Supporting Information

Light-Driven Controllable *Cis–trans* Isomerization in a Cycloparaphenylene Dimer Bridged by 9,9′-Bifluorenylidene

Dongmei Zhang[a], Kai Lan[a], Xiaobo Zhang[a], Jiyong Jiang[a], and Chuyang Cheng*[a]

a. *College of Chemistry, Key Laboratory of Green Chemistry and Technology of Ministry of Education, Sichuan University, Chengdu, Sichuan 610064, China.*

Corresponding Author

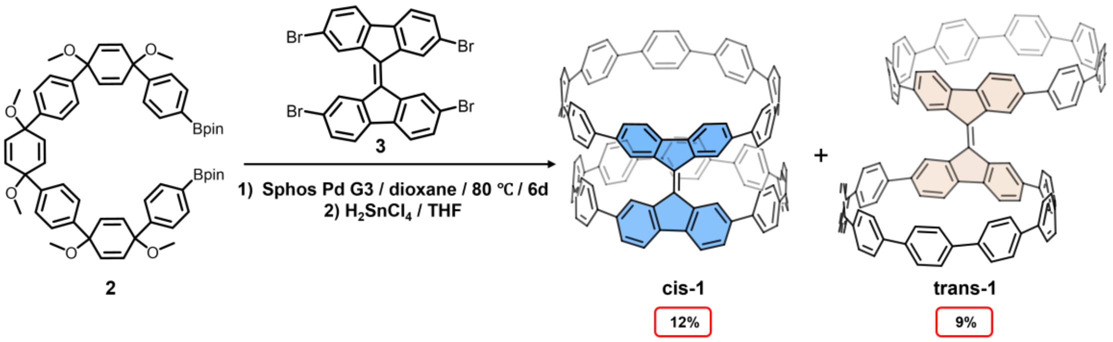
cycheng@scu.edu.cn

1. General Materials and Methods

All reagents were purchased from commercial suppliers: Innochem, Aladdin, Adamas, TCI, KESHI, and used as received. Analytical grade solvents were purchased from commercial suppliers: KESHI and used as received. HPLC grade solvents were purchased from commercial suppliers: Energy Chemical. All reactions were carried out using flame-dried glassware under a nitrogen atmosphere unless otherwise noted. Analytical thin layer chromatography (TLC) was performed using 0.25 mm silica gel 60-F plates. Flash chromatography was performed using 200-400 mesh silica gel. ^{1}H NMR, ^{13}C NMR spectra were recorded on 400 MHz Agilent ProPulse (^{1}H 400 MHz, ^{13}C 100 MHz), Bruker BioSpin GmbH (^{1}H 400 MHz, ^{13}C 100 MHz) instruments. Chemical shifts (δ) are reported in parts per million(ppm). Coupling constants are reported in Hertz (Hz), and signal multiplicity is denoted as singlet (s), doublet (d), multiplet (m) and broad (br). Structural assignments were made with additional information from gCOSY, and gNOESY experiments. Unless otherwise noted, all spectra were acquired at 25 °C (298 K). The high-resolution mass spectra (HR-MS) data was acquired on a Bruker Maxis HD APCI TOF mass spectrometer for high mass accuracy. UV-vis spectra were obtained on a Jasco V-650 UV-vis spectrometer. Single crystal X-ray diffraction data were collected on a Bruker Venture diffractometer using GaKα (λ = 1.34139) micro-focus X-ray sources. The crystals were kept at 173.00 K during data collection. Deposition Number 2444844 and 2520107 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

2. Synthesis

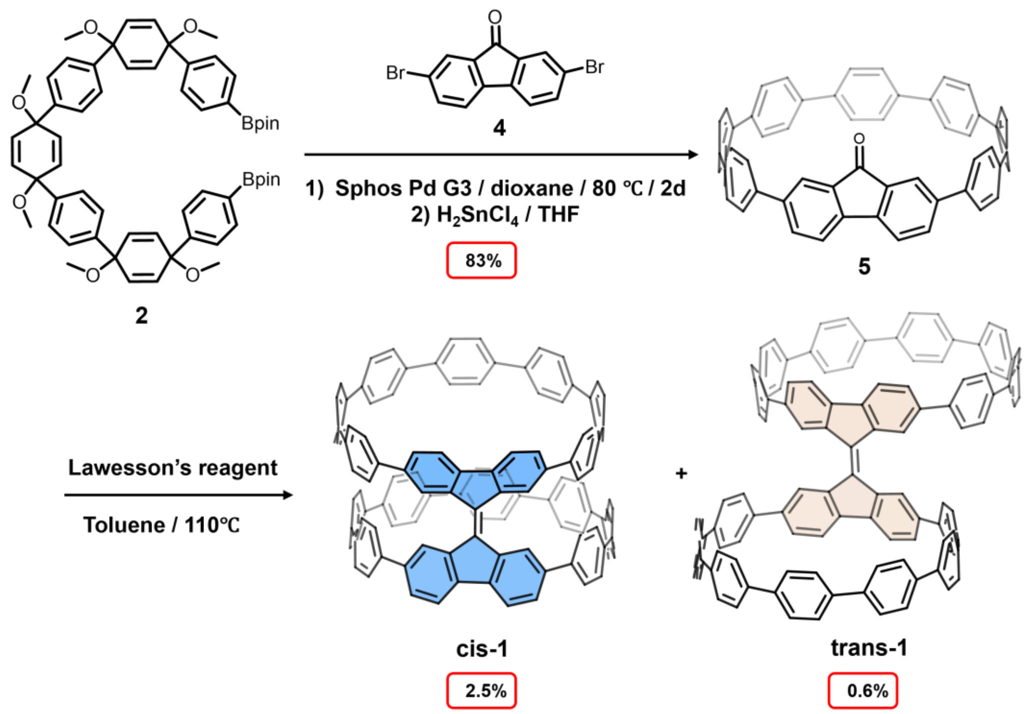
Scheme S1: Synthesis of CPP dimers via the Suzuki coupling reaction.



Compound 1: C_7-Bpin (**2**)[1] (2.43 g, 2.50 mmol), 2,2',7,7'-tetrabromo-9,9'-bifluorenylidene (**3**)[2] (0.81 g, 1.25 mmol), and (2-dicyclohexylphosphino-2',6'- dimethoxybiphenyl)[2-(2'-amino-1,1'-biphenyl)]palladium(II)methanesulfonate (SPhos Pd G_3, 240 mg, 307 µmol) were added to 1,4-dioxane (anhydrous, N_2 sparged for 30.0 min, 500 mL, 2.50 mM) and the resulting solution was sparged with N_2 for 1.0 h. The reaction mixture was heated to 80 °C followed by addition of aqueous K_3PO_4 solution (N_2 sparged for 1 h, 2.00 M, 50.0 mL) via syringe. The reaction was stirred at 80 °C for 6 days before it was allowed to cool to room temperature and water was added (100 mL). The product was extracted with dichloromethane (3 × 50 mL). The combined organic fractions were washed with water (1 × 5 mL), and brine (1 × 50 mL), dried over sodium sulfate and the solvent was removed. The resulting crude product was used on the next step without further purification. In the next step, to a solution of $SnCl_2{\cdot}2H_2O$ (2.51 g, 11.1 mmol) in THF (30 mL) was added concentrated aqueous HCl (1.85 mL, 22.2 mmol) at room temperature and the resulting solution was stirred for 15 min under nitrogen atmosphere. The resulting mixture was added to a dispersion of the as prepared crude product in THF (30 mL) and the mixture was stirred for 4 h at room temperature. The reaction mixture was concentrated under reduced pressure and subjected to silica gel column chromatography under light-protective conditions (20% CH_2Cl_2/PE), yielding deep red solids ***cis*-1** (20.2 mg, 12%) and ***trans*-1** (14.8 mg, 9%). ***cis*-1:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 1.6 Hz, 4H), 7.74 (dd, *J* = 8.2, 1.4 Hz, 4H), 7.72 (s, 8H), 7.67 – 7.61 (m, 12H), 7.62 – 7.54 (m, 32H), 7.51 (d, *J* = 8.5 Hz, 8H). ***trans*-1:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.3, *J* = 1.7 Hz, 4H), 7.70 – 7.65 (dd, 4H), 7.57 – 7.42 (m, 44H).**All characterization data for both *cis*-1 and**

***trans*-1 correspond to samples prepared via the Suzuki route.**

Scheme S2: Synthesis of CPP dimers via Lawesson's reagent.



Compound 5: C_7-Bpin (**2**)[1] (40.4 mg, 93.5 µmol), 2,7-dibromo-9H-fluoren-9-one1 (**4**) (185 mg, 211 µmol), and (2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl)[2-(2'-amino-1,1'-biphenyl)]palladium(II)methanesulfonate (SPhos Pd G_3, 55 mg, 70.5 µmol) were added to 1,4-dioxane (anhydrous, N_2 sparged for 30 min, 22 mL, 500 µM) and the resulting solution was sparged with N_2 for 1.0 h. The reaction mixture was heated to 80 °C followed by addition of aqueous K_3PO_4 solution (N_2 sparged for 1 h, 2.00 M, 2.2 mL) via syringe. The reaction was stirred at 80 °C for 48 h before it was allowed to cool to room temperature and water was added (100 mL). The product was extracted with dichloromethane (3 × 50 mL). The combined organic fractions were washed with water (1 × 5 mL), and brine (1 × 50 mL), dried over sodium sulfate and the solvent was removed. The resulting crude product was used on the next step without further purification. In the next step, to a solution of $SnCl_2 \cdot 2H_2O$ (1.10 g, 4.87 mmol) in THF (30 mL) was added concentrated aqueous HCl (81.0 µL, 9.74 mmol) at room temperature and the resulting solution was stirred for 15 min under nitrogen atmosphere. The resulting mixture was added to a dispersion of the as prepared crude product in THF (30 mL) and the mixture was stirred for 16 h at room temperature. The reaction mixture was concentrated under reduced

pressure and immediately subjected to silica gel column chromatography (50% CH_2Cl_2/PE), yielding **Compound 5** as a pale yellow, yellow-fluorescent solid (55.2 mg, 83%).[1]H NMR (400 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.61 – 7.58 (m, 8H), 7.55 – 7.51 (m, 16H), 7.45-7.41 (m, 6H), 7.29 (d, *J* = 1.8 Hz, 2H).

Compound 1: To a toluene solution (2 mL) of **Compound 5** (72.1 mg, 102 μmol) was added Lawesson's reagent (69.0 mg, 171 μmol) under an inert atmosphere. The reaction was stirred at 110 °C for 12 h before it was allowed to cool to room temperature. The reaction mixture was concentrated under reduced pressure and subjected to silica gel column chromatography (20% CH_2Cl_2/PE), yielding deep red solids ***cis*-1** (175 μg, 2.5%) and ***trans*-1** (45 μg, 0.6%).

3.Nuclear Magnetic Resonance and HR-MS Spectra

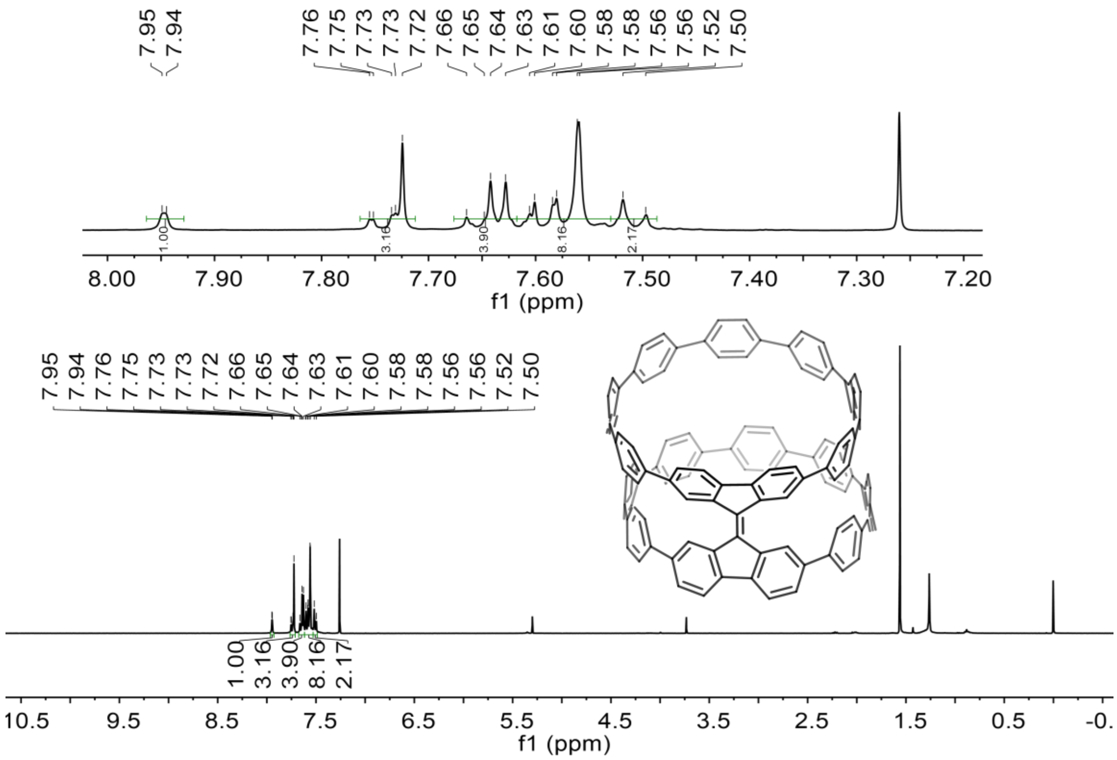


Figure S1 [1]H NMR spectrum (400 MHz) of ***cis*-1** in $CDCl_3$ at room temperature.

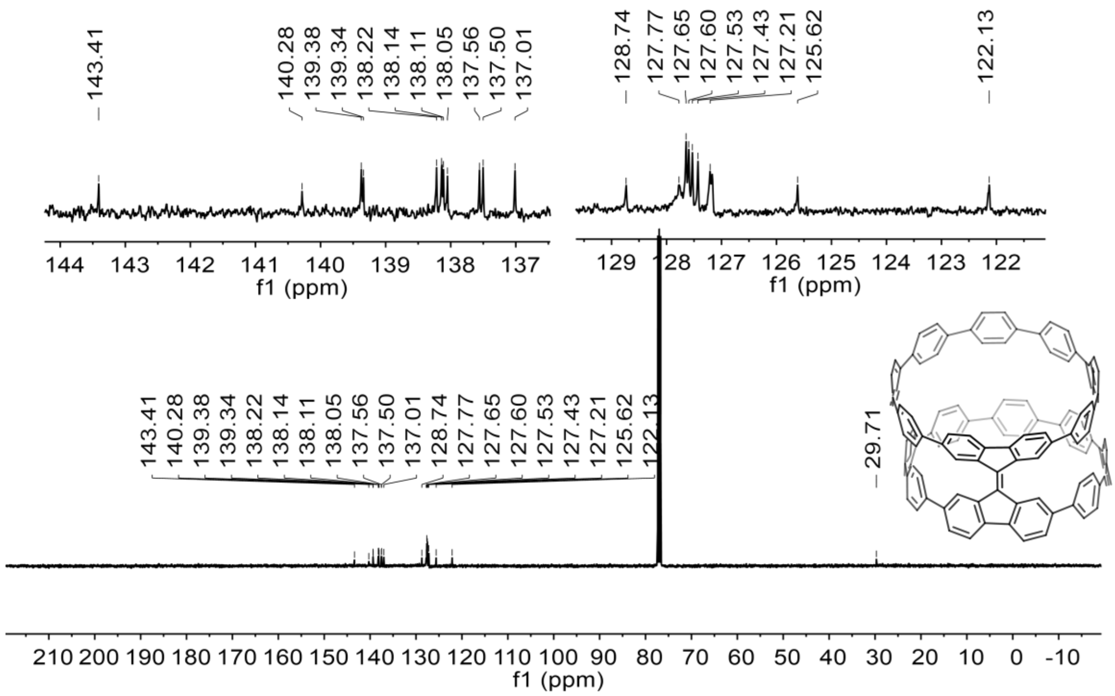


Figure S2 ^{13}C NMR spectrum (101 MHz) of ***cis*-1** in $CDCl_3$ at room temperature.

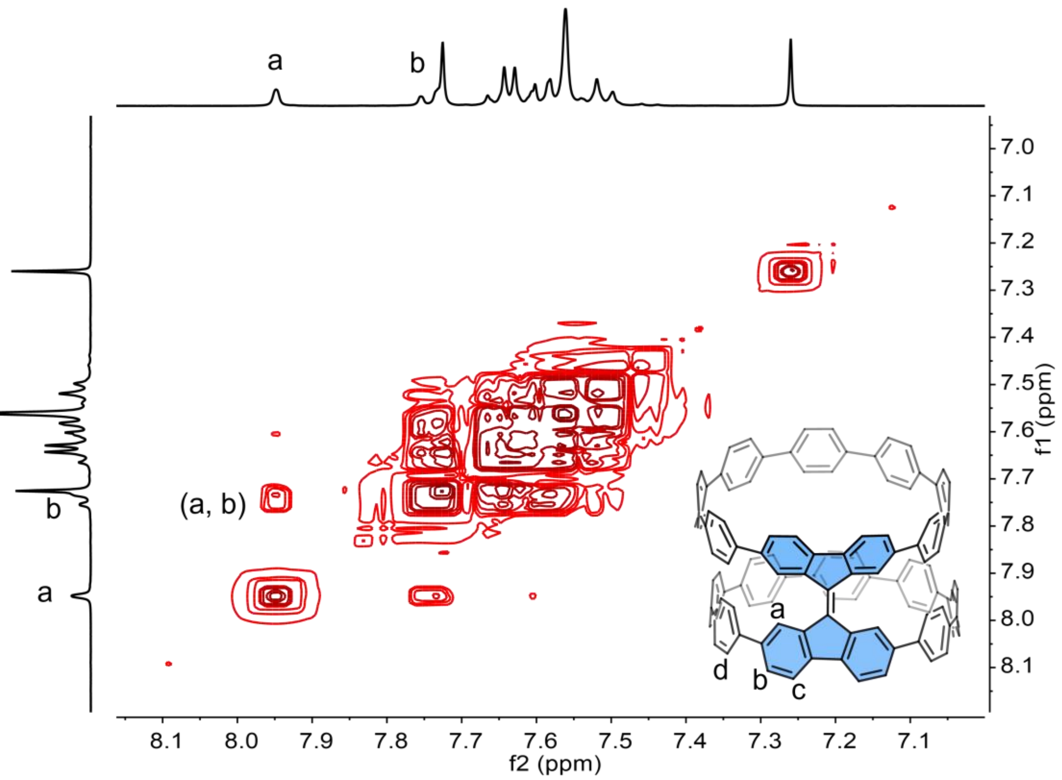


Figure S3 COSY NMR spectrum (400 MHz) of ***cis*-1** in $CDCl_3$ at room temperature.

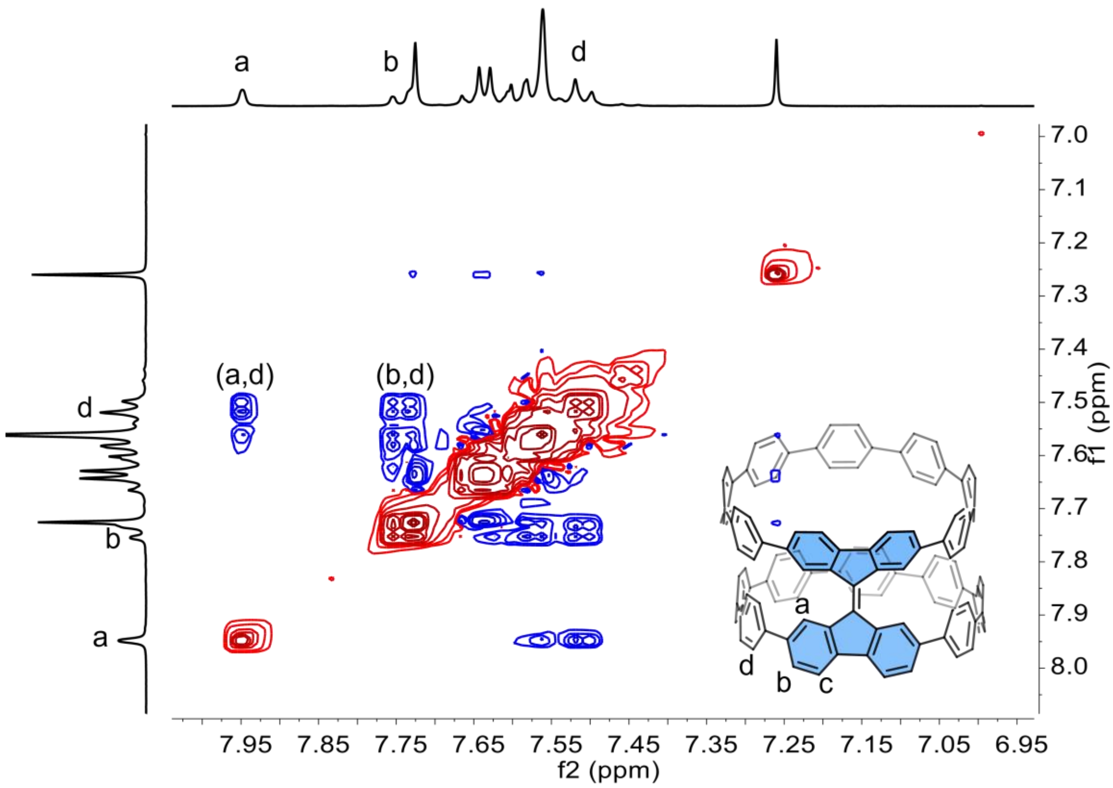


Figure S4 NOESY NMR spectrum (400 MHz) of ***cis*-1** in $CDCl_3$ at room temperature.

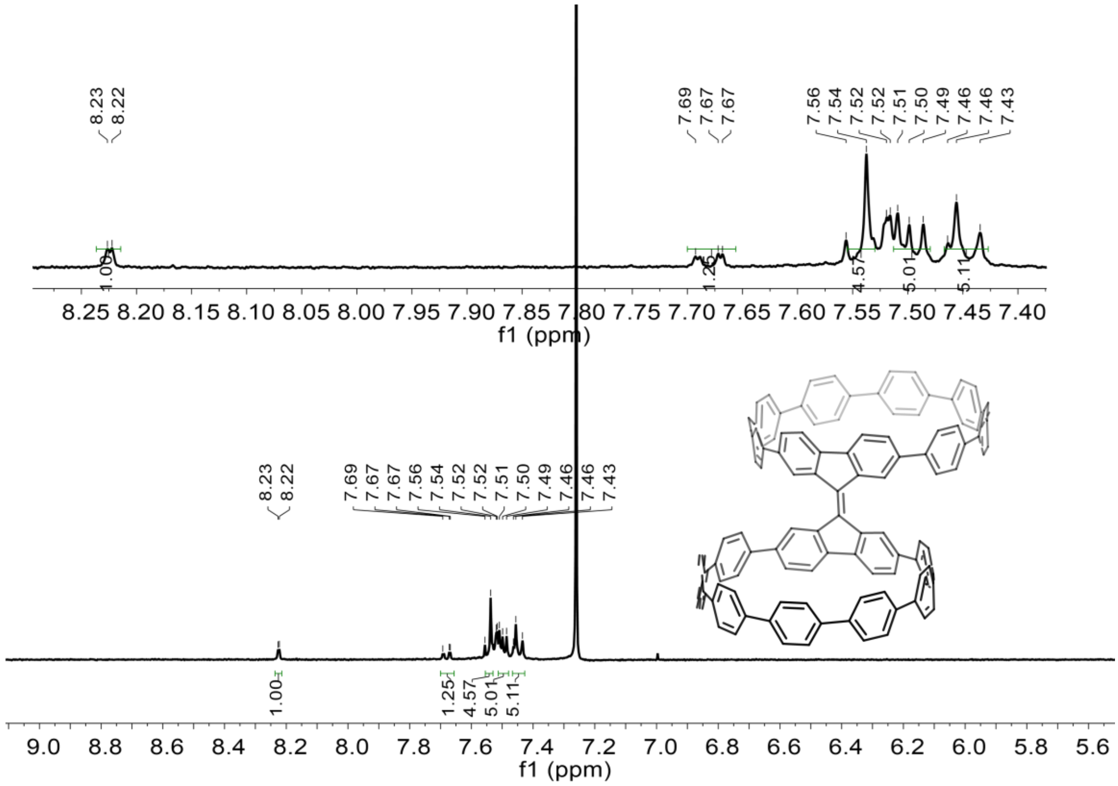


Figure S5 ^{1}H NMR spectrum (400 MHz) of ***trans*-1** in $CDCl_3$ at room temperature.

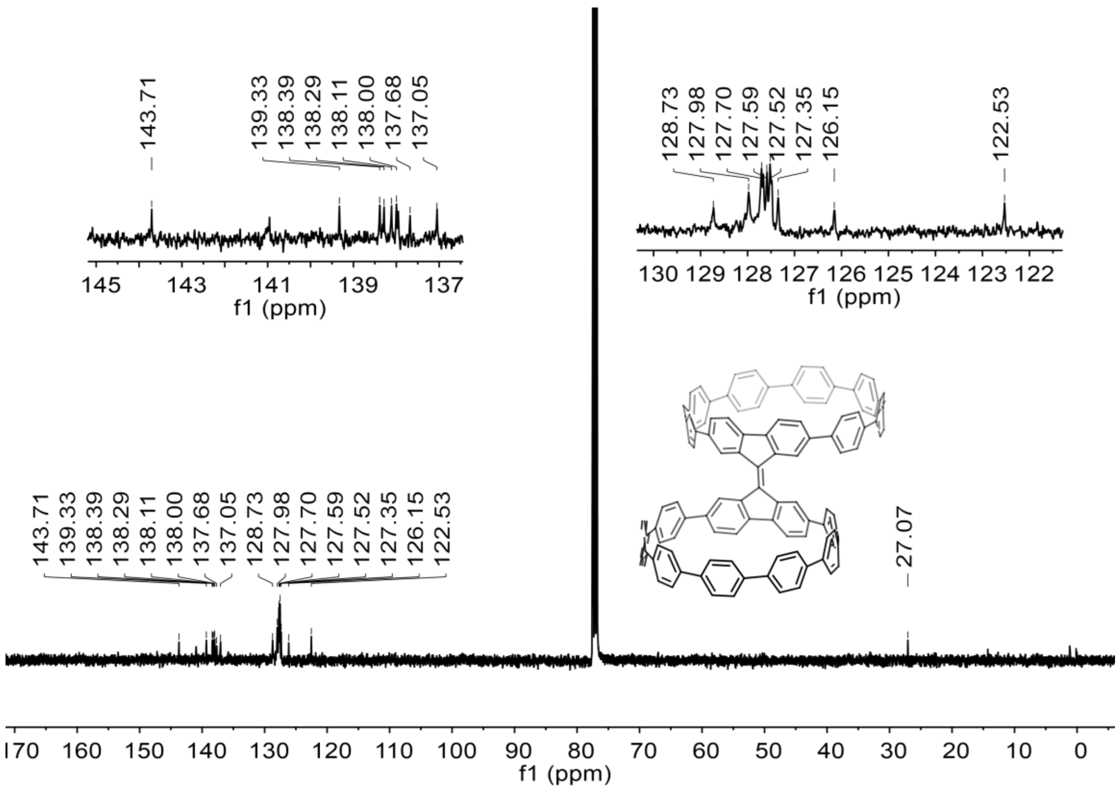


Figure S6 ^{13}C NMR spectrum (101 MHz) of ***trans*-1** in $CDCl_3$ at room temperature.

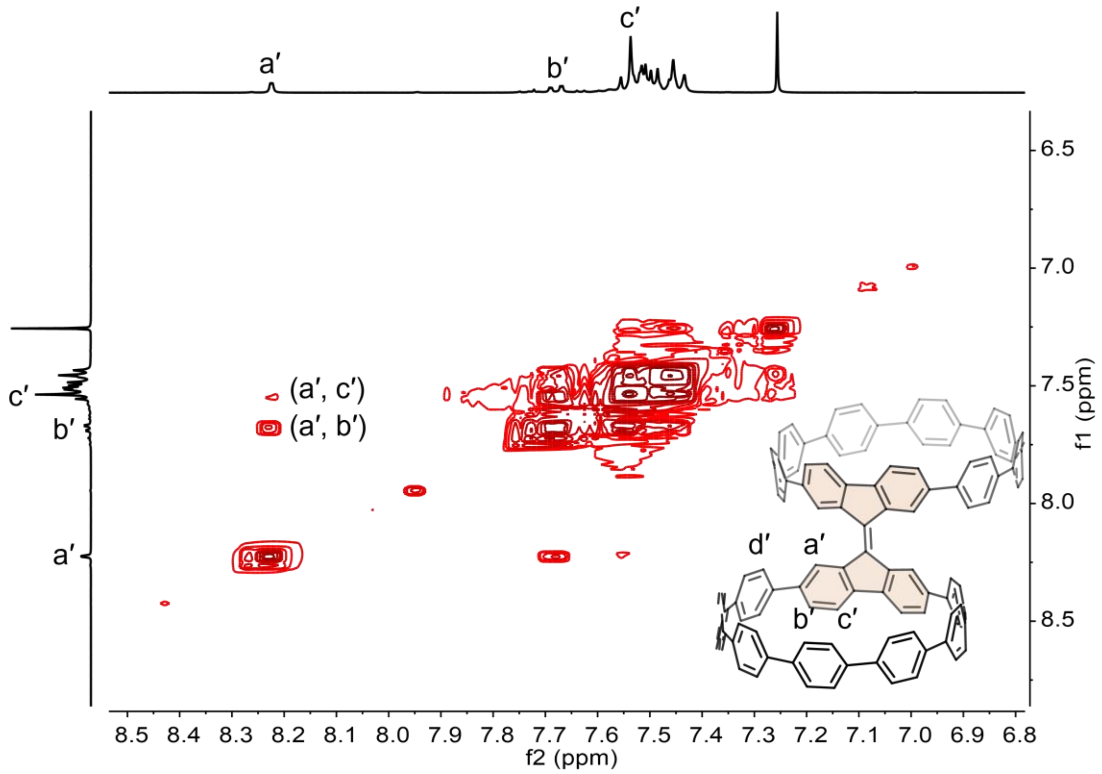


Figure S7 COSY NMR spectrum (400 MHz) of ***trans*-1** in $CDCl_3$ at room temperature.

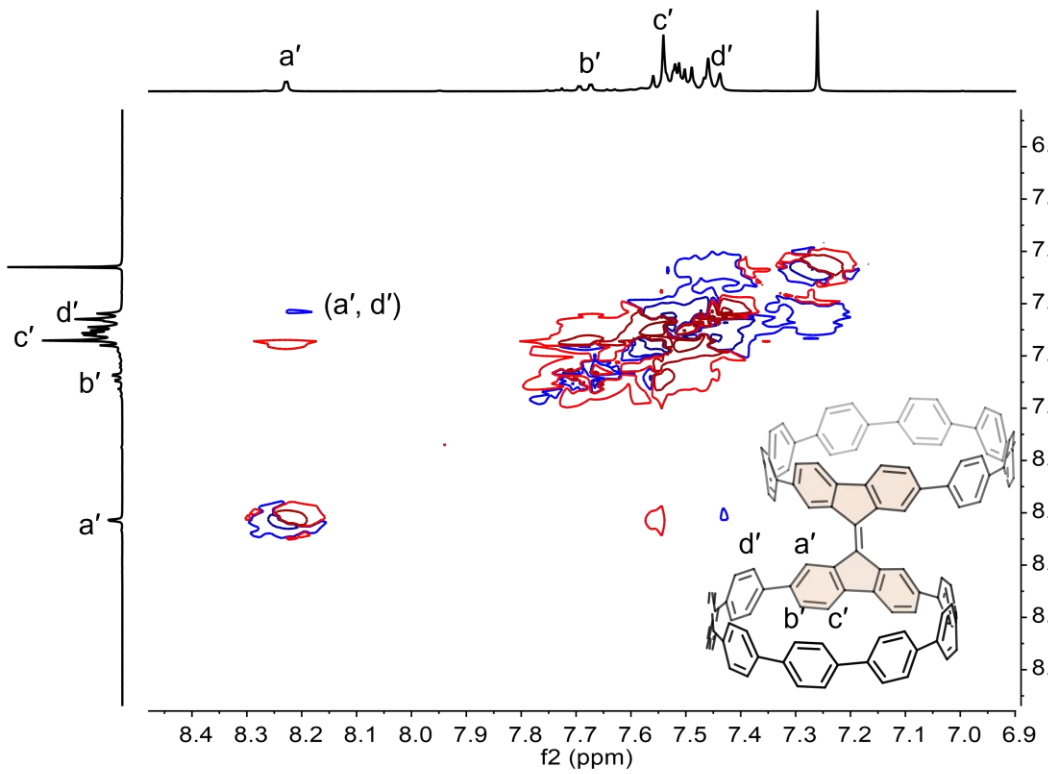


Figure S8 NOESY NMR spectrum (400 MHz) of ***trans*-1** in $CDCl_3$ at room temperature.

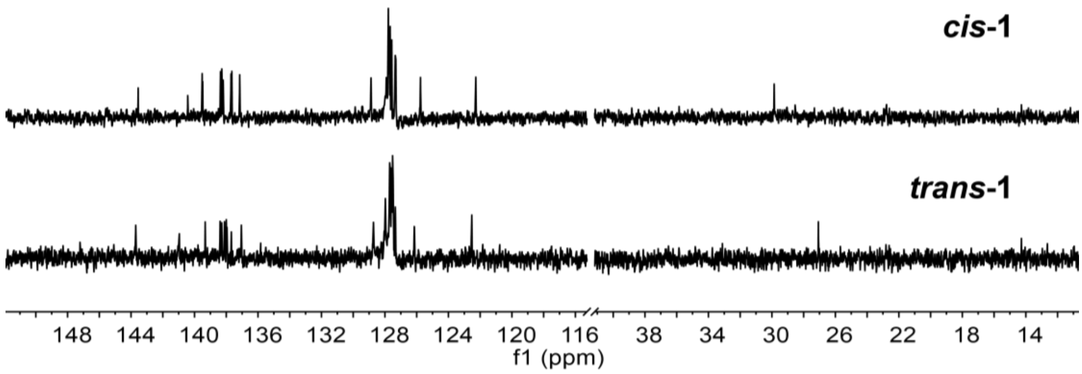


Figure S9 Comparative ^{13}C NMR spectra of the ***cis*-1** and ***trans*-1** isomers.

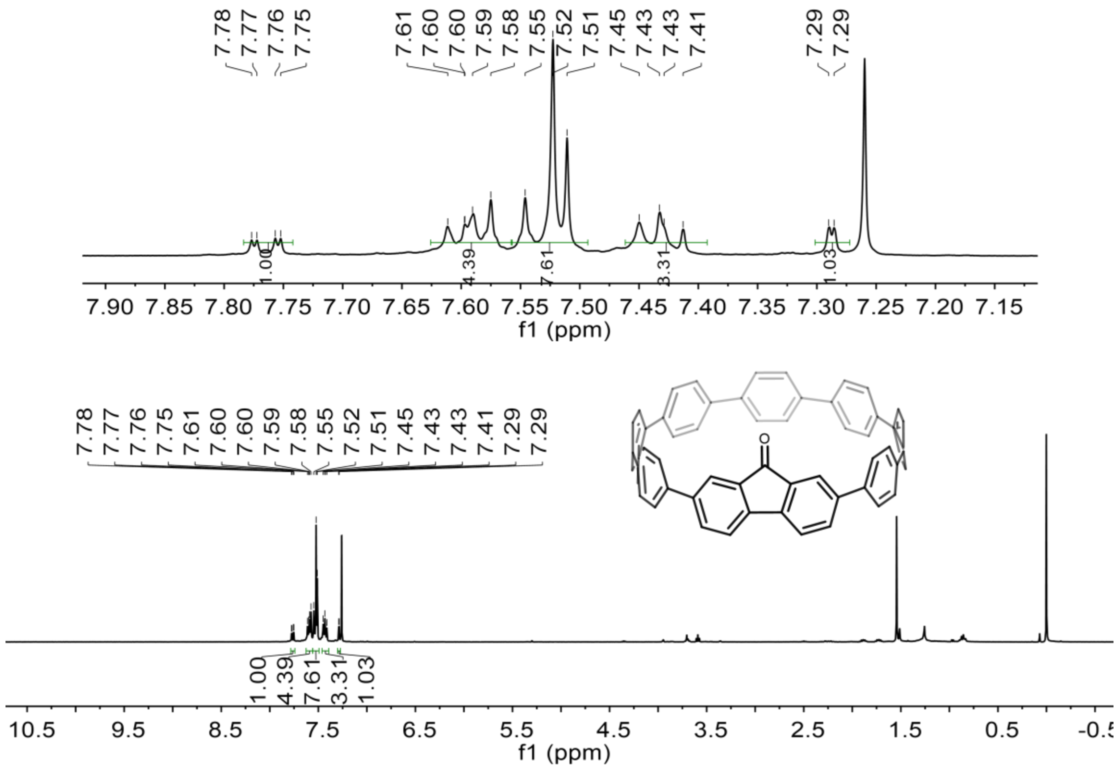


Figure S10 ^{1}H NMR spectrum (400 MHz) of Compound 5 in $CDCl_3$ at room temperature.

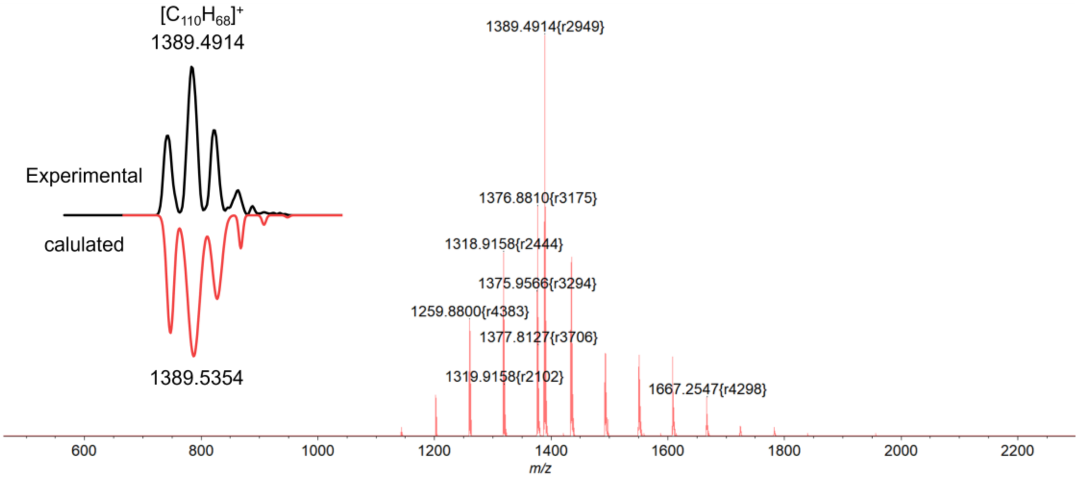


Figure S11 MALDI-HRMS of compound ***cis*-1** (Calcd 1389.5354, found 1389.4914). Using poly(propylene glycol), (average Mn ~1500) for calibration.

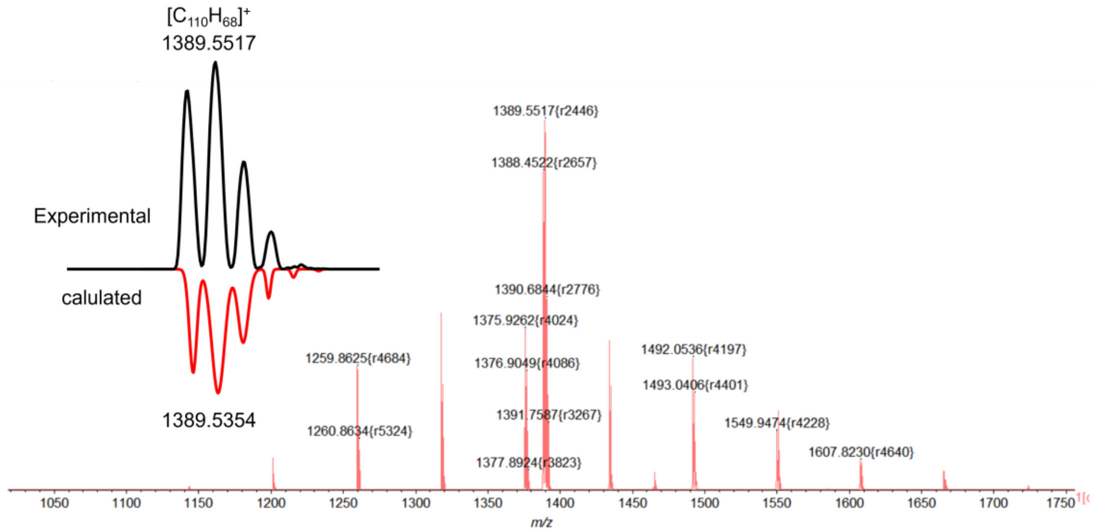


Figure S12 MALDI-HRMS of ***trans*-1** (Calcd 1389.5354, found 1389.5517). Using poly(propylene glycol), (average Mn ~1500) for calibration.

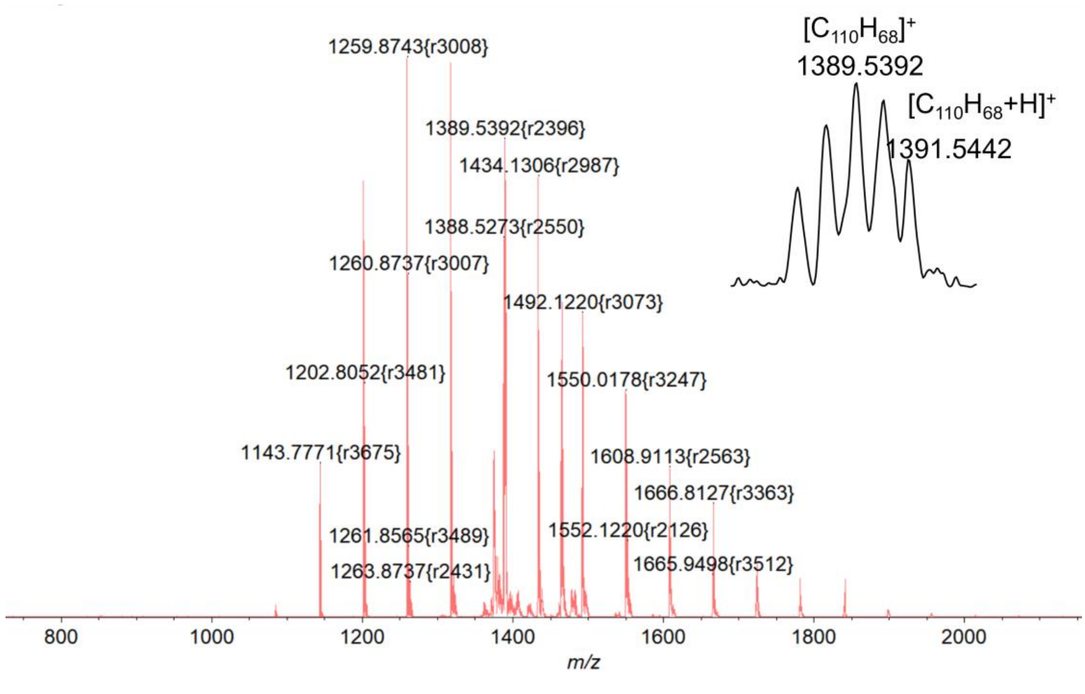


Figure S13 MALDI-HRMS of protonated intermediate (Calcd 1391.5466, found 1391.5442). Using poly(propylene glycol), (average Mn ~1500) for calibration.

4. Photophysical Properties

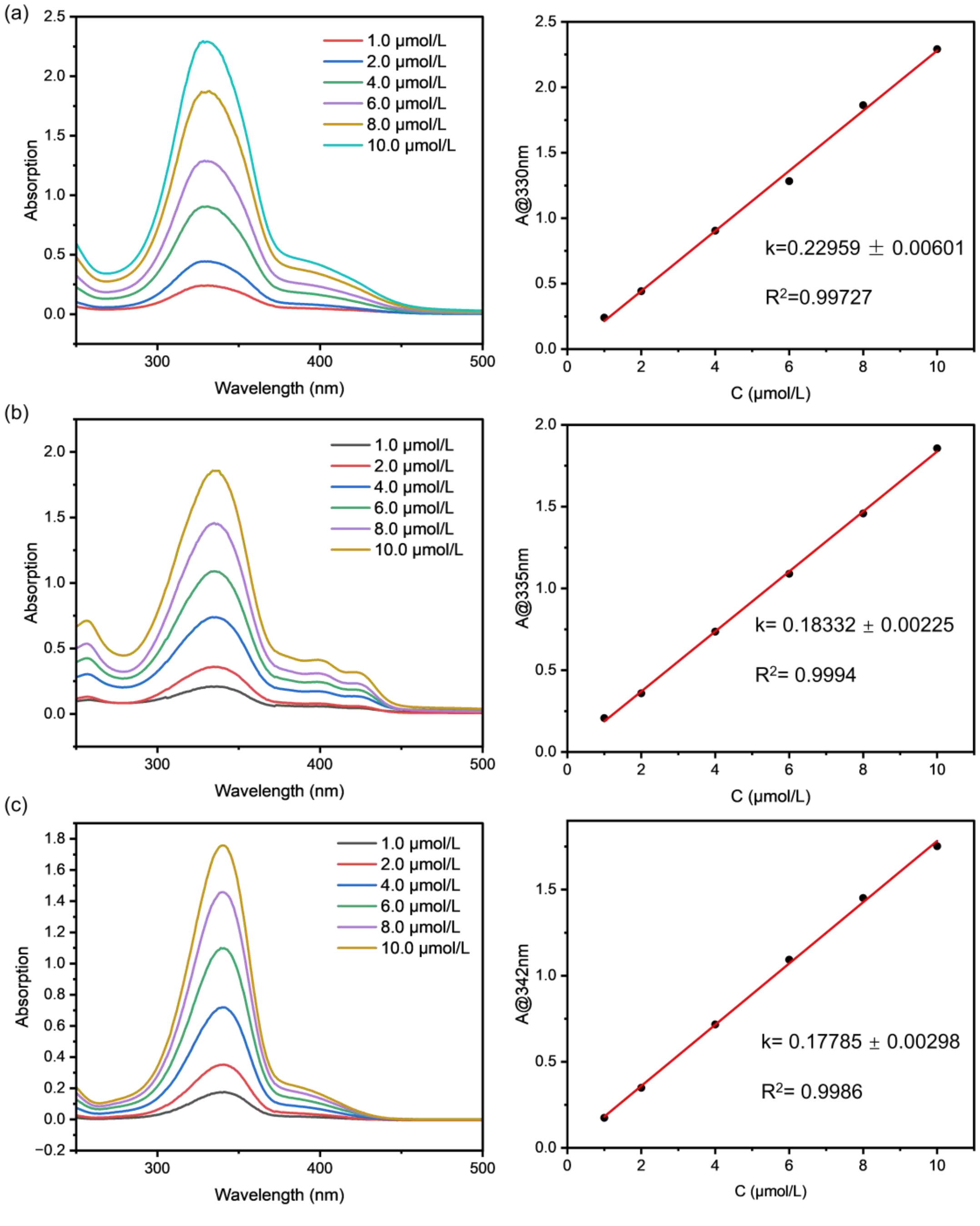


Figure S14 Calibrated absorption spectra of (a) ***cis*-1**, (b) ***trans*-1**, and (c) [9]CPP in dichloromethane at 298 K.

5. Crystallographic Data

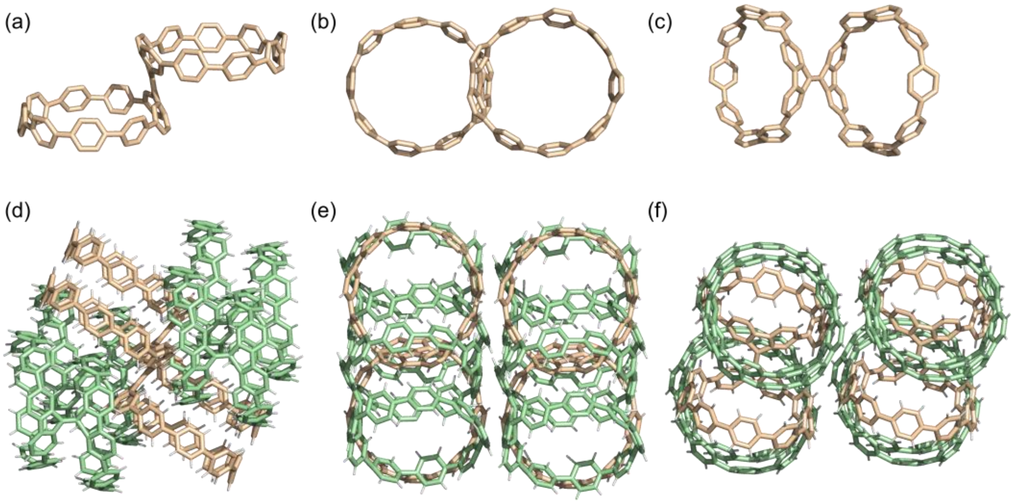


Figure S15 Crystal structure of ***cis*-1@*trans*-1**: (a) front view; (b) top view; (c) side view. Crystal packing structure of ***cis*-1@*trans*-1**: (d) front view; (e) top view. Color code: C, palegreen; H, white; H atoms and solvent molecules have been omitted for clarity.

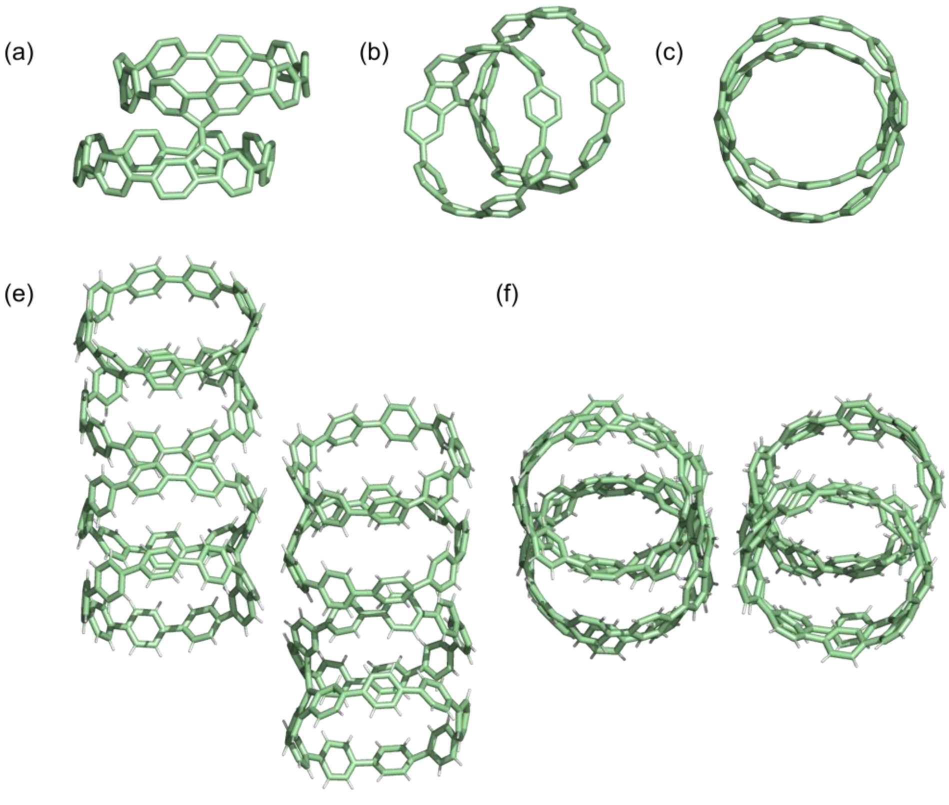


Figure S16 Crystal structure of ***cis-1***: (a) front view; (b) side view; (c) top view. Crystal packing structure of ***cis-1***: (d) front view; (e) top view. Color code: C, palegreen; H, white; H atoms and solvent molecules have been omitted for clarity.

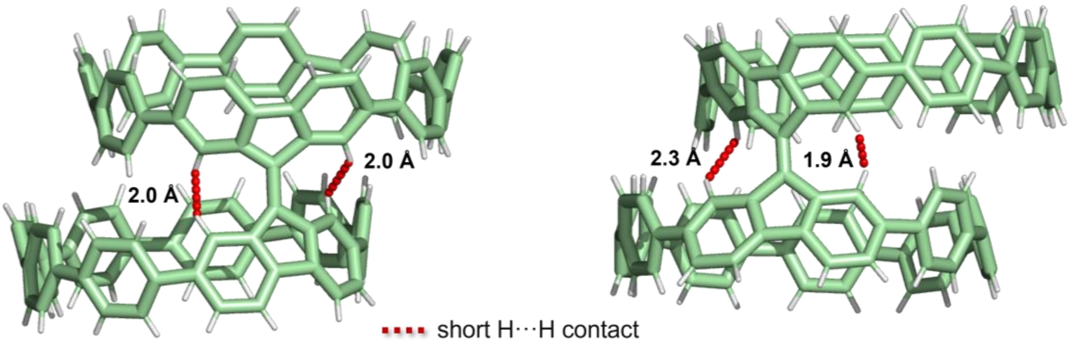


Figure S17 Short H···H contact in ***cis*-1**.

Table S1. Crystal data and structure refinement for ***cis*-1**

Identification code	***cis*-1**	
Empirical formula	C110 H68	
CCDC code	2520107	
Formula weight	1389.64	
Temperature	170.00 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 27.0719(7) Å	a= 90°.
	b = 27.2412(7) Å	b= 90°.
	c = 60.1979(16) Å	g = 90°.
Volume	44394(2) Å^3	
Z	16	
Density (calculated)	0.832 Mg/m^3	
Absorption coefficient	0.238 mm^{-1}	
F(000)	11648	
Crystal size	0.25 x 0.17 x 0.05 mm^3	
Theta range for data collection	3.098 to 55.306°.	
Index ranges	-31<=h<=33, -33<=k<=33, -73<=l<=67	
Reflections collected	221803	
Independent reflections	41985 [R(int) = 0.1495]	
Completeness to theta = 53.594°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.2746	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	41985 / 454 / 1825	
Goodness-of-fit on F^2	0.885	
Final R indices [I>2sigma(I)]	R1 = 0.1884, wR2 = 0.3908	
R indices (all data)	R1 = 0.2788, wR2 = 0.4487	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.474 and -0.417 e.Å^{-3}	

Table S2. Crystal data and structure refinement for ***trans*-1 / *cis*-1.**

Identification code	***trans*-1 / *cis*-1**	
Empirical formula	$C_{110} H_{68}$	
CCDC code	2444844	
Formula weight	1389.64	
Temperature	173.00 K	
Wavelength	1.34139 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.327(2) Å	a= 98.977(5)°.
	b = 15.559(2) Å	b= 93.488(5)°.
	c = 33.396(4) Å	g = 105.655(5)°.
Volume	7530.0(17) $Å^3$	
Z	3	
Density (calculated)	0.919 Mg/m^3	
Absorption coefficient	0.252 mm^{-1}	
F(000)	2184	
Crystal size	0.17 x 0.17 x 0.05 mm^3	
Theta range for data collection	3.130 to 55.275°.	
Index ranges	-18<=h<=18, -18<=k<=19, -40<=l<=40	
Reflections collected	101902	
Independent reflections	28221 [R(int) = 0.1749]	
Completeness to theta = 53.594°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.4477	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	28221 / 2409 / 2045	
Goodness-of-fit on F^2	0.920	
Final R indices [I>2sigma(I)]	R1 = 0.1706, wR2 = 0.3454	
R indices (all data)	R1 = 0.2730, wR2 = 0.4057	
Extinction coefficient	0.00082(16)	
Largest diff. peak and hole	0.531 and -0.457 e.$Å^{-3}$	

6. Controllable conformational transition

6.1 NMR spectra of the controllable conformational transition

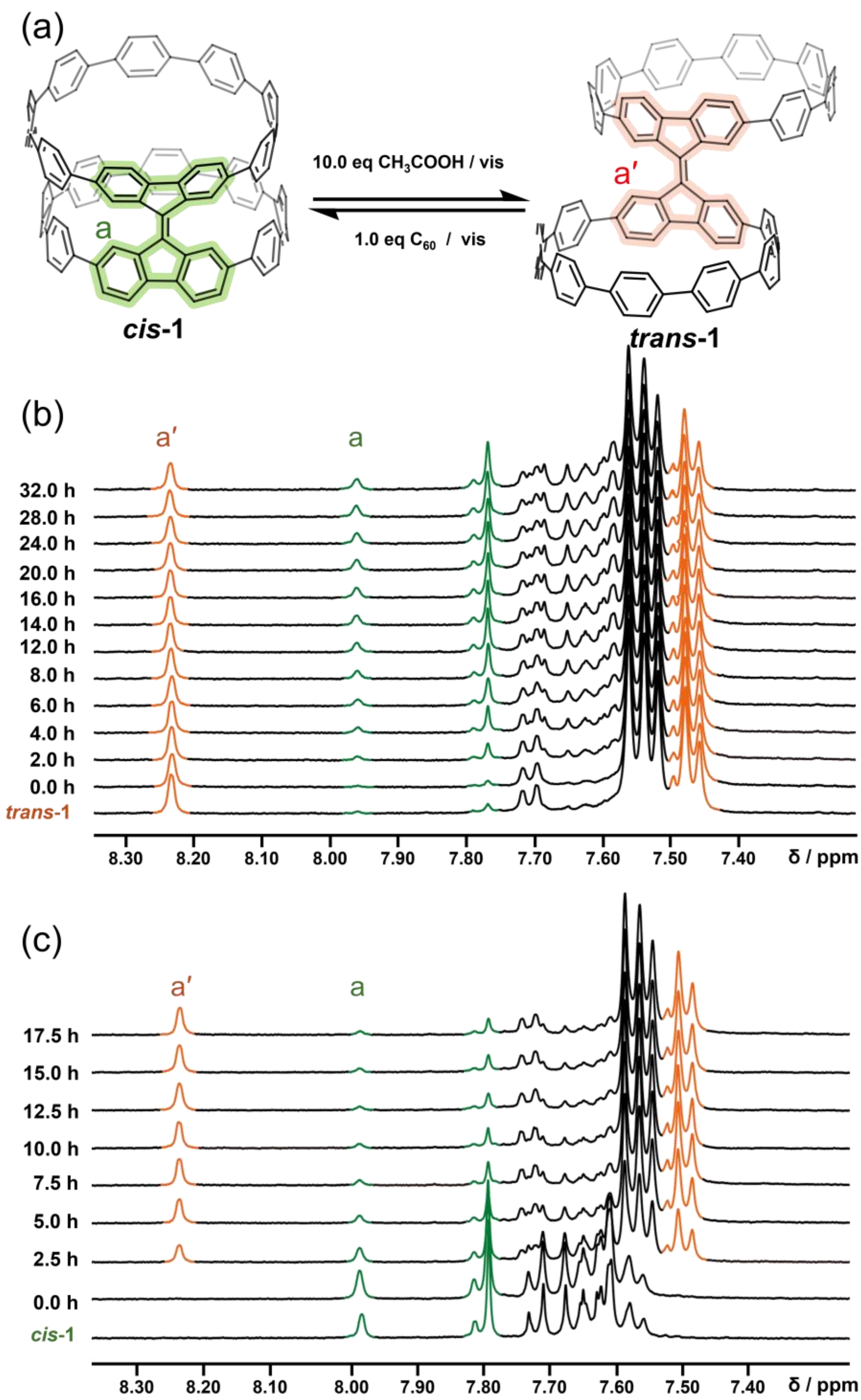


Figure S18 (a) Schematic diagram of the controllable *cis*-*trans* photo-switching process. (b) Time-dependent ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1** under vis and 10.0 eq AcOH. (c) Time-dependent ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***cis*-1** under vis and 1.0 eq C_{60}.

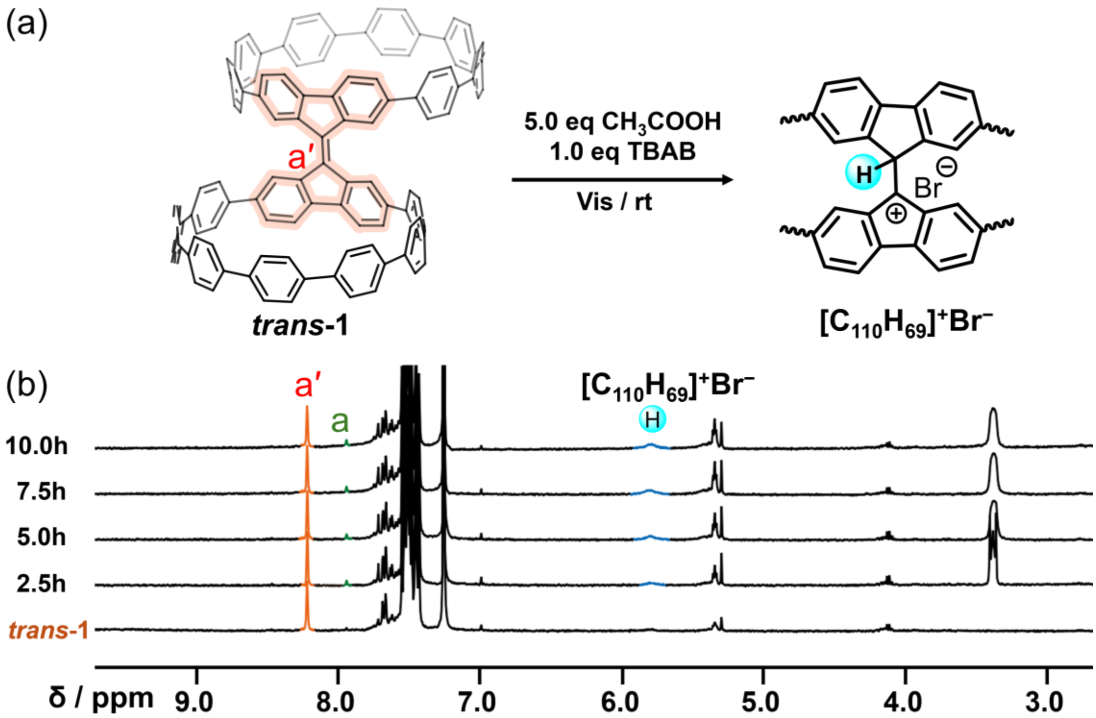


Figure S19. (a) Schematic diagram of the protonation of ***trans*-1**. (b)Time-dependent [1]H NMR spectra (400 MHz, $CDCl_3$-*d*, 298K) of ***trans*-1** under visible light irradiation with the addition of 5.0 eq AcOH and 1.0 eq TBAB.

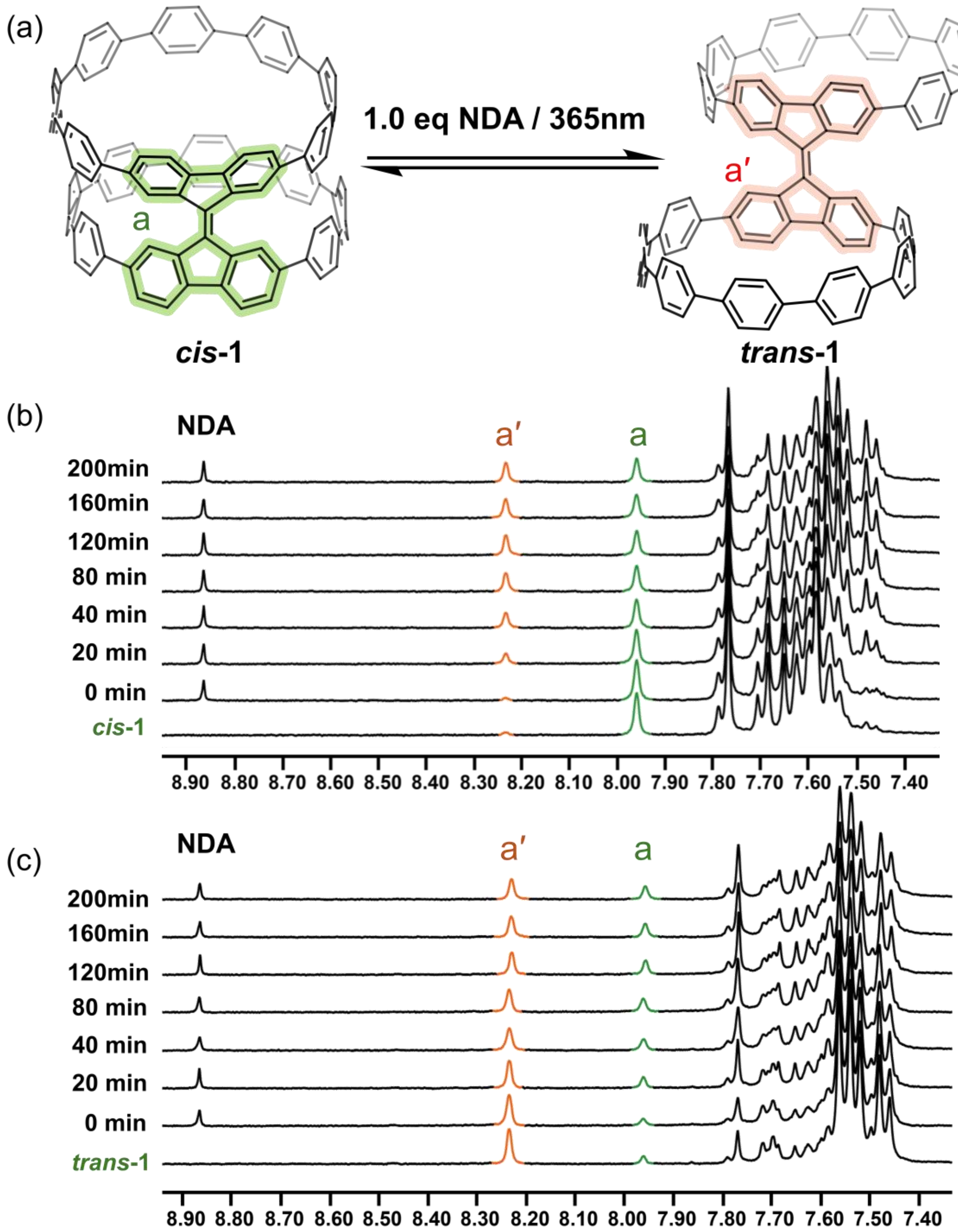


Figure S20. (a) Schematic diagram of the controllable *cis*-*trans* photo-switching process. (b) Time-dependent [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***cis*-1** under 365 nm irradiation with the addition of 1.0 eq naphthalene dianhydride (NDA). (c) Time-dependent [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1** under 365 nm irradiation with the addition of 1.0 eq naphthalene dianhydride (NDA).

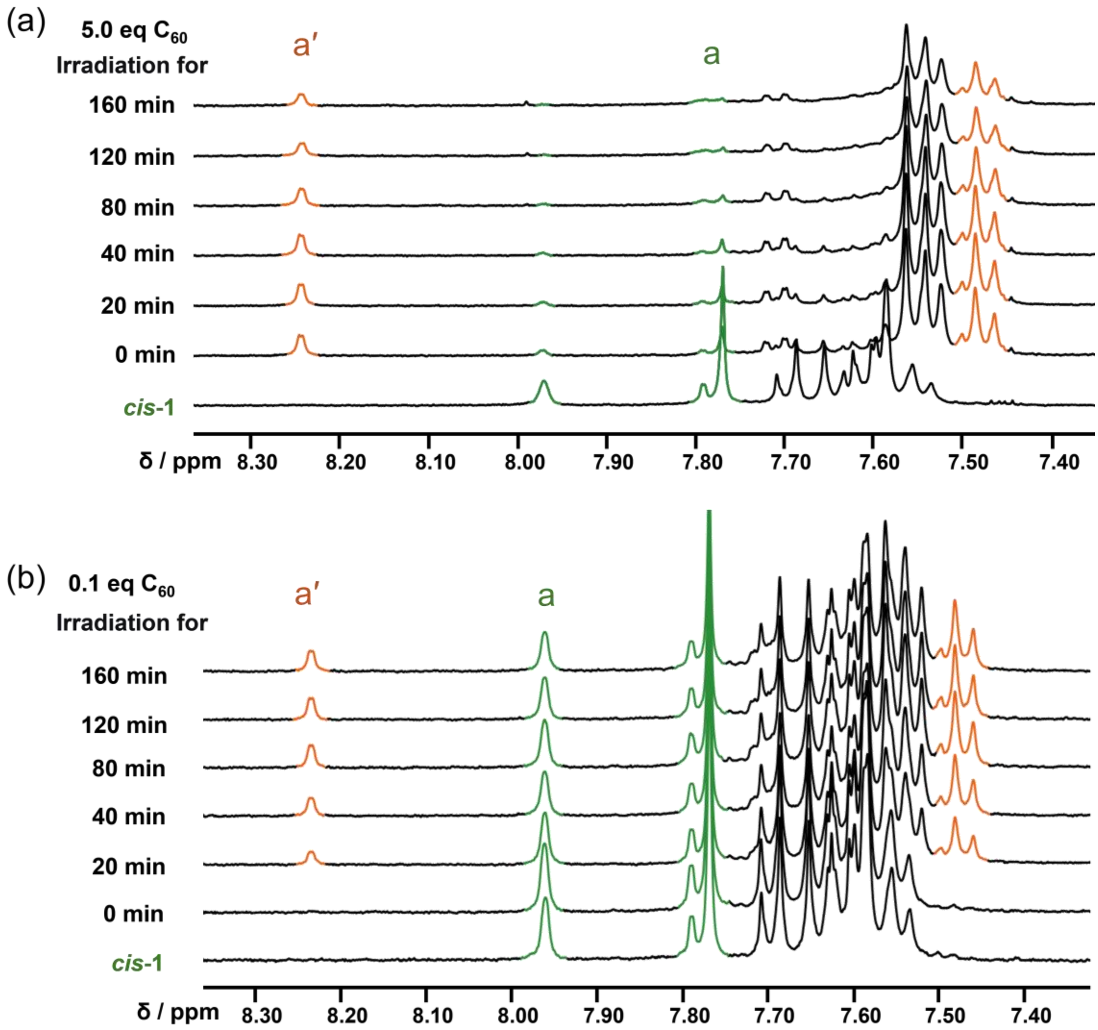


Figure S21. (a)Time-dependent ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***cis*-1** under 365 nm irradiation with the addition of 5.0 eq C_{60}. (b) Time-dependent ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1** under 365 nm irradiation with the addition of 0.1 eq C_{60}.

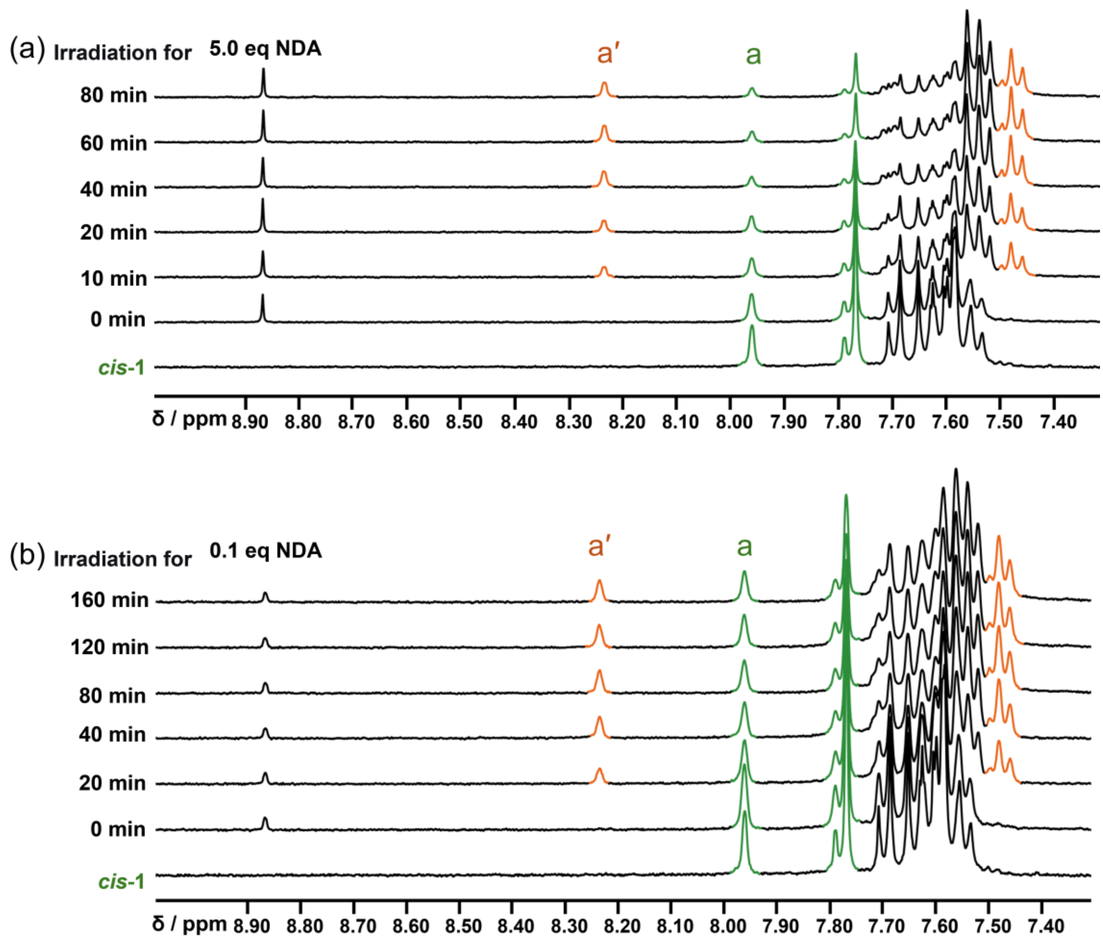


Figure S22. (a)Time-dependent ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***cis*-1** under 365 nm irradiation with the addition of 5.0 eq naphthalene dianhydride (NDA). (b) Time-dependent ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1** under 365 nm irradiation with the addition of 0.1 eq naphthalene dianhydride (NDA).

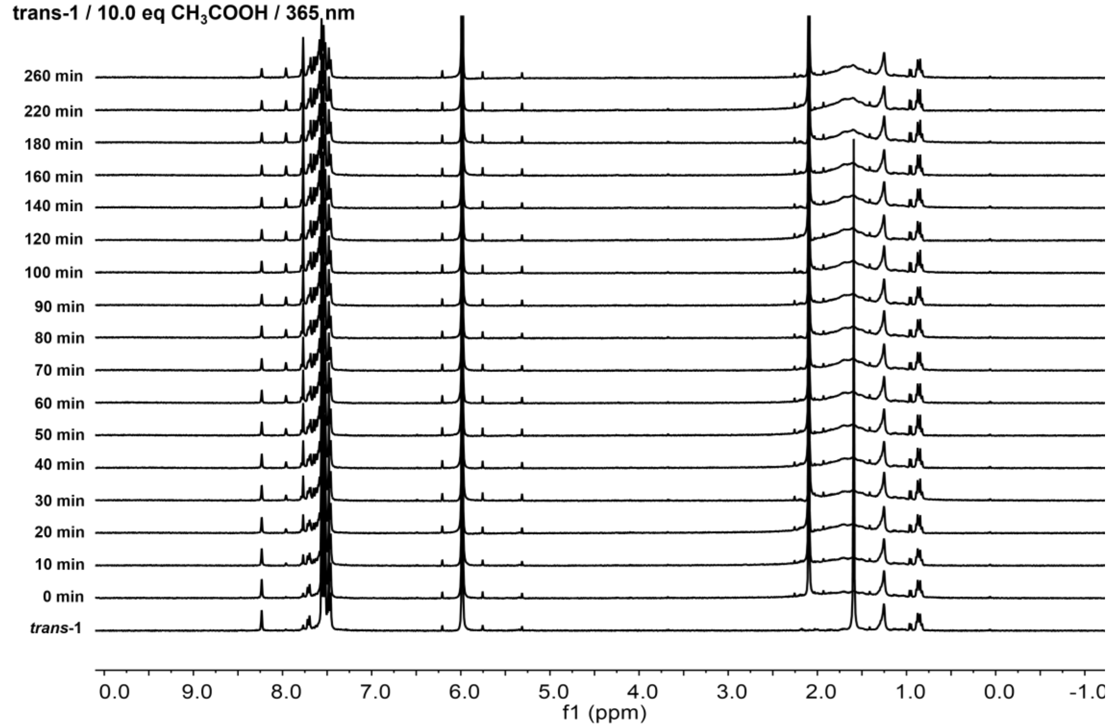


Figure S23 Time-dependent ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1** under 365 nm and 10.0 eq AcOH.

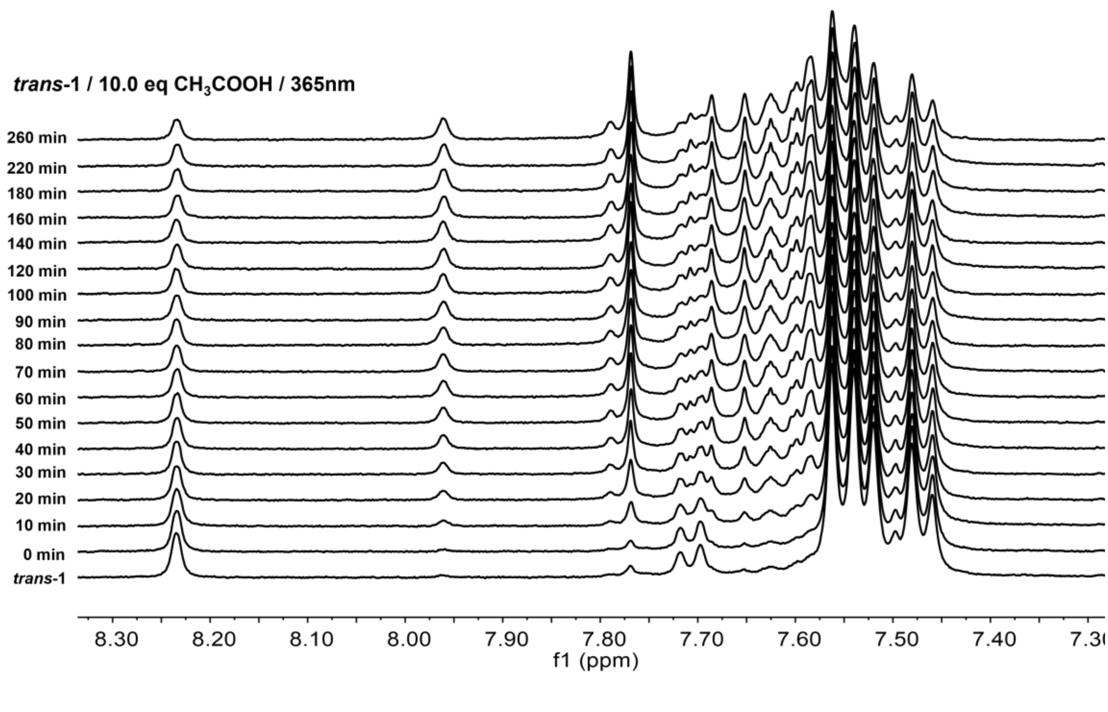


Figure S24 Time-dependent ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1** under 365 nm and 10.0 eq AcOH. Partially enlarged view.

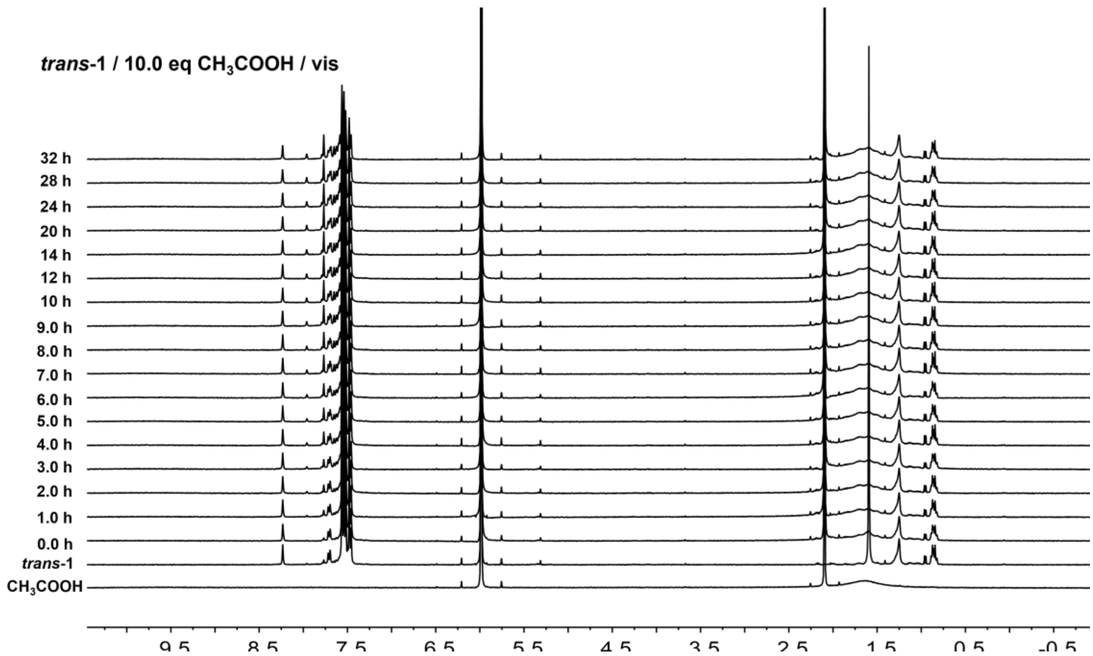


Figure S25 Time-dependent [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1** under vis and 10.0 eq AcOH.

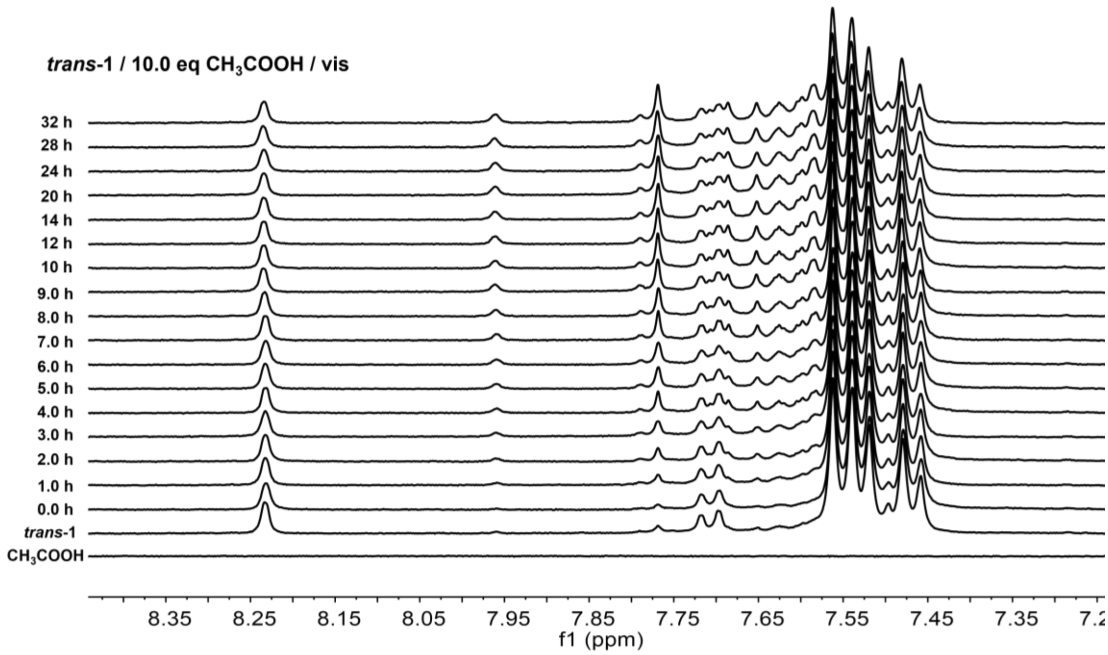


Figure S26 Time-dependent [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1** under vis and 10.0 eq AcOH. Partially enlarged view.

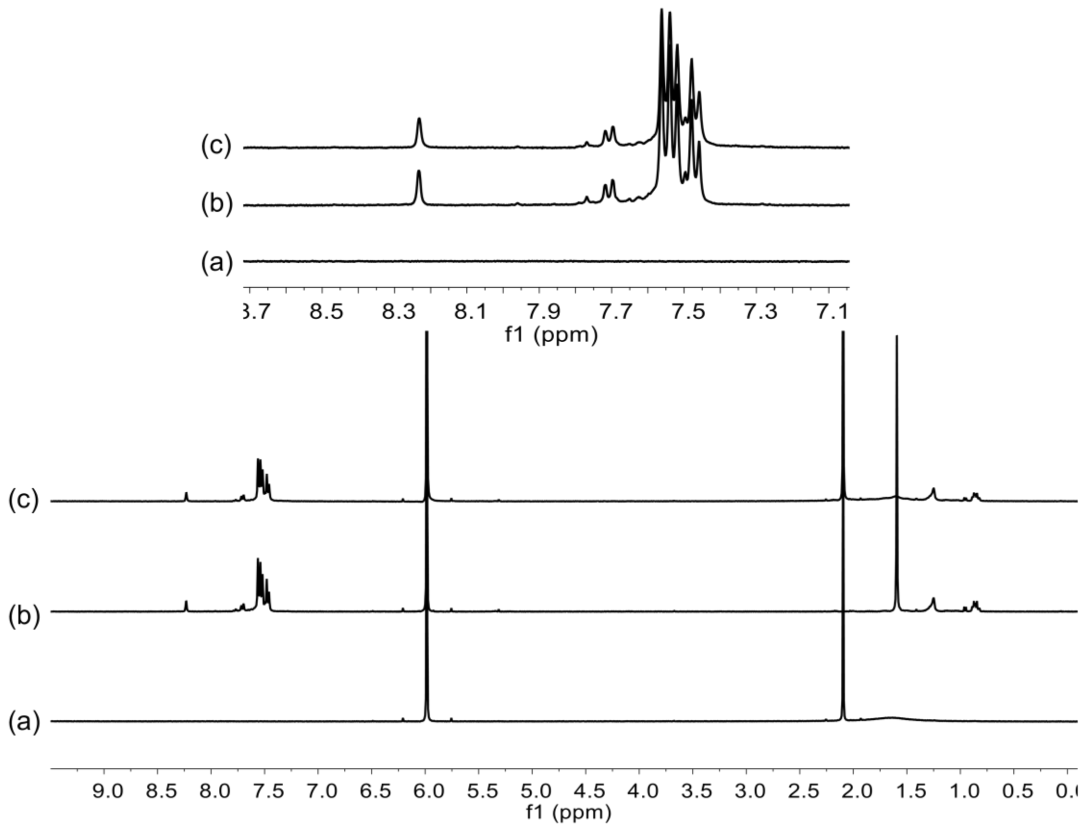


Figure S27 (a) [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of AcOH. (b) [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1**. (c) [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1** and 10.0 eq AcOH reacted for 2.5 h in the dark.

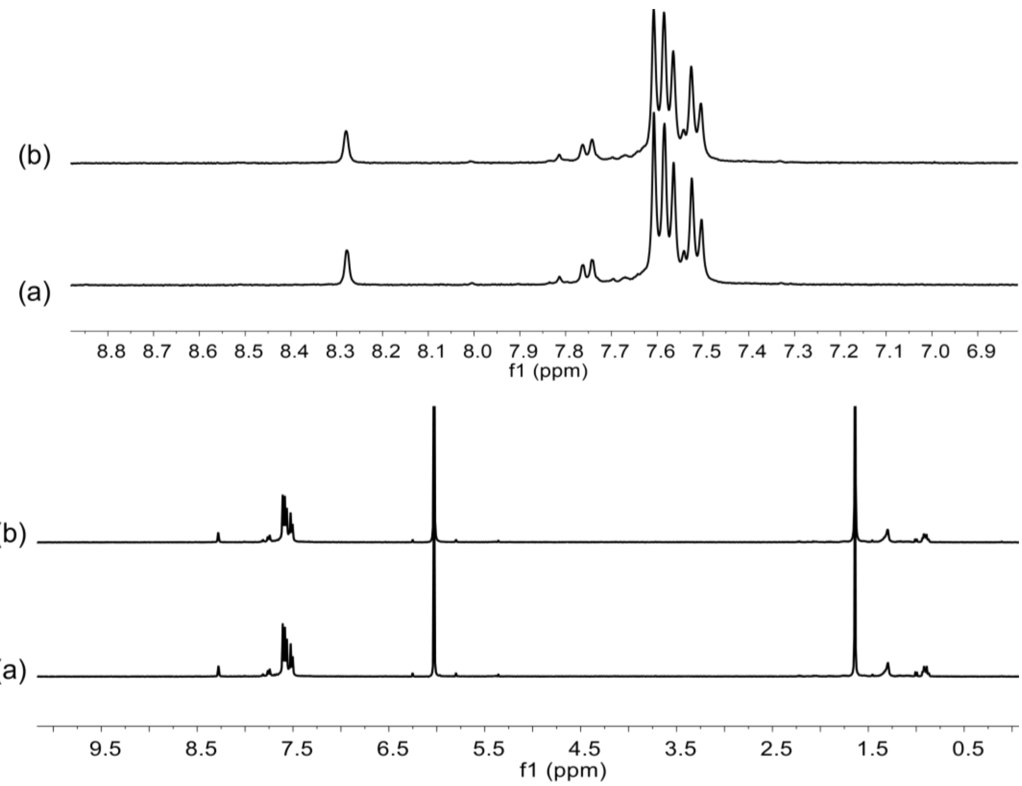


Figure S28 (a) ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1**. (b) ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1** under vis for 12h.

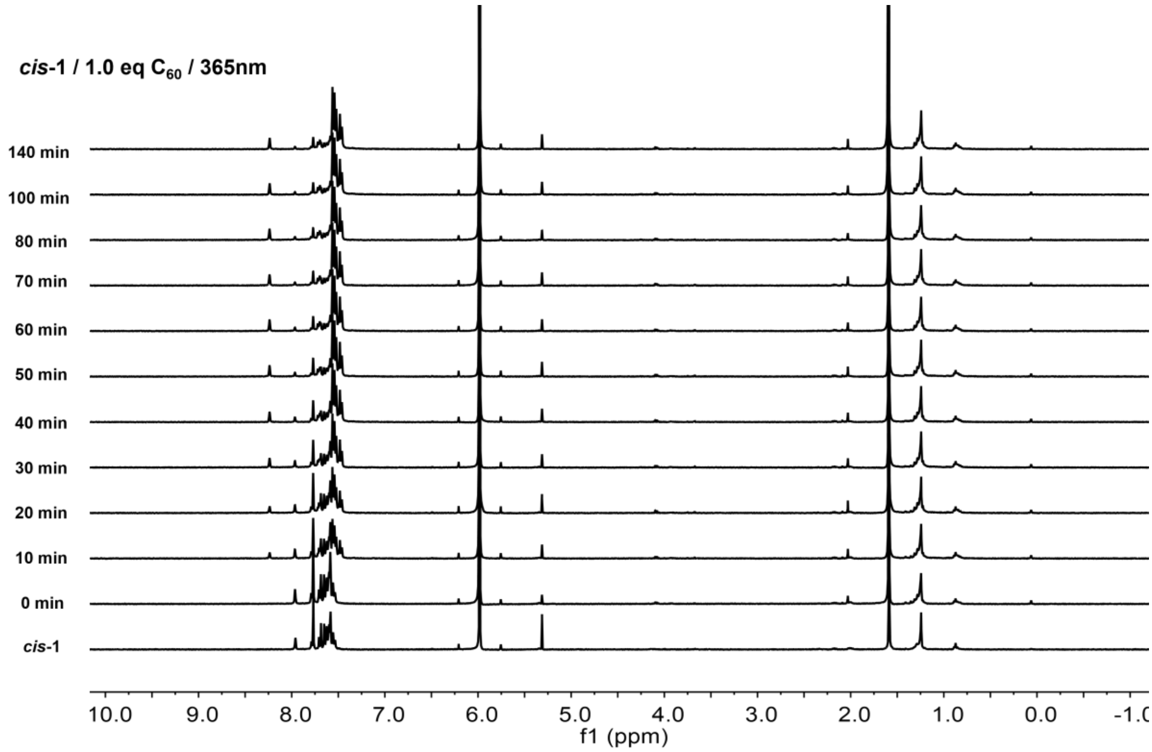


Figure S29 Time-dependent ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***cis*-1** under 365 nm and 1.0 eq C_{60}.

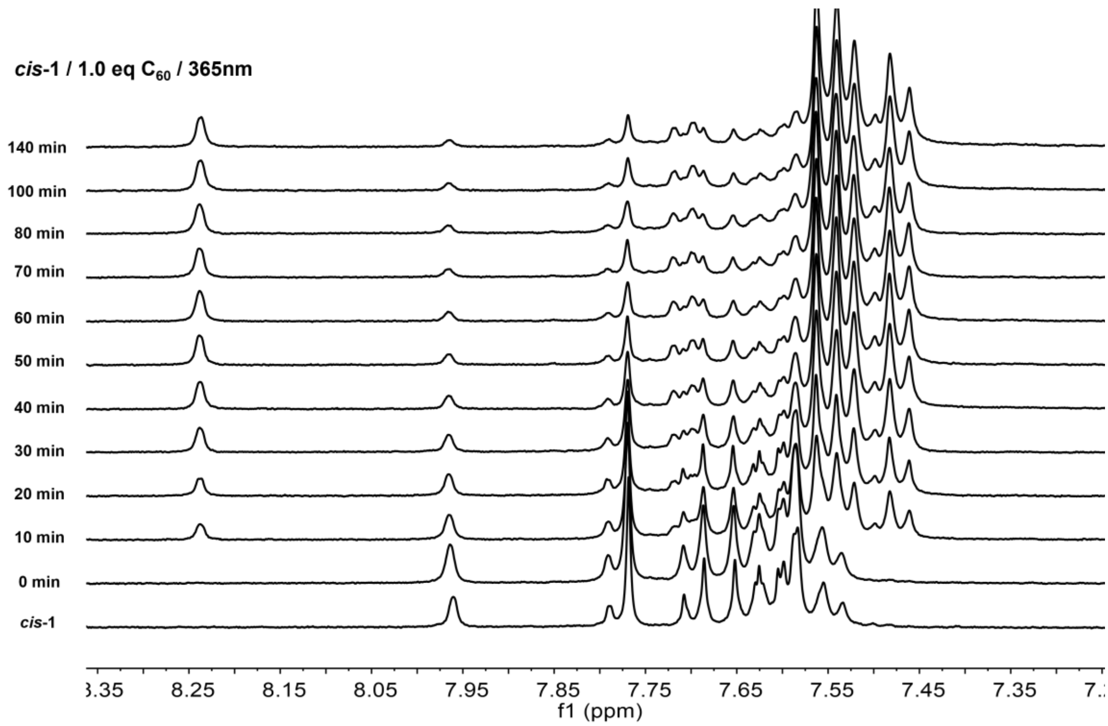


Figure S30 Time-dependent [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***cis*-1** under 365 nm and 1.0 eq C_{60}. Partially enlarged view.

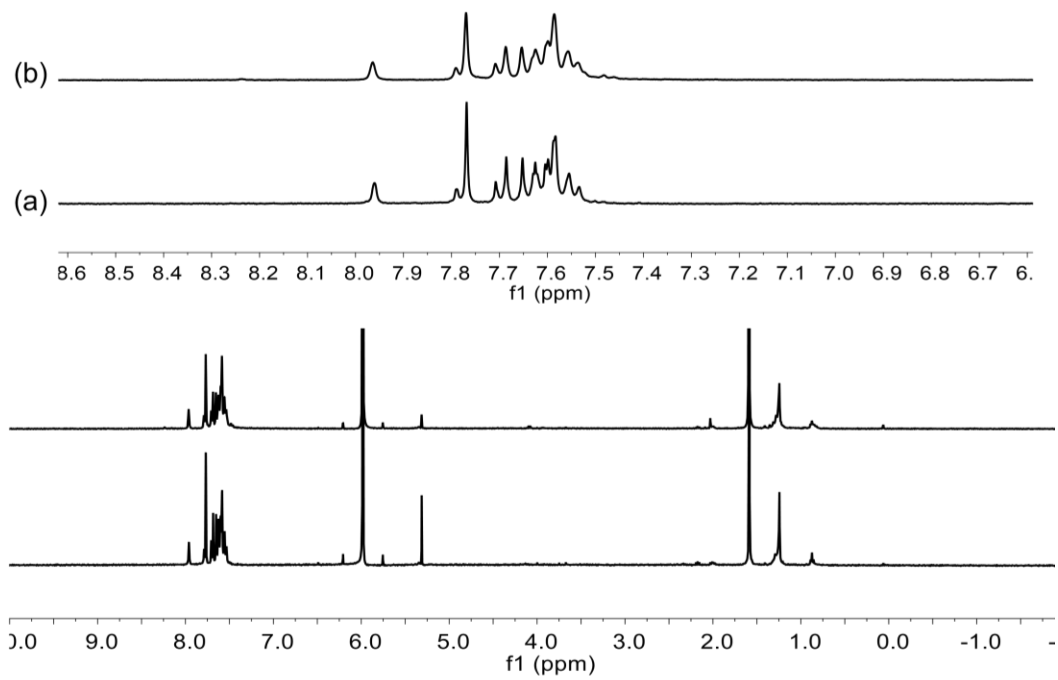


Figure S31 (a) [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***cis*-1**. (c) [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***cis*-1** and 1.0 eq C_{60} reacted for 2.5 h in the dark.

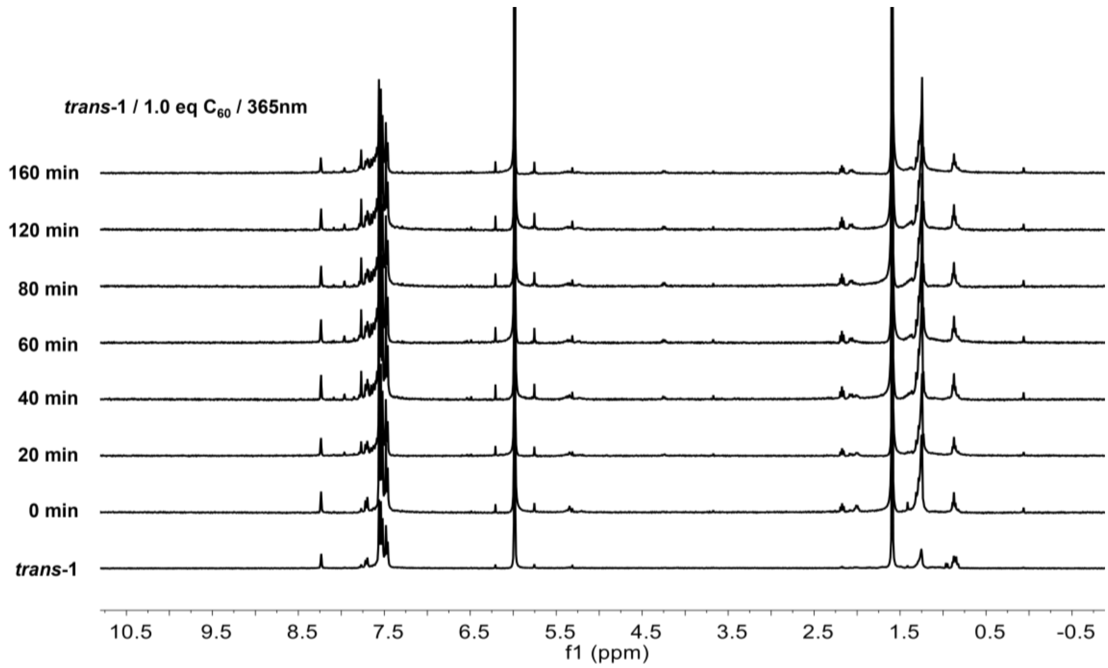


Figure S32 Time-dependent [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1** under 365 nm and 1.0 eq C_{60}.

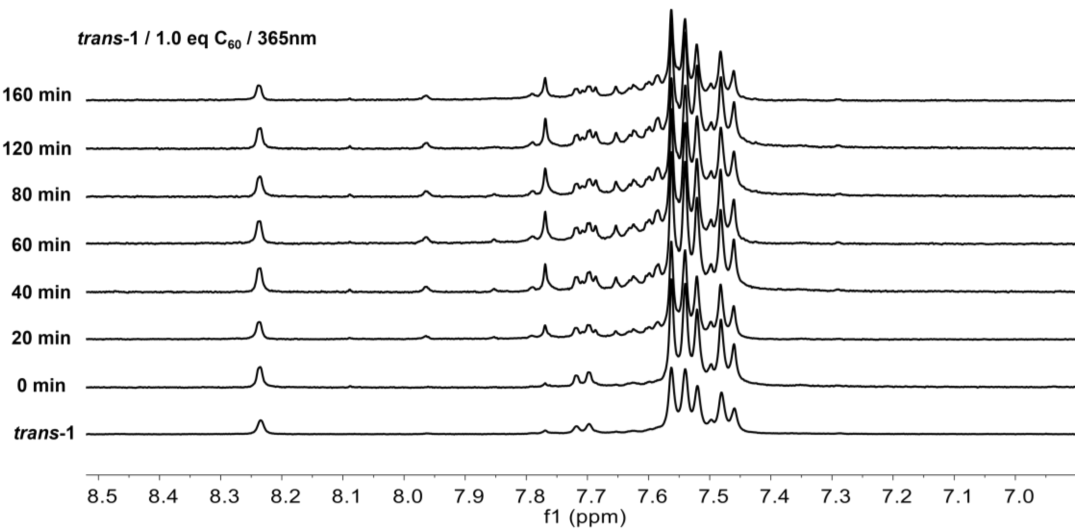


Figure S33 Time-dependent [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1** under 365 nm and 1.0 eq C_{60}. Partially enlarged view.

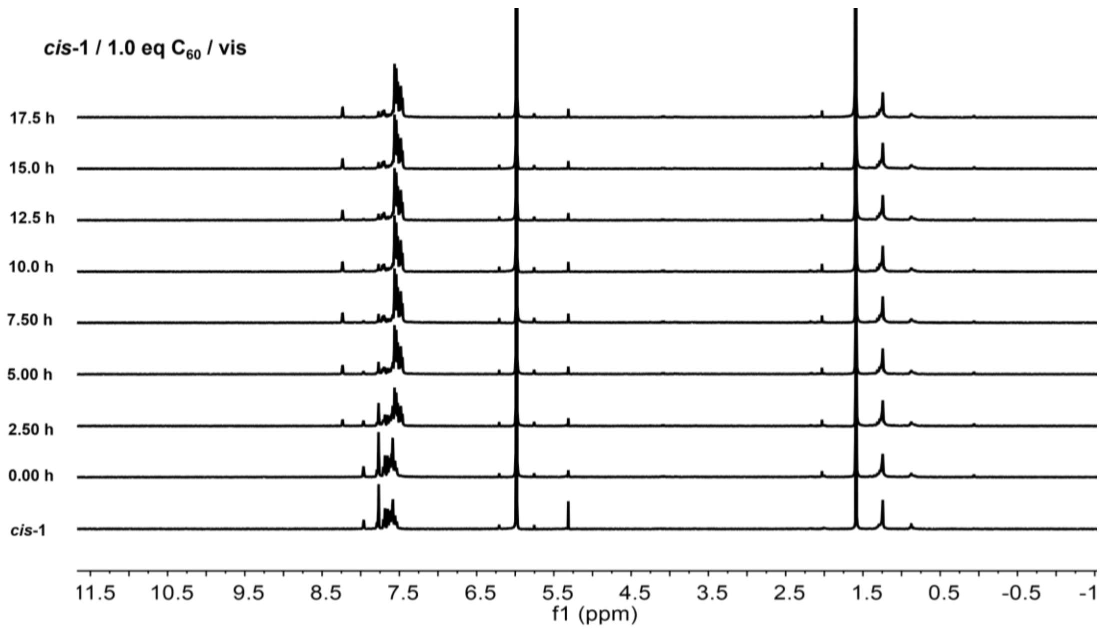


Figure S34 Time-dependent [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-*d*$_2$, 298K) of ***cis*-1** under vis and 1.0 eq C_{60}.

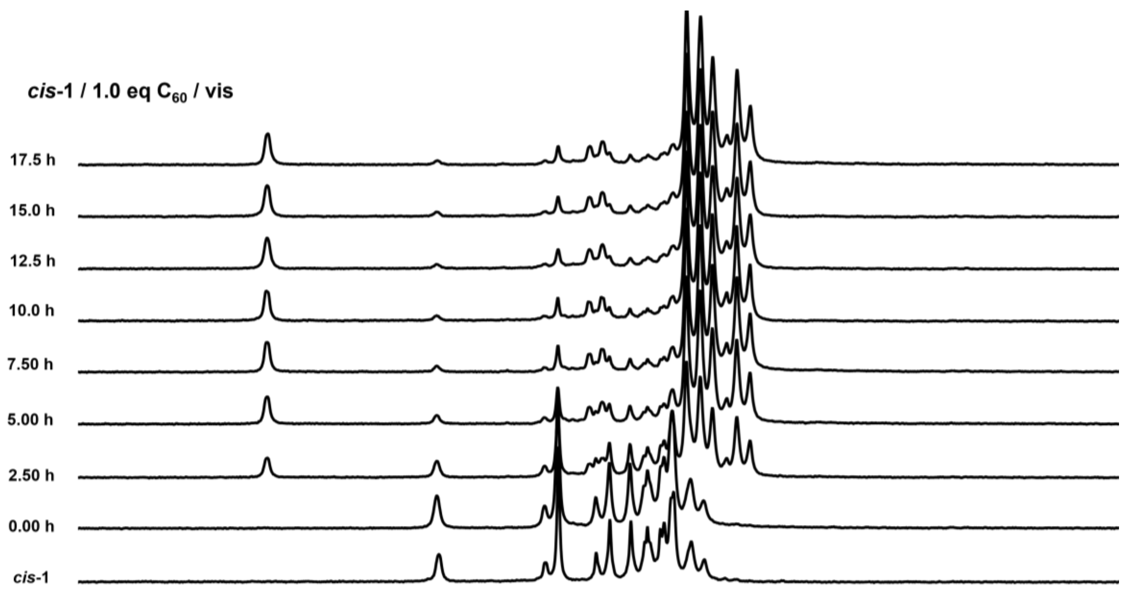


Figure S35 Time-dependent [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-*d*$_2$, 298K) of ***cis*-1** under vis and 1.0 eq C_{60}. Partially enlarged view.

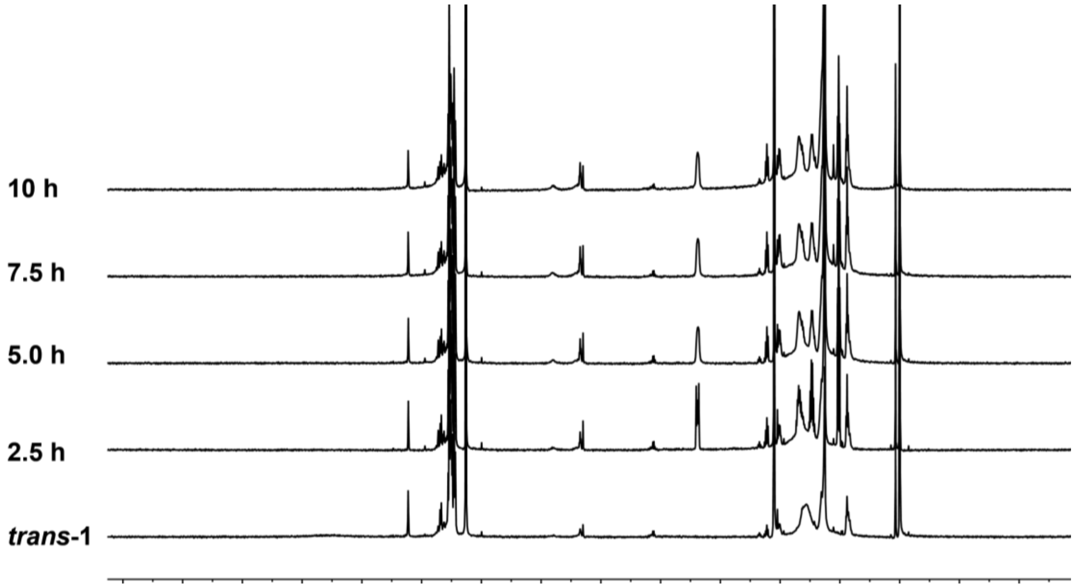


Figure S36 Time-dependent [1]H NMR spectra (400 MHz, $CDCl_3$-*d*, 298K) of ***trans*-1** under visible light irradiation with the addition of 5.0 eq AcOH and 1.0 eq TBAB.

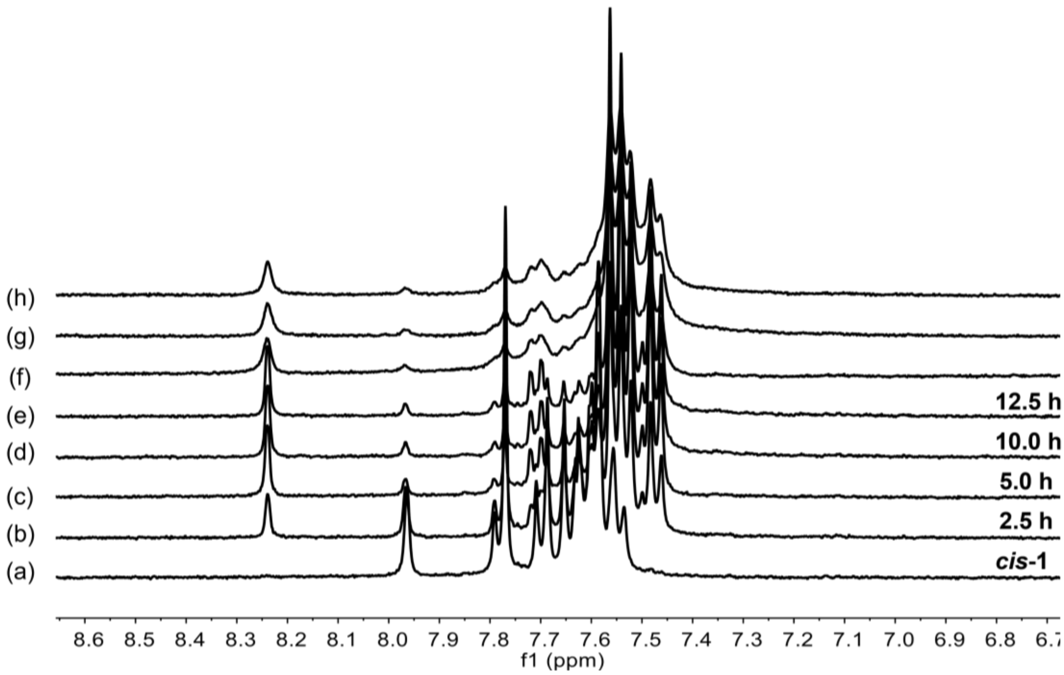


Figure S37 (a)-(e) Time-dependent [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***cis*-1** under vis and 1.0 eq C_{60}. (f) Add 10.0 eq of AcOH to (e). (g) and (h) were obtained by irradiating (f) at 365 nm for 30 and 60 minutes, respectively.

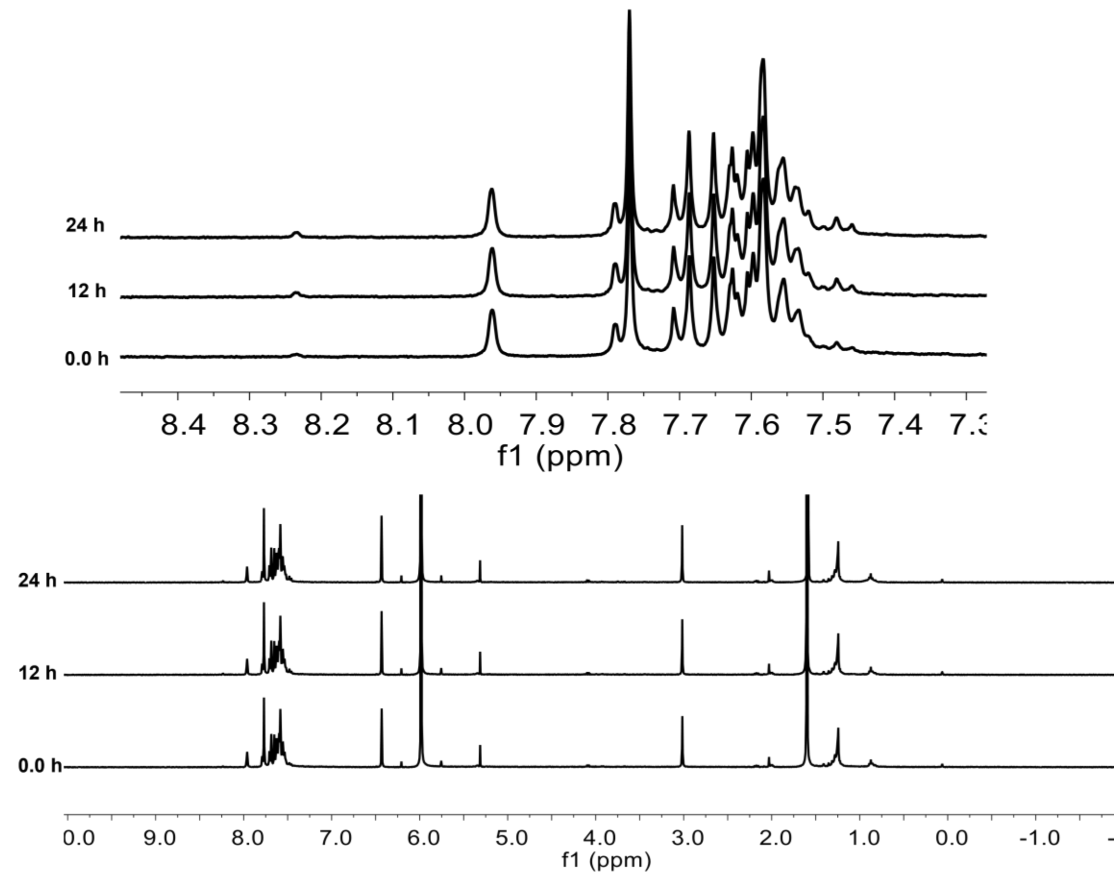


Figure S38 (a) Time-dependent ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1** under visible light irradiation with the addition of 1.0 eq [2.2] paracyclophane.

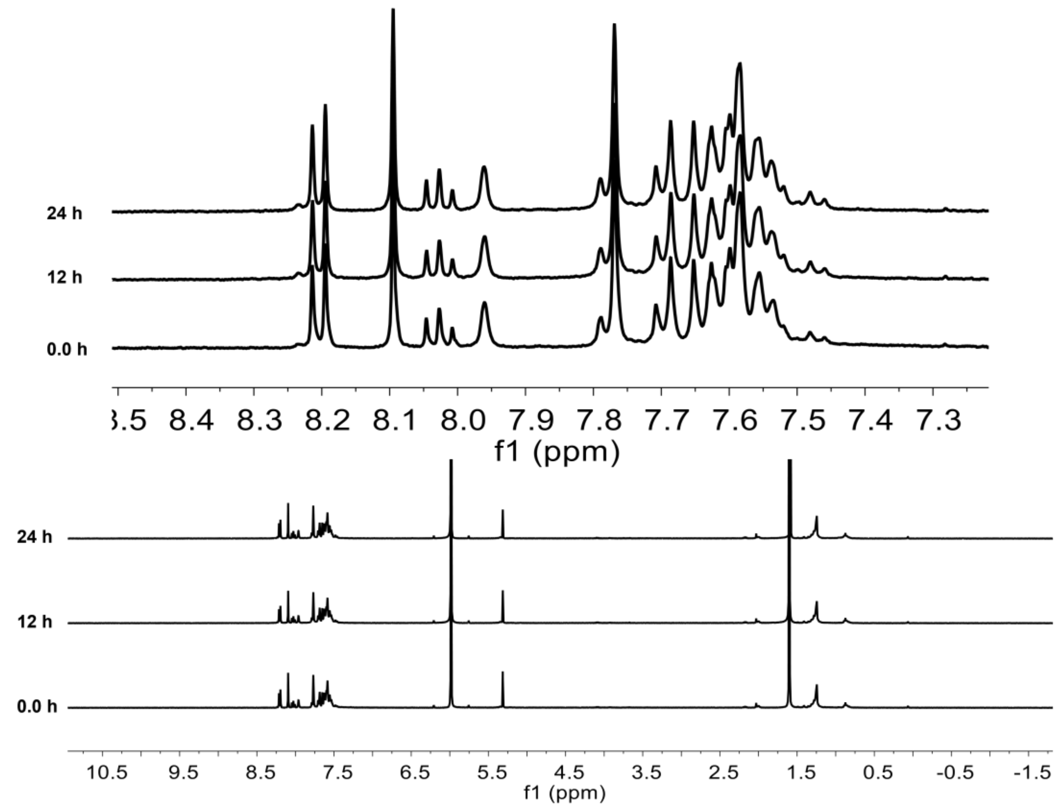


Figure S39 Time-dependent [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***trans*-1** under visible light irradiation with the addition of 1.0 eq pyrene.

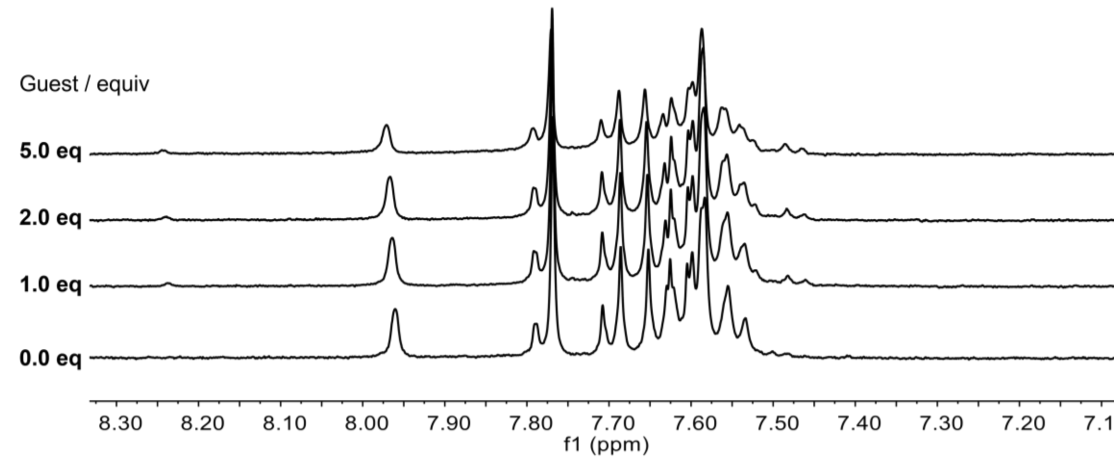


Figure S40. [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298 K) of ***cis*-1** in dark (1.0 mM) upon titration of C_{60} (0.01 M).

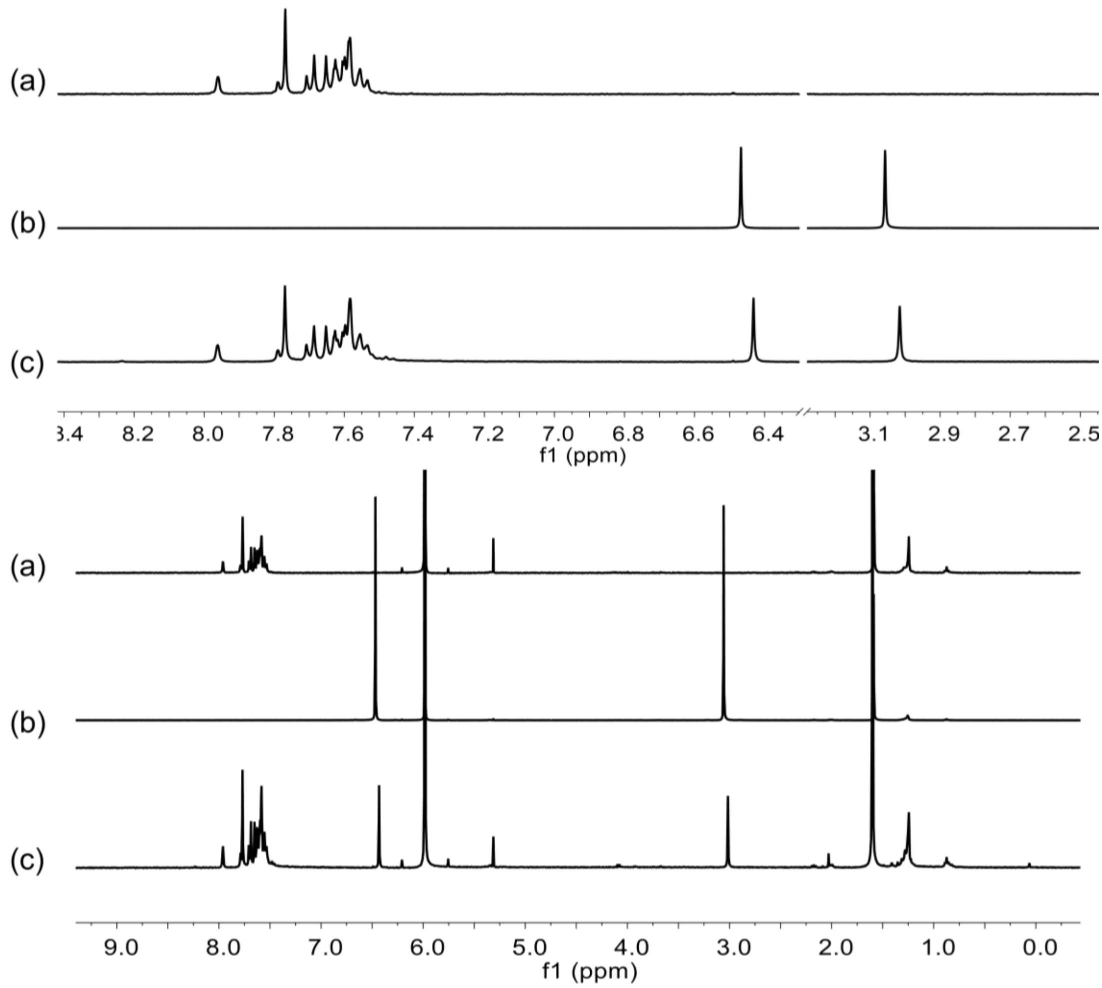


Figure S41 (a) ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***cis*-1**. (b) ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of [2.2] paracyclophane. (c) ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***cis*-1** in dark with the addition of 1.0 eq [2.2] paracyclophane.

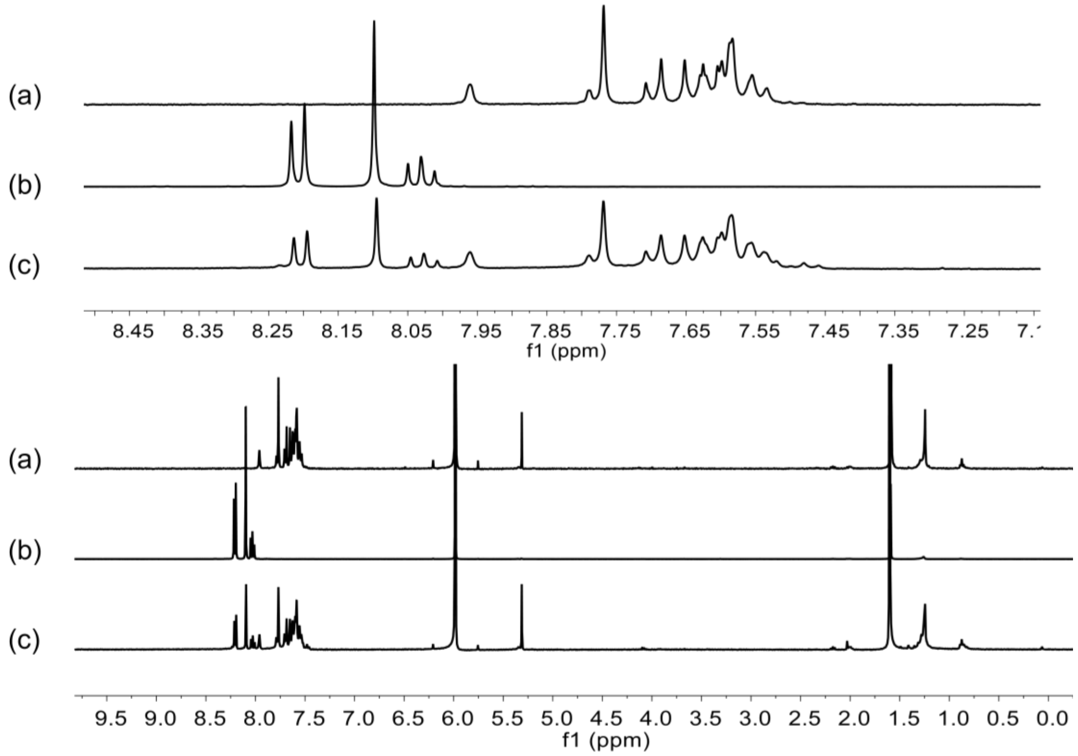


Figure S42 (a) [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-*d₂*, 298K) of ***cis*-1**. (b) [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of pyrene. (c) [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***cis*-1** in dark with the addition of 1.0 eq pyrene.

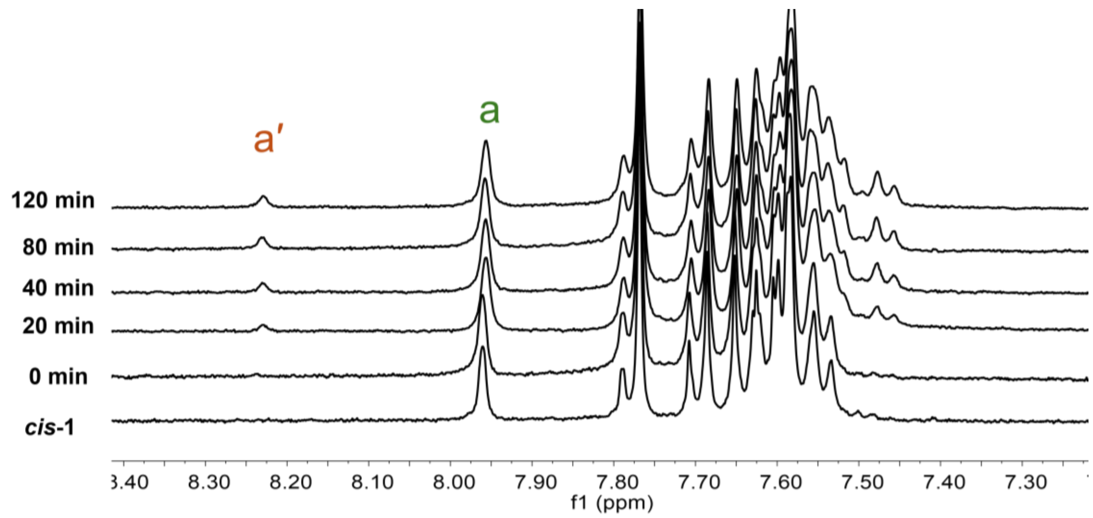


Figure S43 Time-dependent [1]H NMR spectra (400 MHz, $C_2D_2Cl_4$-d_2, 298K) of ***cis*-1** under 365 nm and 10.0 eq AcOH.

6.2 Kinetic study of the controllable conformational transition

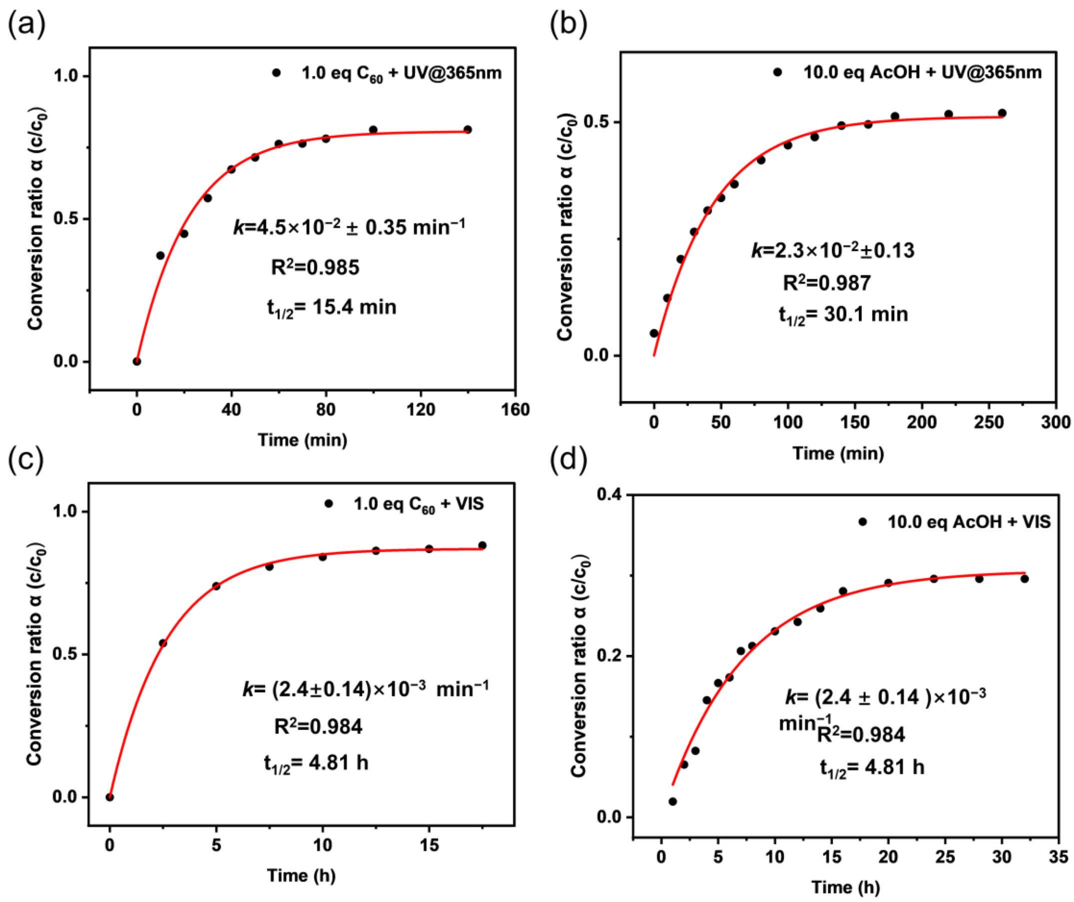


Figure S44 (a) Kinetic profile of ***cis*-1** under 365 nm irradiation in the presence of 1.0 eq C_{60}. (b) Kinetic profile of ***trans*-1** under 365 nm irradiation in the presence of 10.0 eq acetic acid. (c) Kinetic profile of ***cis*-1** under vis irradiation in the presence of 1.0 eq C_{60}. (d) Kinetic profile of ***trans*-1** under vis irradiation in the presence of 10.0 eq acetic acid.

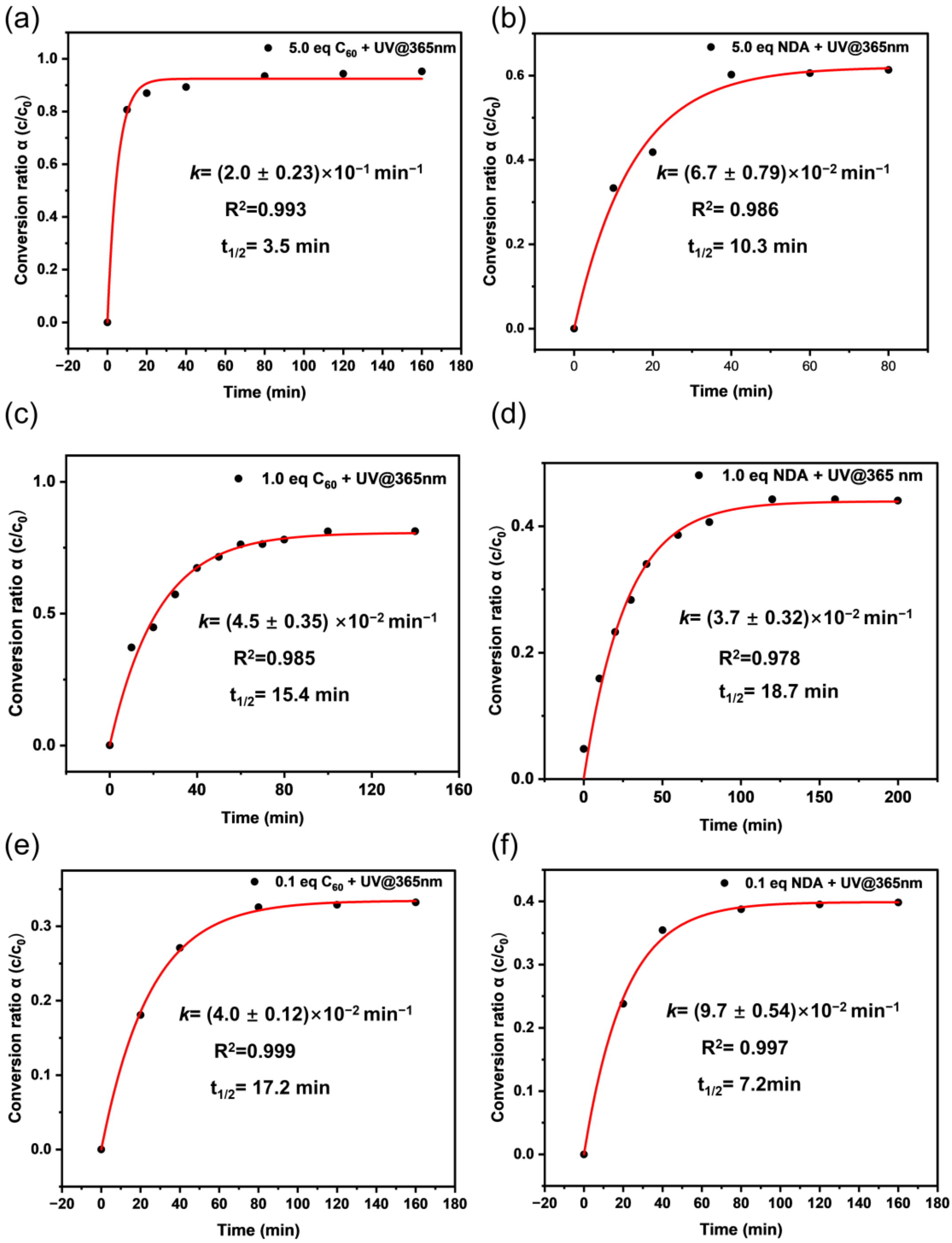


Figure S45 Kinetic profile of ***cis*-1** under 365 nm irradiation in the presence of (a) 5.0 eq C_{60}, (b) 5.0 eq NDA, (c) 1.0 eq C_{60}, (d) 1.0 eq NDA, (e) 0.1 eq C_{60}, (f) 0.1 eq NDA.

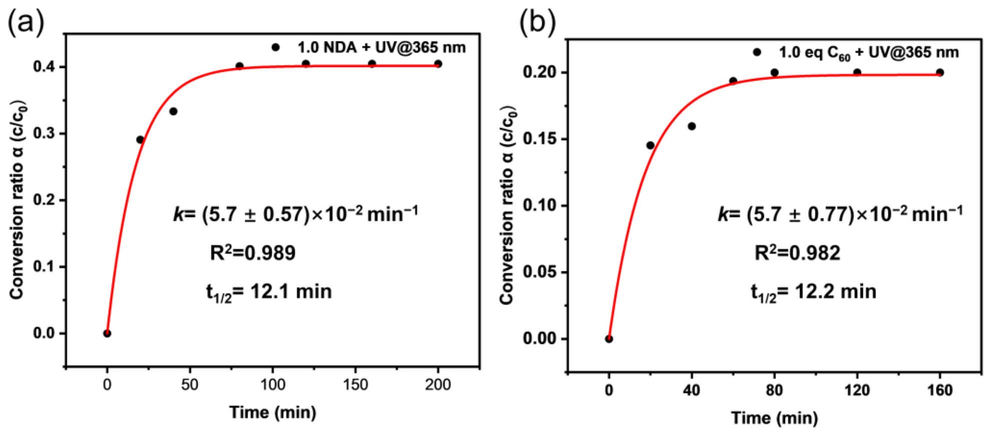


Figure S46 (a) Kinetic profile of ***trans*-1** under 365 nm irradiation in the presence of 1.0 eq NDA. (b) Kinetic profile of ***trans*-1** under 365 nm irradiation in the presence of 1.0 eq C_{60}.

Table S3 Equilibrium Constants and ***cis*-1** Ratios for ***trans*-1** with Various Additives, Equivalents, and Light Sources

Entry	Additive	Substrate	Equivalent	Irradiation Source	***cis*-1** Ratio at Equilibrium (%)	Equilibrium Constant (*K*)
1	C_{60}	***trans*-1**	1.0 eq	365 nm	20	0.25
2	AcOH	***trans*-1**	10.0 eq	vis	30	0.42
3	AcOH	***trans*-1**	10.0 eq	365 nm	52	1.1
4	NDA	***trans*-1**	1.0 eq	365 nm	40	0.68

Table S4 Equilibrium Constants and ***trans*-1** Ratios for ***cis*-1** with Various Additives, Equivalents, and Light Sources

Entry	Substrate	Additive	Equivalent	Irradiation Source	***trans*-1** Ratio at Equilibrium (%)	Equilibrium Constant (*K*)
1	***cis*-1**	C_{60}	1.0 eq	vis	88	7.4
2	***cis*-1**	C_{60}	1.0 eq	365 nm	81	4.3
3	***cis*-1**	AcOH	10.0 eq	365 nm	15	0.18
4	***cis*-1**	NDA	1.0 eq	365 nm	44	0.79

Table S5 Equilibrium Constants and ***cis*-1** Ratios for ***trans*-1** with Various Additives, Equivalents, and Light Sources

Entry	Additive	Substrate	Equivalent	Irradiation Source	***cis*-1** Ratio at Equilibrium (%)	Equilibrium Constant (*K*)
1	C_{60}	***trans*-1**	1.0 eq	365 nm	20	0.25
2	AcOH	***trans*-1**	10.0 eq	vis	30	0.42
3	AcOH	***trans*-1**	10. 0 eq	365 nm	52	1.1

Table S6 Effects of Additives and Equivalents on the Conformational Equilibrium of ***cis*-1**

Entry	Substrate	Additive	Equivalent	***trans*-1**/***cis*-1** ratio at equilibrium (%)	Equilibrium Constant (*K*)
1	***cis*-1**	C_{60}	0.1 eq	33	0.50
2	***cis*-1**	C_{60}	1.0 eq	81	4.3
3	***cis*-1**	C_{60}	5.0 eq	95	20
4	***cis*-1**	NDA	0.1 eq	38	0.66
5	***cis*-1**	NDA	1.0 eq	44	0.79
6	***cis*-1**	NDA	5.0 eq	61	1.6

7. Computational Data

The structures were optimized and calculated at the B3LYP/def2-SVP level and the dispersion correction with the Grimme's D3 version was also considered. All the calculations were performed with the ORCA 5.0.4 program. All the analysis of wave functions used the Multiwfn 3.8(dev) program and VMD 1.9.3. Cartesian coordinates of the optimized structures were listed at the end. The absorption spectrum was calculated at the PBE0 6-31G* level of theory [scrf = (solvent = CH_2Cl_2)].

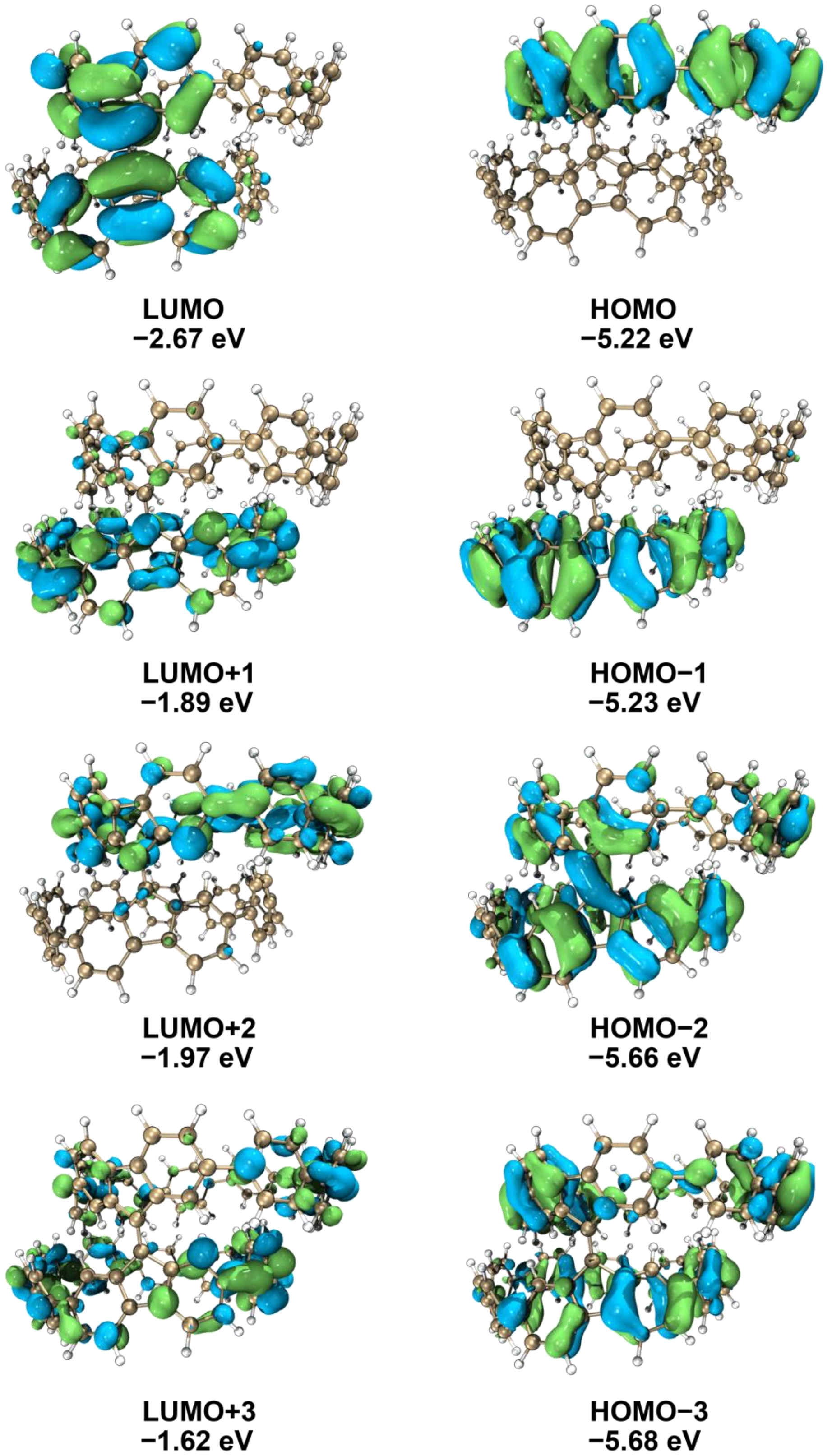


Figure S47 The frontier molecular orbitals and LUMO-HOMO gaps for ***cis*-1** at the optimized geometries of ground state calculated by DFT at the B3LYP/def2-SVP level.

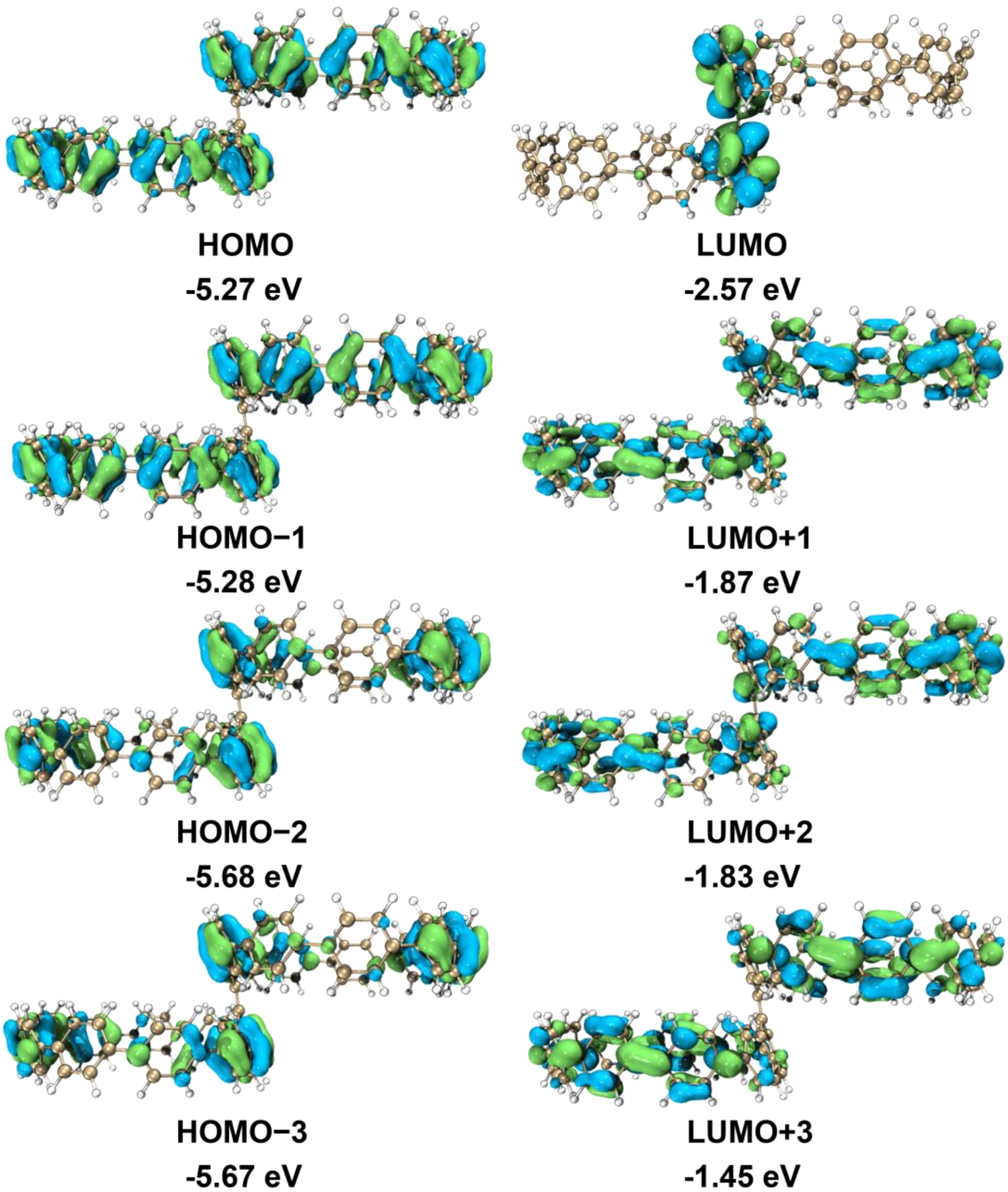


Figure S48 The frontier molecular orbitals and LUMO-HOMO gaps for ***trans*-1** at the optimized geometries of ground state calculated by DFT at the B3LYP/def2-SVP level.

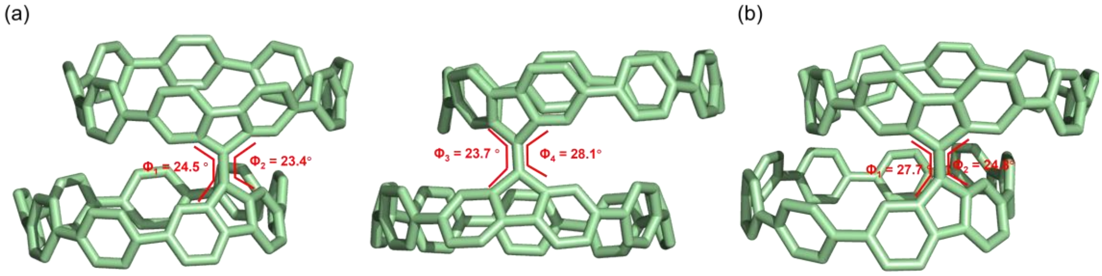


Figure S49 (a) The torsion angles in the ***cis*-1** single crystal. (b) Geometry optimization of ***cis*-1** and torsion angles at the B3LYP/def2-SVP level.

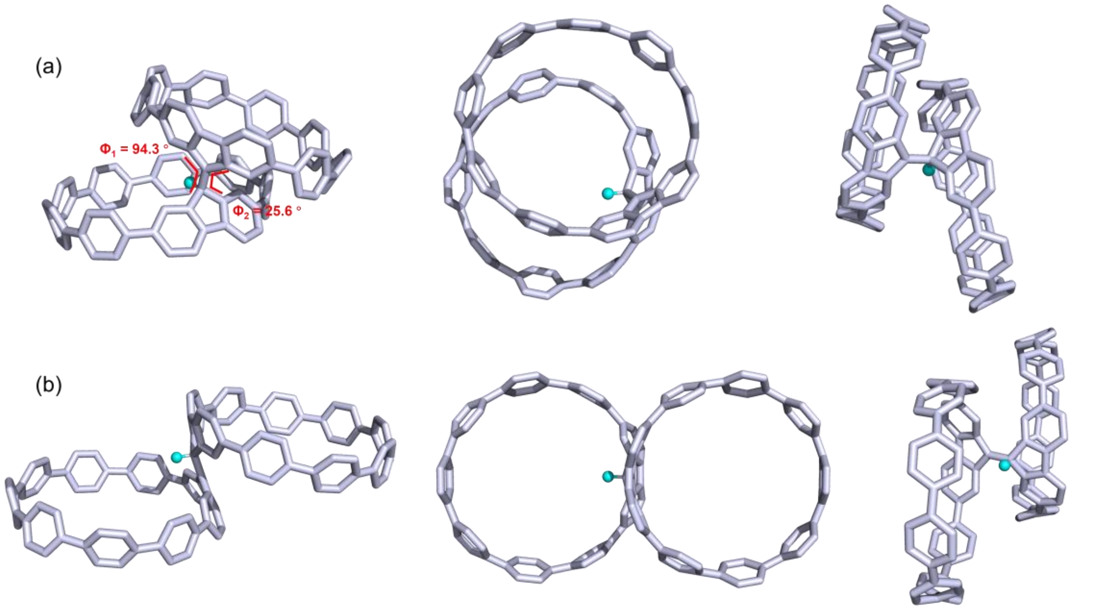


Figure S50 (a) Geometry optimization of sp³-carbocation intermediate (*cis*) and torsion angles at the B3LYP/def2-SVP level. (b) Geometry optimization of sp³-carbocation intermediate (*trans*) at the B3LYP/def2-SVP level. The proton added is highlighted in cyan.

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Table S7 The optimized structure of ***cis*-1** (B3LYP D3 RIJCOSX opt def2-SVP def2/J) (E = −4227.469397247264 Hartree)

C	11.03963	3.25183	-15.80444
C	10.22988	2.67872	-14.64779
C	9.75209	1.35002	-14.69715
C	8.65531	0.94472	-13.93215
C	7.98133	1.84817	-13.08155
C	6.53423	1.58772	-12.68603
C	5.88522	0.38092	-13.02786
C	4.49159	0.31566	-13.13685
C	3.68699	1.45659	-12.90896
C	2.30770	1.60859	-13.53826
C	1.93039	0.71133	-14.57384
C	0.99020	1.09474	-15.54313
C	0.30969	2.29751	-15.37401
C	-0.41709	2.61525	-16.59232
C	-0.99015	3.83154	-16.95497
C	-1.16385	4.10588	-18.32061
C	-0.71639	3.18153	-19.30832
C	-0.26912	1.90743	-18.86115
C	-0.17452	1.61406	-17.49687
C	0.52774	0.47945	-16.84358
C	0.64612	-0.82957	-17.27955
C	1.59550	-1.87669	-16.82183
C	1.14843	-3.12202	-17.18057
C	0.02214	-2.94573	-18.08270

C	-0.60133	-3.92049	-18.85731
C	-1.41074	-3.51333	-19.92412
C	-1.63187	-2.13508	-20.19072
C	-1.11227	-1.18742	-19.26776
C	-0.21473	-1.58591	-18.26471
C	1.88651	-4.27990	-16.94851
C	3.20680	-4.14832	-16.49032
C	3.78912	-2.85942	-16.31763
C	5.29615	-2.65695	-16.36388
C	5.87272	-1.37096	-16.27635
C	7.15754	-1.11800	-16.76670
C	7.92532	-2.14002	-17.37017
C	9.04395	-1.80231	-18.34799
C	9.34264	-0.45950	-18.66649
C	9.97746	-0.12494	-19.86570
C	10.34401	-1.11719	-20.80306
C	10.51918	-0.75699	-22.27194
C	10.45490	0.58301	-22.70616
C	10.12307	0.90034	-24.02606
C	9.83470	-0.10459	-24.97378
C	8.97577	0.20601	-26.19452
C	8.38974	-0.83876	-26.94146
C	7.25137	-0.62197	-27.72142
C	6.64192	0.65019	-27.79253
C	5.17340	0.77393	-28.17588
C	4.43911	1.92747	-27.82046
C	3.04522	1.89638	-27.71437
C	2.31809	0.71085	-27.96128
C	0.92647	0.50469	-27.37570

C	0.29210	-0.75677	-27.42723
C	-0.71880	-1.09804	-26.52231
C	-1.14330	-0.19339	-25.52431
C	-1.81114	-0.68159	-24.24603
C	-2.08205	0.19959	-23.17619
C	-2.20753	-0.27288	-21.86494
C	-2.06639	-1.64867	-21.56772
C	-2.00136	-2.53694	-22.66175
C	-1.87660	-2.06493	-23.96985
C	-0.64428	1.12529	-25.60208
C	0.36629	1.46597	-26.50489
C	3.03828	-0.37908	-28.50015
C	4.43222	-0.34856	-28.60366
C	7.34082	1.72710	-27.20633
C	8.48251	1.51030	-26.42638
C	10.09329	-1.43786	-24.58643
C	10.42868	-1.75649	-23.26686
C	10.22441	-2.46140	-20.39141
C	9.59015	-2.79648	-19.19153
C	7.41941	-3.45596	-17.28030
C	6.13611	-3.70790	-16.78847
C	2.93347	-1.72989	-16.44160
C	0.52728	3.12857	-14.27816
C	1.54108	2.79374	-13.37312
C	4.32579	2.59400	-12.37194
C	5.71629	2.65834	-12.26304
C	8.57771	3.11419	-12.89148
C	9.67667	3.51978	-13.65635
C	11.39875	2.45083	-16.91106

C	11.70478	3.02151	-18.15033
C	11.66383	4.42048	-18.34362
C	11.47559	4.99743	-19.74023
C	10.98342	6.31111	-19.90425
C	10.35239	6.70745	-21.08574
C	10.18292	5.81011	-22.16228
C	9.07607	6.03290	-23.18682
C	8.22396	7.15614	-23.10459
C	6.95033	7.14267	-23.68162
C	6.46797	6.00441	-24.36628
C	4.97021	5.77251	-24.51117
C	4.03806	6.74442	-24.09028
C	2.72845	6.39147	-23.75173
C	2.29048	5.04898	-23.81655
C	1.11181	4.57351	-22.97621
C	0.42705	5.46795	-22.12369
C	-0.30113	5.00785	-21.02357
C	-0.37914	3.63194	-20.72169
C	0.14323	2.73499	-21.67901
C	0.87070	3.19436	-22.78127
C	3.16328	4.12089	-24.42536
C	4.47216	4.47429	-24.76444
C	7.39273	4.96889	-24.61292
C	8.66662	4.98502	-24.03858
C	10.84979	4.56729	-22.06774
C	11.48034	4.16959	-20.88324
C	11.49163	5.21964	-17.19296
C	11.18816	4.64928	-15.95308
H	10.09543	0.62980	-15.41922

H	8.27962	-0.03837	-14.15647
H	6.42020	-0.49360	-13.35774
H	4.10192	-0.60531	-13.53773
H	2.46217	-0.17711	-14.69565
H	-1.15970	4.61524	-16.22836
H	-1.49462	5.10168	-18.56389
H	0.19897	1.21011	-19.52756
H	-0.36939	-4.96959	-18.72885
H	-1.76365	-4.29396	-20.57766
H	-1.28592	-0.17221	-19.42941
H	1.52267	-5.25243	-17.25296
H	3.78223	-5.05751	-16.44068
H	5.31612	-0.50661	-15.95430
H	7.44757	-0.08184	-16.77911
H	8.97371	0.37401	-18.09422
H	10.01714	0.92849	-20.08097
H	10.51347	1.41559	-22.02856
H	9.95968	1.94091	-24.21915
H	8.68267	-1.86871	-26.83812
H	6.79978	-1.51169	-28.12402
H	4.90520	2.83189	-27.47064
H	2.59421	2.78278	-27.30297
H	0.63853	-1.55832	-28.05635
H	-1.04228	-2.12454	-26.55259
H	-2.06158	1.27073	-23.28591
H	-2.27279	0.48707	-21.10404
H	-1.87289	-3.59960	-22.54463
H	-1.67236	-2.82063	-24.70805
H	-0.89220	1.88765	-24.88423

H	0.77635	2.45290	-26.37910
H	2.58471	-1.33005	-28.71792
H	4.89607	-1.27495	-28.89626
H	6.96178	2.73464	-27.21176
H	8.85891	2.37531	-25.91166
H	9.90585	-2.28052	-25.22871
H	10.45393	-2.80894	-23.04403
H	10.47867	-3.29022	-21.02988
H	9.42309	-3.84865	-19.04260
H	7.91872	-4.30620	-17.71029
H	5.78989	-4.72106	-16.90153
H	3.32015	-0.72996	-16.45168
H	0.02005	4.08021	-14.18873
H	1.76610	3.52908	-12.61833
H	3.80868	3.51908	-12.18146
H	6.10688	3.62460	-11.99559
H	8.14433	3.87277	-12.26218
H	9.97032	4.54790	-13.53379
H	11.32132	1.37737	-16.90424
H	11.82027	2.32298	-18.96047
H	10.92349	7.01975	-19.09688
H	9.88414	7.67533	-21.05040
H	8.43731	8.00804	-22.48290
H	6.32728	7.98360	-23.43144
H	4.31613	7.76161	-23.87296
H	2.14500	7.17794	-23.30655
H	0.54276	6.53590	-22.18043
H	-0.65752	5.77227	-20.35440
H	0.12264	1.66632	-21.54429

H	1.34179	2.42764	-23.37127
H	2.93065	3.07449	-24.52170
H	5.09799	3.65646	-25.07604
H	7.12516	4.06227	-25.12497
H	9.23838	4.08895	-24.16858
H	10.78776	3.81355	-22.83121
H	11.83884	3.15478	-20.86148
H	11.44738	6.29456	-17.23243
H	10.93629	5.35052	-15.17699

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Table S8 The optimized structure of ***trans*-1** (B3LYP D3 RIJCOSX opt def2-SVP def2/J) (E = −4227.451890281771 Hartree)

C	12.34000	1.65400	17.34200
C	13.79600	3.40600	16.93500
C	12.37600	3.95000	16.70200
C	13.74100	2.02200	17.17600
C	16.07400	3.43900	17.77100
C	14.94400	4.10100	17.24500
H	14.97400	5.04100	17.10500
C	11.54000	2.80200	17.19800
C	7.14300	3.56600	20.49900
H	6.48800	4.23100	20.32200
C	14.88200	1.35800	17.51800
H	14.88100	0.40700	17.54800
C	7.39700	3.20800	21.77500
C	11.83000	0.51700	17.89500
H	12.32500	-0.29500	17.88900

C	17.48100	5.53700	18.01700
H	17.31800	5.80900	17.12100
C	18.36100	6.06600	20.20100
C	10.30600	2.85800	17.88500
H	9.79900	3.66200	17.86600
C	17.62300	9.12700	22.21700
H	17.13900	9.93700	22.09300
C	17.07100	4.25400	18.45300
C	16.05200	2.05300	17.83000
H	16.83400	1.57800	18.08500
C	13.63100	9.00700	28.20900
H	14.31500	8.66600	28.76900
C	18.58600	7.14500	21.21700
C	9.83200	1.80600	18.57100
C	15.76900	10.83300	25.53900
H	15.32700	11.67400	25.49000
C	18.14500	4.78500	20.52900
H	18.44600	4.49700	21.38400
C	10.09600	8.38500	27.44500
C	18.12500	6.40400	18.90500
H	18.40700	7.25600	18.59700
C	17.88000	8.31000	21.16800
H	17.54100	8.57300	20.31900
C	16.20100	8.71400	26.66700
H	16.02200	8.11800	27.38200
C	18.10000	8.74100	23.53600
C	14.03700	9.89500	27.12600
C	10.54300	0.57900	18.47900
H	10.14700	-0.21500	18.81700

C	15.38400	9.87900	26.52300
C	9.00000	8.90600	26.76600
H	8.91400	9.85100	26.72600
C	11.32400	9.12500	27.57600
C	12.40300	8.63800	28.47400
H	12.20900	8.07700	29.21500
C	17.53300	3.86900	19.74100
H	17.41400	2.97800	20.04600
C	8.02200	8.14200	26.14300
H	7.28200	8.54700	25.70300
C	7.81400	2.98800	19.45600
H	7.58700	3.25400	18.57400
C	19.23800	6.85800	22.43700
H	19.83400	6.12000	22.49300
C	7.42700	6.29200	23.84100
H	7.53700	7.22100	23.67300
C	7.13000	4.07300	22.92900
C	8.79200	2.05000	19.61400
C	11.71500	10.17700	26.70700
H	11.03800	10.65700	26.24100
C	19.01100	7.65400	23.56800
H	19.47700	7.46000	24.37500
C	8.17500	6.71200	26.19200
C	12.99200	10.52200	26.50700
H	13.18200	11.23400	25.91000
C	16.76200	10.53400	24.68300
H	17.01700	11.19100	24.04700
C	17.19400	8.43800	25.84100
H	17.74500	7.68000	26.00200

C	8.29600	2.09500	21.96200
H	8.44300	1.75300	22.83700
C	7.21700	5.48600	22.76500
H	7.12700	5.86500	21.89900
C	8.93200	1.53400	20.91200
H	9.48600	0.77600	21.05300
C	17.45100	9.29100	24.67400
C	10.04000	7.01200	27.66100
H	10.66600	6.64200	28.27100
C	9.15900	6.14600	27.06400
H	9.19900	5.21000	27.22500
C	7.49600	5.86000	25.17200
C	7.06200	3.57200	24.27000
H	6.88000	2.65300	24.43700
C	7.26400	4.45500	25.32600
H	7.24900	4.10300	26.20800
C	12.08400	7.34700	15.45100
C	10.62800	5.59500	15.85800
C	12.04800	5.05000	16.09200
C	10.68300	6.97800	15.61700
C	8.35000	5.56100	15.02300
C	9.48000	4.89900	15.54800
H	9.45000	3.96000	15.68800
C	12.88400	6.19900	15.59500
C	17.28000	5.43400	12.29400
H	17.93500	4.77000	12.47100
C	9.54200	7.64300	15.27500
H	9.54300	8.59400	15.24600
C	17.02700	5.79300	11.01800

C	12.59400	8.48300	14.89800
H	12.09900	9.29500	14.90400
C	6.94200	3.46400	14.77700
H	7.10600	3.19100	15.67200
C	6.06200	2.93500	12.59300
C	14.11800	6.14300	14.90800
H	14.62400	5.33900	14.92700
C	6.80100	-0.12700	10.57600
H	7.28400	-0.93600	10.70000
C	7.35300	4.74600	14.34000
C	8.37100	6.94800	14.96400
H	7.59000	7.42300	14.70800
C	10.79300	-0.00600	4.58400
H	10.10800	0.33400	4.02400
C	5.83800	1.85600	11.57600
C	14.59200	7.19500	14.22200
C	8.65500	-1.83200	7.25400
H	9.09600	-2.67300	7.30300
C	6.27900	4.21600	12.26500
H	5.97700	4.50400	11.40900
C	14.32700	0.61600	5.34900
C	6.29900	2.59700	13.88800
H	6.01700	1.74500	14.19600
C	6.54300	0.69000	11.62500
H	6.88300	0.42700	12.47500
C	8.22200	0.28700	6.12600
H	8.40100	0.88300	5.41100
C	6.32300	0.25900	9.25800
C	10.38600	-0.89400	5.66700

C	13.88000	8.42200	14.31400
H	14.27700	9.21600	13.97600
C	9.04000	-0.87800	6.27000
C	15.42400	0.09500	6.02700
H	15.50900	-0.85000	6.06700
C	13.10000	-0.12500	5.21700
C	12.02100	0.36300	4.31900
H	12.21400	0.92400	3.57800
C	6.89100	5.13100	13.05200
H	7.01000	6.02300	12.74700
C	16.40200	0.85900	6.65000
H	17.14200	0.45400	7.09000
C	16.60900	6.01300	13.33700
H	16.83700	5.74700	14.21900
C	5.18500	2.14300	10.35600
H	4.58900	2.88100	10.30000
C	16.99700	2.70900	8.95300
H	16.88700	1.77900	9.12000
C	17.29400	4.92800	9.86400
C	15.63200	6.95100	13.18000
C	12.70900	-1.17600	6.08600
H	13.38600	-1.65600	6.55200
C	5.41200	1.34700	9.22500
H	4.94700	1.54000	8.41800
C	16.24900	2.28800	6.60100
C	11.43100	-1.52100	6.28600
H	11.24200	-2.23400	6.88300
C	7.66200	-1.53300	8.11000
H	7.40600	-2.19000	8.74600

C	7.23000	0.56300	6.95200
H	6.67900	1.32000	6.79100
C	16.12800	6.90600	10.83200
H	15.98000	7.24800	9.95600
C	17.20700	3.51500	10.02800
H	17.29700	3.13500	10.89400
C	15.49200	7.46600	11.88100
H	14.93800	8.22500	11.74000
C	6.97200	-0.29000	8.12000
C	14.38400	1.98800	5.13200
H	13.75800	2.35900	4.52200
C	15.26500	2.85500	5.72900
H	15.22500	3.79100	5.56800
C	16.92800	3.14000	7.62100
C	17.36200	5.42900	8.52300
H	17.54300	6.34700	8.35600
C	17.16000	4.54500	7.46700
H	17.17500	4.89800	6.58500

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

Table S9 The optimized structure of sp^3-carbocation intermediate (*cis*) (B3LYP D3 RIJCOSX opt def2-SVP def2/J) (E = −4227.835946970529 Hartree)

H	5.258679	0.697637	-0.727020
C	6.270061	1.021567	-1.017445
C	6.633806	2.253133	-0.265489
C	7.539835	3.309945	-0.653408
C	7.629178	4.262264	0.414525
C	8.306665	5.451999	0.195991

C	8.758861	5.769944	-1.107324
C	8.554637	4.903098	-2.195956
C	8.494087	5.323517	-3.617416
C	8.622994	4.392672	-4.670964
C	8.030963	4.620654	-5.907514
C	7.267008	5.784353	-6.148733
C	6.215270	5.840521	-7.190038
C	5.565691	7.044746	-7.539494
C	4.291779	7.036915	-8.094023
C	3.594141	5.827308	-8.315999
C	2.115759	5.785403	-8.403544
C	1.399268	4.654872	-8.847717
C	0.043046	4.498604	-8.569275
C	-0.673103	5.459574	-7.823254
C	0.013503	6.650383	-7.510455
C	1.364564	6.808730	-7.791725
C	4.336699	4.638522	-8.186909
C	5.616178	4.647061	-7.639592
C	7.334162	6.799258	-5.170018
C	7.931569	6.575483	-3.933528
C	8.029261	3.619625	-1.923984
C	6.706021	3.812774	1.476353
C	6.076089	2.613863	1.007636
C	4.923686	2.107212	1.620392
C	4.341355	2.797730	2.700213
C	2.913661	2.536482	3.009984
C	2.319939	1.272244	2.823417
C	0.942250	1.141392	2.663559
C	0.095691	2.270120	2.663863

C	-1.253586	2.259082	2.044303
C	-1.523555	1.373579	0.982729
C	-2.553251	1.624291	0.078718
C	-3.352928	2.778543	0.188710
C	-4.021254	3.298660	-1.030238
C	-3.818542	4.650309	-1.365800
C	-3.936073	5.088525	-2.680761
C	-4.260052	4.198029	-3.723802
C	-3.834360	4.543372	-5.103629
C	-3.301295	3.539766	-5.933053
C	-2.385340	3.844035	-6.937567
C	-1.973534	5.170232	-7.169211
C	-2.717671	6.182007	-6.521246
C	-3.621458	5.877667	-5.510017
C	-4.681690	2.905773	-3.347402
C	-4.563781	2.466487	-2.028632
C	-3.214279	3.545354	1.362650
C	-2.190120	3.288846	2.270979
C	0.675554	3.499350	3.035335
C	2.050604	3.630806	3.204227
C	5.058047	3.890902	3.237202
C	6.229030	4.401113	2.639371
C	7.291954	-0.063736	-0.674343
C	7.361561	-0.801860	0.491980
C	8.174555	-1.954002	0.542660
C	7.871170	-2.971094	1.575070
C	7.943370	-4.344092	1.263657
C	7.188642	-5.280716	1.962992
C	6.300976	-4.887800	2.986827

C	5.103260	-5.689722	3.334174
C	4.232210	-5.336277	4.388052
C	2.899246	-5.737385	4.388705
C	2.371921	-6.517430	3.337941
C	0.933120	-6.530573	2.986215
C	0.159584	-5.377437	3.225206
C	-0.999253	-5.124946	2.497462
C	-1.437729	-6.013443	1.496173
C	-0.785280	-7.261578	1.415728
C	0.372110	-7.514836	2.145033
C	3.297239	-7.054376	2.421149
C	4.626045	-6.649240	2.418168
C	6.426941	-3.559676	3.449807
C	7.196719	-2.627349	2.765356
C	9.031852	-2.200818	-0.559144
C	8.977071	-1.441756	-1.729929
C	8.047179	-0.396043	-1.827517
C	7.502262	0.341299	-2.971677
C	6.407677	1.116983	-2.520026
C	5.573482	1.783902	-3.393732
C	5.774210	1.661632	-4.785718
C	4.630110	2.038823	-5.642232
C	4.148866	1.119511	-6.591281
C	2.807816	1.133215	-6.972134
C	1.908788	2.067897	-6.421767
C	0.483014	1.700921	-6.277114
C	-0.161898	2.037819	-5.070358
C	-1.251243	1.314933	-4.608453
C	-1.765131	0.218910	-5.331752

C	-2.580527	-0.798871	-4.629031
C	-2.592236	-2.146182	-5.043976
C	-2.965652	-3.166863	-4.173815
C	-3.327664	-2.900584	-2.836319
C	-3.252319	-3.935355	-1.777365
C	-3.705769	-3.702520	-0.460434
C	-3.244537	-4.463738	0.609737
C	-2.314202	-5.505393	0.415981
C	-2.025687	-5.862793	-0.915731
C	-2.479524	-5.096013	-1.982702
C	-3.510381	-1.543759	-2.496304
C	-3.151868	-0.525618	-3.370180
C	-1.263807	0.035237	-6.639589
C	-0.161945	0.754115	-7.099359
C	2.467145	3.154351	-5.710787
C	3.795557	3.128155	-5.311782
C	6.912083	0.954158	-5.236205
C	7.776727	0.306135	-4.348397
H	8.416300	6.192003	0.992426
H	9.202211	6.753022	-1.281512
H	9.127167	3.439334	-4.495822
H	8.095805	3.844716	-6.672304
H	6.037292	8.004176	-7.316422
H	3.800250	7.990430	-8.296204
H	1.921868	3.856116	-9.377846
H	-0.454209	3.582326	-8.891462
H	-0.487761	7.433497	-6.941108
H	1.866283	7.706700	-7.428346
H	3.862978	3.674758	-8.377382

H	6.087691	3.688063	-7.426351
H	6.788363	7.731722	-5.319396
H	7.827442	7.335809	-3.156130
H	7.862472	2.941150	-2.751984
H	4.392278	1.265654	1.173341
H	2.949904	0.381628	2.750257
H	0.524245	0.151213	2.470258
H	-0.840240	0.548216	0.773572
H	-2.640160	0.988693	-0.804546
H	-3.421130	5.337790	-0.616186
H	-3.628174	6.108115	-2.917352
H	-3.479533	2.490859	-5.699914
H	-1.890543	3.015968	-7.444794
H	-2.534258	7.231412	-6.758435
H	-4.111494	6.694340	-4.975171
H	-5.029708	2.204625	-4.109237
H	-4.835963	1.437935	-1.781735
H	-3.875098	4.399299	1.529433
H	-2.076502	3.945171	3.136656
H	0.060208	4.399688	3.067088
H	2.464759	4.629094	3.361680
H	4.652498	4.406282	4.110850
H	6.697705	5.295691	3.055833
H	6.676279	-0.578350	1.310184
H	8.502187	-4.676601	0.386531
H	7.213322	-6.319768	1.631011
H	4.579769	-4.676045	5.185290
H	2.238724	-5.380380	5.182235
H	0.541356	-4.598703	3.888298

H	-1.490799	-4.156709	2.611731
H	-1.152917	-8.019688	0.720404
H	0.888243	-8.467746	2.007814
H	2.944874	-7.689161	1.606509
H	5.261977	-6.988533	1.599896
H	5.823934	-3.217142	4.292047
H	7.196542	-1.591448	3.111857
H	9.719050	-3.048381	-0.517316
H	9.609226	-1.709487	-2.579782
H	4.695225	2.311608	-3.018238
H	4.777660	0.283002	-6.905183
H	2.427339	0.300842	-7.566827
H	0.271692	2.794698	-4.416224
H	-1.636594	1.547609	-3.615820
H	-2.208938	-2.418968	-6.028884
H	-2.891092	-4.198175	-4.522426
H	-4.384847	-2.872568	-0.255770
H	-3.567640	-4.208228	1.621633
H	-1.325752	-6.675930	-1.116702
H	-2.119618	-5.342804	-2.982119
H	-3.839571	-1.272495	-1.491619
H	-3.242546	0.505114	-3.034376
H	-1.693868	-0.734335	-7.283656
H	0.246764	0.521373	-8.085680
H	1.828308	3.982494	-5.398229
H	4.185524	3.933085	-4.684454
H	7.096579	0.875660	-6.310288
H	8.627792	-0.259872	-4.734113

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

Table S10 The optimized structure of sp^3-carbocation intermediate (*trans*) (B3LYP D3 RIJCOSX opt def2-SVP def2/J) (E = − 4227.786489369252 Hartree)

C	1.353896	-3.991935	1.039066
C	1.692595	-2.639936	0.389079
C	2.836307	-2.180000	-0.243043
C	2.961445	-0.820010	-0.612920
C	4.317229	-0.305636	-0.905081
C	5.335139	-1.133200	-1.427174
C	6.677101	-0.797354	-1.288567
C	7.069197	0.380360	-0.615875
C	6.048814	1.291694	-0.275459
C	4.706099	0.957355	-0.415968
C	1.842025	0.021819	-0.441020
C	0.712295	-0.415580	0.252425
C	0.673322	-1.723663	0.752084
C	-0.047144	-2.264879	1.912793
C	0.534495	-3.512271	2.257093
C	0.460409	-3.962321	3.564328
C	-0.256539	-3.231186	4.542402
C	0.036011	-3.516504	5.967518
C	0.432657	-4.795006	6.411564
C	1.111968	-4.960662	7.615032
C	1.431345	-3.854207	8.428832
C	2.522724	-3.893194	9.429586
C	2.628276	-2.962118	10.483149
C	3.846468	-2.721482	11.112263
C	5.024110	-3.388778	10.709387

C	6.377966	-2.844136	10.965223
C	7.545548	-3.568041	10.642306
C	8.746874	-2.919433	10.381578
C	8.851410	-1.513030	10.448266
C	9.892631	-0.800390	9.675952
C	9.619311	0.488929	9.171811
C	10.304315	0.998756	8.078525
C	11.304793	0.250329	7.422630
C	11.625036	0.555572	6.011990
C	12.009015	-0.476270	5.127759
C	11.820627	-0.358654	3.756272
C	11.223809	0.790447	3.193140
C	10.521489	0.744390	1.891120
C	9.961535	1.895048	1.290890
C	8.933596	1.798615	0.359205
C	8.418716	0.545002	-0.034194
C	9.122231	-0.595390	0.402990
C	10.142941	-0.498214	1.339750
C	11.075984	1.902254	4.051494
C	11.279328	1.790615	5.420949
C	11.728766	-0.933679	8.067398
C	11.042150	-1.444086	9.164040
C	7.757733	-0.830209	11.023375
C	6.551527	-1.475787	11.265200
C	4.865905	-4.454279	9.798958
C	3.648198	-4.701339	9.177127
C	0.867997	-2.612860	8.073618
C	0.187454	-2.447328	6.871098
C	-1.005123	-2.115704	4.124580

C	-0.888077	-1.618238	2.822751
H	3.714704	-2.812153	-0.326168
H	5.075446	-2.082164	-1.902249
H	7.438059	-1.487450	-1.658901
H	6.304443	2.224931	0.229409
H	3.952329	1.638739	-0.016900
H	1.890368	1.058375	-0.781077
H	-0.090963	0.289093	0.480478
H	1.065715	-4.799208	3.900240
H	0.255070	-5.670245	5.782207
H	1.451110	-5.958588	7.901680
H	1.754768	-2.374860	10.775935
H	3.894309	-1.951067	11.884336
H	7.494943	-4.648776	10.499174
H	9.584521	-3.510948	10.008407
H	8.766494	1.053146	9.549924
H	9.957688	1.938891	7.648504
H	12.352453	-1.433083	5.524499
H	12.057157	-1.217487	3.126088
H	10.287207	2.888181	1.605334
H	8.483200	2.715665	-0.027114
H	8.779853	-1.589031	0.108484
H	10.562523	-1.422630	1.737090
H	10.687016	2.844824	3.663701
H	11.074010	2.657877	6.050704
H	12.568298	-1.502753	7.662855
H	11.364865	-2.397856	9.586261
H	7.815778	0.245465	11.197583
H	5.698401	-0.876098	11.586060

H	5.736681	-5.022302	9.470161
H	3.608963	-5.449324	8.382997
H	1.078532	-1.731914	8.682834
H	-0.115381	-1.441124	6.574706
H	-1.615233	-1.573147	4.849720
H	-1.374440	-0.676601	2.556938
C	-6.856194	-9.863393	-4.565189
C	-5.924491	-10.632728	-5.288157
H	-5.599212	-11.597392	-4.894540
C	-5.271403	-10.114642	-6.401814
H	-4.457009	-10.691977	-6.843059
C	-5.518764	-8.801814	-6.847352
C	-6.600356	-8.119320	-6.253287
H	-6.890046	-7.134523	-6.627217
C	-4.481917	-8.112383	-7.653305
C	-4.183878	-6.762994	-7.381099
H	-4.864843	-6.173356	-6.764673
C	-2.954311	-6.211881	-7.729022
H	-2.711746	-5.207855	-7.375031
C	-1.963897	-6.985644	-8.364462
C	-2.344337	-8.264424	-8.821357
H	-1.638270	-8.864343	-9.400460
C	-0.546190	-6.574589	-8.243965
C	0.420915	-7.553417	-7.942016
H	0.164012	-8.610337	-8.031411
C	1.638042	-7.210162	-7.366035
H	2.290399	-8.016243	-7.028423
C	1.957401	-5.869711	-7.067914
C	1.077479	-4.883571	-7.564486

H	1.320768	-3.825600	-7.446901
C	2.984007	-5.574809	-6.040626
C	2.890610	-4.408413	-5.251305
H	2.232873	-3.594386	-5.558459
C	3.509068	-4.324670	-4.009755
H	3.340606	-3.431548	-3.403475
C	4.248385	-5.407029	-3.488342
C	4.523315	-6.472612	-4.368737
H	5.132456	-7.314828	-4.033721
C	4.457929	-5.561702	-2.031191
C	5.388931	-6.449365	-1.455767
H	6.180930	-6.871421	-2.077806
C	5.262609	-6.906126	-0.125079
H	5.938441	-7.684384	0.237460
C	4.222400	-6.437019	0.663290
C	3.403807	-5.372117	0.164785
C	2.334564	-5.110101	1.106895
C	2.319269	-6.236261	2.006989
C	1.234696	-6.790526	2.698114
H	0.262390	-6.308609	2.637852
C	1.338016	-8.054235	3.309675
C	2.608586	-8.671966	3.310214
H	2.738766	-9.621748	3.833286
C	3.692182	-8.161964	2.565599
H	4.618098	-8.738569	2.504547
C	0.081569	-8.748804	3.677079
C	-1.104865	-8.025921	3.915781
H	-1.063762	-6.955845	4.132092
C	-2.352195	-8.624073	3.777783

H	-3.240180	-7.995684	3.859034
C	-2.479353	-9.977437	3.401280
C	-3.733711	-10.465755	2.776856
C	-3.671294	-11.484916	1.806401
H	-2.757949	-12.068406	1.683168
C	-4.691663	-11.664096	0.878865
H	-4.541069	-12.375761	0.064967
C	-5.823200	-10.826862	0.868374
C	-5.976220	-9.945507	1.957522
H	-6.881111	-9.338676	2.038235
C	-6.597753	-10.700533	-0.390317
C	-6.939979	-9.413753	-0.846414
H	-6.867130	-8.562885	-0.165765
C	-7.193475	-9.173144	-2.194028
H	-7.310687	-8.140334	-2.527424
C	-6.733062	-11.763821	-1.305280
H	-6.563538	-12.790135	-0.970639
C	-6.993200	-11.523149	-2.652127
H	-7.025662	-12.366722	-3.345430
C	-4.956434	-9.771444	2.890526
H	-5.093735	-9.034135	3.684424
C	-1.294213	-10.742574	3.394772
H	-1.339954	-11.814844	3.197812
C	-0.043849	-10.141993	3.513854
H	0.845715	-10.758990	3.368853
C	3.529244	-6.989673	1.840160
C	3.501695	-4.975800	-1.171084
H	2.744105	-4.318790	-1.591195
C	3.918378	-6.545813	-5.619153

H	4.101893	-7.427413	-6.235063
C	-0.144238	-5.226704	-8.136336
H	-0.827389	-4.432867	-8.446694
C	-3.577039	-8.812403	-8.479065
H	-3.812686	-9.829367	-8.800378
C	-7.118363	-10.208152	-3.145622
C	-7.254582	-8.638303	-5.138351
H	-8.041944	-8.048812	-4.662788
H	0.587680	-4.423735	0.346908

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Table S11 The optimized structure of $\mathbf{C_{60}}$ (B3LYP D3 RIJCOSX opt def2-SVP def2/J)

C	5.756142	-1.158475	3.440009
C	4.451668	-1.536634	3.109840
C	4.154990	-2.926211	2.789978
C	5.174970	-3.881758	2.812897
C	5.250105	-4.892190	1.766466
C	4.302103	-4.906377	0.739186
C	4.720389	-5.151100	-0.634600
C	6.069738	-5.372053	-0.925317
C	6.534410	-3.487873	3.156681
C	6.818952	-2.154157	3.463606
C	8.030752	-1.530899	2.949624
C	8.909390	-2.266690	2.149195
C	9.511419	-1.652357	0.973566
C	9.209575	-0.327312	0.645755
C	8.613263	-3.656610	1.829454
C	7.449847	-4.254922	2.322867

C	6.655984	-5.122520	1.463467
C	7.057574	-5.357725	0.145257
C	8.269298	-4.733868	-0.368886
C	9.031142	-3.900878	0.455722
C	9.586461	-2.662575	-0.073283
C	9.357526	-2.306949	-1.405637
C	8.563372	-3.174716	-2.264899
C	8.030566	-4.363240	-1.757130
C	6.671323	-4.757243	-2.100906
C	5.899170	-3.947251	-2.938785
C	6.454183	-2.708585	-3.466983
C	7.758658	-2.330427	-3.136815
C	3.646955	-0.692345	2.237922
C	2.852799	-1.560112	1.378662
C	3.166862	-2.940934	1.719903
C	3.239550	-3.910327	0.715343
C	3.000750	-3.539748	-0.672730
C	3.915679	-4.306656	-1.507296
C	4.492848	-3.717265	-2.636178
C	2.698906	-2.214704	-1.000542
C	2.623864	-1.204485	0.046308
C	3.179183	0.033818	-0.482697
C	3.941028	0.866808	0.341911
C	4.179758	0.496180	1.730155
C	5.539002	0.890183	2.073931
C	6.311155	0.080191	2.911811
C	7.717476	-0.149795	2.609203
C	8.294646	0.439595	1.480321
C	7.489935	1.284038	0.607624

C	6.140587	1.504994	0.898343
C	5.152751	1.490665	-0.172233
C	5.554341	1.255460	-1.490442
C	6.960220	1.025128	-1.793440
C	7.908222	1.039316	-0.766161
C	8.970774	0.043265	-0.742318
C	9.043463	-0.926126	-1.746878
C	8.055336	-0.940849	-2.816954
C	7.035355	0.014697	-2.839872
C	5.675915	-0.379187	-3.183656
C	5.391373	-1.712903	-3.490581
C	4.179574	-2.336161	-2.976599
C	3.300935	-1.600371	-2.176170
C	3.597063	-0.210450	-1.856429
C	4.760478	0.387862	-2.349842

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Table S12 The optimized structure of **NDI** (B3LYP D3 RIJCOSX opt def2-SVP def2/J)

O	1.044720	-0.101310	-0.051690
C	2.265840	-0.093150	-0.050980
C	3.016560	1.188330	-0.049890
C	2.357040	2.427610	-0.049630
C	3.088420	3.618230	-0.048590
C	4.491980	3.590210	-0.047790
C	5.295660	4.839160	-0.046680
O	6.651240	4.771950	-0.045950
O	4.750910	5.932060	-0.046400
C	5.165110	2.352640	-0.048050

C	4.424750	1.147390	-0.049100
C	5.097870	-0.090180	-0.049350
C	6.501430	-0.118200	-0.048550
C	7.232810	1.072420	-0.047520
C	6.573290	2.311700	-0.047270
C	7.324020	3.593180	-0.046190
O	8.545130	3.601340	-0.045520
O	2.938610	-1.271920	-0.051200
C	4.294200	-1.339130	-0.050450
O	4.838950	-2.432030	-0.050700
H	1.275320	2.476390	-0.050230
H	2.555890	4.561060	-0.048410
H	7.033970	-1.061030	-0.048730
H	8.314530	1.023640	-0.046930

Table S13 Energy comparison of relevant structures (B3LYP D3 RIJCOSX opt def2-SVP def2/J)

Compound	E / Hartree	Δ E / Kcal/mol
***cis*-1**	−4227.469397247264	11
***trans*-1**	−4227.451890281771	
sp^3-carbocation intermediate -*cis*	−4227.835946970529	31
sp^3-carbocation intermediate -*trans*	−4227.786489369252	

References

1. X. Zhang, H. Shi, G. Zhuang, S. Wang, J. Wang, S. Yang, X. Shao and P. Du, *Angew. Chem. Int. Ed.*, 2021, **60**, 17368-17372.
2. H. U. Kim, J.-H. Kim, H. Suh, J. Kwak, D. Kim, A. C. Grimsdale, S. C. Yoon and D.-H. Hwang, *Chem. Commun.*, 2013, **49**.