

Supplementary Information

Ethanol vapor-mediated maturing for the enhancement of structural regularity of hexagonal mesoporous silica films

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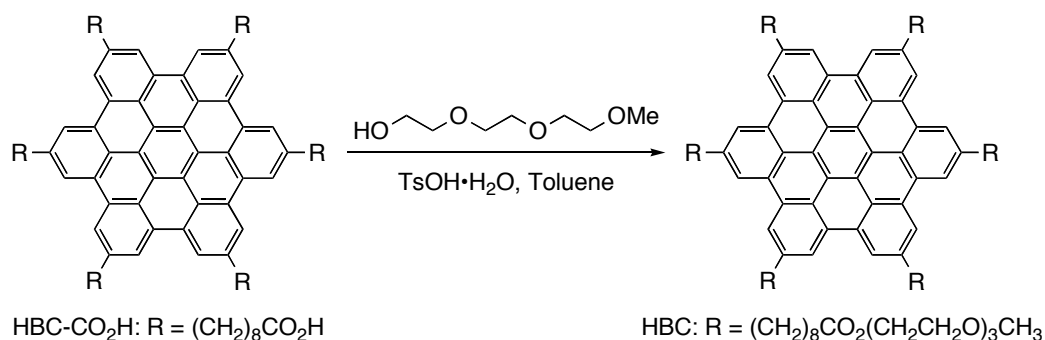
General Measurements. XRD analysis was carried out on a Rigaku model RINT2500PC small and wide-angle X-ray diffractometer using Cu K α radiation. TEM micrographs were taken on a JEOL model JEM-2010 transmission electron microscope. Calcination was carried out at 450 °C for 3 h with a Yamato model F0810 muffle furnace. DSC measurements were carried out on a METTLER TOLEDO model DSC822e differential scanning calorimeter. Preparative SEC was performed at room temperature using columns JAIGEL 1H and 2H on a Japan Analytical Industry Model LC-908 recycling preparative HPLC system, equipped with a JASCO Model MD-2010 variable-wavelength UV-vis detector.

Materials. 1-Cetyl-3-methylimidazolium chloride (CMICl) was prepared by alkylation of 1-methylimidazole with 1-chlorohexadecane in EtOH under reflux for 2 days. The reaction mixture was evaporated to dryness, and the residue was recrystallized from ethyl acetate, affording CMICl as colorless powder. Melting point (DSC) 64 °C.¹ TP was synthesized according to a literature method² and unambiguously characterized. Other reagents including surfactants and TCNB were used as-received from Kanto Chemical Co., Inc., Wako Pure Chemical Industries, Ltd. and Tokyo Kasei Kogyo Co., Ltd.

Preparation of HBC. The precursor carboxylic acid (HBC-CO₂H) was synthesized according to a literature method³ using 8-nonynoic acid as the starting

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- 1 A. E. Bradley, C. Hardacre, J. D. Holbrey, S. Johnston, S. E. J. McMath and M. Nieuwenhuyzen, *Chem. Mater.*, 2002, **14**, 629.
 - 2 A. Okabe, T. Fukushima, K. Ariga and T. Aida, *Angew. Chem., Int. Ed.*, 2002, **41**, 3414.
 - 3 J. D. Brand, C. Kübel, S. Ito and K. Müllen, *Chem. Mater.*, 2000, **14**, 1638.

material. A toluene solution (150 mL) of a mixture of HBC-CO₂H (465 mg, 0.318 mmol), triethylene glycol monomethyl ether (18.5 mL, 116 mmol) and *p*-toluenesulfonic acid monohydrate (35 mg, 0.184 mmol) was heated under reflux for 24 h in a flask equipped with a Dean–Stark trap. Then, the reaction mixture was allowed to cool to room temperature, poured into water and extracted with ethyl acetate. The combined extract was washed successively with saturated aqueous NaHCO₃, water and brine, dried over MgSO₄, and evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel with CH₂Cl₂/MeOH as eluent, and then subjected to preparative SEC with CHCl₃ as eluent, to allow isolation of HBC as yellow waxy solid in 75% yield (559 mg). IR (KBr pellet): 2925, 2854, 1736, 1611, 1457, 1351, 1250, 1179, 1114 and 858 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 8.63 (s, 12H), 4.21 (t, *J* = 4.5 Hz, 12H), 3.66 (t, *J* = 5.0 Hz, 12H), 3.65–3.56 (m, 36H), 3.49 (t, *J* = 4.5 Hz, 12H), 3.33 (s, 18H), 3.13 (t, *J* = 7.5 Hz, 12H), 2.35 (t, *J* = 7.5 Hz, 12H), 2.22–1.94 (m, 12H), 1.72–1.36 (m, 60H); ¹³C NMR (125 MHz, CDCl₃): δ = 173.4, 139.5, 129.2, 122.7, 120.7, 119.0, 71.7, 70.42, 70.38, 70.37, 69.0, 63.2, 58.9, 37.3, 34.1, 32.5, 30.0, 29.7, 29.5, 29.3, 24.9; MALDI–TOF–MS: [*M* + *H*]⁺ (calcd. 2336.40): found. 2336.65.



Preparation of Mesoporous Silica Films. Spin-coated mesoporous silica films with cetylpyridinium chloride (CPyCl) and 1-cetyl-3-methylimidazolium chloride (CMICl) as templates were prepared by a method identical to those templated by cetyltrimethylammonium chloride (CTACl) and immersed in an ethanol vapor as described in the footnote of the paper. Spin-coated and cast mesoporous silica films using an amphiphilic CT complex, TP/TCNB, as a template were prepared according to our previous report.² For the preparation of mesoporous silica films with HBC as a template, tetrabutyl orthosilicate (TBOS, 0.30 mmol) was added to an ethanolic HCl

solution (3.7×10^{-2} N, 0.19 mL) of HBC (6.0 μmol). The mixture ([HBC]/[TBOS]/[H₂O]/[EtOH]/[HCl] = 1.0/50/250/460/1.1) was stirred at 25 °C for 24 h and cast on a glass plate.

Spectral Data

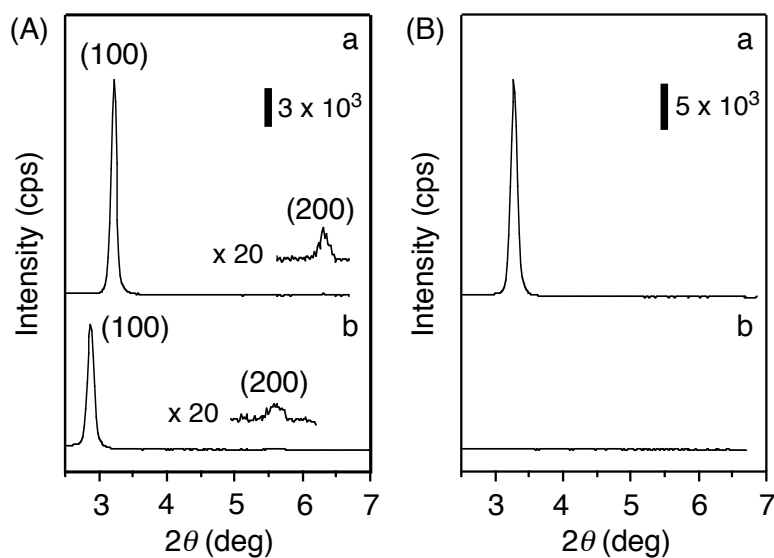


Figure S1. X-ray diffraction patterns of silica films prepared by spin-coating of precursor sols ($[\text{CTACl}]/[\text{TEOS}]/[\text{H}_2\text{O}]/[\text{HCl}]/[\text{EtOH}] = 1.0/10/98/0.088/160$) (a) with and (b) without immersion in an EtOH vapor before dryness, followed by being calcined at 450 °C for 3 h. The sols were aged for (A) 20 h and (B) 125 h at 25 °C before use. Insets in (A): magnified diffraction patterns (x 20).

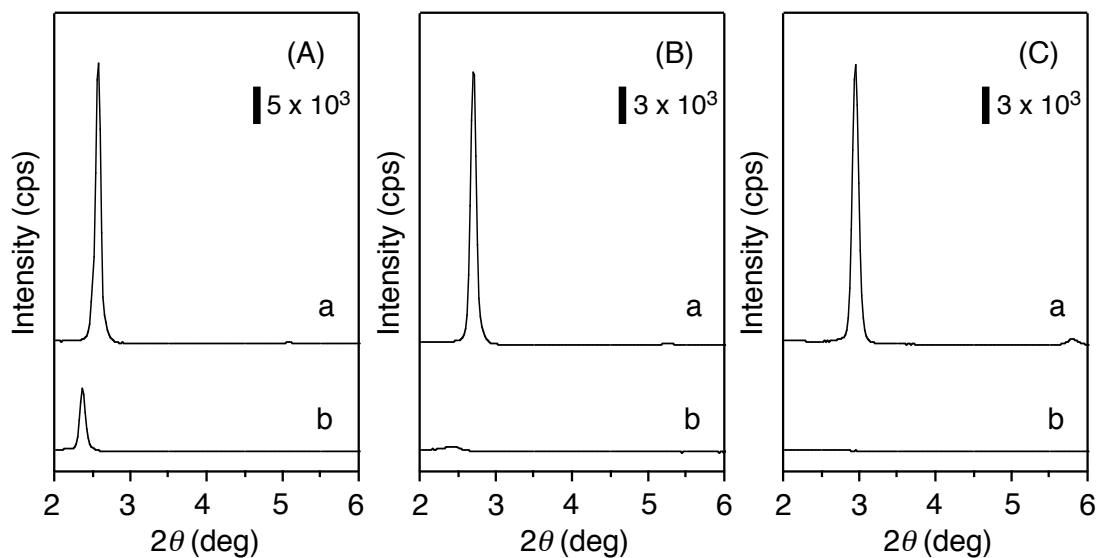


Figure S2. X-ray diffraction patterns of silica films prepared by spin-coating of precursor sols containing (A) CPyCl, (B) CMiCl and (C) TP/TCNB as templates, (a) with and (b) without immersion in an EtOH vapor before dryness. The precursor sols were used after being aged for 118 h, 197 h and 48 days, respectively.