Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Highly Durable Photochromic Radical Complexes Having No Steric Protections of Radicals

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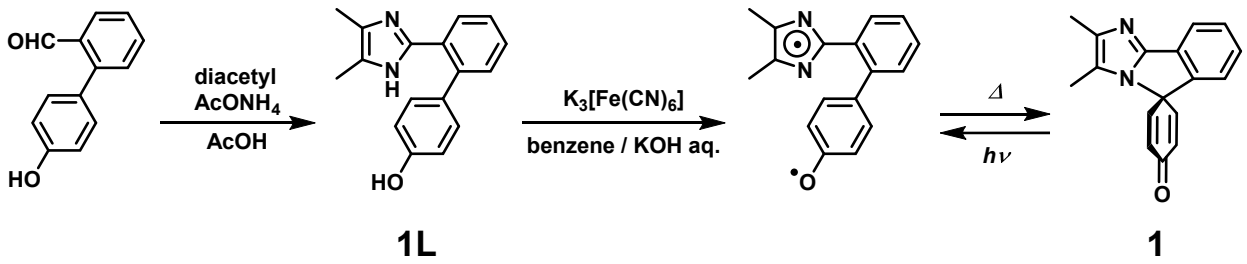
1. Syntheses

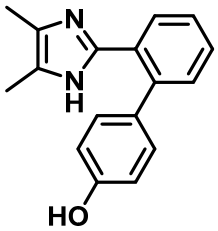
All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Wakogel® C-300). ^{1}H NMR spectra were recorded at 400 MHz on a Bruker AVANCE III 400 NanoBay. DMSO-d_6 and $CDCl_3$ were used as deuterated solvent. ESI–TOF–MS spectra were recorded on a Bruker micrOTOF II-AGA1. All glassware was washed with distilled water and dried. Unless otherwise noted, all reagents and reaction solvents were purchased from TCI, Wako Co. Ltd., Aldrich Chemical Co., Inc., Kanto Chemical Co., Inc. and ACROS Organics and were used without further purification.

4'-hydroxy-[1,1'-biphenyl]-2-carbaldehyde and **3',5'-di-*tert*-butyl-4'-hydroxy-[1,1'-biphenyl]-2-carbaldehyde** were prepared according to a literature procedure[S1].



1L **1**

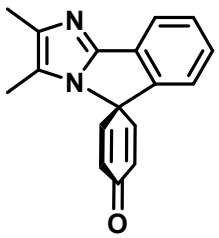
2'-(4,5-dimethyl-1*H*-imidazol-2-yl)-[1,1'-biphenyl]-4-ol (1L)



1L

The mixture of 4'-hydroxy-[1,1'-biphenyl]-2-carbaldehyde (501 mg, 2.53 mmol), diacetyl (1.11 mL, 12.6 mmol) and ammonium acetate (1.95 g, 25.4 mol) in 6 mL of acetic acid in a sealed tube were stirred at 110 °C for 15 h. The reaction mixture was cooled to room temperature and neutralized by aqueous NH_3. The mixture was extracted with ethyl acetate (AcOEt) and the organic extract was washed with water and dried over Na_2SO_4. After removal of the solvents, the crude product was separated by silica gel column chromatography ($CHCl_3$/MeOH = 5/1). The resultant green powder was washed with AcOEt and a small amount of methanol to give desired product as a white powder 347 mg (1.31 mmol, 52 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.83 (s, 1H), 9.43 (s, 1H), 7.50–7.48 (m, 1H), 7.42–7.38 (m, 1H), 7.35–7.32 (m, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.4 Hz, 2H), 1.99 (s, 6H); HRMS (ESI-TOF) calculated for $C_{17}H_{16}N_2O$ $[M+H]^+$: 265.1335, found: 265.1339.

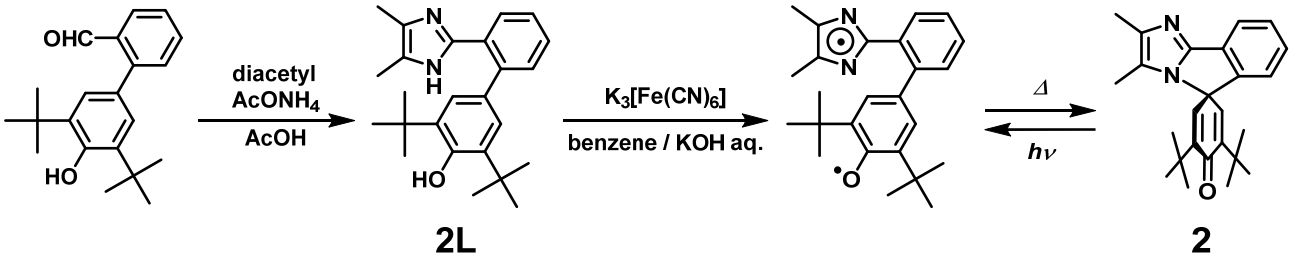
2',3'-dimethylspiro[cyclohexane-1,5'-imidazo[2,1-a]isoindole]-2,5-dien-4-one (1)



1

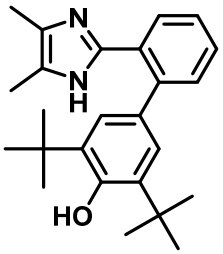
A solution of potassium ferricyanide (12.8 g, 76.0 mmol) and KOH (4.26 g, 76.0 mmol) in water (50 mL) was added to a suspension of **1L** (208 mg, 0.0325 mmol) in 50 mL of benzene. After stirring for 2 h at room temperature, the resultant mixture was then extracted with benzene and the organic extract was washed with water and dried over Na_2SO_4. After removal of the solvents, the crude product was purified by silica gel column chromatography (AcOEt/hexane/CH_2Cl_2 = 14/7/5), to give **1** as a yellow powder, 114 mg (0.438 mmol, 56 %).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 (d, J = 7.6 Hz, 1H), 7.53–7.50 (m, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 6.83 (d, J = 10.0 Hz, 2H), 6.55 (d, J = 9.6 Hz, 2H), 2.14 (s, 3H), 2.06 (s, 3H); HRMS (ESI-TOF) calculated for $C_{17}H_{14}N_2O$ [M+H]$^+$: 263.1178, found: 263.1168.



2L **2**

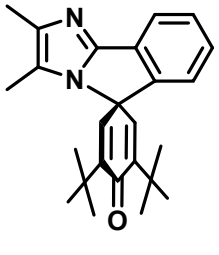
3,5-di-*tert*-butyl-2'-(4,5-dimethyl-1*H*-imidazol-2-yl)-[1,1'-biphenyl]-4-ol (2L)



2L

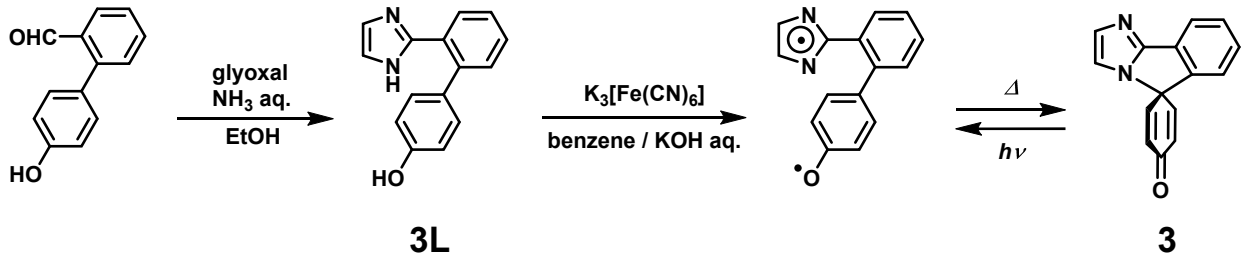
The mixture of 3',5'-di-tert-butyl-4'-hydroxy-[1,1'-biphenyl]-2-carbaldehyde (201 mg, 0.649 mmol), diacetyl (0.17 mL, 1.94 mmol) and ammonium acetate (548 mg, 7.11 mol) in 6 mL of acetic acid in a sealed tube was stirred at 110 °C for 84 h. The reaction mixture was cooled to room temperature and neutralized by aqueous NH_3. The mixture was extracted with $CHCl_3$ and the organic extract was washed with water and dried over $MgSO_4$. After removal of the solvents, the crude product was purified by silica gel column chromatography (AcOEt), to give desired product as a white solid, 124 mg (0.329 mmol, 51 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (s, 1H), 7.46–7.41 (m, 3H), 7.34–7.30 (m, 1H), 6.96 (s, 2H), 6.91 (s, 1H), 1.99 (s, 6H), 1.31 (s, 18H); HRMS (ESI-TOF) calculated for $C_{25}H_{32}N_2O$ [M+H]$^+$: 377.2587, found: 377.2583.

3,5-di-*tert*-butyl-2',3'-dimethylspiro[cyclohexane-1,5'-imidazo[2,1-a]isoindole]-2,5-dien-4-one (2)



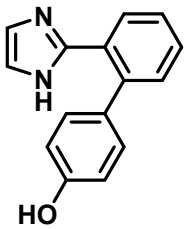
2

A solution of potassium ferricyanide (2.16 g, 6.56 mmol), KOH (742 mg, 13.2 mmol) in water (18 mL) was added to a suspension of **2L** (47.4 mg, 0.128 mmol) in 9 mL of benzene. After stirring for 2 h at room temperature, the resultant mixture was then extracted with benzene and the organic extract was washed with water and dried over Na_2SO_4. After removal of the solvents, the crude product was purified by silica gel column chromatography (AcOEt/$CHCl_3$ = 1/10), to give **2** as a white powder, 25 mg (0.065 mmol, 52 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.33 (td, J = 7.6, 0.8 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.33 (s, 2H), 2.14 (s, 3H), 2.01 (s, 3H), 1.20 (s, 18H); HRMS (ESI-TOF) calculated for $C_{25}H_{30}N_2O$ [M+H]$^+$: 375.2430, found: 375.2437.



3L **3**

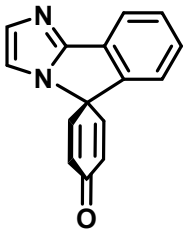
2'-(1*H*-imidazol-2-yl)-[1,1'-biphenyl]-4-ol (3L)



3L

To a solution of 4'-hydroxy-[1,1'-biphenyl]-2-carbaldehyde (1.25 g, 6.33 mmol) in ethanol (15 mL) was added glyoxal (39% in water, 8.3 mL, 73 mmol) and ammonium hydroxide (28% in water, 8.5 mL, 130 mmol) at 0 °C. After stirring for 3 days at room temperature, the reaction mixture was concentrated and the precipitated solid was filtered. The crude solid was purified by silica gel column chromatography (MeOH/$CHCl_3$ = 1/10). The resultant brown powder was further washed with ethyl acetate and a small amount of methanol to give desired product as a white powder, 532 mg (2.25 mmol, 36 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ : 11.42 (s, 1H), 9.42 (s, 1H), 7.53–7.51 (m, 1H), 7.47–7.43 (m, 1H), 7.39–7.36 (m, 2H), 7.01 (s, 1H), 6.92–6.89 (m, 3H), 6.65 (d, *J* = 8.8 Hz, 2H). HRMS (ESI-TOF) calculated for $C_{15}H_{12}N_2O$ $[M+H]^+$: 237.1024, found: 237.1024.

spiro[cyclohexane-1,5'-imidazo[2,1-a]isoindole]-2,5-dien-4-one (3)



3

A solution of potassium ferricyanide (27.89 g, 84.7 mmol), KOH (9.63 g, 170 mmol) in water (100 mL) was added to a suspension of **3L** (467 mg, 1.98 mmol) in benzene (50 mL). After stirring for 1.5 h at room temperature, the resultant mixture was then extracted with benzene and the organic extract was washed with water and dried over Na_2SO_4. The crude product was purified by silica gel column chromatography (AcOEt/hexane = 5/1), to give desired product as white powder, 27 mg (0.11 mmol, 7 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.91 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.38 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.31 (d, *J* = 1.2 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 1.2 Hz, 1H), 6.56–6.51 (m, 4H). HRMS (ESI-TOF) calculated for $C_{15}H_{10}N_2O$ $[M+H]^+$: 235.0865, found: 235.0869.

2. ^{1}H NMR Spectra

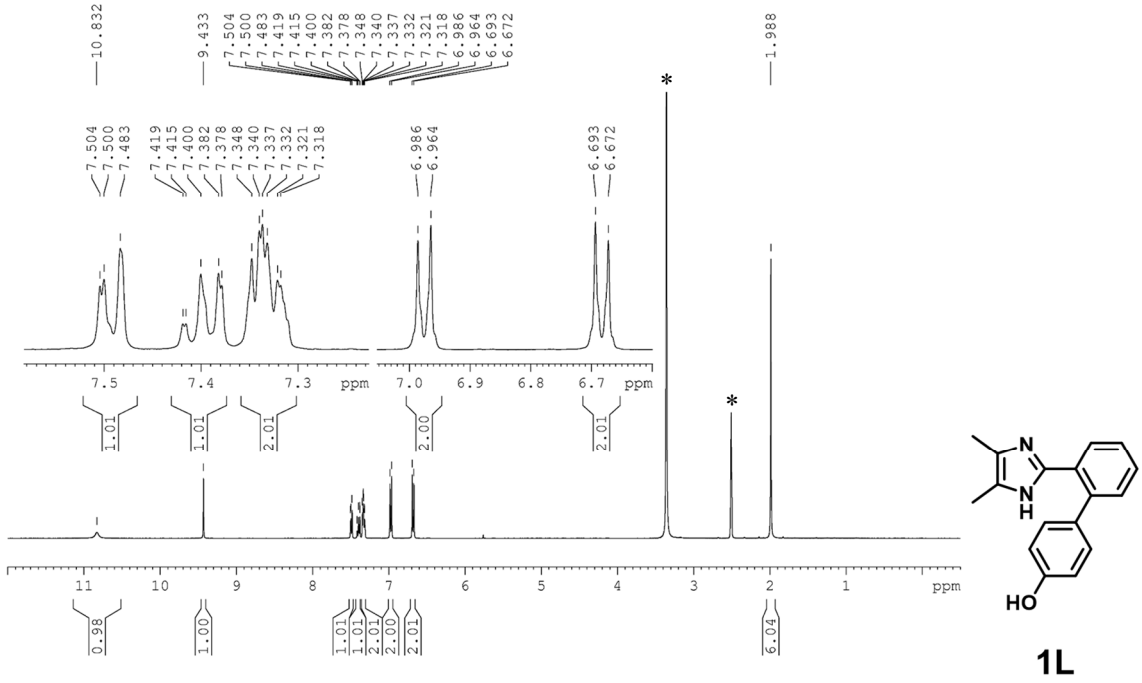


Fig. S1. ^{1}H NMR spectra of **1L** in DMSO-d_6 (* solvent peaks).

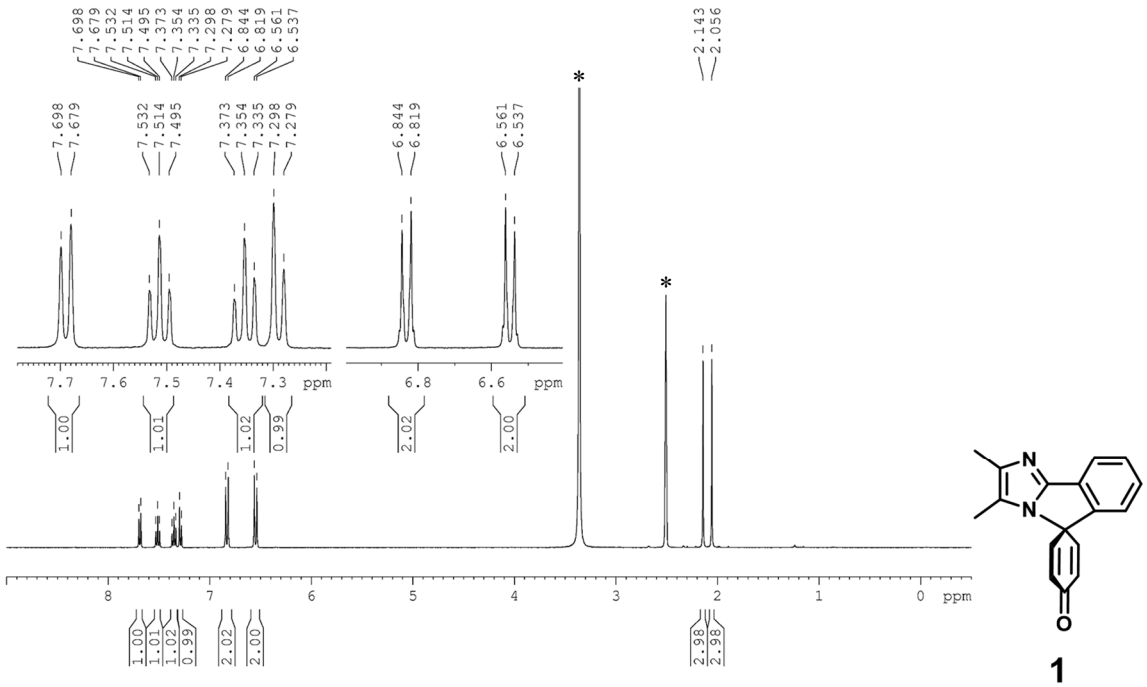


Fig. S2. ^{1}H NMR spectra of **1** in DMSO-d_6 (* solvent peaks).

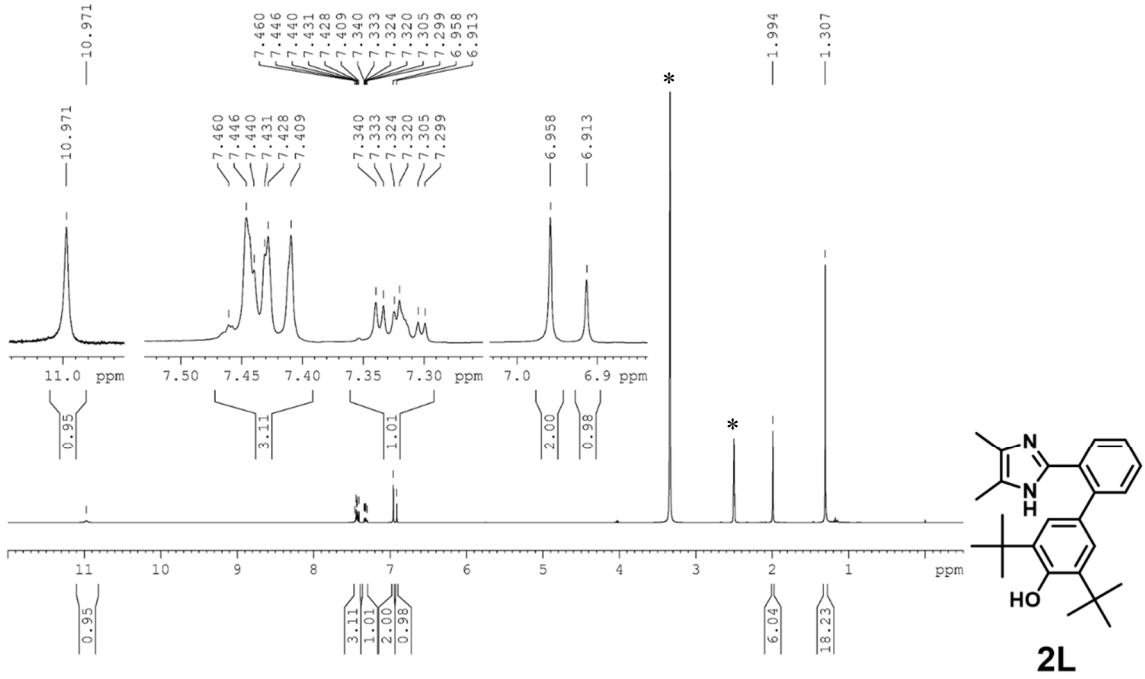


Fig. S3. [1]H NMR spectra of **2L** in DMSO-d_6 (* solvent peaks).

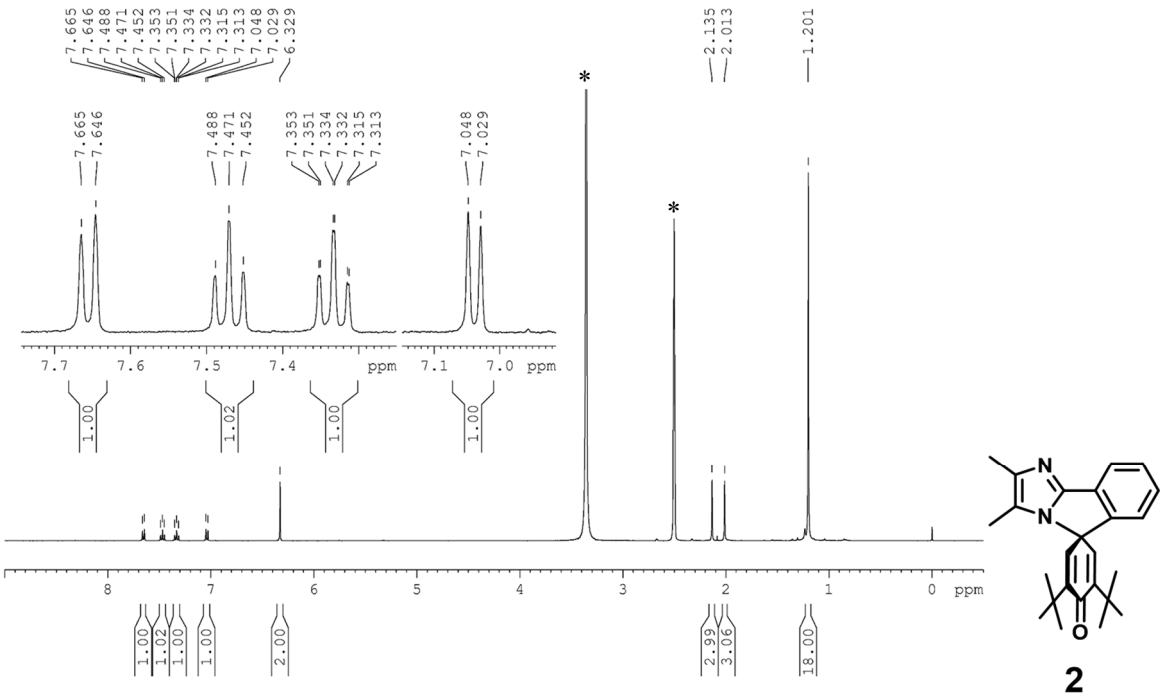


Fig. S4. [1]H NMR spectra of **2** in DMSO-d_6 (* solvent peaks).

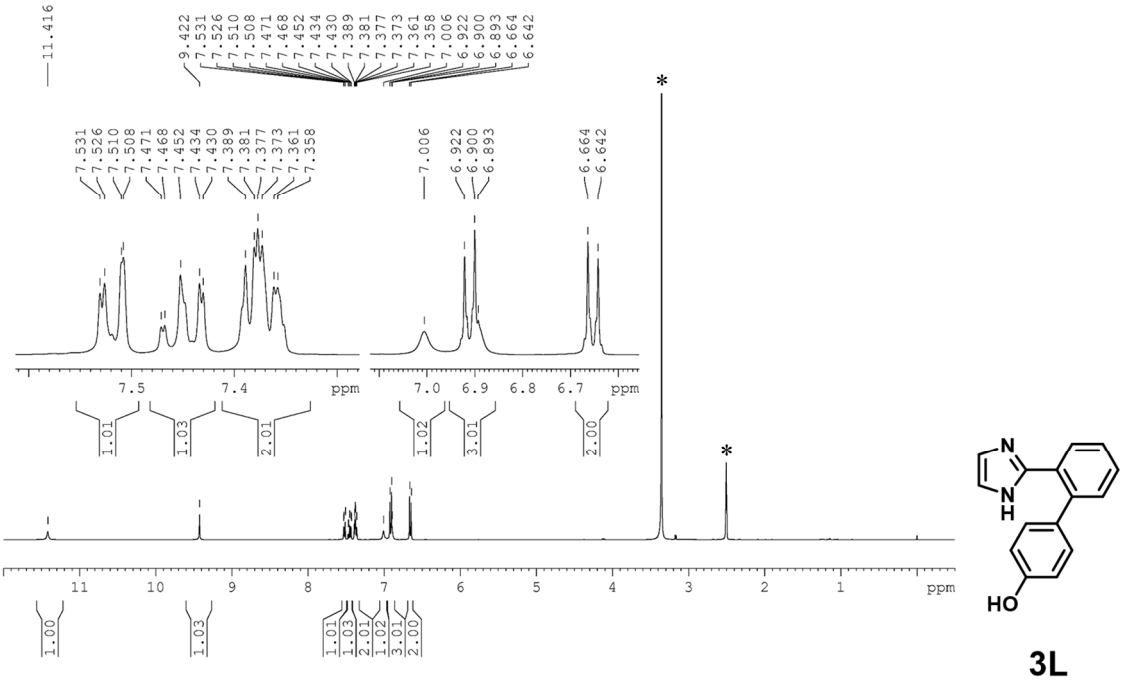


Fig. S5. ^{1}H NMR spectra of **3L** in DMSO-d_6 (* solvent peaks).

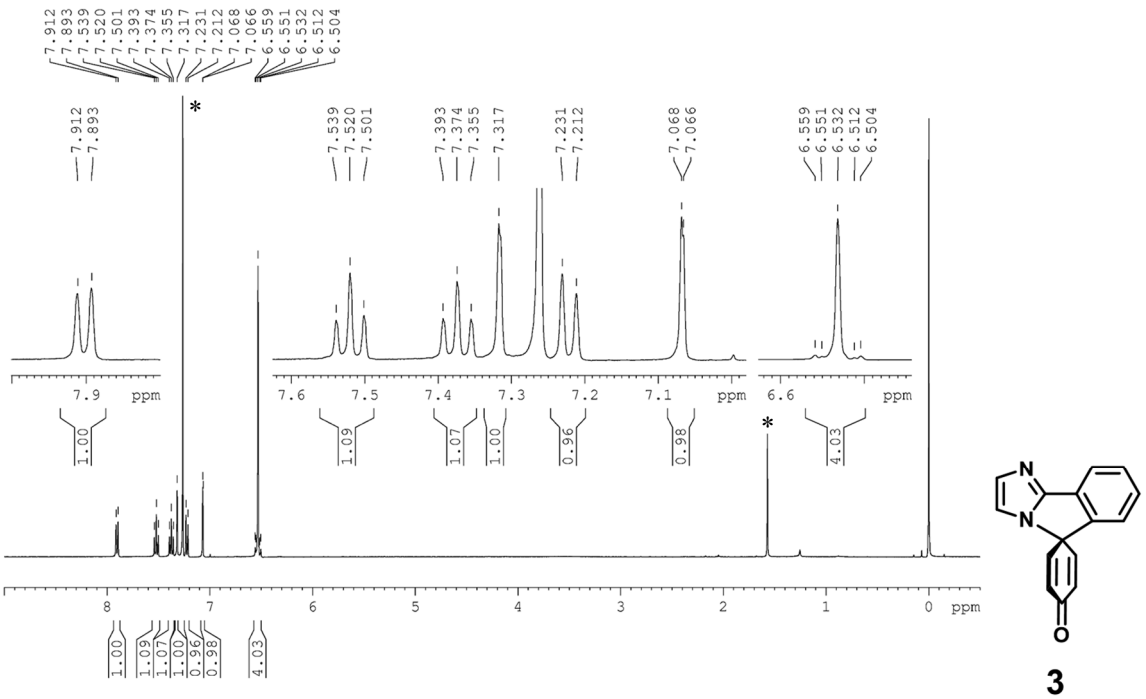


Fig. S6. ^{1}H NMR spectra of **3** in $CDCl_3$ (* solvent peaks).

3. HR-ESI-TOF-MS Spectra

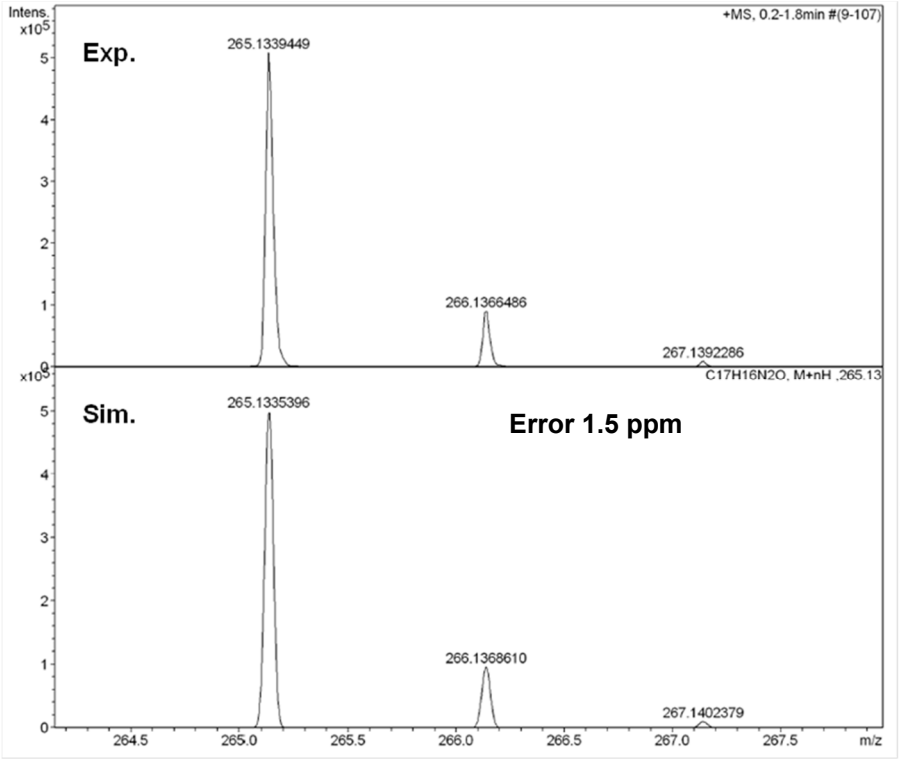


Fig. S7. HR-ESI-TOF-MS of **1L**.

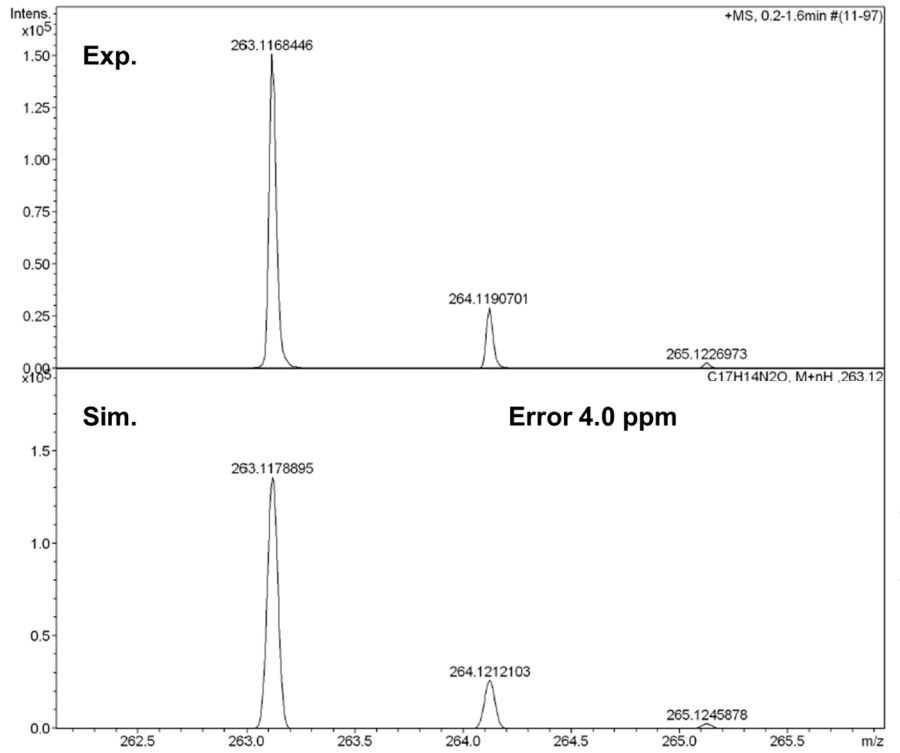


Fig. S8. HR-ESI-TOF-MS of **1**.

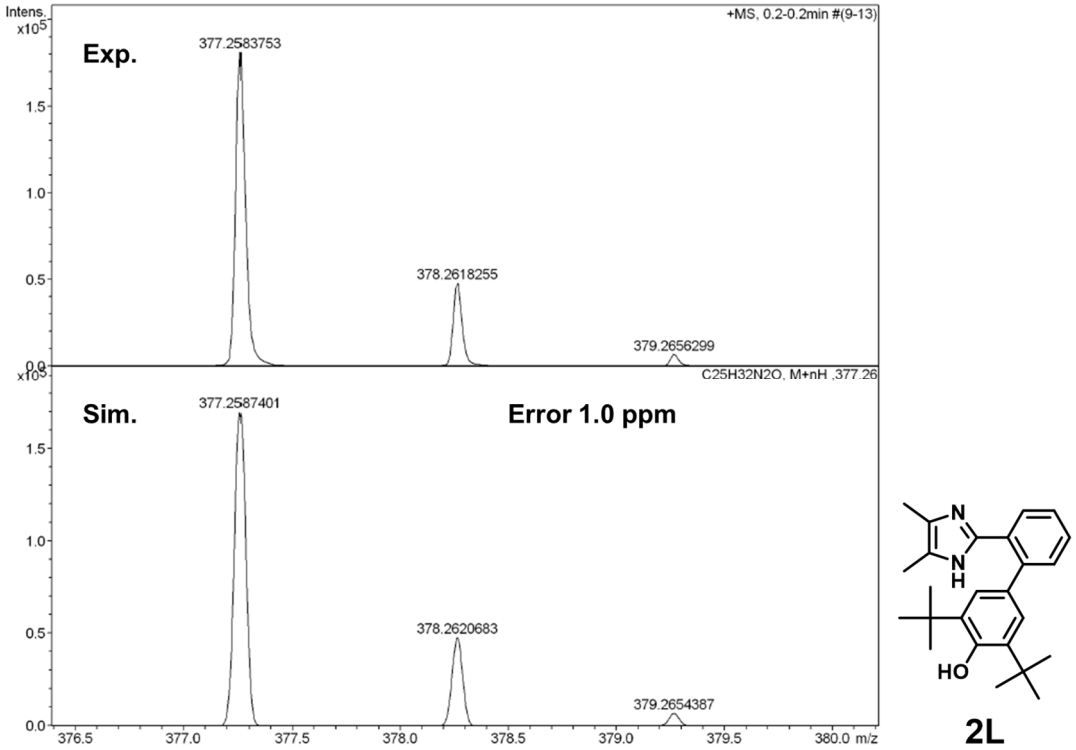


Fig. S9. HR-ESI-TOF-MS of **2L**.

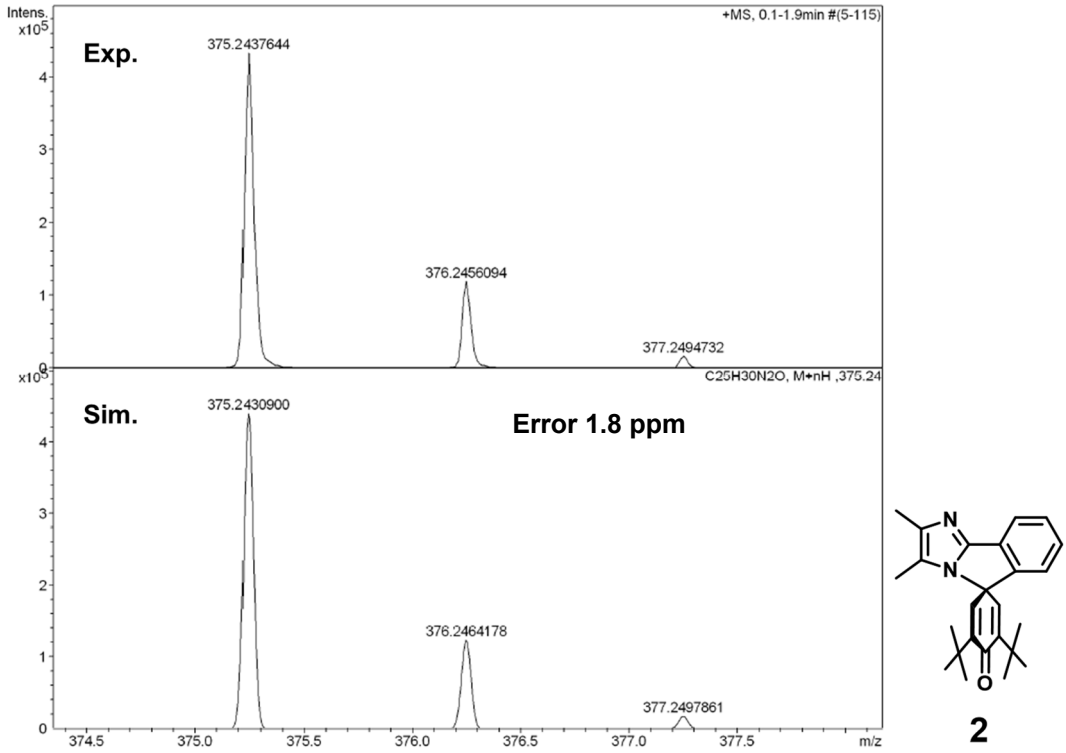


Fig. S10. HR-ESI-TOF-MS of **2**.

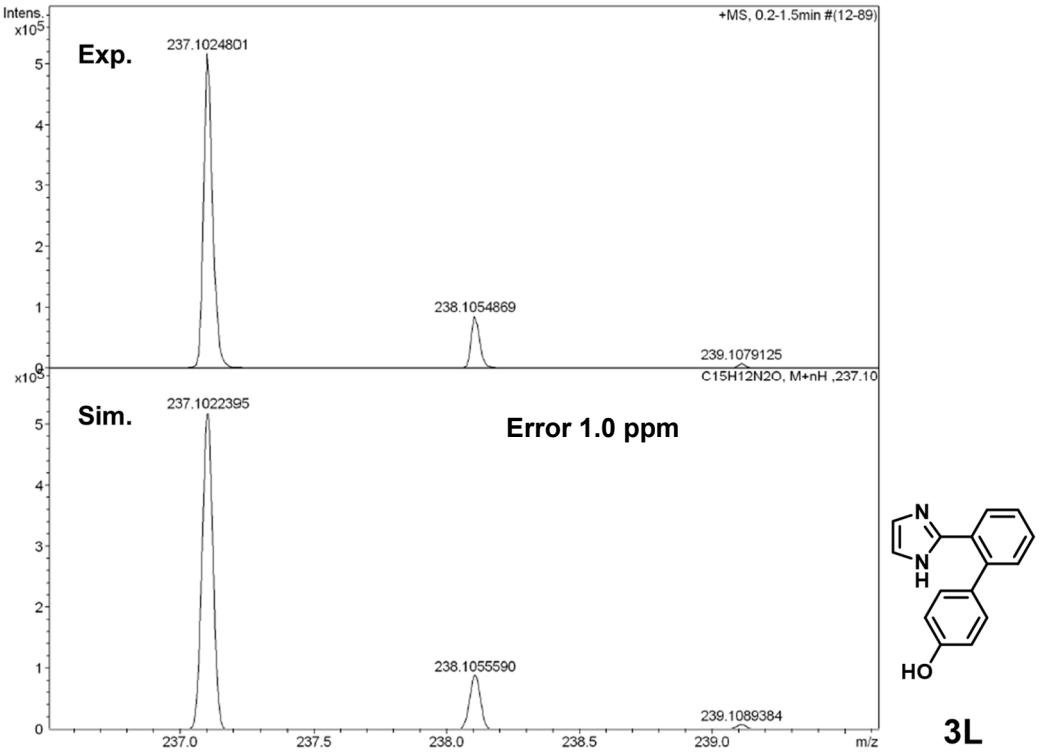


Fig. S11. HR-ESI-TOF-MS of **3L**.

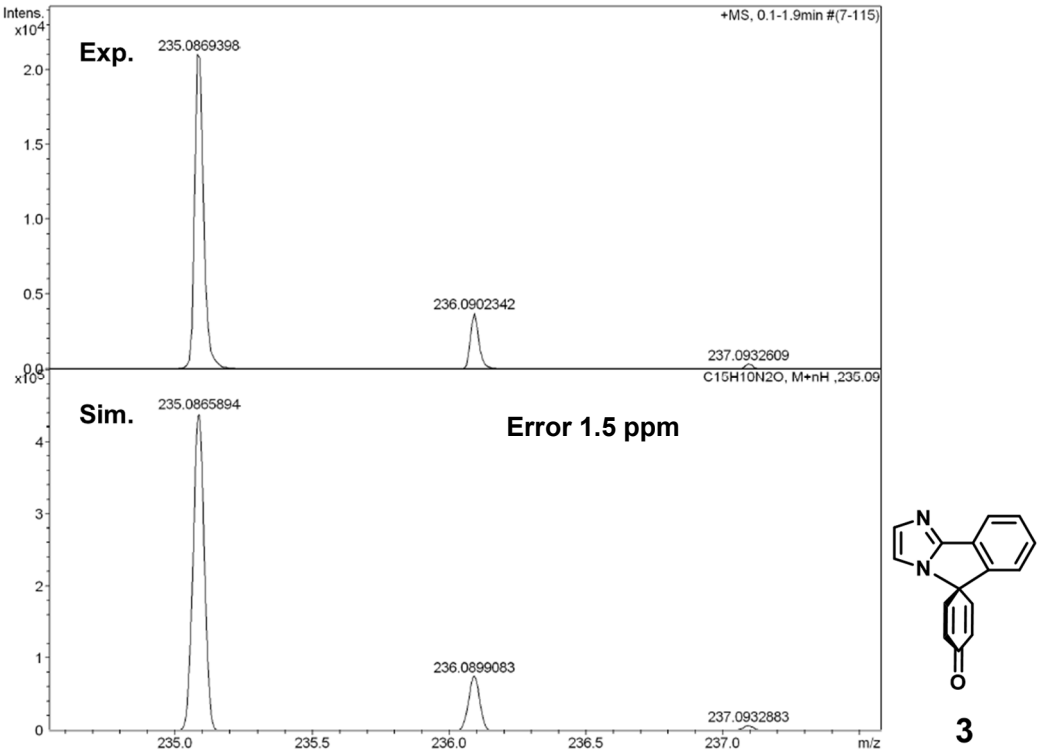


Fig. S12. HR-ESI-TOF-MS of **3**.

4. HPLC Chromatograms

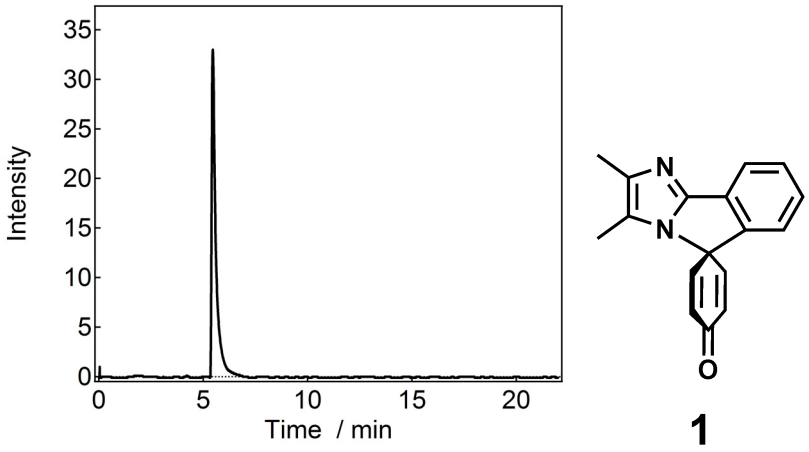


Fig. S13. HPLC chromatogram of **1**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was MeCN/H_2O = 1/1 with a flow rate of 1.0 mL/min (detection wavelength; 254 nm).

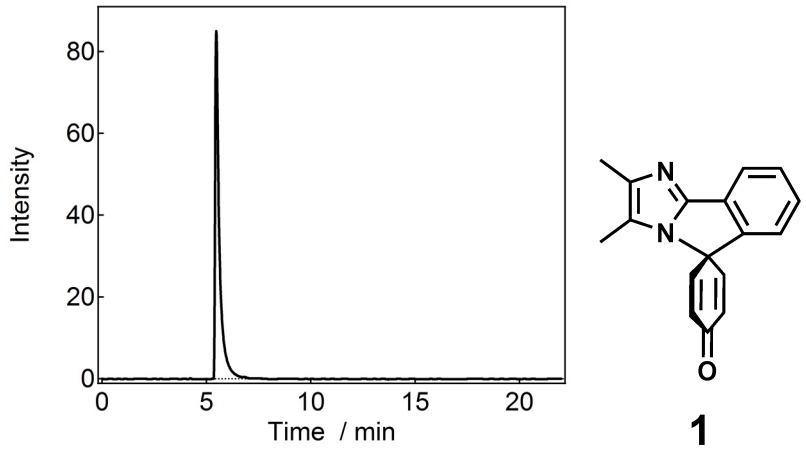


Fig. S14. HPLC chromatogram of **1**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was MeCN/H_2O = 1/1 with a flow rate of 1.0 mL/min (detection wavelength; 300 nm).

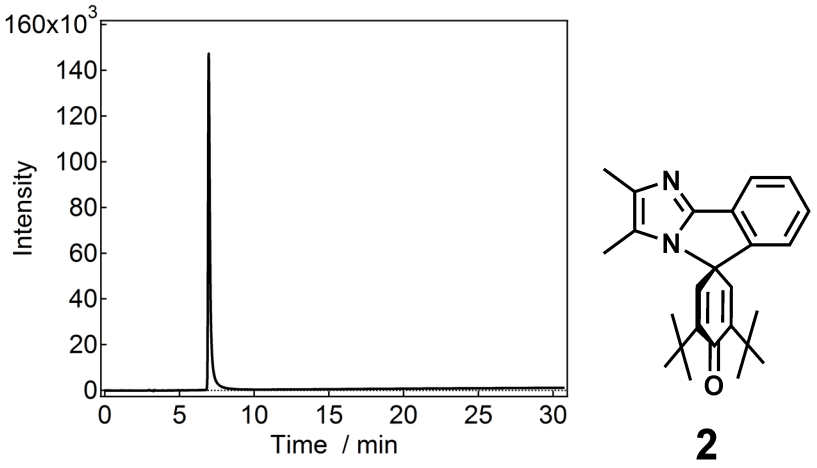


Fig. S15. HPLC chromatogram of **2**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a PDA detector; the mobile phase was MeCN/MeOH = 20/1 with a flow rate of 1.0 mL/min (detection wavelength; 254 nm).

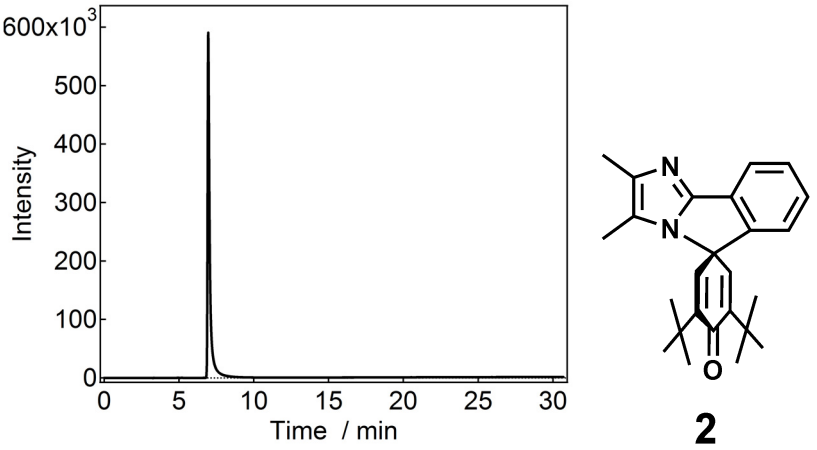


Fig. S16. HPLC chromatogram of **2**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a PDA detector; the mobile phase was MeCN/MeOH = 20/1 with a flow rate of 1.0 mL/min (detection wavelength; 300 nm).

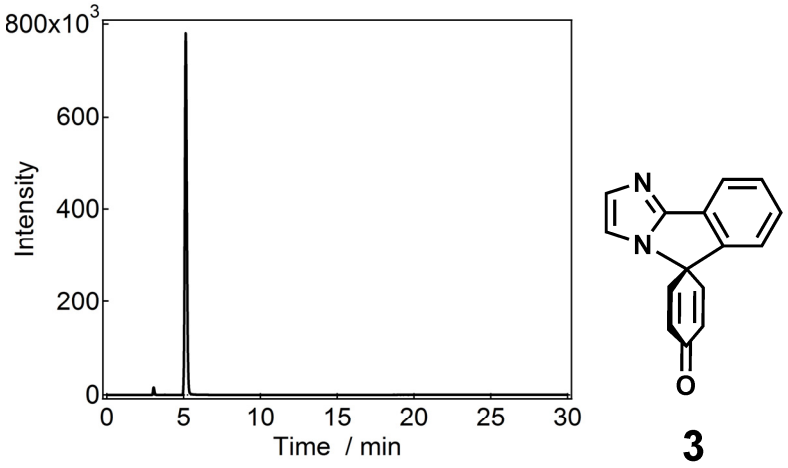


Fig. S17. HPLC chromatogram of **3**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a PDA detector; the mobile phase was MeOH/H_2O = 3/2 with a flow rate of 1.0 mL/min (detection wavelength; 254 nm).

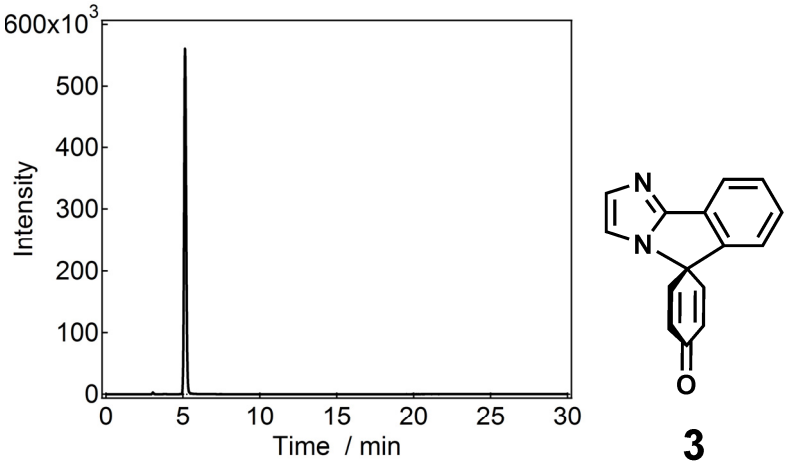
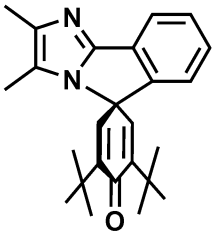


Fig. S18. HPLC chromatogram of **3**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a PDA detector; the mobile phase was MeOH/H_2O = 3/2 with a flow rate of 1.0 mL/min (detection wavelength; 300 nm).

5. X-ray Crystallographic Analysis

The diffraction data of the single crystal were collected on the Bruker APEX II CCD area detector (Mo Kα, λ = 0.71073 nm). The data refinement was carried out by the Bruker APEXII software package with SHELXT program.[S2, S3] All non-hydrogen atoms were anisotropically refined.



2

Table S1. Crystallographic Parameters of **2**

Empirical formula	$C_{25}H_{30}N_2O$	
Formula weight	374.51	
Temperature	90(0) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.2185(9) Å	α = 83.1537(13)°
	b = 9.7237(9) Å	β = 71.5734(13)°
	c = 12.7331(12) Å	γ = 86.3277(12)°
Volume	1074.71(18) $Å^3$	
Z	2	
Density (calculated)	1.157 Mg/m^3	
Absorption coefficient	0.070 mm^{-1}	
F(000)	404	
Theta range for data collection	1.70 to 28.64°	
Index ranges	-11<=h<=12, -11<=k<=12, -6<=l<=17	
Reflections collected	6245	
Independent reflections	4782 [R(int) = 0.0114]	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4782 / 0 / 261	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.1159	
R indices (all data)	R1 = 0.0588, wR2 = 0.1239	
Largest diff. peak and hole	0.494 and -0.207 $eÅ^{-3}$	

6. Experimental Details for Laser Flash Photolysis Measurements

The laser flash photolysis experiments were carried out with a TSP-2000 time resolved spectrophotometer (Unisoku). A 10 Hz Q-switched Nd:YAG (Continuum Minilite II) laser with the third harmonic at 355 nm (time duration: 5 ns) was employed for the excitation light. The probe beam from a halogen lamp (OSRAM HLX64623) was irradiated to the sample solution be arranged in an orientation perpendicular to the exciting laser beam. The transmitted probe beam was monitored with a photomultiplier tube (Hamamatsu R2949) through a spectrometer (Unisoku MD200) for the decay profiles of the open-ring isomers of **1, 2** and **3**. For laser flash photolysis measurements of **2** in nanosecond time scale, a Xe flash lamp (Hamamatsu L2437) was focused into the sample as a probe light. The transmitted light was collected by an optical fiber and monitored by a spectrometer equipped with an intensified charge-coupled device (ICCD) (Shamrock 163 and iStar DH320T-18U-03). The gate duration of the ICCD is set to 10 ns and a spectrum was obtained by the average of 50 scans.

7. Rates, Lifetimes, and Activation Parameters of the Thermal Back Reactions

Table S2. Decoloration Reaction Rates, Half-Lives at 25 °C, and Activation Parameters of the Ring-Closing Reaction of **1**, **2**, **3**, **PIC1** and **PIC2** in Benzene [S1]

	k	$\tau_{1/2}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$
	[s^{-1}]	[s]	[kJ mol^{-1}]	[J mol^{-1} K^{-1}]	[kJ mol^{-1}]
1	6.3×10^{5}	1.1×10^{-6}	37.4	−7.9	39.8
2	3.8×10^{6}	1.8×10^{-7}	31.9	−11.6	35.3
3	2.3×10^{7}	3.0×10^{-8}	17.5	−44.4	30.8
PIC1	2.8×10^{6}	2.5×10^{-7}	31.7	−14.9	36.2
PIC2	2.6×10^{7}	2.6×10^{-7}	26.3	−15.1	30.7

Table S3. First-Order Rate Constants for the Thermal Back-Reaction of **1**.

T / K	k / s^{-1}
278	2.0×10^5
283	2.8×10^5
288	3.8×10^5
293	5.1×10^5
298	6.6×10^5
303	8.5×10^5
308	1.1×10^6
313	1.4×10^6

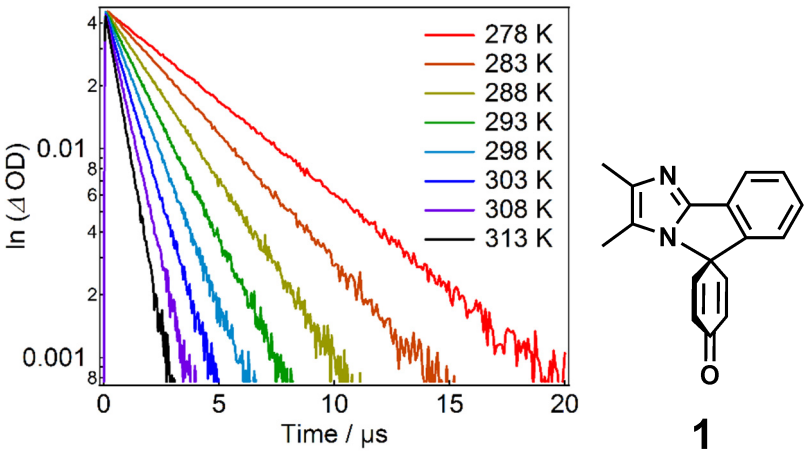


Fig. S19. First-order kinetic plots of **1** monitored at 600 nm in benzene (8.8×10^{-4} M).

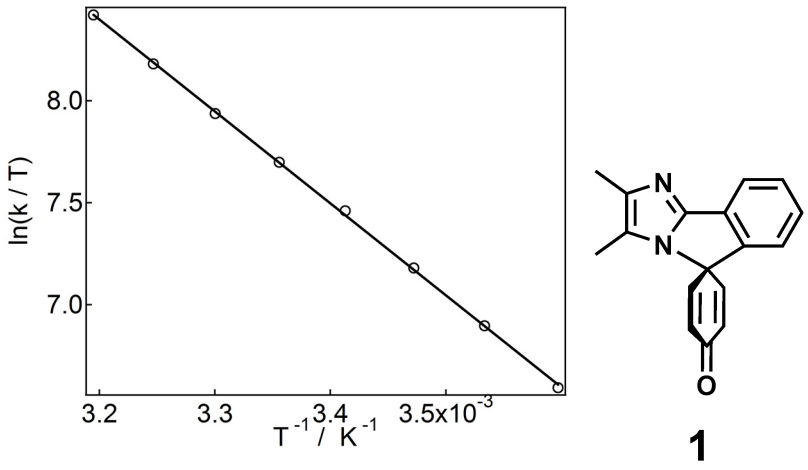


Fig. S20. Eyring plots for the thermal back reaction of **1** in benzene solution (8.8×10^{-4} M).

Table 4. First-Order Rate Constants for the Thermal Back-Reaction of **2**

T / K	k / s^{-1}
278	1.1×10^6
283	1.9×10^6
288	2.4×10^6
293	3.2×10^6
298	3.8×10^6
303	5.0×10^6
308	6.1×10^6
313	7.6×10^6

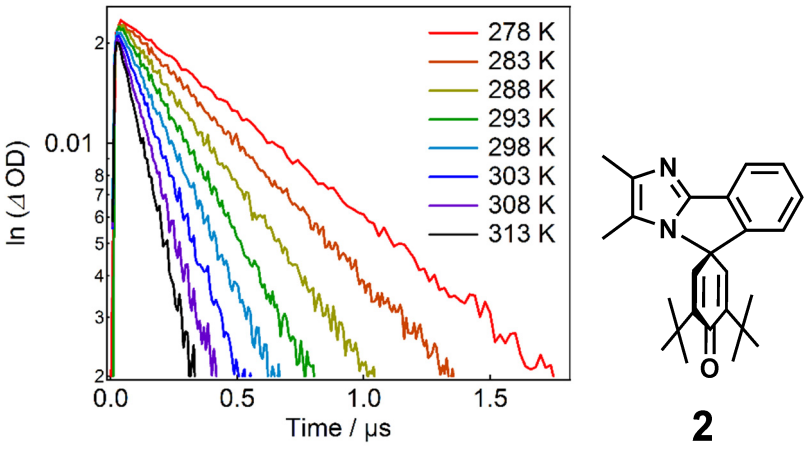


Fig. S21. First-order kinetic plots of **2** monitored at 600 nm in benzene (4.2×10^{-4} M).

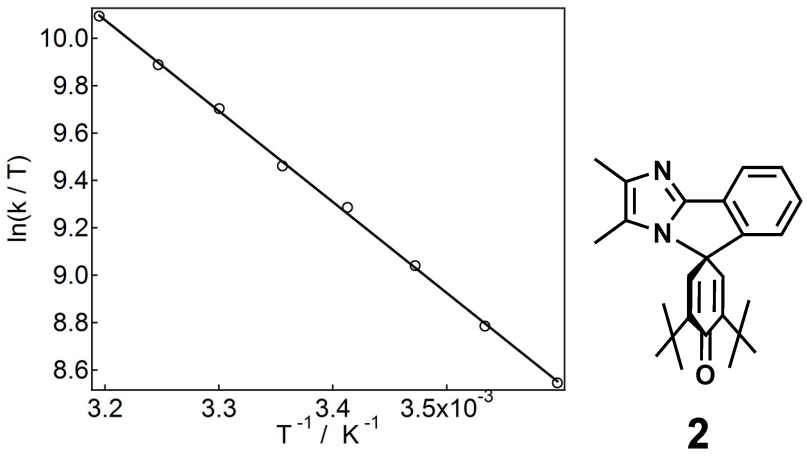


Fig. S22. Eyring plots for the thermal back reaction of **2** in benzene solution (4.2×10^{-4} M).

Table S5. First-Order Rate Constants for the Thermal Back-Reaction of **3**

T / K	k / s^{-1}
278	1.3×10^{-7}
283	1.5×10^{-7}
288	1.8×10^{-7}
293	2.1×10^{-7}
298	2.3×10^{-7}
303	3.0×10^{-7}
308	3.3×10^{-7}
313	3.8×10^{-7}

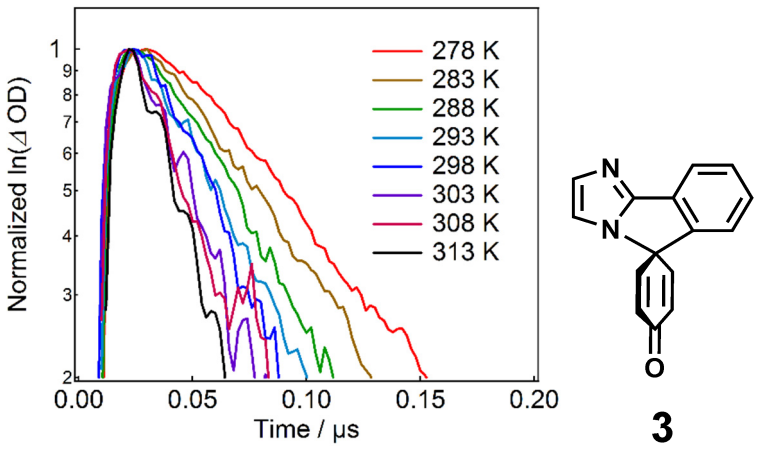


Fig. S23. First-order kinetic plots of **3** monitored at 600 nm in benzene (3.1×10^{-3} M).

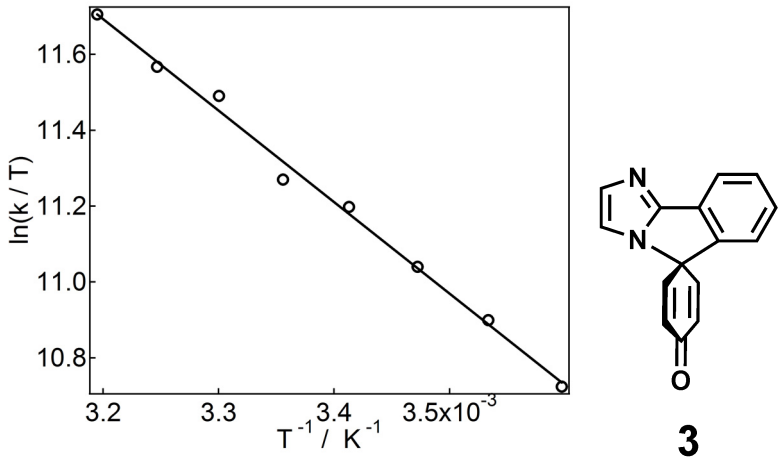


Fig. S24. Eyring plots for the thermal back reaction of **3** in benzene solution (3.1×10^{-3} M).

8. Fatigue Resistances

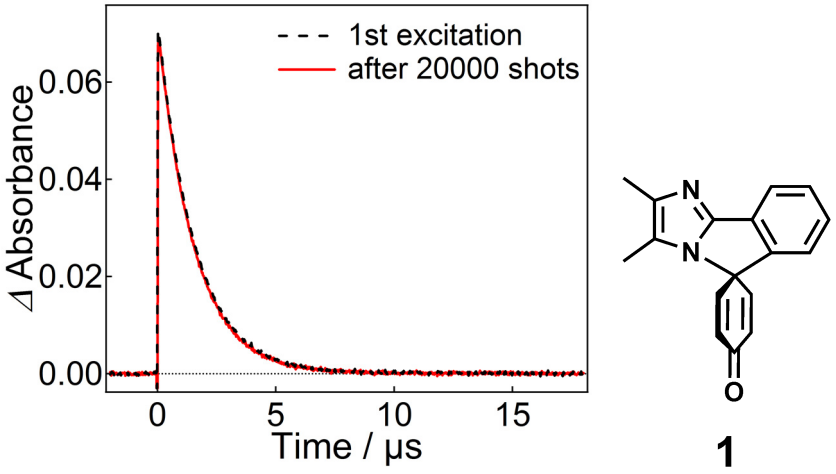


Fig. S25. Decay profiles of the transient absorbance at 600 nm of **1** in O_2 saturated benzene (1.8×10^{-3} M), before (black line) and after (red line) laser pulse irradiation at 298 K (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz).

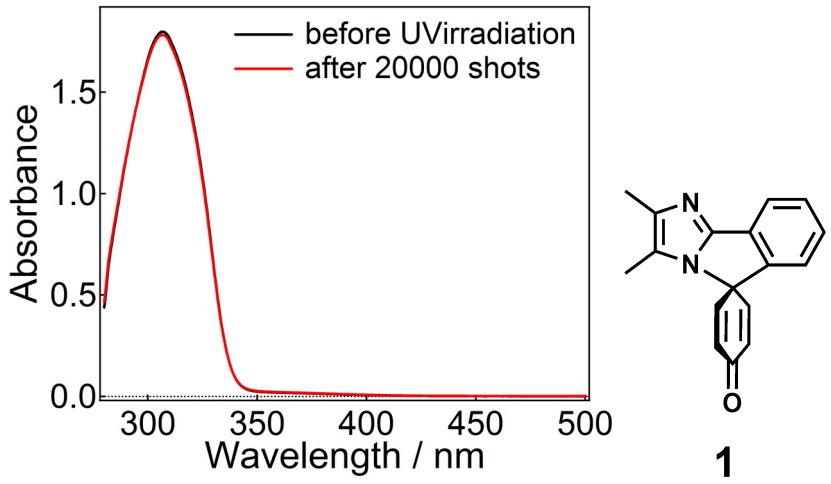


Fig. S26. UV–vis absorption spectra of **1** in O_2 saturated benzene (1.8×10^{-3} M) before (black line) and after (red line) laser pulse irradiation (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz, optical path length: 1 mm).

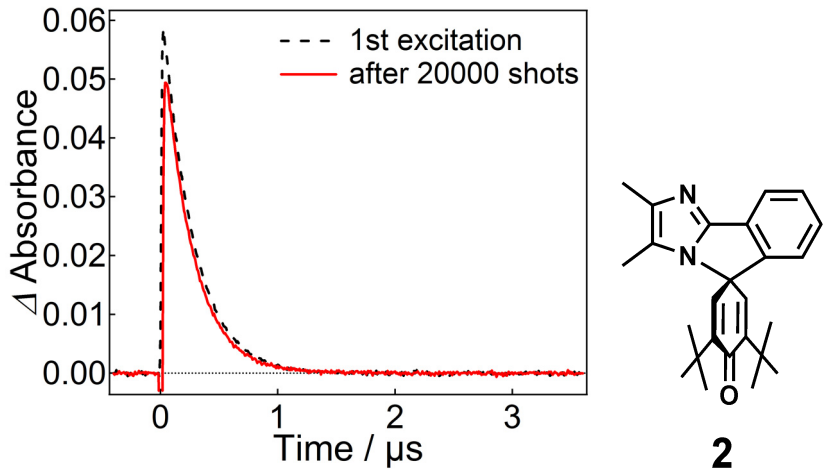


Fig. S27. Decay profiles of the transient absorbance at 600 nm of **2** in O_2 saturated benzene (1.4×10^{-3} M) before (black dash line) and after (red line) laser pulse irradiation measured at 298 K (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz).

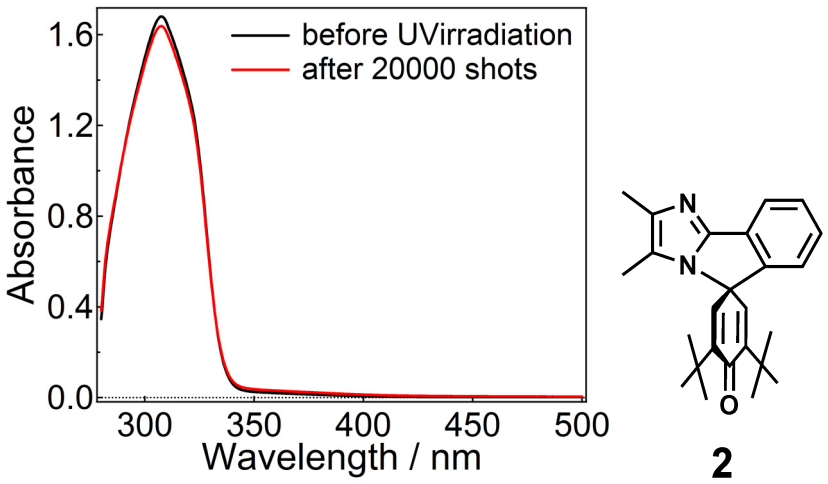


Fig. S28. UV–vis absorption spectra of **2** in O_2 saturated benzene (1.4×10^{-3} M) before (black line) and after (red line) laser pulse irradiation (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz, optical path length: 1 mm).

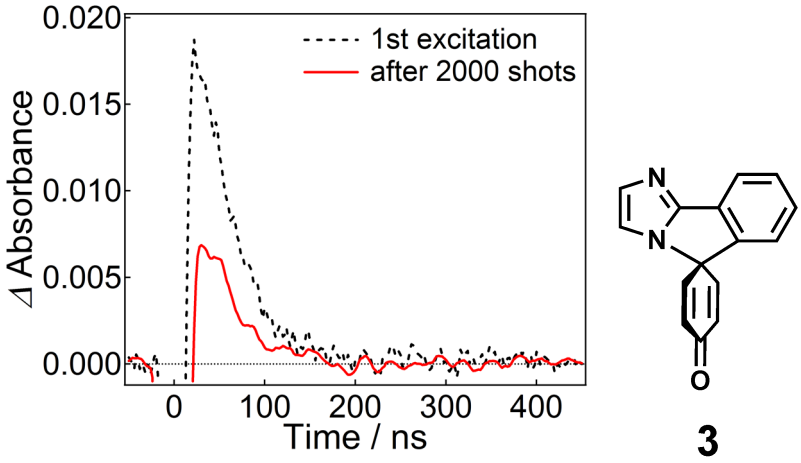


Fig. S29. Decay profiles of the transient absorbance at 600 nm of **3** in benzene (7.2×10^{-3} M) before (black dash line) and after (red line) laser pulse irradiation at 298 K (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz).

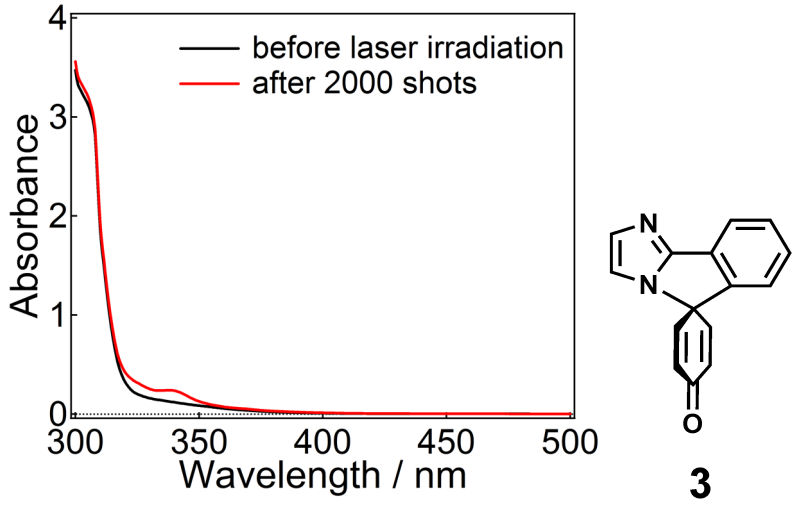


Fig. S30. UV–vis absorption spectra of **3** in benzene (7.2×10^{-3} M) before (black line) and after (red line) laser pulse irradiation (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz, optical path length: 1 mm).

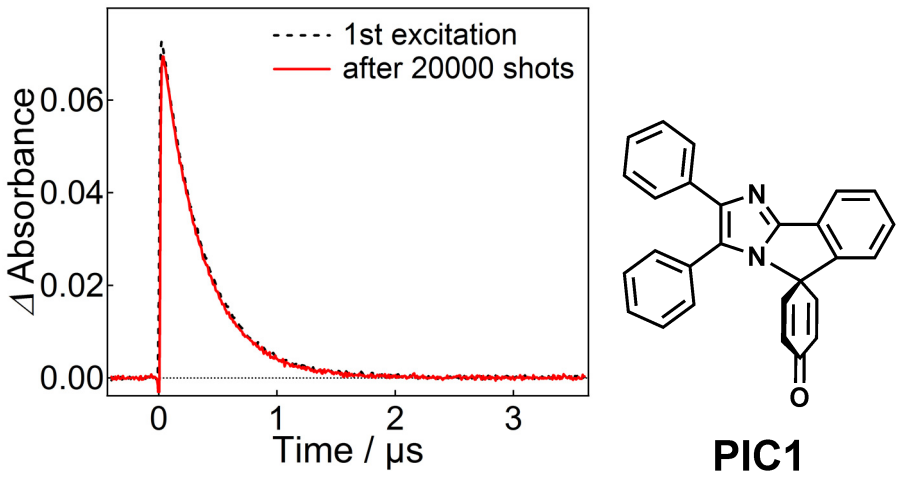


Fig. S31. Decay profiles of the transient absorbance at 650 nm of **PIC1** in O_2 saturated benzene (1.6×10^{-4} M) before (black dash line) and after (red line) laser pulse irradiation at 298 K (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz).

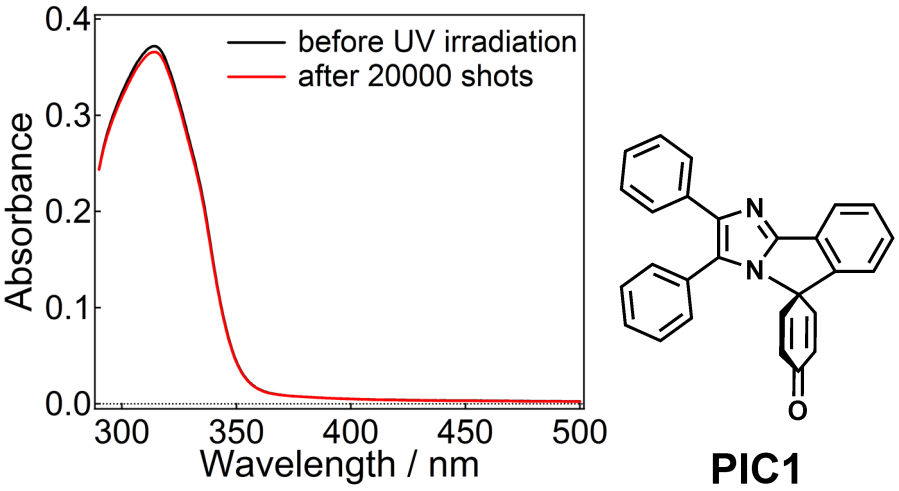


Fig. S32. UV–vis absorption spectra of **PIC1** in O_2 saturated benzene (1.6×10^{-4} M) before (black line) and after (red line) laser pulse irradiation (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz, optical path length: 1 mm).

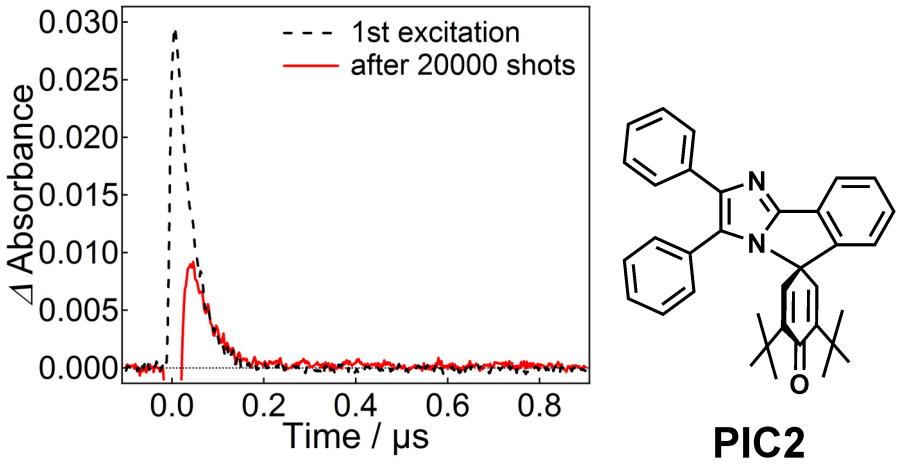


Fig. S33. Decay profiles of the transient absorbance at 650 nm of **PIC2** in O_2 saturated benzene (2.4×10^{-4} M) before (black dash line) and after (red line) laser pulse irradiation at 298 K (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz).

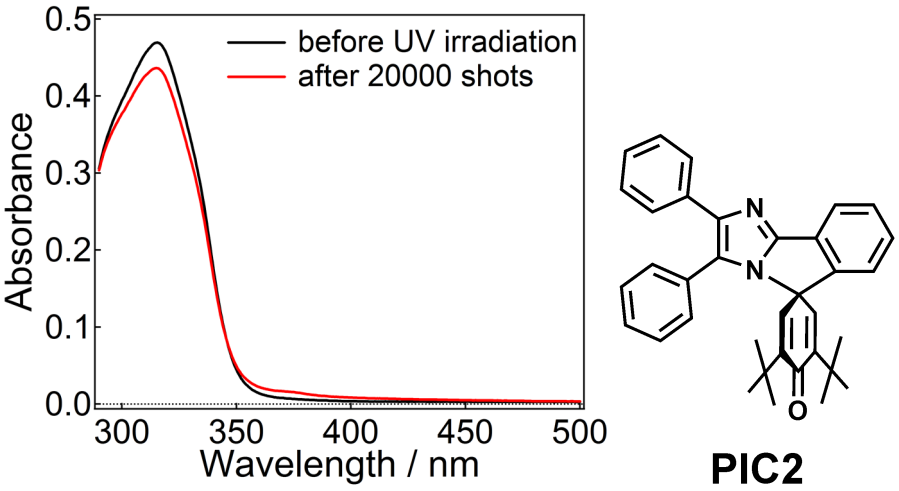


Fig. S34. UV–vis absorption spectra of **PIC2** in O_2 saturated benzene (2.4×10^{-4} M) before (black line) and after (red line) laser pulse irradiation (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz, optical path length: 1 mm).

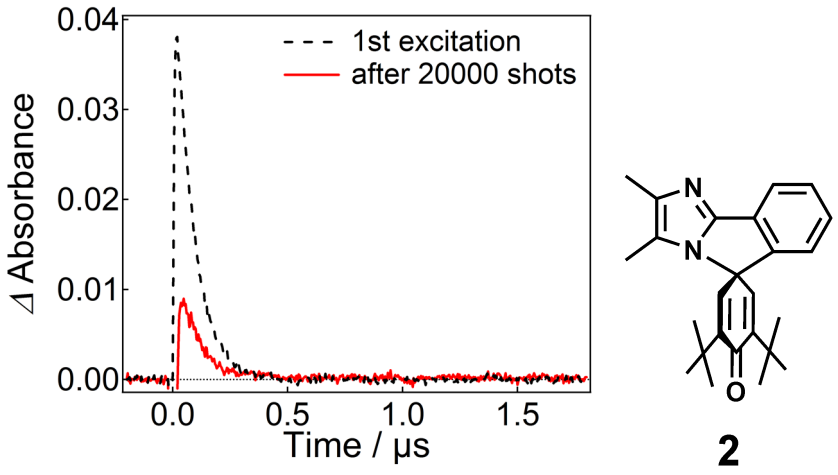


Fig. S35. Decay profiles of the transient absorbance at 600 nm of **2** in O_2 saturated ethanol (2.2×10^{-3} M) before (black dash line) and after (red line) laser pulse irradiation at 298 K (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz).

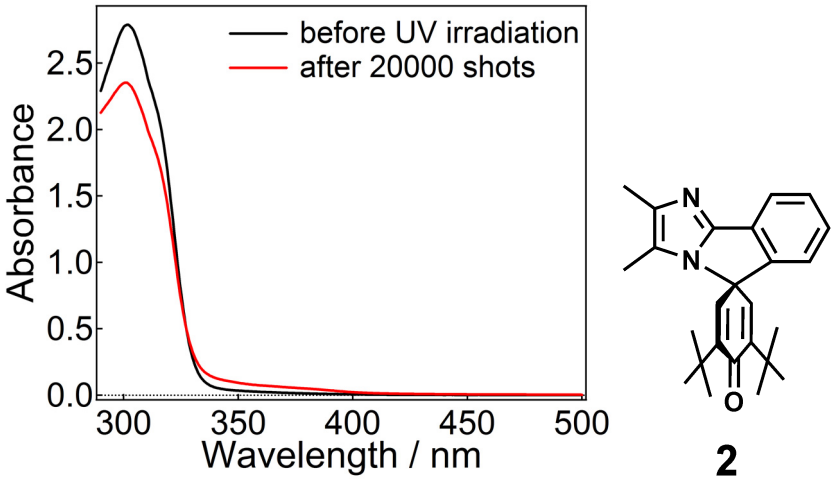


Fig. S36. UV–vis absorption spectra of **2** in O_2 saturated ethanol (2.2×10^{-3} M) before (black line) and after (red line) laser pulse irradiation (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz, optical path length: 1 mm).

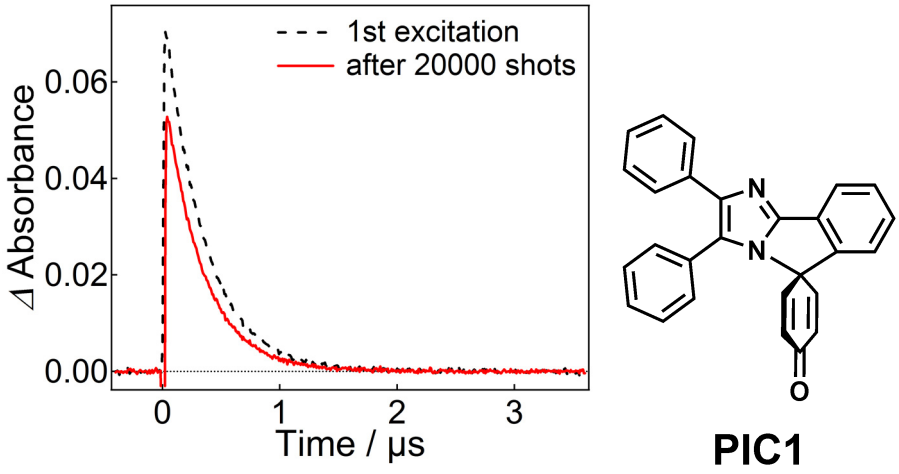


Fig. S37. Decay profiles of the transient absorbance at 650 nm of **PIC1** in O_2 saturated ethanol (6.2×10^{-4} M) before (black dash line) and after (red line) laser pulse irradiation at 298 K (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz).

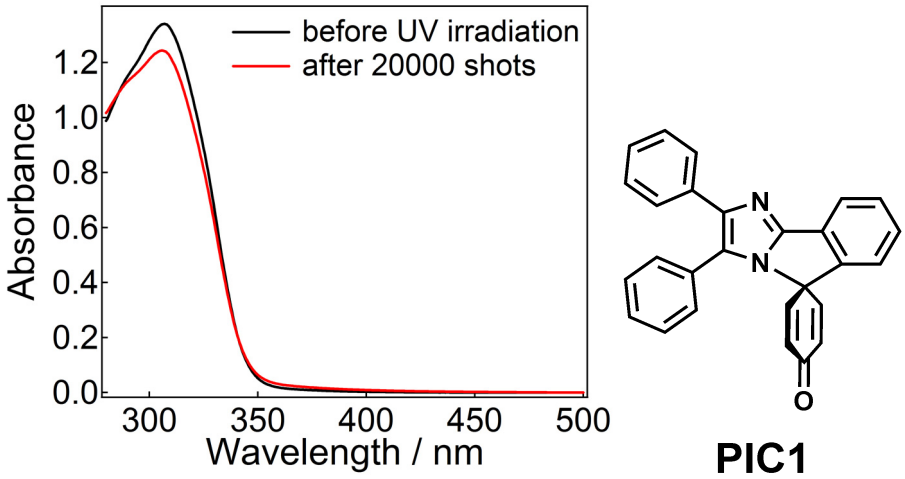


Fig. S38. UV–vis absorption spectra of **PIC1** in O_2 saturated ethanol (6.2×10^{-4} M) before (black line) and after (red line) laser pulse irradiation (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz, optical path length: 1 mm).

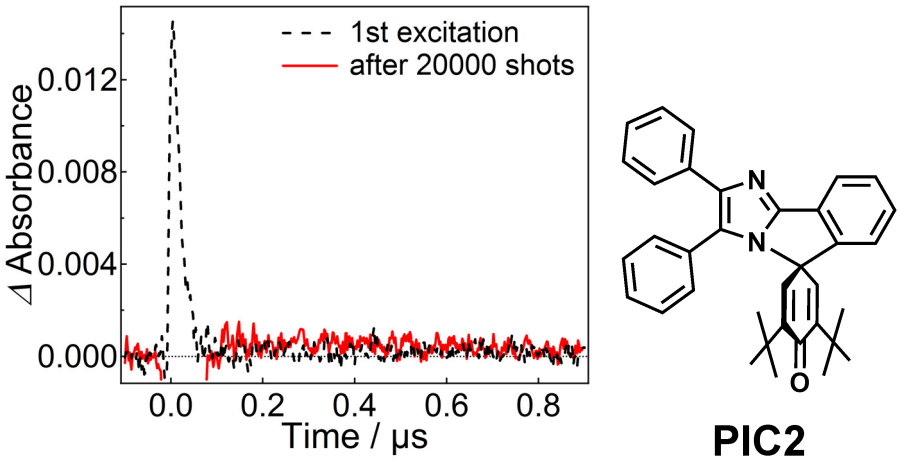


Fig. S39. Decay profiles of the transient absorbance at 650 nm of **PIC2** in O_2 saturated ethanol (7.1×10^{-4} M) before (black dash line) and after (red line) laser pulse irradiation at 298 K (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz).

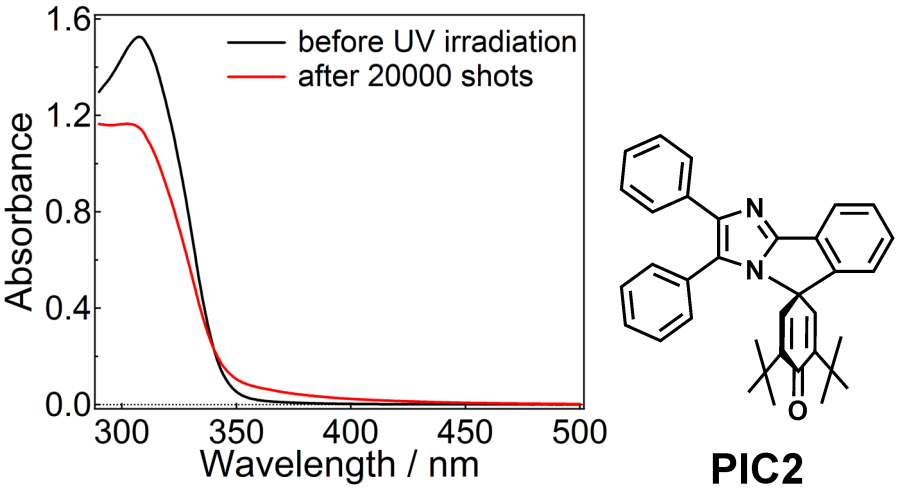


Fig. S40. UV–vis absorption spectra of **PIC2** in O_2 saturated ethanol (7.1×10^{-4} M) before (black line) and after (red line) laser pulse irradiation (excitation wavelength, 355 nm; pulse width, 5 ns; power, 7 mJ/pulse, the pulse repetition rate, 10 Hz, optical path length: 1 mm).

9. DFT Calculations

The calculation was carried out using the Gaussian 09 program (Revision D.01).[S4] The molecular structure was fully optimized at the (U)M052X/6-31+G(d,p) level of 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 (U)MPW1PW91/6-31+G(d,p) level of theory for the optimized structures.

Table S6. Standard Orientation of the Optimized Geometry for the Closed-Ring Form of **1**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	1.0387830	1.7282020	0.0000070
2	C	-0.3328110	1.4382330	0.0000060
3	C	-1.2846040	2.4421260	0.0000110
4	C	-0.8396210	3.7666400	0.0000170
5	C	0.5263070	4.0597920	0.0000180
6	C	1.4828600	3.0449130	0.0000130
7	C	1.7477140	0.4546820	0.0000010
8	C	-0.5662870	-0.0851410	-0.0000020
9	N	2.9732160	-0.0019100	-0.0000040
10	C	2.8343260	-1.3770800	-0.0000160
11	C	1.5003950	-1.7456190	-0.0000160
12	N	0.8214140	-0.5469170	-0.0000060
13	C	-1.2773480	-0.4939000	-1.2612620
14	C	-2.4954660	-1.0411850	-1.2627390
15	C	-3.2121520	-1.3333720	-0.0000040
16	C	-2.4954600	-1.0412020	1.2627310
17	C	-1.2773420	-0.4939170	1.2612550
18	O	-4.3370960	-1.8046410	-0.0000050
19	C	4.0418500	-2.2585460	0.0000100
20	C	0.8076280	-3.0672140	-0.0000190
21	H	-2.3430400	2.2070120	0.0000100
22	H	-1.5610770	4.5736960	0.0000220
23	H	0.8474990	5.0939740	0.0000220
24	H	2.5421510	3.2661150	0.0000130
25	H	-0.7441350	-0.2824140	-2.1822450
26	H	-3.0117530	-1.3021370	-2.1780590
27	H	-3.0117430	-1.3021670	2.1780500
28	H	-0.7441250	-0.2824430	2.1822390
29	H	3.7663690	-3.3129770	-0.0005170
30	H	4.6546330	-2.0610110	-0.8812490

31	H	4.6541040	-2.0617610	0.8818100
32	H	0.1750560	-3.1856790	-0.8830880
33	H	1.5426550	-3.8700570	-0.0000650
34	H	0.1751320	-3.1857210	0.8831000

SCF Done: E(RM052X) = -840. 915554514 A.U.

Zero-point correction = 0.273820 (Hartree/Particle)
Thermal correction to Energy = 0.289496
Thermal correction to Enthalpy = 0.290440
Thermal correction to Gibbs Free Energy = 0.230062
Sum of electronic and zero-point Energies = -840.641734
Sum of electronic and thermal Energies = -840.626059
Sum of electronic and thermal Enthalpies = -840.625115
Sum of electronic and thermal Free Energies = -840.685493

Low frequencies --- -64.3437 -8.4236 -7.1983 -0.0005 -0.0003 0.0003
Low frequencies --- 11.8181 34.4513 51.0121

The Results for the TDDFT calculation

Excited State 1: Singlet-A" 2.7950 eV 443.59 nm f=0.0000 <S**2>=0.0
69 -> 70 0.70605
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -840.701990000
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A" 3.3720 eV 367.69 nm f=0.0000 <S**2>=0.0
66 -> 70 0.20213
67 -> 70 0.29100
68 -> 70 0.60519

Excited State 3: Singlet-A' 3.9844 eV 311.17 nm f=0.0845 <S**2>=0.0
69 -> 71 0.65176
69 -> 72 0.25872

Excited State 4: Singlet-A' 4.2956 eV 288.63 nm f=0.2622 <S**2>=0.0
67 -> 71 0.12443
69 -> 71 -0.25804

69 -> 72 0.63672

Excited State 5: Singlet-A" 4.3625 eV 284.21 nm f=0.0004 <S**2>=0.0
67 -> 70 0.63133
68 -> 70 -0.30728

Excited State 6: Singlet-A" 4.4827 eV 276.59 nm f=0.0004 <S**2>=0.0
64 -> 70 -0.13160
66 -> 70 0.65887
68 -> 70 -0.18244

Excited State 7: Singlet-A' 4.8665 eV 254.77 nm f=0.0174 <S**2>=0.0
65 -> 70 0.38883
69 -> 73 0.56959

Excited State 8: Singlet-A' 4.8751 eV 254.32 nm f=0.0136 <S**2>=0.0
65 -> 70 0.58328
69 -> 73 -0.37683

Excited State 9: Singlet-A" 4.9812 eV 248.90 nm f=0.0006 <S**2>=0.0
64 -> 70 0.68350
66 -> 70 0.13212
69 -> 74 -0.10307

Excited State 10: Singlet-A" 5.0507 eV 245.48 nm f=0.0000 <S**2>=0.0
64 -> 70 0.10466
69 -> 74 0.67532
69 -> 75 -0.10576

Excited State 11: Singlet-A' 5.4190 eV 228.79 nm f=0.0148 <S**2>=0.0
67 -> 71 0.20886
67 -> 72 0.14342
67 -> 73 0.10468
68 -> 71 0.53121
68 -> 72 0.28688
68 -> 73 0.20387

Excited State 12: Singlet-A' 5.4952 eV 225.62 nm f=0.0576 <S**2>=0.0
63 -> 70 -0.13794

64 -> 72 -0.21394
66 -> 72 -0.19255
67 -> 71 0.48936
68 -> 71 -0.22300
68 -> 72 0.15347
69 -> 72 -0.12181
69 -> 73 0.16086

Excited State 13: Singlet-A" 5.5112 eV 224.97 nm f=0.0203 <S**2>=0.0
62 -> 70 0.65311
65 -> 71 0.22315

Excited State 14: Singlet-A' 5.5249 eV 224.41 nm f=0.3096 <S**2>=0.0
63 -> 70 0.57704
64 -> 71 -0.13949
64 -> 72 -0.10275
66 -> 71 0.23756
68 -> 72 0.12203

Excited State 15: Singlet-A" 5.5317 eV 224.13 nm f=0.0009 <S**2>=0.0
69 -> 74 0.10488
69 -> 75 0.67542
69 -> 78 -0.14050

Excited State 16: Singlet-A" 5.5564 eV 223.14 nm f=0.0001 <S**2>=0.0
62 -> 70 -0.23390
65 -> 71 0.59632
65 -> 72 -0.26573

Excited State 17: Singlet-A' 5.6621 eV 218.97 nm f=0.0083 <S**2>=0.0
69 -> 76 0.69058

Excited State 18: Singlet-A' 5.7365 eV 216.13 nm f=0.0025 <S**2>=0.0
63 -> 70 -0.19351
66 -> 71 0.58716
67 -> 72 0.21920
68 -> 71 -0.15003
69 -> 81 -0.11126

Excited State 19: Singlet-A" 5.7379 eV 216.08 nm f=0.0001 <S**2>=0.0

69 -> 74	0.10973
69 -> 77	0.65873
69 -> 78	0.15488
69 -> 79	-0.12649

Excited State 20: Singlet-A" 5.7639 eV 215.11 nm f=0.0035 <S**2>=0.0

69 -> 75	0.14251
69 -> 77	-0.16170
69 -> 78	0.66274

Excited State 21: Singlet-A' 5.8853 eV 210.67 nm f=0.0952 <S**2>=0.0

64 -> 71	-0.13337
66 -> 72	-0.21316
67 -> 71	-0.32924
68 -> 71	-0.17025
68 -> 72	0.51474

Excited State 22: Singlet-A' 5.9521 eV 208.30 nm f=0.1610 <S**2>=0.0

63 -> 70	0.17799
64 -> 71	0.28795
66 -> 71	-0.12595
66 -> 72	-0.17817
67 -> 71	0.11412
67 -> 72	0.52446
68 -> 71	-0.13501

Excited State 23: Singlet-A' 6.0010 eV 206.60 nm f=0.0491 <S**2>=0.0

66 -> 71	-0.17271
66 -> 72	0.57142
68 -> 71	-0.23849
68 -> 72	0.18102
69 -> 81	0.12923

Excited State 24: Singlet-A" 6.0489 eV 204.97 nm f=0.0006 <S**2>=0.0

69 -> 77	0.12838
69 -> 79	0.68705

Excited State 25: Singlet-A" 6.0666 eV 204.37 nm f=0.0003 <S**2>=0.0

65 -> 71 0.28331
65 -> 72 0.64240

Excited State 26: Singlet-A' 6.2469 eV 198.47 nm f=0.0254 <S**2>=0.0
64 -> 71 0.45960
67 -> 72 -0.25039
67 -> 73 -0.10991
68 -> 73 0.13555
69 -> 81 -0.38241
69 -> 89 0.10154

Excited State 27: Singlet-A" 6.2655 eV 197.89 nm f=0.0008 <S**2>=0.0
63 -> 71 0.68254
63 -> 72 0.13284

Excited State 28: Singlet-A" 6.3417 eV 195.50 nm f=0.0000 <S**2>=0.0
69 -> 80 0.68851

Excited State 29: Singlet-A' 6.3964 eV 193.83 nm f=0.0072 <S**2>=0.0
64 -> 72 -0.15291
66 -> 72 -0.12035
68 -> 72 -0.17354
68 -> 73 0.57655
69 -> 81 0.22576

Excited State 30: Singlet-A' 6.4118 eV 193.37 nm f=0.0183 <S**2>=0.0
64 -> 71 0.19730
66 -> 71 0.10937
67 -> 73 -0.34972
68 -> 72 0.14380
68 -> 73 -0.17219
69 -> 81 0.37758
69 -> 83 0.30599

Excited State 31: Singlet-A" 6.4834 eV 191.23 nm f=0.0009 <S**2>=0.0
69 -> 82 0.68317

Excited State 32: Singlet-A' 6.5172 eV 190.24 nm f=0.1634 <S**2>=0.0
62 -> 71 -0.14187

64 -> 72 0.45922
66 -> 73 0.27252
67 -> 71 0.10646
67 -> 72 -0.10710
67 -> 73 0.18446
69 -> 83 0.31515

Excited State 33: Singlet-A' 6.5414 eV 189.54 nm f=0.0609 <S**2>=0.0
62 -> 71 0.24535
64 -> 72 -0.23868
66 -> 73 -0.14200
67 -> 73 0.30514
68 -> 73 -0.12700
69 -> 81 -0.12811
69 -> 83 0.42930
69 -> 85 -0.10387
69 -> 89 0.10749

Excited State 34: Singlet-A" 6.5624 eV 188.93 nm f=0.0003 <S**2>=0.0
63 -> 71 -0.13935
63 -> 72 0.67606

Excited State 35: Singlet-A" 6.5689 eV 188.74 nm f=0.0005 <S**2>=0.0
69 -> 84 0.64591
69 -> 86 0.20303
69 -> 87 -0.13454

Excited State 36: Singlet-A' 6.6252 eV 187.14 nm f=0.0805 <S**2>=0.0
62 -> 71 0.21088
64 -> 72 -0.13779
66 -> 73 0.50593
69 -> 85 0.25058
69 -> 89 0.23079

Excited State 37: Singlet-A' 6.6805 eV 185.59 nm f=0.0294 <S**2>=0.0
66 -> 73 -0.20266
69 -> 83 0.16493
69 -> 85 0.63059

Excited State 38:	Singlet-A"	6.6907 eV	185.31 nm	f=0.0041	<S**2>=0.0	
68 -> 74	0.65841					
68 -> 77	0.12346					
Excited State 39:	Singlet-A"	6.7228 eV	184.42 nm	f=0.0007	<S**2>=0.0	
67 -> 74	0.63959					
67 -> 75	0.17982					
68 -> 75	-0.13148					
Excited State 40:	Singlet-A'	6.7561 eV	183.51 nm	f=0.2792	<S**2>=0.0	
61 -> 70	0.14673					
62 -> 71	0.25237					
62 -> 72	0.22434					
64 -> 71	0.19788					
64 -> 72	0.13178					
64 -> 73	0.26228					
66 -> 71	0.10346					
66 -> 73	-0.14792					
67 -> 72	-0.11382					
67 -> 73	0.26199					
69 -> 81	0.22322					
69 -> 83	-0.17778					

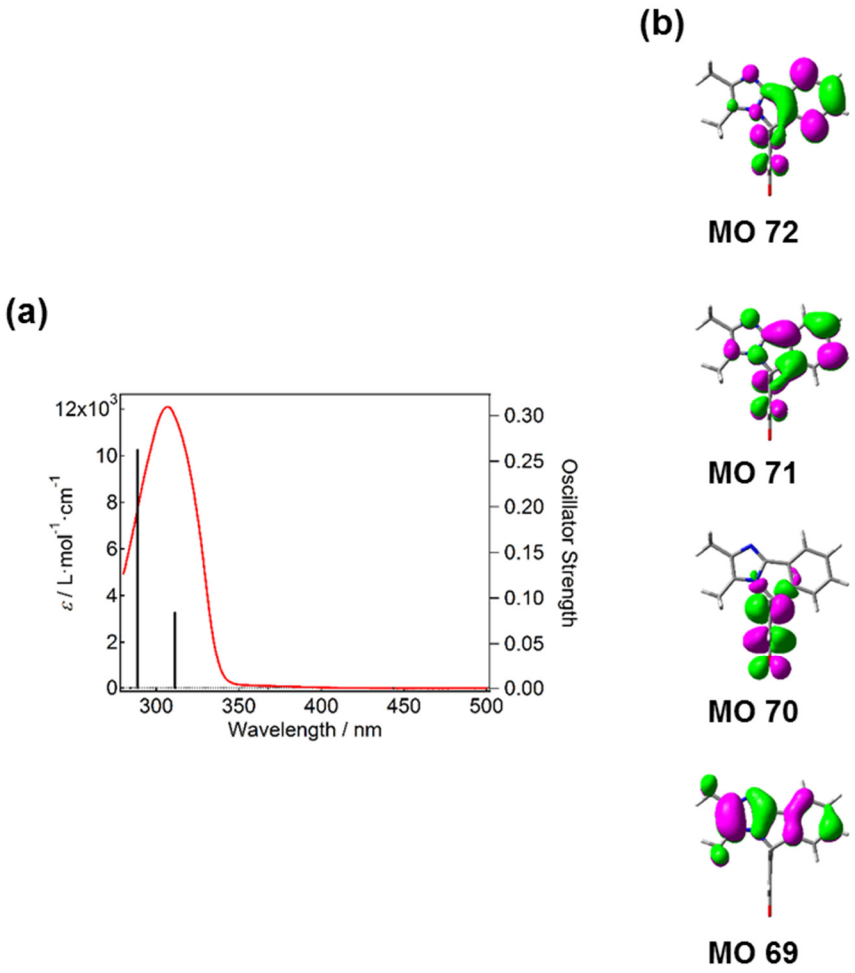


Fig. S41. (a) UV–vis absorption spectrum of the closed-ring isomer of **1** in benzene. The calculated spectrum (MPW1PW91/6-31+G(d,p)//M052X/6-31+G(d,p) level of the theory) is shown by the black lines. (b) The relevant molecular orbitals were calculated at the M052X/6-31+G(d,p) level of the theory.

Table S7. Standard Orientation of the Optimized Geometry for the Biradical Form of **1**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	0.8639480	1.4438450	0.0714620
2	C	-0.5375490	1.6107600	-0.0751990
3	C	1.5112270	0.1549660	-0.0096100
4	N	2.8020330	-0.0351270	0.4258400
5	C	3.0477570	-1.2957140	0.1455680
6	C	1.8621440	-1.8747510	-0.5051800
7	N	0.9339180	-0.9483800	-0.5876520
8	C	-1.4965460	0.5018280	0.0128420
9	C	-2.5789400	0.4226240	-0.8984230
10	C	-3.5174160	-0.5676070	-0.7909550

11	C	-3.4545400	-1.5456290	0.2837460
12	C	-2.3527590	-1.4186400	1.2234140
13	C	-1.4137370	-0.4410960	1.0759210
14	O	-4.3101510	-2.4435700	0.3935420
15	C	-1.0431770	2.9117790	-0.2124140
16	C	-0.2114240	4.0207940	-0.1365290
17	C	1.1587240	3.8543590	0.0877160
18	C	1.6880270	2.5798680	0.1893990
19	H	-2.6286100	1.1360360	-1.7122490
20	H	-0.5991850	-0.3518830	1.7843830
21	H	-2.1126900	3.0477400	-0.3176520
22	H	-0.6324800	5.0144370	-0.2241390
23	H	1.8069890	4.7176370	0.1669770
24	H	2.7496400	2.4230340	0.3249680
25	H	-4.3331880	-0.6655510	-1.4952070
26	H	-2.3186780	-2.1298910	2.0383700
27	C	4.3278370	-1.9915670	0.4415600
28	H	4.7743670	-2.3830600	-0.4765270
29	H	5.0228700	-1.2996980	0.9123450
30	H	4.1588480	-2.8420540	1.1076580
31	C	1.7132220	-3.2624770	-1.0176170
32	H	1.8504500	-3.9881950	-0.2113950
33	H	0.7223010	-3.3891300	-1.4481650
34	H	2.4681150	-3.4763650	-1.7792340

SCF Done: E(UM052X) = -840.869804692 A.U.
S**2 before annihilation 1.0289, after 0.6709

Zero-point correction = 0.269399 (Hartree/Particle)
Thermal correction to Energy = 0.286713
Thermal correction to Enthalpy = 0.287657
Thermal correction to Gibbs Free Energy = 0.222479
Sum of electronic and zero-point Energies = -840.600406
Sum of electronic and thermal Energies = -840.58309
Sum of electronic and thermal Enthalpies = -840.582148
Sum of electronic and thermal Free Energies = -840.64732

Low frequencies --- -14.0900 -9.3628 0.0006 0.0008 0.0010 8.1098
Low frequencies --- 30.7878 39.1034 52.6794

The Results for the TDDFT calculation

Excited State 1: 2.378-A 1.3177 eV 940.93 nm f=0.0000 <S**2>=1.163
68A -> 70A 0.96864
68A -> 71A 0.11973
68A -> 72A 0.10433
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = 74908
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 1.484-A 1.6332 eV 759.16 nm f=0.0126 <S**2>=0.301
69A -> 70A 0.37299
69B -> 70B 0.91112

Excited State 3: 1.320-A 2.0141 eV 615.57 nm f=0.0799 <S**2>=0.185
67A -> 70A -0.10416
69A -> 70A 0.90527
67B -> 70B 0.12053
69B -> 70B -0.35549

Excited State 4: 2.411-A 2.4646 eV 503.06 nm f=0.0091 <S**2>=1.204
66A -> 70A 0.11981
67A -> 70A -0.44228
69A -> 70A -0.13063
63B -> 70B -0.50114
67B -> 70B 0.66070
69B -> 70B 0.15007

Excited State 5: 2.279-A 2.5220 eV 491.62 nm f=0.0022 <S**2>=1.049
64A -> 70A 0.10176
65A -> 70A 0.19698
66A -> 70A -0.21575
67A -> 70A 0.53754
64B -> 70B 0.56448
65B -> 70B -0.12669
66B -> 70B -0.34153
67B -> 70B 0.35342
69B -> 73B 0.10731

Excited State	6:	2.344-A	2.5489 eV	486.42 nm	f=0.0016	<S**2>=1.124
64A -> 70A	-0.15197					
65A -> 70A	-0.14048					
66A -> 70A	0.20515					
67A -> 70A	-0.49634					
63B -> 70B	0.51206					
64B -> 70B	0.47360					
66B -> 70B	-0.34680					

Excited State	7:	2.330-A	2.9531 eV	419.84 nm	f=0.0028	<S**2>=1.107
66A -> 70A	-0.18312					
62B -> 70B	0.21032					
64B -> 70B	0.18487					
66B -> 70B	0.26667					
68B -> 70B	0.87827					

Excited State	8:	2.491-A	2.9862 eV	415.19 nm	f=0.0188	<S**2>=1.302
66A -> 70A	-0.30864					
66A -> 72A	0.10113					
67A -> 70A	-0.17025					
69A -> 71A	-0.19360					
69A -> 72A	0.12609					
62B -> 70B	0.39177					
64B -> 70B	0.21772					
65B -> 70B	-0.43053					
66B -> 70B	0.47511					
66B -> 72B	-0.10071					
68B -> 70B	-0.32910					
69B -> 72B	0.13993					

Excited State	9:	2.455-A	3.0106 eV	411.83 nm	f=0.0376	<S**2>=1.256
69A -> 71A	0.34887					
62B -> 70B	0.33213					
63B -> 70B	-0.13806					
64B -> 70B	0.31383					
65B -> 70B	0.65059					
66B -> 70B	0.16176					
68B -> 70B	-0.31854					

Excited State 10: 2.375-A 3.0302 eV 409.16 nm f=0.0414 <S**2>=1.160

61A -> 70A	0.14761
62A -> 70A	-0.13814
65A -> 70A	-0.14916
66A -> 70A	0.62987
67A -> 70A	0.25316
62B -> 70B	0.54303
63B -> 70B	-0.12565
65B -> 70B	-0.22690
69B -> 71B	0.20446
69B -> 72B	-0.11562

Excited State 11: 2.216-A 3.1785 eV 390.07 nm f=0.0080 <S**2>=0.978

66A -> 70A	0.27990
67A -> 70A	0.13749
69A -> 71A	0.11503
62B -> 70B	-0.38165
63B -> 70B	0.38241
64B -> 70B	0.10936
66B -> 70B	0.59480
67B -> 70B	0.39060
69B -> 71B	0.13046

Excited State 12: 2.423-A 3.3938 eV 365.32 nm f=0.0015 <S**2>=1.218

62A -> 70A	0.20303
64A -> 70A	0.15334
65A -> 70A	0.75191
66A -> 70A	0.31219
66A -> 72A	-0.10459
67A -> 70A	-0.19177
69A -> 71A	0.12765
62B -> 70B	-0.13176
63B -> 70B	-0.16587
64B -> 70B	0.11312
65B -> 70B	-0.20281
67B -> 70B	-0.21355

Excited State 13: 2.226-A 3.5031 eV 353.93 nm f=0.0073 <S**2>=0.988

65A -> 70A	0.36564

62B -> 70B 0.43808
63B -> 70B 0.45106
64B -> 70B -0.43817
65B -> 70B 0.13827
66B -> 70B -0.15372
67B -> 70B 0.42471
69B -> 71B -0.10002

Excited State 14: 2.495-A 3.8181 eV 324.72 nm f=0.0641 <S**2>=1.306
61A -> 70A -0.23271
62A -> 70A 0.20545
64A -> 70A 0.61665
65A -> 70A -0.37863
66A -> 72A -0.15998
69A -> 71A 0.33752
63B -> 70B 0.10608
65B -> 70B -0.24785
65B -> 71B -0.10250
66B -> 72B 0.11517
69B -> 71B -0.21140
69B -> 75B 0.10107
69B -> 76B -0.10914

Excited State 15: 2.440-A 3.8545 eV 321.66 nm f=0.0481 <S**2>=1.238
61A -> 70A -0.21971
62A -> 70A 0.14333
63A -> 70A 0.75872
63A -> 71A -0.13274
64A -> 70A 0.11539
66A -> 70A 0.24868
67A -> 70A 0.10076
69A -> 71A -0.27720
65B -> 70B 0.12153
65B -> 71B 0.14605
69B -> 71B -0.25838

Excited State 16: 2.364-A 3.8880 eV 318.89 nm f=0.0500 <S**2>=1.148
61A -> 70A 0.26866
62A -> 70A -0.25155

64A -> 70A 0.69540
67A -> 70A -0.21307
69A -> 71A -0.29931
65B -> 70B 0.17938
69B -> 71B 0.34697

Excited State 17: 2.788-A 4.0397 eV 306.91 nm f=0.1322 <S**2>=1.694
61A -> 70A -0.10372
62A -> 70A 0.12007
63A -> 70A -0.40186
63A -> 72A 0.12051
64A -> 70A 0.17492
66A -> 70A 0.27641
66A -> 72A 0.29165
67A -> 72A 0.11908
69A -> 72A 0.31420
65B -> 70B 0.25250
65B -> 72B 0.16517
66B -> 72B -0.23593
67B -> 73B 0.11358
69B -> 71B -0.18820
69B -> 72B 0.44820

Excited State 18: 2.592-A 4.0891 eV 303.21 nm f=0.0933 <S**2>=1.430
61A -> 70A 0.32402
62A -> 70A -0.46569
63A -> 70A 0.22621
65A -> 70A 0.10445
66A -> 72A 0.13305
69A -> 71A 0.48507
65B -> 70B -0.15808
66B -> 71B 0.14250
66B -> 72B -0.11281
67B -> 73B 0.10083
69B -> 71B -0.40640
69B -> 75B -0.12277
69B -> 76B 0.12365

Excited State 19: 2.554-A 4.2709 eV 290.30 nm f=0.1039 <S**2>=1.381

61A -> 70A 0.15702
62A -> 70A 0.22630
63A -> 70A 0.35143
67A -> 73A 0.17057
69A -> 71A 0.38631
69A -> 72A 0.46444
63B -> 73B -0.12235
64B -> 73B 0.11079
65B -> 70B -0.11215
66B -> 70B -0.15051
66B -> 72B -0.10109
67B -> 73B -0.22105
69B -> 71B 0.36683
69B -> 72B 0.20179

Excited State 20: 2.506-A 4.3601 eV 284.36 nm f=0.0029 <S**2>=1.319
61A -> 70A 0.39158
62A -> 70A 0.59542
66A -> 72A 0.17935
69A -> 72A -0.52680
66B -> 71B 0.17618
66B -> 72B -0.11354
69B -> 73B 0.11203
69B -> 75B -0.14380
69B -> 76B 0.14421

Excited State 21: 2.603-A 4.4151 eV 280.82 nm f=0.0763 <S**2>=1.444
61A -> 70A -0.15232
62A -> 70A -0.16989
63A -> 70A 0.14309
66A -> 71A -0.10392
67A -> 73A -0.20728
69A -> 71A 0.13636
69A -> 72A -0.24158
63B -> 73B 0.10510
67B -> 73B 0.22339
69B -> 71B 0.38698
69B -> 72B 0.41160
69B -> 73B 0.50387

69B -> 76B -0.10012

Excited State 22: 2.602-A 4.4475 eV 278.77 nm f=0.0104 <S**2>=1.443

61A -> 70A 0.27073
62A -> 70A 0.23123
66A -> 71A 0.10363
66A -> 72A -0.11645
67A -> 70A -0.10204
67A -> 71A 0.10058
67A -> 73A -0.18811
69A -> 72A 0.44253
63B -> 73B 0.10231
67B -> 71B 0.11141
67B -> 73B 0.20378
69B -> 71B -0.17298
69B -> 72B -0.36992
69B -> 73B 0.51530

Excited State 23: 2.868-A 4.4895 eV 276.17 nm f=0.0272 <S**2>=1.806

55A -> 70A -0.12724
61A -> 70A -0.15418
62A -> 70A -0.24535
63A -> 70A -0.11949
65A -> 73A 0.13464
66A -> 70A 0.14234
66A -> 73A -0.14289
67A -> 73A 0.32296
63B -> 73B -0.17176
64B -> 73B 0.18687
67B -> 73B -0.32080
69B -> 71B -0.19024
69B -> 73B 0.60767

Excited State 24: 2.834-A 4.7582 eV 260.57 nm f=0.1079 <S**2>=1.758

61A -> 70A 0.24555
63A -> 71A 0.35775
66A -> 71A -0.12410
67A -> 73A 0.11574
69A -> 71A -0.23995

69A -> 85A -0.14623
57B -> 70B 0.13886
60B -> 70B -0.13478
61B -> 70B -0.32546
65B -> 71B -0.29703
65B -> 72B -0.20361
66B -> 71B -0.14044
69B -> 71B -0.24841
69B -> 72B 0.39165

Excited State 25: 3.190-A 4.8409 eV 256.12 nm f=0.0058 <S**2>=2.295
58A -> 70A -0.22847
59A -> 70A 0.39658
60A -> 70A 0.20340
63A -> 71A 0.14230
68A -> 70A -0.17986
68A -> 71A 0.44876
68A -> 72A 0.25705
68A -> 77A 0.10837
68A -> 78A 0.15377
68A -> 81A -0.14148
65B -> 71B -0.11877
68B -> 71B 0.38047
68B -> 72B -0.17039
68B -> 75B -0.15238
68B -> 76B 0.17238

Excited State 26: 3.140-A 4.9497 eV 250.49 nm f=0.0732 <S**2>=2.215
61A -> 70A -0.26481
63A -> 71A 0.23400
66A -> 71A 0.34774
66A -> 72A 0.26728
67A -> 71A 0.17505
68A -> 71A -0.15494
69A -> 85A -0.10082
57B -> 70B 0.20154
60B -> 70B -0.14143
61B -> 70B -0.10233
65B -> 71B -0.21331

65B -> 72B -0.13126
66B -> 71B 0.31770
66B -> 72B -0.15889
68B -> 71B -0.23573
68B -> 76B -0.10969
69B -> 71B 0.16816
69B -> 72B -0.26090

Excited State 27: 3.239-A 5.0033 eV 247.80 nm f=0.0004 <S**2>=2.372
64A -> 71A -0.15628
65A -> 71A -0.36249
66A -> 72A -0.10145
67A -> 71A 0.67881
60B -> 70B 0.12851
61B -> 70B 0.24277
67B -> 71B 0.26979
69B -> 72B 0.13972

Excited State 28: 3.072-A 5.0246 eV 246.75 nm f=0.0201 <S**2>=2.110
61A -> 70A 0.12450
65A -> 71A 0.36681
66A -> 71A 0.45542
66A -> 72A -0.22600
58B -> 70B -0.15009
61B -> 70B 0.40805
65B -> 72B -0.16141
66B -> 71B 0.25961
66B -> 72B 0.27007
69B -> 72B 0.30178

Excited State 29: 2.463-A 5.0475 eV 245.64 nm f=0.0024 <S**2>=1.267
58A -> 70A 0.15765
59A -> 70A -0.33833
60A -> 70A -0.12665
68A -> 71A -0.32552
68A -> 72A -0.12906
68B -> 71B 0.66069
68B -> 72B -0.26991
68B -> 75B -0.21807

68B -> 76B 0.24296

Excited State 30: 2.641-A 5.1125 eV 242.51 nm f=0.0122 <S**2>=1.493

63A -> 71A 0.14791
66A -> 71A -0.27308
66A -> 72A 0.13854
67A -> 71A -0.12546
69A -> 73A 0.18999
56B -> 70B 0.10227
57B -> 70B 0.15516
58B -> 70B -0.26466
59B -> 70B -0.38826
61B -> 70B 0.57793
65B -> 71B -0.23563
66B -> 72B -0.13892
69B -> 71B -0.11813
69B -> 72B -0.12462

Excited State 31: 2.822-A 5.1682 eV 239.90 nm f=0.0009 <S**2>=1.741

56A -> 70A -0.31068
59A -> 70A -0.16256
60A -> 70A 0.49141
64A -> 71A -0.32204
65A -> 71A 0.18547
66A -> 71A -0.19342
68A -> 73A 0.19420
69A -> 73A -0.40026
60B -> 70B -0.12318
63B -> 71B -0.17560
64B -> 71B -0.13894
68B -> 73B -0.13893

Excited State 32: 2.632-A 5.1783 eV 239.43 nm f=0.0010 <S**2>=1.482

56A -> 70A -0.19289
57A -> 70A 0.12198
58A -> 70A -0.15244
59A -> 70A 0.18699
60A -> 70A 0.40977
64A -> 71A 0.13309

66A -> 72A -0.11594
68A -> 71A -0.37262
68A -> 73A 0.23670
69A -> 73A 0.56176
59B -> 70B 0.10623
68B -> 73B -0.14150

Excited State 33: 2.701-A 5.1864 eV 239.06 nm f=0.0049 <S**2>=1.574
56A -> 70A 0.26856
58A -> 70A -0.16420
59A -> 70A 0.60035
60A -> 70A -0.16479
64A -> 71A -0.18742
65A -> 71A 0.15679
68A -> 71A -0.49309
68A -> 72A -0.10632
68A -> 73A -0.14136
69A -> 73A -0.19395
63B -> 71B -0.10320
68B -> 73B 0.11510

Excited State 34: 3.096-A 5.2079 eV 238.07 nm f=0.0027 <S**2>=2.146
58A -> 70A 0.12080
59A -> 70A -0.12585
60A -> 70A -0.22476
64A -> 71A -0.27217
65A -> 71A 0.40704
66A -> 71A -0.19954
66A -> 73A -0.11633
67A -> 72A 0.13192
68A -> 71A 0.21284
69A -> 73A 0.45365
63B -> 71B -0.12121
63B -> 72B -0.12768
64B -> 71B -0.26075
67B -> 71B 0.23450

Excited State 35: 2.401-A 5.3140 eV 233.32 nm f=0.0134 <S**2>=1.191
65A -> 71A 0.14661

68A -> 73A 0.11187
59B -> 70B -0.26593
60B -> 70B 0.87096
61B -> 70B -0.14276
65B -> 71B -0.11811

Excited State 36: 3.332-A 5.3510 eV 231.70 nm f=0.0012 <S**2>=2.526
56A -> 70A -0.11099
59A -> 70A -0.13414
60A -> 70A 0.36265
64A -> 71A 0.12535
67A -> 72A 0.10381
68A -> 73A -0.50176
68A -> 74A -0.11579
60B -> 70B 0.10457
63B -> 71B 0.11450
68B -> 73B 0.65213

Excited State 37: 2.700-A 5.3566 eV 231.46 nm f=0.0012 <S**2>=1.572
64A -> 71A 0.20913
65A -> 71A 0.11417
67A -> 72A 0.14589
68A -> 73A 0.12705
69A -> 73A -0.21135
69A -> 74A 0.78036
69A -> 75A 0.16291
69A -> 77A -0.10180
63B -> 71B 0.18768
67B -> 71B 0.12262
67B -> 72B -0.10894
68B -> 73B -0.15875

Excited State 38: 2.961-A 5.4140 eV 229.00 nm f=0.0127 <S**2>=1.942
64A -> 71A -0.26648
65A -> 71A -0.19563
66A -> 71A 0.14301
67A -> 71A -0.12686
67A -> 72A -0.23485
69A -> 73A 0.34287

69A -> 74A 0.53661
59B -> 70B -0.16504
63B -> 71B -0.26599
67B -> 71B -0.21878
67B -> 72B 0.16059
68B -> 73B 0.18972
69B -> 75B 0.11791

Excited State 39: 2.610-A 5.4398 eV 227.92 nm f=0.0382 <S**2>=1.453
55A -> 70A -0.20435
57A -> 70A 0.13129
61A -> 70A 0.17418
64A -> 71A 0.10996
67A -> 71A 0.11959
67A -> 72A 0.10632
67A -> 73A 0.10168
58B -> 70B -0.11445
59B -> 70B -0.24448
61B -> 70B -0.13849
65B -> 71B 0.13504
66B -> 71B 0.11145
69B -> 74B 0.21874
69B -> 75B 0.65859
69B -> 76B -0.33559

Excited State 40: 2.480-A 5.4991 eV 225.46 nm f=0.0172 <S**2>=1.288
63A -> 71A 0.10481
67A -> 71A -0.10947
68A -> 72A 0.10703
57B -> 70B -0.11192
58B -> 70B 0.18707
59B -> 70B 0.38491
61B -> 70B 0.23252
65B -> 71B -0.26637
66B -> 71B 0.14843
69B -> 74B 0.65771
69B -> 75B 0.16128
69B -> 77B -0.22464

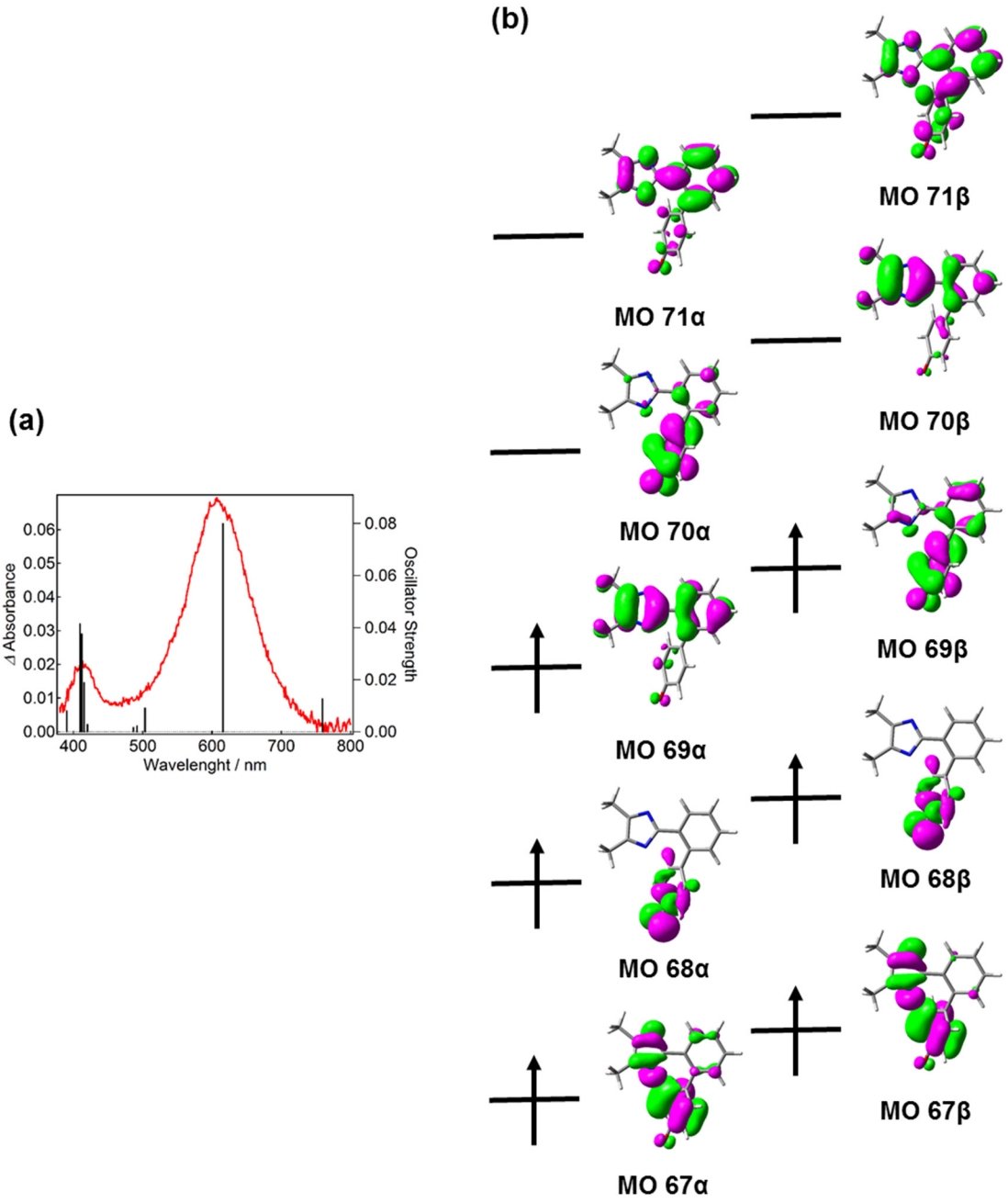


Fig. S42. (a) The transient absorption spectrum of **1** in benzene (excitation wavelength, 355 nm; pulse width, 5ns; power 4 mJ/pulse). The calculated spectrum (UMPW1PW91/6-31+G(d,p)//UM052X/6-31+G(d,p) level of the theory) of the biradical form of the open-ring isomer of **1** is shown by the black lines. (b) The relevant molecular orbitals were calculated at the UM052X/6-31+G(d,p) level of the theory.

Table S8. Standard Orientation of the Optimized Geometry for the Quinoid Form of **1**.

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	0.7903890	1.4171170	0.1776870
2	C	-0.6170470	1.5286110	-0.1770260

3	C	1.4850520	0.2263290	0.0229440
4	N	2.7831300	0.0535640	0.5007100
5	C	3.0884550	-1.1653170	0.1583880
6	C	1.9630130	-1.7534320	-0.5966110
7	N	1.0022020	-0.8797300	-0.6735090
8	C	-1.5091130	0.4618700	-0.0275730
9	C	-2.7656910	0.4307180	-0.7512470
10	C	-3.6449280	-0.5806340	-0.5996660
11	C	-3.4100480	-1.6694870	0.3661670
12	C	-2.1712030	-1.5838190	1.1462520
13	C	-1.2768280	-0.5956270	0.9395550
14	O	-4.2221770	-2.5777890	0.5146170
15	C	-1.0820380	2.8370130	-0.5591610
16	C	-0.3216520	3.9396820	-0.3234150
17	C	0.9766010	3.8265800	0.2782670
18	C	1.5149560	2.6065070	0.5354330
19	H	-2.9592160	1.1933050	-1.4939060
20	H	-0.3885610	-0.5348890	1.5537090
21	H	-2.0948870	2.9590150	-0.9155000
22	H	-0.7176390	4.9223210	-0.5464700
23	H	1.5391270	4.7257200	0.4956460
24	H	2.5194170	2.4896610	0.9178810
25	H	-4.5536400	-0.6439150	-1.1850510
26	H	-2.0243990	-2.3375360	1.9090060
27	C	4.3876070	-1.8276550	0.4582510
28	H	4.8999480	-2.1005810	-0.4684390
29	H	5.0215790	-1.1548540	1.0318160
30	H	4.2294360	-2.7487290	1.0249910
31	C	1.9305840	-3.1022910	-1.2272490
32	H	2.0647310	-3.8833230	-0.4743810
33	H	0.9758950	-3.2494440	-1.7276920
34	H	2.7396380	-3.2082660	-1.9549250

SCF Done: E(RM052X)	=	-840.857424488	A.U.
Zero-point correction	=	0.271461 (Hartree/Particle)	
Thermal correction to Energy	=	0.288608	
Thermal correction to Enthalpy	=	0.289552	
Thermal correction to Gibbs Free Energy	=	0.225211	
Sum of electronic and zero-point Energies	=	-840.585964	

Sum of electronic and thermal Energies = -840.568817

Sum of electronic and thermal Enthalpies = -840.567872

Sum of electronic and thermal Free Energies = -840.632213

Low frequencies --- -13.4656 -8.6711 -0.0007 -0.0003 0.0005 10.4390

Low frequencies --- 32.6568 44.6583 49.6766

The Results for the TDDFT calculation

Excited State 1: Singlet-A 2.0093 eV 617.06 nm f=0.2525 <S**2>=0.000

68 -> 70 0.24299

69 -> 70 0.66849

69 <- 70 -0.16194

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -840.684016310

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.1643 eV 572.86 nm f=0.0505 <S**2>=0.000

68 -> 70 0.64842

68 -> 71 0.10753

69 -> 70 -0.24883

Excited State 3: Singlet-A 2.7864 eV 444.97 nm f=0.0072 <S**2>=0.000

65 -> 70 -0.19519

66 -> 70 0.20325

67 -> 70 0.64074

Excited State 4: Singlet-A 3.0909 eV 401.13 nm f=0.0065 <S**2>=0.000

65 -> 70 -0.40534

66 -> 70 0.44839

67 -> 70 -0.27250

69 -> 71 0.22633

Excited State 5: Singlet-A 3.2651 eV 379.73 nm f=0.0245 <S**2>=0.000

65 -> 70 0.51630

66 -> 70 0.33856

69 -> 71 0.31182

Excited State 6: Singlet-A 3.4347 eV 360.98 nm f=0.0100 <S**2>=0.000

62 -> 70 -0.14208
63 -> 70 0.52968
64 -> 70 0.39998
69 -> 71 0.17920

Excited State 7: Singlet-A 3.5631 eV 347.97 nm f=0.1293 <S**2>=0.000
62 -> 70 0.11312
63 -> 70 -0.40324
64 -> 70 0.44004
66 -> 70 -0.18379
69 -> 70 0.11284
69 -> 71 0.23759
69 -> 72 0.11346

Excited State 8: Singlet-A 3.6806 eV 336.86 nm f=0.0074 <S**2>=0.000
62 -> 70 0.66073
63 -> 70 0.17999
69 -> 71 -0.13103

Excited State 9: Singlet-A 4.1548 eV 298.41 nm f=0.0317 <S**2>=0.000
69 -> 72 0.68128

Excited State 10: Singlet-A 4.2797 eV 289.70 nm f=0.8360 <S**2>=0.000
63 -> 70 0.11500
64 -> 70 -0.34785
66 -> 70 -0.29957
68 -> 71 0.12087
69 -> 71 0.46712

Excited State 11: Singlet-A 4.4450 eV 278.93 nm f=0.0380 <S**2>=0.000
68 -> 70 -0.12883
68 -> 71 0.63735
68 -> 72 -0.14676
68 -> 78 -0.10558

Excited State 12: Singlet-A 4.8378 eV 256.28 nm f=0.0115 <S**2>=0.000
69 -> 73 0.69296

Excited State 13: Singlet-A 4.9500 eV 250.47 nm f=0.0448 <S**2>=0.000

60 -> 70 -0.34898
61 -> 70 0.55563
66 -> 71 0.15352

Excited State 14: Singlet-A 5.0435 eV 245.83 nm f=0.0337 <S**2>=0.000
65 -> 71 -0.22701
66 -> 71 0.17500
67 -> 71 0.61371

Excited State 15: Singlet-A 5.1447 eV 240.99 nm f=0.0032 <S**2>=0.000
60 -> 70 0.10717
69 -> 74 0.68618

Excited State 16: Singlet-A 5.2334 eV 236.91 nm f=0.0329 <S**2>=0.000
60 -> 70 0.50004
61 -> 70 0.24909
66 -> 71 0.17766
68 -> 72 0.20099
68 -> 73 0.11209
69 -> 74 -0.10960
69 -> 75 -0.15741
69 -> 77 0.11429
69 -> 78 0.11148

Excited State 17: Singlet-A 5.2879 eV 234.47 nm f=0.0060 <S**2>=0.000
60 -> 70 -0.21226
68 -> 71 0.10639
68 -> 72 0.53928
68 -> 73 0.34697

Excited State 18: Singlet-A 5.3598 eV 231.32 nm f=0.0037 <S**2>=0.000
60 -> 70 0.10724
66 -> 71 0.16360
69 -> 75 0.65318

Excited State 19: Singlet-A 5.4073 eV 229.29 nm f=0.0093 <S**2>=0.000
59 -> 70 -0.17354
60 -> 70 0.11181
61 -> 70 0.17609

65 -> 71 0.37235
66 -> 71 -0.36521
66 -> 72 -0.15292
67 -> 71 0.26175
69 -> 75 0.11685

Excited State 20: Singlet-A 5.5055 eV 225.20 nm f=0.0011 <S**2>=0.000
59 -> 70 0.58873
64 -> 71 0.12759
65 -> 71 -0.11866
66 -> 71 -0.22226
69 -> 78 0.10415

Excited State 21: Singlet-A 5.5184 eV 224.67 nm f=0.0214 <S**2>=0.000
59 -> 70 0.28986
64 -> 71 -0.14687
65 -> 71 0.47822
66 -> 71 0.30296
67 -> 71 0.10108

Excited State 22: Singlet-A 5.6388 eV 219.88 nm f=0.0039 <S**2>=0.000
69 -> 76 0.70034

Excited State 23: Singlet-A 5.6895 eV 217.92 nm f=0.0003 <S**2>=0.000
68 -> 71 -0.12960
68 -> 72 -0.33463
68 -> 73 0.57676

Excited State 24: Singlet-A 5.7209 eV 216.72 nm f=0.0169 <S**2>=0.000
63 -> 71 -0.27787
64 -> 71 0.42204
66 -> 71 0.22867
66 -> 72 -0.33866
69 -> 77 -0.11736
69 -> 78 -0.16633

Excited State 25: Singlet-A 5.7631 eV 215.13 nm f=0.0086 <S**2>=0.000
58 -> 70 0.51463
62 -> 71 0.12926

63 -> 71 -0.16690
69 -> 77 0.27508
69 -> 78 0.26722

Excited State 26: Singlet-A 5.8194 eV 213.05 nm f=0.0045 <S**2>=0.000
69 -> 77 0.51741
69 -> 78 -0.42561

Excited State 27: Singlet-A 5.8266 eV 212.79 nm f=0.0077 <S**2>=0.000
62 -> 71 -0.15100
63 -> 71 0.39980
64 -> 71 0.28718
65 -> 71 0.16308
67 -> 72 0.39474
69 -> 77 0.11743

Excited State 28: Singlet-A 5.8434 eV 212.18 nm f=0.0086 <S**2>=0.000
57 -> 70 -0.14822
58 -> 70 -0.28185
62 -> 71 0.18290
63 -> 71 -0.29817
66 -> 72 0.17130
67 -> 72 0.40558
69 -> 78 0.22165

Excited State 29: Singlet-A 5.8942 eV 210.35 nm f=0.0079 <S**2>=0.000
57 -> 70 0.19255
58 -> 70 0.26632
64 -> 71 -0.27716
67 -> 72 0.35220
69 -> 77 -0.21444
69 -> 78 -0.24783

Excited State 30: Singlet-A 5.9397 eV 208.74 nm f=0.0142 <S**2>=0.000
62 -> 71 0.56796
63 -> 71 0.20574
64 -> 71 0.15591
66 -> 72 0.14953
69 -> 78 -0.12821

Excited State	31:	Singlet-A	6.0100 eV	206.30 nm	f=0.0037	<S**2>=0.000
69 -> 79	0.65416					
69 -> 80	0.21369					

Excited State	32:	Singlet-A	6.0499 eV	204.94 nm	f=0.0022	<S**2>=0.000
57 -> 70	-0.11324					
66 -> 72	0.12235					
69 -> 79	-0.19089					
69 -> 80	0.61332					

Excited State	33:	Singlet-A	6.1802 eV	200.61 nm	f=0.0824	<S**2>=0.000
56 -> 70	-0.25617					
63 -> 71	0.13025					
65 -> 72	0.42061					
66 -> 72	-0.30726					
67 -> 72	0.12105					
67 -> 73	0.12692					
69 -> 78	0.10990					
69 -> 80	0.13403					

Excited State	34:	Singlet-A	6.1925 eV	200.22 nm	f=0.0230	<S**2>=0.000
56 -> 70	0.60624					
65 -> 72	0.13482					
66 -> 72	-0.15805					
69 -> 81	0.18408					

Excited State	35:	Singlet-A	6.2047 eV	199.82 nm	f=0.0022	<S**2>=0.000
56 -> 70	-0.17866					
69 -> 80	-0.10813					
69 -> 81	0.65421					

Excited State	36:	Singlet-A	6.2730 eV	197.65 nm	f=0.0106	<S**2>=0.000
57 -> 70	-0.29195					
58 -> 70	0.11276					
62 -> 71	-0.15853					
65 -> 72	0.45832					
66 -> 72	0.19173					
67 -> 73	-0.15427					

69 -> 78 -0.12138
69 -> 80 -0.10409

Excited State 37: Singlet-A 6.3196 eV 196.19 nm f=0.0138 <S**2>=0.000
57 -> 70 0.45289
62 -> 71 -0.10962
64 -> 71 0.12500
64 -> 72 -0.10338
65 -> 72 0.17764
66 -> 72 0.17271
69 -> 86 -0.29954
69 -> 87 0.11762

Excited State 38: Singlet-A 6.3708 eV 194.61 nm f=0.0323 <S**2>=0.000
64 -> 72 0.33537
66 -> 72 -0.11421
69 -> 82 -0.33203
69 -> 83 0.45807
69 -> 86 -0.13800

Excited State 39: Singlet-A 6.4056 eV 193.55 nm f=0.0019 <S**2>=0.000
68 -> 72 -0.10808
68 -> 74 0.48303
68 -> 75 -0.24067
68 -> 76 -0.17324
68 -> 77 0.16725
68 -> 78 0.29047
68 -> 80 0.13150

Excited State 40: Singlet-A 6.4179 eV 193.19 nm f=0.0142 <S**2>=0.000
63 -> 72 0.11441
68 -> 74 -0.11697
68 -> 77 0.11811
69 -> 82 0.48351
69 -> 83 0.36978
69 -> 84 -0.10255
69 -> 86 -0.13133

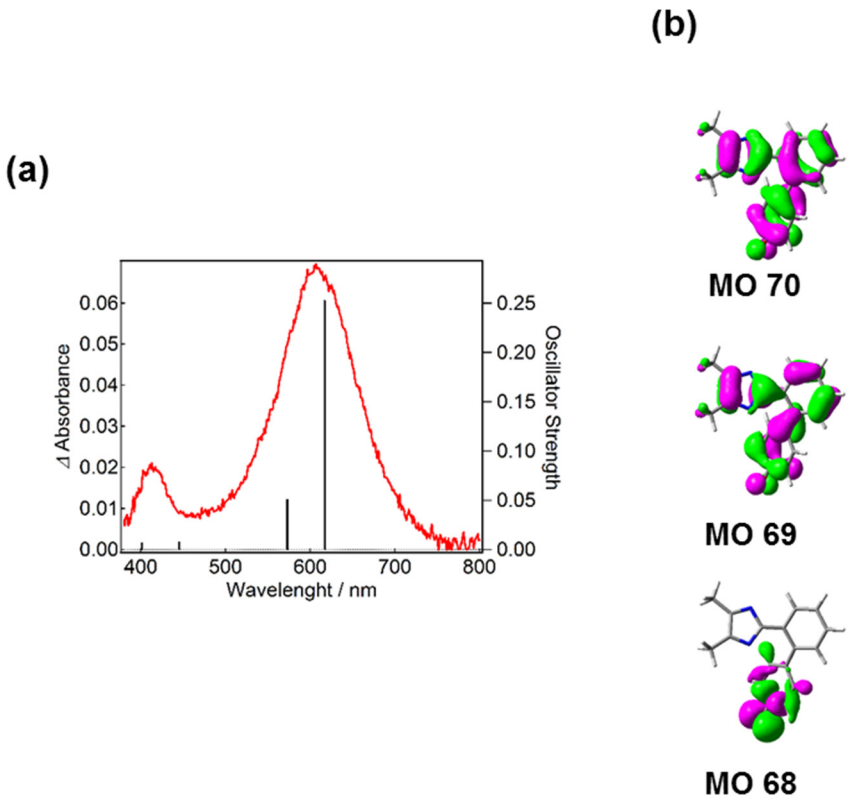


Fig. S43. (a) UV–vis absorption spectrum of **1** in benzene. The calculated spectrum (MPW1PW91/6-31+G(d,p)//M052X/6-31+G(d,p) level of the theory) of the quinoid form of the open-ring isomer of **1** is shown by the black lines. (b) The relevant molecular orbitals were calculated at the M052X/6-31+G(d,p) level of the theory.

Table S9. Standard Orientation of the Optimized Geometry for the Closed-Ring Isomer of **2**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	1.3207890	2.7598000	0.0000000
2	C	1.5272780	1.3732910	0.0000000
3	C	2.8006370	0.8325420	0.0000000
4	C	3.8867390	1.7117660	0.0000000
5	C	3.6848250	3.0942550	0.0000000
6	C	2.3996150	3.6360030	0.0000000
7	C	-0.1206380	2.9791770	0.0000000
8	N	-0.7343740	1.7626670	0.0000000
9	C	0.1824990	0.6206850	0.0000000
10	C	0.0375090	-0.1788680	1.2576480
11	C	-0.0221990	-1.5164460	1.2955640
12	C	0.0390280	-2.2714290	0.0000000
13	C	-0.0221990	-1.5164460	-1.2955640

14	C	0.0375090	-0.1788680	-1.2576480
15	N	-0.9773710	3.9687200	0.0000000
16	C	-2.2165030	3.3571400	0.0000000
17	C	-2.0936210	1.9780650	0.0000000
18	C	-3.4657370	4.1785790	0.0000000
19	C	-3.0883230	0.8654400	0.0000000
20	O	0.1273070	-3.4905530	0.0000000
21	C	-0.1379140	-2.3026350	2.6007030
22	C	-0.1379140	-2.3026350	-2.6007030
23	C	-0.2712310	-1.3608390	3.8030750
24	C	-1.3908060	-3.1979980	2.5670080
25	C	1.1215280	-3.1627600	2.8148930
26	C	1.1215280	-3.1627600	-2.8148930
27	C	-1.3908060	-3.1979980	-2.5670080
28	C	-0.2712310	-1.3608390	-3.8030750
29	H	2.9484330	-0.2418410	0.0000000
30	H	4.8949550	1.3174900	0.0000000
31	H	4.5419970	3.7560100	0.0000000
32	H	2.2367070	4.7058190	0.0000000
33	H	0.0124090	0.4195960	2.1603480
34	H	0.0124090	0.4195960	-2.1603480
35	H	-4.3561790	3.5500940	0.0000000
36	H	-3.4967280	4.8214060	0.8814740
37	H	-3.4967280	4.8214060	-0.8814740
38	H	-4.0982720	1.2717870	0.0000000
39	H	-2.9758270	0.2307590	-0.8828710
40	H	-2.9758270	0.2307590	0.8828710
41	H	-0.3744840	-1.9628290	4.7081560
42	H	0.6115860	-0.7283930	3.9251630
43	H	-1.1555880	-0.7228950	3.7236820
44	H	-1.4887480	-3.7121250	3.5266780
45	H	-1.3272030	-3.9447630	1.7786290
46	H	-2.2889510	-2.5926530	2.4142560
47	H	2.0126050	-2.5300570	2.8477630
48	H	1.0399270	-3.6836790	3.7727410
49	H	1.2379780	-3.9003540	2.0243140
50	H	1.0399270	-3.6836790	-3.7727410
51	H	2.0126050	-2.5300570	-2.8477630
52	H	1.2379780	-3.9003540	-2.0243140

53	H	-1.4887480	-3.7121250	-3.5266780
54	H	-2.2889510	-2.5926530	-2.4142560
55	H	-1.3272030	-3.9447630	-1.7786290
56	H	-1.1555880	-0.7228950	-3.7236820
57	H	0.6115860	-0.7283930	-3.9251630
58	H	-0.3744840	-1.9628290	-4.7081560

SCF Done: E(RM052X) = -1155.41046683 A.U.

Zero-point correction = 0.501976 (Hartree/Particle)
Thermal correction to Energy = 0.528563
Thermal correction to Enthalpy = 0.529507
Thermal correction to Gibbs Free Energy = 0.445453
Sum of electronic and zero-point Energies = -1154.908491
Sum of electronic and thermal Energies = -1154.881904
Sum of electronic and thermal Enthalpies = -1154.880960
Sum of electronic and thermal Free Energies = -1154.965014

Low frequencies --- -21.1957 -11.0803 -10.3911 -0.0010 -0.0005 -0.0003
Low frequencies --- 13.0031 14.4869 29.4901

The Results for the TDDFT calculation

Excited State 1: Singlet-A" 2.8774 eV 430.88 nm f=0.0000 <S**2>=0.000
101 ->102 0.70584
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1155.16684628
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A" 3.3062 eV 375.00 nm f=0.0001 <S**2>=0.000
98 ->102 -0.11503
100 ->102 0.68626

Excited State 3: Singlet-A' 4.0714 eV 304.52 nm f=0.1141 <S**2>=0.000
101 ->103 0.61854
101 ->104 -0.32882

Excited State 4: Singlet-A" 4.2705 eV 290.33 nm f=0.0014 <S**2>=0.000
99 ->102 0.69795

Excited State 5: Singlet-A' 4.2861 eV 289.27 nm f=0.2026 <S**2>=0.000

99 ->103	0.14361
101 ->103	0.32621
101 ->104	0.60224

Excited State 6: Singlet-A" 4.5208 eV 274.25 nm f=0.0002 <S**2>=0.000

96 ->102	0.10287
98 ->102	0.68194
100 ->102	0.12439

Excited State 7: Singlet-A' 4.9480 eV 250.58 nm f=0.0263 <S**2>=0.000

97 ->102	0.69192

Excited State 8: Singlet-A" 4.9762 eV 249.16 nm f=0.0001 <S**2>=0.000

96 ->102	-0.12540
101 ->105	0.65329
101 ->107	-0.12255
101 ->109	0.17434

Excited State 9: Singlet-A" 5.0359 eV 246.20 nm f=0.0018 <S**2>=0.000

96 ->102	0.68443
98 ->102	-0.10603
101 ->105	0.11988

Excited State 10: Singlet-A' 5.0441 eV 245.80 nm f=0.0097 <S**2>=0.000

95 ->102	-0.25202
99 ->103	-0.13424
101 ->106	0.63089

Excited State 11: Singlet-A' 5.2273 eV 237.18 nm f=0.2371 <S**2>=0.000

95 ->102	0.60329
98 ->103	0.10960
99 ->106	-0.10970
101 ->106	0.23808

Excited State 12: Singlet-A" 5.3233 eV 232.91 nm f=0.0099 <S**2>=0.000

94 ->102	0.70050

Excited State 13: Singlet-A" 5.3753 eV 230.66 nm f=0.0008 <S**2>=0.000

101 ->105 0.11433
101 ->107 0.67886

Excited State 14: Singlet-A' 5.3965 eV 229.75 nm f=0.0059 <S**2>=0.000
100 ->103 0.55664
100 ->104 -0.35610
100 ->106 -0.20502

Excited State 15: Singlet-A' 5.4406 eV 227.89 nm f=0.1244 <S**2>=0.000
96 ->104 0.20192
98 ->104 -0.14588
99 ->103 0.56831
100 ->104 -0.14376
101 ->104 -0.13598
101 ->106 0.16218
101 ->108 0.11399

Excited State 16: Singlet-A' 5.5084 eV 225.08 nm f=0.0109 <S**2>=0.000
99 ->103 -0.11341
101 ->108 0.66025
101 ->112 -0.20119

Excited State 17: Singlet-A" 5.5174 eV 224.72 nm f=0.0025 <S**2>=0.000
101 ->105 -0.18164
101 ->109 0.62235
101 ->110 -0.22253
101 ->115 0.11776

Excited State 18: Singlet-A" 5.5665 eV 222.73 nm f=0.0012 <S**2>=0.000
95 ->103 -0.12177
97 ->103 0.66806
97 ->104 0.14206

Excited State 19: Singlet-A' 5.6706 eV 218.64 nm f=0.0132 <S**2>=0.000
98 ->103 0.26545
99 ->103 0.19753
100 ->103 0.35085
100 ->104 0.47098
100 ->106 0.13766

Excited State 20: Singlet-A" 5.7119 eV 217.06 nm f=0.0012 <S**2>=0.000

101 ->109	0.21029
101 ->110	0.62755
101 ->113	-0.20089

Excited State 21: Singlet-A' 5.7698 eV 214.88 nm f=0.0094 <S**2>=0.000

98 ->103	0.57059
99 ->104	0.17230
100 ->103	-0.20191
100 ->104	-0.25248
101 ->117	-0.10436

Excited State 22: Singlet-A' 5.8331 eV 212.55 nm f=0.1424 <S**2>=0.000

95 ->102	0.10760
96 ->103	-0.20055
96 ->104	0.11429
98 ->103	-0.11724
99 ->103	-0.10171
99 ->104	0.61138

Excited State 23: Singlet-A" 5.8741 eV 211.07 nm f=0.0002 <S**2>=0.000

101 ->110	0.10501
101 ->111	0.66985
101 ->116	0.11457

Excited State 24: Singlet-A' 5.9383 eV 208.79 nm f=0.0389 <S**2>=0.000

93 ->102	0.20753
96 ->103	0.20990
98 ->104	0.59386
99 ->103	0.14904

Excited State 25: Singlet-A' 6.0369 eV 205.38 nm f=0.0196 <S**2>=0.000

93 ->102	0.64070
98 ->104	-0.17699
101 ->112	-0.12369

Excited State 26: Singlet-A' 6.0502 eV 204.93 nm f=0.0021 <S**2>=0.000

93 ->102	0.11006

96 ->103 -0.13052
101 ->108 0.19294
101 ->112 0.61053
101 ->117 -0.15506

Excited State 27: Singlet-A" 6.0579 eV 204.67 nm f=0.0090 <S**2>=0.000
95 ->103 0.62331
95 ->104 -0.12783
97 ->103 0.16101
97 ->104 -0.24506

Excited State 28: Singlet-A" 6.1083 eV 202.98 nm f=0.0000 <S**2>=0.000
101 ->110 0.16193
101 ->111 -0.12501
101 ->113 0.64613

Excited State 29: Singlet-A" 6.1179 eV 202.66 nm f=0.0001 <S**2>=0.000
88 ->102 -0.25545
92 ->102 0.58309
97 ->104 0.27060

Excited State 30: Singlet-A" 6.1410 eV 201.90 nm f=0.0003 <S**2>=0.000
88 ->102 0.10549
92 ->102 -0.26415
95 ->103 0.25268
97 ->104 0.58445

Excited State 31: Singlet-A' 6.1614 eV 201.23 nm f=0.0172 <S**2>=0.000
96 ->103 -0.22633
96 ->104 0.11128
101 ->112 -0.15402
101 ->114 0.58375
101 ->117 -0.10450

Excited State 32: Singlet-A' 6.2321 eV 198.94 nm f=0.0161 <S**2>=0.000
94 ->103 0.20706
94 ->104 0.14093
96 ->103 0.32946
96 ->104 -0.10236

98 ->104 -0.17001
99 ->104 0.15662
101 ->112 0.11993
101 ->114 0.33974
101 ->117 0.28837

Excited State 33: Singlet-A" 6.2553 eV 198.21 nm f=0.0003 <S**2>=0.000
101 ->110 0.10420
101 ->115 0.66378
101 ->118 0.10084

Excited State 34: Singlet-A' 6.2637 eV 197.94 nm f=0.0016 <S**2>=0.000
89 ->102 -0.14409
91 ->102 0.12185
100 ->104 -0.23719
100 ->106 0.61686

Excited State 35: Singlet-A" 6.2916 eV 197.06 nm f=0.0000 <S**2>=0.000
88 ->102 0.62613
92 ->102 0.28330

Excited State 36: Singlet-A" 6.3234 eV 196.07 nm f=0.0143 <S**2>=0.000
90 ->102 0.14059
95 ->103 0.13490
95 ->104 0.66726

Excited State 37: Singlet-A' 6.3368 eV 195.66 nm f=0.0139 <S**2>=0.000
89 ->102 -0.12449
91 ->102 0.58244
94 ->103 -0.24330
96 ->103 0.11975
96 ->104 0.15754
99 ->106 0.10398
100 ->106 -0.11097

Excited State 38: Singlet-A" 6.3630 eV 194.85 nm f=0.0012 <S**2>=0.000
101 ->116 0.57934
101 ->118 -0.27285
101 ->120 -0.22716

Excited State	39:	Singlet-A'	6.3974 eV	193.80 nm	f=0.1053	<S**2>=0.000
89 ->102	-0.13348					
91 ->102	0.26690					
94 ->103	0.44343					
96 ->103	-0.18860					
96 ->104	-0.29986					
100 ->106	-0.12021					
101 ->117	-0.12193					

Excited State	40:	Singlet-A"	6.4045 eV	193.59 nm	f=0.0123	<S**2>=0.000
90 ->102	-0.15984					
100 ->105	0.65819					
100 ->109	-0.14880					

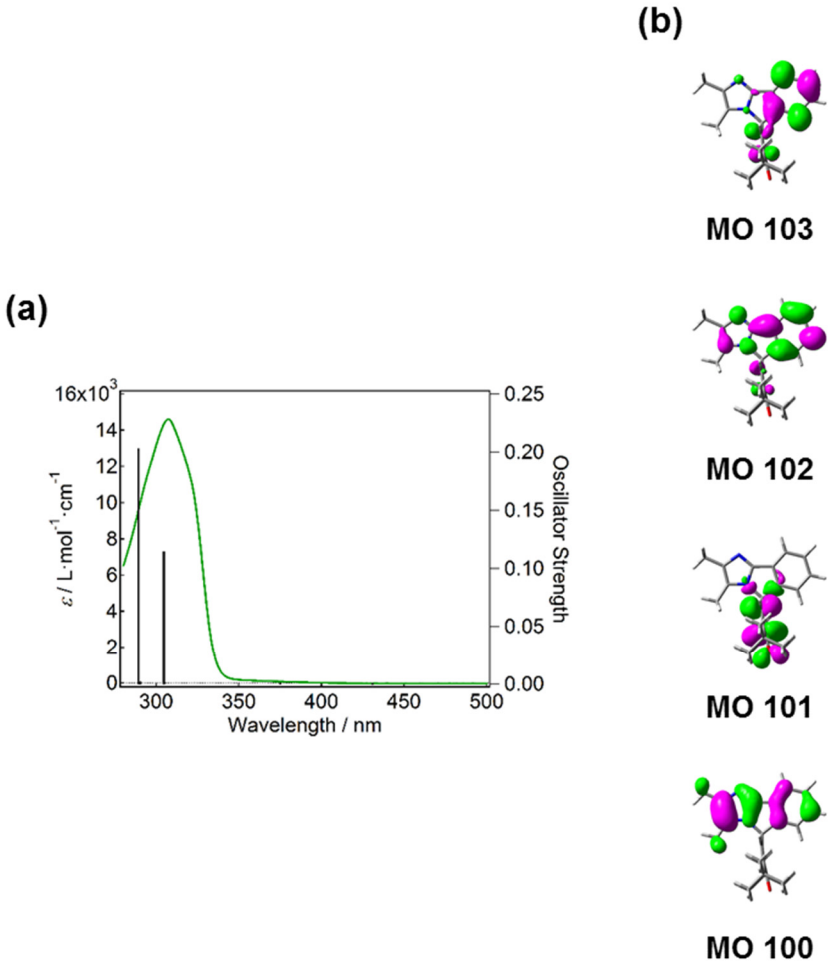


Fig. S44. (a) UV–vis absorption spectrum of the closed-ring isomer of **2** in benzene. The calculated spectrum (MPW1PW91/6-31+G(d,p)//M052X/6-31+G(d,p) level of the theory) is shown by the black lines. (b) The relevant molecular orbitals were calculated at the M052X/6-31+G(d,p) level of the theory.

Table S10. Standard Orientation of the Optimized Geometry for the Biradical Form of **2**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-2.3050360	1.6177950	-0.2957230
2	C	-0.9534410	2.0054310	-0.4885130
3	C	-2.6824210	0.3748740	0.3378900
4	N	-3.9358830	-0.1661720	0.1761040
5	C	-3.9026780	-1.2637920	0.9001010
6	C	-2.5847990	-1.3642220	1.5448010
7	N	-1.8590940	-0.3313850	1.1816370
8	C	0.1724830	1.0716670	-0.3678150
9	C	1.3756140	1.4894650	0.2422490
10	C	2.4660650	0.6615940	0.3452470
11	C	2.3723580	-0.6972000	-0.2267460
12	C	1.1225640	-1.1131720	-0.8886730
13	C	0.0860670	-0.2232110	-0.9380170
14	O	3.3399100	-1.4774110	-0.1532150
15	C	-0.6919120	3.3162530	-0.9163370
16	C	-1.7217910	4.1976970	-1.2124730
17	C	-3.0533280	3.7852750	-1.0943460
18	C	-3.3387590	2.5088390	-0.6434730
19	H	1.3998350	2.4796100	0.6749700
20	H	-0.8394660	-0.4861120	-1.4294170
21	H	0.3358650	3.6174690	-1.0772550
22	H	-1.4901330	5.1958670	-1.5622490
23	H	-3.8586890	4.4644100	-1.3430440
24	H	-4.3597200	2.1762090	-0.5128230
25	C	-5.0327690	-2.2211130	1.0313580
26	H	-5.3166410	-2.3414340	2.0803780
27	H	-5.8891860	-1.8594850	0.4663500
28	H	-4.7466410	-3.2082820	0.6580200
29	C	-2.1228330	-2.4304880	2.4731770
30	H	-2.1537840	-3.4076980	1.9827720
31	H	-1.1028380	-2.2223610	2.7898420
32	H	-2.7699090	-2.4873490	3.3527300
33	C	3.7538240	1.0964300	1.0352630
34	C	1.0135780	-2.5176950	-1.4732780
35	C	3.6551710	2.5329770	1.5643760

36	H	3.4811940	3.2514830	0.7591100
37	H	2.8646300	2.6389300	2.3113110
38	H	4.6018420	2.7933570	2.0422320
39	C	4.9279750	1.0466380	0.0372120
40	H	5.8357240	1.3959710	0.5371770
41	H	5.0920540	0.0348260	-0.3259560
42	H	4.7334200	1.7048860	-0.8138400
43	C	4.0478740	0.1758710	2.2362990
44	H	4.2006270	-0.8517560	1.9151360
45	H	4.9516320	0.5274200	2.7417450
46	H	3.2220920	0.2081000	2.9519180
47	C	-0.3646600	-2.7590260	-2.1021460
48	H	-1.1676320	-2.6604630	-1.3655550
49	H	-0.5614950	-2.0740400	-2.9305400
50	H	-0.3954690	-3.7767620	-2.4971300
51	C	2.0765020	-2.7297370	-2.5677540
52	H	3.0810620	-2.6266160	-2.1634820
53	H	1.9646850	-3.7334110	-2.9875500
54	H	1.9404940	-2.0054650	-3.3752410
55	C	1.1989300	-3.5588590	-0.3513530
56	H	1.0664790	-4.5618370	-0.7669520
57	H	2.1899330	-3.4875640	0.0908690
58	H	0.4481370	-3.4094690	0.4300550

SCF Done: E(UM052X) = -1155.36502250 A.U.
S**2 before annihilation 1.0049, after 0.5705

Zero-point correction = 0.497999 (Hartree/Particle)
Thermal correction to Energy = 0.526079
Thermal correction to Enthalpy = 0.527023
Thermal correction to Gibbs Free Energy = 0.439017
Sum of electronic and zero-point Energies = -1154.867024
Sum of electronic and thermal Energies = -1154.838943
Sum of electronic and thermal Enthalpies = -1154.837999
Sum of electronic and thermal Free Energies = -1154.926005

Low frequencies --- -13.6807 -5.1089 -2.3024 -0.0003 0.0006 0.0009
Low frequencies --- 17.7362 21.6016 30.4214

The Results for the TDDFT calculation

Excited State 1: 2.370-A 1.3896 eV 892.24 nm f=0.0000 <S**2>=1.15
100A ->102A 0.95813
100A ->103A -0.11657
101A ->102A -0.12332
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1155.18261890
Copying the excited state density for this state as the 1-particle RhoCI den

Excited State 2: 1.435-A 1.4623 eV 847.89 nm f=0.0274 <S**2>=0.26
101A ->102A 0.25401
101B ->102B 0.95212

Excited State 3: 1.518-A 2.0079 eV 617.50 nm f=0.0632 <S**2>=0.32
99A ->102A 0.31794
101A ->102A 0.89147
97B ->102B -0.10369
101B ->102B -0.23070

Excited State 4: 2.298-A 2.2640 eV 547.64 nm f=0.0291 <S**2>=1.07
98A ->102A -0.10629
99A ->102A 0.85501
101A ->102A -0.32136
95B ->102B 0.12573
99B ->102B -0.27439
101B ->102B 0.13183
101B ->105B -0.11499

Excited State 5: 2.243-A 2.3903 eV 518.69 nm f=0.0008 <S**2>=1.00
99A ->102A 0.28629
95B ->102B -0.42399
96B ->102B 0.14480
97B ->102B 0.50974
98B ->102B -0.10181
99B ->102B 0.62555

Excited State 6: 2.358-A 2.5469 eV 486.80 nm f=0.0010 <S**2>=1.14

95B ->102B 0.63054
96B ->102B 0.43104
97B ->102B 0.56128
98B ->102B 0.22656

Excited State 7: 2.277-A 2.6999 eV 459.22 nm f=0.0007 <S**2>=1.04
100B ->102B 0.98668

Excited State 8: 2.345-A 2.9029 eV 427.10 nm f=0.0038 <S**2>=1.12
98A ->102A 0.23577
99A ->102A 0.13640
94B ->102B -0.44963
95B ->102B 0.25415
97B ->102B -0.39897
98B ->102B 0.39675
99B ->102B 0.54722

Excited State 9: 2.490-A 2.9815 eV 415.85 nm f=0.0353 <S**2>=1.30
98A ->102A 0.54651
101A ->103A -0.11158
94B ->102B 0.11723
95B ->102B -0.31478
96B ->102B -0.21927
97B ->102B 0.27847
98B ->102B 0.53855
99B ->102B -0.24931
101B ->103B -0.12583
101B ->104B -0.11134

Excited State 10: 2.533-A 3.0061 eV 412.45 nm f=0.0357 <S**2>=1.35
98A ->102A 0.11721
98A ->104A -0.13684
101A ->103A 0.36482
101A ->104A 0.12929
94B ->102B 0.12897
95B ->102B -0.28366
96B ->102B 0.71831
96B ->104B 0.10655
97B ->102B -0.26185

98B ->104B 0.12771
99B ->102B -0.12197
101B ->104B -0.13769

Excited State 11: 2.250-A 3.0534 eV 406.05 nm f=0.0111 <S**2>=1.01
98A ->102A 0.51074
94B ->102B 0.48715
95B ->102B 0.28328
98B ->102B -0.46551
99B ->102B 0.25519
101B ->103B -0.21587

Excited State 12: 2.242-A 3.2022 eV 387.18 nm f=0.0175 <S**2>=1.00
98A ->102A -0.32888
94B ->102B 0.69400
97B ->102B -0.18622
98B ->102B 0.45862
99B ->102B 0.25508
101B ->103B 0.14642

Excited State 13: 2.350-A 3.4597 eV 358.36 nm f=0.0020 <S**2>=1.13
94A ->102A -0.20378
96A ->102A 0.10524
97A ->102A 0.87645
98A ->104A -0.10929
101A ->103A 0.16096
96B ->102B -0.16231
101B ->103B 0.10522

Excited State 14: 2.472-A 3.7750 eV 328.43 nm f=0.0829 <S**2>=1.27
90A ->102A -0.18789
91A ->102A 0.16195
92A ->102A 0.15396
94A ->102A -0.17835
96A ->102A 0.18791
97A ->102A -0.36553
98A ->102A 0.19146
98A ->104A -0.10481
101A ->103A 0.40703

96B ->102B -0.19416
97B ->102B 0.10823
101B ->103B 0.59175
101B ->108B 0.13057

Excited State 15: 2.561-A 3.8408 eV 322.81 nm f=0.0978 <S**2>=1.39
95A ->102A 0.61305
95A ->103A 0.15547
96A ->102A -0.32650
97A ->102A 0.11190
98A ->102A 0.30049
98A ->104A 0.15884
101A ->103A -0.30833
96B ->102B 0.18488
96B ->103B 0.15119
101B ->103B 0.29384
101B ->104B 0.10862

Excited State 16: 2.328-A 3.9033 eV 317.64 nm f=0.0151 <S**2>=1.10
95A ->102A 0.41476
96A ->102A 0.81640
101A ->103A -0.25963
101B ->103B -0.16250

Excited State 17: 2.694-A 3.9888 eV 310.83 nm f=0.1094 <S**2>=1.56
95A ->102A -0.38554
95A ->104A 0.11806
96A ->102A 0.32923
98A ->102A 0.22701
98A ->104A 0.27106
101A ->104A -0.27167
96B ->102B 0.24275
96B ->104B -0.12509
97B ->102B -0.11185
98B ->104B -0.22991
99B ->105B 0.13371
101B ->104B 0.52204

Excited State 18: 2.581-A 4.0607 eV 305.32 nm f=0.0275 <S**2>=1.41

90A ->102A 0.29382
91A ->102A -0.21038
92A ->102A -0.28492
94A ->102A 0.51382
95A ->102A 0.15584
96A ->102A 0.13989
97A ->102A 0.15292
98A ->103A -0.11778
98A ->104A 0.12287
101A ->103A 0.30642
87B ->102B -0.10715
98B ->103B -0.18017
99B ->105B 0.12368
101B ->103B 0.32961
101B ->108B -0.17457

Excited State 19: 2.389-A 4.2235 eV 293.56 nm f=0.1419 <S**2>=1.17
95A ->102A 0.44123
99A ->106A -0.13115
101A ->103A 0.48254
101A ->104A -0.24332
96B ->102B -0.13986
98B ->102B 0.14198
98B ->104B -0.11278
99B ->105B -0.21215
101B ->103B -0.35772
101B ->104B 0.39271

Excited State 20: 2.766-A 4.3284 eV 286.44 nm f=0.0316 <S**2>=1.66
88A ->102A 0.20064
90A ->102A -0.13592
91A ->102A 0.18052
92A ->102A -0.13069
94A ->102A 0.17350
99A ->106A 0.26418
101A ->104A 0.36804
96B ->104B 0.12241
99B ->103B 0.11746
99B ->105B 0.35070

101B ->103B -0.21843
101B ->104B 0.35729
101B ->105B -0.32070
101B ->108B 0.12380

Excited State 21: 2.491-A 4.3518 eV 284.90 nm f=0.0084 <S**2>=1.30
88A ->102A -0.19905
90A ->102A 0.17613
91A ->102A -0.24016
93A ->102A -0.29206
94A ->102A -0.44305
98A ->104A 0.16103
101A ->104A 0.60540
98B ->103B -0.18064
98B ->104B -0.10379
101B ->104B 0.13136
101B ->108B -0.14046

Excited State 22: 2.451-A 4.3873 eV 282.60 nm f=0.0067 <S**2>=1.25
87A ->102A 0.28983
88A ->102A -0.25311
92A ->102A 0.58705
93A ->102A 0.27721
94A ->102A 0.37905
100A ->103A -0.10528
101A ->104A 0.31319
99B ->105B -0.10822
101B ->104B 0.16333
101B ->105B 0.15376

Excited State 23: 2.372-A 4.4115 eV 281.04 nm f=0.0095 <S**2>=1.15
87A ->102A 0.21452
88A ->102A 0.21630
91A ->102A -0.13250
93A ->102A 0.79837
94A ->102A -0.35932
101B ->105B -0.12177

Excited State 24: 2.406-A 4.4235 eV 280.29 nm f=0.0563 <S**2>=1.19

87A ->102A -0.11272
88A ->102A 0.25664
89A ->102A -0.11629
91A ->102A 0.13254
92A ->102A -0.24861
99A ->102A 0.10914
101A ->104A 0.26885
99B ->103B -0.15579
101B ->104B 0.17327
101B ->105B 0.74606

Excited State 25: 2.849-A 4.4810 eV 276.69 nm f=0.0537 <S**2>=1.77
86A ->102A 0.13579
87A ->102A 0.11811
88A ->102A -0.26707
90A ->102A 0.18454
92A ->102A 0.12556
94A ->102A -0.31986
95A ->102A 0.13258
98A ->102A -0.15619
99A ->103A -0.12505
99A ->105A 0.11645
99A ->106A 0.33384
99A ->107A -0.10734
100A ->103A -0.10779
101A ->103A 0.11444
101A ->104A -0.16864
99B ->105B 0.38790
101B ->103B -0.17203
101B ->104B -0.13419
101B ->105B 0.36305

Excited State 26: 2.444-A 4.6040 eV 269.30 nm f=0.0101 <S**2>=1.24
91A ->102A 0.24324
95A ->103A 0.15449
98A ->104A 0.10811
101A ->103A 0.12255
87B ->102B 0.18157
88B ->102B 0.13624

92B ->102B 0.23847
93B ->102B 0.74851
96B ->104B -0.10084
98B ->103B -0.11720
101B ->104B -0.21478

Excited State 27: 2.743-A 4.6362 eV 267.43 nm f=0.0129 <S**2>=1.63
88A ->102A -0.18947
90A ->102A -0.19752
91A ->102A 0.48867
92A ->102A -0.36538
95A ->103A 0.12413
98A ->104A 0.10121
100A ->102A -0.10925
100A ->103A -0.23219
100A ->104A 0.12698
101A ->103A 0.12675
87B ->102B 0.10314
93B ->102B -0.34944
100B ->103B 0.25927
100B ->108B 0.10145
101B ->104B -0.17709

Excited State 28: 2.665-A 4.6463 eV 266.84 nm f=0.0469 <S**2>=1.52
88A ->102A -0.28349
90A ->102A -0.25453
91A ->102A -0.24196
92A ->102A -0.40288
93A ->102A 0.11556
95A ->103A -0.11608
98A ->104A -0.12098
100A ->102A -0.11889
100A ->103A -0.21790
100A ->104A 0.12636
101A ->103A -0.16037
93B ->102B 0.40306
98B ->103B 0.11647
100B ->103B 0.26526
100B ->104B 0.10744

100B ->108B 0.11704
101B ->103B 0.13867
101B ->104B 0.21211

Excited State 29: 2.629-A 4.7321 eV 262.00 nm f=0.0196 <S**2>=1.47
88A ->102A -0.11313
89A ->102A 0.10829
90A ->102A 0.44830
91A ->102A 0.54740
95A ->103A -0.19415
101A ->103A -0.13156
87B ->102B -0.21388
91B ->102B 0.29633
93B ->102B 0.17586
96B ->103B -0.13264
96B ->104B 0.11083
97B ->103B 0.10372
99B ->105B -0.10669
101B ->108B -0.14970

Excited State 30: 2.568-A 4.7937 eV 258.64 nm f=0.0013 <S**2>=1.39
88A ->102A 0.39578
90A ->102A 0.24571
92A ->102A 0.12884
100A ->103A 0.11930
89B ->102B 0.14175
92B ->102B 0.26546
100B ->103B 0.66698
100B ->104B 0.24578
100B ->108B 0.24539
100B ->109B -0.11730
100B ->110B -0.10288

Excited State 31: 2.354-A 4.8051 eV 258.03 nm f=0.0042 <S**2>=1.13
87A ->102A 0.22587
92A ->102A -0.13552
99A ->103A -0.12883
84B ->102B -0.13009
88B ->102B -0.12437

92B ->102B 0.81464
93B ->102B -0.22668
100B ->103B -0.23790

Excited State 32: 2.387-A 4.8237 eV 257.03 nm f=0.0014 <S**2>=1.17
76A ->102A -0.10670
87A ->102A 0.80026
88A ->102A 0.31990
93A ->102A -0.34339
91B ->102B 0.10661
92B ->102B -0.18850

Excited State 33: 3.155-A 4.8411 eV 256.11 nm f=0.0017 <S**2>=2.23
87A ->102A -0.12268
89A ->102A -0.13443
97A ->103A -0.13797
98A ->104A 0.12045
99A ->103A 0.59795
99A ->104A -0.15929
87B ->102B -0.14982
91B ->102B 0.31032
92B ->102B 0.22946
99B ->103B -0.38456
101B ->104B -0.10226
101B ->105B -0.14742

Excited State 34: 2.535-A 4.8829 eV 253.92 nm f=0.0297 <S**2>=1.35
89A ->102A 0.30353
90A ->102A -0.43854
91A ->102A -0.14019
95A ->103A -0.10696
98A ->104A 0.23876
99A ->103A -0.22878
79B ->102B 0.11236
87B ->102B -0.16335
91B ->102B 0.47880
98B ->104B -0.18653
99B ->103B 0.11725
99B ->105B -0.10224

101B ->104B -0.20775

Excited State 35: 2.476-A 4.8955 eV 253.26 nm f=0.0052 <S**2>=1.28

89A ->102A 0.90818
99A ->103A 0.17138
91B ->102B -0.12304
99B ->103B -0.16768
101B ->105B 0.11301

Excited State 36: 3.053-A 4.9419 eV 250.88 nm f=0.0064 <S**2>=2.08

90A ->102A 0.12185
95A ->103A 0.28156
97A ->103A 0.16888
98A ->103A 0.42312
101A ->104A 0.12668
79B ->102B -0.16717
90B ->102B -0.15937
91B ->102B 0.48813
92B ->102B 0.13641
96B ->103B 0.22236
96B ->104B -0.20843
98B ->103B 0.29408
99B ->103B 0.12593

Excited State 37: 2.678-A 4.9700 eV 249.46 nm f=0.0009 <S**2>=1.54

87A ->102A 0.20842
88A ->102A -0.41900
90A ->102A -0.12211
92A ->102A -0.10602
100A ->103A 0.78764
100A ->104A -0.23475
100B ->103B 0.11483

Excited State 38: 2.849-A 5.0012 eV 247.91 nm f=0.0026 <S**2>=1.77

97A ->103A 0.13609
98A ->103A 0.46467
98A ->104A 0.20454
86B ->102B -0.14847
87B ->102B -0.24849

88B ->102B -0.11871
89B ->102B -0.21916
90B ->102B 0.37861
91B ->102B -0.40457
96B ->104B -0.13483
98B ->103B 0.22283
98B ->104B -0.21794
101B ->104B -0.19534

Excited State 39: 2.536-A 5.0493 eV 245.55 nm f=0.0034 <S**2>=1.35
95A ->103A -0.14162
97A ->103A 0.16239
98A ->103A 0.15874
98A ->104A 0.15973
79B ->102B 0.10488
81B ->102B -0.12509
83B ->102B 0.19234
88B ->102B 0.33118
89B ->102B 0.72591
92B ->102B -0.11904
93B ->102B -0.11075
96B ->103B -0.13535
97B ->103B 0.15166
98B ->104B -0.14691
100B ->103B -0.10284

Excited State 40: 3.205-A 5.0913 eV 243.52 nm f=0.0101 <S**2>=2.31
97A ->103A 0.59564
97A ->121A 0.10170
98A ->103A -0.19157
99A ->103A -0.19035
99A ->104A -0.26833
89B ->102B -0.14626
92B ->102B 0.10658
96B ->103B 0.16633
97B ->103B 0.17719
99B ->103B -0.37032
99B ->104B -0.19712
99B ->108B -0.10203

101B ->105B -0.10418

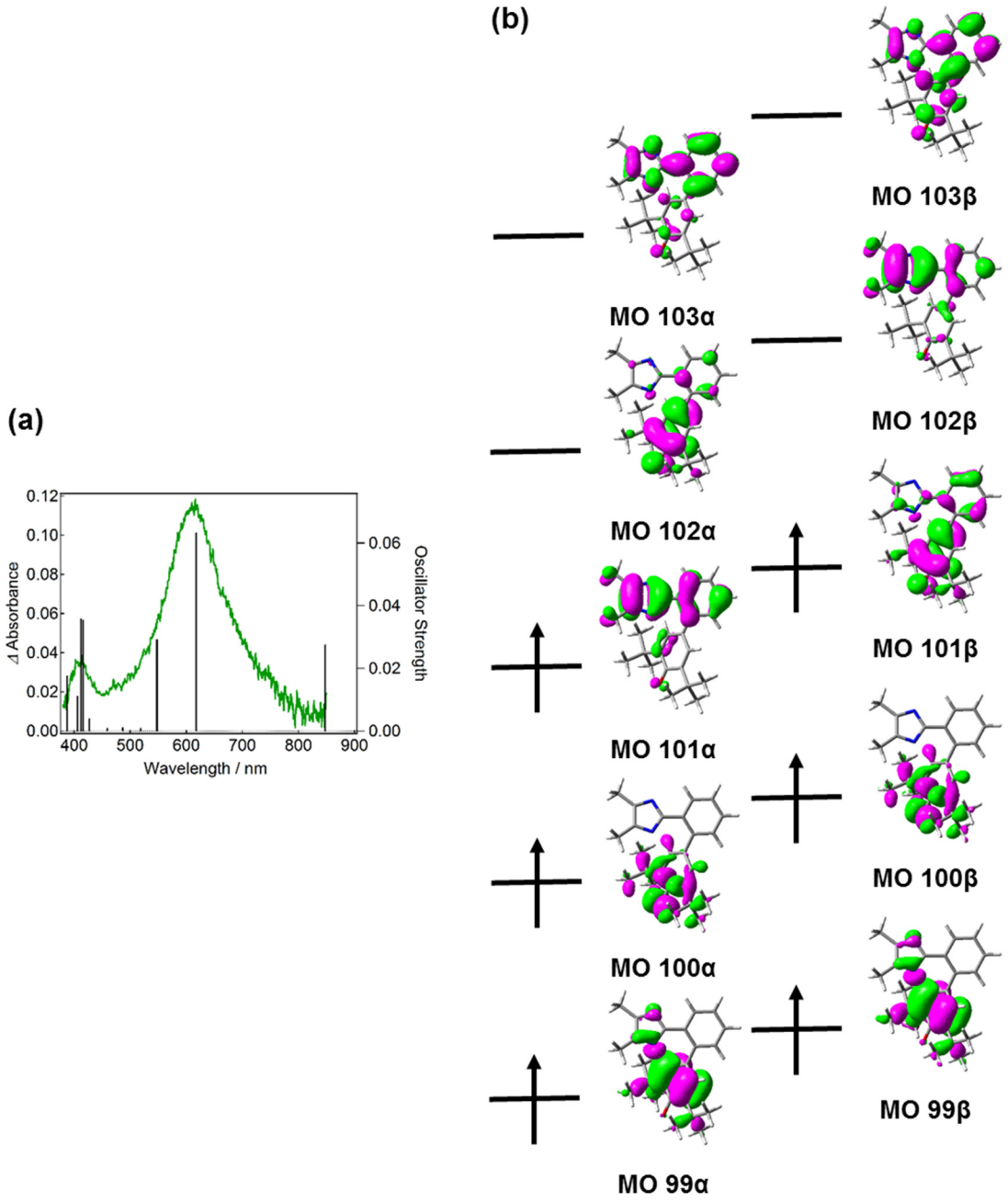


Fig. S45. (a) The transient absorption spectrum of **2** in benzene (excitation wavelength, 355 nm; pulse width, 5ns; power 4 mJ/pulse). The calculated spectrum (UMPW1PW91/6-31+G(d,p)//UM052X/6-31+G(d,p) level of the theory) of the biradical for of the open-ring isomer of 2 is shown by the black lines. (b) The relevant molecular orbitals were calculated at the UM052X/6-31+G(d,p) level of the theory.

Table S11. Standard Orientation of the Optimized Geometry for the Quinoid Form of **2**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-2.1956360	1.6853180	-0.3373520

2	C	-0.7924600	2.0616090	-0.2988810
3	C	-2.6582790	0.5250410	0.2752950
4	N	-3.9403860	0.0302190	0.0589820
5	C	-3.9833290	-1.0630510	0.7698240
6	C	-2.7084260	-1.2211780	1.4910500
7	N	-1.9209980	-0.2297410	1.1816200
8	C	0.2326100	1.1042520	-0.2636490
9	C	1.5560950	1.4536260	0.1910530
10	C	2.5659960	0.5544190	0.2683850
11	C	2.3185270	-0.8459470	-0.1974310
12	C	0.9904970	-1.1825540	-0.7670050
13	C	0.0285420	-0.2317980	-0.7724200
14	O	3.2113270	-1.6891500	-0.1252480
15	C	-0.4944900	3.4616610	-0.4456120
16	C	-1.4497560	4.3367300	-0.8629660
17	C	-2.7842290	3.8918850	-1.1371080
18	C	-3.1467430	2.6036220	-0.8975140
19	H	1.7084040	2.4525590	0.5689960
20	H	-0.9321080	-0.4389560	-1.2172940
21	H	0.5258780	3.8030970	-0.3444020
22	H	-1.1898820	5.3732710	-1.0367510
23	H	-3.5135970	4.6007280	-1.5085990
24	H	-4.1630730	2.2583810	-1.0281740
25	C	-5.1605280	-1.9720160	0.8473630
26	H	-5.5190730	-2.0501540	1.8773970
27	H	-5.9623480	-1.5912460	0.2182260
28	H	-4.8921680	-2.9797200	0.5193480
29	C	-2.3661300	-2.2994660	2.4608360
30	H	-2.3940450	-3.2787750	1.9745160
31	H	-1.3677960	-2.1292060	2.8591350
32	H	-3.0836840	-2.3243490	3.2852820
33	C	3.9374630	0.9125260	0.8309420
34	C	0.7535390	-2.5858340	-1.3182010
35	C	4.0082220	2.3860370	1.2508690
36	H	3.8281600	3.0577290	0.4071080
37	H	3.2977190	2.6178060	2.0485810
38	H	5.0110260	2.5921420	1.6303910
39	C	5.0207350	0.6821410	-0.2420240
40	H	5.9912550	0.9819170	0.1628230

41	H	5.0702340	-0.3638780	-0.5348160
42	H	4.8176430	1.2919940	-1.1263810
43	C	4.2416600	0.0570500	2.0765340
44	H	4.2827720	-1.0008850	1.8287030
45	H	5.2080300	0.3606790	2.4885060
46	H	3.4789120	0.2155880	2.8432220
47	C	-0.6670430	-2.7346890	-1.8770180
48	H	-1.4248220	-2.5608330	-1.1068310
49	H	-0.8508460	-2.0527740	-2.7111680
50	H	-0.7923070	-3.7545570	-2.2471740
51	C	1.7431120	-2.8959970	-2.4561410
52	H	2.7716810	-2.8657840	-2.1031150
53	H	1.5372090	-3.8947690	-2.8512260
54	H	1.6240840	-2.1764430	-3.2705610
55	C	0.9158340	-3.6176870	-0.1844420
56	H	0.6933360	-4.6159310	-0.5724150
57	H	1.9288040	-3.6117960	0.2115630
58	H	0.2149740	-3.4001700	0.6265660

SCF Done: E(M052X) = -1155.35338954 A.U.

Zero-point correction = 0.499677 (Hartree/Particle)
Thermal correction to Energy = 0.527575
Thermal correction to Enthalpy = 0.528520
Thermal correction to Gibbs Free Energy = 0.442108
Sum of electronic and zero-point Energies = -1154.853712
Sum of electronic and thermal Energies = -1154.825814
Sum of electronic and thermal Enthalpies = -1154.824870
Sum of electronic and thermal Free Energies = -1154.911282

Low frequencies --- -10.8239 -0.0009 -0.0006 -0.0006 0.9988 3.4269
Low frequencies --- 26.1540 28.3844 34.2198

The Results for the TDDFT calculation

Excited State 1: Singlet-A 1.9098 eV 649.21 nm f=0.2579 <S**2>=0.000
100 ->102 -0.21025
101 ->102 0.68261

101 <-102 -0.16174

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1155.15575375

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.1195 eV 584.97 nm f=0.0430 <S**2>=0.000

100 ->102 0.66089

100 ->103 0.10257

101 ->102 0.21545

Excited State 3: Singlet-A 2.5557 eV 485.13 nm f=0.0097 <S**2>=0.000

97 ->102 0.12889

99 ->102 0.69181

Excited State 4: Singlet-A 3.0078 eV 412.21 nm f=0.0133 <S**2>=0.000

96 ->102 0.10439

97 ->102 0.62259

98 ->102 -0.24200

99 ->102 -0.12257

101 ->103 0.13097

Excited State 5: Singlet-A 3.1458 eV 394.13 nm f=0.0574 <S**2>=0.000

97 ->102 0.27282

98 ->102 0.55119

101 ->103 -0.32639

Excited State 6: Singlet-A 3.3839 eV 366.39 nm f=0.0155 <S**2>=0.000

95 ->102 0.36543

96 ->102 0.54244

101 ->103 -0.23215

Excited State 7: Singlet-A 3.5228 eV 351.94 nm f=0.0899 <S**2>=0.000

94 ->102 -0.18253

95 ->102 0.53482

96 ->102 -0.25801

98 ->102 0.17168

101 ->103 0.24672

Excited State 8: Singlet-A 3.6416 eV 340.46 nm f=0.0098 <S**2>=0.000

94 ->102 0.66017
95 ->102 0.17622
101 ->103 0.13995

Excited State 9: Singlet-A 4.0742 eV 304.32 nm f=0.0806 <S**2>=0.000
98 ->102 0.15187
101 ->103 0.19556
101 ->104 0.64241

Excited State 10: Singlet-A 4.2028 eV 295.00 nm f=0.6812 <S**2>=0.000
95 ->102 -0.19559
96 ->102 0.32418
98 ->102 0.26120
100 ->103 -0.11536
101 ->103 0.42412
101 ->104 -0.25565

Excited State 11: Singlet-A 4.3626 eV 284.20 nm f=0.0229 <S**2>=0.000
89 ->102 0.17475
92 ->102 -0.14333
100 ->102 -0.11802
100 ->103 0.60194
100 ->104 0.13430

Excited State 12: Singlet-A 4.4579 eV 278.12 nm f=0.0341 <S**2>=0.000
92 ->102 0.16769
93 ->102 0.65668
100 ->103 0.12262

Excited State 13: Singlet-A 4.5728 eV 271.13 nm f=0.0195 <S**2>=0.000
88 ->102 -0.10899
92 ->102 0.63880
93 ->102 -0.20302
100 ->103 0.13515

Excited State 14: Singlet-A 4.7599 eV 260.48 nm f=0.0051 <S**2>=0.000
91 ->102 0.68097

Excited State 15: Singlet-A 4.8303 eV 256.68 nm f=0.0451 <S**2>=0.000

91 ->102 0.13177
97 ->103 0.13357
99 ->103 0.60196
101 ->105 -0.23233
101 ->106 -0.15868

Excited State 16: Singlet-A 4.8633 eV 254.94 nm f=0.0036 <S**2>=0.000
88 ->102 -0.10097
89 ->102 0.62554
90 ->102 -0.17421
92 ->102 0.11472
100 ->103 -0.14616

Excited State 17: Singlet-A 4.9087 eV 252.58 nm f=0.0365 <S**2>=0.000
89 ->102 0.18573
90 ->102 0.30709
97 ->103 0.11131
99 ->103 0.21245
101 ->105 0.47806
101 ->106 0.22626
101 ->107 -0.10489

Excited State 18: Singlet-A 4.9526 eV 250.34 nm f=0.0036 <S**2>=0.000
88 ->102 -0.14013
90 ->102 0.58631
99 ->103 -0.16410
101 ->105 -0.26607
101 ->106 -0.10895

Excited State 19: Singlet-A 4.9930 eV 248.31 nm f=0.0070 <S**2>=0.000
88 ->102 0.65398
92 ->102 0.12949

Excited State 20: Singlet-A 5.0446 eV 245.78 nm f=0.0145 <S**2>=0.000
87 ->102 -0.26988
101 ->105 -0.30112
101 ->106 0.55139

Excited State 21: Singlet-A 5.0950 eV 243.34 nm f=0.0166 <S**2>=0.000

87 ->102 0.53195
97 ->103 0.11457
98 ->103 -0.15979
101 ->105 -0.13358
101 ->106 0.23117
101 ->107 -0.19903
101 ->111 0.11560

Excited State 22: Singlet-A 5.1814 eV 239.29 nm f=0.0017 <S**2>=0.000
87 ->102 0.15125
101 ->106 0.16971
101 ->107 0.65316

Excited State 23: Singlet-A 5.2864 eV 234.53 nm f=0.0151 <S**2>=0.000
87 ->102 -0.11465
97 ->103 0.61621
97 ->104 -0.10859
99 ->103 -0.18365
99 ->104 -0.13618

Excited State 24: Singlet-A 5.2900 eV 234.37 nm f=0.0005 <S**2>=0.000
100 ->103 -0.14052
100 ->104 0.62015
100 ->105 0.16425
100 ->106 0.17757

Excited State 25: Singlet-A 5.3939 eV 229.86 nm f=0.0128 <S**2>=0.000
84 ->102 -0.19463
86 ->102 0.10671
87 ->102 0.11332
96 ->103 -0.14440
96 ->104 -0.11719
97 ->103 0.10808
98 ->103 0.55919
98 ->104 -0.13810

Excited State 26: Singlet-A 5.4515 eV 227.43 nm f=0.0157 <S**2>=0.000
84 ->102 0.45986
85 ->102 -0.12140

86 ->102 -0.36242
98 ->103 0.18568
101 ->108 -0.17573
101 ->112 -0.10424

Excited State 27: Singlet-A 5.4716 eV 226.59 nm f=0.0043 <S**2>=0.000
84 ->102 0.12066
86 ->102 -0.11404
101 ->108 0.66461
101 ->111 0.10097

Excited State 28: Singlet-A 5.5689 eV 222.64 nm f=0.0239 <S**2>=0.000
84 ->102 0.24490
86 ->102 0.30562
97 ->103 0.11190
99 ->104 0.55755

Excited State 29: Singlet-A 5.5835 eV 222.05 nm f=0.0125 <S**2>=0.000
84 ->102 -0.10474
86 ->102 -0.34085
87 ->102 0.11230
98 ->104 -0.10138
99 ->104 0.19378
101 ->109 0.42852
101 ->110 -0.13819
101 ->111 -0.21247
101 ->112 0.14681

Excited State 30: Singlet-A 5.6176 eV 220.71 nm f=0.0051 <S**2>=0.000
84 ->102 0.23820
86 ->102 0.29591
99 ->104 -0.28084
101 ->109 0.46950

Excited State 31: Singlet-A 5.6576 eV 219.15 nm f=0.0060 <S**2>=0.000
81 ->102 -0.12891
84 ->102 -0.17989
86 ->102 -0.10066
96 ->103 0.15313

98 ->104 0.20173
99 ->104 0.17315
101 ->109 0.23639
101 ->110 0.17889
101 ->111 0.40926
101 ->112 -0.12684

Excited State 32: Singlet-A 5.6828 eV 218.18 nm f=0.0057 <S**2>=0.000
81 ->102 0.16913
82 ->102 -0.17353
83 ->102 -0.13612
84 ->102 0.10020
85 ->102 0.39777
95 ->103 -0.23697
96 ->103 0.28830
98 ->103 0.15335
98 ->104 0.22367

Excited State 33: Singlet-A 5.7243 eV 216.59 nm f=0.0186 <S**2>=0.000
84 ->102 0.11273
85 ->102 0.48000
95 ->103 0.16134
96 ->103 -0.22157
98 ->103 -0.12249
98 ->104 -0.16368
100 ->105 -0.10322
101 ->110 0.24601
101 ->111 0.14682

Excited State 34: Singlet-A 5.7292 eV 216.41 nm f=0.0036 <S**2>=0.000
100 ->104 -0.21347
100 ->105 0.41776
100 ->106 0.36080
100 ->107 -0.18343
101 ->110 0.21441
101 ->111 0.10186

Excited State 35: Singlet-A 5.7383 eV 216.06 nm f=0.0008 <S**2>=0.000
85 ->102 -0.18843

95 ->103 -0.12845
101 ->110 0.53091
101 ->111 -0.19299
101 ->112 0.24886

Excited State 36: Singlet-A 5.7678 eV 214.96 nm f=0.0003 <S**2>=0.000
81 ->102 -0.20176
82 ->102 0.30809
83 ->102 0.14011
85 ->102 0.15837
95 ->103 -0.20654
96 ->103 -0.10098
101 ->110 0.11889
101 ->111 -0.27856
101 ->112 -0.26528
101 ->113 -0.19756

Excited State 37: Singlet-A 5.7949 eV 213.95 nm f=0.0082 <S**2>=0.000
82 ->102 -0.10092
94 ->103 -0.20618
95 ->103 0.42720
96 ->103 0.28968
101 ->110 0.13055
101 ->111 -0.16381
101 ->112 -0.29986
101 ->113 -0.11182

Excited State 38: Singlet-A 5.8188 eV 213.07 nm f=0.0184 <S**2>=0.000
78 ->102 -0.12108
81 ->102 -0.13727
82 ->102 0.36908
84 ->102 0.10388
95 ->103 0.14105
96 ->103 0.35014
101 ->112 0.32236

Excited State 39: Singlet-A 5.8772 eV 210.96 nm f=0.0166 <S**2>=0.000
94 ->103 0.58100
96 ->103 0.15294

97 ->104	-0.11582	
98 ->104	-0.19044	
101 ->112	-0.13861	

Excited State 40: Singlet-A 5.9339 eV 208.94 nm f=0.0051 <S**2>=0.000

81 ->102	0.13929
82 ->102	0.13006
101 ->111	-0.19217
101 ->112	-0.18396
101 ->113	0.57513

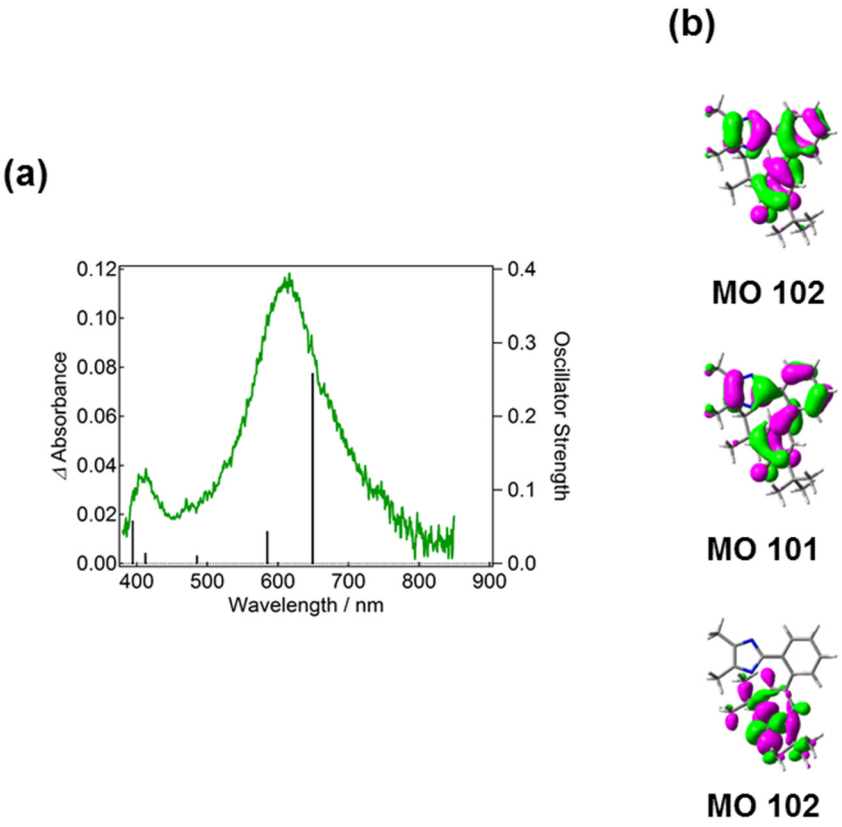


Fig. S46. (a) UV–vis absorption spectrum of **2** in benzene. The calculated spectrum (MPW1PW91/6-31+G(d,p)//M052X/6-31+G(d,p) level of the theory) of the quinoid form of the open-ring isomer of 2 is shown by the black lines. (b) The relevant molecular orbitals were calculated at the M052X/6-31+G(d,p) level of the theory.

Table S12. Standard Orientation of the Optimized Geometry for the Closed-Ring Form of **3**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-1.9015440	-0.2991600	-0.0000010
2	C	-0.6234730	-0.8737150	0.0000030
3	C	-0.4479830	-2.2461290	0.0000090

4	C	-1.5894010	-3.0518560	0.0000120
5	C	-2.8649710	-2.4825100	0.0000080
6	C	-3.0378570	-1.0984970	0.0000010
7	C	-1.7219790	1.1487500	-0.0000070
8	C	0.4645950	0.2159100	-0.0000020
9	N	-2.4450770	2.2414170	-0.0000120
10	C	-1.5189780	3.2597250	-0.0000060
11	C	-0.2292690	2.7711730	-0.0000170
12	N	-0.3827480	1.4096490	-0.0000100
13	C	1.2792800	0.1334140	-1.2618830
14	C	2.5871390	-0.1337190	-1.2629870
15	C	3.3393620	-0.3191290	0.0000050
16	C	2.5871360	-0.1337050	1.2629940
17	C	1.2792760	0.1334280	1.2618820
18	O	4.5265170	-0.5969130	0.0000090
19	H	0.5451240	-2.6810040	0.0000110
20	H	-1.4833820	-4.1291870	0.0000170
21	H	-3.7345740	-3.1276530	0.0000100
22	H	-4.0233740	-0.6516660	-0.0000010
23	H	0.7233970	0.2768370	-2.1823890
24	H	3.1588660	-0.2204090	-2.1784200
25	H	3.1588590	-0.2203850	2.1784290
26	H	0.7233900	0.2768610	2.1823850
27	H	-1.8248050	4.2933930	-0.0000040
28	H	0.7311380	3.2571770	-0.0000230

SCF Done: E(RM052X) = -762.283468925 A.U.

Zero-point correction = 0.218420 (Hartree/Particle)
Thermal correction to Energy = 0.231106
Thermal correction to Enthalpy = 0.232050
Thermal correction to Gibbs Free Energy = 0.178456
Sum of electronic and zero-point Energies = -762.065048
Sum of electronic and thermal Energies = -762.052363
Sum of electronic and thermal Enthalpies = -762.051419
Sum of electronic and thermal Free Energies = -762.105013

Low frequencies --- -8.6455 -8.2907 -0.0005 0.0007 0.0009 12.4810
Low frequencies --- 37.2453 63.2175 101.2002

The Results for the TDDFT calculation

Excited State 1: Singlet-A" 3.1631 eV 391.97 nm f=0.0000 <S**2>=0.000
61 -> 62 0.70553
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -762.059440138
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A" 3.3637 eV 368.59 nm f=0.0000 <S**2>=0.000
59 -> 62 0.23087
60 -> 62 0.65783

Excited State 3: Singlet-A' 4.2900 eV 289.01 nm f=0.0818 <S**2>=0.000
61 -> 63 0.64234
61 -> 64 0.27003

Excited State 4: Singlet-A" 4.3876 eV 282.58 nm f=0.0005 <S**2>=0.000
59 -> 62 0.66272
60 -> 62 -0.23020

Excited State 5: Singlet-A' 4.5946 eV 269.85 nm f=0.2141 <S**2>=0.000
59 -> 63 0.19801
61 -> 63 -0.27052
61 -> 64 0.60404

Excited State 6: Singlet-A" 4.7062 eV 263.45 nm f=0.0015 <S**2>=0.000
56 -> 62 -0.11580
57 -> 62 0.68680

Excited State 7: Singlet-A' 5.0239 eV 246.79 nm f=0.0378 <S**2>=0.000
55 -> 62 -0.10133
58 -> 62 0.69281

Excited State 8: Singlet-A" 5.1679 eV 239.91 nm f=0.0010 <S**2>=0.000
56 -> 62 0.69337
57 -> 62 0.11934

Excited State 9: Singlet-A' 5.1981 eV 238.52 nm f=0.0430 <S**2>=0.000

59 -> 63 -0.18452
61 -> 64 0.13371
61 -> 65 0.64194

Excited State 10: Singlet-A' 5.4016 eV 229.53 nm f=0.0069 <S**2>=0.000
59 -> 63 0.16929
59 -> 64 0.10008
60 -> 63 0.55720
60 -> 64 0.29860
60 -> 65 0.22155

Excited State 11: Singlet-A" 5.5501 eV 223.39 nm f=0.0034 <S**2>=0.000
61 -> 66 0.67711
61 -> 69 0.12472

Excited State 12: Singlet-A' 5.5708 eV 222.56 nm f=0.2962 <S**2>=0.000
55 -> 62 0.60536
56 -> 63 -0.10927
57 -> 63 0.20450
59 -> 64 -0.11216
59 -> 65 -0.10965

Excited State 13: Singlet-A" 5.6028 eV 221.29 nm f=0.0166 <S**2>=0.000
54 -> 62 0.51565
58 -> 63 0.44023
58 -> 64 -0.13011

Excited State 14: Singlet-A' 5.6063 eV 221.15 nm f=0.1434 <S**2>=0.000
56 -> 64 -0.21582
57 -> 64 -0.10470
59 -> 63 0.51692
60 -> 63 -0.18110
61 -> 64 -0.17946
61 -> 65 0.26619

Excited State 15: Singlet-A" 5.6363 eV 219.97 nm f=0.0045 <S**2>=0.000
54 -> 62 -0.45958
58 -> 63 0.47823
58 -> 64 -0.19071

Excited State 16: Singlet-A' 5.8702 eV 211.21 nm f=0.0116 <S**2>=0.000

57 -> 63	0.31502
59 -> 63	-0.17579
59 -> 64	0.20880
60 -> 63	-0.27853
60 -> 64	0.43399
60 -> 65	0.13495
61 -> 68	0.11978

Excited State 17: Singlet-A" 5.9087 eV 209.83 nm f=0.0159 <S**2>=0.000

61 -> 66	0.10308
61 -> 67	0.67306
61 -> 70	-0.14979

Excited State 18: Singlet-A' 5.9148 eV 209.62 nm f=0.0459 <S**2>=0.000

56 -> 63	0.16139
57 -> 63	0.44300
59 -> 63	0.17033
59 -> 64	0.28425
60 -> 63	0.10800
60 -> 64	-0.35641

Excited State 19: Singlet-A' 5.9839 eV 207.20 nm f=0.2198 <S**2>=0.000

55 -> 62	0.16029
56 -> 63	0.16449
57 -> 63	-0.25598
59 -> 63	0.12159
59 -> 64	0.45032
60 -> 63	-0.16842
61 -> 68	-0.30831

Excited State 20: Singlet-A' 6.1128 eV 202.83 nm f=0.0059 <S**2>=0.000

55 -> 62	0.10912
56 -> 63	0.21948
57 -> 63	-0.20495
57 -> 64	-0.18021
59 -> 64	0.13677
61 -> 68	0.55751

Excited State	21:	Singlet-A"	6.1424 eV	201.85 nm	f=0.0002	<S**2>=0.000
61 -> 69	-0.36608					
61 -> 70	0.57744					
Excited State	22:	Singlet-A"	6.1642 eV	201.14 nm	f=0.0001	<S**2>=0.000
55 -> 63	0.22506					
58 -> 63	0.23279					
58 -> 64	0.57375					
61 -> 69	-0.19201					
61 -> 70	-0.12339					
Excited State	23:	Singlet-A"	6.1735 eV	200.83 nm	f=0.0032	<S**2>=0.000
58 -> 64	0.21989					
61 -> 67	0.12335					
61 -> 69	0.52845					
61 -> 70	0.33188					
61 -> 72	0.12840					
Excited State	24:	Singlet-A'	6.1961 eV	200.10 nm	f=0.0070	<S**2>=0.000
56 -> 63	0.11501					
57 -> 64	0.62070					
59 -> 64	-0.10009					
61 -> 68	0.16989					
61 -> 71	-0.15457					
Excited State	25:	Singlet-A"	6.2746 eV	197.60 nm	f=0.0007	<S**2>=0.000
55 -> 63	0.64338					
55 -> 64	0.11296					
58 -> 64	-0.24805					
Excited State	26:	Singlet-A'	6.3397 eV	195.57 nm	f=0.0113	<S**2>=0.000
56 -> 63	0.43056					
59 -> 64	-0.21941					
59 -> 65	-0.18890					
60 -> 65	0.27441					
61 -> 68	-0.11415					
61 -> 71	0.33599					

Excited State 27: Singlet-A' 6.3826 eV 194.25 nm f=0.0055 <S**2>=0.000

56 -> 63	-0.15999
59 -> 65	0.21057
60 -> 64	-0.25780
60 -> 65	0.56188
61 -> 71	-0.11895

Excited State 28: Singlet-A" 6.4748 eV 191.49 nm f=0.0000 <S**2>=0.000

61 -> 69	-0.14429
61 -> 72	0.67444

Excited State 29: Singlet-A' 6.5573 eV 189.08 nm f=0.0202 <S**2>=0.000

54 -> 64	0.11601
56 -> 63	-0.10264
56 -> 64	0.18028
56 -> 65	-0.10566
57 -> 63	-0.11691
59 -> 65	0.42937
61 -> 71	0.44029

Excited State 30: Singlet-A" 6.5996 eV 187.87 nm f=0.0005 <S**2>=0.000

55 -> 63	-0.11483
55 -> 64	0.68309

Excited State 31: Singlet-A' 6.6256 eV 187.13 nm f=0.1601 <S**2>=0.000

54 -> 63	-0.40776
56 -> 64	0.47751
57 -> 65	0.18976
59 -> 63	0.12016

Excited State 32: Singlet-A" 6.7480 eV 183.74 nm f=0.0004 <S**2>=0.000

59 -> 66	0.13227
60 -> 66	-0.18137
61 -> 73	0.64242

Excited State 33: Singlet-A" 6.7658 eV 183.25 nm f=0.0033 <S**2>=0.000

59 -> 66	-0.17069
59 -> 67	-0.11923
60 -> 66	0.59989

60 -> 69 -0.11967
61 -> 73 0.22914

Excited State 34: Singlet-A' 6.7727 eV 183.07 nm f=0.1078 <S**2>=0.000
54 -> 63 0.17699
54 -> 64 0.14715
56 -> 63 0.27192
57 -> 63 0.11290
57 -> 64 -0.13694
57 -> 65 0.33004
59 -> 64 -0.15291
59 -> 65 0.25351
61 -> 71 -0.22216
61 -> 75 -0.13614
61 -> 79 -0.17642

Excited State 35: Singlet-A" 6.7958 eV 182.44 nm f=0.0012 <S**2>=0.000
59 -> 66 0.60970
59 -> 67 0.12014
60 -> 66 0.20057
60 -> 67 -0.13131
60 -> 69 -0.11242

Excited State 36: Singlet-A" 6.8442 eV 181.15 nm f=0.0001 <S**2>=0.000
50 -> 62 0.13889
51 -> 62 0.53640
58 -> 65 -0.38326

Excited State 37: Singlet-A' 6.8461 eV 181.10 nm f=0.0483 <S**2>=0.000
54 -> 63 0.47015
54 -> 64 -0.22314
56 -> 64 0.32203
56 -> 65 0.16110
59 -> 65 -0.19192

Excited State 38: Singlet-A" 6.8663 eV 180.57 nm f=0.0000 <S**2>=0.000
51 -> 62 0.35228
58 -> 65 0.48985
58 -> 71 0.13569

61 -> 74 -0.27310

Excited State 39: Singlet-A" 6.8816 eV 180.17 nm f=0.0000 <S**2>=0.000

51 -> 62 0.14636

58 -> 65 0.22507

61 -> 74 0.61751

Excited State 40: Singlet-A' 6.8972 eV 179.76 nm f=0.3587 <S**2>=0.000

53 -> 62 0.21132

54 -> 64 -0.21357

56 -> 64 -0.19581

56 -> 65 -0.14366

57 -> 65 0.48330

59 -> 63 -0.10429

61 -> 71 0.12380

61 -> 75 0.11812

61 -> 79 -0.13957

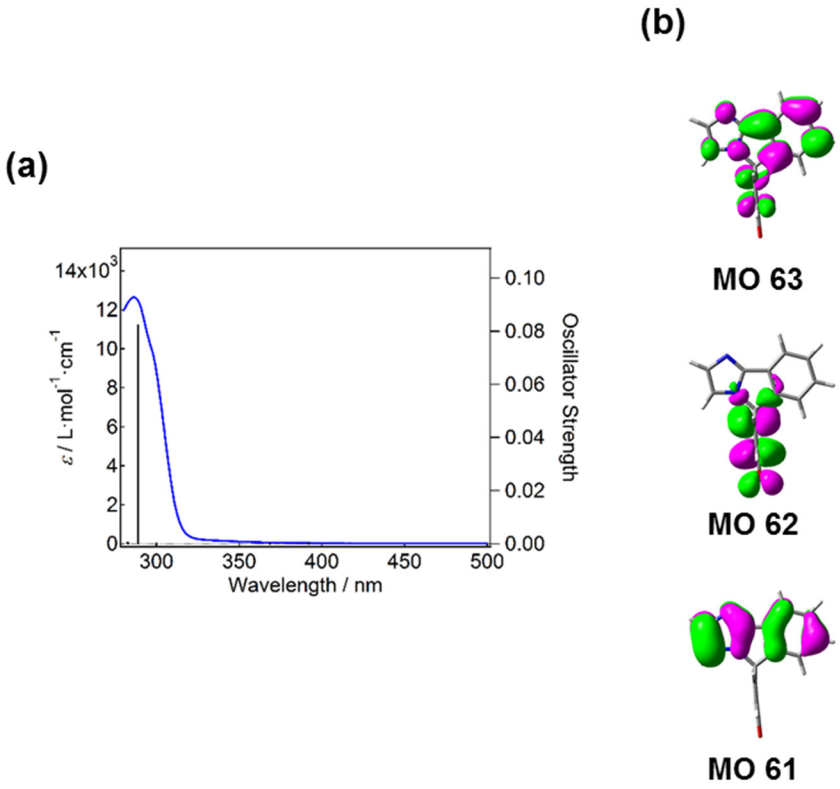


Fig. S47. (a) UV–vis absorption spectrum of the closed-ring isomer of **3** in benzene. The calculated spectrum (MPW1PW91/6-31+G(d,p)//M052X/6-31+G(d,p) level of the theory) is shown by the black lines. (b) The relevant molecular orbitals were calculated at the M052X/6-31+G(d,p) level of the theory.

Table S13. Standard Orientation of the Optimized Geometry for the Biradical Form of **3**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-1.6436590	-0.2571550	0.0814860
2	C	-0.5337600	-1.1355030	-0.0440300
3	C	-1.5330720	1.1683660	-0.0861220
4	N	-2.5337630	2.0257370	0.3189790
5	C	-2.0919520	3.2071210	-0.0391960
6	C	-0.8003710	3.0536170	-0.7027560
7	N	-0.4787060	1.7834500	-0.7236690
8	C	0.8610000	-0.6838550	-0.0056330
9	C	1.8138340	-1.2465970	-0.8933850
10	C	3.1316760	-0.8875510	-0.8282460
11	C	3.6035830	0.0523180	0.1779400
12	C	2.6103760	0.5867170	1.0958430
13	C	1.2969160	0.2363360	0.9895200
14	O	4.8030630	0.3749980	0.2485020
15	C	-0.7819060	-2.5147600	-0.1064310
16	C	-2.0668530	-3.0224320	0.0252570
17	C	-3.1476210	-2.1575280	0.2317240
18	C	-2.9366710	-0.7915740	0.2607180
19	H	1.4724980	-1.9342650	-1.6577250
20	H	0.5659830	0.6349290	1.6824170
21	H	0.0576450	-3.1931570	-0.1937920
22	H	-2.2256550	-4.0930110	-0.0037490
23	H	-4.1471650	-2.5540800	0.3541640
24	H	-3.7586420	-0.0989770	0.3808250
25	H	3.8691280	-1.2776710	-1.5175060
26	H	2.9639150	1.2664540	1.8600340
27	H	-0.1822240	3.8215650	-1.1449070
28	H	-2.6418310	4.1187980	0.1449000

SCF Done: E(UM052X) = -762.228679933 A.U.

S**2 before annihilation 1.0130, after 0.652

Zero-point correction = 0.214510 (Hartree/Particle)

Thermal correction to Energy = 0.227948

Thermal correction to Enthalpy = 0.228892

Thermal correction to Gibbs Free Energy = 0.173370

Sum of electronic and zero-point Energies = -762.014170
Sum of electronic and thermal Energies = -762.000732
Sum of electronic and thermal Enthalpies = -761.999788
Sum of electronic and thermal Free Energies = -762.055310

Low frequencies --- -4.4270 0.0004 0.0006 0.0009 3.6900 12.8796
Low frequencies --- 48.7037 59.8199 71.2935

The Results for the TDDFT calculation

Excited State 1: 2.390-A 1.2939 eV 958.21 nm f=0.0000 <S**2>=1.178
60A -> 62A 0.96577
60A -> 63A -0.12509
60A -> 64A 0.10801
60A -> 69A 0.10060
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -762.079902729
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 1.484-A 1.3954 eV 888.50 nm f=0.0299 <S**2>=0.301
61A -> 62A 0.20104
61B -> 62B 0.96391

Excited State 3: 1.759-A 2.1454 eV 577.90 nm f=0.0426 <S**2>=0.524
59A -> 62A -0.20089
61A -> 62A 0.82066
55B -> 62B 0.16237
57B -> 62B 0.26976
59B -> 62B -0.37900
61B -> 62B -0.10671

Excited State 4: 2.098-A 2.2714 eV 545.84 nm f=0.0306 <S**2>=0.850
61A -> 62A 0.46528
55B -> 62B -0.25284
56B -> 62B -0.19810
57B -> 62B -0.42291
58B -> 62B 0.25603
59B -> 62B 0.60493
61B -> 62B -0.21078

Excited State 5:	2.398-A	2.3500 eV	527.59 nm	f=0.0002	<S**2>=1.188	
56A -> 63A	0.10344					
59A -> 62A	-0.15640					
55B -> 62B	0.70499					
56B -> 62B	-0.24220					
57B -> 62B	-0.47171					
58B -> 62B	0.33529					
59B -> 62B	-0.16921					
Excited State 6:	2.345-A	2.5129 eV	493.39 nm	f=0.0058	<S**2>=1.125	
56A -> 62A	0.11264					
57A -> 62A	0.21921					
58A -> 62A	-0.29540					
59A -> 62A	0.83377					
61A -> 62A	0.14930					
55B -> 62B	0.23010					
57B -> 62B	0.11360					
58B -> 62B	0.12064					
61B -> 65B	0.15444					
Excited State 7:	2.274-A	2.6384 eV	469.92 nm	f=0.0006	<S**2>=1.042	
60B -> 62B	0.98490					
Excited State 8:	2.376-A	2.7848 eV	445.22 nm	f=0.0003	<S**2>=1.162	
58A -> 62A	-0.13261					
59A -> 62A	-0.15575					
54B -> 62B	-0.47512					
55B -> 62B	-0.12404					
57B -> 62B	0.34790					
58B -> 62B	0.73218					
Excited State 9:	2.402-A	2.8986 eV	427.74 nm	f=0.0364	<S**2>=1.192	
61A -> 62A	0.11209					
61A -> 63A	-0.24194					
54B -> 62B	-0.43556					
55B -> 62B	0.33049					
56B -> 62B	0.64349					
57B -> 62B	-0.10011					

58B -> 62B -0.21200
59B -> 62B 0.29086

Excited State 10: 2.403-A 2.9141 eV 425.46 nm f=0.0333 <S**2>=1.194
58A -> 62A -0.30787
61A -> 63A -0.21289
54B -> 62B 0.52310
55B -> 62B -0.18907
56B -> 62B 0.53296
57B -> 62B -0.27538
58B -> 62B 0.28770
59B -> 62B -0.22129

Excited State 11: 2.315-A 3.0609 eV 405.06 nm f=0.0382 <S**2>=1.090
53A -> 62A 0.12791
54A -> 62A -0.12464
57A -> 62A -0.11648
58A -> 62A 0.63773
59A -> 62A 0.32595
61A -> 63A -0.11795
55B -> 62B -0.23538
57B -> 62B -0.20284
58B -> 62B 0.19740
59B -> 62B -0.36171
61B -> 63B 0.21895
61B -> 64B 0.16490

Excited State 12: 2.257-A 3.2277 eV 384.13 nm f=0.0226 <S**2>=1.024
58A -> 62A 0.37803
54B -> 62B 0.49542
55B -> 62B 0.27880
57B -> 62B 0.46320
58B -> 62B 0.23274
59B -> 62B 0.41185
61B -> 63B 0.11355
61B -> 64B 0.10421

Excited State 13: 2.370-A 3.4602 eV 358.32 nm f=0.0047 <S**2>=1.154
53A -> 62A -0.12708

54A -> 62A 0.23362
57A -> 62A 0.82802
58A -> 62A 0.18630
58A -> 64A -0.12274
59A -> 62A -0.14197
61A -> 63A -0.18967
54B -> 62B -0.11287
56B -> 62B -0.12905
58B -> 64B -0.10704
61B -> 63B -0.10728

Excited State 14: 2.721-A 3.8240 eV 324.23 nm f=0.0981 <S**2>=1.601
53A -> 62A 0.23911
54A -> 62A -0.20249
55A -> 62A 0.10275
55A -> 63A 0.11546
56A -> 62A -0.14497
57A -> 62A 0.41177
58A -> 64A 0.22795
59A -> 62A -0.10056
61A -> 63A 0.48183
61A -> 64A 0.11298
56B -> 62B 0.27031
56B -> 63B 0.16330
57B -> 62B -0.10499
58B -> 64B 0.16949
61B -> 63B 0.36718
61B -> 67B 0.11980

Excited State 15: 2.508-A 3.9327 eV 315.26 nm f=0.1107 <S**2>=1.322
53A -> 62A -0.33316
54A -> 62A 0.27394
55A -> 62A 0.45689
55A -> 63A 0.12994
57A -> 62A -0.10552
58A -> 62A 0.36243
58A -> 64A 0.14949
59A -> 62A 0.14373
61A -> 63A 0.22998

56B -> 62B 0.14943
56B -> 63B 0.14645
61B -> 63B -0.38810
61B -> 64B -0.23703
61B -> 67B -0.10076

Excited State 16: 2.462-A 4.0589 eV 305.46 nm f=0.0328 <S**2>=1.265
53A -> 62A -0.12703
54A -> 62A 0.13838
56A -> 62A 0.77853
57A -> 62A -0.11638
58A -> 64A -0.10643
61A -> 63A 0.28473
61B -> 63B 0.36943

Excited State 17: 2.717-A 4.1096 eV 301.69 nm f=0.0596 <S**2>=1.595
53A -> 62A 0.14585
54A -> 62A -0.16859
55A -> 62A -0.32574
56A -> 62A 0.49386
58A -> 62A 0.12758
58A -> 64A 0.25058
61A -> 63A -0.30398
61A -> 64A 0.17391
53B -> 62B 0.13139
58B -> 64B 0.22110
59B -> 65B -0.13822
61B -> 63B -0.20971
61B -> 64B -0.39133

Excited State 18: 2.498-A 4.1140 eV 301.37 nm f=0.0066 <S**2>=1.310
53A -> 62A 0.27907
54A -> 62A -0.39577
55A -> 62A 0.50111
56A -> 62A 0.25581
58A -> 62A -0.10159
61A -> 64A -0.24266
58B -> 63B 0.14226
61B -> 63B -0.35917

61B -> 64B 0.32889
61B -> 67B 0.10716

Excited State 19: 2.612-A 4.3355 eV 285.97 nm f=0.1062 <S**2>=1.455
53A -> 62A 0.14275
55A -> 62A 0.49997
59A -> 65A -0.24731
61A -> 63A -0.44450
61A -> 64A 0.20421
56B -> 62B -0.14121
57B -> 65B 0.15565
58B -> 62B -0.10708
58B -> 64B 0.11486
59B -> 65B 0.28116
61B -> 63B 0.26436
61B -> 64B -0.25674

Excited State 20: 2.801-A 4.4340 eV 279.62 nm f=0.0921 <S**2>=1.711
49A -> 62A -0.10401
54A -> 62A -0.15213
55A -> 62A 0.29147
57A -> 65A 0.12091
58A -> 65A -0.11231
59A -> 65A 0.33229
61A -> 63A -0.17844
61A -> 64A -0.14829
61A -> 65A -0.10391
56B -> 62B -0.10788
57B -> 65B -0.17264
59B -> 65B -0.34719
61B -> 63B 0.34253
61B -> 64B -0.27301
61B -> 65B 0.37654
61B -> 67B -0.11602

Excited State 21: 2.473-A 4.4646 eV 277.71 nm f=0.0054 <S**2>=1.279
53A -> 62A 0.40304
54A -> 62A 0.59144
57A -> 62A -0.10333

58A -> 64A 0.13142
61A -> 64A -0.33874
58B -> 63B 0.16506
61B -> 65B 0.43843
61B -> 67B 0.14463

Excited State 22: 2.460-A 4.5133 eV 274.71 nm f=0.0359 <S**2>=1.263
54A -> 62A -0.23364
59A -> 65A -0.12436
61A -> 64A 0.45746
56B -> 64B -0.11307
59B -> 65B 0.10903
61B -> 63B -0.18851
61B -> 64B 0.14952
61B -> 65B 0.72555

Excited State 23: 2.595-A 4.5408 eV 273.04 nm f=0.0033 <S**2>=1.433
53A -> 62A 0.30051
54A -> 62A 0.36913
55A -> 62A 0.15953
58A -> 64A -0.10051
59A -> 63A -0.10565
59A -> 65A 0.24057
61A -> 64A 0.60081
53B -> 62B 0.14386
57B -> 65B -0.12316
59B -> 65B -0.21756
61B -> 64B 0.26459
61B -> 65B -0.18547

Excited State 24: 2.730-A 4.7325 eV 261.98 nm f=0.0452 <S**2>=1.614
53A -> 62A 0.10921
55A -> 63A -0.23708
58A -> 63A 0.19750
59A -> 65A -0.12554
60A -> 63A 0.16201
61A -> 63A 0.22315
61A -> 75A -0.10061
45B -> 62B 0.10820

50B -> 62B -0.12684
52B -> 62B 0.14120
53B -> 62B 0.61029
56B -> 63B -0.18402
56B -> 64B 0.10030
58B -> 63B -0.20259
59B -> 65B 0.11605
60B -> 63B 0.10865
61B -> 63B -0.13218
61B -> 64B -0.27789

Excited State 25: 3.147-A 4.7889 eV 258.90 nm f=0.0043 <S**2>=2.225
50A -> 62A 0.17451
51A -> 62A 0.21130
52A -> 62A -0.35069
55A -> 63A 0.11834
60A -> 62A 0.18758
60A -> 63A 0.51514
60A -> 64A -0.25936
60A -> 69A -0.17868
52B -> 62B -0.12600
53B -> 62B -0.23458
60B -> 63B 0.34565
60B -> 64B 0.17548
60B -> 67B 0.16922

Excited State 26: 2.819-A 4.9091 eV 252.56 nm f=0.1160 <S**2>=1.737
53A -> 62A -0.30693
57A -> 63A -0.20345
58A -> 63A -0.30581
58A -> 64A 0.25061
59A -> 63A 0.10192
60A -> 63A 0.11293
61A -> 63A -0.15614
49B -> 62B -0.12055
50B -> 62B -0.20023
51B -> 62B 0.18123
52B -> 62B 0.14205
53B -> 62B 0.34043

58B -> 63B 0.26057
58B -> 64B 0.17704
60B -> 63B 0.18480
61B -> 63B 0.19161
61B -> 64B 0.34323

Excited State 27: 2.998-A 4.9328 eV 251.35 nm f=0.0045 <S**2>=1.997
55A -> 62A -0.10358
55A -> 63A 0.30775
58A -> 63A 0.30601
59A -> 63A 0.33535
60A -> 63A -0.13157
61A -> 63A -0.11103
61A -> 64A -0.13965
61A -> 75A 0.11765
46B -> 62B -0.11682
49B -> 62B 0.19669
50B -> 62B -0.16095
51B -> 62B 0.21638
52B -> 62B -0.28407
53B -> 62B 0.34751
56B -> 63B 0.27928
56B -> 64B -0.18748
58B -> 63B -0.17563
59B -> 63B 0.12572
61B -> 64B 0.11725

Excited State 28: 3.099-A 4.9630 eV 249.82 nm f=0.0193 <S**2>=2.151
53A -> 62A 0.20411
57A -> 63A -0.45596
57A -> 75A 0.10288
59A -> 63A 0.55182
50B -> 62B 0.11054
52B -> 62B 0.31544
53B -> 62B -0.14727
57B -> 63B -0.11095
59B -> 63B 0.21751
60B -> 63B -0.17718

Excited State 29: 2.442-A 4.9991 eV 248.01 nm f=0.0077 <S**2>=1.240

51A -> 62A	-0.15339
52A -> 62A	0.18697
57A -> 63A	-0.10787
59A -> 63A	0.13415
60A -> 63A	-0.40540
60A -> 64A	0.12639
60B -> 63B	0.66211
60B -> 64B	0.29869
60B -> 66B	0.13983
60B -> 67B	0.25443
60B -> 68B	0.11981

Excited State 30: 3.044-A 5.0268 eV 246.65 nm f=0.0081 <S**2>=2.067

57A -> 63A	0.21729
58A -> 63A	0.50019
58A -> 64A	0.28649
59A -> 63A	0.11040
49B -> 62B	-0.14353
50B -> 62B	0.10293
51B -> 62B	-0.17624
52B -> 62B	0.33755
53B -> 62B	-0.13646
56B -> 63B	-0.10846
56B -> 64B	-0.12627
58B -> 63B	-0.25377
58B -> 64B	0.28257
61B -> 64B	0.34940

Excited State 31: 2.539-A 5.0755 eV 244.28 nm f=0.0060 <S**2>=1.362

51A -> 62A	0.16473
55A -> 63A	0.14474
57A -> 63A	0.10733
58A -> 64A	-0.11911
59A -> 63A	-0.19955
60A -> 63A	-0.14827
49B -> 62B	0.14243
51B -> 62B	0.52722
52B -> 62B	0.65372

53B -> 62B -0.11446
56B -> 63B 0.14199

Excited State 32: 2.638-A 5.1347 eV 241.46 nm f=0.0027 <S**2>=1.489
49A -> 62A 0.10422
50A -> 62A -0.23789
51A -> 62A -0.37331
52A -> 62A 0.59423
55A -> 63A 0.10202
58A -> 64A -0.10015
60A -> 63A 0.54332
49B -> 62B 0.12966

Excited State 33: 2.620-A 5.1922 eV 238.79 nm f=0.0020 <S**2>=1.466
48A -> 62A -0.41305
49A -> 62A 0.21250
51A -> 62A 0.60226
52A -> 62A 0.30522
57A -> 63A -0.14457
60A -> 65A -0.34854
52B -> 62B -0.18021
60B -> 65B 0.23615

Excited State 34: 3.346-A 5.2197 eV 237.53 nm f=0.0005 <S**2>=2.549
48A -> 62A -0.10822
51A -> 62A 0.10060
52A -> 62A 0.15436
56A -> 63A -0.26232
57A -> 63A 0.49712
58A -> 63A -0.25315
58A -> 65A -0.10818
59A -> 63A 0.20462
59A -> 64A -0.21227
60A -> 65A -0.11041
61A -> 65A 0.11891
55B -> 62B 0.10223
55B -> 63B -0.14608
55B -> 64B 0.11772
56B -> 63B 0.13015

57B -> 63B 0.24896
59B -> 63B 0.32008
59B -> 64B 0.13877

Excited State 35: 3.009-A 5.2908 eV 234.34 nm f=0.0057 <S**2>=2.013
55A -> 63A 0.14611
56A -> 63A 0.42056
58A -> 65A -0.10051
59A -> 64A -0.15510
61A -> 65A 0.42553
50B -> 62B 0.22517
51B -> 62B -0.28883
52B -> 62B 0.14764
53B -> 62B 0.16371
55B -> 62B -0.11761
55B -> 63B 0.33645
56B -> 63B 0.14645
59B -> 64B 0.12602
61B -> 66B -0.10430
61B -> 67B -0.12229

Excited State 36: 2.795-A 5.3529 eV 231.62 nm f=0.0167 <S**2>=1.702
51A -> 62A 0.12259
52A -> 62A 0.14247
55A -> 63A -0.14081
56A -> 63A 0.19408
58A -> 63A 0.12199
59A -> 63A 0.10199
60A -> 65A 0.26560
61A -> 65A 0.26531
50B -> 62B -0.29486
51B -> 62B 0.38895
52B -> 62B -0.23444
53B -> 62B -0.26601
55B -> 63B 0.10606
56B -> 63B -0.21783
57B -> 63B 0.11881
60B -> 65B -0.29055
61B -> 66B 0.13996

61B -> 67B 0.15002

Excited State 37: 3.249-A 5.3599 eV 231.32 nm f=0.0016 <S**2>=2.388

48A -> 62A 0.10403
49A -> 62A -0.11249
51A -> 62A -0.30983
52A -> 62A -0.22648
56A -> 63A 0.21518
60A -> 65A -0.45893
50B -> 62B -0.10264
51B -> 62B 0.17627
53B -> 62B -0.11193
55B -> 63B 0.15586
56B -> 63B -0.10632
60B -> 65B 0.58703

Excited State 38: 2.571-A 5.4754 eV 226.44 nm f=0.0286 <S**2>=1.402

47A -> 62A 0.11558
53A -> 62A -0.20361
56A -> 63A 0.15274
58A -> 63A -0.16927
59A -> 63A 0.19101
59A -> 64A -0.10759
60A -> 64A -0.11417
61A -> 65A -0.42115
55B -> 63B 0.17905
56B -> 63B 0.11793
58B -> 63B -0.20392
59B -> 64B 0.10345
60B -> 65B -0.19490
61B -> 66B 0.45391
61B -> 67B 0.38443
61B -> 68B 0.13426

Excited State 39: 2.609-A 5.4847 eV 226.05 nm f=0.0293 <S**2>=1.452

53A -> 62A -0.17244
56A -> 63A -0.19624
57A -> 63A -0.12681
59A -> 63A -0.26234

60A -> 64A -0.16934
60A -> 65A 0.11304
61A -> 65A 0.47262
55B -> 63B -0.16854
57B -> 63B -0.14591
58B -> 63B -0.11883
59B -> 63B 0.23220
60B -> 65B 0.25433
61B -> 66B 0.39513
61B -> 67B 0.28545
61B -> 68B 0.11028

Excited State 40: 2.522-A 5.5023 eV 225.33 nm f=0.0252 <S**2>=1.340
58A -> 63A 0.14719
59A -> 63A -0.33900
60A -> 64A 0.25403
60A -> 65A -0.19570
61A -> 65A -0.27643
56B -> 63B -0.16479
57B -> 63B -0.26971
57B -> 64B 0.14795
58B -> 63B 0.16750
59B -> 63B 0.61317
60B -> 65B -0.24297

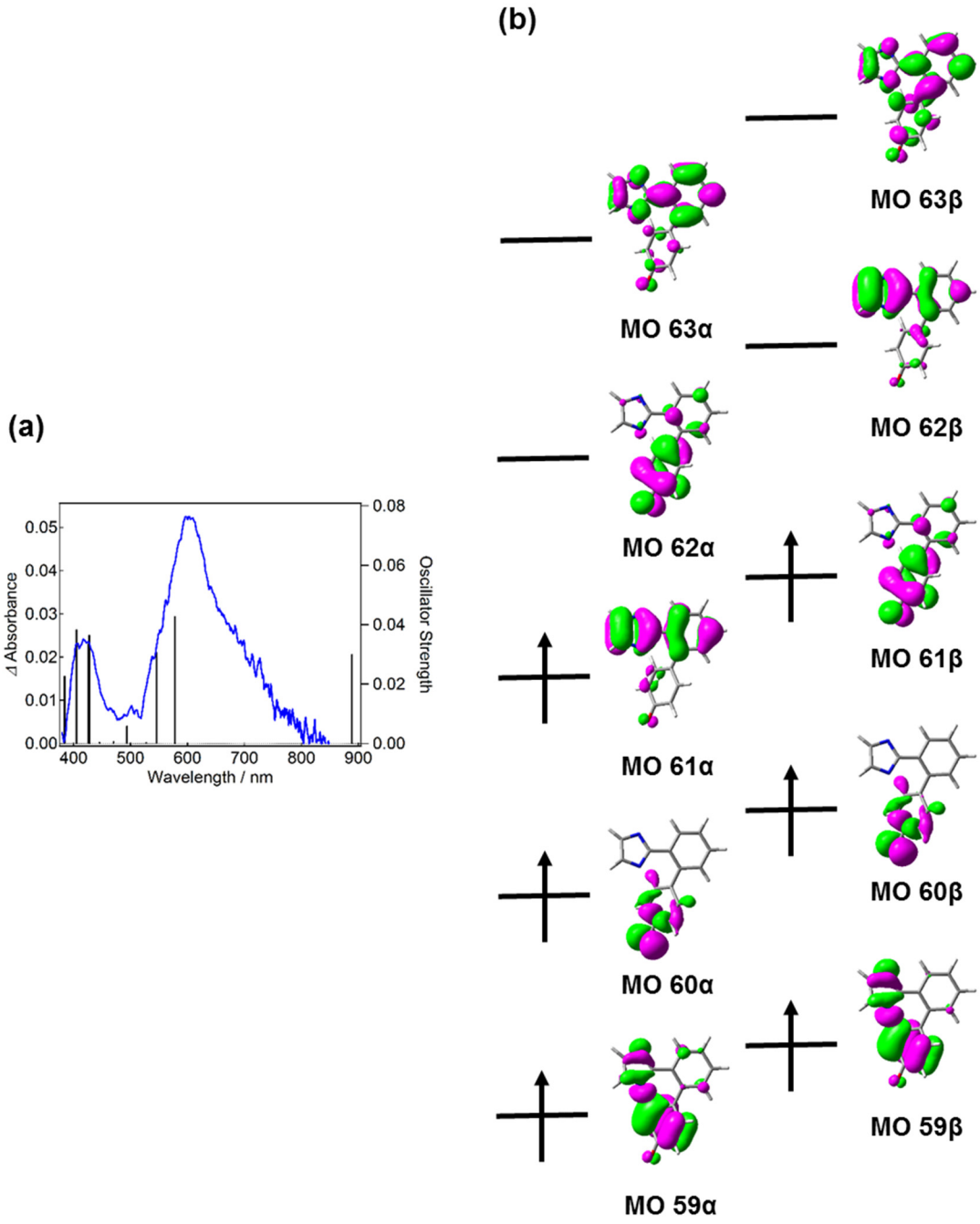


Fig. S48. (a) The transient absorption spectrum of **3** in benzene (excitation wavelength, 355 nm; pulse width, 5ns; power 4 mJ/pulse). The calculated spectrum (UMPW1PW91/6-31+G(d,p)//UM052X/6-31+G(d,p) level of the theory) of the biradical form of the open-ring isomer of **3** is shown by the black lines. (b) The relevant molecular orbitals were calculated at the UM052X/6-31+G(d,p) level of the theory.

Table S14. Standard Orientation of the Optimized Geometry for the Quinoid Form of **3**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-1.6147410	-0.2455550	0.1554000

2	C	-0.4948050	-1.1219630	-0.1372480
3	C	-1.5426320	1.1226270	-0.0994770
4	N	-2.5084670	2.0142630	0.3446460
5	C	-2.0826320	3.1713600	-0.0888020
6	C	-0.8583030	2.9836540	-0.8543420
7	N	-0.5452690	1.7163160	-0.8629300
8	C	0.8327010	-0.6848030	-0.0438520
9	C	1.8948270	-1.3865510	-0.7414500
10	C	3.1803840	-0.9953760	-0.6423820
11	C	3.5835410	0.1129640	0.2462460
12	C	2.5074340	0.7622570	1.0042390
13	C	1.2193420	0.3991820	0.8439850
14	O	4.7579500	0.4468460	0.3512290
15	C	-0.7974920	-2.5067730	-0.3843020
16	C	-2.0295110	-3.0073290	-0.0942930
17	C	-3.0607110	-2.1607490	0.4280130
18	C	-2.8610080	-0.8215910	0.5636260
19	H	1.6314850	-2.1808410	-1.4268860
20	H	0.4468630	0.8694640	1.4367110
21	H	-0.0065700	-3.1815410	-0.6793250
22	H	-2.2225600	-4.0655910	-0.2144770
23	H	-4.0196490	-2.5933060	0.6843660
24	H	-3.6465590	-0.1511110	0.8839140
25	H	3.9708500	-1.4656390	-1.2137000
26	H	2.8030600	1.5287020	1.7087210
27	H	-0.2896720	3.7285060	-1.3929680
28	H	-2.6130650	4.0944100	0.0996420

SCF Done: E(RM052X) = -762.217817715 A.U.

Zero-point correction	=	0.215841 (Hartree/Particle)
Thermal correction to Energy	=	0.229247
Thermal correction to Enthalpy	=	0.230191
Thermal correction to Gibbs Free Energy	=	0.174871
Sum of electronic and zero-point Energies	=	-762.001977
Sum of electronic and thermal Energies	=	-761.988571
Sum of electronic and thermal Enthalpies	=	-761.98762
Sum of electronic and thermal Free Energies	=	-762.042947

Low frequencies --- -10.0262 -0.0004 -0.0001 0.0001 1.7979 11.6539

Low frequencies --- 43.5414 68.3771 82.0791

The Results for the TDDFT calculation

Excited State 1: Singlet-A 1.9718 eV 628.80 nm f=0.1811 <S**2>=0.000

60 -> 62 0.31817

61 -> 62 0.62917

61 <- 62 -0.15423

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -762.048238369

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.1013 eV 590.03 nm f=0.0649 <S**2>=0.000

60 -> 62 0.61607

61 -> 62 -0.32161

Excited State 3: Singlet-A 2.6240 eV 472.50 nm f=0.0137 <S**2>=0.000

57 -> 62 0.13511

58 -> 62 -0.18326

59 -> 62 0.65659

Excited State 4: Singlet-A 2.9758 eV 416.65 nm f=0.0092 <S**2>=0.000

57 -> 62 -0.44016

58 -> 62 0.47392

59 -> 62 0.23378

61 -> 63 -0.13635

Excited State 5: Singlet-A 3.2048 eV 386.87 nm f=0.0614 <S**2>=0.000

54 -> 62 0.12227

55 -> 62 0.10575

56 -> 62 -0.10004

57 -> 62 0.49693

58 -> 62 0.36346

61 -> 63 -0.27239

Excited State 6: Singlet-A 3.3295 eV 372.38 nm f=0.0017 <S**2>=0.000

54 -> 62 -0.10033

55 -> 62 -0.41163

56 -> 62 0.52494
61 -> 63 -0.17203

Excited State 7: Singlet-A 3.5487 eV 349.37 nm f=0.1231 <S**2>=0.000
54 -> 62 0.17607
55 -> 62 0.47165
56 -> 62 0.35613
58 -> 62 -0.13035
61 -> 62 -0.12536
61 -> 63 -0.25094

Excited State 8: Singlet-A 3.6110 eV 343.35 nm f=0.0059 <S**2>=0.000
54 -> 62 0.64532
55 -> 62 -0.17890
61 -> 63 0.20355

Excited State 9: Singlet-A 4.2274 eV 293.29 nm f=0.2284 <S**2>=0.000
53 -> 62 -0.10895
56 -> 62 0.11329
58 -> 62 0.18510
61 -> 63 0.30945
61 -> 64 0.55269

Excited State 10: Singlet-A 4.3214 eV 286.91 nm f=0.5540 <S**2>=0.000
55 -> 62 -0.20944
56 -> 62 -0.23697
58 -> 62 -0.20487
61 -> 63 -0.39437
61 -> 64 0.41341

Excited State 11: Singlet-A 4.5064 eV 275.13 nm f=0.0186 <S**2>=0.000
60 -> 62 -0.12559
60 -> 63 0.63514
60 -> 64 0.14413
60 -> 69 0.13167

Excited State 12: Singlet-A 4.8838 eV 253.87 nm f=0.0671 <S**2>=0.000
52 -> 62 -0.35316
53 -> 62 0.55034

58 -> 63 -0.14724
60 -> 63 -0.11587

Excited State 13: Singlet-A 4.9103 eV 252.50 nm f=0.0133 <S**2>=0.000
59 -> 63 -0.13024
61 -> 65 0.68165

Excited State 14: Singlet-A 4.9697 eV 249.48 nm f=0.0249 <S**2>=0.000
57 -> 63 0.18321
58 -> 63 -0.14651
59 -> 63 0.62524
61 -> 65 0.13757

Excited State 15: Singlet-A 5.2023 eV 238.33 nm f=0.0340 <S**2>=0.000
52 -> 62 0.54473
53 -> 62 0.28106
58 -> 63 -0.20826
61 -> 66 -0.11113
61 -> 69 -0.12720

Excited State 16: Singlet-A 5.3565 eV 231.47 nm f=0.0014 <S**2>=0.000
51 -> 62 0.12208
60 -> 63 -0.11217
60 -> 64 0.54483
60 -> 65 0.39021

Excited State 17: Singlet-A 5.3814 eV 230.39 nm f=0.0035 <S**2>=0.000
51 -> 62 -0.25068
61 -> 66 0.63287

Excited State 18: Singlet-A 5.3837 eV 230.29 nm f=0.0072 <S**2>=0.000
51 -> 62 0.41050
57 -> 63 0.29046
58 -> 63 -0.33333
59 -> 63 -0.17707
61 -> 66 0.21623

Excited State 19: Singlet-A 5.4314 eV 228.27 nm f=0.0129 <S**2>=0.000
51 -> 62 0.47555

53 -> 62 0.12624
57 -> 63 -0.26532
58 -> 63 0.28120
59 -> 63 0.15811
61 -> 66 0.14994

Excited State 20: Singlet-A 5.5316 eV 224.14 nm f=0.0194 <S**2>=0.000
50 -> 62 -0.15156
53 -> 62 0.10117
55 -> 64 -0.11330
56 -> 63 -0.17211
57 -> 63 0.48604
58 -> 63 0.34126

Excited State 21: Singlet-A 5.6652 eV 218.85 nm f=0.0037 <S**2>=0.000
50 -> 62 -0.37533
61 -> 67 0.56472

Excited State 22: Singlet-A 5.7326 eV 216.28 nm f=0.0122 <S**2>=0.000
50 -> 62 0.46573
55 -> 63 -0.19103
56 -> 63 -0.11998
58 -> 64 -0.20956
59 -> 64 0.15503
60 -> 65 -0.11966
61 -> 67 0.28511
61 -> 69 -0.10339

Excited State 23: Singlet-A 5.7575 eV 215.34 nm f=0.0018 <S**2>=0.000
55 -> 63 -0.13144
60 -> 63 0.13428
60 -> 64 -0.34599
60 -> 65 0.54475

Excited State 24: Singlet-A 5.7645 eV 215.08 nm f=0.0056 <S**2>=0.000
50 -> 62 0.21463
54 -> 63 0.11093
55 -> 63 0.42571
56 -> 63 -0.10474

58 -> 63 0.14909
58 -> 64 0.20153
59 -> 64 -0.27667
61 -> 67 0.19319
61 -> 69 -0.17931

Excited State 25: Singlet-A 5.7969 eV 213.88 nm f=0.0157 <S**2>=0.000
55 -> 63 0.20832
56 -> 63 0.32976
57 -> 63 0.17100
58 -> 63 0.10705
58 -> 64 0.14936
59 -> 64 0.49252

Excited State 26: Singlet-A 5.8320 eV 212.59 nm f=0.0015 <S**2>=0.000
54 -> 63 -0.19935
55 -> 63 -0.27044
56 -> 63 0.42248
58 -> 63 0.10941
58 -> 64 0.13210
59 -> 64 -0.28992
61 -> 67 0.10349
61 -> 69 -0.24777

Excited State 27: Singlet-A 5.8533 eV 211.82 nm f=0.0039 <S**2>=0.000
61 -> 68 0.69850

Excited State 28: Singlet-A 5.9135 eV 209.66 nm f=0.0019 <S**2>=0.000
49 -> 62 -0.18380
50 -> 62 0.12283
54 -> 63 0.20906
56 -> 63 0.31604
57 -> 64 -0.12613
58 -> 64 -0.17631
59 -> 64 -0.15776
61 -> 69 0.42534

Excited State 29: Singlet-A 5.9667 eV 207.79 nm f=0.0170 <S**2>=0.000
49 -> 62 0.14268

54 -> 63 0.55272
55 -> 63 -0.14177
58 -> 63 -0.10521
61 -> 69 -0.29096

Excited State 30: Singlet-A 6.1351 eV 202.09 nm f=0.0080 <S**2>=0.000
48 -> 62 0.58475
49 -> 62 0.15182
61 -> 70 0.31407

Excited State 31: Singlet-A 6.1449 eV 201.77 nm f=0.0179 <S**2>=0.000
48 -> 62 -0.25375
57 -> 64 0.22572
58 -> 64 -0.16665
61 -> 69 -0.11080
61 -> 70 0.54920

Excited State 32: Singlet-A 6.1682 eV 201.01 nm f=0.0765 <S**2>=0.000
48 -> 62 0.17230
55 -> 63 0.14525
57 -> 64 0.42121
58 -> 64 -0.34898
59 -> 64 -0.10876
61 -> 70 -0.27358

Excited State 33: Singlet-A 6.2846 eV 197.28 nm f=0.0269 <S**2>=0.000
49 -> 62 0.32618
50 -> 62 0.11252
54 -> 63 0.16226
55 -> 63 -0.11200
57 -> 64 0.39446
58 -> 64 0.19180
59 -> 65 0.18478
61 -> 69 0.19774

Excited State 34: Singlet-A 6.2926 eV 197.03 nm f=0.0091 <S**2>=0.000
49 -> 62 -0.17490
57 -> 64 0.10395
61 -> 71 0.60553

61 -> 73 0.23668

Excited State 35: Singlet-A 6.3830 eV 194.24 nm f=0.0120 <S**2>=0.000
48 -> 62 -0.11742
49 -> 62 0.34715
55 -> 63 0.11248
56 -> 64 0.27625
57 -> 64 -0.15960
58 -> 64 -0.19535
61 -> 71 0.30712
61 -> 73 -0.21060
61 -> 77 -0.11153

Excited State 36: Singlet-A 6.4127 eV 193.34 nm f=0.0025 <S**2>=0.000
56 -> 64 0.10654
61 -> 72 0.60046
61 -> 73 0.29597

Excited State 37: Singlet-A 6.4420 eV 192.46 nm f=0.0183 <S**2>=0.000
56 -> 64 0.38491
58 -> 64 -0.10051
61 -> 71 -0.12880
61 -> 72 -0.31415
61 -> 73 0.41613
61 -> 74 0.11014

Excited State 38: Singlet-A 6.4682 eV 191.68 nm f=0.0022 <S**2>=0.000
60 -> 63 -0.12429
60 -> 64 -0.14786
60 -> 66 0.28534
60 -> 67 0.34066
60 -> 69 0.42675
61 -> 73 -0.13747

Excited State 39: Singlet-A 6.4898 eV 191.05 nm f=0.0247 <S**2>=0.000
49 -> 62 -0.25638
55 -> 63 -0.10978
55 -> 64 -0.12073
56 -> 64 0.42279

61 -> 72 0.12035

61 -> 73 -0.29972

61 -> 77 0.18928

Excited State 40: Singlet-A 6.5578 eV 189.06 nm f=0.0059 <S**2>=0.000

54 -> 64 -0.11011

55 -> 64 -0.35158

57 -> 65 0.11649

59 -> 65 0.32838

61 -> 74 -0.19328

61 -> 75 0.37447

61 -> 77 -0.11769

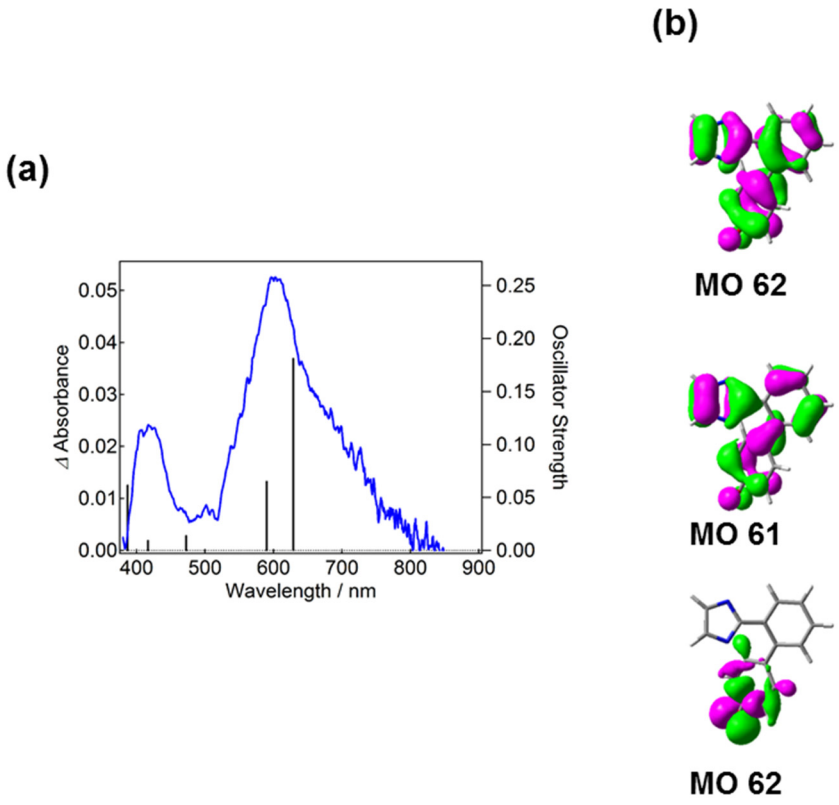


Fig. S49. (a) The transient absorption spectrum of **3** in benzene (excitation wavelength, 355 nm; pulse width, 5ns; power 4 mJ/pulse). The calculated spectrum (MPW1PW91/6-31+G(d,p)//M052X/6-31+G(d,p) level of the theory) of the quinoid form of the open-ring isomer of **3** is shown by the black lines. (b) The relevant molecular orbitals were calculated at the M052X/6-31+G(d,p) level of the theory.

Table S15. Standard Orientation of the Optimized Geometry for the Closed-Ring Form of **PIC1**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	3.4316450	-4.0485470	0.1329430
2	C	2.0643800	-3.8060560	0.0058140
3	C	1.6387330	-2.4843310	-0.0472750
4	C	2.5598450	-1.4320530	0.0301960
5	C	3.9176550	-1.6688020	0.1514120
6	C	4.3484110	-2.9965100	0.2053780
7	C	1.8449030	-0.0698730	-0.0587300
8	C	0.3138840	-1.8856110	-0.1496310
9	N	-0.9387810	-2.2577680	-0.1336570
10	C	-1.6580630	-1.0789190	-0.1363140
11	C	-0.8063360	0.0213540	-0.1413850
12	N	0.4564910	-0.5290360	-0.1806790
13	C	-3.1303730	-1.0994690	-0.1297930
14	C	-1.0374310	1.4710570	-0.0107010
15	C	-3.7929500	-2.2186430	0.3871980
16	C	-5.1829680	-2.2667890	0.4091340
17	C	-5.9312820	-1.2002800	-0.0859770
18	C	-5.2774870	-0.0883640	-0.6130860
19	C	-3.8870240	-0.0385680	-0.6410430
20	C	-0.5485900	2.3715160	-0.9619370
21	C	-0.7327480	3.7413800	-0.7939970
22	C	-1.4227420	4.2221650	0.3163150
23	C	-1.9309460	3.3281470	1.2581670
24	C	-1.7346060	1.9603150	1.0998760
25	C	2.3254850	0.6340030	-1.2989790
26	C	3.0179320	1.7744030	-1.2601490
27	C	3.2786110	2.4772220	0.0172990
28	C	2.7138110	1.8711470	1.2441260
29	C	2.0384410	0.7205200	1.2061420
30	O	3.9204830	3.5138550	0.0527310
31	H	3.7901280	-5.0693050	0.1765010
32	H	1.3488470	-4.6159590	-0.0501550
33	H	4.6234730	-0.8477160	0.2063650
34	H	5.4044190	-3.2124660	0.3052540
35	H	-3.2031390	-3.0441550	0.7641360
36	H	-5.6824900	-3.1384910	0.8140470

37	H	-7.0135780	-1.2379950	-0.0677870
38	H	-5.8500130	0.7392800	-1.0138230
39	H	-3.3893400	0.8212010	-1.0714540
40	H	-0.0330800	1.9965660	-1.8367420
41	H	-0.3430960	4.4309140	-1.5325670
42	H	-1.5670400	5.2875520	0.4459940
43	H	-2.4723060	3.6968720	2.1205680
44	H	-2.1201170	1.2594020	1.8307440
45	H	2.1168180	0.1218570	-2.2328160
46	H	1.6133830	0.2774730	2.1005070
47	H	3.3998880	2.2498020	-2.1550520
48	H	2.8682790	2.4194560	2.1647640

SCF Done: E(RM052X) = - 1224.38986695 A.U.

Zero-point correction = 0.382234 (Hartree/Particle)
Thermal correction to Energy = 0.404521
Thermal correction to Enthalpy = 0.405466
Thermal correction to Gibbs Free Energy = 0.328600
Sum of electronic and zero-point Energies = -1224.007633
Sum of electronic and thermal Energies = -1223.985345
Sum of electronic and thermal Enthalpies = -1223.984401
Sum of electronic and thermal Free Energies = -1224.061267

Low frequencies --- -8.6683 -4.9196 -3.3754 0.0001 0.0003 0.0007
Low frequencies --- 21.1190 24.8821 36.4628

The Results for the TDDFT calculation

Excited State 1: Singlet-A 2.7857 eV 445.08 nm f=0.0003 <S**2>=0.000
101 ->102 0.70388
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1224.10883118
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.3694 eV 367.98 nm f=0.0000 <S**2>=0.000
95 ->102 -0.11136
96 ->102 0.66309
97 ->102 0.18471

Excited State	3:	Singlet-A	3.7965 eV	326.58 nm	f=0.1562	<S**2>=0.000
101 ->103		0.68409				
101 ->104		0.15268				
Excited State	4:	Singlet-A	4.0977 eV	302.57 nm	f=0.2471	<S**2>=0.000
95 ->103		0.10031				
101 ->103		-0.15110				
101 ->104		0.67529				
Excited State	5:	Singlet-A	4.1626 eV	297.86 nm	f=0.0458	<S**2>=0.000
99 ->102		0.48060				
100 ->102		0.41688				
101 ->105		0.25391				
Excited State	6:	Singlet-A	4.1900 eV	295.90 nm	f=0.1671	<S**2>=0.000
99 ->102		-0.16259				
100 ->102		-0.19705				
101 ->105		0.64497				
Excited State	7:	Singlet-A	4.2774 eV	289.86 nm	f=0.0035	<S**2>=0.000
97 ->102		0.25218				
99 ->102		-0.43593				
100 ->102		0.48452				
Excited State	8:	Singlet-A	4.3461 eV	285.27 nm	f=0.0042	<S**2>=0.000
95 ->102		0.30517				
97 ->102		0.16284				
98 ->102		0.59777				
99 ->102		0.10582				
Excited State	9:	Singlet-A	4.4217 eV	280.40 nm	f=0.0145	<S**2>=0.000
101 ->106		0.67354				
Excited State	10:	Singlet-A	4.4647 eV	277.70 nm	f=0.0057	<S**2>=0.000
95 ->102		0.32678				
97 ->102		0.49667				
98 ->102		-0.31005				
100 ->102		-0.18254				

Excited State 11:	Singlet-A	4.5051 eV	275.21 nm	f=0.0011	<S**2>=0.000
95 ->102	0.52056				
96 ->102	0.18409				
97 ->102	-0.35093				
98 ->102	-0.16430				
99 ->102	-0.13498				
100 ->102	0.10182				
101 ->106	0.10183				
Excited State 12:	Singlet-A	4.8415 eV	256.09 nm	f=0.0222	<S**2>=0.000
101 ->107	0.65375				
101 ->108	-0.12042				
101 ->110	0.12853				
Excited State 13:	Singlet-A	4.8729 eV	254.44 nm	f=0.0399	<S**2>=0.000
100 ->104	-0.10401				
100 ->105	-0.17605				
101 ->108	0.49560				
101 ->109	0.11224				
101 ->110	0.37140				
Excited State 14:	Singlet-A	4.9322 eV	251.38 nm	f=0.0362	<S**2>=0.000
94 ->102	0.14810				
100 ->103	0.11262				
100 ->105	0.20233				
101 ->107	0.16241				
101 ->108	0.40953				
101 ->109	-0.15986				
101 ->110	-0.36642				
Excited State 15:	Singlet-A	4.9525 eV	250.35 nm	f=0.0100	<S**2>=0.000
91 ->102	-0.10997				
93 ->102	0.44697				
94 ->102	0.47631				
101 ->107	-0.10751				
Excited State 16:	Singlet-A	5.0520 eV	245.42 nm	f=0.0031	<S**2>=0.000
101 ->109	0.64538				

101 ->110 -0.15671
101 ->114 0.13120

Excited State 17: Singlet-A 5.1069 eV 242.78 nm f=0.1530 <S**2>=0.000
99 ->103 0.44373
100 ->103 0.49643
101 ->110 0.10272

Excited State 18: Singlet-A 5.1774 eV 239.47 nm f=0.0134 <S**2>=0.000
99 ->103 0.48213
99 ->105 0.11789
100 ->103 -0.45113

Excited State 19: Singlet-A 5.2006 eV 238.40 nm f=0.0399 <S**2>=0.000
91 ->102 0.14800
92 ->102 0.15581
93 ->102 -0.42057
94 ->102 0.43967
95 ->103 0.11209
98 ->103 0.14538
99 ->104 -0.11674

Excited State 20: Singlet-A 5.2637 eV 235.55 nm f=0.0338 <S**2>=0.000
93 ->102 0.11462
94 ->102 -0.14546
95 ->103 0.37557
96 ->103 0.10681
97 ->103 0.12511
98 ->104 -0.20472
99 ->104 -0.35428
100 ->104 -0.17980
101 ->104 -0.10069
101 ->108 -0.14644

Excited State 21: Singlet-A 5.3309 eV 232.58 nm f=0.0064 <S**2>=0.000
96 ->103 0.46039
96 ->104 0.26526
96 ->105 -0.17044
96 ->107 0.11705

96 ->108 -0.13263
97 ->103 0.25673
97 ->104 0.11650
100 ->104 0.12147

Excited State 22: Singlet-A 5.3581 eV 231.40 nm f=0.0375 <S**2>=0.000
96 ->103 0.27328
96 ->104 0.12480
97 ->103 -0.25626
97 ->105 -0.25710
98 ->103 -0.12963
98 ->106 -0.22508
99 ->103 -0.12007
100 ->104 -0.19419
100 ->105 -0.16636
100 ->106 0.11570

Excited State 23: Singlet-A 5.3775 eV 230.56 nm f=0.0512 <S**2>=0.000
94 ->103 -0.19117
97 ->103 -0.16422
98 ->103 0.57836
99 ->105 0.15115

Excited State 24: Singlet-A 5.4444 eV 227.73 nm f=0.0003 <S**2>=0.000
92 ->102 0.10479
100 ->105 -0.20481
101 ->110 -0.20009
101 ->111 0.53985
101 ->112 -0.17344

Excited State 25: Singlet-A 5.4531 eV 227.37 nm f=0.0205 <S**2>=0.000
91 ->102 -0.11947
92 ->102 0.19867
97 ->103 -0.11955
99 ->106 0.11452
99 ->110 -0.10187
100 ->104 0.22854
100 ->105 0.32211
101 ->110 0.27450

101 ->111 0.33081

Excited State 26: Singlet-A 5.4681 eV 226.74 nm f=0.0092 <S**2>=0.000
91 ->102 -0.36820
92 ->102 0.50557
101 ->111 -0.24923

Excited State 27: Singlet-A 5.5032 eV 225.30 nm f=0.0061 <S**2>=0.000
99 ->105 0.10254
100 ->104 -0.27277
101 ->112 0.57902
101 ->113 -0.12032

Excited State 28: Singlet-A 5.5123 eV 224.92 nm f=0.0153 <S**2>=0.000
91 ->102 0.16063
95 ->103 0.18429
98 ->104 -0.22113
99 ->104 0.18740
99 ->105 0.18403
100 ->104 0.38448
100 ->105 -0.22876
101 ->112 0.21949

Excited State 29: Singlet-A 5.5384 eV 223.86 nm f=0.1066 <S**2>=0.000
91 ->102 0.29595
92 ->102 0.20230
95 ->104 -0.10271
99 ->104 0.15133
99 ->105 0.31654
100 ->104 -0.22493
100 ->105 0.25742
101 ->112 -0.14791

Excited State 30: Singlet-A 5.5623 eV 222.90 nm f=0.0651 <S**2>=0.000
91 ->102 -0.22759
93 ->102 -0.11059
94 ->103 0.16818
97 ->103 0.25315
98 ->104 0.16804

99 ->105	0.43148				
100 ->104	0.13891				
101 ->112	-0.11321				
Excited State 31:	Singlet-A	5.6025 eV	221.30 nm	f=0.0187	<S**2>=0.000
91 ->102	-0.25837				
92 ->102	-0.18461				
93 ->102	-0.12942				
95 ->103	0.19736				
97 ->103	-0.10228				
98 ->104	-0.19695				
99 ->104	0.35367				
100 ->104	-0.10209				
100 ->105	0.18628				
101 ->113	-0.20703				
Excited State 32:	Singlet-A	5.6267 eV	220.35 nm	f=0.0094	<S**2>=0.000
99 ->104	0.15739				
101 ->113	0.60360				
101 ->114	0.10910				
101 ->115	-0.14605				
Excited State 33:	Singlet-A	5.6601 eV	219.05 nm	f=0.0136	<S**2>=0.000
97 ->103	0.21903				
97 ->105	-0.14800				
99 ->104	0.14045				
100 ->106	0.10610				
101 ->109	-0.10178				
101 ->114	0.54832				
Excited State 34:	Singlet-A	5.6677 eV	218.76 nm	f=0.0595	<S**2>=0.000
96 ->103	0.12590				
97 ->103	-0.32422				
97 ->105	0.22364				
98 ->106	0.11133				
99 ->104	-0.17141				
99 ->105	0.15472				
99 ->106	-0.10688				
100 ->106	-0.17780				

101 ->114 0.35782

Excited State 35: Singlet-A 5.7158 eV 216.92 nm f=0.0071 <S**2>=0.000
90 ->102 0.65662
92 ->102 -0.10407
98 ->105 0.12276

Excited State 36: Singlet-A 5.7349 eV 216.19 nm f=0.1328 <S**2>=0.000
91 ->102 0.10171
92 ->102 0.10518
93 ->103 -0.10723
94 ->103 0.35462
94 ->104 -0.15944
95 ->103 0.24105
96 ->103 -0.11456
96 ->104 0.24780
96 ->105 -0.11325
97 ->103 -0.15906
98 ->103 0.12451
98 ->104 0.19399
98 ->105 0.12059
100 ->106 -0.11093

Excited State 37: Singlet-A 5.7603 eV 215.24 nm f=0.0675 <S**2>=0.000
94 ->104 0.10269
96 ->103 -0.32369
96 ->104 0.35871
96 ->105 -0.22887
97 ->104 0.16223
98 ->104 -0.15601
98 ->105 -0.26577

Excited State 38: Singlet-A 5.7839 eV 214.36 nm f=0.0099 <S**2>=0.000
90 ->102 -0.10748
94 ->103 -0.27551
94 ->105 -0.10805
95 ->104 -0.13690
96 ->103 -0.16335
96 ->104 0.12569

97 ->105	-0.18525					
98 ->105	0.47530					
99 ->106	0.10934					
Excited State 39:	Singlet-A	5.8383 eV	212.36 nm	f=0.0016	<S**2>=0.000	
101 ->113	0.16644					
101 ->115	0.66215					
Excited State 40:	Singlet-A	5.8579 eV	211.65 nm	f=0.0705	<S**2>=0.000	
94 ->103	0.12885					
97 ->105	0.13908					
98 ->104	-0.10673					
98 ->105	0.18268					
98 ->106	0.10868					
99 ->105	0.11947					
100 ->106	0.58089					

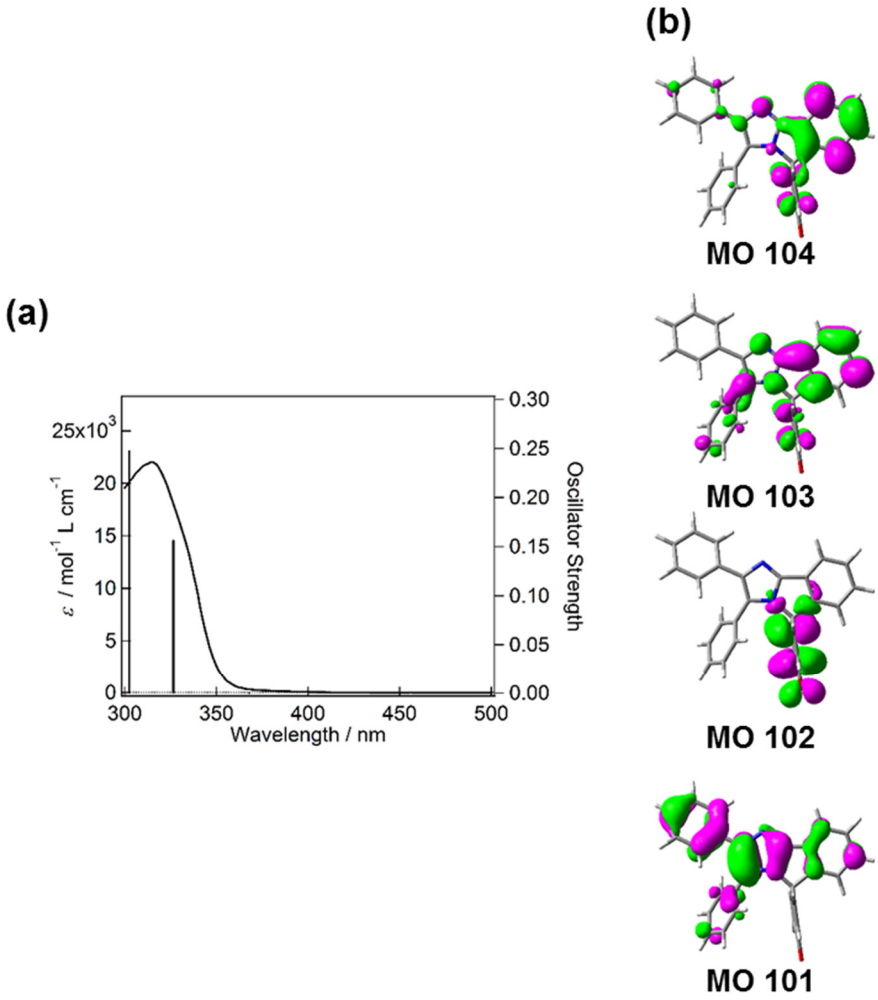


Fig. S50. (a) UV–vis absorption spectrum of the closed-ring isomer of **PIC1** in benzene. The calculated spectrum

(MPW1PW91/6-31+G(d,p)//M052X/6-31+G(d,p) level of the theory) is shown by the black lines. (b) The relevant molecular orbitals were calculated at the M052X/6-31+G(d,p) level of the theory.

Table S16. Standard Orientation of the Optimized Geometry for the Biradical Form of **PIC1**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	1.5163320	-2.1690790	-0.1726410
2	C	2.8216140	-1.6174260	-0.1627760
3	C	0.3164620	-1.3540240	-0.1367430
4	N	-0.9123320	-1.8958650	0.1243840
5	C	-1.7487770	-0.8787110	0.0225400
6	C	-0.9620210	0.3353650	-0.2920530
7	N	0.3064890	-0.0234810	-0.4127280
8	C	-3.1946840	-1.0644070	0.1549500
9	C	-1.3659570	1.7339420	-0.4091510
10	C	-4.1049130	-0.3341420	-0.6212250
11	C	-5.4700840	-0.5752420	-0.5081590
12	C	-5.9396200	-1.5401160	0.3815100
13	C	-5.0377520	-2.2774250	1.1488560
14	C	-3.6725840	-2.0495620	1.0306450
15	C	-0.5613630	2.6027700	-1.1637970
16	C	-0.8842650	3.9490960	-1.2600740
17	C	-2.0022940	4.4507340	-0.5922410
18	C	-2.7918390	3.5997090	0.1788260
19	C	-2.4788950	2.2478740	0.2723510
20	C	3.1132370	-0.2095420	0.1572520
21	C	4.0065790	0.5268860	-0.6574560
22	C	4.3319490	1.8218330	-0.3516240
23	C	3.7977340	2.4660160	0.8369700
24	C	2.9138510	1.6722450	1.6740920
25	C	2.5841510	0.3938520	1.3316590
26	O	4.0903330	3.6432830	1.1219950
27	C	3.9081250	-2.4715270	-0.3955590
28	C	3.7287590	-3.8369960	-0.5769110
29	C	2.4450950	-4.3852610	-0.5259610
30	C	1.3526990	-3.5575030	-0.3268230
31	H	-3.7425400	0.4041500	-1.3252780
32	H	-6.1661160	-0.0138100	-1.1186490

33	H	-7.0034210	-1.7215840	0.4720650
34	H	-5.3999250	-3.0315990	1.8362670
35	H	-2.9588780	-2.6215660	1.6092180
36	H	0.3126680	2.2007130	-1.6595350
37	H	-0.2605050	4.6107670	-1.8477040
38	H	-2.2493680	5.5026730	-0.6636410
39	H	-3.6468440	3.9901200	0.7164030
40	H	-3.0812300	1.5984760	0.8938010
41	H	4.3992260	0.0614170	-1.5536070
42	H	1.9218740	-0.1888260	1.9602210
43	H	4.9086830	-2.0567420	-0.3798710
44	H	4.5888440	-4.4751160	-0.7368100
45	H	2.3002670	-5.4503190	-0.6543910
46	H	0.3458410	-3.9525790	-0.3182810
47	H	2.5318460	2.1436910	2.5700370
48	H	4.9885750	2.4131440	-0.9765380

SCF Done: E(UM052X) = -1224.34544920 A.U.
S**2 before annihilation 1.0121, after 0.6048

Zero-point correction = 0.378684 (Hartree/Particle)
Thermal correction to Energy = 0.401682
Thermal correction to Enthalpy = 0.402626
Thermal correction to Gibbs Free Energy = 0.322648
Sum of electronic and zero-point Energies = -1223.966766
Sum of electronic and thermal Energies = -1223.943768
Sum of electronic and thermal Enthalpies = -1223.942823
Sum of electronic and thermal Free Energies = -1224.022801

Low frequencies --- -13.6244 -7.1678 -0.0005 -0.0001 0.0007 2.9836
Low frequencies --- 10.7577 25.2558 25.7381

The Results for the TDDFT calculation

Excited State 1: 2.375-A 1.2996 eV 954.05 nm f=0.0000 <S**2>=1.161
100B ->102B 0.96867
100B ->104B 0.10579
100B ->105B -0.10291
This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1224.12867018

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 1.462-A 1.4746 eV 840.78 nm f=0.0283 <S**2>=0.284

101A ->102A	0.96159
101B ->102B	-0.20598

Excited State 3: 1.300-A 1.8499 eV 670.22 nm f=0.0477 <S**2>=0.172

100A ->102A	-0.11212
101A ->102A	0.19078
101B ->102B	0.96016

Excited State 4: 2.371-A 2.0300 eV 610.75 nm f=0.0342 <S**2>=1.156

90A ->102A	-0.16291
91A ->102A	-0.18021
100A ->102A	0.91850
101B ->102B	0.10603
101B ->103B	0.14397

Excited State 5: 2.326-A 2.3687 eV 523.42 nm f=0.0075 <S**2>=1.103

93A ->102A	-0.45423
94A ->102A	0.18649
95A ->102A	-0.42396
96A ->102A	0.14122
97A ->102A	0.52729
98A ->102A	-0.44605
101A ->102A	0.13589
98B ->102B	-0.11013

Excited State 6: 2.317-A 2.4727 eV 501.41 nm f=0.0061 <S**2>=1.092

93A ->102A	-0.14403
97A ->102A	0.11995
101A ->107A	0.14912
93B ->102B	0.22709
95B ->102B	-0.10879
96B ->102B	0.58510
98B ->102B	0.49390
99B ->102B	-0.49668

Excited State 7:	2.408-A	2.5543 eV	485.40 nm	f=0.1272	<S**2>=1.200
93A ->102A	-0.19351				
95A ->102A	-0.28163				
97A ->102A	0.30015				
98A ->102A	0.82483				
101B ->104B	0.18815				

Excited State 8:	2.377-A	2.6692 eV	464.50 nm	f=0.0129	<S**2>=1.162
93A ->102A	0.30911				
94A ->102A	-0.14820				
95A ->102A	0.43186				
96A ->102A	-0.28863				
97A ->102A	0.74291				
101B ->104B	-0.10250				

Excited State 9:	2.303-A	2.7747 eV	446.84 nm	f=0.0002	<S**2>=1.076
96A ->102A	-0.10790				
99A ->102A	0.97844				

Excited State 10:	2.364-A	2.8245 eV	438.96 nm	f=0.0008	<S**2>=1.147
90A ->102A	-0.10463				
91A ->102A	0.21752				
94A ->102A	-0.11027				
95A ->102A	0.39441				
96A ->102A	0.84163				
99A ->102A	0.13642				

Excited State 11:	2.373-A	2.9184 eV	424.84 nm	f=0.0012	<S**2>=1.157
90A ->102A	-0.10792				
91A ->102A	0.58918				
92A ->102A	-0.15547				
93A ->102A	-0.50941				
94A ->102A	-0.34075				
95A ->102A	0.14679				
96A ->102A	-0.33091				
97A ->102A	-0.12458				
100A ->102A	0.13507				
95B ->102B	-0.10612				

Excited State 12: 2.447-A 2.9331 eV 422.71 nm f=0.0489 <S**2>=1.247

91A ->102A	0.26208
92A ->102A	-0.12152
93A ->102A	-0.11979
94A ->102A	0.60905
95A ->102A	0.23577
96A ->102A	-0.10714
101A ->105A	-0.13298
92B ->102B	0.11637
93B ->102B	-0.12934
95B ->102B	0.36525
96B ->102B	-0.29826
98B ->102B	0.15033
99B ->102B	-0.26113

Excited State 13: 2.272-A 2.9929 eV 414.27 nm f=0.0219 <S**2>=1.040

94A ->102A	0.59869
95A ->102A	0.28729
101A ->103A	0.16057
101A ->105A	0.10054
93B ->102B	0.10863
95B ->102B	-0.34269
96B ->102B	0.32511
98B ->102B	-0.14237
99B ->102B	0.38442
101B ->104B	0.12330

Excited State 14: 2.336-A 3.1847 eV 389.31 nm f=0.0009 <S**2>=1.114

90B ->102B	-0.10828
95B ->102B	0.33847
96B ->102B	0.17523
98B ->102B	0.51646
99B ->102B	0.67824

Excited State 15: 2.762-A 3.2791 eV 378.11 nm f=0.0051 <S**2>=1.658

91A ->102A	0.27208
92A ->102A	0.64443
94A ->105A	0.11487
95A ->102A	-0.10032

97A ->108A 0.10149
98A ->103A 0.12987
100A ->103A -0.11775
93B ->102B -0.15180
95B ->102B 0.12453
95B ->105B -0.12673
96B ->104B -0.15462
98B ->104B 0.11798
99B ->103B 0.19696
101B ->103B 0.10019
101B ->104B 0.26446
101B ->108B -0.22590

Excited State 16: 2.399-A 3.3216 eV 373.27 nm f=0.0027 <S**2>=1.189
91A ->102A -0.24910
92A ->102A 0.23523
93A ->102A -0.28876
95A ->102A 0.18897
92B ->102B -0.10699
93B ->102B 0.35808
95B ->102B 0.51908
96B ->102B 0.19043
97B ->102B 0.18361
98B ->102B -0.42123

Excited State 17: 2.901-A 3.3432 eV 370.86 nm f=0.0452 <S**2>=1.854
90A ->102A 0.31737
92A ->102A -0.10053
96A ->108A -0.15075
97A ->106A -0.17294
98A ->103A 0.10007
98A ->104A 0.17173
100A ->102A -0.11898
100A ->109A 0.15225
101A ->103A 0.10687
94B ->107B 0.14574
95B ->102B -0.11697
96B ->102B -0.10229
96B ->103B 0.10222

97B ->106B 0.18313
98B ->103B -0.14418
99B ->102B -0.10588
99B ->108B -0.14417
101B ->103B 0.67197

Excited State 18: 2.271-A 3.3603 eV 368.96 nm f=0.0008 <S**2>=1.039
91A ->102A 0.50216
92A ->102A -0.18227
93A ->102A 0.46329
94A ->102A 0.10430
95A ->102A -0.37860
93B ->102B 0.14635
95B ->102B 0.24694
96B ->102B 0.33849
98B ->102B -0.27877

Excited State 19: 2.367-A 3.4416 eV 360.26 nm f=0.0025 <S**2>=1.150
91A ->102A 0.13613
92A ->102A 0.14455
93B ->102B 0.28375
94B ->102B -0.22174
95B ->102B -0.19217
96B ->102B -0.24412
97B ->102B 0.77335
98B ->102B 0.15301
101B ->104B -0.13871

Excited State 20: 2.474-A 3.5538 eV 348.88 nm f=0.0684 <S**2>=1.281
91A ->102A -0.10384
92A ->102A -0.14522
98A ->102A -0.13283
101A ->103A -0.11745
89B ->102B 0.10599
92B ->102B 0.18396
93B ->102B -0.44710
94B ->102B -0.19334
96B ->102B 0.30292
97B ->102B 0.50154

98B ->102B -0.19800
101B ->104B 0.35708

Excited State 21: 2.681-A 3.6059 eV 343.83 nm f=0.0965 <S**2>=1.547
90A ->102A 0.58368
91A ->102A 0.11190
92A ->102A 0.21156
96A ->106A -0.12960
97A ->108A -0.12840
98A ->102A -0.13969
100A ->102A 0.17252
100A ->103A 0.14607
100A ->104A 0.13605
101A ->103A -0.15159
93B ->102B 0.29730
94B ->106B 0.13379
96B ->102B -0.14605
97B ->107B 0.14119
99B ->103B -0.16877
101B ->103B -0.27165
101B ->104B 0.25360

Excited State 22: 2.654-A 3.6182 eV 342.67 nm f=0.1501 <S**2>=1.511
90A ->102A 0.62990
92A ->102A -0.14765
93A ->102A -0.10826
96A ->106A 0.13403
97A ->108A 0.12616
98A ->102A 0.18273
100A ->102A 0.14606
100A ->103A -0.11832
100A ->104A -0.16041
93B ->102B -0.26239
94B ->106B -0.13854
97B ->107B -0.12667
99B ->103B 0.16907
101B ->103B -0.19233
101B ->104B -0.33797

Excited State 23: 2.611-A 3.7965 eV 326.57 nm f=0.0639 <S**2>=1.455

92A ->102A	-0.39408
96A ->106A	0.10343
98A ->104A	-0.10179
100A ->103A	-0.13221
100A ->104A	-0.11806
89B ->102B	0.10143
93B ->102B	0.27039
94B ->102B	0.59184
94B ->106B	-0.12448
95B ->105B	-0.11593
96B ->102B	-0.14285
97B ->102B	0.13845
97B ->107B	-0.11498
98B ->104B	0.10435
99B ->103B	0.15836
101B ->104B	0.31133

Excited State 24: 2.476-A 3.8198 eV 324.58 nm f=0.0914 <S**2>=1.283

92A ->102A	0.31545
92B ->102B	0.13092
93B ->102B	-0.23651
94B ->102B	0.63766
95B ->102B	-0.29353
96B ->102B	0.11011
97B ->102B	0.19006
98B ->102B	-0.14952
99B ->103B	-0.11252
101B ->104B	-0.32445

Excited State 25: 2.380-A 3.8982 eV 318.05 nm f=0.0913 <S**2>=1.166

101A ->103A	0.42373
101A ->104A	-0.22698
101A ->105A	0.24277
101A ->109A	0.10333
101A ->112A	0.11726
89B ->102B	-0.36196
90B ->102B	0.21792
91B ->102B	-0.12094

92B ->102B -0.31777
93B ->102B -0.27340
94B ->102B 0.32138
95B ->102B 0.21254
97B ->102B 0.15822
98B ->102B 0.15132

Excited State 26: 2.962-A 4.0068 eV 309.43 nm f=0.0798 <S**2>=1.943
94A ->103A -0.11011
94A ->105A -0.17024
96A ->108A 0.16601
97A ->106A 0.21669
98A ->103A -0.13714
100A ->104A -0.11363
101A ->103A -0.31291
101A ->105A -0.11078
89B ->102B -0.18237
90B ->102B 0.12847
92B ->102B -0.23363
93B ->102B -0.17316
94B ->107B -0.16428
95B ->105B 0.18581
97B ->106B -0.18986
98B ->103B 0.11254
99B ->104B 0.12601
101B ->103B 0.41639
101B ->104B 0.25996

Excited State 27: 3.074-A 4.0148 eV 308.82 nm f=0.0118 <S**2>=2.113
90A ->102A 0.13111
94A ->105A 0.21227
96A ->108A 0.17587
97A ->106A 0.22070
97A ->108A -0.12217
98A ->104A -0.15282
100A ->103A 0.11122
101A ->103A 0.12319
101A ->105A 0.25485
89B ->102B 0.15277

90B ->102B -0.10603
92B ->102B 0.18910
93B ->102B 0.11474
94B ->107B -0.16686
95B ->102B 0.11846
95B ->105B -0.23476
97B ->106B -0.21056
97B ->107B 0.11882
101B ->103B 0.38226
101B ->104B -0.27860
101B ->105B 0.18166

Excited State 28: 2.670-A 4.1454 eV 299.09 nm f=0.0233 <S**2>=1.532
94A ->102A 0.12637
94A ->104A 0.11131
94A ->105A 0.14233
101A ->103A -0.39496
101A ->104A 0.44407
101A ->105A 0.35986
89B ->102B -0.10508
92B ->102B -0.24286
93B ->102B -0.10585
95B ->104B -0.10711
95B ->105B -0.17456
101B ->104B -0.23087
101B ->105B 0.33644
101B ->106B 0.10215

Excited State 29: 2.715-A 4.2784 eV 289.79 nm f=0.0148 <S**2>=1.593
97A ->103A -0.14041
97A ->104A -0.14653
98A ->106A 0.14263
100A ->108A 0.13836
98B ->106B -0.11364
99B ->107B -0.16056
101B ->105B -0.18615
101B ->106B 0.84507

Excited State 30: 2.600-A 4.3192 eV 287.06 nm f=0.0041 <S**2>=1.441

93A ->107A 0.11874
95A ->107A -0.17077
101A ->105A 0.16842
101A ->107A -0.14989
101A ->111A -0.10289
101A ->112A 0.14982
89B ->102B -0.32761
90B ->102B 0.19586
92B ->102B 0.67216
93B ->102B 0.10316
96B ->109B 0.11858
101B ->105B 0.13580
101B ->106B 0.12046

Excited State 31: 2.579-A 4.3319 eV 286.21 nm f=0.0200 <S**2>=1.413
95A ->107A 0.12577
98A ->105A -0.11464
101A ->103A 0.13717
101A ->104A -0.33752
101A ->105A -0.31066
96B ->105B -0.10491
98B ->105B 0.12275
101B ->105B 0.73646
101B ->106B 0.14214

Excited State 32: 2.555-A 4.3557 eV 284.65 nm f=0.0211 <S**2>=1.383
95A ->107A -0.16792
101A ->103A -0.46497
101A ->104A -0.52367
101A ->107A 0.54148
96B ->109B 0.12708

Excited State 33: 3.137-A 4.4185 eV 280.60 nm f=0.0063 <S**2>=2.210
89A ->102A -0.10961
93A ->107A -0.24084
95A ->103A -0.12052
95A ->107A 0.36388
101A ->103A -0.15407
101A ->104A -0.22528

89B ->102B -0.17823
90B ->102B 0.15910
91B ->102B -0.16464
92B ->102B 0.27734
93B ->109B -0.14133
96B ->104B -0.10132
96B ->109B -0.27445
98B ->102B 0.11806
98B ->103B 0.10238
98B ->109B -0.20492
99B ->103B -0.12182
99B ->104B 0.11799
99B ->109B 0.16410
101B ->105B -0.24175

Excited State 34: 3.396-A 4.4674 eV 277.53 nm f=0.0295 <S**2>=2.633
96A ->106A -0.29919
97A ->108A -0.28809
98A ->104A -0.10404
98A ->108A -0.11664
100A ->103A -0.23315
100A ->104A -0.23261
101A ->104A 0.16394
101A ->105A -0.10506
101A ->107A 0.21197
89B ->102B -0.13261
92B ->102B 0.14843
94B ->106B 0.28901
97B ->107B 0.29770
99B ->103B 0.39650
101B ->107B -0.12886

Excited State 35: 3.115-A 4.4938 eV 275.90 nm f=0.0054 <S**2>=2.175
96A ->103A -0.17025
96A ->104A -0.20265
97A ->103A 0.15198
97A ->108A -0.11601
97A ->109A -0.11943
98A ->108A 0.12466

100A ->106A	0.28703
94B ->103B	0.18097
96B ->107B	0.11992
98B ->106B	-0.14756
98B ->107B	-0.12043
99B ->106B	-0.28002
101B ->107B	0.64782
101B ->108B	-0.12092

Excited State 36: 2.648-A 4.4984 eV 275.62 nm f=0.0373 <S**2>=1.503

95A ->107A	0.11988
96A ->106A	0.11236
98A ->104A	0.11147
100A ->104A	0.10127
101A ->103A	0.31530
101A ->104A	0.27995
101A ->107A	0.71262
92B ->102B	0.18305
94B ->106B	-0.10659
96B ->109B	-0.11408
98B ->104B	-0.10140

Excited State 37: 2.749-A 4.5787 eV 270.78 nm f=0.0493 <S**2>=1.640

89A ->102A	0.12699
92A ->104A	0.10932
98A ->103A	-0.15055
100A ->104A	-0.15509
101A ->103A	0.10589
101A ->104A	-0.14027
101A ->105A	0.21802
89B ->102B	0.11677
91B ->102B	0.69274
91B ->104B	-0.12876
96B ->104B	0.10799
98B ->103B	0.16967
99B ->104B	0.20975
101B ->104B	0.13853

Excited State 38: 3.262-A 4.6217 eV 268.27 nm f=0.0018 <S**2>=2.411

96A ->109A	-0.12106
97A ->103A	-0.21713
97A ->104A	-0.26428
100A ->103A	-0.18195
100A ->104A	0.14669
101A ->103A	-0.14671
101A ->104A	-0.20755
101A ->105A	0.11937
101A ->107A	-0.14191
91B ->102B	0.23923
94B ->104B	0.11387
94B ->108B	0.16176
96B ->103B	0.15108
97B ->103B	0.44531
98B ->103B	-0.22650
98B ->104B	-0.11305
99B ->103B	0.12031
99B ->104B	-0.27748
101B ->106B	-0.25196

Excited State 39: 3.315-A 4.6632 eV 265.88 nm f=0.0005 <S**2>=2.497

96A ->108A	-0.12677
96A ->109A	-0.10573
97A ->103A	-0.17201
97A ->104A	-0.12127
97A ->106A	-0.21008
98A ->103A	-0.21794
98A ->104A	-0.17407
100A ->103A	0.15646
100A ->104A	-0.14739
100A ->108A	0.10138
101A ->103A	0.10713
101A ->104A	0.11298
89B ->102B	0.11911
91B ->102B	-0.33619
94B ->104B	0.15968
94B ->107B	0.13866
94B ->108B	0.13756
97B ->103B	0.45267

97B ->105B -0.10391
97B ->106B 0.17465
99B ->104B 0.28438
101B ->106B -0.13508

Excited State 40: 2.923-A 4.6927 eV 264.21 nm f=0.0258 <S**2>=1.886
89A ->102A -0.15859
92A ->103A 0.11528
96A ->104A -0.15190
98A ->104A -0.19426
100A ->103A 0.14314
101A ->104A 0.12538
101A ->105A -0.40354
90B ->102B 0.25094
91B ->102B 0.44031
91B ->104B 0.13860
94B ->103B 0.14993
96B ->104B -0.16398
97B ->104B 0.14544
98B ->103B -0.10372
98B ->104B 0.16579
99B ->103B -0.21437
101B ->104B -0.14237
101B ->105B -0.11536

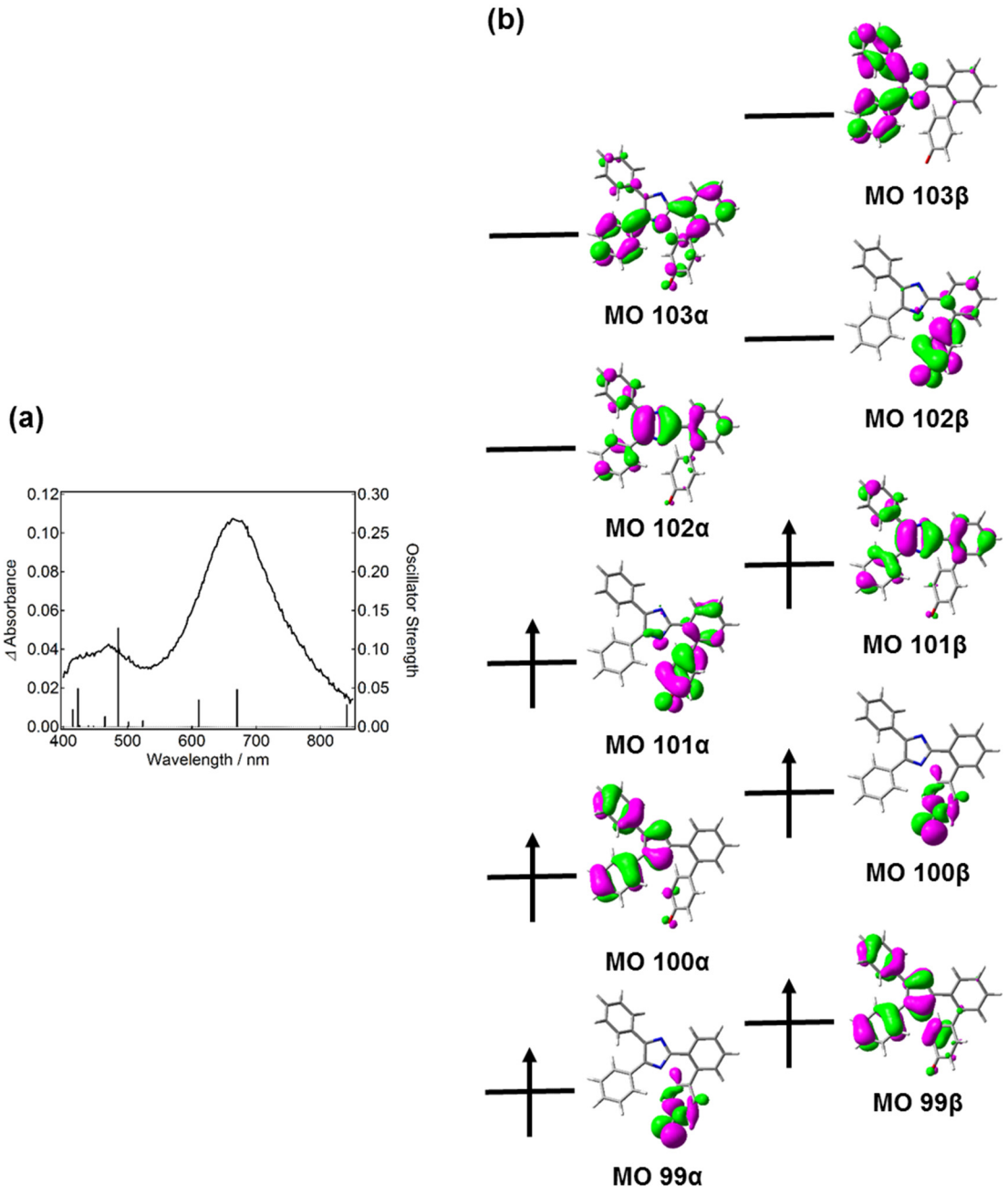


Fig. S51. (a) The transient absorption spectrum of **PIC1** in benzene (excitation wavelength, 355 nm; pulse width, 5ns; power 4 mJ/pulse). The calculated spectrum (UMPW1PW91/6-31+G(d,p)//UM052X/6-31+G(d,p) level of the theory) of the biradical form of the open-ring isomer of **PIC1** is shown by the black lines. (b) The relevant molecular orbitals were calculated at the UM052X/6-31+G(d,p) level of the theory.

Table S17. Standard Orientation of the Optimized Geometry for the Quinoid Form of **PIC1**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	1.5673920	-2.0691660	-0.1734190
2	C	2.8636410	-1.4375620	-0.3405330

3	C	0.3858380	-1.3246520	-0.1471510
4	N	-0.8362530	-1.8925450	0.1617890
5	C	-1.6936410	-0.9078020	0.0605720
6	C	-0.9606710	0.3174840	-0.3411560
7	N	0.3034580	0.0120530	-0.4879740
8	C	-3.1338020	-1.1179840	0.2595050
9	C	-1.4571310	1.6820960	-0.5580000
10	C	-4.0859130	-0.4578340	-0.5269960
11	C	-5.4409550	-0.7177100	-0.3480310
12	C	-5.8581900	-1.6296490	0.6196400
13	C	-4.9137090	-2.2948910	1.4006950
14	C	-3.5583350	-2.0478480	1.2170000
15	C	-0.8187360	2.4969120	-1.5020340
16	C	-1.2386920	3.8075280	-1.6927330
17	C	-2.2897650	4.3234110	-0.9346330
18	C	-2.9171540	3.5233730	0.0181840
19	C	-2.5060410	2.2075830	0.2066800
20	C	3.1426080	-0.1494280	0.1405970
21	C	4.2405970	0.6236000	-0.4055960
22	C	4.5392230	1.8537870	0.0605230
23	C	3.8144380	2.4429040	1.2017660
24	C	2.7538820	1.6180680	1.7902240
25	C	2.4308340	0.4150880	1.2719790
26	O	4.1069840	3.5520430	1.6376220
27	C	3.9113970	-2.2484510	-0.9011910
28	C	3.7610360	-3.5959820	-1.0228330
29	C	2.5431400	-4.2360350	-0.6279560
30	C	1.4802330	-3.4992240	-0.2048760
31	H	-3.7658940	0.2425660	-1.2879180
32	H	-6.1701410	-0.2104440	-0.9672540
33	H	-6.9139620	-1.8249640	0.7611270
34	H	-5.2342090	-3.0072980	2.1507050
35	H	-2.8130640	-2.5648590	1.8077000
36	H	0.0049150	2.0867320	-2.0721420
37	H	-0.7436130	4.4294540	-2.4280060
38	H	-2.6129720	5.3465940	-1.0809190
39	H	-3.7222620	3.9251330	0.6206140
40	H	-2.9858180	1.5947250	0.9592550
41	H	4.7722010	0.2387540	-1.2656920

42	H	1.6682040	-0.1884620	1.7444190
43	H	4.8739890	-1.8028710	-1.1083040
44	H	4.5869090	-4.1988380	-1.3784840
45	H	2.4614750	-5.3132280	-0.7013950
46	H	0.5253250	-3.9511680	0.0252140
47	H	2.2601900	2.0141420	2.6679790
48	H	5.3132640	2.4654400	-0.3859490

SCF Done: E(M052X) = - 1224.33091697 A.U.

Zero-point correction = 0.379677 (Hartree/Particle)
Thermal correction to Energy = 0.402614
Thermal correction to Enthalpy = 0.403558
Thermal correction to Gibbs Free Energy = 0.324208
Sum of electronic and zero-point Energies = -1223.951240
Sum of electronic and thermal Energies = -1223.928303
Sum of electronic and thermal Enthalpies = -1223.927359
Sum of electronic and thermal Free Energies = -1224.006709

Low frequencies --- -15.6257 -7.8941 -0.0004 0.0004 0.0007 6.4754
Low frequencies --- 13.0248 23.5190 28.1903

The Results for the TDDFT calculation

Excited State 1: Singlet-A 1.7322 eV 715.77 nm f=0.3623 <S**2>=0.000
101 ->102 0.71305
101 <-102 -0.18182
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1224.10313650
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.0429 eV 606.91 nm f=0.0105 <S**2>=0.000
100 ->102 0.68150
100 ->103 -0.10664

Excited State 3: Singlet-A 2.5081 eV 494.34 nm f=0.0598 <S**2>=0.000
95 ->102 -0.17254
97 ->102 -0.10756

99 ->102	0.65445					
100 ->102	0.10130					
Excited State	4:	Singlet-A	2.6378 eV	470.03 nm	f=0.0059	<S**2>=0.000
93 ->102	-0.15454					
95 ->102	0.33580					
97 ->102	0.42549					
98 ->102	-0.35415					
99 ->102	0.19336					
Excited State	5:	Singlet-A	2.8067 eV	441.74 nm	f=0.0283	<S**2>=0.000
97 ->102	0.42101					
98 ->102	0.53956					
101 ->103	-0.14238					
Excited State	6:	Singlet-A	2.9472 eV	420.68 nm	f=0.0182	<S**2>=0.000
95 ->102	0.54024					
97 ->102	-0.31017					
98 ->102	0.16135					
101 ->103	-0.24801					
Excited State	7:	Singlet-A	3.0774 eV	402.88 nm	f=0.0037	<S**2>=0.000
93 ->102	-0.31328					
94 ->102	0.46297					
95 ->102	-0.13952					
96 ->102	0.35574					
101 ->103	-0.17160					
Excited State	8:	Singlet-A	3.0833 eV	402.11 nm	f=0.0062	<S**2>=0.000
93 ->102	0.11275					
94 ->102	-0.31607					
96 ->102	0.58939					
97 ->102	0.10843					
101 ->103	0.14000					
Excited State	9:	Singlet-A	3.2315 eV	383.67 nm	f=0.1068	<S**2>=0.000
93 ->102	0.58246					
94 ->102	0.30810					
101 ->103	-0.15999					

Excited State 10:	Singlet-A	3.5860 eV	345.75 nm	f=0.0137	<S**2>=0.000
90 ->102	-0.12900				
91 ->102	0.27335				
92 ->102	0.62403				
Excited State 11:	Singlet-A	3.7287 eV	332.51 nm	f=0.3987	<S**2>=0.000
91 ->102	0.32603				
92 ->102	-0.11481				
94 ->102	0.19886				
95 ->102	0.14842				
98 ->102	0.19840				
101 ->103	0.48649				
Excited State 12:	Singlet-A	3.9658 eV	312.64 nm	f=0.1030	<S**2>=0.000
101 ->104	0.66046				
101 ->105	0.18312				
Excited State 13:	Singlet-A	4.0644 eV	305.05 nm	f=0.0482	<S**2>=0.000
90 ->102	0.62847				
91 ->102	0.26874				
Excited State 14:	Singlet-A	4.0914 eV	303.04 nm	f=0.0418	<S**2>=0.000
101 ->104	-0.20846				
101 ->105	0.65016				
Excited State 15:	Singlet-A	4.1924 eV	295.74 nm	f=0.4358	<S**2>=0.000
90 ->102	-0.22040				
91 ->102	0.46571				
92 ->102	-0.25276				
94 ->102	-0.16270				
95 ->102	-0.10826				
101 ->103	-0.28268				
101 ->105	-0.11170				
Excited State 16:	Singlet-A	4.3919 eV	282.31 nm	f=0.0121	<S**2>=0.000
100 ->102	0.12461				
100 ->103	0.63360				
100 ->105	0.14123				

Excited State 17:	Singlet-A	4.4838 eV	276.52 nm	f=0.0179	<S**2>=0.000
101 ->106	0.68578				

Excited State 18:	Singlet-A	4.7255 eV	262.38 nm	f=0.0141	<S**2>=0.000
101 ->107	0.65028				
101 ->108	0.12148				
101 ->109	0.17627				

Excited State 19:	Singlet-A	4.7682 eV	260.02 nm	f=0.0207	<S**2>=0.000
89 ->102	0.13215				
95 ->103	-0.21427				
97 ->103	-0.20402				
98 ->103	0.19263				
99 ->103	0.55714				
100 ->103	0.10410				

Excited State 20:	Singlet-A	4.8537 eV	255.44 nm	f=0.0211	<S**2>=0.000
85 ->102	-0.12068				
86 ->102	-0.14013				
87 ->102	-0.15061				
89 ->102	0.42917				
95 ->103	0.10335				
97 ->103	0.19521				
101 ->108	0.36367				

Excited State 21:	Singlet-A	4.8741 eV	254.37 nm	f=0.0500	<S**2>=0.000
85 ->102	0.10251				
86 ->102	0.13175				
87 ->102	0.13590				
89 ->102	-0.33601				
96 ->104	-0.11533				
98 ->103	0.15717				
101 ->108	0.47729				

Excited State 22:	Singlet-A	4.9254 eV	251.72 nm	f=0.0247	<S**2>=0.000
89 ->102	0.12249				
93 ->103	0.11976				
95 ->103	-0.20558				

97 ->103 -0.30659
98 ->103 0.39670
99 ->103 -0.38348

Excited State 23: Singlet-A 5.0354 eV 246.22 nm f=0.0136 <S**2>=0.000
97 ->103 -0.13996
98 ->103 -0.10547
99 ->104 -0.10348
101 ->107 -0.14798
101 ->109 0.60108
101 ->110 -0.13782

Excited State 24: Singlet-A 5.0713 eV 244.48 nm f=0.0033 <S**2>=0.000
97 ->103 -0.27935
98 ->103 -0.32233
101 ->108 0.20733
101 ->110 0.45566

Excited State 25: Singlet-A 5.0900 eV 243.59 nm f=0.0068 <S**2>=0.000
97 ->103 0.27517
98 ->103 0.28357
99 ->104 -0.10630
101 ->108 -0.19018
101 ->109 0.19697
101 ->110 0.47146

Excited State 26: Singlet-A 5.1593 eV 240.31 nm f=0.0200 <S**2>=0.000
85 ->102 0.19363
86 ->102 0.31830
87 ->102 0.32997
88 ->102 0.16551
89 ->102 0.24783
94 ->103 0.17845
101 ->109 -0.11196
101 ->110 0.12818
101 ->111 -0.10305
101 ->115 -0.10903

Excited State 27: Singlet-A 5.2374 eV 236.73 nm f=0.0523 <S**2>=0.000

88 ->102	-0.34667
93 ->103	-0.10425
94 ->103	-0.13511
95 ->103	0.38965
96 ->103	0.20414
97 ->103	-0.19385
97 ->104	-0.14779
98 ->103	0.12783
101 ->111	-0.10062

Excited State 28: Singlet-A 5.2491 eV 236.20 nm f=0.0546 <S**2>=0.000

83 ->102	0.13217
85 ->102	-0.13359
88 ->102	0.44297
94 ->103	-0.17637
95 ->103	0.30872
97 ->103	-0.16386
99 ->104	-0.17224
101 ->111	0.13572

Excited State 29: Singlet-A 5.2636 eV 235.55 nm f=0.0100 <S**2>=0.000

88 ->102	-0.23306
95 ->103	0.15607
96 ->103	-0.29345
97 ->103	-0.13282
97 ->104	0.33118
98 ->106	0.15170
99 ->108	0.12177
100 ->105	0.10443
101 ->111	0.24340

Excited State 30: Singlet-A 5.2806 eV 234.79 nm f=0.0002 <S**2>=0.000

87 ->102	-0.11335
100 ->103	-0.13390
100 ->104	0.17204
100 ->105	0.53419
100 ->107	-0.25577
100 ->109	-0.14818

Excited State 31:	Singlet-A	5.3100 eV	233.49 nm	f=0.0143	<S**2>=0.000
94 ->103	0.11715				
96 ->103	0.17668				
97 ->104	-0.15279				
99 ->104	0.10857				
101 ->111	0.57353				
101 ->113	-0.15036				

Excited State 32:	Singlet-A	5.3266 eV	232.76 nm	f=0.0992	<S**2>=0.000
93 ->103	-0.13200				
94 ->103	-0.28207				
98 ->104	0.26075				
98 ->105	0.13679				
99 ->104	0.43356				
100 ->104	0.13909				

Excited State 33:	Singlet-A	5.3573 eV	231.43 nm	f=0.0070	<S**2>=0.000
83 ->102	-0.12879				
84 ->102	-0.14543				
85 ->102	0.18029				
87 ->102	-0.24766				
88 ->102	0.20553				
89 ->102	-0.13235				
93 ->103	-0.16396				
94 ->103	0.33664				
95 ->103	0.10553				
98 ->103	0.14065				
98 ->105	-0.10469				
99 ->104	0.17889				

Excited State 34:	Singlet-A	5.3882 eV	230.10 nm	f=0.0095	<S**2>=0.000
83 ->102	-0.28993				
84 ->102	-0.23582				
85 ->102	0.34162				
86 ->102	-0.20181				
88 ->102	0.16100				
94 ->103	-0.18769				
96 ->103	0.12175				
99 ->104	-0.14116				

Excited State 35:	Singlet-A	5.4139 eV	229.01 nm	f=0.0246	<S**2>=0.000
85 ->102	-0.10077				
93 ->103	-0.10841				
95 ->103	-0.10612				
96 ->103	0.50201				
97 ->104	0.28743				
97 ->105	-0.11506				
98 ->104	0.15538				
98 ->106	0.11520				
99 ->104	-0.10268				

Excited State 36:	Singlet-A	5.4174 eV	228.86 nm	f=0.0008	<S**2>=0.000
85 ->102	-0.15914				
86 ->102	-0.36336				
87 ->102	0.42122				
88 ->102	0.10402				
93 ->103	-0.21569				
96 ->103	-0.15149				
97 ->104	-0.11415				
98 ->104	0.13261				

Excited State 37:	Singlet-A	5.4448 eV	227.71 nm	f=0.0013	<S**2>=0.000
86 ->102	-0.18430				
87 ->102	0.14818				
93 ->103	0.32038				
96 ->104	0.24271				
96 ->105	-0.10035				
97 ->103	0.16425				
98 ->104	-0.23744				
99 ->106	-0.23287				

Excited State 38:	Singlet-A	5.4621 eV	226.99 nm	f=0.0104	<S**2>=0.000
93 ->103	0.34366				
95 ->103	0.15108				
96 ->103	0.10958				
96 ->104	-0.19455				
98 ->104	0.21986				
98 ->105	-0.19483				

99 ->104	0.10631				
99 ->106	0.20964				
100 ->104	0.28557				

Excited State 39:	Singlet-A	5.4903 eV	225.82 nm	f=0.0033	<S**2>=0.000
93 ->103	-0.15600				
98 ->104	-0.13842				
99 ->104	-0.23093				
100 ->104	0.56552				
100 ->107	0.12811				
100 ->109	0.10185				

Excited State 40:	Singlet-A	5.5026 eV	225.32 nm	f=0.0161	<S**2>=0.000
97 ->104	-0.11018				
98 ->104	0.15055				
101 ->112	0.58576				
101 ->113	-0.15455				
101 ->114	0.16733				

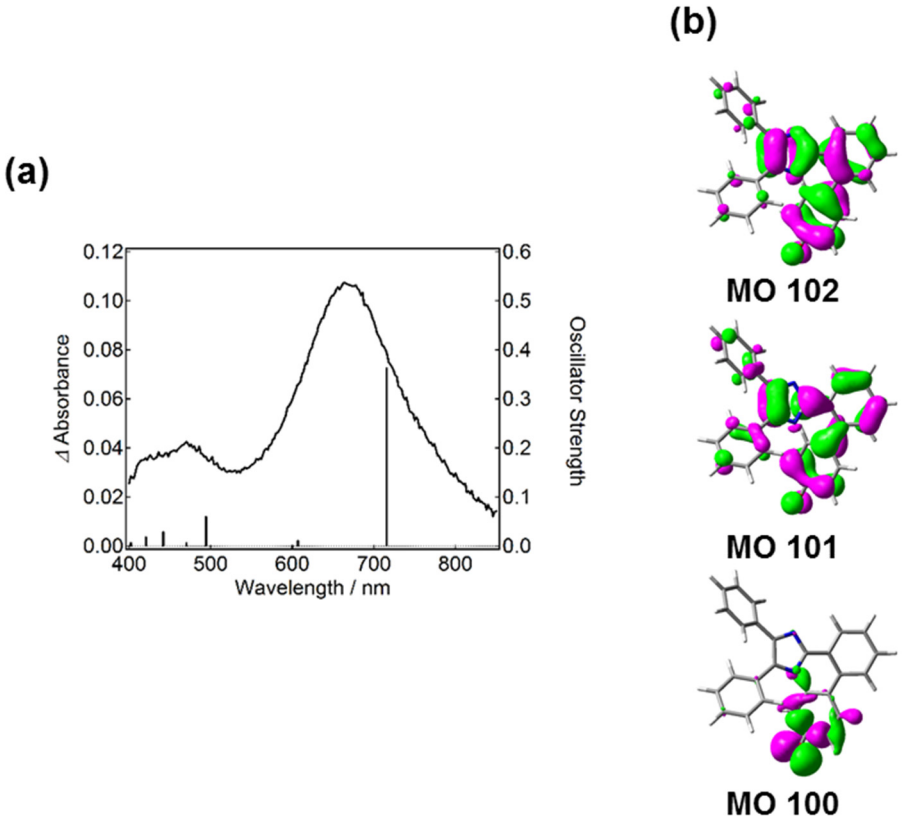


Fig. S52. (a) UV–vis absorption spectrum of the quinoid form of **PIC1** in benzene. The calculated spectrum (MPW1PW91/6-31+G(d,p)//M052X/6-31+G(d,p) level of the theory) of the quinoid form of the open-ring isomer of **PIC1** is shown by the black lines. (b) The relevant molecular orbitals were calculated at the M052X/6-31+G(d,p)

level of the theory.

Table S18. Standard Orientation of the Optimized Geometry for the Closed-Ring Form of **PIC2**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	0.6852800	5.3358140	-0.6535070
2	C	-0.4852260	4.6169880	-0.4130310
3	C	-0.3822140	3.2421810	-0.2382500
4	C	0.8621000	2.6025610	-0.3074810
5	C	2.0259190	3.3136730	-0.5404180
6	C	1.9257250	4.6956170	-0.7173640
7	C	0.7168700	1.0879270	-0.0695450
8	C	-1.3818710	2.2069280	-0.0041470
9	N	-2.6836060	2.0841750	0.0413730
10	C	-2.9054820	0.7276300	0.1686280
11	C	-1.7019100	0.0280530	0.1855630
12	N	-0.7405400	1.0096050	0.1048910
13	C	-4.2759180	0.1983500	0.2643350
14	C	-1.3799260	-1.4098860	0.1470580
15	C	-5.3322790	0.9422080	-0.2738800
16	C	-6.6380240	0.4685670	-0.1991640
17	C	-6.9091670	-0.7528330	0.4153150
18	C	-5.8634590	-1.4923540	0.9641820
19	C	-4.5565600	-1.0191320	0.8960890
20	C	-0.5412420	-1.9976010	1.0993260
21	C	-0.2224170	-3.3507080	1.0170470
22	C	-0.7518780	-4.1338590	-0.0063610
23	C	-1.5995290	-3.5573480	-0.9515030
24	C	-1.9073150	-2.2025520	-0.8793730
25	C	1.4440140	0.7350500	1.1913180
26	C	2.5101510	-0.0730510	1.2412260
27	C	2.9694890	-0.7312130	-0.0277300
28	C	2.1662210	-0.5561820	-1.2826650
29	C	1.1346130	0.2966510	-1.2682510
30	O	3.9836760	-1.4135570	-0.0337540
31	C	2.5459210	-1.3679340	-2.5196380
32	C	3.9544040	-0.9805760	-3.0059830
33	C	1.5636210	-1.1121640	-3.6692670

34	C	2.4880900	-2.8713470	-2.1880840
35	C	3.2650320	-0.3644370	2.5374310
36	C	3.2437760	-1.8759190	2.8326720
37	C	2.6173250	0.3505920	3.7291940
38	C	4.7183770	0.1328730	2.4250060
39	H	0.6327960	6.4082550	-0.7936370
40	H	-1.4491760	5.1063020	-0.3631230
41	H	2.9844960	2.8089850	-0.5880230
42	H	2.8191860	5.2768960	-0.9068990
43	H	-5.1124780	1.8920100	-0.7438480
44	H	-7.4455090	1.0542000	-0.6216850
45	H	-7.9259720	-1.1213630	0.4727150
46	H	-6.0653000	-2.4352650	1.4575660
47	H	-3.7544580	-1.5912710	1.3452090
48	H	-0.1443630	-1.3943580	1.9063050
49	H	0.4336740	-3.7944390	1.7559070
50	H	-0.5052420	-5.1866240	-0.0675410
51	H	-2.0156850	-4.1608590	-1.7486850
52	H	-2.5629730	-1.7469930	-1.6121160
53	H	1.0599460	1.2324790	2.0739020
54	H	0.5258410	0.4703600	-2.1470360
55	H	4.7099510	-1.2048640	-2.2565460
56	H	3.9945110	0.0853110	-3.2466600
57	H	4.1849210	-1.5418600	-3.9155600
58	H	0.5422290	-1.3898230	-3.3949040
59	H	1.5756320	-0.0680350	-3.9926120
60	H	1.8594760	-1.7257660	-4.5225320
61	H	1.4918840	-3.1417000	-1.8277390
62	H	3.2240430	-3.1422080	-1.4339140
63	H	2.6926160	-3.4443700	-3.0965450
64	H	3.7399640	-2.4435100	2.0485350
65	H	2.2136760	-2.2298640	2.9320080
66	H	3.7568240	-2.0634300	3.7795260
67	H	2.6329560	1.4368240	3.6100840
68	H	1.5846540	0.0271260	3.8867900
69	H	3.1819270	0.1070130	4.6313500
70	H	4.7377080	1.2065300	2.2188630
71	H	5.2570630	-0.3903350	1.6385000
72	H	5.2297200	-0.0387700	3.3760460

SCF Done: E(RM052X) = -1538.88732493 A.U.

Zero-point correction = 0.610672 (Hartree/Particle)
Thermal correction to Energy = 0.643767
Thermal correction to Enthalpy = 0.644711
Thermal correction to Gibbs Free Energy = 0.54563
Sum of electronic and zero-point Energies = -1538.276653
Sum of electronic and thermal Energies = -1538.243558
Sum of electronic and thermal Enthalpies = -1538.242614
Sum of electronic and thermal Free Energies = -1538.341692

Low frequencies --- -9.3856 -3.3150 -0.0036 -0.0033 -0.0029 3.2764
Low frequencies --- 12.9822 20.3475 33.7426

The Results for the TDDFT calculation

Excited State 1: Singlet-A 2.8767 eV 430.99 nm f=0.0003 <S**2>=0.000
133 ->134 0.70391
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1538.57303310
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.2924 eV 376.58 nm f=0.0000 <S**2>=0.000
130 ->134 0.67026
131 ->134 -0.16370

Excited State 3: Singlet-A 3.8528 eV 321.80 nm f=0.1731 <S**2>=0.000
133 ->135 0.68097
133 ->136 0.16096

Excited State 4: Singlet-A 4.1091 eV 301.73 nm f=0.3301 <S**2>=0.000
133 ->135 -0.15689
133 ->136 0.67174

Excited State 5: Singlet-A 4.1967 eV 295.43 nm f=0.0952 <S**2>=0.000
133 ->137 0.67665

Excited State 6: Singlet-A 4.2562 eV 291.30 nm f=0.0009 <S**2>=0.000

129 ->134 0.41421
130 ->134 0.15176
131 ->134 0.36195
132 ->134 -0.38487

Excited State 7: Singlet-A 4.2978 eV 288.48 nm f=0.0052 <S**2>=0.000
128 ->134 0.17770
129 ->134 0.52780
131 ->134 -0.27427
132 ->134 0.29940

Excited State 8: Singlet-A 4.3501 eV 285.01 nm f=0.0143 <S**2>=0.000
133 ->138 0.67589

Excited State 9: Singlet-A 4.4189 eV 280.57 nm f=0.0028 <S**2>=0.000
127 ->134 -0.18683
131 ->134 0.47442
132 ->134 0.45624
133 ->138 0.12152

Excited State 10: Singlet-A 4.5507 eV 272.45 nm f=0.0080 <S**2>=0.000
127 ->134 0.20755
128 ->134 0.63768
129 ->134 -0.18836

Excited State 11: Singlet-A 4.6313 eV 267.71 nm f=0.0057 <S**2>=0.000
127 ->134 0.62904
128 ->134 -0.20735
131 ->134 0.13325
132 ->134 0.17106

Excited State 12: Singlet-A 4.8236 eV 257.04 nm f=0.0716 <S**2>=0.000
132 ->136 -0.10887
133 ->139 0.56596
133 ->142 -0.30486

Excited State 13: Singlet-A 4.8896 eV 253.57 nm f=0.0069 <S**2>=0.000
125 ->134 0.34053
126 ->134 -0.31007

132 ->136 0.14739
132 ->137 -0.10857
133 ->139 0.23672
133 ->140 0.14096
133 ->142 0.33528

Excited State 14: Singlet-A 4.8997 eV 253.04 nm f=0.0483 <S**2>=0.000
125 ->134 -0.33220
126 ->134 0.36562
132 ->136 0.11929
133 ->139 0.28492
133 ->140 0.12361
133 ->142 0.30018

Excited State 15: Singlet-A 5.0139 eV 247.28 nm f=0.0057 <S**2>=0.000
125 ->134 -0.12903
129 ->135 -0.12673
133 ->140 0.42510
133 ->141 -0.42173
133 ->142 -0.20296
133 ->145 0.11187

Excited State 16: Singlet-A 5.0614 eV 244.96 nm f=0.0187 <S**2>=0.000
125 ->134 0.15816
126 ->134 0.12269
133 ->140 0.46150
133 ->141 0.38193
133 ->143 0.11073
133 ->145 0.17323

Excited State 17: Singlet-A 5.1248 eV 241.93 nm f=0.2049 <S**2>=0.000
125 ->134 0.30806
126 ->134 0.29976
131 ->135 0.33800
131 ->136 0.11571
132 ->135 -0.32670
133 ->141 -0.17538

Excited State 18: Singlet-A 5.1688 eV 239.87 nm f=0.0445 <S**2>=0.000

124 ->134	0.16109				
125 ->134	0.28583				
126 ->134	0.29953				
131 ->135	-0.29939				
132 ->135	0.34572				
133 ->141	-0.18709				
133 ->142	-0.11284				

Excited State 19:	Singlet-A	5.2354 eV	236.82 nm	f=0.0727	<S**2>=0.000
128 ->135	0.11546				
129 ->135	0.31920				
131 ->135	0.33498				
131 ->136	0.21106				
132 ->135	0.30733				
132 ->137	-0.10113				

Excited State 20:	Singlet-A	5.2406 eV	236.58 nm	f=0.0221	<S**2>=0.000
127 ->135	-0.11868				
128 ->135	-0.14824				
129 ->135	-0.29210				
129 ->136	0.10845				
130 ->135	-0.15525				
131 ->135	0.29689				
131 ->137	-0.16072				
132 ->135	0.33883				
132 ->136	0.12384				
133 ->141	0.16814				

Excited State 21:	Singlet-A	5.2851 eV	234.59 nm	f=0.0082	<S**2>=0.000
124 ->134	-0.11894				
129 ->135	-0.12709				
130 ->135	0.58352				
130 ->136	0.16909				
130 ->137	0.18109				
130 ->141	-0.13368				
131 ->137	-0.11730				

Excited State 22:	Singlet-A	5.3372 eV	232.30 nm	f=0.0047	<S**2>=0.000
133 ->141	-0.14924				

133 ->143 0.62514

Excited State 23: Singlet-A 5.3502 eV 231.74 nm f=0.0414 <S**2>=0.000
124 ->134 0.53583
127 ->135 -0.14750
127 ->136 -0.11352
128 ->138 -0.11933
132 ->135 -0.14618
132 ->136 0.11771
133 ->143 0.17237

Excited State 24: Singlet-A 5.3728 eV 230.76 nm f=0.0270 <S**2>=0.000
124 ->134 0.31750
127 ->135 0.21007
127 ->136 0.13438
127 ->137 -0.13995
128 ->138 0.16630
129 ->135 -0.16859
129 ->138 -0.10815
131 ->135 0.18098
132 ->135 0.10236
132 ->136 -0.28742
132 ->138 0.10092
133 ->142 0.10038
133 ->143 -0.14893

Excited State 25: Singlet-A 5.3995 eV 229.62 nm f=0.0216 <S**2>=0.000
124 ->134 -0.10198
128 ->135 -0.12104
133 ->143 -0.11243
133 ->144 0.61436
133 ->149 -0.16484

Excited State 26: Singlet-A 5.4281 eV 228.41 nm f=0.0323 <S**2>=0.000
124 ->135 -0.14727
125 ->135 -0.13812
127 ->135 -0.18771
128 ->135 0.38154
128 ->138 -0.11633

129 ->135 -0.25749
131 ->135 -0.10364
131 ->136 0.21731
132 ->136 -0.19284

Excited State 27: Singlet-A 5.4426 eV 227.80 nm f=0.0050 <S**2>=0.000
127 ->135 -0.11260
129 ->135 0.16371
131 ->136 -0.25978
131 ->138 0.12233
131 ->142 0.10977
132 ->136 -0.25162
132 ->137 0.18676
132 ->138 -0.12218
133 ->142 0.28527
133 ->144 -0.22323
133 ->145 0.18129

Excited State 28: Singlet-A 5.5046 eV 225.24 nm f=0.0068 <S**2>=0.000
132 ->136 0.21949
132 ->137 -0.10660
133 ->140 -0.17784
133 ->145 0.58038
133 ->146 0.12321

Excited State 29: Singlet-A 5.5391 eV 223.84 nm f=0.0205 <S**2>=0.000
123 ->134 0.17409
128 ->135 -0.22840
129 ->136 0.15579
130 ->136 0.10581
131 ->135 -0.10416
131 ->136 0.36003
131 ->137 -0.28078
132 ->136 -0.12589
133 ->145 0.14420

Excited State 30: Singlet-A 5.5497 eV 223.41 nm f=0.0131 <S**2>=0.000
123 ->134 0.27130
125 ->135 -0.11530

128 ->135 0.22016
129 ->135 0.10754
130 ->135 -0.22105
130 ->136 0.22659
130 ->137 0.28118
130 ->141 -0.11139
131 ->136 -0.19531
131 ->137 -0.15794
132 ->136 0.15488
132 ->137 0.17467

Excited State 31: Singlet-A 5.5589 eV 223.04 nm f=0.0143 <S**2>=0.000
123 ->134 0.60527
130 ->135 0.12990
130 ->136 -0.13657
130 ->137 -0.19604
131 ->137 0.12521

Excited State 32: Singlet-A 5.6047 eV 221.21 nm f=0.0003 <S**2>=0.000
133 ->145 -0.14794
133 ->146 0.58260
133 ->147 0.28749
133 ->148 0.10872

Excited State 33: Singlet-A 5.6230 eV 220.50 nm f=0.0170 <S**2>=0.000
122 ->134 0.64693
132 ->137 0.12429

Excited State 34: Singlet-A 5.6331 eV 220.10 nm f=0.0692 <S**2>=0.000
122 ->134 -0.18487
126 ->135 0.11222
127 ->135 0.11683
128 ->135 0.12138
129 ->135 0.14918
129 ->136 0.11093
130 ->135 0.14859
130 ->136 -0.20255
130 ->137 -0.28293
131 ->137 -0.20664

132 ->136	0.15529				
132 ->137	0.35467				
Excited State 35:	Singlet-A	5.6509 eV	219.41 nm	f=0.0686	<S**2>=0.000
125 ->135	-0.35539				
126 ->135	-0.10916				
127 ->135	-0.16168				
127 ->136	0.11296				
128 ->136	-0.16821				
129 ->135	0.19281				
129 ->136	0.35743				
132 ->137	-0.12138				
Excited State 36:	Singlet-A	5.7029 eV	217.40 nm	f=0.0150	<S**2>=0.000
126 ->135	-0.28840				
127 ->135	-0.29791				
128 ->135	-0.14234				
129 ->136	-0.17629				
130 ->136	-0.15649				
130 ->137	0.14088				
131 ->136	0.14524				
131 ->137	0.17106				
132 ->136	0.13741				
132 ->137	0.32753				
Excited State 37:	Singlet-A	5.7239 eV	216.61 nm	f=0.0208	<S**2>=0.000
127 ->135	-0.24020				
128 ->136	0.19480				
129 ->136	-0.28515				
129 ->137	0.14036				
130 ->137	-0.14609				
131 ->136	-0.15203				
131 ->137	-0.24622				
132 ->136	-0.12728				
132 ->137	-0.12216				
132 ->138	0.30104				
Excited State 38:	Singlet-A	5.7313 eV	216.33 nm	f=0.0050	<S**2>=0.000
130 ->136	0.54089				

130 ->137 -0.33123
131 ->137 0.18015
132 ->137 0.15325

Excited State 39: Singlet-A 5.7530 eV 215.51 nm f=0.0004 <S**2>=0.000
133 ->146 -0.29535
133 ->147 0.61604

Excited State 40: Singlet-A 5.7681 eV 214.95 nm f=0.0002 <S**2>=0.000
125 ->136 -0.14844
127 ->138 -0.10026
128 ->136 0.37464
128 ->137 -0.21305
129 ->136 0.13185
129 ->137 0.34426
131 ->136 0.13624
131 ->137 0.18376

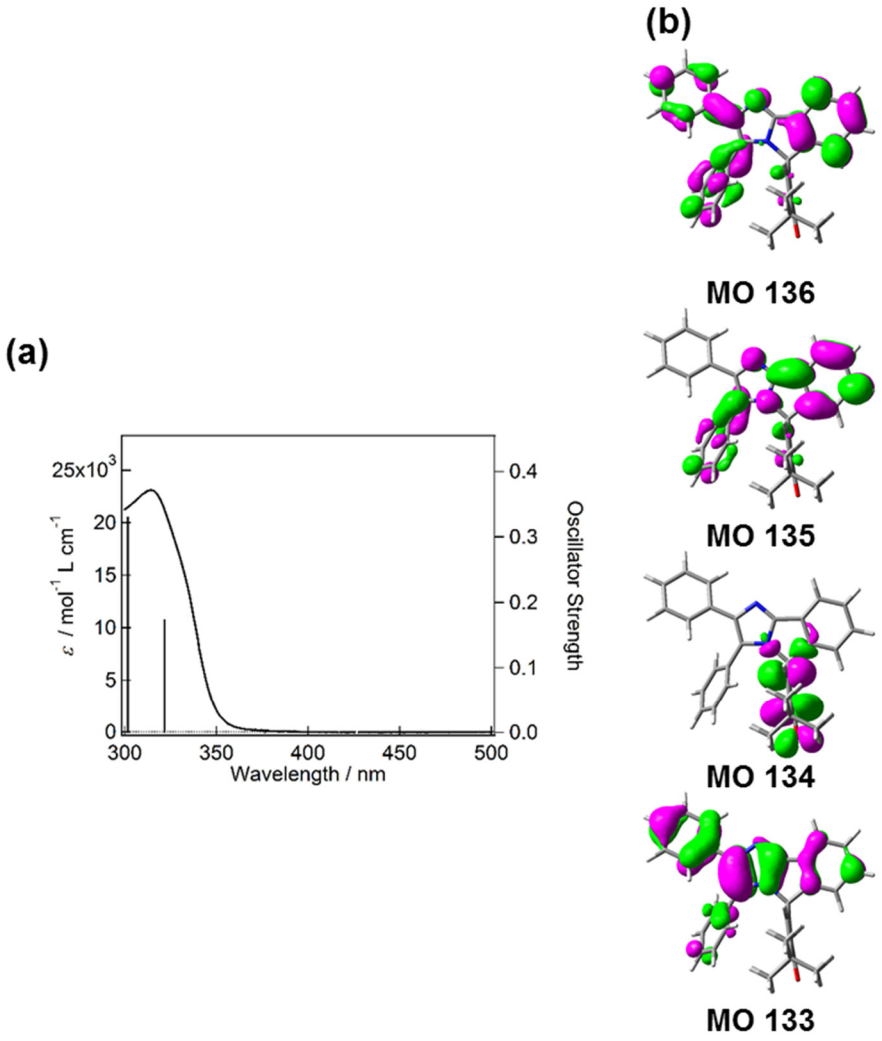


Fig. S53. (a) UV–vis absorption spectrum of the closed-ring isomer of **PIC2** in benzene. The calculated spectrum (MPW1PW91/6-31+G(d,p)//M052X/6-31+G(d,p) level of the theory) is shown by the black lines. (b) The relevant molecular orbitals were calculated at the M052X/6-31+G(d,p) level of the theory.

Table S19. Standard Orientation of the Optimized Geometry for the Biradical Form of **PIC2**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	0.2232340	2.9462972	-0.0846358
2	C	-1.1827504	2.7890606	0.0131253
3	C	1.1278559	1.8255805	-0.2590534
4	N	2.4594663	1.9210046	0.0283303
5	C	2.9418478	0.7195064	-0.2421510
6	C	1.8219814	-0.1321660	-0.7014890
7	N	0.7311416	0.6126117	-0.7354217
8	C	4.3697044	0.4237136	-0.1320500

9	C	1.7625129	-1.5627083	-0.9982582
10	C	5.0016261	-0.4867336	-0.9904562
11	C	6.3708576	-0.7081983	-0.8886305
12	C	7.1209458	-0.0294502	0.0702304
13	C	6.4996631	0.8859669	0.9202064
14	C	5.1345156	1.1191467	0.8158173
15	C	0.7662242	-2.0292902	-1.8694845
16	C	0.6284784	-3.3898435	-2.1093387
17	C	1.4686044	-4.3026060	-1.4700215
18	C	2.4469940	-3.8479350	-0.5879422
19	C	2.5974989	-2.4851284	-0.3520847
20	C	-1.8402153	1.4886575	0.2172479
21	C	-3.0048963	1.1707518	-0.5136319
22	C	-3.6663831	-0.0217569	-0.3459520
23	C	-3.1441854	-0.9807226	0.6478219
24	C	-1.9376731	-0.6318003	1.4182429
25	C	-1.3482897	0.5803630	1.1875377
26	O	-3.7225075	-2.0682001	0.8330626
27	C	-4.9052669	-0.3837149	-1.1567896
28	C	-1.3694200	-1.6324032	2.4194007
29	C	-0.9936711	-2.9386140	1.6901824
30	C	-2.3972329	-1.9246685	3.5286445
31	C	-0.0952465	-1.0966101	3.0845954
32	C	-4.6448348	-1.6627494	-1.9768543
33	C	-5.2829432	0.7300747	-2.1417566
34	C	-6.1055018	-0.6003149	-0.2139516
35	C	-1.9821435	3.9418236	-0.0016813
36	C	-1.4203871	5.2103422	-0.0503325
37	C	-0.0311831	5.3602967	-0.0812397
38	C	0.7793528	4.2379748	-0.0964209
39	H	4.4257551	-1.0032269	-1.7476302
40	H	6.8524947	-1.4062030	-1.5619312
41	H	8.1859962	-0.2082904	0.1509651
42	H	7.0811748	1.4189174	1.6620351
43	H	4.6386680	1.8339512	1.4595805
44	H	0.1062319	-1.3095964	-2.3364277
45	H	-0.1409988	-3.7415643	-2.7849651
46	H	1.3527173	-5.3640343	-1.6505289
47	H	3.0861696	-4.5545638	-0.0737011

48	H	3.3419501	-2.1385785	0.3532396
49	H	-3.3427291	1.8827829	-1.2537882
50	H	-0.4712794	0.8774534	1.7448134
51	H	-0.2728084	-2.7389093	0.8927853
52	H	-0.5304845	-3.6244054	2.4056068
53	H	-1.8723477	-3.4163441	1.2627362
54	H	-2.6519300	-1.0060486	4.0639548
55	H	-3.3054262	-2.3592673	3.1165240
56	H	-1.9624517	-2.6274085	4.2451526
57	H	-0.2829050	-0.1810848	3.6514867
58	H	0.2770688	-1.8497393	3.7824277
59	H	0.6919485	-0.9041694	2.3495274
60	H	-4.4395645	-2.5098224	-1.3264986
61	H	-5.5281071	-1.8849886	-2.5821750
62	H	-3.7971450	-1.5155217	-2.6516882
63	H	-5.5157004	1.6666220	-1.6283206
64	H	-4.4911422	0.9140016	-2.8723100
65	H	-6.1758278	0.4219668	-2.6897492
66	H	-6.3012631	0.3047444	0.3672295
67	H	-6.9945018	-0.8197192	-0.8118717
68	H	-5.9243269	-1.4282559	0.4674103
69	H	-3.0562864	3.8315158	0.0849829
70	H	-2.0621581	6.0824738	-0.0402150
71	H	0.4107347	6.3481607	-0.1046533
72	H	1.8562422	4.3265878	-0.1519452

SCF Done: E(UM052X) = -1538.84216912 A.U.
S**2 before annihilation 0.8824, after 0.5040

Zero-point correction = 0.607098 (Hartree/Particle)
Thermal correction to Energy = 0.640919
Thermal correction to Enthalpy = 0.641863
Thermal correction to Gibbs Free Energy = 0.539895
Sum of electronic and zero-point Energies = -1538.235071
Sum of electronic and thermal Energies = -1538.201251
Sum of electronic and thermal Enthalpies = -1538.200306
Sum of electronic and thermal Free Energies = -1538.302275

Low frequencies --- -8.6793 -5.2488 -4.6661 -0.0026 -0.0024 -0.0020

Low frequencies --- 8.6030 17.9672 28.3181

The Results for the TDDFT calculation

Excited State 1: 1.393-A 1.2505 eV 991.52 nm f=0.0409 <S**2>=0.235
133A ->134A 0.14253
133B ->134B 0.97948
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1538.59757430
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.376-A 1.3698 eV 905.15 nm f=0.0001 <S**2>=1.161
132A ->134A 0.96227
132A ->136A 0.10806
132A ->138A -0.10468

Excited State 3: 1.562-A 1.8963 eV 653.83 nm f=0.0322 <S**2>=0.360
131A ->134A -0.22224
133A ->134A 0.89543
131B ->134B -0.29231
133B ->134B -0.10112

Excited State 4: 2.262-A 1.9991 eV 620.20 nm f=0.0431 <S**2>=1.029
133A ->134A 0.34222
133A ->135A 0.12458
121B ->134B 0.12950
123B ->134B -0.17260
130B ->134B 0.31143
131B ->134B 0.78880
132B ->134B -0.18217
133B ->134B -0.12085

Excited State 5: 2.335-A 2.2105 eV 560.89 nm f=0.0060 <S**2>=1.114
129A ->134A -0.16417
130A ->134A 0.32777
131A ->134A 0.82445
133A ->134A 0.18778
130B ->134B -0.30079
133B ->140B -0.10634

Excited State 6:	2.270-A	2.3081 eV	537.17 nm	f=0.0186	<S**2>=1.038
131A ->134A	0.22285				
125B ->134B	0.54611				
128B ->134B	0.30620				
130B ->134B	0.66188				
131B ->134B	-0.22688				
Excited State 7:	2.279-A	2.4578 eV	504.45 nm	f=0.0028	<S**2>=1.049
131B ->134B	0.19551				
132B ->134B	0.97127				
Excited State 8:	2.413-A	2.5680 eV	482.80 nm	f=0.1180	<S**2>=1.206
133A ->136A	0.19234				
125B ->134B	-0.30110				
129B ->134B	0.87244				
130B ->134B	0.14411				
Excited State 9:	2.309-A	2.6531 eV	467.32 nm	f=0.0068	<S**2>=1.083
131A ->134A	-0.13081				
123B ->134B	-0.19444				
125B ->134B	0.21162				
128B ->134B	0.74962				
129B ->134B	0.20614				
130B ->134B	-0.43822				
131B ->134B	0.25122				
Excited State 10:	2.350-A	2.7572 eV	449.67 nm	f=0.0080	<S**2>=1.130
123B ->134B	-0.17886				
124B ->134B	-0.10379				
125B ->134B	0.66373				
126B ->134B	0.10913				
127B ->134B	0.13405				
128B ->134B	-0.53818				
129B ->134B	0.24236				
130B ->134B	-0.24731				
131B ->134B	0.16984				
Excited State 11:	2.394-A	2.8466 eV	435.56 nm	f=0.0041	<S**2>=1.183

127A ->134A -0.11307
129A ->134A -0.14947
123B ->134B -0.12544
125B ->134B -0.12341
126B ->134B -0.15974
127B ->134B 0.91828

Excited State 12: 2.435-A 2.8817 eV 430.25 nm f=0.0101 <S**2>=1.232
127A ->134A 0.16595
129A ->134A 0.25869
130A ->134A -0.10053
131A ->134A 0.10413
126B ->134B 0.86293
127B ->134B 0.22003

Excited State 13: 2.310-A 2.9645 eV 418.23 nm f=0.0404 <S**2>=1.084
124A ->134A 0.11310
127A ->134A 0.26942
129A ->134A 0.51895
130A ->134A -0.27694
131A ->134A 0.19983
133A ->136A 0.10107
123B ->134B -0.43455
124B ->134B -0.12419
126B ->134B -0.36298
131B ->134B -0.12745
133B ->135B 0.11897
133B ->136B 0.19212
133B ->137B 0.14582

Excited State 14: 2.306-A 3.0916 eV 401.03 nm f=0.0058 <S**2>=1.079
127A ->134A 0.17735
129A ->134A 0.27317
130A ->134A -0.10365
123B ->134B 0.76484
124B ->134B 0.11676
125B ->134B 0.19059
126B ->134B -0.17136
127B ->134B 0.21036

129B ->134B 0.13200
131B ->134B 0.20697
133B ->136B 0.10181

Excited State 15: 2.491-A 3.2572 eV 380.64 nm f=0.0143 <S**2>=1.301
127A ->134A 0.28070
129A ->136A -0.11525
130A ->134A 0.69167
131A ->134A -0.26393
133A ->135A -0.22384
133A ->136A 0.14897
133A ->140A 0.10104
124B ->134B -0.28498

Excited State 16: 2.710-A 3.2904 eV 376.80 nm f=0.0019 <S**2>=1.586
127A ->134A 0.26510
128A ->139A -0.10634
129A ->134A 0.10796
129A ->136A 0.13141
130A ->134A 0.20878
130A ->135A 0.16656
131A ->135A -0.12246
133A ->135A -0.23003
133A ->136A -0.14143
133A ->140A -0.22208
123B ->134B -0.13728
124B ->134B 0.65512
128B ->139B -0.11069
129B ->135B 0.11079
131B ->135B -0.13001

Excited State 17: 2.806-A 3.3337 eV 371.91 nm f=0.0312 <S**2>=1.718
126A ->139A 0.13666
127A ->134A 0.25172
128A ->137A -0.16467
129A ->135A 0.14758
130A ->134A 0.31507
130A ->140A -0.12986
131A ->134A -0.14639

133A ->135A 0.63190
121B ->134B -0.24993
122B ->134B 0.10472
124B ->134B 0.12966
127B ->139B -0.10575
128B ->138B -0.15359
129B ->135B -0.13238
130B ->141B -0.10474
133B ->135B 0.16767

Excited State 18: 2.385-A 3.4046 eV 364.16 nm f=0.0068 <S**2>=1.173
124A ->134A -0.11123
125A ->134A 0.40575
127A ->134A 0.54028
127A ->138A 0.12778
128A ->134A -0.23670
129A ->134A -0.42225
130A ->134A -0.33794
133A ->136A 0.20002
129B ->134B -0.11152
133B ->136B -0.12134

Excited State 19: 2.483-A 3.4959 eV 354.66 nm f=0.0323 <S**2>=1.291
124A ->134A 0.11670
125A ->134A -0.36083
126A ->134A 0.12819
127A ->134A 0.42355
128A ->134A 0.44695
129A ->134A -0.36898
133A ->136A -0.35672
124B ->134B -0.15274
133B ->136B 0.13658
133B ->137B 0.10058

Excited State 20: 2.668-A 3.5813 eV 346.19 nm f=0.1029 <S**2>=1.530
125A ->134A -0.20587
126A ->134A 0.13033
126A ->137A 0.12642
128A ->134A 0.54346

128A ->139A	-0.12555
130A ->135A	0.15236
133A ->136A	0.43947
121B ->134B	-0.16736
124B ->134B	-0.13947
127B ->138B	-0.10105
128B ->139B	-0.11604
129B ->134B	-0.17118
130B ->135B	-0.12287
131B ->135B	-0.13353
133B ->135B	-0.18204
133B ->136B	-0.31119

Excited State 21: 2.402-A 3.6302 eV 341.54 nm f=0.0965 <S**2>=1.193

128A ->134A	0.21458
133A ->135A	0.29843
133A ->136A	0.12846
119B ->134B	-0.15824
120B ->134B	0.11736
121B ->134B	0.73284
122B ->134B	-0.31225
130B ->134B	-0.17620
131B ->134B	-0.13341

Excited State 22: 2.576-A 3.6493 eV 339.74 nm f=0.0204 <S**2>=1.409

124A ->134A	-0.15127
125A ->134A	0.47747
126A ->134A	0.24093
126A ->137A	-0.13041
128A ->134A	0.52468
128A ->139A	0.13123
129A ->134A	0.10567
130A ->135A	-0.14596
131A ->135A	0.10407
133A ->135A	-0.10213
121B ->134B	-0.17282
124B ->134B	0.32715
128B ->139B	0.11407
130B ->135B	0.10335

131B ->135B 0.13666

Excited State 23: 2.751-A 3.7891 eV 327.22 nm f=0.0362 <S**2>=1.642

125A ->134A 0.45738
126A ->134A 0.18206
126A ->137A 0.16612
127A ->134A -0.13905
128A ->134A 0.13001
128A ->139A -0.16635
130A ->135A 0.16087
131A ->135A -0.12259
133A ->136A -0.22038
124B ->134B -0.34624
127B ->138B -0.12205
128B ->139B -0.13125
130B ->135B -0.14921
131B ->135B -0.17132
133B ->135B 0.19007
133B ->136B 0.38583

Excited State 24: 2.491-A 3.8342 eV 323.37 nm f=0.2883 <S**2>=1.302

118A ->134A 0.13390
120A ->134A 0.12311
121A ->134A 0.12458
122A ->134A 0.11185
124A ->134A 0.17286
125A ->134A -0.17669
127A ->134A -0.26379
127A ->138A 0.15124
129A ->134A -0.34331
129A ->136A -0.10594
133A ->136A 0.32502
124B ->134B 0.28633
129B ->134B -0.15243
129B ->136B -0.12537
133B ->135B 0.24770
133B ->136B 0.37016
133B ->137B 0.26334

Excited State 25: 2.349-A 3.9196 eV 316.32 nm f=0.0108 <S**2>=1.130

124A ->134A	0.12354
126A ->134A	0.89739
128A ->134A	-0.29443
133B ->135B	-0.11366
133B ->136B	-0.12810

Excited State 26: 2.854-A 3.9887 eV 310.84 nm f=0.0267 <S**2>=1.786

118A ->134A	0.11676
124A ->134A	0.13983
125A ->134A	0.16538
126A ->134A	-0.11733
126A ->139A	-0.20771
128A ->137A	0.25214
129A ->135A	-0.12060
131A ->136A	0.10898
133A ->135A	0.52050
133A ->138A	0.11633
121B ->134B	-0.13293
126B ->139B	0.11524
127B ->139B	0.16841
128B ->138B	0.26565
129B ->135B	0.15529
131B ->136B	-0.10984
133B ->135B	-0.29491
133B ->137B	0.19538

Excited State 27: 2.737-A 4.0016 eV 309.84 nm f=0.0249 <S**2>=1.623

118A ->134A	0.22290
120A ->134A	0.11847
121A ->134A	0.15216
122A ->134A	0.10491
124A ->134A	0.28309
125A ->134A	0.21083
126A ->134A	-0.13960
127A ->134A	0.13265
127A ->138A	-0.27874
133A ->136A	0.42639
133A ->138A	-0.14450

126B ->137B -0.21179
127B ->137B 0.17139
133B ->135B -0.14579
133B ->136B 0.17627
133B ->137B -0.36368
133B ->141B 0.10104
133B ->145B 0.12955

Excited State 28: 2.535-A 4.0353 eV 307.25 nm f=0.0179 <S**2>=1.357
118A ->134A -0.20948
120A ->134A -0.13955
121A ->134A -0.15243
122A ->134A -0.11884
124A ->134A -0.27773
125A ->134A -0.23292
126A ->134A 0.13275
126A ->139A -0.10301
128A ->137A 0.12390
133A ->135A 0.21674
133A ->136A 0.12448
128B ->138B 0.12962
133B ->136B 0.52440
133B ->137B -0.41897
133B ->145B -0.12836

Excited State 29: 2.608-A 4.1437 eV 299.21 nm f=0.0104 <S**2>=1.451
126A ->139A -0.13955
128A ->137A 0.17942
133A ->136A 0.12116
127B ->139B 0.10258
128B ->138B 0.16417
133B ->135B 0.78769
133B ->136B -0.29420
133B ->137B -0.20579
133B ->140B -0.14220

Excited State 30: 2.704-A 4.2456 eV 292.03 nm f=0.0131 <S**2>=1.577
129A ->137A 0.13449
130A ->139A 0.14937

133A ->137A 0.85558
133A ->138A -0.17610
128B ->135B 0.17681
129B ->138B 0.12155
133B ->138B -0.14764

Excited State 31: 2.947-A 4.2840 eV 289.41 nm f=0.0017 <S**2>=1.922
116A ->134A 0.13288
119A ->134A 0.13936
122A ->134A 0.10063
124A ->134A 0.19732
130A ->143A -0.13309
131A ->143A -0.27427
133A ->136A -0.11481
133A ->138A 0.47721
129B ->140B 0.13010
130B ->140B -0.21022
131B ->140B 0.26333
133B ->136B 0.14834
133B ->137B -0.24025
133B ->145B -0.11345

Excited State 32: 2.581-A 4.3163 eV 287.25 nm f=0.0098 <S**2>=1.415
116A ->134A 0.23319
119A ->134A 0.14939
122A ->134A 0.30906
124A ->134A 0.22770
129A ->138A 0.13562
133A ->138A -0.48691
120B ->134B 0.10334
121B ->134B 0.18096
122B ->134B 0.53083

Excited State 33: 2.414-A 4.3237 eV 286.76 nm f=0.0115 <S**2>=1.207
116A ->134A -0.11360
119A ->134A -0.12616
124A ->134A -0.30138
133A ->138A 0.34804
120B ->134B 0.10053

121B ->134B 0.29112
122B ->134B 0.70141

Excited State 34: 2.310-A 4.3455 eV 285.32 nm f=0.0024 <S**2>=1.084
115A ->134A 0.11001
116A ->134A 0.27984
121A ->134A -0.15504
122A ->134A 0.63010
123A ->134A 0.47123
124A ->134A -0.29199
133A ->138A 0.11232
122B ->134B -0.19480
133B ->140B -0.11662

Excited State 35: 2.656-A 4.3557 eV 284.65 nm f=0.0206 <S**2>=1.513
115A ->134A 0.20774
119A ->134A -0.16842
120A ->134A -0.27148
121A ->134A -0.24730
122A ->134A 0.10230
123A ->134A 0.15140
124A ->134A 0.40460
131A ->135A 0.15402
131A ->136A -0.16888
131A ->143A 0.14194
133A ->137A 0.10225
133A ->138A 0.28069
131B ->135B 0.13220
131B ->136B 0.10613
131B ->140B -0.11511
133B ->137B -0.15020
133B ->139B -0.11865
133B ->140B 0.36196

Excited State 36: 2.593-A 4.4091 eV 281.20 nm f=0.0418 <S**2>=1.430
115A ->134A -0.32261
116A ->134A 0.26343
119A ->134A 0.39728
120A ->134A 0.23813

121A ->134A 0.27315
124A ->134A -0.19567
131A ->143A 0.10830
132A ->136A -0.15036
132A ->138A 0.10131
133A ->138A 0.13920
131B ->135B 0.10162
133B ->137B -0.17132
133B ->139B -0.12239
133B ->140B 0.36798
133B ->141B 0.11823

Excited State 37: 2.896-A 4.4356 eV 279.52 nm f=0.0545 <S**2>=1.846
120A ->134A -0.18154
124A ->134A -0.12088
126A ->137A -0.18881
128A ->139A 0.18171
129A ->136A 0.14212
130A ->135A 0.13014
131A ->135A -0.24479
131A ->136A 0.12522
131A ->143A -0.13228
133A ->136A 0.13991
133A ->139A -0.11498
126B ->138B 0.12005
127B ->138B 0.16128
128B ->139B 0.16442
129B ->136B 0.13764
131B ->135B -0.16444
133B ->135B 0.14205
133B ->137B 0.20259
133B ->139B -0.19389
133B ->140B 0.49949

Excited State 38: 2.890-A 4.4559 eV 278.24 nm f=0.0136 <S**2>=1.838
115A ->134A -0.15116
116A ->134A 0.19375
118A ->134A -0.18957
119A ->134A 0.18871

122A ->134A -0.12091
124A ->134A 0.35913
126A ->137A -0.15847
127A ->136A -0.10203
128A ->139A 0.15258
130A ->135A 0.17659
131A ->136A -0.12400
131A ->143A 0.15554
133A ->138A 0.15848
133A ->139A -0.25855
115B ->134B -0.13619
119B ->134B 0.20176
126B ->138B 0.10408
127B ->135B -0.11038
127B ->138B 0.12140
128B ->139B 0.13016
129B ->140B -0.10626
130B ->136B 0.10126
131B ->140B -0.13909
133B ->139B 0.15108
133B ->140B -0.28021

Excited State 39: 3.118-A 4.4658 eV 277.63 nm f=0.0079 <S**2>=2.181
126A ->135A 0.12960
126A ->137A -0.12028
128A ->139A 0.12780
129A ->139A 0.13951
130A ->135A 0.16473
130A ->137A 0.26505
131A ->135A -0.15244
131A ->137A -0.14890
133A ->139A 0.60069
133A ->140A -0.10077
126B ->135B 0.12942
127B ->135B 0.14433
127B ->138B 0.12610
128B ->139B 0.18094
130B ->138B 0.20054
131B ->135B -0.11035

131B ->138B 0.19291
133B ->139B -0.10692
133B ->140B -0.12178

Excited State 40: 2.885-A 4.5340 eV 273.45 nm f=0.0331 <S**2>=1.830
118A ->134A -0.15495
119A ->134A 0.19500
120A ->134A -0.14209
122A ->134A -0.17319
123A ->134A 0.17424
123A ->136A -0.13374
126A ->135A 0.10197
126A ->137A 0.13067
128A ->139A -0.12649
129A ->136A 0.16624
130A ->135A -0.21086
131A ->135A 0.22264
133A ->136A 0.16988
133A ->139A 0.14941
115B ->134B -0.19840
119B ->134B 0.29156
120B ->134B -0.15947
121B ->134B 0.12270
124B ->136B -0.12826
127B ->135B 0.14018
127B ->138B -0.10174
129B ->136B 0.11834
130B ->135B 0.13990
131B ->135B 0.12590
133B ->136B 0.10599
133B ->137B 0.30372
133B ->140B -0.10554

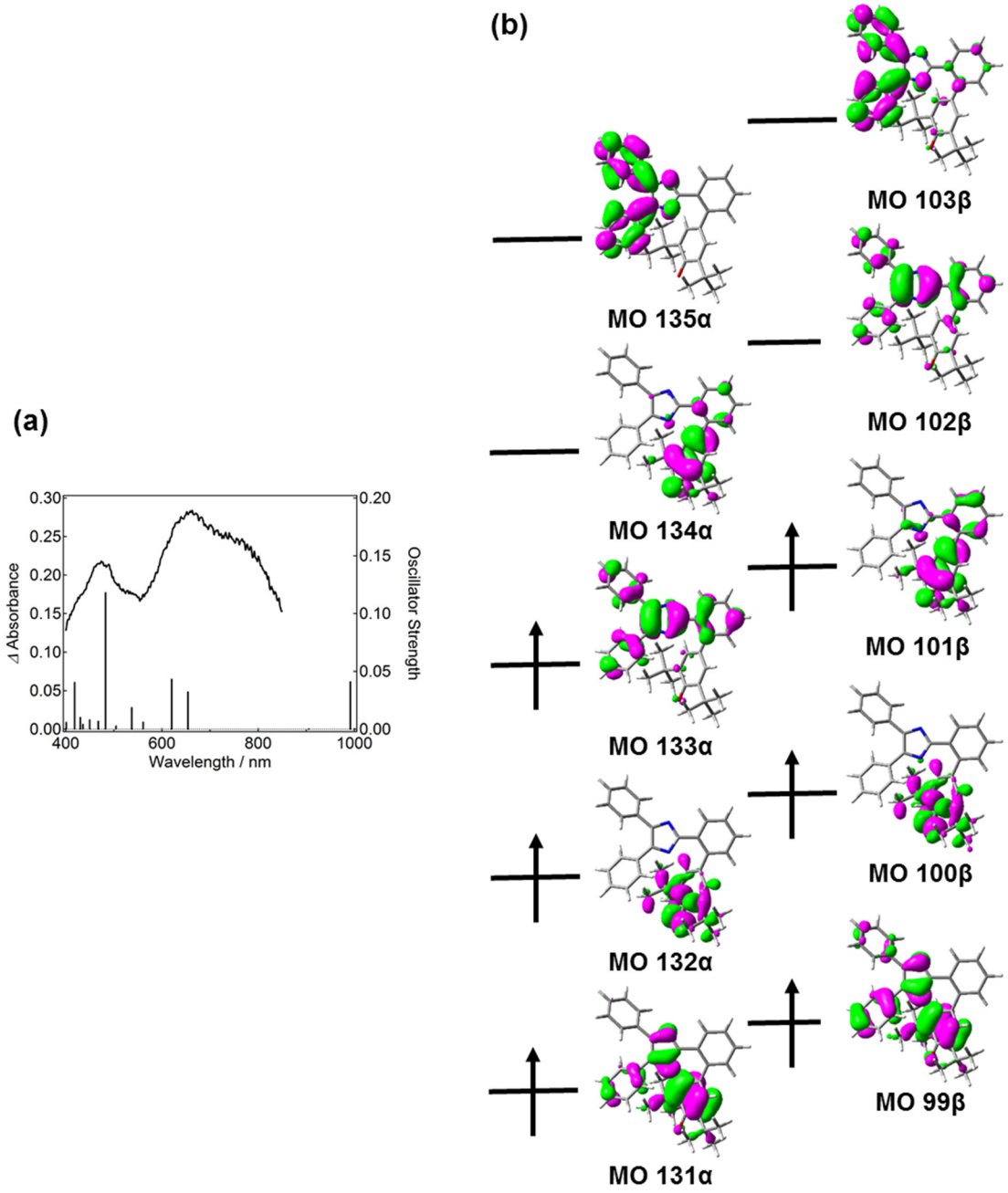


Fig. S54. (a) The transient absorption spectrum of **PIC2** in benzene (excitation wavelength, 355 nm; pulse width, 5ns; power 4 mJ/pulse). The calculated spectrum (UMPW1PW91/6-31+G(d,p)//UM052X/6-31+G(d,p) level of the theory) of the biradical form of the open-ring isomer of **PIC2** is shown by the black lines. (b) The relevant molecular orbitals were calculated at the UM052X/6-31+G(d,p) level of the theory.

Table S20. Standard Orientation of the Optimized Geometry for the Quinoid Form of **PIC2**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	0.1440150	2.8985690	-0.0596470
2	C	-1.2857100	2.6905770	-0.1608060

3	C	1.0586690	1.8518050	-0.2480220
4	N	2.3945610	1.9733360	0.0691800
5	C	2.9067650	0.7941230	-0.2009580
6	C	1.8335230	-0.0756620	-0.7229570
7	N	0.7248400	0.6238950	-0.7762310
8	C	4.3421620	0.5242350	-0.0456040
9	C	1.8543770	-1.4957610	-1.0977380
10	C	5.0287120	-0.3179400	-0.9291210
11	C	6.3974010	-0.5196310	-0.7826430
12	C	7.0930820	0.1119080	0.2465850
13	C	6.4163300	0.9591130	1.1236260
14	C	5.0507010	1.1705810	0.9755510
15	C	0.9636980	-1.9548460	-2.0773070
16	C	0.9007090	-3.3074210	-2.3886340
17	C	1.7163100	-4.2199760	-1.7189200
18	C	2.5948380	-3.7717020	-0.7346990
19	C	2.6663480	-2.4168330	-0.4243000
20	C	-1.8913840	1.4515030	0.1301970
21	C	-3.1836440	1.1239490	-0.4172890
22	C	-3.7844180	-0.0721000	-0.2074940
23	C	-3.1099680	-1.0667260	0.6876000
24	C	-1.8306870	-0.6897830	1.3396090
25	C	-1.2867180	0.5135960	1.0456550
26	O	-3.6262900	-2.1640420	0.8871390
27	C	-5.1050880	-0.4513550	-0.8673400
28	C	-1.1642410	-1.6771930	2.2923700
29	C	-0.8053940	-2.9663250	1.5243780
30	C	-2.0954150	-2.0077090	3.4730160
31	C	0.1379260	-1.1047250	2.8657320
32	C	-4.9091060	-1.6823150	-1.7743700
33	C	-5.6486210	0.6868150	-1.7396050
34	C	-6.1635340	-0.7559570	0.2122720
35	C	-2.0941850	3.8449250	-0.4403430
36	C	-1.5668400	5.1005070	-0.3806850
37	C	-0.1867210	5.2960240	-0.0690940
38	C	0.6439840	4.2284710	0.0985740
39	H	4.4951870	-0.8006510	-1.7381070
40	H	6.9210590	-1.1660660	-1.4759220
41	H	8.1575690	-0.0512220	0.3617600

42	H	6.9538710	1.4555780	1.9220530
43	H	4.5136100	1.8324530	1.6427580
44	H	0.3210660	-1.2382230	-2.5726380
45	H	0.2106280	-3.6528610	-3.1483570
46	H	1.6605550	-5.2749450	-1.9571970
47	H	3.2176230	-4.4774410	-0.1992430
48	H	3.3339770	-2.0767360	0.3574510

SCF Done: E(M052X) = - 1538.82900557 A.U.

Zero-point correction = 0.608517 (Hartree/Particle)
Thermal correction to Energy = 0.642148
Thermal correction to Enthalpy = 0.643093
Thermal correction to Gibbs Free Energy = 0.542577
Sum of electronic and zero-point Energies = -1538.220488
Sum of electronic and thermal Energies = -1538.186857
Sum of electronic and thermal Enthalpies = -1538.185913
Sum of electronic and thermal Free Energies = -1538.286429

Low frequencies --- -12.2072 -7.2089 -0.0029 -0.0025 -0.0024 4.4986
Low frequencies --- 14.6969 18.1597 27.3826

The Results for the TDDFT calculation

Excited State 1: Singlet-A 1.7322 eV 715.77 nm f=0.3623 <S**2>=0.000
101 ->102 0.71305
101 <-102 -0.18182
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1224.10313650
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.0429 eV 606.91 nm f=0.0105 <S**2>=0.000
100 ->102 0.68150
100 ->103 -0.10664

Excited State 3: Singlet-A 2.5081 eV 494.34 nm f=0.0598 <S**2>=0.000
95 ->102 -0.17254
97 ->102 -0.10756

99 ->102	0.65445					
100 ->102	0.10130					
Excited State	4:	Singlet-A	2.6378 eV	470.03 nm	f=0.0059	<S**2>=0.000
93 ->102	-0.15454					
95 ->102	0.33580					
97 ->102	0.42549					
98 ->102	-0.35415					
99 ->102	0.19336					
Excited State	5:	Singlet-A	2.8067 eV	441.74 nm	f=0.0283	<S**2>=0.000
97 ->102	0.42101					
98 ->102	0.53956					
101 ->103	-0.14238					
Excited State	6:	Singlet-A	2.9472 eV	420.68 nm	f=0.0182	<S**2>=0.000
95 ->102	0.54024					
97 ->102	-0.31017					
98 ->102	0.16135					
101 ->103	-0.24801					
Excited State	7:	Singlet-A	3.0774 eV	402.88 nm	f=0.0037	<S**2>=0.000
93 ->102	-0.31328					
94 ->102	0.46297					
95 ->102	-0.13952					
96 ->102	0.35574					
101 ->103	-0.17160					
Excited State	8:	Singlet-A	3.0833 eV	402.11 nm	f=0.0062	<S**2>=0.000
93 ->102	0.11275					
94 ->102	-0.31607					
96 ->102	0.58939					
97 ->102	0.10843					
101 ->103	0.14000					
Excited State	9:	Singlet-A	3.2315 eV	383.67 nm	f=0.1068	<S**2>=0.000
93 ->102	0.58246					
94 ->102	0.30810					
101 ->103	-0.15999					

Excited State 10:	Singlet-A	3.5860 eV	345.75 nm	f=0.0137	<S**2>=0.000
90 ->102	-0.12900				
91 ->102	0.27335				
92 ->102	0.62403				
Excited State 11:	Singlet-A	3.7287 eV	332.51 nm	f=0.3987	<S**2>=0.000
91 ->102	0.32603				
92 ->102	-0.11481				
94 ->102	0.19886				
95 ->102	0.14842				
98 ->102	0.19840				
101 ->103	0.48649				
Excited State 12:	Singlet-A	3.9658 eV	312.64 nm	f=0.1030	<S**2>=0.000
101 ->104	0.66046				
101 ->105	0.18312				
Excited State 13:	Singlet-A	4.0644 eV	305.05 nm	f=0.0482	<S**2>=0.000
90 ->102	0.62847				
91 ->102	0.26874				
Excited State 14:	Singlet-A	4.0914 eV	303.04 nm	f=0.0418	<S**2>=0.000
101 ->104	-0.20846				
101 ->105	0.65016				
Excited State 15:	Singlet-A	4.1924 eV	295.74 nm	f=0.4358	<S**2>=0.000
90 ->102	-0.22040				
91 ->102	0.46571				
92 ->102	-0.25276				
94 ->102	-0.16270				
95 ->102	-0.10826				
101 ->103	-0.28268				
101 ->105	-0.11170				
Excited State 16:	Singlet-A	4.3919 eV	282.31 nm	f=0.0121	<S**2>=0.000
100 ->102	0.12461				
100 ->103	0.63360				
100 ->105	0.14123				

Excited State 17:	Singlet-A	4.4838 eV	276.52 nm	f=0.0179	<S**2>=0.000
101 ->106	0.68578				

Excited State 18:	Singlet-A	4.7255 eV	262.38 nm	f=0.0141	<S**2>=0.000
101 ->107	0.65028				
101 ->108	0.12148				
101 ->109	0.17627				

Excited State 19:	Singlet-A	4.7682 eV	260.02 nm	f=0.0207	<S**2>=0.000
89 ->102	0.13215				
95 ->103	-0.21427				
97 ->103	-0.20402				
98 ->103	0.19263				
99 ->103	0.55714				
100 ->103	0.10410				

Excited State 20:	Singlet-A	4.8537 eV	255.44 nm	f=0.0211	<S**2>=0.000
85 ->102	-0.12068				
86 ->102	-0.14013				
87 ->102	-0.15061				
89 ->102	0.42917				
95 ->103	0.10335				
97 ->103	0.19521				
101 ->108	0.36367				

Excited State 21:	Singlet-A	4.8741 eV	254.37 nm	f=0.0500	<S**2>=0.000
85 ->102	0.10251				
86 ->102	0.13175				
87 ->102	0.13590				
89 ->102	-0.33601				
96 ->104	-0.11533				
98 ->103	0.15717				
101 ->108	0.47729				

Excited State 22:	Singlet-A	4.9254 eV	251.72 nm	f=0.0247	<S**2>=0.000
89 ->102	0.12249				
93 ->103	0.11976				
95 ->103	-0.20558				

97 ->103 -0.30659
98 ->103 0.39670
99 ->103 -0.38348

Excited State 23: Singlet-A 5.0354 eV 246.22 nm f=0.0136 <S**2>=0.000
97 ->103 -0.13996
98 ->103 -0.10547
99 ->104 -0.10348
101 ->107 -0.14798
101 ->109 0.60108
101 ->110 -0.13782

Excited State 24: Singlet-A 5.0713 eV 244.48 nm f=0.0033 <S**2>=0.000
97 ->103 -0.27935
98 ->103 -0.32233
101 ->108 0.20733
101 ->110 0.45566

Excited State 25: Singlet-A 5.0900 eV 243.59 nm f=0.0068 <S**2>=0.000
97 ->103 0.27517
98 ->103 0.28357
99 ->104 -0.10630
101 ->108 -0.19018
101 ->109 0.19697
101 ->110 0.47146

Excited State 26: Singlet-A 5.1593 eV 240.31 nm f=0.0200 <S**2>=0.000
85 ->102 0.19363
86 ->102 0.31830
87 ->102 0.32997
88 ->102 0.16551
89 ->102 0.24783
94 ->103 0.17845
101 ->109 -0.11196
101 ->110 0.12818
101 ->111 -0.10305
101 ->115 -0.10903

Excited State 27: Singlet-A 5.2374 eV 236.73 nm f=0.0523 <S**2>=0.000

88 ->102	-0.34667				
93 ->103	-0.10425				
94 ->103	-0.13511				
95 ->103	0.38965				
96 ->103	0.20414				
97 ->103	-0.19385				
97 ->104	-0.14779				
98 ->103	0.12783				
101 ->111	-0.10062				

Excited State 28:	Singlet-A	5.2491 eV	236.20 nm	f=0.0546	<S**2>=0.000
83 ->102	0.13217				
85 ->102	-0.13359				
88 ->102	0.44297				
94 ->103	-0.17637				
95 ->103	0.30872				
97 ->103	-0.16386				
99 ->104	-0.17224				
101 ->111	0.13572				

Excited State 29:	Singlet-A	5.2636 eV	235.55 nm	f=0.0100	<S**2>=0.000
88 ->102	-0.23306				
95 ->103	0.15607				
96 ->103	-0.29345				
97 ->103	-0.13282				
97 ->104	0.33118				
98 ->106	0.15170				
99 ->108	0.12177				
100 ->105	0.10443				
101 ->111	0.24340				

Excited State 30:	Singlet-A	5.2806 eV	234.79 nm	f=0.0002	<S**2>=0.000
87 ->102	-0.11335				
100 ->103	-0.13390				
100 ->104	0.17204				
100 ->105	0.53419				
100 ->107	-0.25577				
100 ->109	-0.14818				

Excited State 31:	Singlet-A	5.3100 eV	233.49 nm	f=0.0143	<S**2>=0.000
94 ->103	0.11715				
96 ->103	0.17668				
97 ->104	-0.15279				
99 ->104	0.10857				
101 ->111	0.57353				
101 ->113	-0.15036				

Excited State 32:	Singlet-A	5.3266 eV	232.76 nm	f=0.0992	<S**2>=0.000
93 ->103	-0.13200				
94 ->103	-0.28207				
98 ->104	0.26075				
98 ->105	0.13679				
99 ->104	0.43356				
100 ->104	0.13909				

Excited State 33:	Singlet-A	5.3573 eV	231.43 nm	f=0.0070	<S**2>=0.000
83 ->102	-0.12879				
84 ->102	-0.14543				
85 ->102	0.18029				
87 ->102	-0.24766				
88 ->102	0.20553				
89 ->102	-0.13235				
93 ->103	-0.16396				
94 ->103	0.33664				
95 ->103	0.10553				
98 ->103	0.14065				
98 ->105	-0.10469				
99 ->104	0.17889				

Excited State 34:	Singlet-A	5.3882 eV	230.10 nm	f=0.0095	<S**2>=0.000
83 ->102	-0.28993				
84 ->102	-0.23582				
85 ->102	0.34162				
86 ->102	-0.20181				
88 ->102	0.16100				
94 ->103	-0.18769				
96 ->103	0.12175				
99 ->104	-0.14116				

Excited State 35:	Singlet-A	5.4139 eV	229.01 nm	f=0.0246	<S**2>=0.000
85 ->102	-0.10077				
93 ->103	-0.10841				
95 ->103	-0.10612				
96 ->103	0.50201				
97 ->104	0.28743				
97 ->105	-0.11506				
98 ->104	0.15538				
98 ->106	0.11520				
99 ->104	-0.10268				

Excited State 36:	Singlet-A	5.4174 eV	228.86 nm	f=0.0008	<S**2>=0.000
85 ->102	-0.15914				
86 ->102	-0.36336				
87 ->102	0.42122				
88 ->102	0.10402				
93 ->103	-0.21569				
96 ->103	-0.15149				
97 ->104	-0.11415				
98 ->104	0.13261				

Excited State 37:	Singlet-A	5.4448 eV	227.71 nm	f=0.0013	<S**2>=0.000
86 ->102	-0.18430				
87 ->102	0.14818				
93 ->103	0.32038				
96 ->104	0.24271				
96 ->105	-0.10035				
97 ->103	0.16425				
98 ->104	-0.23744				
99 ->106	-0.23287				

Excited State 38:	Singlet-A	5.4621 eV	226.99 nm	f=0.0104	<S**2>=0.000
93 ->103	0.34366				
95 ->103	0.15108				
96 ->103	0.10958				
96 ->104	-0.19455				
98 ->104	0.21986				
98 ->105	-0.19483				

99 ->104	0.10631					
99 ->106	0.20964					
100 ->104	0.28557					

Excited State 39:	Singlet-A	5.4903 eV	225.82 nm	f=0.0033	<S**2>=0.000
93 ->103	-0.15600				
98 ->104	-0.13842				
99 ->104	-0.23093				
100 ->104	0.56552				
100 ->107	0.12811				
100 ->109	0.10185				

Excited State 40:	Singlet-A	5.5026 eV	225.32 nm	f=0.0161	<S**2>=0.000
97 ->104	-0.11018				
98 ->104	0.15055				
101 ->112	0.58576				
101 ->113	-0.15455				
101 ->114	0.16733				

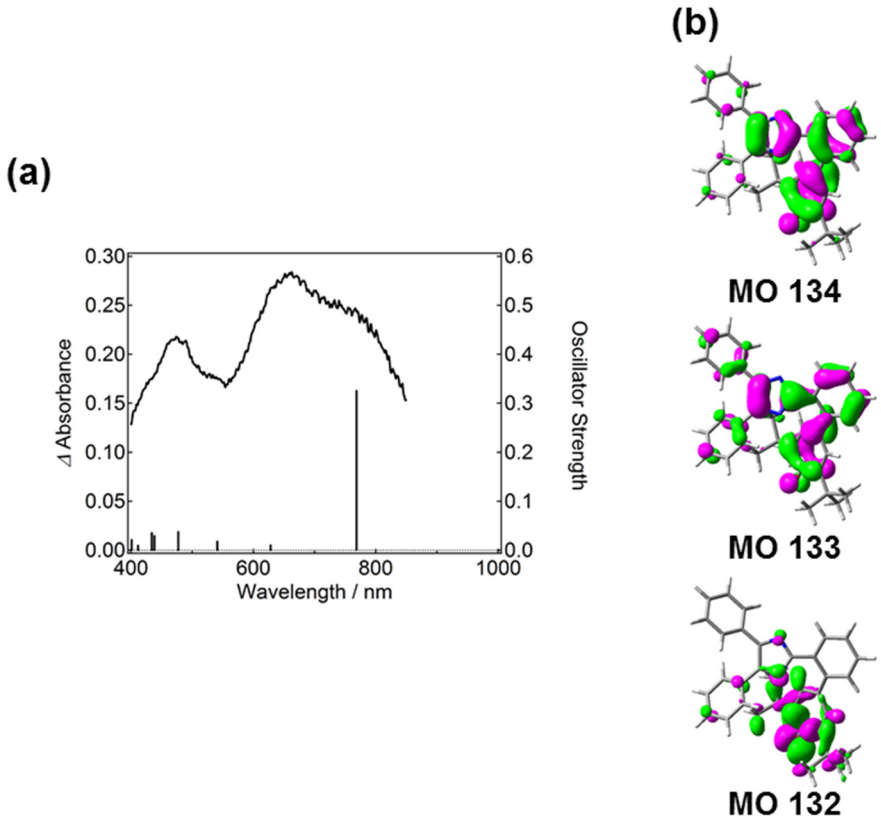


Fig. S55. (a) UV–vis absorption spectrum of **PIC2** in benzene. The calculated spectrum (MPW1PW91/6-31+G(d,p)//M052X/6-31+G(d,p) level of the theory) of the quinoid form of the open-ring isomer of **PIC2** is shown by the black lines. (b) The relevant molecular orbitals were calculated at the M052X/6-31+G(d,p) level of the theory.

10. References

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