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Electronic supporting information

Porous surface of an achiral trimer in the chiral conglomerate phase catalyzes a direct aldol reaction

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1. Characterization of trimer **I-(9,9)** and the DSC thermogram. The rate of cooling and heating was 5 °C min⁻¹.

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1. Characterization of trimer **I-(9,9)** and the DSC thermogram. The rate of cooling and heating was 5 °C min⁻¹.

2-{4-[9-(4-(4-Octyloxyphenyl)phenyloxy)nonyloxy]phenyl}-5-{9-[4-(5-octyloxypyrimidin-2-yl)phenyloxy]nonyloxy}pyrimidine (I-(9,9)).

¹HNMR (500 MHz, CDCl₃, TMS): δ =8.40 (s, 4H, Ar-H), 8.26 (d, 4H, Ar-H, J = 8.6 Hz), 6.96 (d, 4H, Ar-H, J = 8.3 Hz), 6.93 (d, 4H, Ar-H, J = 8.0 Hz), 4.07 (t, 4H, - OCH₂-, J = 6.3 Hz), 4.02 (t, 2H, -OCH₂-, J = 6.3 Hz), 4.05 (t, 2H, -OCH₂-, J = 6.3 Hz), 3.99 (t, 2H, -OCH₂-, J = 6.9 Hz), 3.97 (t, 2H, -OCH₂-, J = 6.9 Hz), 1.85–1.69 (m, 12H, aliphatic-H), 1.47–1.29 (m, 40H, aliphatic-H), 0.89 (t, 6H, -CH₃, J = 6.9 Hz). IR (KBr):v cm⁻¹: 2933, 2851 (C-H str), 1608 (Ar-H str), 1246 (C-O str). Elemental Analysis Calcd. for C,76.6; H, 8.76; N, 5.43. Found C, 76.8; H, 8.40; N, 5.43.



DSC thermograms of trimer I-(9,9). The rate of cooling and heating was 5 °C min⁻¹.

2. Experimental procedure of the reaction of acetone with benzaldehyde using **90PYP50** as a catalyst.

90PYP50 (40 mg, 0.11 mmol) was added into a DMSO (5 ml)/acetone (5 ml) mixture. **90PYP50** was not dissolved in the solvent. Then, benzaldehyde (60 mg, 0.60 mmol) was added to the reaction mixture and it was stirred at room temperature. A spot corresponding to the product did not appear on a thin layer chromatography even after 149 h. After working up the reaction, no product was detected.

 $C_5H_{11}O \longrightarrow OC_9H_{19}$ **90PYP50**



Fig. S1 (a) Polarized optical textures of trimer **I-(9,9)** quenched from the isotropic liquid on a glass slide with a cover glass in the crystal between crossed and uncrossed polarizers at room temperature. (b) SEM image of the surface structure.



Fig. S2 Polarized optical textures of trimer **I-(9,9)** on a glass slide with a cover glass in the crystal between uncrossed polarizers.

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P-8-O-PIMB

Fig. S3 Molecular structure of P-8-O-PIMB