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Supporting Information

Nonclassical Dual Controlling Circularly Polarized Luminescence Modes of Binaphthyl–Pyrene Organic Fluorophores in Fluidic and Glassy Media

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1. Experimental

1.1. General methods

Chloroform ($CHCl_3$), purchased from Wako Pure Chemical (Osaka, Japan), was used for optical measurements. Compounds (*R*)-**1** and (*S*)-**1** were prepared using a previously reported method.[1]

1.2. Syntheses of (*R*)-2 and (*S*)-2

The reaction mixture of (*R*)-2′-ethoxy-1,1′-binaphthalene-2ol (314 mg, 1.00 mmol), 2(2-chloroethoxy)ethanol (0.22 mL, 2.00 mmol) and potassium carbonate (K_2CO_3) (415 mg, 3.00 mmol) in dry *N,N*-dimethylformamide (DMF) (30 mL) was stirred for 24 h under argon atmosphere at 120 ºC. After filtration, the reaction mixture was concentrated under vacuum. Dichloromethane (CH_2Cl_2) was added to the residue, and the mixture was washed with brine. The organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$) and concentrated under vacuum. The crude product was purified by silica gel column chromatography (eluent: ethyl acetate/hexane = 1/1). The (*R*)-binaphthyl intermediate was obtained as a pale yellow viscous liquid [369 mg (Yield: 92%)].

The (*R*)-binaphthyl intermediate (403 mg, 1.00 mmol) was added to a mixture of 1-pyreneacetic acid (390 mg, 1.50 mmol), *N,N′*-dicyclohexylcarbodilmide (413 mg, 2.00 mmol), and 4-*N,N*-dimethylaminopyridine (122 mg, 1.00 mmol) in dry CH_2Cl_2 (50 mL). The reaction mixture was stirred for 24 h under argon atmosphere at room temperature. Then, CH_2Cl_2 was added to the reaction mixture and washed with saturated aqueous sodium bicarbonate ($NaHCO_3$) and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude product was purified by silica gel column chromatography (eluent: ethyl acetate/hexane = 1/2). (*R*)-**2** was obtained as a pale yellow viscous solid [438 mg (Yield: 68%)]. (*S*)-**2** was prepared by the same procedure in 62% overall yield, from (*S*)-2′-ethoxy-1,1′-binaphthalene-2-al. ^1H NMR (acetone-d_6, 400 MHz) δ 8.08-8.26 (m, 7H), 8.03 (t, *J* = 7.8 Hz, 1H), 7.87-7.96 (m, 4H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.11-7.32 (m, 4H), 7.03 (d, *J* = 8.7 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 4.32 (s, 2H), 3.95-4.02 (m, 4H), 3.84-3.87 (m, 2H), 3.32 (t, *J* = 4.6 Hz, 2H), 3.09-3.19 (m, 2H), 0.94 (t, *J* = 6.9 Hz, 3H).

1.3. Measurement of the fluorescence spectra

Fluorescence spectra and absolute photoluminescence quantum yields in $CHCl_3$ solution and poly(methyl methacrylate) (PMMA) film were measured using an absolute unpolarized photoluminescence (PL) quantum yield measurement system (Hamamatsu Photonics C9920-02, Hamamatsu, Japan) under air atmosphere at room temperature. PMMA films doped with chiral **1** or **2** were prepared using a spin coater at 3000 rpm (Opticoat MS-A100, Mikasa, Tokyo, Japan). Chiral **1** or **2**-doped PMMA films were prepared by drop-casting tetrahydrofuran (THF) solutions, in which the PMMA concentration was fixed at 0.1 g/mL, onto quartz plates. Chiral **1** (or **2**) was added to the PMMA/THF solutions at concentrations of 0.01 mol/L. The cast films were dried at room temperature. Chiral **1**, dissolved in $CHCl_3$, was also excited at 340 nm, at all measured concentrations. Chiral **1** in PMMA film was excited at 340 nm. Chiral **2**, both when dissolved in $CHCl_3$ and when dispersed in a PMMA film, was excited at 340 nm.

The circularly polarized luminescence (CPL) spectra in $CHCl_3$ solution and PMMA film were measured using a JASCO CPL-200 spectrofluoropolarimeter (Tokyo, Japan), at room temperature. The instrument used a scattering angle of 0° from the excitation of unpolarized, monochromated incident light with a bandwidth of 10 nm. Chiral **1** and **2** were excited at 340 nm, both when dissolved in $CHCl_3$ and when dispersed in a PMMA film. The CPL spectra were approximated using the simple moving average (SMA) method.

1.4. Measurement of the circular dichroism (CD) and UV absorption spectra

CD and UV absorption spectra for all compounds when dissolved in $CHCl_3$ or dispersed in PMMA film were measured using a JASCO J-820 spectropolarimeter, at room temperature. The CD spectra were approximated using the SMA method.

References

1. E. J. Jun, H. N. Won, J. S. Kim, K-H. Lee and J. Yoon, *Tetrahedron Lett.*, 2006, **47**, 4577.