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Supplementary Data

Multi-constituent Co-assembling Ordered Mesoporous Thiol-functionalized Hybrid Materials: Synthesis and Adsorption Properties

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Synthesis of low-polymerized phenolic resols: The polymer precursors, low-molecular-weight, soluble phenolic resols, were prepared from phenol and formaldehyde in a base-catalyzed process.[43] In a typical procedure, 8.0 g of phenol was melted at 42 ~ 45 °C in a flask and mixed with 0.34 g of 20 *wt*% sodium hydroxide aqueous solution under stirring. After 10 min, 5.24 g of formalin was added. Then the mixture was heated to 70 °C. Upon further stirring for 1 h at this temperature, the mixture was cooled to room temperature. The pH value was adjusted with 2 M HCl solution until it reached a value of ~ 7.0. Subsequently, water was removed by vacuum evaporation below 45 °C. The water- and ethanol-soluble phenolic resols were then dissolved in ethanol (20 *wt* %) for further use.

Characterization: The small-angle X-ray diffraction (XRD) measurements were taken on a Rigaku D/max B diffractometor using Cu Kα radiation (40 kV, 20 mA). The *d*-spacing values were calculated by the formula of $d = 0.15408/2\sin\theta$, and the unit cell parameters were calculated from the formula of $a_0 = 2d_{10}/\sqrt{3}$. N_2 adsorption-desorption isotherms were measured at 77 K with a Quantachrome NOVA 4000e analyzer. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}). By using the Barett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms. The micropore volumes (V_m) were calculated from the *V*-*t* plot method. The *t* values were calculated as a function of the relative pressure using the de Boer equation, t (nm) $= [0.1399/(\log(p_0/p) + 0.0340)]^{1/2}$. V_m was obtained using the equation of V_m (cm^3/g) $= 0.001547I$, where *I* represents the *Y* intercept in the *V*-*t* plot.

Transmission electron microscopy (TEM) experiments were conduced on a JEOL 2011 microscope operated at 200 kV. The samples for TEM measurements were suspended in ethanol and supported onto a holey carbon film on a Cu grid. Weight losses and the associated temperature were determined by thermogravimetry analysis with a Mettler Toledo TG/SDTA 851e apparatus. Samples were heated from room temperature to 1000 °C at a rate of 10 °C/min in air flow. ^{29}Si solid state nuclear magnetic resonance (NMR) experiments were performed on a Bruker DSX300 spectrometer (Germany) under condition of magic angle sample spinning (MAS). ^{29}Si solid state MAS NMR spectra were collected at room temperature with a frequency of 59.6 MHz, a recycling delay of 600 s, a radiation frequency intensity of 62.5 kHz, and a reference sample of Q_8M_8 ($[(CH_3)_3SiO]_8Si_8O_{12}$). Energy dispersive X-ray spectroscopy (EDX) was performed on a Philips EDAX instrument. The S content was measured on a Vario EL III elemental analyzer (Germany). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin- Elmer PHI 5000CESCA system with a base pressure of 10^{-9} Torr.

Fig. S1. TG curves for extracted SH-PS0.5-3.36, which are carried out in air from room temperature to 1000 ºC.

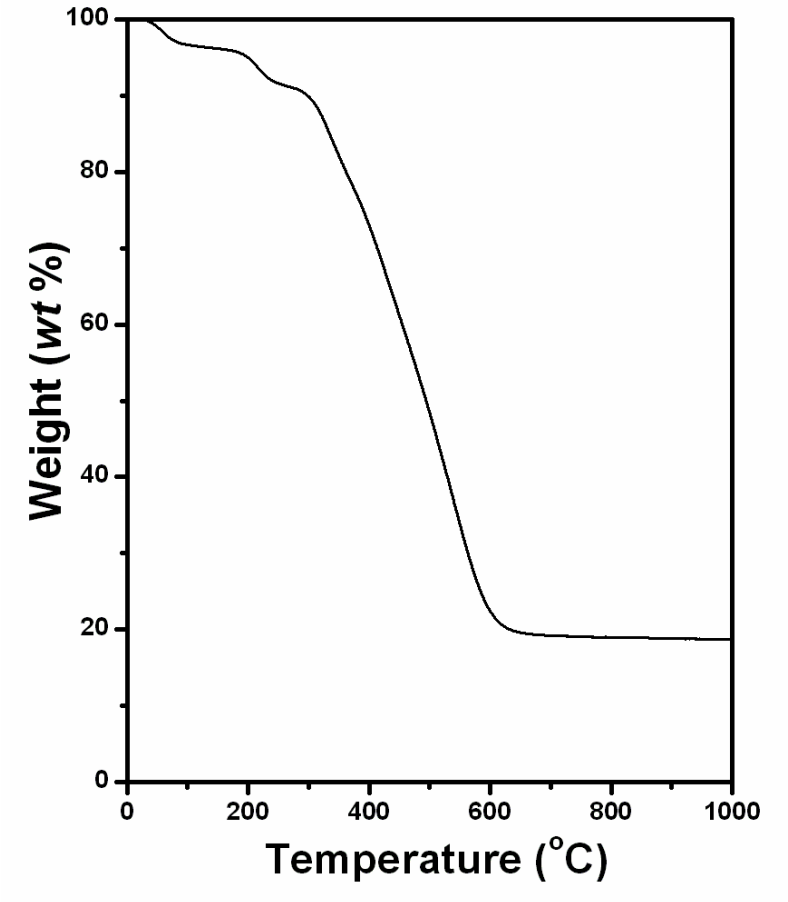

Fig. S2. XRD patterns for SH-PS(1) synthesized from co-assembly of triblock copolymer F127, phenolic resols, MPTMS after sulfuric acid extraction.

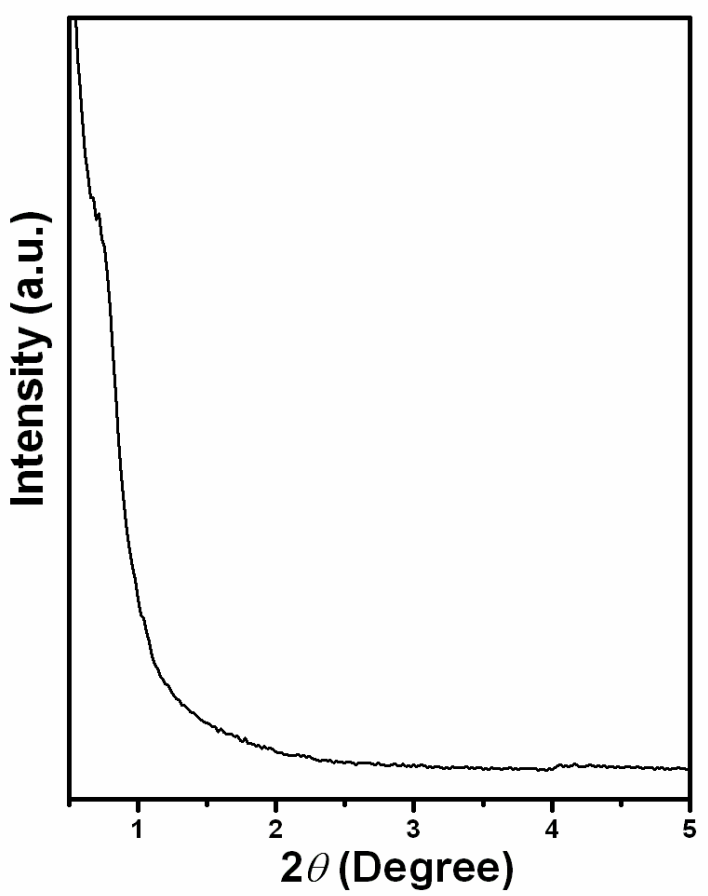

Fig. S3. TG curves for SH-PS*n*-*x* synthesized from co-assembly of triblock copolymer F127, phenolic resols, MPTMS and TEOS with a total silicon amount/quality of phenolic resols of (a) 10 mmol : 1.0 g and (b) 10 mmol : 0.16 g, and different MPTMS/TEOS ratios. PS1 and PS2 were synthesized from phenolic resols, and TEOS with a total silicon amount/quality of phenolic resols of 10 mmol : 1.0 g and 10 mmol : 0.16 g, respectively.

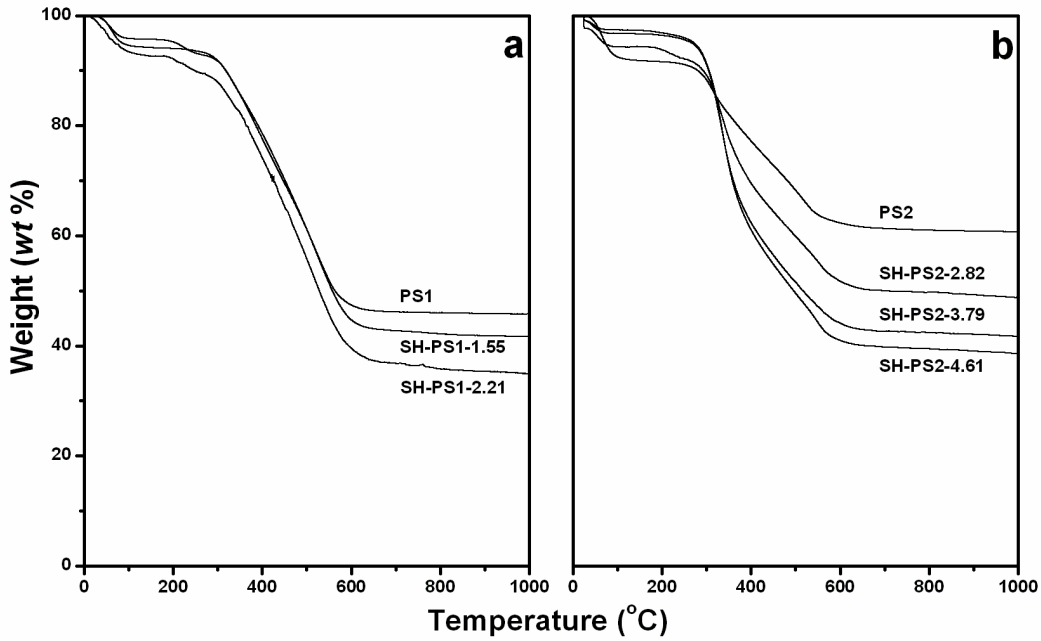

Fig. S4. *t*-plot analysis for mesoporous thiol-functionalized organic-inorganic hybrid materials SH-PS1-*x* with the silica/resins mass ratio of 1 and different thiol contents. *x* represents the thiol content estimated by the elemental analysis.

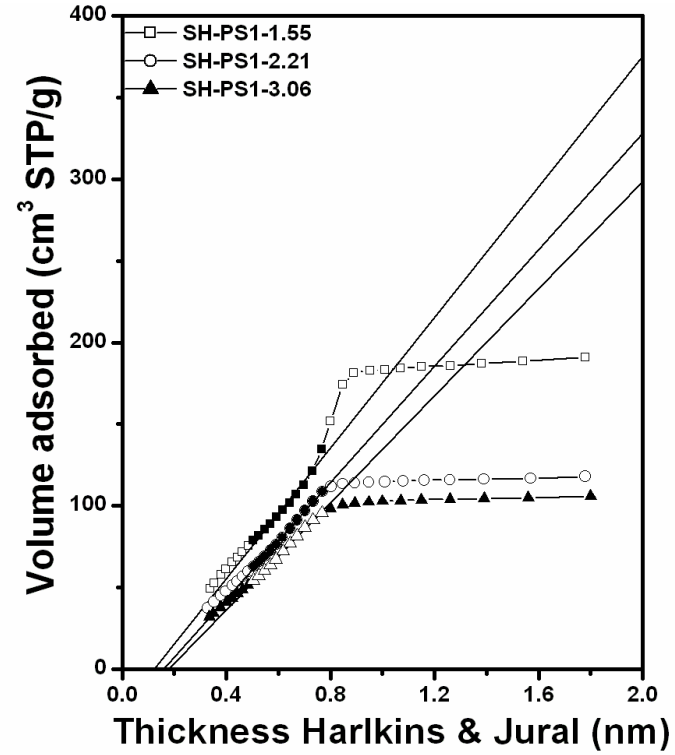

Fig. S5. NMR spectra for SH-PS2-*x* with the silica/resins mass ratio of 2 and different thiol contents.

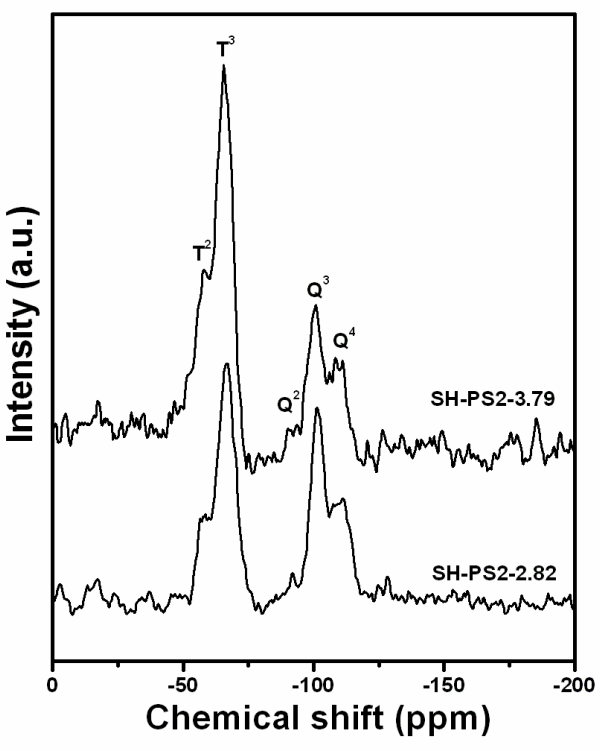

Fig. S6 (a) XRD patterns and (b) N_2 sorption isotherms for SH-PS2-3.79 after adsorption of Ag^+(SH-PS2-3.79-adsorption) and desorption by 1.0 M HNO_3 acid (SH-PS2-3.79-desorption).