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## Photoresponsive rolling and bending of thin crystals of chiral diarylethenes

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## Photoresponsive rolling and bending of thin crystals of chiral diarylethenes

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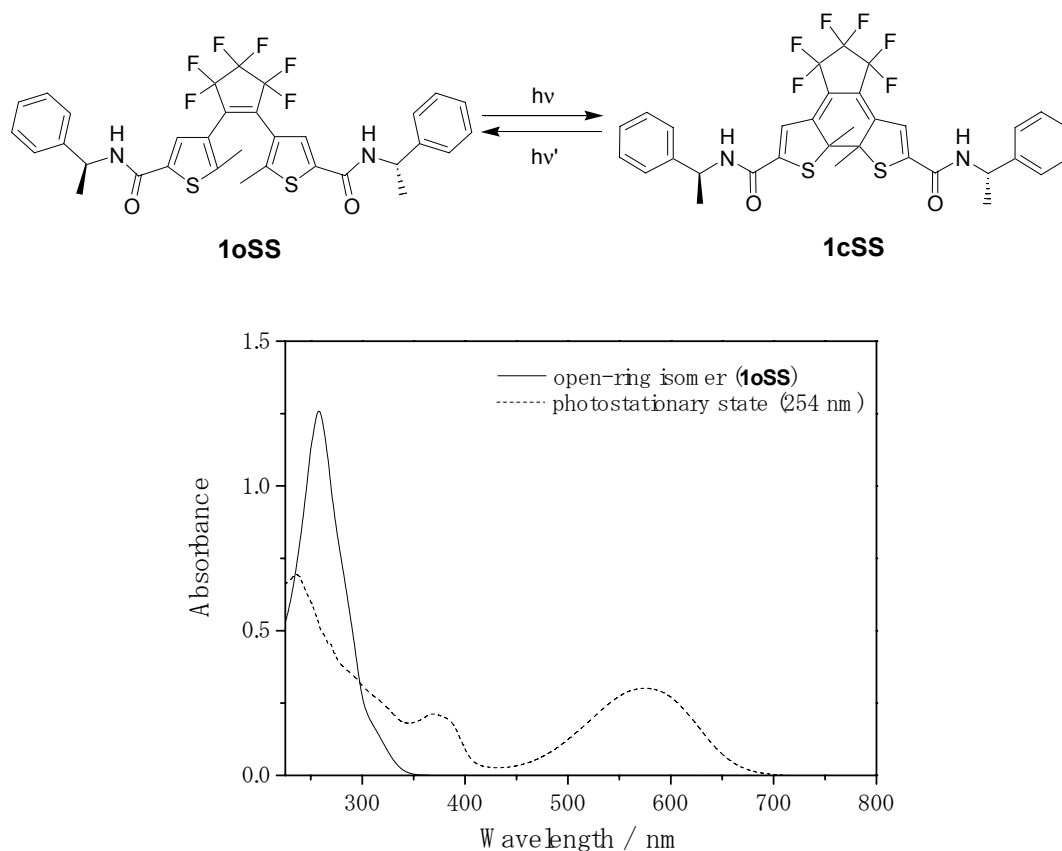
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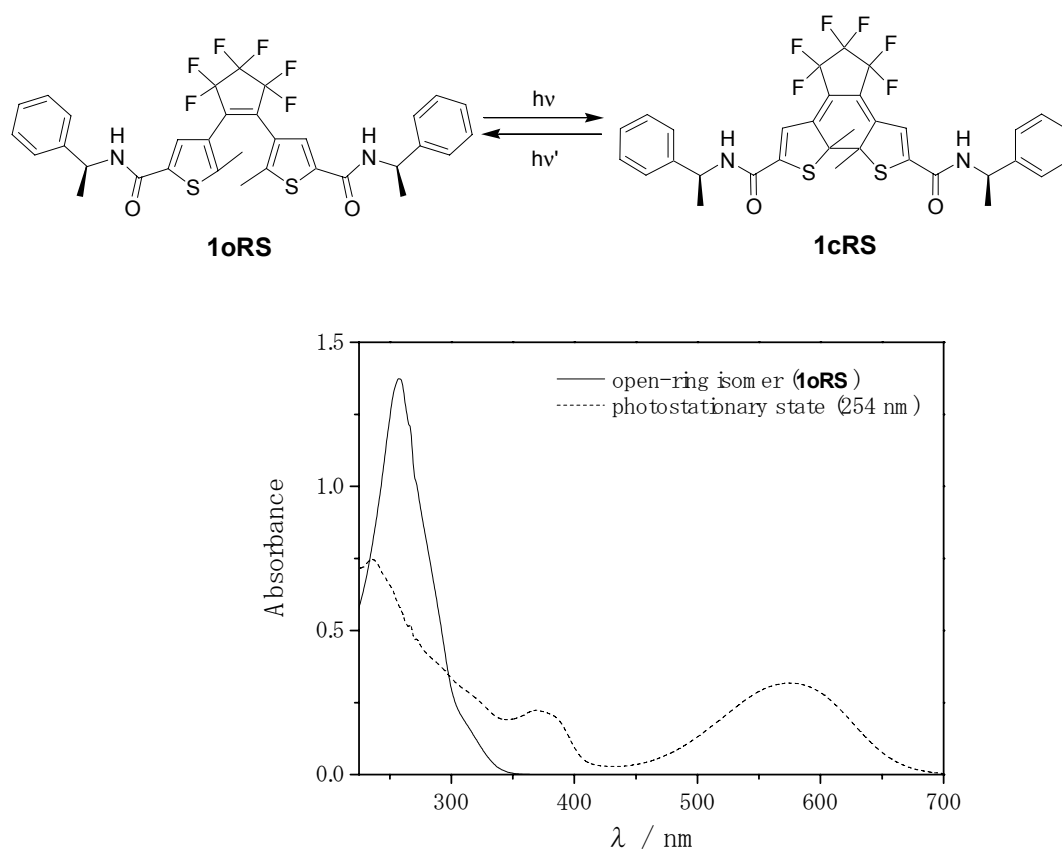
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## 1. Photochromism of the diarylethene derivatives in solution



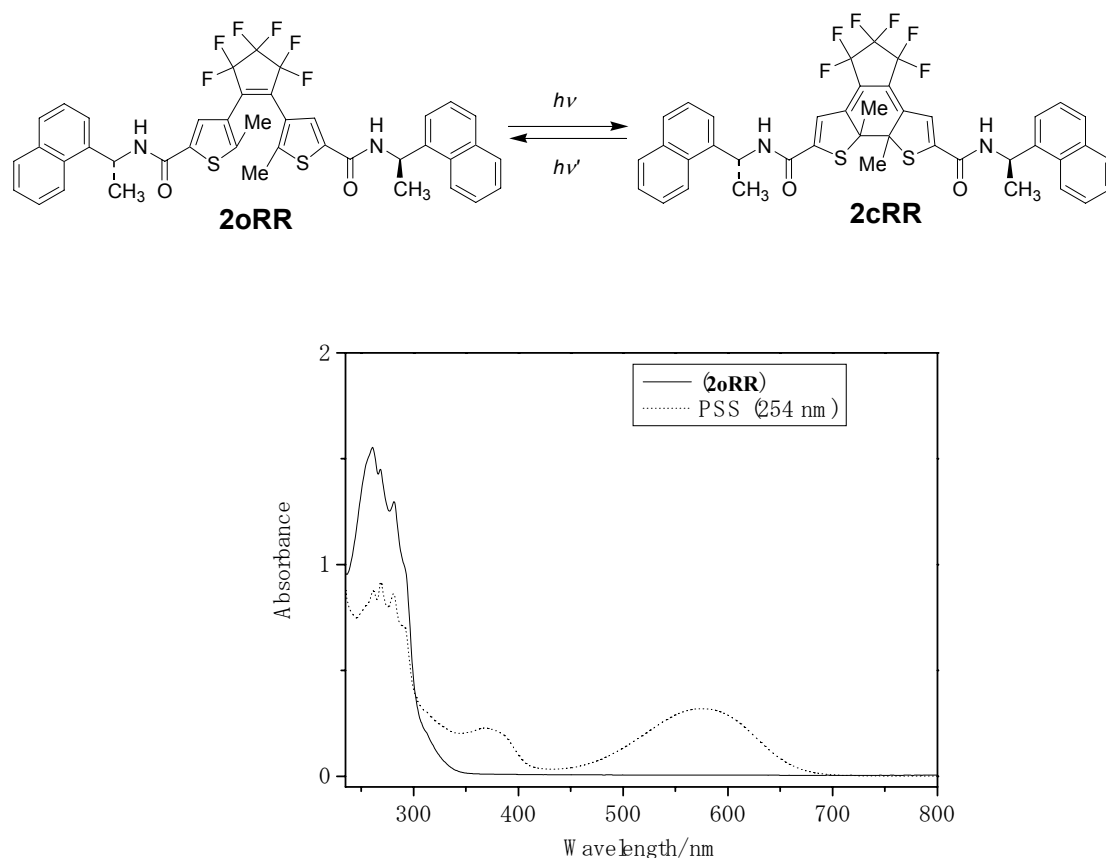
**Figure S1** UV-vis spectra of diarylethene **1oSS** in acetonitrile (solid line) and after reaching the photostationary state (254 nm) (dotted line).

An absorption maximum in the UV-vis spectrum ( $\text{CH}_3\text{CN}$ ) of **1oSS** was observed at 258 nm ( $\epsilon$ :  $3.91 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ). Upon UV (254 nm) irradiation, the solution turned to blue-purple and a new band appeared at 575 nm ( $\epsilon$ :  $1.02 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ), attributed to the closed-ring isomer **1cSS**. Upon visible light irradiation, the color disappeared and the original spectrum was recovered.



**Figure S2** UV-vis spectra of diarylethene **1oRS** in acetonitrile (solid line) and after reaching the photostationary state (254 nm) (dotted line)

An absorption maximum in the UV-vis spectrum ( $\text{CH}_3\text{CN}$ ) of **1oRS** was observed at 258 nm ( $\epsilon$ :  $3.40 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ). Upon UV (254 nm) irradiation, the solution turned to blue-purple and a new band appeared at 574 nm ( $\epsilon$ :  $9.0 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ ), attributed to the closed-ring isomer **1cRS**. Upon visible light irradiation, the color disappeared and the original spectrum was recovered.



**Figure S3** Absorption spectra of diarylethene **2oRR** in acetonitrile (solid line) and after reaching the photostationary state (254 nm) (dotted line)

An absorption maximum in the UV-vis spectrum ( $\text{CH}_3\text{CN}$ ) of **2oRR** was observed at 261 nm ( $\epsilon: 4.18 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ). Upon UV (254 nm) irradiation, the solution turned to blue-purple and new bands appeared at 576 nm ( $\epsilon: 8.62 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ ) and 368.0 nm ( $\epsilon: 6.15 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ ), attributed to the closed-ring isomer **2cRR**. Upon visible light irradiation, the color disappeared and the original spectrum was recovered.

## 2. X-ray analysis of diarylethene 1oRR

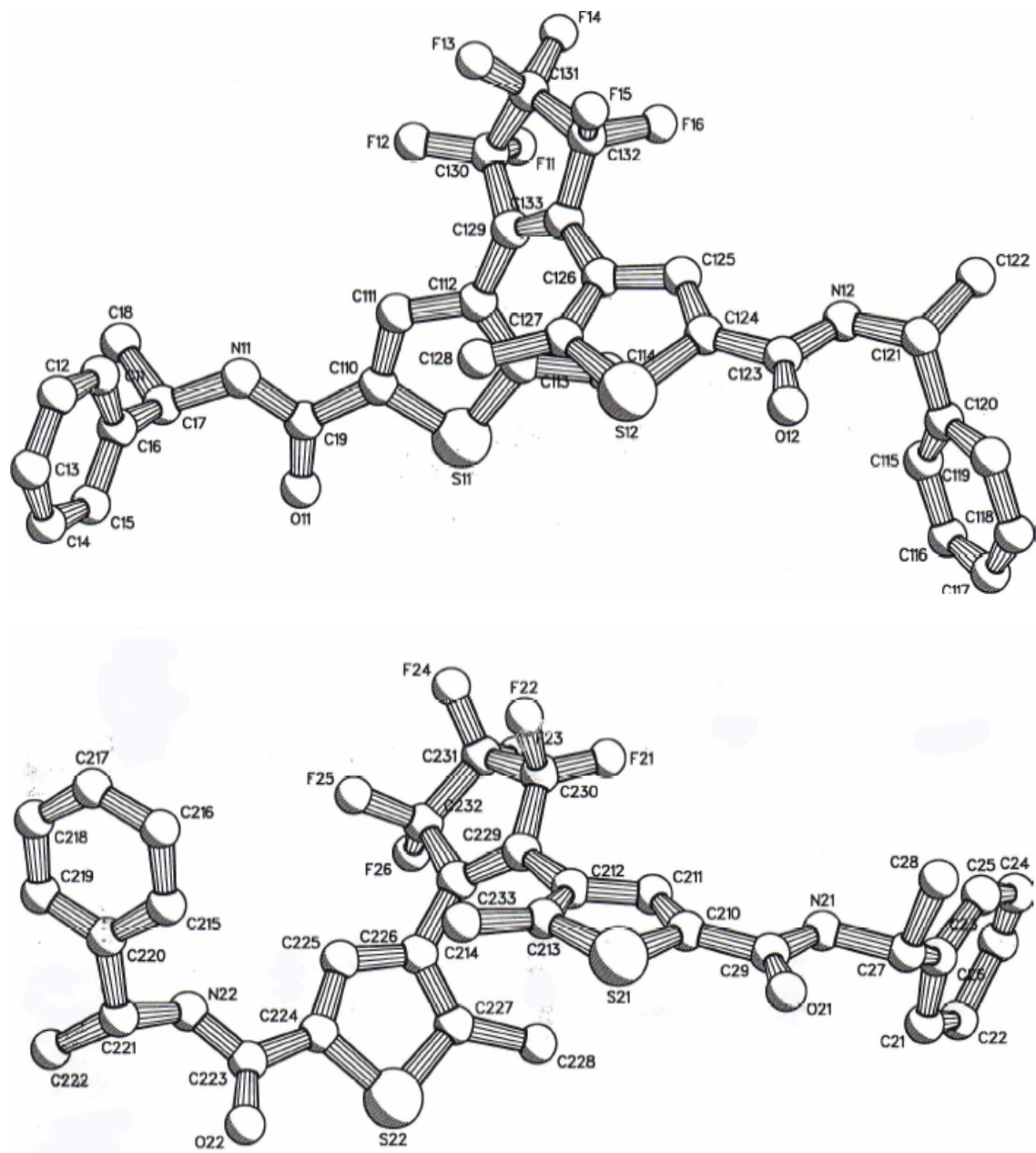


Fig. S4. ORTEP drawing of the two conformers of **1oRR** present in the single crystal

In the single crystal, the two conformers form a ladder-like structure through multiple intermolecular hydrogen bonding, Fig. S5. Each molecule participates in four hydrogen bonds that connect it to four (perpendicularly orientated) other molecules of different conformation.

The amide moieties, linked by hydrogen bonds, form an infinite two-dimensional network along the base vectors  $[1\ 0\ 0]$  and  $[0\ 1\ 0]$ , i.e. in the plane  $(0\ 0\ 1)$ .

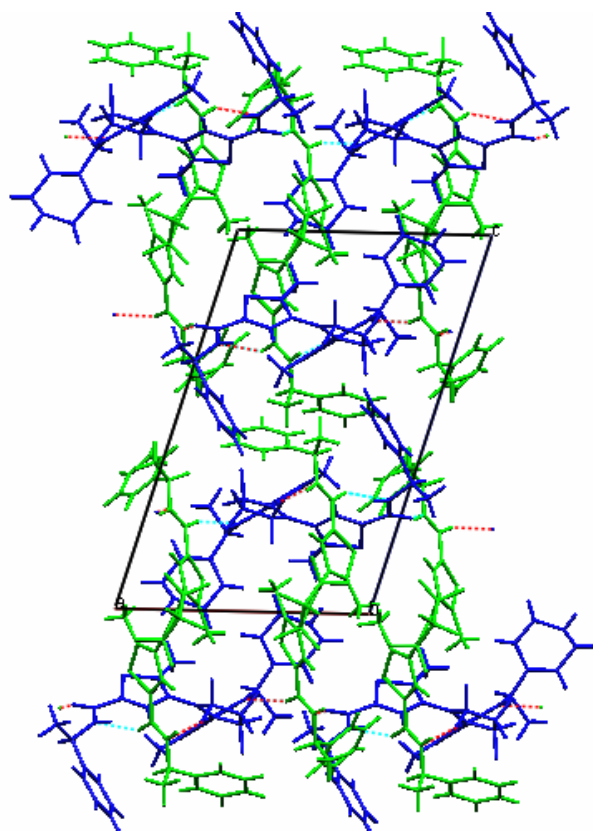


Fig. S5. Molecular packing of **1oRR**. Conformers A and B, drawn in green and blue, respectively, are hydrogen bonded (red dotted line).

### 3. Description of **1oRR** and **2oRR** crystals and polar plots

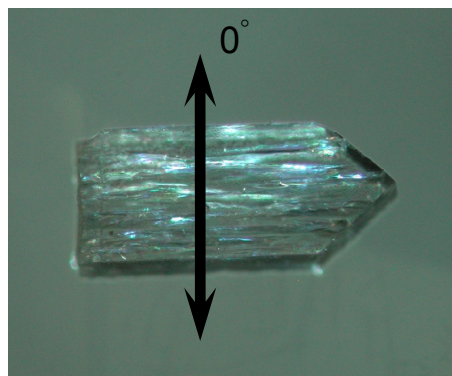


Fig. S6. Appearance of the single crystal of **1oRR** (0.6 mm x 1.5 mm).

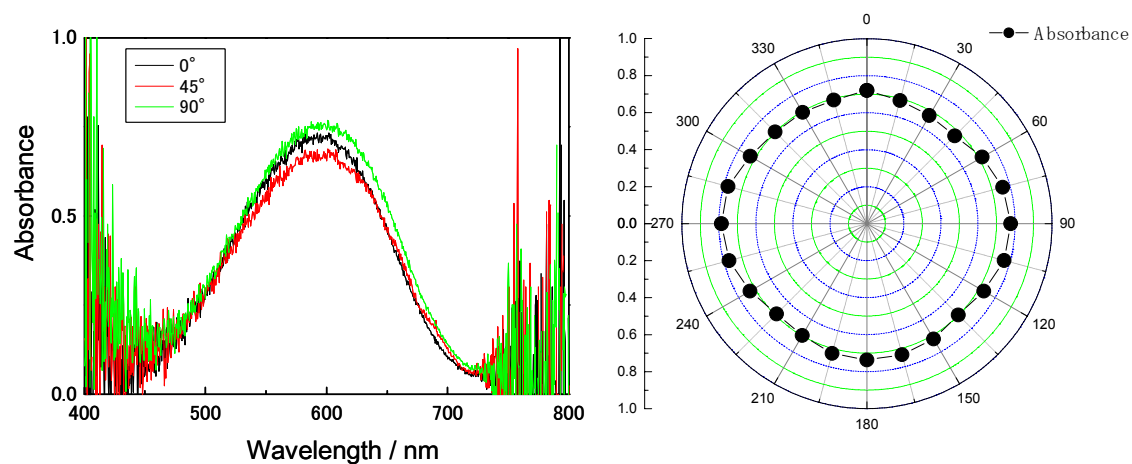


Fig. S7 Absorption spectra (left) of the photochemically coloured crystal of **1oRR** at several orientations and polar plot of the absorbance at 598 nm.



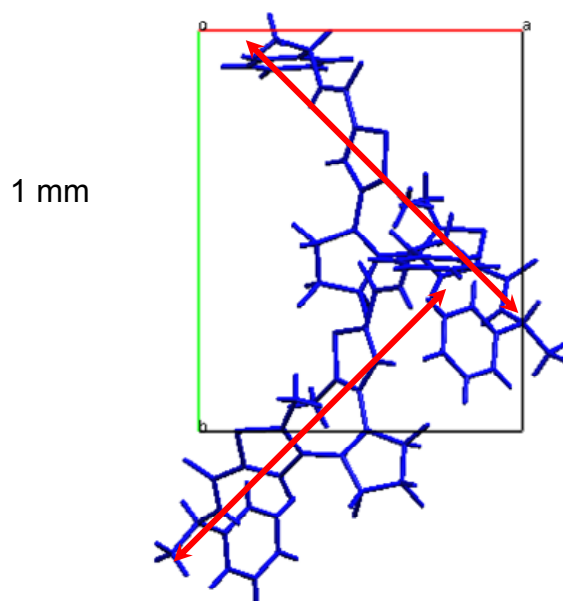
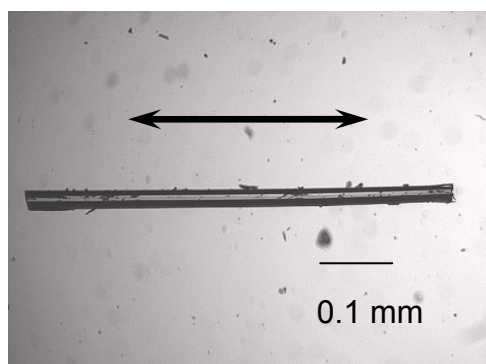
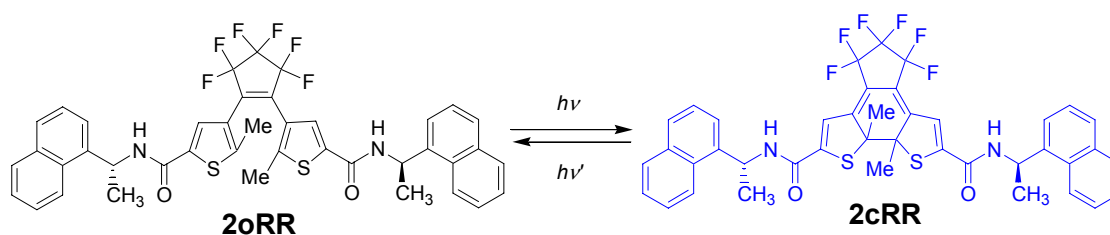


Fig. S8. Molecular packing of two conformers of **1oRR** from the (001) face. The long axes of the molecules are oriented perpendicular to each other. The packing pattern is in agreement with the polar plot in Fig. 3b (Fig. S7).



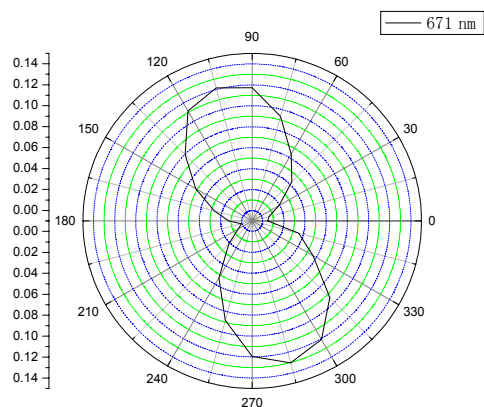


Fig. S9. Microscopic picture of the sublimated crystal of **2oRR** and the polar plot at 571 nm after UV irradiation of the crystal.

#### 4. IR spectra of **1oRR** and **2oRR**

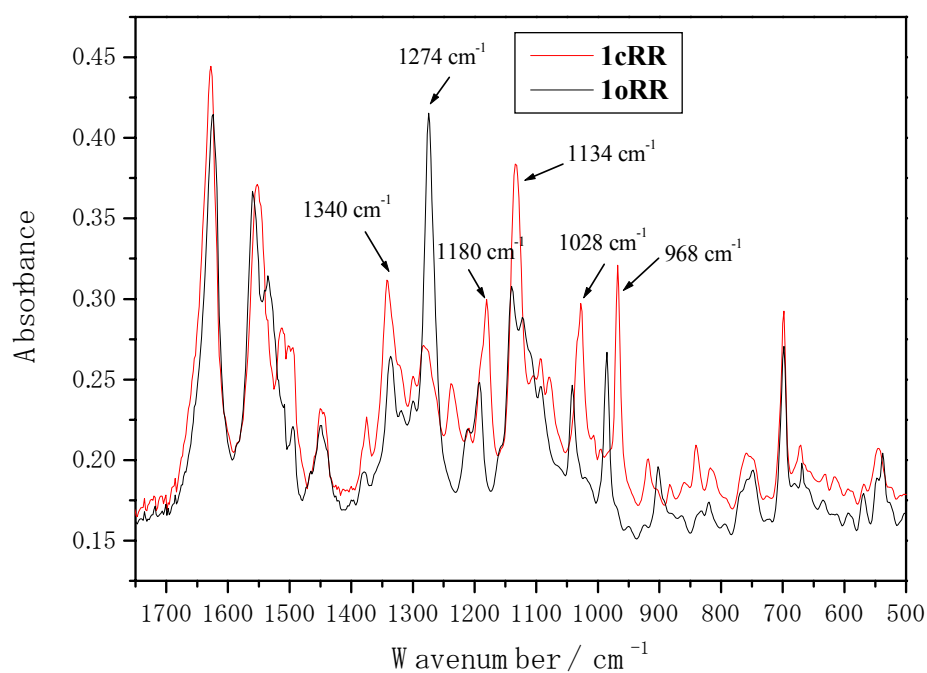


Fig. S10. IR spectra of open-ring isomer **1oRR** (black line) and the closed-ring isomer **1cRR** (red line).

## 5. ATR-IR spectra of the surface of the crystal before and after irradiation

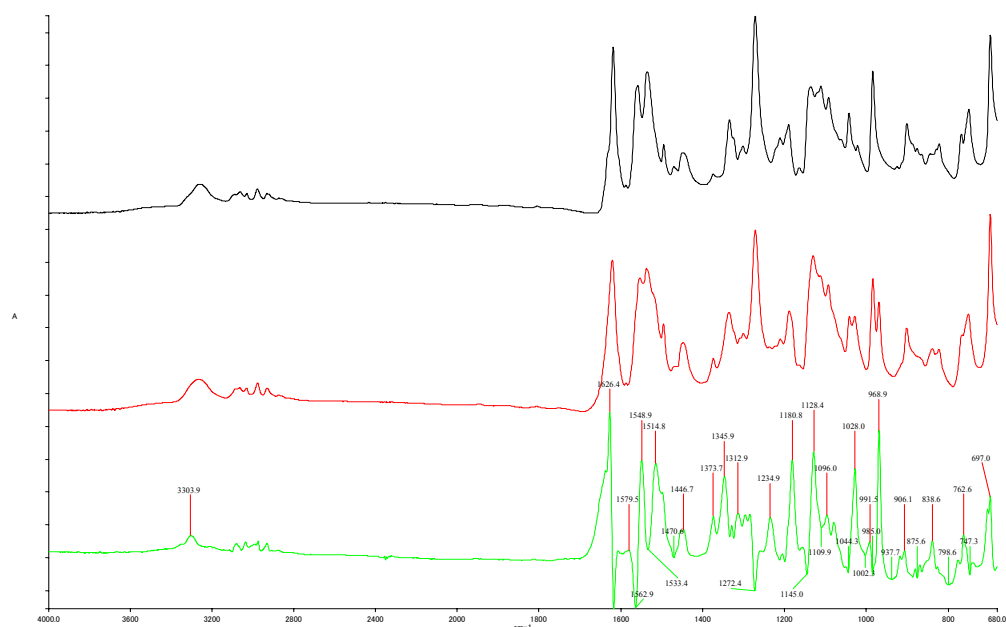
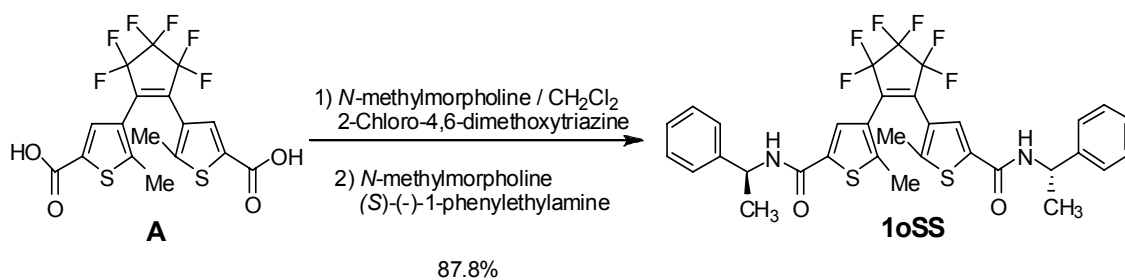


Fig. S11 ATR-IR spectra of the thin film crystal (a) before UV irradiation, (b) after UV irradiation, (c) differential spectrum ((b)-(a)).

## 6. Synthesis of diarylethenes

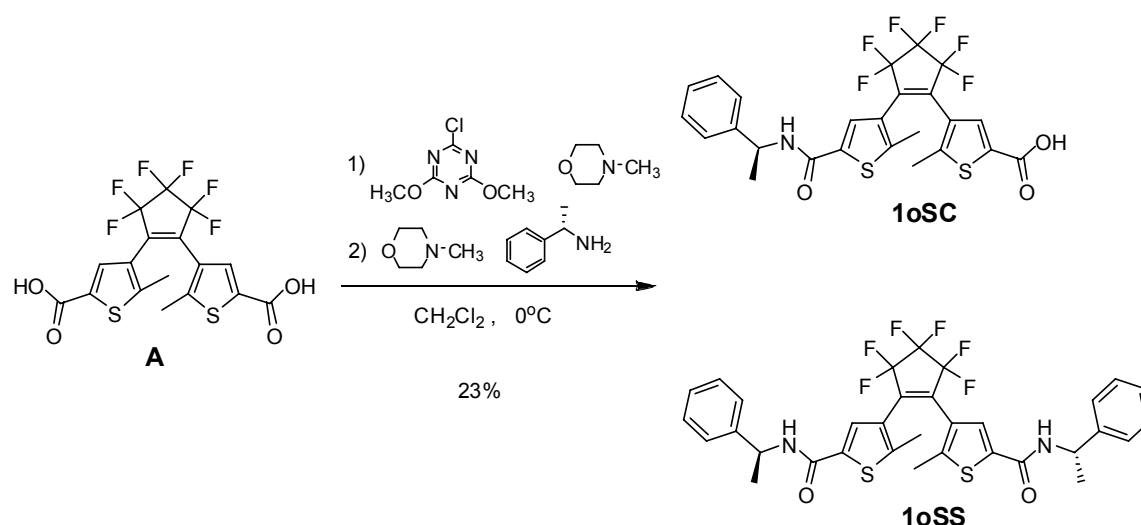
### 1,2-Bis(2-methyl-5-[[[(S)-1-phenylethyl]amino]carbonyl]thien-3-yl)perfluorocyclopentene (1oSS)<sup>i</sup>



To a mixture of 1,2-bis(5-carbonyl-2-methylthien-3-yl)perfluorocyclopentene (**A**) (0.80 g, 1.75 mmol) and dichloromethane (DCM) (30.0 ml) cooled in a water-ice bath, was added *N*-methylmorpholine (0.48 ml, 4.38 mmol). 2-Chloro-4,6-dimethoxy-1,3,5-triazine (0.84 g, 4.73 mmol) was added and the mixture was stirred for 2 h at 0 °C. *N*-methylmorpholine (0.52 ml, 4.73 mmol) and (*S*)-(-)-1-phenylethylamine (0.60 ml, 4.73 mmol) were added successively, and stirring was continued for another 3 h at 0 °C. To the reaction mixture, 100 ml of DCM and small amount of ether was added and the organic mixture was washed with 1M aq. HCl (2×50 ml) followed by 100 ml of brine, saturated sodium bicarbonate solution, and 100 ml of distilled water. The mixture was dried over anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo to yield 2.27 g of a yellow solid. The crystalline material was dissolved into ether and a small volume of methanol was added resulting in the precipitation of 1.07 g (1.61 mmol, 88%) of pure **1oSS**.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>); 1.61 (d, *J*=7.0 Hz, 6H), 1.91 (s, 6H), 5.27 (dq, *J*=7.8, 7.0 Hz, 2H), 6.07 (d, *J*=7.8 Hz, 2H), 7.30-7.40 ppm (m, 12H).

**1-(5-Carbonyl-2-methylthien-3-yl)-2-(2-methyl-5-[(*S*)-1-(phenylethyl)amino]-carbonyl]thien-3-yl)perfluorocyclopentene (**1oSC**)**



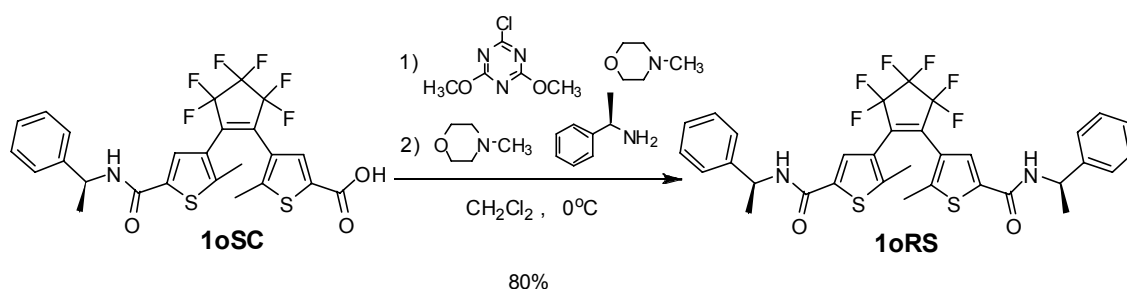
To 1,2-bis(5-carboxy-2-methylthien-3-yl)-perfluorocyclopentene (**A**) (0.5 g, 1.1 mmol) in 20 ml of DCM at 0 °C was added *N*-methylmorpholine (0.13 ml, 1.21 mmol) to yield a brown clear solution. Subsequently, 2-chloro-4,6-dimethoxy-1,3,5-triazine (0.21 g, 1.21 mmol) was added and the mixture was stirred for 2 h at 0 °C. Then *N*-methylmorpholine (0.13 ml, 1.21 mmol) and (*S*)-(-)-1-phenylethylamine (0.15 ml, 1.21 mmol) were added successively, and stirring was continued for another 3 h at 0 °C. DCM (80 ml) was added and the DCM layer was washed twice with 1M aq.HCl (2x50 ml) followed by brine (1×50 ml), and distilled water (1×80 ml). The organic layer was separated and dried over anhydrous sodium sulfate.

After filtration, the solvent was removed in vacuo. The crystalline material was dissolved into ether followed by the addition of small amount of methanol whereupon up 0.12 g of **1oSS** precipitated. The filtrate was evaporated in vacuo, and the residue was purified by preparative TLC (Merck 9717) by using a mixture of dichloromethane: methanol: triethylamine (60 ml:1.5 ml:3 drops) as an eluent to provide 0.14 g (0.25 mmol, 23%) of **1oSC**.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ = 1.61 (d, *J*=7.0 Hz, 3H), 1.93 (s, 3H), 1.97 (s, 3H), 5.27 (dq, *J*=7.7, 7.0 Hz, 1H), 6.06 (d, *J*=7.7 Hz, 1H), 7.28-7.41 (m, 6H), 7.82 ppm (s, 1H); FAB-MS (NBA) *m/z* 560 (M<sup>+</sup>)

Anal. Calcd. for C<sub>33</sub>H<sub>40</sub>N<sub>2</sub>F<sub>6</sub>O<sub>2</sub>S<sub>2</sub> : C, 59.81; H, 4.26; N, 4.23; Found: C, 59.61; H, 4.25; N, 4.22

**1-(2-Methyl-5-[(*R*)-1-(phenylethyl)amino]carbonyl]thien-3-yl)-2-(2-methyl-5-[(*S*)-1-(phenylethyl)amino]carbonyl]thien-3-yl)perfluorocyclopentene (**1oRS**)**



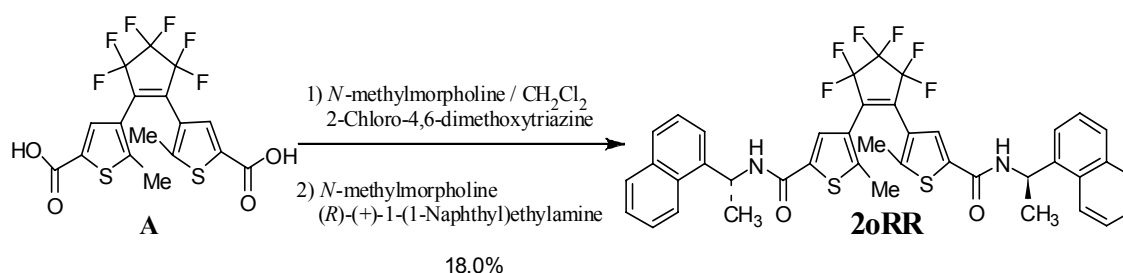
To 1-(5-carbonyl-2-methylthien-3-yl)-2-(2-methyl-5-[(*S*)-1-(phenylethyl)amino]carbonyl]thien-3-yl)perfluorocyclopentene (**1oSC**) (0.25 g, 0.447 mmol) in anhydrous DCM (10 ml) stirred at 0 °C *N*-methylmorpholine (0.054 ml, 0.49 mmol) was added, resulting in a brownish transparent solution. Subsequently, 2-chloro-4,6-dimethoxy-1,3,5-triazine (0.09 g, 0.49 mmol) was added and stirring continued for 2 h at 0 °C. Then *N*-methylmorpholine (0.054 ml, 0.49 mmol), 2-chloro-4,6-dimethoxy-1,3,5-triazine (0.05 g, 0.29 mmol), and *R*-(+)-1-phenylethylamine (0.15 ml, 1.21 mmol) were added successively, followed by stirring for another 3 h at 0 °C. DCM (80 ml) was then added and the DCM layer was washed twice with 1M aq. HCl (50 ml) followed by brine (1 × 50 ml), saturated sodium bicarbonate solution (50 ml) and distilled water (1 × 80 ml). The organic layer was dried over sodium sulfate anhydrous and after the filtration, the solvent was removed in vacuo. The crystalline material was dissolved into ether followed by the addition of small amount of methanol to yield **1oRS** (0.238 g, 0.359 mmol, 80%) as white crystals.

m.p. 260.6-262.4°C

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ = 1.61 (d, *J*=7.0 Hz, 6H), 1.91 (s, 6H), 5.27 (dq, *J*=7.7, 7.0 Hz, 1H), 6.09 (d, *J*=7.7 Hz, 1H), 7.28-7.40 ppm (m, 12H)

Anal. Calcd. for C<sub>33</sub>H<sub>40</sub>N<sub>2</sub>F<sub>6</sub>O<sub>2</sub>S<sub>2</sub> : C, 59.81; H, 4.26; N, 4.23.; Found: C, 60.11; H, 4.19; N, 4.27.

**1,2-Bis(2-methyl-5-[[*[(R)-1-(1-naphthylethyl)amino]carbonyl*thien-3-yl]perfluorocyclopentene (2oRR)**



To 1,2-bis(5-carboxyl-2-methylthien-3-yl)- perfluorocyclopentene (**A**) (1.0 g, 2.2 mmol) in 20 ml of DCM stirred at 0 °C was added *N*-methylmorpholine (0.44 ml, 4.4 mmol) was added to yield a brown clear solution. Next 2-chloro-4,6-dimethoxy-1,3,5-triazine (0.77 g, 4.38 mmol) was added followed by stirring for 2 h at 0 °C. Then *N*-methylmorpholine (0.443 ml, 4.38 mmol) and (*R*)-(+)-1-(1-naphthyl)ethylamine (0.80 g, 4.38 mmol) were added successively, and stirring continued for 1 h at 0 °C, followed by stirring at room temperature overnight. Ether (200 ml) was added and the organic layer was washed with twice 1M aq. HCl (2x100 ml) followed by brine (2x100 ml), saturated aq. sodium bicarbonate solution (2x100 ml), and distilled water (2x100 ml). The organic layer was dried over anhydrous sodium sulfate, filtered, and the solvent was removed in vacuo to yield 3.1 g of yellow crystals . Recrystallization from chloroform provided **2oRR** (0.30 g, 0.41 mmol, 18% yield) as white crystals.

mp 267.0-268.0 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>); 1.77 (d, *J*=6.5 Hz, 6H), 1.85 (s, 6H), 6.09 (dq, *J*=8.0, 6.6 Hz, 2H), 6.14 (d, *J*=8.1 Hz, 2H), 7.32 (s, 2H) , 7.48 (dd, *J*=8.5, 7.5 Hz, 2H), 7.50-7.61 (m, 6H), 7.83 (d, *J*=8.0 Hz, 2H), 7.88 (d, *J*=8.5 Hz, 2H), 8.13 ppm (d, *J*=8.3 Hz, 2H)

FAB-MS(NBA) *m/z* 764 (M<sup>+</sup>, 10)

Anal. Calcd. for C<sub>41</sub>H<sub>32</sub>N<sub>2</sub>F<sub>6</sub>O<sub>2</sub>S<sub>2</sub> : C, 64.55; H, 4.23; N, 3.67.; Found: C, 64.37; H, 4.17; N, 3.61.

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<sup>i</sup> K. Uchida, M. Walko, J. J. D. de Jong, S. Sukata, S. Kobatake, A. Meetsma, J. van Esch and B. L. Feringa, *Org. Biomol. Chem.*, 2006, **4**, 1002.