Electronic Supplementary Material (ESI) for Soft Matter

Supporting information for

Charged Carrier Mobility in the Cubic (*Ia*3*d*) mesophase of 1,2-bis(4'-*n*-nonyloxybenzoyl)hydrazine (BABH-9)

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(1) Synthesis of BABH-9[1]

The first step: Ethyl 4-hydroxybenzoate (5.03 g, 30 mmol) and 1-bromo-*n*-nonane (12.07 g, 58 mmol) were dissolved in acetone (100 mL). K_2CO_3 (17.25 g, 125 mmol) was then added and the resulting mixture was stirred under reflux for 12 h. After cooling to room temperature, the solvent was evaporated under a reduced pressure. The residue was dissolved in ethanol (150 mL), and then NaOH (6.21 g, 155 mmol) was added. The mixture was stirred under reflux for 1 h. The precipitated product was collected and washed with water (500 mL). The crude product was then recrystallised from acetic acid and from a 1/1 hexane/ethanol mixture, dried under vacuum, yielding 2.37 g (30%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ 8.05 (d, J = 9.3 Hz, 2H, Ar−H), 6.93 (d, J = 8.8 Hz, 2H, Ar−H), 4.02 (t, J = 6.8 Hz, 2H, OCH_2), 1.81 (quin, 2H, CH_2), 1.50−1.25 (m, 12H, $(CH_2)_6$), 0.89 (t, J = 6.8 Hz, 3H, CH_3). *Second step*: A mixture of 4-*n*-nonyloxybenzoic acid (2.00 g, 7.6 mmol) and thionyl chloride (20 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 $CHCl_3$ (200 mL), and then hydrazine monohydrate (0.19 g, 3.8 mmol) was added dropwise. After stirring for 1 h, water (200 mL) was added and the aqueous layer was separated. The organic layer was evaporated into dryness to obtain a white solid. The crude product was recrystallised from a mixture of ethanol and benzene, finally dried under vacuum, yielding 1.20 g (30%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ 9.15 (s, 2H, CONH), 7.82 (d, J = 8.8 Hz, 4H, Ar−H), 6.94 (d, J = 8.8 Hz, 4H, Ar−H), 4.01 (t, J = 6.6 Hz, 4H, OCH_2), 1.81 (quin, 4H, CH_2), 1.50−1.25 (m, 24H, $(CH_2)_6$), 0.88 (t, J = 6.8 Hz, 6H, CH_3). Elemental anal. Calcd for $C_{32}H_{48}N_2O_4$: C, 73.25; H, 9.22; N, 5.34. Found: C, 73.49; H, 9.13; N, 5.38%.

To remove ionic impurities for the TOF measurements, the final product was further recrystallised from mixture of tetrahydrofuran and water and dried under vacuum.

(2) DSC and XRD measurements of BABH-9[1]

Phase transitions were examined using a Seiko Denshi DSC-210 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 °C min^{-1}. The instrument was calibrated by various standard materials (indium, tin, lead, zinc). First-order transition temperatures were reported as the maxima and minima of their endothermic and exothermic peaks.

X-ray diffraction (XRD) patterns at elevated temperatures were obtained for powder samples with a Rigaku NANO-Viewer IP system which was operated with a copper target 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 nm) and 2θ the scattering angle) to produce a circularly averaged pattern.

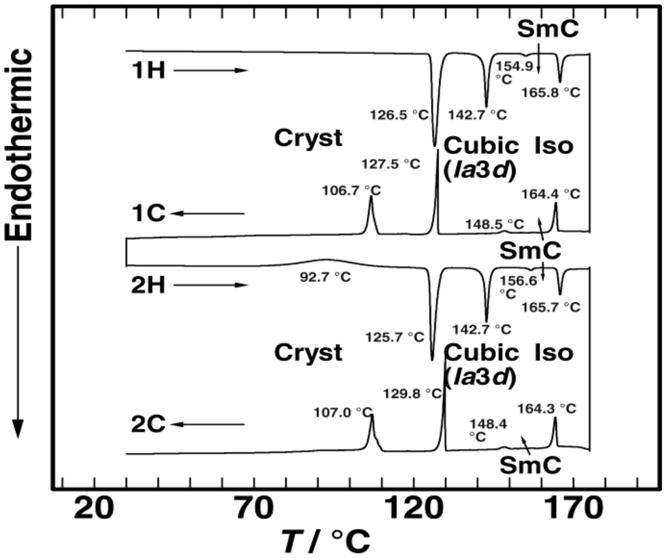

Figure S1 : DSC thermograms of BABH-9 (5 °C min^{-1}).

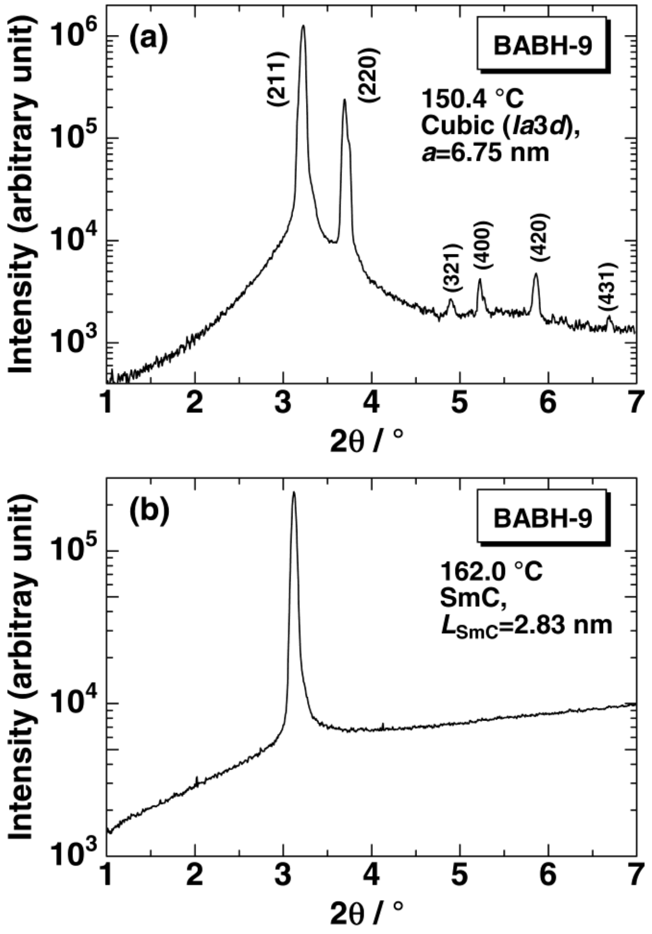

Figure S2 : XRD patterns of BABH-9 in (a) cubic (*Ia*3*d*) and (b) SmC phases.

(2) Mobility measurements[2]

Experimental: Time-Of-Flight (TOF) measurements were conducted to determine the mobility (see, SEI). using a TOF setup with a polarized optical microscope and a hot stage for the temperature control. The setup is described in the previous paper.[2] A sandwich- type cell with TiO_2-ITO electrodes was used for measurements. Carriers were injected by illumination of the positive TiO_2 electrode, since the compound BABH-9 does not show any significant photon absorption at 337nm (800 psec-pulsed N_2 gas laser). The cell gaps (distance between electrodes) were 3-7 μm and the mobility was calculated by means of the following equation:

$$\mu = d / \tau E$$

where μ is the mobility, d is the distance between the electrodes, τ is the determined transit time, and E the applied electric field.

The measurements were carried out successively starting at 135 °C to heat up to 160 °C and afterwards, the measurements were continued on cooling to 135 °C. The compound shows slight decomposition under the applied field and at the field above 10000 Vcm-1, it gets remarkable. Therefore, the measurements had to be operated so carefully and required new cells injected with the sample by each successive measurement.

References

1. S. Kutsumizu, H. Mori, M. Fukatami, S. Naito, K. Sakajiri and K. Saito, *Chem. Mater.*, 2008, **11**, 3675.

2. F. Nekelson, H. Monobe, M. Shiro and Y. Shimizu, *J. Mater. Chem.*, 2007, **17**, 2607.

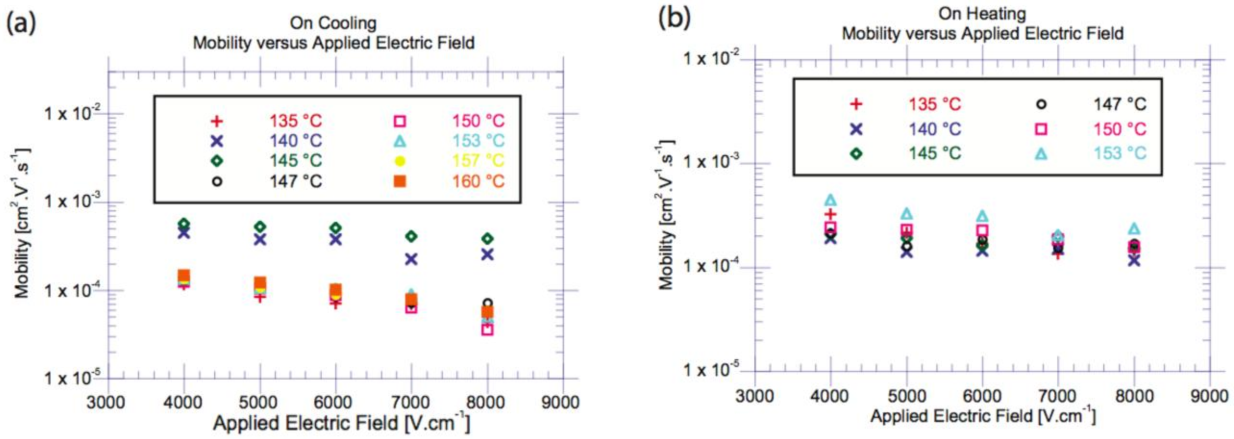

Figure S3 : Electric field dependence of the charge carrier mobility of BABH-9 obtained by TOF measurements for the positive illumination of the TiO_2 electrode. The temperatures range from 133°C to 153°C on cooling (a) and on heating (b).

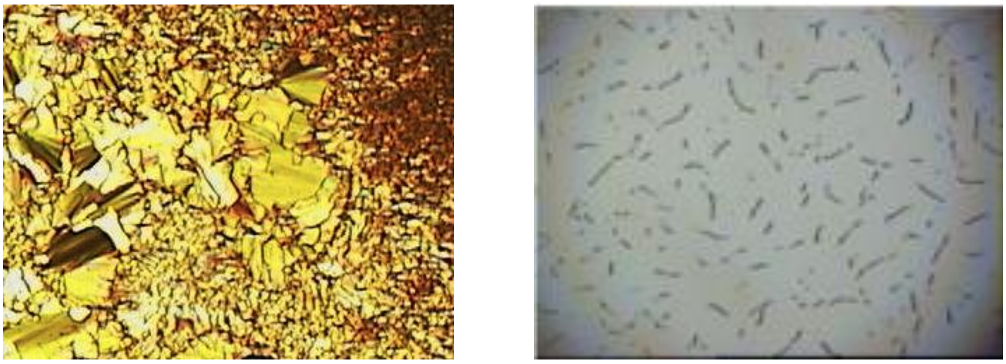
(a) (b)

Figure S4 : Optical textures of (a) the SmC (162 °C) and (b) cubic (*Ia*3*d*) phases in the TOF cell used for the mobility measurements. The former was a texture observed under crossed polarisers and the latter under non-polarisers where one sees domain boundaries.