Supplementary Information

Titanium and manganese complexes supported by a xanthene-bridged bis(tripodal N$_2$O$_2$) ligand: isomerization, intramolecular hydrogen bonding and metal-binding ability

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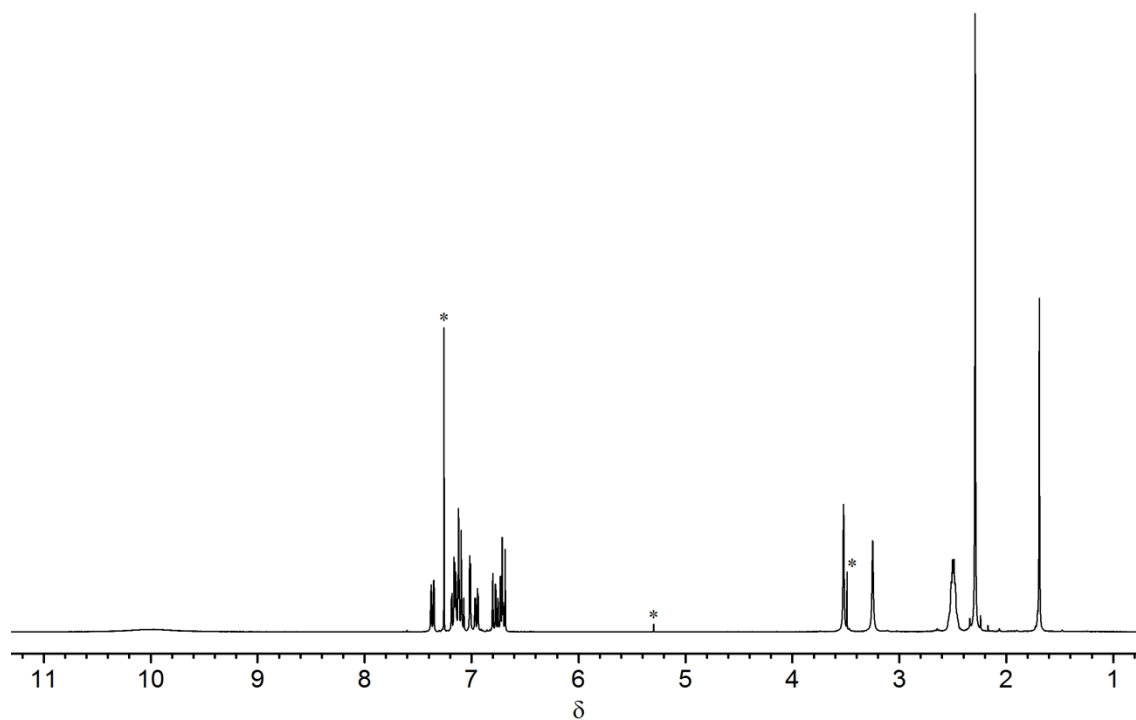
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Figure S1. ^{1}H NMR spectrum (300 MHz, CDCl$_3$) of H$_4$L. Residual solvent signals are marked with an asterisk.
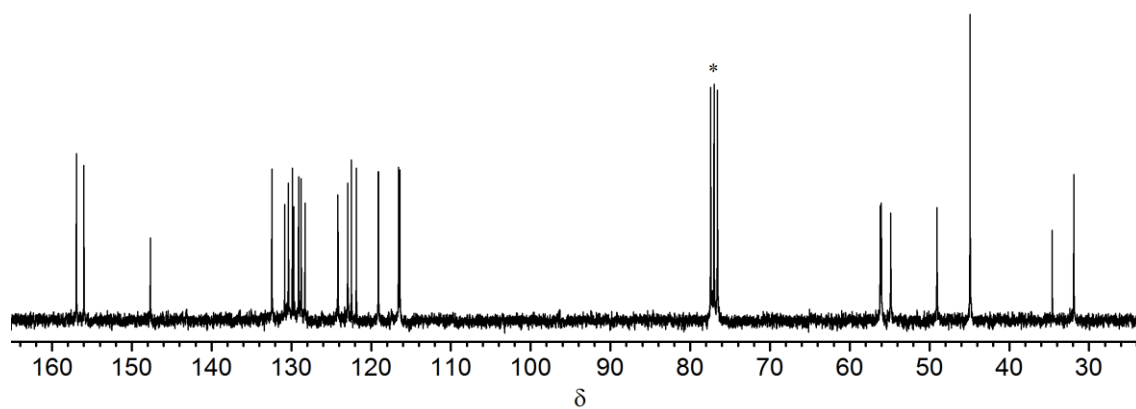

Figure S2. ^{13}C{^{1}H} NMR spectrum (75.5 MHz, CDCl$_3$) of H$_4$L. Residual solvent signals are marked with an asterisk.
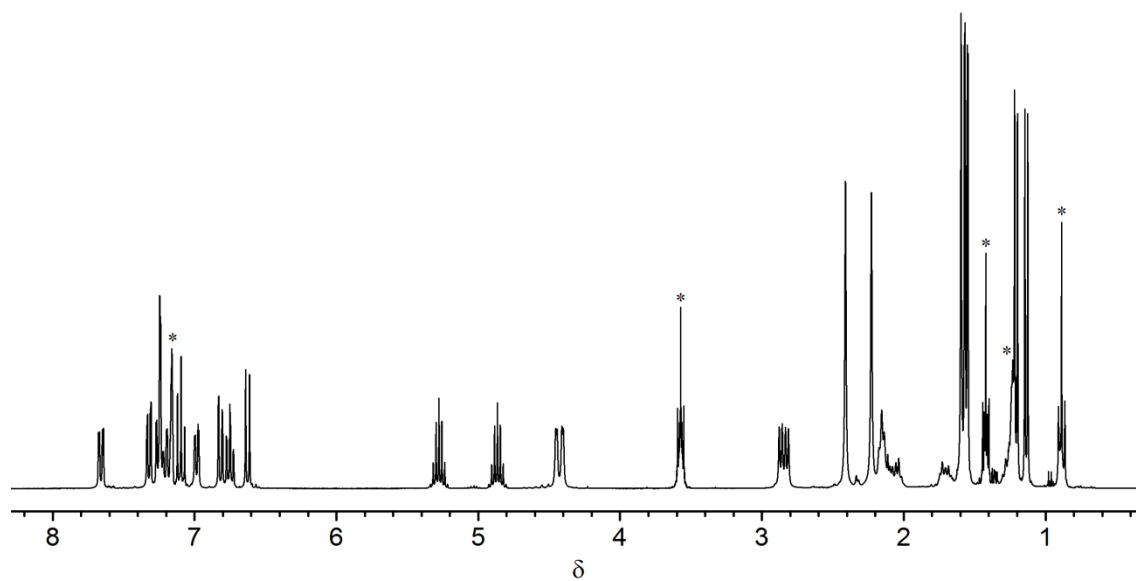
Figure S3. ^{1}H NMR spectrum (300 MHz, C_6D_6) of **1a**. Residual solvent signals are marked with an asterisk.
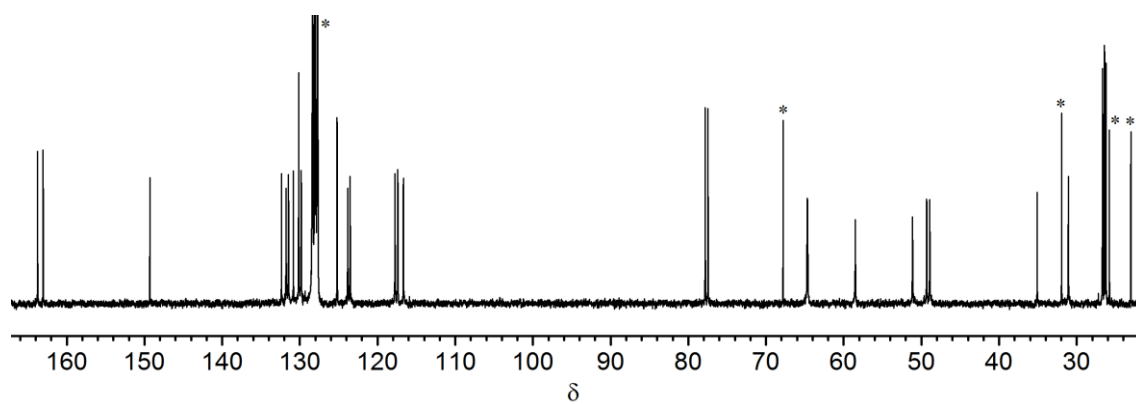
Figure S4. $^{13}C\{^1H\}$ NMR spectrum (75.5 MHz, C_6D_6) of **1a**. Residual solvent signals are marked with an asterisk.
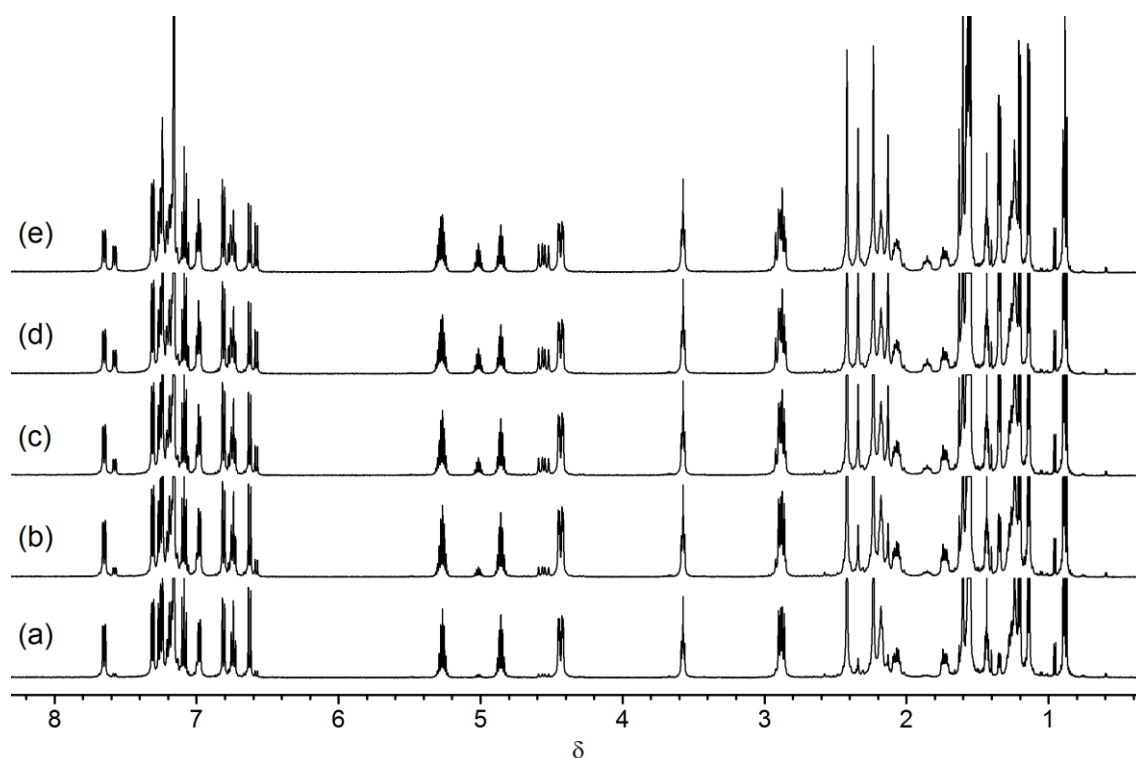
Figure S5. ^{1}H NMR spectra (300 MHz) of a C_6D_6 solution of **1a**, which is isomerized to **1b** at 40 °C: (a) 0 min, (b) 30 min, (c) 90 min, (d) 240 min, (e) 600 min.
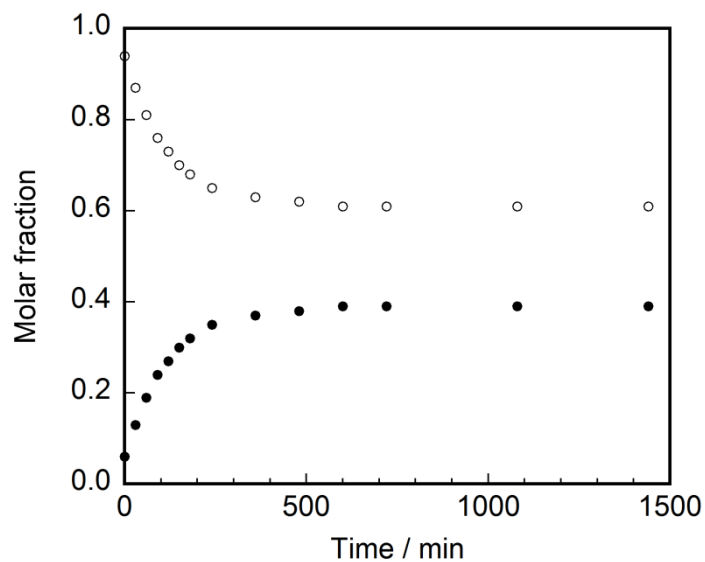
Figure S6. Isomerization of **1a** (open circle) to **1b** (solid circle) at 40 °C in C_6D_6 monitored by ^{1}H NMR spectroscopy.
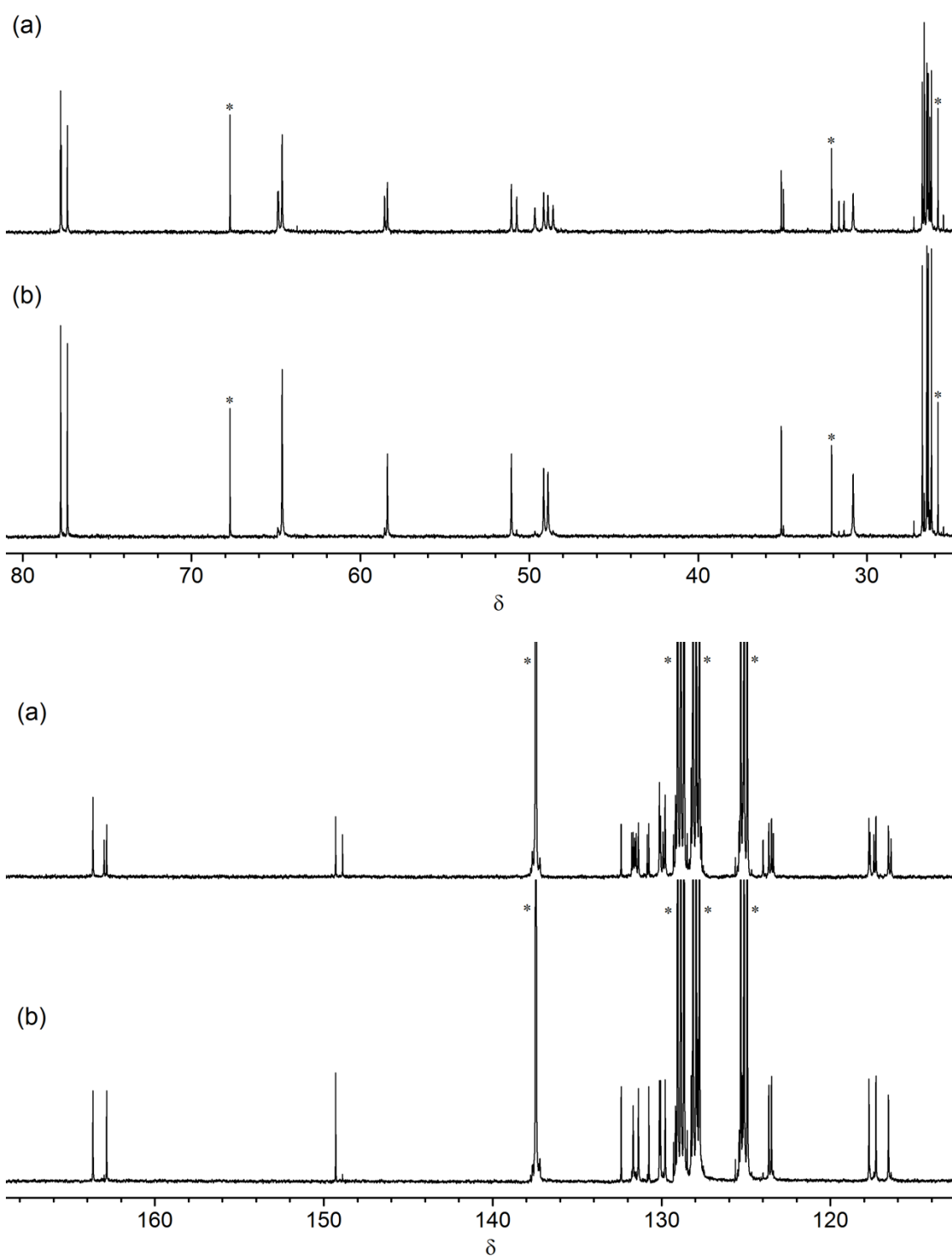
Figure S7. $^{13}C\{^1H\}$ NMR spectrum (125.7 MHz, toluene-d_8, 0 °C) of (a) **1a** and (b) a mixture of **1a** and **1b** after isomerization experiments. Residual solvent signals are marked with an asterisk.
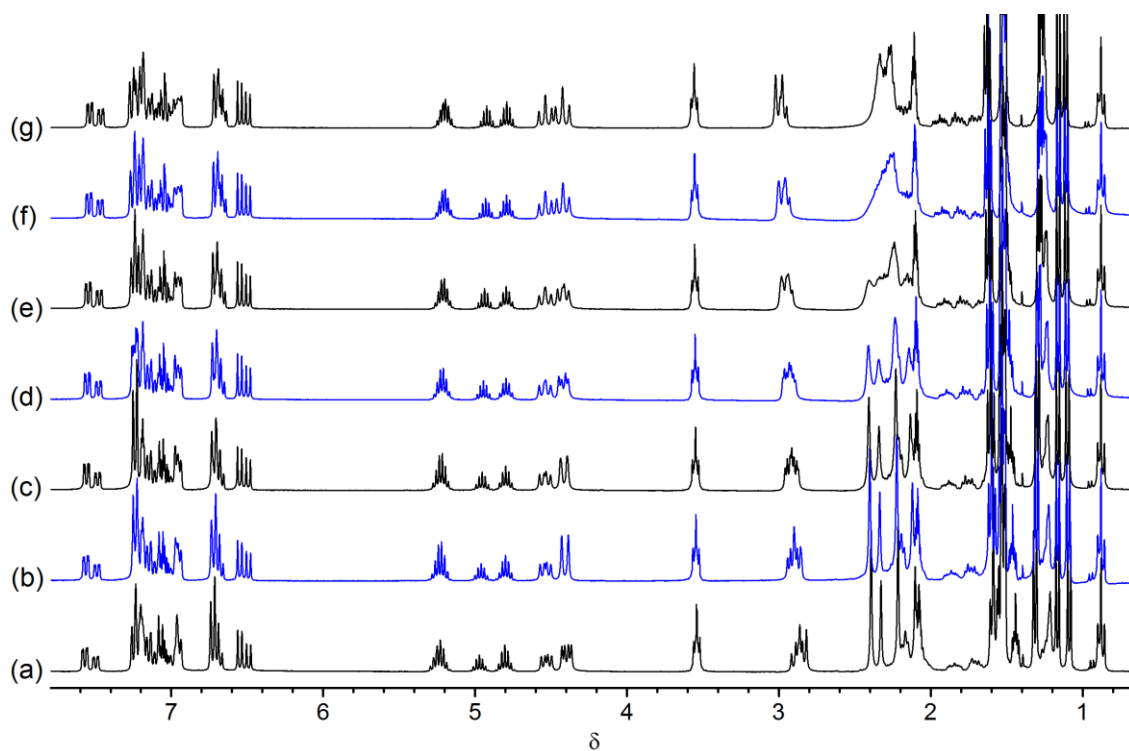
Figure S8. Temperature-dependent ^1H NMR spectra of a toluene-d_8 solution containing **1a** and **1b** in equilibrium at (a) 20 °C, (b) 40 °C, (c) 50 °C, (d) 60 °C, (e) 70 °C, (f) 80 °C, and (g) 90 °C.
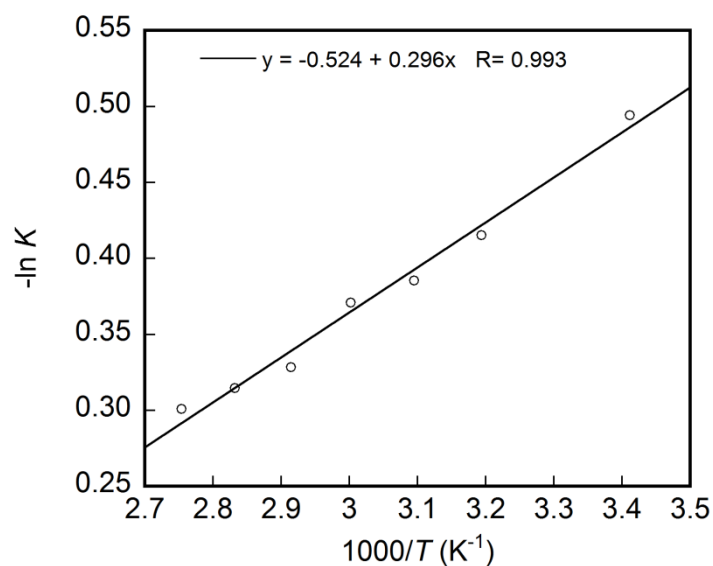
Figure S9. A van't Hoff plot of ln K vs. 1/T for the temperature dependence of the equilibrium between **1a** and **1b** in toluene-d_8.
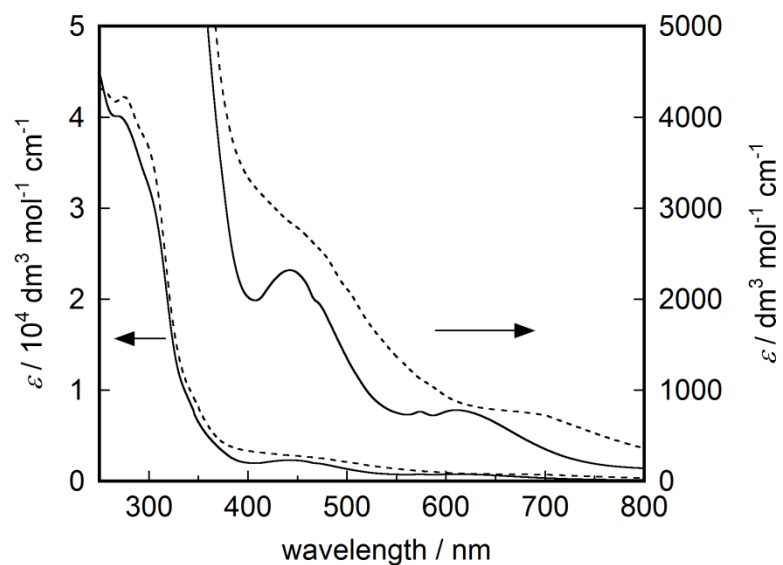
Figure S10. Absorption spectra of complexes **2** (- - -) and **3** (—).

Table S1. UV-vis absorption spectral data for **2** and **3**

complex	$\lambda_{\text{max or sh}}$ / nm, (ε / $M^{-1}cm^{-1}$)
2	680 (760),[a] 480 (2400),[a] 300 (34600),[a] 275 (42200)
3	612 (780), 574 (750), 470 (1960),[a] 442 (2320), 305 (30200),[a] 268 (40100)

[a] Shoulder.

A1 (**1a**)   A2 (**1a**)   B (**1b**)
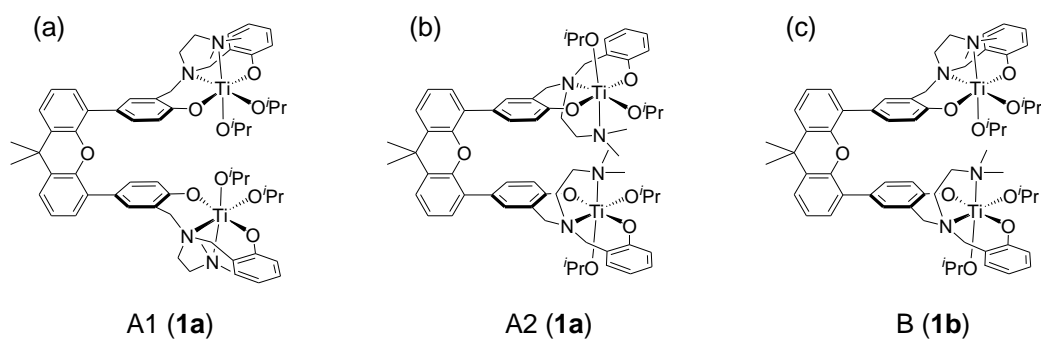
Figure S11.   Schematic models (a) A1, (b) A2, and (c) B.

(a)   (b)

(c)
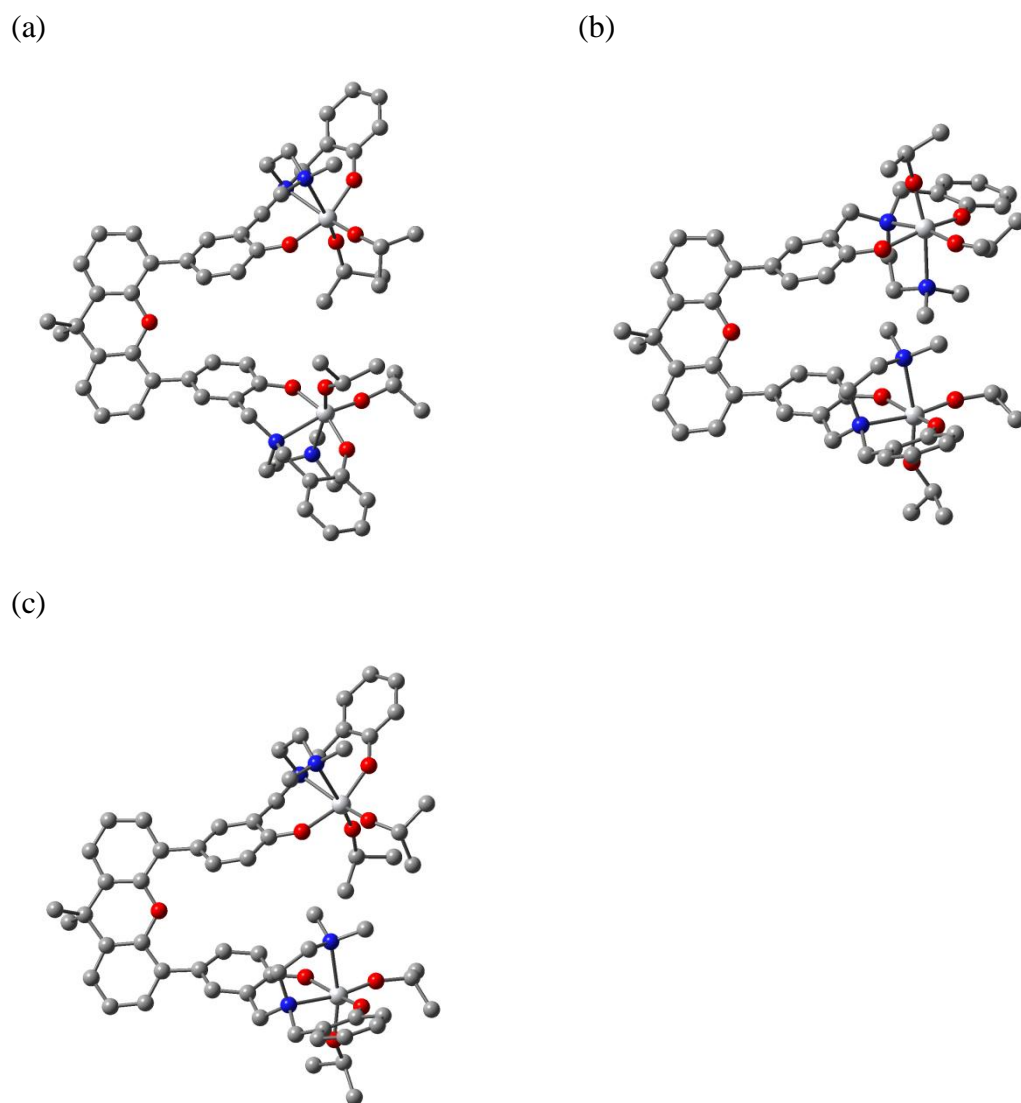
Figure S12.   Optimized structures of (a) A1, (b) A2, and (c) B.

Table S2. Molecular coordinates of A1 optimized by the DFT calculation at the B3LYP/LANL2DZ level

	Atomic number	x/Å	y/Å	z/Å
1	6	0.576758	8.997383	-1.302669
2	6	-3.342654	7.235024	-0.480621
3	6	-2.149577	7.954267	-0.343658
4	6	0.21677	9.067602	1.219967
5	6	0.369201	8.129446	-0.019956
6	6	-0.912227	7.295486	-0.181472
7	6	-3.308271	5.832452	-0.456697
8	6	-0.907134	5.88554	-0.168847
9	6	-2.098986	5.119409	-0.296525
10	6	1.597884	7.227281	0.180659
11	6	2.867277	7.818842	0.353876
12	6	-1.275437	2.796714	-0.9911
13	6	1.514864	5.819832	0.185396
14	6	-2.162672	3.62852	-0.267606
15	6	8.922673	-2.025425	-1.114377
16	6	4.015068	7.035969	0.524786
17	6	9.740687	-3.135097	-0.823998
18	6	-1.472368	1.408419	-1.051746
19	6	6.644034	-0.92173	-1.319082
20	6	2.659439	4.989305	0.34507
21	6	3.902834	5.637516	0.521381
22	6	7.536366	-2.058089	-0.87546
23	6	3.690438	2.800074	-0.307837
24	6	-3.220929	3.002021	0.436874
25	6	4.877329	0.694217	-1.063388
26	6	9.154692	-4.299275	-0.286457
27	6	6.212091	0.079837	0.95107
28	6	2.635774	3.497812	0.329076
29	6	3.79249	1.399664	-0.28151
30	6	-2.556791	0.803725	-0.376049
31	6	-3.422781	1.614578	0.404908
32	6	6.954085	-3.228438	-0.315139
33	6	-3.992914	-0.978575	-3.273319
34	6	7.77396	-4.346711	-0.029162
35	6	6.329837	-1.010786	2.027695
36	6	-5.442218	0.464152	-1.922663
37	6	1.652759	2.72691	0.99613
38	6	2.815562	0.64577	0.425108

39	6	-4.476835	0.95547	1.262309
40	6	1.744985	1.329948	1.049971
41	6	-6.166349	0.608111	-0.574631
42	6	-6.226634	-1.747324	-2.701429
43	6	4.12967	-0.864232	3.144131
44	6	5.264514	-3.005041	2.975316
45	6	-6.368702	-0.484429	1.650723
46	6	-7.424745	-1.475839	1.217858
47	6	-7.057082	-2.616377	0.450676
48	6	-8.762606	-1.32988	1.634617
49	6	-8.039144	-3.586186	0.131256
50	6	-9.737122	-2.295259	1.320019
51	6	-9.364618	-3.428002	0.566515
52	7	5.608103	-0.419513	-0.330659
53	7	-5.054429	-0.955231	-2.215705
54	7	5.02286	-1.699764	2.28369
55	7	-5.415659	-0.013579	0.567933
56	8	0.285225	5.154565	0.000848
57	8	3.677575	-2.182601	-1.677936
58	8	-2.797694	-0.526384	-0.48566
59	8	5.631835	-3.260262	-0.027658
60	8	2.911231	-0.700798	0.511407
61	8	-3.34022	-3.197132	-1.15598
62	8	3.0072	-3.427112	0.82242
63	8	-3.628547	-2.230155	1.532154
64	8	-5.78452	-2.774681	0.012625
65	1	7.30619	-5.23694	0.383347
66	1	9.772505	-5.167521	-0.06623
67	1	10.809315	-3.094619	-1.01798
68	1	9.366072	-1.12761	-1.544172
69	1	7.272025	-0.068266	-1.6282
70	1	6.061093	-1.246405	-2.190089
71	1	5.828211	-2.856205	3.912995
72	1	4.300778	-3.465332	3.208584
73	1	5.815118	-3.671611	2.310203
74	1	4.541002	-0.787531	4.166199
75	1	4.016488	0.138076	2.730653
76	1	3.137146	-1.319586	3.180435
77	1	6.708088	-0.547763	2.957741
78	1	7.054673	-1.765688	1.720677
79	1	7.213082	0.502757	0.764623

80	1	5.578311	0.892939	1.318203
81	1	4.449497	0.214242	-1.950932
82	1	5.617553	1.438161	-1.404805
83	1	4.439305	3.364847	-0.861091
84	1	0.989525	0.741853	1.562895
85	1	0.817081	3.22407	1.475702
86	1	4.78686	5.028162	0.684881
87	1	4.983843	7.506551	0.669776
88	1	2.956474	8.901591	0.357702
89	1	1.474424	9.620644	-1.213568
90	1	-0.278949	9.662712	-1.468177
91	1	0.689857	8.35961	-2.187281
92	1	-0.640816	9.740289	1.10184
93	1	0.067481	8.479924	2.133414
94	1	1.110575	9.687734	1.354968
95	1	-2.177773	9.040102	-0.364883
96	1	-4.286213	7.757093	-0.615166
97	1	-4.227529	5.269672	-0.591306
98	1	-0.433965	3.239136	-1.51356
99	1	-0.792406	0.773655	-1.612705
100	1	-3.887128	3.613899	1.043051
101	1	-3.984289	0.359559	2.040865
102	1	-5.082708	1.734325	1.757047
103	1	-7.14545	0.122376	-0.628903
104	1	-6.344249	1.679103	-0.381704
105	1	-4.533667	1.067689	-1.928127
106	1	-6.101184	0.852935	-2.720398
107	1	-3.095095	-0.483138	-2.900932
108	1	-4.345075	-0.478907	-4.192474
109	1	-3.74146	-2.017686	-3.495391
110	1	-5.944622	-2.801136	-2.762494
111	1	-6.546812	-1.39086	-3.696147
112	1	-7.064902	-1.666992	-2.008685
113	1	-6.862503	0.395851	2.098089
114	1	-5.72924	-0.929297	2.421735
115	1	-9.042054	-0.454311	2.219916
116	1	-10.76337	-2.168353	1.654419
117	1	-10.10623	-4.184118	0.317269
118	1	-7.735019	-4.451824	-0.451205
119	6	-3.906921	-3.133663	2.628602
120	1	-4.99735	-3.30145	2.658623

121	6	-3.446804	-2.478096	3.9423
122	1	-2.368115	-2.281522	3.903509
123	1	-3.961422	-1.522538	4.105165
124	1	-3.656911	-3.133758	4.798471
125	6	-3.212605	-4.485351	2.382768
126	1	-3.416209	-5.179793	3.209622
127	1	-3.57946	-4.933069	1.453096
128	1	-2.128266	-4.340548	2.300825
129	6	-2.697978	-4.456144	-1.432712
130	1	-2.111053	-4.722848	-0.53915
131	6	-1.737013	-4.293254	-2.623261
132	1	-1.169857	-5.219634	-2.788633
133	1	-2.296117	-4.062358	-3.539687
134	1	-1.031933	-3.477528	-2.430961
135	6	-3.764465	-5.539584	-1.679544
136	1	-4.456741	-5.594578	-0.832005
137	1	-4.34559	-5.302761	-2.580461
138	1	-3.290922	-6.521368	-1.817764
139	6	2.229463	-4.542538	1.283596
140	1	2.274378	-4.535029	2.386697
141	6	2.809927	-2.280465	-2.826463
142	1	3.349693	-1.821493	-3.67236
143	6	2.560193	-3.763831	-3.155307
144	1	2.018883	-4.246566	-2.332624
145	1	1.965147	-3.861467	-4.073943
146	1	3.514403	-4.285193	-3.293848
147	6	1.506484	-1.496212	-2.579673
148	1	0.974036	-1.905945	-1.713649
149	1	1.72343	-0.442132	-2.370619
150	1	0.853184	-1.553124	-3.461634
151	6	0.763381	-4.365383	0.851143
152	1	0.685384	-4.392316	-0.242896
153	1	0.142386	-5.171132	1.266712
154	1	0.373825	-3.401717	1.1974
155	6	2.84897	-5.856119	0.769337
156	1	2.309697	-6.722003	1.177744
157	1	2.799253	-5.893856	-0.325812
158	1	3.902567	-5.921507	1.063069
159	22	-4.100072	-1.88467	-0.198187
160	22	4.049878	-2.176753	0.093881

Table S3. Molecular coordinates of A2 optimized by the DFT calculation at the B3LYP/LANL2DZ level

	Atomic number	x/Å	y/Å	z/Å
1	6	1.141252	9.034996	-1.189355
2	6	-2.888032	7.38876	-1.501056
3	6	-1.755369	8.070195	-1.041792
4	6	0.10824	9.111991	1.141064
5	6	0.569351	8.172112	-0.018833
6	6	-0.641077	7.373432	-0.527941
7	6	-2.920467	5.988134	-1.438698
8	6	-0.69425	5.964417	-0.490251
9	6	-1.8393	5.23675	-0.923601
10	6	1.673923	7.238931	0.500205
11	6	2.868834	7.800182	0.998371
12	6	-0.957935	2.849881	-1.221683
13	6	1.552073	5.834038	0.485885
14	6	-1.987577	3.752683	-0.865384
15	6	7.998589	-2.310282	-2.22372
16	6	3.913009	6.9916	1.461051
17	6	8.339438	-3.483489	-2.923319
18	6	-1.188488	1.467785	-1.248352
19	6	6.578382	-1.038533	-0.544752
20	6	2.601798	4.97814	0.924732
21	6	3.772501	5.596707	1.419411
22	6	6.872559	-2.263355	-1.379418
23	6	3.733051	2.77901	0.517735
24	6	-3.248159	3.201769	-0.525554
25	6	5.139064	0.687719	0.314277
26	6	7.532672	-4.630692	-2.776182
27	6	4.630623	-0.315225	-1.934709
28	6	2.563415	3.486799	0.890446
29	6	3.818078	1.378795	0.569643
30	6	-2.457817	0.933278	-0.926542
31	6	-3.504337	1.821723	-0.56036
32	6	6.056508	-3.420213	-1.243704
33	6	6.398069	-4.599908	-1.948846
34	6	3.11599	-0.531434	-2.073198
35	6	1.446682	2.725106	1.306752
36	6	2.685633	0.631744	0.991996
37	6	-4.903204	1.297438	-0.32461
38	6	1.507266	1.325491	1.355079

39	6	-5.621471	-1.937983	-3.203846
40	6	3.010064	-2.943219	-2.593282
41	6	1.215563	-1.894756	-1.338
42	6	-6.515766	-0.208665	0.637171
43	6	-6.962991	-1.417273	1.427702
44	6	-6.367452	-2.684529	1.177497
45	6	-8.040287	-1.329023	2.328869
46	6	-6.881722	-3.835025	1.823092
47	6	-8.549285	-2.472413	2.975267
48	6	-7.965967	-3.72802	2.710703
49	7	5.131849	-0.564388	-0.539728
50	7	2.692352	-1.884872	-1.585598
51	7	-5.024383	0.05982	0.551008
52	8	0.384889	5.201114	0.00671
53	8	4.917672	-2.065608	1.979525
54	8	-2.6675	-0.405358	-0.946203
55	8	4.951786	-3.39091	-0.46104
56	8	2.720813	-0.72278	1.010538
57	8	-3.036136	-3.159587	-1.131095
58	8	2.637074	-3.505446	0.979327
59	8	-5.296671	-2.78718	0.353046
60	1	5.76637	-5.475619	-1.825911
61	1	7.786263	-5.546121	-3.306807
62	1	9.21482	-3.503937	-3.56709
63	1	8.620663	-1.42175	-2.327099
64	1	6.80822	-1.245445	0.507008
65	1	7.222264	-0.20784	-0.88066
66	1	0.65748	-1.61824	-2.248353
67	1	0.91478	-2.898437	-1.026579
68	1	0.979029	-1.20073	-0.531809
69	1	2.384985	-2.816327	-3.494416
70	1	4.060852	-2.907459	-2.88092
71	1	2.820661	-3.925882	-2.154475
72	1	2.834404	-0.400189	-3.133865
73	1	2.574532	0.219579	-1.49605
74	1	4.874522	0.711674	-2.252428
75	1	5.164165	-0.996914	-2.603796
76	1	5.840386	1.411274	-0.136097
77	1	5.562984	0.36735	1.274356
78	1	4.601421	3.339363	0.174929
79	1	0.64848	0.744633	1.676213

80	1	0.529716	3.23092	1.588904
81	1	4.569453	4.966296	1.802512
82	1	4.821049	7.438591	1.856584
83	1	2.980085	8.880462	1.02662
84	1	1.993927	9.637277	-0.854245
85	1	0.380608	9.721264	-1.579564
86	1	1.477946	8.394075	-2.012752
87	1	-0.670593	9.80406	0.800288
88	1	-0.296057	8.526413	1.975182
89	1	0.945841	9.710439	1.518017
90	1	-1.733278	9.155495	-1.086354
91	1	-3.731603	7.937673	-1.910748
92	1	-3.785848	5.455572	-1.821426
93	1	0.024863	3.23277	-1.473098
94	1	-0.396412	0.778634	-1.523355
95	1	-4.051972	3.870145	-0.221501
96	1	-5.520404	2.101066	0.112172
97	1	-5.349697	1.006501	-1.2827
98	1	-4.989299	-2.793028	-3.499098
99	1	-6.837572	-0.323032	-0.405143
100	1	-7.006296	0.691329	1.04623
101	1	-8.494288	-0.356867	2.518678
102	1	-9.384292	-2.386403	3.665508
103	1	-8.353027	-4.621441	3.196356
104	1	-6.421385	-4.796544	1.610327
105	6	-3.876531	-1.019317	2.538033
106	6	-2.648093	-4.499599	-1.485152
107	1	-2.007062	-4.875671	-0.669039
108	6	-1.824191	-4.462324	-2.784264
109	1	-1.466286	-5.468249	-3.043498
110	1	-2.439779	-4.084165	-3.610098
111	1	-0.961431	-3.796949	-2.668246
112	6	-3.892222	-5.401716	-1.592997
113	1	-4.501992	-5.311898	-0.688161
114	1	-4.508529	-5.100501	-2.449864
115	1	-3.595387	-6.450829	-1.728135
116	6	2.07261	-4.816732	1.167401
117	1	1.42481	-5.01772	0.295746
118	6	5.209811	-2.05744	3.39346
119	1	6.028708	-1.333441	3.545008
120	6	3.978745	-1.593396	4.195577

121	1	3.149834	-2.297474	4.053954
122	1	4.219149	-1.537826	5.266386
123	1	3.644753	-0.607027	3.855672
124	6	5.702872	-3.451974	3.821248
125	1	4.900847	-4.190015	3.696017
126	1	6.553915	-3.760499	3.203052
127	1	6.014018	-3.445927	4.87509
128	6	3.189751	-5.876568	1.209699
129	1	3.807361	-5.742476	2.106493
130	1	2.759823	-6.887651	1.226645
131	1	3.839993	-5.772895	0.335192
132	6	1.204696	-4.815733	2.437959
133	1	0.71255	-5.789051	2.571453
134	1	1.827778	-4.614594	3.318426
135	1	0.437777	-4.035182	2.374492
136	6	-4.39276	0.278628	1.897452
137	1	-3.564495	0.980787	1.762673
138	1	-5.112645	0.751818	2.585228
139	1	-3.366387	-0.766229	3.485248
140	1	-4.711668	-1.676675	2.782764
141	7	-2.945039	-1.768127	1.631248
142	6	-2.826426	-3.189154	2.084622
143	1	-2.474886	-3.242712	3.129637
144	1	-3.794746	-3.683017	1.992576
145	1	-2.107496	-3.706543	1.443176
146	6	-1.582245	-1.153201	1.638672
147	1	-1.103013	-1.284688	2.624416
148	1	-0.966636	-1.627498	0.872125
149	1	-1.640073	-0.089542	1.40709
150	8	-5.041761	-1.361807	-2.009701
151	6	-5.597205	-0.888192	-4.327351
152	1	-6.222501	-0.027064	-4.056819
153	1	-4.57315	-0.532845	-4.490508
154	1	-5.978239	-1.314131	-5.266004
155	6	-7.041057	-2.450115	-2.896719
156	1	-7.465428	-2.961299	-3.77203
157	1	-7.016949	-3.150265	-2.054406
158	1	-7.700742	-1.612544	-2.633062
159	22	-3.972575	-1.737415	-0.582646
160	22	3.817943	-2.226998	0.548774

Table S4. Molecular coordinates of B optimized by the DFT calculation at the B3LYP/LANL2DZ level

	Atomic number	x/Å	y/Å	z/Å
1	6	-0.041327	9.146586	1.113192
2	6	3.827873	7.193784	0.648529
3	6	2.676125	7.945523	0.389351
4	6	0.445622	9.04555	-1.387349
5	6	0.193115	8.19322	-0.102374
6	6	1.428468	7.321592	0.177419
7	6	3.740395	5.794856	0.700786
8	6	1.370893	5.913668	0.231645
9	6	2.519964	5.113596	0.488426
10	6	-1.060414	7.329199	-0.313884
11	6	-2.298643	7.958536	-0.563059
12	6	1.531744	2.866318	1.217736
13	6	-1.028908	5.920514	-0.263419
14	6	2.530369	3.622484	0.557375
15	6	-8.7425	-1.646513	0.909269
16	6	-3.46749	7.212292	-0.753617
17	6	-9.584022	-2.734496	0.605277
18	6	1.659857	1.47905	1.369519
19	6	-6.441945	-0.608529	1.184998
20	6	-2.196302	5.127781	-0.448536
21	6	-3.407065	5.811662	-0.698278
22	6	-7.349526	-1.727019	0.725654
23	6	-3.321949	2.988415	0.222555
24	6	3.643085	2.917838	0.036301
25	6	-4.609799	0.941419	0.974699
26	6	-9.01583	-3.925587	0.1094
27	6	-5.882804	0.333878	-1.079671
28	6	-2.226101	3.637358	-0.395149
29	6	-3.4703	1.591255	0.222841
30	6	2.79333	0.793038	0.871578
31	6	3.797357	1.529954	0.186924
32	6	-6.784405	-2.925306	0.20878
33	6	-7.628434	-4.021317	-0.092226
34	6	-5.988437	-0.771815	-2.141471
35	6	-1.254	2.821272	-1.021672
36	6	-2.496853	0.790284	-0.433854
37	6	5.067857	0.84926	-0.272908
38	6	-1.393153	1.42816	-1.049251

39	6	5.747915	-1.679301	3.063736
40	6	-3.737301	-0.719535	-3.161866
41	6	-4.956593	-2.81247	-3.017814
42	6	6.31295	-0.916735	-1.33363
43	6	6.474392	-2.229871	-2.064935
44	6	5.837311	-3.39677	-1.559757
45	6	7.3341	-2.340615	-3.173251
46	6	6.093157	-4.649514	-2.167327
47	6	7.585565	-3.585934	-3.782232
48	6	6.963879	-4.741268	-3.266705
49	7	-5.348742	-0.160429	0.233962
50	7	-4.69564	-1.509292	-2.328222
51	7	4.900329	-0.480654	-0.988657
52	8	0.163835	5.21866	0.004518
53	8	-3.530909	-1.990332	1.676916
54	8	2.909647	-0.547414	1.028836
55	8	-5.452909	-3.00697	-0.024367
56	8	-2.624532	-0.557339	-0.485472
57	8	3.068994	-3.283587	1.459114
58	8	-2.809837	-3.311094	-0.766653
59	8	4.967122	-3.30309	-0.526027
60	1	-7.174818	-4.932505	-0.473423
61	1	-9.652495	-4.777134	-0.121743
62	1	-10.65744	-2.656719	0.756392
63	1	-9.173044	-0.727618	1.306223
64	1	-7.056678	0.269931	1.447915
65	1	-5.912326	-0.930389	2.090376
66	1	-5.473177	-2.650542	-3.980069
67	1	-4.001219	-3.310032	-3.201705
68	1	-5.561366	-3.449649	-2.371315
69	1	-4.099707	-0.649841	-4.202539
70	1	-3.60958	0.286861	-2.762636
71	1	-2.761402	-1.210606	-3.144303
72	1	-6.308435	-0.314128	-3.095566
73	1	-6.751414	-1.496847	-1.855888
74	1	-6.877556	0.789581	-0.943743
75	1	-5.210377	1.121037	-1.433942
76	1	-4.237354	0.471098	1.891601
77	1	-5.3351	1.719076	1.27033
78	1	-4.069014	3.589872	0.738231
79	1	-0.652105	0.806657	-1.541407

80	1	-0.390991	3.281588	-1.490189
81	1	-4.305252	5.228017	-0.878363
82	1	-4.41137	7.71185	-0.954664
83	1	-2.346315	9.04282	-0.610843
84	1	-0.907669	9.79619	0.941998
85	1	0.830815	9.789188	1.280964
86	1	-0.221318	8.569672	2.027958
87	1	1.326769	9.686657	-1.267025
88	1	0.611013	8.396847	-2.255653
89	1	-0.41251	9.693049	-1.602884
90	1	2.744102	9.029272	0.356716
91	1	4.779322	7.688823	0.823241
92	1	4.624339	5.212037	0.941576
93	1	0.655736	3.367554	1.61444
94	1	0.894533	0.901974	1.880287
95	1	4.411633	3.46913	-0.503281
96	1	5.625938	1.537023	-0.931431
97	1	5.699928	0.623959	0.593804
98	1	5.095913	-2.411218	3.570451
99	1	6.82628	-0.980329	-0.36587
100	1	6.790493	-0.114306	-1.921938
101	1	7.821647	-1.445263	-3.557824
102	1	8.254713	-3.654013	-4.635933
103	1	7.155147	-5.71117	-3.721362
104	1	5.605995	-5.531258	-1.75888
105	6	3.253372	-1.629304	-2.54111
106	6	2.770214	-4.573793	2.030131
107	1	2.14915	-5.11559	1.296609
108	6	1.95826	-4.376436	3.321471
109	1	1.66501	-5.346645	3.745567
110	1	2.557667	-3.834023	4.063654
111	1	1.054401	-3.791072	3.118532
112	6	4.072013	-5.366269	2.257689
113	1	4.658009	-5.40263	1.333425
114	1	4.681454	-4.882681	3.032018
115	1	3.84489	-6.391116	2.582364
116	6	-2.190847	-4.607689	-0.874961
117	1	-1.558508	-4.584403	-1.778231
118	6	-2.896849	-1.850749	2.963656
119	1	-3.39065	-1.006996	3.478813
120	6	-3.136034	-3.127303	3.789846

121	1	-2.643258	-3.984514	3.315168
122	1	-2.73397	-3.010441	4.805493
123	1	-4.209047	-3.341693	3.85639
124	6	-1.403172	-1.516311	2.794813
125	1	-0.87968	-2.34442	2.303305
126	1	-1.277191	-0.621351	2.175912
127	1	-0.936472	-1.339404	3.773362
128	6	-1.294788	-4.861129	0.35121
129	1	-1.907645	-4.92269	1.258316
130	1	-0.74266	-5.803963	0.234719
131	1	-0.575846	-4.043225	0.473996
132	6	-3.265231	-5.700454	-1.037625
133	1	-2.793556	-6.690292	-1.107871
134	1	-3.944156	-5.687429	-0.177303
135	1	-3.85861	-5.532915	-1.94344
136	6	4.013402	-0.338951	-2.193545
137	1	3.300712	0.464242	-1.982664
138	1	4.604992	-0.029104	-3.070671
139	1	2.566993	-1.417145	-3.381297
140	1	3.950958	-2.398009	-2.875928
141	7	2.488172	-2.173933	-1.37116
142	6	2.149415	-3.611144	-1.612598
143	1	1.564341	-3.72707	-2.541813
144	1	3.067603	-4.197015	-1.675759
145	1	1.555295	-3.980013	-0.772721
146	6	1.217233	-1.414131	-1.158232
147	1	0.514497	-1.592989	-1.989922
148	1	0.751524	-1.730507	-0.22303
149	1	1.418472	-0.345942	-1.078652
150	8	5.358708	-1.645281	1.670156
151	6	5.526982	-0.295446	3.701964
152	1	6.17814	0.452352	3.229578
153	1	4.485564	0.019811	3.574322
154	1	5.758187	-0.325301	4.775938
155	6	7.208291	-2.152233	3.161924
156	1	7.517755	-2.244599	4.212394
157	1	7.325113	-3.125703	2.671548
158	1	7.873598	-1.434243	2.664491
159	22	3.981252	-2.043342	0.544836
160	22	-3.827981	-1.990394	-0.099412

Table S5. Bond distances (Å) for optimized structures of A1, A2, and B (B3LYP/LANL2DZ)

	A1	A2	B
$Ti_a–O_a(1)$	1.910	1.918	1.911
$Ti_a–O_a(2)$	1.921	1.913	1.918
$Ti_a–O_a(3)$	1.784	1.793	1.796
$Ti_a–O_a(4)$	1.811	1.812	1.801
$Ti_a–N_a(c)$	2.387	2.382	2.403
$Ti_a–N_a(t)$	2.443	2.437	2.440
$Ti_b–O_b(1)$	1.904	1.900	1.903
$Ti_b–O_b(2)$	1.917	1.932	1.925
$Ti_b–O_b(3)$	1.794	1.789	1.791
$Ti_b–O_b(4)$	1.826	1.822	1.823
$Ti_b–N_b(c)$	2.412	2.371	2.375
$Ti_b–N_b(t)$	2.418	2.441	2.433

A1 (**1a**)   A2 (**1a**)   B (**1b**)
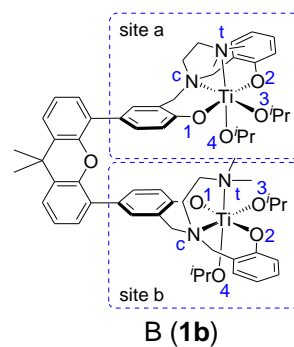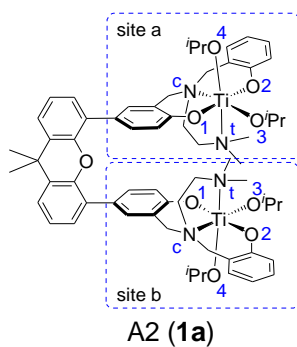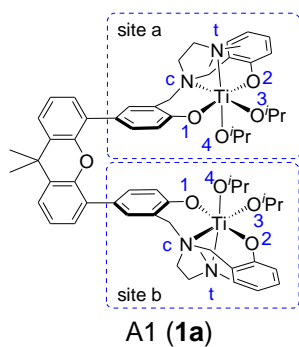
Table S6. Calculated results for models A1, A2, and B[a]

	A1	A2	B
	[Hartree/Particle]	[Hartree/Particle]	[Hartree/Particle]
E_{el}(RB+HF-LYP)	-3462.372666	-3462.373298	-3462.372672
E_{el} + zero-point energy	-3461.012864	-3461.013904	-3461.012854
E_{el} + thermal energy	-3460.933609	-3460.936272	-3460.933610
E_{el} + thermal enthalpy	-3460.932665	-3460.935328	-3460.932666
E_{el} + thermal free energy	-3461.132649	-3461.130326	-3461.132338
	Δ (B-A1)	Δ (B-A2)	Δ (A2-A1)
	[kJ mol^{-1}]	[kJ mol^{-1}]	[kJ mol^{-1}]
E_{el}(RB+HF-LYP)	-0.016	1.643	-1.659
E_{el} + zero-point energy	0.026	2.756	-2.731
E_{el} + thermal energy	-0.003	6.988	-6.992
E_{el} + thermal enthalpy	-0.003	6.988	-6.992
E_{el} + thermal free energy	0.816	-5.283	6.099

[a] Zero-point energy and enthalpic and entropic thermal contributions to thermodynamic properties at 298.15 K and 1 atm were calculated from harmonic vibrational frequencies without scaling factors.