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Supplementary Information

Flying-seed-like liquid crystals 3: New guideline for induction of mesomorphism by using bulky groups instead of long alkyl chains

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Synthesis

4-[4-(1,1-diphenylethyl)phenoxy]benzoic acid (3b)

A 50 ml of three-necked flask with a condenser was dried by a heat gun under nitrogen atmosphere. Into this flask, *p*-nitrobenzoic acid (0.18 g, 1.1mmol), distilled DMF (5 ml), K_2CO_3 (0.35 g, 2.5mmol), and 4-(1,1-diphenylethyl)phenol (**2b**: 0.30 g, 1.1mmol) was poured. It was heated with stirring under dry nitrogen atmosphere at 150 ^oC for 12 hours. After cooling to rt, it was neutralised by adding a 10% hydrochloric acid dilute aqueous solution, and then extracted with diethyl ether and washed with with NaCl saturated aqueous solution. The organic layer was dried over sodium sulphate and dried in vacuo. The residue was recrystallised from $CHCl_3$ to afford 0.14 g of light yellow solid in a 33% yield. M.p.: see Table 2.

IR(KBr): 3390 (- OH), 1725 (C=O), 1279 (ether) cm^{-1}

^{1}H-NMR (DMSO-d_6: TMS) δ 2.14 (3H, s, -C*H*$_3$), 6.74 (2H, d, J = 9.1 Hz, aromatic -*H*), 6.90 (2H, d, J = 9.0 Hz, aromatic -*H*), 7.10 ~ 7.35(14H, m, aromatic –*H*), 9.42 (1H, s, COO-*H*).

4-[4-(1-Methyl-1-phenylethyl)phenoxy]benzoic acid (3c)

A 100 ml of three-necked flask with a condenser was dried by a heat gun under nitrogen atmosphere. Into this flask, *p*-nitrobenzoic acid (0.41 g, 2.5mmol), distilled DMF (5 ml), K_2CO_3 (0.83 g, 6.0mmol), and 4-α-cumylphenol (**2c**: 0.58 g, 2.7mmol) was poured. It was heated with stirring under dry nitrogen atmosphere at 150 ^oC for 12 hours. After cooling to rt, it was neutralised by adding a 10% hydrochloric acid dilute aqueous solution, and then extracted with diethyl ether and washed with with NaCl saturated aqueous solution. The organic layer was dried over sodium sulphate and dried in vacuo. The residue was recrystallised from $CHCl_3$ to afford 0.46 g of white solid in a 58% yield. M.p.: see Table 2.

IR(KBr): 3400 (- OH), 1695 (C=O), 1254 (ether) cm^{-1}

^{1}H-NMR (DMSO-d_6: TMS) δ 1.75 (6H, s, -C*H*$_3$), 7.05 (2H, d, J = 9.1 Hz, aromatic -*H*), 7.26~7.45 (9H, m,aromatic -*H*), 7.91 (2H, 9.0Hz, aromatic -*H*), 9.18 (1H, s, COO-*H*).

4-(4-tert-butylphenoxy)benzoic acid (3d)

A 100 ml of three-necked flask with a condenser was dried by a heat gun under nitrogen atmosphere. Into this flask, *p*-nitrobenzoic acid (0.33 g, 2.0mmol), distilled DMF (5 ml), K_2CO_3 (0.69 g, 5.0mmol), and 4-α-cumylphenol (**2d**: 0.58 g, 2.7mmol) was poured. It was heated with stirring under dry nitrogen atmosphere at 110 ^oC for 3 hours. After cooling to rt, it was neutralised by adding a 10% hydrochloric acid dilute aqueous solution, and then extracted with diethyl ether and washed with with NaCl saturated aqueous solution. The organic layer was dried over sodium sulphate and dried in vacuo. The residue was recrystallised from $CHCl_3$ to afford 0.24 g of white solid in a 45% yield. M.p.: see Table 2.

IR(KBr): 3556 (Ar-OH), 1693 (C=O), 1239 (ether) cm^{-1}

^{1}H-NMR (DMSO-d_6: TMS) δ 1.31(9H, s, -C*H*$_3$), 7.04 (4H, m, aromatic -*H*), 7.43 (2H, d, J = 9.1 Hz, aromatic -*H*), 7.89 (2H, d, J = 8.9Hz, aromatic - *H*), 13.7 (1H, s, COO-*H*).

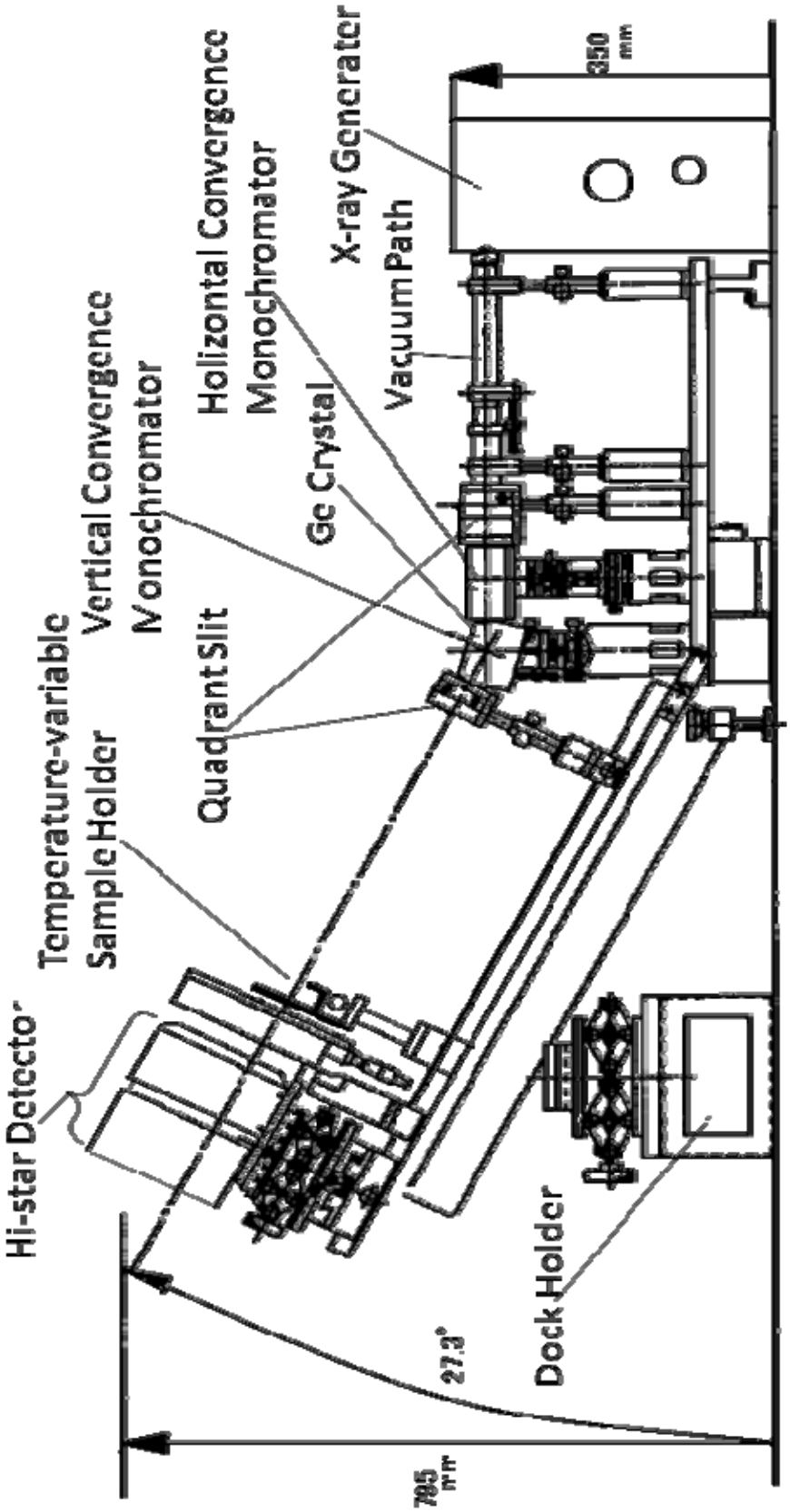

Fig. S1. Setup of Small-Angle X-ray Scattering (Bruker MACSAXS) equipped with a temperature-variable sample holder.

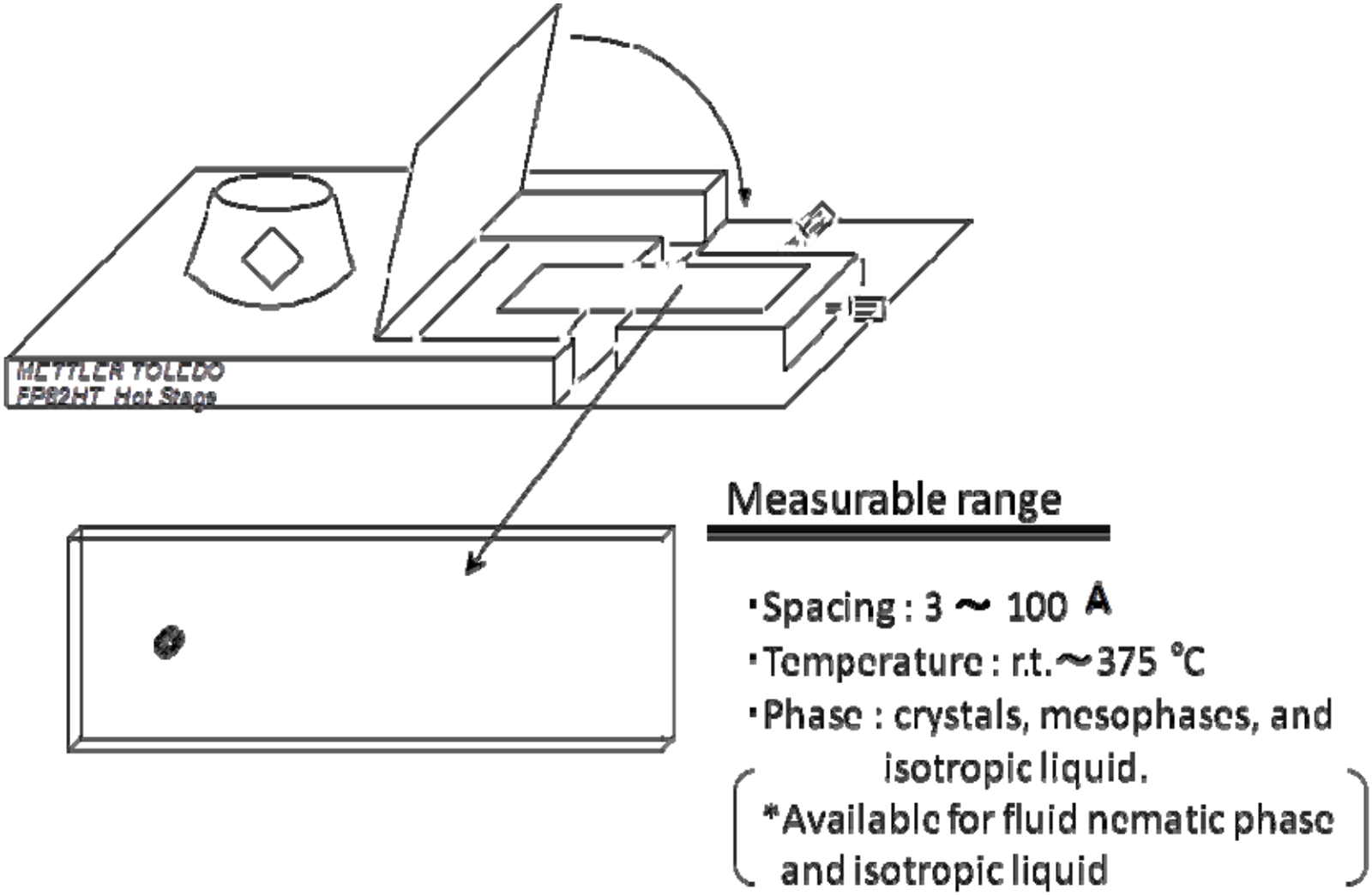

Fig. S2. Setup of the temperature-variable sample holder.