Electronic Supplementary Information

Facile preparation of oriented nanoporous silica films from solvent-free liquid-crystalline mixtures

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1. Conventional synthesis of nanostructured silica hybrids from 1 and TEOS

Synthesis of nanostructured silica films: A mixture of **1** (20 mg), TEOS (20–40 mg), THF (0.5 mL), ethanol (0.5 mL), water (10 μL), and 2 M hydrochloric acid (5 μL) was stirred at room temperature for 20 h. The acidic sol mixture was cast onto glass substrates and the solvents were removed under reduced pressure. The formation of periodic nanostructures was confirmed by XRD measurements (Fig. S1).

Synthesis of nanostructured and nanoporous silica powders: To a mixture of water (5 mL), ethanol (1 mL), **1** and TEOS was added 36% hydrochloric acid (1 mL). Rod-like red powders yielded in the reaction mixture after standing for 24 h. The as-synthesized **1**/silica hybrid was collected by filtration and calcined at 700 °C for 4 h to completely remove the PBI template. The structural properties of the powders were examined by optical microscopic observation, nitrogen adsorption–desorption isotherms, XRD measurements, and TEM observation (Fig. S2).

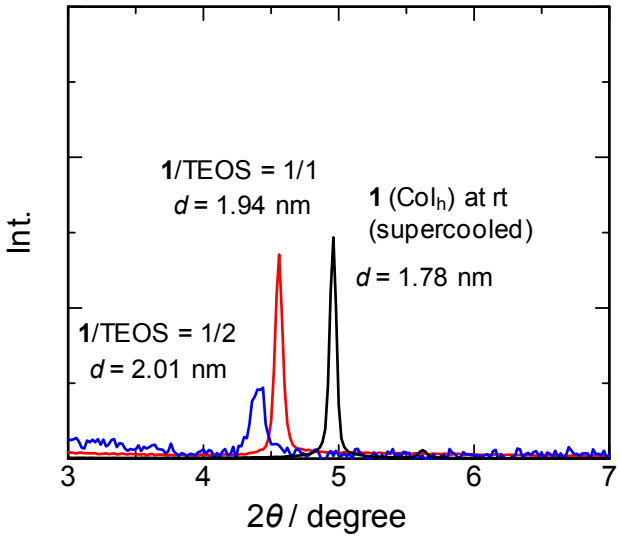

Fig. S1 XRD patterns of the nanostructured **1**/silica films prepared by a conventional sol–gel polycondensation method.

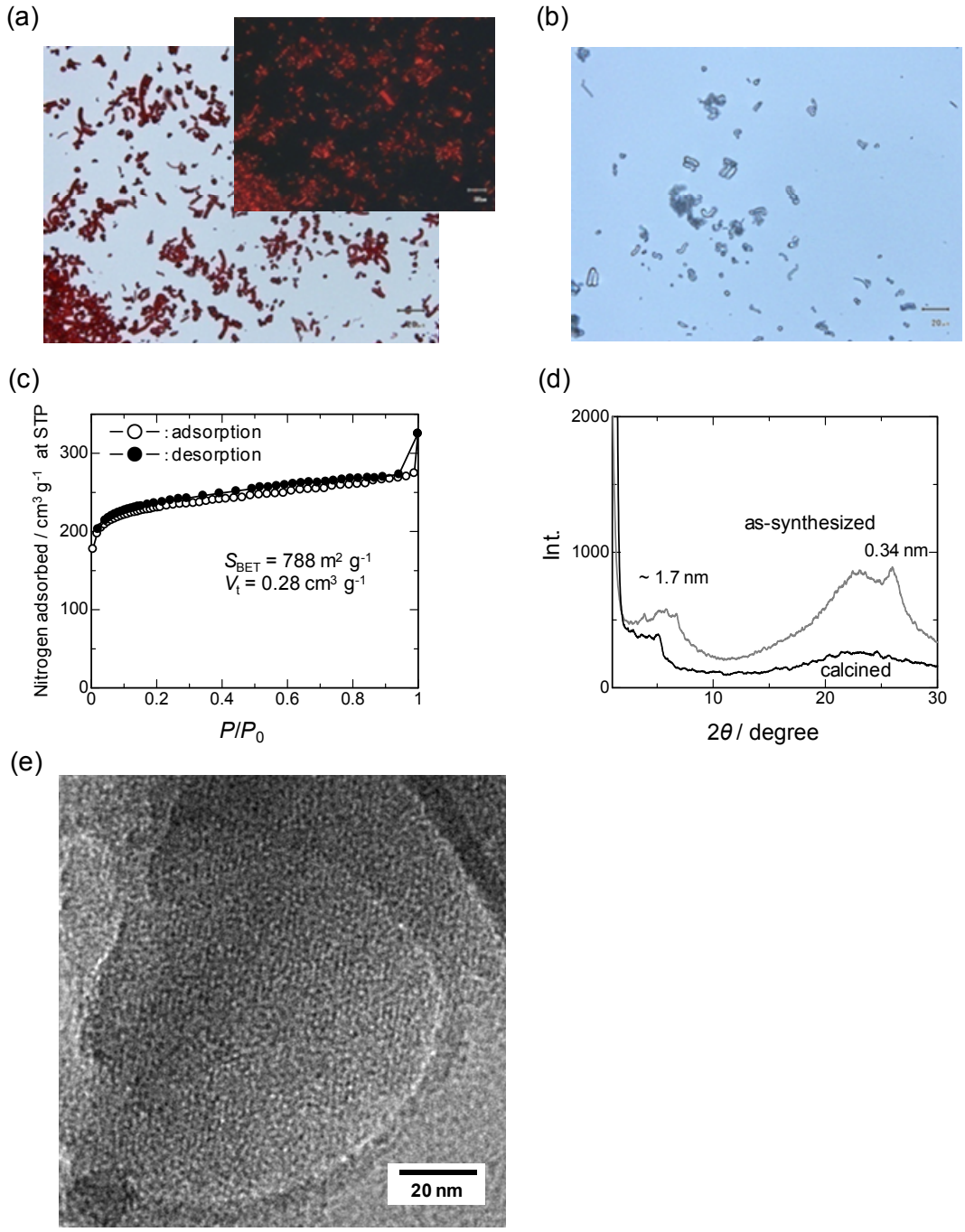

Fig. S2 (a) An optical microscopic image of the as-synthesized **1**/silica powder. The inset shows a polarized microscopic image. (b) An optical microscopic image of the calcined powder. (c) Nitrogen adsorption–desorption isotherm of the calcined powder. (d) XRD patterns of the as-synthesized and calcined powders. (e) A TEM image of the calcined nanoporous powder.

2. Optical microscopy observation of 1/TEOS and 1/TMOS mixtures

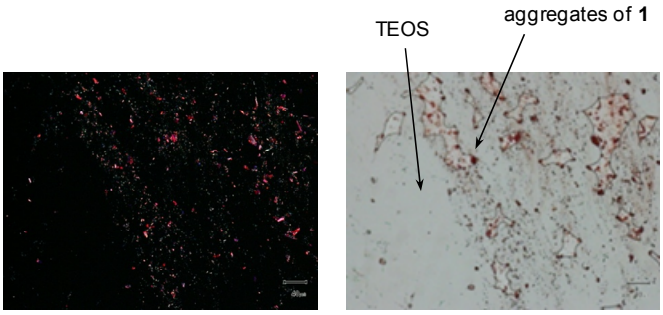

Fig. S3 Polarized (left) and non-polarized (right) microscopic images of the mixture of **1** and TEOS (10/90, w/w) exhibiting macroscopic phase separation.

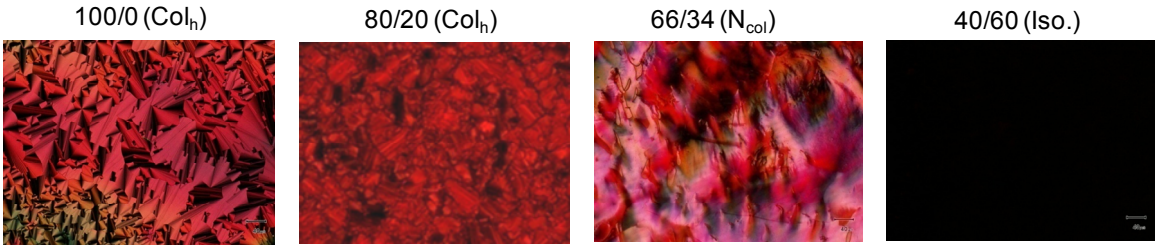

Fig. S4 Polarized optical photomicrographs of the **1**/TMOS (w/w) mixtures.

3. Supplementary data for the liquid-crystalline 1/TMOS mixtures

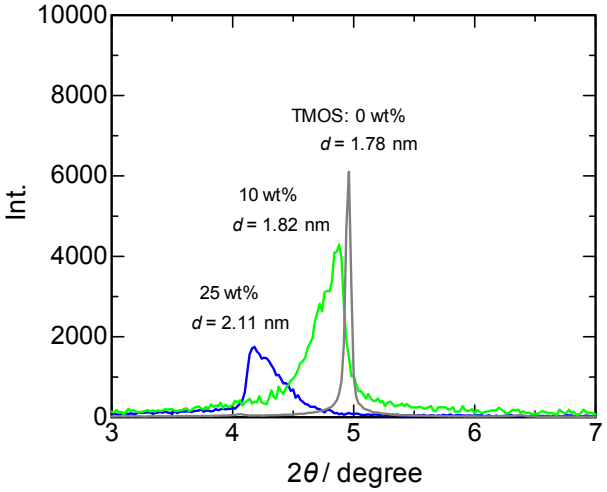

Fig. S5 X-ray diffraction pattern of the **1**/TMOS mixtures.

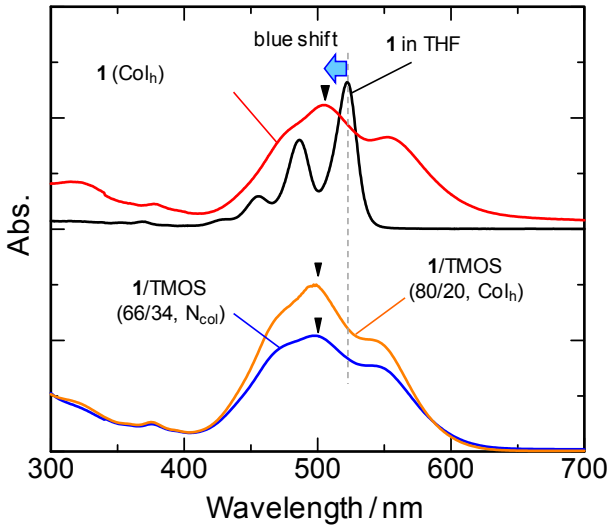

Fig. S6 UV-vis spectra of a THF solution of **1**, neat **1** film (Col_h), **1**/TMOS (80/20, Col_h) and **1**/TMOS (66/34, N_{col}).

4. Orientation behavior of the 1/TMOS/HCl aq. mixture

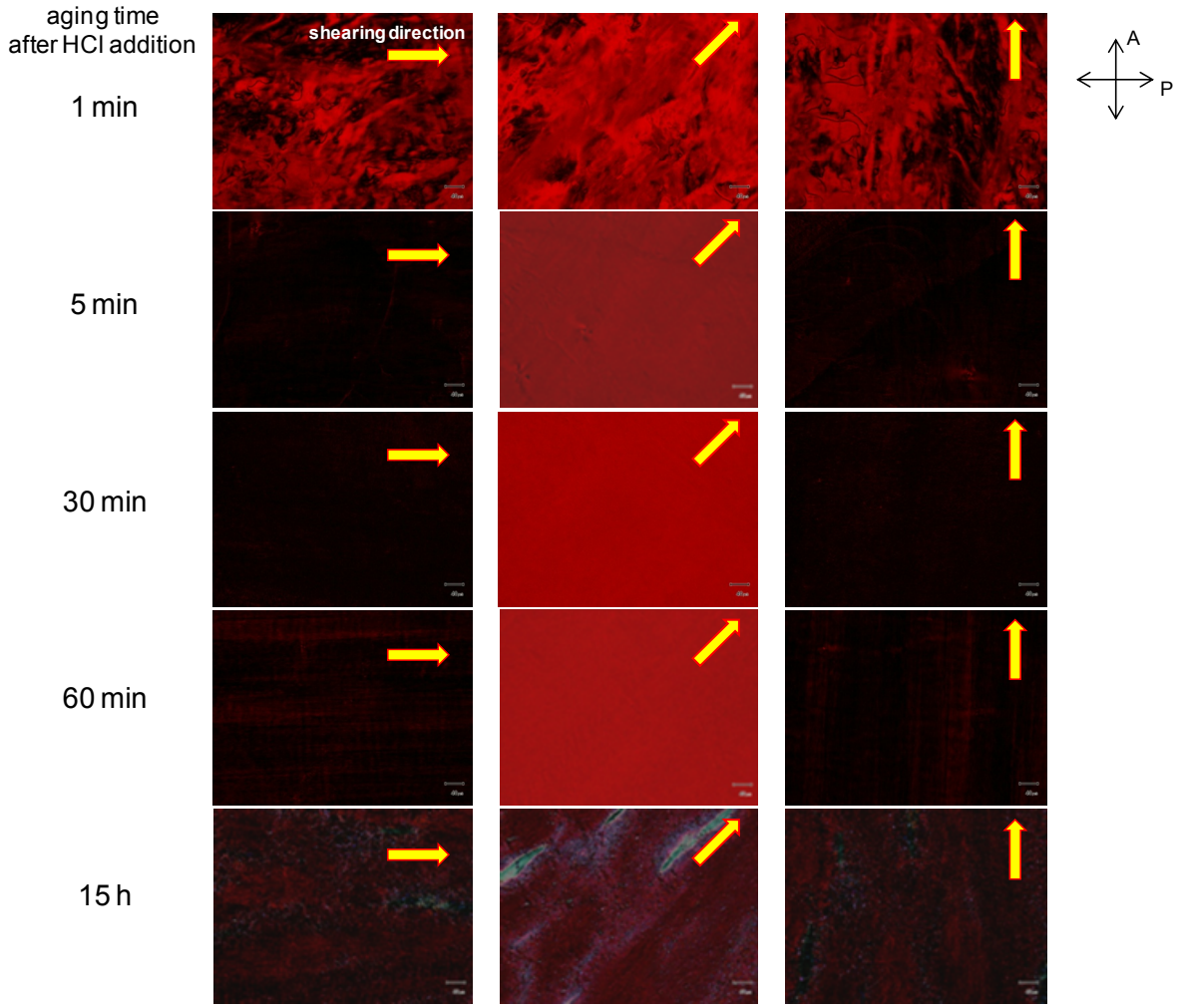

Fig. S7 Polarized optical photomicrographs of the LC sol mixture sheared between tow glass substrates after HCl addition (P: polarizer; A: analyzer).

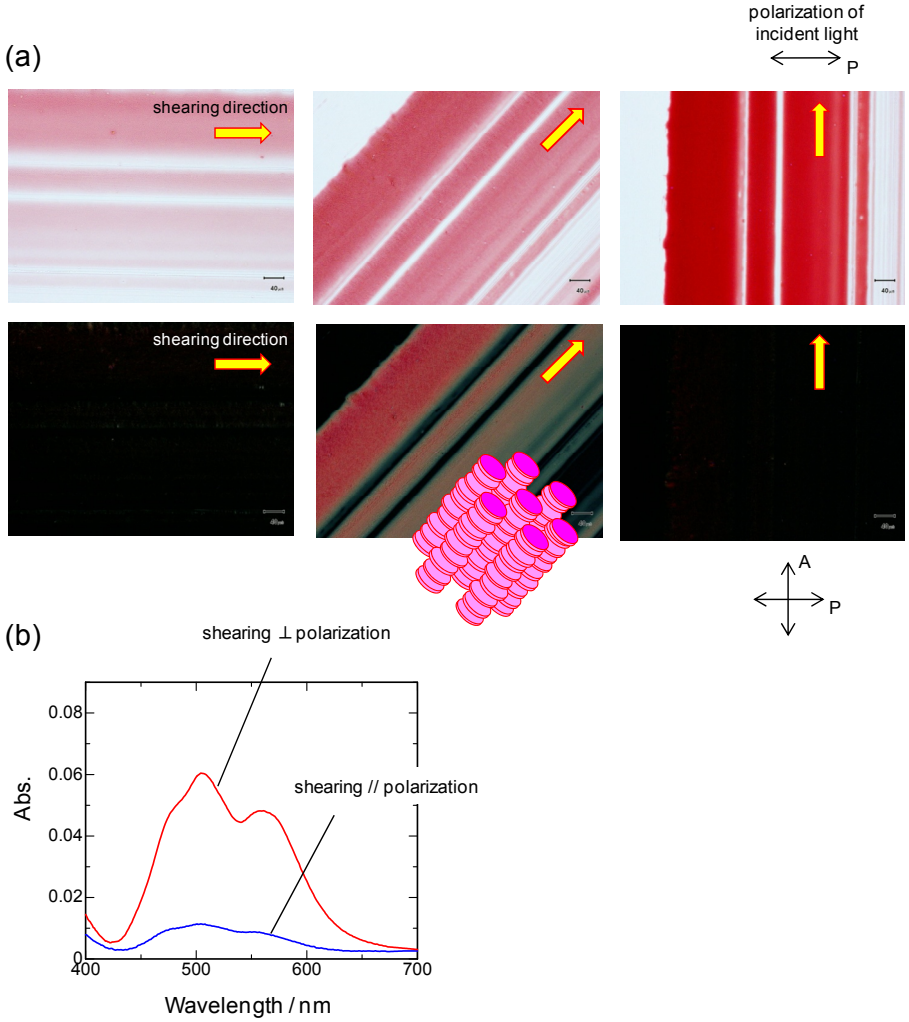

Fig. S8 (a) Polarized optical microscopy observation of the sheared **1**/TMOS (66/34) mixture under open nicol (top) and crossed nicols (bottom) conditions. (b) Polarized UV-vis spectra of the sheared **1**/TMOS mixture. The maximum absorption intensity was obtained when the polarization direction of the incident light was perpendicular to the shearing direction; therefore, the transition dipole moment of **1** is distributed perpendicularly to the shearing direction, i.e., the columnar aggregates of **1** are aligned along the shearing direction.

5. Characterization of the nanoporous material prepared from 1/TMOS mixtures

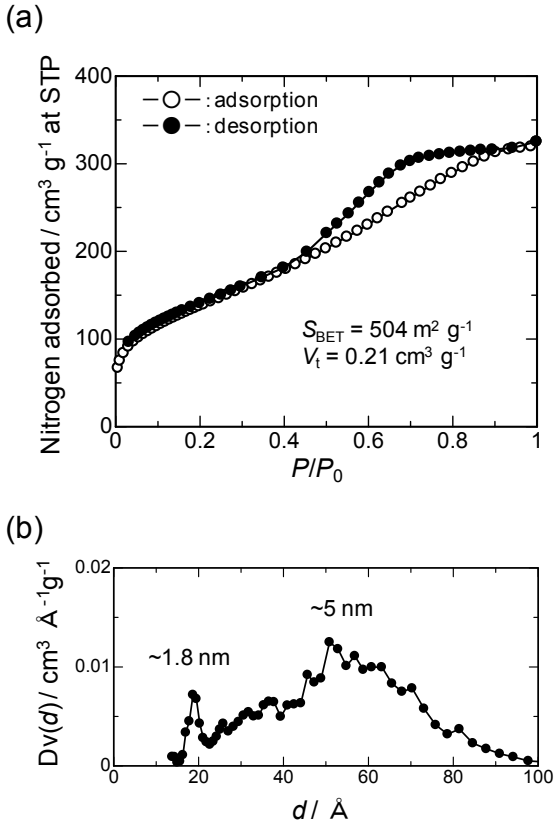

Fig. S9 (a) Nitrogen adsorption–desorption isotherm of the calcined silica film prepared from the **1**/TMOS (66/34, w/w) mixture. (b) Pore size distribution of the calcined material determined using the density functional theory (DFT) method (the DFT kernel used: N_2 at 77K on silica, cylindrical pore, NLDFT equilibrium model). The small pores with a diameter less than 2 nm correspond to nanochannels templated by a single PBI column. The meso-scale pores centered at ~ 5 nm are thought to be formed by fusion of the PBI-templated microchannels.