

Supporting information for
Partial-crosslinked bicontinuous cubic phase exhibiting
a temperature range more than 100 degrees

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Syntheses of **1** and **2**:

4-(9'-decenyloxy)benzoic acid (**2**)

10-bromo-1-decene (5.18 g, 24 mmol), Ethyl 4-hydroxybenzoate (2.53 g, 15 mmol), and K₂CO₃ (4.34 g, 31 mmol) were dissolved in acetone (100 mL) and refluxed for 24 h. After that, the solution was filtered, and the solvent was removed in vacuo. The residue was dissolved in ethanol (50 mL), and then an aqueous solution (10 mL) of NaOH (1.38 g, 35 mmol) was added with stirring. The resulting mixture was refluxed for 2 h. After evaporating the solvent, a white solid was obtained. The crude product was dissolved in a mixture (200 mL) of water and a small volume of ethanol, to which was added 6 N aqueous HCl (40 mL), and then water (200 mL) in an ice bath. Shiny white crystals were collected by filtration, recrystallized from a mixture of hexane and a small volume of ethanol, dried under vacuum, to afford 3.49 g (84.2 %) of **2**.

¹H NMR (400 MHz, CDCl₃, r.t.): δ 1.33-1.46 (m, 10H), 1.81 (quin, *J* = 7.0 Hz, 2H), 2.05 (q, *J* = 6.7 Hz, 2H), 4.02 (t, *J* = 6.6 Hz, 2H), 4.93 (d, *J* = 10.2 Hz, 1H), 5.00 (d, *J* = 17.1 Hz, 1H), 5.82 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.8 Hz, 2H).

1,2-bis[4'-(9''-decenyloxy)benzoyl]hydrazine (**1**):

A mixture of compound **2** (3.38 g, 12 mmol) and thionyl chloride (12 mL) was stirred under reflux for 3 h. After cooling to room temperature, the remaining thionyl chloride was removed thoroughly under a reduced pressure. The resulting oil was dissolved in CHCl₃ (60 mL), and then hydrazine monohydrate (0.35 g, 7 mmol) was added dropwise. After stirring for 0.5 h, CHCl₃ (200 mL) and water (100 mL) were added and the aqueous layer was separated. The organic layer was evaporated into dryness to obtain a brownish white solid. The crude product was recrystallized from a mixture of hexane/THF (3/1 v/v) (200 mL), dried under vacuum, yielding 0.24 g (7.3 %) of a white solid **1**.

¹H NMR (400 MHz, CDCl₃, r.t.): δ 1.34-1.48 (m, 20H), 1.80 (quin, *J* = 7.0 Hz, 4H), 2.05 (q, *J* = 7.0 Hz, 4H), 4.01 (t, *J* = 6.5 Hz, 4H), 4.94 (d, *J* = 10.2 Hz, 2H), 5.00 (d, *J* = 17.1 Hz, 2H), 5.82 (m, 2H), 6.95 (d, *J* = 9.0 Hz, 4H), 7.82 (d, *J* = 9.0 Hz, 4H), 9.09 (s, 2H); ¹³C NMR (100 MHz, CDCl₃, r.t.): δ 25.95-29.29 (2C), 33.77 (2C), 68.23 (2C), 114.17 (2C), 114.46 (4C), 123.33 (2C), 129.07 (4C), 139.16 (2C), 162.50 (2C), 163.78 (2C); Elemental Anal. Calcd for C₄₃H₈₀N₂O₄(%): C, 74.42; H, 8.82; N, 5.10; Found: C, 74.18; H, 8.90; N 4.98.

Measurements: ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL JNM- α 400 spectrometer, and tetramethylsilane ($\delta = 0.00$) and CDCl_3 ($\delta = 77.0$) were used as internal standards, respectively. CDCl_3 or $(\text{CD}_3)_2\text{SO}$ was used as solvent.

Phase transitions were examined using a Seiko Denshi DSC-200 interfaced to a TA data station (SSC 5000 system). The measurements were performed under a dry N_2 flow of *c.* 40 mL min^{-1} and the scanning rate was $5 \text{ }^\circ\text{C min}^{-1}$ or $1 \text{ }^\circ\text{C min}^{-1}$. The texture of each mesophase was observed using a Nikon Optiphot-pol XTP-11 polarizing optical microscope (POM) equipped with a Mettler FP82 hot stage and a Mettler FP80 central processor at a heating/cooling rate of $5 \text{ }^\circ\text{C min}^{-1}$.

X-ray diffraction (XRD) patterns at elevated temperatures were obtained for powder samples using a Rigaku NANO-Viewer IP system. $\text{CuK}\alpha$ radiation was used at 45 kV and 60 mA. The scattered X-rays were recorded on a two-dimensional imaging plate (IP). The intensities were radially integrated and averaged, and redistributed when converting the pixel number into the corresponding scattering vector q ($q = (4\pi/\lambda)\sin\theta$, with λ being the X-rays wavelength ($= 0.15418 \text{ nm}$) and 2θ the scattering angle) to produce a circularly averaged pattern.

Temperature-variable IR spectra were recorded with a JASCO IRT-30 Fourier transform IR spectrometer equipped with a Mettler FP82 hot stage for powder samples on a KBr pellet ($5\times 5\times 1 \text{ mm}$). Resolution was 4 cm^{-1} and the number of scans was 18.

Preparation of photopolymerizable samples and photopolymerization procedure

The photopolymerizable sample was prepared by dissolving the compound **1**, 1,6-hexanediol diacrylate as the bi-functional linker, and 2,2-dimethoxy-1,2-diphenylethan-1-one as the photo-initiator, with a molar ratio of 66.8 : 24.7 : 8.5, in THF, and then, removing the solvent at $100 \text{ }^\circ\text{C}$. After that, the mixture was heated up to $160 \text{ }^\circ\text{C}$ and then cooled to room temperature. Then, the mixture was replaced on a Teflon sheet in a Mettler FP82 hot stage, heated up to isotropization, mixed again, then cooled to room temperature. The mixture was again heated up to and held at around a temperature ($\sim 140 \text{ }^\circ\text{C}$) of the Cub_{bi} LC phase, where photopolymerization was carried out for 10 min under the exposure of UV light (365 nm , 24 mW cm^{-2}), which was obtained from an ultra-high-pressure mercury lamp (Ushio, SX-UI501HQ, 500 W) with appropriate glass filters (Ushio UG-11 and Sigma Optics HAF-50S-30H).

^1H NMR spectra of the mixture were compared between before and after photopolymerization. It is evident that the signals at $\delta = 4.16$, 6.12 and 6.40 from

1,6-hexanediol diacrylate linker completely vanished after polymerization, although severe overlapping of signals from the components in the mixture makes the analysis quite difficult. This implies that 10 min-exposure of UV light was enough for the reaction. On the other hand, the signals ($\delta = 4.95, 5.02$ and 2.05) from the C=C bond and neighbouring methylene unit of the compound **1**, respectively, decreased only by $\sim 5\%$ but almost remained. Thus, as expected from low reactivity of the C=C bond, we concluded that its contribution to the network formation within the TPMS region of the *Ia3d*-Cub_{bi} phase, which is mainly produced from the bi-functional linker, is quite low. However, as mentioned in the main text of the article, it should be stressed that this partial contribution is important for preserving the dynamic nature of the phase as well as preventing from the macrophase separation seen in the photopolymerized mixture of BABH-10.

Time-resolved small-angle XRD measurements

The time-resolved small-angle XRD measurements were performed using the BL-15A instrument at the Photon Factory (PF) in the High-energy Accelerator Research Organization (KEK). Sample was packed into a drilled hole of diameter of 3 mm in a brass plate (21×5×1 mm), sandwiched with two Kapton windows; the plate was inserted into a notch of the same size of a Teflon sheet 1 mm thick, which was placed in a Mettler FP82HT hot stage. A ramp mode of temperature with a rate of $5\text{ }^{\circ}\text{C min}^{-1}$ was controlled by a FP90 central processor. The exposure time was typically 5 s and the temperature variation in that interval was $0.4\text{ }^{\circ}\text{C}$. The scattered X-rays were recorded using a charge-coupled device (CCD) area detector (Hamamatsu Photonics C7300) with an image intensifier. Recording was performed within the intensity range of the CCD detector where linearity satisfactorily holds. The covering modulus of scattering vector q ($q = (4\pi/\lambda)\sin\theta$, with λ being the X-rays wavelength and 2θ the scattering angle) ranged from 0.5 to 4.1 nm^{-1} . The area intensities in the detector were circularly averaged in terms of q , and the q values (or the reciprocal spacings) of the pattern were calibrated using standard materials (chicken tendon collagen and α -stearic acid at 298 K), and BABH-18 in the Cub_{bi} state.

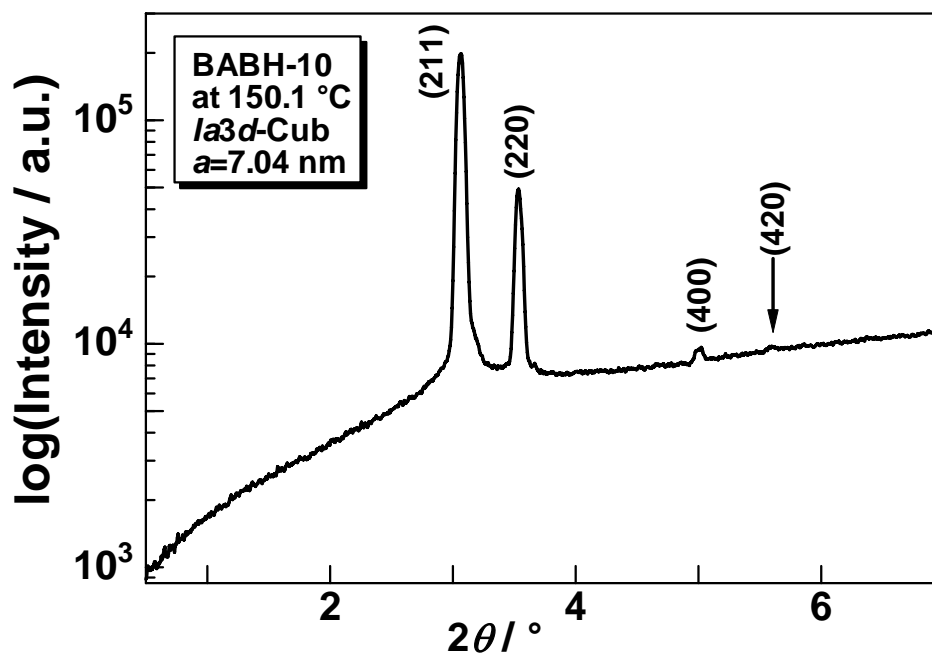


Figure S1. X-ray diffraction pattern of BABH-10 at 150.1 °C in the Cub_{bi} phase.

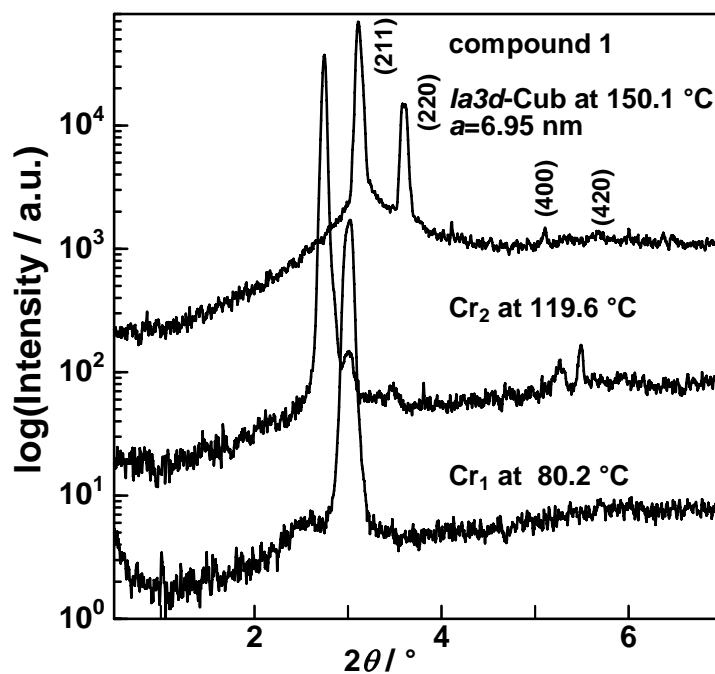


Figure S2. X-ray diffraction pattern of compound **1** at 150.1 °C in the Cub_{bi} phase (top), 119.6 °C in the Cr_2 phase (middle), and 80.2 °C in the Cr_1 phase (bottom).

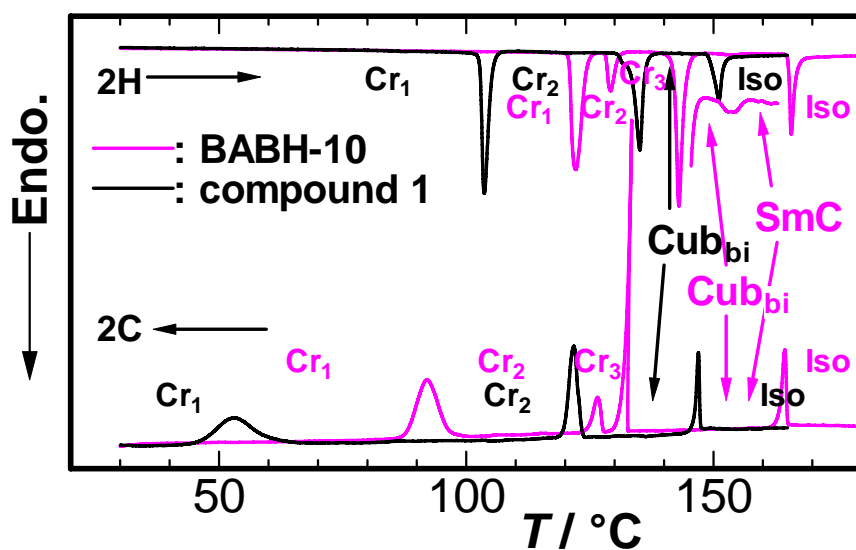


Figure S3. DSC thermograms of BABH-10 (purple) and compound **1** (black) on the second heating and cooling (5 K min^{-1}). Numbering of the crystalline phases is made only from the low temperature side and so two phases with the same number but for different compounds are not necessarily identical.

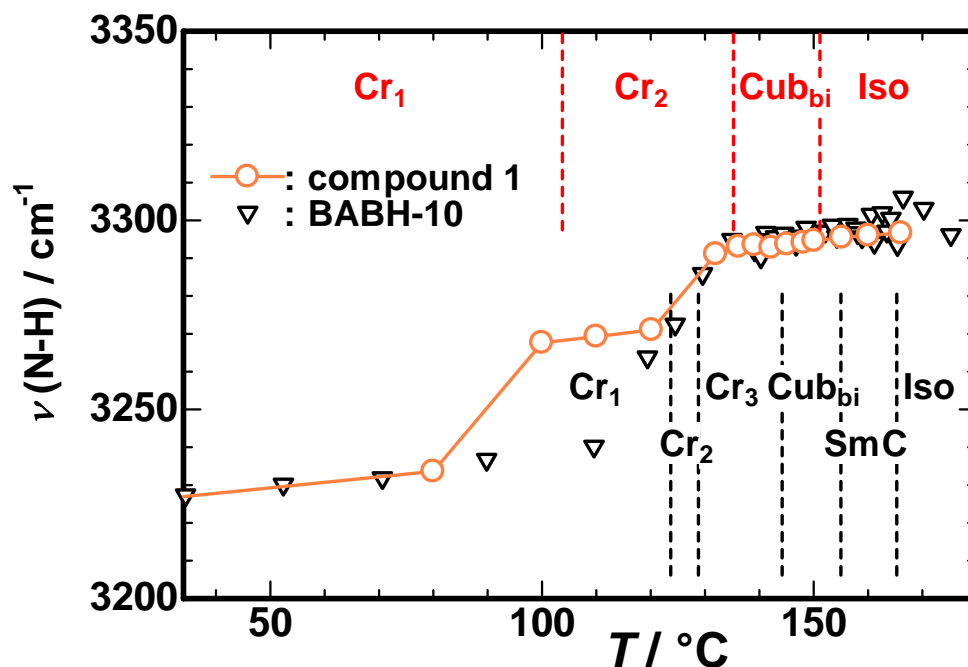


Figure S4. Temperature variations of $\nu(\text{N-H})$ peak frequency for compound **1** and BABH-10.

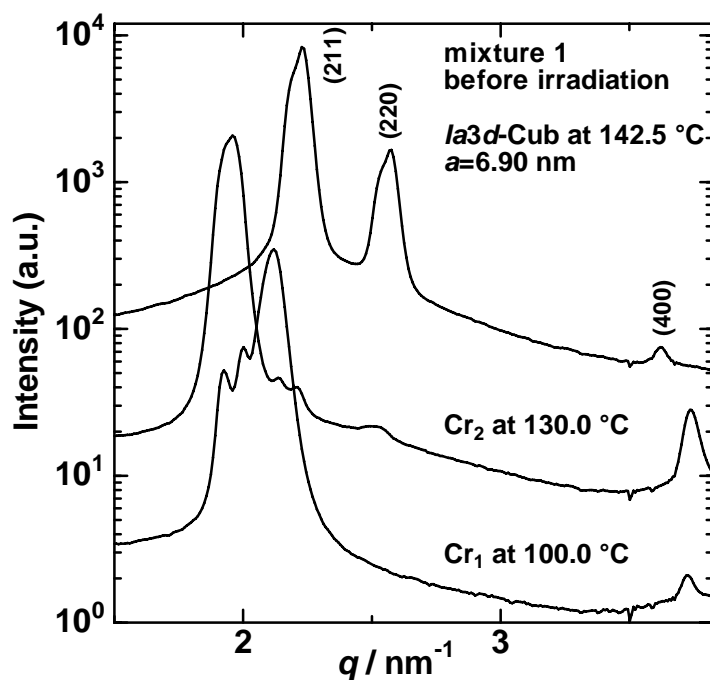


Figure S5. XRD patterns of the mixture **1** with diacrylate and photo-initiator at 142.5 °C (top), 130.0 °C (middle), and 100.0 °C (bottom) on heating before photopolymerization.

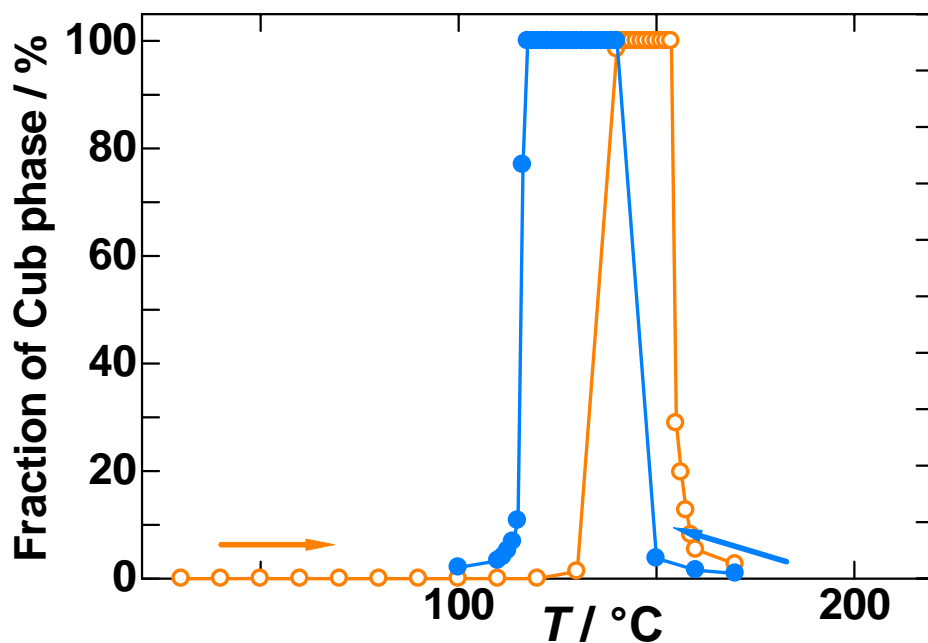


Figure S6. Fraction of Cub_{bi} phase evaluated from the XRD pattern as a function of temperature for the mixture **1** before photopolymerization.

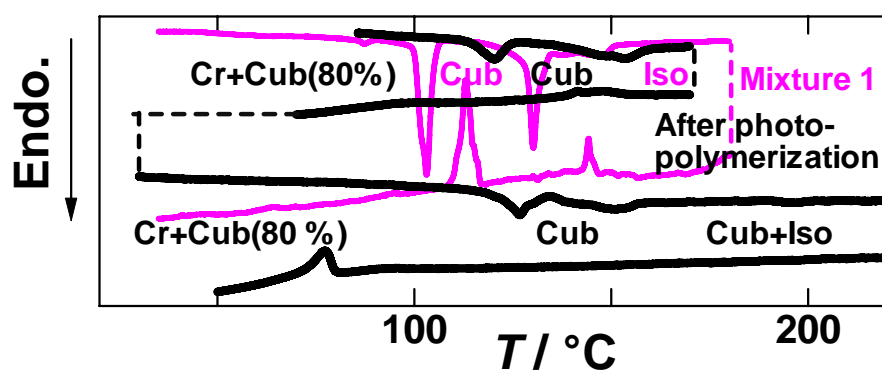


Figure S7. DSC thermograms of the mixture (mixture 1) of compound 1 /diacrylates/photo-initiator (66.8/24.7/8.5 mol/mol/mol), before (purple) and after photopolymerization (black).

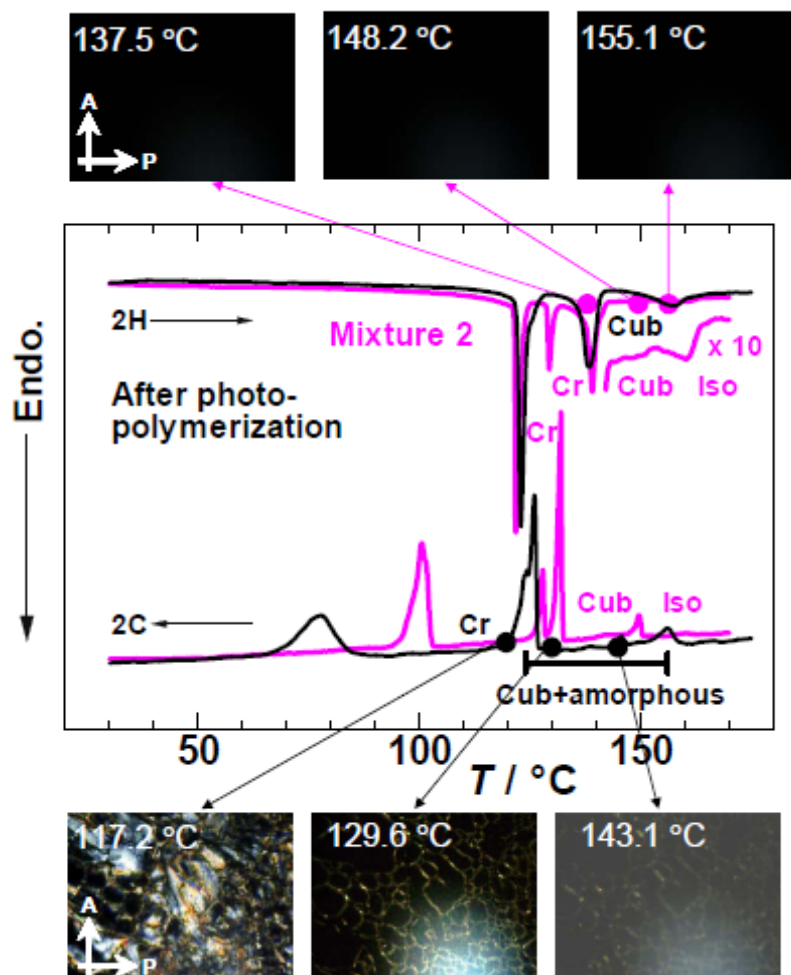


Figure S8. DSC thermograms and polarizing optical microphotographs under crossed polarizers of the mixture (mixture 2) of BABH-10/diacrylates/photo-initiator (66.7/23.6/9.7 mol/mol/mol), before (purple) and after photopolymerization (black). The mixture 2 after polymerization exhibited a phase-separation, where polymerized substances were present in the boundary region of the BABH-10.