Electronic Supporting Information

An Unprecedented Photochromic System with cis-Oriented Dithienyl-Dithiolenes Supported by Metal Chelation

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Table S1. Selected Atomic Distances (Å) and Angles (°) of **1o**.

Ni(1)-S(2)	2.1443(11)	Ni(1)-P(2)	2.1721(12)
Ni(1)-S(1)	2.1445(12)	Ni(1)-P(1)	2.1744(12)
S(1)-C(1)	1.765(3)	S(2)-C(2)	1.774(4)
C(2)-C(1)	1.336(5)	C(25)-C(26)	1.750(5)
S(2)-Ni(1)-S(1)	91.48(5)	S(2)-Ni(1)-P(2)	91.60(5)
S(1)-Ni(1)-P(2)	171.14(5)	S(2)-Ni(1)-P(1)	170.91(5)
S(1)-Ni(1)-P(1)	91.14(5)	P(2)-Ni(1)-P(1)	87.10(5)
C(1)-S(1)-Ni(1)	104.73(12)	C(2)-S(2)-Ni(1)	105.03(12)
C(25)-P(1)-Ni(1)	108.12(15)	C(26)-P(2)-Ni(1)	107.69(14)
C(1)-C(2)-S(2)	118.7(3)	C(2)-C(1)-S(1)	120.1(3)
C(26)-C(25)-P(1)	106.7(3)	C(25)-C(26)-P(2)	106.6(3)

Table S2. Selected Atomic Distances (Å) and Angles (°) of **2o**.

Pd(1)-P(1)	2.3181(16)	Pd(1)-P(1)#1	2.3181(16)
Pd(1)-S(1)#1	2.3247(15)	Pd(1)-S(1)	2.3247(15)
S(1)-C(1)	1.801(6)	C(1)-C(1)#1	1.366(11)
C(13)-C(13)#1	1.540(14)	P(1)-C(13)	1.879(7)
P(1)-Pd(1)-P(1)#1	85.42(9)	P(1)#1-Pd(1)-S(1)#1	93.39(6)
P(1)-Pd(1)-S(1)#1	172.93(6)	P(1)-Pd(1)-S(1)	93.39(6)
P(1)#1-Pd(1)-S(1)	172.93(6)	S(1)#1-Pd(1)-S(1)	88.63(7)
C(1)-S(1)-Pd(1)	104.18(18)	C(13)-P(1)-Pd(1)	107.0(2)
C(1)#1-C(1)-C(2)	126.1(3)	C(1)#1-C(1)-S(1)	121.47(18)
C(2)-C(1)-S(1)	112.4(4)	C(13)#1-C(13)-P(1)	107.8(4)
C(21)-C(20)-P(1)	120.7(5)	C(25)-C(20)-P(1)	122.4(6)

Table S3. The Partial Molecular Orbital Compositions (%) and the Absorption Transitions for Complex **1o'** in Toluene, Calculated by the TD-DFT Method.

orbital	energy (eV)	MO contribution (%)		
		Ni (s/p/d)	$H_2P(CH_2)_2PH_2$	Lo
LUMO+5	0.05	15.16 (93/0/7)	61.92	22.92
LUMO+4	-0.44	5.39 (0/53/47)	76.58	18.03
LUMO+3	-0.54	5.25 (0/51/49)	48.51	46.24
LUMO+2	-0.62	0.91 (60/33/7)	0.30	98.79
LUMO+1	-0.86	34.21 (66/32/2)	64.50	1.29
LUMO	-1.55	28.89 (0/7/93)	40.30	30.80
HOMO	-4.79	5.23 (0/52/48)	3.97	90.81
HOMO-1	-5.44	2.94 (0/28/72)	1.57	95.50
HOMO-2	-5.55	5.56 (4/0/96)	0.54	93.90
HOMO-4	-6.49	10.85 (0/11/89)	3.42	85.73

states	*E*, nm (eV)	O.S.	transition	contrib.	assignment
S_6	387 (3.21)	0.0056	HOMO→LUMO+1	96%	LLCT/LMCT
S_{10}	352 (3.52)	0.0675	HOMO→LUMO+3	71%	IL/LLCT
			HOMO→LUMO+4	22%	LLCT/IL
S_{13}	313 (3.96)	0.1143	HOMO→LUMO+5	80%	LLCT/IL/LMCT
S_{16}	295 (4.20)	0.6570	HOMO-1→LUMO+2	81%	IL
S_{18}	289 (4.30)	0.4773	HOMO-4→LUMO	58%	LLCT/IL/LMCT/MC
			HOMO-2→LUMO+2	12%	IL
			HOMO-1→LUMO+3	10%	LLCT/IL
S_{22}	281 (4.42)	0.3229	HOMO-2→LUMO+3	57%	LLCT/IL
			HOMO-2→LUMO+4	18%	LLCT/IL

Table S4. The Partial Molecular Orbital Compositions (%) and the Absorption Transitions for Complex **1c'** in Toluene, Calculated by the TD-DFT Method.

orbital	energy (eV)	MO contribution (%)		
		Ni (s/p/d)	$H_2P(CH_2)_2PH_2$	Lc
LUMO+4	-0.41	1.92 (77/6/17)	3.26	94.82
LUMO+3	-0.62	6.20 (0/57/43)	87.84	5.96
LUMO+1	-1.56	3.18 (0/44/56)	8.08	88.74
LUMO	-1.76	29.39 (0/7/93)	39.91	30.70
HOMO	-4.11	1.89 (6/6/88)	0.21	97.90
HOMO-1	-5.28	4.39 (0/40/60)	2.68	92.93
HOMO-2	-5.93	14.66 (1/0/99)	0.51	84.84
HOMO-4	-6.58	1.59 (3/0/97)	0.06	98.35
HOMO-5	-6.72	4.12 (0/6/94)	0.79	95.10
HOMO-9	-7.13	14.33 (0/25/75)	12.13	73.54

state	*E*, nm (eV)	O.S.	transition	contrib.	assignment	exp. (nm)
S_4	608 (2.04)	0.4591	HOMO→LUMO+1	97%	IL	620
S_{11}	383 (3.23)	0.6335	HOMO→LUMO+4	51%	IL	420
			HOMO-1→LUMO+1	45%	IL	
S_{26}	289 (4.29)	0.3185	HOMO-4→LUMO	48%	LLCT/IL/LMCT	302
			HOMO-4→LUMO+1	29%	IL	
S_{28}	283 (4.38)	0.1682	HOMO-2→LUMO+3	42%	LLCT	
			HOMO-4→LUMO+1	24%	IL	
S_{32}	274 (4.52)	0.4532	HOMO-9→LUMO	47%	IL/LLCT/LMCT/MC	
			HOMO-5→LUMO+1	38%	IL	

Table S5. The Partial Molecular Orbital Compositions (%) and the Absorption Transitions for Complex **2o'** in Toluene, Calculated by the TD-DFT Method.

orbital	energy (eV)	MO contribution (%)		
		Pd (s/p/d)	$H_2P(CH_2)_2PH_2$	Lo
LUMO+9	0.45	17.88 (94/0/6)	37.71	44.41
LUMO+4	-0.34	8.95 (0/62/38)	85.53	5.52
LUMO+3	-0.53	3.03 (0/43/57)	11.80	85.18
LUMO+2	-0.63	0.92 (76/7/17)	0.61	98.47
LUMO	-1.77	25.35 (0/7/93)	39.72	34.92
HOMO	-4.79	5.42 (0/44/56)	4.54	90.04
HOMO-1	-5.43	2.47 (0/27/73)	1.39	96.14
HOMO-2	-5.59	4.20 (8/0/92)	0.61	95.19
HOMO-3	-6.09	16.18 (3/1/96)	1.02	82.81
HOMO-6	-6.88	34.52 (16/2/82)	0.67	64.81
HOMO-12	-7.73	56.03 (5/4/91)	16.54	27.42

states	*E*, nm (eV)	O.S.	transition	contrib.	assignment
S_3	416 (2.98)	0.0081	HOMO-1→LUMO	93%	LLCT/IL/LMCT
S_5	370 (3.35)	0.0062	HOMO-3→LUMO	37%	LLCT/IL/MC/LMCT
			HOMO-2→LUMO	35%	LLCT/IL/LMCT
			HOMO-6→LUMO	14%	LLCT/IL/MC
S_7	355 (3.49)	0.0274	HOMO→LUMO+2	89%	IL
S_9	337 (3.67)	0.0334	HOMO→LUMO+4	86%	LLCT
S_{15}	296 (4.19)	0.6275	HOMO-1→LUMO+2	88%	IL
S_{20}	280 (4.44)	0.3542	HOMO-2→LUMO+3	40%	IL/LLCT
			HOMO-2→LUMO+4	13%	LLCT
			HOMO-12→LUMO	12%	IL/MLCT/MC
			HOMO→LUMO+9	12%	IL/LLCT/LMCT

Table S6. The Partial Molecular Orbital Compositions (%) and the Absorption Transitions for Complex **2c'** in Toluene, Calculated by the TD-DFT Method.

orbital	energy (eV)	MO contribution (%)		
		Pd (s/p/d)	$H_2P(CH_2)_2PH_2$	Lc
LUMO+4	-0.45	1.66 (70/4/26)	1.50	96.84
LUMO+1	-1.56	1.76 (0/58/42)	4.93	93.32
LUMO	-1.97	25.87 (0/7/93)	40.34	33.79
HOMO	-4.15	2.05 (10/6/84)	0.28	97.67
HOMO-1	-5.27	4.50 (0/35/65)	3.07	92.43
HOMO-4	-6.6	1.35 (9/1/90)	0.07	98.58

states	*E*, nm (eV)	O.S.	transition	contrib.	assignment	exp. (nm)
S_2	600 (2.07)	0.4571	HOMO→LUMO+1	100%	IL	617
S_8	384 (3.23)	0.6411	HOMO→LUMO+4	52%	IL	418
			HOMO-1→LUMO+1	44%	IL	
S_{27}	285 (4.34)	0.5923	HOMO-4→LUMO+1	84%	IL	294

Table S7. The Partial Molecular Orbital Compositions (%) and the Absorption Transitions for Complex [**4oo'**]$^{2-}$ in Toluene, Calculated by the TD-DFT Method.

orbital	energy (eV)	MO contribution (%)		
		Zn (s/p/d)	Lo	Lo'
LUMO+11	1.33	1.13 (0/93/7)	49.41	49.46
LUMO+3	-0.46	0.13 (0/88/12)	49.78	50.09
LUMO+2	-0.47	0.23 (0/95/5)	50.04	49.73
LUMO+1	-0.57	0.20 (0/96/4)	49.93	49.87
LUMO	-0.59	0.86 (98/0/2)	49.54	49.60
HOMO	-3.96	2.56 (0/50/50)	48.72	48.72
HOMO-2	-4.94	3.42 (0/44/56)	48.29	48.29
HOMO-3	-5.16	0.65 (0/40/60)	49.67	49.68
HOMO-4	-5.33	0.32 (0/73/27)	49.84	49.84
HOMO-5	-5.34	3.00 (0/60/40)	48.50	48.50
HOMO-7	-5.43	0.68 (10/0/90)	49.65	49.66
HOMO-8	-5.75	0.91 (0/92/8)	49.55	49.54
HOMO-9	-5.87	1.64 (20/0/80)	49.18	49.18

states	*E*, nm (eV)	O.S.	transition	contrib.	assignment	exp. (nm)
S_{12}	324 (3.82)	0.6266	HOMO-2→LUMO+1	81%	IL	330
S_{21}	306 (4.05)	0.5481	HOMO-3→LUMO	49%	IL	301
			HOMO-5→LUMO+1	22%	IL	
S_{35}	290 (4.28)	0.3101	HOMO-4→LUMO+2	65%	IL	
			HOMO-7→LUMO+3	26%	IL	
S_{47}	270 (4.59)	0.3525	HOMO-8→LUMO	41%	IL	287
			HOMO-9→LUMO+1	25%	IL	
			HOMO→LUMO+11	16%	IL	

Table S8. The Partial Molecular Orbital Compositions (%) and the Absorption Transitions for Complex [**4co'**]$^{2-}$ in Toluene, Calculated by the TD-DFT Method.

orbital	energy (eV)	MO contribution (%)		
		Zn (s/p/d)	Lc	Lo
LUMO+8	0.46	32.54 (100/0/0)	34.93	32.53
LUMO+7	0.44	24.57 (99/0/0)	52.72	22.71
LUMO+4	0.35	0.48 (94/1/5)	0.22	99.31
LUMO+3	-0.34	0.45 (59/19/22)	99.42	0.13
LUMO+1	-0.6	0.58 (81/16/3)	0.15	99.27
LUMO	-1.43	0.92 (0/68/32)	97.12	1.96
HOMO	-3.88	0.52 (25/34/41)	99.24	0.24
HOMO-1	-4.14	2.86 (0/58/42)	11.47	85.67
HOMO-3	-5.13	1.71 (0/46/54)	14.35	83.94
HOMO-6	-5.62	5.62 (0/55/45)	82.01	12.37
HOMO-11	-6.48	0.05 (46/9/45)	99.70	0.24

states	*E*, nm (eV)	O.S.	transition	contrib.	assignment	exp. (nm)
S_1	647 (1.92)	0.0279	HOMO→LUMO	100%	IL	
S_2	559 (2.22)	0.5170	HOMO-1→LUMO	99%	LLCT/IL	601
S_6	418 (2.97)	0.4769	HOMO→LUMO+3	78%	IL	416
S_9	387 (3.20)	0.2180	HOMO-3→LUMO	61%	LLCT/IL	
			HOMO-6→LUMO	29%	IL/LLCT	
S_{22}	326 (3.81)	0.3067	HOMO-1→LUMO+8	43%	IL/LMCT/LLCT	
			HOMO-1→LUMO+7	33%	LLCT/IL/LMCT	
			HOMO-1→LUMO+4	11%	IL/LLCT	
S_{24}	315 (3.93)	0.5669	HOMO-3→LUMO+1	87%	IL/LLCT	302
S_{40}	286 (4.34)	0.6692	HOMO-11→LUMO	72%	IL	

Table S9. The Partial Molecular Orbital Compositions (%) and the Absorption Transitions for Complex [**4cc'**]$^{2-}$ in Toluene, Calculated by the TD-DFT Method.

Orbital	Energy (eV)	MO contribution (%)		
		Zn (s/p/d)	Lc	Lc'
LUMO+3	-0.35	0.20 (0/99/1)	49.90	49.91
LUMO+2	-0.37	0.68 (74/0/26)	49.66	49.65
LUMO+1	-1.43	0.70 (0/51/49)	49.65	49.65
LUMO	-1.47	1.13 (0/76/24)	49.44	49.44
HOMO	-3.89	0.37 (0/96/4)	49.81	49.81
HOMO-1	-3.97	0.74 (39/0/61)	49.63	49.63
HOMO-3	-4.83	2.83 (0/45/55)	48.58	48.58
HOMO-11	-6.51	0.08 (39/0/61)	49.09	50.82
HOMO-12	-6.51	0.35 (0/82/18)	50.69	48.95

states	*E*, nm (eV)	O.S.	transition	contrib.	assignment	exp. (nm)
S_3	586 (2.12)	0.2775	HOMO-1→LUMO	62%	IL	601
			HOMO→LUMO+1	38%	IL	
S_4	583 (2.13)	0.7252	HOMO-1→LUMO+1	75%	IL	
			HOMO→LUMO	25%	IL	
S_9	421 (2.95)	0.5446	HOMO→LUMO+2	58%	IL	416
			HOMO-1→LUMO+3	26%	IL	
			HOMO-3→LUMO+1	12%	IL	
S_{12}	382 (3.24)	0.8733	HOMO-1→LUMO+3	67%	IL	
			HOMO→LUMO+2	32%	IL	
S_{45}	285 (4.35)	0.4608	HOMO-12→LUMO	51%	IL	290
			HOMO-11→LUMO+1	39%	IL	
S_{46}	285 (4.36)	0.8245	HOMO-11→LUMO	43%	IL	
			HOMO-12→LUMO+1	43%	IL	

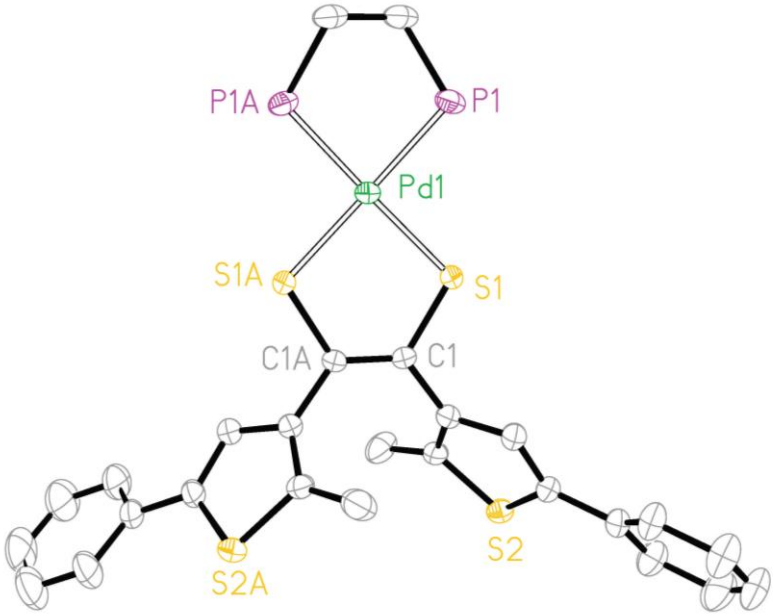

Fig. S1 ORTEP drawings of the complex cation of **2o** with atom labeling scheme showing 30% thermal ellipsoids. Phenyl rings on the phosphorus atoms are omitted for clarity.

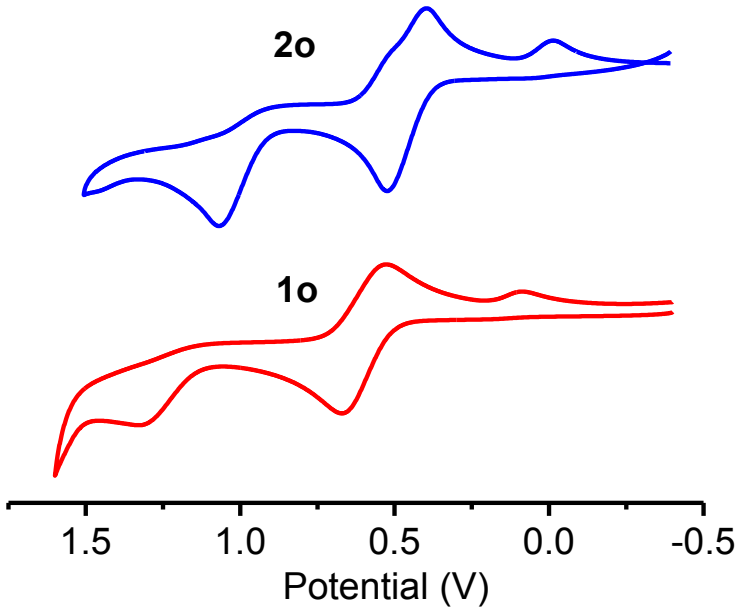

Fig. S2 Plots of cyclic voltammogram of **1o** and **2o** in 0.1 M $(Bu_4N)(PF_6)$ dichloromethane.

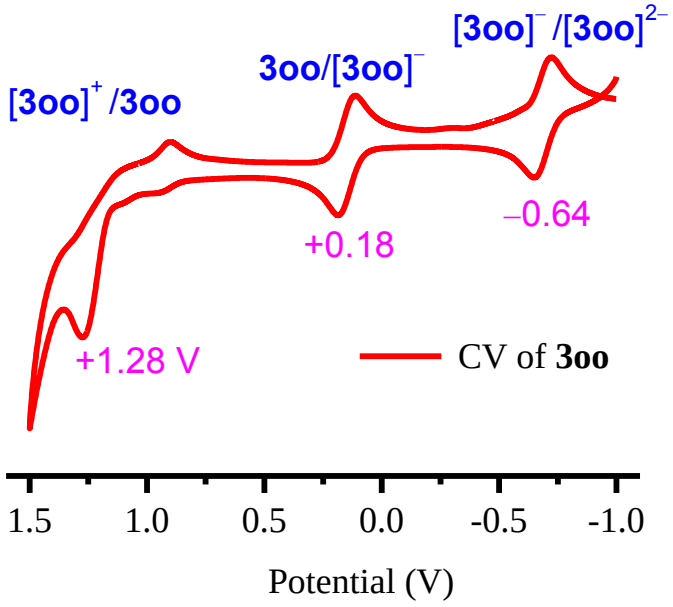

Fig. S3 Plots of cyclic voltammogram of **3oo** in 0.1 M (Bu_4N)(PF_6) dichloromethane.

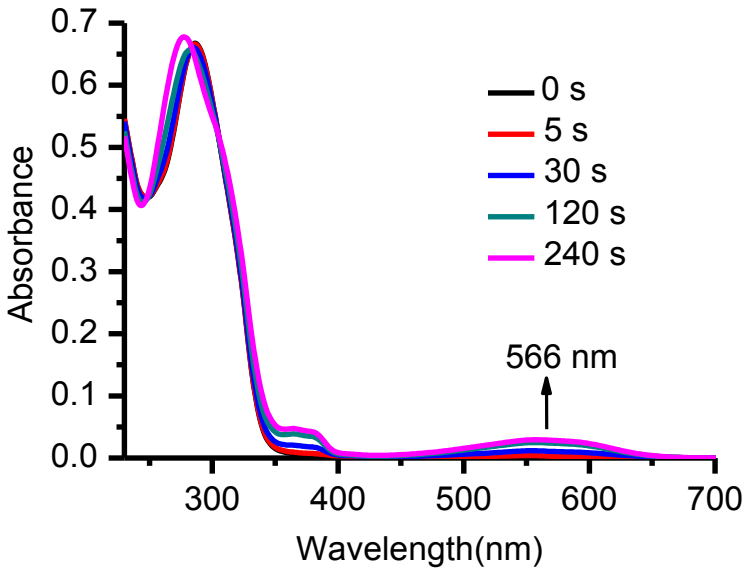

Fig. S4 The UV-vis spectral changes of L1o (1×10^{-5} M) in toluene upon irradiation at 312 nm.

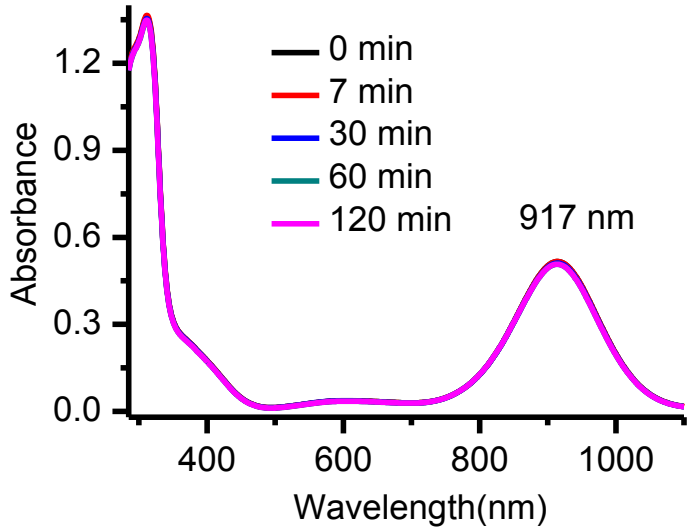

Fig. S5 The UV-vis-NIR spectral changes of **3oo** (1×10^{-5} M) in toluene upon irradiation with UV light at 312 nm.

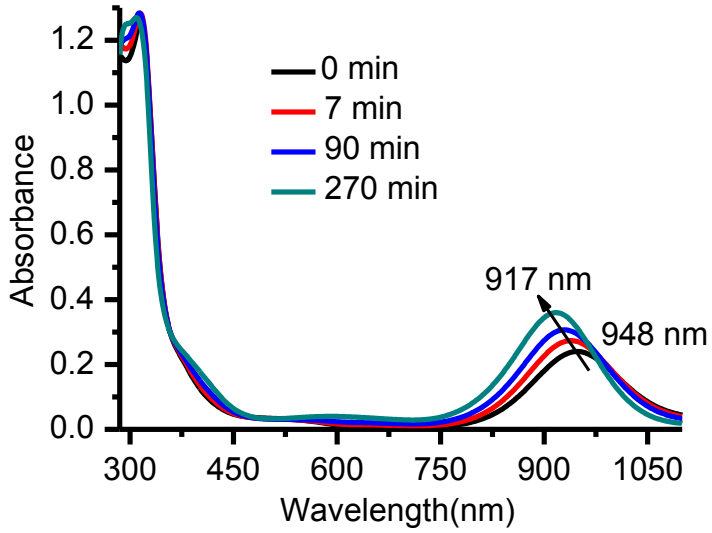

Fig. S6 The UV-vis-NIR spectral changes of $[\mathbf{3oo}]^-$ (1×10^{-5} M) in toluene upon irradiation with UV light at 312 nm.

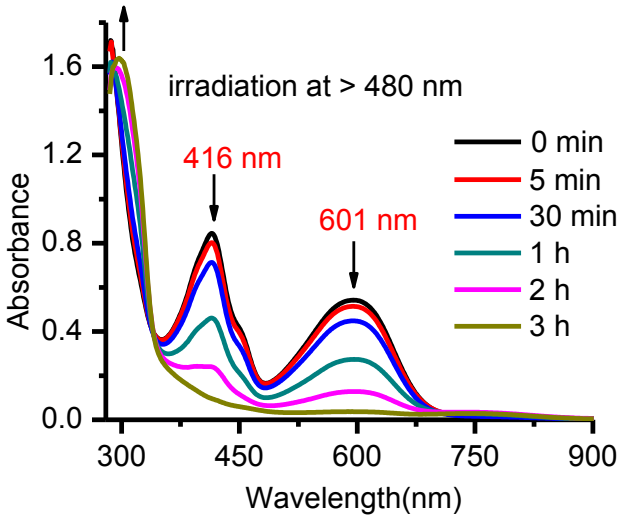

Fig. S7 The UV-vis spectral changes of $[\mathbf{4cc}]^{2-}$ (1×10^{-5} M) in DMSO upon irradiation with visible light at > 480 nm.

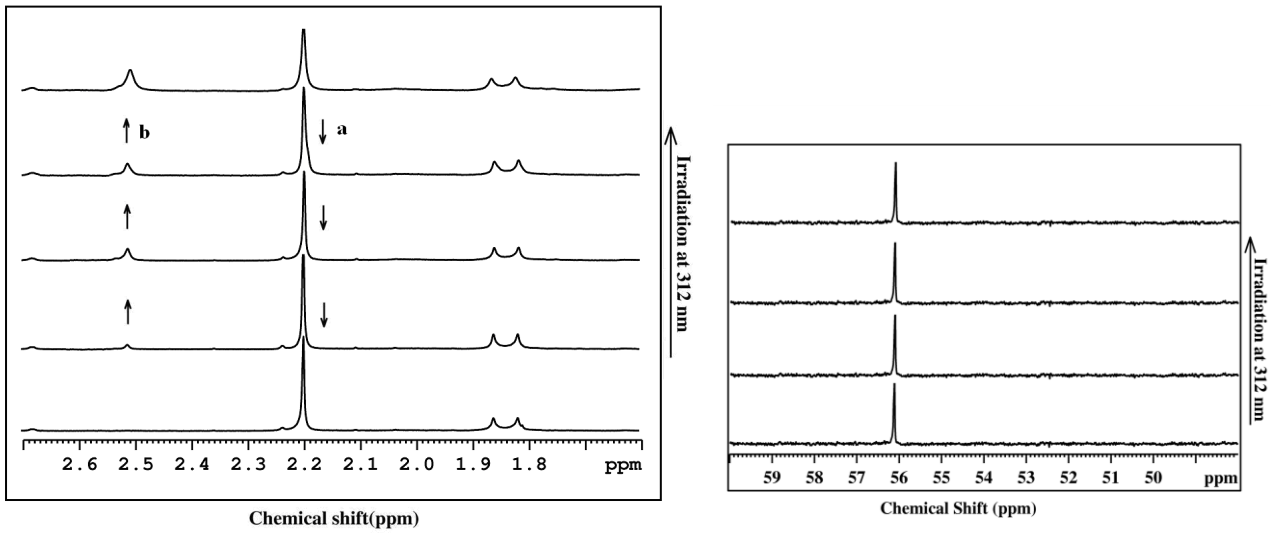

Fig. S8 The ^{1}H NMR (left) and ^{31}P NMR (right) spectral changes of **1o** in C_6D_6 upon irradiation with UV light at 312 nm.

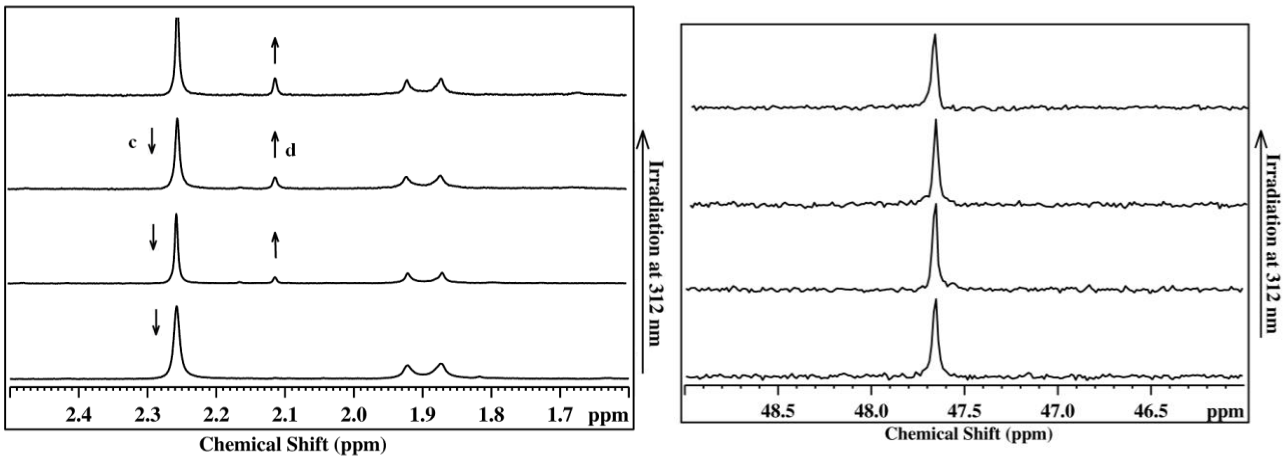

Fig. S9 The ^{1}H NMR (left) and ^{31}P NMR (right) spectral changes of **2o** in C_6D_6 upon irradiation with UV at 312 nm.

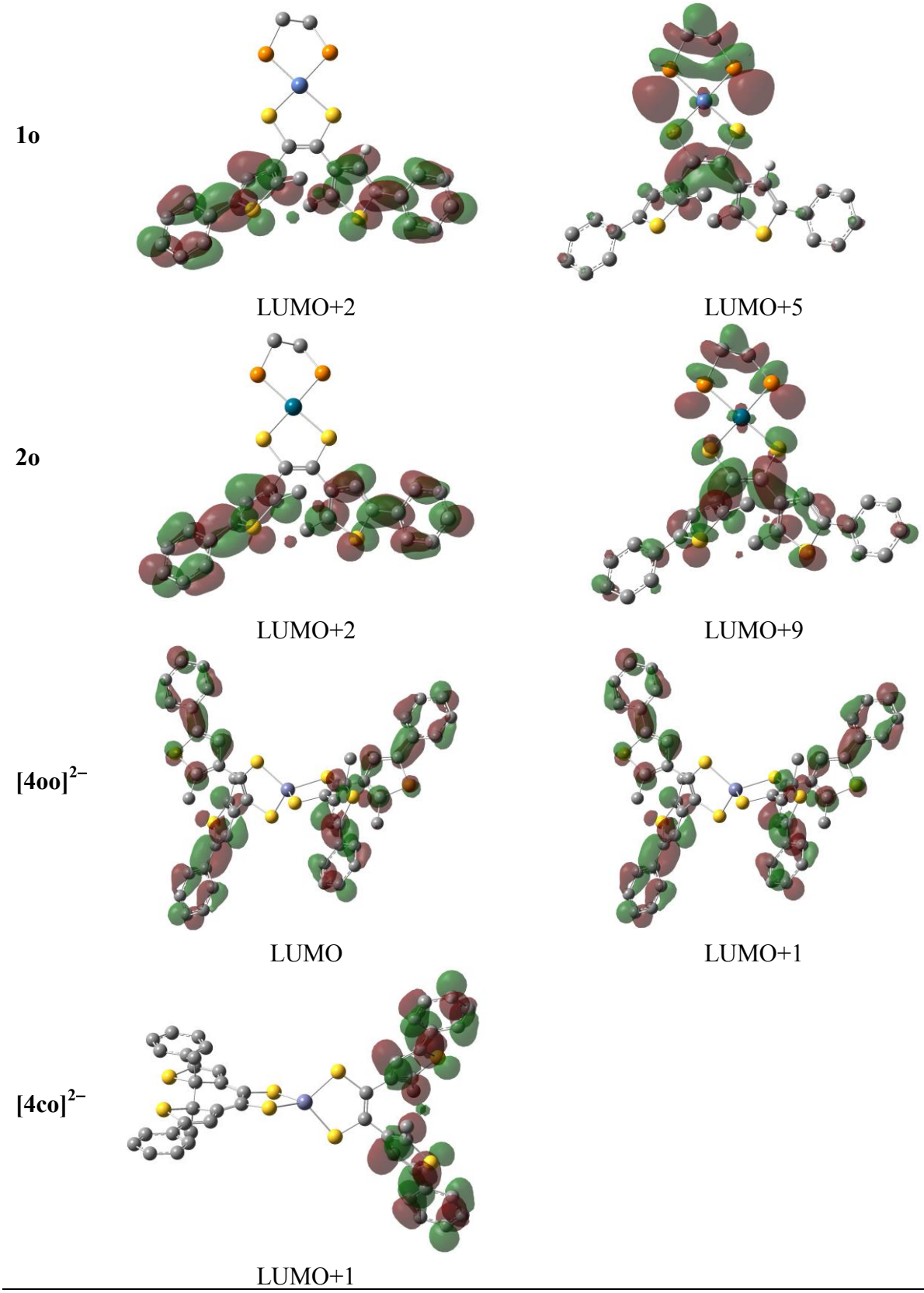

Fig. S10 The unoccupied frontier orbitals involving UV absorption and photocyclization upon irradiation at 312 nm.