Supporting Informtion

Synthesis of panchromatic Ru(II) thienyl-dipyrrin complexes and evaluation of their light-harvesting capacity

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Table S1. TD-DFT calculation of electronic transitions in **1a**, **1b**, and **2** S9

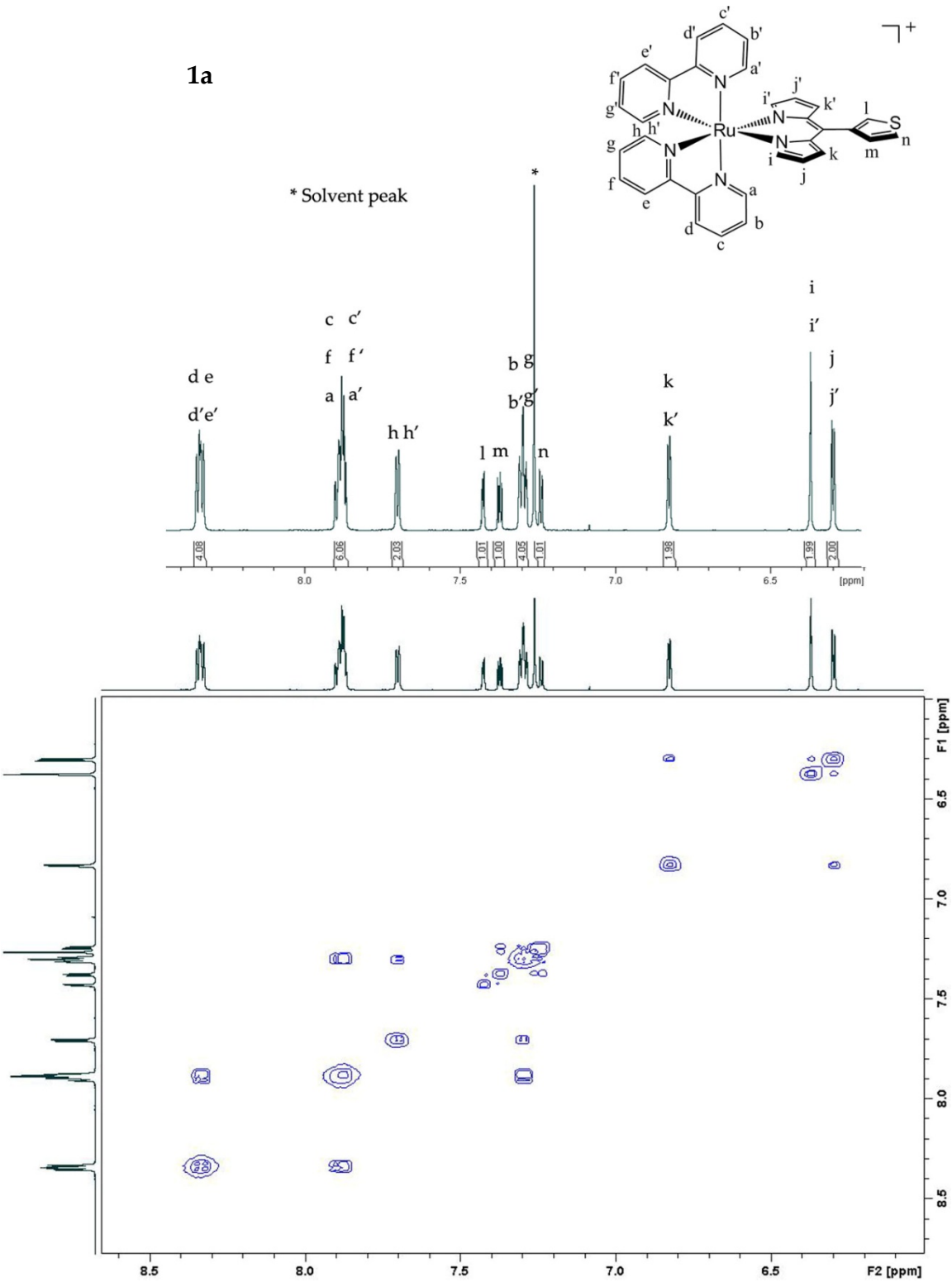

Figure S1. ^{1}H NMR spectra of **1a**, **1b**, and **2** in $CDCl_3$ at room temperature.

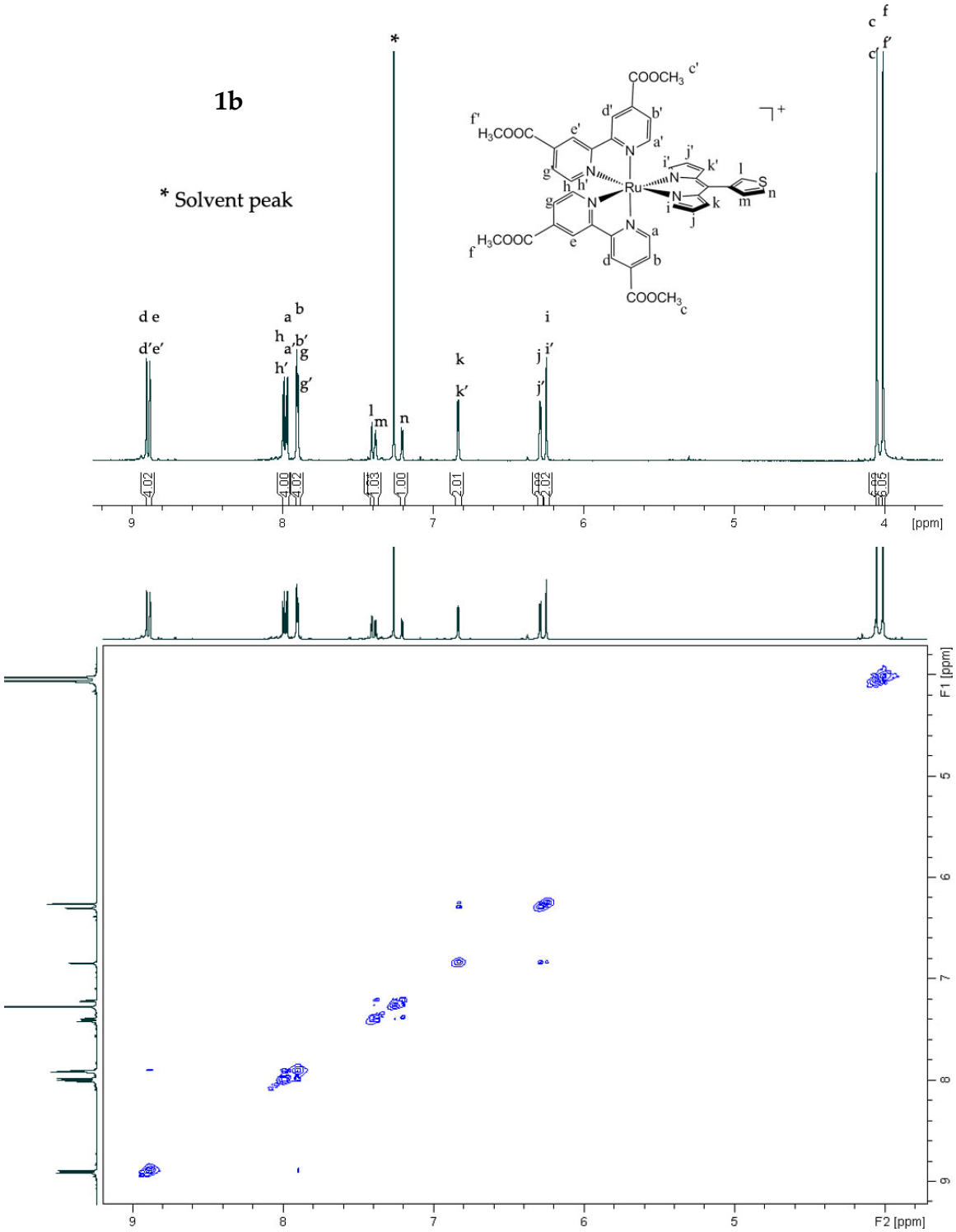

Figure S1 (continued). ^{1}H NMR spectra of **1a**, **1b**, and **2** in $CDCl_3$ at room temperature.

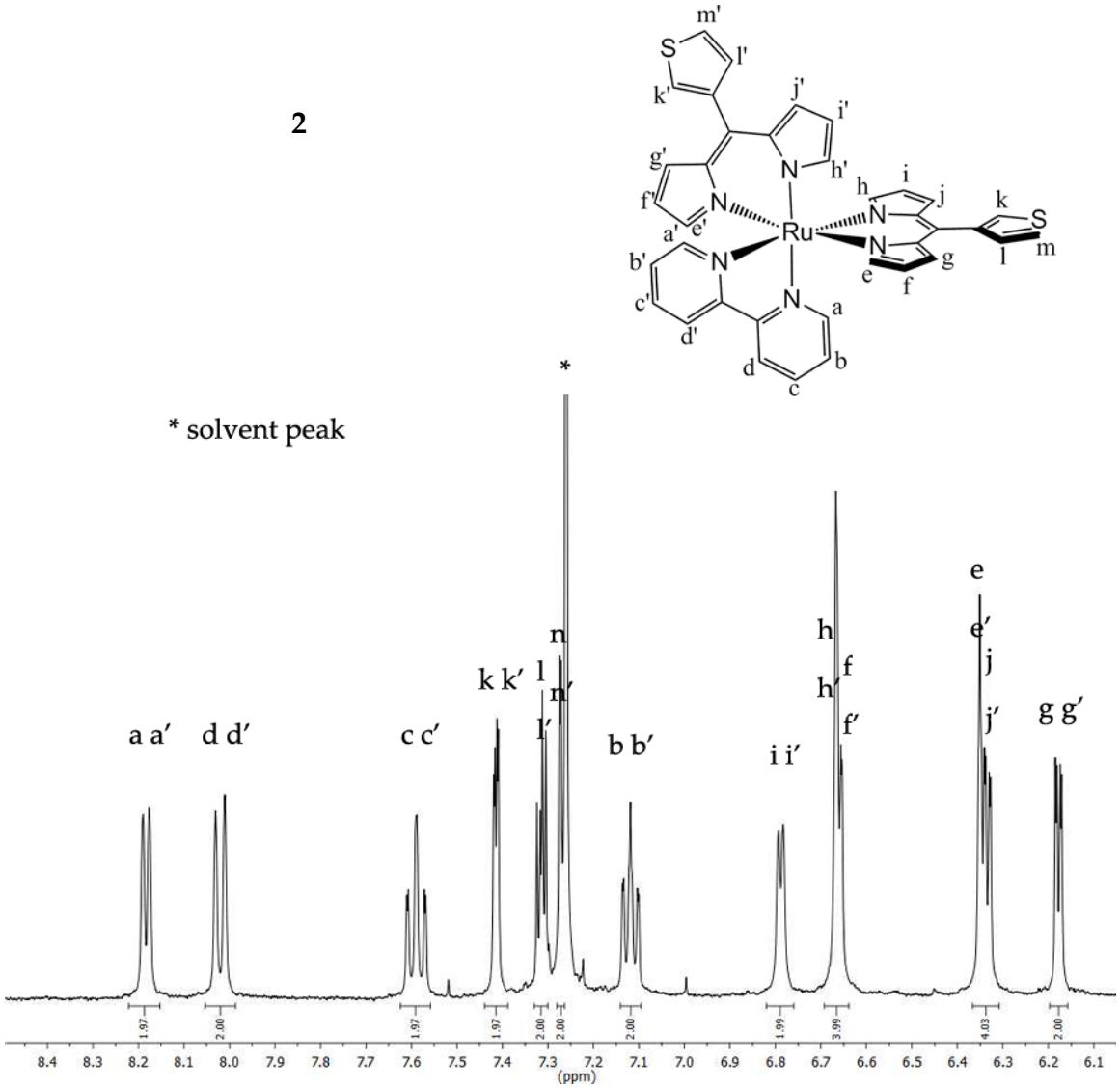

Figure S1 (continued). ^{1}H NMR spectra of **1a**, **1b** and **2** in $CDCl_3$ at room temperature.

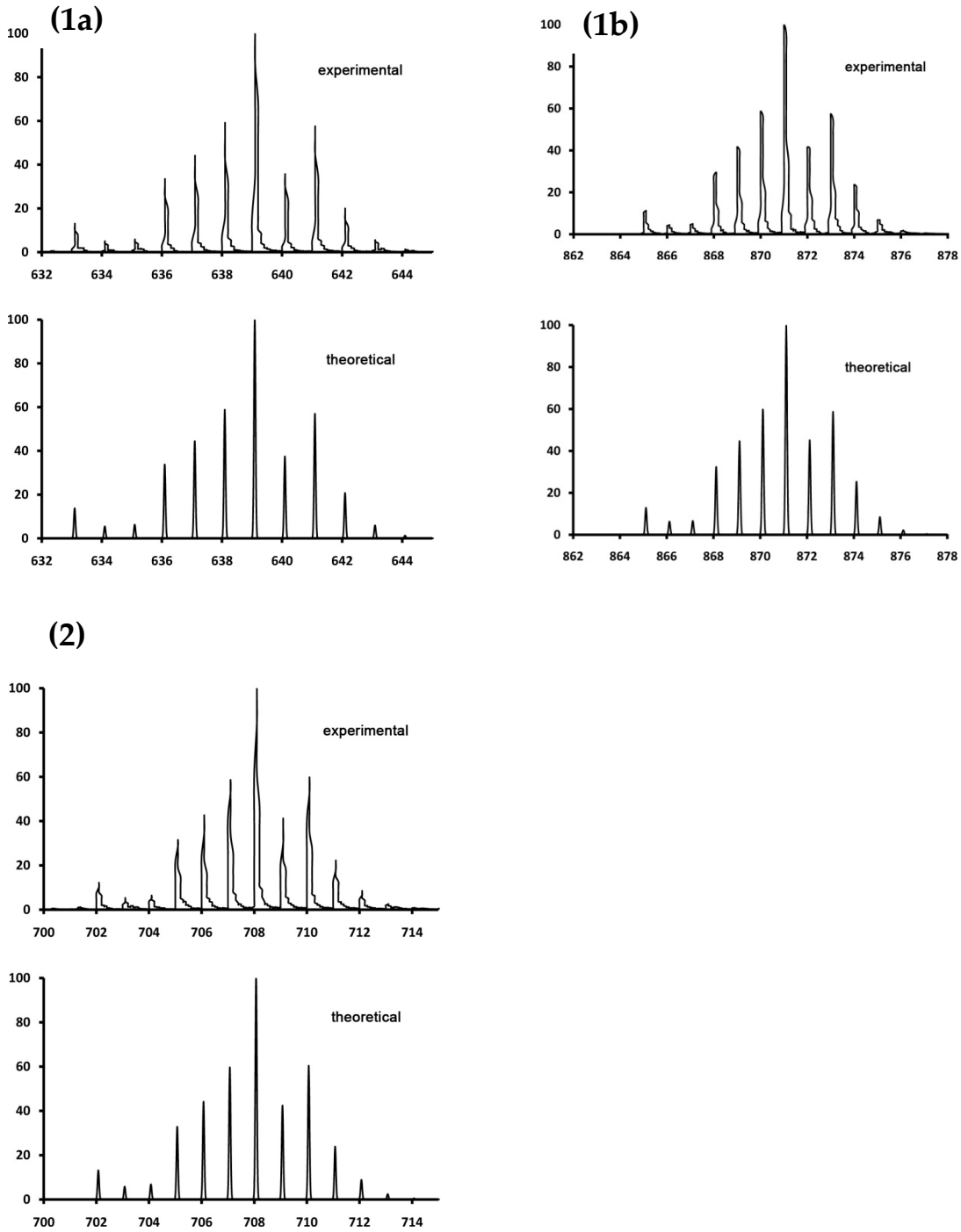

Figure S2. Experimental and simulated mass spectra of **1a**, **1b** and **2** corresponding to $[Ru(bpy)_2(3\text{-}TDP)]^+$ (m/z = 639.09005), $[Ru(dcmb)_2(3\text{-}TDP)]^+$ (871.11151) and $[Ru(bpy)(3\text{-}TDP)_2]^+$ (708.07271) respectively.

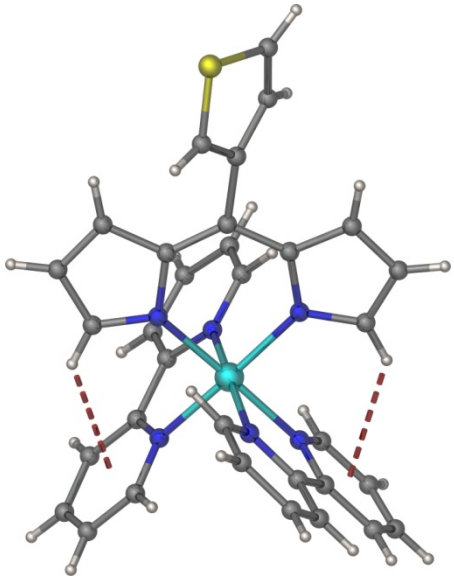

Figure S3. Molecular structure of $[Ru(bpy)_2(3\text{-TDP})]^+$ showing the proximity of the α-protons of coordinated 3-TDP to the π-system of bpy.

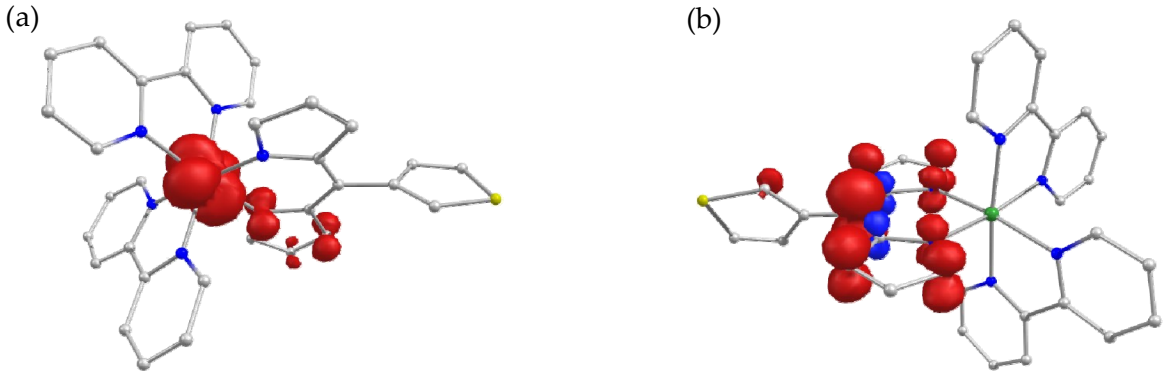

Figure S4. Calculated spin density of 1e-oxidized (a) and 1e-reduced (b) forms of **1a**.

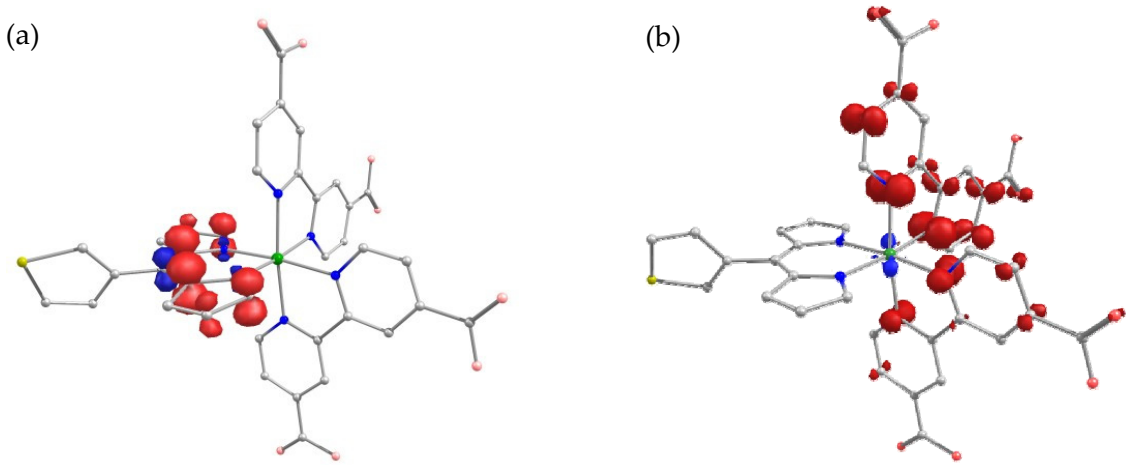

Figure S5. Calculated spin density of 1e-oxidized (a) and 1e-reduced (b) forms of **1b**.

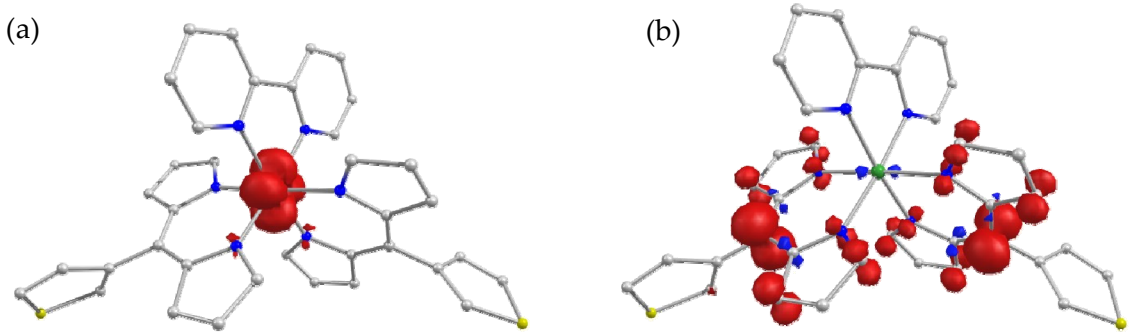

Figure S6. Calculated spin density of 1e-oxidized (a) and 1e-reduced (b) forms of **2**.

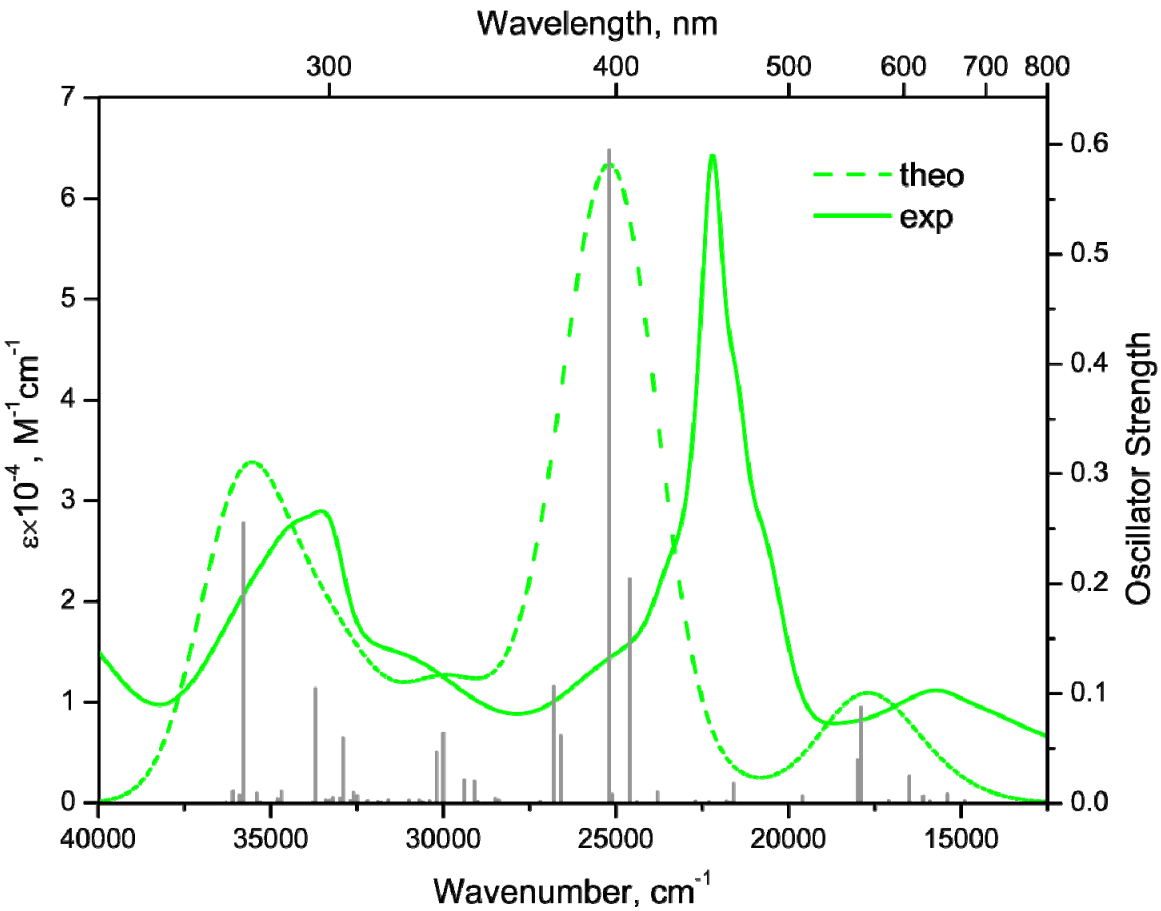

Figure S7. Experimental (solid line) and simulated (dashed line) absorption spectra of **2**. The grey bars indicate the energy and oscillator strength of each electronic excitation.

Table S1. Spin-allowed absorption bands calculated for **1a**, **1b** and **2**.

1a			**1b**		
Energy (cm^{-1})	f^b	Assignment	Energy (cm^{-1})	f^b	Assignment
19100	0.016	HOMO-1→LUMO+2 (89%)	16100	0.007	HOMO-1→LUMO (89%)
19400	0.012	HOMO-1→LUMO (84%)	16900	0.031	HOMO-2→LUMO+1 (87%)
20100	0.068	HOMO-1→LUMO+1 (76%)	19500	0.137	HOMO-3→LUMO (88%)
21000	0.022	HOMO-3→LUMO+1 (92%)	20600	0.061	HOMO-3→LUMO+1 (64%)
21400	0.070	HOMO-3→LUMO (91%)	21800	0.046	HOMO-2→LUMO+2 (77%)
22700	0.018	HOMO-3→LUMO+2 (76%)	22400	0.035	HOMO-1→LUMO+3 (68%)
24700	0.389	HOMO-2→LUMO+1 (63%)	22900	0.126	HOMO-2→LUMO+4 (81%)
		HOMO-2→LUMO (30%)			
25300	0.014	HOMO→LUMO+3 (97%)	23400	0.029	HOMO-3→LUMO+2 (86%)
27700	0.012	HOMO-3→LUMO+3 (77%)	23900	0.099	HOMO→LUMO+2 (45%)
					HOMO→LUMO+5 (37%)
28000	0.014	HOMO→LUMO+6 (62%)	24300	0.025	HOMO-1→LUMO+5 (93%)
28200	0.031	HOMO-2→LUMO+3 (87%)	24900	0.029	HOMO-2→LUMO+5 (73%)
28500	0.091	HOMO-1→LUMO+5 (33%)	25200	0.023	HOMO-3→LUMO+3 (87%)
		HOMO→LUMO+6 (29%)			
28700	0.054	HOMO-4→LUMO+1 (59%)	25700	0.298	HOMO→LUMO+5 (46%)
		HOMO-4→LUMO (28%)			HOMO→LUMO+2 (30%)
			25900	0.030	HOMO-2→LUMO+6 (89%)
			26000	0.057	HOMO-3→LUMO+4 (49%)
			28200	0.062	HOMO-4→LUMO+2 (50%)
					HOMO-3→LUMO+6 (39%)
			28600	0.039	HOMO-5→LUMO (58%)
					HOMO-6→LUMO (32%)
			29600	0.041	HOMO-6→LUMO (43%)
					HOMO-5→LUMO (32%)

2		
Energy (cm^{-1})	f [b]	Assignment
15400	0.008	HOMO→LUMO (70%)
		HOMO→LUMO+1 (26%)
16500	0.025	HOMO-1→LUMO (86%)
17900	0.087	HOMO-2→LUMO (40%)
		HOMO-2→LUMO+1 (27%)
		HOMO-1→LUMO+2 (26%)
18000	0.039	HOMO-2→LUMO+2 (95%)
21600	0.018	HOMO-3→LUMO (74%)
23800	0.010	HOMO-1→LUMO+3 (97%)
24600	0.204	HOMO-4→LUMO+2 (72%)
		HOMO-3→LUMO (22%)
25200	0.595	HOMO-3→LUMO+2 (52%)
		HOMO-4→LUMO (42%)
26600	0.061	HOMO-2→LUMO+4 (94%)
26800	0.106	HOMO-1→LUMO+4 (56%)
		HOMO-2→LUMO+3 (27%)
29100	0.020	HOMO-4→LUMO+3 (92%)
29400	0.021	HOMO-5→LUMO+2 (50%)
		HOMO-6→LUMO (39%)
30000	0.063	HOMO-7→LUMO (60%)
		HOMO-6→LUMO+2 (30%)
30200	0.046	HOMO-5→LUMO+2 (43%)
		HOMO-7→LUMO+2 (27%)
		HOMO-6→LUMO (26%)

[a]Transitions in the visible and near-UV region (10,000–30,000 cm^{-1}). Excitation contributions greater than 10% are shown, smaller contributions are omitted.
[b] f = oscillator strength.