

## Supporting Information

### **Photochromism of a spiro-functionalized diarylethene derivative: multi-colour fluorescence modulation with a photon-quantitative photocyclization reactivity**

Tetsuya Nakagawa,\* Yosuke Miyasaka and Yasushi Yokoyama

Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University,  
79-5, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

E-mail address: [tnakagawa@ynu.ac.jp](mailto:tnakagawa@ynu.ac.jp)

#### **Contents**

1. Synthesis details
  - 1-1. Synthesis of **Spiro-DAE<sub>O</sub>**
  - 1-2. Synthesis of Spiro-DAE<sub>2O</sub>
2. Scheme for Spiro-DAE<sub>2O</sub>
3. Experimental Details
4. Experimental data
  - 4-1 <sup>1</sup>H NMR spectrum of **Spiro-DAE<sub>O</sub>**
  - 4-2 <sup>1</sup>H NMR spectrum of **Spiro-DAE<sub>C</sub>**
  - 4-3 <sup>1</sup>H NMR spectrum of **Spiro-DAE<sub>2O</sub>**
  - 4-4 <sup>13</sup>C NMR spectrum of **Spiro-DAE<sub>O</sub>**
  - 4-5 <sup>13</sup>C NMR spectrum of **Spiro-DAE<sub>C</sub>**

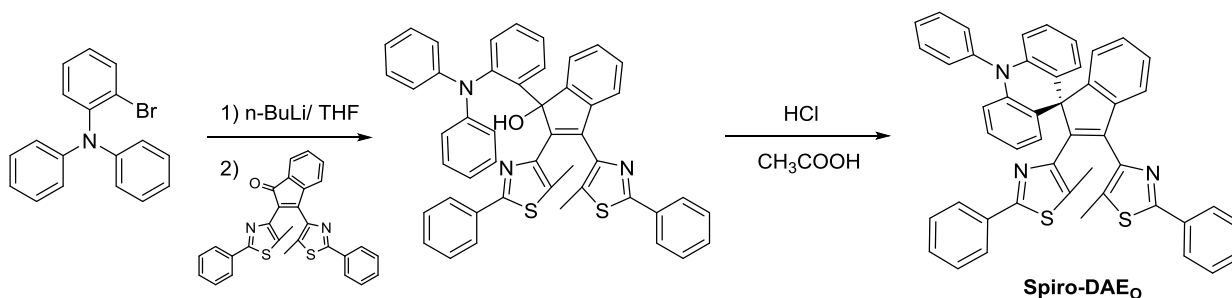
- 4-6  $^{13}\text{C}$  NMR spectrum of **Spiro-DAE2<sub>0</sub>**
- 4-7 ESI-Mass spectrum of **Spiro-DAE<sub>0</sub>**
- 4-8 ESI-Mass spectrum of **Spiro-DAE2<sub>0</sub>**
- 4-9 Photographs of single crystal of **Spiro-DAE**
- 4-10 Crystallographic parameters and refinement details of **Spiro-DAE**
- 4-11 Space-filling model of **Spiro-DAE**
- 4-12 Absorption spectral change of **Spiro-DAE2**
- 4-13 Fluorescence spectral change of **Spiro-DAE**
- 4-14 Fast fluorescence spectrum measurement results of **Spiro-DAE**
- 4-15 Solvent polarity dependence of the fluorescence spectra of **Spiro-DAE**
- 4-16 Molecular orbitals of **Spiro-DAE**

## 5. References

## 6. Complete reference 18.

### 1. Synthesis details

#### 1-1. Synthesis of **Spiro-DAE<sub>0</sub>**



*n*-BuLi 0.2 mL (0.33 mmol, 1.60 mol dm<sup>-3</sup> hexane solution) was added to a stirred solution of 2-bromotriphenylamine 104 mg (0.32 mmol) in anhydrous THF (10 mL) at -78 °C under a N<sub>2</sub> atmosphere. The mixture was stirred for 1 h at -78 °C and then 2,3-bis(5-methyl-2-phenyl-4-thiazolyl)indenone<sup>1)</sup> 100 mg (0.21 mmol) in anhydrous THF (10 mL) was added to the reaction solution. The resulting solution was stirred for overnight at room temperature. The reaction was quenched by adding water, and the resultant was extracted with chloroform four times. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the drying agent filtered off, the solvent evaporated,

and the remaining material dried at room temperature. The resulting product was used in the next reaction without any further purification. The resulting mixture, acetic acid (5 mL), and HCl (0.2 mL) were stirred for 1.5 h under reflux. The reaction mixture was neutralized with 10% aq. sodium carbonate and then the resultant was extracted with chloroform four times. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the drying agent filtered off, and the solvent evaporated. The residue was purified by a silica gel column chromatography using 5% ethyl acetate / hexane as eluent and then recrystallized with chloroform and hexane to give 71 mg of 4,4'-(10-phenyl-10H-spiro[acridine-9,1'-indene]-2',3'-diyl)bis(5-methyl-2-phenylthiazole): **Spiro-DAE<sub>0</sub>** as a white solid in 48% yield.

<sup>1</sup>H NMR: (500MHz CD<sub>2</sub>Cl<sub>2</sub> TMS) δ/ppm 1.75 (3 H, s), 1.99 (3 H, s), 6.15 (2 H, d, J/Hz = 8.51), 6.63 (2 H, td, J/Hz = 6.60, 0.95), 6.75 (2 H, dd, J/Hz = 7.88, 1.58), 6.90 (2 H, ddd, J/Hz = 8.43, 7.01, 1.58), 7.05 (2 H, m), 7.28 (2 H, m), 7.32 (2 H, m), 7.40 (5 H, m), 7.47 (3 H, m), 7.53 (2 H, m), 7.73 (1 H, d, J/Hz = 7.25), 8.02 (2 H, m).

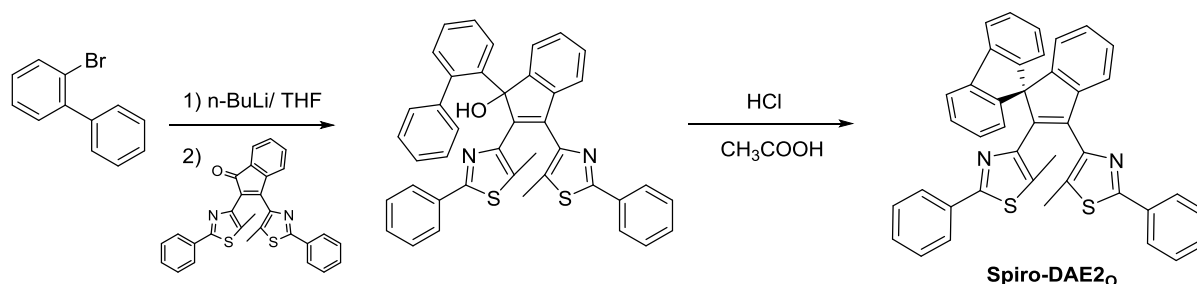
<sup>13</sup>C NMR: (500MHz CD<sub>2</sub>Cl<sub>2</sub> TMS) δ/ppm 12.03, 12.63, 61.69, 114.99, 120.25, 122.23, 122.76, 125.30, 126.63, 126.73, 127.44, 127.53, 127.62, 128.05, 128.48, 128.94, 129.36, 129.79, 130.18, 131.78, 132.97, 132.99, 133.15, 134.20, 134.41, 141.58, 142.38, 143.86, 147.39, 148.41, 152.61, 159.71, 163.47, 165.16.

ESI-Mass [M]<sup>+</sup>: calcd. for C<sub>47</sub>H<sub>34</sub>S<sub>2</sub>N<sub>3</sub>: 704.2189; found: 704.2211.

<sup>1</sup>H NMR (**Spiro-DAE<sub>C</sub>**): (500 MHz, DICHLOROMETHANE-d<sub>2</sub>) δ/ ppm 1.94 (3 H, s), 1.97 (3 H, s), 6.24 (1 H, dd, J/Hz = 8.51, 0.95), 6.30 (1 H, dd, J/Hz = 8.51, 0.95), 6.63 (2 H, m), 6.74 (2 H, td, J/Hz = 7.72, 1.58), 6.84 (1 H, ddd, J/Hz = 8.43, 7.01, 1.58), 6.89 (1 H, ddd, J/Hz = 8.51, 7.09, 1.73), 7.22 (1 H, d, J/Hz = 7.57), 7.31 (1 H, td, J/Hz = 7.41, 1.26), 7.40 (3 H, m), 7.48 (3 H, m), 7.56 (4 H, m), 7.68 (4 H, m), 8.09 (2 H, dd, J/Hz = 7.88, 1.58), 8.39 (1 H, d, J/Hz = 7.57).

<sup>13</sup>C NMR (**Spiro-DAE<sub>C</sub>**): (500 MHz, DICHLOROMETHANE-d<sub>2</sub>) δ/ ppm 26.69, 27.20, 54.98, 69.32, 70.16, 114.41, 114.97, 120.45, 124.69, 125.94, 126.45, 126.60, 127.21, 128.12, 128.72, 128.79, 128.84, 129.01, 129.07, 129.18, 129.86, 130.02, 131.44, 131.89, 132.13, 132.27, 134.18, 134.28, 136.51, 140.10, 141.12, 141.95, 143.39, 152.06, 153.84, 157.14, 170.85, 171.59.

## 1-2. Synthesis of **Spiro-DAE<sub>2o</sub>**



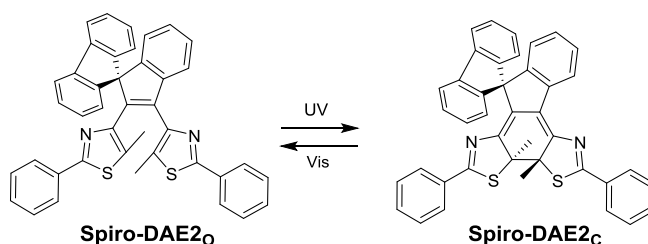
*n*-BuLi 0.09 mL (0.14 mmol, 1.60 mol dm<sup>-3</sup> hexane solution) was added to a stirred solution of 2-bromobiphenyl 44 mg (0.19 mmol) in anhydrous THF (5 mL) at -78 °C under a N<sub>2</sub> atmosphere. The mixture was stirred for 1 h at -78 °C and then 2,3-bis(5-methyl-2-phenyl-4-thiazolyl)indenone<sup>1</sup> 56.5 mg (0.12 mmol) in anhydrous THF (5 mL) was added to the reaction solution. The resulting solution was stirred for overnight at room temperature. The reaction was

quenched by adding water, and the resultant mixture was extracted with chloroform four times. The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , the drying agent filtered off, and the solvent evaporated. The residue was dried in vacuo at room temperature. The resulting product was used in the next reaction without any further purification. The resulting mixture, acetic acid (4 mL), and HCl (0.2 mL) were mixed and stirred for 1 h under reflux. The reaction mixture was neutralized with 10% aq. sodium carbonate and then the resultant mixture was extracted with chloroform four times. The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , the drying agent filtered off, and the solvent evaporated. The residue was purified by silica gel column chromatography using 5% ethyl acetate / hexane as eluent and then recrystallized with chloroform and hexane to give 5 mg of 4,4'-(spiro[fluorene-9,1'-indene]-2',3'-diyl)bis(5-methyl-2-phenylthiazole): **Spiro-DAE2<sub>O</sub>** as a white solid in 7% yield.

$^1\text{H}$  NMR: (500MHz  $\text{CDCl}_3$  TMS)  $\delta$ /ppm 1.88 (3 H, s), 2.00 (3 H, s), 6.75 (1 H, d,  $J/\text{Hz} = 6.94$ ), 7.10 (3 H, m), 7.16 (2 H, t,  $J/\text{Hz} = 6.60$ ), 7.22 (5 H, m), 7.34 (3 H, m), 7.48 (3 H, m), 7.76 (3 H, t,  $J/\text{Hz} = 7.90$ ), 8.05 (2 H, d,  $J/\text{Hz} = 6.30$ )  
 $^{13}\text{C}$  NMR: (500MHz  $\text{CDCl}_3$  TMS)  $\delta$ /ppm 12.05, 12.65, 70.57, 119.79, 122.23, 122.63, 123.58, 125.95, 126.45, 126.65, 127.30, 127.35, 128.43, 128.96, 129.08, 129.78, 131.49, 132.59, 133.83, 133.96, 136.97, 142.74, 143.10, 144.76, 146.61, 147.05, 147.35, 148.49, 162.66, 164.74

ESI-Mass  $[\text{M}]^+$ : calcd. for  $\text{C}_{41}\text{H}_{29}\text{S}_2\text{N}_2$ : 613.1767; found: 613.1779.

## 2. Scheme for Spiro-DAE2<sub>O</sub>



**Scheme S1** Photochromism of **Spiro-DAE2**.

## 3. Experimental details

### General

$^1\text{H}$  NMR Spectrum was recorded in dideuteromethylene chloride ( $\text{CD}_2\text{Cl}_2$ ) on a 500 MHz NMR spectrometers (DRX500, Bruker).  $J$  values are expressed in Hz and quoted chemical shifts are in ppm. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High-resolution mass spectrum was measured by an electrospray ionization mass spectroscopy (NanoFrontierLD, Hitachi High-Technology). X-ray crystallographic analysis at 223 K was carried out using a single-crystal X-ray diffractometer (XtaLAB PRO, Rigaku) with  $\text{Cu K}\alpha$  radiation (1.54 Å). The chemical structure was solved by a direct method program (SIR2011) and refined by the full-matrix least squares method and anisotropic temperature factors were applied to all non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and refined applying a riding model.

## Optical Measurements

Absorption spectra of **Spiro-DAE** in ethyl acetate ( $2.27 \times 10^{-5}$  mol dm<sup>-3</sup>) and **Spiro-DAE2** in ethyl acetate ( $2.12 \times 10^{-5}$  mol dm<sup>-3</sup>) were measured on a UV-visible spectrophotometer (V-670, JASCO). Fatigue resistance of **Spiro-DAE** in ethyl acetate ( $2.27 \times 10^{-5}$  mol dm<sup>-3</sup>) were monitored on a UV-visible spectrophotometer (PRA-201, Asahi Spectra) equipped with a 300 W xenon lamp (MAX-303, Asahi Spectra) as an excitation source. Fluorescence spectra of **Spiro-DAE** in ethyl acetate ( $2.27 \times 10^{-5}$  mol dm<sup>-3</sup>) were measured on a spectrofluorometer (FP-8300, JASCO). Fast fluorescence spectra measurements of **Spiro-DAE** in ethyl acetate ( $2.39 \times 10^{-5}$  mol dm<sup>-3</sup>) were carried out using a photonic multichannel analyzer (PMA12 C10027-01, Hamamatsu). Fluorescence quantum yields of **Spiro-DAE<sub>O</sub>** and **Spiro-DAE<sub>C</sub>** in ethyl acetate (**Spiro-DAE<sub>O</sub>**:  $2.39 \times 10^{-5}$  mol dm<sup>-3</sup>, **Spiro-DAE<sub>C</sub>**:  $2.12 \times 10^{-5}$  mol dm<sup>-3</sup>) were determined using absolute photoluminescence quantum yield spectrometer equipped with a photonic multichannel analyzer (Quantaaurus-QY Plus C13534-01, Hamamatsu). **Spiro-DAE<sub>C</sub>** was separated by using a high performance liquid chromatography equipped with a UV/Vis detector (SPD-20A, Shimadzu) and a silica gel column (Wakosil 5SIL, Wako). CIE coordinate change was estimated from the fluorescence spectra (Fig. S12(a) and Fig. S12(b)).

Photochemical reaction were carried out in a quartz cell with 10 nm optical path length. Photo irradiations with 313 nm and 506 nm were carried out using a 250 W super-high presser mercury lamp (REX-250, Asahi Spectra) and 100 W xenon lamp (LAX-C100, Asahi Spectra), respectively. UV light (313 nm) was obtained by passing the light through a glass filter (HQBP313-UV, Asahi Spectra). Visible light (506 nm) was obtained by passing the light through filters (a 5 cm water filter, a pyrex glass filter, a Y-47 glass filter and a KL-50 glass filter). High performance liquid chromatography equipped with a UV/Vis detector (SPD-10A, Shimadzu) and a silica gel column (Wakosil 5SIL, Wako) was used to determine the concentration of isomers during photoirradiation. Photocyclization and photocycloreversion quantum yields were determined with the procedures described elsewhere.<sup>2)</sup>

## 4. Experimental data

### 4-1 <sup>1</sup>H NMR spectrum of **Spiro-DAE<sub>O</sub>**

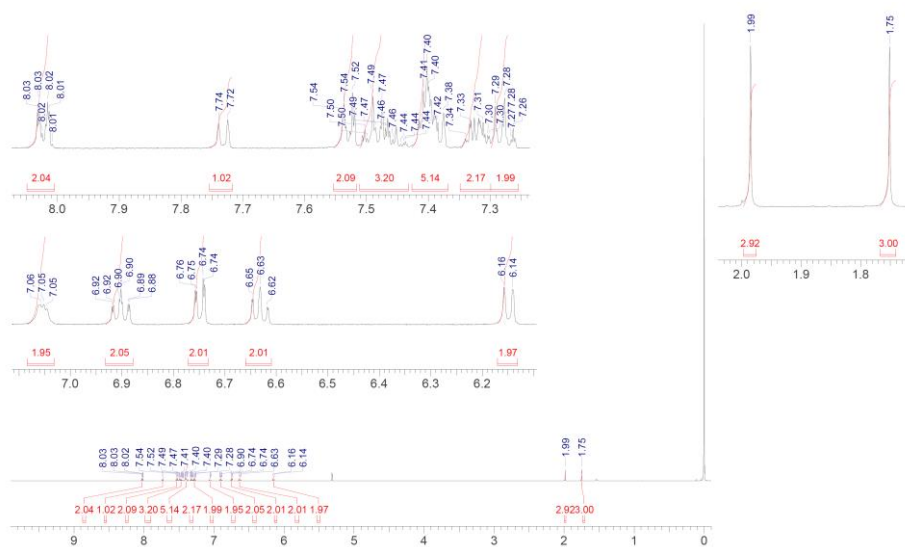


Fig. S1 <sup>1</sup>H NMR spectrum of **Spiro-DAE<sub>O</sub>**

#### 4-2 $^1\text{H}$ NMR spectrum of **Spiro-DAEc**

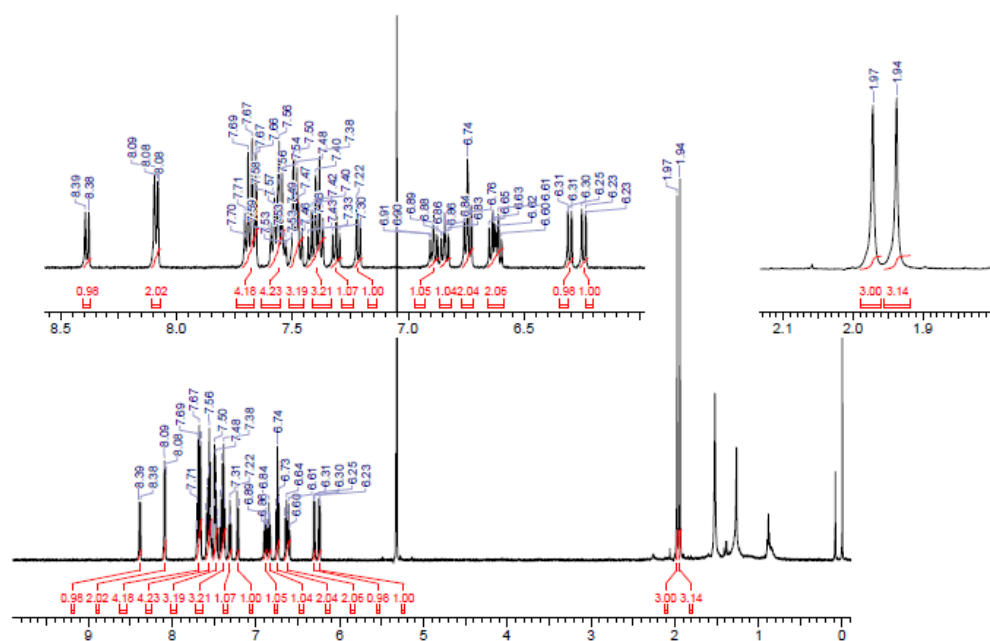


Fig. S2  $^1\text{H}$  NMR spectrum of **Spiro-DAEc**

#### 4-3 $^1\text{H}$ NMR spectrum of **Spiro-DAE2o**

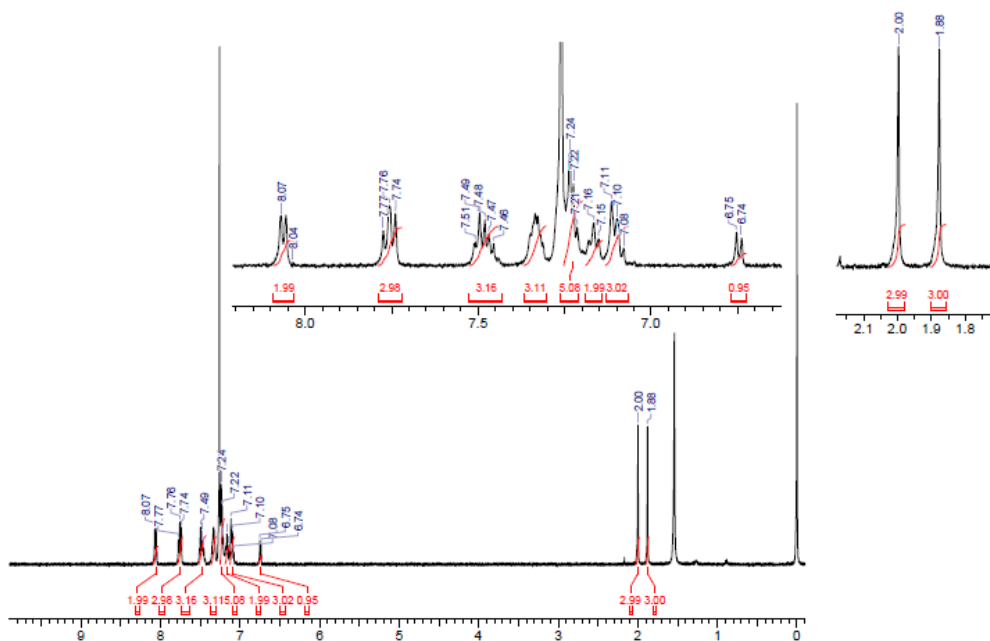


Fig. S3  $^1\text{H}$  NMR spectrum of **Spiro-DAE2o**

4-4  $^{13}\text{C}$  NMR spectrum of **Spiro-DAE<sub>0</sub>**

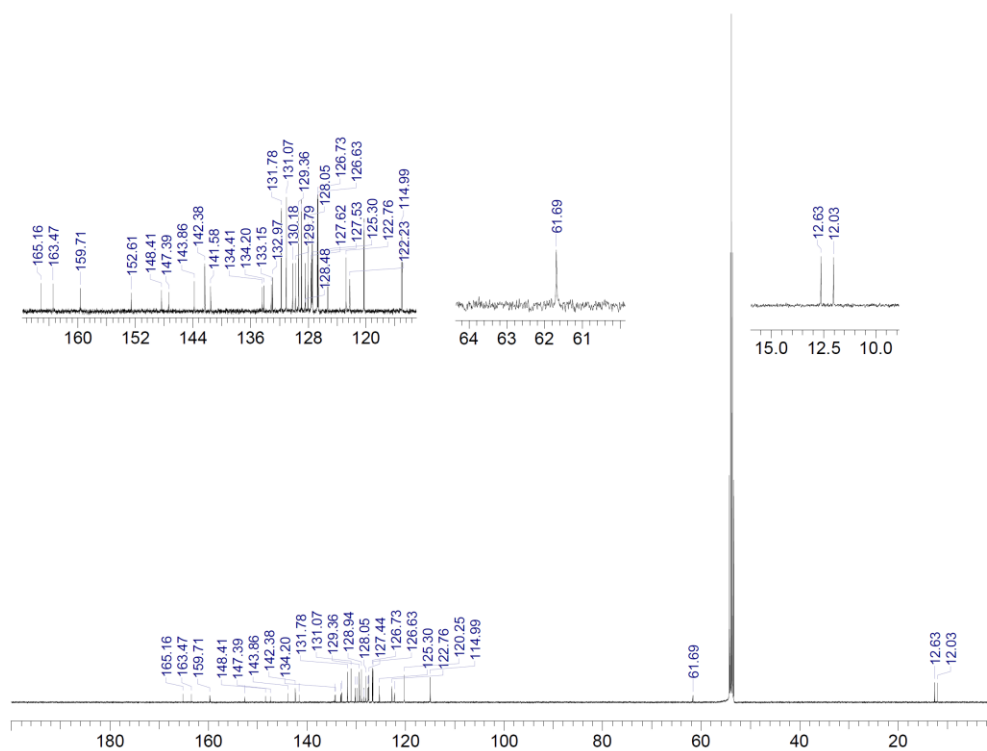


Fig. S4  $^{13}\text{C}$  NMR spectrum of **Spiro-DAE<sub>0</sub>**

4-5  $^{13}\text{C}$  NMR spectrum of **Spiro-DAE<sub>c</sub>**

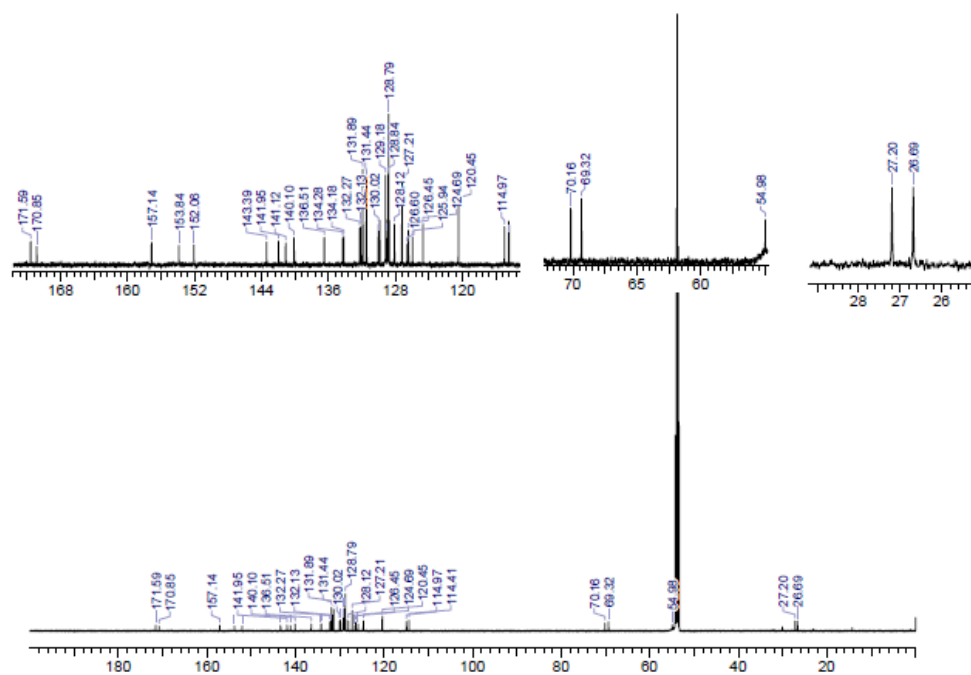


Fig. S5  $^{13}\text{C}$  NMR spectrum of **Spiro-DAE<sub>c</sub>**

4-6  $^{13}\text{C}$  NMR spectrum of **Spiro-DAE2<sub>o</sub>**

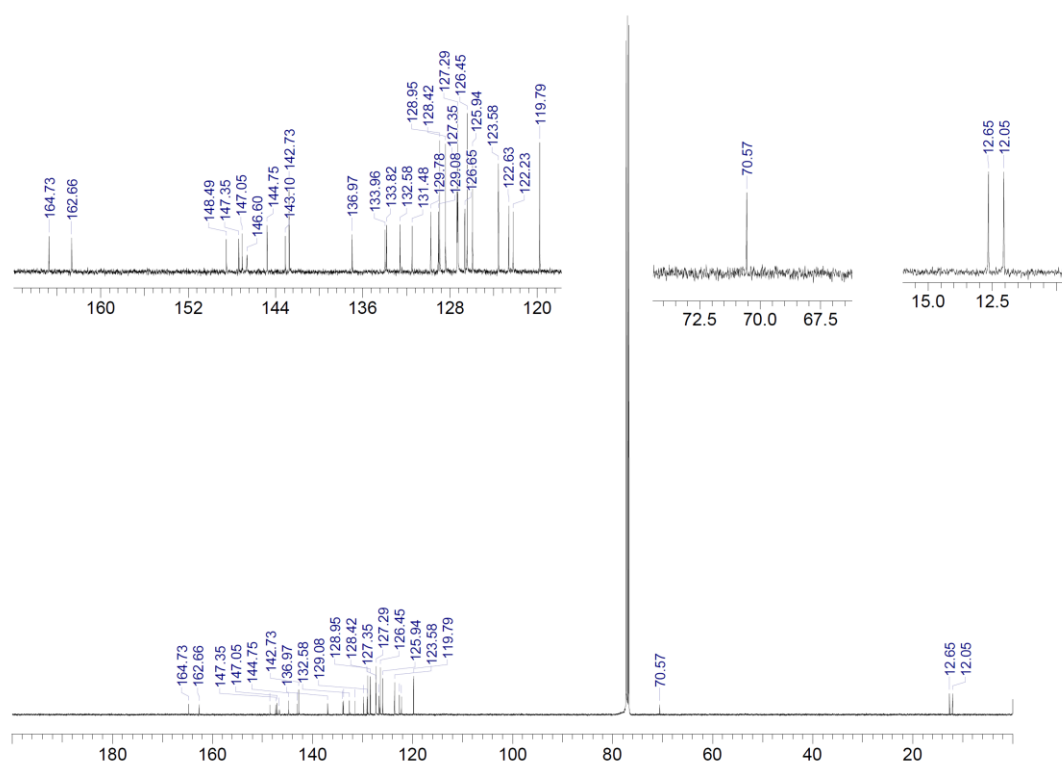


Fig. S6  $^{13}\text{C}$  NMR spectrum of **Spiro-DAE2<sub>o</sub>**

4-7 ESI-Mass spectrum of **Spiro-DAE<sub>o</sub>**

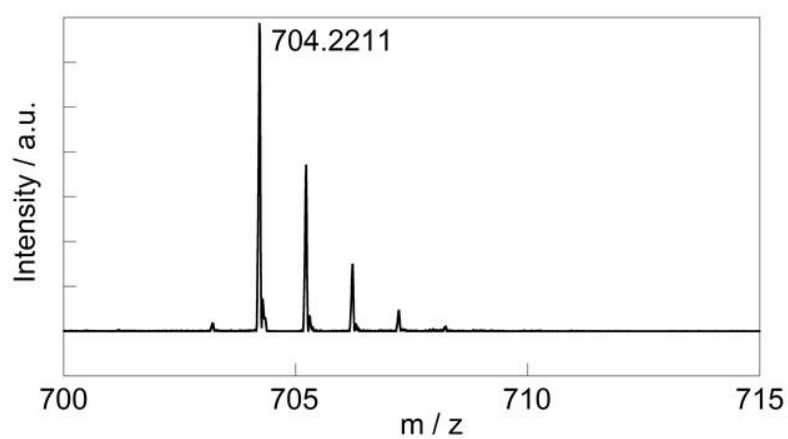


Fig. S7 ESI-Mass spectrum of **Spiro-DAE<sub>o</sub>**



#### 4-8 ESI-Mass spectrum of **Spiro-DAE2o**

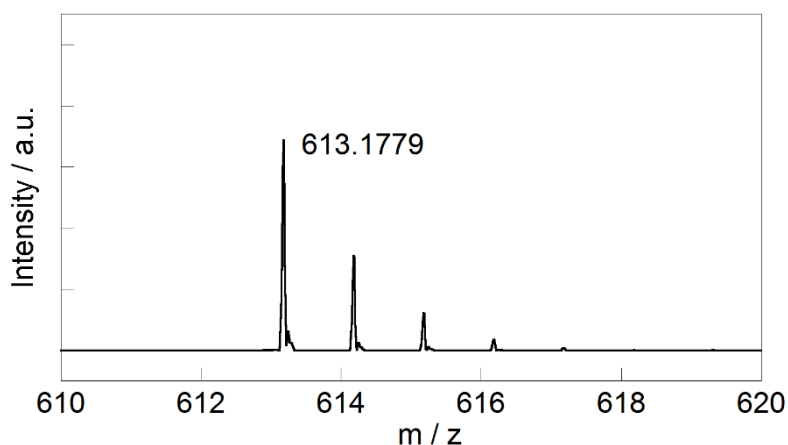


Fig. S8 ESI-Mass spectrum of **Spiro-DAE2o**

#### 4-9 Photographs of single crystal of **Spiro-DAE**

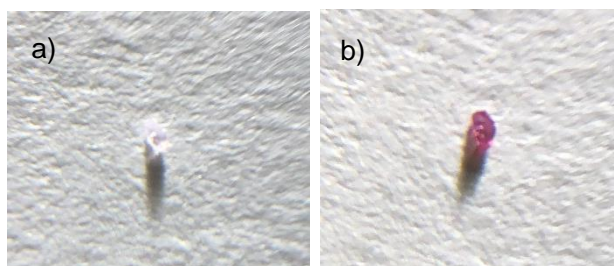


Fig. S9 Photographs of a single crystal of **Spiro-DAE** a) before and b) after irradiation with 365 nm light.

#### 4-10 Crystallographic parameters and refinement details of **Spiro-DAE**

Table S1. Crystallographic parameters and refinement details for **Spiro-DAE**.

formula	C47 H33 N3 S2	T (K)	223
formula weight	703.92	V (Å <sup>3</sup> )	1808.03(4)
Crystal system	Monoclinic	r (gcm <sup>-3</sup> )	1.293
space group	P 1 21 1	Z	2
a (Å)	9.99169 (11)	R <sub>1</sub>	0.0373
b (Å)	14.13348 (14)	wR <sub>2</sub>	0.1005
c (Å)	13.64326 (15)	CCDC No.	CCDC 1810980
α (deg)	90		
β (deg)	110.2112 (12)		
γ (deg)	90		

#### 4-11 Space-filling model of **Spiro-DAE**

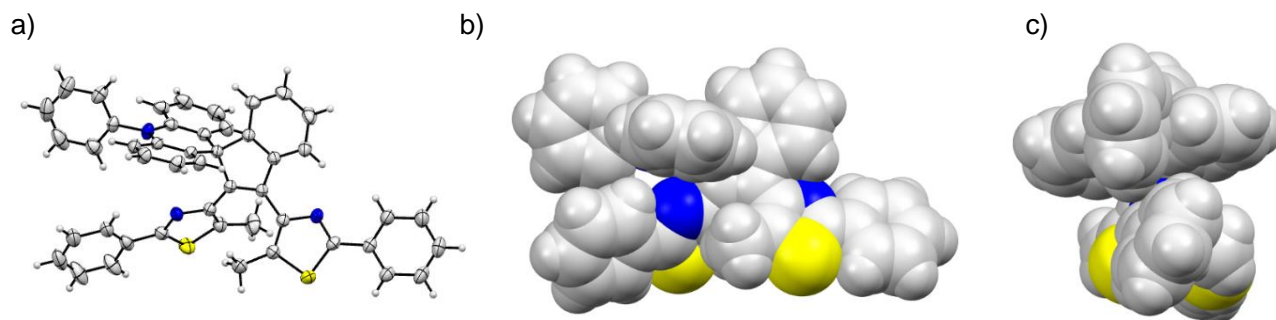


Fig. S10 a) 2 ORTEP drawing of **Spiro-DAE<sub>o</sub>**. Space-filling model of **Spiro-DAE**. b) front view. c) side view.

#### 4-12 Absorption spectral change of **Spiro-DAE2**

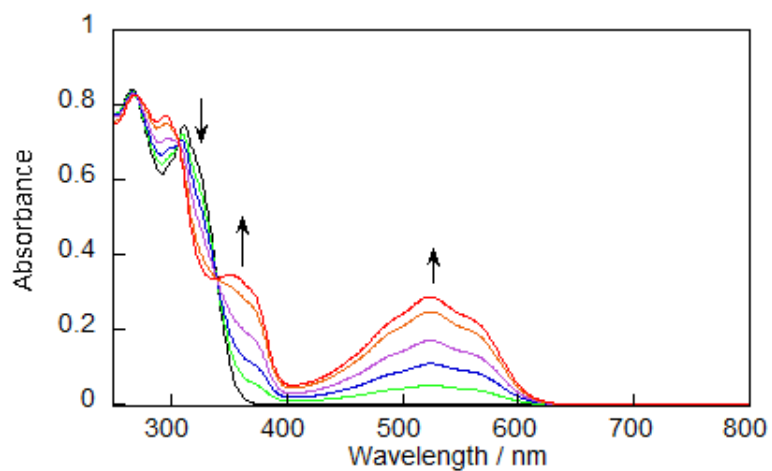


Fig. S11 Absorption spectral change of **Spiro-DAE<sub>2o</sub>** in ethyl acetate upon 313 nm light irradiation. Concentration:  $2.12 \times 10^{-5} \text{ mol dm}^{-3}$ . Irradiation time/ sec: 0, 15, 30, 60, 120, 360. ( $\epsilon_{310} = 3.49 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$ : **Spiro-DAE<sub>2o</sub>**,  $\epsilon_{524} = 1.52 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$ : **Spiro-DAE<sub>2c</sub>**).

#### 4-13 Fluorescence spectral change of **Spiro-DAE**

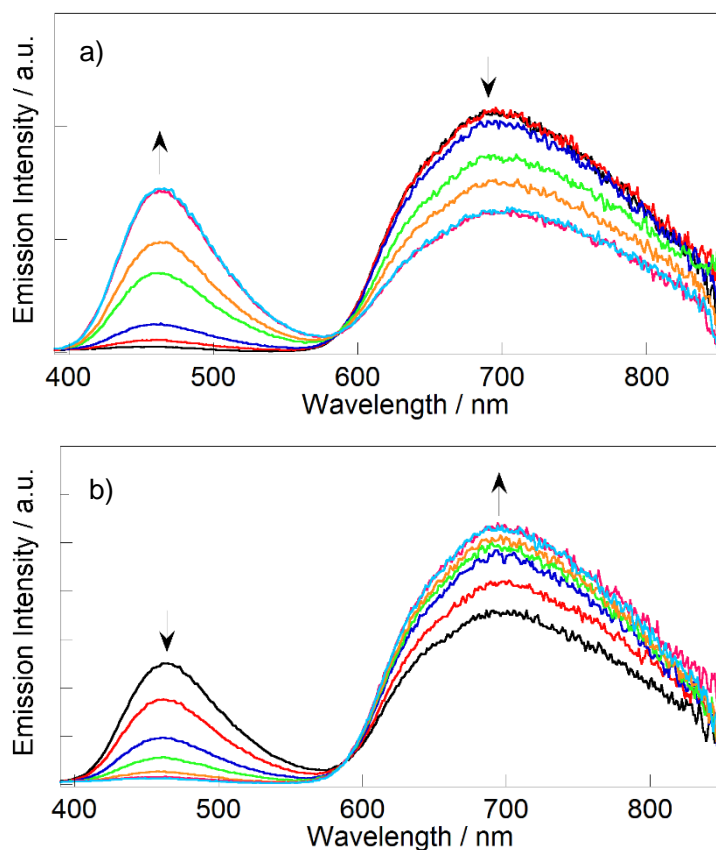


Fig. S12 Fluorescence spectral change of **Spiro-DAE** in ethyl acetate ( $2.27 \times 10^{-5} \text{ mol dm}^{-3}$ ) upon irradiation with a) a 506 nm light (Irradiation time/min: 0, 2, 8, 32, 60, 150, 270) and b) a 313 nm light irradiation (Irradiation time/min: 0, 0.17, 0.33, 0.5, 1, 2, 4), respectively. Excitation wavelength: 339 nm.

#### 4-14 Fast fluorescence spectrum measurement results of **Spiro-DAE**

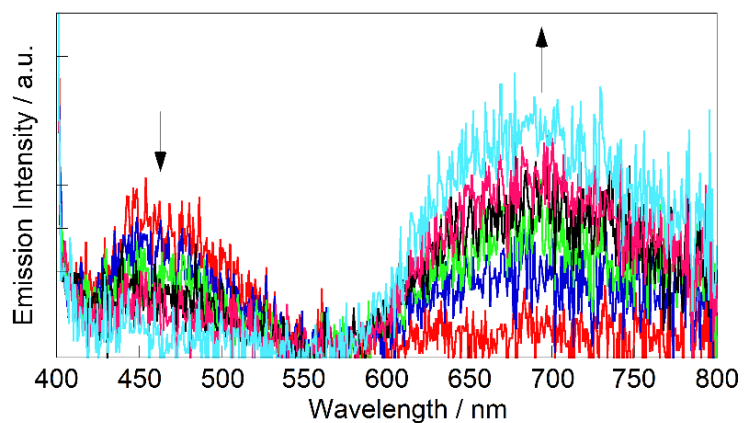


Fig. S13 Fast fluorescence spectra measurement results of **Spiro-DAE** in ethyl acetate ( $2.39 \times 10^{-5} \text{ mol dm}^{-3}$ ) upon excitation with 375 nm. Irradiation time/s: 0, 0.4, 0.8, 1.2, 1.6, 5.7.

#### 4-15 Solvent polarity dependence of the fluorescence spectra of **Spiro-DAE**

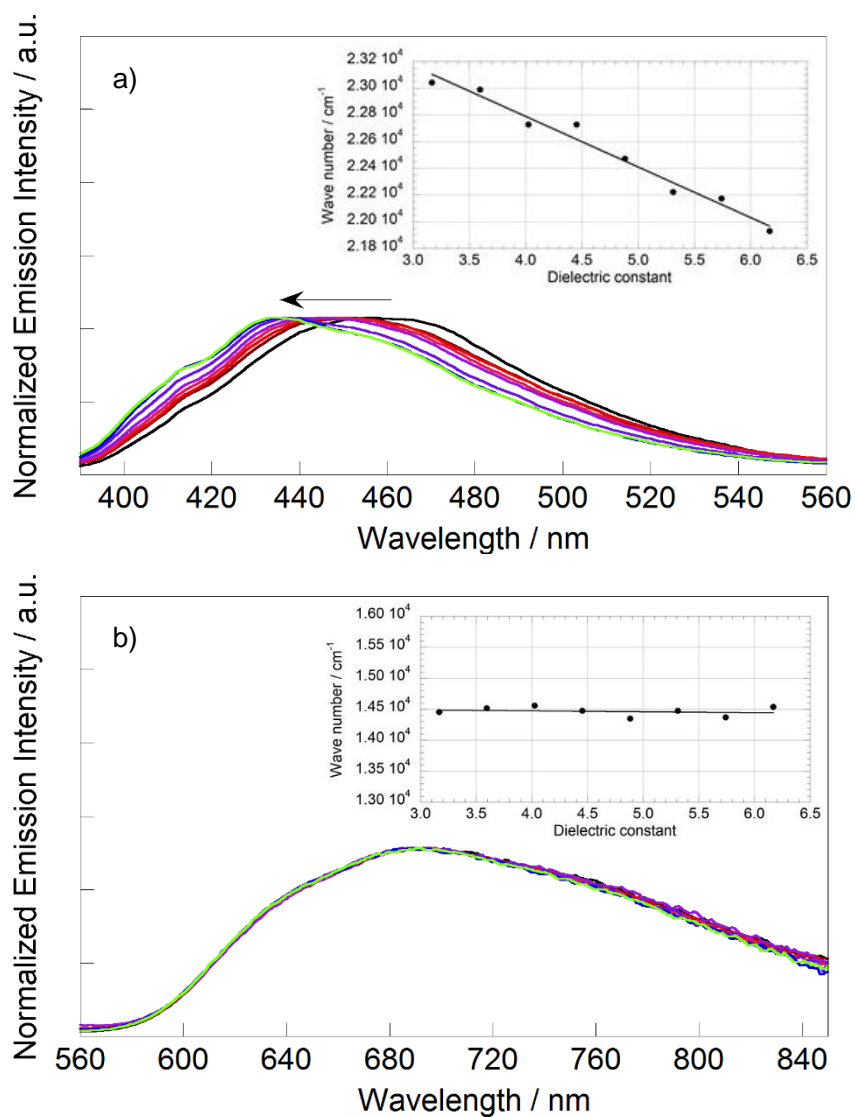


Fig. S14 Fluorescence spectra of **Spiro-DAE** a) before and b) after irradiation with 313 nm light. Excitation wavelength: 339 nm. Solvent: ethyl acetate: hexane = 1.0 : 0 ( $1.90 \times 10^{-5} \text{ mol dm}^{-3}$ ), 0.9 : 0.1 ( $1.71 \times 10^{-5} \text{ mol dm}^{-3}$ ), 0.8 : 0.2 ( $1.52 \times 10^{-5} \text{ mol dm}^{-3}$ ), 0.7 : 0.3 ( $1.33 \times 10^{-5} \text{ mol dm}^{-3}$ ), 0.6 : 0.4 ( $1.14 \times 10^{-5} \text{ mol dm}^{-3}$ ), 0.5 : 0.5 ( $0.95 \times 10^{-5} \text{ mol dm}^{-3}$ ), 0.4 : 0.6 ( $0.76 \times 10^{-5} \text{ mol dm}^{-3}$ ), 0.3 : 0.7 ( $0.57 \times 10^{-5} \text{ mol dm}^{-3}$ ) (right to left). Inset: the relationship between the emission wave number and the dielectric constant values of the solvents.

#### 4-16 Molecular orbitals of **Spiro-DAE**

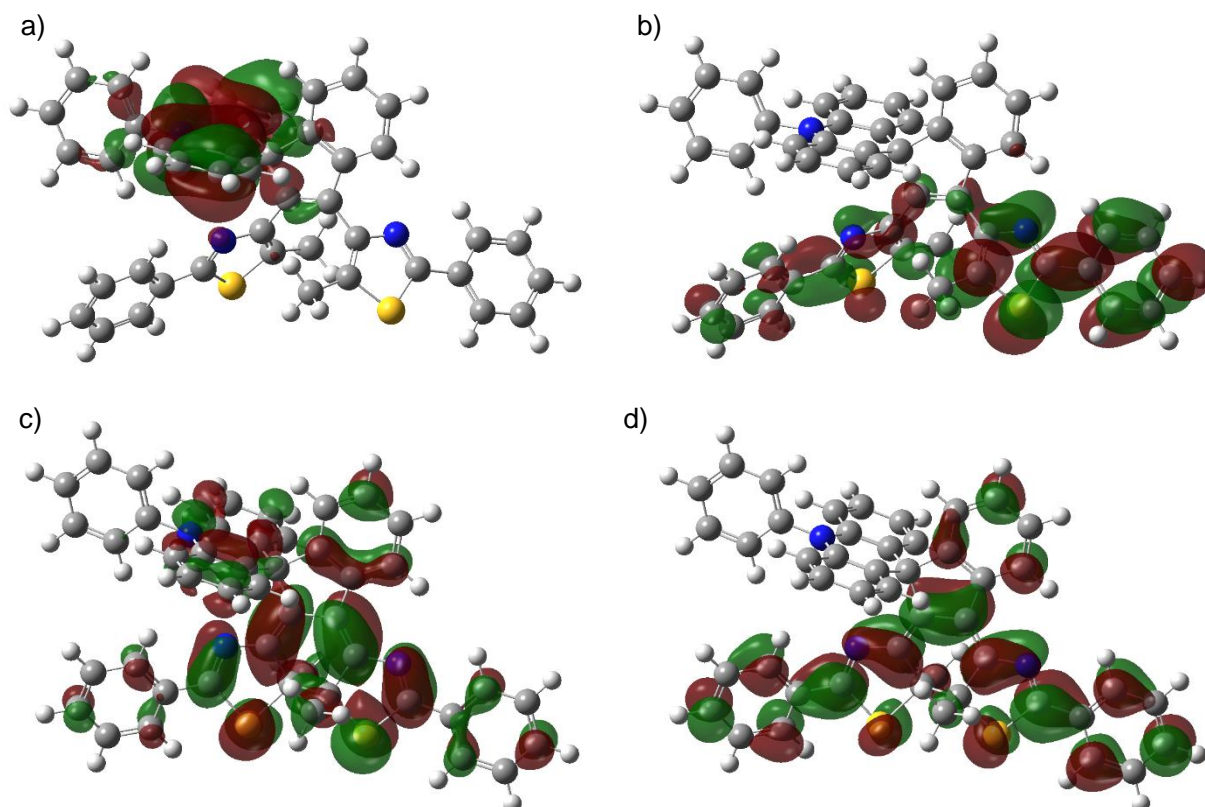


Fig. S15 Molecular orbitals of **Spiro-DAE<sub>o</sub>** (a): HOMO, b): LUMO) and **Spiro-DAE<sub>c</sub>** (c): HOMO, d): LUMO) at B3LYP/ 6-31G(d).

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- 1) K. Morinaka, T. Ubukata and Y. Yokoyama, *Org. Lett.*, 2009, **11**, 3890.
- 2) Y. Yokoyama, T. Inoue, M. Yokoyama, T. Goto, T. Iwai, N. Kera, I. Hitomi, Y. Kurita, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 3297.

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