

Supporting Information

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69451 Weinheim, Germany

**Photoinduced Deformation of Crosslinked Liquid-Crystalline Polymer
Film Oriented by a Highly Aligned Carbon Nanotube Sheet****

Wei Wang, Xuemei Sun, Wei Wu, Huisheng Peng, and Yanlei Yu**

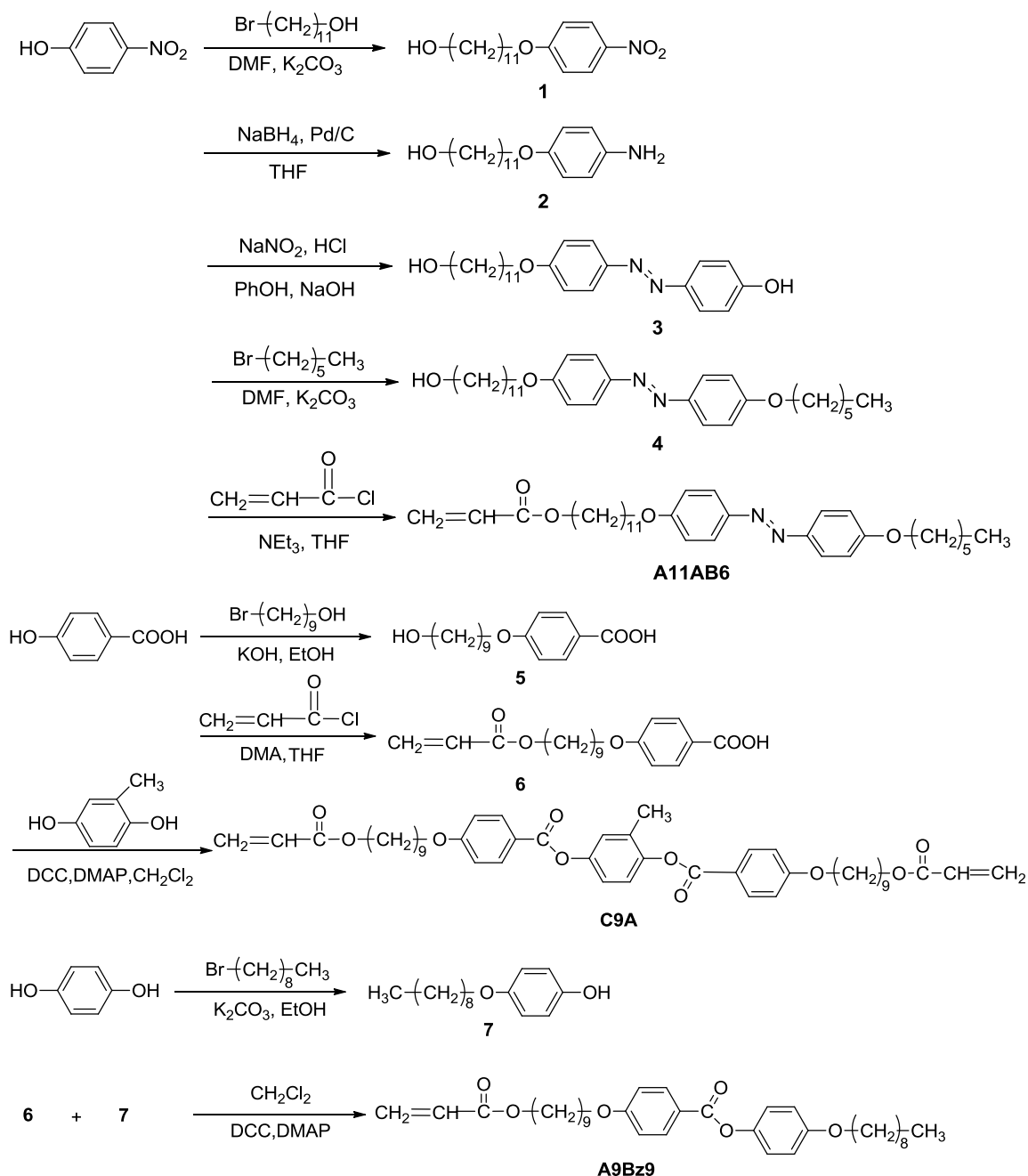
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Supporting Information

Preparation and characterization of monomers and crosslinker

The syntheses of LC monomers (**A11AB6** and **A9Bz9**) and crosslinker (**C9A**) are outlined in Scheme S1.

They were synthesized according to the literature.^[S1,S2]



Scheme S1. Synthetic routes of the LC monomers and crosslinker.

4-(11-Hydroxyundecyloxy)nitrobenzene (1). A mixture of 4-nitrophenol (3.32 g, 24 mmol), potassium carbonate (3.3 g, 24 mmol) and 11-bromo-1-nonanol (6 g, 24 mmol) was dissolved in dimethylformamide (DMF, 20 mL). The resulting solution was heated at 120 °C for 3 h. After the reacting mixture was cooled

to room temperature, 100 mL of water was added to the mixture. The precipitate was collected and extracted with ethyl acetate. The ethyl acetate solution was washed with water and dried with magnesium sulfate. After the solvent was evaporated, **1** (6.12 g, 20 mmol) was obtained in 83 % yield.

¹H-NMR (500 MHz, CDCl₃, 25 °C, TMS): δ 1.23-1.81 (m, 18H), 3.64 (t, *J* = 6.5 Hz, 2H), 4.11 (t, *J* = 6.5 Hz, 2H), 6.92-6.95 (m, 2H), 8.18-8.21 (m, 2H).

4-(11-Hydroxyundecyloxy)aniline (2). A mixture of **1** (6.12 g, 20 mmol) and 5 % Pd/C (1 g) was added to 40 mL tetrahydrofuran (THF), and the resulting suspension was stirred vigorously at 0 °C. Sodium borohydride (1.66 g, 44 mmol) was added to the solution. The suspension was stirred at room temperature for 4 h. About 60 mL HCl of hydrochloric acid (1 M) was added to the mixture at 0 °C. The precipitate was removed and an aqueous solution of potassium carbonate was added to the mixture to give pH = 10. The mixture solution was extracted with ethyl acetate and washed with water. Then the solution was dried with magnesium sulfate. After the solvent was evaporated, **2** (5.2 g, 17 mmol) was obtained in 85 % yield.

¹H-NMR (500 MHz, CDCl₃, 25 °C, TMS): δ 1.31-1.76 (m, 18H), 3.64 (t, *J* = 6.5 Hz, 2H), 3.87 (t, *J* = 6.5 Hz, 2H), 6.63-6.66 (m, 2H), 6.71-6.76 (m, 2H).

4-Hydroxy-4'-(11-hydroxyundecyloxy)azobenzene (3). **2** (5.2 g, 17 mmol) was dissolved in 100 mL hydrochloric acid (1 M) and the resulting solution was cooled at 0 °C. With stirred, sodium nitrite (1.2 g, 17 mmol) in water (10 mL) was added dropwise into the solution to produce diazonium salt. A mixture of phenol (1.6 g, 17 mmol) and sodium hydroxide (0.68 g, 17 mmol) in water (10 mL) was added slowly at 0 °C. An aqueous solution of potassium carbonate was added to the mixture to give pH = 8, and then a yellow solid precipitated. The reacting mixture was stirred at 0 °C for 3 h. After hydrochloric acid (1 M) was added to the reacting mixture to give pH = 4, the precipitated solid was collected and washed with water. The crude product was recrystallized from ethanol to give **3** (4.6 g, 12 mmol) in 70 % yield.

¹H-NMR (500 MHz, CDCl₃, 25 °C, TMS): δ 1.36-1.92 (m, 18H), 3.53 (t, *J* = 6.5 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 6.87-7.02 (m, 4H), 7.73-7.81 (m, 4H).

4-Hexyloxy-4'-(11-hydroxynonyloxy)azobenzene (4). A mixture of **3** (2.2 g, 5.6 mmol) and 1-bromohexane (1.1 g, 6.7 mmol) was dissolved in 10 mL of DMF, and potassium carbonate (0.9 g, 6.7 mmol) was then added to the solution. The resulting solution was heated at 120 °C for 3 h. After the reacting mixture was cooled to room temperature, 60 mL of water was added to the mixture. The precipitate was collected and extracted with ethyl acetate. The ethyl acetate solution was washed with water and dried with magnesium sulfate. After the solvent was evaporated, **4** (2.4 g, 5.1 mmol) was obtained in 91 % yield.

¹H-NMR (500 MHz, CDCl₃, 25 °C, TMS): δ 0.9 (t, *J* = 6.5 Hz, 3H), 1.42-1.84 (m, 26H), 3.65 (t, *J* = 6.5

Hz, 2H), 3.81 (t, $J = 6.5$ Hz, 2H), 4.02 (t, $J = 6.5$ Hz, 2H), 6.95-6.99 (m, 4H), 7.82-7.87 (m, 4H).

6-4-(4'-hexyloxyphenylazo)phenoxy]undecyl acrylate (A11AB6). A mixture of **4** (1.2 g, 2.5 mmol), triethylamine (0.7 ml, 5 mmol) and a trace amount of hydroquinone was dissolved in dried THF (100 mL), and the resulting solution was cooled at 0 °C. With stirring, 0.4 ml (5 mmol) of acryloyl chloride in dried THF (20 mL) was added dropwise to the solution, and the reacting mixture was stirred at room temperature for 24 h. The reacting mixture was poured into saturated sodium hydrogen carbonate solution, and the product was extracted with chloroform. The chloroform solution was washed with water and dried with magnesium sulfate. After the solvent was removed, a yellow solid obtained and it was purified by column chromatography on silica gel (chloroform) and recrystallized from ethyl acetate and methanol to give **A11AB6** (0.6g, 1.1mmol) in 46 % yield.

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25 °C, TMS, shown in **Figure S1**): δ 0.90 (t, $J = 6.5$ Hz, 3H), 1.32-1.81 (m, 26H), 3.91-4.00 (m, 4H), 4.13 (t, $J = 6.5$ Hz, 2H), 5.81 (dd, $J = 10$, 2 Hz, 1H), 6.11 (dd, $J = 17$, 10 Hz, 1H), 6.40 (dd, $J = 17$, 2 Hz, 1H), 6.94-7.06 (m, 4H), 7.4-7.5 (m, 4H). Anal Calcd for $\text{C}_{32}\text{H}_{46}\text{N}_2\text{O}_4$: C, 73.55 %; H, 8.94 %; N, 5.36%. Found: C, 73.53 %; H, 8.87%; N, 5.36 %.

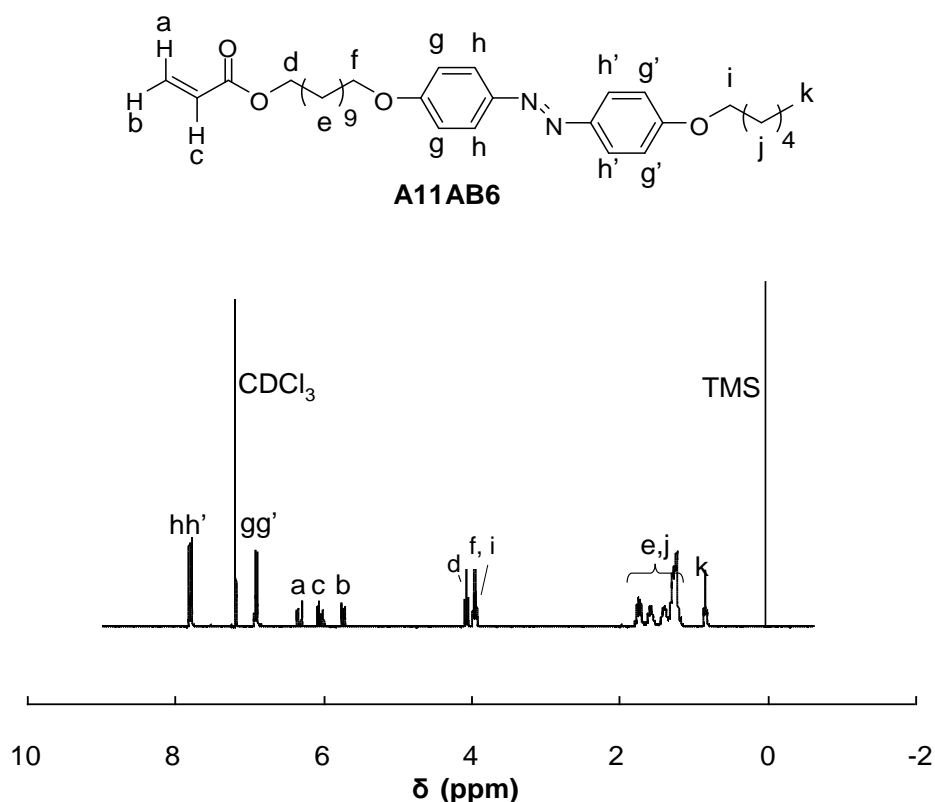


Figure S1. $^1\text{H-NMR}$ spectrum of the monomer **A11AB6**.

4-(9-hydroxynonyloxy) benzoic acid (5). A solution of KOH (3 g, 54 mmol) in water (100 mL) was added to a solution of 4-hydroxybenzoic acid (3 g, 22 mmol) in ethanol (50 mL). The mixture was heated to 90 °C for 30 min and a solution of 9-bromo-1-nonanol in 30 mL of ethanol was then added. After

refluxed for additional 36 h, the reaction mixture was cooled and acidified with 2.5 M HCl to pH = 3~4. A white precipitate was formed and filtered. The residue was recrystallized to give **5** (4.2 g) in 70 % yield. ¹H-NMR (500 MHz, CDCl₃, 25 °C, TMS): δ 1.35-1.97 (m, 14H), 3.53 (t, *J* = 6.5 Hz, 2H), 4.03 (t, *J* = 6.5 Hz, 2H), 6.93-6.97 (m, 2H), 7.91-7.96 (m, 2H).

4-(9-acryloyloxynonyloxy) benzoic acid (6). A mixture of **5** (4.2 g, 15.2 mmol), N,N-dimethylaniline (DMA, 5.7 mL, 45.6 mmol) was dissolved in dried THF (60 mL) under Ar atmosphere, and the resulting solution was cooled at 0 °C. With stirring, acryloyl chloride (3.7 mL, 45.6 mmol) in dried THF (30 mL) was added dropwise to the solution, and then the reaction mixture was stirred at room temperature for 48 h. The reaction mixture was evaporated and extracted with chloroform. The chloroform solution was washed with water and dried with magnesium sulfate. After the solvent was removed, a white solid obtained was purified by column chromatography on silica gel (chloroform) and recrystallized from ethanol to give **6** (3.5 g, 10.6 mmol) in 70% yield.

¹H-NMR (500 MHz, CDCl₃, 25 °C, TMS): δ 1.26-1.85 (m, 14H), 4.03 (t, *J* = 6.5 Hz, 2H), 4.20 (t, *J* = 6.5 Hz, 2H), 5.84 (dd, *J* = 2, 10 Hz, 1H), 6.16 (dd, *J* = 10, 17 Hz, 1H), 6.43 (dd, *J* = 2, 17 Hz, 1H), 6.90-6.95 (m, 2H), 8.00-8.07 (m, 2H).

1,4-bis[4-(9-acryloyloxynonyloxy)benzoyloxy]-2-methylbenzene (C9A).

A mixture of **6** (1.72 g, 5.2 mmol), methylhydroquinone (0.32 g, 2.6 mmol), 4-dimethylaminopyridine (DMAP, 1 g, 5.2 mmol) and dicyclohexyl carbodiimide (DCC, 3.4 g, 15.6 mmol) was dissolved in dried CH₂Cl₂ (40 mL) under Ar atmosphere. The mixture was then stirred at room temperature for 48 h. The precipitate formed during the reaction was filtered off and the organic solution was washed with water. The mixture was dried with magnesium sulfate and the solvent was removed. The crude product was purified by silica gel column chromatography using chloroform as the eluent and recrystallized from methanol to give **C9A** (1.2 g, 1.56 mmol) in 60 % yield.

¹H-NMR (500 MHz, CDCl₃, 25 °C, TMS, shown in **Figure S2**): δ 1.35-1.85 (m, 28H), 2.24 (s, 3H), 4.05 (t, *J* = 6.5 Hz, 4H), 4.18 (t, *J* = 6.5 Hz, 4H), 5.74 (dd, *J* = 2, 10 Hz, 2H), 6.07 (dd, *J* = 10, 17 Hz, 2H), 6.33 (dd, *J* = 2, 17 Hz, 2H), 6.95-6.99 (m, 4H), 7.12-7.36 (m, 4H), 8.12-8.17 (m, 3H). Anal Calcd for C₄₅H₅₆O₁₀: C, 71.43 %; H, 7.41 %. Found: C, 71.68 %; H, 7.48 %.

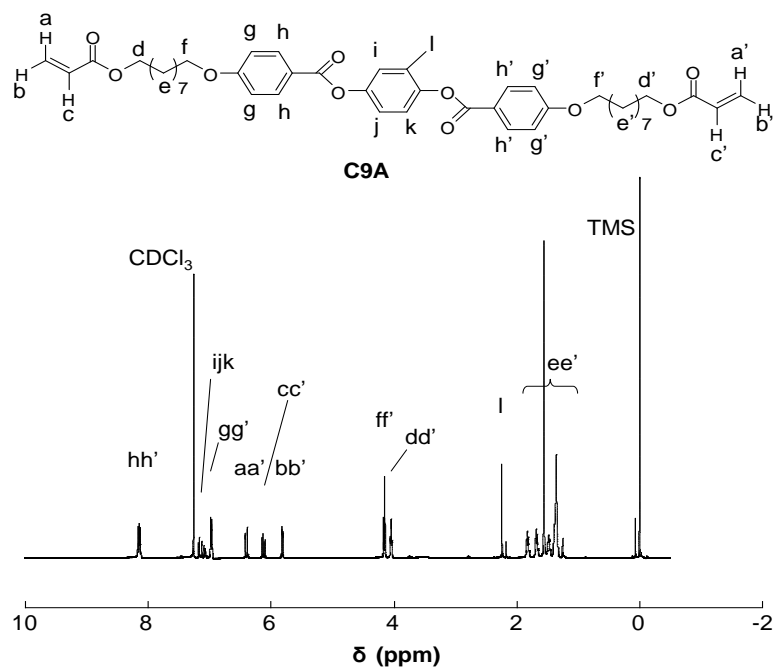


Figure S2. $^1\text{H-NMR}$ spectrum of the crosslinker **C9A**.

4-(Nonyloxy)phenol (7). Hydroquinone (4.0 g, 36 mmol), 9-bromononane (5.2 g, 38mmol) and potassium carbonate (1.6 g, 36 mmol) were dissolved in 20 mL of 2-butanone. The resulting solution was heated at 65 °C for 6 h. After cooled to room temperature, the reaction mixture was filtered to eliminate by-products. After the solvent was removed, a white solid obtained was purified by column chromatography on silica gel (chloroform: acetone = 3:1) and recrystallized from ethyl acetate and *n*-hexane to give **7** (1.6 g, 6.9 mmol) in 43 % yield.

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25 °C, TMS): δ 0.89 (t, $J = 6.5$ Hz, 3H), 0.76-1.30 (m, 14H), 4.10 (t, $J = 6.5$ Hz, 2H), 6.81-7.01 (m, 4H).

4-Nonyloxyphenyl-4'-(9-Acryloyloxynonyloxy)benzoate (A9Bz9). A mixture of **7** (1.13 g, 3.2 mmol), **6** (1.6 g, 6.7 mmol), DMAP (0.7 g, 3.4 mmol) and DCC (0.4 g, 3.4 mmol) was dissolved in dried CH_2Cl_2 (60 mL). The reaction mixture was stirred at room temperature for 24 h. The precipitate formed during the reaction was filtered off and the organic solution was washed with water. The mixture was dried with magnesium sulfate and the solvent was removed. The crude product was purified by silica gel column chromatography (chloroform: acetone = 3:1) and recrystallized from *n*-hexane/ethyl acetate to give **A9Bz9** (0.4 g, 0.22 mmol) in 7 % yield.

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , 25 °C, TMS, shown in **Figure S3**): δ 0.90 (t, $J = 6.5$ Hz, 3H), 1.31-1.80 (m, 28H), 3.95 (t, $J = 6.5$ Hz, 2H), 4.01 (t, $J = 6.5$ Hz, 2H), 4.17 (t, $J = 6.5$ Hz, 2H), 5.83 (dd, $J = 2, 10$ Hz, 1H), 6.11 (dd, $J = 10, 17$ Hz, 1H), 6.43 (dd, $J = 2, 17$ Hz, 1H), 6.90-7.16 (m, 4H), 7.39-7.51 (m, 4H). Anal Calcd for $\text{C}_{34}\text{H}_{48}\text{O}_6$: C, 73.88 %; H, 8.75 %; O, 17.37 %. Found: C, 73.90 %; H, 8.72 %; O, 17.23 %.

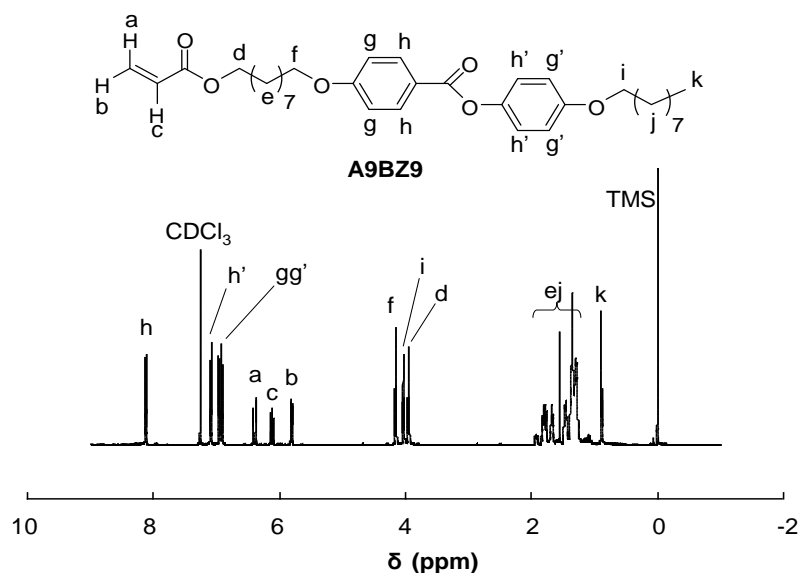


Figure S3. ¹H-NMR spectrum of the monomer **A9Bz9**.

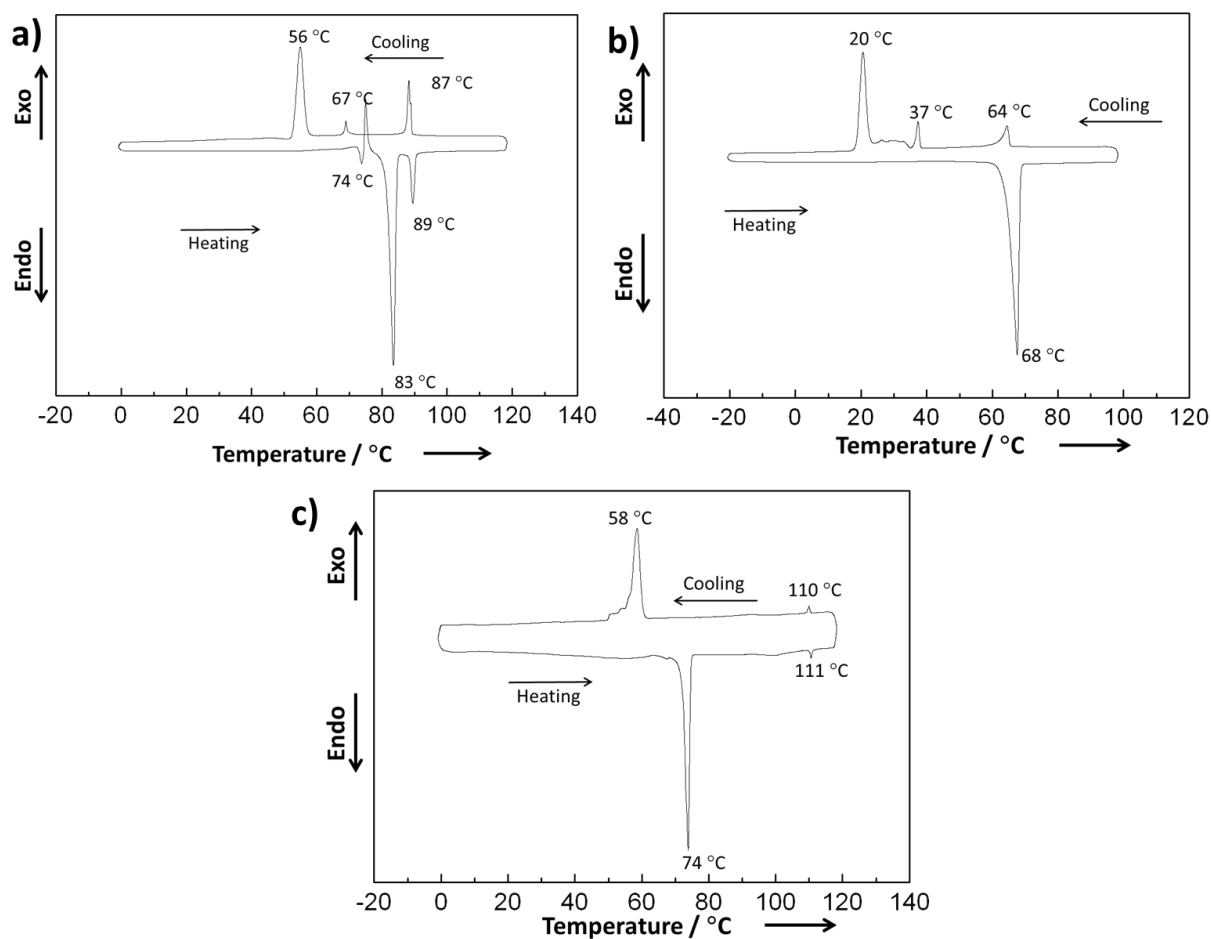


Figure S4. DSC thermograms of **a) A11AB6**, **b) A9Bz9**, and **c) C9A**. The peak at 75 °C in **a)** results from the crystallization of **A11AB6**. The thermodynamic properties of **A11AB6** have been reported in our previous work.^[S3]

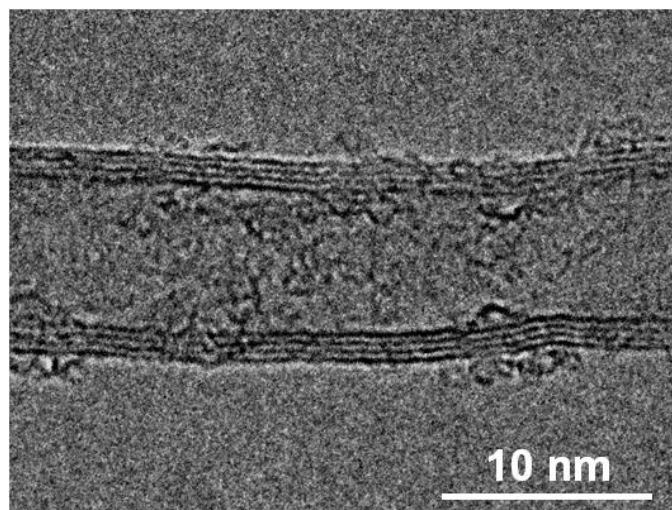


Figure S5. High-resolution transmission electron microscopy image of a CNT.

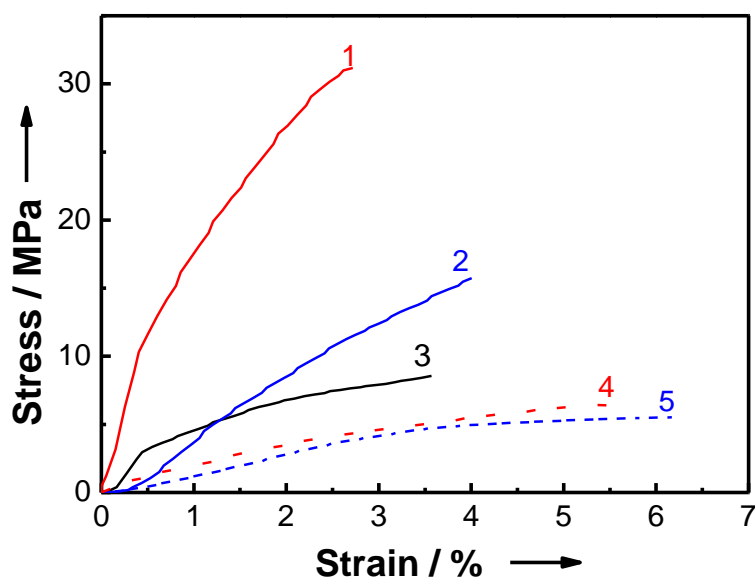


Figure S6. Stress-strain curves of the CLCP/CNT composite film measured with the tensile direction of being parallel (1) and perpendicular (4) to the CNT-aligned direction, the pure unoriented CLCP film (3), and the pure oriented CLCP film measured with the tensile direction of being parallel (2) and perpendicular (5) to the rubbing direction of the polyimide. The tensile rate was 1 mm min^{-1} .

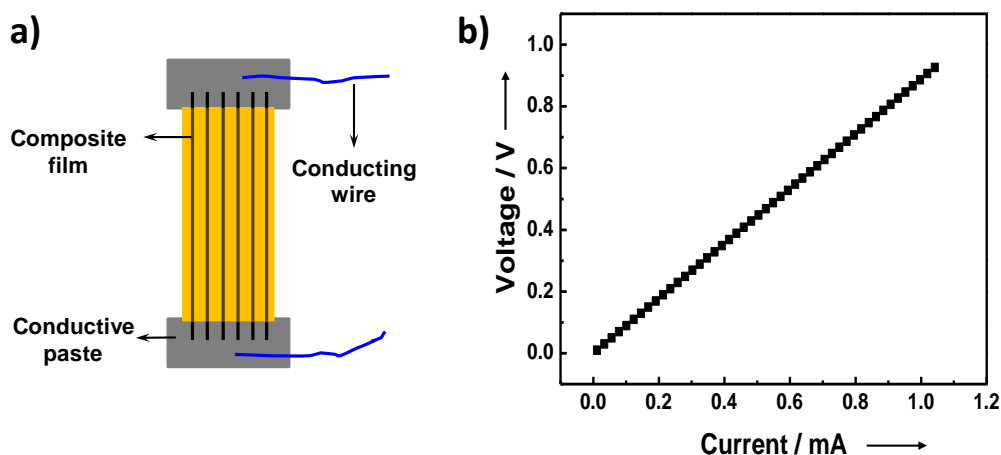


Figure S7. a) Schematic illustration to the measurement of electrical conductivity by a two-probe method. b) A typical I-V curve of the CLCP/CNT composite film at room temperature. The electrical resistance (R) of the composite film at **b** was measured to be 889.2 Ω . The width (W) and thickness (D) in the rectangular cross section were 1.52 mm and 0.22 μm , respectively, and the length (L) of the composite film was 8.02 mm, so the electrical conductivity (σ) could be finally calculated by the equation of $\sigma = [(1/R) \times (L)] / (W \times D)$, i.e., $\sigma = [(1/889.2) \times (8.02 \times 10^{-1})] / (1.52 \times 10^{-1} \times 0.22 \times 10^{-4}) = 269.7 \text{ S/cm}$.

References for the Supporting Information

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