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Electronic Supporting Information

Spectroscopic and Electrochemical Properties of Ruthenium Complexes with Photochromic Triarylamine-Dithienylethene -Acetylide Ligands

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Table S1. Partial Molecular Orbital Compositions (%) obtained by the SCPA Approach (C-squared Population Analysis Proposed by Ros and Schuit) for the Ground State and Vertical Absorption Transitions for **1o'** in Toluene. The Excitation Energies have been determined with TD-DFT Method using the PBE0 Functional.

MO	Energy (eV)	Contribution (%)				
		$(p\text{-}MeOC_6H_4)_2N$	DTE (o)	Ru (s/p/d)	P ligand	Cl
LUMO+5	0.13	0.07	0.09	21.62 (1/2/97)	78.18	0.03
LUMO+2	-0.29	6.92	68.60	13.97 (13/74/12)	10.25	0.25
LUMO+1	-0.40	15.68	77.99	3.37 (25/55/20)	2.89	0.07
LUMO	-1.30	0.95	98.15	0.62 (24/40/37)	0.29	0.00
HOMO	-4.96	26.89	46.53	20.13 (0/7/93)	4.17	2.28
HOMO-1	-5.03	55.58	30.19	10.84 (0/6/94)	2.07	1.31

State	*E*, nm (eV)	O.S.	Transition	Contrib.	Assignment	Exp. (nm)
S_1	414 (2.99)	0.0146	HOMO→LUMO	92%	IL/MLCT	
S_5	332 (3.73)	0.3026	HOMO-1→LUMO+1	46%	IL	331
			HOMO→LUMO+1	22%	IL/MLCT	
S_7	319 (3.89)	0.4976	HOMO→LUMO+1	29%	IL/MLCT	
			HOMO→LUMO+2	22%	IL/MC	

Table S2. The Partial Molecular Orbital Compositions and Absorption Transitions for **1c'** in Toluene. See Caption of Table S1 for more Details.

MO	Energy (eV)	Contribution (%)				
		$(p\text{-}MeOC_6H_4)_2N$	DTE (c)	Ru (s/p/d)	P ligand	Cl
LUMO+4	-0.01	52.31	28.74	11.79 (26/64/11)	7.00	0.15
LUMO+2	-0.25	58.79	15.44	19.85 (89/6/6)	5.73	0.18
LUMO	-1.86	8.43	85.18	3.50 (4/32/64)	2.79	0.10
HOMO	-4.50	16.07	75.49	6.00 (0/12/88)	2.02	0.43
HOMO-1	-5.47	56.30	32.72	8.62 (0/2/98)	0.94	1.42
HOMO-3	-5.83	13.02	48.36	28.96 (0/0/100)	2.06	7.59

State	*E*, nm (eV)	O.S.	Transition	Contrib.	Assignment	Exp.(nm)
S_1	608 (2.04)	0.7826	HOMO→LUMO	81%	IL	668
S_3	409 (3.03)	0.0946	HOMO-1→LUMO	88%	IL	406
S_4	378 (3.28)	0.2343	HOMO-3→LUMO	82%	IL/MLCT	
S_9	330 (3.76)	0.2894	HOMO→LUMO+4	23%	IL	311
			HOMO→LUMO+2	23%	IL/LMCT	

Table S3. The Partial Molecular Orbital Compositions and Absorption Transitions for [**1o'**]$^+$ in CH_2Cl_2. See Caption of Table S1 for more Details.

MO	Energy (eV)	Contribution (%)				
		$(p\text{-}MeOC_6H_4)_2N$	DTE (o)	Ru (s/p/d)	P ligand	Cl
αLUMO+8	-0.18	79.94	18.84	0.80 (12/86/1)	0.41	0.01
αLUMO+3	-0.84	19.79	78.82	1.18 (74/18/8)	0.21	0.00
αLUMO	-2.12	0.62	96.65	1.43 (4/32/63)	1.27	0.03
αHOMO	-5.22	74.65	25.30	0.04 (11/6/83)	0.01	0.00
αHOMO-1	-6.51	2.92	65.73	24.18 (0/1/99)	4.25	2.93
βLUMO+9	-0.16	80.70	18.30	0.65 (10/87/2)	0.34	0.00
βLUMO+4	-0.80	20.87	77.63	1.26 (73/18/9)	0.23	0.01
βLUMO+2	-1.30	0.35	86.77	6.59 (0/31/68)	6.06	0.23
βLUMO	-4.52	5.95	52.82	33.13 (0/2/98)	5.53	2.56
βHOMO	-5.12	68.21	27.59	3.44 (0/1/99)	0.45	0.31
βHOMO-1	-6.63	95.29	4.65	0.04 (0/1/98)	0.00	0.01
βHOMO-3	-6.80	39.57	55.83	3.31 (0/2/98)	0.34	0.95
βHOMO-4	-7.20	2.97	47.66	23.08 (0/10/90)	10.07	16.23
βHOMO-5	-7.30	29.76	54.18	6.38 (0/14/86)	3.98	5.70

State	*E*, nm (eV)	O.S.	Transition	Contrib.	Assignment	Exp.(nm)
S_3	760 (1.63)	0.2718	βHOMO-4→βLUMO	53%	IL/MC/LMCT	846
			βHOMO-3→βLUMO	35%	IL/LMCT	
S_4	713 (1.74)	0.022	βHOMO-1→βLUMO	98%	IL/LMCT	
S_6	678 (1.83)	0.0588	βHOMO-3→βLUMO	61%	IL/LMCT	
			βHOMO-4→βLUMO	30%	IL/MC/LMCT	
S_7	582 (2.13)	0.002	βHOMO-5→βLUMO	53%	IL/LMCT	598
			βHOMO-4→βLUMO	14%	IL/MC/LMCT	
S_{16}	420 (2.95)	0.1077	αHOMO-1→αLUMO	39%	IL/MLCT	418
			βHOMO→βLUMO+2	12%	IL	
S_{26}	351 (3.53)	0.4128	αHOMO→αLUMO+3	40%	IL	
			βHOMO→βLUMO+4	39%	IL	
S_{46}	296 (4.18)	0.2881	βHOMO→βLUMO+9	40%	IL	
			αHOMO→αLUMO+8	36%	IL	

Table S4. The Partial Molecular Orbital Compositions and Absorption Transitions for [**1c'**]$^+$ in CH_2Cl_2. See Caption of Table S1 for more Details.

MO	Energy	Contribution (%)				
		$(p\text{-}MeOC_6H_4)_2N$	DTE (c)	Ru (s/p/d)	P ligand	Cl
αLUMO	-2.99	9.70	82.87	4.55 (1/16/83)	2.72	0.15
αHOMO	-5.32	14.97	74.82	7.65 (0/4/96)	2.01	0.55
αHOMO-3	-6.68	7.97	44.77	35.66 (0/1/99)	1.84	9.76
βLUMO+1	-2.67	12.32	78.87	5.36 (1/18/81)	3.27	0.18
βLUMO	-3.89	11.37	78.56	6.92 (0/10/89)	2.83	0.33
βHOMO	-6.23	25.44	35.92	31.70 (0/0/100)	1.57	5.37
βHOMO-1	-6.25	23.34	31.34	36.35 (0/0/100)	2.77	6.20
βHOMO-2	-6.44	23.64	39.80	28.42 (0/1/99)	1.92	6.22
βHOMO-3	-7.01	61.48	35.06	1.90 (2/9/89)	0.48	1.08
βHOMO-4	-7.10	37.51	57.59	2.35 (3/13/84)	0.90	1.65
βHOMO-8	-7.73	83.90	15.07	0.08 (8/71/20)	0.57	0.38

State	*E*, nm (eV)	O.S.	Transition	Contrib.	Assignment	Exp.(nm)
S_1	928 (1.34)	0.0372	αHOMO→αLUMO	79%	IL	926
			βHOMO→βLUMO	22%	$IL/Ru^{II}\rightarrow DTE^+$	
S_3	810 (1.53)	0.9814	βHOMO→βLUMO	44%	$IL/Ru^{II}\rightarrow DTE^+$	
			βHOMO-1→βLUMO	25%	$IL/Ru^{II}\rightarrow DTE^+$	
			αHOMO→αLUMO	17%	IL	
S_4	706 (1.76)	0.0126	βHOMO-2→βLUMO	78%	IL/MLCT	
S_5	569 (2.18)	0.0527	βHOMO-4→βLUMO	44%	IL	666
			βHOMO-3→βLUMO	40%	IL	
S_8	482 (2.57)	0.0223	βHOMO-3→βLUMO	53%	IL	502
			βHOMO-4→βLUMO	41%	IL	
S_9	460 (2.69)	0.0209	αHOMO-3→αLUMO	30%	IL/MLCT	
			βHOMO-1→βLUMO+1	17%	IL/MLCT	
S_{17}	394 (3.15)	0.2852	βHOMO-8→βLUMO	43%	IL	
			αHOMO-3→αLUMO	13%	IL/MLCT	

Table S5. The Partial Molecular Orbital Compositions and Absorption Transitions for **2oo'** in Toluene. See Caption of Table S1 for more Details.

MO	Energy (eV)	Contribution (%)					
		$(p\text{-}MeOC_6H_4)_2N$	DTE (o)	Ru (s/p/d)	P ligand	DTE' (o)	$(p\text{-}MeOC_6H_4)_2N$
LUMO+2	-0.53	1.02	33.36	12.76 (0/99/1)	16.36	35.36	1.14
LUMO	-1.28	0.10	13.24	0.87 (40/47/13)	0.41	84.72	0.67
HOMO	-4.89	2.92	33.23	26.75 (0/0/100)	1.86	32.02	3.23
HOMO-1	-5.00	26.65	8.03	0.27 (0/28/72)	0.16	14.08	50.80

State	*E*, nm (eV)	O.S.	Transition	Contrib.	Assignment	Exp. (nm)
S_1	410 (3.02)	0.0211	HOMO→LUMO	66%	IL/MLCT/LLCT	418
			HOMO-1→LUMO	15%	IL/LLCT	
S_9	340 (3.64)	1.4445	HOMO→LUMO+2	67%	IL/MLCT/MC	337

Table S6. The Partial Molecular Orbital Compositions and Absorption Transitions for **2co'** in Toluene. See Caption of Table S1 for more Details.

MO	Energy (eV)	Contribution (%)					
		$(p\text{-}MeOC_6H_4)_2N$	DTE (c)	Ru (s/p/d)	P	DTE (o)	$(p\text{-}MeOC_6H_4)_2N$
LUMO+7	-0.14	0.39	1.38	0.92 (1/86/13)	0.46	11.04	85.80
LUMO+4	-0.27	68.00	14.80	6.89 (76/10/15)	1.36	8.29	0.66
LUMO+2	-0.52	2.58	12.11	11.19 (2/92/6)	14.02	57.53	2.57
LUMO+1	-1.34	0.01	0.09	0.72 (32/33/34)	0.28	98.01	0.88
LUMO	-1.89	8.40	84.72	3.01 (4/44/51)	3.25	0.61	0.00
HOMO	-4.52	16.01	74.74	5.74 (1/9/91)	1.52	1.99	0.01
HOMO-1	-5.03	0.09	0.25	0.55 (0/22/77)	0.24	19.78	79.09
HOMO-2	-5.20	5.01	10.03	23.10 (0/15/85)	7.18	51.63	3.04
HOMO-3	-5.50	34.92	27.45	24.76 (0/1/99)	1.67	11.17	0.03
HOMO-4	-5.59	26.31	30.07	25.22 (0/5/95)	3.70	14.68	0.03

State	*E*, nm (eV)	O.S.	Transition	Contrib.	Assignment	Exp. (nm)
S_1	611 (2.03)	0.9202	HOMO→LUMO	82%	IL	664
S_5	415 (2.99)	0.1307	HOMO-3→LUMO	59%	IL/MLCT/LLCT	
			HOMO-2→LUMO	21%	LLCT/MLCT/IL	
S_7	404 (3.07)	0.1983	HOMO-4→LUMO	67%	IL/MLCT/LLCT	403
			HOMO-3→LUMO	16%	IL/MLCT/LLCT	
S_{10}	347 (3.58)	0.3498	HOMO→LUMO+2	49%	LLCT/IL	
			HOMO→LUMO+4	17%	IL	
S_{21}	313 (3.97)	0.3139	HOMO-2→LUMO+2	23%	IL/MLCT/MC	323
			HOMO-3→LUMO+1	22%	LLCT/MLCT/IL	
			HOMO-1→LUMO+2	10%	IL/LLCT/LMCT	
			HOMO-4→LUMO+1	9%	LLCT/MLCT/IL	
S_{23}	309 (4.01)	0.2699	HOMO-4→LUMO+1	32%	LLCT/MLCT/IL	
			HOMO-2→LUMO+2	23%	IL /MLCT/MC	
			HOMO-1→LUMO+7	12%	IL	
			HOMO-3→LUMO+1	10%	LLCT/MLCT/IL	

Table S7. The Partial Molecular Orbital Compositions and Absorption Transitions for **2cc'** in Toluene. See Caption of Table S1 for more Details.

MO	Energy	Contribution (%)					
	(eV)	$(p\text{-}MeOC_6H_4)_2N$	DTE (c)	Ru (s/p/d)	P ligand	DTE' (c)	$(p\text{-}MeOC_6H_4)_2N$
LUMO+1	-1.85	4.70	44.99	3.23 (0/5/95)	0.15	42.49	4.44
LUMO	-2.01	3.84	40.75	2.54 (7/92/1)	5.73	43.07	4.07
HOMO	-4.52	8.14	38.79	6.59 (1/0/99)	0.44	38.07	7.97
HOMO-1	-4.65	9.24	37.70	1.80 (1/95/4)	3.79	38.12	9.35
HOMO-2	-5.50	21.74	13.85	8.38 (0/0/100)	0.44	20.70	34.89
HOMO-3	-5.56	36.50	23.84	6.87 (1/6/93)	1.34	13.36	18.08
HOMO-5	-5.90	7.62	32.71	22.10 (0/0/100)	1.58	30.18	5.81
HOMO-6	-6.14	4.78	42.26	1.16 (2/75/24)	2.53	44.21	5.06
HOMO-7	-6.24	2.88	42.62	7.93 (1/2/97)	1.10	42.54	2.93

State	*E*, nm (eV)	O.S.	Transition	Contrib.	Assignment	Exp. (nm)
S_1	638 (1.94)	1.7441	HOMO→LUMO	71%	IL	681
			HOMO-1→LUMO+1	15%	IL	
S_6	416 (2.98)	0.1696	HOMO-2→LUMO	50%	IL	
			HOMO-3→LUMO+1	31%	IL/LLCT	
S_9	383 (3.24)	0.469	HOMO-5→LUMO	65%	IL/MLCT	400
			HOMO-3→LUMO+1	10%	IL/LLCT	
			HOMO-6→LUMO+1	8%	IL	
S_{13}	353 (3.51)	0.1842	HOMO-3→LUMO+1	29%	IL/LLCT	
			HOMO-7→LUMO	24%	IL	
			HOMO-5→LUMO	20%	IL/MLCT	

Table S8. The Partial Molecular Orbital Compositions and Absorption Transitions for **[2oo']$^+$** in CH_2Cl_2. See Caption of Table S1 for more Details.

MO	Energy (eV)	Contribution (%)					
		(p-$MeOC_6H_4)_2N$	DTE (o)	Ru (s/p/d)	P ligand	DTE' (o)	(p-$MeOC_6H_4)_2N$
αLUMO+12	-0.06	9.85	2.47	1.14 (15/78/7)	0.88	16.09	69.57
αLUMO+11	-0.07	68.47	16.68	1.78 (1/98/1)	1.57	2.81	8.68
αLUMO+6	-0.71	2.39	9.92	3.19 (75/18/7)	0.61	67.44	16.45
αHOMO	-5.13	0.04	0.02	0.02 (5/22/73)	0.01	22.82	77.10
αHOMO-1	-5.14	77.24	22.68	0.02 (8/19/73)	0.01	0.01	0.04
βLUMO+13	-0.06	12.61	2.91	0.68 (12/77/11)	0.50	15.02	68.27
βLUMO+6	-0.06	5.47	22.23	4.23 (41/11/47)	6.25	49.53	11.48
βLUMO	-4.59	1.41	30.40	35.35 (0/0/100)	2.25	29.24	1.34
βHOMO	-5.10	19.99	6.42	0.12 (1/33/65)	0.10	16.97	56.40
βHOMO-2	-6.09	0.75	31.79	10.15 (0/95/5)	22.53	34.02	0.76
βHOMO-21	-8.33	2.05	25.39	5.32 (1/95/4)	37.77	27.19	2.28
βHOMO-22	-8.84	0.22	28.48	27.20 (0/0/99)	12.85	30.81	0.44

State	*E*, nm (eV)	O.S.	Transition	Contrib.	Assignment
S_4	1306 (0.95)	0.6172	βHOMO-2→βLUMO	83%	IL/LMCT/MC
S_{28}	427 (2.90)	0.1723	βHOMO-21→βLUMO	29%	IL/LMCT
			βHOMO-22→βLUMO	14%	IL/MC/LMCT
S_{51}	349 (3.55)	0.3484	αHOMO→αLUMO+6	34%	IL/LLCT
			βHOMO→βLUMO+6	25%	IL
S_{89}	294 (4.22)	0.2574	αHOMO→αLUMO+12	21%	IL/LLCT
			βHOMO→βLUMO+13	16%	IL/LLCT
S_{92}	293 (4.23)	0.322	αHOMO-1→αLUMO+11	32%	IL/LLCT

Table S9. The Partial Molecular Orbital Compositions and Absorption Transitions for [**2co'**]$^+$ in CH_2Cl_2. See Caption of Table S1 for more Details.

MO	Energy (eV)	Contribution (%)					
		$(p\text{-}MeOC_6H_4)_2N$	DTE (c)	Ru (s/p/d)	P ligand	DTE (o)	$(p\text{-}MeOC_6H_4)_2N$
αLUMO+2	-1.51	9.20	52.45	2.09 (8/37/55)	2.53	33.49	0.23
αLUMO+1	-1.55	4.51	25.99	1.86 (3/80/17)	3.41	63.79	0.44
αLUMO	-3.11	9.75	82.82	3.77 (1/24/75)	3.07	0.59	0.00
αHOMO	-5.16	0.01	0.05	0.07 (1/22/77)	0.02	21.40	78.45
αHOMO-1	-5.40	13.39	69.31	9.15 (0/0/99)	0.96	6.98	0.20
αHOMO-5	-6.53	65.19	24.86	1.58 (1/20/79)	1.50	1.73	5.15
αHOMO-7	-6.97	2.19	28.89	18.42 (0/4/96)	8.91	39.06	2.52
αHOMO-8	-7.06	2.06	14.59	7.23 (0/11/89)	6.22	63.51	6.38
βLUMO+1	-2.78	12.25	78.78	4.35 (1/28/71)	3.81	0.80	0.00
βLUMO	-4.01	11.39	79.22	5.64 (1/12/87)	2.70	1.05	0.00
βHOMO	-5.16	0.00	0.02	0.05 (1/39/60)	0.03	21.38	78.52
βHOMO-1	-5.72	0.45	7.40	21.82 (0/26/74)	8.80	60.74	0.79
βHOMO-2	-6.23	1.58	25.53	48.87 (0/1/99)	2.25	21.77	0.00
βHOMO-3	-6.39	66.99	27.85	1.76 (1/21/78)	1.39	1.95	0.06
βHOMO-5	-6.68	1.25	6.52	4.43 (0/1/99)	0.98	58.60	28.22
βHOMO-6	-6.82	5.04	41.37	16.56 (0/11/89	12.56	20.09	4.39
βHOMO-16	-7.91	1.72	8.18	8.69 (0/55/45)	19.05	37.75	24.61

State	*E*, nm (eV)	O.S.	Transition	Contrib.	Assignment
S_1	1296 (0.96)	0.0037	βHOMO→ βLUMO	99%	LLCT
S_2	1051 (1.18)	0.1285	βHOMO-1→ βLUMO	83%	LLCT/MLCT
S_4	873 (1.42)	0.6553	βHOMO-2→ βLUMO	62%	MLCT/IL/LLCT
			αHOMO-1→ αLUMO	19%	IL
S_5	754 (1.64)	0.3109	βHOMO-3→ βLUMO	85%	IL
S_7	627 (1.98)	0.0749	βHOMO-6→ βLUMO	59%	IL/LLCT/MLCT
			βHOMO-5→ βLUMO	14%	LLCT
S_{22}	439 (2.82)	0.1232	βHOMO-2→βLUMO+1	21%	MLCT/IL/LLCT
			αHOMO-1→ αLUMO+2	19%	IL/LLCT
			αHOMO-5→ αLUMO	14%	IL
			αHOMO-1→ αLUMO+1	11%	LLCT/IL
S_{28}	406 (3.05)	0.131	αHOMO-7→ αLUMO	22%	LLCT/IL/MLCT
			βHOMO-3→ βLUMO+1	17%	IL
			αHOMO-1→ αLUMO+2	16%	IL/LLCT
			αHOMO-8→ αLUMO	8%	LLCT/IL
S_{36}	376 (3.30)	0.1711	βHOMO-6→ βLUMO+1	20%	IL/LLCT/MLCT
			βHOMO-16→ βLUMO	14%	LLCT

Table S10. The Partial Molecular Orbital Compositions and Absorption Transitions for [**2cc'**]$^+$ in CH_2Cl_2. See Caption of Table S1 for more Details.

MO	Energy (eV)	Contribution (%)					
		$(p\text{-}MeOC_6H_4)_2N$	DTE (c)	Ru (s/p/d)	P ligand	DTE' (c)	$(p\text{-}MeOC_6H_4)_2N$
αLUMO+2	-1.09	4.37	23.47	3.31 (9/84/7)	7.36	51.95	9.55
αLUMO+1	-2.49	6.74	59.69	3.52 (0/6/94)	0.41	26.53	3.12
αLUMO	-2.67	2.63	25.57	2.50 (5/88/7)	5.39	57.75	6.16
αHOMO	-5.03	12.85	58.47	5.38 (1/3/96)	0.60	18.75	3.95
αHOMO-5	-6.54	4.13	33.94	29.64 (0/0/100)	1.62	27.40	3.26
βLUMO+4	-2.37	12.27	44.10	3.76 (8/5/87)	0.81	29.61	9.45
βLUMO+2	-2.58	7.11	51.52	4.33 (0/3/97)	0.24	32.29	4.52
βLUMO+1	-4.15	4.33	31.48	2.29 (4/91/4)	5.06	49.83	7.01
βLUMO	-4.66	5.34	36.28	9.08 (1/0/99)	0.57	42.45	6.28
βHOMO	-5.96	6.30	42.78	2.83 (1/96/3)	6.18	36.66	5.26
βHOMO-2	-6.17	27.68	17.39	9.04 (0/3/97)	1.04	17.20	27.65
βHOMO-3	-6.31	0.56	17.86	40.19 (0/0/100)	2.04	23.24	16.10
βHOMO-4	-6.68	10.94	29.80	23.70 (0/0/100)	1.83	25.28	8.44
βHOMO-5	-6.89	9.35	51.49	1.85 (3/57/40)	3.59	28.67	5.06

State	E, nm (eV)	O.S.	Transition	Contrib.	Assignment
S_2	1241 (1.00)	0.0033	βHOMO→βLUMO+1	76%	IL
			αHOMO→αLUMO+1	29%	IL
S_3	1102 (1.13)	0.3024	βHOMO→βLUMO+2	48%	IL
			αHOMO→αLUMO	37%	IL/LLCT
S_4	1086 (1.14)	0.0315	βHOMO-3→βLUMO	56%	IL/MLCT/LLCT
			βHOMO-2→βLUMO	28%	IL
S_8	674 (1.84)	0.4895	βHOMO→βLUMO+2	35%	IL
			αHOMO→αLUMO	17%	IL/LLCT
			βHOMO-5→βLUMO	12%	IL/LLCT
S_{10}	629 (1.97)	0.3835	βHOMO-5→βLUMO	73%	IL/LLCT
			αHOMO→αLUMO	7%	IL/LLCT
S_{37}	389 (3.19)	0.4753	αHOMO-5→αLUMO	40%	IL/MLCT/LLCT
			βHOMO-4→βLUMO+1	14%	IL/MLCT
S_{58}	342 (3.63)	0.1798	αHOMO→αLUMO+2	13%	IL/LLCT
			βHOMO→βLUMO+4	11%	IL

Table S11. The Partial Molecular Orbital Compositions and Absorption Transitions for **[2oo']$^{2+}$** in CH_2Cl_2. See Caption of Table S1 for more Details.

MO	Energy (eV)	Contribution (%)					
		$(p\text{-}MeOC_6H_4)_2N$	DTE (o)	Ru (s/p/d)	P ligand	DTE' (o)	$(p\text{-}MeOC_6H_4)_2N$
αLUMO+8	-1.03	5.85	37.24	4.36 (1/97/1)	10.83	34.44	7.28
αLUMO+5	-1.33	0.01	0.00	0.01 (22/32/45)	0.01	12.28	87.70
αHOMO	-5.31	0.09	31.41	33.85 (0/0/100)	1.30	33.25	0.10
αHOMO-3	-6.35	8.92	3.21	0.21 (0/15/85)	0.14	22.26	65.26
βLUMO+8	-1.04	3.36	38.81	4.51 (2/97/1)	11.11	38.10	4.11
βLUMO+1	-4.65	11.23	5.15	0.91 (0/1/99)	0.05	25.11	57.56
βLUMO	-4.66	59.24	23.73	0.14 (3/23/74)	0.10	4.88	11.91
βHOMO	-5.27	1.68	30.19	32.70 (0/0/100)	1.30	32.22	1.92
βHOMO-1	-5.86	0.19	29.61	36.38 (0/6/94)	8.48	25.20	0.14
βHOMO-2	-6.03	0.34	30.29	19.67 (0/22/78)	16.18	33.12	0.40
βHOMO-5	-7.22	88.98	6.04	0.95 (1/2/97)	0.20	1.19	2.63
βHOMO-6	-7.22	5.55	3.58	2.45 (0/2/98)	0.49	8.22	79.71
βHOMO-8	-7.32	13.35	31.39	0.28 (1/68/31)	1.18	35.01	18.78
βHOMO-9	-7.42	13.16	24.93	14.36 (0/2/98)	2.91	28.24	16.39

State	*E*, nm (eV)	O.S.	Transition	Contrib.	Assignment	Exp. (nm)
S_4	1287 (0.96)	0.0005	βHOMO-1→βLUMO+1	57%	MLCT/IL/LLCT	1265
			βHOMO-1→βLUMO	42%	MLCT/IL/LLCT	
S_5	1194 (1.04)	0.0014	βHOMO-2→βLUMO+1	98%	LLCT/IL/MLCT	
S_7	703 (1.76)	0.2567	βHOMO-5→βLUMO	55%	IL	
S_8	698 (1.78)	0.2851	βHOMO-6→βLUMO+1	52%	IL	
			βHOMO-6→βLUMO	13%	LLCT/IL	
S_{61}	350 (3.55)	0.7927	βHOMO→βLUMO+8	18%	IL/MLCT	
			αHOMO→αLUMO+8	15%	IL/MLCT	
			αHOMO-3→αLUMO+5	9%	IL	

Table S12. The Partial Molecular Orbital Compositions and Absorption Transitions for **[2co']$^{2+}$** in CH_2Cl_2. See Caption of Table S1 for more Details.

MO	Energy (eV)	Contribution (%)					
		$(p\text{-}MeOC_6H_4)_2N$	DTE (c)	Ru (s/p/d)	P ligand	DTE'(o)	$(p\text{-}MeOC_6H_4)_2N$
αLUMO+6	-1.04	2.26	9.92	6.28 (4/72/24)	9.66	65.67	6.22
αLUMO	-3.11	10.72	82.93	3.29 (1/26/73)	2.63	0.43	0.00
αHOMO	-5.44	12.72	74.86	8.32 (1/3/96)	1.79	2.30	0.00
αHOMO-1	-5.85	0.52	7.70	29.12 (0/12/88)	6.40	55.89	0.37
αHOMO-13	-7.90	88.30	11.37	0.12 (9/10/81)	0.15	0.07	0.00
βLUMO+6	-1.16	12.71	55.43	4.81 (3/80/17)	8.98	17.05	1.02
βLUMO+2	-2.78	12.58	79.02	4.17 (1/32/68)	3.59	0.63	0.00
βLUMO+1	-4.01	12.01	79.77	4.99 (1/17/82)	2.61	0.62	0.00
βLUMO	-4.64	0.00	0.01	0.05 (3/27/70)	0.03	28.11	71.80
βHOMO	-5.83	0.18	7.04	29.64 (0/12/88)	6.32	56.36	0.47
βHOMO-1	-6.30	11.61	28.49	39.41 (0/2/98)	2.75	17.74	0.00
βHOMO-2	-6.44	59.13	25.92	7.70 (0/11/89)	2.05	5.18	0.01
βHOMO-6	-7.23	0.00	0.02	0.00 (1/44/54)	0.01	5.23	94.73
βHOMO-7	-7.36	0.51	18.16	3.25 (1/68/30)	11.20	43.62	23.27
βHOMO-20	-8.80	0.45	26.96	23.26 (0/9/91)	23.23	24.55	1.54

State	*E*, nm (eV)	O.S.	Transition	Contrib.	Assignment	Exp. (nm)
S_2	1196 (1.04)	0.0185	βHOMO→βLUMO+1	86%	LLCT/MLCT	1194
S_3	924 (1.34)	0.1633	αHOMO→αLUMO	85%	IL	
S_5	818 (1.52)	0.6185	βHOMO-1→βLUMO+1	75%	IL/MLCT/LLCT	
S_8	695 (1.78)	0.2553	βHOMO-6→βLUMO	73%	IL	662
			βHOMO-7→βLUMO	12%	IL/LLCT	
S_{30}	422 (2.94)	0.2215	βHOMO-1→βLUMO+2	36%	IL/MLCT/LLCT	401
			βHOMO-2→βLUMO+2	16%	IL	
S_{86}	308 (4.03)	0.2805	αHOMO-1→αLUMO+6	14%	IL/MLCT	
			βHOMO→βLUMO+6	12%	LLCT/MLCT/IL	
			αHOMO-13→αLUMO	12%	IL	
			βHOMO-20→βLUMO+1	12%	LLCT/IL/MLCT	

Table S13. The Partial Molecular Orbital Compositions and Absorption Transitions for **[2cc']$^{2+}$** in CH_2Cl_2. See Caption of Table S1 for more Details.

MO	Energy (eV)	Contribution (%)					
		$(p\text{-}MeOC_6H_4)_2N$	DTE (c)	Ru (s/p/d)	P ligand	DTE' (c)	$(p\text{-}MeOC_6H_4)_2N$
αLUMO+1	-3.15	5.92	40.66	3.60 (0/1/99)	0.11	43.44	6.27
αLUMO	-3.31	5.86	42.67	1.70 (3/95/2)	4.31	40.00	5.45
αHOMO	-5.49	5.77	38.33	10.01 (1/0/99)	0.52	39.50	5.88
αHOMO-1	-5.70	6.67	40.49	2.11 (1/87/12)	5.26	39.10	6.37
αHOMO-3	-6.58	55.32	18.96	5.23 (0/1/99)	0.40	5.70	14.41
αHOMO-4	-6.63	16.61	12.07	14.56 (0/1/99)	1.39	19.46	35.90
αHOMO-5	-7.01	2.43	29.61	34.55 (0/0/100)	2.26	29.11	2.04
βLUMO+2	-2.98	6.67	40.04	2.70 (2/96/2)	6.17	38.08	6.34
βLUMO+1	-4.05	7.09	39.71	4.39 (2/1/97)	0.34	41.23	7.24
βLUMO	-4.19	5.89	41.06	2.53 (1/95/4)	5.38	39.56	5.58
βHOMO	-6.46	6.97	8.77	14.70 (0/0/100)	0.63	25.53	43.41
βHOMO-1	-6.48	57.97	26.48	7.28 (0/1/99)	0.56	4.09	3.62
βHOMO-3	-6.72	6.22	28.02	34.38 (0/0/100)	2.54	25.46	3.38

State	*E*, nm (eV)	O.S.	Transition	Contrib.	Assignment	Exp. (nm)
S_1	1052 (1.18)	0.3611	αHOMO→αLUMO	69%	IL/MLCT	1160
			αHOMO-1→αLUMO+1	27%	IL	
S_2	900 (1.38)	0.0011	αHOMO→αLUMO+1	42%	IL/MLCT	995
			αHOMO-1→αLUMO	38%	IL	
S_3	829 (1.49)	0.5585	βHOMO→βLUMO	50%	IL/LLCT/MLCT	
			βHOMO-1→βLUMO+1	20%	IL/LLCT	
			βHOMO-1→βLUMO	7%	IL/LLCT	
S_7	679 (1.83)	0.2501	βHOMO-3→βLUMO	72%	IL/MLCT	660
S_{42}	395 (3.14)	0.4836	βHOMO-3→βLUMO+2	39%	IL/MLCT	395
			αHOMO-5→αLUMO	16%	IL/MLCT	
			αHOMO-4→αLUMO+1	12%	IL/MLCT	
			αHOMO-3→αLUMO	10%	IL/LLCT	

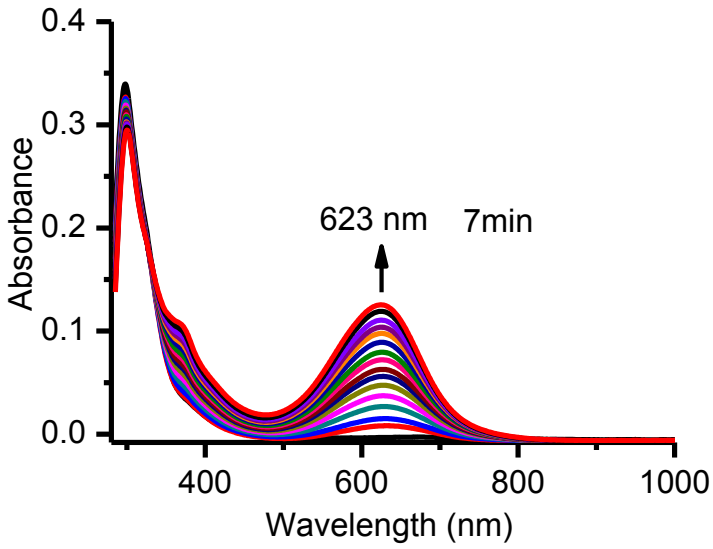

Fig. S1 UV-Vis absorption spectral changes of L1o (2×10^{-5} M) in toluene at 298 K upon irradiation at 312 nm due to the conversion of L1o into L1c.

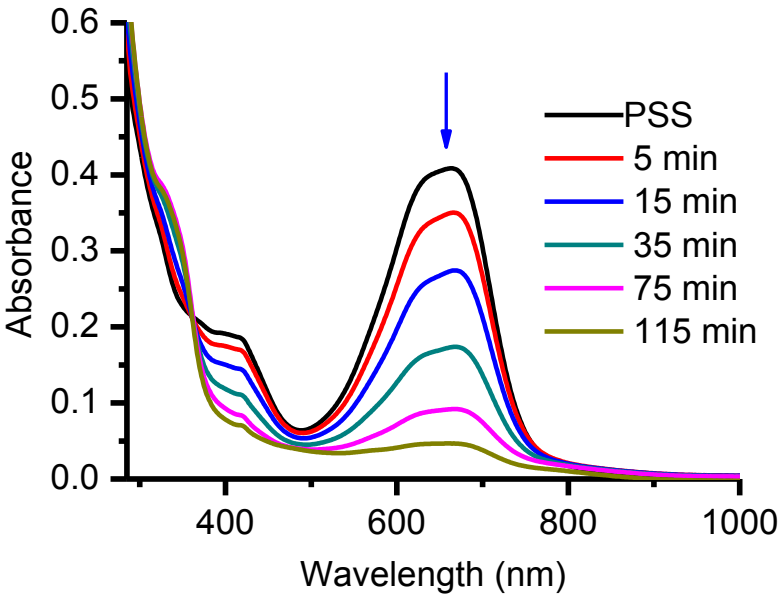

Fig. S2 UV-Vis absorption spectral changes of ring-closed **1c** (2×10^{-5} M) in toluene at 298 K upon irradiation at λ = 675 nm, showing the conversion of **1c** to **1o** through photo-induced cycloreversion.

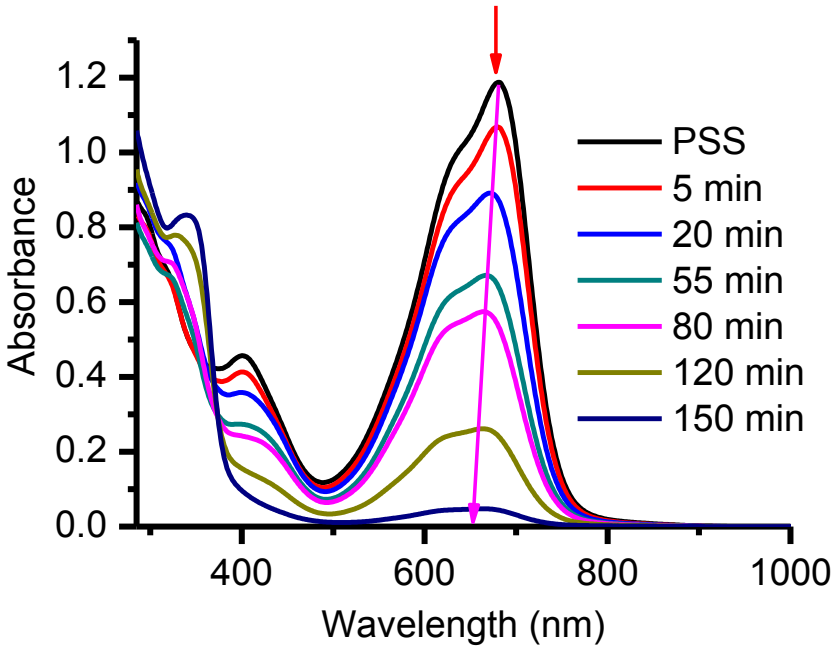

Fig. S3 UV-Vis absorption spectral changes of dually ring-closed **2cc** (2×10^{-5} M) in toluene at 298 K upon irradiation at λ = 675 nm, showing the stepwise conversion of **2cc** → **2co** → **2oo** through photo-induced cycloreversion.

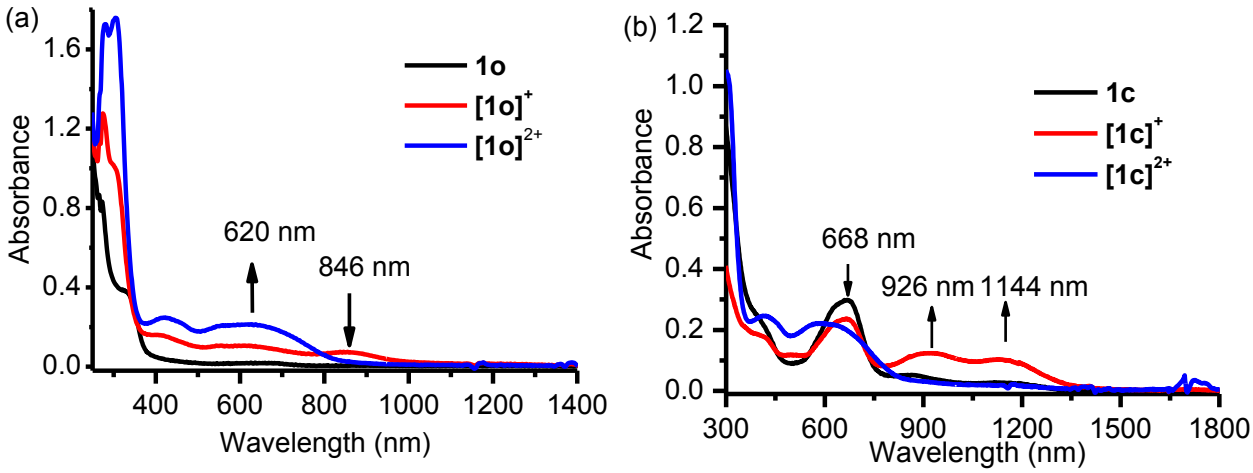

Fig. S4 UV-Vis-NIR absorption spectra of dichloromethane solutions of (a) open form of molecule **1o** (2×10^{-5} M) and (b) closed form of molecule **1c** (2×10^{-5} M) following addition of $[N(C_6H_5Br\text{-}4)_3](SbCl_6)$.

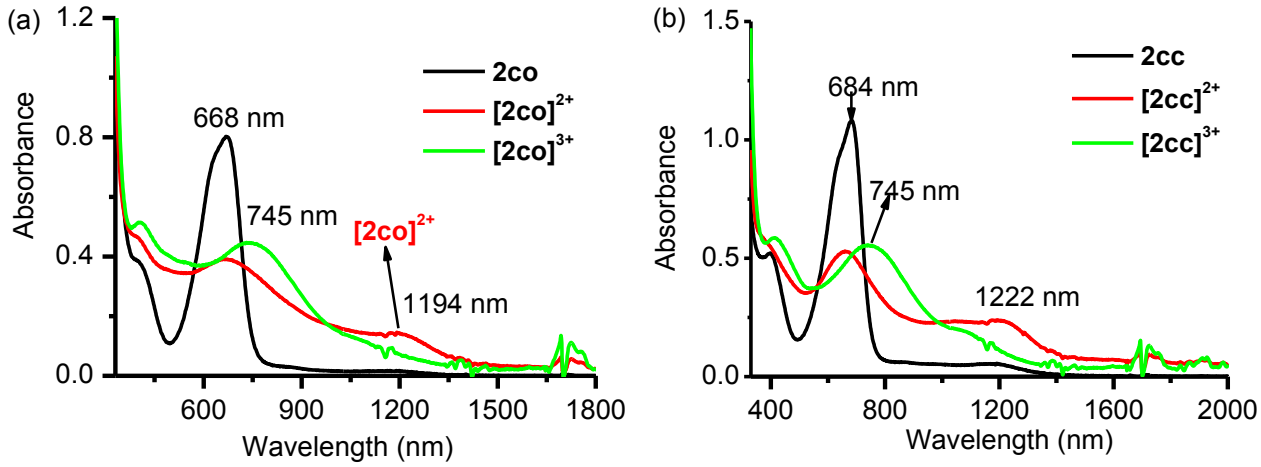

Fig. S5 Optical absorption spectra of dichloromethane solutions of (a) single closed form of molecule **2co** (2×10^{-5} M) and (b) dual closed form of molecule **2cc** (2×10^{-5} M) following the addition of $[N(C_6H_5Br\text{-}4)_3](SbCl_6)$.

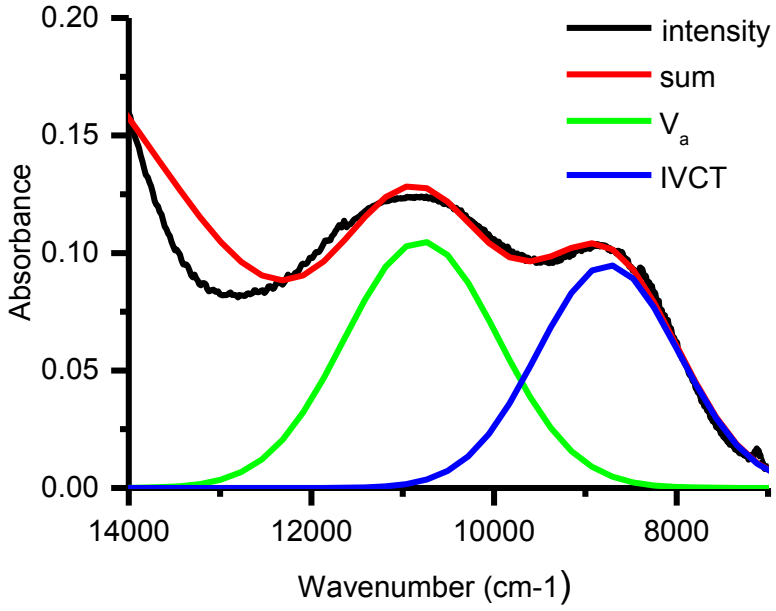

Fig. S6 Gaussian deconvolution for the NIR band of **[1c]**$^{+}$.

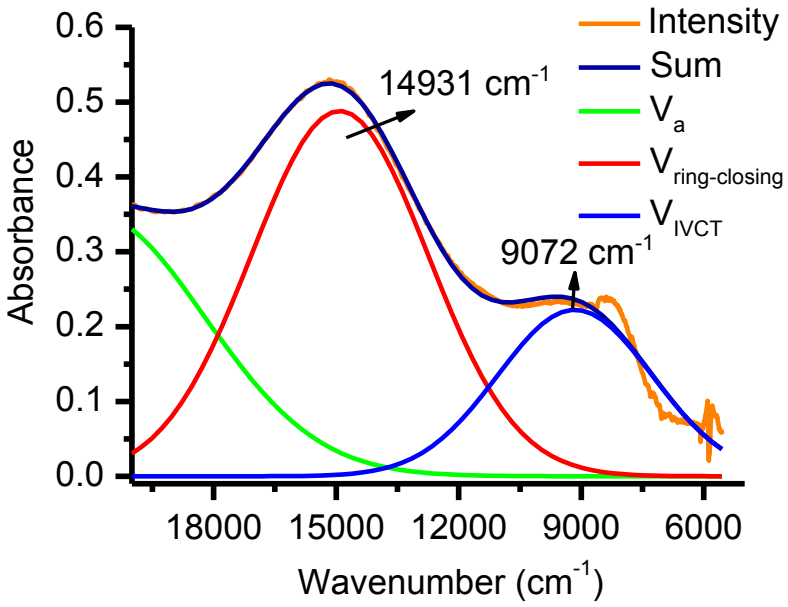

Fig. S7 Gaussian deconvolution for the NIR band of **[2cc]**$^{2+}$.

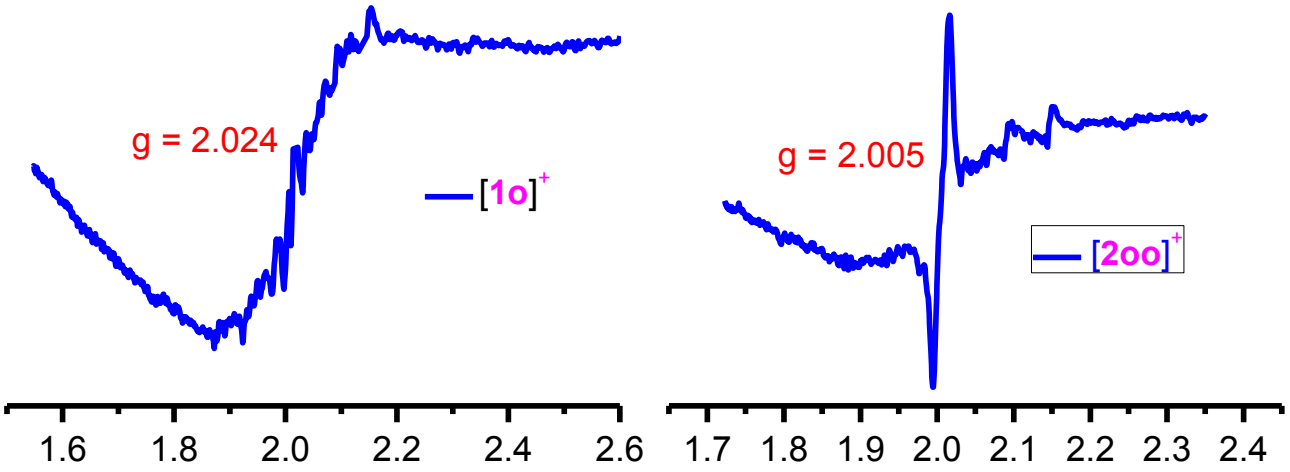

Fig. S8 The ESR spectra of [**1o**]$^+$ and [**2oo**]$^+$ in CH_2Cl_2 solutions at room temperature. One-electron oxidized species [**1o**]$^+$ and [**2oo**]$^+$ were accessed by the addition of one equivalent $[N(C_6H_4Br\text{-}4)_3](SbCl_6)$ to CH_2Cl_2 solutions of **1o** and **2oo**, respectively.

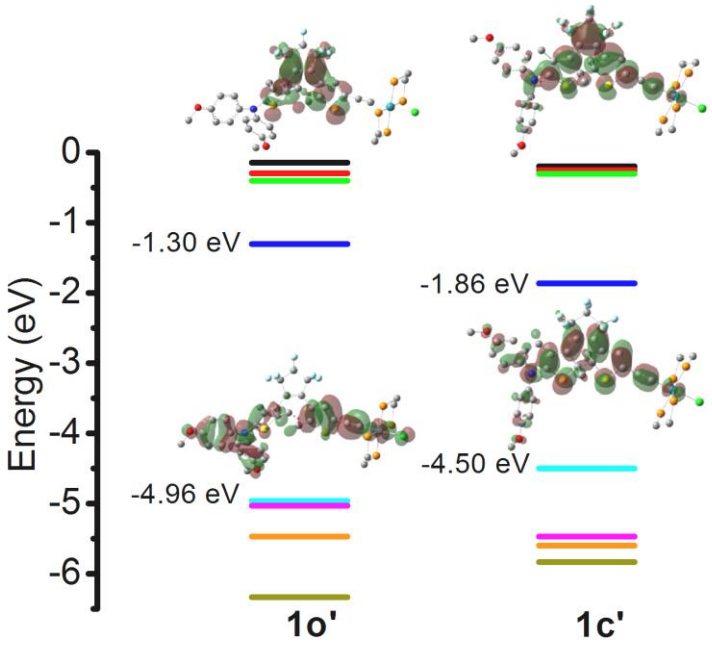

Fig. S9 Energy levels of the frontier orbitals of **1o'** and **1c'** as obtained with the PBE0 functional. The topology of the HOMO and LUMO are also given (isovalue = 0.02).

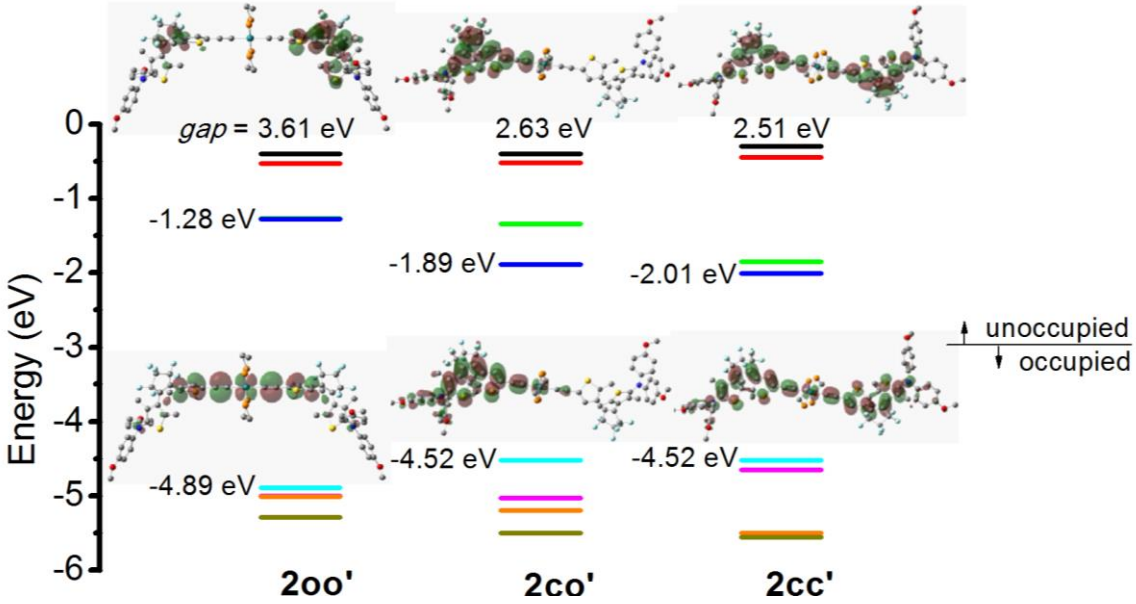

Fig. S10 Energy levels of frontier orbitals for **2oo'**, **2co'**, and **2cc'**. See the caption of Fig. S6 for more details.

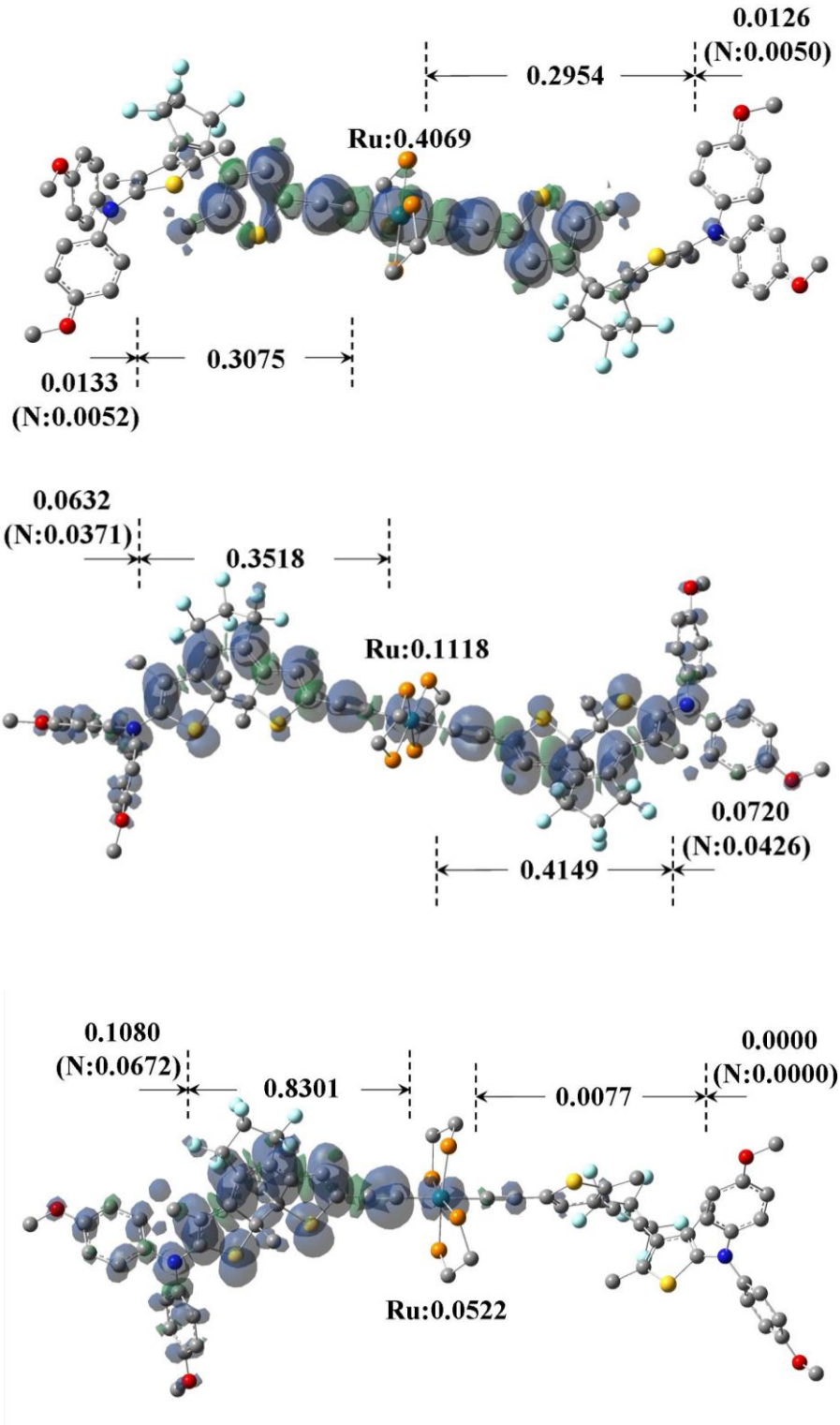

Fig. S11 Spin density of **[2oo']**$^+$ (top), **[2co']**$^+$ (middle), and **[2cc']**$^+$ (down) determined at the DFT(PBE0) level (isovalue = 0.0008).

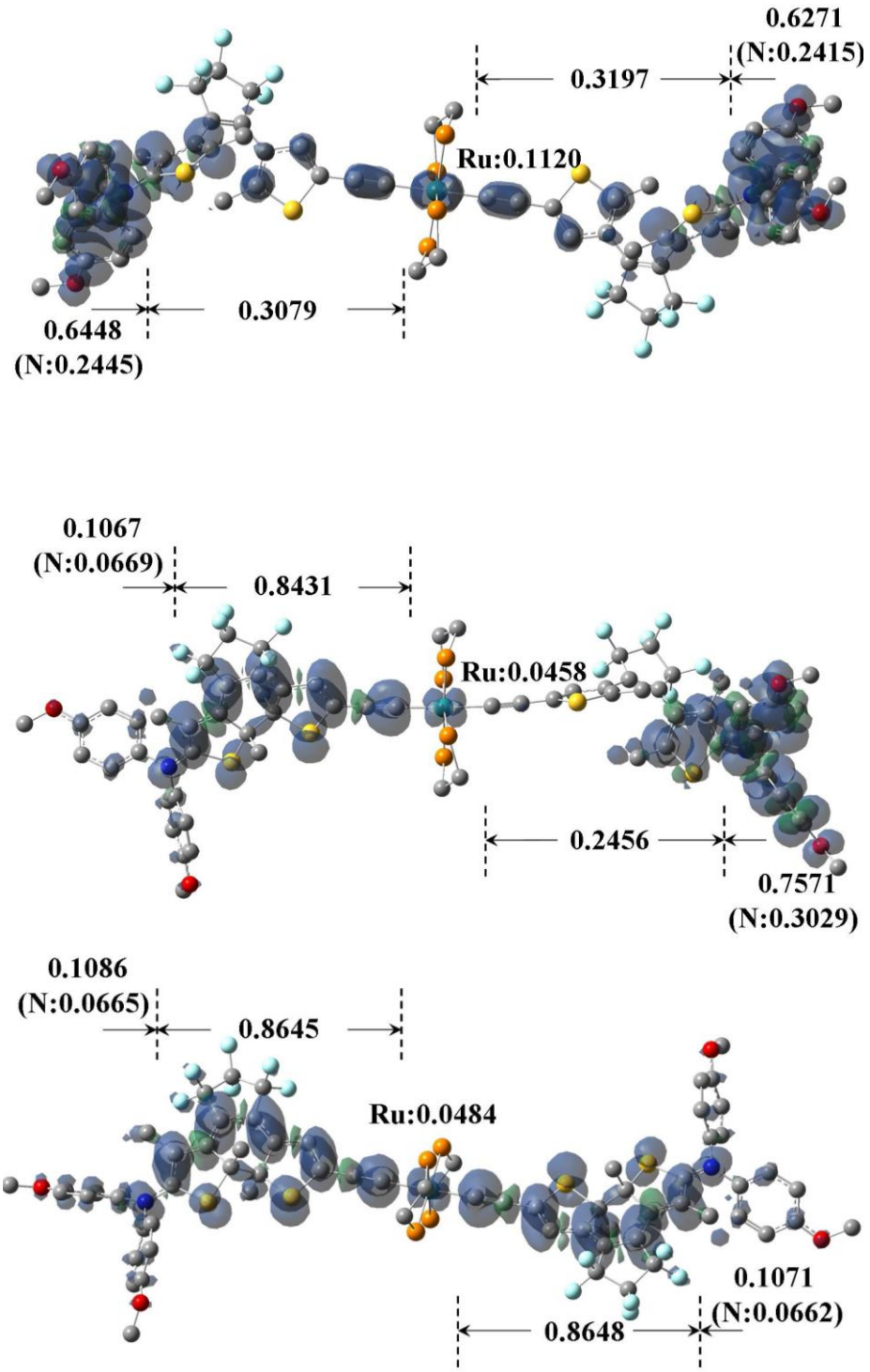

Fig. S12 Spin density of **[2oo']**$^{2+}$ (top), **[2co']**$^{2+}$ (middle), and **[2cc']**$^{2+}$ (down) determined at the DFT(PBE0) level (isovalue = 0.0008).

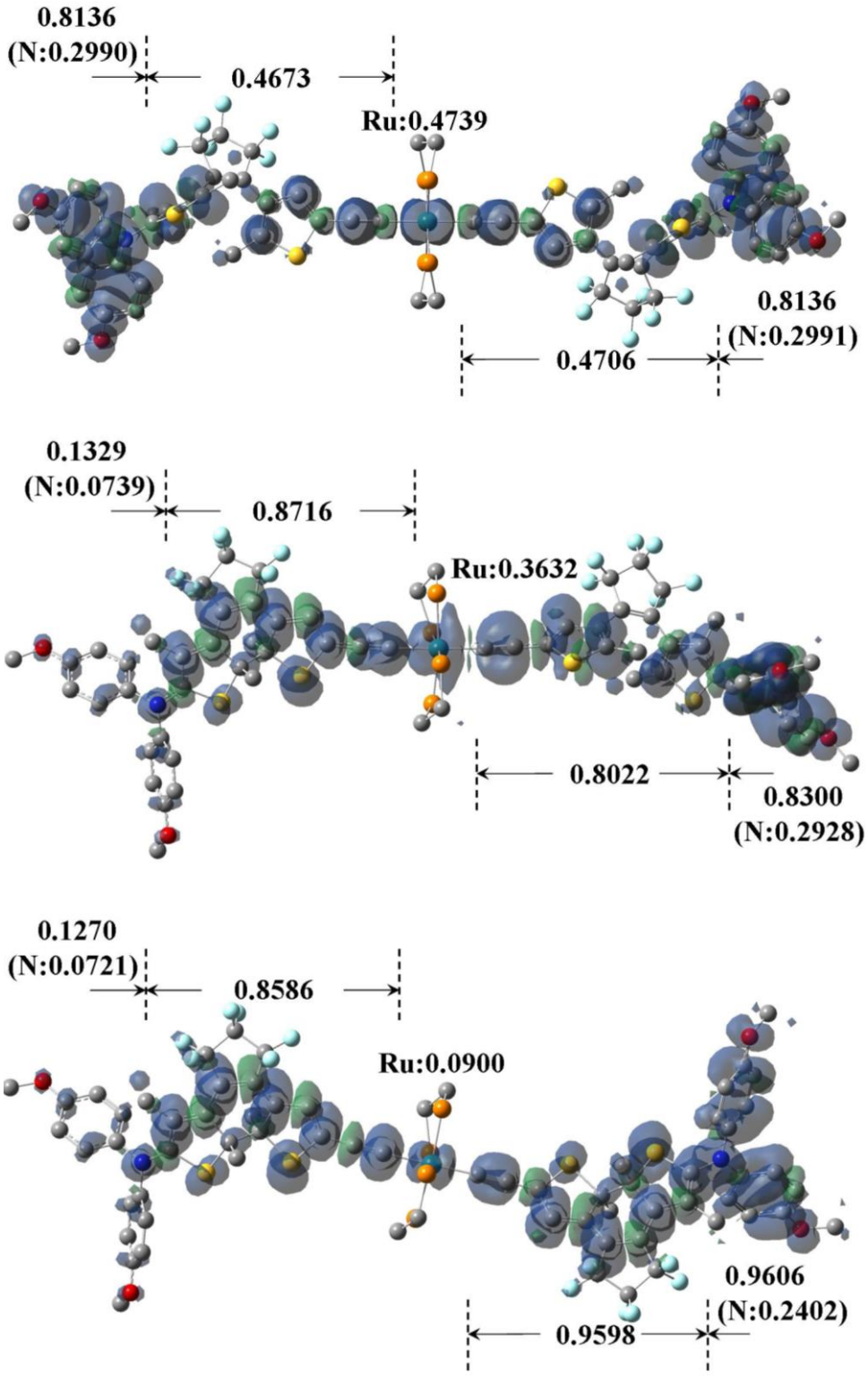

Fig. S13 Spin density of **[2oo']**$^{3+}$ (top), **[2co']**$^{3+}$ (middle), and **[2cc']**$^{3+}$ (down) determined at the DFT(PBE0) level (isovalue = 0.0008)

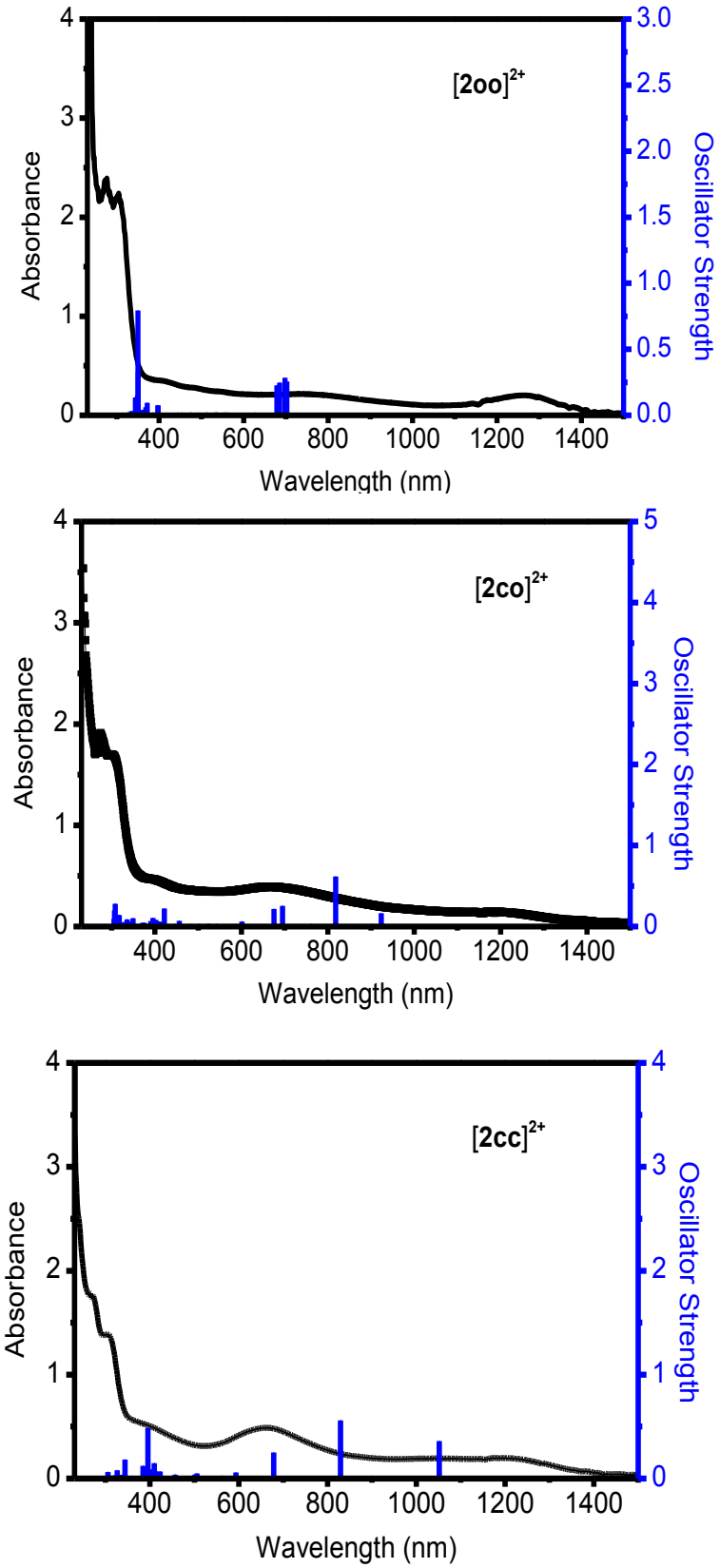

Fig. S14 The calculated (blue vertical bars) and measured (black line) absorption spectra of **[2oo]**$^{2+}$, **[2co]**$^{2+}$, and **[2cc]**$^{2+}$ in CH_2Cl_2.

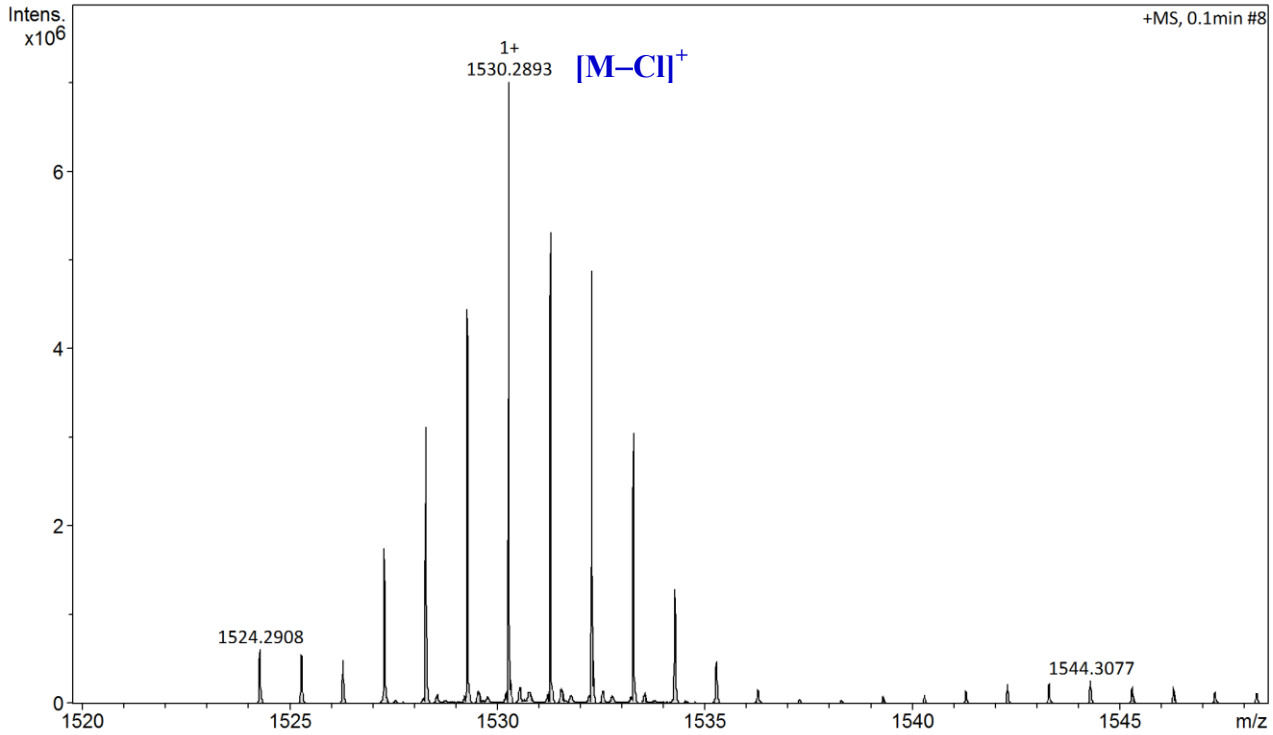

Fig. S15 The high resolution mass spectrometry with isotopic patters for **1o**.

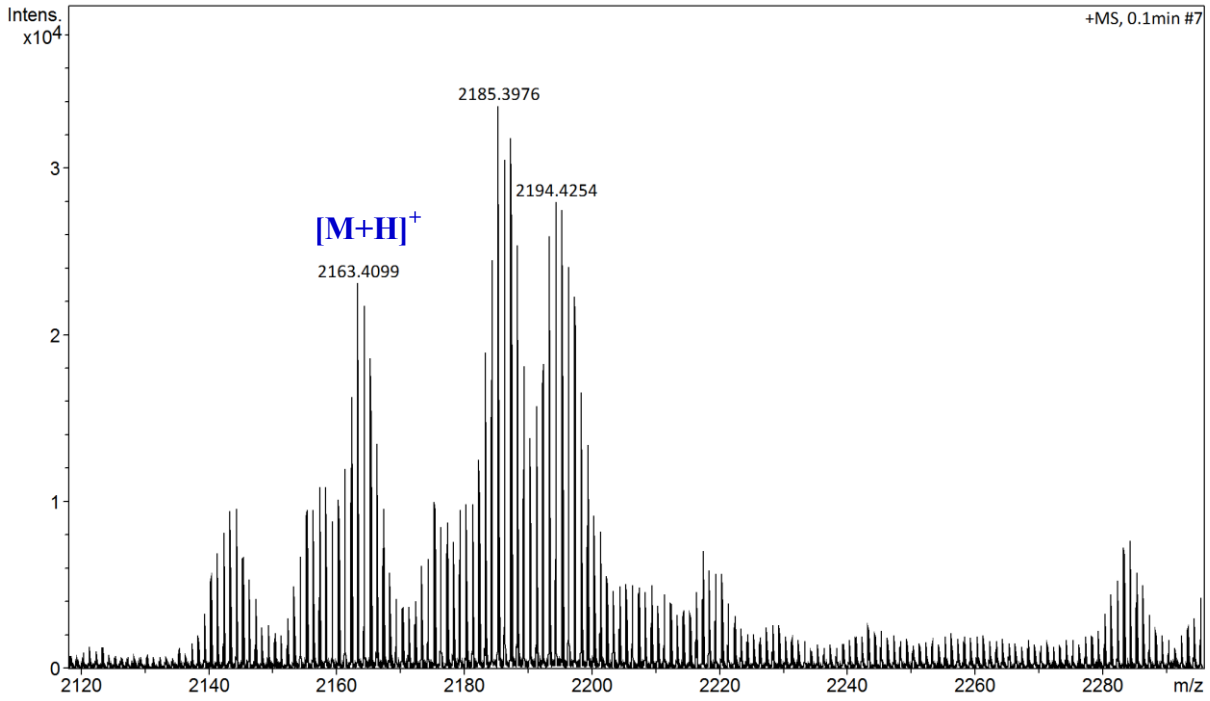

Fig. S16 The high resolution mass spectrometry with isotopic patters for **2oo**.