Supplementary Information

Simple and Extremely Efficient Blue Emitters Based on Mononuclear Cu(I)-Halide Complexes with Delayed Fluorescence

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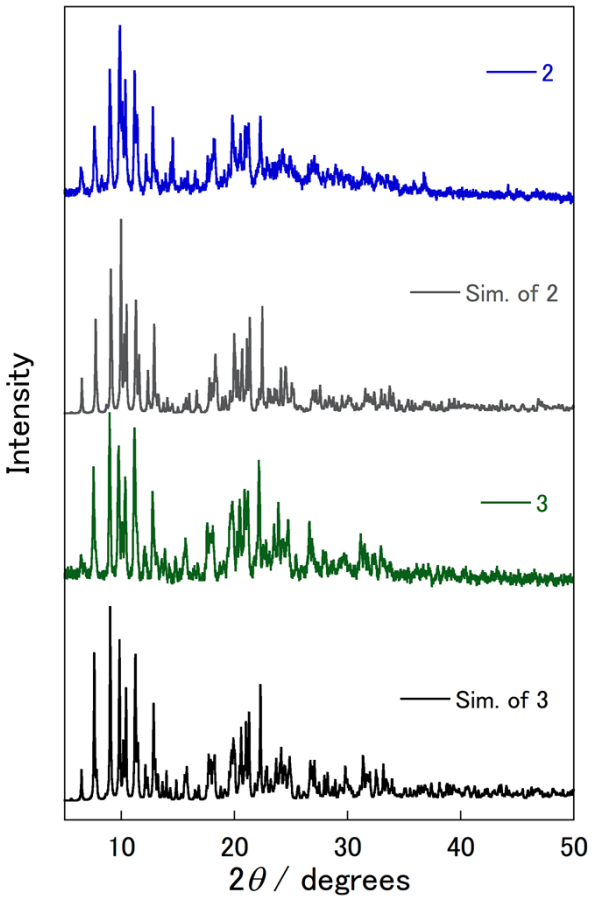

Fig. S1. PXRD patterns of **2** and **3** prepared by Method 2 and simulated diffraction pattern based on the single crystal structure of **2** and **3**.

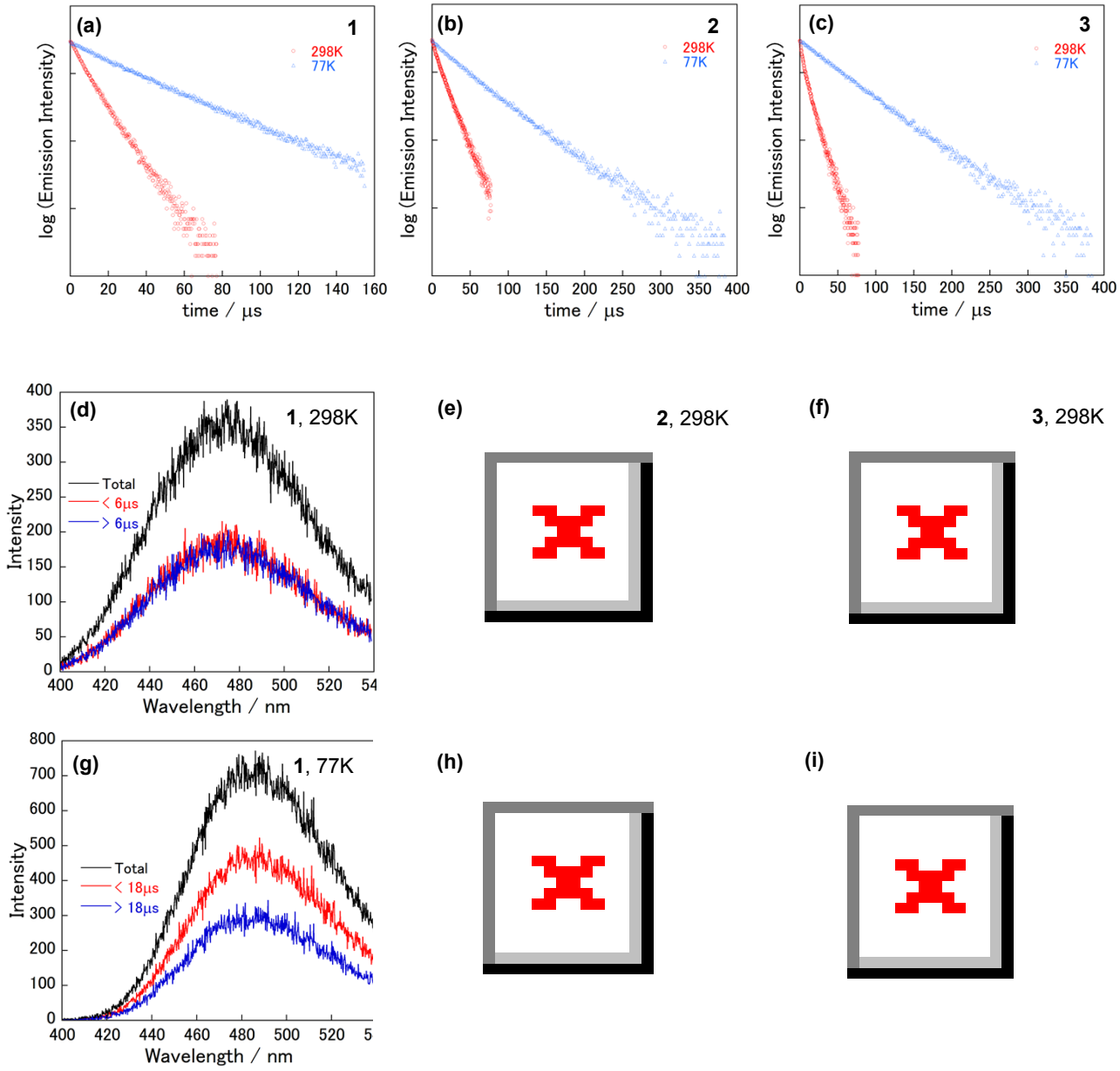

Fig. S2. Emission decays of **1**-**3** in the solid states (a, b and c) and time-resolved emission spectra of **1**-**3** at 298 K (d, e and f) and 77 K (g, h and i).

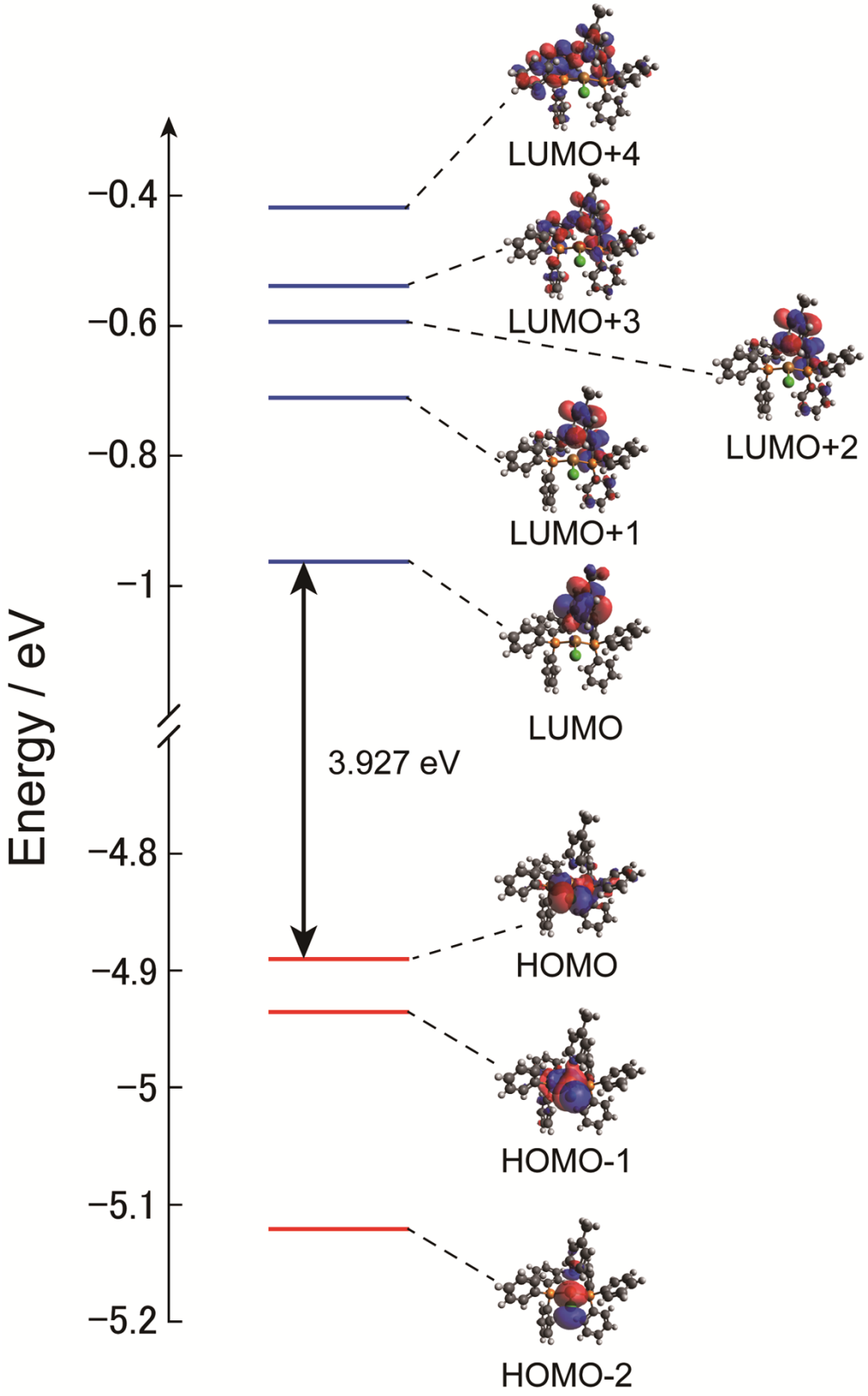

Fig. S3. Schematic molecular orbital diagrams and orbital shapes related to calculated transition of **1**. Molecular structure is determined by X-ray crystallographic analysis.

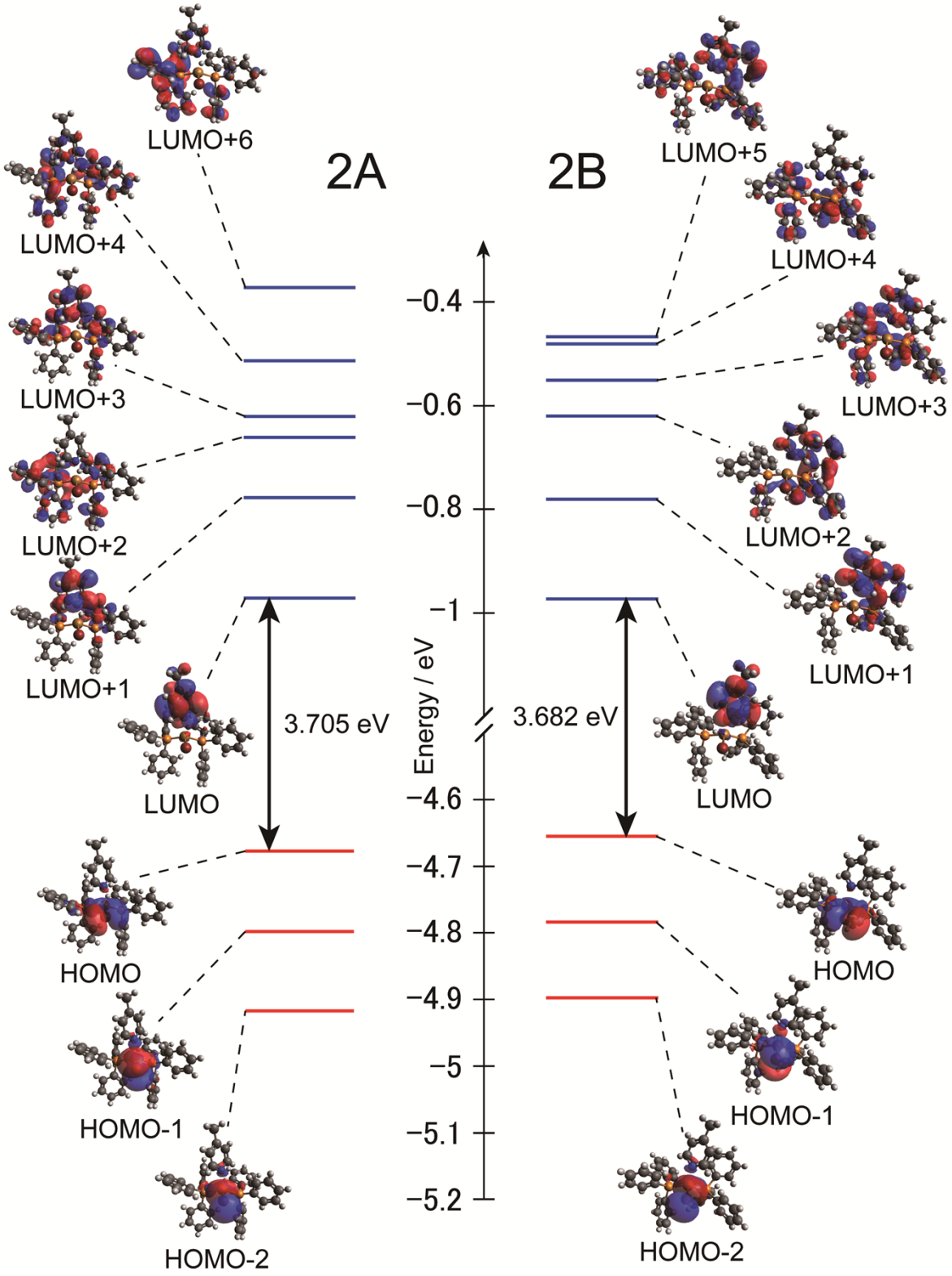

Fig. S4. Schematic molecular orbital diagrams and orbital shapes related to calculated transition of **2A** (left) and **2B** (right) which are based on two geometries determined by X-ray crystallography (see Fig. 1 (b) and (c)).

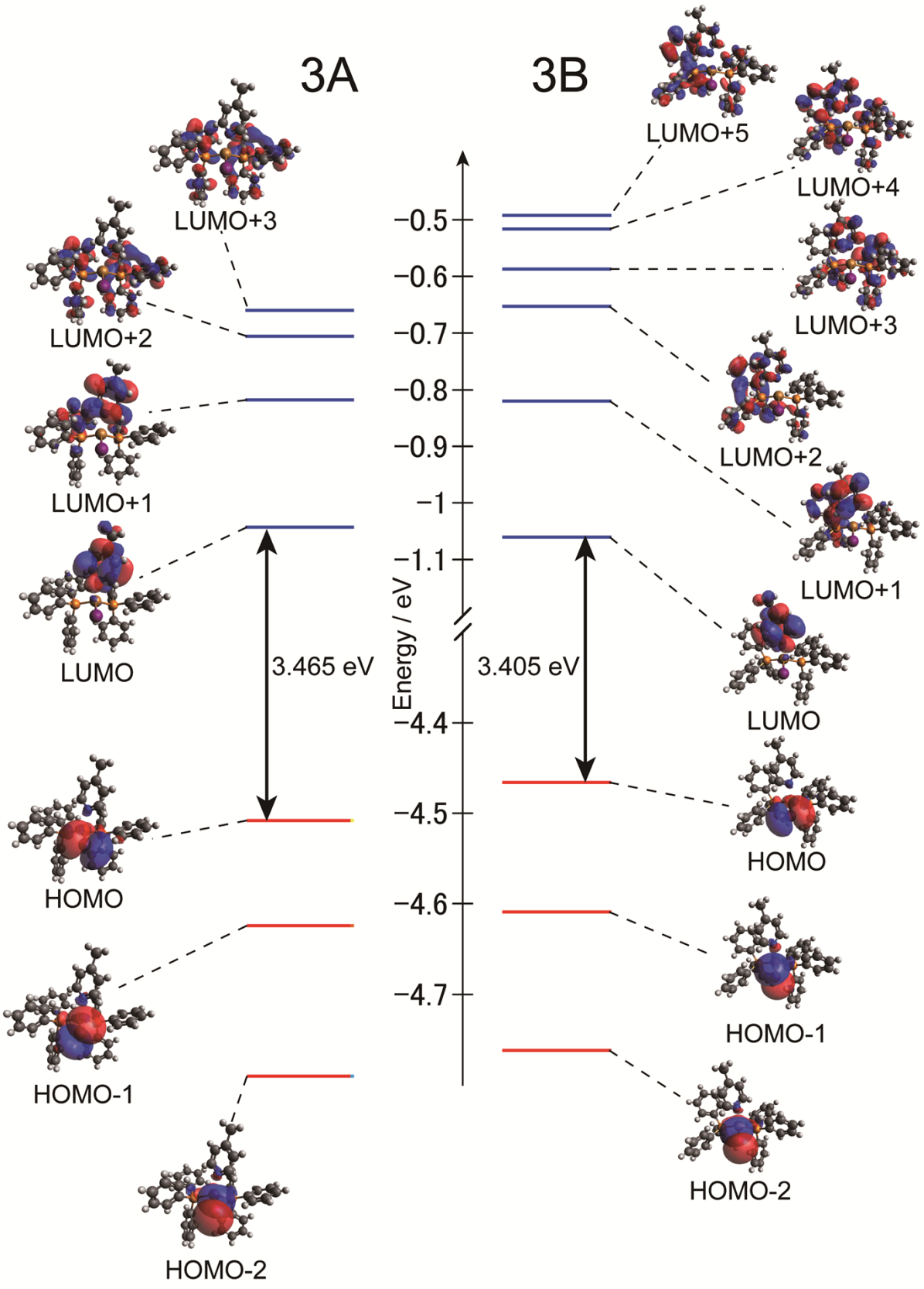

Fig. S5. Schematic molecular orbital diagrams and orbital shapes related to calculated transition of **3A** (left) and **3B** (right) which are based on two geometries determined by X-ray crystallography (see Fig. 1 (d) and (e)).

Table S1. Energy, oscillator strength and major contribution of calculated transition for **1**.

Excited state	Energy / eV (nm)	Oscillator strength	Major contribution (%)
1	3.2234 (384.64)	0.0079	HOMO-1->LUMO (74) HOMO->LUMO (26)
2	3.2396 (382.72)	0.0118	HOMO->LUMO (74) HOMO-1->LUMO (26)
3	3.3467 (370.46)	0.0004	HOMO-2->LUMO (100)
4	3.5358 (350.65)	0.0100	HOMO->LUMO+1 (63) HOMO-1->LUMO+1 (24) HOMO->LUMO+2 (13)
5	3.5700 (347.29)	0.0008	HOMO-1->LUMO+1 (58) HOMO->LUMO+1 (23) HOMO-1->LUMO+2 (19)
6	3.6725 (337.60)	0.0099	HOMO->LUMO+2 (47) HOMO-1->LUMO+2 (17) HOMO->LUMO+3 (14) HOMO->LUMO+1 (12) HOMO-2 ->LUMO+1 (10)
7	3.6971 (335.35)	0.0021	HOMO-2 ->LUMO+1 (39) HOMO-2->LUMO+2 (16) HOMO->LUMO+2 (14) HOMO-1->LUMO+2 (12) HOMO-2->LUMO+3 (10) HOMO-1->LUMO+1 (9)
8	3.7154 (333.70)	0.0163	HOMO-1->LUMO+2 (48) HOMO-2->LUMO+1 (17) HOMO-1->LUMO+1 (13) HOMO->LUMO+2 (12) HOMO-2->LUMO+2 (10)
9	3.7584 (329.89)	0.0040	HOMO->LUMO+3 (55) HOMO-1->LUMO+3 (19) HOMO->LUMO+2 (16) HOMO->LUMO+4 (10)
10	3.7993 (326.33)	0.0392	HOMO-1->LUMO+3 (67) HOMO->LUMO+3 (20) HOMO-1->LUMO+4 (13)

Table S2. Energy, oscillator strength and major contribution of calculated transition for **2**.

Excited state	Energy / eV (nm)		Oscillator strength		Major contribution (%)	
	A	B	A	B	A	B
1	3.0315 (408.98)	3.0045 (412.67)	0.0035	0.0026	HOMO->LUMO (100)	HOMO->LUMO (100)
2	3.1365 (395.30)	3.1128 (398.30)	0.0032	0.0046	HOMO-1 ->LUMO (86) HOMO-2 ->LUMO (14)	HOMO-1 ->LUMO (78) HOMO-2 ->LUMO (22)
3	3.2298 (383.88)	3.2030 (387.09)	0.0087	0.0066	HOMO-2 ->LUMO (84) HOMO-1 ->LUMO (16)	HOMO-2 ->LUMO (77) HOMO-1 ->LUMO (23)
4	3.2820 (377.77)	3.2693 (379.24)	0.0032	0.0070	HOMO ->LUMO+1 (83) HOMO ->LUMO+3 (17)	HOMO ->LUMO+1 (83) HOMO ->LUMO+2 (13)
5	3.3890 (365.84)	3.3771 (367.13)	0.0033	0.0030	HOMO-1 ->LUMO+1 (84) HOMO-1 ->LUMO+3 (16)	HOMO-1 ->LUMO+1 (86) HOMO-1 ->LUMO+2 (14)
6	3.4618 (358.15)	3.4603 (358.30)	0.0068	0.0044	HOMO ->LUMO+2 (100)	HOMO-2 ->LUMO+1 (86) HOMO-2 ->LUMO+2 (14)
7	3.4799 (356.29)	3.4911 (355.15)	0.0022	0.0038	HOMO-2 ->LUMO+1 (81) HOMO-2 ->LUMO+3 (19)	HOMO ->LUMO+2 (86) HOMO ->LUMO+1 (14)
8	3.4900 (355.26)	3.5546 (348.80)	0.0024	0.0196	HOMO ->LUMO+3 (83) HOMO ->LUMO+1 (17)	HOMO ->LUMO+3 (100)
9	3.5855 (345.79)	3.6101 (343.43)	0.0059	0.0013	HOMO-1 ->LUMO+2 (70) HOMO-1 ->LUMO+3 (16) HOMO-2 ->LUMO+2 (14)	HOMO-1 ->LUMO+2 (45) HOMO ->LUMO+4 (40) HOMO ->LUMO+5 (15)
10	3.6154 (342.93)	3.6194 (342.55)	0.0028	0.0018	HOMO ->LUMO+4 (60) HOMO-1 ->LUMO+3 (29) HOMO ->LUMO+6 (11)	HOMO ->LUMO+4 (39) HOMO-1 ->LUMO+2 (36) HOMO ->LUMO+5 (14) HOMO-1 ->LUMO+3 (11)

A and B denote the results based on two geometries determined by X-ray crystallography (see Fig. 1 (b) and (c)).

Table S3. Energy, oscillator strength and major contribution of calculated transition for **3**.

Excited state	Energy / eV (nm)		Oscillator strength		Major contribution (%)	
	A	B	A	B	A	B
1	2.8255 (438.81)	2.7742 (446.91)	0.0018	0.0014	HOMO->LUMO (100)	HOMO->LUMO (100)
2	2.9330 (422.72)	2.8958 (428.16)	0.0011	0.0015	HOMO-1 ->LUMO (100)	HOMO-1 ->LUMO (100)
3	3.0650 (404.51)	3.0184 (410.76)	0.0084	0.0075	HOMO-2 ->LUMO (100)	HOMO-2 ->LUMO (87) HOMO-1 ->LUMO (13)
4	3.1046 (399.36)	3.0622 (404.89)	0.0029	0.0031	HOMO ->LUMO+1 (80) HOMO ->LUMO+3 (20)	HOMO ->LUMO+1 (100)
5	3.2156 (385.57)	3.1957 (387.97)	0.0055	0.0079	HOMO-1 ->LUMO+1 (81) HOMO-1 ->LUMO+3 (19)	HOMO-1 ->LUMO+1 (100)
6	3.2899 (376.86)	3.3010 (375.60)	0.0030	0.0042	HOMO ->LUMO+2 (100)	HOMO ->LUMO+2 (84) HOMO-2 ->LUMO+1 (16)
7	3.3120 (374.35)	3.3065 (374.97)	0.0013	0.0008	HOMO ->LUMO+3 (80) HOMO ->LUMO+1 (20)	HOMO-2 ->LUMO+1 (83) HOMO ->LUMO+2 (17)
8	3.3406 (371.15)	3.3649 (368.47)	0.0031	0.0114	HOMO-2 ->LUMO+1 (80) HOMO-2 ->LUMO+3 (20)	HOMO ->LUMO+3 (100)
9	3.4103 (363.56)	3.4334 (361.12)	0.0055	0.0009	HOMO-1 ->LUMO+2 (78) HOMO-1 ->LUMO+3 (22)	HOMO ->LUMO+4 (48) HOMO ->LUMO+5 (34) HOMO-1 ->LUMO+2 (18)
10	3.4408 (360.34)	3.4494 (359.44)	0.0034	0.0001	HOMO-1 ->LUMO+3 (64) HOMO-1 ->LUMO+2 (20) HOMO-1 ->LUMO+1 (16)	HOMO-1 ->LUMO+2 (66) HOMO ->LUMO+5 (34)

A and B denote the results based on two geometries determined by X-ray crystallography (see Fig. 1 (d) and (e)).

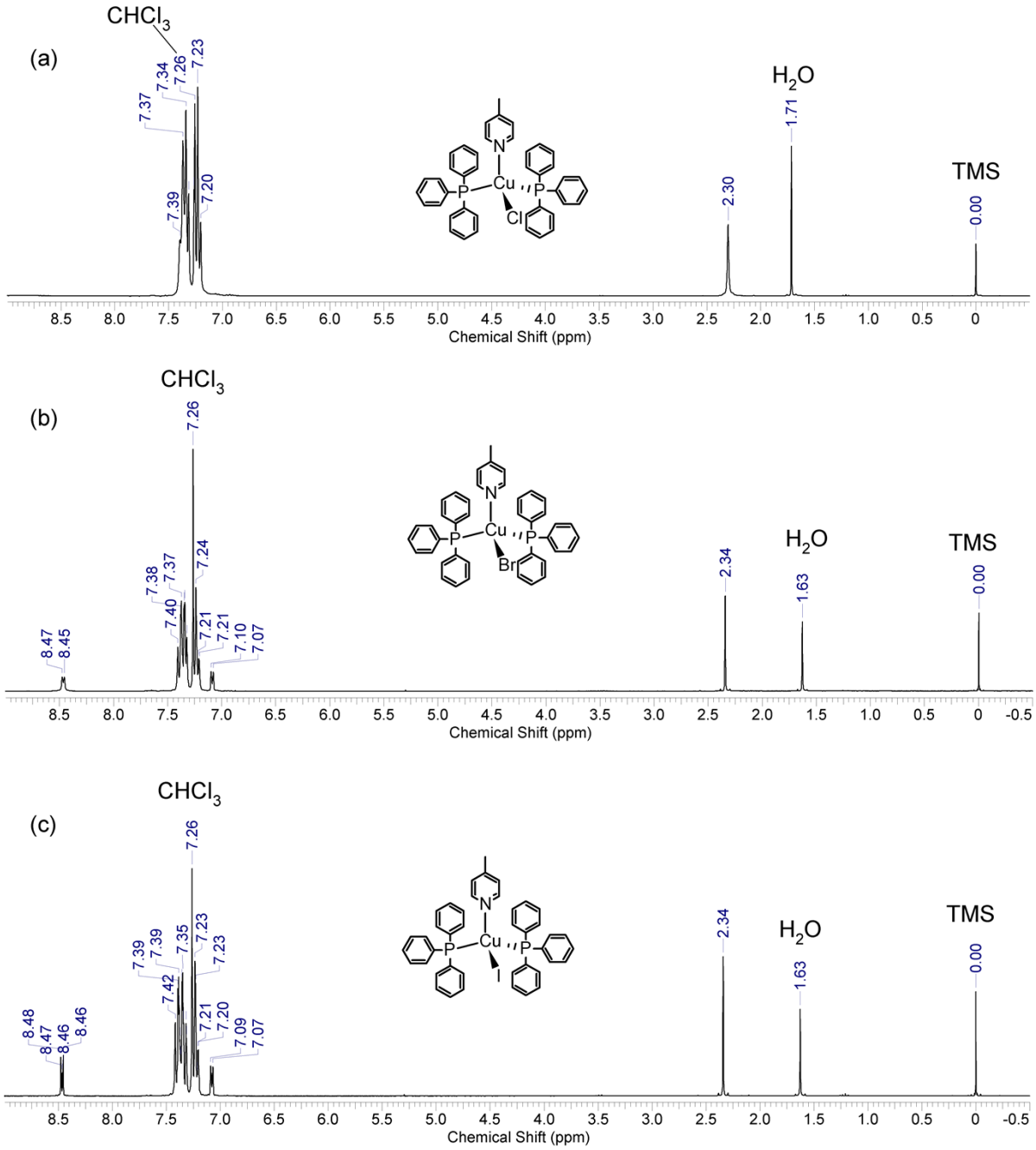

Fig. S6. ^{1}H NMR spectra ($CDCl_3$) of **1** (a), **2** (b) and **3** (c).