

Supporting Information For:

Phase Structure and Phase Transition Mechanism for Light-Induced *Ia3d* Cubic Phase

in 4'-*n*-Docosyloxy-3'-nitrobiphenyl-4-carboxylic acid /

Ethyl 4-(4'-*n*-Docosyloxyphenylazo)benzoate Binary Mixture

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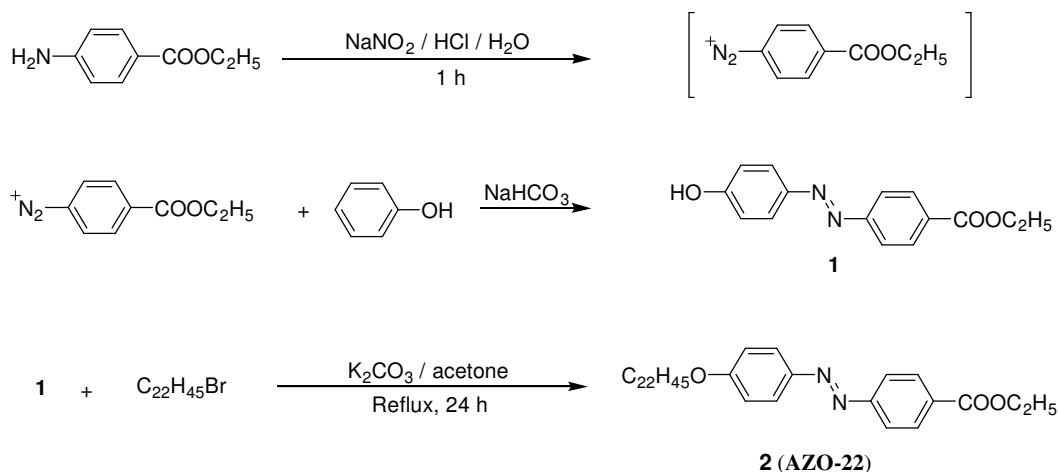
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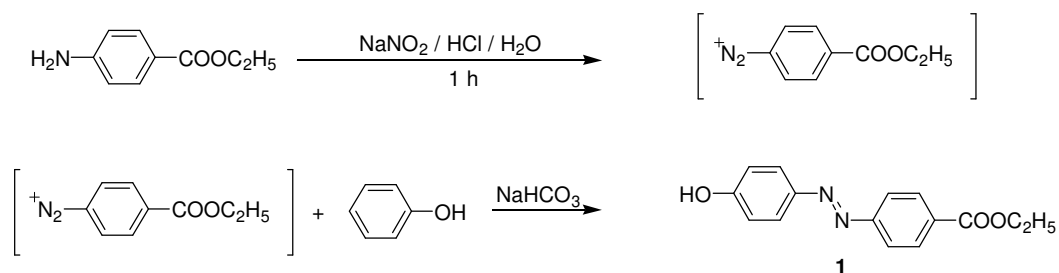
Sample Preparation

1-1. AZO-22 was prepared according to Scheme 1, which is essentially the same as the procedure described by J. Ortega et al. (tetradecyloxy analogue of azo-1)^[1] and Serrano et al.^[2] Very recently, Lizu et al. reported the syntheses of hexyloxy and decyloxy analogues of the two compounds.^[3]



Scheme S1. Synthetic route for **AZO-22 (2)**.

1-1-1. Preparation of Compound 1

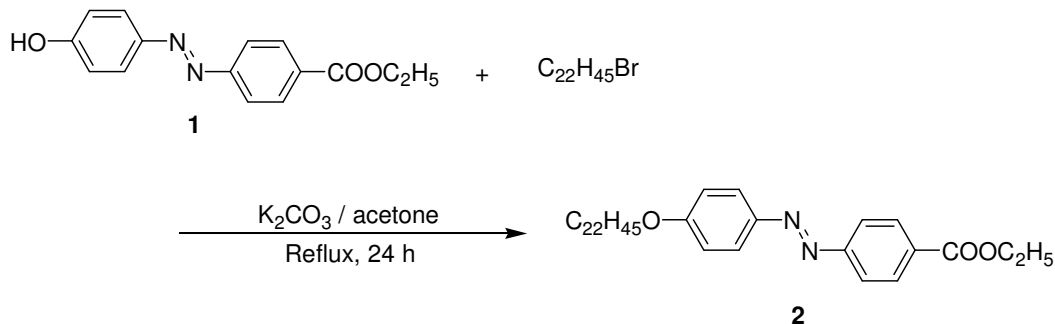


To ethyl *p*-aminobenzoate (9.07 g, 54.9 mmol) in water (30 mL) was added slowly 2 N aqueous solution of HCl (120 mL). The solution was kept at a temperature lower than 5 °C in an iced bath, to which NaNO₂ (4.64 g, 67.2 mmol) in water (30 mL) was added dropwise. After stirring for 1 h, the diazonium intermediate was formed. Then, phenol (6.16 g, 65.5 mmol) was added and stirred for a while, a saturated aqueous solution of NaHCO₃ (200 mL) was added slowly. The precipitate was collected and recrystallized from ethanol to give a brown solid, which was identified by ¹H NMR. Yield 13.10 g (48.5 mmol), 88.3 %.

¹H NMR (400 MHz, CDCl₃, TMS) : δ = 8.18 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.92 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.90 (d, *J* = 8.1 Hz, 2H, Ar-H), 6.97 (d, *J* = 9.5 Hz, 2H, Ar-H), 5.47 (s, 1H, OH), 4.42 (q, *J* = 7.1 Hz, 2H,

COOCH₂), 1.43 ppm (t, *J* = 7.0 Hz, 3H, CH₃).

1-1-2. Preparation of AZO-22 (Compound 2)

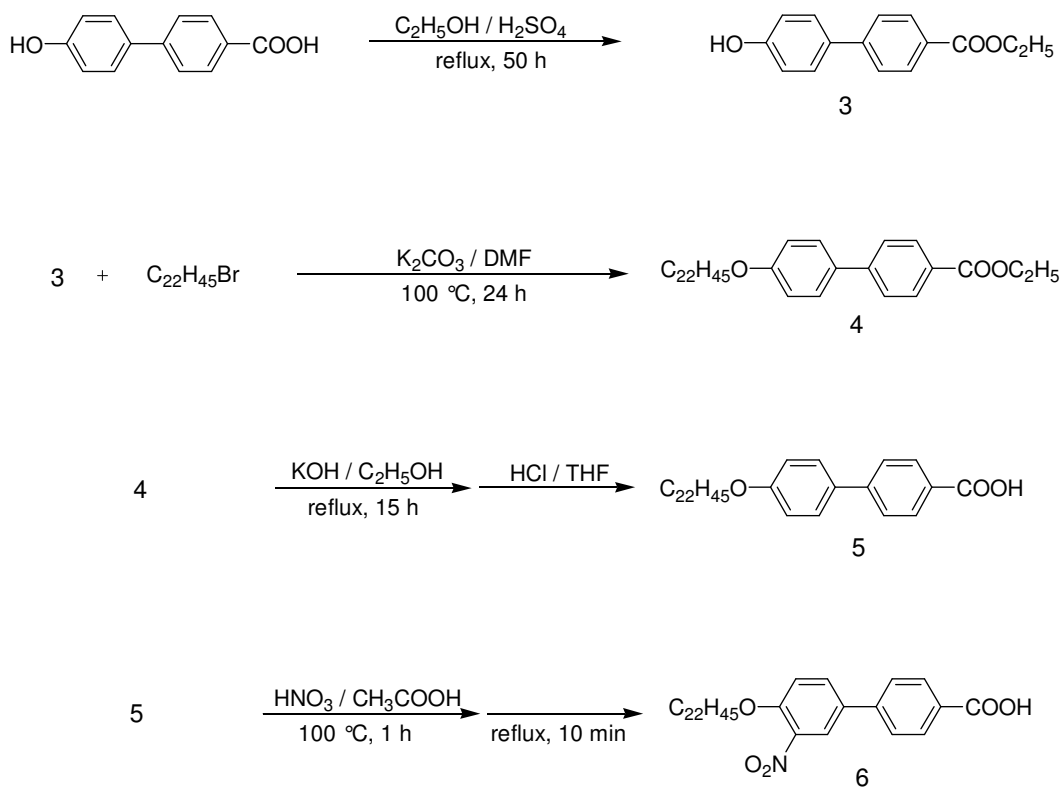


Compound **1** (4.99 g, 18.4 mmol), 1-bromodocosane (7.07 g, 18.1 mmol), and K₂CO₃ (5.11 g, 37.0 mmol) were dissolved in acetone (100 mL) and refluxed for 24 h. The resulting solution was extracted with water and CHCl₃. The organic layer was separated and the solvent was evaporated with a rotary evaporator. The resulting solid was recrystallized from acetone to obtain bright reddish orange crystals, which was identified by ¹H NMR. Yield 8.44 g (14.5 mmol), 81 %.

¹H NMR (600 MHz, CDCl₃, TMS): δ = 8.16 (d, *J* = 8.2 Hz, 2H, Ar-H), δ 7.92 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.88 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.00 (d, *J* = 9.0 Hz, 2H, Ar-H), 4.41 (q, *J* = 7.1 Hz, 2H, COOCH₂), 4.05 (t, *J* = 6.5 Hz, 2H, OCH₂), 1.82 (m, 2H, OCH₂CH₂), 1.49-1.46 (m, 2H, OCH₂CH₂CH₂), 1.42 (t, *J* = 7.2 Hz, 3H, COOCH₂CH₃), 1.40-1.21 (m, 36H, (CH₂)₁₈), 0.88 ppm (t, *J* = 7.2 Hz, 3H, CH₃) ; elemental analysis calcd (%) for C₃₇H₅₈N₂O₃: C 76.77, H 10.10, N 4.84; found: C 76.52, H 10.37, N 4.89.

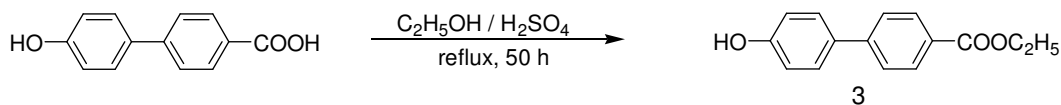
1-2. Preparation of 4'-docosyloxy-3'-nitrophenyl-4-carboxylic acid (ANBC-22)

ANBC-22 was prepared according to Scheme 2. The ANBC series was first synthesized by Gray et al.,^[4,5] and extended to the C26 compound by our group.^[6-8]



Scheme S2. Synthetic route for ANBC-22 (Compound 6)

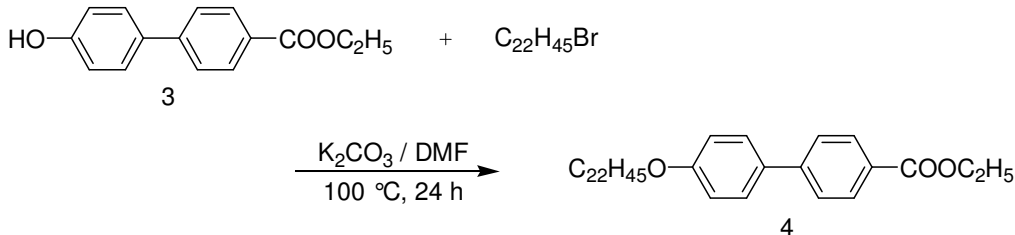
1-2-1. Preparation of Compound 3



4'-Hydroxy-4-biphenylcarboxylic acid (10.00 g, 46.7 mmol) was dissolved in ethanol (200 mL), to which concentrated H_2SO_4 (5.09 g, 51.9 mmol) was added dropwise. The mixture was then refluxed for 50 h. After cooled, the solvent was removed with a rotary evaporator. The product in the organic layer was extracted with CHCl_3 and 5 % K_2CO_3 aqueous solution, and washed with water thoroughly until neutral. After that, the solvent was dried (MgSO_4), removed under reduced pressure to give a white solid, identified by ^1H NMR. Yield 8.94 g (36.9 mmol), 79 %.

^1H NMR (600 MHz, CDCl_3 , TMS) : δ = 8.07 (d, J = 8.2 Hz, 2H, Ar-H), 7.59 (d, J = 8.3 Hz, 2H, Ar-H), 7.51 (d, J = 9.0 Hz, 2H, Ar-H), 6.92 (d, J = 8.2 Hz, 2H, Ar-H), 5.03 (s, 1H, OH), 4.39 (q, J = 7.1 Hz, 2H, COOCH_2), 1.40 ppm (t, J = 7.2 Hz, 3H, $\text{COOCH}_2\text{CH}_3$).

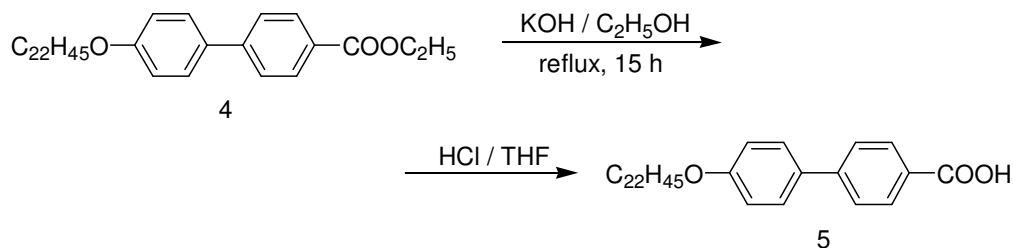
1-2-2. Preparation of compound 4



Compound **3** (8.94 g, 36.9 mmol), 1-bromodocosane (20.50 g, 52.6 mmol), and K_2CO_3 (8.08 g, 58.5 mmol) were dissolved in *N,N*-dimethylformamide (DMF) (300 mL), followed by reflux for 24 h. After cooled, the resulting solution was extracted with water and CHCl_3 . The organic layer was washed with 1 N aqueous solution of NaOH, and of NaCl, dried with MgSO_4 . After that, the solvent was removed under reduced pressure to give the crude product. The product was recrystallised from ethyl acetate and from ethanol to give a white solid, which was identified by ^1H NMR. Yield 17.22 g (31.3 mmol), 85 %.

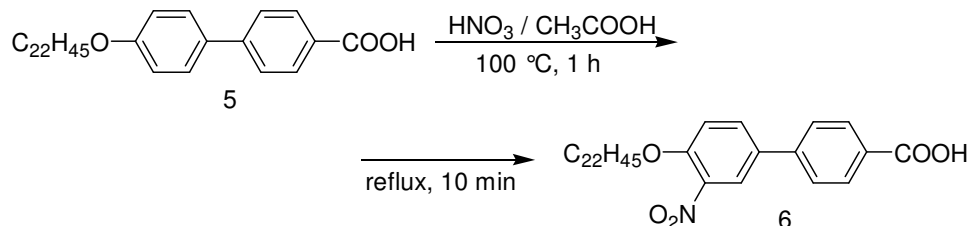
^1H NMR (600 MHz, CDCl_3 , TMS): δ = 8.07 (d, J = 8.3 Hz, 2H, Ar-H), 7.60 (d, J = 8.3 Hz, 2H, Ar-H), 7.55 (d, J = 8.2 Hz, 2H, Ar-H), 6.97 (d, J = 8.9 Hz, 2H, Ar-H), 4.38 (q, J = 7.1 Hz, 2H, COOCH_2), 3.99 (t, J = 6.6 Hz, 2H, OCH_2), 1.79 (qn, J = 6.9 Hz, 2H, OCH_2CH_2), 1.46 (qn, J = 7.4 Hz, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.40 (t, J = 6.9 Hz, 3H, $\text{COOCH}_2\text{CH}_3$), 1.32-1.19 (m, 36H, $(\text{CH}_2)_{18}$), 0.87 ppm (t, J = 7.2 Hz, 3H, CH_3).

1-2-3. Preparation of compound 5



To a solution of Compound **4** (17.22 g, 31.3 mmol) in ethanol (500 mL) was added KOH (15.37 g, 307 mmol) in ethanol (500 mL) dropwise, followed by reflux for 15 h. After cooled, the precipitate were collected and then dissolved in hot THF, acidified with 2 N HCl (50 mL). The precipitate was collected. Recrystallization from acetic acid gave 14.50 g (27.7 mmol) of white solid (88 %). The product was checked by differential scanning calorimetry (DSC). Peak transition temperatures determined by DSC (5 K min⁻¹) are: 395.1, 407.2, 409.7, 420.3, 452.7, and 499.7 K.

1-2-4. Preparation of ANBC-22 (compound 6)



Compound **5** (4.50 g, 8.6 mmol) was dissolved in acetic acid (600 mL), stirred at 100 °C, to which was added dropwise a mixture of fuming nitric acid (10 mL) and acetic acid (30 mL). The solution was stirred at 100 °C for 1 h, heated up to 125 °C, further refluxed for 10 min. After cooled, the crude product was collected and recrystallized from ethanol to give a pale yellow solid, which was identified by ¹H NMR and DSC. Yield 3.28 g (5.8 mmol), 67 %.

¹H NMR (400 MHz, CDCl₃, TMS): δ = 8.17 (d, J = 8.2 Hz, 2H, Ar-H), 8.11 (d, J = 2.1 Hz, 1H, Ar-H), 7.78 (d,d J = 8.6, 2.4 Hz, 1H, Ar-H), 7.65 (d, J = 8.2 Hz, 2H, Ar-H), 7.16 (d, J = 8.9 Hz, 1H, Ar-H), 4.15 (t, J = 6.2 Hz, 2H, OCH₂), 1.86 (qn, J = 7.1 Hz, 2H, OCH₂CH₂), 1.48 (qn, J = 7.6 Hz, 2H, OCH₂CH₂CH₂), 1.32-1.18 (m, 36H, CH₂), 0.86 ppm (t, J = 7.2 Hz, 3H, CH₃); elemental analysis calcd (%) for C₃₅H₅₃N₁O₅: C 74.04, H 9.41, N 2.48; found: C 73.89, H 9.23, N 2.57. Peak transition temperatures determined by DSC (5 K min⁻¹) are: 376.2, 411.6, 468.9, and 474.8 K.

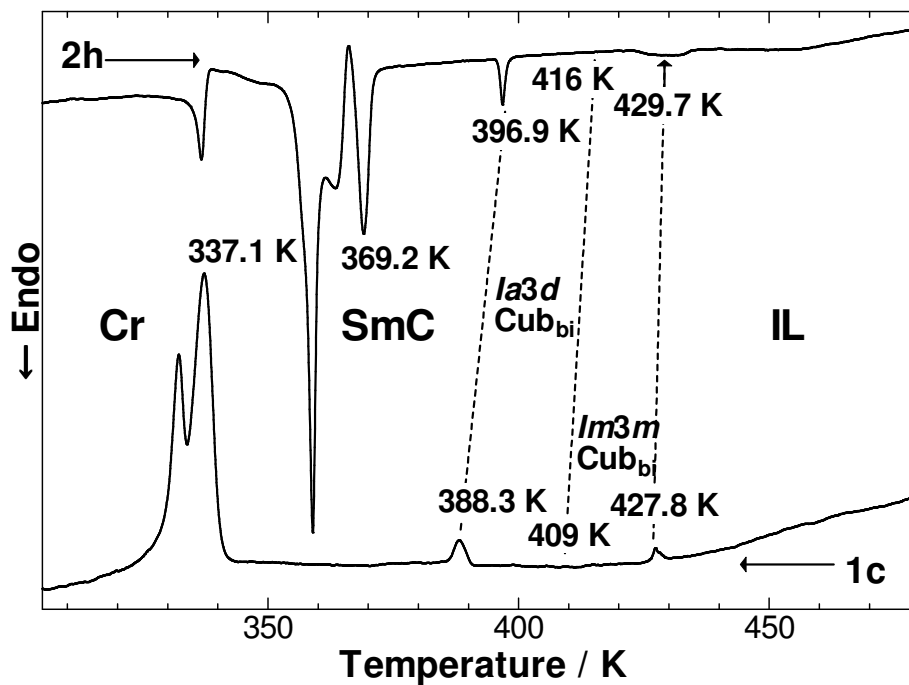


Figure S1. DSC thermograms for ANBC-22 / AZO-22 binary mixture on first cooling (bottom) and second heating (IL, isotropic liquid; *Cub_{bi}*, bicontinuous cubic; SmC, smectic C; Cr, crystalline). Transition temperatures of *Ia3d* to *Im3m* phases (416 K on second heating) and *Im3m* to *Ia3d* phases (409 K on first cooling) were determined by GI-XRD, and the others were determined by DSC.

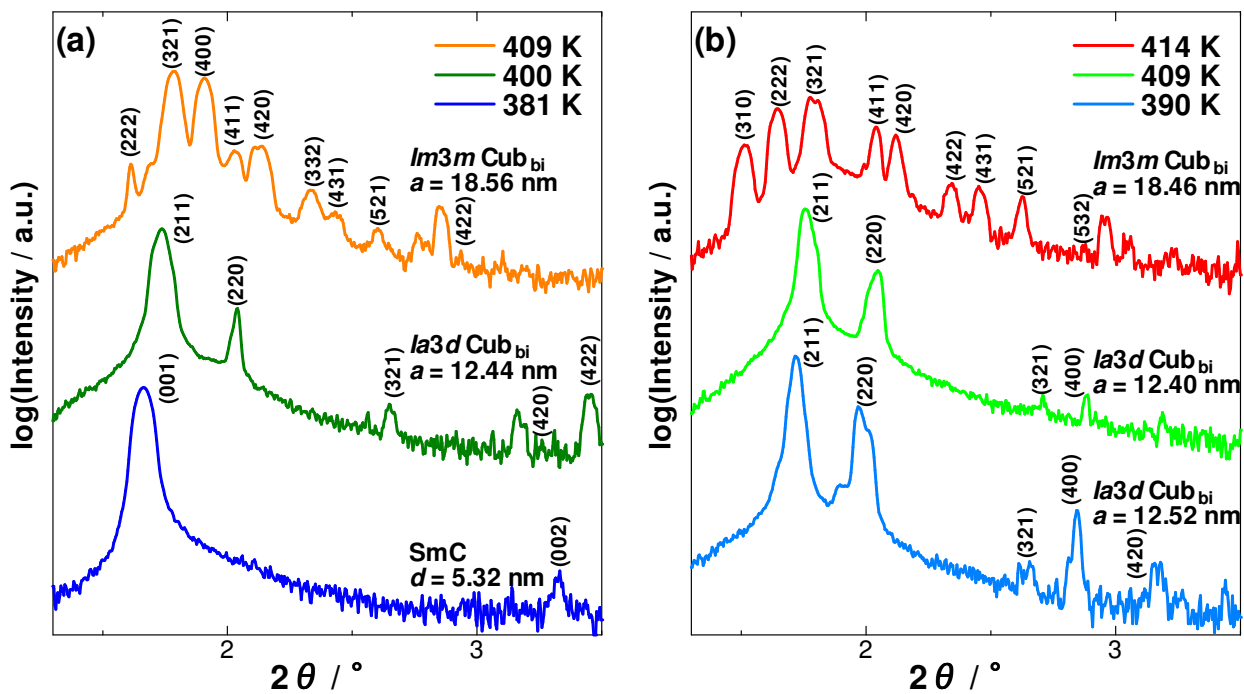


Figure S2. Transmission XRD patterns for ANBC-22 / AZO-22 binary mixture on first cooling (a) and on second heating (b).

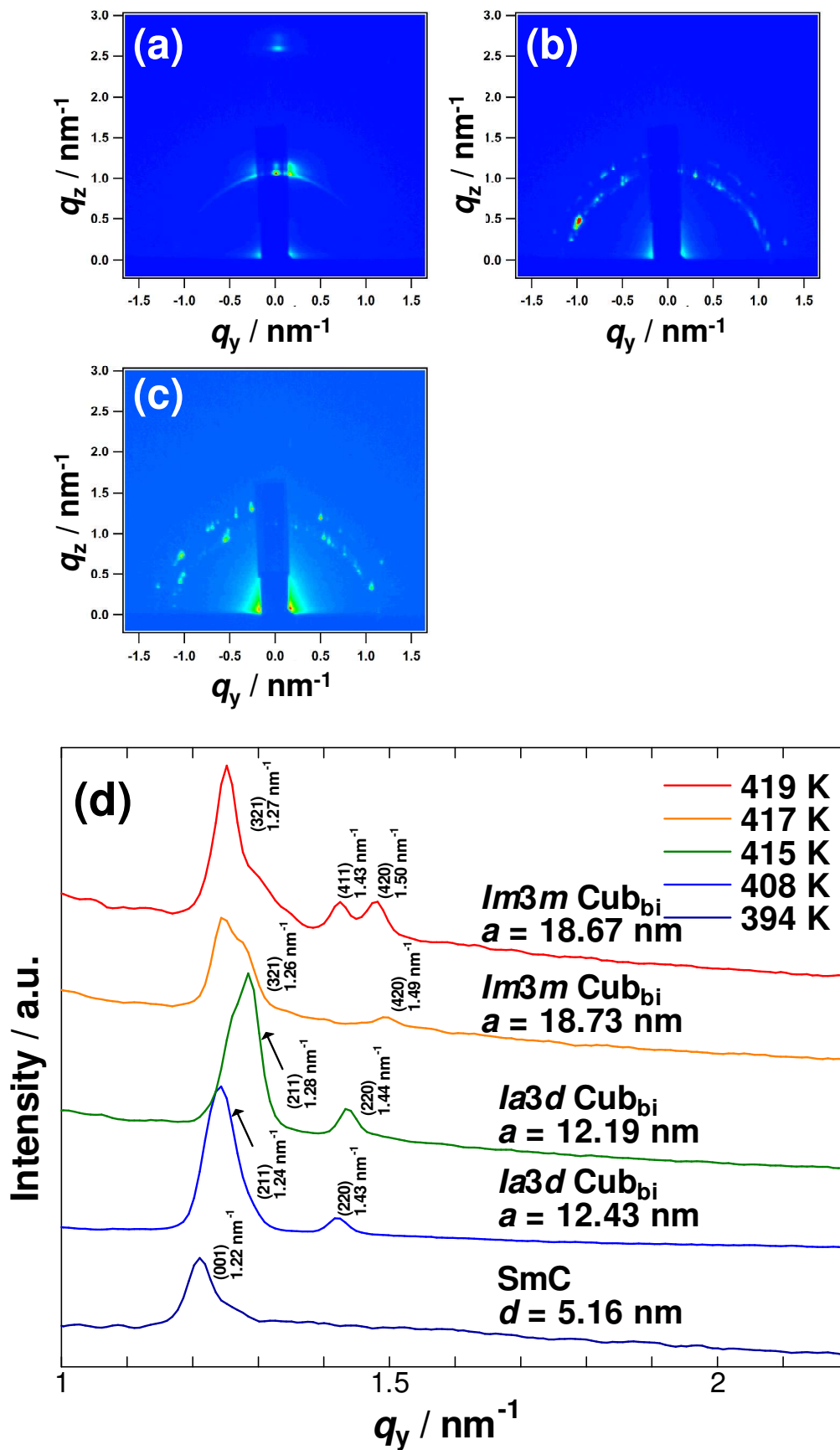


Figure S3. Two-dimensional GI-XRD patterns for ANBC-22 / AZO-22 binary mixture containing 20 mol% of AZO-22 at (a) 394 K, (b) 408 K, and (c) 419 K on first heating and (d) 1D-XRD profiles at $q_z=0$ at various temperatures.

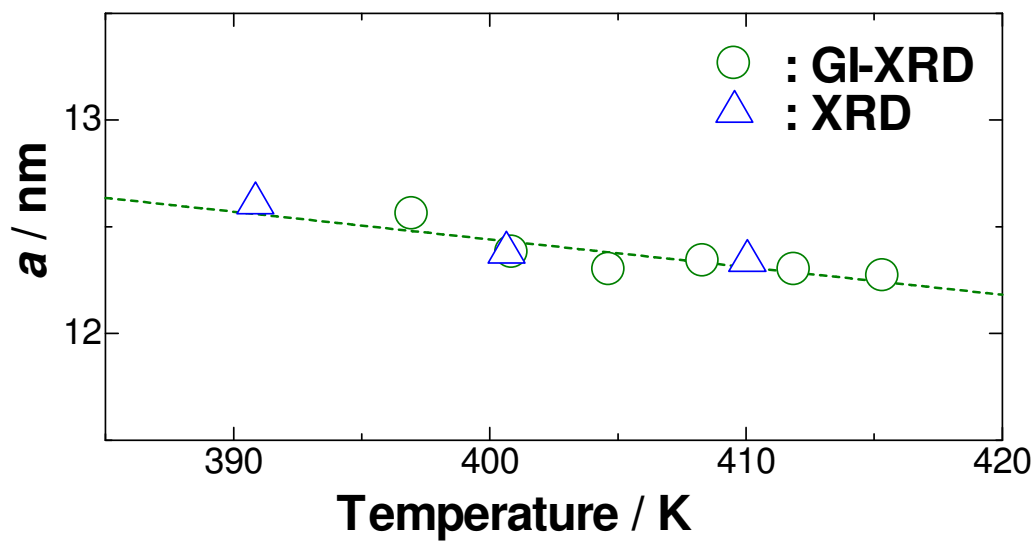


Figure S4. Plots of lattice parameter a versus temperature for ANBC-22 / AZO-22 binary mixture, where circle and triangle symbols indicate thin film and bulk samples, respectively.

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