

-Supporting Information- Flexible and Iridescent Chiral Nematic Mesoporous Organosilica Films

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1. Materials and Characterization

1,2-Bis(trimethoxysilyl)ethane (BTMSE) (Aldrich, 96%), 1,2-bis(triethoxysilyl)ethane (BTSE) (Aldrich, 96%), and tetramethyl orthosilicate (TMOS) (Acros, 99%) were used without further purification. Polarized optical microscopy was performed on an Olympus BX41 microscope. All images were taken with the polarizers in a perpendicular (crossed) arrangement. Thermogravimetric analysis was performed on a PerkinElmer Pyris 6 thermogravimetric analyzer (all samples were run at 10 °C/min under air). Elemental analysis (C N H) was carried out at UBC Microanalytical Services Laboratory. UV-visible/near-IR spectroscopy was conducted on a Cary 5000 UV-Vis/NIR spectrophotometer by mounting the films on glass microscope slides so that the films surfaces were perpendicular to the beam path. CD experiments were performed using a JASCO J-710 spectropolarimeter by mounting the films in the same manner. For CD spectra of the dry films, small pieces that did not completely cover the aperture were used in order to avoid saturating the detector. Due to the different sizes of the films used, the CD signals were all normalized to 1000 mdeg. For the films loaded with different solvents, the CD signals were greatly reduced allowing for the aperture to be covered without saturating the detector. The intensity of the CD signals for films loaded with different liquids can therefore be compared. Nitrogen adsorption data were obtained at 77 K using a Micromeritics ASAP 2000 analyzer. Sample weights of ~100 mg were used for all measurements. The pore-size distributions were derived from the adsorption branches using the Barrett-Joyner-Helenda (BJH) method. SEM experiments were conducted on a Hitachi S4700 electron microscope. Samples were typically sputter-coated with 5 nm of gold prior to observation. TEM micrographs were obtained with a Hitachi H7600 at an acceleration voltage of 80 kV. The samples were prepared by drop-casting a dilute NCC suspension onto a carbon-coated TEM grid followed by negative staining with a 2% uranyl acetate solution. Solid-state NMR spectra were collected on a 400 MHz Varian Unity Inova. ¹³C CP/MAS experiments (100 MHz, 3000 acquisitions) used glycine as a reference and ²⁹Si CP/MAS experiments (80 MHz, 16000 acquisitions) used DSS as a reference. Tensile strength measurements were carried out on a Deben microtensile stage equipped with a 200 N load cell. Films were cut into ~15 mm x 5 mm strips and elongated at a constant rate of 0.1 mm/min until fracture occurred.

2. Experimental

Preparation of nanocrystalline cellulose (NCC). Fully-bleached, commercial kraft softwood pulp was first milled to pass through a 0.5-mm screen in a Wiley mill to ensure particle size uniformity and to increase surface area. The milled pulp was hydrolyzed in sulfuric acid (8.75 mL of a sulfuric acid solution/g pulp) at a concentration of 64 wt. % and a temperature of 45 °C with vigorous stirring for 25 min. The cellulose suspension was then diluted with cold de-ionized (DI) water (~10 times the volume of the acid solution used) to stop the hydrolysis, and allowed to settle overnight. The clear top layer was decanted and the remaining cloudy

layer was centrifuged. The supernatant was decanted and the resulting thick white suspension was washed 3 times with DI water to remove all soluble cellulose materials. The thick white suspension obtained after the last centrifugation step was placed inside dialysis membrane tubes (12,000-14,000 molecular weight cut-off) and dialyzed against slow running DI water, for 1-4 days. The membrane tubes containing the extracted cellulose materials were placed periodically in DI H₂O, and the procedure was continued until the pH of the water became constant over a period of one hour, indicating that residual sulfuric acid had been completely removed. The suspension from the membrane tubes was dispersed by subjecting it to ultrasound treatment in a Fisher Sonic Dismembrator (Fisher Scientific) for 10 minutes at 60% power and then diluted to the desired concentration (3 wt. %). The final suspension had a pH of 2.4. NCC produced by sulfuric acid hydrolysis contains strongly acidic surface sulfate groups that provide the NCC with a negative surface charge when suspended in water. The acidity of the suspension is due only to the surface sulfate groups; no additional acid was added.

Synthesis of ethylene-bridged chiral nematic mesoporous organosilica. The preparation of composite sample **C1** is given as a representative example. 25 mL of a 3 wt. % aqueous NCC suspension was sonicated for 10 min using an Aquasonic 50T sonic cleaner. BTMSE (625 μ L, 2.5 mmol) was added to the NCC suspension with stirring and allowed to continue stirring at room-temperature for 1 h. 5 mL portions were then transferred to 60 mm polystyrene Petri dishes and allowed to dry for 48 h under ambient conditions. For the removal of NCC, the composite films (640 mg) were placed in 900 mL of 6 M sulfuric acid and heated to 100 °C for 18 h. The films were then filtered and alternately washed with a solution of piranha (20 mL 30% H₂O₂ / 100 mL H₂SO₄) and water until they appeared colorless. The films were then washed with 2 L of water and allowed to air-dry yielding 202 mg of **CMO1**. The remaining samples were prepared using the exact same procedure with the only difference being the volume of BTMSE that was added. The volume of BTMSE per 25 mL of 3 wt. % NCC used for the preparation of samples **C2-C4** are as follows: **C2** (850 μ L), **C3** (1000 μ L), and **C4** (1250 μ L). The average thicknesses measured for the free-standing mesoporous organosilica films were 40 μ m, 53 μ m, 65 μ m, and 77 μ m for **CMO1-CMO4** respectively.

3. Supporting Figures

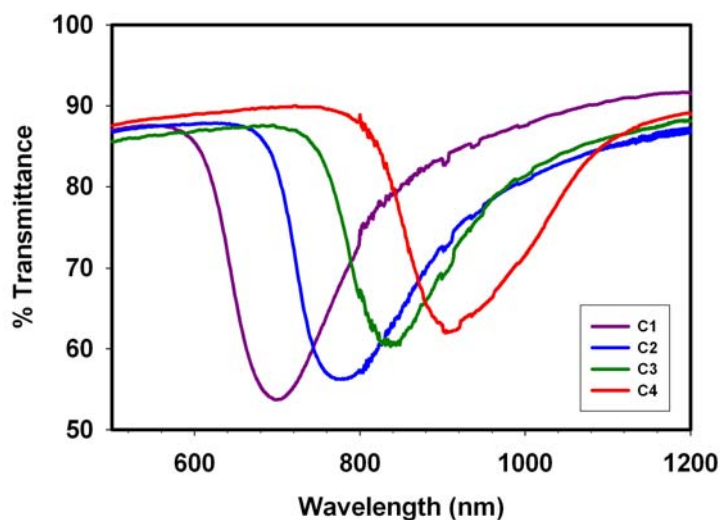


Figure S1. UV-Vis/NIR transmittance spectra of NCC-organosilica composite films.

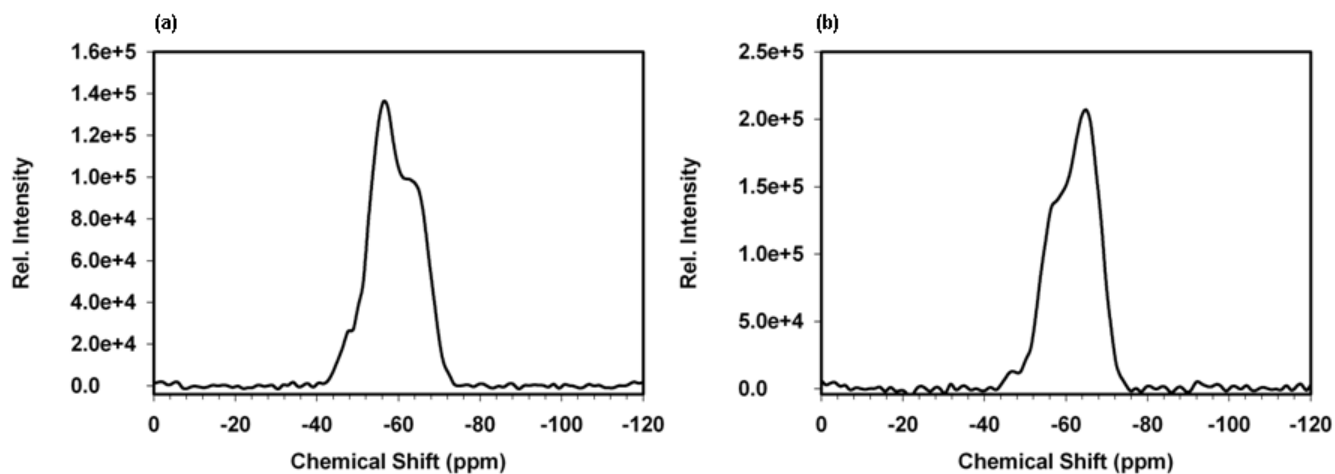


Figure S2. Solid-state ^{29}Si CP-MAS NMR spectra. (a) NCC-organosilica composite **C3**. (b) Mesoporous organosilica **CMO3**.

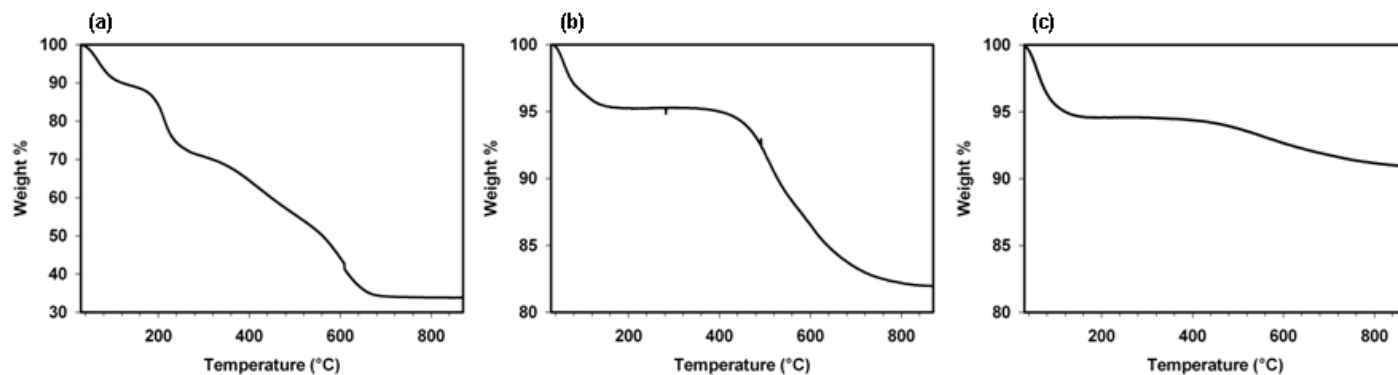


Figure S3. (a) TGA of NCC-organosilica composite sample **C3**. (b) TGA of mesoporous organosilica sample **CMO3**. (c) TGA of mesoporous silica obtained by acid hydrolysis of NCC-silica composite films.

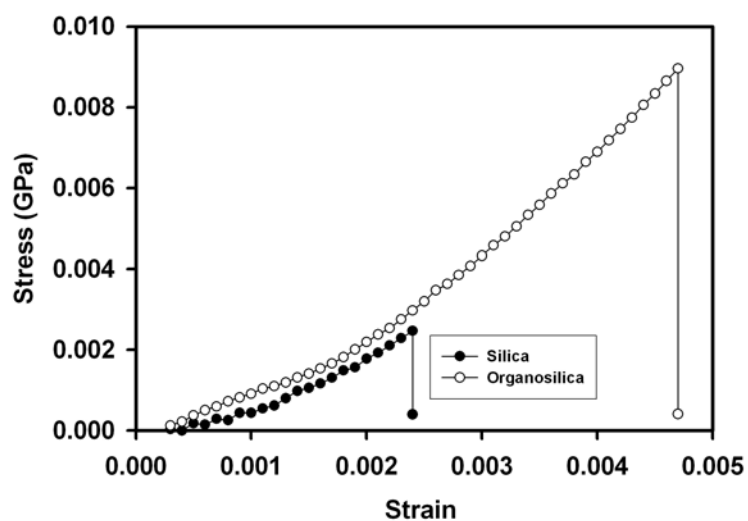


Figure S4. Tensile stress-strain curves for free-standing films of mesoporous organosilica **CMO2** and mesoporous silica obtained by acid hydrolysis of an NCC-silica composite.

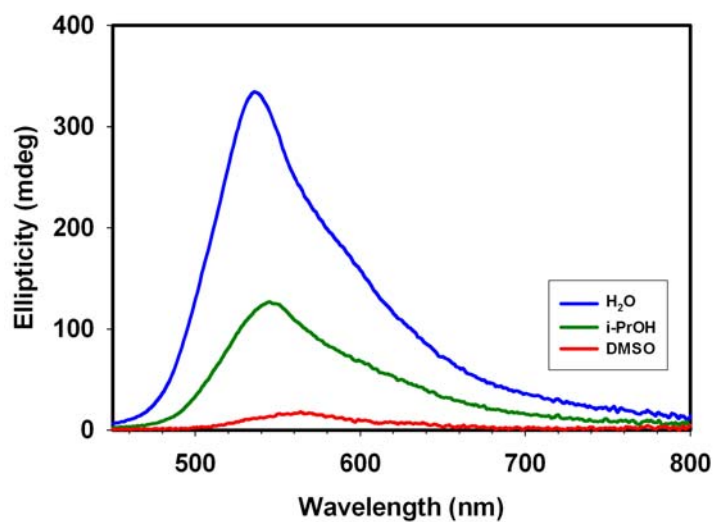


Figure S5. CD spectra of mesoporous organosilica film **CMO2** after absorbing different liquids.