Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

Intense Blue Emission and Reversible Hypsochromic Shift of Luminescence Caused by Grinding Based on Silver(I) Complexes

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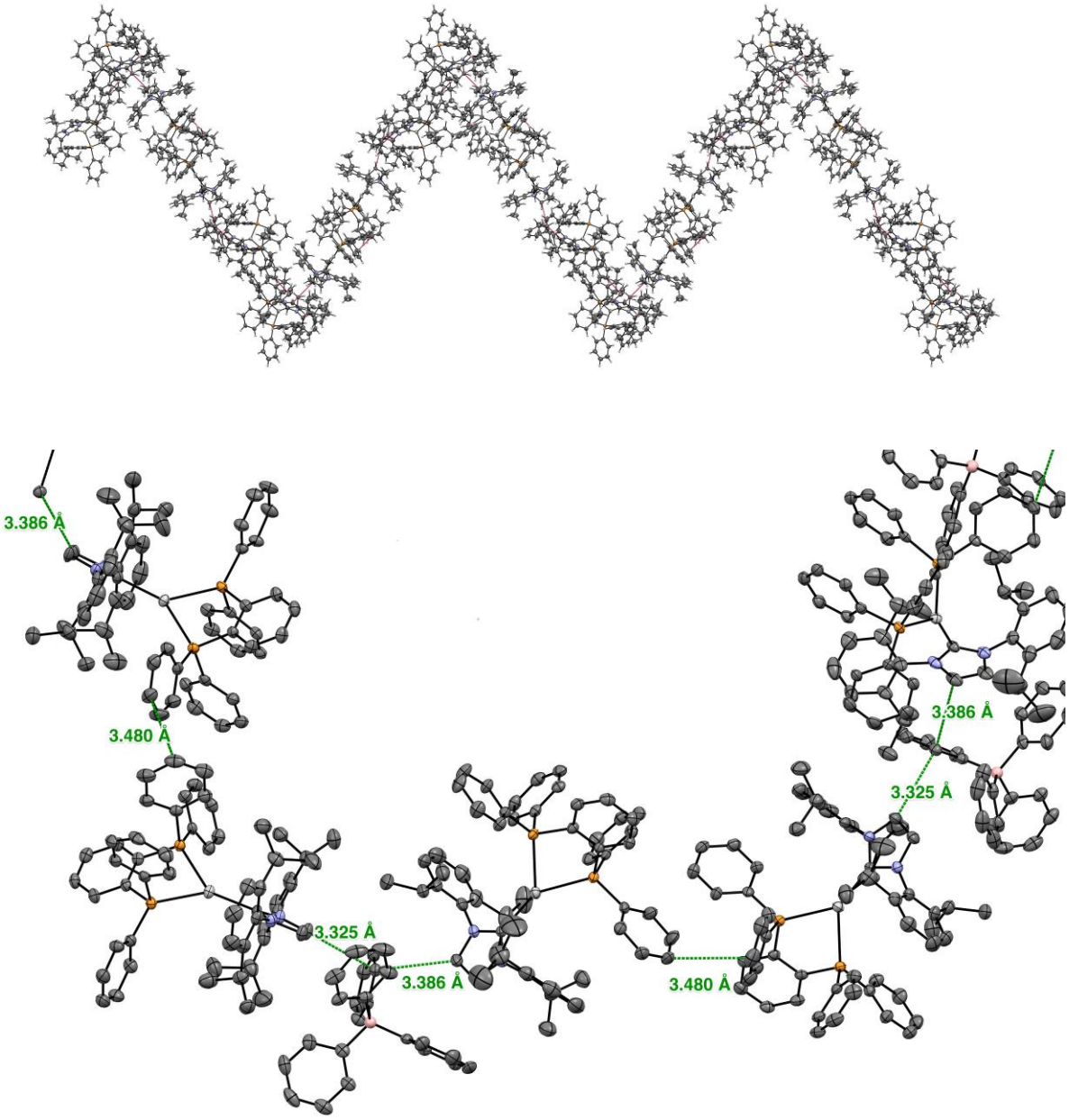

Fig. S1. (Upper) The helix formed by 1 in the crystal by the intermolecular interaction between the ligand and the counter anion. (Lower) Detailed illustration showing the intermolecular distances.

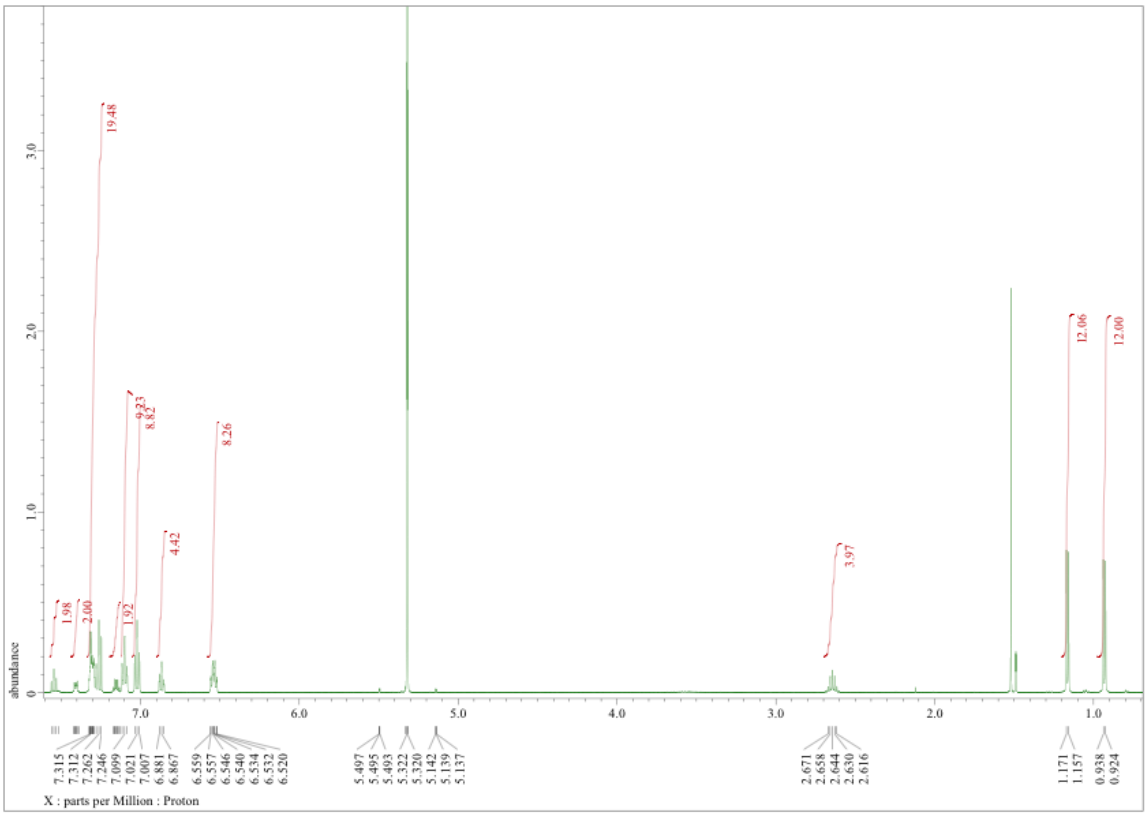

Fig. S2. ^{1}H NMR spectrum of **1** in CD_2Cl_2 at room temperature.

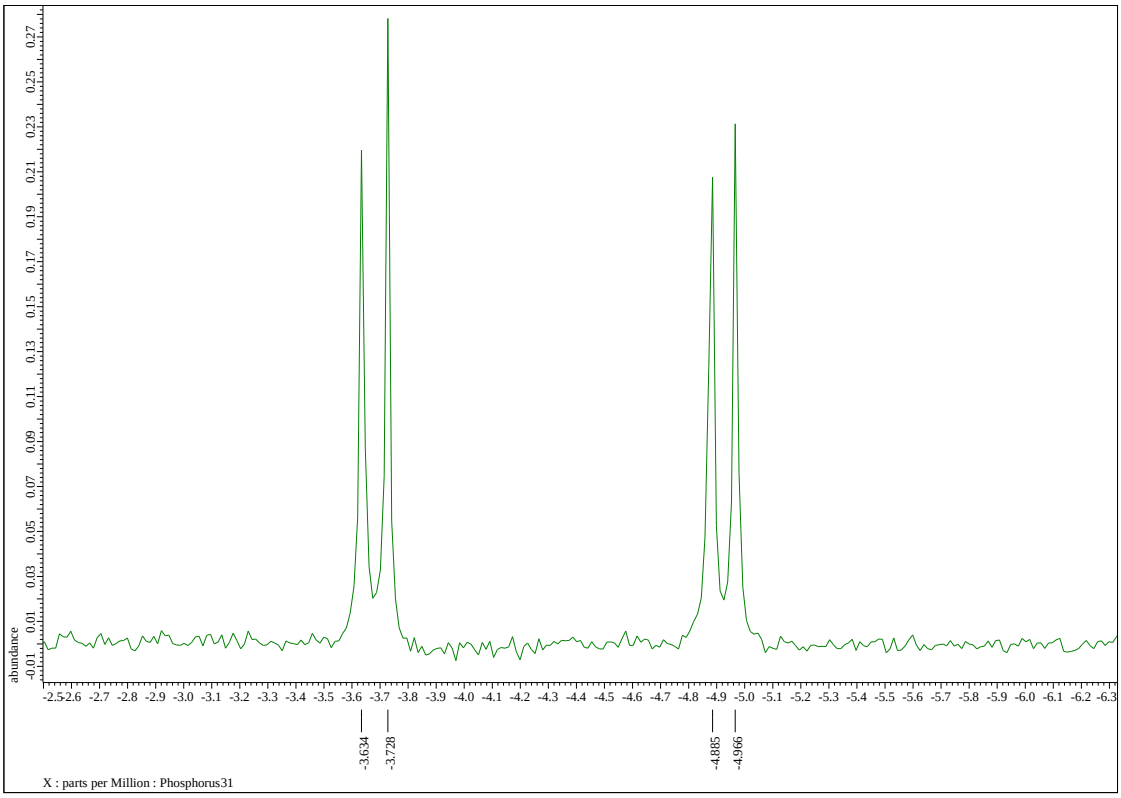

Fig. S3. ^{31}P{^{1}H}NMR spectrum of **1** in CD_2Cl_2 at room temperature.

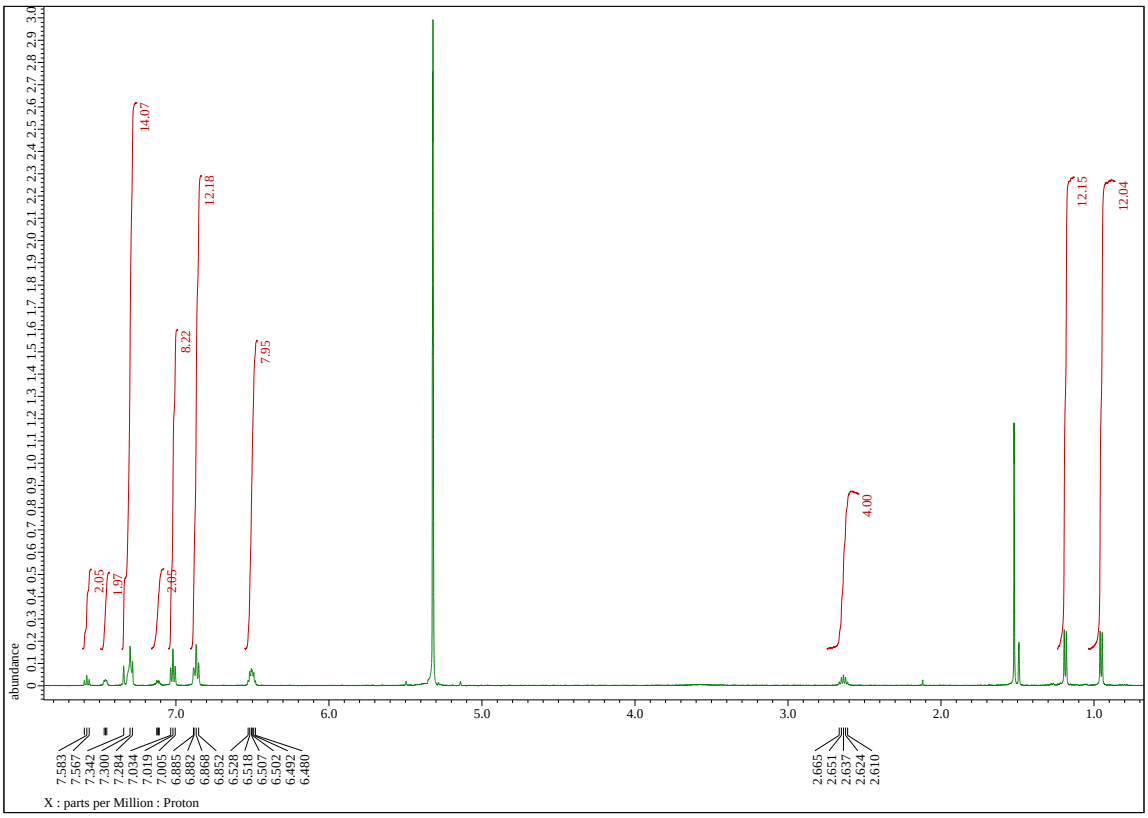

Fig. S4. ^{1}H NMR spectrum of **2** in CD_2Cl_2 at room temperature.

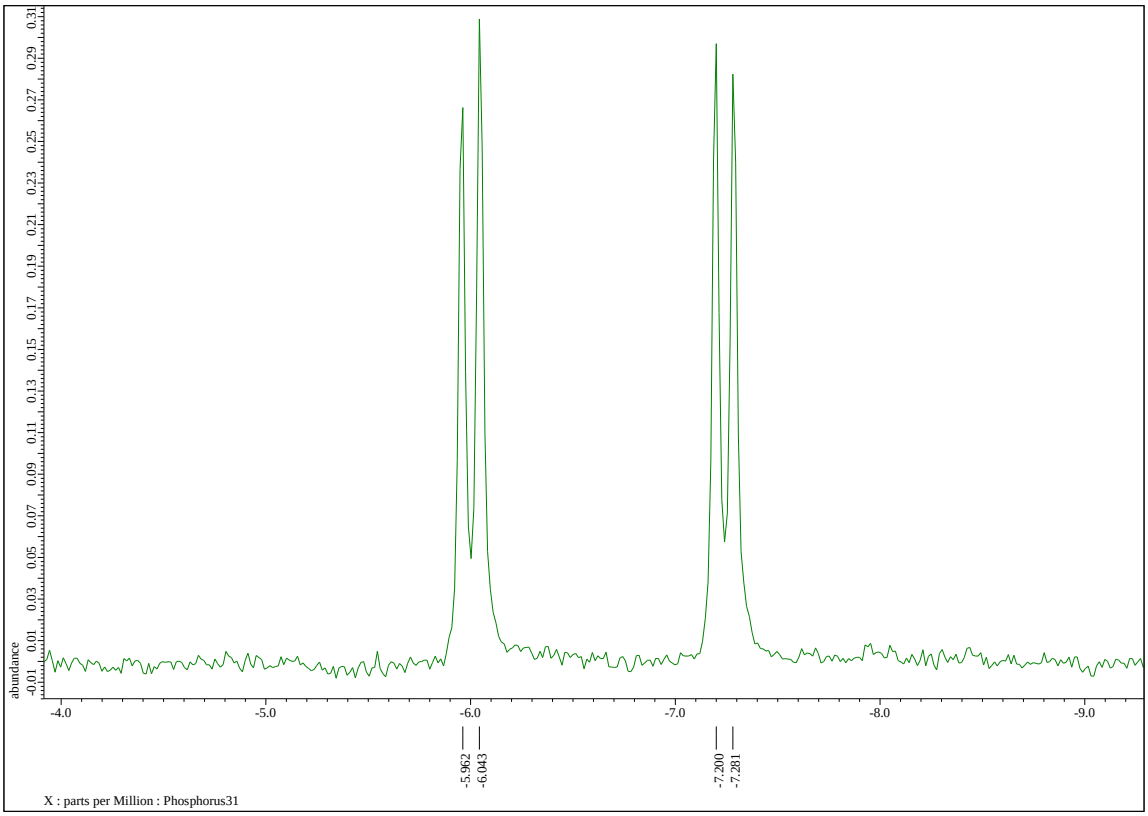

Fig. S5. ^{31}P{^{1}H}NMR spectrum of **2** in CD_2Cl_2 at room temperature.

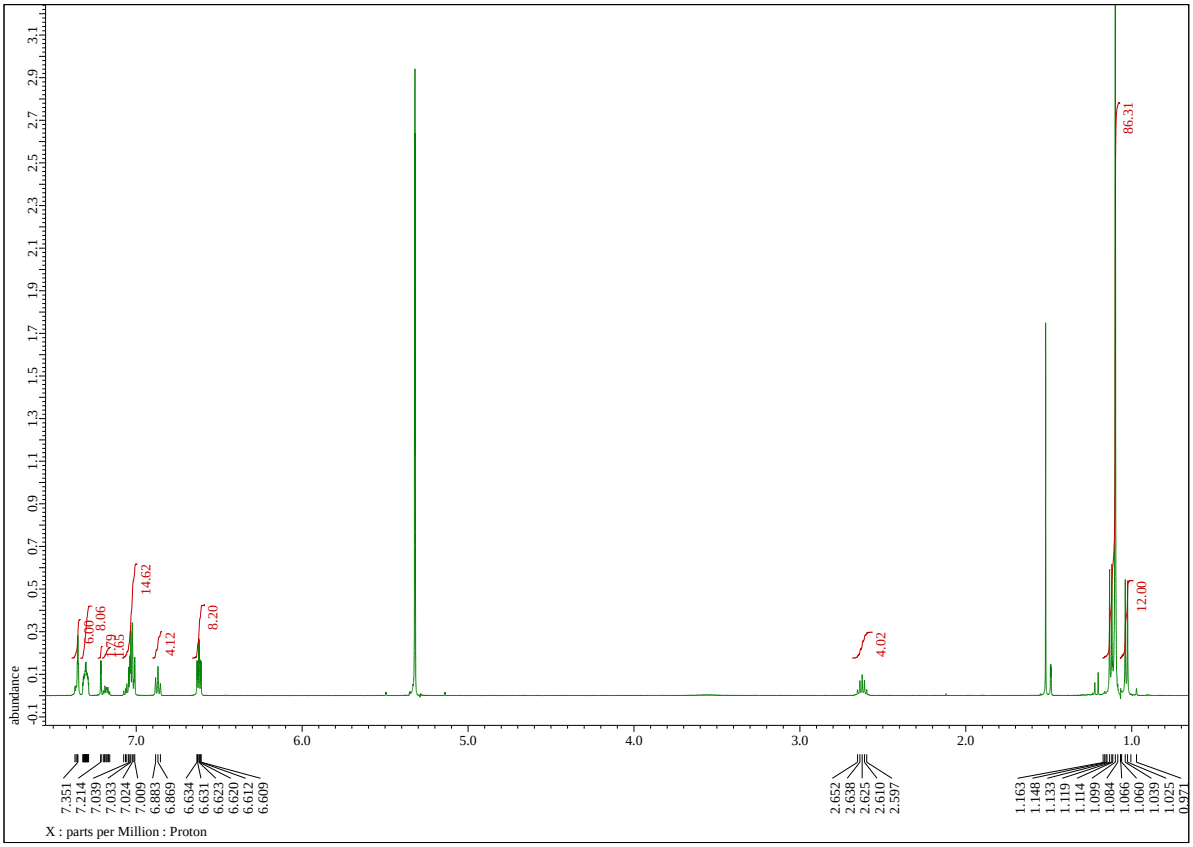

Fig. S6. ^{1}H NMR spectrum of **3** in CD_2Cl_2 at room temperature.

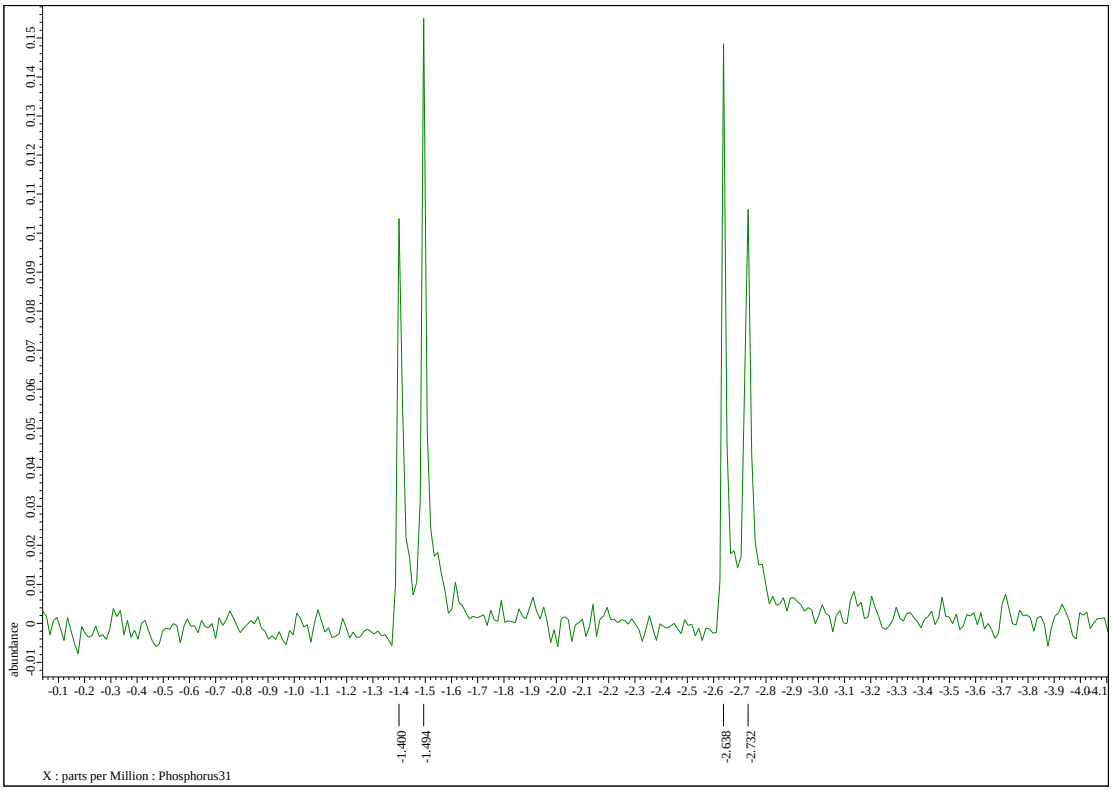

Fig. S7. ^{31}P{^{1}H}NMR spectrum of **3** in CD_2Cl_2 at room temperature.

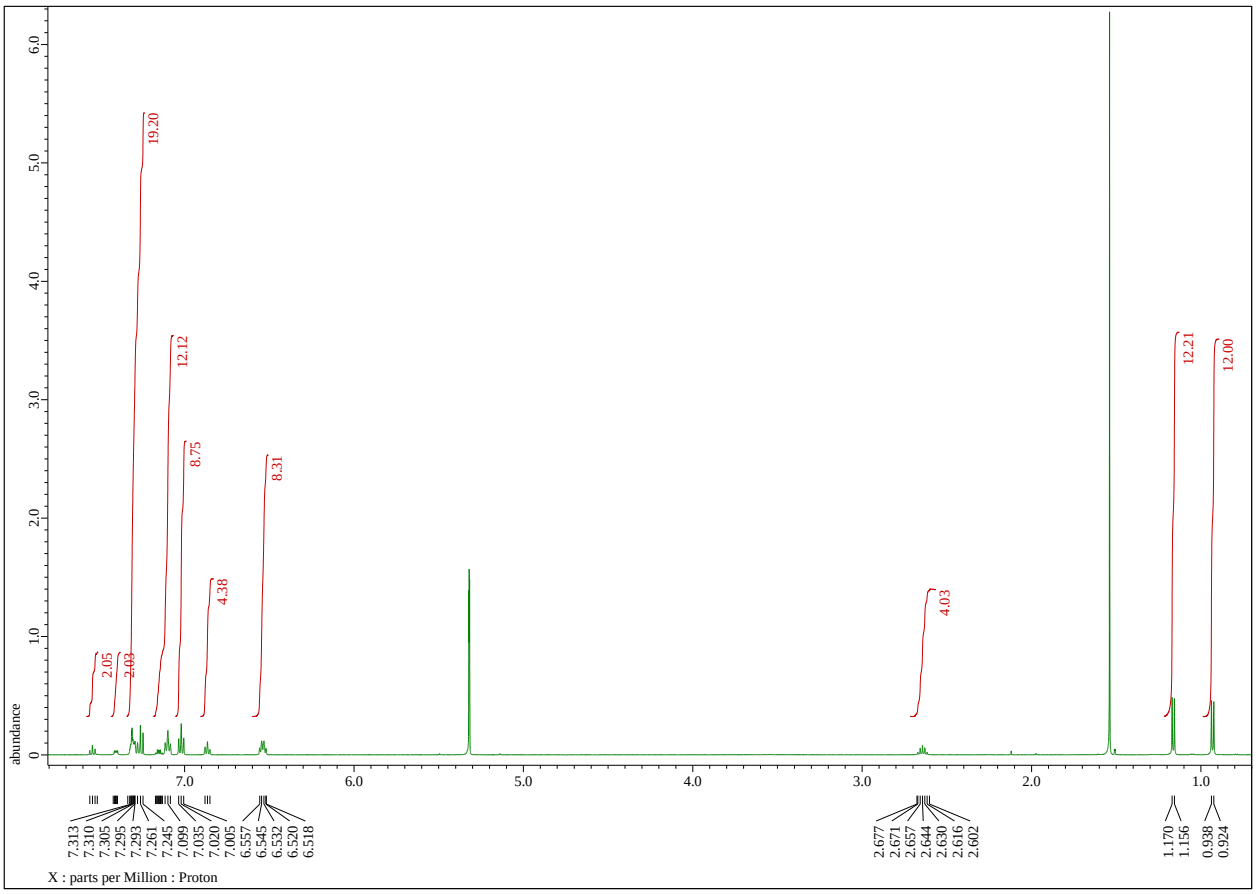

Fig. S8. ^{1}H NMR spectrum after 3 days of **1** in CD_2Cl_2 at room temperature.

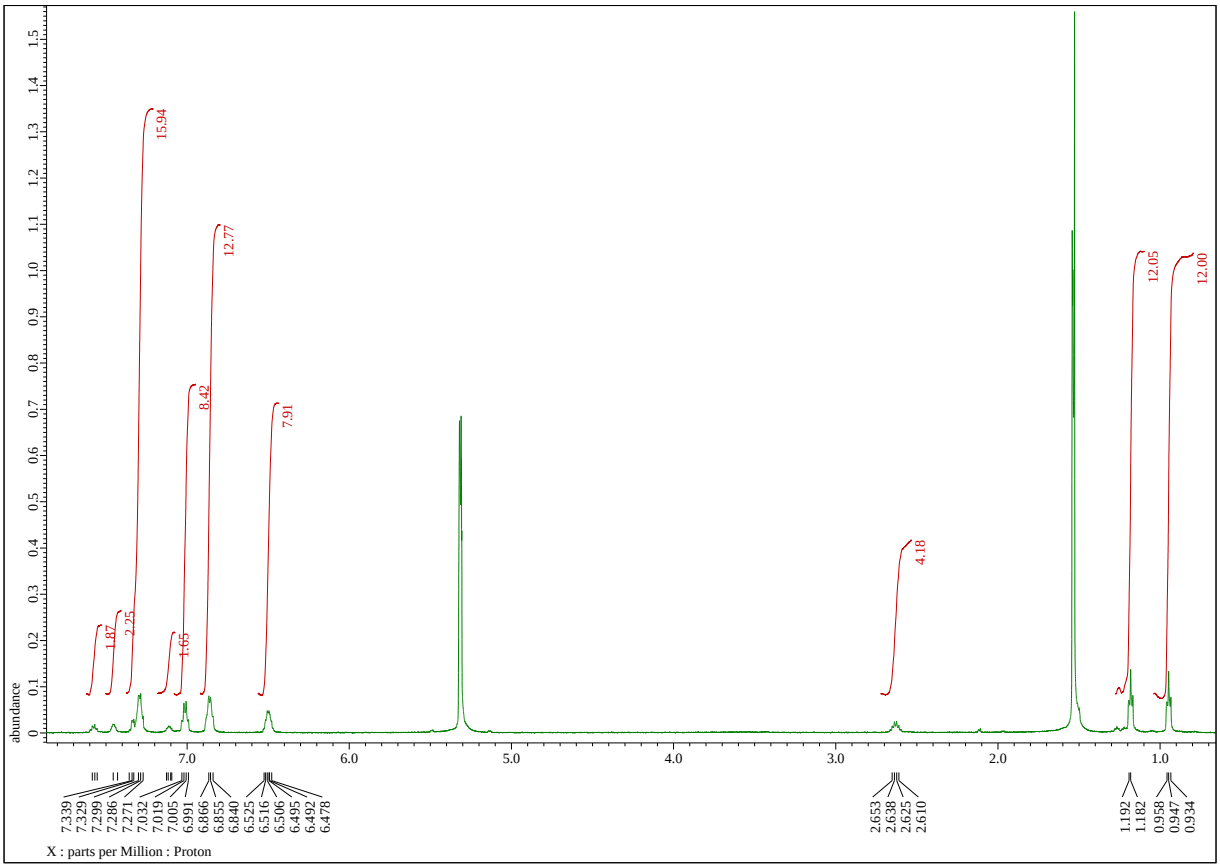

Fig. S9. ^{1}H NMR spectrum after 3 days of **2** in CD_2Cl_2 at room temperature.

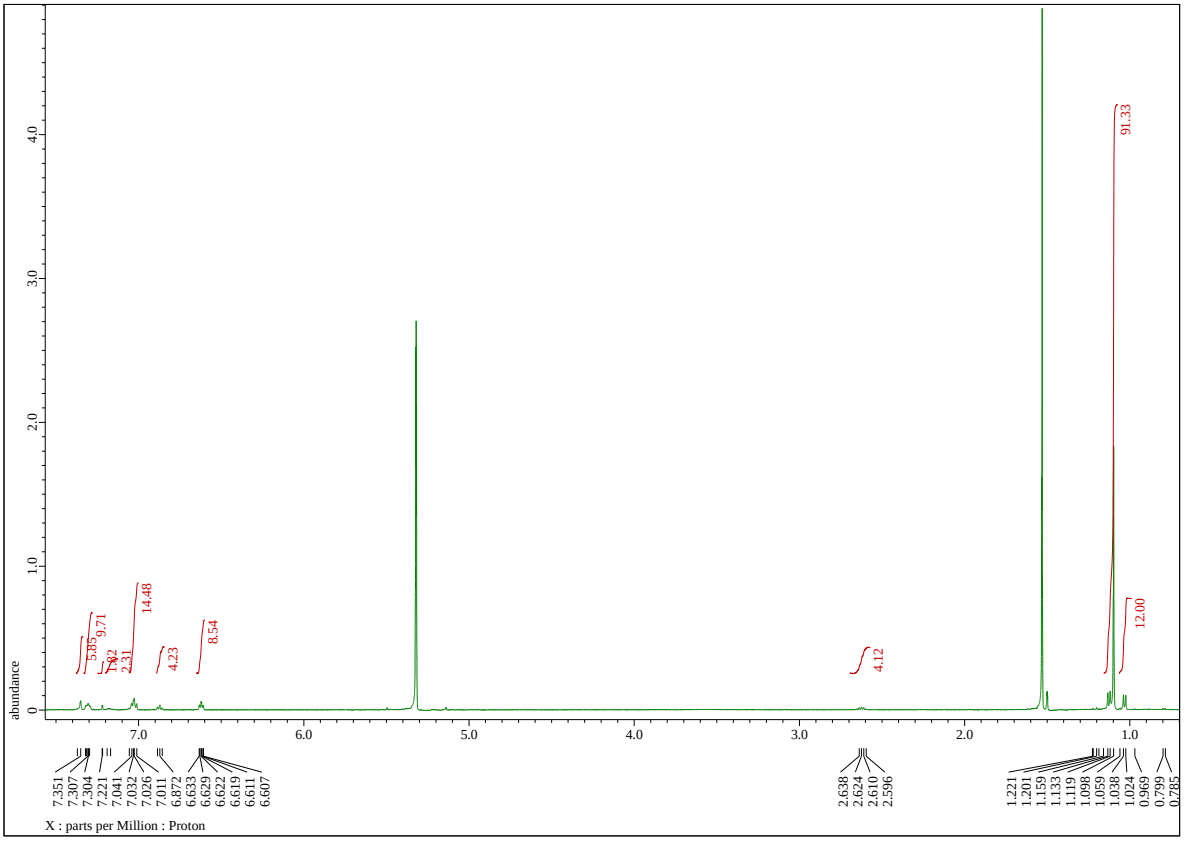

Fig. S10. ^{1}H NMR spectrum after 3 days of **3** in CD_2Cl_2 at room temperature.

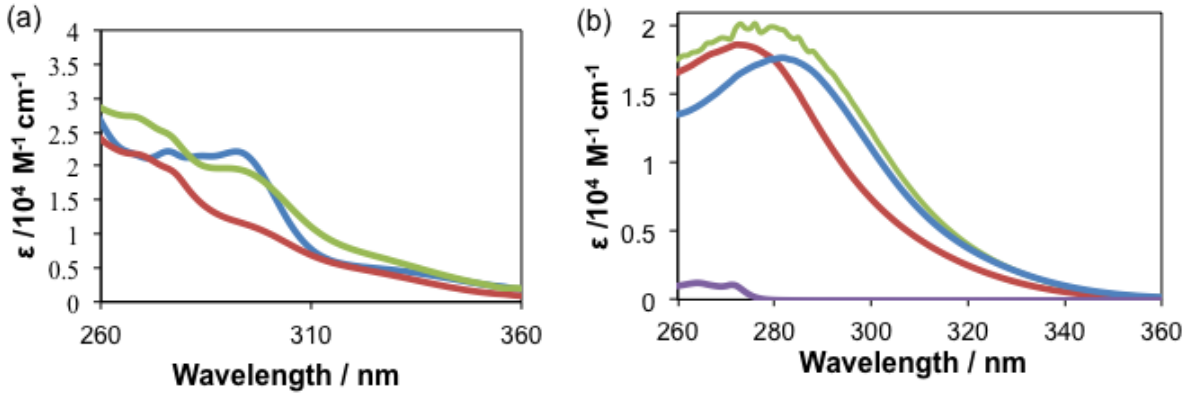

Fig. S11. (a) Absorption spectra of **1** (green), **2** (red) and **3** (blue) in dichloromethane at room temperature. (b) Absorption spectra of dppbz (red), dfpbz (green), dtbpbz (blue) and Ag(IPr)Cl (purple) in dichloromethane at room temperature.

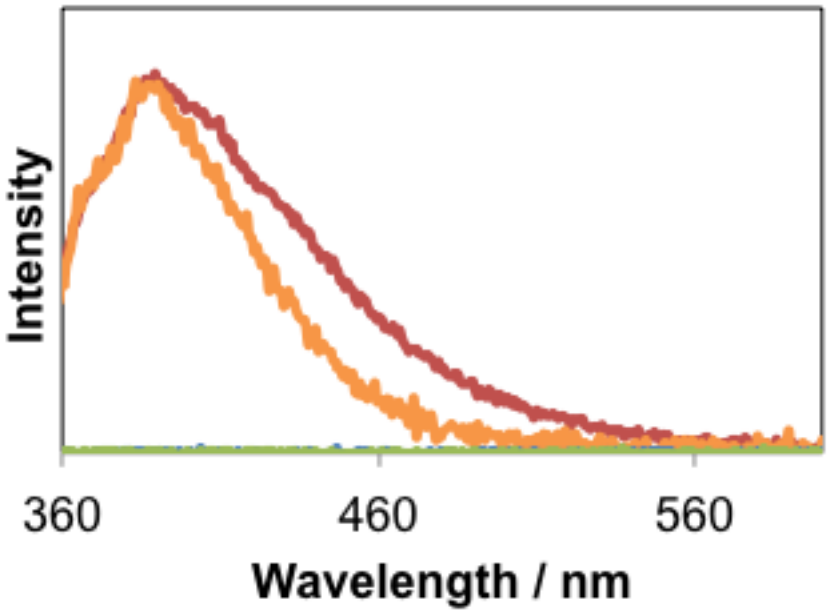

Fig. S12. Emission spectrum of ligands,dppbz (green dash,excited 345nm), **2** (orange dot, excited 335nm), dfpbz (red, excited 330nm) and dtbpbz (blue dash, excited 345nm), in degassed dichloromethane at room temperture (uncorrected).

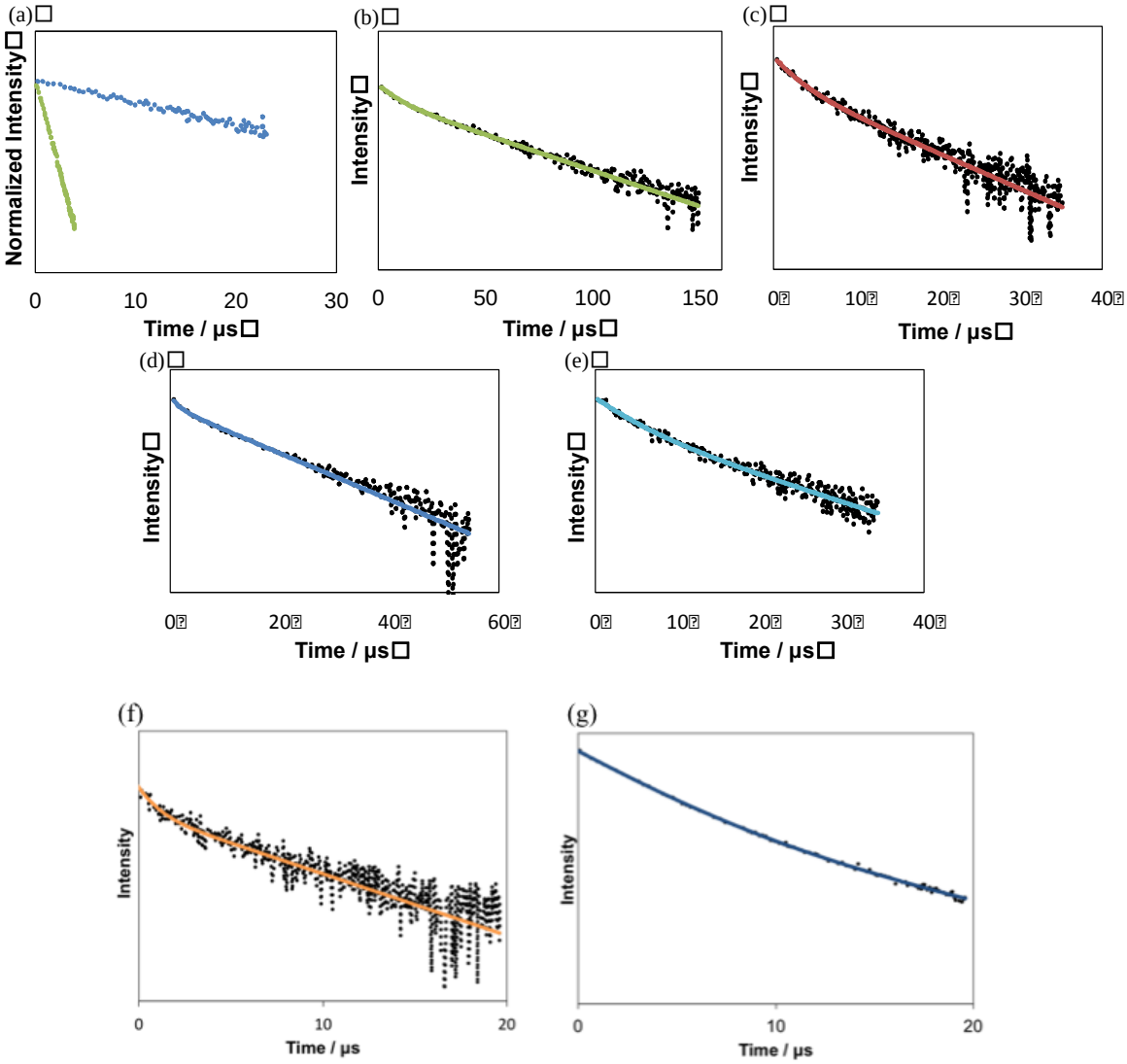

Fig. S13. (a) The emission decay curves of **1** (green dot) and **3** (blue dot) in the degassed dichloromethane at room temperature. (b) The emission decay curves of **1** as synthesis (green, 36 μs (88%), 7.8 μs (12%)) in solid state. (c) The emission decay curves of **2** (red, 9.8 μs (80%), 2.5 μs (20%)) in solid state.

(d) The emission decay curves of **3** (blue, 14 μs (96%), 1.4 μs (4%)) in solid state.

(e) The emission decay curves of grinding **1** (**G_1**) (light blue, 12.2 μs (72%), 4.0 μs (28%)) in solid state. (f) The emission decay curves of grinding **2** (orange, 5.8 μs (87%), 0.82 μs (13%)) in solid state. (g) The emission decay curves of grinding **3** (dark blue, 9.2 μs (37%), 3.3 μs (63%)) in solid state.

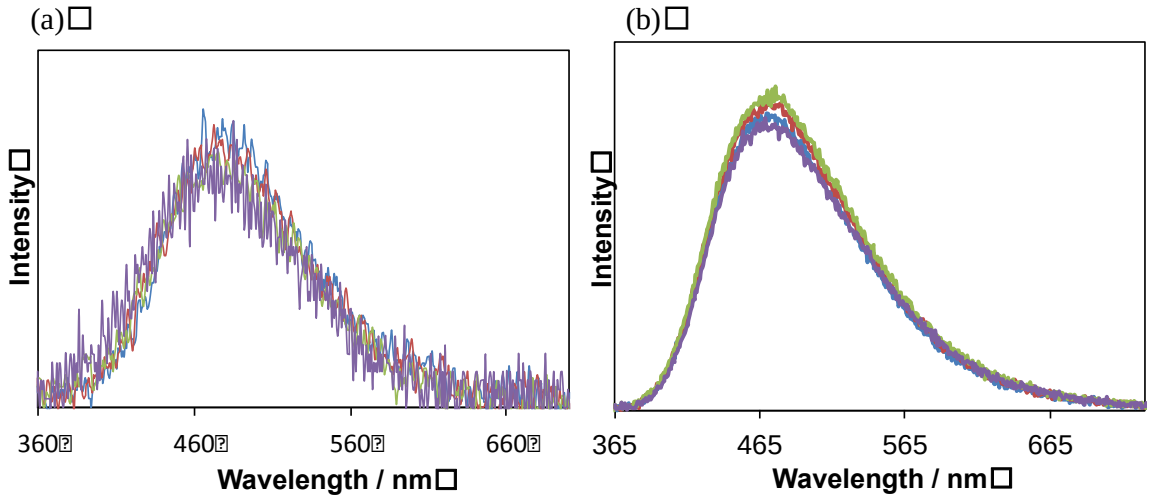

Fig. S14. (a) Emission spectrum of **1** at 0 min (blue), 10 min later (red), 30 min later (green), and 1 h later (purple) in the degassed dichloromethane at room temperature. (b) Emission spectrum of **3** at 0 min (blue), 15min later (red), 30min later (green) and 1h later (purple) in the degassed dichloromethane at room temperature.

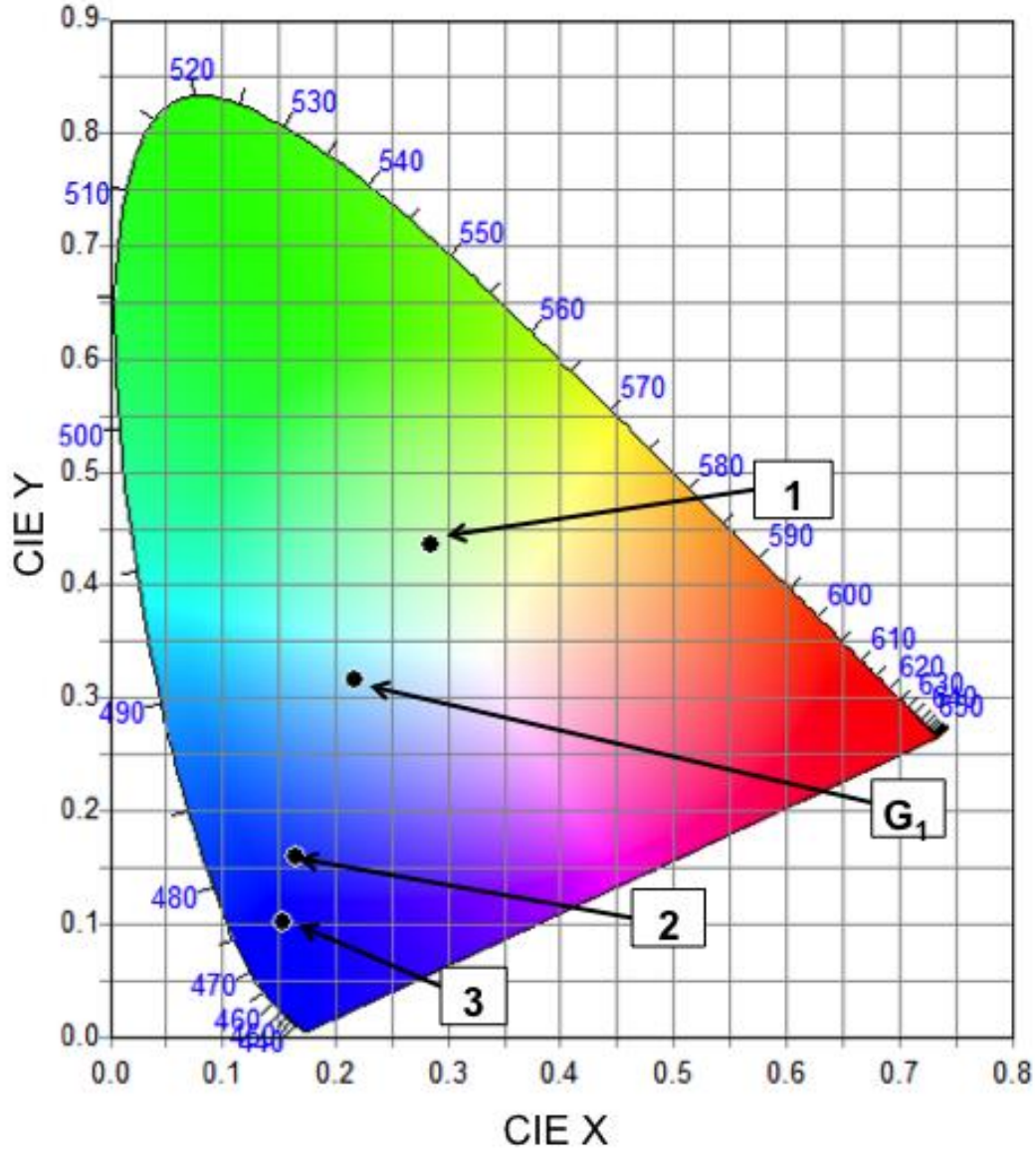

Fig. S15. CIE graph of **1** (0.29, 0.43), **2** (0.16, 0.16), **3** (0.15, 0.10) and $\mathbf{G_1}$ (0.22, 0.32) in the solid state.

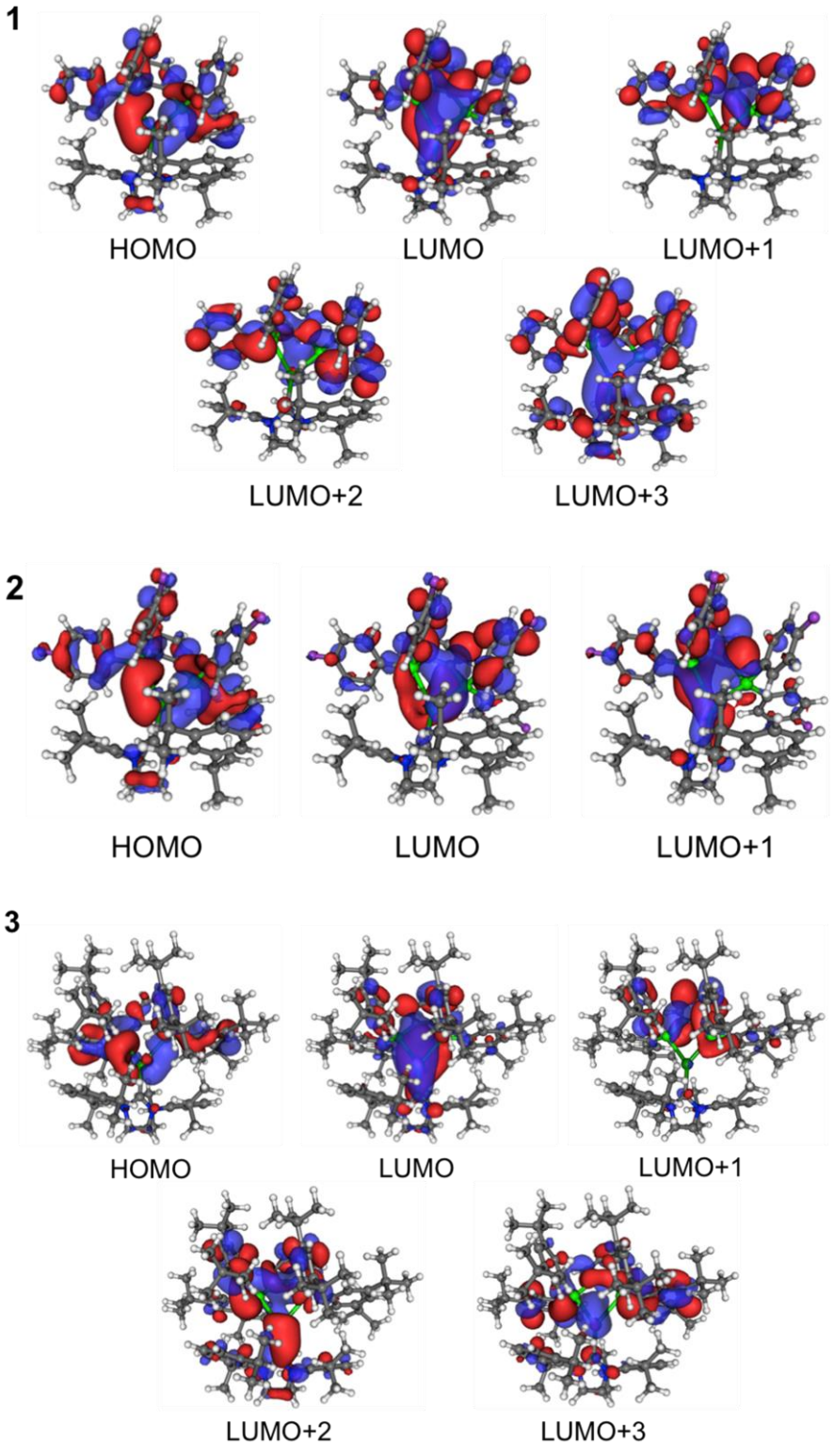

Fig. S16. Kohn-Sham orbitals of **1** (upper), **2**$^{+}$**(**centre**)** and **3**$^{+}$ (lower). Orbitals calculated based on the optimized structure in the S_0 (singlet ground) states (contour value 0.02).

Table S1. k_r (=Φ/τ) and k_{nr} (=(1-Φ)/τ) value of **1** and **3** measured in degassed CH_2Cl_2 solution.

	k_r /10^4 s^{-1}	k_{nr} /10^4 s^{-1}
1	1.6	89
3	1.5	14

Table S2. Important bond lengths and angles of the optimized structure of **1** and **2**

	Ag-C (Å)	Ag-P1 (Å)	Ag-P2 (Å)	C-Ag-P1 (°)	C-Ag-P2 (°)	P1-Ag-P2 (°)
1	2.156	2.541	2.563	142.43	138.29	79.27
2	2.153	2.545	2.559	141.85	138.93	79.18

Table S3. TDDFT results of singlets and triplets calculated using singlet-optimized structures. Calculated transition wavelength, oscillator strength (*f*), components of the transitions.

	Singlets calculated using singlet-optimized structures				Triplets calculated using singlet-optimized structures			
	λ / nm	f	Components	Coefficients	λ / nm	f	Components	Coefficients
1	321	0.0145	HOMO -> LUMO	0.664	370	0	HOMO-16 -> LUMO	0.116
			HOMO -> LUMO+1	0.173			HOMO -> LUMO	0.377
	315	0.0416	HOMO -> LUMO	-0.179	364	0	HOMO-1 -> LUMO+4	-0.155
			HOMO -> LUMO+1	0.668			HOMO -> LUMO+2	0.414
	288	0.1411	HOMO -> LUMO+2	0.657				
			HOMO -> LUMO+3	-0.164				
2	320	0.023	HOMO -> LUMO	0.595	370	0	HOMO -> LUMO	0.238
			HOMO -> LUMO+1	0.341			HOMO -> LUMO+1	0.353
	315	0.0349	HOMO -> LUMO	-0.347	360	0	HOMO -> LUMO+2	0.381
			HOMO -> LUMO+1	0.596			HOMO -> LUMO+3	0.132
3	327	0.0097	HOMO -> LUMO	0.695	374	0	HOMO -> LUMO	0.389
	318	0.0302	HOMO -> LUMO+1	0.700			HOMO -> LUMO+1	-0.138
	287	0.0243	HOMO -> LUMO+2	0.678	368	0	HOMO-1 -> LUMO+12	-0.109
			HOMO -> LUMO+3	-0.125			HOMO -> LUMO+3	0.339