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. $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ with a JNM ECP–500 spectrometer. Chemical shifts of $^1$H and $^{13}$C NMR signals were quoted to internal standard 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 °C/min.

2. Synthesis and analytical data

The synthesis were performed by using modified procedures reported previously (Scheme S1).$^{12b}$

![Scheme S1](image)
**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 overnight at room temperature and a saturated aq. solution of NH4Cl was then added. The resulting mixture was extracted with diethyl ether, dried over MgSO4, and concentrated under vacuum. The crude residue was purified by column chromatography (SiO2, hexane : ethyl acetate = 20 :1), affording 2.0 g (38%) as a white solid. \(^1\)H NMR (CDCl \(_3\), 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 MgSO4, 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\(_2\) (2.5 mL, 34 mmol) and DMF (2 drops) in CH\(_2\)Cl\(_2\) was refluxed for 1h. All volatiles were removed under reduced pressure, giving the crude acid chloride, which was dissolved in CH\(_2\)Cl\(_2\) and cooled to 0 °C. To the solution AlCl\(_3\) (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\(_3\) and extracted with CH\(_2\)Cl\(_2\), which was dried over MgSO\(_4\) and concentrated under low pressure. The crude residue was purified by recrystallization, affording 0.43 g (84%) as a white solid. \(^1\)H NMR (CDCl\(_3\), 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\(_4\) and concentrated under low pressure. The crude residue was purified by column chromatography (SiO\(_2\), hexane : ethyl acetate = 20
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 MnO₂ (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 (SiO₂, hexane : ethyl acetate = 7 : 1), affording 0.76 g (77%) as a white solid. ¹H NMR (CDCl₃, 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 (I)**, A reaction mixture of d, and e in toluene (130 mL) was refluxed for 1h, added PPh₃ (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 PPh₃. The suspension generated was filtered, and the solution was concentrated under reduced pressure. The crude residue was purified by column chromatography (SiO₂, hexane : dichloromethane = 10 : 1), affording 0.11 g (29%) as an yellow solid. ¹H NMR (CDCl₃, 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). ¹³C-NMR (CDCl₃) 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⁺).

Resolution of cis-I 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$^{-2}$) for 30 min.
Figure S3. Polarized absorption spectra of parallel ($A_\parallel$) 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 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.