Supporting Information

Tris(tropolonato) ruthenium as a hub for connecting π-conjugated systems

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Single crystal X-ray diffraction analysis

The crystal structures of **4b** was determined by the single-crystal X-ray diffraction method. A Rigaku XtaLAB Synergy-S (Cu-Kα radiation) with a HyPix-6000 area detector was used for the data collection. The structures were solved using the program *SHELXT*.[1] The refinement and all further calculations were carried out using the program *SHELXL*[2] via *OLEX2*.[3] All H atoms were generated geometrically.

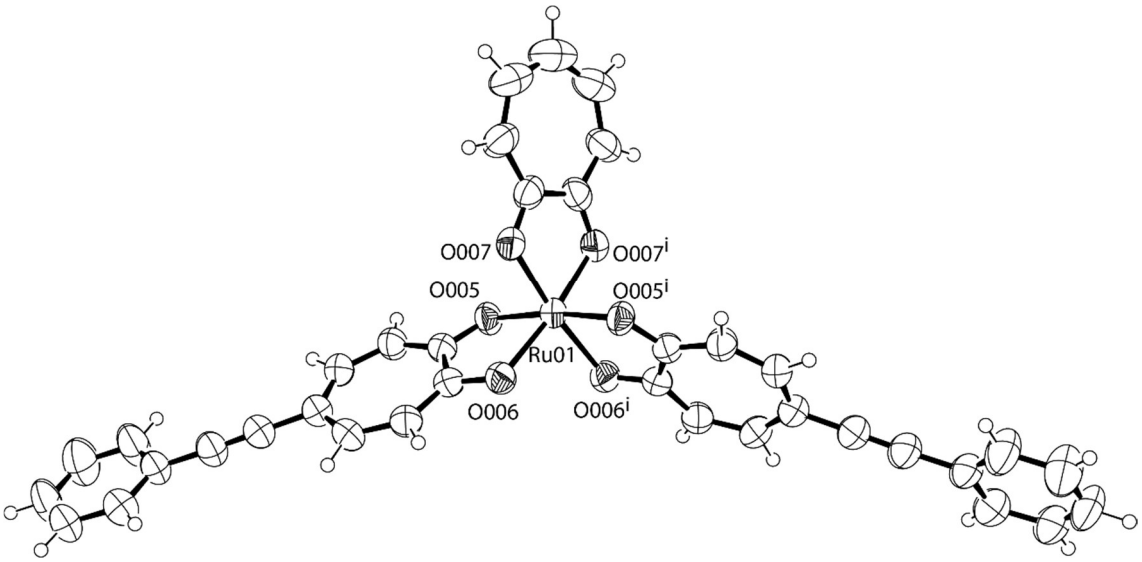


Figure S1 ORTEP representation of **4b** (50% probability level, symmetry code: (i) −x+1, y, −z+1/2).

Table S1 Crystallographic and experimental data for **4b.**

Compound	**4b**
Formula	$C_{37}H_{23}O_6Ru{\cdot}2(CHCl_3)$
Formula weight	903.36
Crystal system	Monoclinic
Space group	*C*2/c
a / Å	24.5500 (4)
b / Å	10.6232 (2)
c / Å	14.7279 (3)
α / °	-
β / °	96.420 (2)
γ / °	-
V / Å^3	3816.94 (12)
Z	4
μ (mm−1)	7.58
T / K	173(2)
Crystal size / mm	0.1, 0.03, 0.03
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18613, 3930, 3618
R_{int}	0.096
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.080, 0.220, 1.03
No. of parameters	236

Table S2 Selected bond lengths (Å) angles (°) for **1** and **4b**.

	1	**4b**
Ru-O	2.045(1)	2.004 (3)
	2.009(1)	2.004 (3)
	2.008(1)	2.058 (4)
	2.008(1)	2.058 (4)
	2.009(1)	2.024 (4)
	2.045(1)	2.024 (4)
O-Ru-O	79.32 (4)	79.26 (1)
(chelate ring)	79.31(5)	79.26 (1)
	80.94(6)	79.6(2)

ESI mass spectra

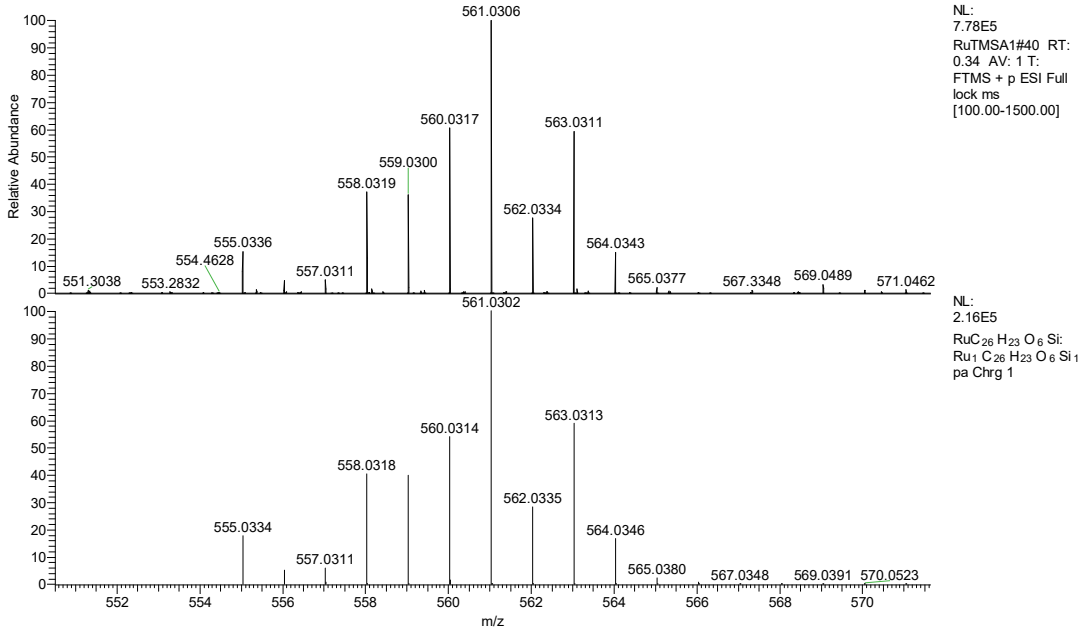


Figure S2 Experimental isotropic pattern of **3a** (top) and theoretical isotopic pattern for $[C_{26}H_{23}O_6SiRu]^+$ (bottom).

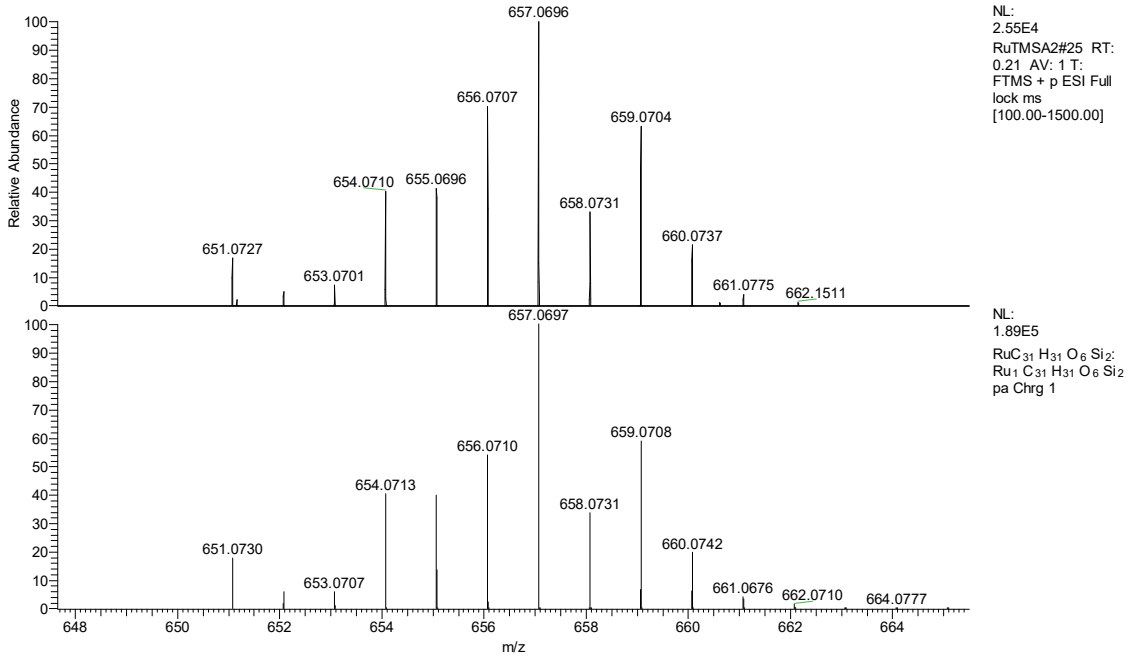


Figure S3 Experimental isotropic pattern of **3b** (top) and theoretical isotopic pattern for $[C_{31}H_{31}O_6Si_2Ru]^+$ (bottom).

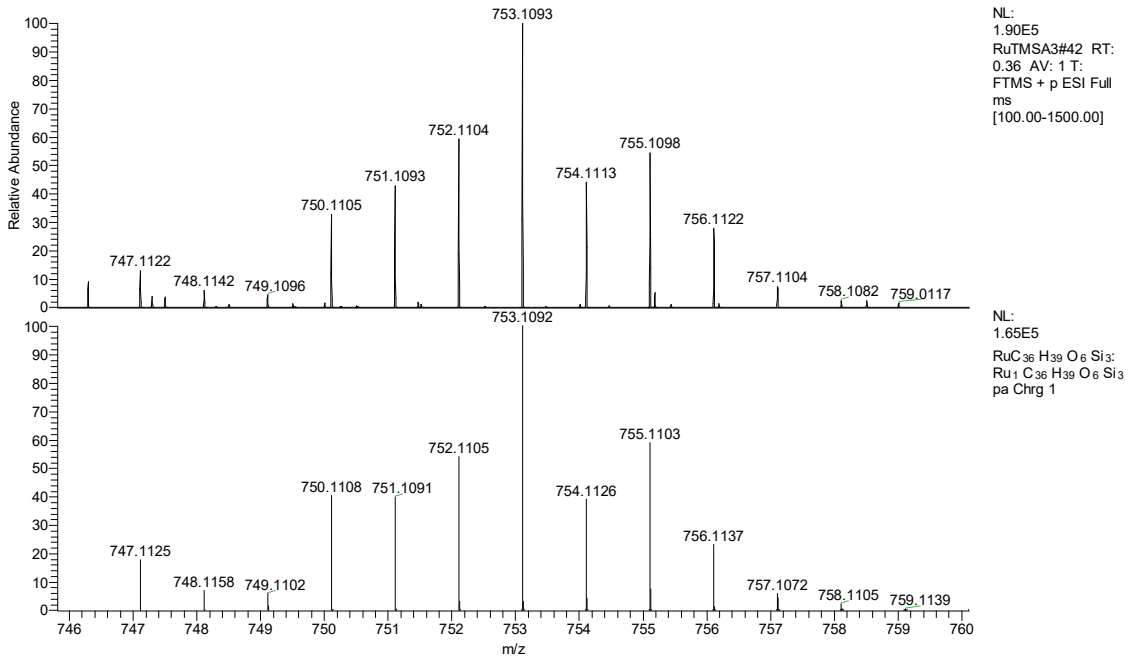


Figure S4 Experimental isotropic pattern of **3c** (top) and theoretical isotopic pattern for $[C_{36}H_{39}O_6Si_3Ru]^+$ (bottom).

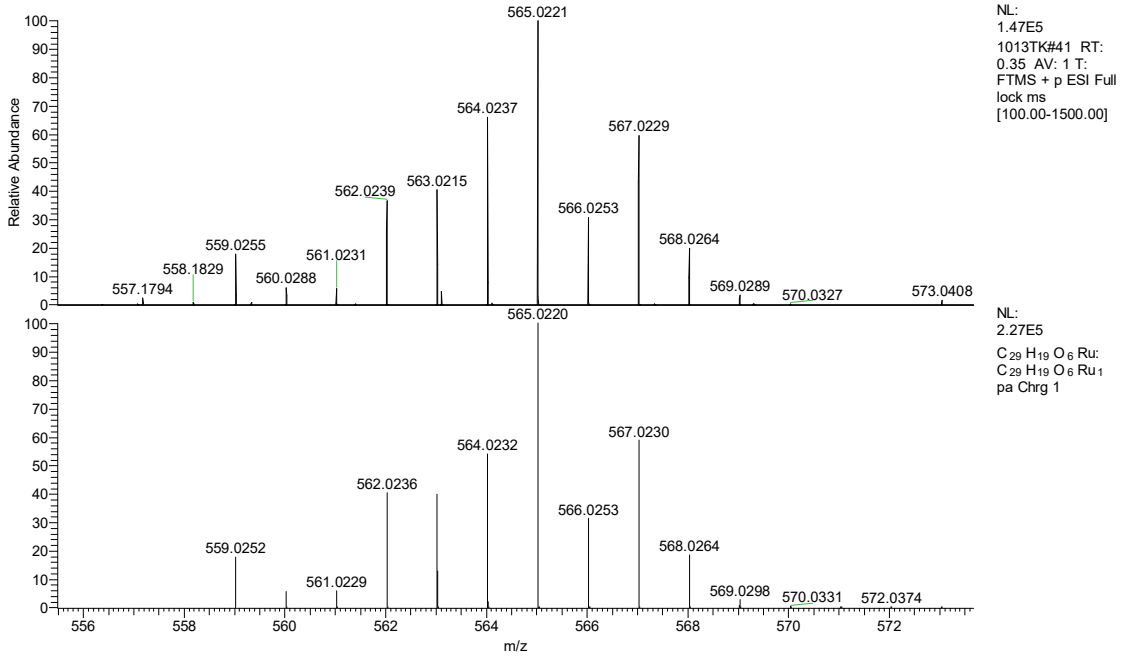


Figure S5 Experimental isotropic pattern of **4a** (top) and theoretical isotopic pattern for $[C_{29}H_{19}O_6Ru]^+$ (bottom).

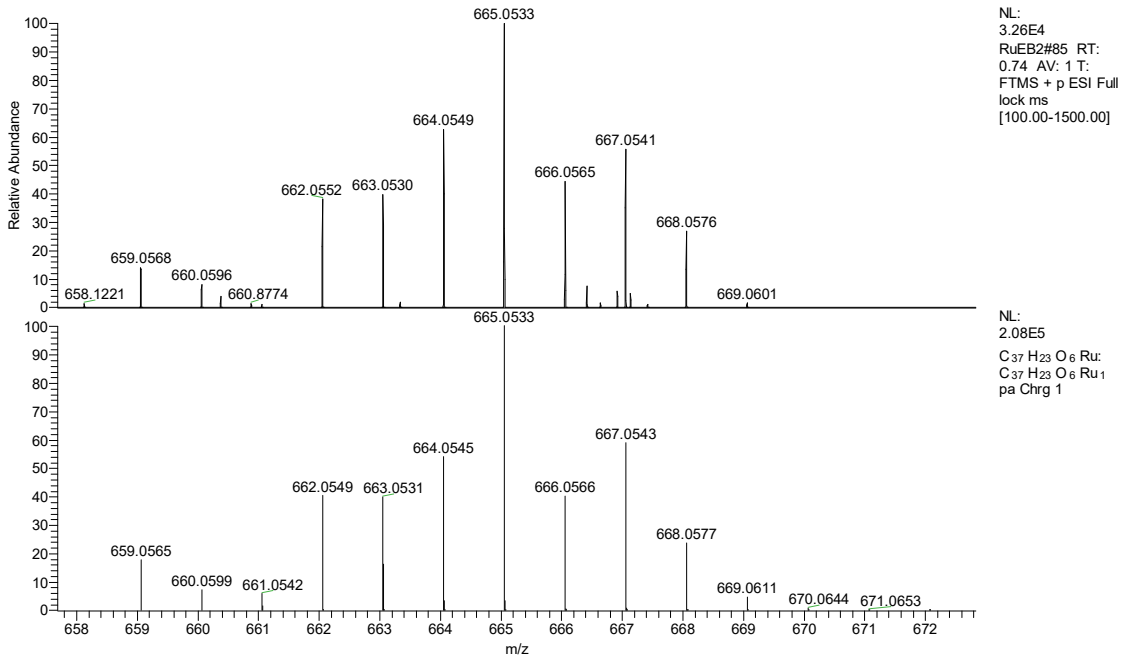


Figure S6 Experimental isotropic pattern of **4b** (top) and theoretical isotopic pattern for $[C_{37}H_{23}O_6Ru]^+$ (bottom).

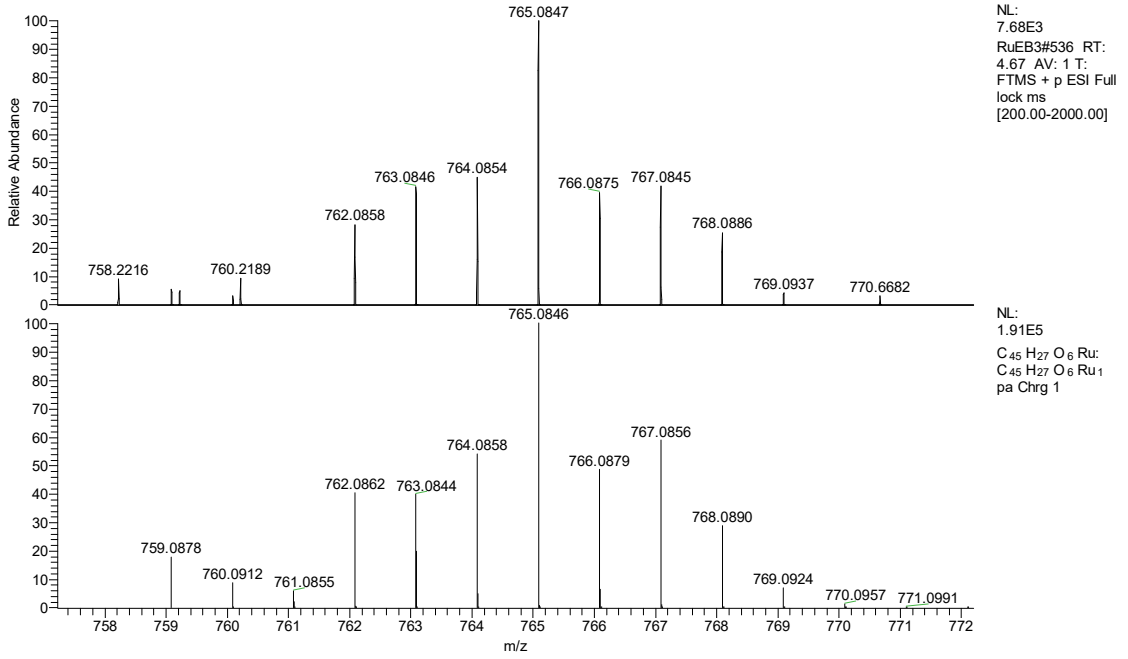


Figure S7 Experimental isotropic pattern of **4c** (top) and theoretical isotopic pattern for $[C_{45}H_{27}O_6Ru]^+$ (bottom).

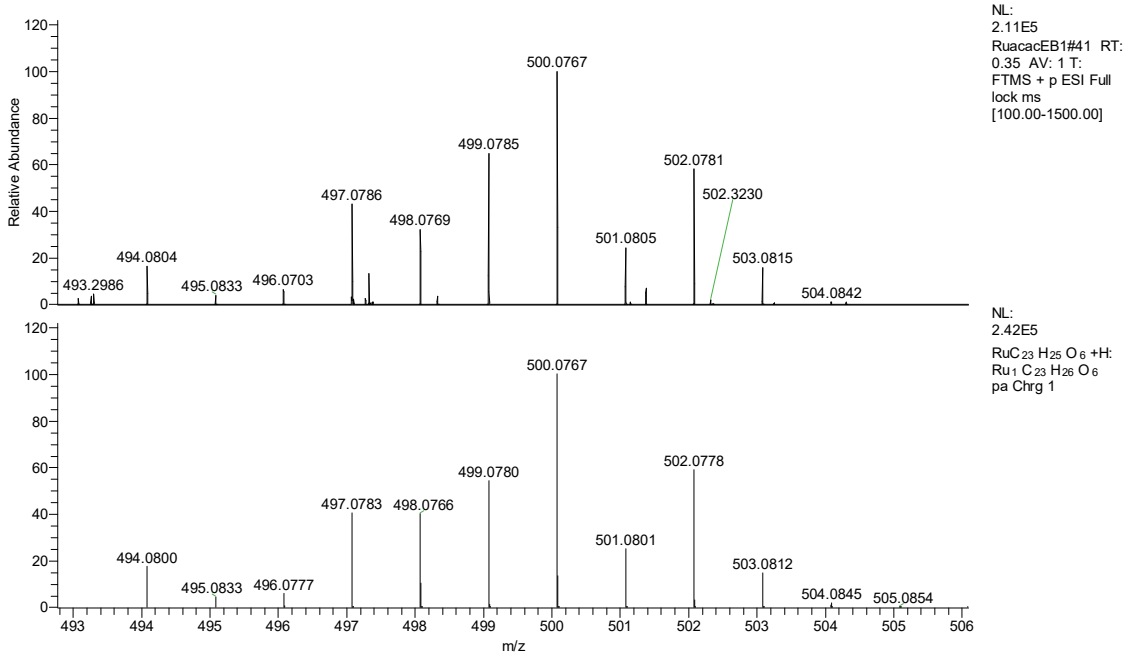


Figure S8 Experimental isotropic pattern of **6a** (top) and theoretical isotopic pattern for $[C_{23}H_{25}O_6Ru + H]^+$ (bottom).

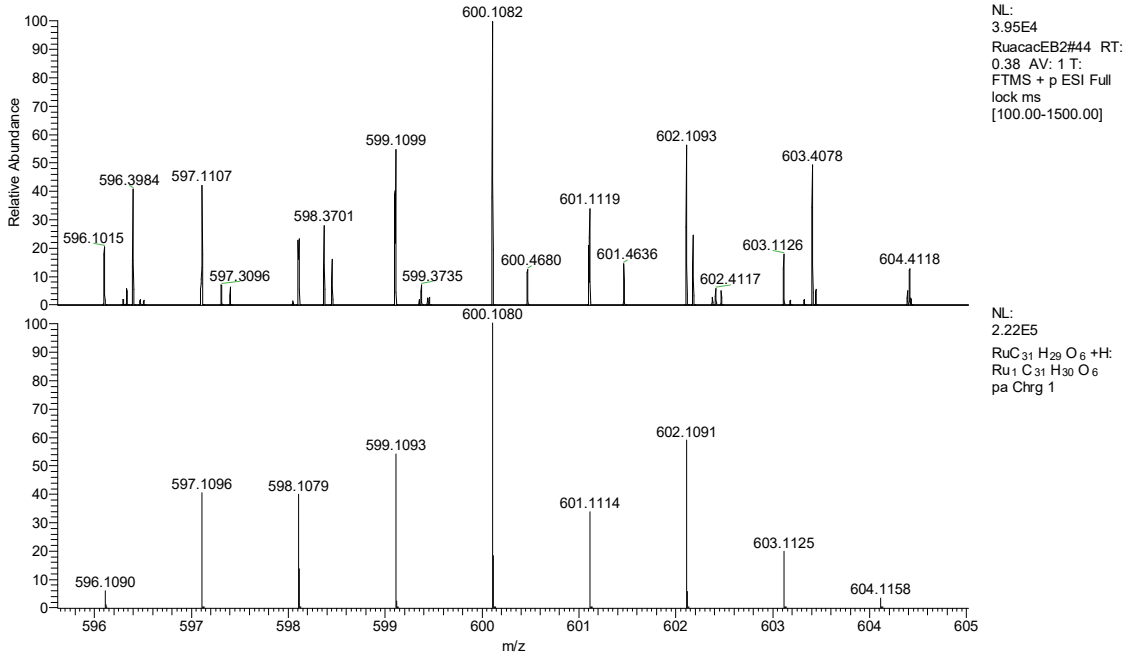


Figure S9 Experimental isotropic pattern of **6b** (top) and theoretical isotopic pattern for $[C_{31}H_{29}O_6Ru + H]^+$ (bottom).

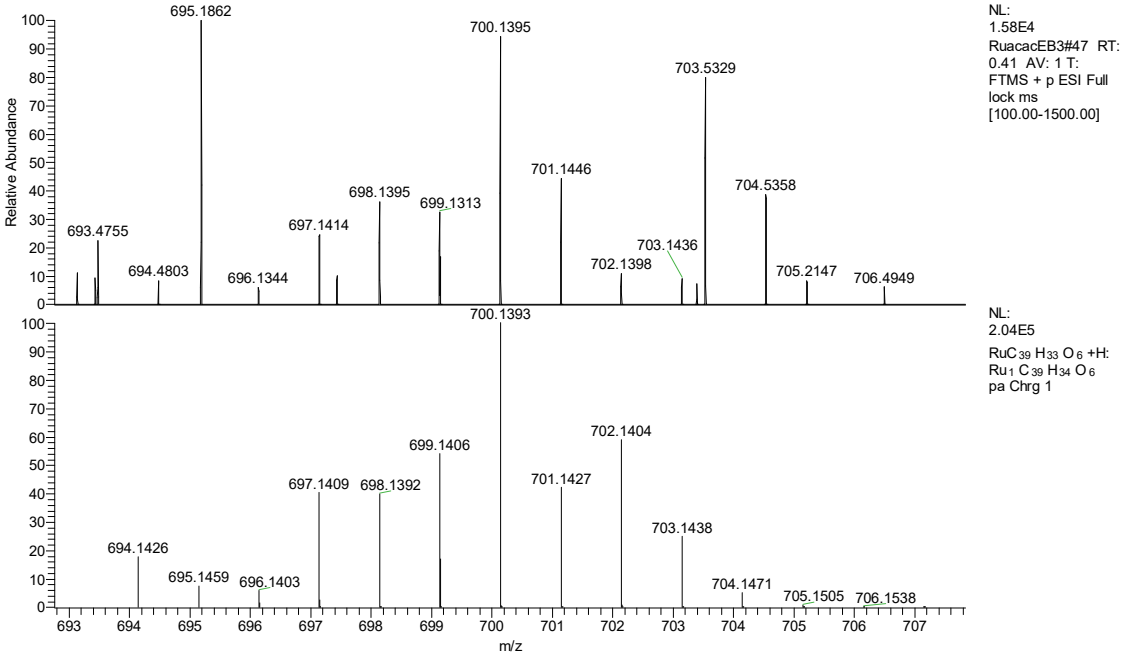


Figure S10 Experimental isotropic pattern of **6c** (top) and theoretical isotopic pattern for $[C_{39}H_{33}O_6Ru + H]^+$ (bottom).

^{1}H NMR Spectra

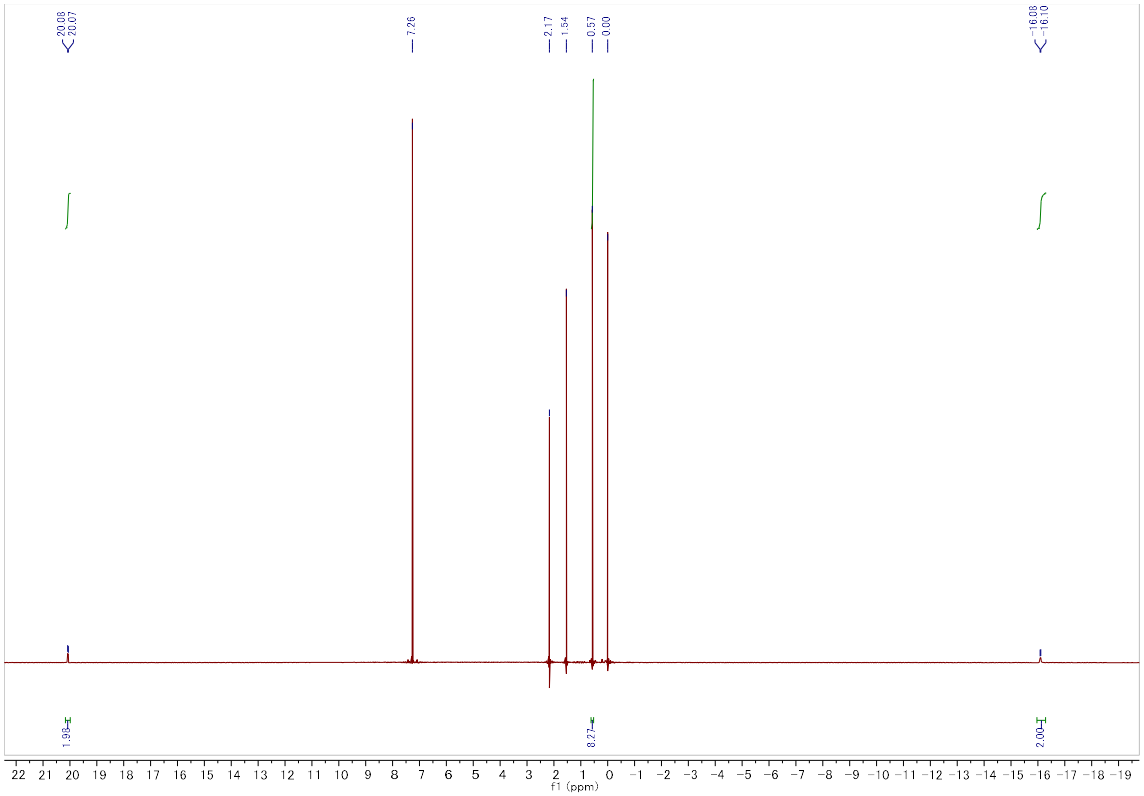


Figure S11 ^{1}H NMR spectrum of **3c** measured in $CDCl_3$.

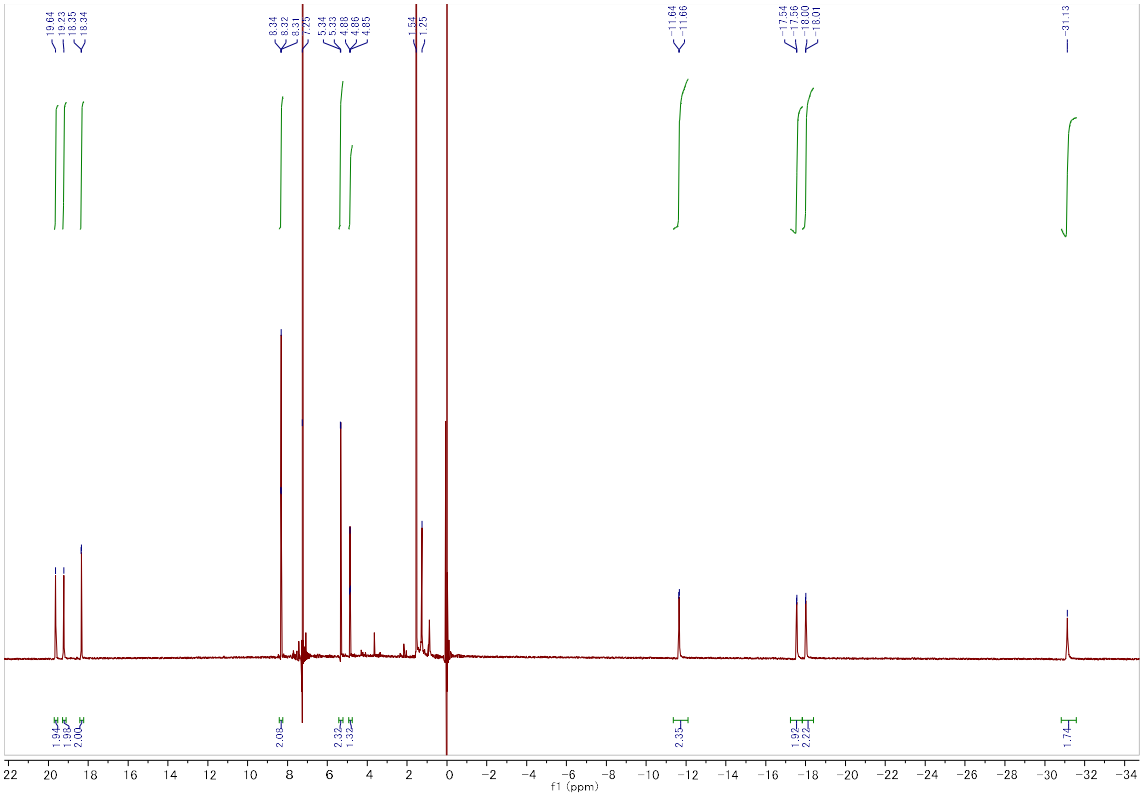


Figure S12 ^{1}H NMR spectrum of **4a** measured in $CDCl_3$.

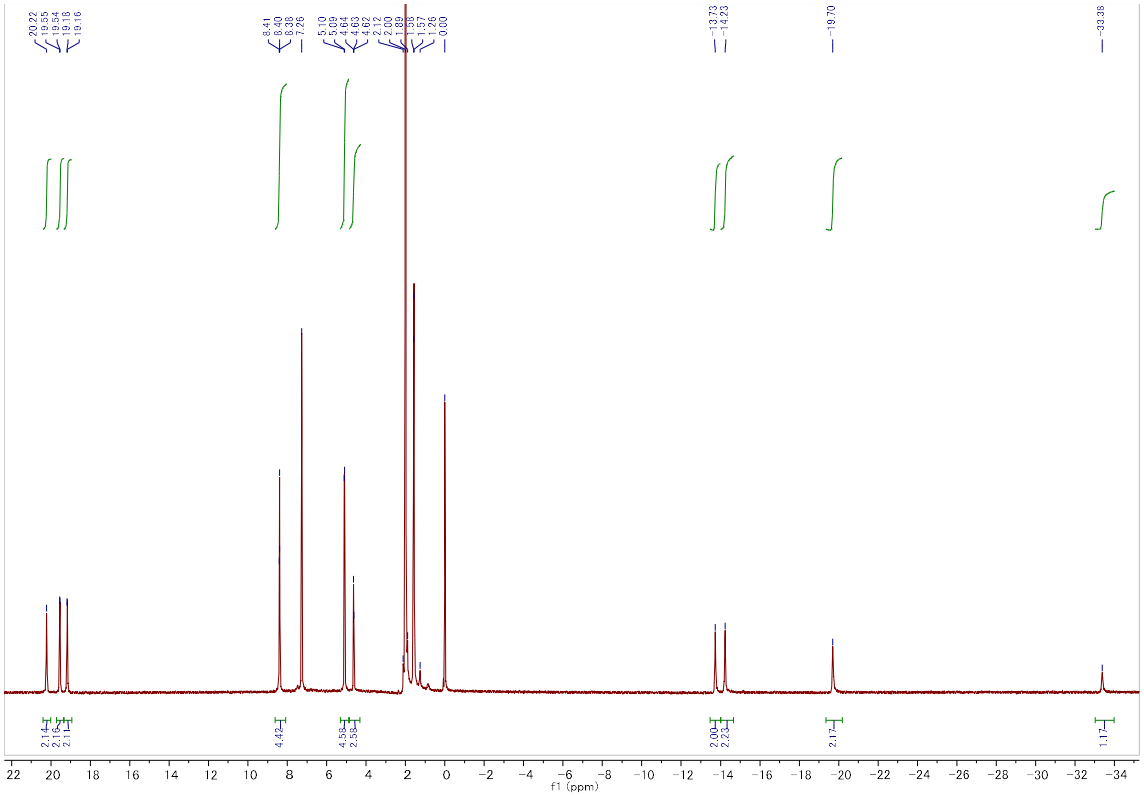


Figure S13 ^{1}H NMR spectrum of **4b** measured in $CDCl_3$.

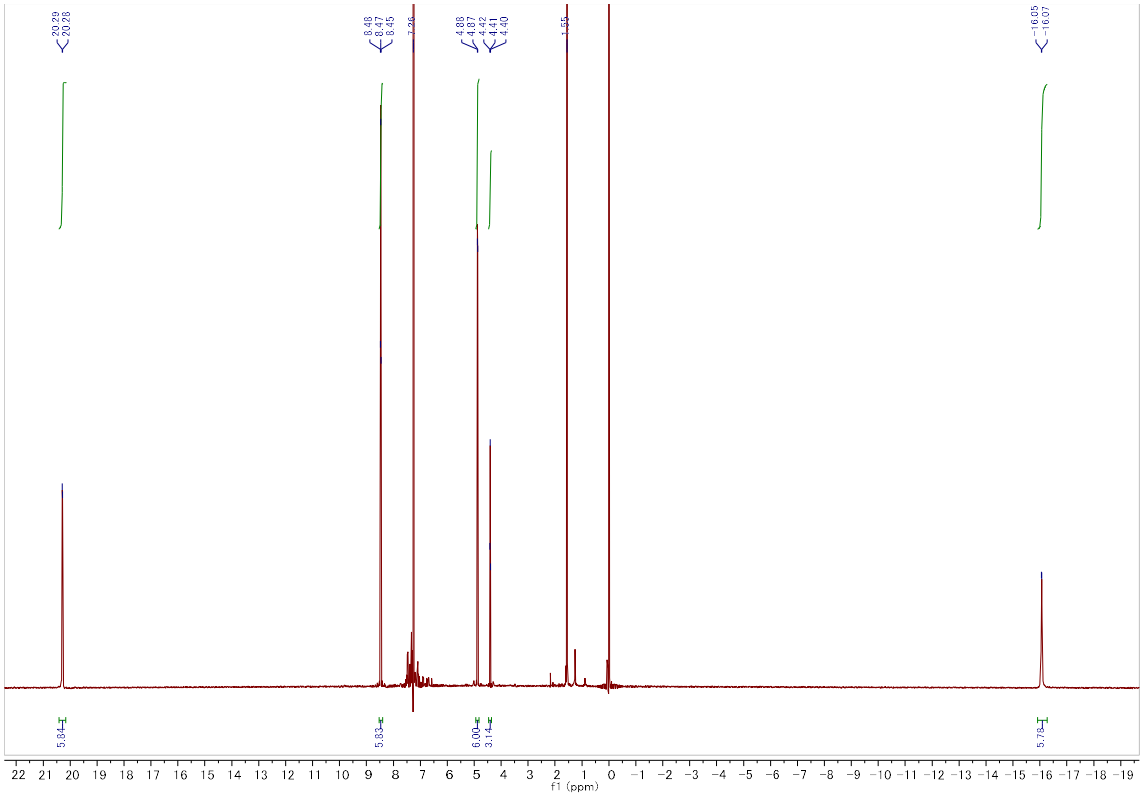


Figure S14 ^{1}H NMR spectrum of **4c** measured in $CDCl_3$.

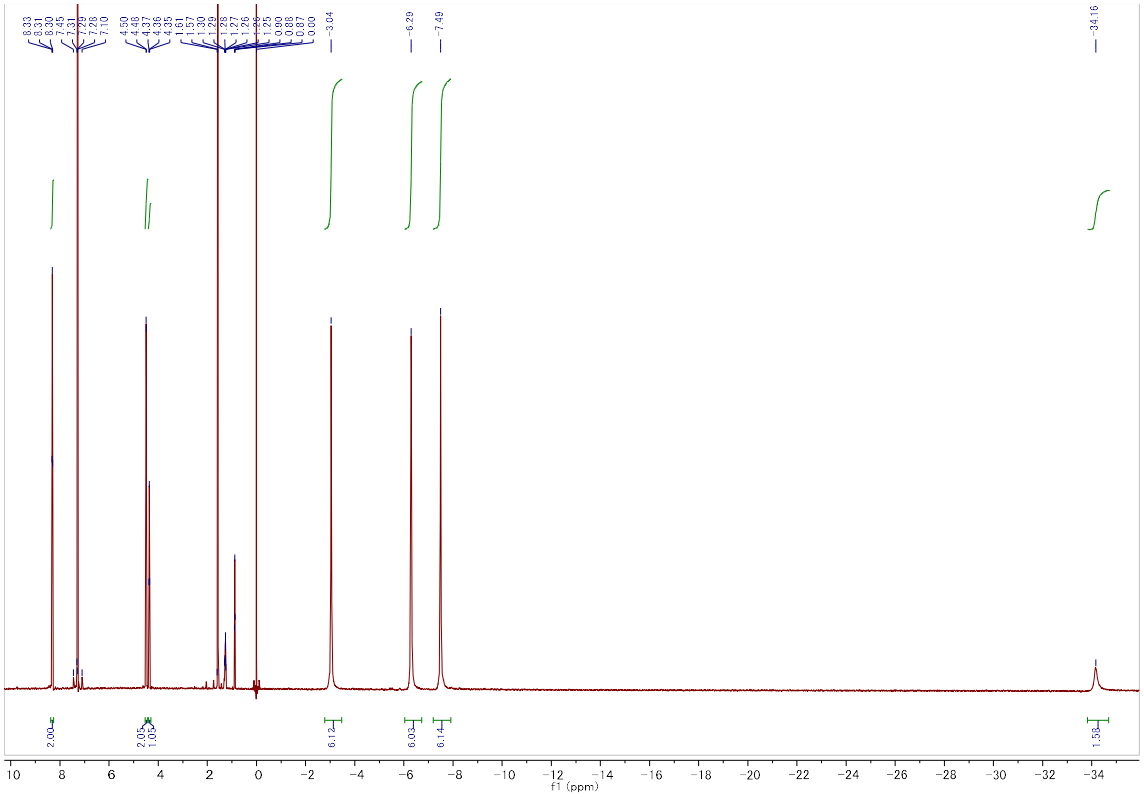


Figure S15 ^{1}H NMR spectrum of **6a** measured in $CDCl_3$.

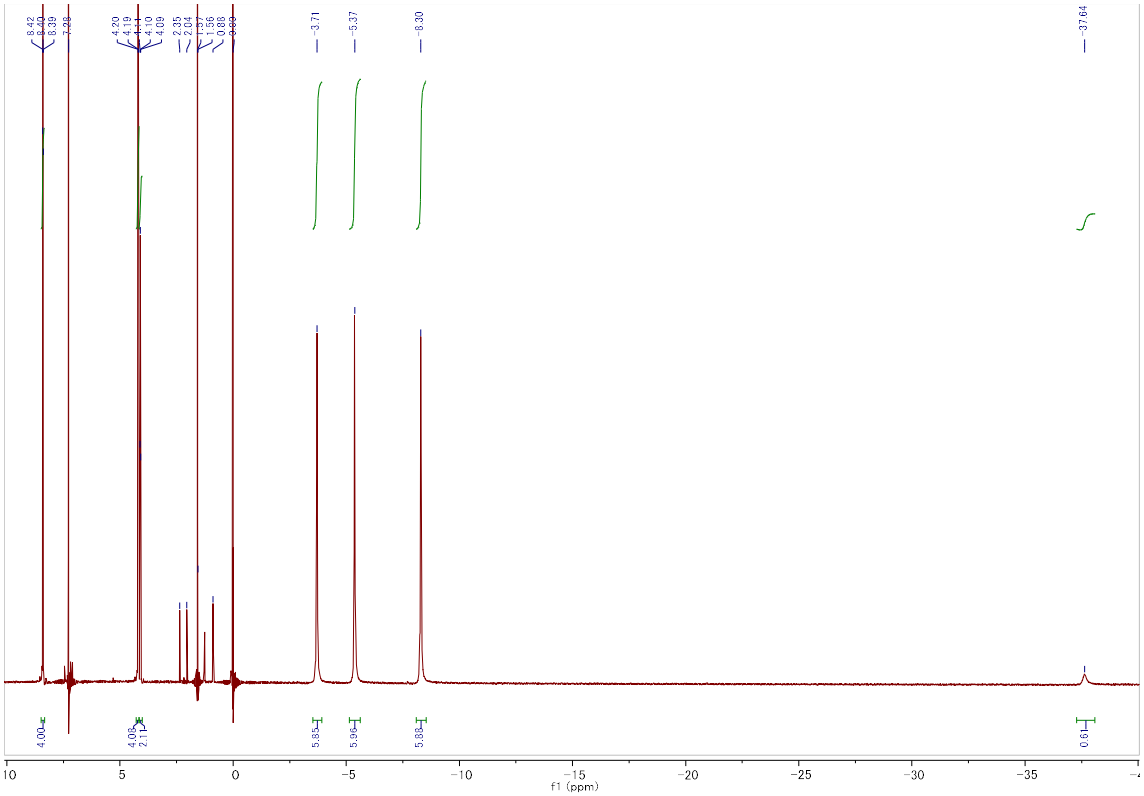


Figure S16 ^{1}H NMR spectrum of **6b** measured in $CDCl_3$.

UV-vis-NIR spectra

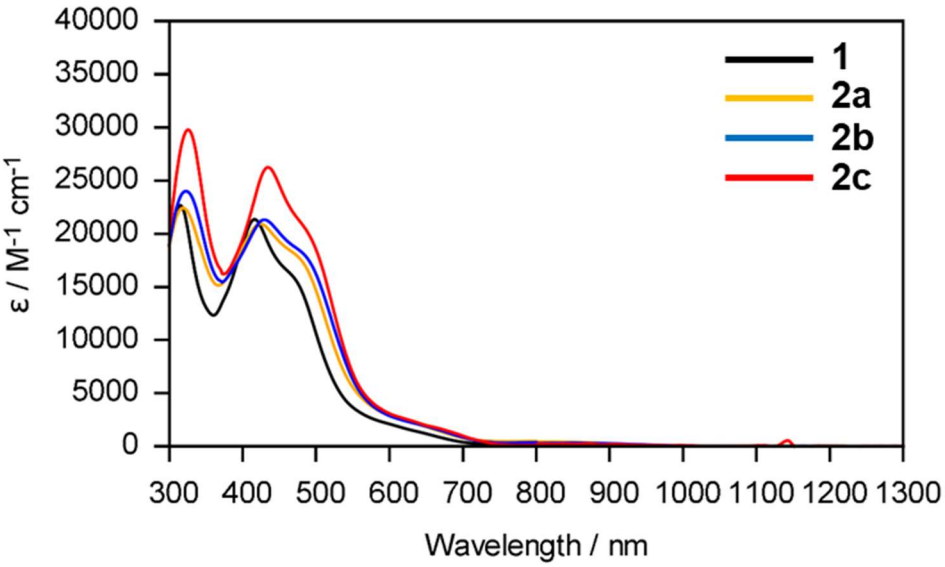


Figure S17 UV-Vis-NIR spectra of **1**, **2a**, **2b**, and **2c** measured in CH_2Cl_2**.**

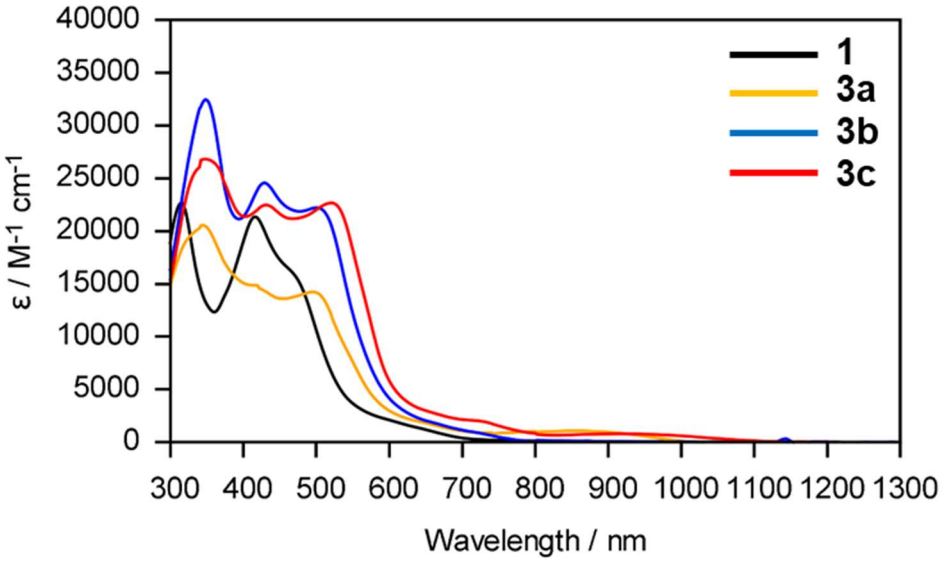


Figure S18 UV-Vis-NIR spectra of **1**, **3a**, **3b**, and **3c** measured in CH_2Cl_2.

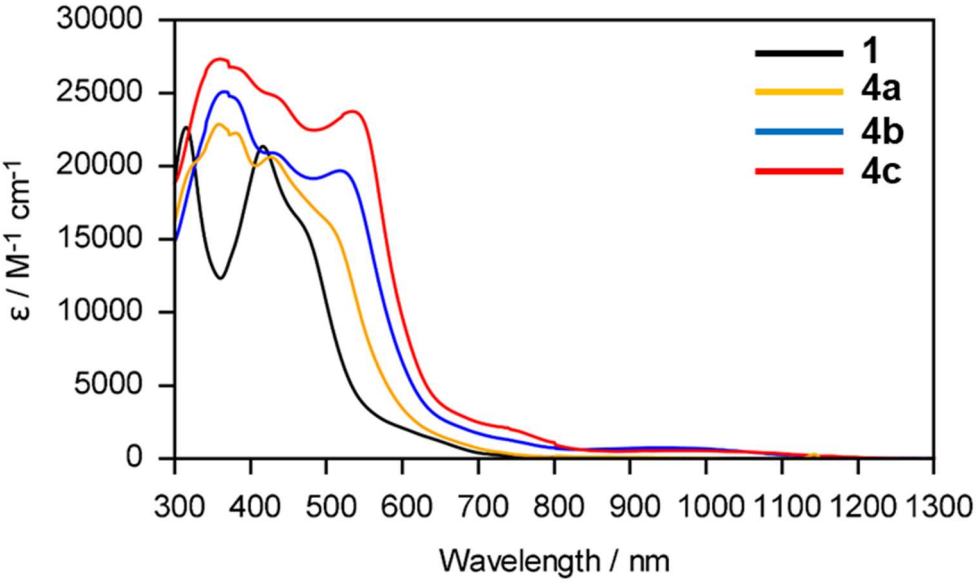


Figure S19 UV-Vis-NIR spectra of **1**, **4a**, **4b**, and **4c** measured in CH_2Cl_2.

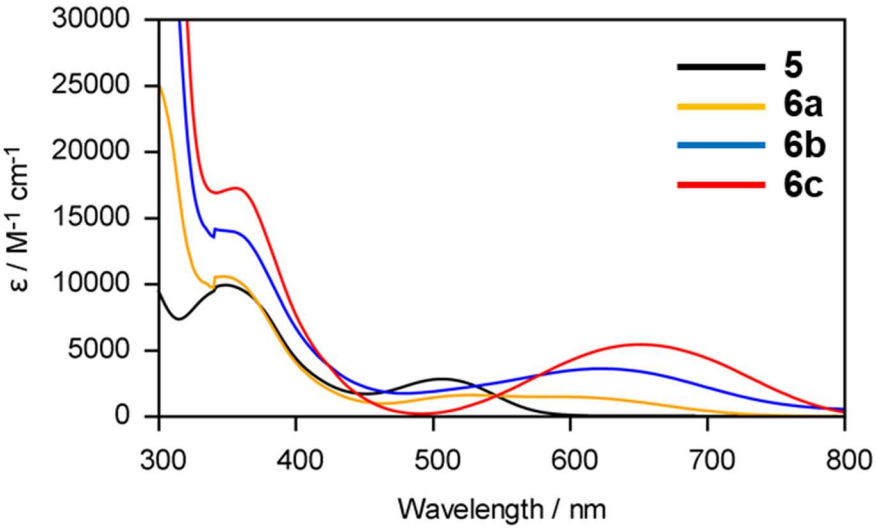


Figure S20 UV-Vis-NIR spectra of **5**, **6a**, **6b** and **6c** measured in CH_2Cl_2.

Cyclic voltammograms

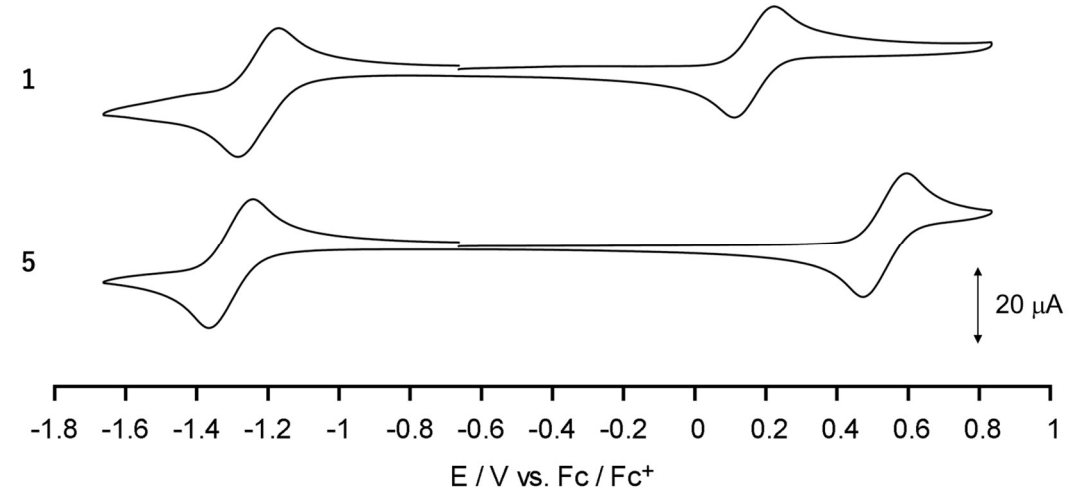


Figure S21 Cyclic voltammograms of **1** and **5** (1.0 mmol dm^{-3}) in 0.10 mol dm^{-3} $[Bu_4N](ClO_4)$-CH_2Cl_2. The scan rate is 100 mV s^{-1}.

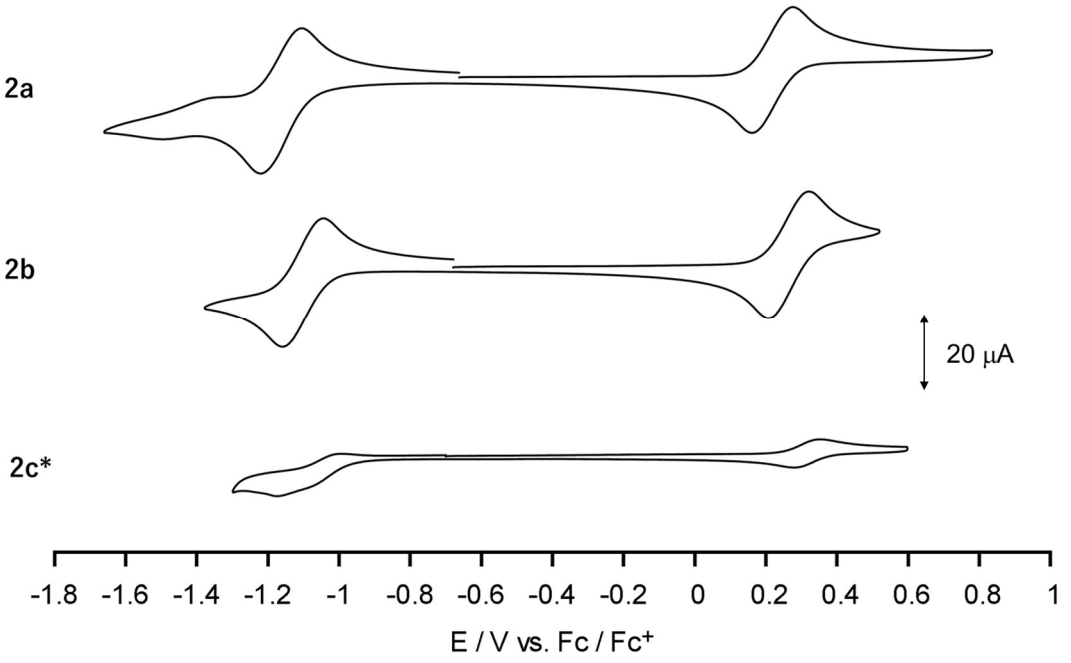


Figure S22 Cyclic voltammograms of **2a** ~ **2c** (**2a** and **2b**: 1.0 mmol dm^{-3}, **2c**: 0.16 mmol dm^{-3}) in 0.1 mol dm^{-3} $[Bu_4N](ClO_4)$-CH_2Cl_2. The scan rate is 100 mV s^{-1}.

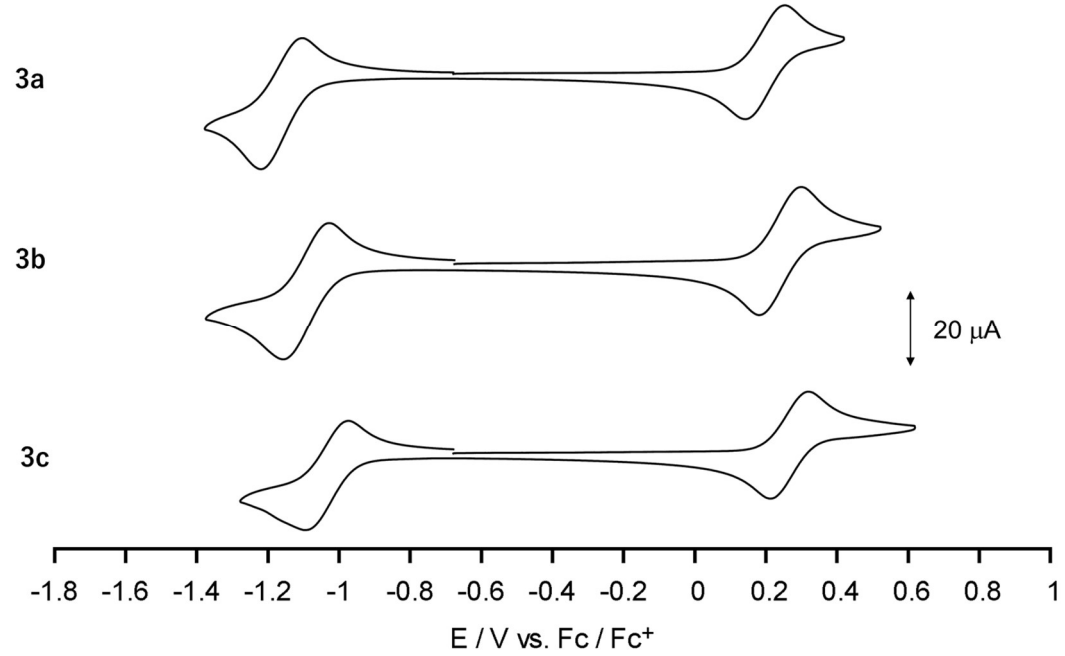


Figure S23 Cyclic voltammograms of **3a** ~ **3c** (1.0 mmol dm^{-3}) in 0.10 mol dm^{-3} $[Bu_4N](ClO_4)$-CH_2Cl_2. The scan rate is 100 mV s^{-1}.

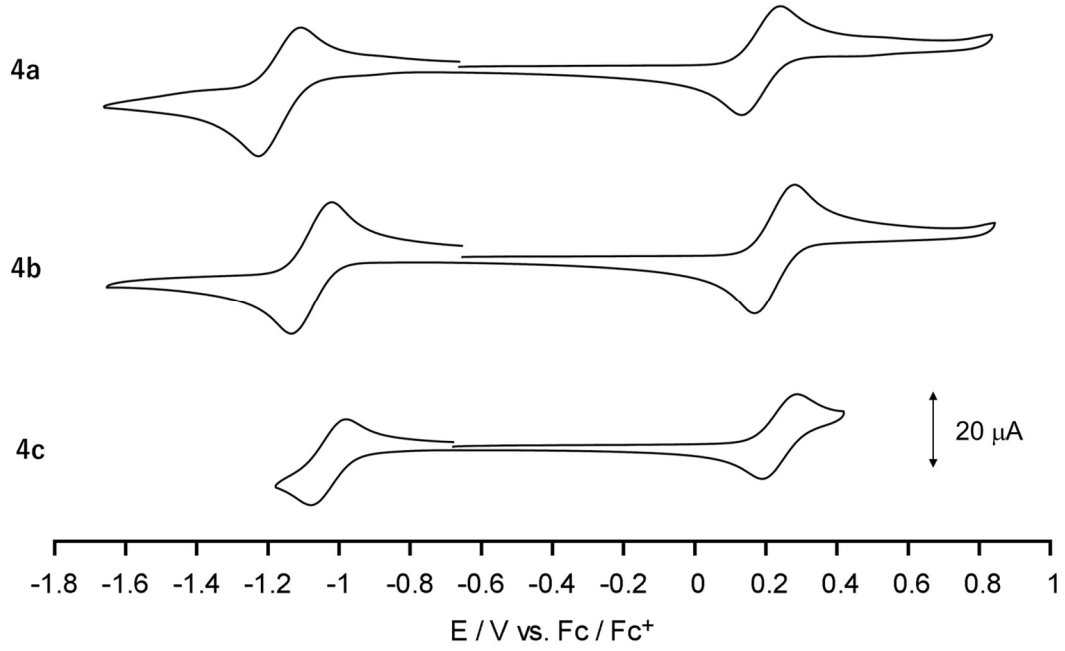


Figure S24 Cyclic voltammograms of **4a** ~ **4c** (1.0 mmol dm^{-3}) in 0.10 mol dm^{-3} $[Bu_4N](ClO_4)$-CH_2Cl_2. The scan rate is 100 mV s^{-1}.

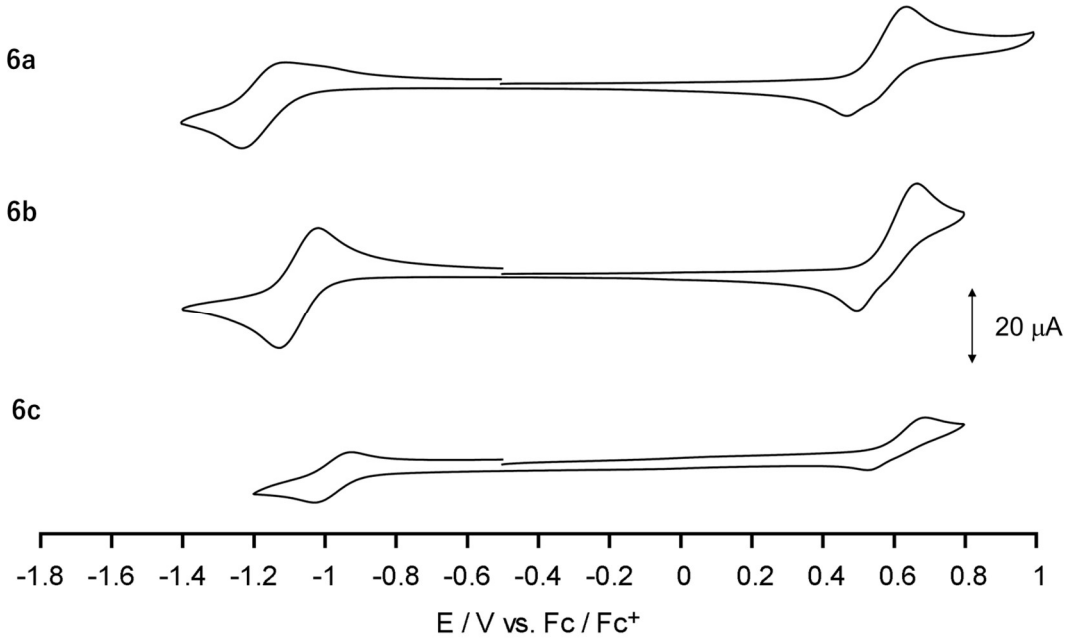
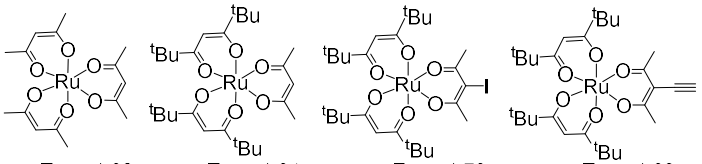


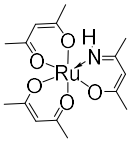
Figure S25 Cyclic voltammograms of **6a** ~ **6c** (1.0 mmol dm^{-3}) in 0.10 mol dm^{-3} $[Bu_4N](ClO_4)$-CH_2Cl_2. The scan rate is 100 mV s-1.

ΔE values of related complexes



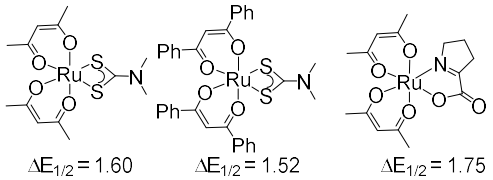
$\Delta E_{1/2}$ = 1.82 in DCM | $\Delta E_{1/2}$ = 1.84 in AN | $\Delta E_{1/2}$ = 1.78 in AN | $\Delta E_{1/2}$ = 1.83 in AN

Organometallics **1992,** *11*, 1968-1971.



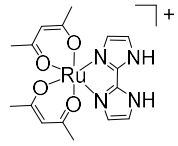
$\Delta E_{1/2}$ = 1.71 in AN

Chem. Lett., **2003,** *32*, 874-875.



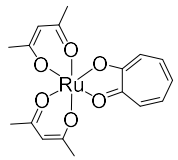
$\Delta E_{1/2}$ = 1.60 in AN | $\Delta E_{1/2}$ = 1.52 in AN | $\Delta E_{1/2}$ = 1.75 in AN

Inorganica Chimica Acta, **2003**, *353*, 107-118.



$\Delta E_{1/2}$ = 1.75 in AN

Dalton Trans., **2010,** *39*, 4232-4242.



$\Delta E_{1/2}$ = 1.61 in CH_2Cl_2

J. Organomet. Chem. **2014,** *756*, 19-26.

Figure S26 ΔE = $E_{1/2}(Ru^{III}/Ru^{IV})$ - $E_{1/2}(Ru^{II}/Ru^{III})$ values of $[Ru(acac)_3]$ and its selected derivatives based on the reported articles.[4–8]

Spectroelectrochemical study (electrochemical reduction)

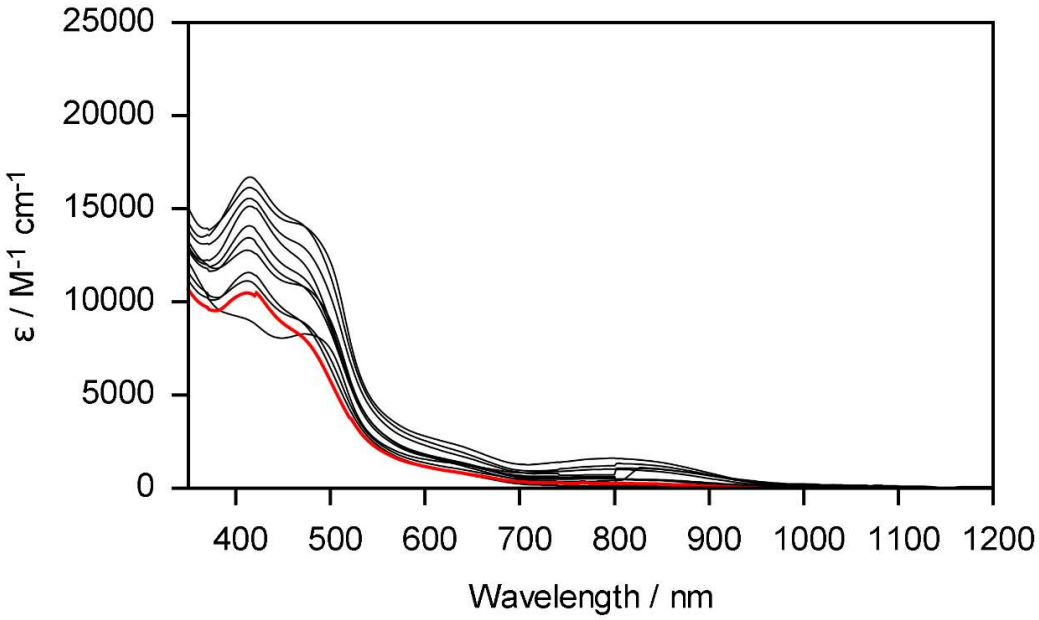


Figure S27 UV-Vis-NIR spectral changes of **1** (0.5 mM in CH_2Cl_2 with 0.05 M $^nBu_4NClO_4$) on the application of -1.30 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the last measured spectrum.

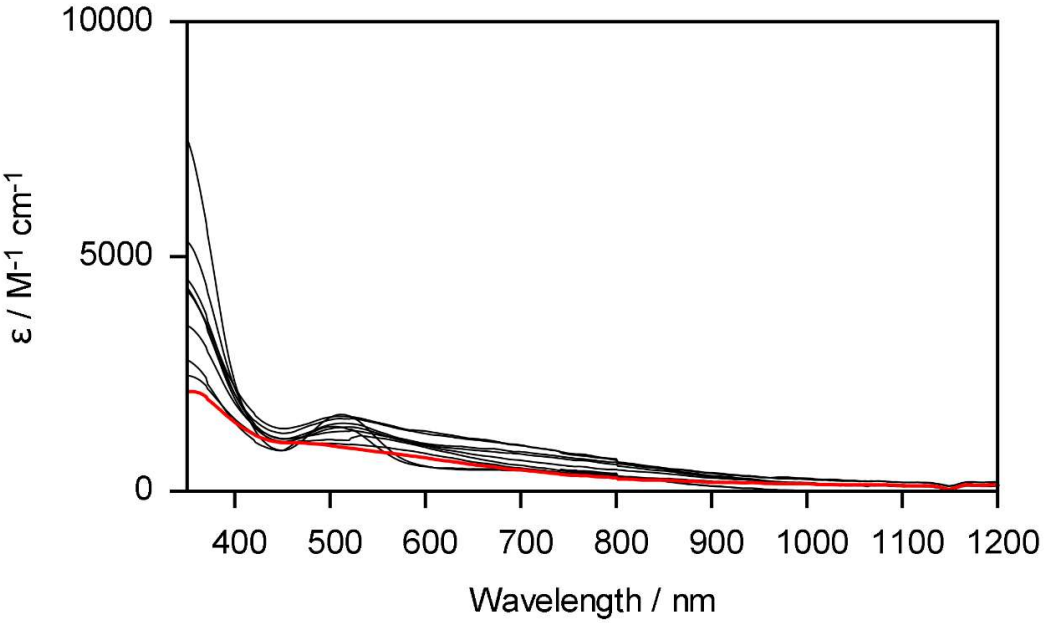


Figure S28 UV-Vis-NIR spectral changes of **5** (0.5 mM in CH_2Cl_2 with 0.05 M $^nBu_4NClO_4$) on the application of -1.30 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the last measured spectrum.

Spectroelectrochemical study (electrochemical oxidation)

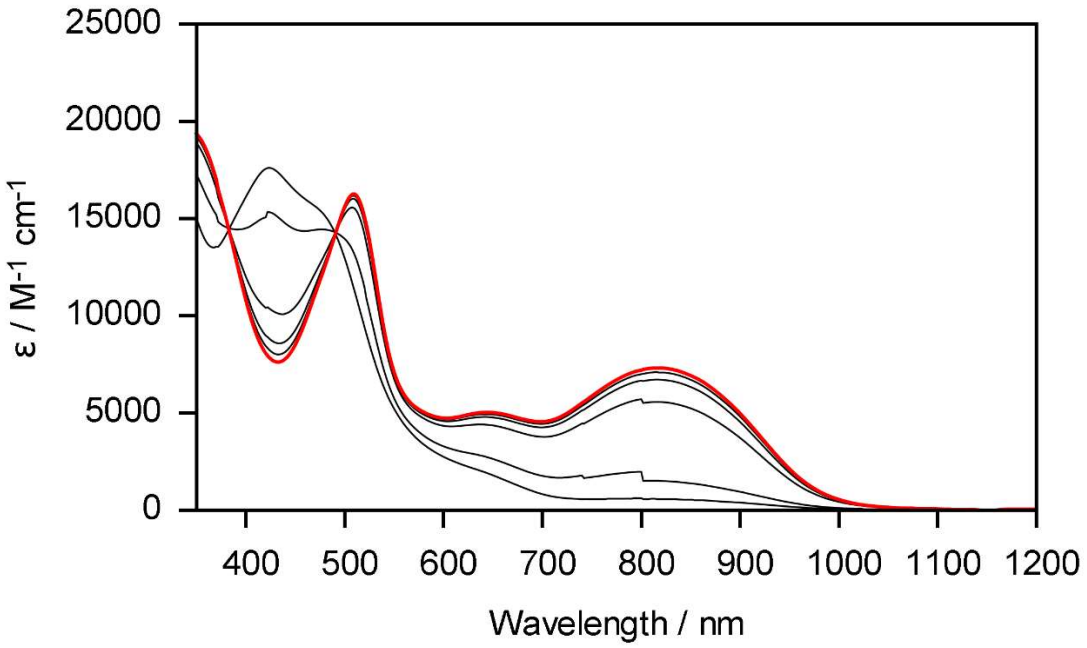


Figure S29 UV-Vis-NIR spectral changes of **2a** (0.5 mM in CH_2Cl_2 with 0.05 M $^nBu_4NClO_4$) on the application of 0.60 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the equilibrated state.

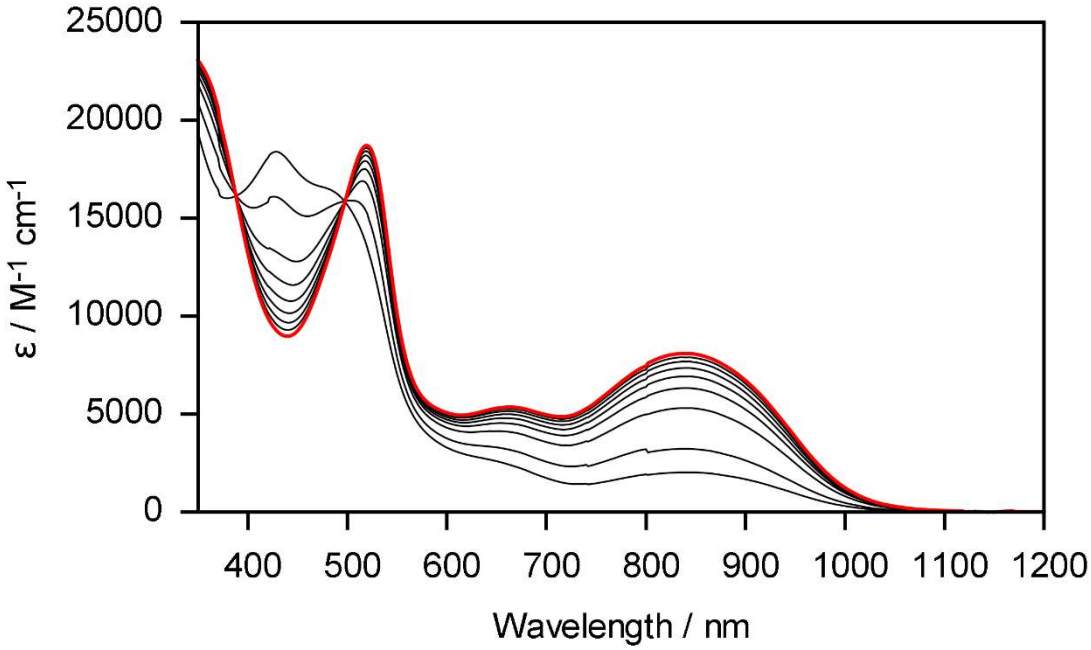


Figure S30 UV-Vis-NIR spectral changes of **2b** (0.5 mM in CH_2Cl_2 with 0.05 M $^nBu_4NClO_4$) on the application of 0.54 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the equilibrated state.

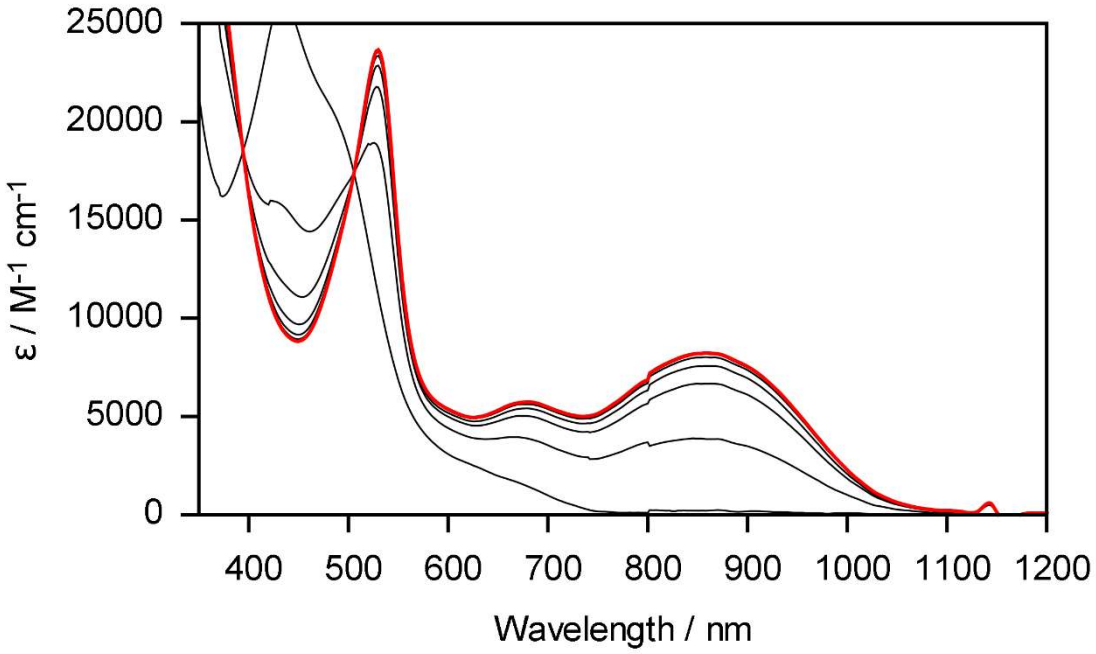


Figure S31 UV-Vis-NIR spectral changes of **2c** (0.16 mM in CH_2Cl_2 with 0.05 M $^nBu_4NClO_4$) on the application of 0.60 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the equilibrated state.

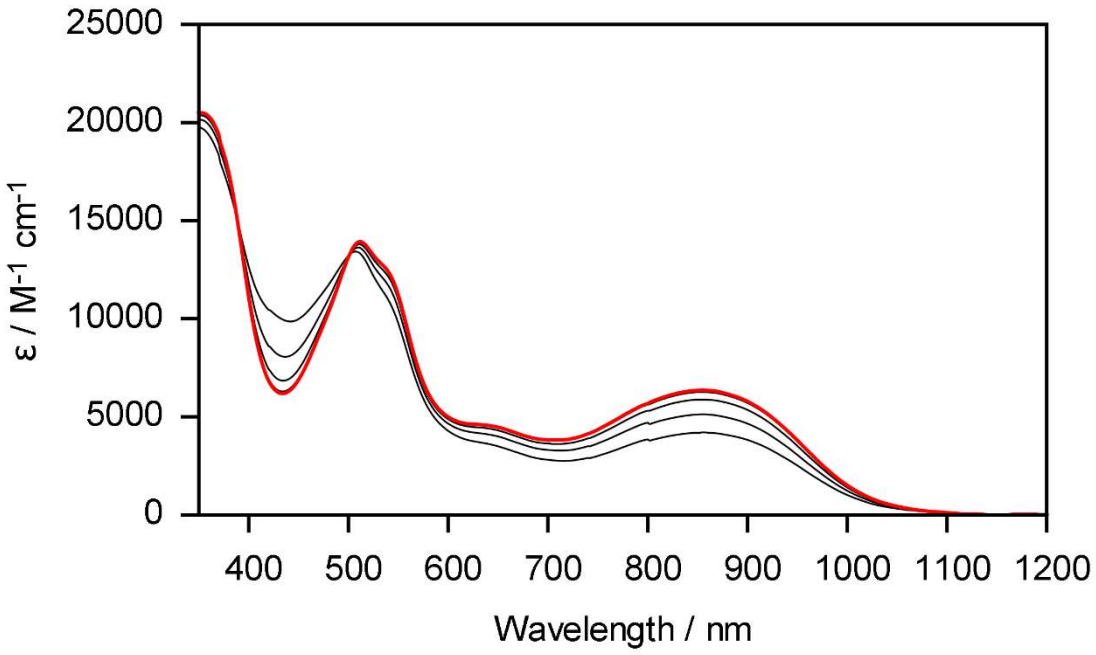


Figure S32 UV-Vis-NIR spectral changes of **3a** (0.5 mM in CH_2Cl_2 with 0.05 M $^nBu_4NClO_4$) on the application of 0.60 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the equilibrated state.

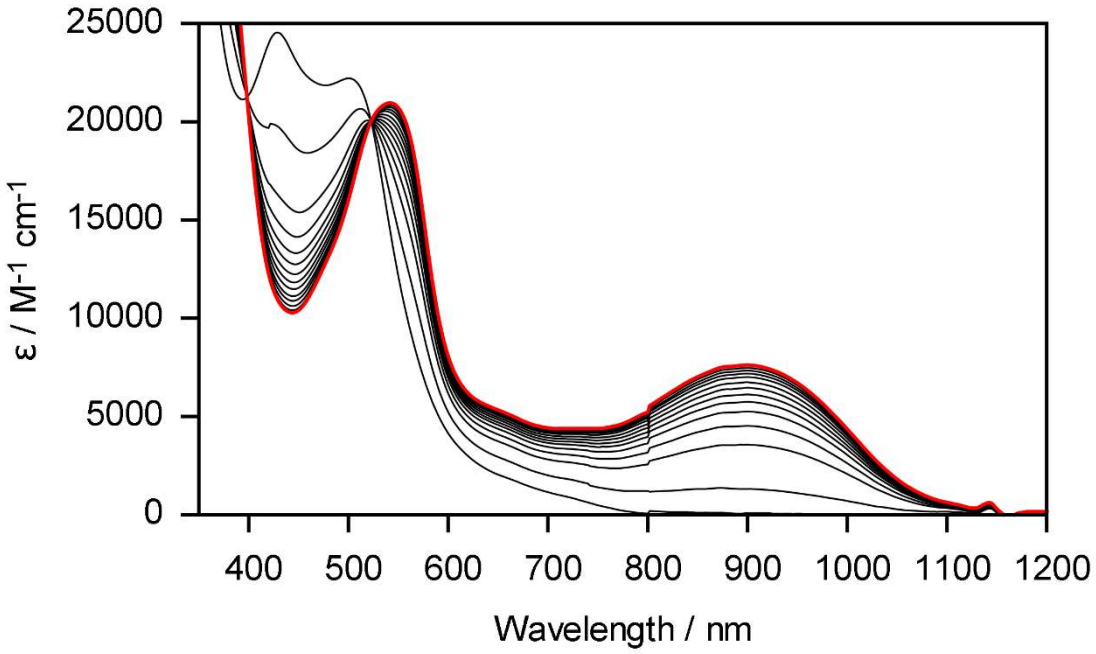


Figure S33 UV-Vis-NIR spectral changes of **3b** (0.25 mM in CH_2Cl_2 with 0.05 M $^nBu_4NClO_4$) on the application of 0.60 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the equilibrated state.

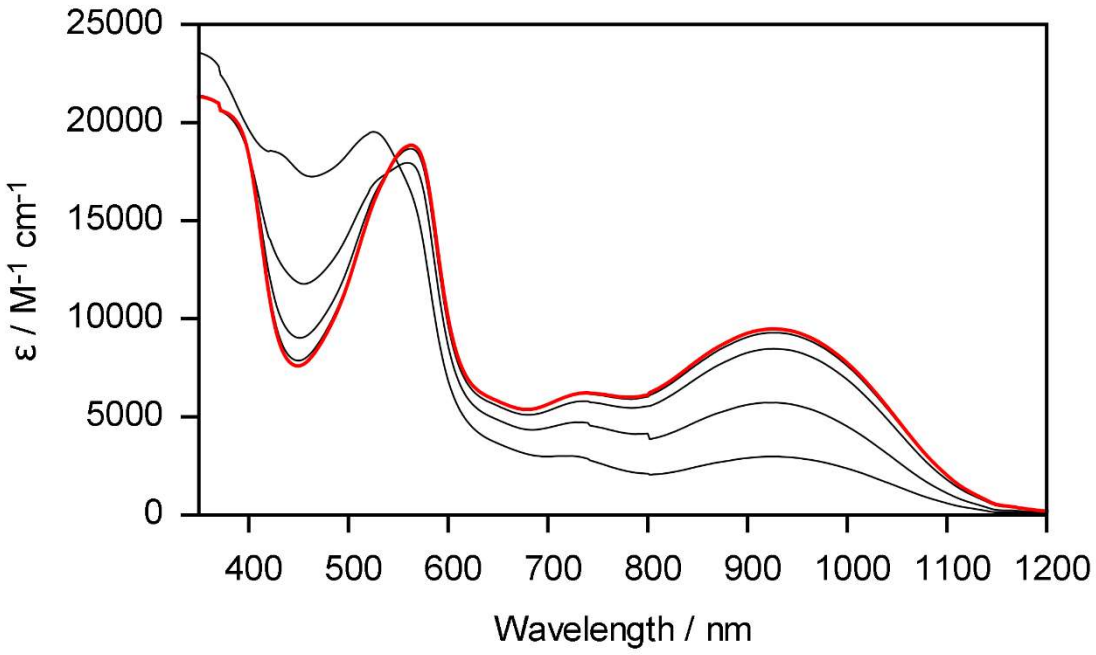


Figure S34 UV-Vis-NIR spectral changes of **3c** (0.5 mM in CH_2Cl_2 with 0.05 M $^nBu_4NClO_4$) on the application of 0.60 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the equilibrated state.

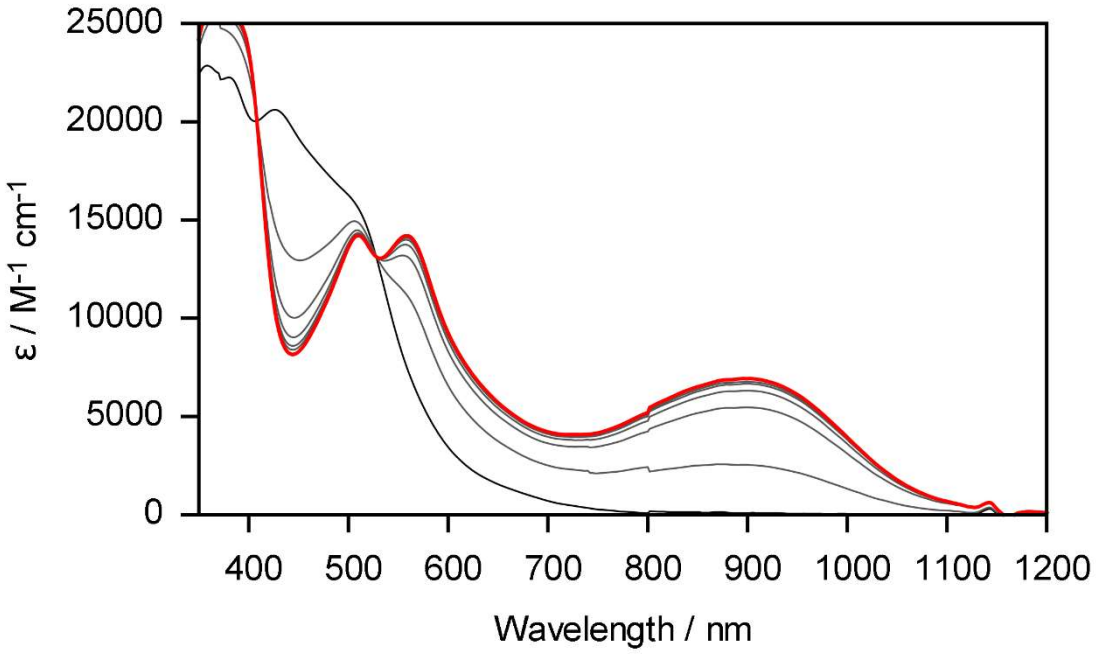


Figure S35 UV-Vis-NIR spectral changes of **4a** (0.5 mM in CH_2Cl_2 with 0.05 M $^nBu_4NClO_4$) on the application of 0.55 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the equilibrated state.

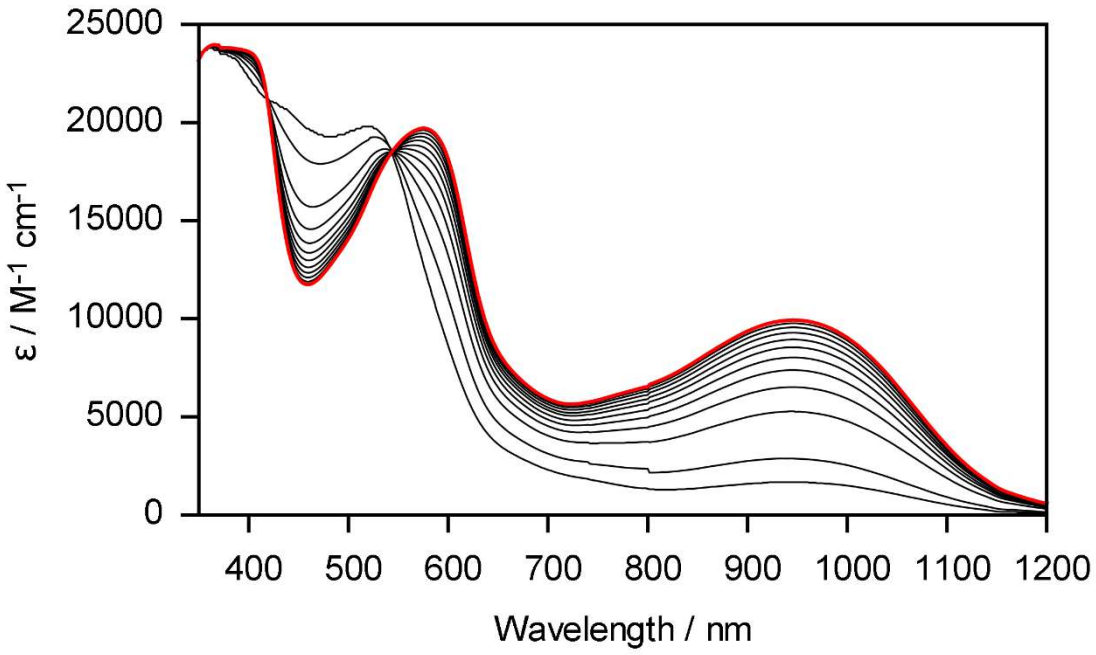


Figure S36 UV-Vis-NIR spectral changes of **4b** (0.25 mM in CH_2Cl_2 with 0.05 M $^nBu_4NClO_4$) on the application of 0.60 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the equilibrated state.

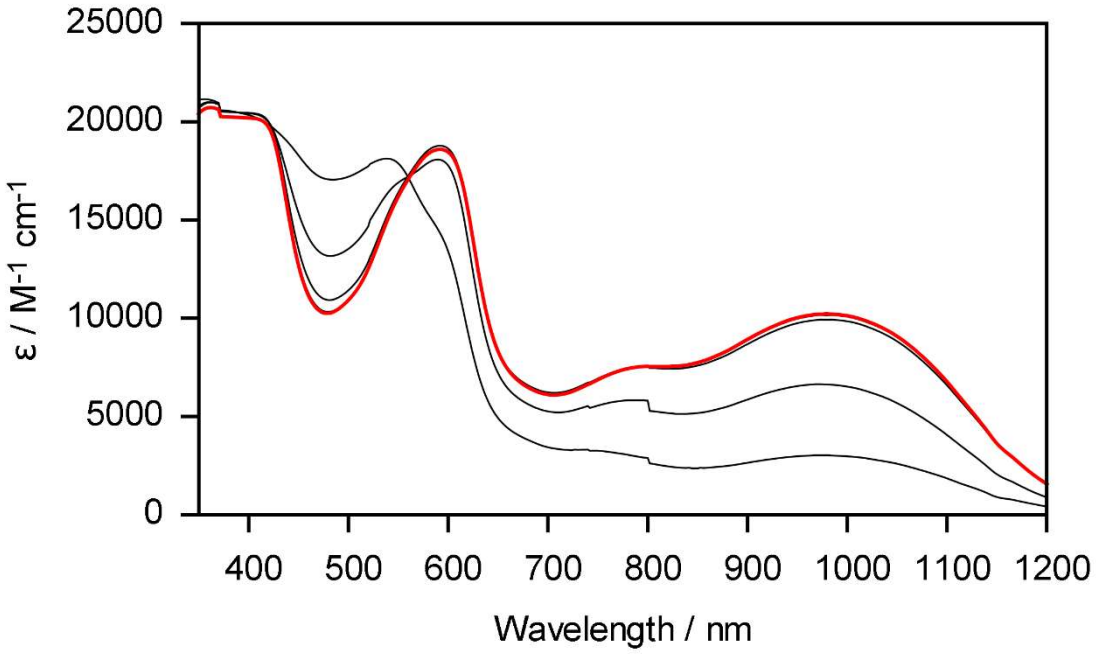


Figure S37 UV-Vis-NIR spectral changes of **4c** (0.5 mM in CH_2Cl_2 with 0.05 M $^nBu_4NClO_4$) on the application of 0.60 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the equilibrated state.

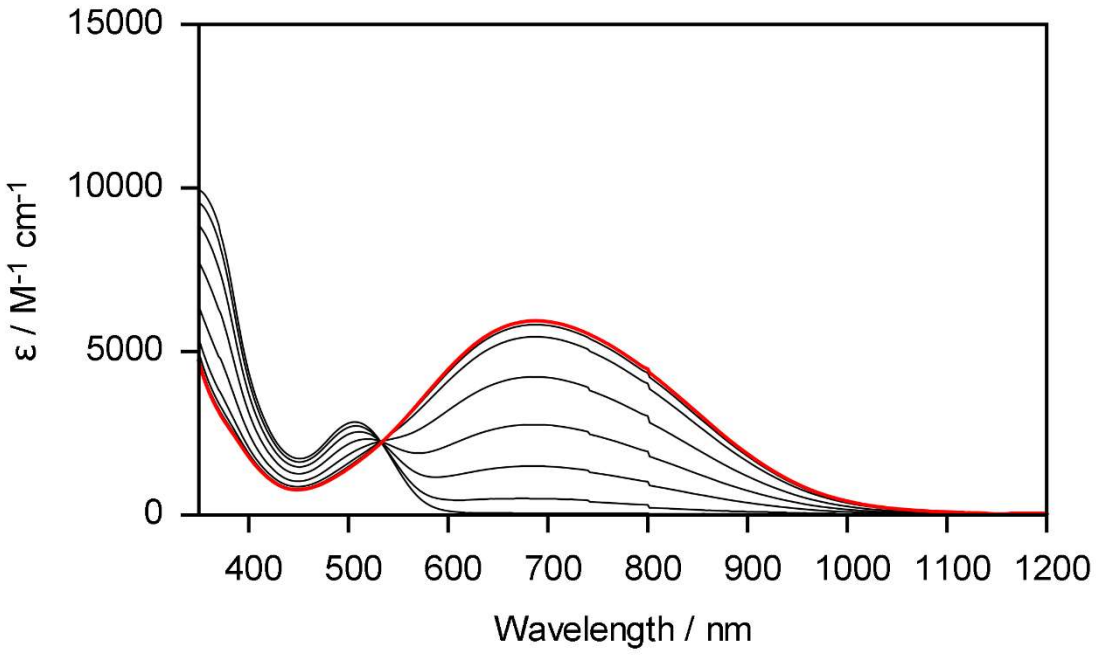


Figure S38 UV-Vis-NIR spectral changes of **5** (1.0 mM in CH_2Cl_2 with 0.1 M $^nBu_4NClO_4$) on the application of 0.85 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the equilibrated state.

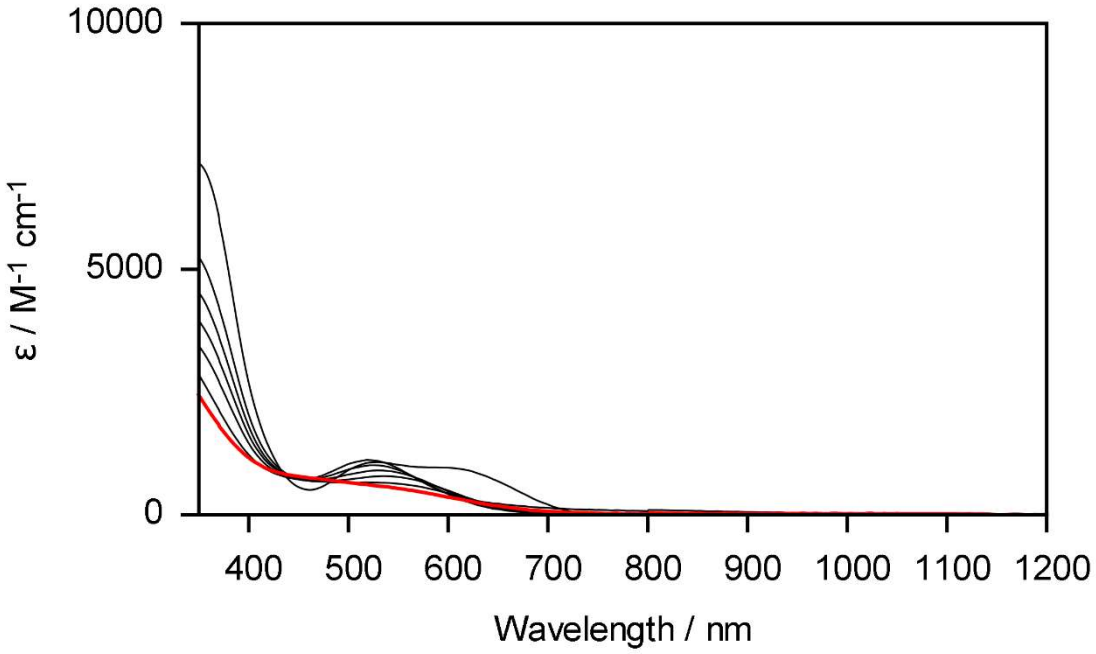


Figure S39 UV-Vis-NIR spectral changes of **6a** (0.5 mM in CH_2Cl_2 with 0.05 M $^nBu_4NClO_4$) on the application of 0.85 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the equilibrated state.

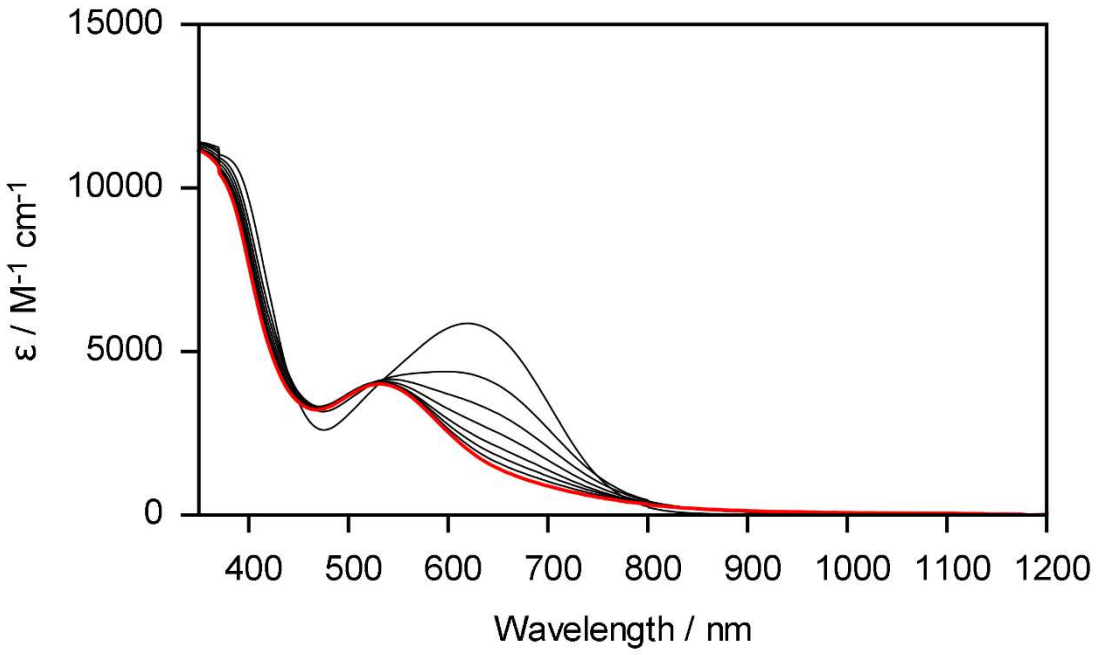


Figure S40 UV-Vis-NIR spectral changes of **6b** (0.5 mM in CH_2Cl_2 with 0.05 M $^nBu_4NClO_4$) on the application of 0.85 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the equilibrated state.

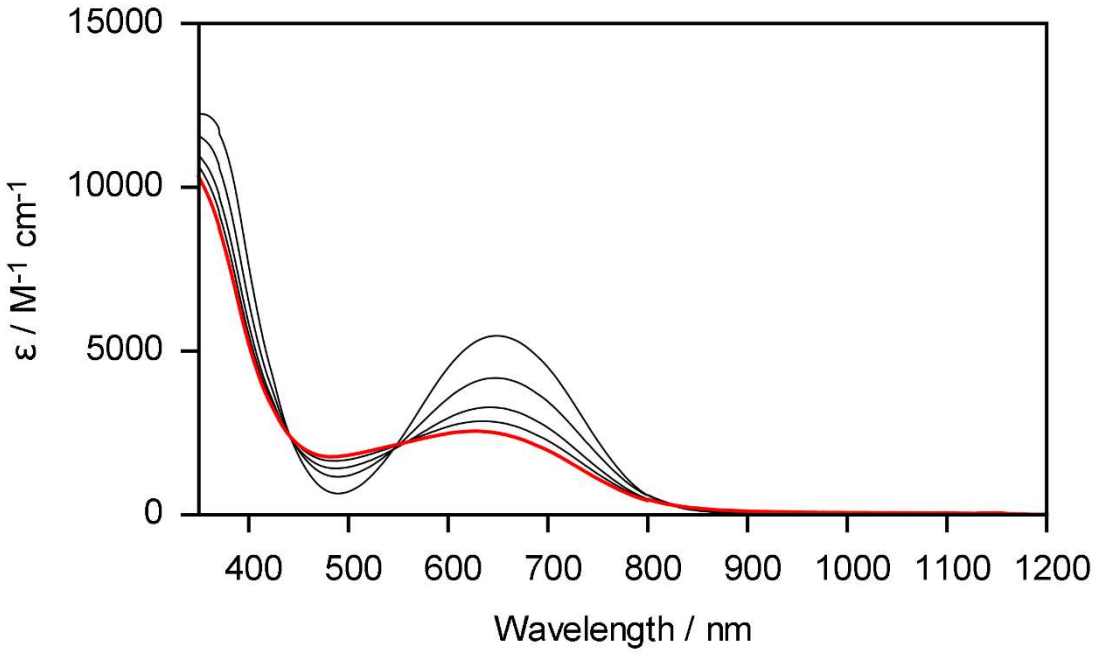


Figure S41 UV-Vis-NIR spectral changes of **6c** (0.5 mM in CH_2Cl_2 with 0.05 M $^nBu_4NClO_4$) on the application of 0.85 V vs. Ag/Ag^+. The measurements were performed every 3 minutes. The red line corresponds to the equilibrated state.

Chemical oxidation

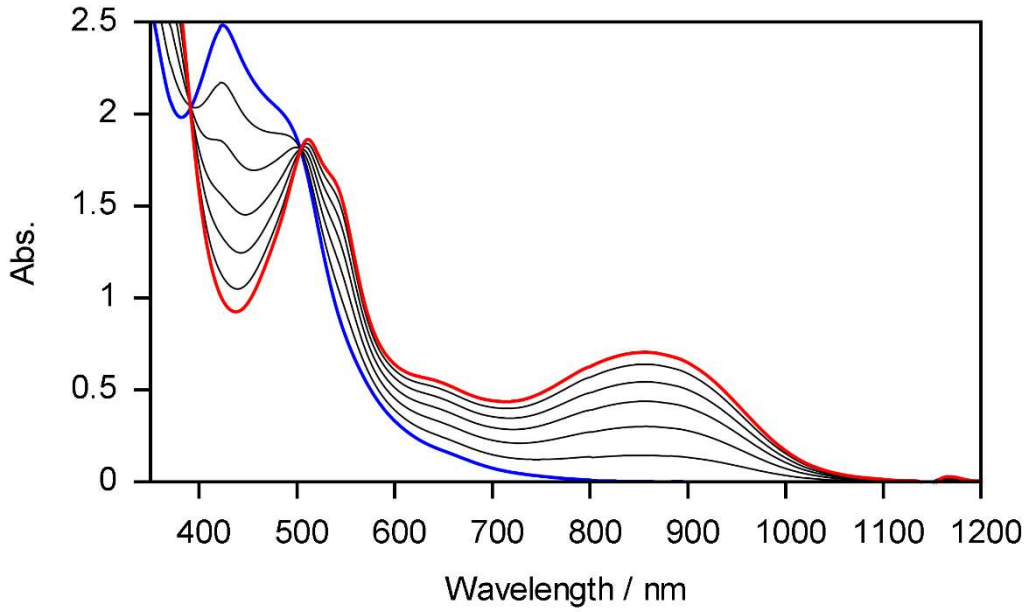


Figure S42 UV-Vis-NIR spectral changes of **3a** in CH_2Cl_2 upon the sequential additions of 0.2 equiv. of CAN in CH_3CN up to 1.2 equiv. The blue and red lines correspond to the initial and equilibrated state.

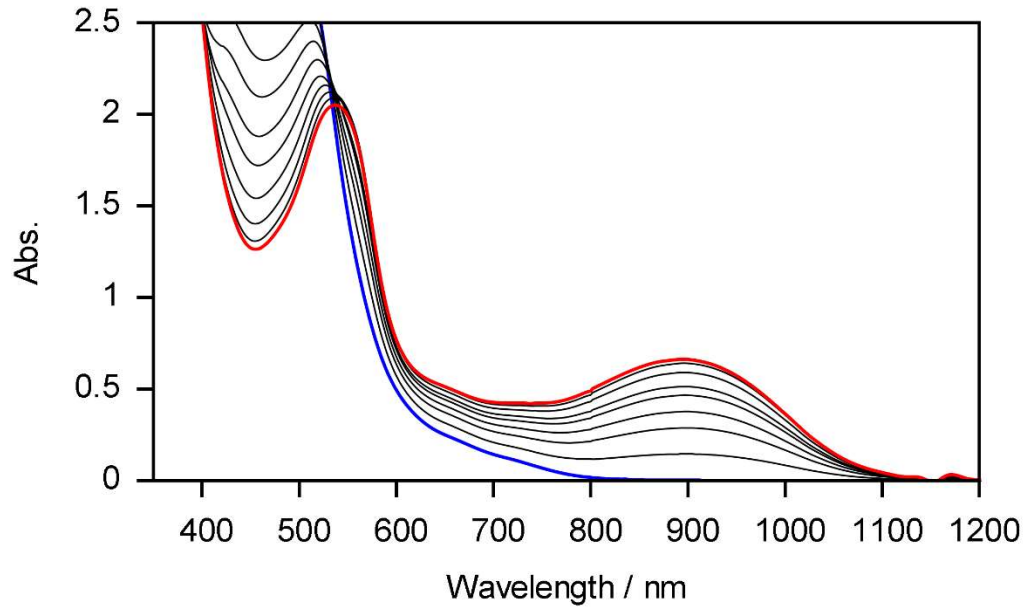


Figure S43 UV-Vis-NIR spectral changes of **3b** in CH_2Cl_2 upon the sequential additions of 0.2 equiv. of CAN in CH_3CN up to 1.6 equiv. The blue and red lines correspond to the initial and equilibrated state.

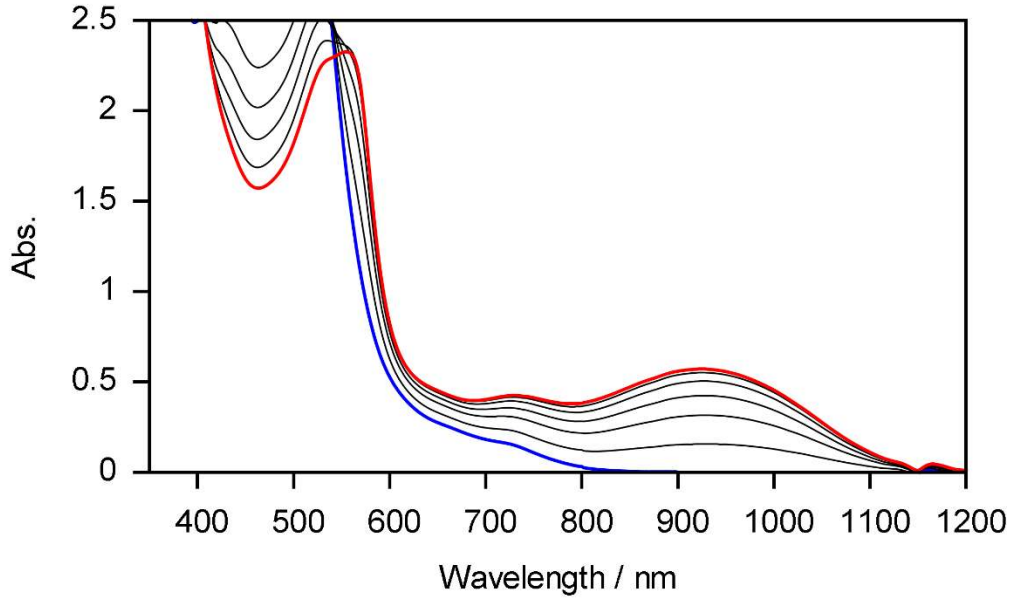


Figure S44 UV-Vis-NIR spectral changes of **3c** in CH_2Cl_2 upon the sequential additions of 0.2 equiv. of CAN in CH_3CN up to 1.0 equiv. The blue and red lines correspond to the initial and equilibrated state.

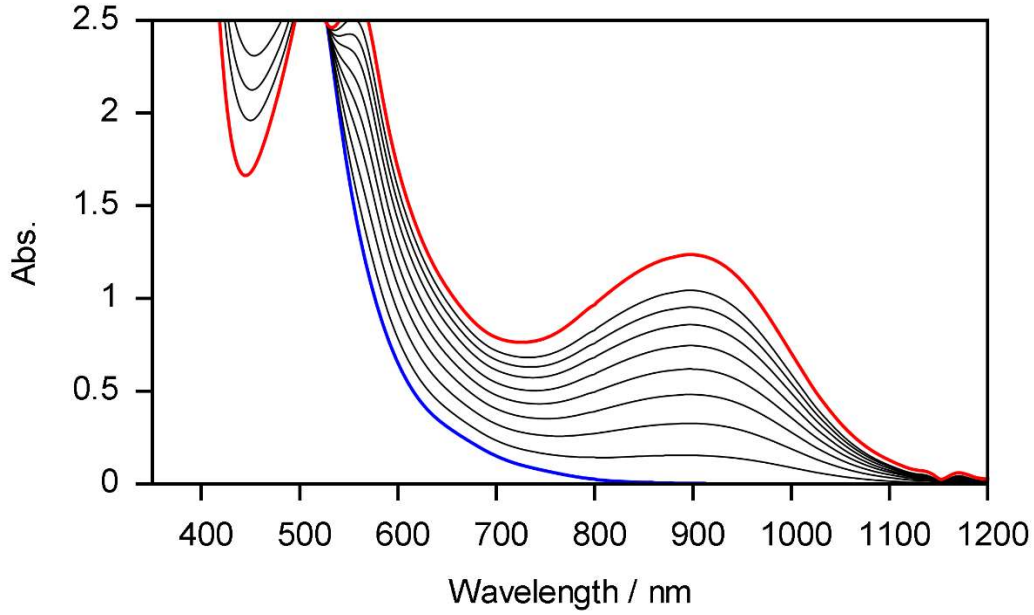


Figure S45 UV-Vis-NIR spectral changes of **4a** in CH_2Cl_2 upon the sequential additions of 0.2 equiv. of CAN in CH_3CN up to 1.8 equiv. The blue and red lines correspond to the initial and equilibrated state.

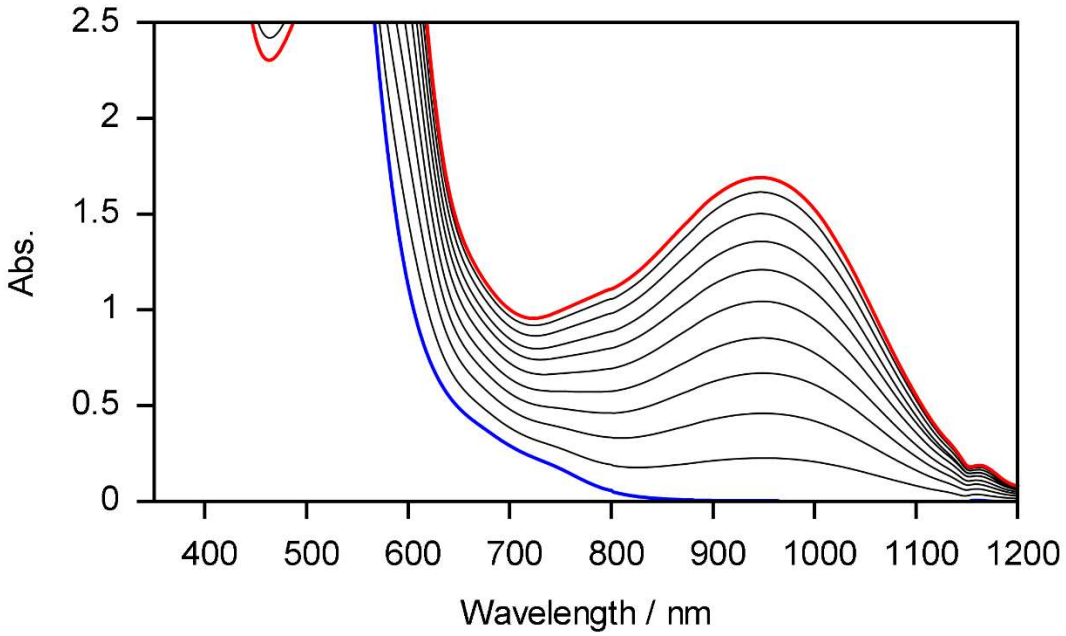


Figure S46 UV-Vis-NIR spectral changes of **4b** in CH_2Cl_2 upon the sequential additions of 0.2 equiv. of CAN in CH_3CN up to 2.0 equiv. The blue and red lines correspond to the initial and equilibrated state.

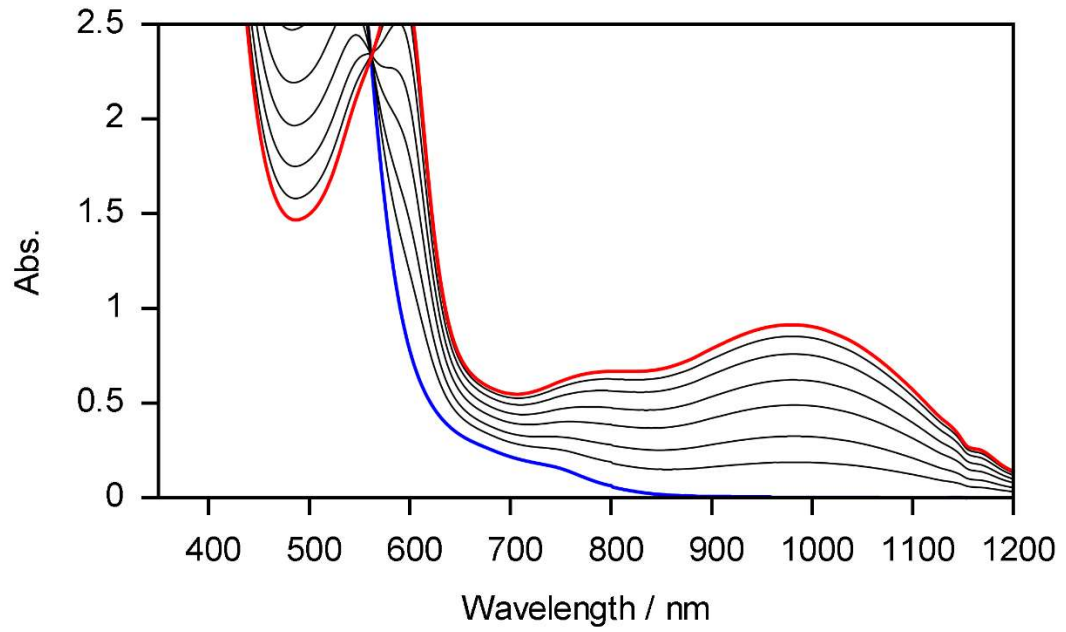


Figure S47 UV-Vis-NIR spectral changes of **4c** in CH_2Cl_2 upon the sequential additions of 0.2 equiv. of CAN in CH_3CN up to 1.4 equiv. The blue and red lines correspond to the initial and equilibrated state.

DFT calculations

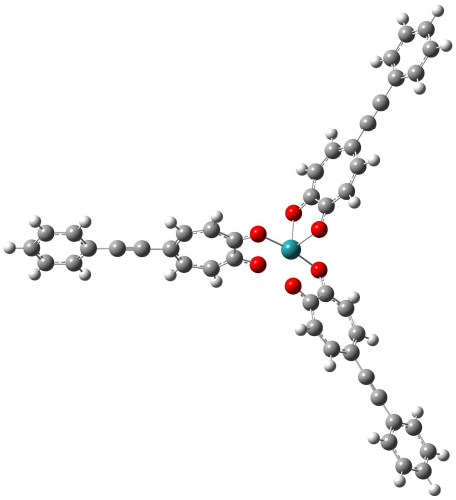


Figure S 48 DFT-optimized structure of **4c**.

Table S3 The atom list of the optimized structure of **4c**.

Tag	Symbol	Bond	Angle	Dihedral	X	Y	Z
1	O				-1.65842	-0.73964	-1.02833
2	O	2.547009			-1.64919	0.763262	1.027992
3	C	1.274742	65.01235		-2.81187	-0.42302	-0.58759
4	C	1.403762	119.2293	-179.042	-3.95346	-0.92489	-1.23215
5	H	1.084883	112.4246	0.809088	-3.70643	-1.57015	-2.06856
6	C	1.377848	131.0021	-178.806	-5.29373	-0.72692	-0.98128
7	H	1.085202	114.6515	179.797	-5.96278	-1.24956	-1.65721
8	C	1.400102	130.7081	-0.0883	-5.93583	0.038359	-0.00028
9	C	1.400149	124.972	-0.22805	-5.28433	0.795492	0.980904
10	H	1.085202	114.6396	179.8998	-5.94689	1.326361	1.656814
11	C	1.377801	130.7079	-0.21466	-3.94176	0.976709	1.231923
12	H	1.084882	116.5742	-179.69	-3.68676	1.618737	2.068428
13	C	1.274678	65.01341	-1.00724	-2.8064	0.460834	0.587302
14	Ru	2.058243	116.79	-178.569	-0.03681	0.001074	0.000309
15	O	2.015116	170.4352	-31.1427	1.352201	0.988572	1.075575
16	C	1.291099	115.5001	-61.3059	1.696467	2.143353	0.612004
17	C	1.394866	118.3049	-177.204	2.696936	2.851725	1.277528
18	H	1.085027	112.3652	0.352931	3.081042	2.313798	2.137981

19	C	1.38444	131.2641	-179.674	3.260929	4.090563	1.024808
20	H	1.084917	114.7033	-179.745	4.036848	4.38644	1.722986
21	C	1.393322	130.4071	0.335723	2.99144	5.017632	0.020187
22	O	2.068554	96.32122	-87.6631	0.090325	1.789136	-1.03197
23	C	1.270485	114.1766	175.0997	0.968914	2.588686	-0.58149
24	C	1.411974	118.5621	177.9349	1.164897	3.819701	-1.24471
25	H	1.084991	112.039	-0.07774	0.50648	3.930754	-2.0999
26	C	1.371412	131.2495	-179.733	2.027633	4.855451	-0.99236
27	H	1.085048	114.8593	179.665	1.957154	5.687062	-1.68575
28	O	2.068432	88.69276	96.28424	0.066091	-1.78853	1.032359
29	O	2.015169	95.30739	174.5968	1.340351	-1.00403	-1.07398
30	C	1.27053	114.173	98.86568	0.933999	-2.59974	0.581892
31	C	1.411946	118.5588	177.9656	1.112842	-3.8336	1.244617
32	H	1.084996	112.038	-0.0829	0.452568	-3.93603	2.099464
33	C	1.371431	131.252	-179.743	1.9614	-4.881	0.992173
34	H	1.085047	114.8593	179.67	1.879173	-5.71189	1.685124
35	C	1.407267	130.5607	-0.33326	2.923338	-5.0559	-0.02
36	C	1.393358	125.0688	-0.22016	3.205955	-4.13213	-1.0241
37	H	1.084915	114.8897	-179.803	3.978013	-4.43832	-1.72211
38	C	1.384407	130.4056	0.116696	2.659136	-2.88558	-1.27643
39	H	1.08503	116.3719	-179.694	3.050941	-2.35253	-2.13645
40	C	1.291084	115.4922	-91.0371	1.668253	-2.16376	-0.61092
41	C	1.427559	117.5157	179.7743	-7.36336	0.047357	-0.00037
42	C	1.42699	117.2318	179.9168	3.661991	-6.27683	-0.01489
43	C	1.426999	117.6999	179.976	3.746757	6.228332	0.014838
44	C	1.203498	179.9935	-161.647	-8.56683	0.055056	-0.00038
45	C	1.203407	179.8333	-3.5262	4.283302	-7.30742	-0.00763
46	C	1.203407	179.8348	177.29	4.382115	7.250317	0.007415
47	C	1.426204	179.9971	-59.1379	-9.99301	0.064176	-0.00031
48	C	1.398759	120.5367	40.21951	-10.699	0.797819	0.958796
49	C	1.39877	120.5373	-139.78	-10.7084	-0.66039	-0.95935
50	C	1.384639	120.3832	-180	-12.0836	0.804426	0.955908
51	H	1.083551	119.2436	-0.00555	-10.15	1.360891	1.704191
52	C	1.384628	120.383	179.998	-12.093	-0.64931	-0.9563
53	H	1.083551	119.2429	-0.00744	-10.1667	-1.23042	-1.70481

54	C	1.38861	120.2806	0.00182	-12.7852	0.082008	-0.00015
55	H	1.084291	119.6479	179.9981	-12.6188	1.377262	1.704978
56	H	1.084291	119.6485	179.9984	-12.6356	-1.21526	-1.7053
57	H	1.084181	120.1271	179.999	-13.8694	0.088925	-8.7E-05
58	C	1.426111	179.9388	169.2541	5.020076	-8.52844	-0.00043
59	C	1.398674	120.4915	14.17659	5.991982	-8.77664	-0.97516
60	C	1.398668	120.4988	-165.817	4.781514	-9.49569	0.981295
61	C	1.38455	120.338	-179.992	6.705306	-9.96325	-0.96526
62	H	1.083517	119.2749	0.000743	6.180237	-8.03032	-1.73777
63	C	1.384547	120.3378	179.9918	5.498647	-10.68	0.985021
64	H	1.08352	119.2786	-0.00427	4.029555	-9.30796	1.738481
65	C	1.388644	120.2565	0	6.46172	-10.9179	0.013304
66	H	1.084205	119.6653	179.995	7.456163	-10.1443	-1.72613
67	H	1.084204	119.6648	-179.997	5.304781	-11.4223	1.751135
68	H	1.084147	120.0999	179.9963	7.021724	-11.8462	0.018616
69	C	1.426115	179.9383	170.788	5.135585	8.461115	2.36E-05
70	C	1.398674	120.4922	11.90753	6.109716	8.696804	0.97563
71	C	1.398667	120.4987	-168.084	4.91139	9.430712	-0.98277
72	C	1.38455	120.3381	-179.989	6.839219	9.873538	0.965557
73	H	1.083517	119.275	0.002454	6.286889	7.948627	1.739076
74	C	1.384548	120.3382	179.9889	5.644665	10.60513	-0.98666
75	H	1.083521	119.2782	-0.00665	4.15778	9.25265	-1.74065
76	C	1.388642	120.257	-0.00043	6.609815	10.83065	-0.01406
77	H	1.084206	119.6652	179.9948	7.591638	10.04498	1.727118
78	H	1.084204	119.6647	-179.996	5.461826	11.34936	-1.75361
79	H	1.084147	120.1002	179.9964	7.182475	11.75119	-0.0195

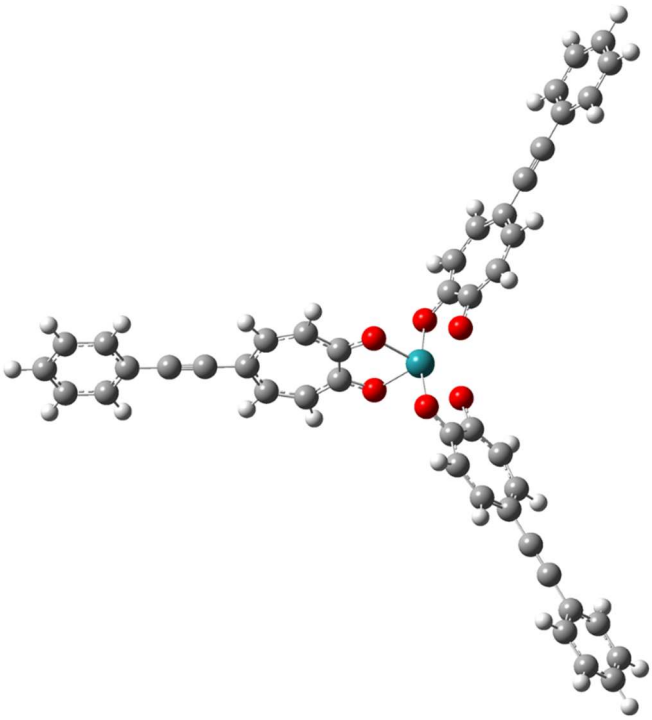


Figure S49 DFT-optimized structure of **4c**$^{+}$.

Table S4 The atom list of the optimized structure of **4c**$^{+}$.

Tag	Symbol	Bond	Angle	Dihedral	X	Y	Z
1	O				1.569594	-0.65103	-1.06238
2	O	2.52833			0.578751	-1.59958	1.061516
3	C	1.29401	65.20613		2.170164	-1.70234	-0.60575
4	C	1.400341	118.5246	179.9443	3.274708	-2.19962	-1.30835
5	H	1.084834	112.9066	-0.01973	3.508093	-1.61861	-2.19425
6	C	1.376529	130.3277	-179.901	4.080721	-3.28485	-1.04864
7	H	1.084218	115.0214	-179.987	4.877528	-3.44639	-1.76595
8	C	1.404691	130.2612	0.056871	4.035387	-4.21925	-0.00078
9	C	1.404651	125.4603	-0.00661	3.100005	-4.22376	1.047116
10	H	1.084218	114.7184	-179.964	3.226571	-5.02693	1.764357
11	C	1.376564	130.2605	-0.00963	2.051079	-3.37103	1.306984
12	H	1.084835	116.7651	-179.821	1.460472	-3.57887	2.192905
13	C	1.294072	65.20528	-0.15854	1.602724	-2.24563	0.604656
14	Ru	2.004523	50.90746	179.8887	-0.00107	-0.00091	0.000299
15	O	2.004616	94.52132	172.302	-1.67471	0.295684	1.063049

16	C	1.294051	116.1066	-92.8812	-2.74665	-0.26712	0.606118
17	C	1.400322	118.5233	-179.982	-3.94512	-0.09267	1.309068
18	H	1.084837	112.9067	-0.02738	-3.8291	0.521838	2.195516
19	C	1.376539	130.3274	-179.91	-5.20846	-0.57355	1.049106
20	H	1.084217	115.0216	-179.986	-5.96691	-0.28167	1.766797
21	C	1.404682	130.2613	0.057131	-5.67314	-1.38459	0.000573
22	O	2.004563	93.6495	93.8736	-1.3501	-1.03533	-1.06195
23	C	1.294073	116.1077	93.79868	-2.56078	-1.02929	-0.60495
24	C	1.400303	118.5226	179.9986	-3.54433	-1.736	-1.30782
25	H	1.084837	112.9068	-0.02498	-3.15842	-2.22814	-2.19424
26	C	1.376548	130.3278	-179.902	-4.88723	-1.89071	-1.04789
27	H	1.084217	115.0215	-179.994	-5.42614	-2.499	-1.76559
28	O	2.004682	94.53456	-92.7468	1.094448	1.299789	1.061795
29	O	2.004557	169.4777	-46.9812	-0.22382	1.685138	-1.06078
30	C	1.293992	116.1132	172.2246	1.142509	2.509639	0.605322
31	C	1.400345	118.5263	-179.974	1.894179	3.45993	1.307395
32	H	1.084834	112.9069	-0.02312	2.36982	3.051764	2.192849
33	C	1.376522	130.3273	-179.902	2.10909	4.794533	1.047667
34	H	1.084217	115.0211	-179.989	2.742384	5.305034	1.764503
35	C	1.4047	130.2613	0.056267	1.6373	5.603015	0.000311
36	C	1.404652	125.4599	-0.00509	0.804171	5.176051	-1.0469
37	H	1.084218	114.7186	-179.967	0.545656	5.947255	-1.76379
38	C	1.376563	130.2608	-0.01134	0.266075	3.935886	-1.30645
39	H	1.084834	116.7647	-179.822	-0.35465	3.848252	-2.19183
40	C	1.294058	116.1183	-46.9285	0.387499	2.730409	-0.60439
41	C	1.419122	117.2688	179.9978	5.016747	-5.24435	-0.00082
42	C	1.419114	117.2702	179.9935	2.035665	6.965068	0.000202
43	C	1.419118	117.2698	179.9991	-7.05189	-1.72067	0.000483
44	C	1.204807	179.9913	147.2361	5.849902	-6.11465	-0.00067
45	C	1.204808	179.9992	53.18839	2.373889	8.121427	0.00011
46	C	1.204814	179.9934	72.2662	-8.22246	-2.00587	0.00037
47	C	1.422854	179.9933	-39.1521	6.833918	-7.14238	-0.00037
48	C	1.399309	120.2783	71.5489	6.851801	-8.10174	1.018143
49	C	1.399307	120.2779	-108.446	7.791963	-7.20215	-1.01853
50	C	1.383581	120.084	-179.991	7.810593	-9.09923	1.01459

51	H	1.083387	119.5002	-0.00047	6.11054	-8.05627	1.806935
52	C	1.383584	120.0843	179.9968	8.747036	-8.20321	-1.01425
53	H	1.083388	119.5003	-0.0116	7.778903	-6.45991	-1.8076
54	C	1.389133	120.1347	-0.00613	8.758351	-9.15197	0.000352
55	H	1.083659	119.7739	179.9932	7.819854	-9.83955	1.805892
56	H	1.083659	119.7739	179.9938	9.486543	-8.2448	-1.80528
57	H	1.083848	119.9409	-179.996	9.507985	-9.93477	0.00064
58	C	1.42285	179.9934	51.66433	2.773429	9.48703	-0.00012
59	C	1.399313	120.2784	74.7116	2.347471	10.3466	-1.01884
60	C	1.399308	120.2782	-105.288	3.59563	9.981754	1.018357
61	C	1.38358	120.0843	-179.995	2.738489	11.67377	-1.01517
62	H	1.083389	119.4999	-0.00587	1.710966	9.964505	-1.80789
63	C	1.383581	120.0843	-179.998	3.981681	11.31038	1.014215
64	H	1.083388	119.5002	-0.00675	3.92588	9.317085	1.807585
65	C	1.389134	120.135	-0.00746	3.554787	12.1575	-0.00059
66	H	1.08366	119.7737	179.9922	2.405771	12.33497	-1.80664
67	H	1.08366	119.7738	179.9933	4.618421	11.68821	1.805494
68	H	1.083848	119.941	-179.996	3.859156	13.19774	-0.00078
69	C	1.422862	179.9871	41.39584	-9.60492	-2.34251	-3.1E-05
70	C	1.399316	120.2792	-114.021	-10.4445	-1.8782	1.018638
71	C	1.399306	120.2784	65.97356	-10.1364	-3.14058	-1.01916
72	C	1.383577	120.0849	179.9945	-11.7882	-2.2079	1.01423
73	H	1.083385	119.4994	-0.01221	-10.0339	-1.26034	1.808198
74	C	1.383582	120.085	-179.988	-11.4814	-3.46529	-1.01575
75	H	1.083388	119.4995	0	-9.48731	-3.50049	-1.80835
76	C	1.389133	120.135	-0.00692	-12.3084	-3.00056	-0.00101
77	H	1.083659	119.7742	179.9951	-12.4337	-1.84565	1.805641
78	H	1.08366	119.774	179.9924	-11.8877	-4.08358	-1.80754
79	H	1.083848	119.941	-179.997	-13.3615	-3.25688	-0.00141

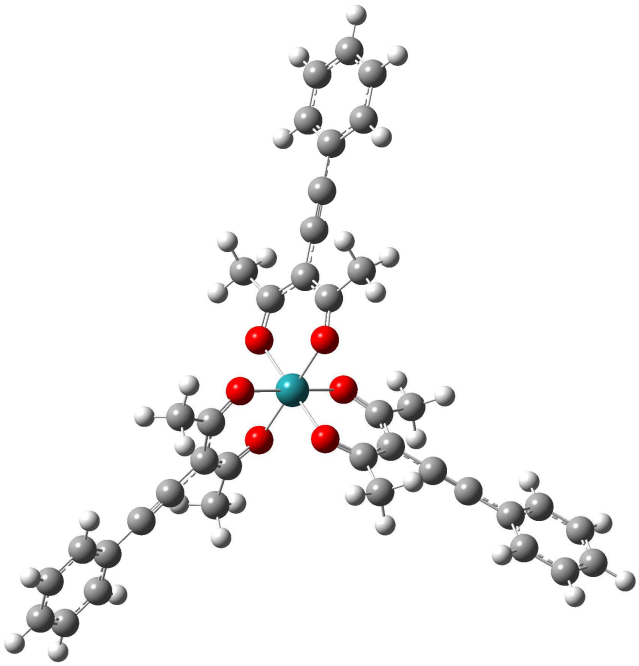


Figure S50 DFT-optimized structure of **6c**.

Table S5 The atom list of the optimized structure of **6c**.

Tag	Symbol	Bond	Angle	Dihedral	X	Y	Z
1	Ru				-3.3E-06	-0.46227	8.79E-05
2	O	2.026827			0.99222	0.960234	1.048897
3	C	1.26352	126.0882		0.860071	2.209909	0.917243
4	C	1.418881	126.0897	-0.63818	-5.1E-05	2.867388	0.000109
5	C	1.418882	124.7888	0.356196	-0.86018	2.209895	-0.91701
6	O	1.263518	126.0897	0.35355	-0.99232	0.960221	-1.04866
7	C	1.503084	119.1057	-179.766	-1.71578	3.034858	-1.83714
8	H	1.091462	110.5768	59.32621	-1.09548	3.677962	-2.46399
9	H	1.091447	110.6711	-58.9232	-2.37549	3.690121	-1.2656
10	H	1.08734	109.0968	-179.87	-2.30726	2.371211	-2.46327
11	C	1.425875	117.6057	-179.644	-3.8E-05	4.293262	0.000083
12	C	1.204268	179.9986	127.9282	-2.3E-05	5.49753	3.26E-05
13	C	1.503084	114.8044	179.4789	1.715664	3.034883	1.837373
14	H	1.08734	109.0967	0.016008	2.307061	2.371243	2.463584
15	H	1.091461	110.5773	-120.788	1.095378	3.678085	2.464129
16	H	1.091448	110.6706	120.9622	2.375461	3.69005	1.26581
17	O	2.018084	91.16713	-89.0217	-1.49708	-0.47435	1.353338

18	C	1.269973	126.9236	162.1577	-2.66905	-0.93564	1.190451
19	C	1.502332	114.6916	-169.961	-3.63605	-0.59429	2.288346
20	H	1.087401	109.2027	-0.68709	-3.12401	-0.0055	3.045697
21	H	1.091235	110.8372	-121.843	-4.04785	-1.49921	2.738157
22	H	1.091823	110.3333	119.9579	-4.47892	-0.0269	1.888697
23	C	1.409198	125.7811	11.31736	-3.098	-1.73288	0.110518
24	C	1.424558	118.2114	-179.643	-4.45753	-2.15764	0.085346
25	C	1.204439	179.7651	91.73572	-5.60817	-2.51277	0.06142
26	C	1.42586	123.6044	4.487416	-2.22763	-2.2085	-0.91384
27	O	1.254601	125.3663	-5.39418	-1.01636	-1.90536	-1.0362
28	C	1.502366	119.0885	173.1731	-2.75871	-3.17726	-1.93195
29	H	1.09189	110.1019	62.35822	-3.56378	-2.71436	-2.50623
30	H	1.091102	110.9146	-55.7621	-3.18101	-4.05897	-1.44744
31	H	1.087373	109.1918	-177.254	-1.95347	-3.46891	-2.60196
32	O	2.018075	179.3192	-63.2927	1.497073	-0.47417	-1.35315
33	C	1.269977	126.9234	-63.2381	2.669081	-0.93538	-1.19027
34	C	1.409193	125.7811	11.32526	3.098052	-1.73275	-0.11045
35	C	1.425867	123.6044	4.480652	2.227688	-2.20851	0.913863
36	O	1.254596	125.3664	-5.3968	1.016438	-1.90537	1.036295
37	C	1.502367	119.0882	173.1711	2.758782	-3.17744	1.931812
38	H	1.087373	109.1917	-177.263	1.953589	-3.46905	2.601891
39	H	1.091889	110.1029	62.34793	3.564002	-2.71471	2.506029
40	H	1.091104	110.9134	-55.7725	3.180893	-4.05916	1.447143
41	C	1.424554	118.2116	-179.652	4.457569	-2.15753	-0.08536
42	C	1.204439	179.7641	91.79405	5.608214	-2.51266	-0.06149
43	C	1.502334	114.6916	-169.957	3.636093	-0.59383	-2.2881
44	H	1.091241	110.8341	-121.796	4.04734	-1.49871	-2.7385
45	H	1.091816	110.3361	120.0037	4.479314	-0.02709	-1.88828
46	H	1.087401	109.2027	-0.64613	3.1242	-0.00439	-3.04506
47	C	1.427166	179.9996	68.96098	-1.3E-05	6.924696	-3.2E-05
48	C	1.398847	120.626	-16.5273	-0.82898	7.63728	-0.87285
49	C	1.398848	120.626	163.4731	0.828969	7.637347	0.872717
50	C	1.384842	120.4775	-179.997	-0.82645	9.022117	-0.87036
51	H	1.083725	119.2651	0.001174	-1.47463	7.093608	-1.55257
52	C	1.384842	120.4775	-179.998	0.826471	9.022184	0.870088

53	H	1.083725	119.2651	0.000643	1.474608	7.093728	1.552487
54	C	1.388474	120.3393	-0.00554	1.62E-05	9.720388	-0.00017
55	H	1.084412	119.603	179.9975	-1.47478	9.560218	-1.55304
56	H	1.084412	119.603	179.9975	1.474816	9.560338	1.552721
57	H	1.084151	120.1908	-179.997	2.73E-05	10.80454	-0.00022
58	C	1.426997	179.9359	35.04411	6.971628	-2.93282	-0.03173
59	C	1.398928	120.6303	54.3024	7.445467	-3.74244	1.006054
60	C	1.39892	120.6435	-125.704	7.85997	-2.54321	-1.03971
61	C	1.384842	120.4877	-179.995	9.182428	-2.95293	-1.00769
62	C	1.38484	120.4886	179.9793	8.769083	-4.14884	1.031794
63	C	1.388477	120.3457	0.017538	9.642963	-3.75669	0.026598
64	H	1.083726	119.2535	0.002593	7.50197	-1.91609	-1.8478
65	H	1.084435	119.5984	-179.997	9.858636	-2.64235	-1.79654
66	H	1.083727	119.254	-0.03038	6.764734	-4.049	1.791603
67	H	1.084433	119.5986	-179.994	9.121004	-4.77646	1.843115
68	H	1.08416	120.1974	179.9915	10.67875	-4.07613	0.049208
69	C	1.427003	179.9339	33.66718	-6.97161	-2.93287	0.031569
70	C	1.398918	120.6431	-124.256	-7.86002	-2.54311	1.039427
71	C	1.398927	120.6303	55.75067	-7.44538	-3.74256	-1.00619
72	C	1.384844	120.4875	-179.995	-9.1825	-2.95276	1.007316
73	H	1.083725	119.2536	0.002021	-7.50206	-1.91593	1.847497
74	C	1.38484	120.4884	179.9798	-8.76902	-4.14888	-1.03202
75	H	1.083726	119.254	-0.0296	-6.76458	-4.04924	-1.79163
76	C	1.388477	120.3456	0.017321	-9.64298	-3.75659	-0.02695
77	H	1.084435	119.5985	-179.997	-9.85877	-2.64208	1.796072
78	H	1.084433	119.5987	-179.994	-9.1209	-4.77656	-1.84331
79	H	1.08416	120.1973	179.9915	-10.6788	-4.07598	-0.04963

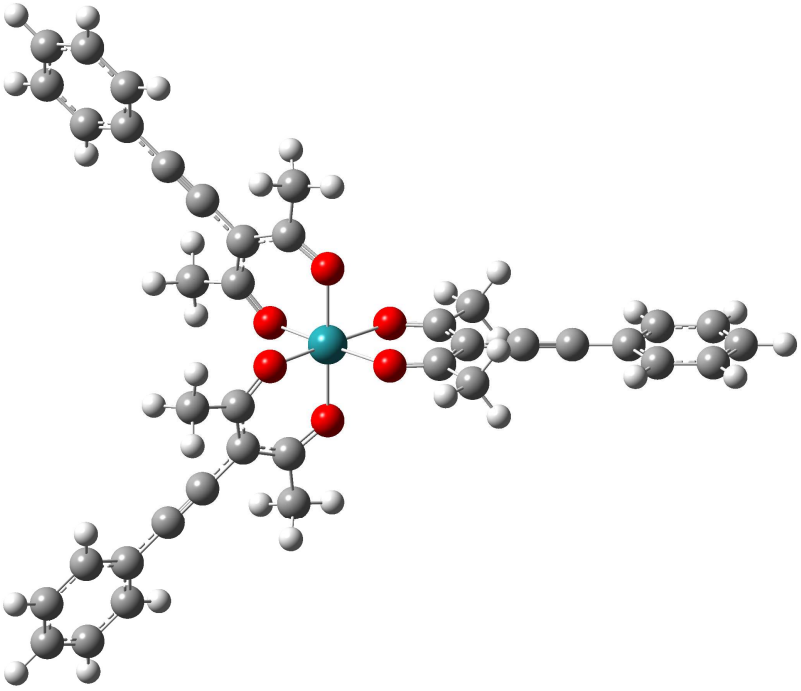


Figure S51 DFT-optimized structure of **6c**$^{+}$.

Table S6 The atom list of the optimized structure of **6c**$^{+}$.

Tag	Symbol	Bond	Angle	Dihedral	X	Y	Z
1	Ru				0.457072	-0.00013	4.13E-05
2	O	2.014349			0.456858	1.872624	0.741935
3	C	1.269216	125.4596		-0.50696	2.694872	0.665254
4	C	1.417019	124.9576	-13.6702	-1.63435	2.547755	-0.18048
5	C	1.413518	123.6509	-6.3434	-1.76212	1.521425	-1.144
6	O	1.27318	125.3438	7.579976	-0.96639	0.537106	-1.28152
7	C	1.497885	119.8324	-170.831	-2.88815	1.561899	-2.13096
8	H	1.091035	110.8143	55.5254	-2.88679	2.503382	-2.68229
9	H	1.091973	110.0637	-62.3065	-3.84575	1.504276	-1.60934
10	H	1.087155	109.559	177.0947	-2.79756	0.726648	-2.82092
11	C	1.425151	118.0833	179.4588	-2.63944	3.55733	-0.14036
12	C	1.203701	179.6591	-93.8237	-3.49199	4.406188	-0.10164
13	C	1.497956	115.4491	168.1524	-0.38045	3.916695	1.522585
14	H	1.087285	109.58	1.904531	0.568337	3.892948	2.053076
15	H	1.092093	109.9017	-118.377	-1.1994	3.95087	2.244264
16	H	1.090945	111.0115	123.7903	-0.45277	4.824858	0.922443

17	O	1.989282	88.6237	68.71999	-0.96632	-0.53744	1.281634
18	C	1.273177	125.9044	68.71582	-1.76205	-1.52176	1.144103
19	C	1.497884	114.8066	-169.812	-2.888	-1.56232	2.131142
20	H	1.087156	109.5585	-1.5317	-2.79683	-0.72766	2.821754
21	H	1.091026	110.8186	-123.108	-2.88731	-2.50425	2.68168
22	H	1.091982	110.0593	119.0583	-3.84558	-1.50353	1.609599
23	C	1.413525	125.3435	11.70444	-1.63437	-2.54799	0.180467
24	C	1.42514	118.0212	-178.212	-2.63951	-3.55749	0.14025
25	C	1.203703	179.659	91.36925	-3.49213	-4.40628	0.10148
26	C	1.417019	123.65	7.587436	-0.50698	-2.69507	-0.6653
27	O	1.269215	124.9574	-6.34345	0.456877	-1.87287	-0.74188
28	C	1.497958	119.5686	171.7628	-0.38054	-3.91682	-1.52275
29	H	1.092089	109.9034	63.31121	-1.19977	-3.95119	-2.24409
30	H	1.09095	111.0089	-54.5224	-0.45237	-4.82501	-0.92258
31	H	1.087285	109.5799	-176.403	0.568051	-3.89283	-2.05359
32	O	2.090914	178.0777	-90.2691	1.998084	0.523015	-1.31279
33	C	1.23251	131.9887	-21.7917	3.224945	0.479939	-1.20306
34	C	1.467999	123.561	0.068681	3.915776	-3.9E-05	1.25E-05
35	C	1.467995	123.8564	-0.03155	3.224994	-0.48012	1.203072
36	O	1.232511	123.561	-0.03994	1.998137	-0.52324	1.31283
37	C	1.497593	118.7775	179.8382	4.04396	-0.94816	2.366262
38	H	1.086694	109.0164	-179.739	3.377438	-1.27014	3.161865
39	H	1.09178	110.5759	59.7714	4.686757	-0.14459	2.731045
40	H	1.091684	110.6832	-59.0263	4.692761	-1.77568	2.072921
41	C	1.372144	118.0717	179.9695	5.28792	8.57E-05	3.14E-05
42	C	1.224094	179.9993	123.0361	6.512014	0.000205	6.02E-05
43	C	1.497592	117.6615	-179.809	4.043866	0.947956	-2.3663
44	H	1.091776	110.5782	-120.368	4.687008	0.144544	-2.73081
45	H	1.091687	110.681	120.8346	4.692321	1.775789	-2.07308
46	H	1.086694	109.0164	0.124927	3.377312	1.269522	-3.16204
47	C	1.42772	179.9282	10.57767	-4.50393	5.412227	-0.05429
48	C	1.3983	120.447	-108.739	-5.50773	5.45389	-1.02686
49	C	1.398299	120.438	71.25827	-4.50444	6.369032	0.965399
50	C	1.384519	120.278	179.9728	-6.48767	6.430693	-0.97725
51	H	1.083661	119.4814	-0.07264	-5.51238	4.715965	-1.82044

52	C	1.384516	120.2804	179.9558	-5.48681	7.343732	1.007653
53	H	1.083668	119.4749	-0.12439	-3.73043	6.340937	1.723336
54	C	1.388532	120.2384	0.074779	-6.48035	7.377659	0.038252
55	H	1.083938	119.6874	-179.983	-7.26145	6.453883	-1.73597
56	H	1.083951	119.6925	-179.993	-5.478	8.080847	1.802343
57	H	1.083849	120.0775	179.9577	-7.24852	8.141435	0.074234
58	C	1.398811	179.9992	49.51662	7.910825	0.000337	0.000113
59	C	1.409393	120.2155	7.352438	8.620108	-0.44908	1.132071
60	C	1.409392	120.2155	-172.648	8.620107	0.449889	-1.13179
61	C	1.378645	119.8874	-180	9.998729	0.447098	-1.12441
62	C	1.378645	119.8874	-180	9.99873	-0.44604	1.124786
63	C	1.39294	120.0227	-0.00051	10.68876	0.000594	0.000214
64	H	1.083061	119.4961	-0.00348	8.073861	0.794939	-2.00103
65	H	1.083084	119.9407	179.9986	10.54466	0.79236	-1.99379
66	H	1.083061	119.496	-0.0039	8.073861	-0.79423	2.001272
67	H	1.083084	119.9407	179.9987	10.54467	-0.7912	1.994205
68	H	1.083637	119.6946	-180	11.7724	0.000696	0.000254
69	C	1.427709	179.9286	9.939291	-4.50416	-5.41221	0.054092
70	C	1.398302	120.4468	-107.2	-5.51536	-5.44602	1.01928
71	C	1.3983	120.4383	72.79714	-4.49737	-6.37677	-0.95825
72	C	1.384517	120.278	179.9753	-6.49534	-6.42279	0.969685
73	H	1.083661	119.4817	-0.0667	-5.52575	-4.70201	1.807097
74	C	1.384514	120.2804	179.9584	-5.4799	-7.3513	-1.00058
75	H	1.083669	119.4754	-0.11867	-3.71756	-6.35485	-1.71041
76	C	1.388533	120.2387	0.069742	-6.48078	-7.37745	-0.03851
77	H	1.083938	119.6872	-179.984	-7.27486	-6.43987	1.72266
78	H	1.083951	119.6924	-179.994	-5.46541	-8.09445	-1.78955
79	H	1.083849	120.0776	179.9603	-7.24903	-8.14115	-0.07452

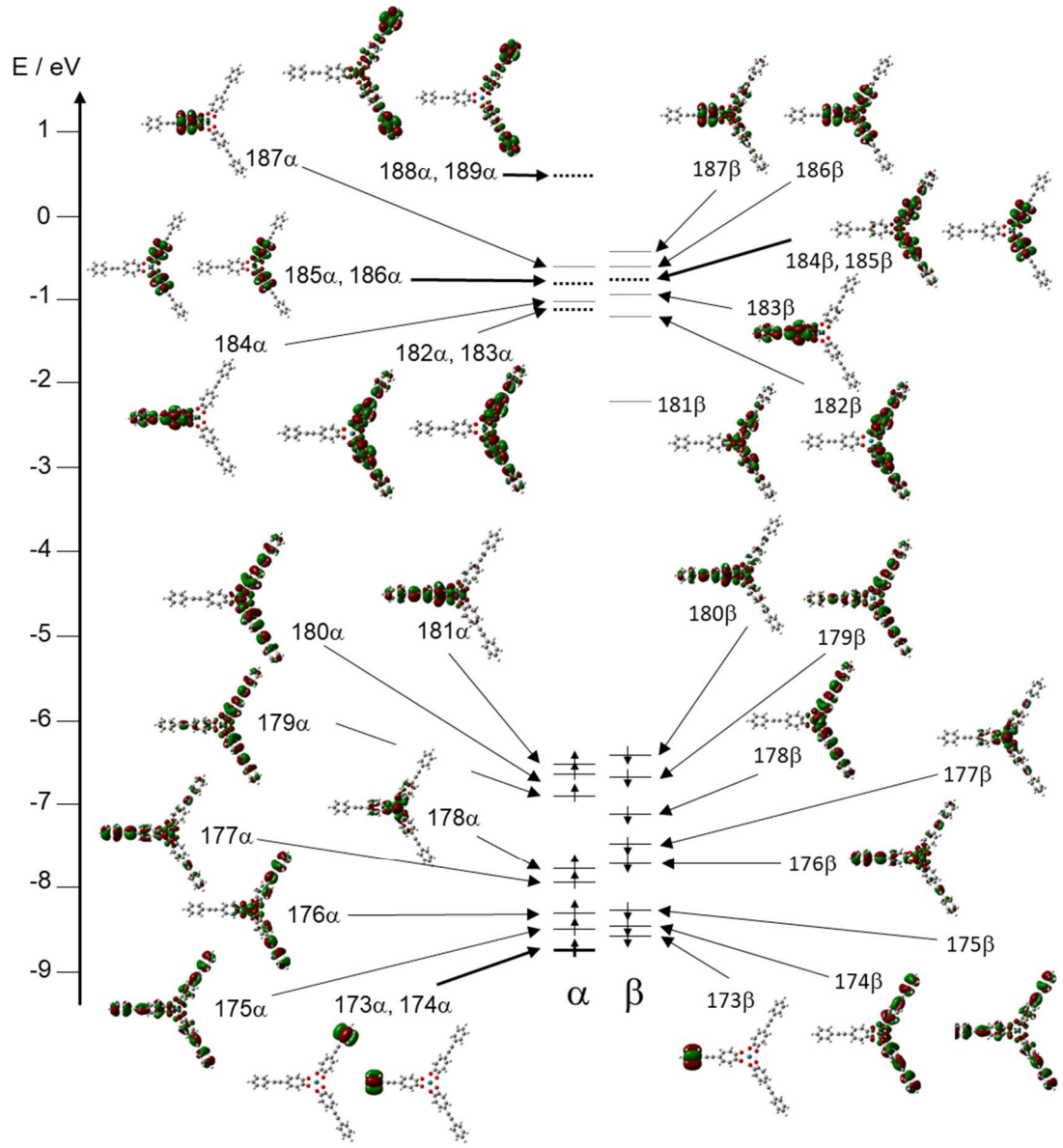


Figure S52 Frontier MO diagrams of **4c** calculated by DFT/ucam-b3lyp.

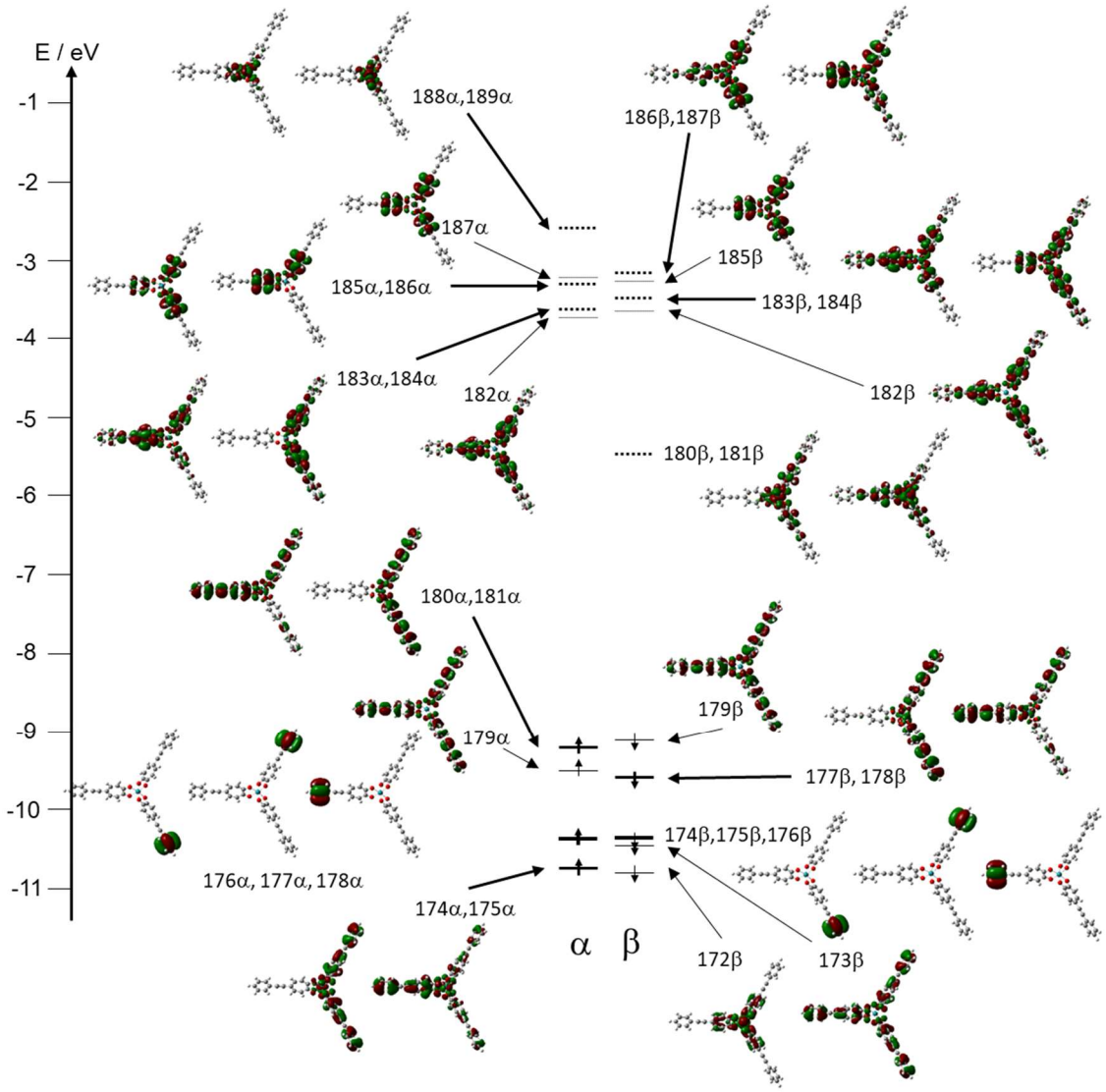


Figure S53 Frontier MO diagrams of **4c**$^{+}$ calculated by DFT/ucam-b3lyp.

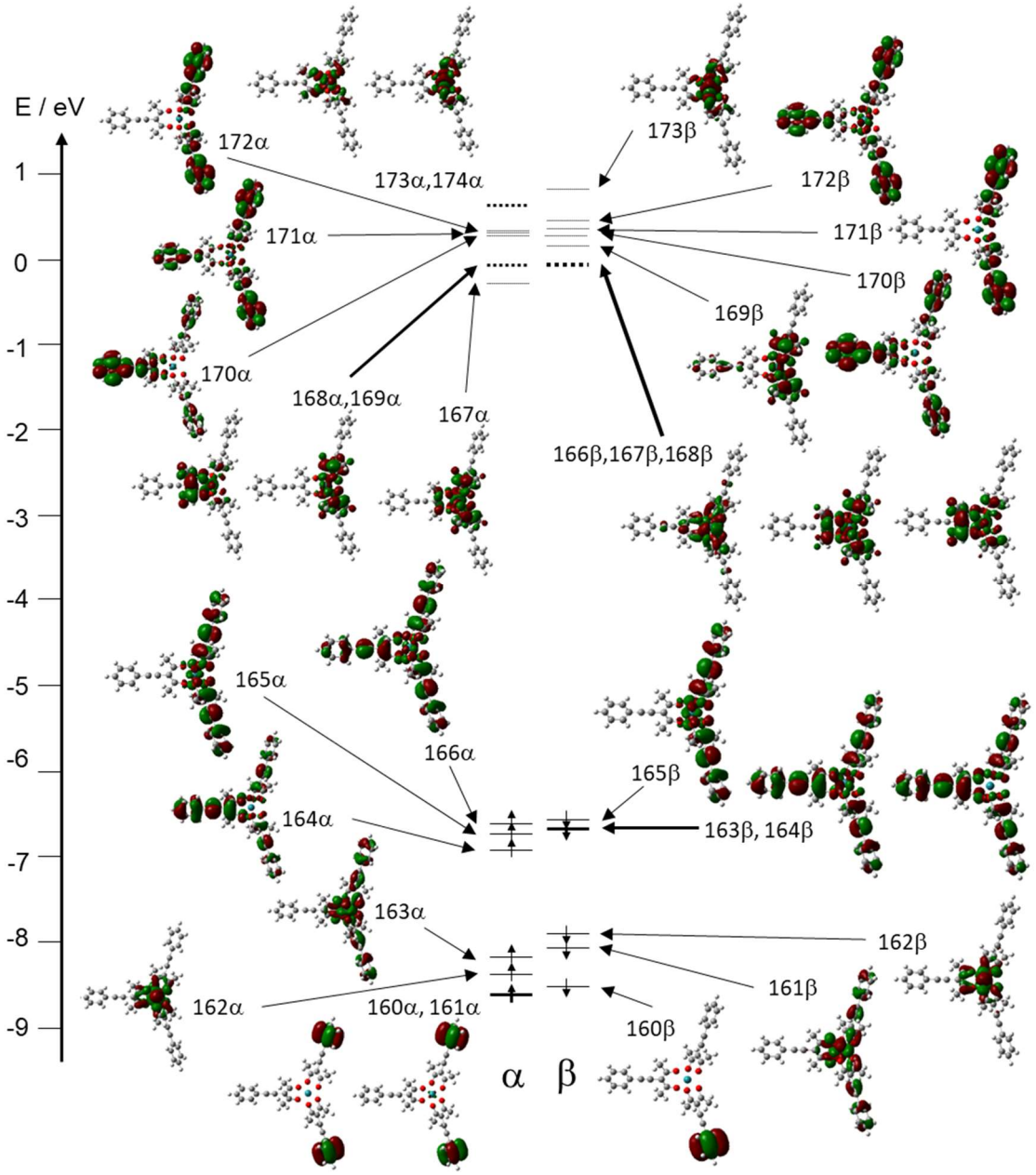


Figure S54 Frontier MO diagrams of **6c** calculated by DFT/ucam-b3lyp.

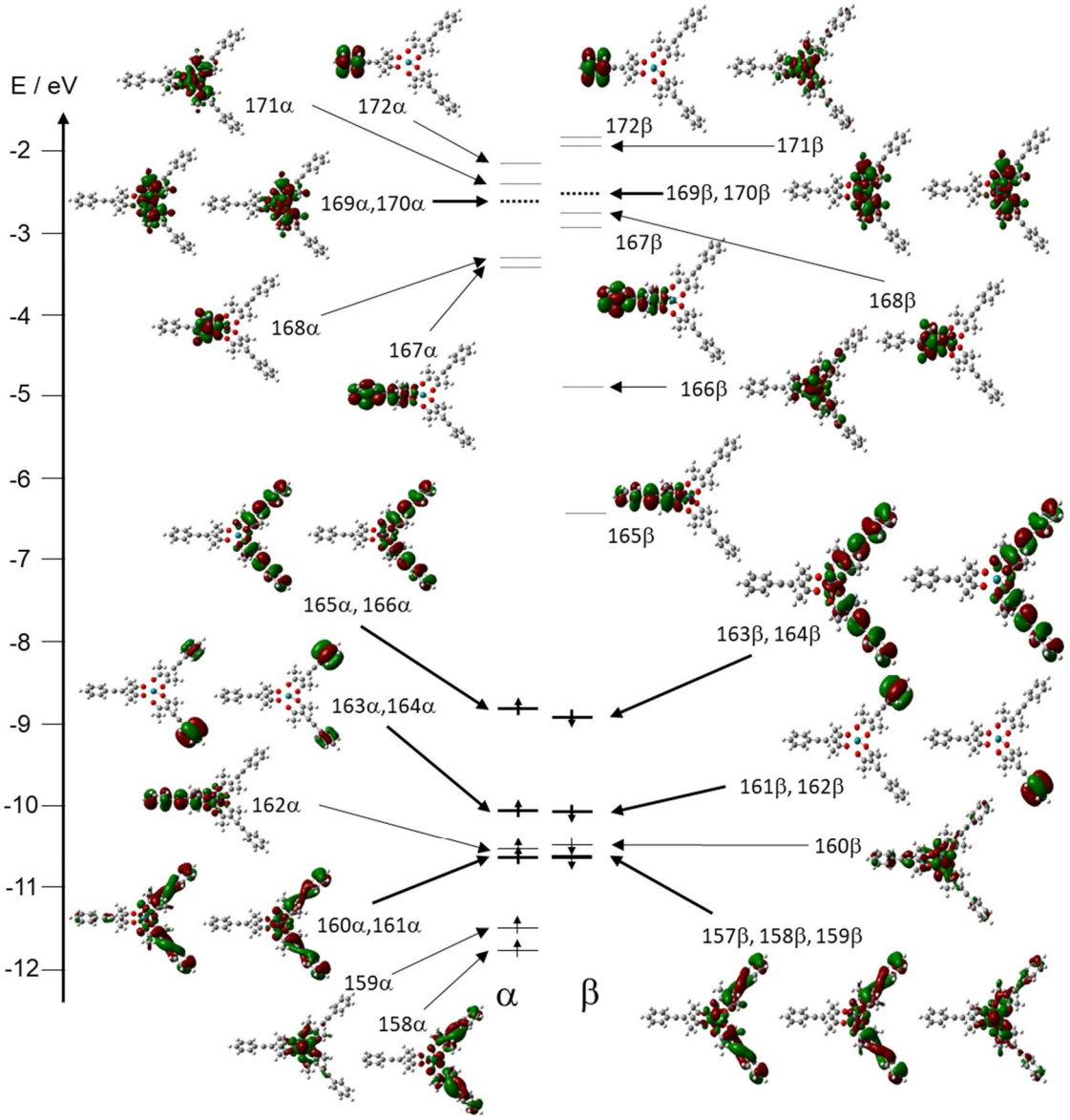


Figure S55 Frontier MO diagrams of **6c**$^{+}$ calculated by DFT/ucam-b3lyp.

Time-course UV-vis spectra

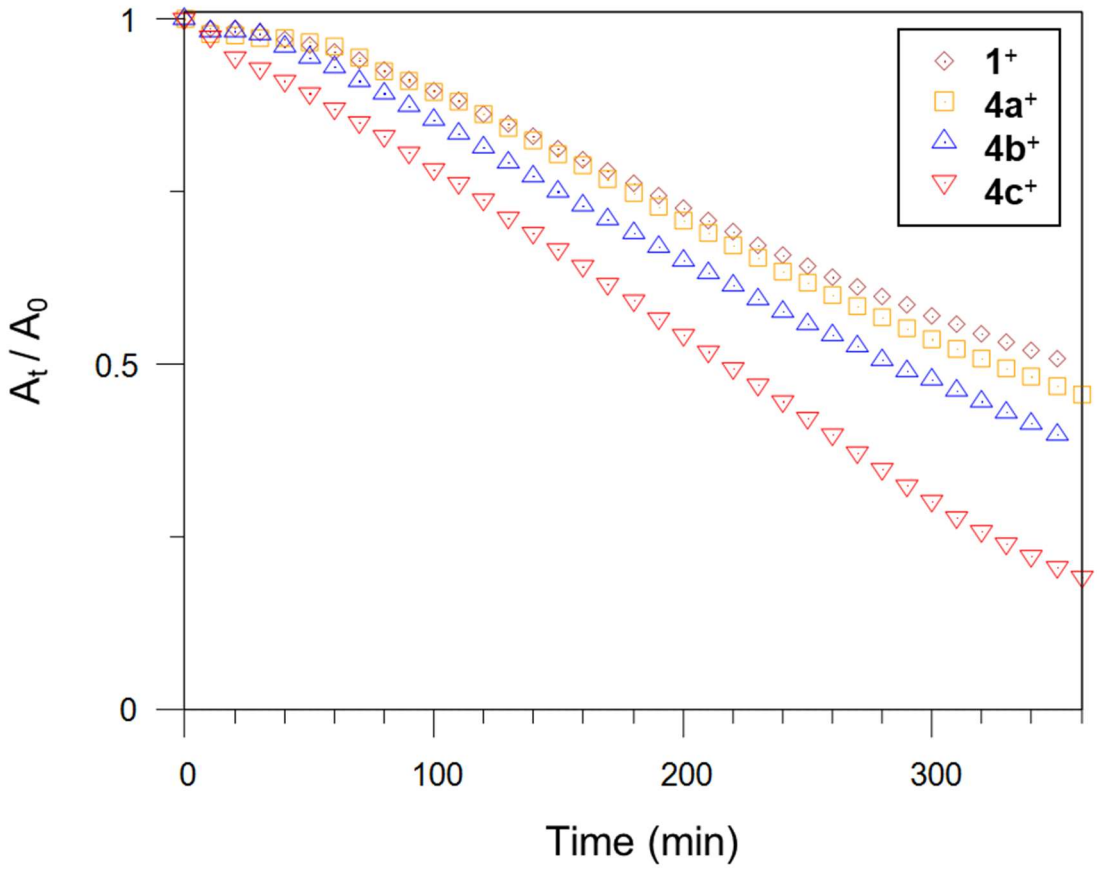


Figure S56 Time-dependent absorption changes of oxidized complexes **1**$^+$, **4a**$^+$, **4b**$^+$ and **4c**$^+$, in-situ prepared by the addition of CAN. The relative absorption at 800 nm (A_t / A_0, A_t: absorption at an arbitrary time, A_0: absorption in the initial state) is plotted against the time after the addition of CAN.

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