Electronic Supplementary Information for:

Visible Light Intensity Dependent Negative Photochromism of Binaphthyl-Bridged Phenoxyl-Imidazolyl Radical Complex

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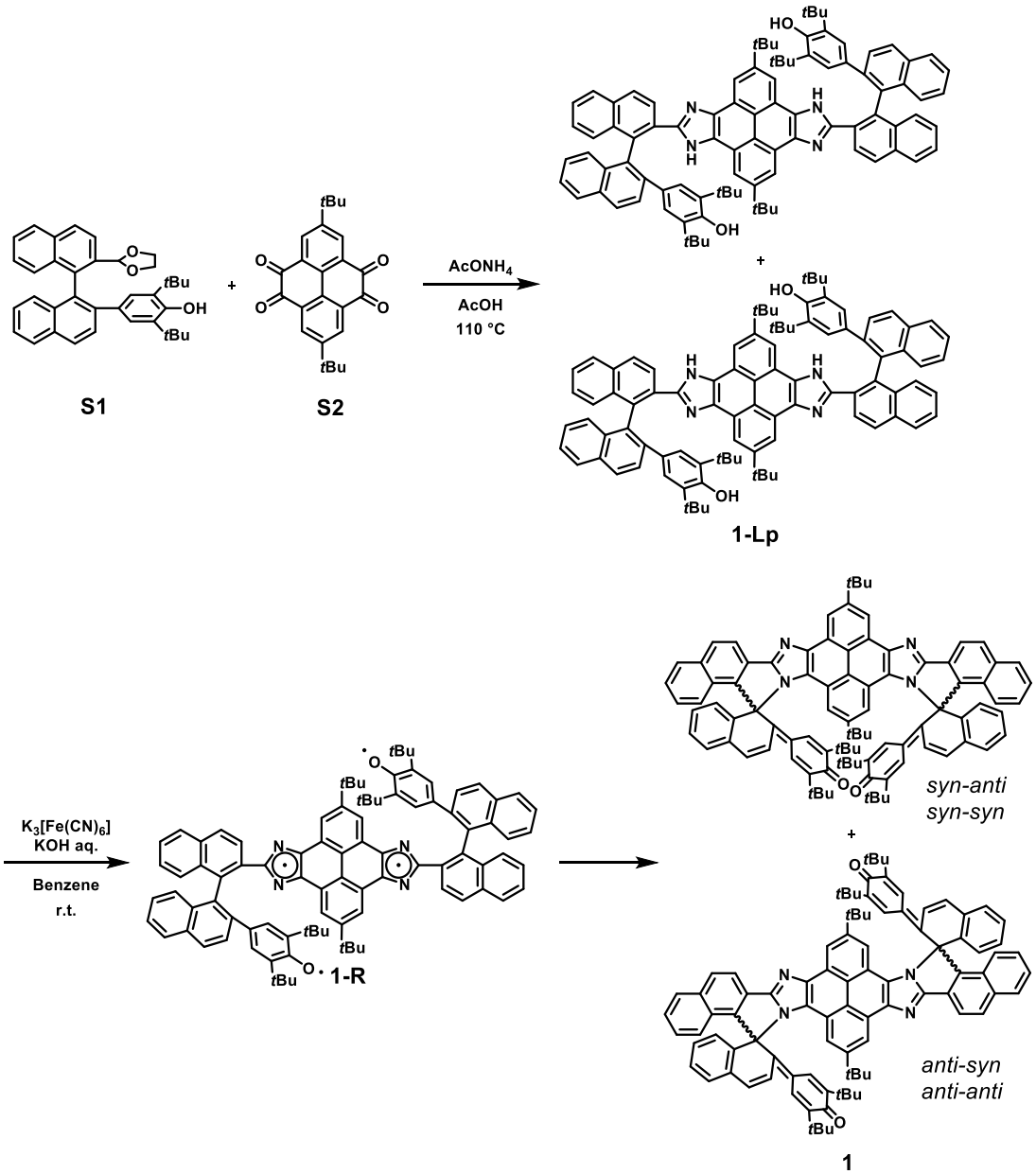
CONTENTS

1. Synthesis

All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Silica gel 60N, Kanto Chemical Co., Inc.). NMR spectra were recorded at 400 MHz on a Bruker AVANCE III 400 NanoBay. DMSO–d_6 and $CDCl_3$ were used as deuterated solvent. ESI–TOF–MS spectra were recorded on a Bruker micrOTOF II-AGA1. Unless otherwise noted, all reagents and reaction solvents were purchased from Tokyo Chemical Industry Co., Ltd., Wako Pure Chemical Industries, Ltd., Sigma-Aldrich Inc. and Kanto Chemical Co., Inc. and were used without further purification.

Scheme S1. Synthesis of **1**.



2,6-Di-*tert*-butyl-4-[2'-(1,3-dioxolan-2-yl)-[1,1'-binaphthalen]-2-yl]phenol (S1) and 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone (S2) were synthesized according to a literature procedure.[S1,S2] The syntheses of **NN-Lp** and **NN** are described below.

NN-Lp and **NN**

A mixture of **S1** (205 mg, 0.385 mmol), **S2** (71 mg, 0.19 mmol), and ammonium acetate (625 mg, 8.11 mmol) in acetic acid (25 mL) was stirred for 2 days at 110 °C. The reaction mixture was allowed to cool to room temperature and was neutralized with aqueous ammonia. The precipitate was collected by filtration and washed with water. The solid was purified by silica gel column chromatography twice (hexane/ethyl acetate = 4:1 and toluene) to give a mixture of the structural isomers of **1-Lp** as yellow solid (81 mg, 30% yield). This was used in the next step without further purification. **1-Lp** was identified by HRMS, (ESI-TOF) calcd for $C_{94}H_{90}N_4O_2$ $[M+H]^+$, 1308.7169; found, 1308.7168. The mixture of structural isomers of **1-Lp** (99 mg, 0.076 mmol) was dissolved in degassed benzene (100 mL). A degassed aqueous solution (15 mL) of potassium ferricyanide (2.216 g, 6.723 mmol) and KOH (1.865 mg, 33.24 mmol) was added to the benzene solution. After vigorous stirring for 4 hours at room temperature, the resulting solution was extracted with benzene. The organic layer was washed with water and brine, and the solvent was removed by evaporation under reduced pressure. The residual solid was purified by silica gel column chromatography (ethyl acetate/CH_2Cl_2 = 1:100) to give **1** as the mixture of *anti-anti* and *anti-syn* isomers (mixture 1, R_f = 0.51) and the mixture of *syn-anti* and *syn-syn* isomers (mixture 2, R_f = 0.19). The *anti-anti* and anti-syn isomers were isolated from the mixture 1 by silica gel column chromatography (hexane/THF = 4:1) to give *anti-anti* isomer (R_f = 0.27, 34 mg, 34% yield) and *anti-syn* isomer (R_f = 0.16, 37 mg, 37% yield) as red solid. The *syn-anti* and *syn-syn* isomers were isolated from the mixture 2 by silica gel column chromatography (hexane/THF = 3:1) to give *syn-anti* isomer (R_f = 0.22, 7.2 mg, 7% yield) and *syn-syn* isomer (R_f = 0.10, 11.0 mg, 14% yield) as red solid. The *syn-anti* isomer was used for spectroscopic experiments. ^{1}H NMR for the *syn-anti* isomer (400 MHz, DMSO-d_6) δ: 9.03 (s, 2H), 8.48 (d, J = 4.2 Hz, 2H), 8.31 (d, J = 4.2 Hz, 2H), 8.22 (d, J = 5.1 Hz, 2H), 8.15 (d, J = 4.1 Hz, 2H), 8.09 (d, J = 4.1 Hz, 2H), 7.77 (d, J = 5.1 Hz, 2H), 7.69 (s, 2H), 7.62–7.53 (m, 8H), 7.13 (dd, J_1 = 5.2 Hz, J_2 = 3.4 Hz, 2H), 6.84 (t, J = 3.6 Hz, 2H), 6.60 (d, J = 1.2 Hz, 2H), 6.30 (d, J = 4.0 Hz, 2H), 1.70 (s, 9H), 1.34 (s, 9H), 0.97 (s, 18H), 0.62 (s, 18H). HRMS (ESI-TOF) calcd for $C_{94}H_{86}N_4O_2$ $[M+H]^+$, 1303.6824; found, 1303.6831.

2. ^{1}H NMR Spectra

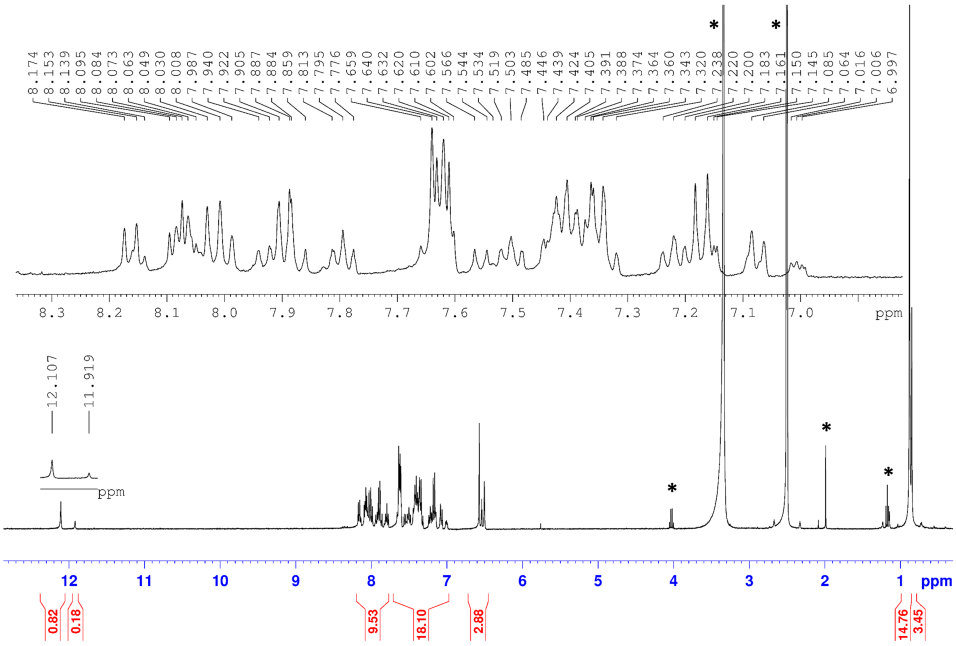


Figure S1. ^{1}H NMR spectrum of 1-(4-(2-(2'-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-[1,1'-binaphthalen]-2-yl)-5-phenyl-1*H*-imidazol-4-yl)phenyl)-2-phenylethane-1,2-dione (**1-Lp**) in DMSO-d_6 (* solvent peak).

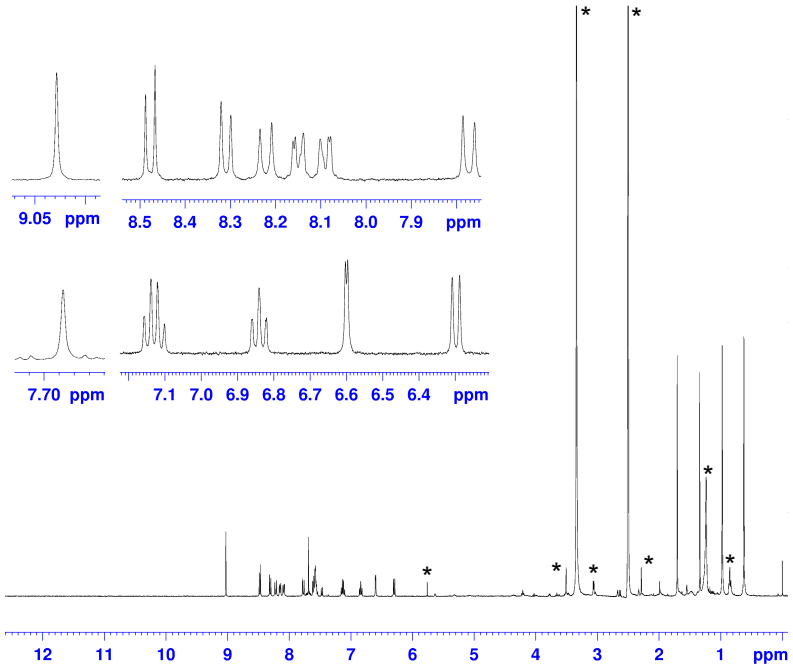


Figure S2. ^{1}H NMR spectrum of the *syn-anti* isomer of 1 in DMSO-d_6 (* solvent peak).

3. HR-ESI-TOF-MS Spectra

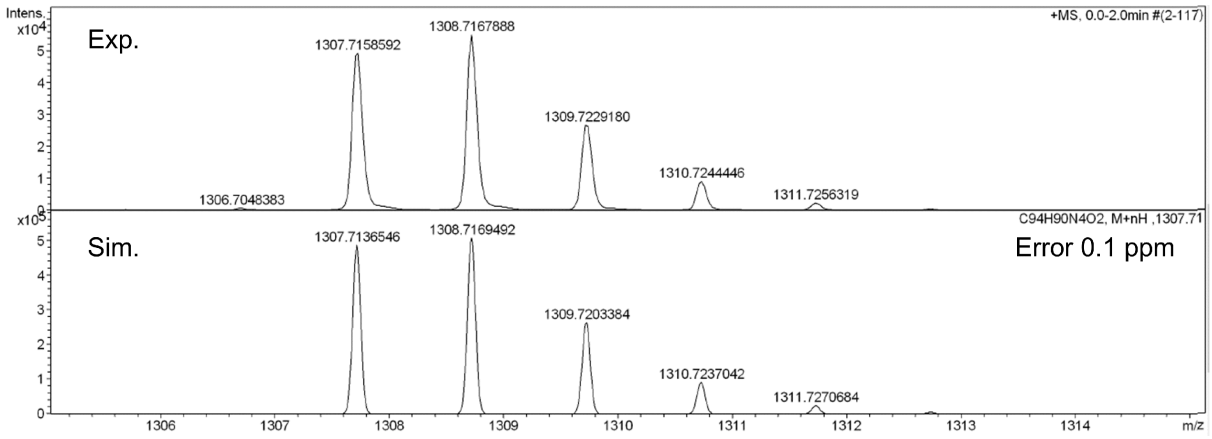


Figure S3. HR-ESI-TOF-MS of **1-Lp**.

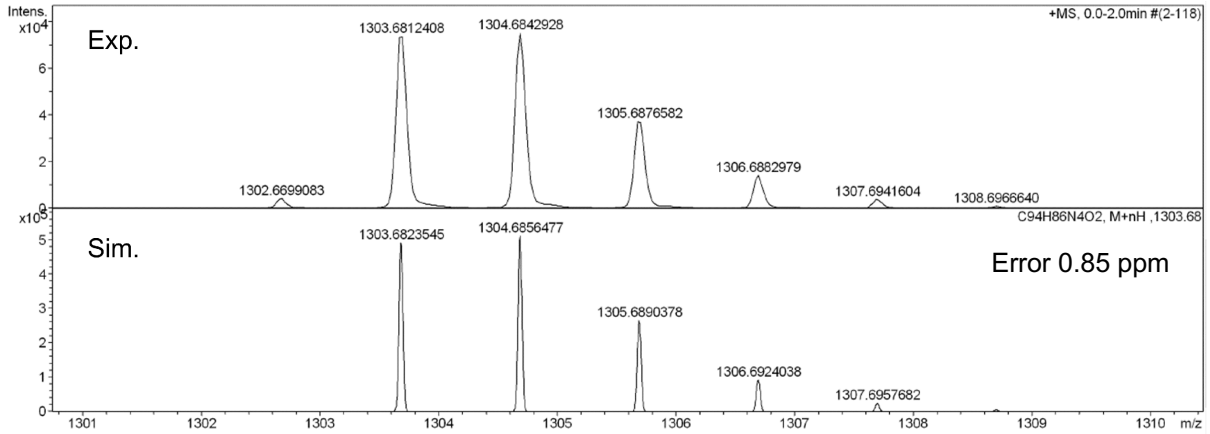


Figure S4. HR-ESI-TOF-MS of the *anti*-type isomers for **1**.

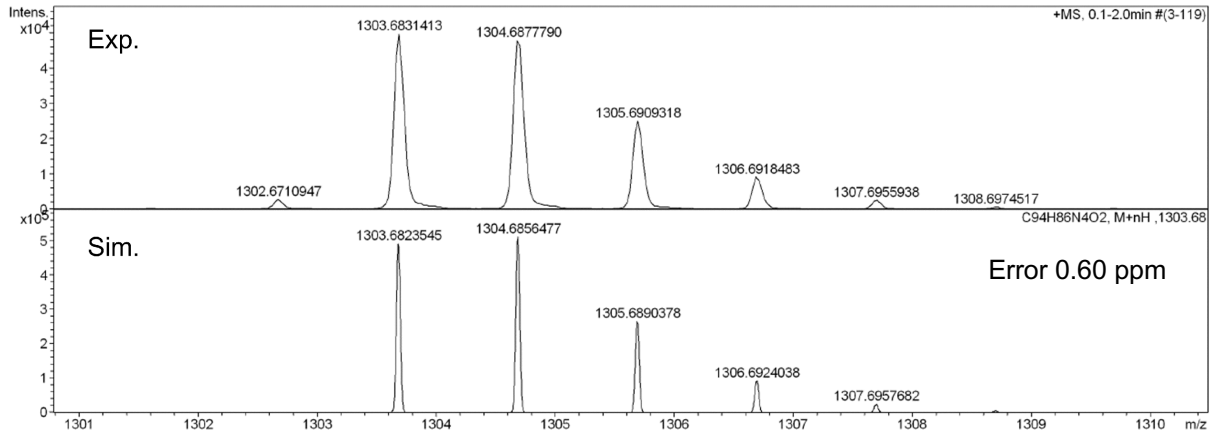


Figure S5. HR-ESI-TOF-MS of the *syn*-type isomers for **1**.

4. HPLC Chromatogram

HPLC analysis was performed using a normal phase analytical column (Mightysil Si60, 25cm×4.6mm, 5μm particle) from Kanto Chemical Co., Inc. The mobile phase was THF/hexane = 1/2 with a flow rate of 1.0 mL/min (detection wavelength; 254, 300 and 355 nm). The HPLC analytical system consists of a pump unit (PU-2080 plus, JASCO), a photodiode array detector (MD-2018, JASCO), and a control unit (LCNetII/ADC, JASCO).

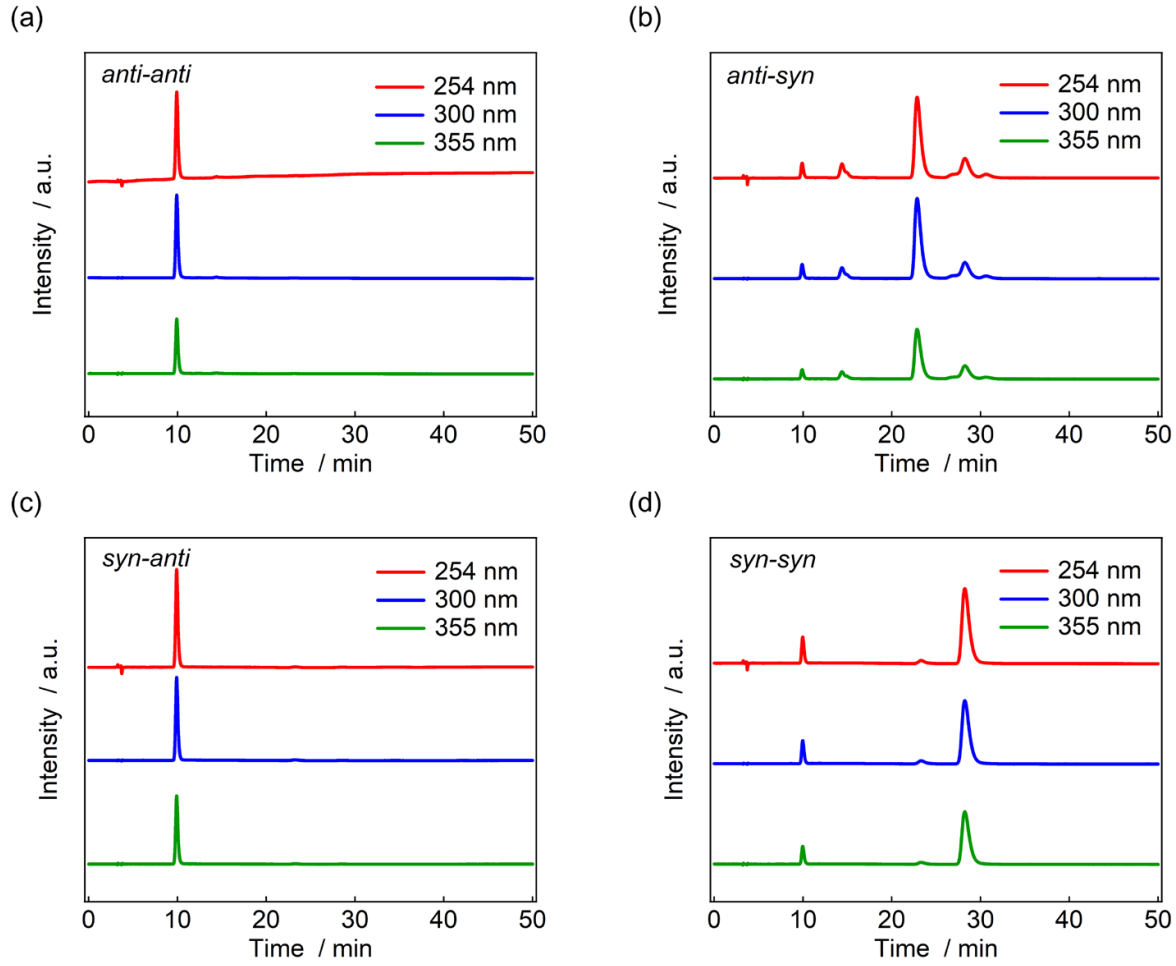


Figure S6. HPLC chromatograms of the structural isomers of **1**, (a) *anti-anti* isomer; 99 % purity, (b) *anti-syn* isomer; 84 % purity, (c) *syn-anti* isomer; 98 % purity, (d) *syn-syn* isomer; 88 % purity.

Compound **1** has four structural isomers (Figure S7). The HPLC peaks at 9.9 min, 22.8 min, 10.0 min and 28.4 min for *anti-anti*, *anti-syn*, *syn-anti*, and *syn-syn* isomers were observed. We succeeded to isolate *anti-anti* and *syn-anti* isomers by purification with silica gel column chromatography. Although the four structural isomers have different absorption spectral shape in UVA region, all isomers have the characteristic similar absorption bands in visible light region (Figure S7).

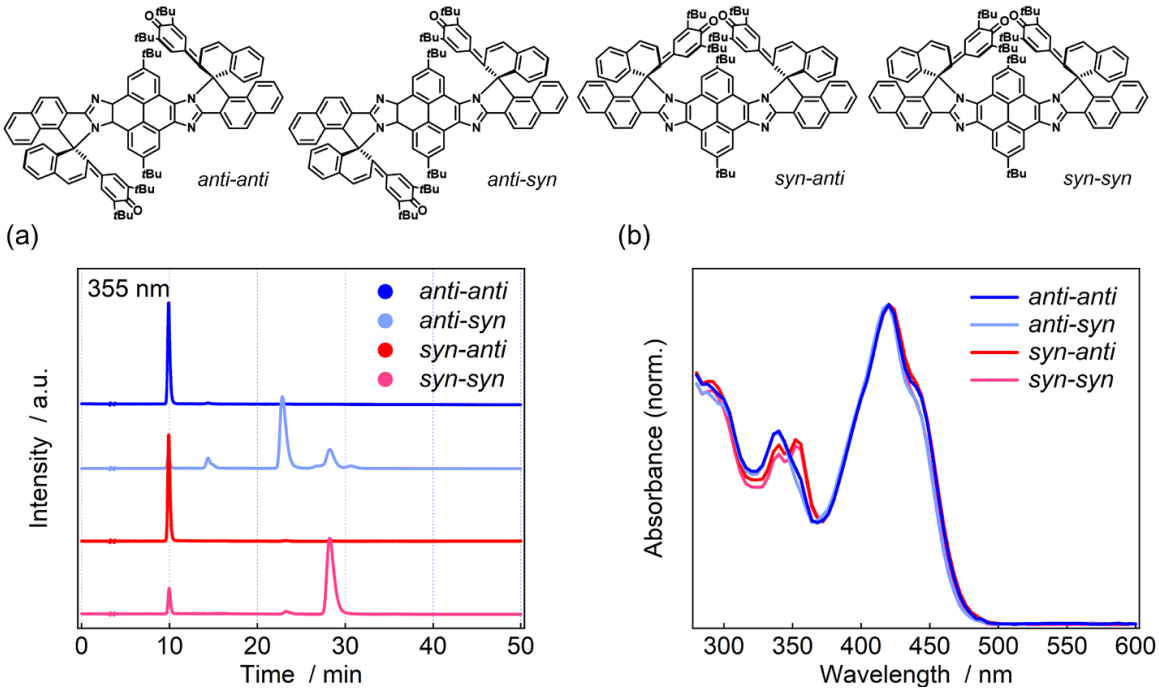


Figure S7. (a) HPLC chromatograms of the four structural isomers of **1** detected at 355 nm. (b) The absorption spectra of the structural isomers of **1**.

5. X-ray Crystallographic Analysis

The diffraction data of the single crystal of **1** were collected on the Bruker APEX II CCD area detector (Mo Kα, λ = 0.71073 nm). During the data collection, the lead glass doors of the diffractometer were covered to exclude the room light. The data refinement was carried out by the Bruker APEXII software package with SHELXT program.[S3,S4] All non-hydrogen atoms were anisotropically refined.

Table S1. X-ray Crystallographic Data of **1**

Empirical formula moiety	C94 H86 N4 O2, 3.75(C6 H14)	
Empirical formula sum	C116.50 H138.50 N4 O2	
Empirical formula weight	1626.80	
Temperature	103 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 17.5774(13) Å	α= 90°
	b = 19.6323(13) Å	β= 105.803(3)°
	c = 29.878(3) Å	γ= 90°
Volume	9920.7(13) $Å^3$	
Z	4	
Density(calculated)	1.089 g/cm^3	
Absorption coefficient	0.063 mm^{-1}	
F(000)	3526	
Theta range for data collection	2.19 to 25.05°	
Index ranges	−20<=h<=20, −23<=k<=23, −35<=l<=31	
Reflections collected	58478	
Independent reflections	17505 [R(int) = 0.0696]	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restrains / parameters	17505 / 0 / 1175	
Goodness-of-fit on F^2	1.039	
Final R indices [I>sigma (I)]	R1 = 0.0839, wR2 = 0.2525	
R indices (all data)	R1 = 0.1200, wR2 = 0.2867	
Largest diff. peak and hole	0.783 and −0.688 e. $Å^{-3}$	

6. TDDFT Calculations for the UV–vis Absorption Spectrum

All calculations were carried out using the Gaussian 09 program (Revision D.01).[S5] The molecular structure was fully optimized at the MPW1PW91/6-31G(d) level of the theory, and analytical second derivative was computed using vibrational analysis to confirm each stationary point to be a minimum. TDDFT calculations were performed at the MPW1PW91/6-31G(d) level of the theory for the optimized structures.

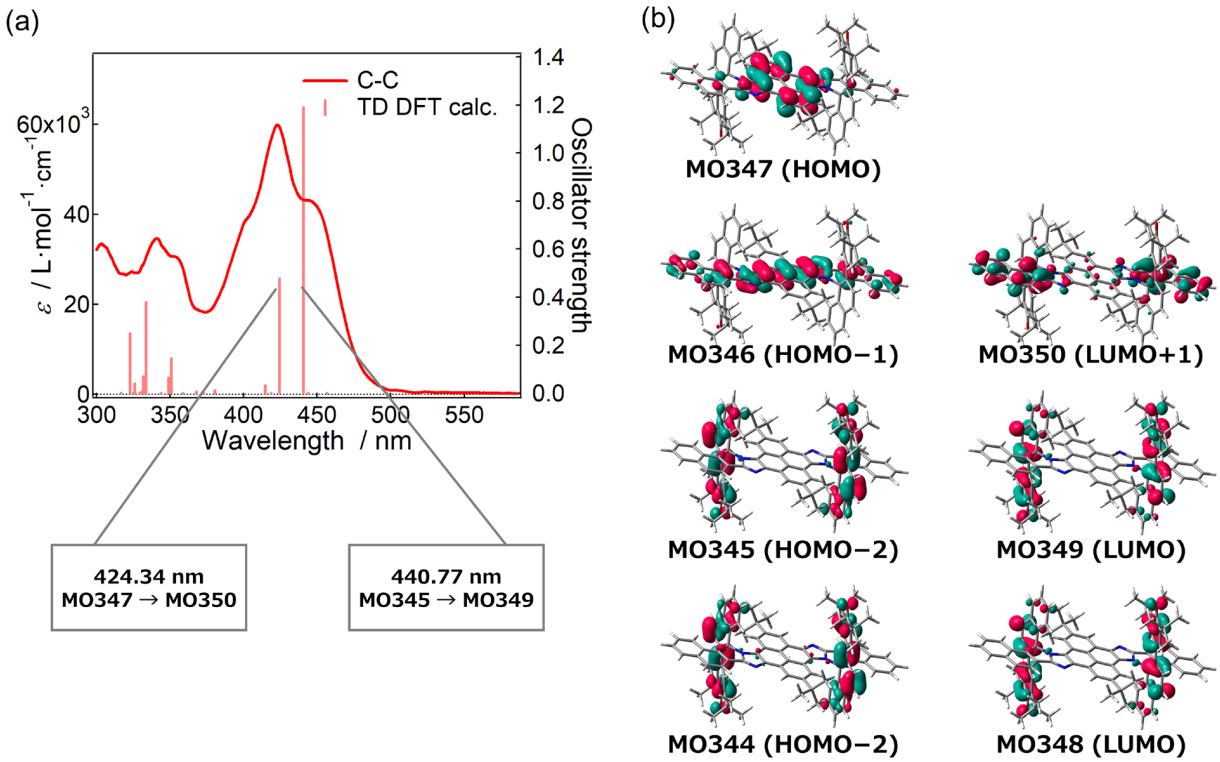


Figure S8. (a) UV–vis absorption spectrum of **C-C** estimated by global analysis method using Glotaran. The calculated spectra are shown by the perpendicular lines. (b) The calculated molecular orbitals of **C-C**.

Table S2. Standard Orientation of the Optimized Geometry for **C-C**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	6.0467660	1.8090050	-3.2934110
2	C	7.3919210	2.1003060	-3.2382100
3	C	8.0900040	2.1399880	-1.9928720
4	C	7.4031360	1.8800500	-0.7682250
5	C	6.0223370	1.5730140	-0.8427410
6	C	5.3701610	1.5453760	-2.0841810
7	C	5.0429430	1.2742970	0.3224440
8	C	5.4519330	0.0418360	1.1228460
9	C	5.8163720	0.2607550	2.5274060
10	C	5.6797070	1.4335070	3.1683350
11	C	5.1519140	2.6176690	2.4952090
12	C	4.8379170	2.5560400	1.1245730
13	C	3.9719560	1.1912710	-1.8765420
14	N	2.8459420	0.9601170	-2.5688100
15	C	1.8920560	0.6276040	-1.5966380
16	C	2.4464280	0.6590090	-0.2796870
17	N	3.7790090	1.0084930	-0.4610890
18	C	1.6553110	0.3667390	0.8914180
19	C	0.5083170	0.2784270	-1.8158540
20	C	0.2862830	0.0218890	0.6718540
21	C	-0.5083790	-0.2788740	1.8157300
22	C	0.0369310	-0.2317810	3.1082000
23	C	1.3733930	0.1176950	3.2914150
24	C	2.1781010	0.4167330	2.1905960
25	C	-0.0369770	0.2312520	-3.1083250
26	C	-1.3734280	-0.1182720	-3.2915400
27	C	-2.1781480	-0.4172600	-2.1907150
28	C	-1.6553660	-0.3671610	-0.8915380
29	C	-0.2863400	-0.0223090	-0.6719660
30	C	4.9596000	3.8158470	3.2070200
31	C	9.4912020	2.4454720	-1.9513320
32	C	4.3423930	3.7025310	0.4820430
33	C	4.1511490	4.8866840	1.1944340
34	C	8.1340330	1.9465940	0.4633730
35	C	9.4709030	2.2436940	0.4672610
36	C	10.1612490	2.4943030	-0.7577700
37	C	4.4589130	4.9437240	2.5592860
38	H	5.4954520	1.7777730	-4.2336970
39	H	7.9465090	2.3082200	-4.1538690
40	H	6.2163560	-0.6086100	3.0622020
41	H	5.9578220	1.5432730	4.2175360
42	H	3.2190470	0.6954140	2.3466880
43	H	0.5998480	0.4711400	-3.9629410
44	H	5.1994560	3.8592120	4.2681570
45	H	10.0079060	2.6384410	-2.8909110
46	H	4.0984870	3.6719700	-0.5827700
47	H	3.7578580	5.7671200	0.6870400
48	H	7.6002070	1.7618020	1.3960730
49	H	10.0296530	2.2966160	1.4007300

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54	C	5.7951460	-2.3974380	1.4511500
55	C	4.5564160	-2.7552110	-1.0709200
56	H	5.4308930	-0.8719050	-1.5529500
57	C	5.2411070	-3.5958110	1.2065320
58	H	6.4993280	-2.2336720	2.2694760
59	C	4.2485640	-3.6876020	0.0703560
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63	C	2.6050850	-3.0807400	-2.5537130
64	H	2.1177510	-3.6895620	-1.7777740
65	H	2.2290550	-3.4181060	-3.5230100
66	H	2.2689180	-2.0454800	-2.4118370
67	C	4.5802500	-4.6544950	-2.6949150
68	H	4.3564300	-4.9807680	-3.7156370
69	H	4.0518550	-5.3404920	-2.0200820
70	H	5.6545820	-4.7795400	-2.5354080
71	C	4.7753320	-2.3096280	-3.5579450
72	H	5.8672400	-2.3142600	-3.5000970
73	H	4.4293440	-1.2697490	-3.4865730
74	H	4.4977010	-2.6606100	-4.5578160
75	C	4.2671850	-5.1503790	2.8708040
76	H	4.3790320	-6.0757830	3.4421980
77	H	3.3679890	-5.2581360	2.2424280
78	H	4.0699520	-4.3393110	3.5776460
79	C	5.7523700	-6.0320310	1.0263480
80	H	4.8509920	-6.2582360	0.4405200
81	H	6.0200000	-6.9492150	1.5605110
82	H	6.5617360	-5.8083100	0.3253130
83	C	6.7453290	-4.7184200	2.9123520
84	H	6.6048270	-3.9435030	3.6717650
85	H	7.6422620	-4.4749430	2.3338990
86	H	6.9485370	-5.6534740	3.4468950
87	H	-3.2190820	-0.6959880	-2.3467980
88	H	-0.5999000	-0.4716970	3.9628060
89	C	-1.8921270	-0.6279880	1.5965120
90	N	-2.8460290	-0.9604680	2.5686810
91	C	-2.4465050	-0.6593570	0.2795580
92	C	-3.9720590	-1.1915460	1.8764120
93	N	-3.7790940	-1.0087920	0.4609590
94	C	-5.3703230	-1.5454130	2.0840560
95	C	-5.0431080	-1.2742850	-0.3225580
96	C	-6.0469550	-1.8090130	3.2932760
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99	C	-4.8383760	-2.5560560	-1.1247200
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107	C	-8.0902810	-2.1395140	1.9927560
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120	H	-5.9580620	-1.5429410	-4.2176550
121	C	-4.5560570	2.7550680	1.0710890
122	H	-5.4308520	0.8718630	1.5529650
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130	H	-10.0300380	-2.2955090	-1.4008100
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132	C	-4.1368590	3.1946000	2.4720160
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134	H	-4.3065460	-5.8692140	-3.1134820
135	H	-11.2252560	-2.7245370	0.7198850
136	O	-3.2891770	4.4270960	-0.0959860
137	C	-2.6048240	3.0803650	2.5540740
138	C	-4.5798910	4.6542610	2.6951540
139	C	-4.7752210	2.3093850	3.5580900
140	C	-4.2663400	5.1504480	-2.8704600
141	C	-5.7514490	6.0321840	-1.0259780
142	C	-6.7445470	4.7188630	-2.9121100
143	H	-2.1173720	3.6891430	1.7781700
144	H	-2.2288560	3.4176980	3.5234020
145	H	-2.2687250	2.0450780	2.4122110
146	H	-4.3561360	4.9804910	3.7159070
147	H	-4.0513970	5.3402400	2.0203880
148	H	-5.6542040	4.7793780	2.5355670
149	H	-5.8671280	2.3141680	3.5001980
150	H	-4.4293720	1.2694640	3.4866570
151	H	-4.4975940	2.6602700	4.5579930
152	H	-4.3780400	6.0759030	-3.4418020
153	H	-3.3671470	5.2580400	-2.2420520

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158	H	-6.6041380	3.9439820	-3.6715760
159	H	-7.6415320	4.4754760	-2.3336990
160	H	-6.9475990	5.6539860	-3.4465890
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162	C	-2.2539926	-1.6240036	-5.0483242
163	C	-3.2410607	0.6394042	-4.7292754
164	C	-0.9501847	0.4023322	-5.6744844
165	H	-1.3148007	-2.2263980	-5.0096285
166	H	-2.9833052	-2.0541640	-4.3206484
167	H	-2.6864518	-1.7093312	-6.0742846
168	H	-3.0275659	1.7005128	-4.4555179
169	H	-3.7029781	0.6228258	-5.7457836
170	H	-3.9775380	0.2247549	-3.9998008
171	H	-1.3427179	0.3779145	-6.7196097
172	H	-0.7215593	1.4620214	-5.4075664
173	H	-0.0021686	-0.1863186	-5.6393700
174	C	1.9656229	0.1755312	4.7118088
175	C	3.2408719	-0.6404631	4.7289933
176	C	2.2544023	1.6231724	5.0482783
177	C	0.9500675	-0.4027717	5.6743748
178	H	3.0268843	-1.7015913	4.4557278
179	H	3.9771194	-0.2261950	3.9990835
180	H	3.7032032	-0.6236801	5.7452928
181	H	1.3155145	2.2260261	5.0091417
182	H	2.6864358	1.7082788	6.0744535
183	H	2.9842036	2.0531512	4.3209721
184	H	1.3430700	-0.3794533	6.7193488
185	H	0.0025200	0.1866577	5.6399846
186	H	0.7204878	-1.4621191	5.4068796

SCF Done: E(RmPW1PW91) = -4002.50239122 A.U.

Zero-point correction = 1.572297 (Hartree/Particle)
Thermal correction to Energy = 1.658443
Thermal correction to Enthalpy = 1.659388
Thermal correction to Gibbs Free Energy = 1.450182
Sum of electronic and zero-point Energies = -4000.930094
Sum of electronic and thermal Energies = -4000.843948
Sum of electronic and thermal Enthalpies = -4000.843004
Sum of electronic and thermal Free Energies = -4001.052209

Low frequencies --- -2.2482 -0.0027 -0.0015 0.0022 3.5467 3.7987
Low frequencies --- 6.4093 10.5252 11.0875

The Result for the TDDFT calculation

Excited State 1: Singlet-A 1.5791 eV 785.16 nm f=0.0000 <S**2>=0.000
346 -> 349 0.10841
347 -> 348 0.69672
This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -4002.44436066
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State	2:	Singlet-A	1.5799 eV	784.75 nm	f=0.0006	<S**2>=0.000
346 -> 348		0.10854				
347 -> 349		0.69664				

Excited State	3:	Singlet-A	2.3788 eV	521.20 nm	f=0.0010	<S**2>=0.000
340 -> 349		0.15698				
341 -> 348		-0.20284				
342 -> 349		0.20190				
343 -> 349		-0.16411				
344 -> 348		0.13491				
346 -> 348		0.56964				

Excited State	4:	Singlet-A	2.3795 eV	521.05 nm	f=0.0000	<S**2>=0.000
340 -> 348		0.16222				
341 -> 349		-0.20767				
342 -> 348		0.20406				
343 -> 348		-0.16808				
344 -> 349		0.13037				
346 -> 349		0.56537				

Excited State	5:	Singlet-A	2.4199 eV	512.36 nm	f=0.0008	<S**2>=0.000
339 -> 348		0.16510				
340 -> 349		-0.37465				
341 -> 348		0.37934				
342 -> 349		-0.14950				
343 -> 349		0.13497				
344 -> 348		0.11313				
346 -> 348		0.33313				

Excited State	6:	Singlet-A	2.4202 eV	512.29 nm	f=0.0000	<S**2>=0.000
339 -> 349		0.16360				
340 -> 348		-0.37259				
341 -> 349		0.37567				
342 -> 348		-0.14658				
343 -> 348		0.13362				
344 -> 349		0.11522				
346 -> 349		0.34160				

Excited State	7:	Singlet-A	2.4914 eV	497.65 nm	f=0.0000	<S**2>=0.000
340 -> 348		0.11703				
341 -> 349		-0.11400				
343 -> 348		0.66189				
345 -> 348		0.11054				

Excited State	8:	Singlet-A	2.4923 eV	497.48 nm	f=0.0002	<S**2>=0.000
340 -> 349		0.11596				
341 -> 348		-0.11306				
343 -> 349		0.66248				
345 -> 349		0.11061				

Excited State	9:	Singlet-A	2.7154 eV	456.60 nm	f=0.0000	<S**2>=0.000
344 -> 348		0.34998				
344 -> 349		0.33592				
345 -> 348		0.34514				
345 -> 349		0.35122				

Excited State 10:	Singlet-A	2.7154 eV	456.60 nm	f=0.0000	<S**2>=0.000
344 -> 348	-0.34007				
344 -> 349	0.34657				
345 -> 348	0.35478				
345 -> 349	-0.34085				
Excited State 11:	Singlet-A	2.7912 eV	444.19 nm	f=0.0000	<S**2>=0.000
344 -> 349	-0.47339				
345 -> 348	0.48257				
346 -> 349	0.13461				
Excited State 12:	Singlet-A	2.8129 eV	440.77 nm	f=1.1889	<S**2>=0.000
344 -> 348	-0.43229				
345 -> 349	0.45381				
346 -> 348	0.13031				
347 -> 350	0.26090				
Excited State 13:	Singlet-A	2.9218 eV	424.34 nm	f=0.4770	<S**2>=0.000
344 -> 348	0.18534				
345 -> 349	-0.18221				
347 -> 350	0.63400				
Excited State 14:	Singlet-A	2.9623 eV	418.54 nm	f=0.0000	<S**2>=0.000
339 -> 349	0.12294				
342 -> 348	0.16331				
347 -> 351	0.65519				
Excited State 15:	Singlet-A	2.9902 eV	414.63 nm	f=0.0323	<S**2>=0.000
339 -> 348	0.36476				
340 -> 349	-0.25625				
341 -> 348	-0.13078				
342 -> 349	0.50545				
347 -> 350	0.10475				
Excited State 16:	Singlet-A	2.9911 eV	414.51 nm	f=0.0000	<S**2>=0.000
339 -> 349	0.34792				
340 -> 348	-0.24578				
341 -> 349	-0.12419				
342 -> 348	0.48539				
347 -> 351	-0.22515				
Excited State 17:	Singlet-A	3.2590 eV	380.44 nm	f=0.0120	<S**2>=0.000
336 -> 348	-0.30284				
337 -> 349	-0.35962				
338 -> 348	0.47380				
341 -> 348	-0.17434				
Excited State 18:	Singlet-A	3.2593 eV	380.40 nm	f=0.0000	<S**2>=0.000
336 -> 349	-0.30405				
337 -> 348	-0.36162				
338 -> 349	0.47189				
341 -> 349	-0.17358				
Excited State 19:	Singlet-A	3.3253 eV	372.85 nm	f=0.0017	<S**2>=0.000
335 -> 349	-0.12571				
336 -> 348	-0.22674				
337 -> 349	-0.17789				
339 -> 348	-0.20364				
340 -> 349	0.14760				

341 -> 348 0.44013
342 -> 349 0.36139

Excited State 20: Singlet-A 3.3255 eV 372.82 nm f=0.0000 <S**2>=0.000
335 -> 348 -0.12569
336 -> 349 -0.22604
337 -> 348 -0.17763
339 -> 349 -0.20296
340 -> 348 0.14871
341 -> 349 0.44128
342 -> 348 0.35998

Excited State 21: Singlet-A 3.3699 eV 367.91 nm f=0.0060 <S**2>=0.000
336 -> 348 0.31184
337 -> 349 0.26285
338 -> 348 0.43043
339 -> 348 -0.29574
341 -> 348 0.10426
342 -> 349 0.17068

Excited State 22: Singlet-A 3.3703 eV 367.87 nm f=0.0000 <S**2>=0.000
336 -> 349 0.30990
337 -> 348 0.26177
338 -> 349 0.43198
339 -> 349 -0.29670
341 -> 349 0.10476
342 -> 348 0.17054

Excited State 23: Singlet-A 3.4554 eV 358.82 nm f=0.0003 <S**2>=0.000
338 -> 348 0.22575
339 -> 348 0.42619
340 -> 349 0.45760
341 -> 348 0.19519

Excited State 24: Singlet-A 3.4555 eV 358.80 nm f=0.0000 <S**2>=0.000
338 -> 349 0.22647
339 -> 349 0.42705
340 -> 348 0.45661
341 -> 349 0.19467

Excited State 25: Singlet-A 3.5333 eV 350.91 nm f=0.1443 <S**2>=0.000
343 -> 352 0.11825
344 -> 351 0.21571
345 -> 350 0.23371
347 -> 352 0.28631
347 -> 354 0.50110
347 -> 359 0.13872

Excited State 26: Singlet-A 3.5403 eV 350.20 nm f=0.0000 <S**2>=0.000
344 -> 350 0.46249
345 -> 351 0.47077
346 -> 350 -0.18667

Excited State 27: Singlet-A 3.5421 eV 350.03 nm f=0.0560 <S**2>=0.000
344 -> 351 0.38267
345 -> 350 0.42966
346 -> 351 -0.19674
347 -> 352 -0.24300
347 -> 354 -0.19182

Excited State 28: Singlet-A 3.5517 eV 349.09 nm f=0.0637 <S**2>=0.000
343 -> 350 -0.30921
343 -> 352 -0.10927
343 -> 359 -0.11127
347 -> 352 0.52295
347 -> 354 -0.26393

Excited State 29: Singlet-A 3.6064 eV 343.79 nm f=0.0000 <S**2>=0.000
346 -> 350 0.13830
347 -> 353 0.66862

Excited State 30: Singlet-A 3.7148 eV 333.76 nm f=0.3797 <S**2>=0.000
335 -> 349 -0.12976
344 -> 351 0.17954
346 -> 351 0.61396
347 -> 354 -0.10733

Excited State 31: Singlet-A 3.7152 eV 333.73 nm f=0.0000 <S**2>=0.000
344 -> 350 0.18306
346 -> 350 0.61049
347 -> 353 -0.12048
347 -> 356 -0.15045

Excited State 32: Singlet-A 3.7355 eV 331.91 nm f=0.0000 <S**2>=0.000
331 -> 349 -0.11359
332 -> 349 -0.12792
333 -> 349 0.29102
334 -> 348 -0.18145
335 -> 348 0.52850
337 -> 348 -0.12411
346 -> 350 -0.10706

Excited State 33: Singlet-A 3.7369 eV 331.78 nm f=0.0710 <S**2>=0.000
331 -> 348 -0.11643
332 -> 348 -0.11939
333 -> 348 0.27893
334 -> 349 -0.17493
335 -> 349 0.50716
337 -> 349 -0.11914
346 -> 351 0.14047
347 -> 355 -0.17670

Excited State 34: Singlet-A 3.7534 eV 330.32 nm f=0.0048 <S**2>=0.000
335 -> 349 0.15692
343 -> 350 -0.15065
346 -> 356 0.10584
347 -> 355 0.64347

Excited State 35: Singlet-A 3.7670 eV 329.13 nm f=0.0000 <S**2>=0.000
343 -> 351 -0.14542
346 -> 350 0.11806
346 -> 355 0.10952
347 -> 356 0.63191

Excited State 36: Singlet-A 3.8019 eV 326.11 nm f=0.0000 <S**2>=0.000
332 -> 349 -0.30893
333 -> 349 -0.29903
334 -> 348 0.44071

335 -> 348 0.21819
337 -> 348 -0.16185
343 -> 351 0.10232

Excited State 37: Singlet-A 3.8030 eV 326.01 nm f=0.0412 <S**2>=0.000
332 -> 348 -0.31241
333 -> 348 -0.30921
334 -> 349 0.45005
335 -> 349 0.20805
337 -> 349 -0.16040

Excited State 38: Singlet-A 3.8121 eV 325.24 nm f=0.0000 <S**2>=0.000
343 -> 351 0.65535
345 -> 351 0.10011
347 -> 356 0.14855

Excited State 39: Singlet-A 3.8399 eV 322.88 nm f=0.2479 <S**2>=0.000
330 -> 349 -0.13601
331 -> 348 -0.12865
343 -> 350 0.51588
343 -> 352 0.10737
346 -> 351 -0.12855
347 -> 352 0.19329
347 -> 354 -0.25554
347 -> 359 0.12625

Excited State 40: Singlet-A 3.9185 eV 316.41 nm f=0.0000 <S**2>=0.000
330 -> 348 0.42370
331 -> 349 0.38717
332 -> 349 -0.14284
333 -> 349 0.12781
344 -> 352 -0.12921
344 -> 355 0.14334
345 -> 353 -0.15388
345 -> 356 -0.13121

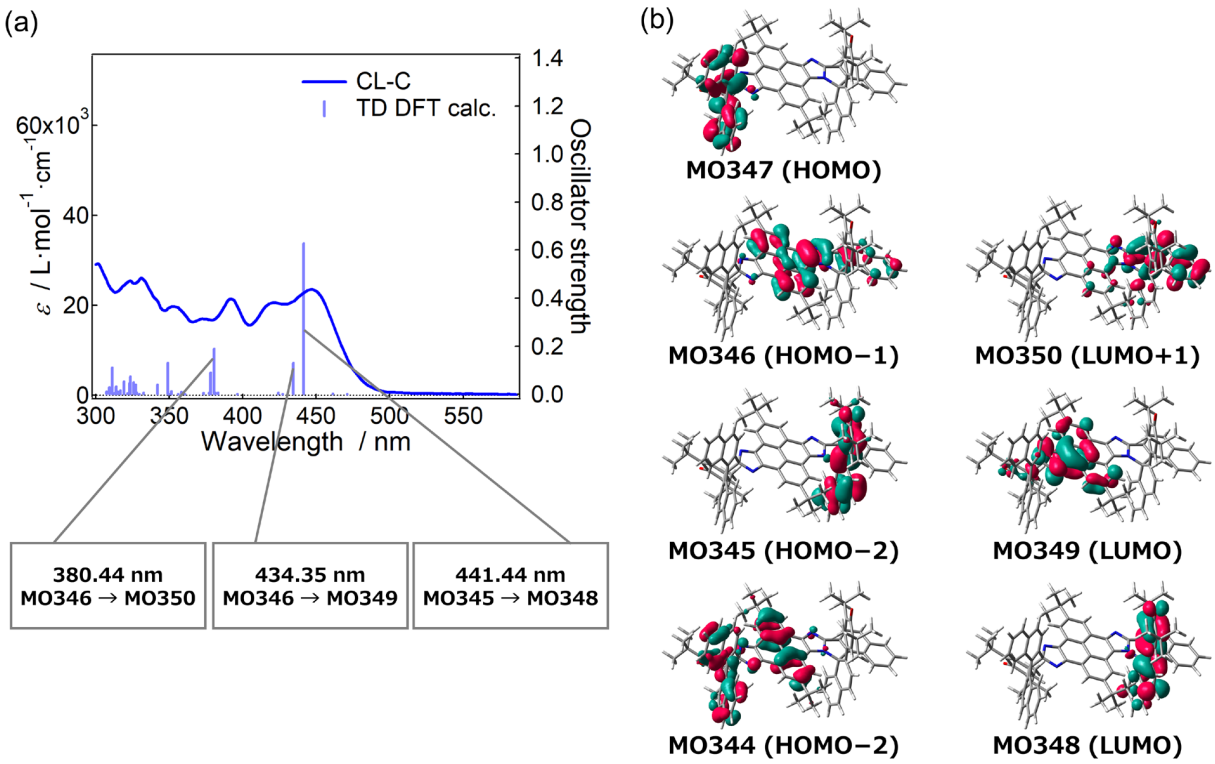

Figure S9. (a) UV–vis absorption spectrum of **CL-C** estimated by global analysis method using Glotaran. The calculated spectra are shown by the perpendicular lines. (b) The calculated molecular orbitals of **CL-C**.

Table S3. Standard Orientation of the Optimized Geometry for **CL-C**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	6.793413	3.346649	0.365859
2	C	8.11725	3.242926	0.032752
3	C	8.599685	2.165888	-0.757692
4	C	7.701332	1.152101	-1.233117
5	C	6.338866	1.279054	-0.867734
6	C	5.914305	2.349063	-0.097204
7	C	5.12716	0.393733	-1.26253
8	C	5.292756	-1.088852	-0.871709
9	C	5.464233	-2.02554	-1.95304
10	C	5.357342	-1.707304	-3.264256
11	C	5.009764	-0.381119	-3.710012
12	C	4.853994	0.638577	-2.759339
13	C	4.497064	2.206634	0.125374
14	N	3.557601	2.872182	0.746176
15	C	2.43128	2.128019	0.505681
16	C	2.694218	0.999906	-0.279226
17	N	4.059492	1.062974	-0.493204
18	C	1.658354	0.092769	-0.685121
19	C	1.116039	2.428534	0.980477
20	C	0.342308	0.391146	-0.218179
21	C	-0.698459	-0.48484	-0.609677
22	C	-0.458995	-1.586538	-1.418186
23	C	0.823269	-1.881408	-1.888035

24	C	1.859356	-1.02959	-1.506746
25	C	0.863614	3.557882	1.777506
26	C	-0.408778	3.86126	2.239276
27	C	-1.449006	2.986695	1.880582
28	C	-1.224898	1.865479	1.098325
29	C	0.073958	1.550842	0.617896
30	C	4.802882	-0.103445	-5.069556
31	C	9.972123	2.078553	-1.091403
32	C	4.48571	1.911464	-3.188512
33	C	4.273161	2.175061	-4.53736
34	C	8.229377	0.104551	-2.028149
35	C	9.567611	0.055726	-2.332789
36	C	10.451063	1.048383	-1.861331
37	C	4.436173	1.165976	-5.484455
38	H	6.414197	4.162227	0.970602
39	H	8.827063	3.991146	0.372114
40	H	5.742029	-3.041284	-1.707462
41	H	5.525877	-2.472343	-4.01636
42	H	2.863768	-1.234016	-1.858684
43	H	1.712669	4.186758	2.015166
44	H	4.926068	-0.904226	-5.792796
45	H	10.643812	2.848916	-0.724223
46	H	4.356605	2.710925	-2.466989
47	H	3.980081	3.172575	-4.846673
48	H	7.568757	-0.668391	-2.397908
49	H	9.949377	-0.756545	-2.942891
50	H	11.506092	0.995379	-2.108766
51	H	4.273956	1.370727	-6.537263
52	C	5.317592	-1.531699	0.447345
53	C	5.430041	-0.648354	1.585485
54	C	5.227178	-2.947647	0.746246
55	C	5.489665	-1.078	2.86997
56	H	5.535407	0.405893	1.394336
57	C	5.236084	-3.460955	1.99791
58	H	5.077302	-3.630168	-0.076696
59	C	5.379094	-2.533233	3.149258
60	O	5.403655	-2.961371	4.303622
61	C	5.089644	-4.958592	2.267501
62	C	5.674623	-0.117105	4.044836
63	C	4.453635	-0.200866	4.981273
64	H	4.334766	-1.203997	5.390351
65	H	4.582935	0.50106	5.812328
66	H	3.537319	0.07476	4.448964
67	C	6.955447	-0.477813	4.821801
68	H	7.088527	0.225758	5.650756
69	H	6.904029	-1.487005	5.229301
70	H	7.835963	-0.402833	4.174673
71	C	5.808462	1.336738	3.58027
72	H	6.67653	1.481743	2.928542
73	H	4.916436	1.692875	3.055375
74	H	5.947677	1.977438	4.456615
75	C	3.837886	-5.217913	3.127166

76	H	3.730701	-6.293553	3.305167
77	H	3.908665	-4.712902	4.090229
78	H	2.93479	-4.870679	2.614127
79	C	6.341958	-5.480454	2.997982
80	H	6.476302	-4.981864	3.957421
81	H	6.241318	-6.556777	3.17554
82	H	7.23998	-5.323002	2.391006
83	C	4.940196	-5.762326	0.971219
84	H	4.045788	-5.476952	0.406834
85	H	5.81347	-5.657158	0.31793
86	H	4.844635	-6.823787	1.218376
87	H	-2.46801	3.169629	2.205362
88	H	-1.309635	-2.207113	-1.67066
89	C	-2.0419	-0.191277	-0.138365
90	C	-2.304116	0.970243	0.726677
91	N	-3.133037	-0.830266	-0.382746
92	N	-3.551733	1.030158	1.038939
93	C	-4.161044	-0.102855	0.364754
94	C	-4.819469	-1.052997	1.356235
95	C	-5.277931	0.433468	-0.629529
96	C	-4.479804	-1.001357	2.722146
97	C	-5.781846	-1.935511	0.885202
98	C	-5.895376	-0.803111	-1.29391
99	C	-6.334903	1.163262	0.137008
100	C	-4.604403	1.289412	-1.650971
101	C	-5.126312	-1.80021	3.628079
102	H	-3.708894	-0.312862	3.04541
103	C	-6.580752	-2.650135	1.842508
104	C	-6.01676	-1.986747	-0.576006
105	C	-6.308003	-0.740134	-2.641059
106	C	-6.677187	2.448106	-0.050184
107	H	-6.853125	0.564091	0.876153
108	C	-4.865619	2.587878	-1.867187
109	H	-3.84536	0.778358	-2.232599
110	C	-6.212052	-2.609124	3.223512
111	H	-4.849233	-1.776064	4.677808
112	C	-7.778087	-3.335366	1.503268
113	C	-6.298383	-3.198081	-1.291628
114	C	-6.74079	-1.861897	-3.298003
115	H	-6.276206	0.215057	-3.15423
116	C	-5.934257	3.252506	-1.061172
117	C	-7.789435	3.122662	0.758032
118	C	-4.104198	3.414915	-2.906729
119	C	-6.975304	-3.332188	4.174527
120	C	-8.515165	-3.998443	2.453116
121	H	-8.126377	-3.317409	0.478831
122	C	-6.693668	-3.123012	-2.662789
123	C	-6.120833	-4.488868	-0.726418
124	H	-7.072753	-1.801473	-4.330268
125	O	-6.195419	4.439904	-1.234042
126	C	-7.203694	4.287907	1.576855
127	C	-8.887132	3.645741	-0.185977

128	C	-8.444009	2.145593	1.740558
129	C	-3.37233	4.57738	-2.210229
130	C	-5.078966	3.968814	-3.961901
131	C	-3.052421	2.573492	-3.638319
132	C	-8.099117	-4.022308	3.801011
133	H	-6.662326	-3.306247	5.214378
134	H	-9.431636	-4.502488	2.163486
135	C	-6.989828	-4.31397	-3.372035
136	C	-6.382407	-5.626061	-1.44988
137	H	-5.74929	-4.574011	0.287024
138	H	-6.77384	5.051175	0.928292
139	H	-7.993607	4.748513	2.180716
140	H	-6.425694	3.927587	2.258365
141	H	-9.687723	4.109803	0.400692
142	H	-8.493358	4.387658	-0.88063
143	H	-9.327377	2.824382	-0.761581
144	H	-8.909108	1.296198	1.229173
145	H	-7.729351	1.757389	2.473689
146	H	-9.231227	2.667335	2.293646
147	H	-2.803978	5.15104	-2.95082
148	H	-4.075651	5.248814	-1.718009
149	H	-2.666317	4.199976	-1.463003
150	H	-5.82839	4.616449	-3.507602
151	H	-4.524681	4.548427	-4.708267
152	H	-5.59056	3.153494	-4.485453
153	H	-2.295545	2.173093	-2.955849
154	H	-3.499988	1.73708	-4.185927
155	H	-2.535198	3.203325	-4.368653
156	H	-8.681872	-4.563496	4.539403
157	C	-6.845927	-5.542148	-2.780223
158	H	-7.311436	-4.233039	-4.406497
159	H	-6.223716	-6.598827	-0.995459
160	H	-7.064527	-6.448143	-3.336333
161	C	1.09381	-3.085585	-2.795036
162	C	1.644623	-2.591224	-4.142737
163	C	2.121138	-4.012486	-2.125047
164	C	-0.174348	-3.90083	-3.06857
165	H	0.916623	-1.949589	-4.648755
166	H	2.565919	-2.016241	-4.019291
167	H	1.861279	-3.441987	-4.798457
168	H	1.748728	-4.376795	-1.162455
169	H	2.3209	-4.880161	-2.763473
170	H	3.070836	-3.500789	-1.948928
171	H	0.070627	-4.749148	-3.715253
172	H	-0.609926	-4.302186	-2.148374
173	H	-0.93957	-3.308431	-3.579479
174	C	-0.712739	5.086329	3.102113
175	C	-1.723266	5.984266	2.367483
176	C	-1.315932	4.626984	4.440672
177	C	0.543179	5.911237	3.397017
178	H	-1.316588	6.33212	1.412858
179	H	-2.660718	5.460656	2.159805

180	H	-1.961007	6.862927	2.976777
181	H	-0.615118	3.988399	4.987421
182	H	-1.547042	5.494379	5.068188
183	H	-2.242616	4.06385	4.298502
184	H	0.278771	6.772913	4.017693
185	H	1.293686	5.329192	3.941265
186	H	1.003796	6.293177	2.480521

SCF Done: E(RmPW1PW91) = -4002.48814308 A.U.

Zero-point correction = 1.571781 (Hartree/Particle)
Thermal correction to Energy = 1.657678
Thermal correction to Enthalpy = 1.658622
Thermal correction to Gibbs Free Energy = 1.449370
Sum of electronic and zero-point Energies = -4000.916362
Sum of electronic and thermal Energies = -4000.830465
Sum of electronic and thermal Enthalpies = -4000.829521
Sum of electronic and thermal Free Energies = -4001.038773

Low frequencies --- -0.4962 -0.0019 -0.0007 0.0012 2.9470 3.4733
Low frequencies --- 6.7010 9.8885 12.3979

The Result for the TDDFT calculation

Excited State 1: Singlet-A 1.9206 eV 645.54 nm f=0.0005 <S**2>=0.000
346 -> 348 0.70341
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -4002.41756109
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.2431 eV 552.73 nm f=0.0000 <S**2>=0.000
347 -> 348 0.70560

Excited State 3: Singlet-A 2.3898 eV 518.80 nm f=0.0006 <S**2>=0.000
338 -> 348 -0.19794
339 -> 348 0.51797
341 -> 348 0.39567

Excited State 4: Singlet-A 2.6319 eV 471.08 nm f=0.0001 <S**2>=0.000
343 -> 348 0.45046
344 -> 348 0.52695

Excited State 5: Singlet-A 2.6875 eV 461.33 nm f=0.0022 <S**2>=0.000
347 -> 349 0.70105

Excited State 6: Singlet-A 2.8086 eV 441.44 nm f=0.6280 <S**2>=0.000
345 -> 348 0.66292
346 -> 349 0.20386
345 <- 348 -0.10296

Excited State 7: Singlet-A 2.8545 eV 434.35 nm f=0.1302 <S**2>=0.000
345 -> 348 -0.20278
346 -> 349 0.66612

Excited State 8: Singlet-A 2.9024 eV 427.17 nm f=0.0008 <S**2>=0.000
339 -> 348 0.14407
341 -> 348 -0.19824

343 -> 348 0.50805
344 -> 348 -0.42212

Excited State 9: Singlet-A 2.9229 eV 424.18 nm f=0.0064 <S**2>=0.000
339 -> 348 -0.37551
341 -> 348 0.52645
343 -> 348 0.16969
344 -> 348 -0.18808

Excited State 10: Singlet-A 3.1281 eV 396.35 nm f=0.0001 <S**2>=0.000
342 -> 348 0.69799

Excited State 11: Singlet-A 3.2362 eV 383.11 nm f=0.0068 <S**2>=0.000
334 -> 348 0.37327
336 -> 348 0.11079
337 -> 348 0.35245
338 -> 348 -0.33388
339 -> 348 -0.10021
340 -> 348 0.21851
341 -> 348 -0.10621

Excited State 12: Singlet-A 3.2511 eV 381.36 nm f=0.0071 <S**2>=0.000
342 -> 349 0.38643
342 -> 352 0.48272
343 -> 349 -0.13786
344 -> 349 -0.21036
346 -> 350 -0.11518
347 -> 352 -0.11180

Excited State 13: Singlet-A 3.2590 eV 380.44 nm f=0.1898 <S**2>=0.000
342 -> 349 0.15228
342 -> 352 0.15750
343 -> 349 0.21010
344 -> 349 0.21388
346 -> 350 0.57517

Excited State 14: Singlet-A 3.2799 eV 378.01 nm f=0.0900 <S**2>=0.000
342 -> 349 0.11332
342 -> 352 0.10461
343 -> 349 0.36665
344 -> 349 0.43927
346 -> 350 -0.34947

Excited State 15: Singlet-A 3.2875 eV 377.14 nm f=0.0061 <S**2>=0.000
333 -> 348 -0.11093
334 -> 348 -0.26456
340 -> 348 0.63249

Excited State 16: Singlet-A 3.3220 eV 373.23 nm f=0.0048 <S**2>=0.000
333 -> 348 0.21493
334 -> 348 0.44830
336 -> 348 -0.10424
337 -> 348 -0.20836
338 -> 348 0.35778
339 -> 348 0.13284
340 -> 348 0.19448

Excited State 17: Singlet-A 3.4371 eV 360.72 nm f=0.0003 <S**2>=0.000
345 -> 349 0.69874

Excited State 18:	Singlet-A	3.4612 eV	358.21 nm	f=0.0092	<S**2>=0.000
343 -> 349	0.53437				
344 -> 349	-0.44383				
Excited State 19:	Singlet-A	3.4816 eV	356.11 nm	f=0.0007	<S**2>=0.000
336 -> 348	0.16093				
337 -> 348	0.48964				
338 -> 348	0.44732				
339 -> 348	0.10903				
Excited State 20:	Singlet-A	3.5276 eV	351.47 nm	f=0.0093	<S**2>=0.000
345 -> 350	-0.34318				
347 -> 350	0.58058				
347 -> 351	0.14685				
Excited State 21:	Singlet-A	3.5287 eV	351.36 nm	f=0.0124	<S**2>=0.000
345 -> 350	0.56947				
347 -> 350	0.35439				
Excited State 22:	Singlet-A	3.5460 eV	349.65 nm	f=0.0010	<S**2>=0.000
333 -> 348	0.36647				
334 -> 348	-0.12740				
335 -> 348	0.10273				
336 -> 348	0.52988				
337 -> 348	-0.14848				
345 -> 350	0.16161				
Excited State 23:	Singlet-A	3.5519 eV	349.06 nm	f=0.1292	<S**2>=0.000
347 -> 350	-0.16588				
347 -> 351	0.64736				
347 -> 352	-0.17273				
Excited State 24:	Singlet-A	3.6263 eV	341.90 nm	f=0.0385	<S**2>=0.000
342 -> 349	0.18529				
347 -> 351	0.18874				
347 -> 352	0.64412				
Excited State 25:	Singlet-A	3.7282 eV	332.56 nm	f=0.0068	<S**2>=0.000
331 -> 349	0.13653				
336 -> 349	-0.11413				
340 -> 349	0.61200				
342 -> 349	-0.17961				
342 -> 352	0.11131				
Excited State 26:	Singlet-A	3.7622 eV	329.55 nm	f=0.0009	<S**2>=0.000
333 -> 348	0.49543				
334 -> 348	-0.22401				
336 -> 348	-0.37935				
337 -> 348	0.16866				
Excited State 27:	Singlet-A	3.7819 eV	327.84 nm	f=0.0064	<S**2>=0.000
336 -> 349	-0.10101				
338 -> 349	0.37638				
340 -> 349	0.12545				
341 -> 349	0.11506				
342 -> 349	0.33489				
342 -> 352	-0.27775				
346 -> 353	-0.22829				

347 -> 352 -0.11132

Excited State 28: Singlet-A 3.7908 eV 327.07 nm f=0.0393 <S**2>=0.000
332 -> 348 0.64247
335 -> 348 0.19363

Excited State 29: Singlet-A 3.8075 eV 325.63 nm f=0.0489 <S**2>=0.000
337 -> 349 0.11695
342 -> 349 0.26215
342 -> 352 -0.21179
343 -> 350 -0.19324
344 -> 350 -0.22036
346 -> 351 -0.20142
346 -> 353 0.43876

Excited State 30: Singlet-A 3.8329 eV 323.48 nm f=0.0730 <S**2>=0.000
336 -> 349 -0.10199
337 -> 349 0.14779
338 -> 349 0.42089
340 -> 349 -0.21303
341 -> 349 0.17747
342 -> 349 -0.22620
342 -> 352 0.20915
346 -> 351 -0.10325
346 -> 353 0.15226
346 -> 354 -0.10658

Excited State 31: Singlet-A 3.8383 eV 323.02 nm f=0.0464 <S**2>=0.000
341 -> 350 0.11516
343 -> 350 -0.23106
344 -> 350 -0.25829
346 -> 352 -0.17159
346 -> 353 -0.19907
346 -> 354 0.44148

Excited State 32: Singlet-A 3.8557 eV 321.56 nm f=0.0031 <S**2>=0.000
332 -> 348 -0.19174
333 -> 348 -0.14836
335 -> 348 0.65527

Excited State 33: Singlet-A 3.8848 eV 319.15 nm f=0.0526 <S**2>=0.000
330 -> 348 -0.17193
344 -> 350 -0.11304
346 -> 351 0.60394
346 -> 352 -0.12038
346 -> 353 0.17003

Excited State 34: Singlet-A 3.9140 eV 316.77 nm f=0.0149 <S**2>=0.000
330 -> 348 0.54579
337 -> 349 0.13574
345 -> 353 -0.15951
345 -> 354 0.10423
345 -> 355 0.17751
346 -> 351 0.19318
346 -> 353 0.14637

Excited State 35: Singlet-A 3.9398 eV 314.70 nm f=0.0102 <S**2>=0.000
329 -> 349 0.16695
330 -> 348 -0.15532

331 -> 349 0.24093
335 -> 349 -0.11008
336 -> 349 -0.11222
337 -> 349 0.37624
338 -> 349 -0.13736
340 -> 349 -0.11896
341 -> 349 -0.11687
343 -> 350 0.15764
344 -> 350 0.18793
346 -> 354 0.14410
347 -> 353 0.14491

Excited State 36: Singlet-A 3.9500 eV 313.88 nm f=0.0310 <S**2>=0.000
343 -> 351 -0.12880
344 -> 351 0.14091
346 -> 352 -0.36487
346 -> 354 -0.15106
347 -> 353 0.37915
347 -> 354 0.19759
347 -> 356 -0.21728

Excited State 37: Singlet-A 3.9628 eV 312.87 nm f=0.0053 <S**2>=0.000
341 -> 349 -0.13829
346 -> 351 0.13476
346 -> 352 0.53525
347 -> 353 0.28146
347 -> 354 0.13759
347 -> 356 -0.14956

Excited State 38: Singlet-A 3.9859 eV 311.06 nm f=0.1097 <S**2>=0.000
329 -> 349 0.11359
331 -> 349 0.23612
335 -> 349 -0.11097
336 -> 349 -0.22940
337 -> 349 -0.17702
338 -> 349 -0.26274
339 -> 349 -0.10863
341 -> 349 0.31358
343 -> 350 -0.14783
344 -> 350 -0.17733
346 -> 353 -0.13097
346 -> 354 -0.13048

Excited State 39: Singlet-A 4.0085 eV 309.30 nm f=0.0287 <S**2>=0.000
331 -> 349 -0.17438
341 -> 349 0.41547
341 -> 350 0.10341
343 -> 351 -0.12613
344 -> 350 0.12118
344 -> 351 0.17952
346 -> 353 0.11978
346 -> 354 0.21351
346 -> 355 -0.13435
347 -> 356 -0.23539

Excited State 40: Singlet-A 4.0354 eV 307.24 nm f=0.0116 <S**2>=0.000
341 -> 349 0.23015
343 -> 351 0.22305
344 -> 351 -0.23864

347 -> 353	0.38105
347 -> 356	0.36444

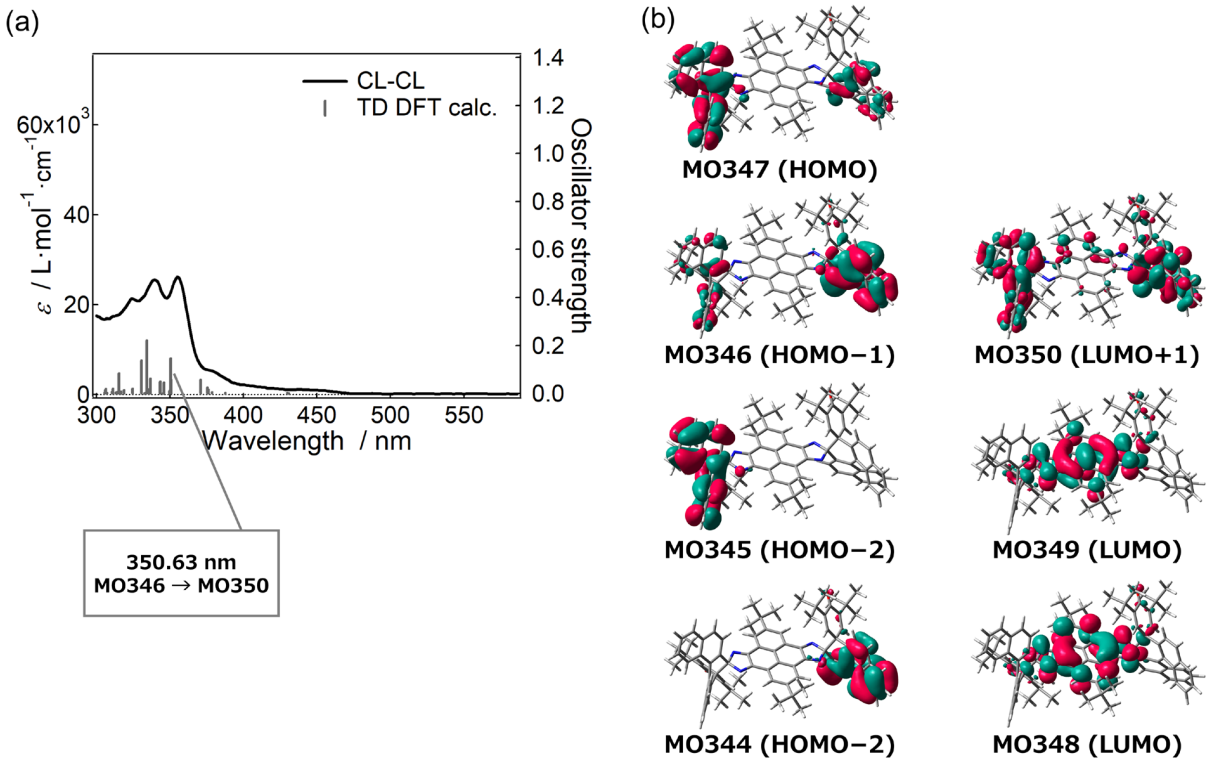

Figure S10. (a) UV–vis absorption spectrum of **CL-CL** estimated by global analysis method using Glotaran. The calculated spectra are shown by the perpendicular lines. (b) The calculated molecular orbitals of **CL-CL**.

Table S4. Standard Orientation of the Optimized Geometry for **CL-CL**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	4.974578	-0.719388	2.641159
2	C	5.772439	-0.703058	3.755034
3	C	7.00889	-0.019275	3.740674
4	C	7.385208	0.726996	2.580431
5	C	6.457825	0.834501	1.488205
6	C	5.326351	0.030515	1.502261
7	C	6.709659	1.653776	0.280647
8	C	6.348937	1.119142	-0.950283
9	C	6.744853	1.751213	-2.147051
10	C	7.40474	2.951908	-2.123344
11	C	7.62165	3.622942	-0.89906
12	C	7.245078	2.984096	0.322417
13	C	4.492458	-0.061587	0.230693
14	N	3.644848	-1.240697	0.232976
15	C	2.443909	-0.786659	0.146048
16	C	2.449252	0.684554	0.101658
17	N	3.654618	1.134804	0.124952
18	C	1.202877	1.429898	0.044718
19	C	1.196474	-1.527631	0.076536
20	C	0.000123	0.69005	0.001742

21	C	-1.198068	1.43111	-0.04108
22	C	-1.187059	2.82797	-0.041506
23	C	0.001166	3.555524	-0.000706
24	C	1.191251	2.82186	0.042856
25	C	1.185728	-2.924674	0.075152
26	C	-0.000317	-3.653085	0.00093
27	C	-1.18843	-2.918749	-0.074072
28	C	-1.200137	-1.526545	-0.075122
29	C	0.000401	-0.785893	0.001239
30	C	8.16773	4.930577	-0.865687
31	C	7.905524	-0.113203	4.83481
32	C	7.344953	3.740593	1.520316
33	C	7.846568	5.018555	1.516425
34	C	8.703586	1.254477	2.537916
35	C	9.561739	1.117333	3.600786
36	C	9.153931	0.449464	4.774832
37	C	8.286665	5.615641	0.31578
38	H	4.072921	-1.318839	2.617944
39	H	5.491087	-1.265362	4.640379
40	H	6.5177	1.271958	-3.093349
41	H	7.7205	3.42427	-3.048813
42	H	2.153875	3.32152	0.079463
43	H	2.146636	-3.421781	0.132309
44	H	8.469471	5.38872	-1.803248
45	H	7.589491	-0.665179	5.715299
46	H	6.997908	3.305788	2.449244
47	H	7.898158	5.576901	2.445657
48	H	9.04489	1.755726	1.641649
49	H	10.566989	1.520528	3.532422
50	H	9.836515	0.361567	5.61386
51	H	8.696062	6.620601	0.328427
52	C	5.486324	-0.146786	-1.007332
53	C	6.362706	-1.351951	-0.86961
54	C	4.663753	-0.164722	-2.253794
55	C	6.408703	-2.377181	-1.734914
56	H	7.00649	-1.348366	0.001527
57	C	4.631905	-1.16827	-3.144348
58	H	4.053005	0.719229	-2.40056
59	C	5.493304	-2.368077	-2.910199
60	O	5.44742	-3.325228	-3.677488
61	C	3.73624	-1.136597	-4.385555
62	C	7.347858	-3.570472	-1.537737
63	C	6.521467	-4.854952	-1.339836
64	H	5.906763	-5.069345	-2.213942
65	H	7.193846	-5.703451	-1.170584
66	H	5.869021	-4.762074	-0.465111
67	C	8.271943	-3.724483	-2.759191
68	H	8.951867	-4.569182	-2.602995
69	H	7.701161	-3.906056	-3.669825
70	H	8.882031	-2.825764	-2.900466
71	C	8.234664	-3.39143	-0.300338
72	H	8.867877	-2.500766	-0.372379

73	H	7.648248	-3.324436	0.621905
74	H	8.895775	-4.258354	-0.20577
75	C	2.720328	-2.292708	-4.324138
76	H	2.0611	-2.250659	-5.198343
77	H	3.223054	-3.259554	-4.314886
78	H	2.095786	-2.213185	-3.427903
79	C	4.592812	-1.261114	-5.65896
80	H	5.139612	-2.203515	-5.679919
81	H	3.947794	-1.214097	-6.543157
82	H	5.311348	-0.436805	-5.726409
83	C	2.947163	0.173796	-4.481759
84	H	2.274548	0.316184	-3.6294
85	H	3.603918	1.047494	-4.552722
86	H	2.329582	0.154053	-5.384904
87	H	-2.149695	-3.418946	-0.131173
88	H	-2.149099	3.324886	-0.079293
89	C	-2.446374	0.689612	-0.097956
90	C	-2.445671	-0.781606	-0.144224
91	N	-3.650867	1.143024	-0.1208
92	N	-3.647462	-1.232344	-0.232398
93	C	-4.491892	-0.050692	-0.228856
94	C	-5.324127	0.045548	-1.501258
95	C	-5.487039	-0.136239	1.007983
96	C	-4.97151	-0.701742	-2.641641
97	C	-6.454634	0.85091	-1.486865
98	C	-6.348334	1.13059	0.952296
99	C	-6.364629	-1.340222	0.867552
100	C	-4.665956	-0.15683	2.255387
101	C	-5.767718	-0.681737	-3.756627
102	H	-4.070392	-1.302037	-2.618933
103	C	-7.380704	0.746848	-2.580575
104	C	-6.707124	1.66798	-0.277967
105	C	-6.74564	1.760232	2.149893
106	C	-6.412358	-2.366847	1.731113
107	H	-7.00749	-1.334574	-0.00428
108	C	-4.636588	-1.16143	3.144871
109	H	-4.054651	0.726409	2.404087
110	C	-7.003559	0.003147	-3.742192
111	H	-5.485593	-1.241965	-4.643042
112	C	-8.698704	1.275304	-2.538439
113	C	-7.241798	2.998691	-0.317587
114	C	-7.405098	2.961171	2.127856
115	H	-6.520059	1.278799	3.095459
116	C	-5.498293	-2.360371	2.907477
117	C	-7.351834	-3.559326	1.530615
118	C	-3.743693	-1.13166	4.388105
119	C	-7.898799	-0.087168	-4.837771
120	C	-9.555582	1.141609	-3.602781
121	H	-9.04078	1.774538	-1.641347
122	C	-7.62	3.634942	0.904729
123	C	-7.339568	3.757914	-1.513908
124	H	-7.722079	3.431604	3.053892

125	O	-5.453534	-3.319178	3.672756
126	C	-6.525481	-4.843433	1.330074
127	C	-8.276727	-3.716267	2.751067
128	C	-8.237801	-3.377144	0.29308
129	C	-2.727492	-2.287508	4.327578
130	C	-4.603338	-1.258033	5.659259
131	C	-2.954973	0.178686	4.488046
132	C	-9.146789	0.476451	-4.778017
133	H	-7.58207	-0.637166	-5.719248
134	H	-10.560585	1.545464	-3.534679
135	C	-8.165733	4.942756	0.873468
136	C	-7.840883	5.035983	-1.507919
137	H	-6.991056	3.325169	-2.443244
138	H	-5.910339	-5.05941	2.203506
139	H	-7.197783	-5.691707	1.159415
140	H	-5.873655	-4.748658	0.455046
141	H	-8.956726	-4.56041	2.592236
142	H	-7.706605	-3.900266	3.661619
143	H	-8.886716	-2.817782	2.894192
144	H	-8.870612	-2.48634	0.366771
145	H	-7.650825	-3.308296	-0.628672
146	H	-8.899252	-4.243548	0.196109
147	H	-2.071373	-2.247337	5.204218
148	H	-3.229766	-3.254529	4.314236
149	H	-2.099776	-2.205925	3.433801
150	H	-5.149994	-2.200572	5.677656
151	H	-3.960455	-1.212148	6.545065
152	H	-5.322203	-0.433959	5.726133
153	H	-2.280319	0.322278	3.637498
154	H	-3.611973	1.05224	4.558645
155	H	-2.339534	0.157682	5.392623
156	H	-9.828326	0.391331	-5.618182
157	C	-8.282736	5.63047	-0.306643
158	H	-8.468731	5.398886	1.811605
159	H	-7.890802	5.596473	-2.435947
160	H	-8.69184	6.635567	-0.317662
161	C	0.042803	5.084086	-0.002326
162	C	0.734846	5.572032	1.281988
163	C	0.838564	5.566826	-1.227204
164	C	-1.358175	5.69975	-0.061467
165	H	0.185802	5.247168	2.171187
166	H	1.758556	5.195828	1.362881
167	H	0.780796	6.66612	1.291972
168	H	0.365697	5.237048	-2.15743
169	H	0.884253	6.660866	-1.238576
170	H	1.86611	5.192112	-1.220721
171	H	-1.276792	6.790851	-0.062289
172	H	-1.895018	5.408446	-0.969755
173	H	-1.967052	5.415725	0.802624
174	C	-0.041662	-5.18134	-0.001621
175	C	-0.872322	-5.666618	1.199018
176	C	-0.696203	-5.665613	-1.306988

177	C	1.357568	-5.796305	0.095135
178	H	-0.426287	-5.339978	2.143488
179	H	-1.899274	-5.291517	1.16655
180	H	-0.918806	-6.760584	1.205858
181	H	-0.123149	-5.336389	-2.179325
182	H	-0.739707	-6.759657	-1.322058
183	H	-1.71844	-5.29151	-1.414115
184	H	1.276966	-6.887363	0.091706
185	H	1.990629	-5.510511	-0.750879
186	H	1.867143	-5.506882	1.019731

SCF Done: E(RmPW1PW91) = -4002.47241591 A.U.

Zero-point correction = 1.570438 (Hartree/Particle)
Thermal correction to Energy = 1.656361
Thermal correction to Enthalpy = 1.657305
Thermal correction to Gibbs Free Energy = 1.446739
Sum of electronic and zero-point Energies = -4000.901978
Sum of electronic and thermal Energies = -4000.816055
Sum of electronic and thermal Enthalpies = -4000.815111
Sum of electronic and thermal Free Energies = -4001.025677

Low frequencies --- -0.0010 -0.0004 0.0010 0.4497 2.3413 3.8189
Low frequencies --- 8.2810 10.4356 13.2383

The Result for the TDDFT calculation

Excited State 1: Singlet-A 2.5429 eV 487.58 nm f=0.0014 <S**2>=0.000
346 -> 348 -0.19018
346 -> 349 -0.22313
347 -> 348 0.45776
347 -> 349 0.44340
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -4002.37896721
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.5448 eV 487.21 nm f=0.0009 <S**2>=0.000
346 -> 348 0.46532
346 -> 349 -0.42869
347 -> 348 0.20239
347 -> 349 -0.22502

Excited State 3: Singlet-A 2.8785 eV 430.72 nm f=0.0001 <S**2>=0.000
346 -> 348 0.10299
346 -> 349 0.45463
347 -> 348 0.47750
347 -> 349 -0.22123

Excited State 4: Singlet-A 2.8843 eV 429.86 nm f=0.0020 <S**2>=0.000
346 -> 348 0.48088
346 -> 349 0.23206
347 -> 348 -0.11913
347 -> 349 0.44589

Excited State 5: Singlet-A 3.1985 eV 387.63 nm f=0.0017 <S**2>=0.000
341 -> 348 -0.26951

341 -> 353 0.25627
342 -> 348 -0.17281
342 -> 349 0.32515
342 -> 352 -0.31902
342 -> 353 0.13194
343 -> 348 0.14611

Excited State 6: Singlet-A 3.1989 eV 387.59 nm f=0.0005 <S**2>=0.000
341 -> 348 -0.14620
341 -> 349 -0.29778
341 -> 352 0.28724
341 -> 353 0.16863
342 -> 348 0.30061
342 -> 353 -0.28359
343 -> 349 0.14735
343 -> 352 -0.10477

Excited State 7: Singlet-A 3.2750 eV 378.58 nm f=0.0056 <S**2>=0.000
341 -> 348 0.24155
343 -> 348 0.56041
344 -> 348 -0.17388
345 -> 348 0.21007
345 -> 349 0.12991

Excited State 8: Singlet-A 3.2966 eV 376.10 nm f=0.0156 <S**2>=0.000
343 -> 349 0.11702
344 -> 348 0.28781
344 -> 349 -0.31336
345 -> 348 0.37132
345 -> 349 0.36241

Excited State 9: Singlet-A 3.3024 eV 375.44 nm f=0.0244 <S**2>=0.000
343 -> 348 0.28442
344 -> 348 0.37091
344 -> 349 -0.35232
345 -> 348 -0.21913
345 -> 349 -0.30378

Excited State 10: Singlet-A 3.3439 eV 370.78 nm f=0.0576 <S**2>=0.000
341 -> 349 0.21801
343 -> 349 0.63072
345 -> 348 -0.13845

Excited State 11: Singlet-A 3.5360 eV 350.63 nm f=0.0574 <S**2>=0.000
346 -> 350 0.49243
346 -> 351 0.26324
346 -> 352 -0.10610
346 -> 353 0.13965
347 -> 351 0.31681
347 -> 352 -0.11572

Excited State 12: Singlet-A 3.5377 eV 350.46 nm f=0.1460 <S**2>=0.000
346 -> 351 0.31513
346 -> 352 -0.10807
347 -> 350 0.42042
347 -> 351 -0.35682
347 -> 352 0.11448
347 -> 353 0.15315

Excited State 13:	Singlet-A	3.5450 eV	349.74 nm	f=0.0108	<S**2>=0.000
343 -> 348	0.10075				
344 -> 348	0.25473				
344 -> 349	0.22054				
345 -> 348	-0.39831				
345 -> 349	0.43238				
Excited State 14:	Singlet-A	3.5466 eV	349.58 nm	f=0.0010	<S**2>=0.000
344 -> 348	0.39594				
344 -> 349	0.45306				
345 -> 348	0.27276				
345 -> 349	-0.22549				
Excited State 15:	Singlet-A	3.5847 eV	345.87 nm	f=0.0456	<S**2>=0.000
339 -> 348	0.34973				
340 -> 349	0.36961				
341 -> 348	-0.13518				
342 -> 349	0.20542				
342 -> 352	0.10601				
346 -> 352	-0.20762				
347 -> 353	0.20229				
Excited State 16:	Singlet-A	3.5924 eV	345.13 nm	f=0.0007	<S**2>=0.000
339 -> 349	0.36562				
340 -> 348	0.38142				
341 -> 349	-0.14613				
342 -> 348	0.20061				
346 -> 353	-0.19245				
347 -> 352	0.19971				
Excited State 17:	Singlet-A	3.6105 eV	343.40 nm	f=0.0492	<S**2>=0.000
339 -> 348	-0.20249				
339 -> 349	-0.14824				
340 -> 348	-0.18948				
340 -> 349	-0.22328				
346 -> 352	-0.15985				
346 -> 353	-0.12674				
347 -> 350	-0.14862				
347 -> 351	0.14902				
347 -> 352	0.27108				
347 -> 353	0.33200				
Excited State 18:	Singlet-A	3.6120 eV	343.25 nm	f=0.0483	<S**2>=0.000
339 -> 348	0.20622				
339 -> 349	-0.21787				
340 -> 348	-0.18936				
340 -> 349	0.14515				
346 -> 350	0.15513				
346 -> 351	0.11896				
346 -> 352	0.31419				
346 -> 353	-0.29075				
347 -> 352	0.18535				
Excited State 19:	Singlet-A	3.6840 eV	336.55 nm	f=0.0614	<S**2>=0.000
336 -> 349	-0.18894				
337 -> 348	0.31105				
338 -> 349	0.36532				
341 -> 353	-0.15193				
342 -> 349	0.17936				

342 -> 352 0.15769
346 -> 352 0.19217
347 -> 353 -0.18552

Excited State 20: Singlet-A 3.6943 eV 335.61 nm f=0.0167 <S**2>=0.000
336 -> 348 -0.14265
337 -> 349 0.22752
338 -> 348 0.20787
341 -> 349 -0.13452
341 -> 352 -0.22221
342 -> 348 0.30722
342 -> 353 0.24034
346 -> 353 0.19668
347 -> 352 -0.19960

Excited State 21: Singlet-A 3.7091 eV 334.27 nm f=0.2198 <S**2>=0.000
334 -> 348 -0.14093
336 -> 349 0.42091
337 -> 348 -0.14616
339 -> 348 -0.14357
341 -> 348 0.17423
342 -> 349 0.35188

Excited State 22: Singlet-A 3.7109 eV 334.10 nm f=0.0040 <S**2>=0.000
337 -> 348 0.18100
338 -> 349 0.26887
340 -> 349 0.10152
341 -> 348 0.44397
341 -> 353 0.22655
342 -> 352 -0.23121
343 -> 348 -0.10846
346 -> 352 -0.11583
347 -> 353 0.10216

Excited State 23: Singlet-A 3.7205 eV 333.25 nm f=0.0018 <S**2>=0.000
336 -> 348 -0.27406
337 -> 349 0.35440
338 -> 348 0.29999
340 -> 348 0.12553
341 -> 352 0.14966
342 -> 348 -0.21985
342 -> 353 -0.16387

Excited State 24: Singlet-A 3.7275 eV 332.62 nm f=0.0003 <S**2>=0.000
341 -> 349 0.51782
342 -> 348 0.39832
343 -> 349 -0.19882

Excited State 25: Singlet-A 3.7501 eV 330.61 nm f=0.1368 <S**2>=0.000
334 -> 348 0.12655
336 -> 349 -0.32287
338 -> 349 -0.31700
341 -> 348 0.24322
342 -> 349 0.39406
343 -> 348 -0.10894

Excited State 26: Singlet-A 3.8203 eV 324.54 nm f=0.0198 <S**2>=0.000
334 -> 349 -0.23214
336 -> 348 0.41720

338 -> 348 0.41223
339 -> 349 -0.14390

Excited State 27: Singlet-A 3.8915 eV 318.60 nm f=0.0143 <S**2>=0.000
327 -> 349 -0.12625
328 -> 348 0.11938
331 -> 349 0.13565
333 -> 348 -0.13599
335 -> 349 0.39671
336 -> 349 -0.14320
337 -> 348 -0.19178
338 -> 349 0.11672
339 -> 348 -0.10007
340 -> 349 0.11113
343 -> 354 -0.11322
346 -> 351 0.11754
347 -> 350 -0.17767
347 -> 354 -0.24633

Excited State 28: Singlet-A 3.9149 eV 316.70 nm f=0.0002 <S**2>=0.000
328 -> 349 -0.10534
337 -> 349 -0.10391
339 -> 349 -0.38832
340 -> 348 0.45284
340 -> 349 -0.16496
346 -> 354 -0.11489

Excited State 29: Singlet-A 3.9169 eV 316.53 nm f=0.0073 <S**2>=0.000
327 -> 349 0.10449
328 -> 348 -0.11790
334 -> 348 0.11314
337 -> 348 -0.12019
339 -> 348 -0.39335
339 -> 349 -0.15537
340 -> 349 0.44161

Excited State 30: Singlet-A 3.9223 eV 316.10 nm f=0.0064 <S**2>=0.000
339 -> 349 -0.16767
340 -> 348 0.15823
346 -> 350 0.26584
346 -> 354 0.33206
347 -> 350 -0.20983
347 -> 351 -0.28178
347 -> 354 -0.17700
347 -> 355 0.10768

Excited State 31: Singlet-A 3.9338 eV 315.18 nm f=0.0833 <S**2>=0.000
335 -> 349 0.30106
337 -> 348 -0.18767
338 -> 349 0.10923
339 -> 348 0.12696
346 -> 350 0.12913
346 -> 351 -0.28821
346 -> 354 0.21364
346 -> 355 0.11249
347 -> 350 0.23235
347 -> 354 0.25375

Excited State 32: Singlet-A 3.9483 eV 314.02 nm f=0.0066 <S**2>=0.000

327 -> 349 0.25798
328 -> 348 -0.25515
329 -> 349 0.15924
330 -> 348 0.19538
331 -> 349 -0.17591
334 -> 348 0.13262
335 -> 349 0.16132
337 -> 348 -0.20678
339 -> 348 0.21647
346 -> 351 0.14278
347 -> 350 -0.13681

Excited State 33: Singlet-A 3.9599 eV 313.10 nm f=0.0031 <S**2>=0.000
327 -> 348 0.27880
328 -> 349 -0.27300
329 -> 348 0.18650
330 -> 349 0.21280
331 -> 348 -0.15832
333 -> 349 0.16912
336 -> 348 0.23610
338 -> 348 0.10182
339 -> 349 0.12606
346 -> 350 0.15770
346 -> 351 -0.12571
347 -> 351 -0.14658

Excited State 34: Singlet-A 3.9854 eV 311.10 nm f=0.0193 <S**2>=0.000
333 -> 349 -0.10381
335 -> 348 0.33846
336 -> 348 -0.12011
337 -> 349 -0.29693
338 -> 348 0.26644
339 -> 349 0.14370
346 -> 350 -0.18387
346 -> 354 0.11243
347 -> 351 0.18364
347 -> 355 0.10833

Excited State 35: Singlet-A 3.9884 eV 310.86 nm f=0.0111 <S**2>=0.000
344 -> 350 0.19982
344 -> 351 0.14570
345 -> 350 -0.13180
345 -> 351 0.18301
346 -> 350 -0.10004
346 -> 351 0.31408
346 -> 355 0.24994
347 -> 350 -0.27927
347 -> 354 0.23576
347 -> 356 0.21657

Excited State 36: Singlet-A 3.9923 eV 310.56 nm f=0.0074 <S**2>=0.000
335 -> 348 -0.22305
336 -> 348 0.10665
337 -> 349 0.19250
338 -> 348 -0.14394
344 -> 350 0.14428
344 -> 351 0.13632
345 -> 350 0.16333
345 -> 351 -0.18014

346 -> 350 -0.19041
346 -> 354 0.19275
346 -> 356 0.19244
347 -> 350 0.10913
347 -> 351 0.20141
347 -> 355 0.22594
347 -> 356 -0.11332

Excited State 37: Singlet-A 4.0378 eV 307.06 nm f=0.0013 <S**2>=0.000
332 -> 349 0.38625
333 -> 348 0.30070
334 -> 348 -0.36518
335 -> 349 -0.10017

Excited State 38: Singlet-A 4.0468 eV 306.38 nm f=0.0179 <S**2>=0.000
345 -> 350 -0.15964
345 -> 351 0.19726
346 -> 353 0.15588
346 -> 355 0.10720
347 -> 350 0.12730
347 -> 351 0.13019
347 -> 352 0.31367
347 -> 353 -0.25545
347 -> 354 -0.29392
347 -> 356 0.19177

Excited State 39: Singlet-A 4.0495 eV 306.17 nm f=0.0151 <S**2>=0.000
344 -> 350 -0.23770
344 -> 351 -0.19580
346 -> 351 0.14100
346 -> 352 -0.18053
346 -> 354 0.42541
346 -> 355 -0.17218
346 -> 356 -0.19589
347 -> 351 0.10468
347 -> 353 -0.12446
347 -> 354 0.13958
347 -> 355 -0.10342

Excited State 40: Singlet-A 4.0612 eV 305.29 nm f=0.0019 <S**2>=0.000
346 -> 352 0.38184
346 -> 353 0.47763
346 -> 354 0.10328
347 -> 352 0.18670
347 -> 353 0.21719

7. Time-resolved UV-vis absorption spectroscopy

The transient absorption spectra and the time profiles of the transient absorbance of **1** were recorded on a USB 4000 or Ocean FX multichannel detector (Ocean Optics). CUV-QPOD (Ocean Optics) equipped TC 125 temperature controller (QUANTUM) was used as a cuvette holder. The probe beam from a deuterium and a halogen lamps, DH-2000-BAL (Ocean Optics) were guided with a QP-600-1-SR optical fiber (Ocean Optics). Optical grade solvents were used for all measurements.

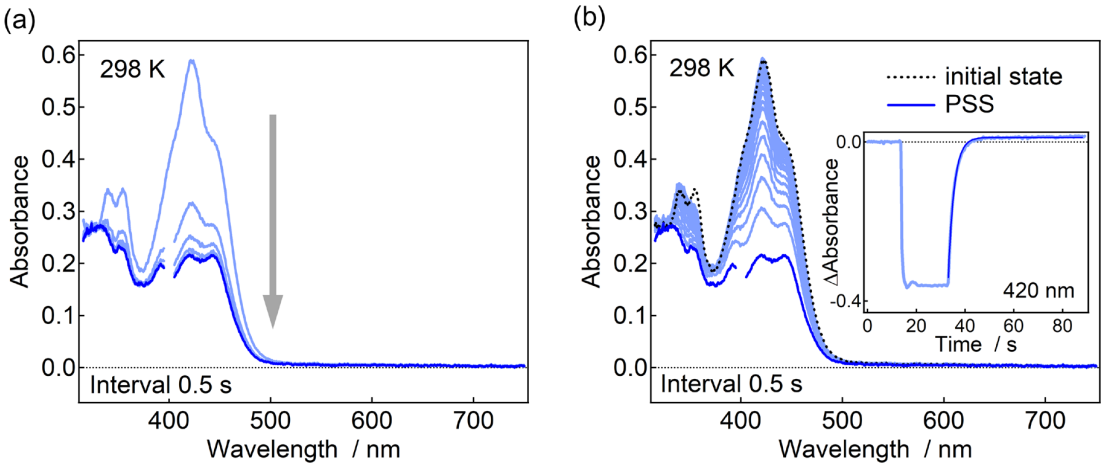

Figure S11. Time evolution of the UV–vis absorption spectrum of **1** in degassed toluene (1.0×10^{-5} M) (a) under the irradiation with 260 mW, 405-nm CW laser at 298 K and (b) after turning off the laser at 298 K. The inset shows the time variation of the transient absorbance at 420 nm.

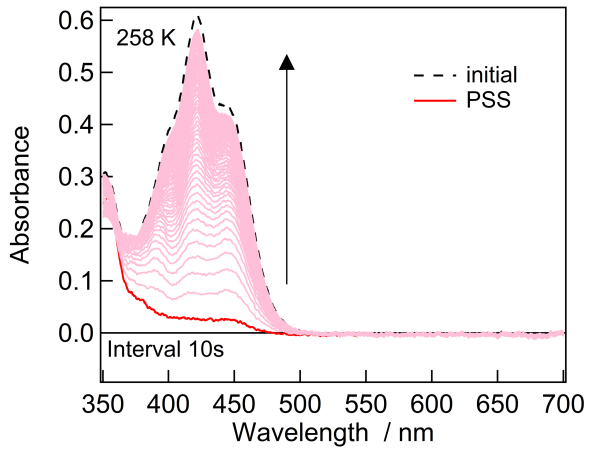

Figure S12. Transient absorption spectra of **1** in degassed toluene (1×10^{-5} M) upon 430-nm light irradiation (350 mW) at 258 K.

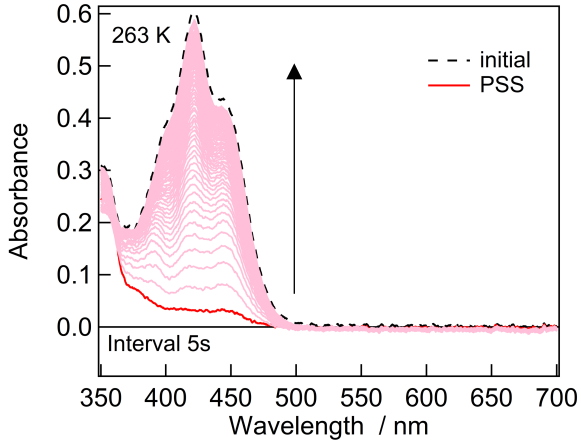

Figure S13. Transient absorption spectra of **1** in degassed toluene (1×10^{-5} M) upon 430-nm light irradiation (350 mW) at 263 K.

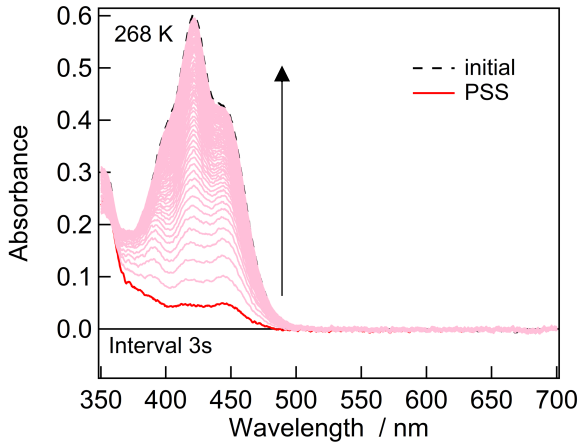

Figure S14. Transient absorption spectra of **1** in degassed toluene (1×10^{-5} M) upon 430-nm light irradiation (350 mW) at 268 K.

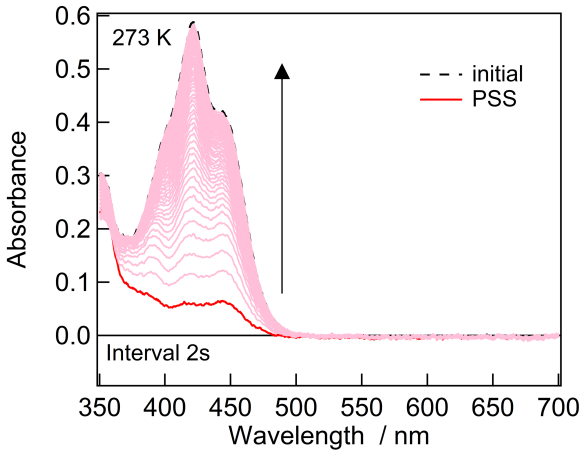

Figure S15. Transient absorption spectra of **1** in degassed toluene (1×10^{-5} M) upon 430-nm light irradiation (350 mW) at 273 K.

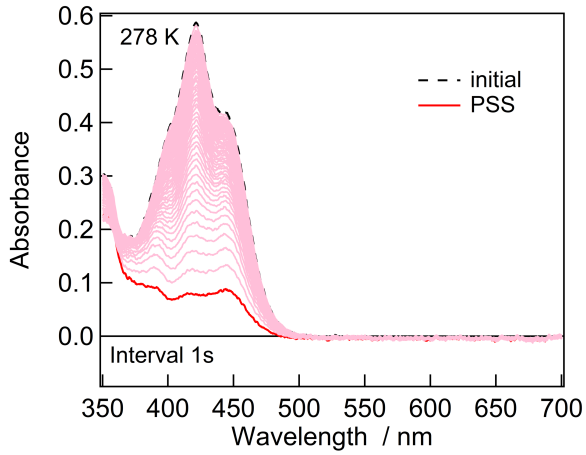

Figure S16. Transient absorption spectra of **1** in degassed toluene (1×10^{-5} M) upon 430-nm light irradiation (350 mW) at 278 K.

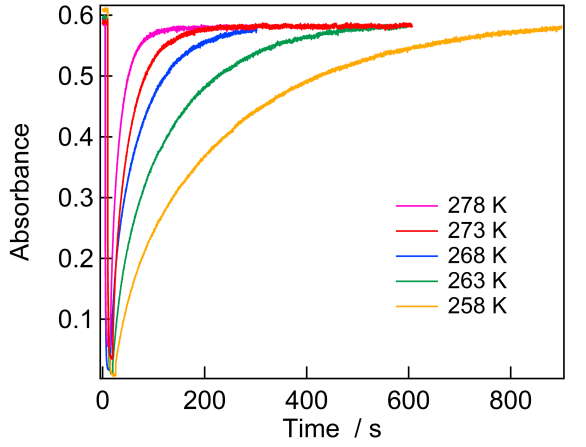

Figure S17. Time profiles of the transient absorbance at 421 nm of **1** in degassed toluene (1×10^{-5} M) upon 430-nm light irradiation (350 mW).

Table S5. Rate Constants for the Thermal Back-Reaction, **CL-C** to **C-C** (k_1) and **CL-CL** to **CL-C** (k_2).

T / K	k_1 / s^{-1}	k_2 / s^{-1}
258	0.0039607	0.028335
263	0.0076033	0.047908
268	0.014193	0.10053
273	0.025086	0.15699
278	0.045635	0.27238

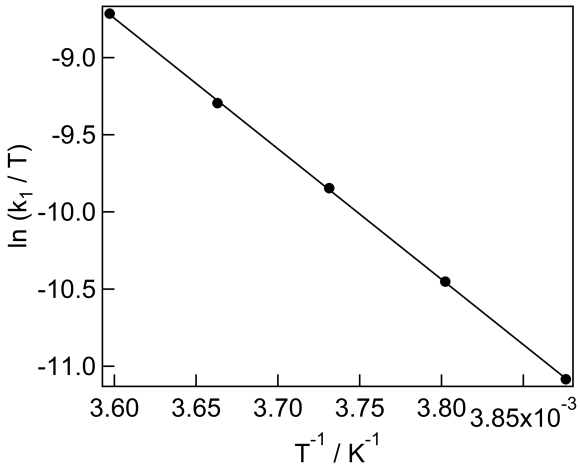

Figure S18. Eyring plot for the thermal back reaction from **CL-C** to **C-C**.

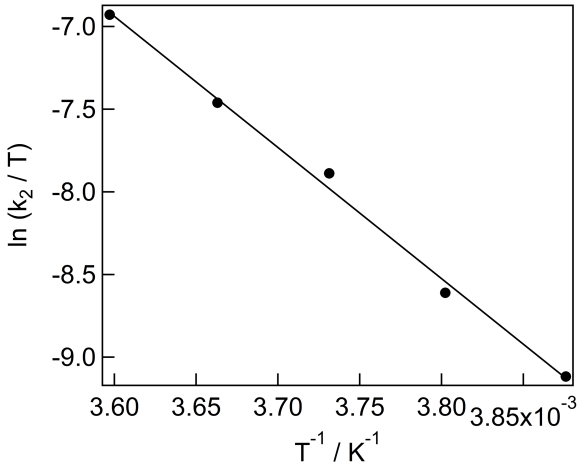

Figure S19. Eyring plot for the thermal back reaction from **CL-CL** to **CL-C**.

Table S6. Activation Parameters for the Thermal Back-Reaction, **CL-C** to **C-C** and **CL-CL** to **CL-C**.

	$\Delta H^{\ddagger}$/ kJ•mol^{-1}	$\Delta S^{\ddagger}$/ J•mol^{-1}•K^{-1}	$\Delta G^{\ddagger}$/ kJ•mol^{-1}	$t_{1/2}$ @ 298K
CL-C to **C-C**	70.3	−17.1	75.4	1.82 s
CL-CL to **CL-C**	65.9	−17.8	71.3	0.340 s

8. Laser Flash Photolysis

The laser flash photolysis experiments were carried out with a TSP-1000 time resolved spectrophotometer (UNISOKU). A 10 Hz Q-switched Nd:YAG laser (Continuum Minilite II) with the third harmonic at 355 nm (pulse width, 5 ns) was employed for the excitation light. The excitation pulse at 450 nm and 420 nm (pulse width, 5 ns) were provided by a Continuum Surelite II Q-Switched Nd:YAG coupled to a Continuum Panther EX OPO. The probe beam from a halogen lamp (OSRAM HLX64623) was guided with an optical fiber scope to be arranged in an orientation perpendicular to the exciting laser beam. The probe beam was monitored with a photomultiplier tube (Hamamatsu R2949) through a spectrometer (UNISOKU MD200) for time evolutions of the transient absorbance. The excitation intensity of one pulse was estimated by an energy detector (Gentec Electro-Optics QE12LP-S-MB) with an energy monitor (Gentec Electro-Optics MAESTRO). Optical grade solvents were used for all measurements.

Figure S20 shows the time profiles for the transient absorbance at 650 nm of **1** in benzene upon 450-nm or 355-nm laser pulse irradiation. The decay profiles follow the first-order kinetics and the half-life of the transient species was estimated to be 1.4 μs. Both transient absorption spectra obtained by the irradiation with UV and visible laser show similar broad absorption bands in vis-NIR region, corresponding to the generation of a transient radical species (Figure S21). This indicates that the biradical species was generated upon UV or visible light irradiation.

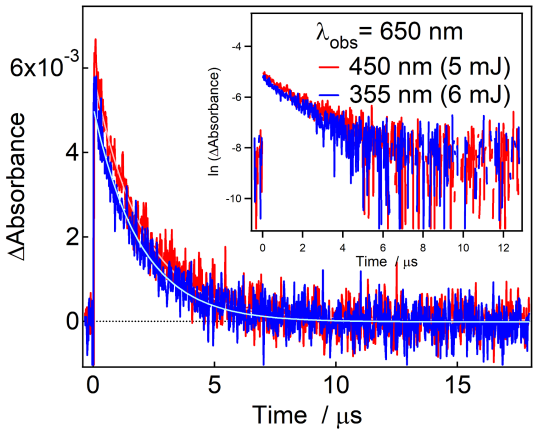

Figure S20. Time profiles of the transient absorbance at 650 nm for **1** in degassed benzene (1.5×10^{-5} M) upon 450 nm (5 mJ) or 255 nm (6mJ) laser irradiation. The inset shows the logarithmic plots of the decay profiles.

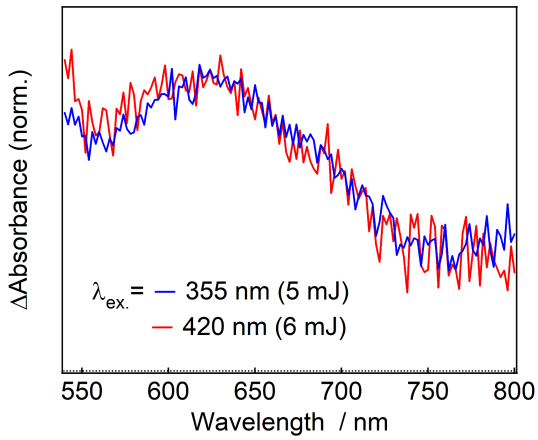

Figure S21. Normalized transient absorption spectra for **1** in degassed benzene upon laser irradiation.

9. Irradiation power dependence at PSS

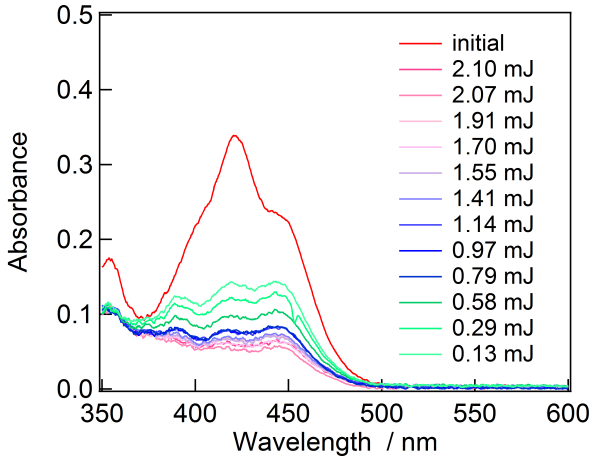

Figure S22. (a) Absorption spectra of the PSS for **1** at 298 K under 0.13-2.10 mJ laser irradiation (450 nm, pulse width = 5 ns, 10 Hz).

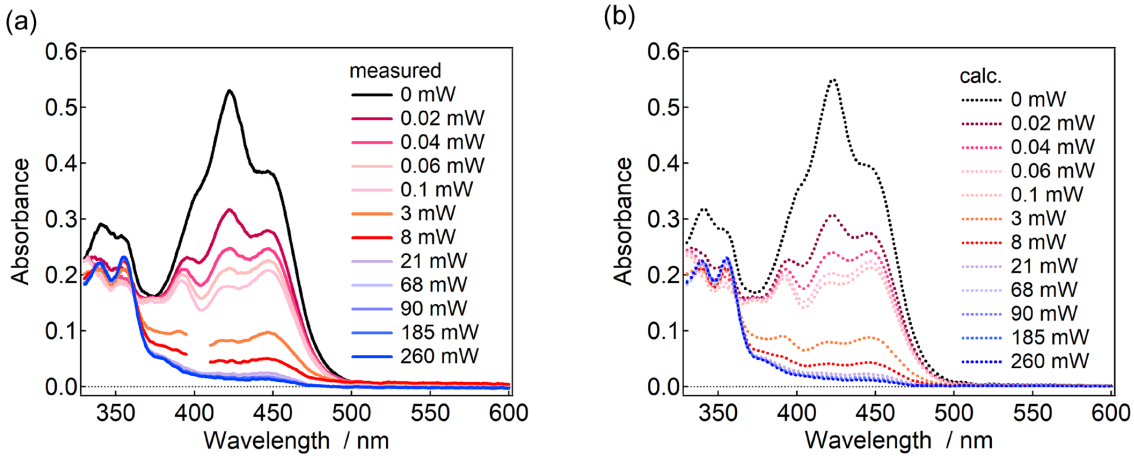

Figure S23. (a) Experimental absorption spectra at 245 K under 0-260 mW CW laser irradiation (405 nm) at PSS. (b) Calculated absorption spectra with the molecular coefficients and estimated concentration by the global analyses for **C-C**, **CL-C** and **CL-CL**.

10. Reference

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