Electronic Supplementary Information for "Striped Fullerene Patterns Constructed in the Elastically Anisotropic Cholesteric Liquid Crystals"

Soeun Kim,^a Shin-Woong Kang^{*b} and Kwang-Un Jeong^{*a}

^a Department of Polymer-Nano Science and Technology and Department of Flexible and Printable Electronics, Chonbuk National University, Jeonju 561-756, Korea ^b Department of BIN Fusion Technology, Chonbuk National University, Jeonju 561-756 Korea

* To whom the correspondence should be addressed. E-mail: kujeong@jbnu.ac.kr and swkang@jbnu.ac.kr

1. Synthesis of fullerene-based reactive molecule (C60RM)

Materials: 6-bromohexanoic acid (95%, TCI), 1,5-hexadien-3-ol (95 %, Aldrich), 4,4biphenol (95%, TCI), 6-bromohexan-1-ol (95%, TCI), malonyl chloride (95%, TCI), fullerene (C₆₀, 99%, MER), *N*,*N*'-dicyclohexylcarbodiimide (DCC, 99%, Fluka), dimethylaminopyridine (DMAP, 99%, Fluka), triethylamine (TEA, 99%, Sigma-Aldrich), 1,8-diazabicyclo [5,4,0]undec-7-ene (DBU, 98%, Sigma-Aldrich), tetrabromomethane (99%, Sigma-Aldrich), and potassium carbonate (K₂CO₃, 99.5%, Showa) were used as received. Methylene chloride (MC), *N*,*N*-dimethylformamide (DMF) and toluene were purified before use.



Fig. S1 ¹H NMR spectrum of compound 1

6-bromohexa

Hexa-1,5-dien-3-yl6-bromohexanoate (1): With stirring the solution of 6-bromohexanoic acid (7.32 g, 30 mmol) and 1,5-hexadien-3-ol (4.1 g, 41 mmol) in 80 mL of dried CH₂Cl₂, DMAP (0.45 g, 3 mmol) was added and cooled to 0 °C. DCC (7.74 g, 30 mmol) was additionally added. After stirring for 30 min at 0 °C, the reacting mixture was additionally stirred at room temperature for 24 h. Dicyclohexylurea was filtered off and the organic mixture was washed twice with 2 M HCl and aqueous NaHCO₃ solution. It was purified by column chromatography with silica gel using CH₂Cl₂. For confirming the purity, thin layer chromatography (TLC) was identified by iodine colour developing reagent. Resulting product was colourless and transparent viscous liquid (yield: 96%, 7.9 g). ¹H NMR (CDCl₃): δ =1.47 (m; 2H), 1.66 (m; 2H), 1.87 (m; 2H), 2.3-2.4 (m; 4H), 3.38 (t; 2H), 5.00-5.35 (m; 5H), 5.60-5.85 (m; 2H)



Fig. S2 ¹H NMR spectrum of compound 2

Hexa-1,5-dien-3-yl6-(4-hydroxy-4'-biphenoxy)hexanoate (2): A solution of compound 1 (7.9 g, 28.8 mmol), 4,4-biphenol (11.94 g, 63.8 mmol) and K₂CO₃ (8.81 g, 63.8 mmol) in 150 mL of dried DMF was refluxed at 90 °C for 16 h. After reaction, solvent was removed in

vacuum and the residue was dissolved in ethyl acetate and washed with distilled water several times. The organic layer was dried over MgSO₄. It was purified by column chromatography with silica gel using ethyl acetate: hexane = 2:8 (volume ratio). Resulting product was viscous and light yellowish liquid (yield: 54%, 5.95 g). ¹H NMR (CDCl₃): δ =1.52 (m: 2H), 1.72 (m: 2H), 1.81 (m: 2H), 2.3-2.4 (m: 4H), 3.97 (t; 2H), 4.96 (s; 1H), 5.00-5.35 (m; 5H), 5.60-5.85 (m; 2H), 6.88 (d; 2H), 6.92 (d; 2H), 7.42 (q; 4H).



Fig. S3 ¹H NMR spectrum of compound 3

Hexa-1,5-dien-3-yl6-(4-6-hydroxyhexanoxy-4'-biphenoxy)hexanoate (3): A solution of compound **2** (7.4 g, 19.46 mmol), 6-bromohexan-1-ol (4.15 g, 23.05 mmol) and K₂CO₃ (2.76 g, 20 mmol) in 100 mL of dried DMF was refluxed at 90 °C for 24 h. After reaction, solvent was evaporated and the residue was dissolved in chloroform and washed with distilled water several times. After drying the organic layer with MgSO₄, it was purified by column chromatography with silica gel using ethyl acetate: hexane = 3: 7 (volume ratio). Resulting product was white powder (yield: 48.5%, 4.53 g). ¹H NMR (CDCl₃): δ =1.42-1.85 (m; 14H), 2.3-2.4 (m; 4H), 3.67 (t; 2H), 3.99 (m; 4H), 5.06-5.35 (m; 5H), 5.69-5.84 (m; 2H), 6.92 (d;

2H), 6.93 (d; 2H), 7.46 (d; 4H)



Fig. S4 ¹H NMR spectrum of compound 4

Bis[Hexa-1,5-dien-3-yl6-(4-6-hydroxyhexanoxy-4'-biphenoxy)hexanoate] malonate (4): A solution of compound **3** (2.4 g, 4.99 mmol) and triethylamine (0.7 mL, 4.99 mmol) in 40 mL of dried methylene chloride was stirred at room temperature and cooled to 0 °C for 10 min. At 0 °C, malonyl chloride (0.219 mL, 2.77 mmol) was drop-wisely added and stirred at room temperature for 20 h under nitrogen atmosphere. After reaction, the organic solvent was removed in vacuum. It was purified by column chromatography with silica gel using ethyl acetate: hexane=3:7 (volume ratio). Resulting product was white waxy solid (yield: 76.6%, 1.79 g). ¹H NMR (CDCl₃): δ =1.42-1.85 (m; 28H), 2.3-2.4 (m; 8H), 3.77 (s; 2H), 3.97 (t; 8H), 4.16 (t; 4H), 5.06-5.35 (m; 10H), 5.69-5.84 (m; 4H), 6.92 (d; 4H), 6.93 (d; 4H), 7.46 (d; 8H).



Fig. S5 ¹H NMR spectrum of C60RM

Bis[Hexa-1,5-dien-3-yl6-(4-6-hydroxyhexanoxy-4'-biphenoxy)hexanoate]*1,2-ethano*[60]*fullerene-61,61-dicarboxylate (5) (C60RM*): A solution of compound **4** (0.156 g, 0.152 mmol) and fullerene (0.22 mg, 0.304 mmol) in 200 mL of dried toluene was stirred at room temperature under nitrogen atmosphere. After 1 h, tetrabromomethane (52 mg, 0.152 mmol) and DBU (46 μ L, 0.304 mmol) were added and stirred at room temperature for 24 h. After reaction, the organic solvent was removed in vacuum. It was first purified by column chromatography with silica gel using methylene chloride: methanol = 50:1 (volume ratio) to remove the unreacted fullerene. Afterwards, it was further purified by column chromatography with silica gel using methylene chloride. Resulting product was dark brownish solid (yield: 41.43%, 0.11 g) which showed a good solubility relative to pristine fullerene. ¹H NMR (CDCl₃): δ =1.42-1.85 (m; 28H), 2.36-2.4 (m; 8H), 3.97 (5; 8H), 4.51 (t; 4H), 5.16-5.29 (m; 10H), 5.73-5.80 (m; 4H), 6.93 (d; 8H), 7.46 (d; 8H).

2. ¹H Nuclear Magnetic Resonance of C60RM and Its Intermediates

All the chemical compounds synthesized in this research were purified by several column chromatograpies. Their chemical structures and purity were confirmed by proton (¹H) nuclear magnetic resonance (NMR, JNM-EX400) in deuterated chloroform (CDCl₃). Chemical shifts were quoted in part per million (ppm) with a reference of tetramethylsilane (TMS). Chemical structure of compound 1 was confirmed from the ¹H chemical shift at –Br-CH₂- (3.38 ppm) in Fig. S1. Protons of the methyl group created a resonance signal (Br-CH₃) at 2.5 ppm. The α protons in esters were deshielded by the anisotropy of the adjacent (C=O) group.⁷ The protons on a carbon next to a carbonyl group gave the chemical shift at the 2.33 ppm.⁷ The peak in the 3.5- to 4.8 -ppm region is the key to identify an ester group.⁷ The protons of esters appeared in the 5.07 ppm which was a little bit highly shifted than theoretical value because of adjacent to a double bond (allyic hydrogens). Chemical structure of compound 2 was confirmed by the chemical shift of 6.5-8.0 ppm which was a typical chemical shift of aromatic ring in Fig. S2. In ethers, the protons on the carbon next to oxygen were deshielded due to the electronegativity of the attached oxygen, and they appeared in the range 3.2-3.8 ppm.⁷ The protons of ether in compound 2 appeared at the 3.97 ppm as triplet. Also, the highly variable chemical shift of the -OH hydrogen showed up in the 4.96 ppm as a singlet. Chemical structure of compound 3 was identified by increased integration of protons in ethers (R-O-CH-, 3.99 ppm), alkanes (R-CH₂-R, 1.2-1.4 ppm) and protons on the α carbon (CH-O-H, 3.67 ppm) in Fig. S3. Chemical structure of compound 4 was confirmed by new peak (C=O-CH₂-C=O, 3.77 ppm) as a singlet and highly shifted chemical shift in esters adjacent to malonyl group (3.67 ppm \rightarrow 4.16 ppm) in Fig. S4. Chemical structure of compound 5 (C60RM) was identified by the disappearance of the singlet peak (C=O-CH₂-C=O, 3.77 ppm) and further shifted the proton chemical shift (4.16 ppm \rightarrow 4.51 ppm) due to the electron-withdrawing properties of fullerene, as shown in Fig. S5.

3. Preparation of antiparallel-rubbed electro-optic LC cells

The antiparallel-rubbed electro-optic LC cells were fabricated with planar alignment layer (Japan Synthetic Rubber, AL-16139, Japan) coated on indium tin oxide (ITO) glass substrates. Using a spin coater (Korea Spin Coater system, ECF-2, Korea), planar alignment layer was first coated on ITO glass substrates. The spinning rate was increased up to 3000 rpm and maintained for 70 s after spin coating at 600 rpm for 23 s. The spin coated substrates were cured in a drying oven (JEIO TECH, NO-600M, Korea) with two-step processes. After soft baking for 5 min at 80 °C, the spin coated substrates were cured at 200 °C for 60 min. After rubbing process, two substrates were anti-parallel assembled into a standard EO cell separated by 10 µm thick tape-spacers by utilizing automatic press machine (Neo system, APD-01, Japan).

4. Thermal Properties

Differential scanning calorimetry (DSC): The thermal behaviour of the phase transitions was studied using a Perkin-Elmer PYRIS Diamond differential scanning calorimetry (DSC). For DSC experiments, the sample weights were about 4.0 mg and the pan weights were kept constant with a precision of ± 0.001 mg. The temperature and heat flow scales were calibrated using standard materials at 5 °C min⁻¹ cooling and heating rates ranging from 2.5 to 40 °C min⁻¹. Transition temperatures were determined using the onset temperatures. Heating experiments always preceded the cooling experiments in order to eliminate previous thermal histories, and the cooling and heating rates were always kept identical. The onset temperature was defined by the cross-point of the peak slope and the baseline in the DSC trace. In cooling, the onset temperature was determined on the high-temperature side, and upon heating the onset temperature determined was on the low temperature side.



Fig. S6 Sets of DSC cooling (a) and subsequent heating (b) thermal diagrams for a C60RM molecule at scanning rates ranging from 2.5 to 40 $^{\circ}$ C min⁻¹.

DSC experiments were conducted during cooling and subsequent heating rates ranging from 2.5 to 40 °C min⁻¹ to detect various thermal transitions and to obtain quantitative thermodynamic properties of the thermal transitions. DSC results of C60RM showed only one peak both on cooling and on heating in Fig. S6. Although C60RM molecules contain

mosogenic group, it did not reveal liquid crystalline phase. The C60RM melts to isotropic state above 74.09 °C. The exothermic transition of 9.55 kJ/mol should indicate the crystallization process of C60RM. This result also was confirmed by POM experiments.



Fig. S7 Sets of DSC cooling (a) and subsequent heating (b) thermal diagrams for a c ompound 4 molecule at scanning rates ranging from 2.5 to 40 $^{\circ}$ C min⁻¹.

Fig. S7 represents DSC results of compound **4**. During cooling, the high transition with 21.93 kJ/mol (68.62 °C) indicated the phase transition from an isotropic melt to LC phase. On the other hand, the transition of the low temperature exothermic transition with 22.35 kJ/mol (43.04 °C) must be the crystal melting process. The compound **4** exhibits a LC phase between 68.62 °C and 43.04 °C which was also identified by POM observation.

Thermogravimetric analysis (TGA): To figure out the thermal stability and contents of fullerenes in C60RM molecules, thermogravimetric analysis (TGA, Q-50, TA instrument) was employed. The scanning rate was 10 °C min⁻¹ from 30 °C to 500 °C under nitrogen atmosphere.



Fig. S8 TGA results of compound 4 and C60RM

Thermal stability of C60RM and compound 4 was identified by utilizing thermogravimetric analysis (TGA), as shown in Fig. S8. C60RM began to degrade at 330 °C (5 % weight loss). Above 500 °C, compound 4 degraded completely, approximately 63 wt% of C60RM compound still remained. This result may come from the outstanding thermal stability of fullerene. According to the previous reports, the degradation temperature of fullerene (C₆₀) is known as above 927 °C.

5. Optical Properties: Ultraviolet-Visible (UV-Vis) spectroscopy

To investigate optical absorbance properties of C60RM, UV-Vis spectroscopy experiment was carried out. Solution for UV-Vis spectroscopy was prepared as 2 % (w/v) of C60RM compound in chloroform. UV-Vis spectroscopy experiment of C60RM was performed by utilizing SCINCO S-3100 UV-Vis spectrometer.



Fig. S9 UV-Vis spectra of C60RM, fullerene (C_{60}), and compound 4; the characteristic a bsorption spectrum of fullerene is shown in the area of square box around at 330 nm.

As shown in Fig. S9, a strong absorbance at 330 nm was observed. It is a characteristic absorption wavelength of the fullerene (C_{60}). With this result, the presence of fullerene in C60RM molecules is verified.

6. Identification of Phase Structures: 1D Wide Angle X-ray Diffraction (WAXD)

1D WAXD experiments were conducted in the reflection mode of a Rigaku 12 kW rotatinganode X-ray (Cu K α radiation) generator coupled to a diffractometer. The diffraction peak positions and widths were calibrated with silicon crystals in the high 2 θ -angle region (> 15°), and silver behenate in the low 2 θ -angle region. A hot stage was coupled to the diffractometer to study the structural evolutions with temperature changes during heating and cooling. The temperature of the hot stage was calibrated to be within ±1 °C error. Samples were scanned across a 2 θ -angle range of 1.5-35° at the scanning rate of 2.5° min⁻¹. In 1D WAXD experiments, background scattering was subtracted from the sample scans.



Fig. S10 Set of 1D WAXD powder patterns of C60RM molecules during heating at the rate of 2.5 °C min⁻¹ at different temperatures between 35 and 130 °C (a) and set of 1D WAXD powder patterns of compound 4 molecules during heating at the rate o f 2.5 °C min⁻¹ at different temperatures between 30 and 100 °C (b).

To identify molecular arrangement of the C60RM, 1D WAXD experiments were performed at different temperatures between 35 and 130 °C during heating at the rate of 2.5 °C min⁻¹ and

its 1D WAXD powder pattern is shown in Fig. S10a. In this 1D WAXD powder pattern, diffraction information on the molecular arrangements of the C60RM appears at $2\theta = 10.68^{\circ}$ and 20.15°. Flexible alkyl chains and rigid mosogens in the C60RM exhibit broad reflections. Attaching mesogens to fullerene (C₆₀) was intended to manage molecular orientation. However, it causes to poor molecular packing in reality. These results are supported later by POM observation (Fig. S11). Molecular arrangement of compound **4** was also investigated by 1D WAXD experiment at different temperatures between 30 and 100 °C during heating at the rate of 2.5 °C min⁻¹ (Fig. S10b). In this 1D WAXD powder pattern, diffraction information on molecular arrangements of the compound **4** appears at $2\theta = 8.98^{\circ}$, 12.05°, 20.06°, 22.98° and 27.68° at the temperature below 55 °C and $2\theta = 20.514$ at the temperature between 60 °C and 75 °C as a sharp peak. Above 80 °C, the peak at $2\theta = 20.514$ becomes broad. These results well match with DSC date (Fig. S7) and POM observation (Fig. S12). Information on more detailed molecular structure and packing could be acquired by further investigation.

7. Morphological Observation: Polarized Optical Microscopy (POM)

Optical textures of the ordered phases at different temperatures were observed with crosspolarized optical microscopy (POM, Nikon ECLIPSE LV100POL) coupled with a METTER FP 90 heating stage to investigate morphology on the micrometer scale. A tint retardation plate (530 nm) was also placed between the objective lenses and the eyepieces to identify the orientation of molecules in the POM textures.



Fig. S11 POM textural observation of C60RM at room temperature.

POM observation was employed to examine the morphology of C60RM and to support the results of DSC. POM observation of C60RM was conducted upon cooling at 1 °C min⁻¹ from 80 °C (isotropic phase) to room temperature (crystalline phase). As shown in Fig. S11, the optical texture is dark and shapeless, and its birefringence is relatively weak. It indicates the fact that the crystalline structure of C60RM has immature anisotropy crystalline formation as discussed in Fig. S10a. Even though the C60RM contains mesogenic group, it does not reveal liquid crystalline phase. It is believed that the C60RM does not show the liquid crystalline phase because of the relatively bulky fullerene molecule. To figure out the cause of obstructing liquid crystalline phase, POM observation of the compound **4** was conducted.



Fig. S12 POM morphological observation of the compound 4 at 68 °C (a) and 30 °C (b) during cooling at 5 °C min⁻¹.

The optical textures of the compound 4 have been recorded upon cooling 5 °C min⁻¹ from 75 °C to room temperature, and textures at 68 °C and 30 °C are shown in Fig. S12a and S12b, respectively. The photograph taken at 68 °C (Fig. S12a) shows typical nematic droplets. The further decreasing the temperature to 30 °C (Fig. S12b) results in a focal-conic like texture often observed in a layered phase. These results are matched with those of DSC as shown in Fig. S7.



Fig. S13 (a) POM morphological observation of the compound **4** sheared at 60 °C an d then annealed at room temperature. (b) POM texture with a tint plate between the objective lenses and eyepieces.

In order to confirm the macroscopic molecular orientation of the highly ordered liquid crystalline phase of compound **4**, a mechanically oriented liquid crystalline phase film was

observed under POM image. Fig. S13a shows the POM image of compound **4** sheared at 60 °C and then annealed at room temperature. The bright "lines" are the oriented bulk sample, and the shear direction is along these "lines". The "lines" are bright because the molecules are in the ordered liquid crystalline phase, and the direction of uniaxial optic axis is not parallel to the directions of the polarizer or analyzer of the POM.¹⁰⁻¹¹ A tint retardation plate (530 nm) was also applied between polarizers to identify the orientation of molecules (i.e., optic axis) in the POM textures, as shown in Fig. S13b. The sheared "lines" are yellow in color, which means that retardation of the sample is subtracted by the tint plate. The refractive index parallel to the "lines" is higher than the refractive index perpendicular to the "lines". The uniaxial optic axis with a positive birefringence is aligned along the shear direction.



Fig. S14 Size distribution of C60RM particles in Fig. 2c of the main manuscript.