

# Photoinduced mass migration in polymer films containing a photoresponsive molecular motor

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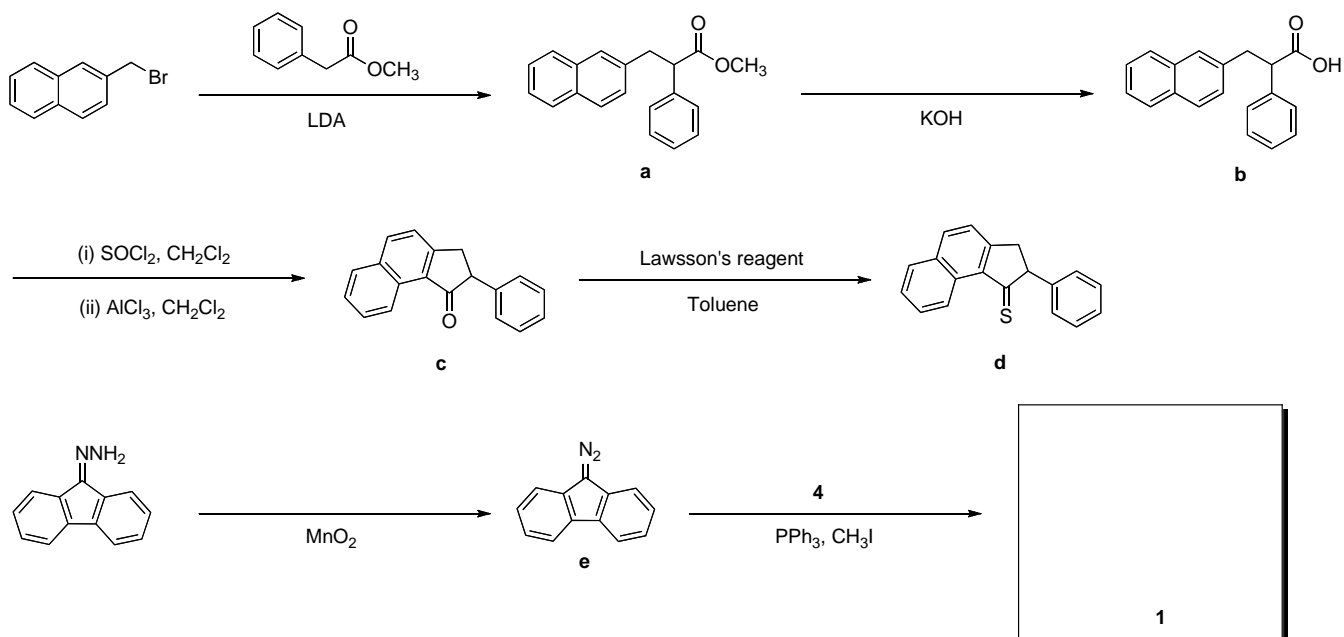
## 1. General

Unless otherwise noted, all commercial reagents were used as received.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  with a JNM ECP-500 spectrometer. Chemical shifts of  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals were quoted to internal standard  $\text{CDCl}_3$  ( $\delta = 7.26$  and  $77.0$ ), and listed as chemical shifts in ppm ( $\delta$ ). UV measurements were performed on a JASCO V-550 spectrophotometer, and CD spectra were recorded on a JASCO J-820 spectropolarimeter. High-resolution mass spectra were obtained with a JMS-SX102A spectrometer with fast atom bombardment (FAB). Thermal properties of samples were determined with a differential scanning calorimeter (Seiko I&E SSC-5200 and DSC220C) at a scanning rate of  $10^\circ\text{C}/\text{min}$ .

## 2. Synthesis and analytical data

The synthesis were performed by using modified procedures reported previously (Scheme S1).<sup>12b</sup>

Scheme S1



**Methyl 3-naphthalen-2-yl-2-phenyl propanoate (a).** n-BuLi in hexane (20 mL, 33 mmol) was added dropwise to THF solution (100 mL) containing diisopropylamine (4.0 mL, 28 mmol) at -60 °C, and it was stirred for 15 min. Then, methyl phenylacetate (2.5 mL, 18 mmol) was added to the mixture, the reaction was stirred at -60 °C for 1 h, and 2-(Bromomethyl)naphthalen (4.0 g, 18 mmol) was added. The solution was stirred over night at room temperature and a saturated aq. solution of NH<sub>4</sub>Cl was then added. The resulting mixture was extracted with diethyl ether, dried over MgSO<sub>4</sub>, and concentrated under vacuum. The crude residue was purified by column chromatography (SiO<sub>2</sub>, hexane : ethyl acetate = 20 :1), affording 2.0 g (38%) as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 7.80-7.71 (3H , m) , 7.45-7.41 (2H , m) , 7.36-7.24(6H , m) , 3.96 (1H , dd , J=8.8 , 6.6 Hz) , 3.59 (3H , s) , 3.58 (1H , m) , 3.18 (1H , dd , J=13.9 , 6.6 Hz).

**3-Naphthalen-2-yl-2-phenyl-propionic acid (b),** The mixture of EtOH (40 mL), water (40 mL), KOH (7.0 g, 130 mmol), and **a** was refluxed for 3 h, and HCl solution was added for neutralization. The resulting mixture was extracted with diethyl ether, dried over MgSO<sub>4</sub>, and concentrated under vacuum. The crude residue was purified by recrystallization from hexane, affording 1.4 g (79%) as a white solid. (1H , dd , J=8.2 , 7.1 Hz) , 3.56 (1H , dd , J=13.9 , 8.4 Hz) , 3.19 (1H , dd , J=13.9 , 7.0 Hz) .

**2-Phenyl-2,3-dihydro-cyclopenta[a]naphthalene-1-one (c),** A solution of **b** (0.56 g, 2.0 mmol), SOCl<sub>2</sub> (2.5 mL, 34 mmol) and DMF (2drops) in CH<sub>2</sub>Cl<sub>2</sub> was refluxed for 1h. All volatiles were removed under reduced pressure, giving the crude acid chloride, which was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and cooled to 0 °C. To the solution AlCl<sub>3</sub> (0.86 g, 6.4 mmol) was added and the reaction mixture was stirred at 0 for 30 min. The reaction was quenched with a saturated aqueous solution of NaHCO<sub>3</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub>, which was dried over MgSO<sub>4</sub> and concentrated under low pressure. The crude residue was purified by recrystallization, affording 0.43 g (84%) as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 9.14 (1H , d , J=8.1 Hz) , 8.12 (1H , d , J=8.4 Hz) , 7.93 (1H , d , J=8.1 Hz) , 7.71-7.65 (1H , m) , 7.61-7.56 (2H , m) , 7.36-7.22 (5H , m) , 4.01 (1H , dd , J=7.9 , 3.5 Hz) , 3.79 (1H , dd , J=17.8 , 7.9 Hz) , 3.37 (1H , dd , J=17.8 , 3.5 Hz).

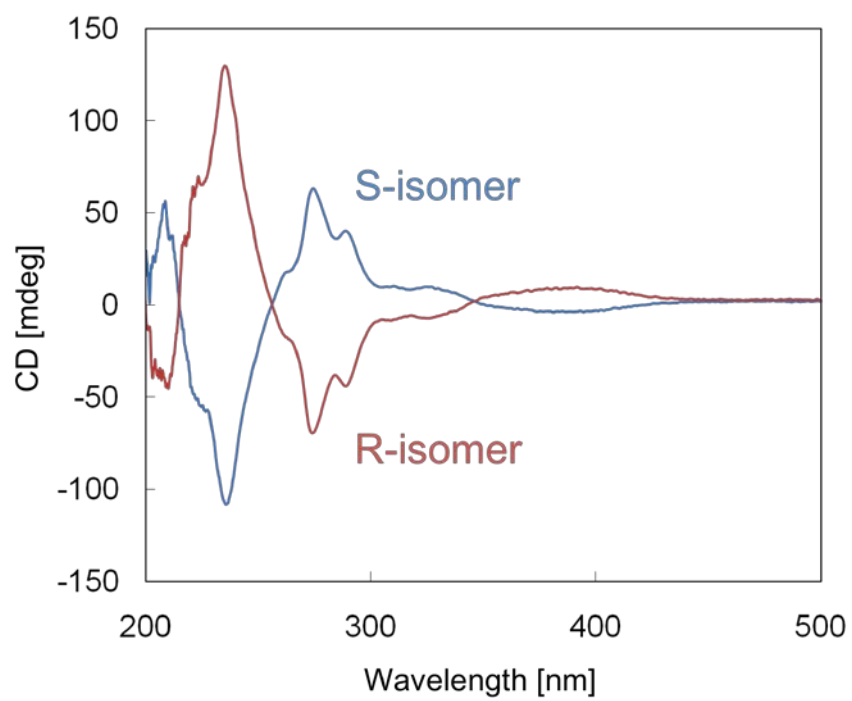
**2-Phenyl-2,3-dihydro-1H-cyclopenta[a]naphthalene-1-thione (d),** A mixture of **c**, toluene (5 mL), and lawesson's reagent (0.39 g, 0.97 mmol) was refluxed for 3 h. After finished the reaction, the mixture was extracted with ethyl acetate, and then it was dried over MgSO<sub>4</sub> and concentrated under low pressure. The crude residue was purified by column chromatography (SiO<sub>2</sub>, hexane : ethyl acetate = 20

:1), affording 0.12 g (37%) as a green solid. The obtained compound was used to the next reaction immediately.

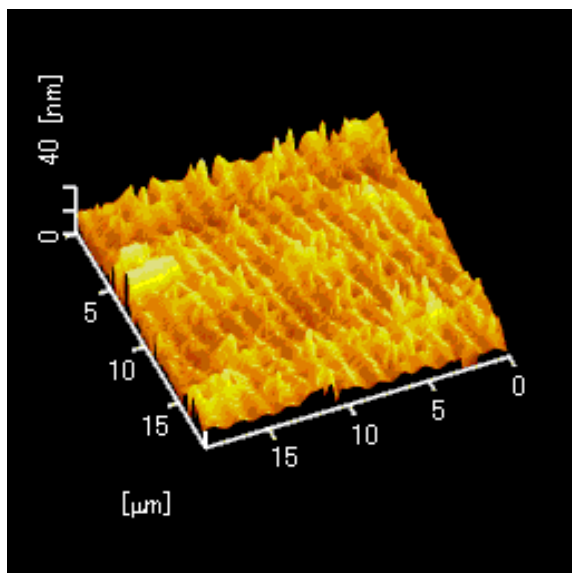
**9-diazo-9H-fluorene (e)**, A reaction mixture of **d**, THF (50 mL), and MnO<sub>2</sub> (0.32 g, 3.7 mmol) was stirred for 6 h. After the reaction, the mixture was concentrated under low pressure. The crude residue was purified by column chromatography (SiO<sub>2</sub>, hexane : ethyl acetate = 7 : 1), affording 0.76 g (77%) as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 7.94 (2H, d, J=7.8 Hz), 7.51 (2H, d, J=7.8 Hz), 7.38 (2H, t, J=7.6 Hz), 7.32 (2H, t, J=7.6 Hz).

**9-(2-phenyl-2,3-dihydro-1H-cyclopenta[*a*]naphthalen-1-ylidene)-9H-fluoren (1)**, A reaction mixture of **d**, and **e** in toluene (130 mL) was refluxed for 1h, added PPh<sub>3</sub> (0.29 g, 1.5 mmol), and refluxed for 1 hour. The reaction mixture was cooled to room temperature, and MeI (1.3 g, 9.0 mmol) was added to remove the excess of PPh<sub>3</sub>. The suspension generated was filtered, and the solution was concentrated under reduced pressure. The crude residue was purified by column chromatography (SiO<sub>2</sub>, hexane : dichloromethane = 10 : 1), affording 0.11 g (29%) as an yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 8.00 (1H, d, J=8.7 Hz), 7.95 (1H, d, J=8.2 Hz), 7.87 (1H, d, J=8.2 Hz), 7.80 (1H, d, J=7.8 Hz), 7.76 (1H, d, J=7.3 Hz), 7.49-7.44 (4H, m), 7.31 (1H, t, J=7.8 Hz), 7.21-7.13 (7H, m), 6.84-6.80 (2H, m), 5.37 (1H, d, J=6.4 Hz), 3.98 (1H, dd, J=15.4, 6.6 Hz), 3.22 (1H, d, J=15.1 Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 146.38, 146.16, 143.94, 140.06, 139.85, 139.50, 137.60, 137.03, 133.03, 132.74, 131.14, 129.01, 128.86, 128.77, 127.55, 127.23, 127.22, 127.20, 127.01, 127.00, 126.39, 126.12, 125.81, 125.47, 124.39, 123.67, 119.49, 119.06, 56.55, 44.07. MS (FAB) 406.1704 (M<sup>+</sup>).

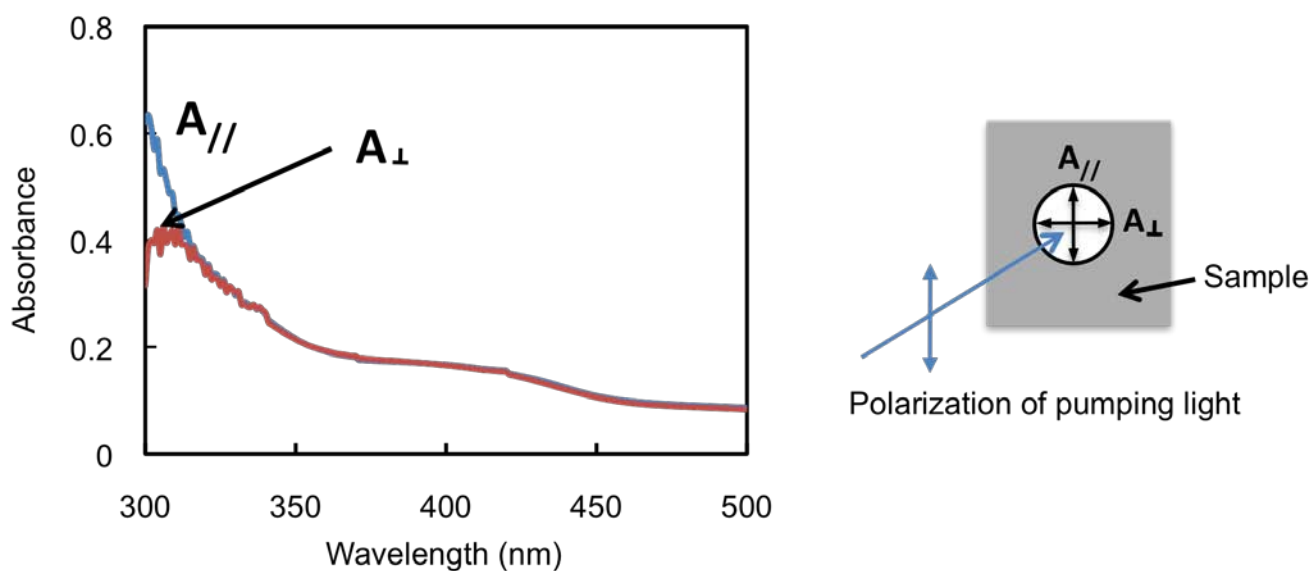
Resolution of *cis*-**1** was performed by chiral HPLC using a Daicel Chiralpak IA column as the stationary phase and a mixture of hexane:chloroform in a ratio of 1: 1 as the eluent at a rate of 2 mL/min.



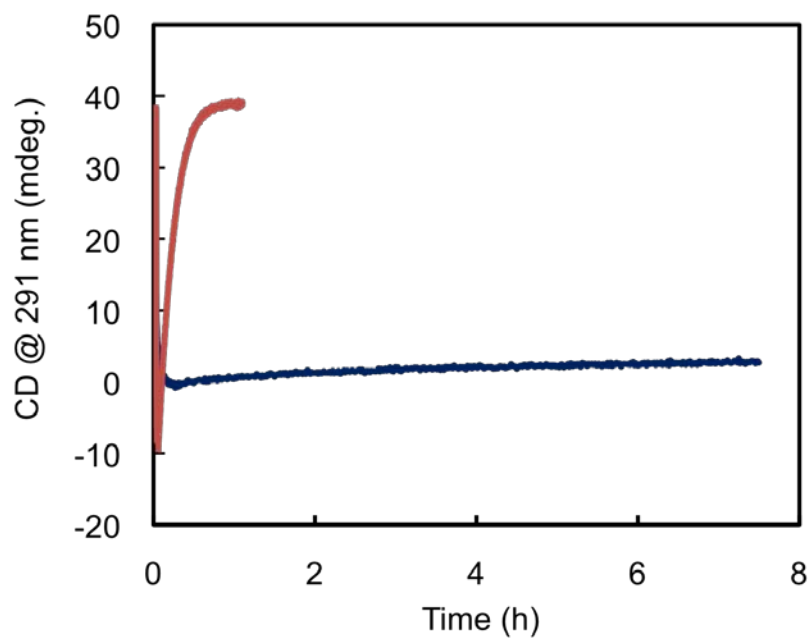
**Figure S1.** CD spectra of resolved isomers in diethyl ether ( $3.0 \times 10^{-5}$  M).



**Figure S2** AFM image of surface morphology of the film added (*R*)-isomer (initial state). The film was irradiated with interfered UV beams (364 nm, 130 mW cm<sup>-2</sup>) for 30 min.



**Figure S3** Polarized absorption spectra of parallel ( $A_{//}$ ) and perpendicular ( $A_{\perp}$ ) to the polarization of pumping light. The film containing an (*S*)-isomer (initial state) after irradiation of polarized UV light at  $300 \text{ mW cm}^{-2}$  for 30 min.



**Figure S4.** Thermal relaxation processes of an (*S*)-isomer (initial state) of **1** in the PMMA matrix (blue line) and diethyl ether (red line), respectively. These profiles were recorded by CD spectroscopy at 291 nm.