Supplementary Information

Terpyridine platinum(II) complexes containing triazine di- or tri-thiolate bridges: structures, luminescence, electrochemistry and aggregation

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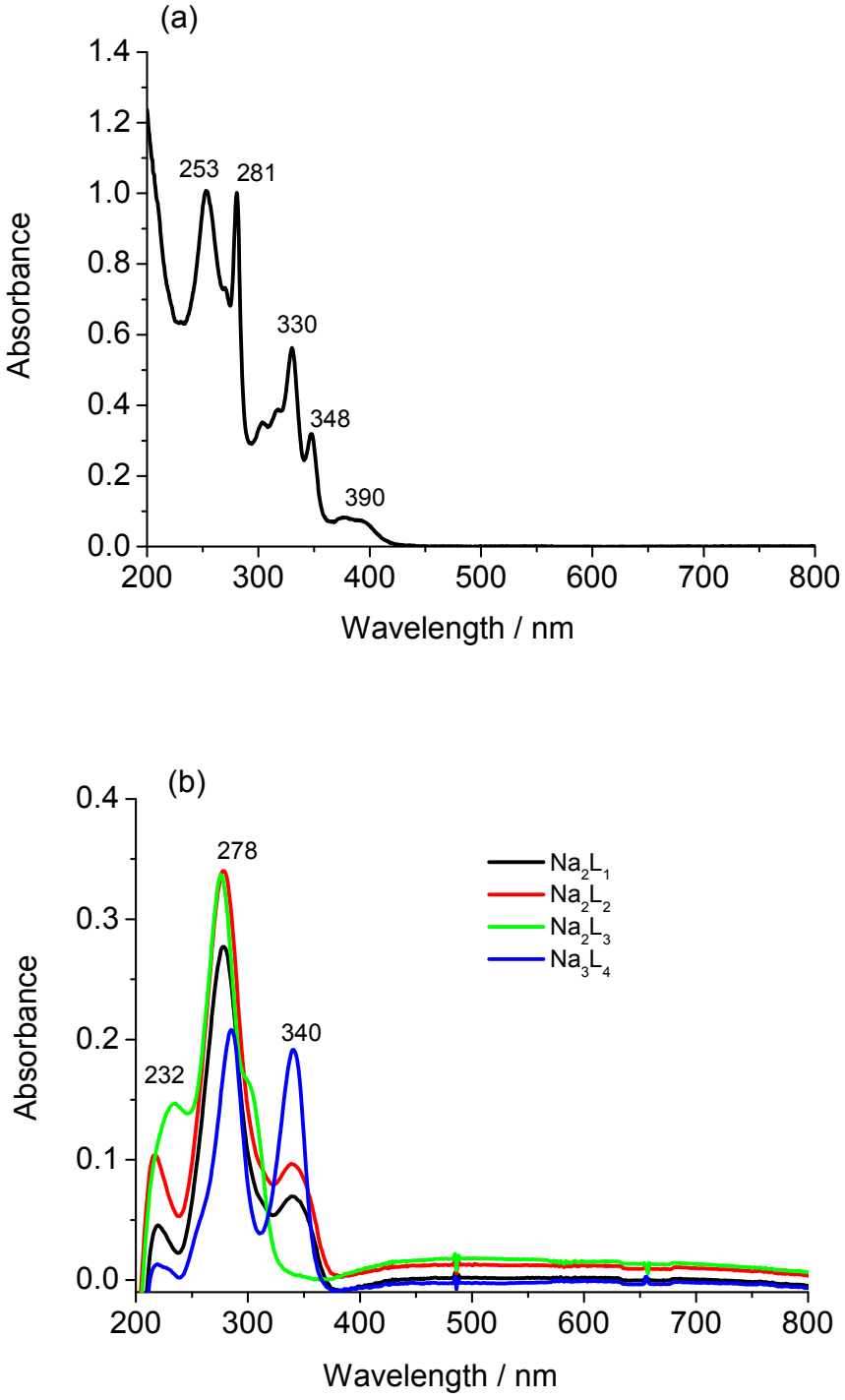

Fig. S1 Absorption spectra of (a) [Pt(tpy)Cl]Cl (1.5×10^{-5} M), (b) Sodium salts of L_1–L_4 (1.0×10^{-5} M) in CH_3CN.

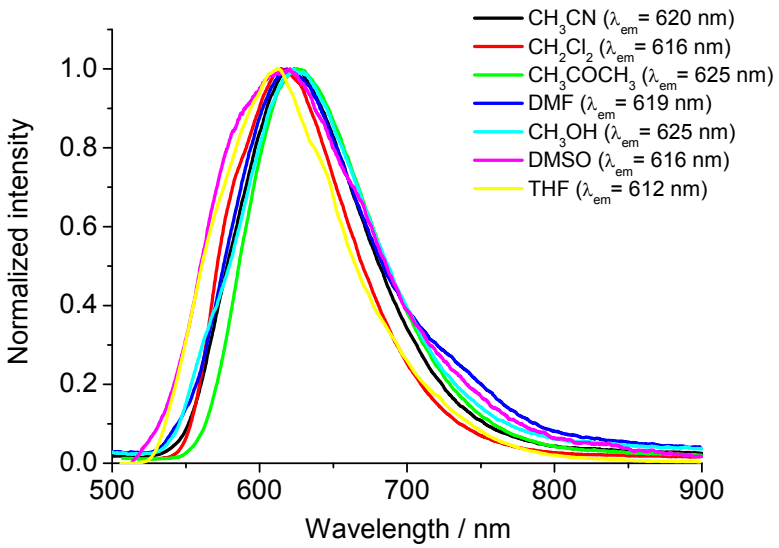

Fig. S2 Emission spectra of **1** in various solvents. Excitation at 450 nm.

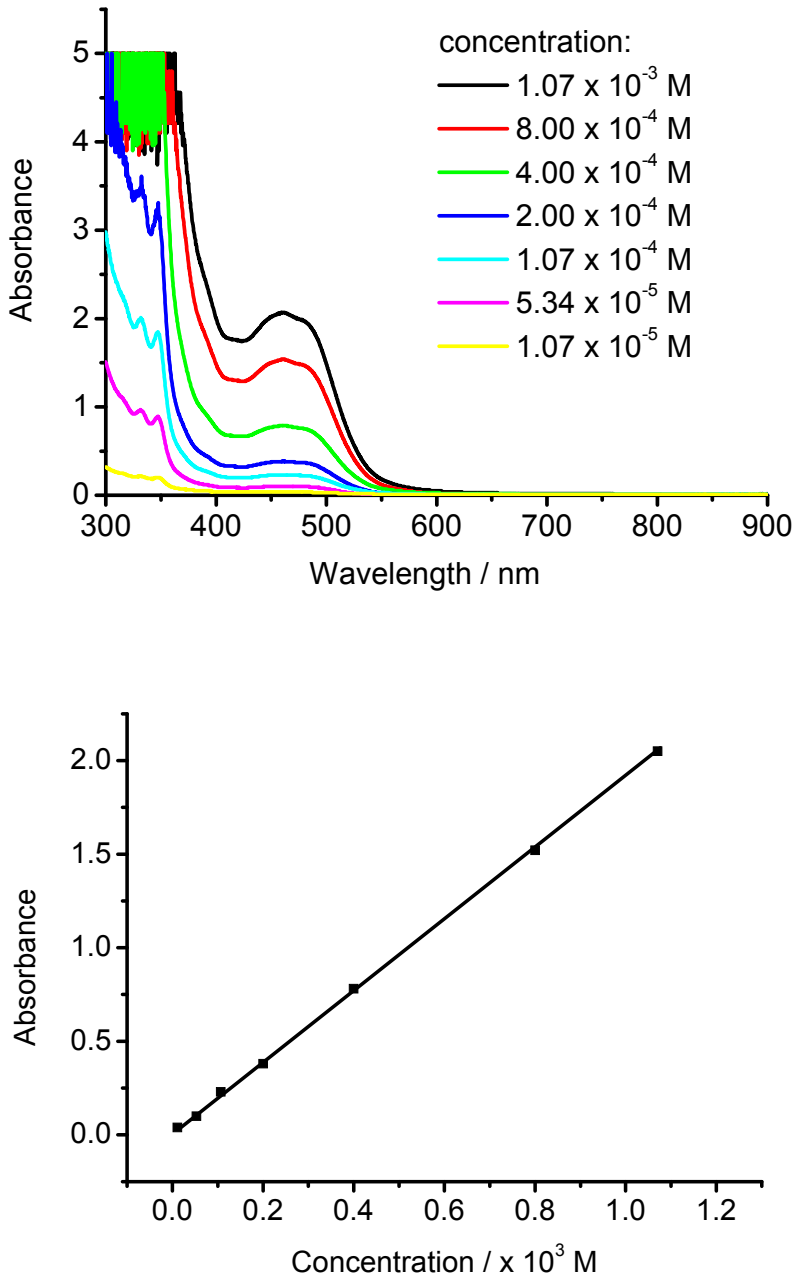

Fig. S3 Absorption spectra of **2** in CH_3CN solution: (a) at concentrations from 1.07×10^{-5} M to 1.07×10^{-3} M; (b) plot of the absorbance at 466 nm *vs*. concentration.

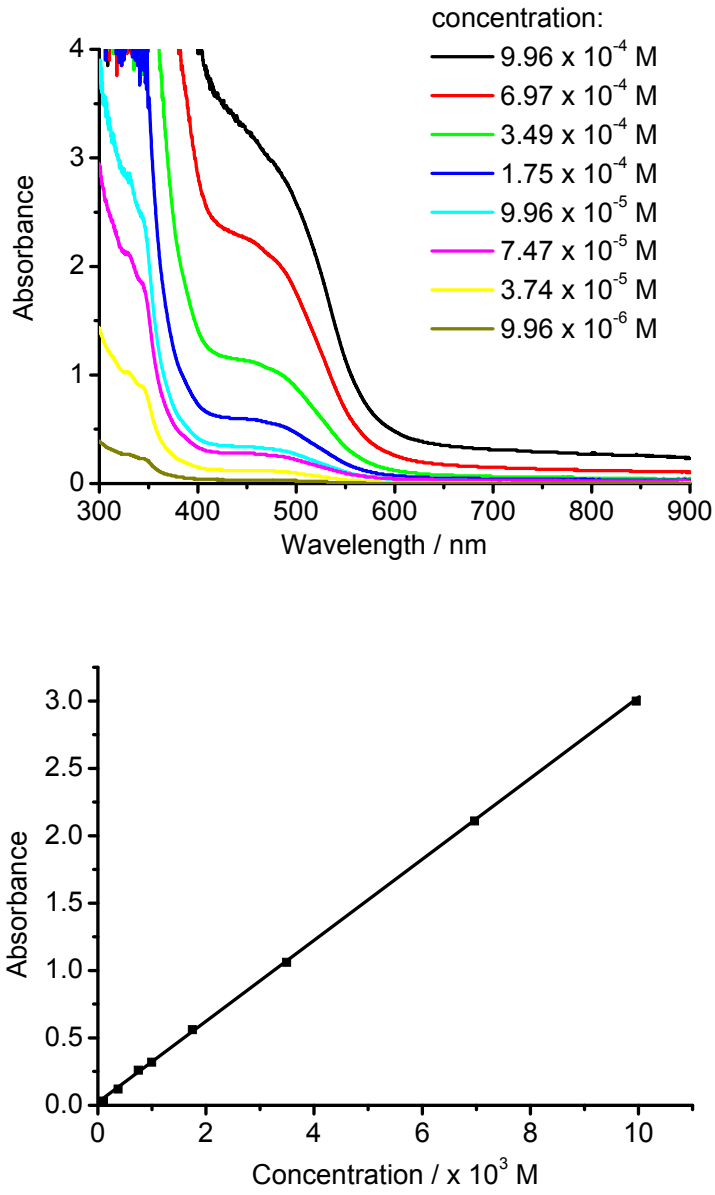

Fig. S4 Absorption spectra of **4** in CH_3CN solution: (a) at concentrations from 9.96×10^{-6} M to 9.96×10^{-4} M; (b) plot of the absorbance at 472 nm *vs*. concentration.

Table S1. Mulliken population of MOs near frontier orbitals for **1**.

Orbital	Energy (eV)	Symmetry	S (%)	Triazine (%)	Pt (%)	trpy (%)
L+20	-3.25	A	1	1	13	86
L+19	-3.67	A	1	2	91	6
L+18	-3.79	A	1	1	100	-1
L+17	-3.99	A	6	0	95	0
L+16	-4.16	A	6	2	90	2
L+15	-5.13	A	5	30	2	63
L+14	-5.18	A	8	57	3	32
L+13	-5.31	A	3	20	1	76
L+12	-5.35	A	9	56	4	31
L+11	-5.99	A	18	2	45	36
L+10	-6.08	A	2	1	5	92
L+9	-6.17	A	17	2	46	36
L+8	-6.21	A	0	0	1	98
L+7	-6.71	A	0	0	3	97
L+6	-6.87	A	0	0	3	97
L+5	-6.89	A	0	0	1	99
L+4	-6.99	A	0	0	1	98
L+3	-7.97	A	0	0	2	98
L+2	-8.05	A	0	0	3	97
L+1	-8.25	A	1	1	5	94
LUMO	-8.39	A	1	1	5	93
HOMO	-10.05	A	69	30	1	1
H-1	-10.53	A	60	26	10	4
H-2	-10.68	A	67	16	12	5
H-3	-11.15	A	10	78	10	2
H-4	-11.19	A	9	86	5	1
H-5	-11.27	A	3	94	2	0
H-6	-11.55	A	22	78	0	0
H-7	-11.82	A	5	92	3	1
H-8	-11.89	A	36	15	43	6
H-9	-12.17	A	13	79	7	2
H-10	-12.25	A	8	26	49	17
H-11	-12.25	A	8	3	62	26
H-12	-12.28	A	25	27	40	9
H-13	-12.35	A	9	81	8	2
H-14	-12.45	A	2	1	57	40
H-15	-12.5	A	15	13	60	13
H-16	-12.63	A	9	64	22	4
H-17	-12.79	A	8	2	37	53
H-18	-12.88	A	9	35	28	28
H-19	-12.93	A	4	65	12	20
H-20	-12.95	A	1	4	7	88

Table S2. Mulliken population of MOs near frontier orbitals for **3**.

Orbital	Energy (eV)	Symmetry	S (%)	Triazine (%)	Pt (%)	trpy (%)
L+20	-3.04	A	1	1	48	50
L+19	-3.49	A	2	2	83	14
L+18	-3.6	A	1	3	100	-3
L+17	-3.83	A	6	-1	96	0
L+16	-3.87	A	4	15	80	0
L+15	-4.35	A	2	73	22	3
L+14	-4.78	A	10	83	5	2
L+13	-4.98	A	0	1	0	99
L+12	-5.06	A	0	1	1	98
L+11	-5.71	A	17	1	47	34
L+10	-5.77	A	17	2	48	33
L+9	-5.93	A	1	0	2	97
L+8	-6.09	A	0	0	1	99
L+7	-6.6	A	0	0	3	97
L+6	-6.67	A	0	0	3	97
L+5	-6.73	A	0	0	1	99
L+4	-6.78	A	0	0	1	99
L+3	-7.7	A	0	0	2	98
L+2	-7.86	A	0	0	2	98
L+1	-8.12	A	2	1	6	91
LUMO	-8.15	A	1	1	7	90
HOMO	-9.75	A	2	96	1	1
H-1	-10.25	A	59	26	10	5
H-2	-10.38	A	67	16	12	6
H-3	-10.73	A	7	90	2	1
H-4	-10.88	A	11	74	12	3
H-5	-11.62	A	41	6	47	6
H-6	-11.93	A	1	96	2	0
H-7	-11.99	A	6	64	25	5
H-8	-12.02	A	9	41	42	8
H-9	-12.08	A	18	55	23	5
H-10	-12.11	A	1	9	61	28
H-11	-12.11	A	10	68	16	6
H-12	-12.14	A	1	92	5	2
H-13	-12.18	A	3	9	53	35
H-14	-12.22	A	3	77	13	7
H-15	-12.23	A	0	99	0	0
H-16	-12.27	A	5	17	70	8
H-17	-12.57	A	14	4	52	30
H-18	-12.68	A	4	1	18	77
H-19	-12.75	A	15	11	41	33
H-20	-12.87	A	0	5	4	91

Table S3. Energy, oscillator strength and major contribution of calculated transitions for **1**.

Excited state	Energy / eV (/ nm)	Oscillator strength	Main contribution (%)	
1	2.45 (506)	0.0237	H-1 → LUMO	88
2	2.51 (493)	0.0194	HOMO → LUMO	24
			HOMO → L+1	62
3	2.64 (469)	0.0017	H OMO→ LUMO	69
			HOMO → L+1	20
4	2.68 (463)	0.0018	H-1 → L+1	81
			HOMO→ L+1	13
5	2.79 (445)	0.0074	H-3 → LUMO	18
			H-3 → L+1	72
6	2.91 (426)	0.0026	H-1 → L+2	89
7	2.94 (421)	0.0071	HOMO→ L+2	39
			HOMO→ L+3	47
8	2.95 (420)	0.0035	H-4 → LUMO	28
			H-3 → LUMO	43
			H-3→ L+1	11
9	2.98 (416)	0.0022	H-4 → LUMO	44
			H-3 → LUMO	31
10	3.01 (412)	0.0008	HOMO → L+2	55
			HOMO → L+3	36

Table S4. Energy, oscillator strength and major contribution of calculated transitions for **3**.

Excited state	Energy / eV (/ nm)	Oscillator strength	Main contribution (%)	
1	2.32 (533)	0.0015	H-2→LUMO	23
			H-1→L+1	38
			HOMO→LUMO	34
2	2.35 (526)	0.0604	H-2→L+1	20
			H-1→LUMO	46
			HOMO→L+1	28
3	2.48 (499)	0.0000	H-1→LUMO	19
			H-1→L+1	33
			HOMO→LUMO	14
			HOMO→L+1	17
4	2.49 (498)	0.0000	H-2→L+1	10
			H-1→LUMO	31
			H-1→L+1	25
			HOMO→LUMO	10
			HOMO→L+1	13
5	2.57 (480)	0.0002	H-2→LUMO	59
			HOMO→LUMO	40
6	2.60 (477)	0.0048	H-2→L+1	59
			HOMO→L+1	40
7	2.77 (448)	0.008	H-3→LUMO	34
			H-3→L+1	43
8	2.79 (445)	0.0079	H-3→LUMO	44
			H-3→L+1	32
9	2.80 (443)	0.0012	H-2→L+2	29
			H-1→L+3	11
			HOMO→L+2	52
10	2.81 (441)	0.009	H-1→L+2	77

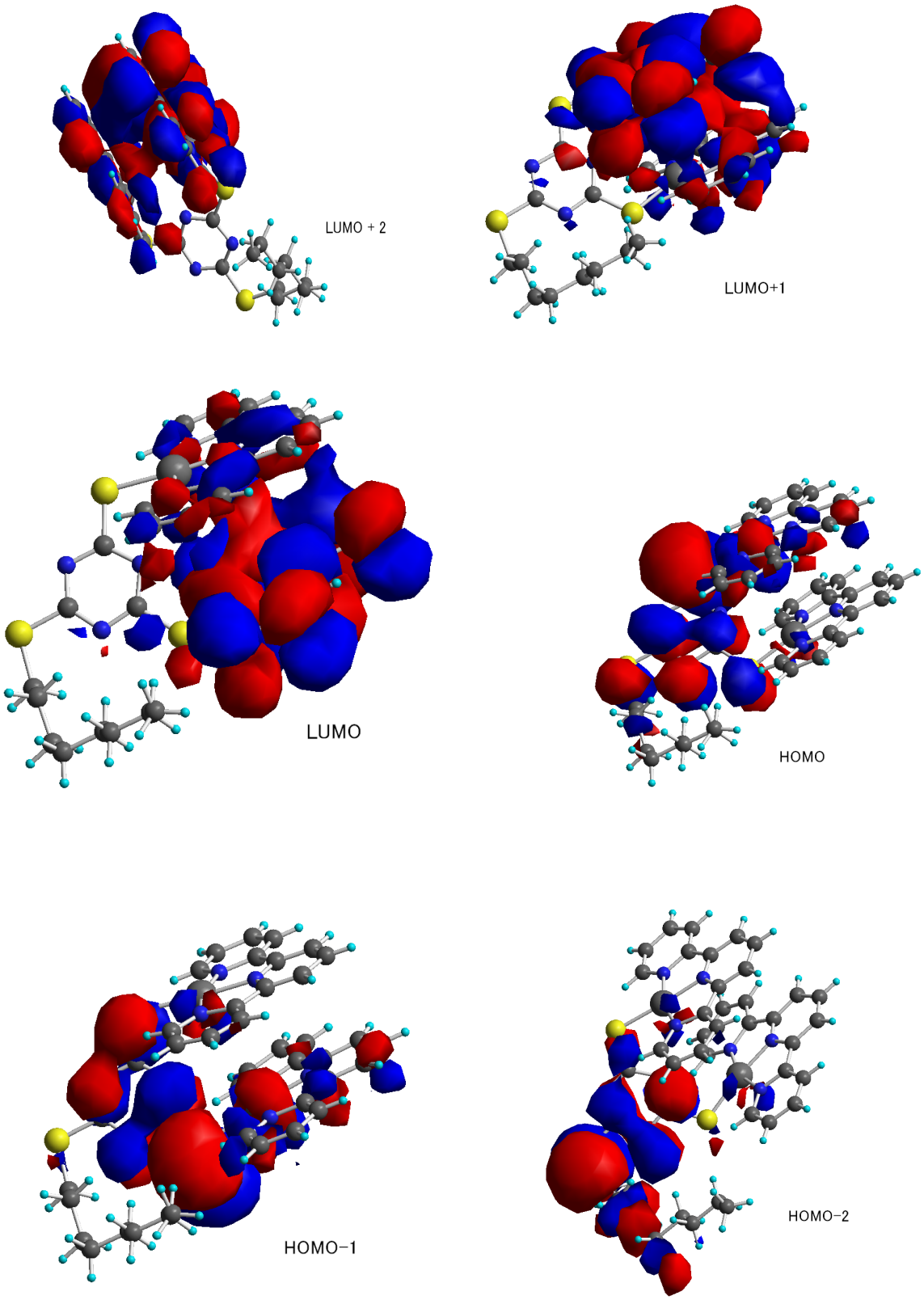

Fig. S5 Contour plots of the frontier orbitals of **1**: LUMO+2, LUMO+1, LUMO, HOMO, HOMO−1 and HOMO−2.

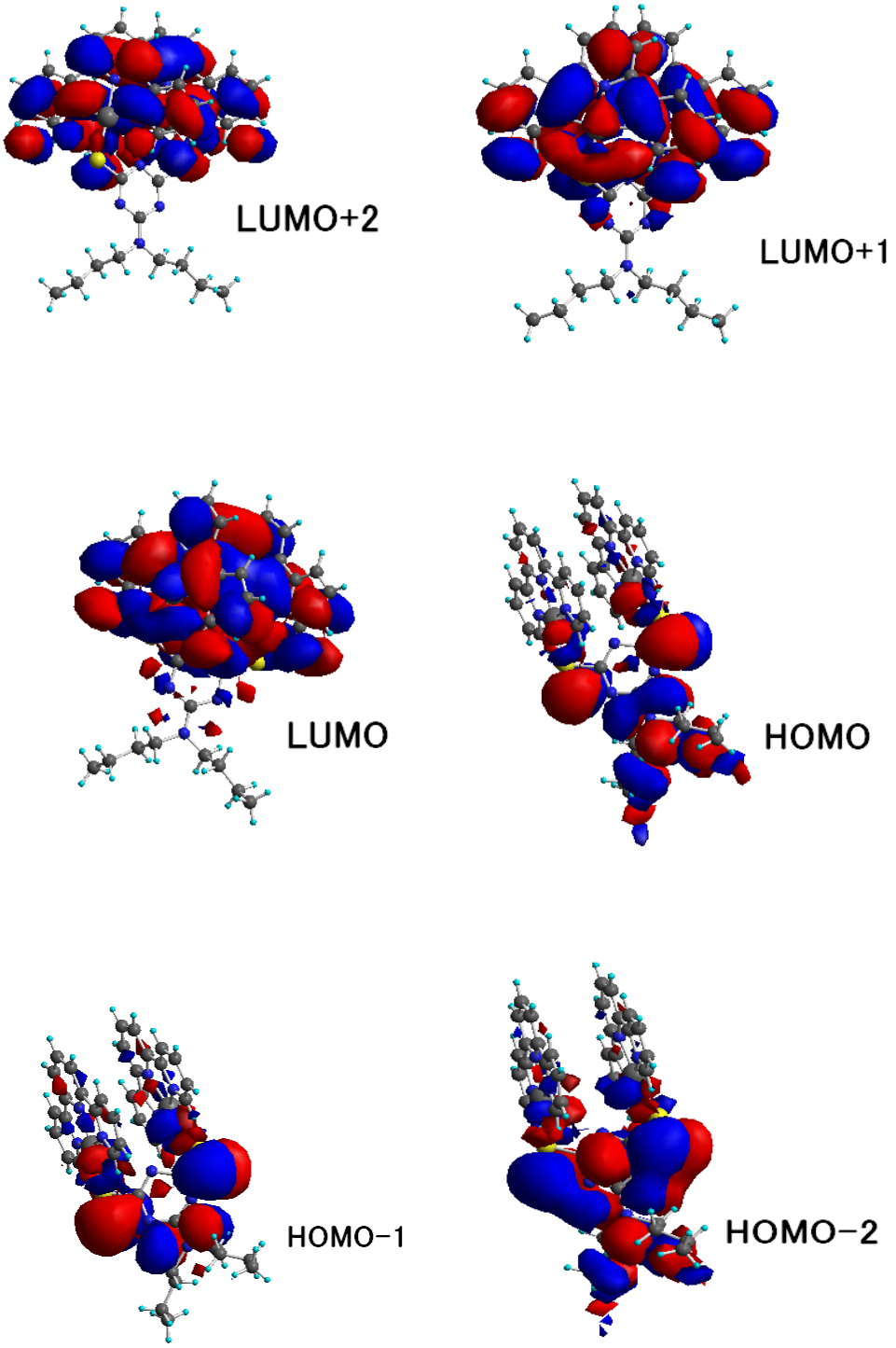

Fig. S6 Contour plots of the frontier orbitals of **3**: LUMO+2, LUMO+1, LUMO, HOMO, HOMO−1 and HOMO−2.

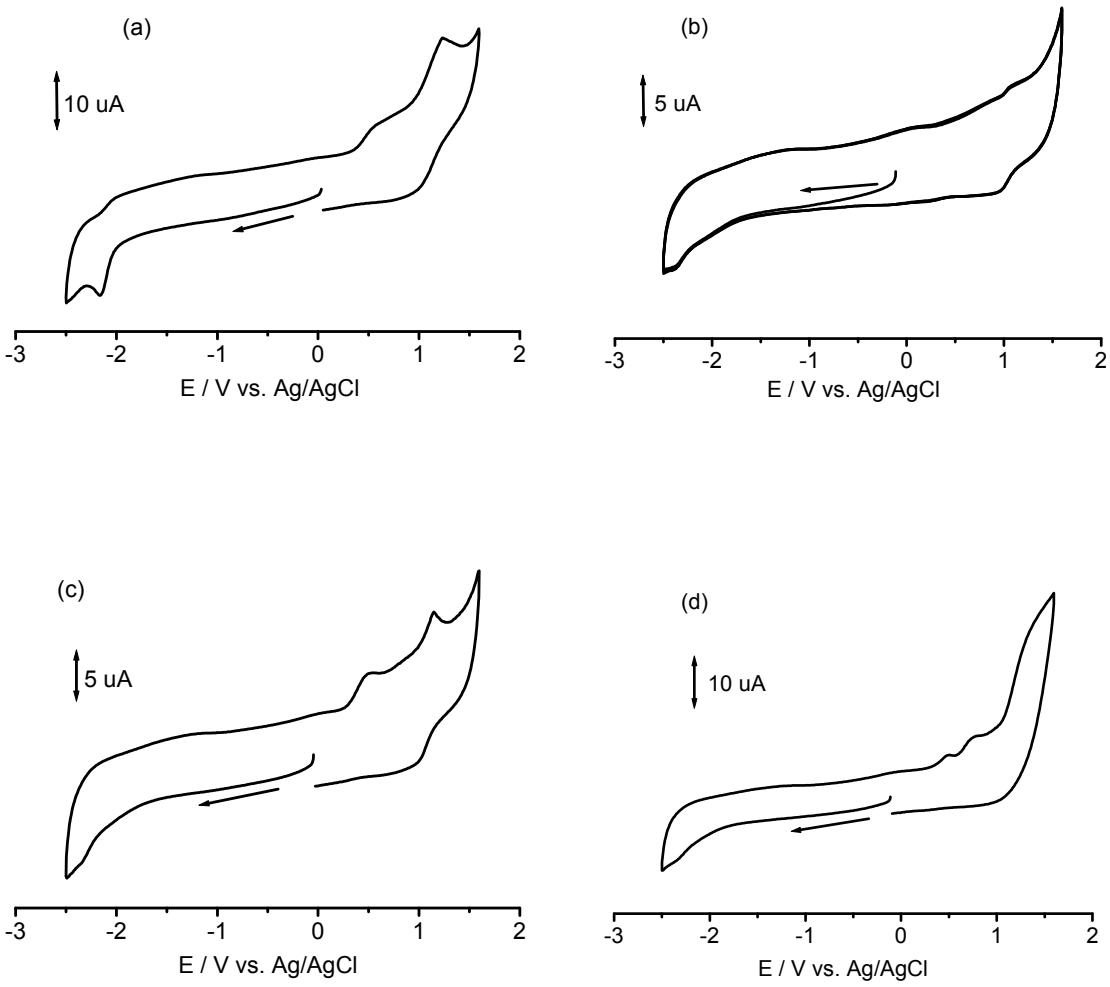

Fig. S7 Cyclic voltammograms of Na_2L_1 (a), Na_2L_2 (b), Na_3L_3 (c) and Na_2L_4 (d) (0.5 mM) in 0.1 M *n*-Bu_4NPF_6/DMF solution with a glassy carbon working electrode. Scan rate: 100 mV s^{-1}.

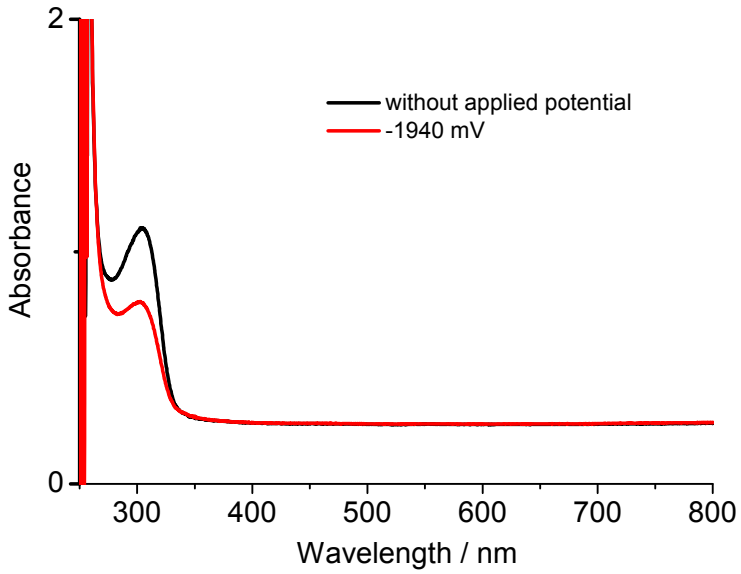

Fig. S8 Controlled-potential absorption spectra of H_2L_3 in 0.1 M *n*-Bu_4NPF_6/DMF solution.

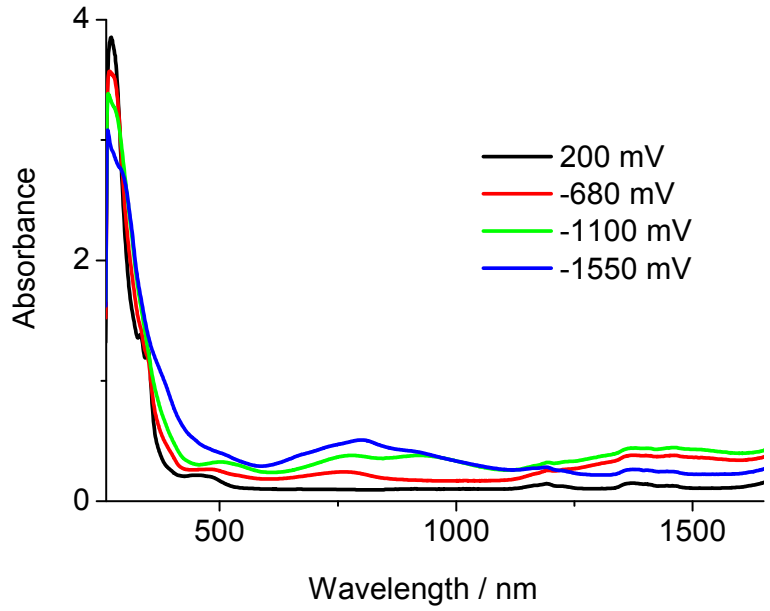

Fig. S9 Controlled-potential absorption spectra of **3** in 0.1 M *n*-Bu_4NPF_6/DMF solution: black line, 200 mV; red line, –680 mV; green line, –1100 mV; blue line, –1550 mV.