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Supporting information

Blue phases induced by rod-shaped hydrogen-bonded supermolecules possessing no chirality or mesomorphic behaviour

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Experimental details

Measurements

The specific optical rotations (SOR) were carried out on a PerkinElmer 341 polarimeter (PerkinElmer, USA). The element analysis (EA) was measured on Elementar Vario EL III (Elementar, Germany). Fourier Transform Infrared Spectroscopy (FT-IR) spectra were obtained from a Perkin–Elmer spectrum One (B) spectrometer (PerkinElmer, USA) using KBr pellets. Nuclear magnetic resonance (NMR) spectra got from Bruker AV 600 (600 MHz) NMR spectrometer (Bruker, Germany) with tetramethylsilane (TMS) as an internal standard. The thermal properties were characterized by use of a TA Q2000 DSC (TA, USA). A ZEISS Axio Scope A1 pol (Zeiss, Germany) polarizing optical microscope (POM) equipped with a Linkam THMSE-600 (Linkam, England) hot stage was used to observe the phase transition temperatures and analyse the mesomorphic properties through the observation of optical textures. X-ray diffraction (XRD) measurements of the samples were performed using Cu Kα(λ=1.54 Å) radiation monochromatized with a Bruker D8 ADVANCE X-ray diffractometer (Bruker, Germany).

Synthesis of M, PAB and supermolecules

4-(Menthyloxyacetoxy)phenyl-4'-(undec-10-enoyloxyphenyldiazenyl)benzoate ***(M)***

4-(undec-10-enoyloxyphenyldiazenyl)benzoic acid and 4-menthyloxyacetoxy phenol were synthesised according to the relative method in reported papers.[1-6] 4-menthyloxyacetoxy phenol (3.06 g, 10.0 mmol) and 4-(undec-10-enoyloxyphenyldiazenyl)benzoic acid (4.08 g, 12.0 mmol) were dissolved in 120 mL of THF and 20 mL of pyridine. DCC (2.47 g, 12.0 mmol), DMAP (0.12 g, 1 mmol) were dissolved in 60 mL of THF, and then added dropwise to the former solution. The reaction mixture was stirred for 30 h at 30 ℃. The resulting mixture was washed with 20 mL of water, stirred for 30 min, and filtered. The filtrate was concentrated by a rotary evaporator. The crude product was purified by means of silica gel column chromatography (toluene/ethyl acetate, 15/1, v/v). M (4.67g, 67%). mp 92.3 ℃ (from Ethyl acetate). SOR: $[\alpha]D^{25}$ -37.2 (c 1.02 in THF). Elemental analysis: Found: C 71.6; H 7.3; N 4.1; O 15.9. $C_{42}H_{52}N_2O_7$ requires C 72.4; H 7.5; N 4.0; O 16.1%. IR absorptions: 3079 (=C–H), 2958 and 2868 (–CH_3, –CH_2–), 1775, 1755 and 1727 (C=O), 1640 (C=C), 1601 and 1506 (Ar–), 1468 (N=N), 1271 (C–O–C). ^{1}H-NMR: δH (600MHz; $CDCl_3$; Me_4Si) 0.84-2.63 (30 H, m, –$(CH_2)_6$– and menthyl–H); 2.05 (2 H, m –CH_2–); 2.60 (2 H, t, –CH_2COO–); 3.28 (1 H, m, –CH< in menthyl); 4.38 (2 H, t, –OOCCH_2O–); 5.00 (2 H, m, CH_2=); 5.82 (1 H, m, =CH–); 7.21-8.36 (12 H, m, Ar–H). The ^{1}H-NMR spectrum of **M** is shown as Fig. S1.

Pyridin-4-yl 4-(allyloxy)benzoate ***(PAB)***

4-(allyloxy)benzoic acid were synthesised according the reported method.[7] A solution of 4-(allyloxy)benzoic acid (3.56 g, 20.0 mmol) in dry THF (150 mL) was added to a solution of 4-hydroxypyridine (2.28 g, 24.0 mmol) in THF (150 mL) containing DCC (4.94 g, 24.0 mmol) and DMAP (0.24 g, 2.0 mmol). The reaction mixture was stirred for 48 h at 30 ℃. The resulting mixture was washed with 25 mL of water, stirred for 30 min, and filtered. The filtrate was concentrated by a rotary evaporator. The crude product was purified by means of silica gel column chromatography (petroleum ether/THF, 7/2, v/v). **PAB** (3.21 g, 63%). mp 135.2 ℃ (from Ethyl acetate). Elemental analysis: Found: C 70.7; H 5.2; N 5.5; O 18.7. $C_{15}H_{13}NO_3$ requires C 70.6; H 5.1; N 5.5; O 18.8%. IR absorptions: 3060 (=C–H), 2967 and 2888 (–CH3, –CH2–), 1742 (C=O), 1643 (C=C), 1611-1506 (Ar–), 1580 (pridine). ^{1}H-NMR: δH (600MHz; CDCl3; Me4Si) 4.60 (2 H, d, –CH2–O–); 5.35 (2 H, m, CH2=); 6.05 (1 H, m, =CH–); 6.64, 7.81 (4 H, m, Ar–H); 6.94, 8.05 (4H, m, in pyridyl). The ^{1}H-NMR spectrum of **PAB** is shown as Fig. S2.

Synthesis of mixtures containing hydrogen-bonded supermolecules

Mixtures containing supermolecules were prepared by mixing **M**, proton donor and proton acceptor with designed requirements in tetrahydrofuran and heated to 60℃， followed by stirring for 24h. THF was slowly removed under reduced pressure. The resulting mixture was then dried in vacuum at room temperature for about 24h.

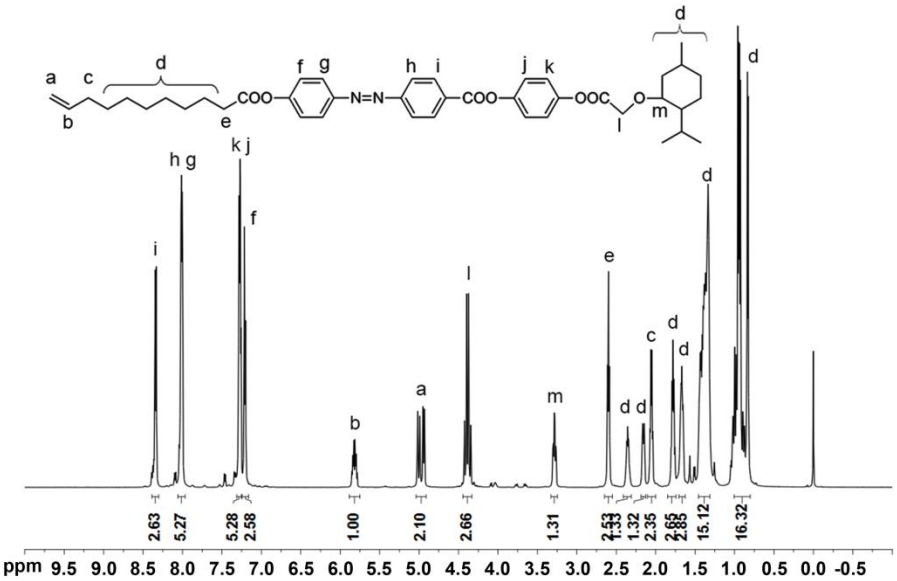

Fig. S1 ^{1}H NMR spectrum of **M**

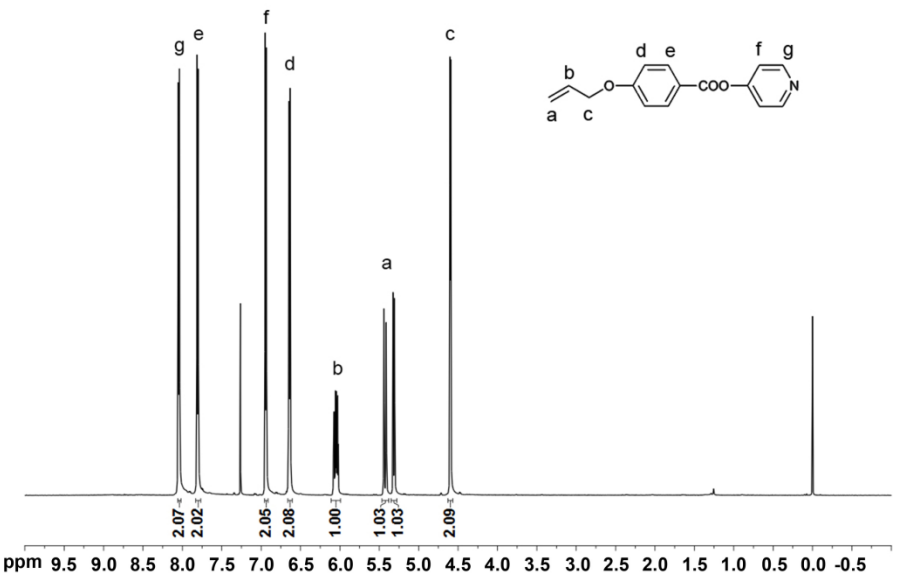

Fig. S2 ^{1}H NMR spectrum of **PAB**

Optical textures of M

The observations of POM showed that M exhibited two different types of liquid crystalline phases. The optical textures at the indicated temperatures are shown as follows.

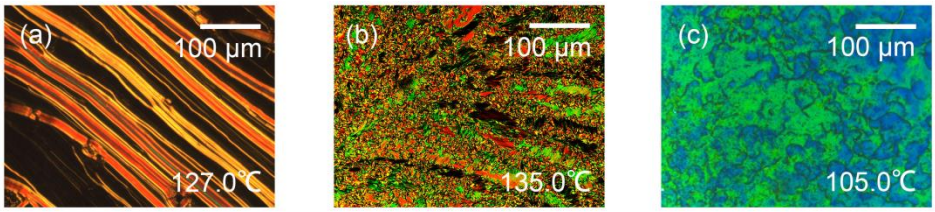

Fig. S3 Optical textures of **M**. (a) Oily streak texture of N* phase on heating to 127.0 ℃. (b) Focal conic texture of N* phase on cooling to 135.0 ℃. (c) Marble texture of SmC* phase on cooling to 105℃.

Reflection spectra of the mixture M(82mol%)/10A-PAB(18mol%)

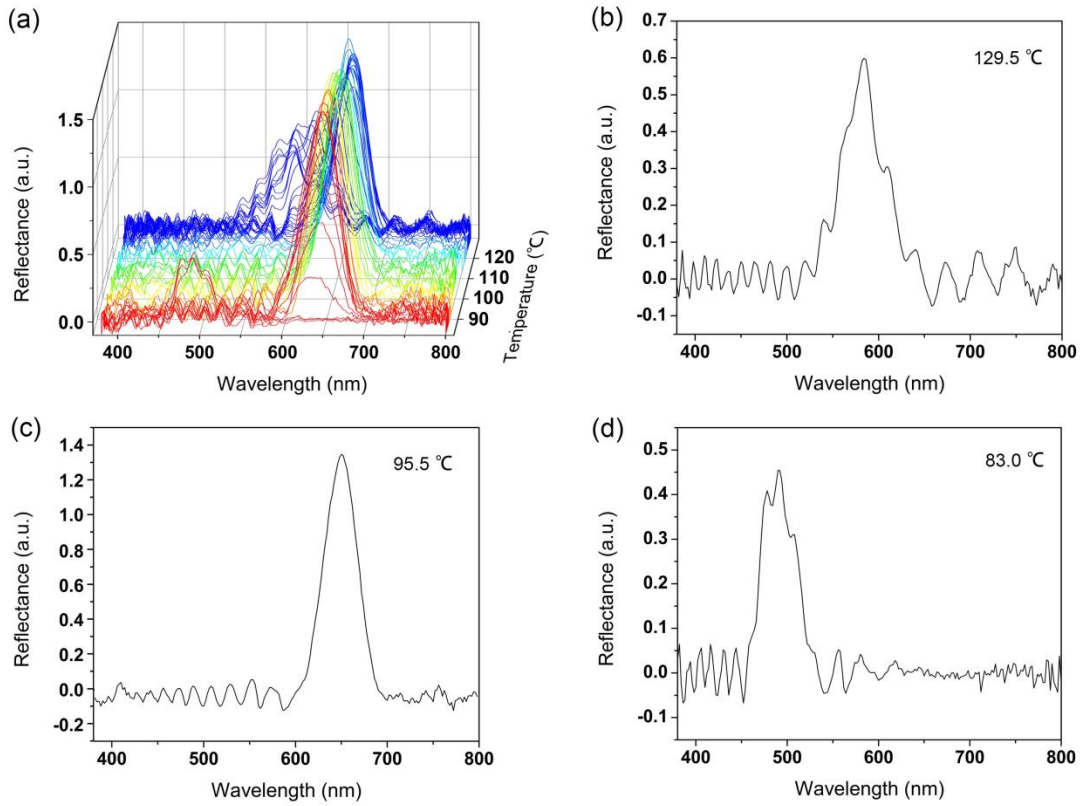

Fig. S4 (a)The reflection spectra of **M(82mol%)/10A-PAB(18mol%)** in BP and N* phase. (b)(c)(d) The reflection spectra of **M(82mol%)/10A-PAB(18mol%)** at 129.5, 95.5 and 83.0 ℃, respectively.

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