Electronic Supplementary Material (ESI) for ChemComm.

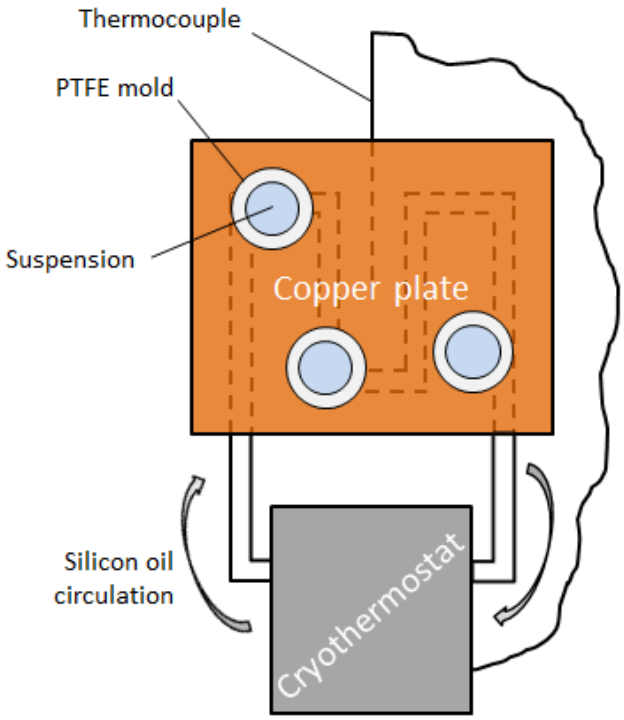
Freezing-induced ordering of block copolymer micelles

Supporting Information

S1:Detailed freezing protocol and characterization

Freezing protocol

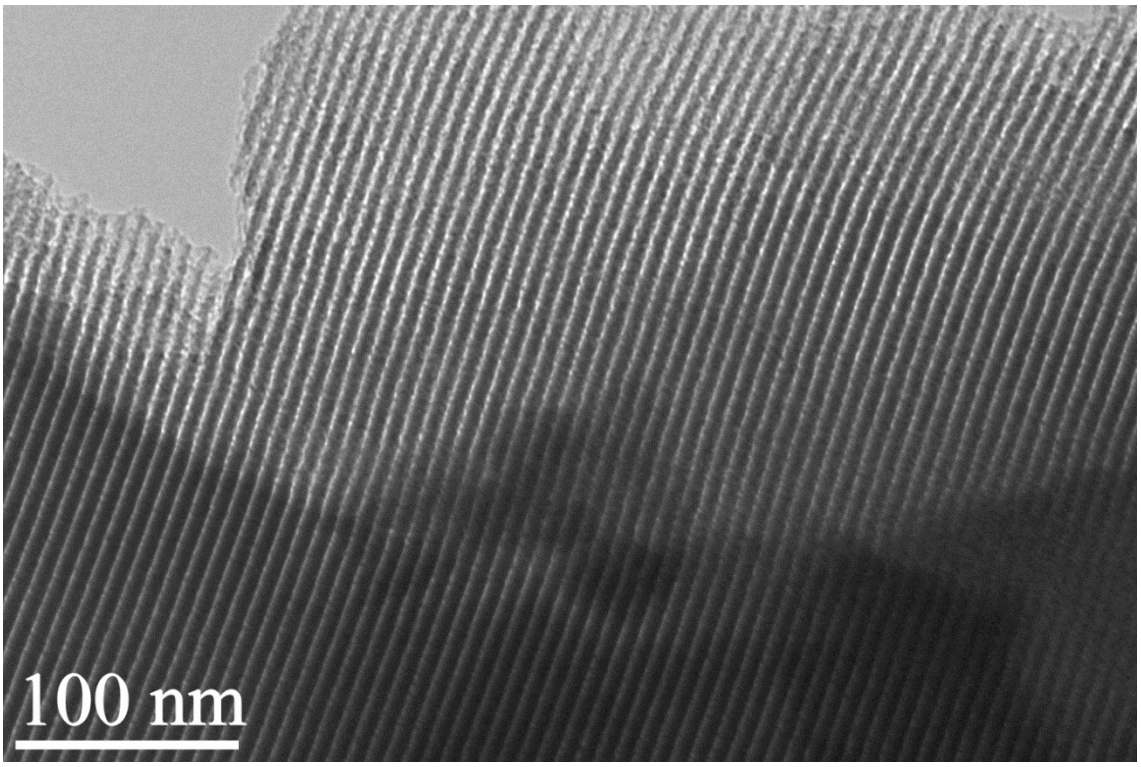
The suspension containing almost no ethanol trace is poured into PTFE molds, formerly deposited on a copper plate. This copper plate is cooled from the bottom at constant -2°C/minute cooling rate until complete freezing of the suspension. The cooling rate is controlled by a thermocouple located inside of the copper plate and connected to a Huber CC 905 cryothermostat (see figure below). Alternatively, a cooling rate of about -10°C/minute can be reached by placing the PTFE molds on the top of copper rods, then sunken in a liquid nitrogen-filled Dewar, with only few consequences on the material properties at the mesoscale. After complete freezing samples are demolded, then placed in a Labconco FreeZone 2.5 freeze-dryer to sublime the ice crystals (-80°C ; 0.120 mbar) for 48h.



Characterization

Small-angle powder X-ray diffraction patterns were recorded with a 0.05° step size (step time = 1 s) on a Siemens D5000 X-ray diffractometer equipped with a CuKα1 monochromatic radiation source (40 kV, 35 mA) and a 0.1 mm reception slit. Nitrogen physisorption was performed on a Micromeritics Tristar II instrument, after treatment of the samples under primary vacuum (20 mTorr) at 280 °C for four hours. Surface areas were calculated using the Brunauer-Emmet-Teller (BET) method over the range P/Po = 0.07-0.30, where a linear relationship was maintained. Mesopore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) model applied to the desorption branch of the isotherm. Mesopore volumes were evaluated on the volume adsorbed at P/Po = 0.99. Scanning electron micrographs were acquired on a scanning electron microscope FEI Nova NanoSEM 230. Prior analysis, a thin coating of platinum was deposited onto the samples. High-resolution transmission electron microscopy was carried out by using a FEI Tecnai G2 20 operating at 200 kV. Samples were prepared by depositing a drop of solution containing the sample in ethanol on a holey-carbon filmed copper grid. Mercury intrusion porosimetry was performed on a Micromeritics AutoPore IV 9500.

S2: TEM image of FISA-templated mesoporous silica, view of the hexagonal channels



S3: Small angle XRD patterns (shifted vertically) of FISA-templated mesoporous silica with variation of sol-gel and process parameters.

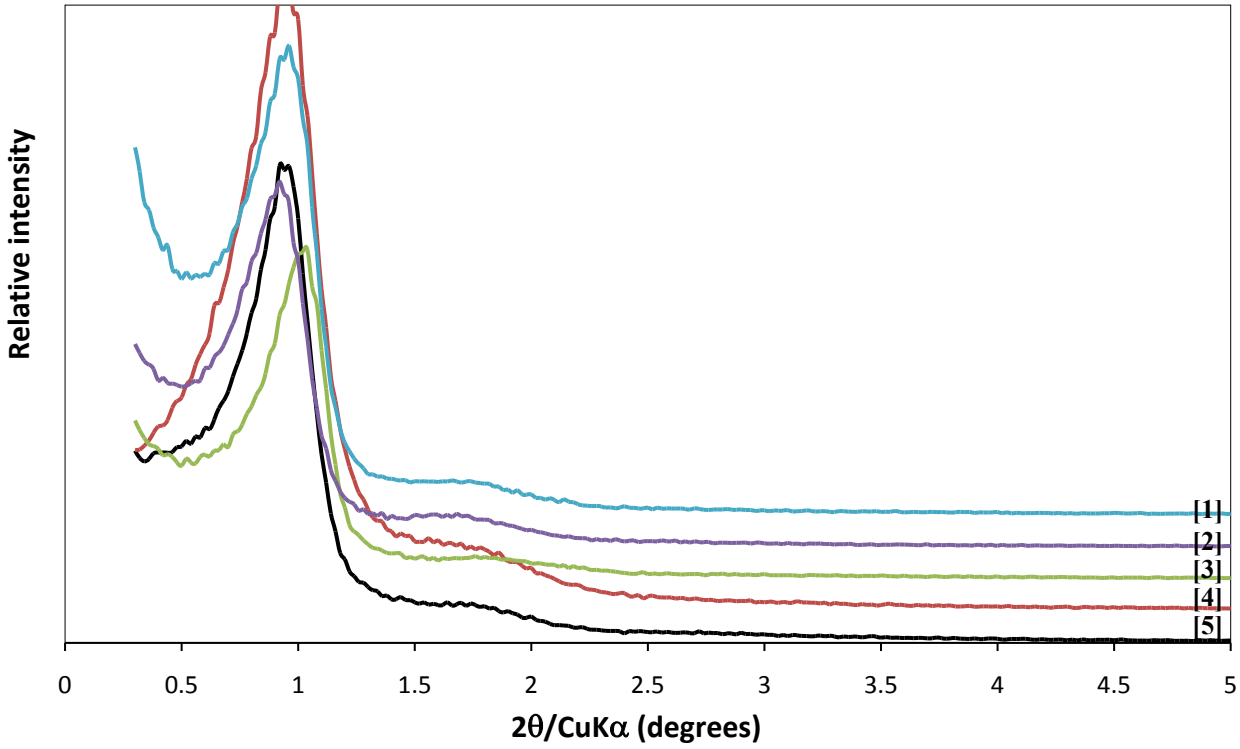
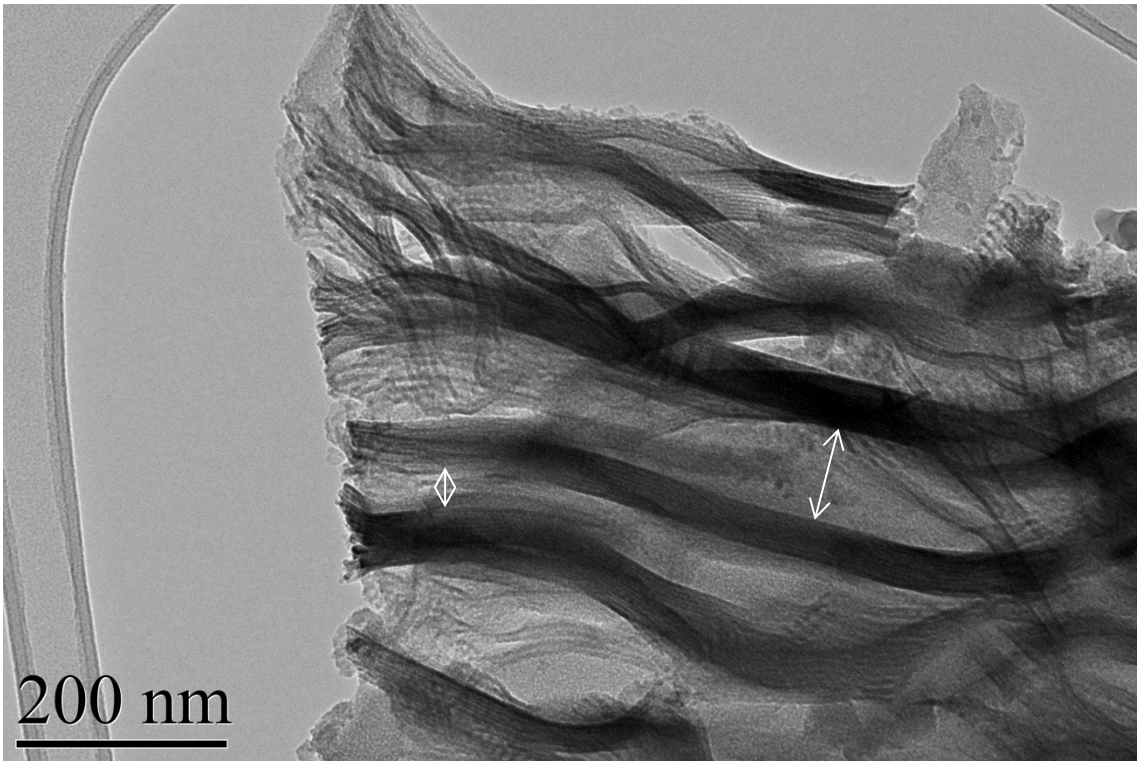


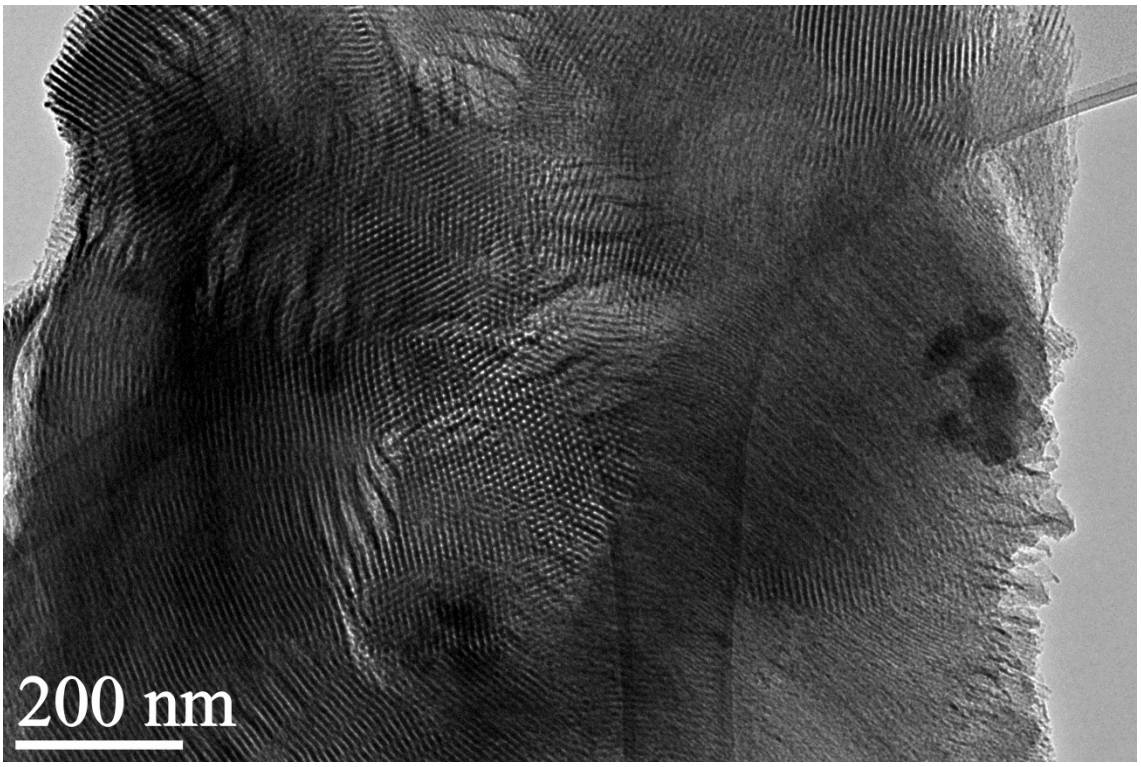
Table S1: Structural properties of FISA-templated mesoporous silica, influence of sol-gel and process parameters.

[X]	Ageing temperature (°C)	Cooling rate (°C/min)	pH	d_{10} (nm)
1	22	-2	1.3	9.2
2	35	-2	1.3	9.6
3	35	-10	1.3	8.5
4	35	-2	1.1	9.2
5	35	-2	1.8	9.6

S4: TEMimage of Bundle-like channels at the surface of the macropore walls



S5: TEM image of the mesostructuration state of macropore walls core



S6: Nitrogen adsorption-desorption isotherms (shifted vertically by 100 cm^3/g) and BJH pore size distributions of FISA-templated mesoporous silica with variation of sol-gel and process parameters

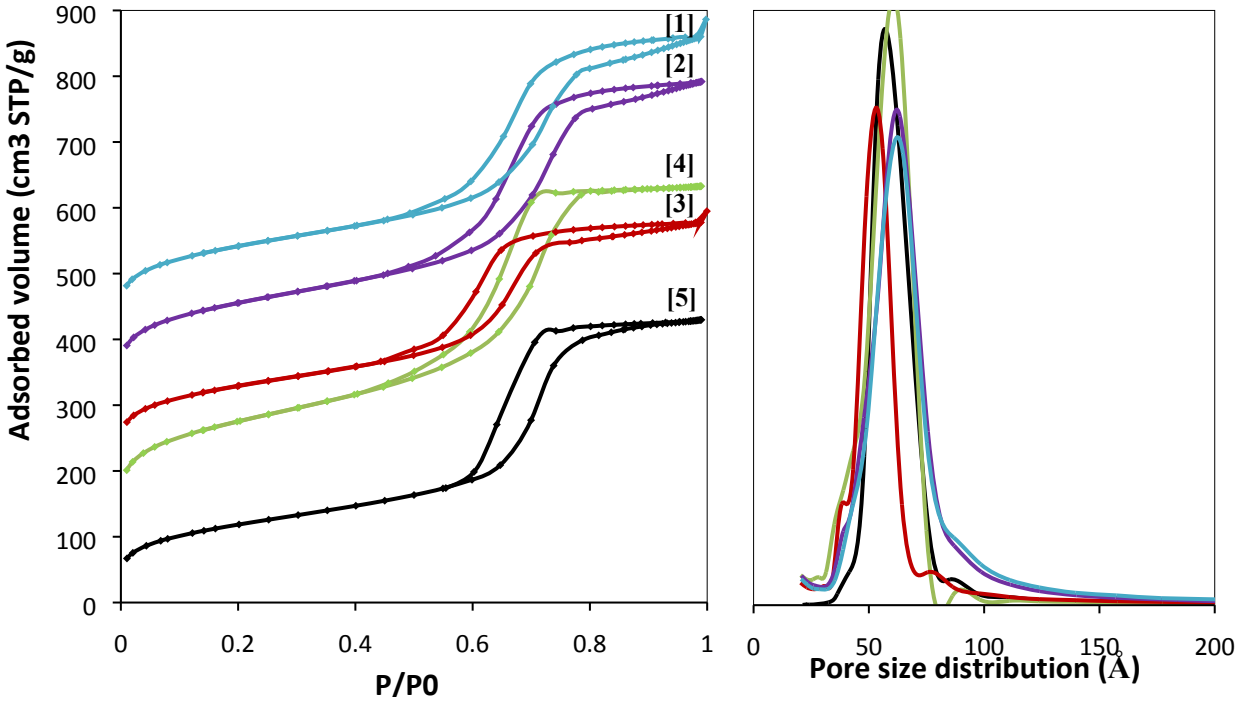
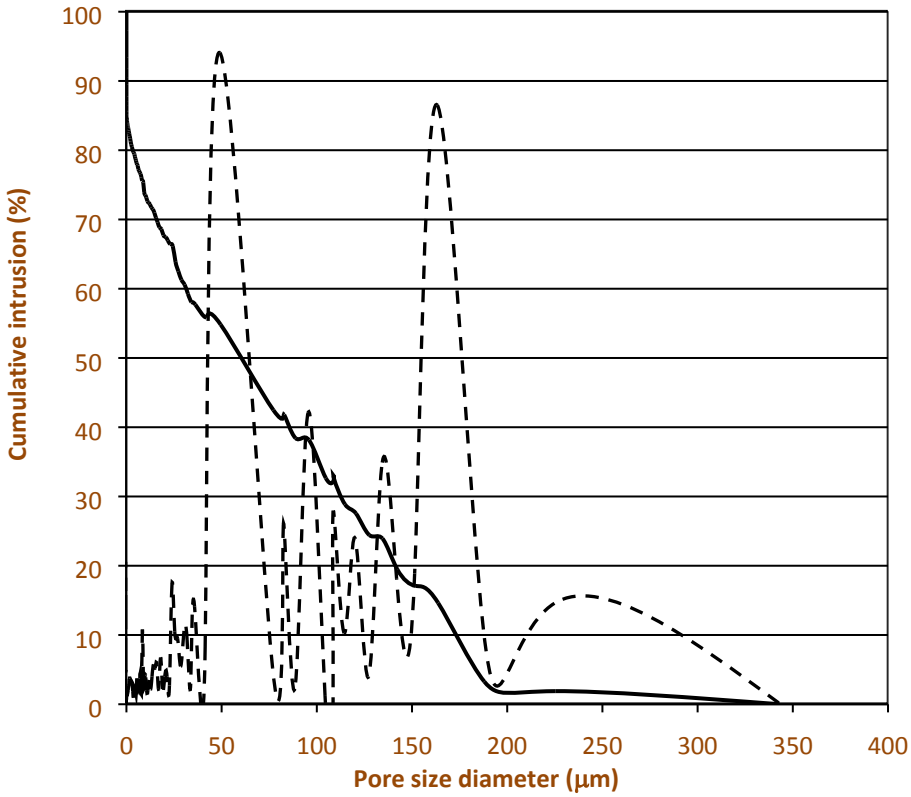


Table S2: Textural properties of FISA-templated mesoporous silica, influence of sol-gel and process parameters.

[X]	Ageing temperature (°C)	Cooling rate (°C/min)	pH	SSA (m^2/g)	$d_{mesopores}$ (nm)	V_{porous} (cm^3/g)
1	22	-2	1.3	487	6.2	0.74
2	35	-2	1.3	535	6.3	0.78
3	35	-10	1.3	446	5.4	0.61
4	35	-2	1.1	607	6.2	0.85
5	35	-2	1.8	412	5.7	0.67

S7: Mercury porosimetry of FISA-templated mesoporous silica



SiO_2 : 71 H_2O : 0.017 P123 (pH = 1.3)

Apparent density = 0,99 g/ml

Porosity (> 6 nm) = 43,0 %