Characterization of 4,4′-biphenylene-silicas and a chiral sensor for silicas

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General methods

The FT-IR spectrum was taken on a Jasco FS-420 spectrometer. The ^{1}H NMR spectrum was recorded on a Bruker AVANCE 400 spectrometer in DMSO-d^6 solutions using TMS as an internal standard. Elemental analysis was performed on a Perkin Elmer series II CHNS/O analyzer 2400. Field emission scanning electron microscopy (FESEM) images were taken on a Hitachi S-4700 operating at 15 kV. Transmission electron microscopy (TEM) images were obtained using a TecnaiG220. Specific surface area and pore-size distribution were determined by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods using N_2 adsorption isotherm measured by a Micromeritics ASAP 2020M+C instrument. Small angle X-ray diffraction (SAXRD) and wide angle X-ray diffraction (WAXRD) patterns were taken on an X′ Pert-Pro MPD X-ray diffractometer. Circular dichroism (CD) spectra were taken on an AVIV 410 spectrometer.

Chemicals

BTSB and tetraethoxysilane (TEOS) were purchased from Aldrich. Sodium hydroxide and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd.

Characterization of L-***18Phg4PyBr***: FT-IR (KBr): 3276 cm^{-1} (ν_{N-H}, amide A), 1636 cm^{-1} ($\nu_{C=O}$, amide I), 1543 cm^{-1} (ν_{N-H}, amide II). ^{1}H-NMR (400 MHz, DMSO-d_6, TMS, 25 °C): δ = 0.84 (t, J = 6.3 Hz, 3H; C$\underline{H}_3$), 1.22 (br, 30$\underline{H}$; alkyl), 1.68-1.88 (m, 2H; CONHCH$_2$C$\underline{H}_2$), 2.14-2.16 (m, 2H; C$\underline{H}_2$CONH), 3.02-3.04 (m, 2H; PyCH$_2$C$\underline{H}_2$), 2.26-2.31 (m, 2H; CONHC$\underline{H}_2$), 5.36 (d, J = 7.8 Hz , 1H; NHC$\underline{H}$CO), 7.31(m, 2H; 4-Ph$\underline{H}$) , 7.38 (t, J = 7.6 Hz , 1H; 3-Ph$\underline{H}$), 7.52 (d, J = 7.2 Hz, 1H; 2-Ph$\underline{H}$), 7.53 (s, 1H; CON$\underline{H}$CH$_2$), 8.13 (d, J = 6.6 Hz, 1H; CON$\underline{H}$CH), 8.62 (t, J = 8.7 Hz, 2H; 3-Py$\underline{H}$), 8.68 (t, J = 7.8 Hz, 1H; 4-Py$\underline{H}$), 9.07 (d, J = 6.3 Hz, 2H; 2-Py$\underline{H}$). $C_{35}H_{56}BrN_3O_2$ (Mw: 630.74). Elemental analysis calcd (%): C, 66.65; H, 8.95; N, 6.66. Found: C, 65.87; H, 9.85; N, 6.63.

Synthetic procedure for ***S1***: Amphiphile L-**18Phg4PyBr** (100 mg, 0.16 mmol) was dissolved in a mixture of ethanol (5.0 mL), deionized water (20 mL) and aqueous NaOH solution (2.0 M, 0.175 mL) under stirring at 60 °C. To this solution, BTSB (0.4 mL, 0.87 mmol) was added. The mixture was continuously stirred and kept 60 °C for additional 2.0 h. After that, the products were collected by filtration, and extracted with a mixture of methanol and hydrochloric acid for 48 h. Finally, the sample was dried in air.

Synthetic procedure for ***S2***: Amphiphile L-**18Phg4PyBr** (100 mg, 0.16 mmol) was dissolved in a mixture of ethanol (10.0 mL), deionized water (15 mL) and aqueous NaOH solution (2.0 M, 0.175 mL) under stirring at 60 °C. To this solution, BTSB (0.4 mL, 0.87 mmol) was added. The mixture was continuously stirred and kept 60 °C for additional 2.0 h. After that, the products were collected by

filtration, and extracted with a mixture of methanol and hydrochloric acid for 48 h. Finally, the sample was dried in air.

*Synthetic procedure for C**S100***: Amphiphile L-**18Phg4PyBr** (100 mg, 0.16 mmol) was dissolved in a mixture of deionized water (25 mL) and aqueous NaOH solution (2.0 M, 0.175 mL) under stirring at 60 °C. To this solution, BTSB (0.4 mL, 0.87 mmol) was added. The mixture was continuously stirred and kept 60 °C for additional 2.0 h. After that, the products were collected by filtration, and and extracted with a mixture of methanol and hydrochloric acid for 48 h. Finally, the sample was dried in air.

*Synthetic procedure for C**S10***: Amphiphile L-**18Phg4PyBr** (100 mg, 0.16 mmol) was dissolved in a mixture of deionized water (25 mL) and aqueous NaOH solution (2.0 M, 0.175 mL) under stirring at 60 °C. To this solution, a mixture of TEOS (0.45 mL, 2.0 mmol) and BTSB (50 μL, 0.11 mmol) was added. The mixture was continuously stirred and kept 60 °C for additional 2.0 h. After that, the products were collected by filtration, and and extracted with a mixture of methanol and hydrochloric acid for 48 h. Finally, the sample was dried in air.

*Synthetic procedure for C**S1***: Amphiphile L-**18Phg4PyBr** (100 mg, 0.16 mmol) was dissolved in a mixture of deionized water (25 mL) and aqueous NaOH solution (2.0 M, 0.175 mL) under stirring at 60 °C. To this solution, a mixture of TEOS (0.495 mL, 2.2 mmol) and BTSB (5.0 μL, 0.011 mmol) was added. The mixture was continuously stirred and kept 60 °C for additional 2.0 h. After that, the products were collected by filtration, and and extracted with a mixture of methanol and hydrochloric acid for 48 h. Finally, the sample was dried in air.

*Synthetic procedure for C**S0***: Amphiphile L-**18Phg4PyBr** (100 mg, 0.16 mmol) was dissolved in a mixture of deionized water (25 mL) and aqueous NaOH solution (2.0 M, 0.175 mL) under stirring at 60 °C. To this solution, TEOS (0.5 mL, 2.2 mmol) was added. The mixture was continuously stirred and kept 60 °C for additional 2.0 h. After that, the products were collected by filtration, and and extracted with a mixture of methanol and hydrochloric acid for 48 h. Finally, the sample was dried in air.

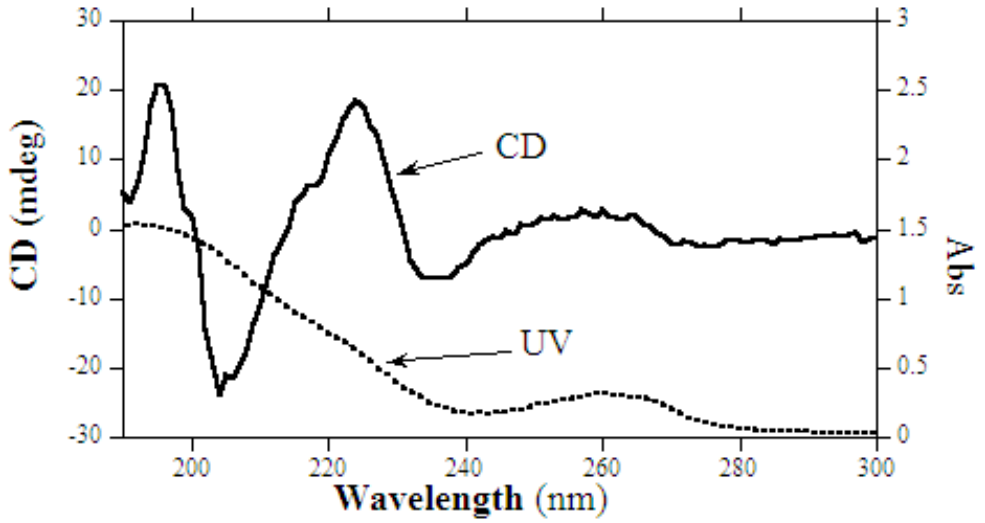

Figure S1. CD and UV spectra of L-**18Phg4PyBr** hydrogel.

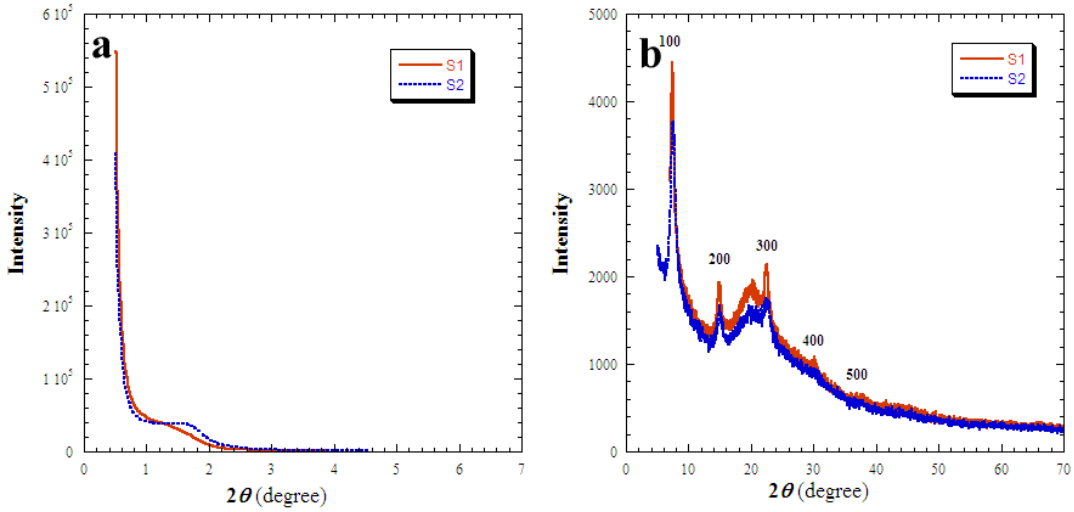

Figure S2. (a) SAXRD and (b) WAXRD patterns of the 4,4′-biphenylene-silicas, **S1** and **S2**.

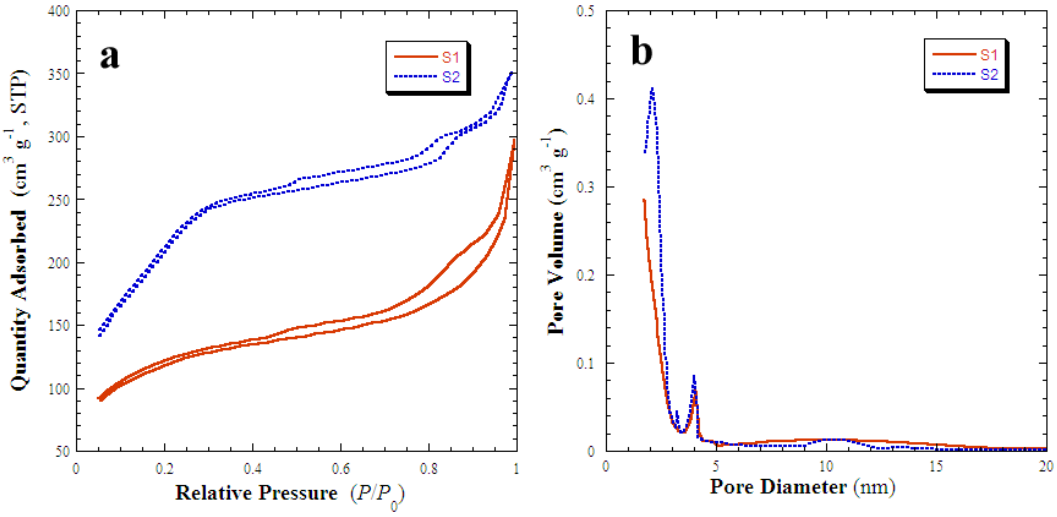

Figure S3. Sorption isotherms (a) and BJH pore size distribution (b) of the 4,4′-biphenylene-silicas, **S1** and **S2**. The sorption isotherms were determined by N_2 sorption-desorption measurements, and the pore size distributions were evaluated from the desorption branches.

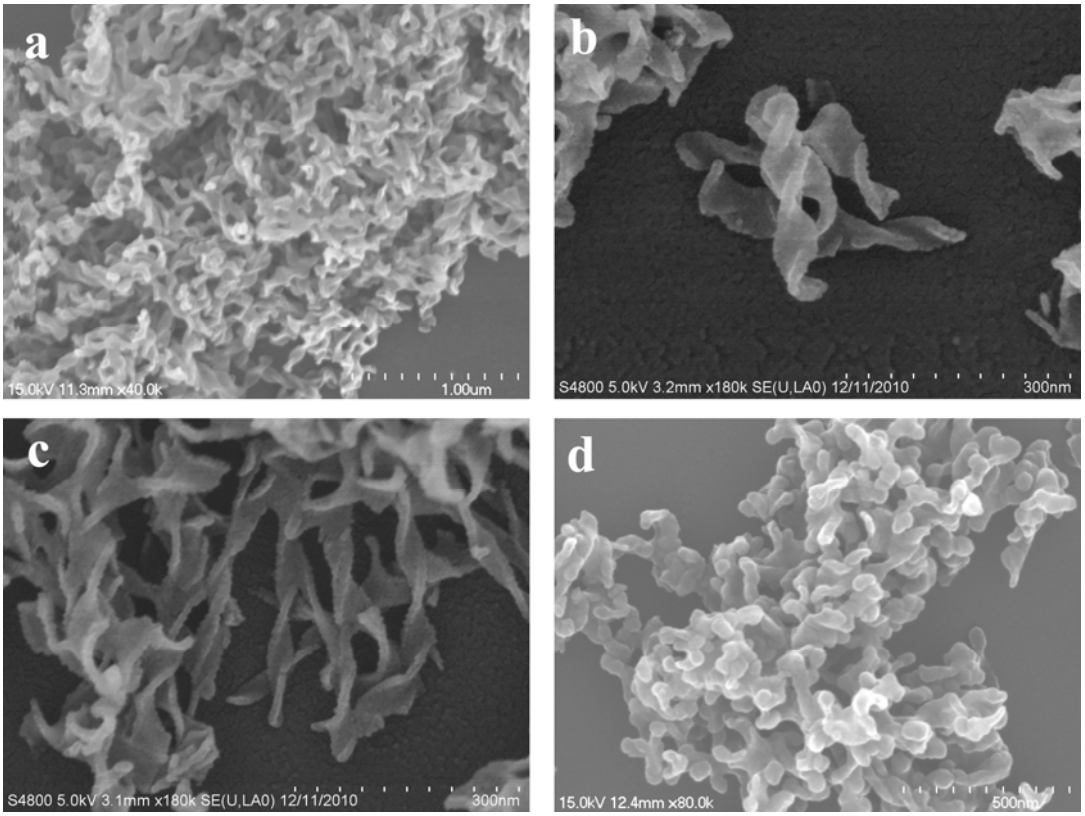

Figure S4. FESEM images of the samples (a) **CS0**, (b) **CS1**, (c) **CS10**, and (d) **CS100**.

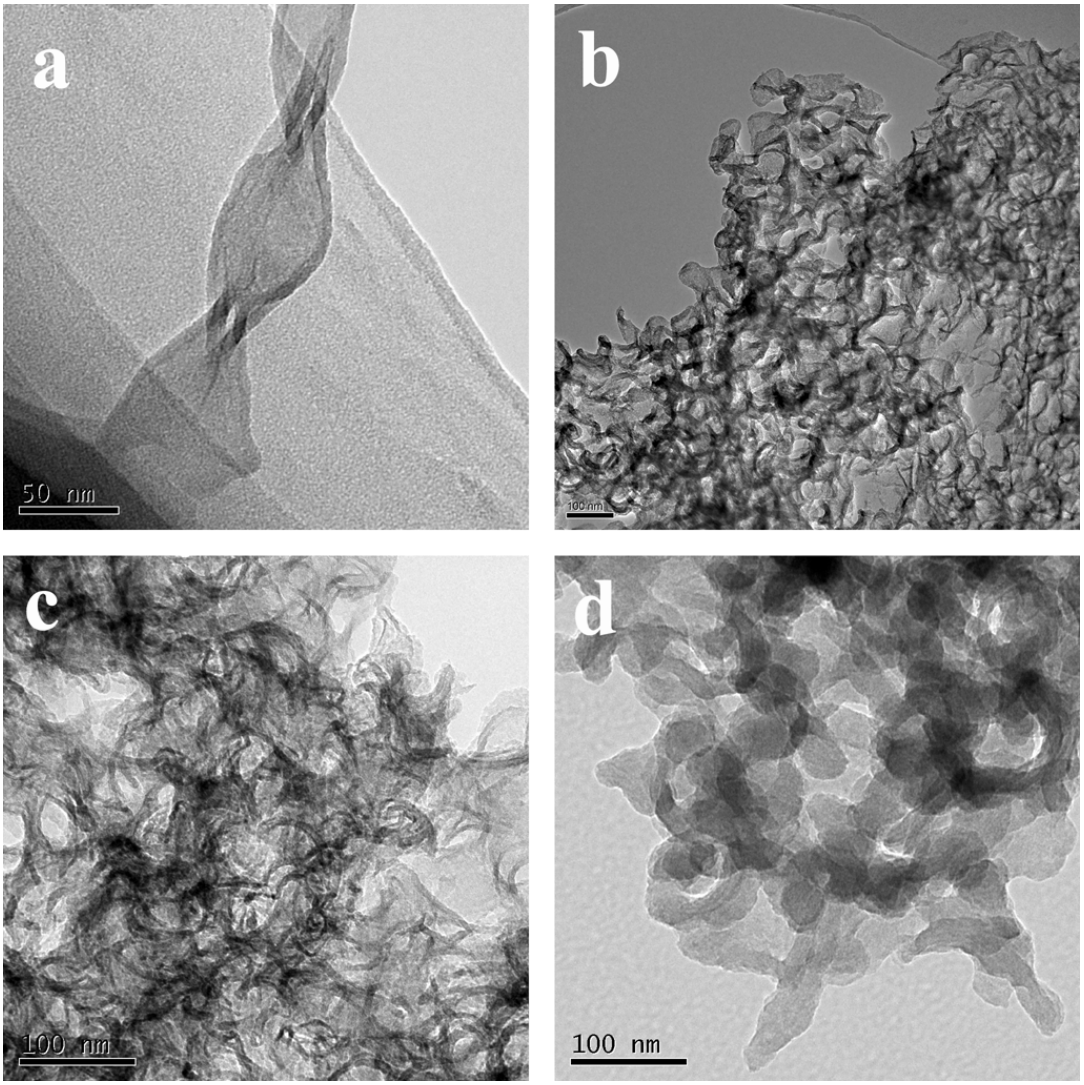

Figure S5. TEM images of the samples (a) **CS0**, (b) **CS1**, (c) **CS10**, and (d) **CS100**.

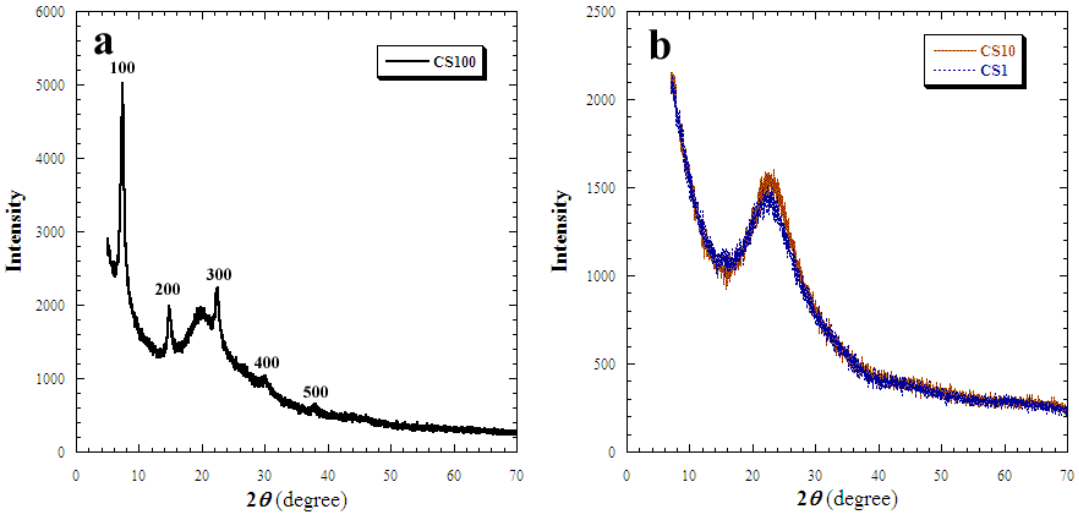

Figure S6. WAXRD patterns of the organic-inorganic hybrid silicas, **CS100**, **CS10**, and **CS1**.