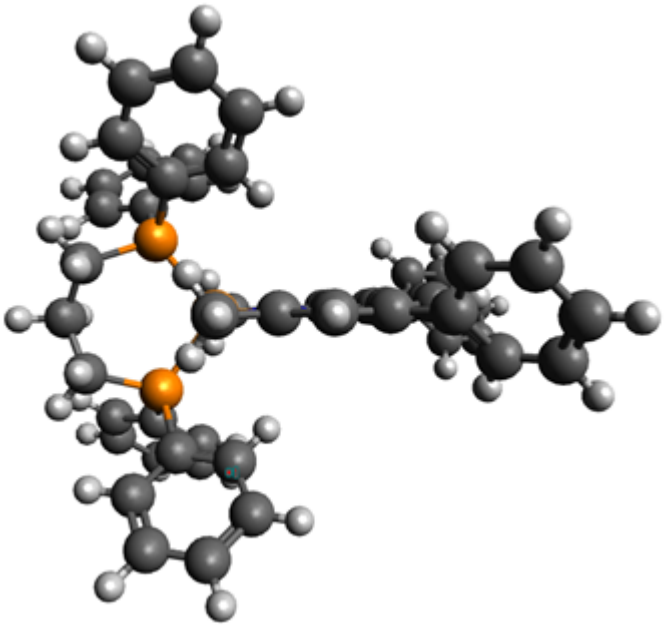
3b Orbitals calculated based on the optimized structure in the singlet ground state.		
HOMO 	LUMO 	LUMO + 1 
HOMO - 1 	HOMO - 2 	HOMO - 3 

Fig. S12. Side views of the structures of **1b**, **2b**, and **3b**, which were clarified by X-ray crystallography.

1b



2b



3b