

## Electronic Supplementary Information

### Bis(corannulenyl)ethene as an Efficient Photochromic Materials

*Ryuta Imai, Shohei Katao, Fumio Asanoma, Tsuyoshi Kawai\* and Mihoko Yamada\**

*Division of Materials Science, Graduate School of Science and Technology, Nara Institute of Science and  
Technology (NAIST)*

*Ikoma 630-0192, Japan*

*Corresponding Authors: myamada@ms.naist.jp, tkawai@ms.naist.jp*

### Table of Contents

<b>Experimental Section</b>	S3–6
<b>1. Synthesis of <b>1</b></b>	
<b>Figure S1.</b> $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ NMR of <b>1</b> in $\text{CDCl}_3$	S7–8
<b>Figure S2.</b> $^1\text{H}$ and $^{19}\text{F}$ NMR of <b>1</b> in toluene- $d_8$	S9
<b>Figure S3.</b> EI mass spectrum of <b>1</b>	S10
<b>Figure S4.</b> GPC spectrum of <b>1</b>	S10
<b>Table S1.</b> Crystallographic parameters of <b>1</b>	S11
<b>Figure S5.</b> The intermolecular interactions in single-crystal X-ray structure of <b>1o</b>	S12
<b>Figure S6.</b> VT NMR of <b>1o</b> and <b>1c</b> in 1,1,2,2-tetrachloroethane- $d_2$	S13
<b>Figure S7.</b> VT NMR of <b>1o</b> and <b>1c</b> in $\text{CD}_2\text{Cl}_2$	S13
<b>Figure S8.</b> VT NMR of <b>1o</b> in toluene- $d_8$	S14
<b>Figure S9.</b> The optimized structure, bowl depth and dipole moment of <b>1</b>	S15
<b>Figure S10.</b> The molecular orbitals of <b>1o</b> calculated by DFT (enantiomers are omitted)	S16
<b>Figure S11.</b> The molecular orbitals of <b>1c</b> calculated by DFT	S17
<b>Figure S12.</b> NICS(0) values of <b>1</b>	S18

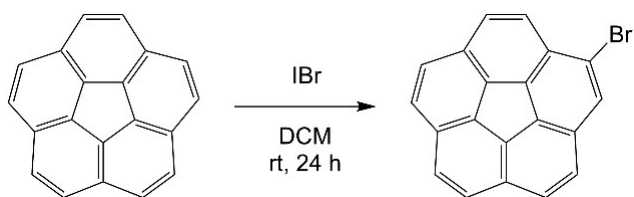
<b>Figure S13.</b> Predicted absorption spectra of the atropisomers <b>1o</b>	S19
<b>Figure S14.</b> Predicted absorption spectra of the atropisomers <b>1c</b>	S19
<b>Figure S15.</b> Emission and excitation spectra of <b>1o</b> in toluene	S20
<b>Figure S16.</b> UV-vis spectral change under photoirradiation of <b>1</b> in chloroform	S21
<b>Figure S17.</b> The repeated colouration and bleaching cycles of <b>1</b>	S21
<b>Figure S18.</b> NMR spectral change under photoirradiation of <b>1</b> in chloroform	S22
<b>Figure S19.</b> NMR spectral change under photoirradiation of <b>1</b> in toluene	S23
<b>Figure S20.</b> Two conformations of <b>1o-1</b>	S24
<b>Table S2.</b> Oxygen effect on the quantum yields	S24
<b>Figure S21.</b> Arrhenius plot and Eyring plot of <b>1</b>	S25
<b>Figure S22.</b> UV-vis spectral change and emission spectrum of PMMA film of <b>1</b>	S26
<b>Figure S23.</b> UV-vis spectral change of a neat film of <b>1</b>	S27
<b>Figure S24.</b> PXRD pattern of a neat film of <b>1</b>	S28
<b>References</b>	S28

## EXPERIMENTAL SECTION

**General.** Chemicals were purchased from FUJIFILM Wako Pure Chemical Corporation, Tokyo Chemical Industry Co., Ltd. (TCI), Kanto Chemical Co., Inc. or Sigma-Aldrich Japan G.K. and used as received without further purification.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were measured with JEOL JNM-ECA600 (600 MHz), JEOL JNM-ECZ500R (500 MHz) or JEOL JNM-ECX400P (400 MHz). Silica gel column chromatography was performed using Silica gel 60N (spherical neutral, particle size 63-210  $\mu\text{m}$ ). Recycling preparative GPC separation was performed with a LaboACE LC-5060 (Japan Analytical Industry Co., Ltd.). HPLC separation was performed with COSMOSIL 5SL-II Packed column (20 mmI.D.  $\times$  250 mm, Nacalai Tesque, Inc.), UV/vis detector (JASCO UV-2075 Plus) and HPLC pump (JASCO PU-2080 Plus). Mass spectra were measured with mass spectrometers (JEOL JMS-700 MStation for EI). UV-vis absorption spectra and quantum yields of photochromic reactions were measured using a JASCO V-550 or V-760 spectrometer and Shimadzu QYM-01, respectively. For kinetic thermal analyses, the temperature was controlled by a JASCO ETC 505T temperature controller. Emission and excitation spectra were measured using a JASCO FP-8500 spectrometer. Emission quantum yield was measured by using a Hamamatsu Photonics C9920-02 instrument with an integrating sphere. Single crystal X-ray crystallographic analysis was performed using a Rigaku XtaLAB Synergy (1.2 kW) diffractometer with photon Jet-R rotating anode X-ray source  $\text{CuK}\alpha$  radiation and Hypix-6000HE detector. Powder X-ray diffraction (PXRD) pattern was recorded on a Rigaku SmartLab9kW/IP/HY/N diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.540593 \text{ \AA}$ ) in the  $2\theta$  range of  $4^\circ$ – $40^\circ$  with a step size of  $0.02^\circ$  and a scan rate of  $1^\circ \text{ min}^{-1}$ . UV irradiation was carried out with an AS ONE SLUV-4 handy lamp or UJ30/ANUJ6186 (Panasonic). Calculations were performed with the Gaussian16 package.

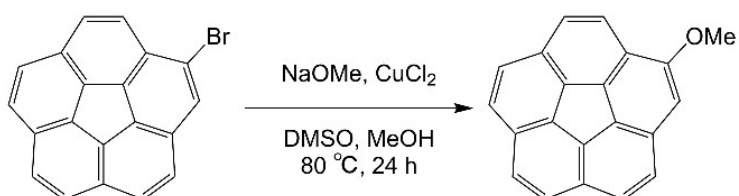
## 1. Synthesis of **1**

### Bromocorannulene<sup>[S1]</sup>



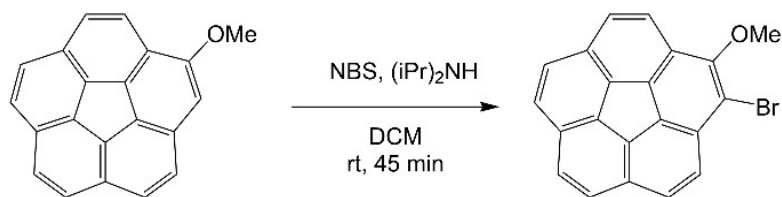
Corannulene (2.0 g, 8.0 mmol, 1.0 eq) was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (150 mL) and iodine monobromide (3.3 g, 16.0 mmol, 2.0 eq) was added under nitrogen. The mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with dichloromethane (100 mL) and sat.  $\text{Na}_2\text{S}_2\text{O}_3$  aq. (150 mL) was added. The solution was extracted with  $\text{CH}_2\text{Cl}_2$  (150 mL  $\times$  3) and washed with water (150 mL  $\times$  2). The organic layer was dried over anhydrous  $\text{MgSO}_4$  and the solvent was evaporated. The mixture of corannulene and bromocorannulene (the ratio of NMR is corannulene:bromocorannulene = 1:2) was obtained as a yellow solid (2.6 g).

### Methoxycorannulene<sup>[S2]</sup>



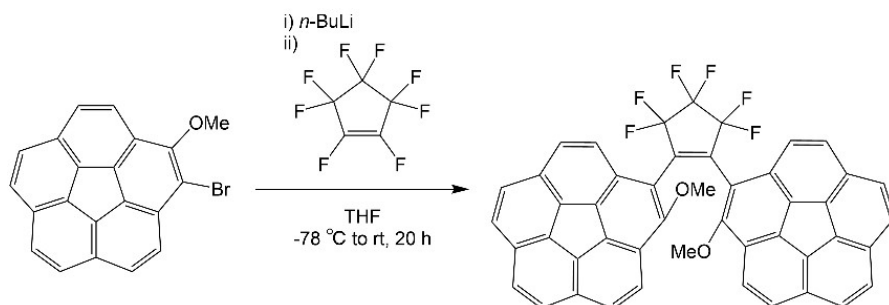
The mixture (corannulene:bromocorannulene = 1:2) (680 mg) and  $\text{CuCl}_2$  (27 mg) was dissolved in a mixture of DMSO (20 mL) and MeOH (1.3 mL) and 5 M NaOMe in MeOH (7.2 mL) was added under nitrogen. The mixture was stirred at 80 °C for 24 h. The reaction mixture was poured into water (50 mL). The solution was extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL  $\times$  3) and washed with water. The organic layer was dried over anhydrous  $\text{MgSO}_4$  and the solvent was evaporated. After purification by silica gel column chromatography (Hexane: $\text{CH}_2\text{Cl}_2$  = 10:1), methoxycorannulene (190 mg, 0.68 mmol) was obtained as a yellow solid.

### 1-Bromo-2-methoxycorannulene <sup>[S2]</sup>



Methoxycorannulene (559 mg, 2.00 mmol) and NBS (408 mg, 2.29 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (20 mL) and  $(i\text{-Pr})_2\text{NH}$  (28  $\mu\text{L}$ , 0.20 mmol) was added. The mixture was stirred at room temperature for 45 min and then sat.  $\text{Na}_2\text{S}_2\text{O}_3$  aq. (10 mL) was added. The solution was extracted with  $\text{CH}_2\text{Cl}_2$  and washed with water. The organic layer was dried over anhydrous  $\text{MgSO}_4$  and the solvent was evaporated. 1-Bromo-2-methoxycorannulene (708 mg, 1.97 mmol, 99 %) was obtained as a brown solid.

### 1,2-Bis(2-methoxy-corannulenyl)perfluorocyclopentene (1)



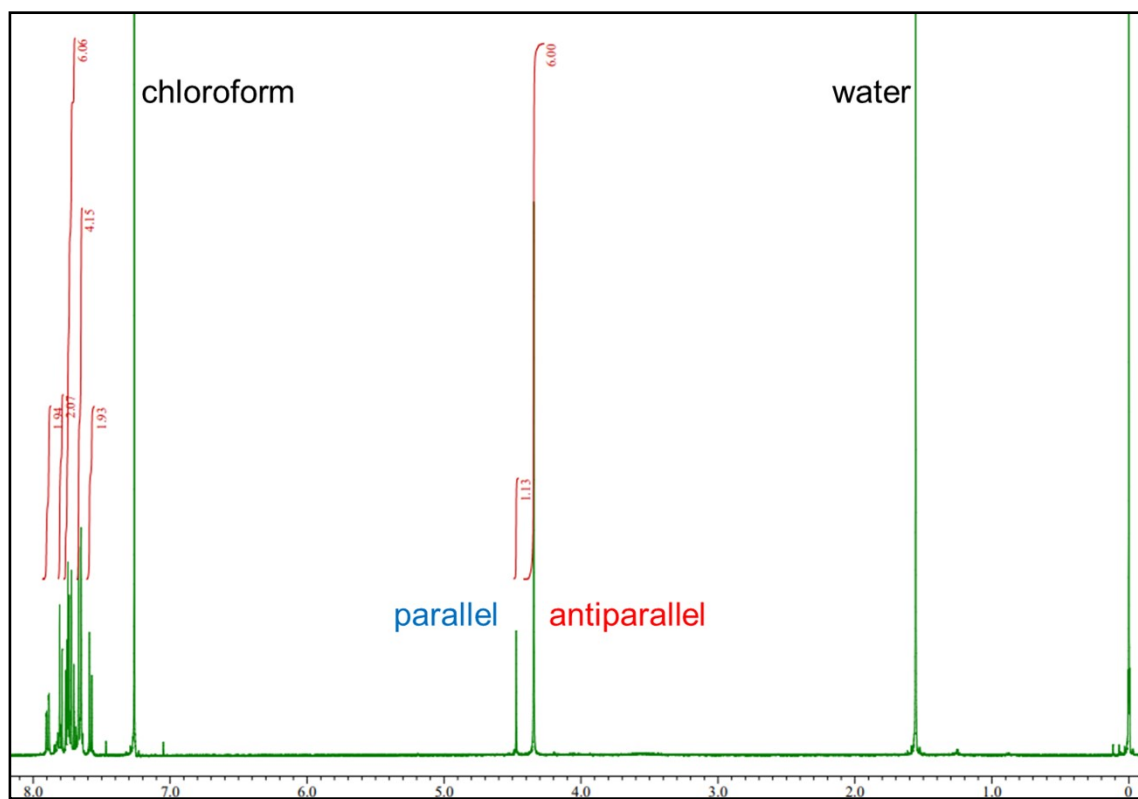
1-Bromo-2-methoxycorannulene (360 mg, 1.00 mmol, 1.00 eq) dissolved in dry THF at  $-78\text{ }^\circ\text{C}$  under nitrogen. 1.6 M  $n\text{-BuLi}$  in hexane (660  $\mu\text{L}$ , 1.05 mmol, 1.05 eq) was slowly added and stirred for 3 h at  $-78\text{ }^\circ\text{C}$ . Then, 0.75 M perfluorocyclopentene in THF (530  $\mu\text{L}$ , 0.40 mmol, 0.40 eq) was gradually added dropwise. The mixture was stirred for 4 h at  $-78\text{ }^\circ\text{C}$  and then overnight at room temperature. The reaction mixture was poured into 1 M HCl (6 mL). The solution was extracted with  $\text{CH}_2\text{Cl}_2$  (5 mL  $\times$  2) and washed with water. The organic layer was dried over anhydrous  $\text{MgSO}_4$  and the solvent was evaporated. After purification by silica gel column chromatography (Hexane: $\text{CH}_2\text{Cl}_2$  = 5:1), 1,2-bis(2-methoxy-corannulenyl)perfluorocyclopentene (58 mg, 0.08 mmol, 16%) was obtained as a yellow solid.

$^1\text{H}$  NMR (500 MHz, toluene- $d_8$ ):  $\delta$  8.08 (dd,  $J = 2, 9$  Hz, 2H, ap), 7.60 (d,  $J = 9$  Hz, 2H, ap), 7.43 (d,  $J = 9$  Hz, 2H, ap), 7.30 (d,  $J = 9$  Hz, 2H, ap), 7.23 (d,  $J = 9$  Hz, 2H, ap), 7.10 (d,  $J = 9$  Hz, 2H, ap), 6.88 (m, 4H, ap), 4.11 (s, 0.75H, p), 3.82 (s, 6H, ap).

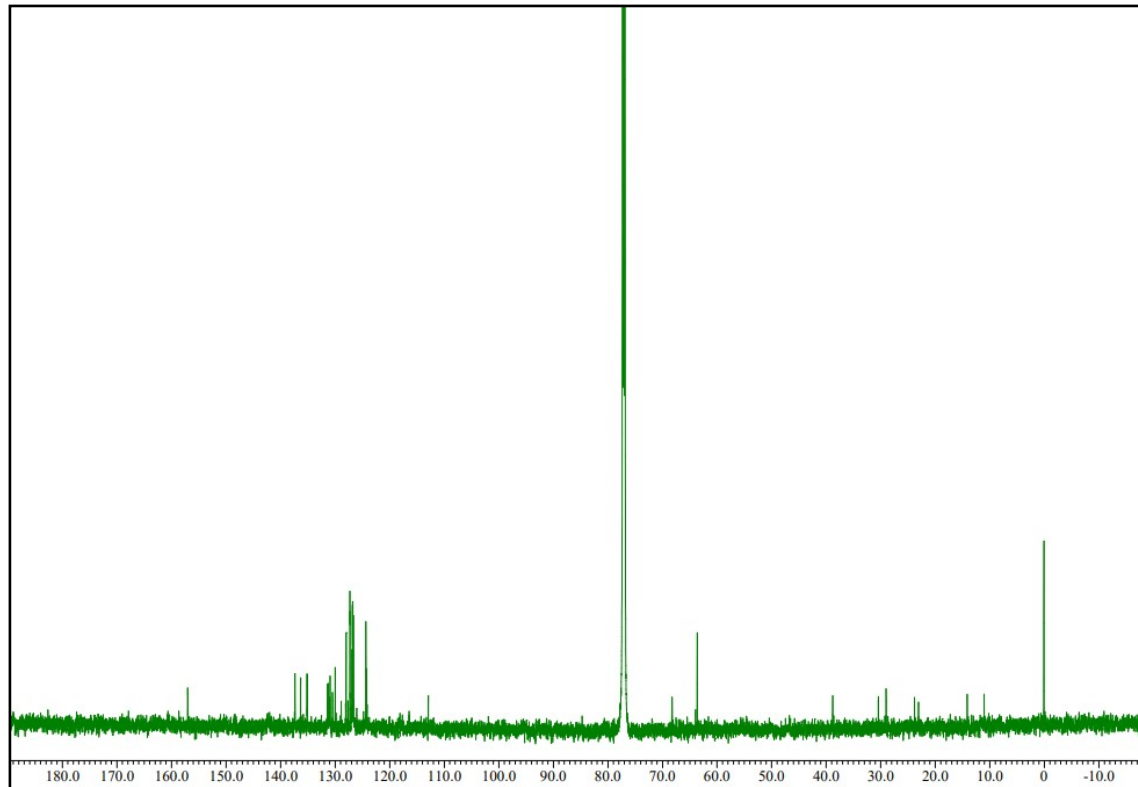
$^{19}\text{F}$  NMR (470 MHz, toluene- $d_8$ ):  $\delta$  -107.53 (dd,  $J = 9, 263$  Hz, 0.3F, p), -108.99 (d,  $J = 263$  Hz, 2F, ap), -110.13 (d,  $J = 263$  Hz, 2F, ap), -111.92 (dd,  $J = 9, 263$  Hz, 0.3F, p), -131.84 (quin,  $J = 6$  Hz 2F, ap), -131.5--133.2 (m, 0.3F, p).

HRMS (EI)  $m/z$ : calcd for  $\text{C}_{47}\text{H}_{22}\text{F}_6\text{O}_2$   $\{[\mathbf{1}]^+\}$ : 732.1524; found: 732.1524.

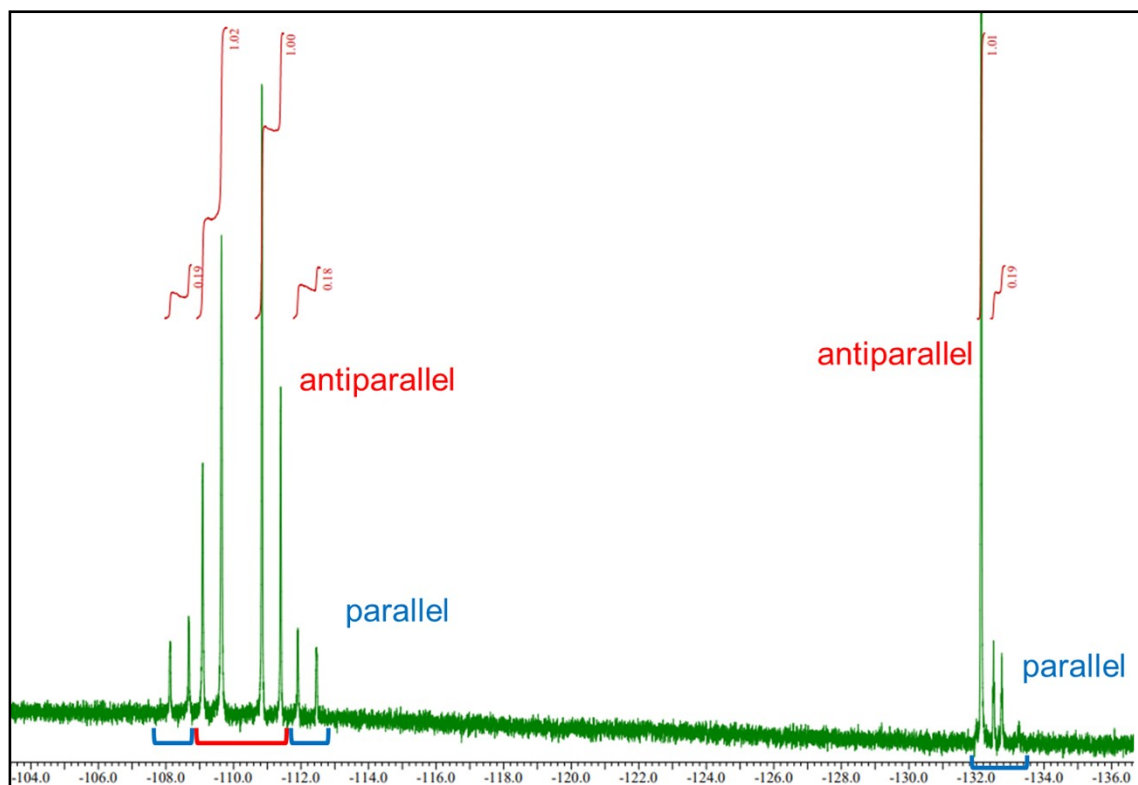
(a)



(b)



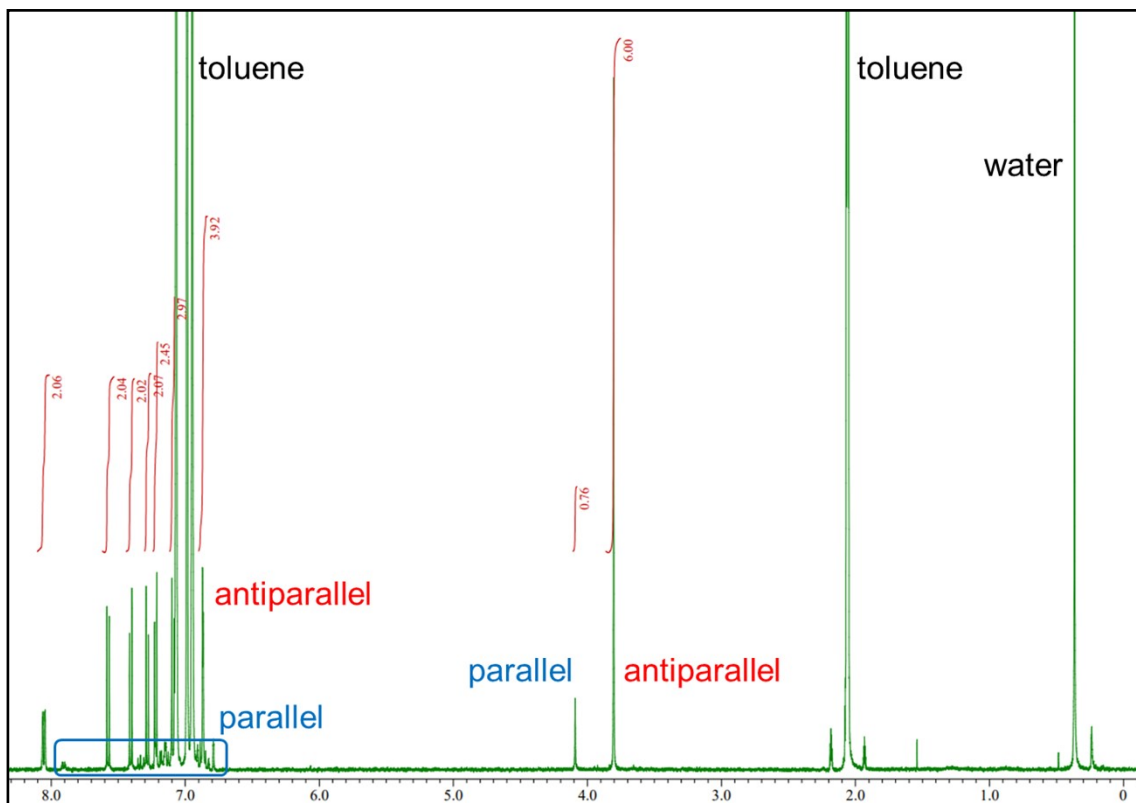
(c)



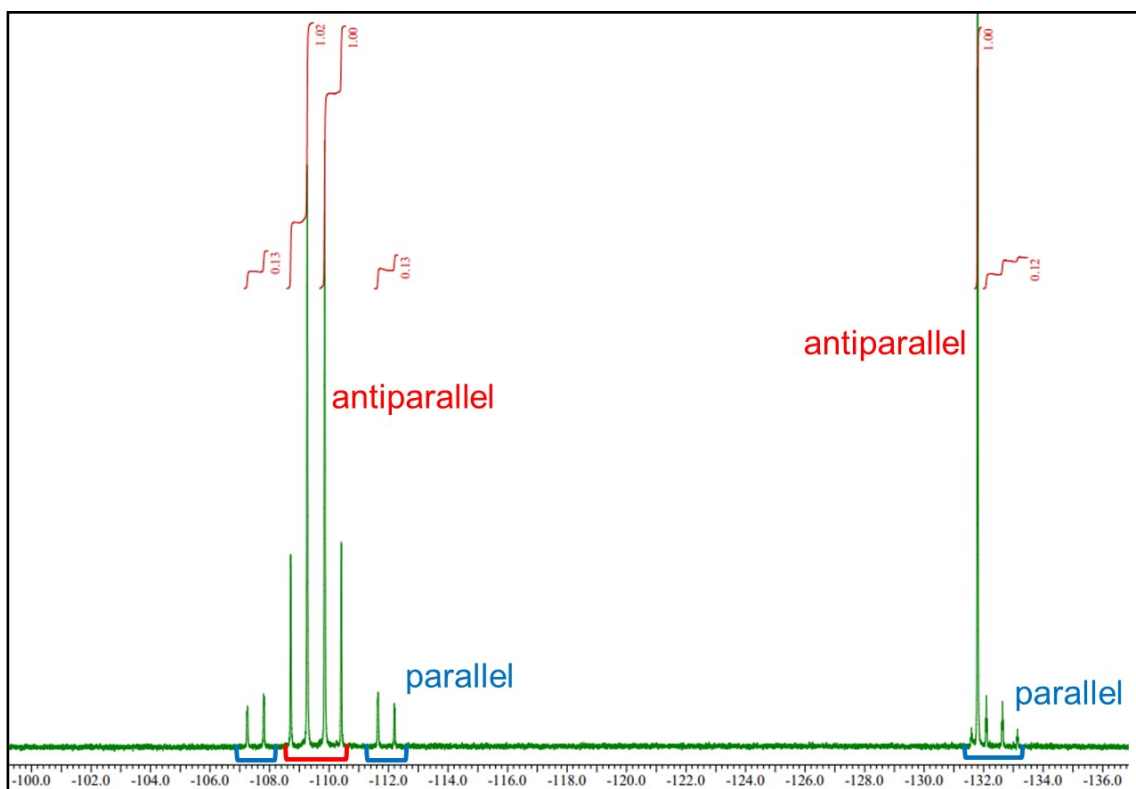
**Figure S1.** (a)  $^1\text{H}$  (500 MHz), (b)  $^{13}\text{C}$  (150 MHz) and (c)  $^{19}\text{F}$  (470 MHz) NMR spectra of **1** in  $\text{CDCl}_3$  at 20 °C. The major component with the singlet peak and the minor component with the double doublet peak due to the central  $\text{CF}_2$  unit was expected  $C_2$  symmetric anti-parallel and  $C_s$  symmetric parallel conformations, respectively.



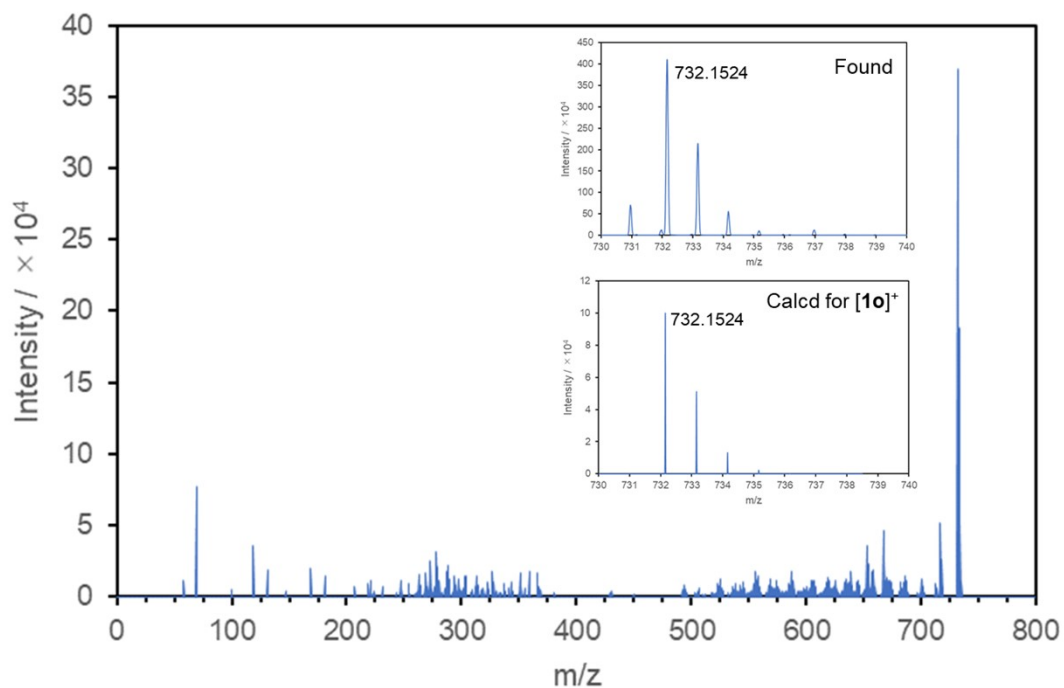
(a)



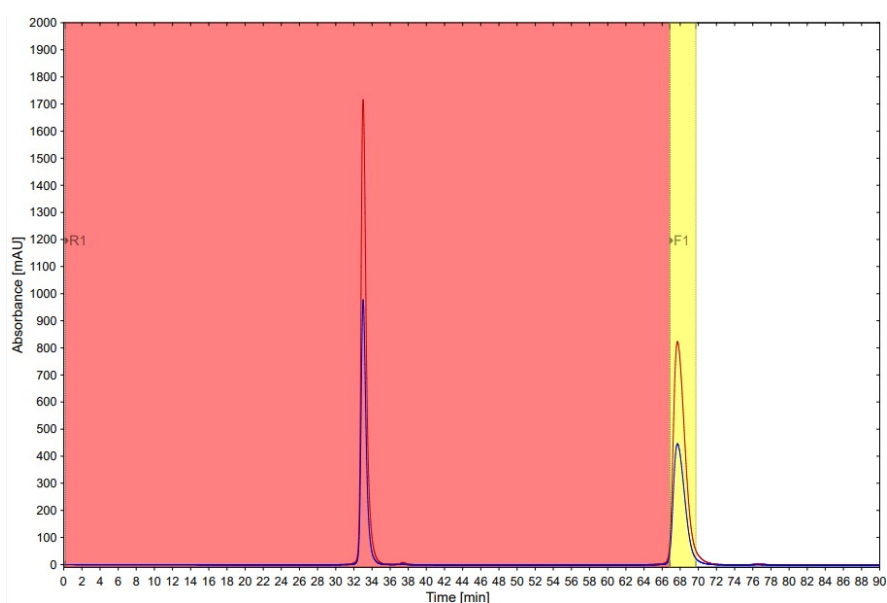
(b)



**Figure S2.** (a)  $^1\text{H}$  (500 MHz) and (b)  $^{19}\text{F}$  (470 MHz) NMR spectra of **1** in toluene- $d_8$  at 20 °C.



**Figure S3.** EI mass spectrum of **1** (positive,  $\text{CHCl}_3$ ).



**Figure S4.** GPC spectrum of **1**. The eluent is chloroform and the observed wavelengths are 254 nm (red line) and 300 nm (blue line). We confirmed the peak of **1o** was single component in the first cycle (red region) and collected **1o** in the second cycle (yellow region).

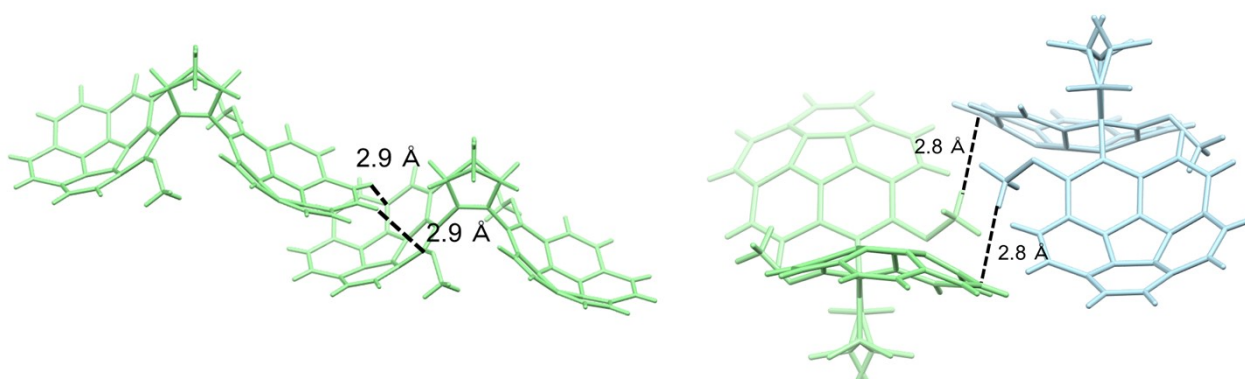
**Table S1.** Crystallographic parameters of **1**

Formula	C <sub>47</sub> H <sub>22</sub> F <sub>6</sub> O <sub>2</sub>
Colour, shape	Colourless, needle
<i>M</i>	732.64
Crystal system	Monoclinic
Space group	<i>I</i> 1 2/a 1
<i>a</i> / Å	17.5895(3)
<i>b</i> / Å	7.4912(1)
<i>c</i> / Å	25.2551(4)
$\beta$ / °	109.857(2)
<i>V</i> / Å <sup>3</sup>	3129.92(9)
<i>Z</i>	4
<i>T</i> / K	103
<i>F</i> (000)	1496.0
$\rho_{\text{calcd}}$ / g cm <sup>-3</sup>	1.555
$\mu(\text{Mo K}\alpha)$ / mm <sup>-1</sup>	1.001
Crystal size / mm <sup>3</sup>	0.13 × 0.04 × 0.03
	-16 ≤ <i>h</i> ≤ 21
Limiting indices	-9 ≤ <i>k</i> ≤ 9
	-31 ≤ <i>l</i> ≤ 31
<i>R</i> <sub>1</sub> <sup>a</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0955
<i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.2690
GOF	1.058
CCDC number	2345853

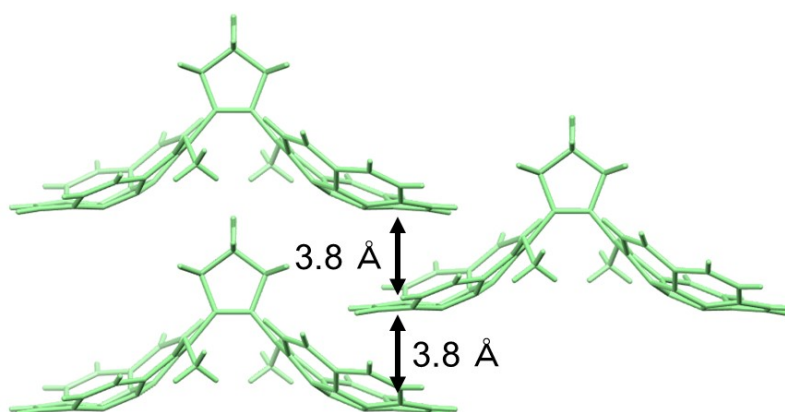
<sup>a</sup>  $R_1 = \Sigma (|F_o| - |F_c|) / \Sigma (|F_o|)$ .

<sup>b</sup>  $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ .

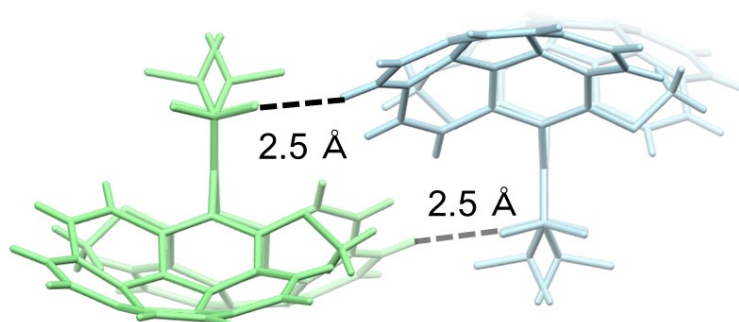
(a)



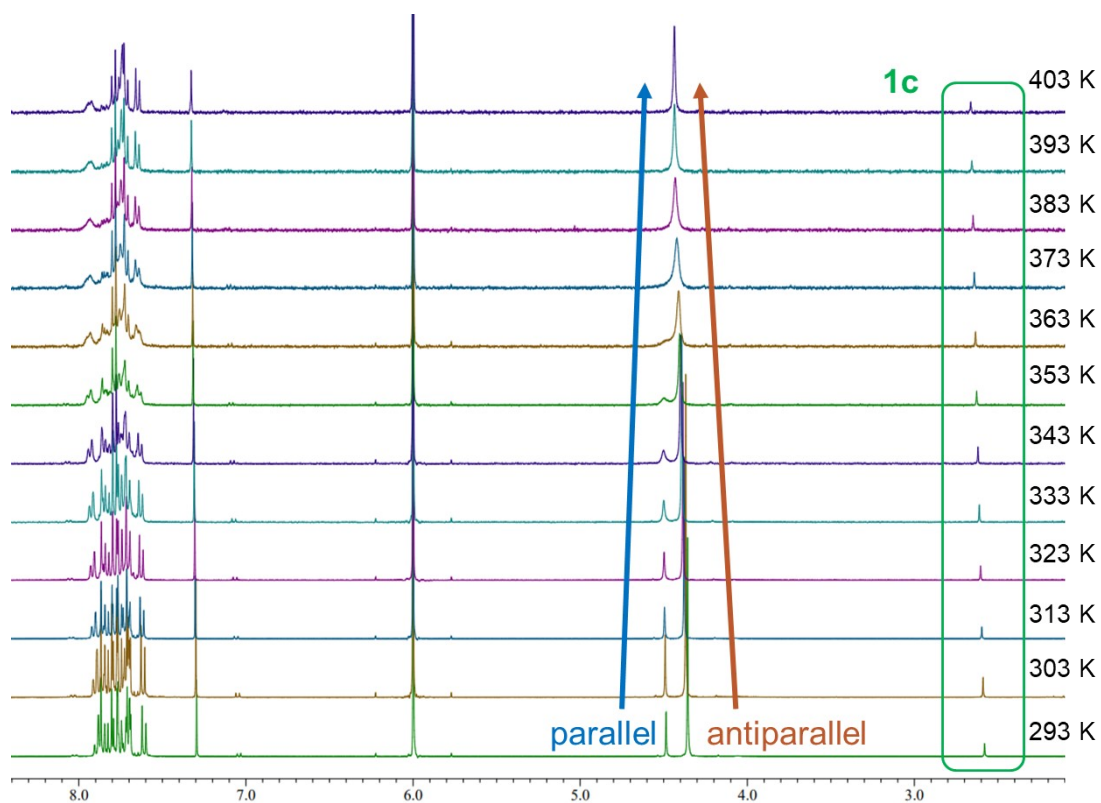
(b)



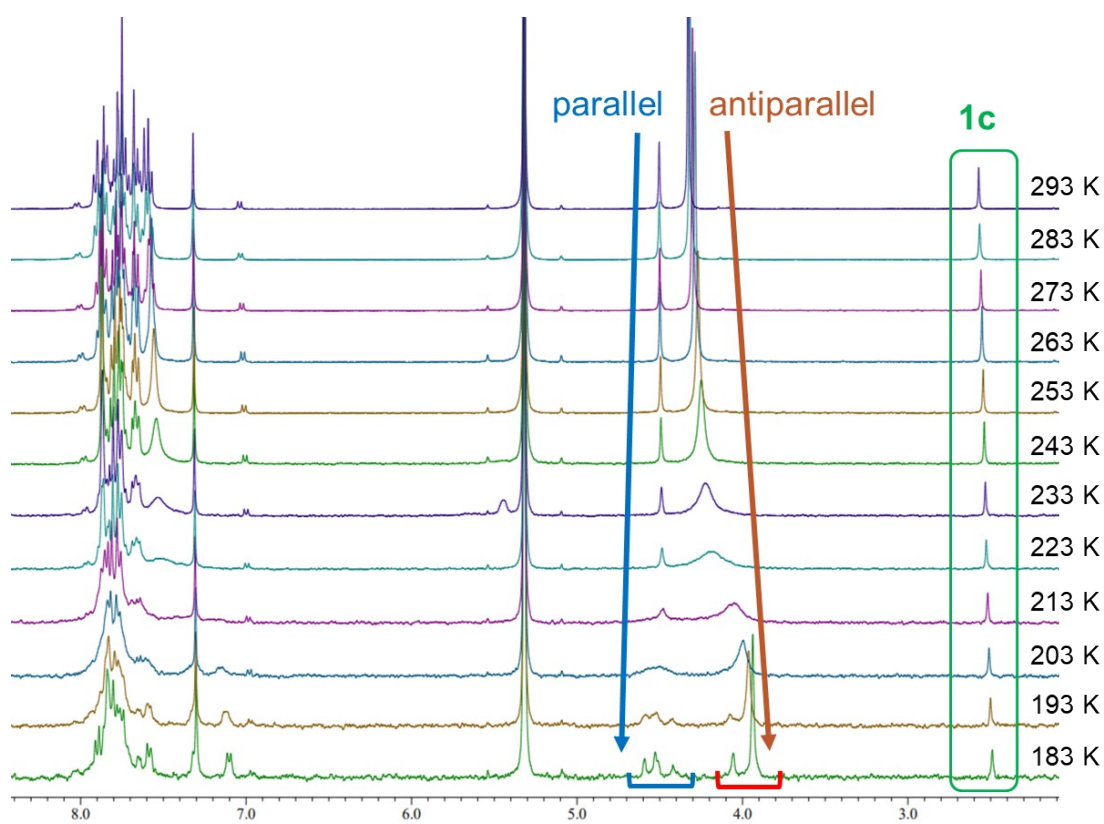
(c)



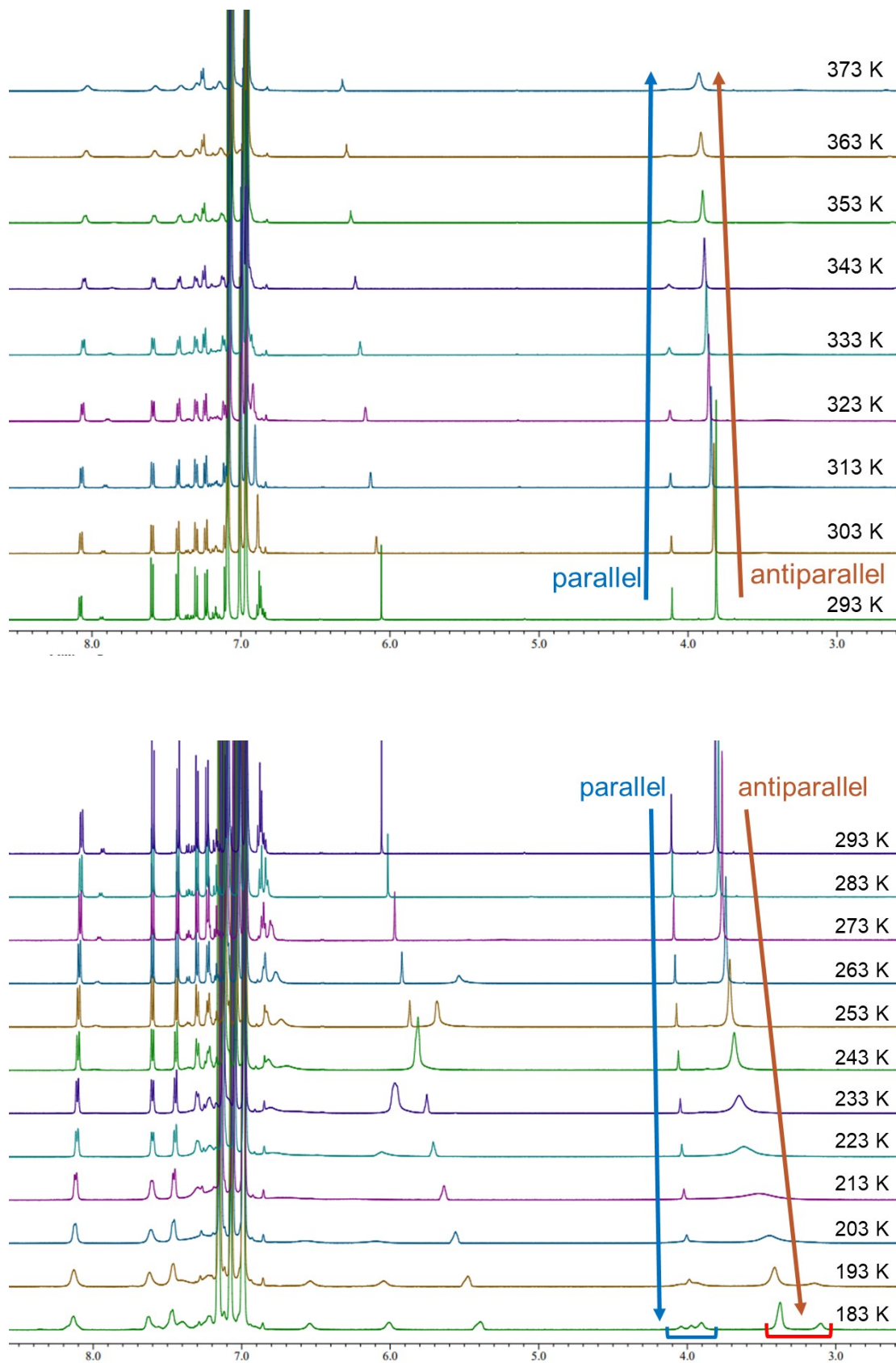
**Figure S5.** The intermolecular interactions in single-crystal X-ray structure of **10**. (a)  $\text{CH}\cdots\pi$  interactions between intermolecular corannulenes, or methoxy group and corannulene, (b) intermolecular  $\pi$ - $\pi$  interaction, (c) intermolecular  $\text{CH}\cdots\text{F}$  interaction. The chirality of corannulene moieties are *PP* (green) and *MM* (blue) isomers.



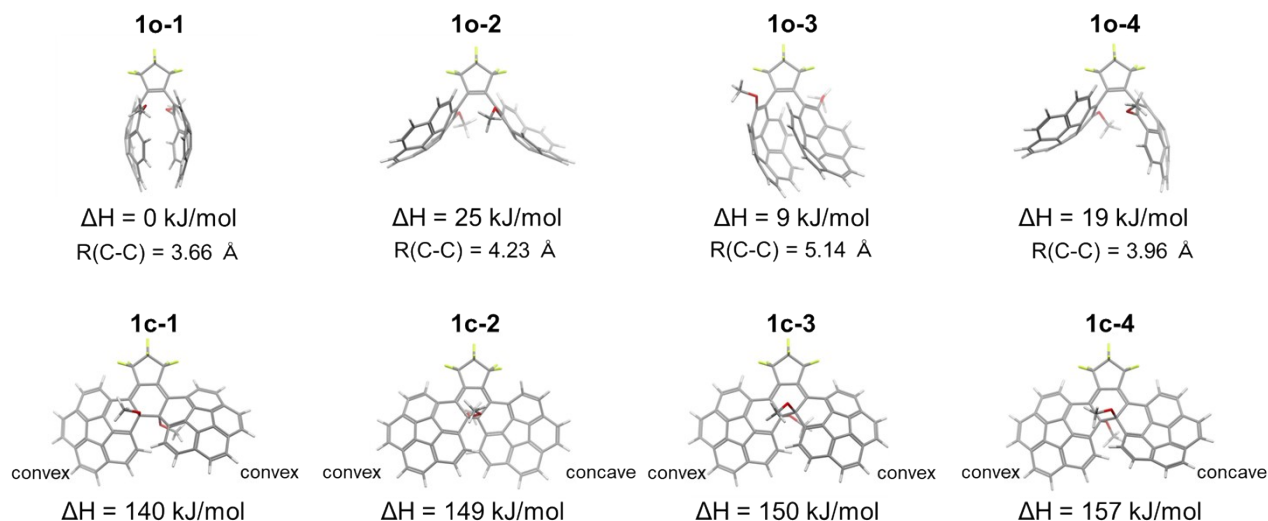
**Figure S6.** VT-NMR (400 MHz) spectra of **1o** and **1c** in 1,1,2,2-tetrachloroethane- $d_2$  at 293–403 K.



**Figure S7.** VT-NMR (400 MHz) spectra of **1o** and **1c** in  $CD_2Cl_2$  at 183–293 K.



**Figure S8.** VT-NMR (600 MHz) spectra of **1o** in toluene- $d_8$  at 183–373 K.



	<b>1o-1</b>		<b>1o-2</b>		<b>1o-3</b>		<b>1o-4</b>	
Bowl depth / Å	0.86	0.88	0.86	0.86	0.93	0.87	0.86	0.86
Dipole moment / Debye	5.22		4.62		6.01		5.49	
	<b>1c-1</b>		<b>1c-2</b>		<b>1c-3</b>		<b>1c-4</b>	
Bowl depth / Å	0.79	0.76	0.69	0.60	0.76	0.73	0.76	0.73
Dipole moment / Debye	6.54		6.25		7.93		6.48	

**Figure S9.** The optimized structure, bowl depth of corannulene moiety and dipole moment by DFT in  $\omega$ B97XD/6-31+G(d) level.

$\Delta H$ : The energy difference from the most stable atropisomer **1o-1**.

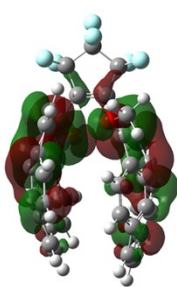
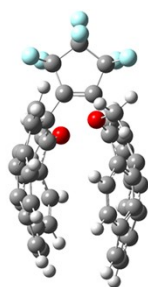
$R(C-C)$ : The distance between the two reactive carbon atoms.

Corannulene direction: A corannulene with five-membered ring in front is “convex” and one in the back is “concave”.

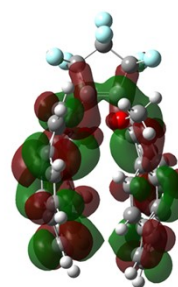
Corannulene bowl depth: The distance between the centroid of the five interior carbon atoms and the centroid of the ten carbon atoms on the rim.



**1o-1**

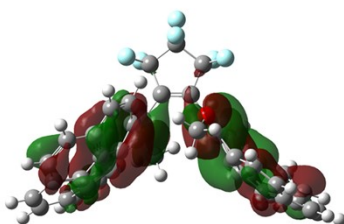
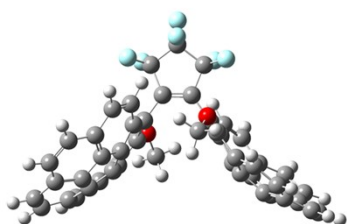


HOMO

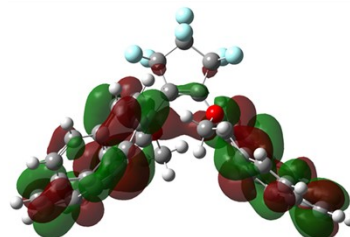


LUMO

**1o-2**

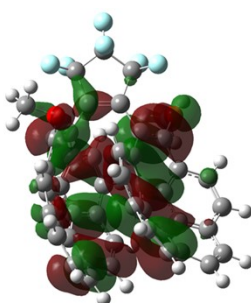
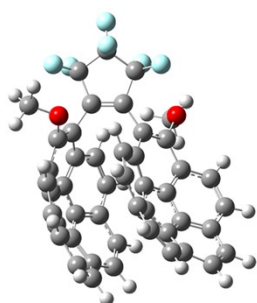


HOMO

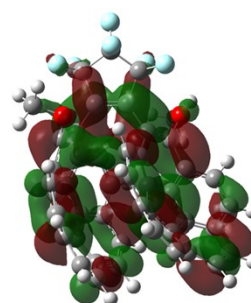


LUMO

**1o-3**

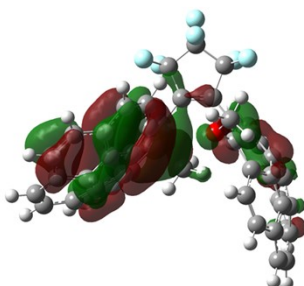
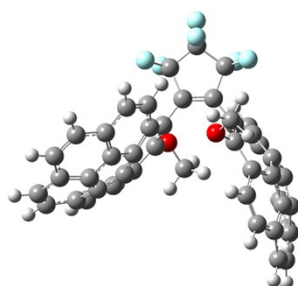


HOMO

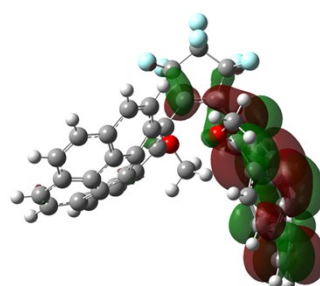


LUMO

**1o-4**



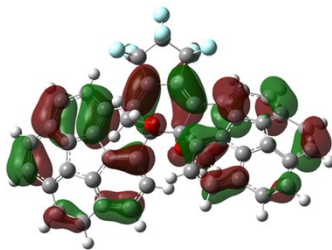
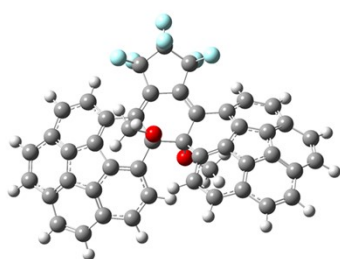
HOMO



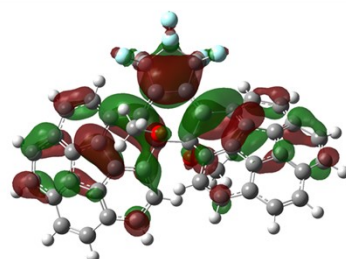
LUMO

**Figure S10.** The molecular orbitals of **1o** calculated by DFT in  $\omega$ B97XD/6-31+G(d) level.

1c-1

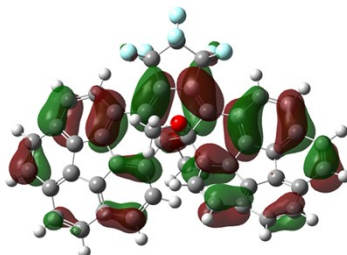
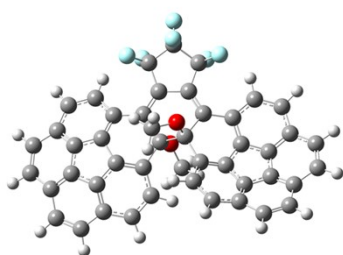


HOMO

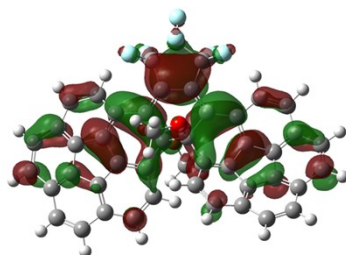


LUMO

1c-2

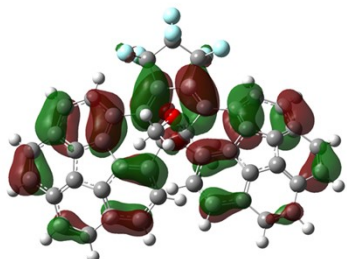
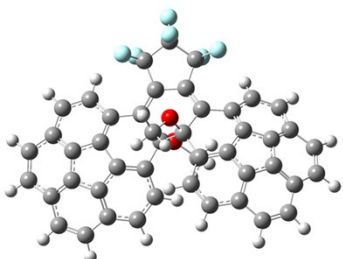


HOMO

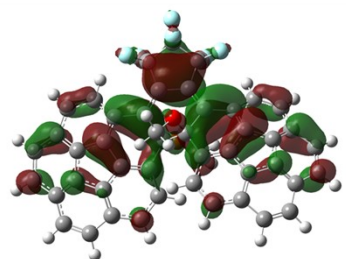


LUMO

1c-3

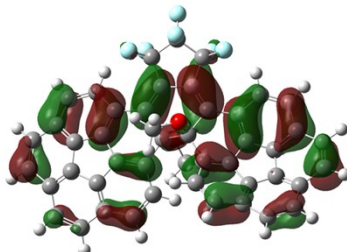
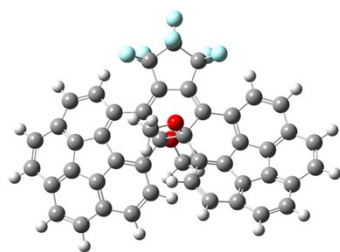


HOMO

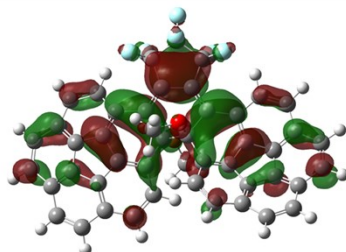


LUMO

1c-4

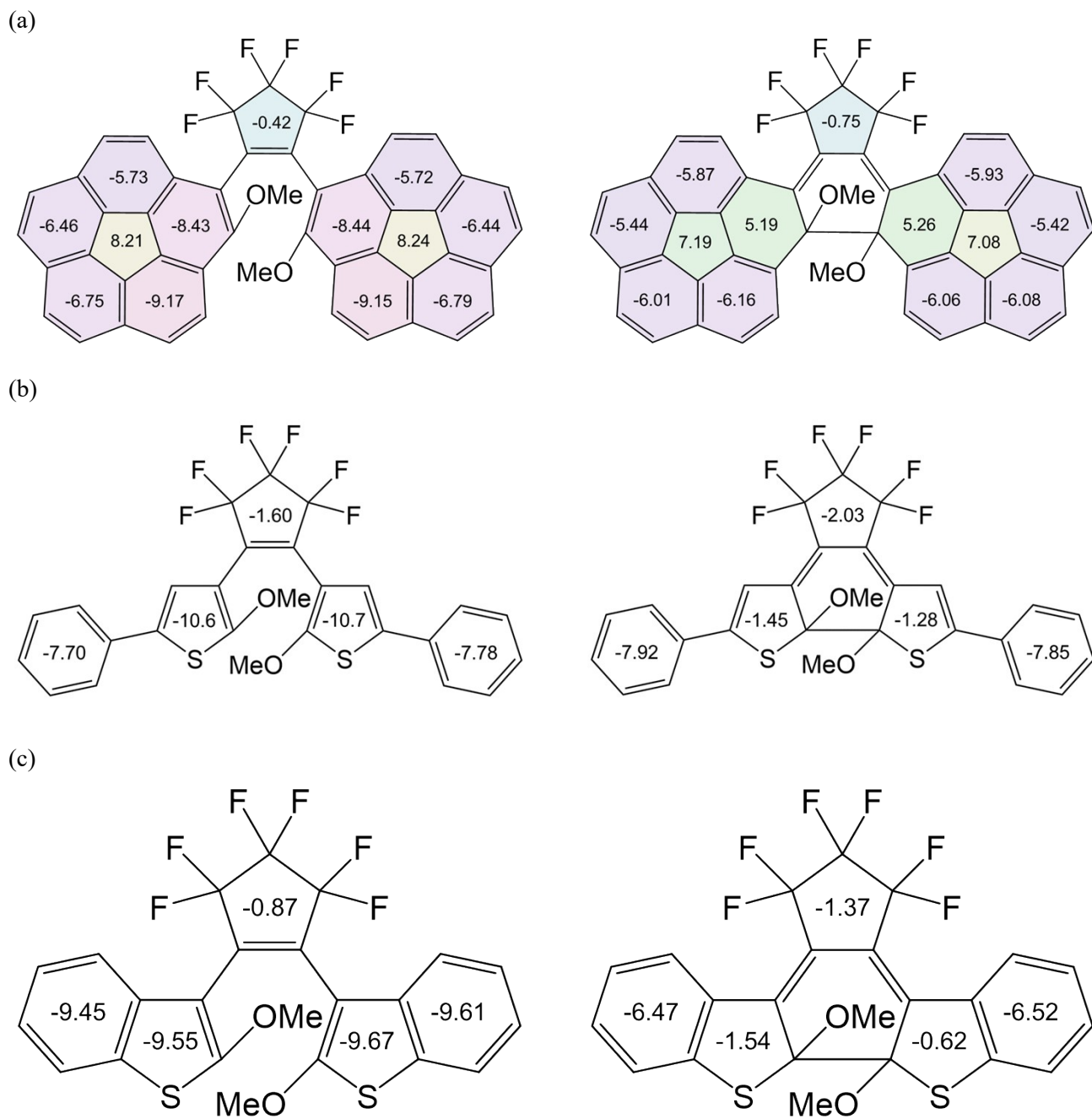


HOMO

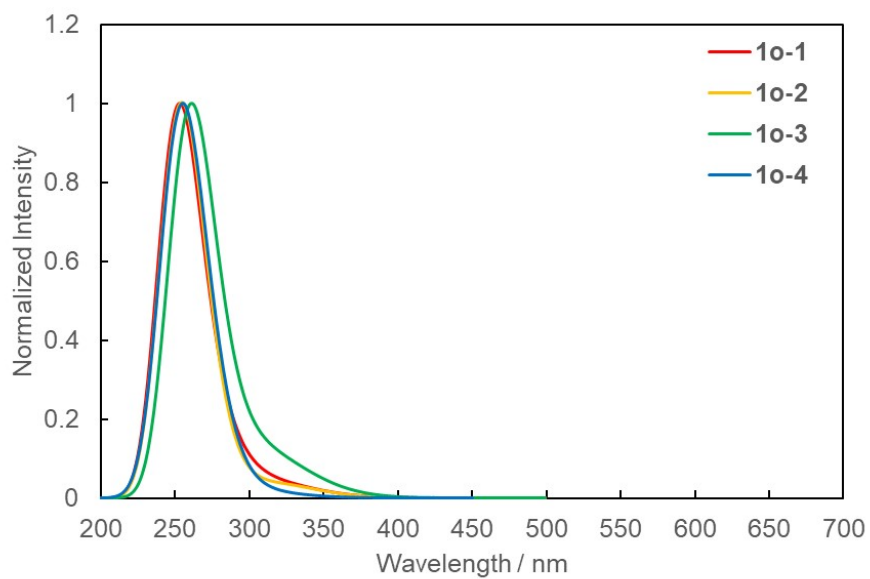


LUMO

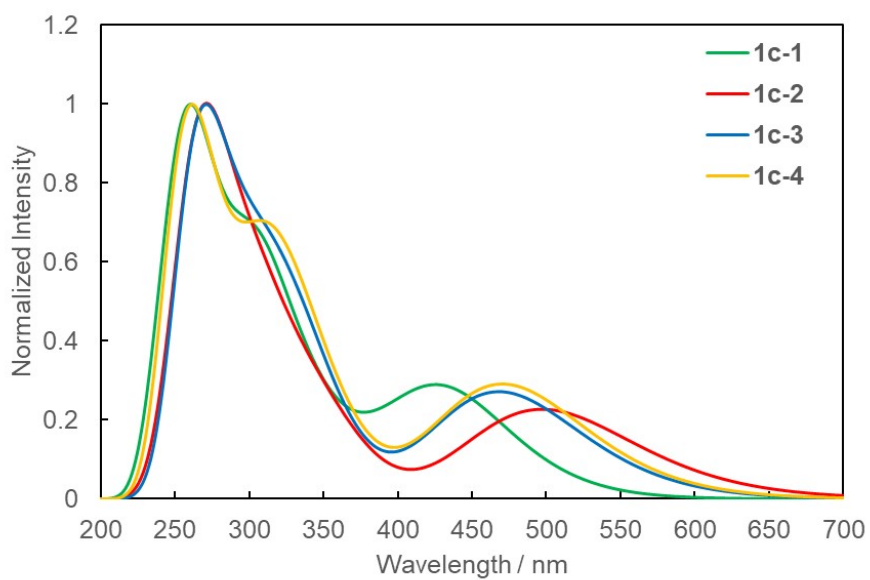
**Figure S11.** The molecular orbitals of **1c** calculated by DFT in  $\omega$ B97XD/6-31+G(d) level.



**Figure S12.** Nucleus-independent chemical shift (NICS(0)) of open and closed form of variable diarylethene derivatives, (a) **1**, (b) 1,2-bis(2-methoxy-5-phenyl-3-thienyl)perfluorocyclopentene and (c) 1,2-bis(2-methoxy-1-benzothien-3-yl)perfluorocyclopentene. Calculations were performed GIAO method in  $\text{r}\omega\text{B97XD}/6\text{-}31\text{+G(d)}$  level.

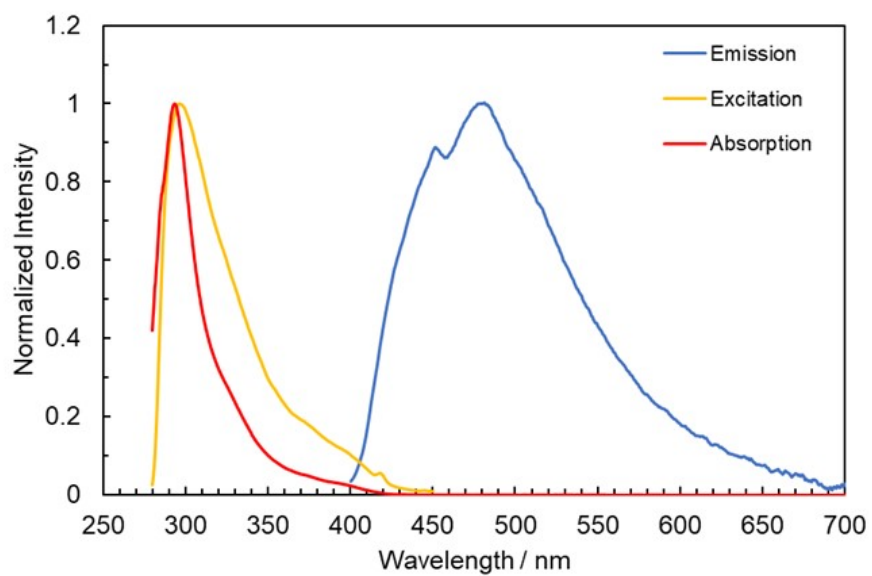


**Figure S13.** Predicted absorption spectra of the atropisomers **1o** by DFT in  $\omega$ B97XD/6-31+G(d) level.

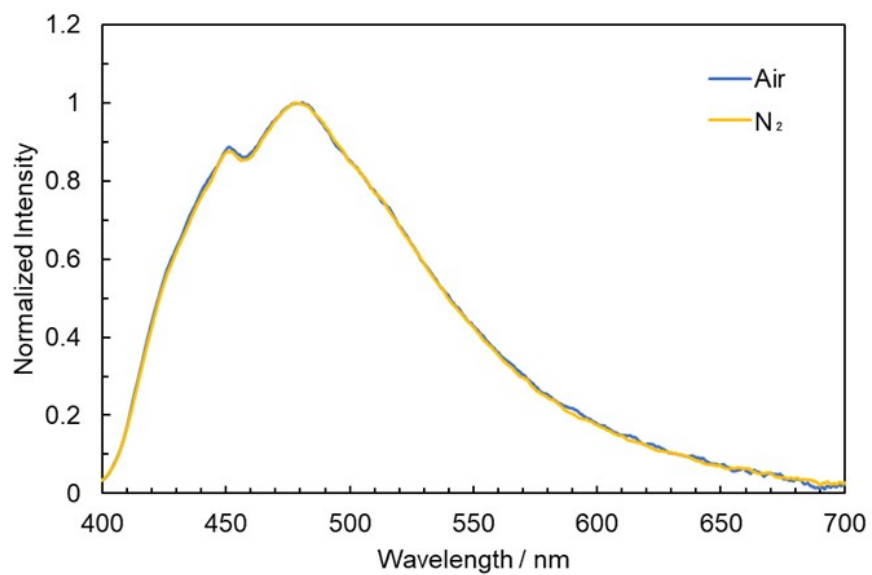


**Figure S14.** Predicted absorption spectra of the atropisomers **1c** by DFT in  $\omega$ B97XD/6-31+G(d) level.

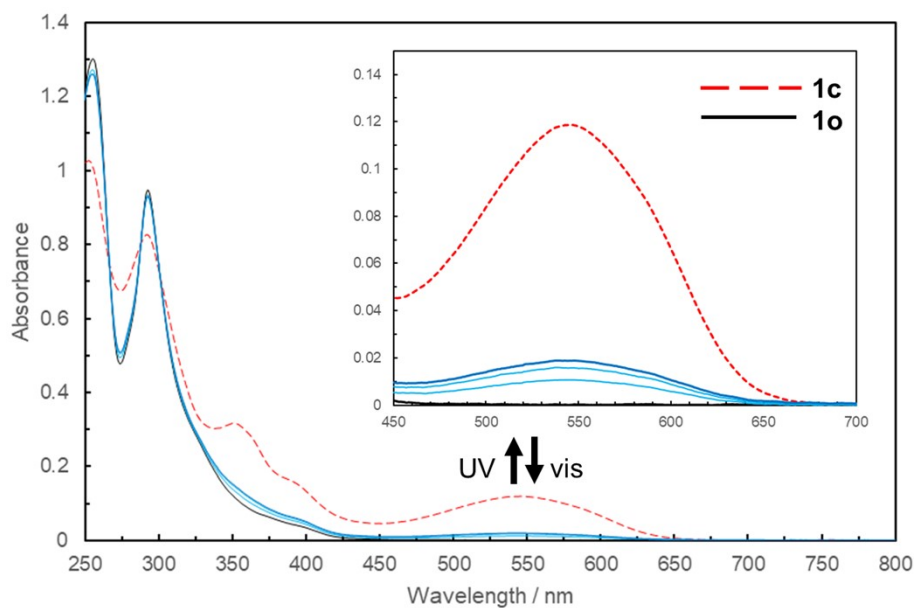
(a)



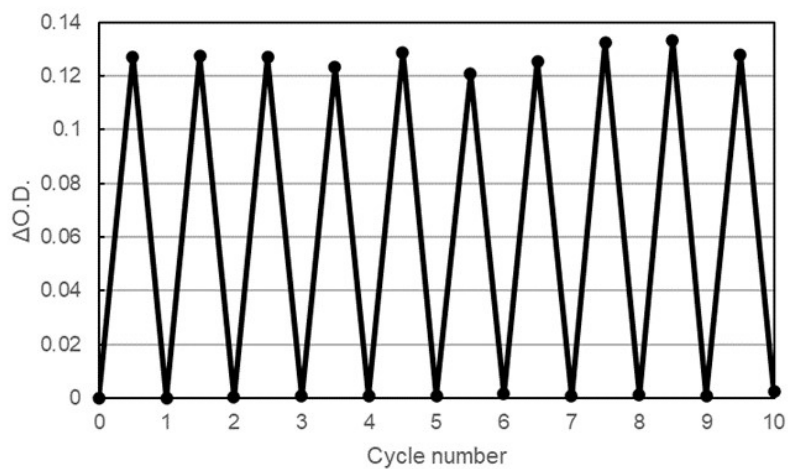
(b)



**Figure S15.** (a) Emission, excitation and absorption spectra of **1o** in toluene (15  $\mu\text{M}$ ) and (b) emission spectra under air and  $\text{N}_2$  condition ( $\lambda_{\text{ex}} = 350 \text{ nm}$ ,  $\lambda_{\text{em}} = 480 \text{ nm}$ ).

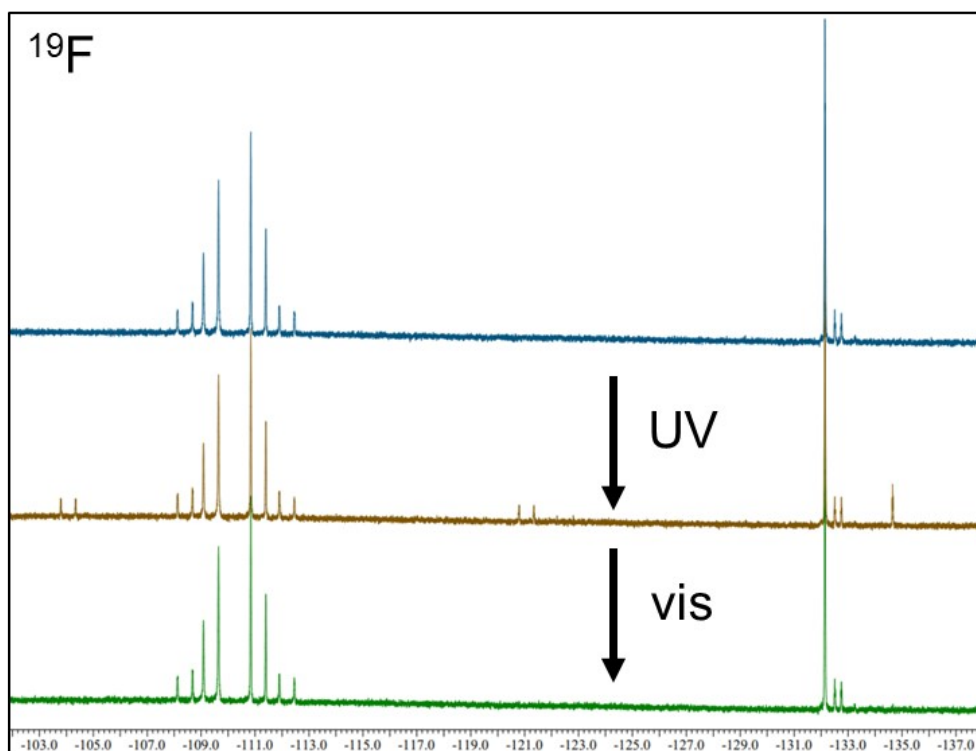
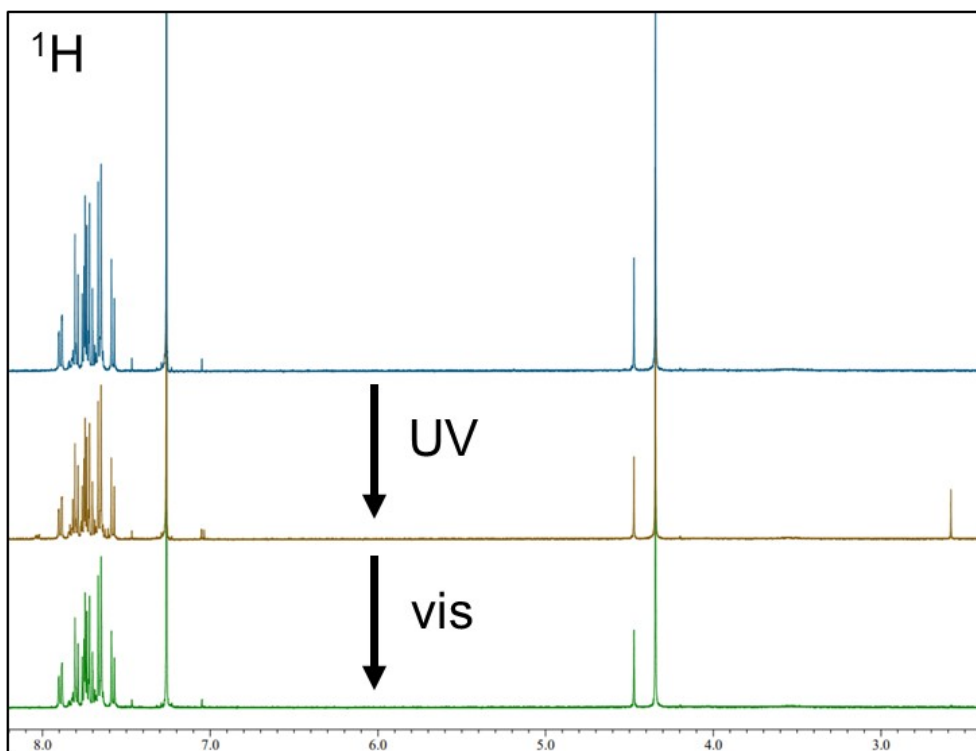


**Figure S16.** UV-vis absorption spectral change under photoirradiation of **1** in  $\text{CHCl}_3$  ( $\lambda_{\text{ex}} = 365$  nm).

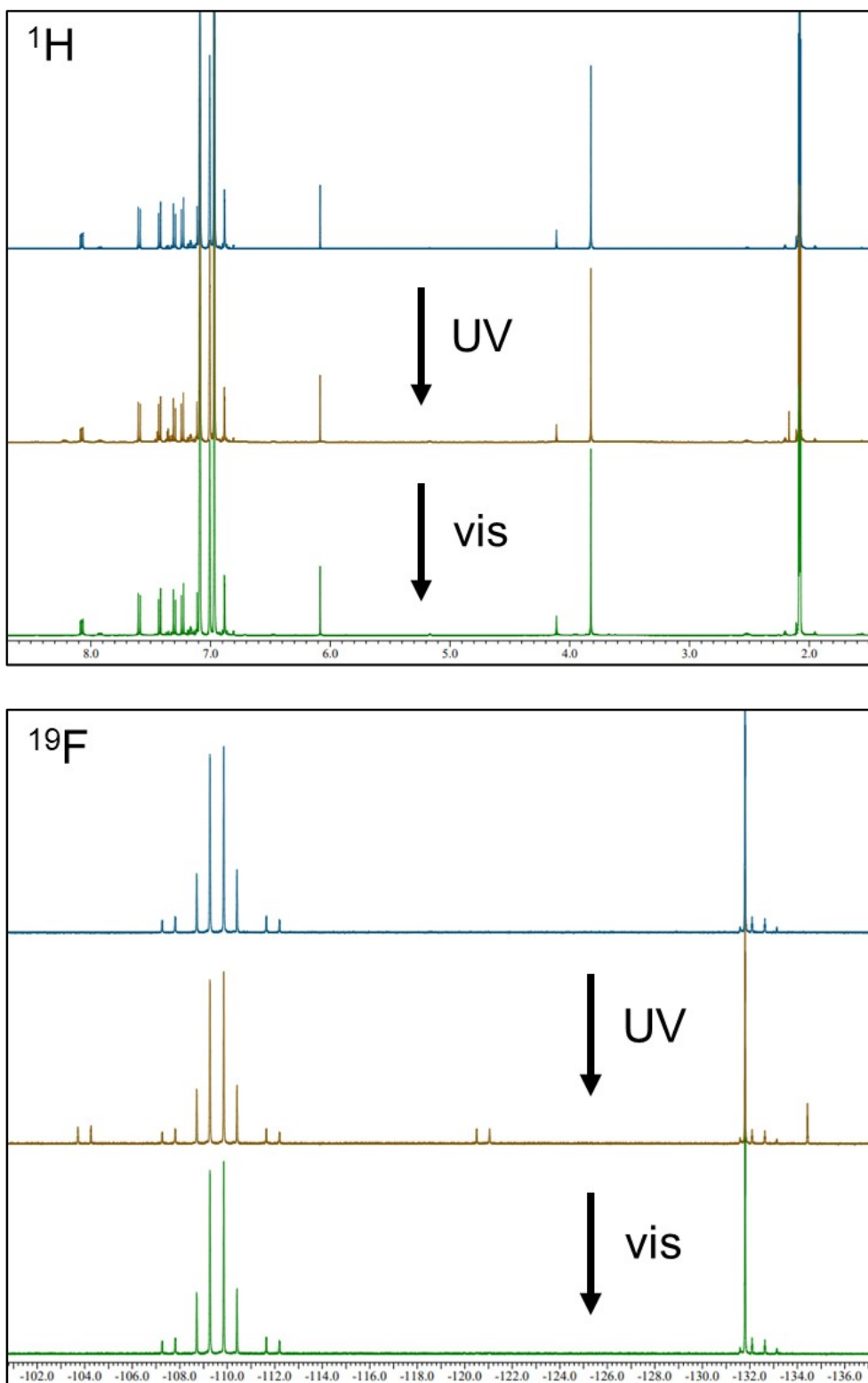


**Figure S17.** The repeated colouration ( $\lambda_{\text{ex}} = 300$  nm) and bleaching ( $\lambda_{\text{ex}} = 540$  nm) cycles of **1** in toluene.  $\Delta\text{O.D.}$  was observed at 546 nm.



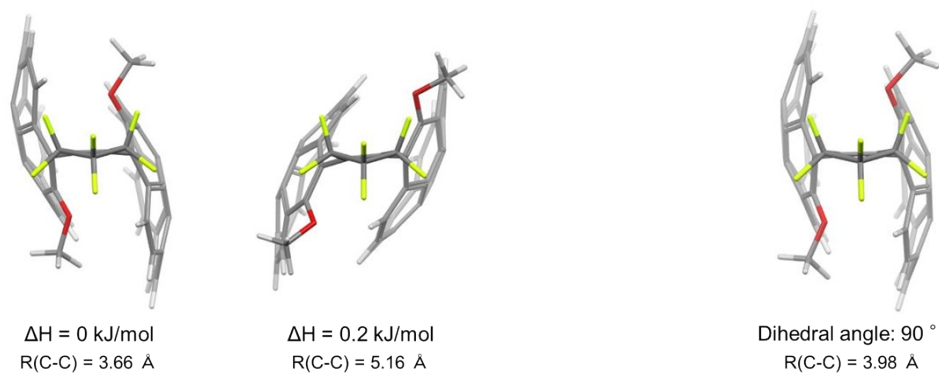


**Figure S18.** NMR spectral changes of **1** under photoirradiation by UV at 365 nm in  $\text{CDCl}_3$ .



**Figure S19.** NMR spectral changes of **1** under photoirradiation by UV at 365 nm in toluene-*d*<sub>8</sub>.

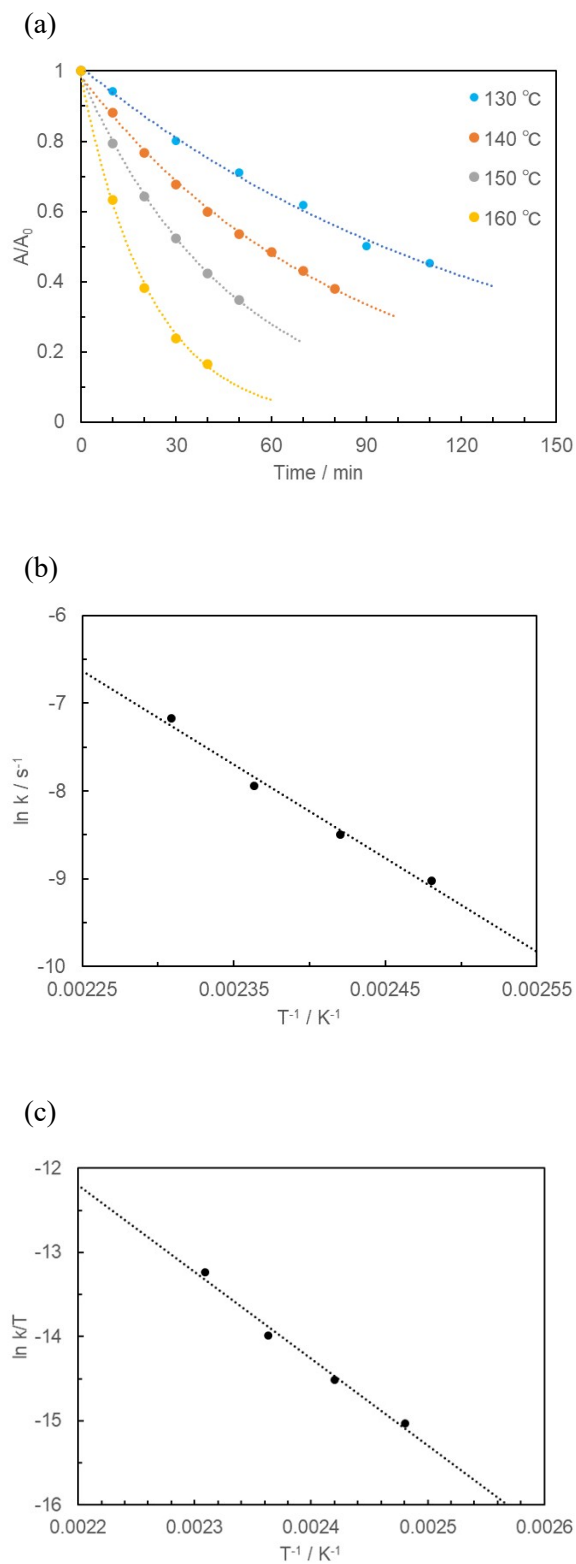




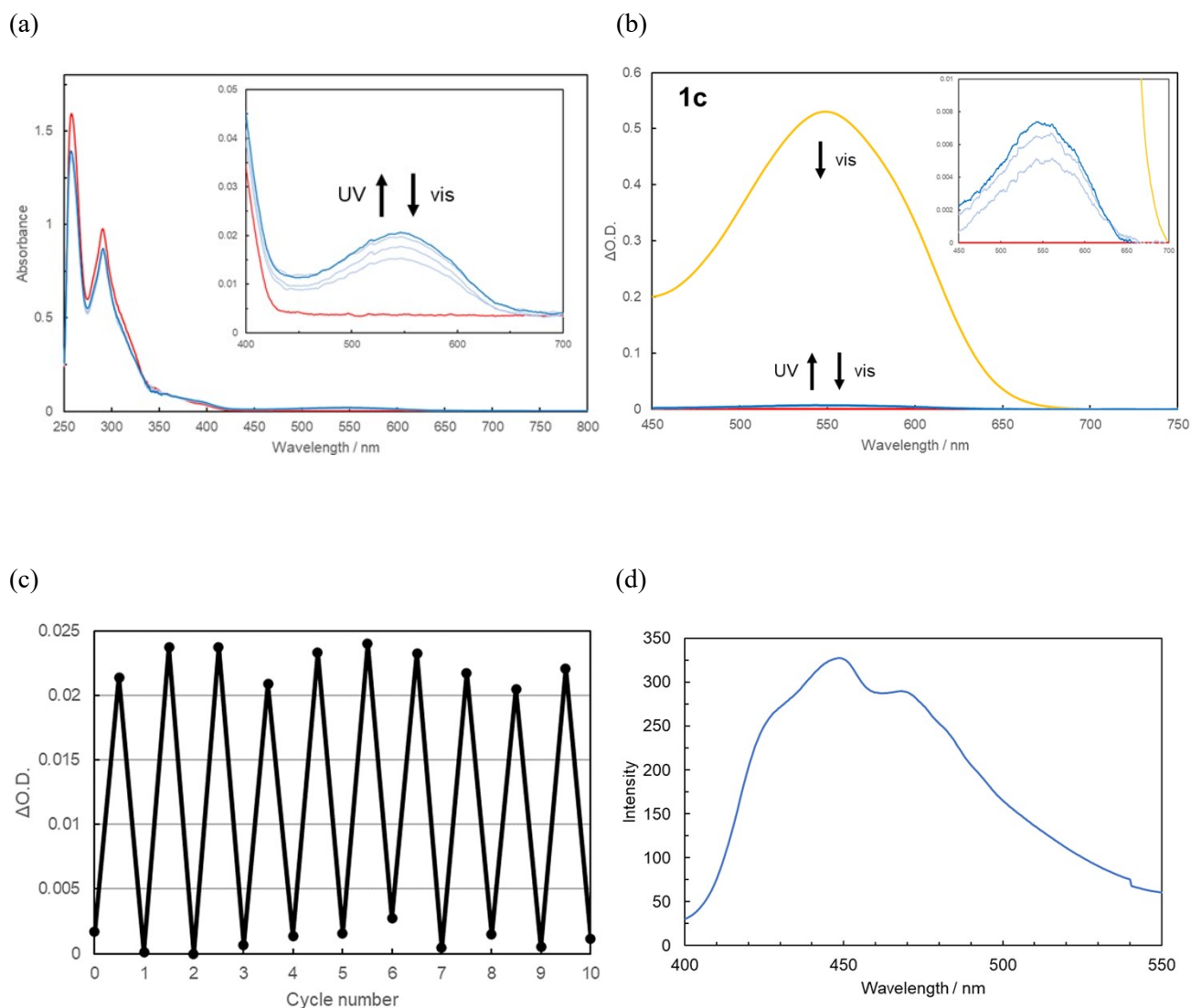
**Figure S20.** Two energy minima of **10-1** by DFT calculations in  $\omega$ B97XD/6-31+G(d) level and the structure with both dihedral angles fixed to  $90^\circ$  like the twisted conformation.

**Table S2.** Oxygen effect on the quantum yields in  $\text{CHCl}_3$ .

	$\lambda_{\text{ex}} / \text{nm}$	Air	$\text{O}_2$	$\text{N}_2$
$\Phi_{\text{o-c}}$	365	0.30	0.26	0.33
$\Phi_{\text{c-o}}$	540	0.31	0.28	0.28

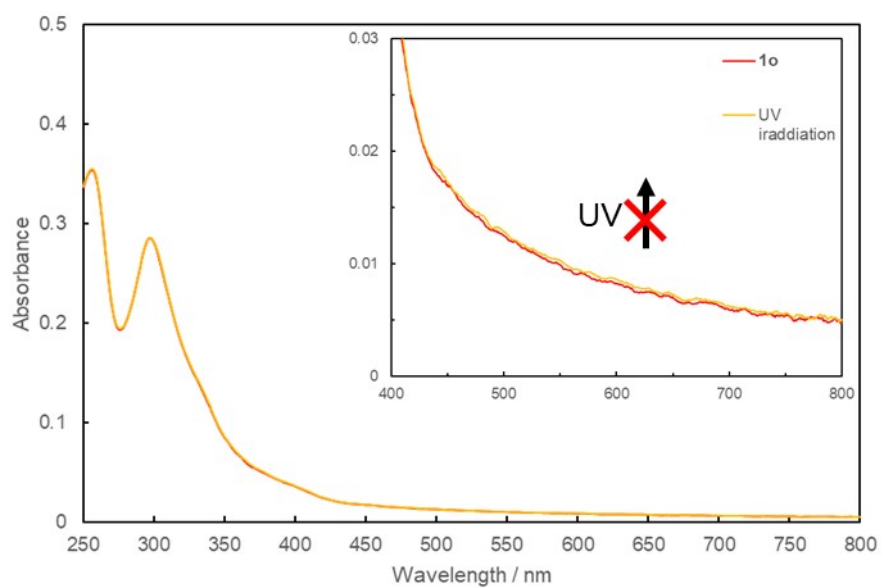


**Figure S21.** (a) Decay time of the thermal cycloreversion of closed form (**1c**) in decalin (absorbance was observed at 546 nm.), (b) Arrhenius plot of **1c** and (c) Eyring plot of **1c**.

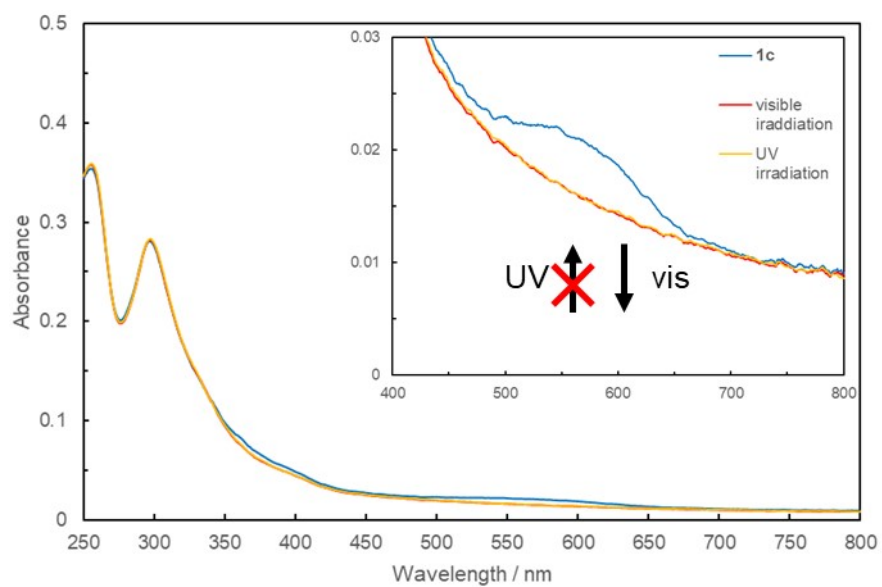


**Figure S22.** UV-vis absorption spectral change of (a) a solution of **1o** (27  $\mu\text{M}$ ) with PMMA (20 wt%) in  $\text{CHCl}_3$  and (b) a PMMA film of **1c**, prepared by drop-casting chloroform solution containing **1c** (5 mM) and PMMA (5 wt%), (**1c**/PMMA = ca. 4 wt%). (c) The repeated colouration and bleaching cycles of **1** in a PMMA film, prepared by drop-casting chloroform solution containing **1o** (12 mM), PMMA (10 wt%), (**1o**/PMMA = ca. 5 wt%). Irradiation was carried out with UV at 365 nm. The absorption spectrum of **1o** was subtracted as baseline. (d) Emission spectrum of **1o** in PMMA film ( $\lambda_{\text{ex}} = 300 \text{ nm}$ ).

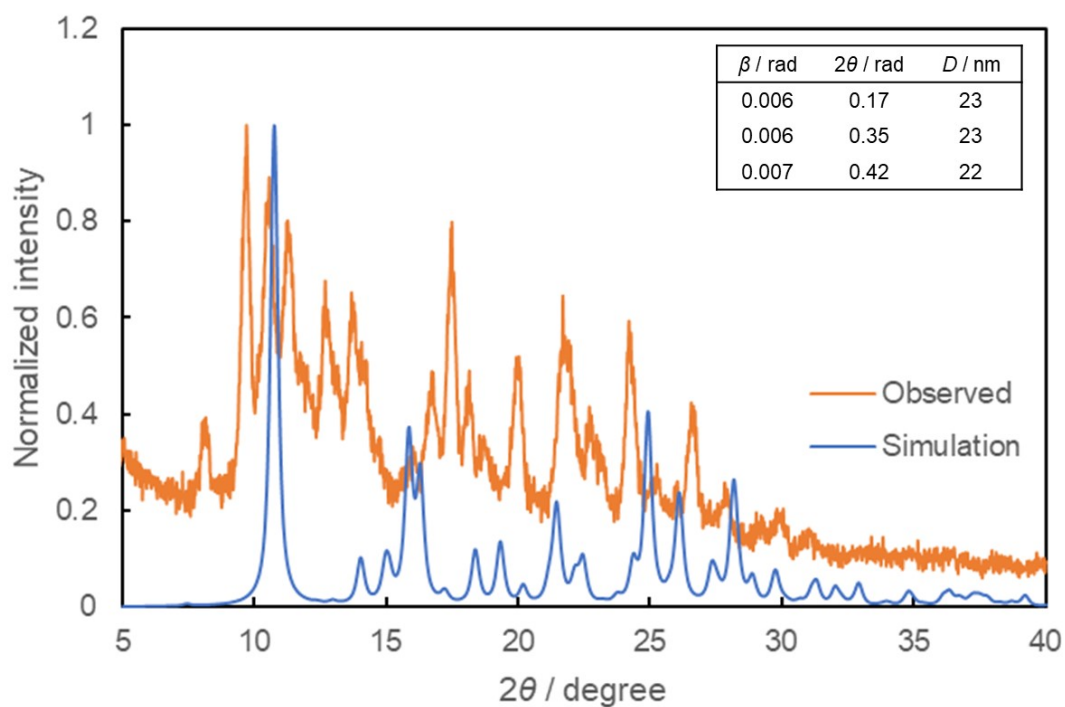
(a)



(b)



**Figure S23.** UV-vis spectral change of a neat film of (a) **1o** and (b) **1c**. Irradiation was carried out with UV at 365 nm.



**Figure S24.** PXRD pattern of a neat film of **1** and the simulation of PXRD pattern from single-crystal structure.

The crystallite size  $D$  was calculated by Scherrer's equation:  $D = \frac{K\lambda}{\beta \cos\theta}$  ( $K$ : Scherrer constant,  $\lambda$ : X-ray wavelength,  $\beta$ : the full width at half maximum of the diffraction peak,  $\theta$ : Bragg angle).<sup>[S3]</sup>

## REFERENCES

[S1] B. D. Steinberg, E. A. Jackson, A. S. Filatov, A. Wakamiya, M. A. Petrukhina and L. T. Scott, *J. Am.*

*Chem. Soc.*, 2009, **131**, 10537.

[S2] A. Sygula, R. Sygula and L. Kobryn, *Org. Lett.*, 2008, **10**, 3927.

[S3] A. Monshi, M. R. Foroughi and M. R. Monshi, *World J. Nano Sci. Eng.*, 2012, **2**, 154.