

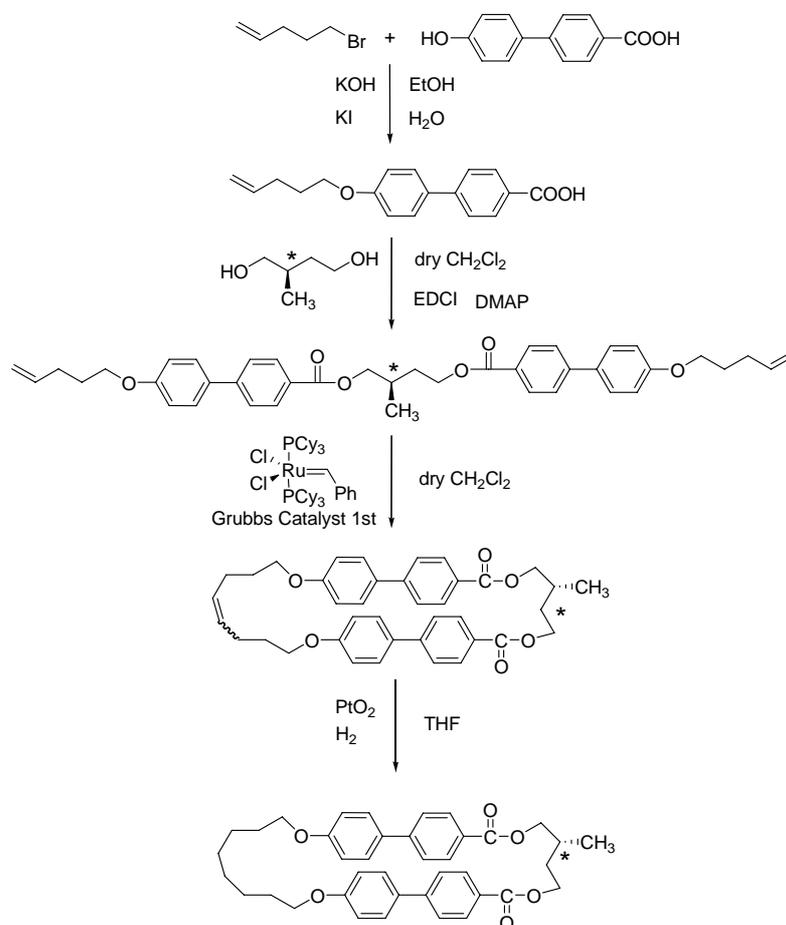
## Cholesteric induction power enhanced by macrocyclization in liquid crystalline dimers having chiral spacer

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### Supporting Information

#### 1. Synthesis of dimers

The synthetic route of the dimers is shown in Fig. S1 and each step are described below.



**Figure S1.** Synthetic route leading to L-dimer and C-dimer.

#### *Synthesis of 4'-(4-Penten-1-yloxy) biphenyl-4-carboxylic acid*

4'-Hydroxy-4-biphenylcarboxylic acid (3.0 g, 14.0 mmol) was dissolved with potassium hydroxide (1.77 g, 31.5 mmol) and potassium iodide (0.1 g) in a mixture of ethanol (60 ml) and water (20 ml). 5-Bromo-1-pentene (2.23 g, 15.0 mmol) was dropped into the solution and

the mixture was refluxed for 24 h. The solution was cooled, poured into 200 ml of water, and acidified with concentrated hydrochloric acid. The solid carboxylic acid was removed by filtration and washed with water. The crude product was recrystallized from acetic acid to give (2.93 g, 74%) as white plates.  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ):  $\delta$  7.98 (2H, m, *ortho* to the carboxyl group on the biphenyl), 7.74 (2H, m, *meta* to the carboxyl group on the biphenyl), 7.67 (2H, m, *meta* to the ether on the biphenyl), 7.04 (2H, m, *ortho* to the ether on the biphenyl), 5.93–5.83 (1H, m,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ), 5.04 (2H, m,  $-\text{CH}=\text{CH}_2$ ), 4.04 (2H, t,  $J=6.5$  Hz,  $-\text{OCH}_2\text{CH}_2-$ ), 2.23–2.17 (2H, m,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ), 1.87–1.80 (2H, m,  $-\text{OCH}_2\text{CH}_2-$ ).

#### *Synthesis of L-dimer*

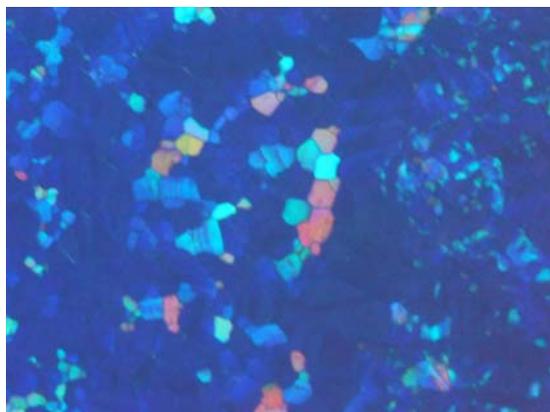
To a solution of (R)-(+)-2-methyl-1,4-butanediol (0.118 g, 1.14 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 ml) we added 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (0.720 g, 3.76 mmol), 4-dimethylaminopyridine (0.306 g, 2.50 mmol), and 4'-(4-penten-1-yloxy)biphenyl-4-carboxylic acid, (0.706 g, 2.50 mmol). The mixture was stirred at room temperature for 1 day. The reaction mixture was evaporated under reduced pressure and poured into methanol. The precipitate was filtered and recrystallized from chloroform/ethanol to give L-dimer (0.528 g, 73 %) in the form of white crystals. For L-dimer,  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.07 (4H, m, *ortho* to the ester on the biphenyl), 7.60 (4H, m, *meta* to the ester on the biphenyl), 7.55 (4H, m, *meta* to the ether on the biphenyl), 6.98 (4H, m, *ortho* to the ether on the biphenyl), 5.92–5.82 (2H, m,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ), 5.05 (4H, m,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ), 4.47 (2H, m,  $-\text{COOCH}_2\text{CH}_2-$ ), 4.28 (2H, m,  $-\text{COOCH}_2\text{CH}(\text{CH}_3)-$ ), 4.02 (4H, t,  $J=6.3$  Hz,  $-\text{OCH}_2\text{CH}_2-$ ), 2.25 (5H, m,  $-\text{OCH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$ ), 2.05 (1H, m,  $-\text{CH}(\text{CH}_3)\text{CH}_2-$ ), 1.92 (4H, m,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ), 1.77 (1H, m,  $-\text{CH}(\text{CH}_3)\text{CH}_2-$ ), 1.15 (3H, d,  $J=6.6$  Hz,  $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$ ). The spectrum is shown in Supporting Information Figure 5(a).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  16.9, 28.4, 30.1, 30.3, 32.6, 62.9, 67.3, 69.3, 114.9, 115.3, 126.4, 128.3, 130.1, 132.2, 137.7, 145.2, 159.3, 166.5.  $[\alpha]_D^{28} -23.0^\circ$  ( $c$  1.00,  $\text{CHCl}_3$ )

#### *Synthesis of C-dimer*

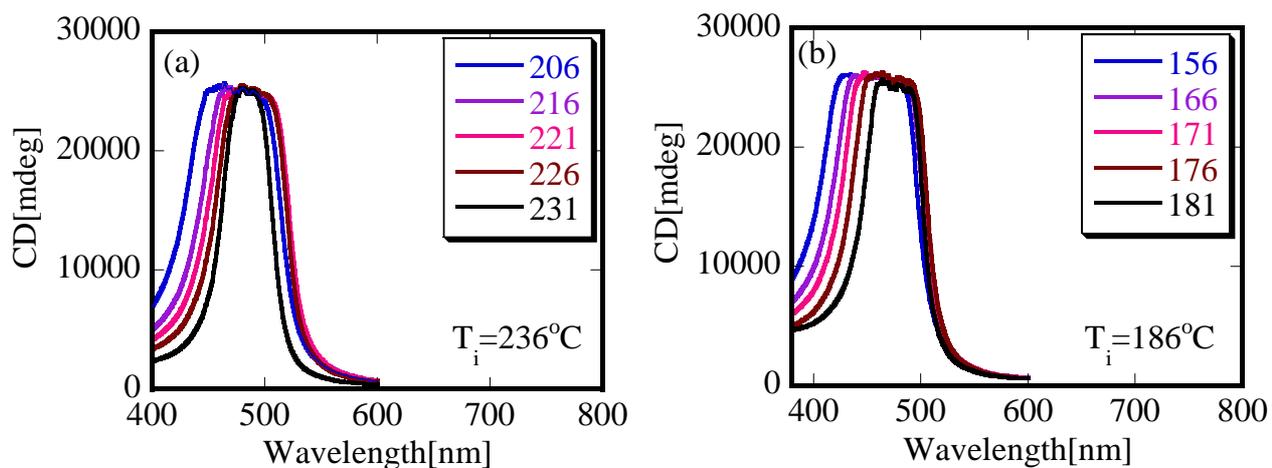
The cyclization of L-dimer (0.250 g, 0.396 mmol) was performed under reflux in dry  $\text{CH}_2\text{Cl}_2$  at a concentration of  $0.25 \text{ g L}^{-1}$  in the presence of the first Grubbs catalyst. The catalyst (0.032 g, 0.0396 mmol) was added. After evaporation of the solvent under reduced pressure, the concentrated solution was recovered by alumina flash chromatography to remove the catalyst residues. The crude product was purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ).

The product was hydrogenated in tetrahydrofuran under H<sub>2</sub> atmosphere in the presence of Adams' catalyst (PtO<sub>2</sub>). The reaction solution was filtered by celite545 to remove the catalyst residues and then evaporated. The residue was recrystallized from toluene/hexane to give C-dimer (0.092g, 38%) as white needles. The absence of the resonances of molecular ends of -CH=CH<sub>2</sub> in <sup>1</sup>H-NMR spectra establishes the cyclic structure. For C-dimer, <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.98-7.87 (4H, m, *ortho* to the ester on the biphenyl), 7.38-7.34 (8H, m, *meta* to the ester on the biphenyl, *meta* to the ether on the biphenyl), 6.84 (4H, m, *ortho* to the ether on the biphenyl), 4.56(1H, m, -COOCH<sub>2</sub>CH(CH<sub>3</sub>)-), 4.44 (1H, m, -COOCH<sub>2</sub>CH(CH<sub>3</sub>)-), 4.32 (1H, t, J=10.7Hz, -COOCH<sub>2</sub>CH<sub>2</sub>-), 4.04 (4H, t, J=6.3Hz, -OCH<sub>2</sub>CH<sub>2</sub>-), 4.00 (1H, t, J=10.5Hz, -COOCH<sub>2</sub>CH<sub>2</sub>-), 2.20, 1.66 (3H, m, -COOCH<sub>2</sub>CH<sub>2</sub>-, -COOCH<sub>2</sub>CH(CH<sub>3</sub>)-), 1.82 (4H, m, -OCH<sub>2</sub>CH<sub>2</sub>-), 1.55 (4H, m, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.44 (4H, m, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.10 (3H, d, J=6.8Hz, -CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>-). The spectrum is shown in Supporting Information Figure 5(b). <sup>13</sup>C-NMR(CDCl<sub>3</sub>): δ 17.0, 25.1, 27.7, 28.0, 31.1, 33.9, 62.7, 67.8, 69.0, 115.0, 126.1, 128.2, 130.1, 131.9, 144.9, 159.2, 166.5. [α]<sub>D</sub><sup>28</sup> -213.7° (c 1.00, CHCl<sub>3</sub>)

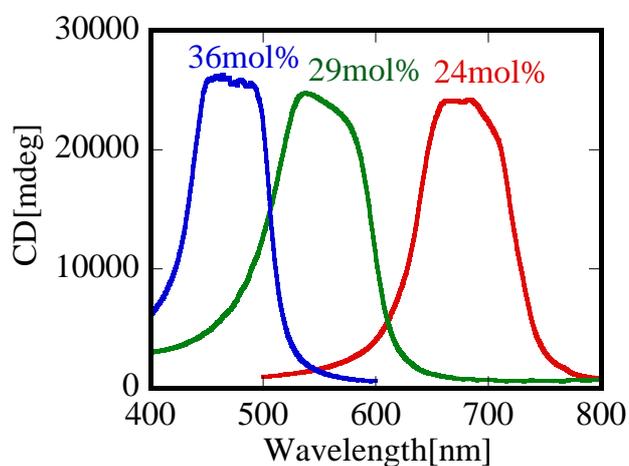
### Other experimental data



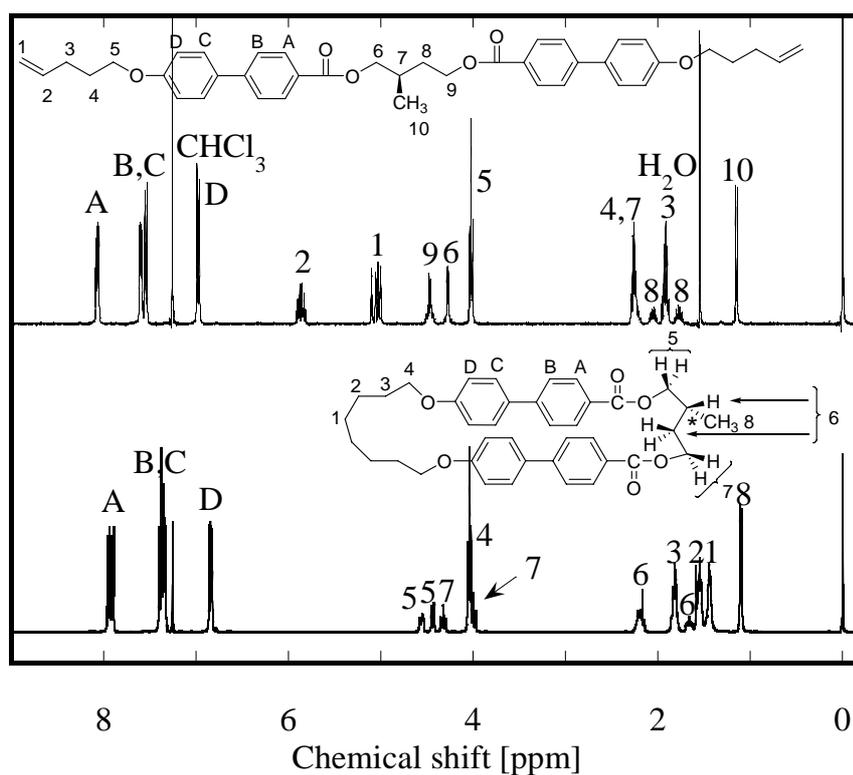
**Fig. S2** Polarized optical micrograph observed for C-dimer(R)/CBPBB with the dimer content of 8 mol% at 233°C (the BP phase) on cooling.



**Fig. S3** Reflection CD spectra of the chiral nematic LCs of (a) C-dimer(R) / CBPBB (8.1mol%) and (b) L-dimer(R) / CBPBB (36mol%) mixtures observed at temperatures indicated in the figure.



**Fig. S4** Reflection CD spectra of the chiral nematic LCs of the L-dimer(R) / CBPBB mixtures measured at  $T = T_i - 10$ . The chiral dimer concentrations are indicated in the figure.



**Fig. S5** <sup>1</sup>H-NMR spectra of L-dimer(R) and C-dimer(R) in chloroform measured at 25 °C.