Supporting information

UiO-66@SiO_2core-shell microparticles as stationary phases for the separation of small organic molecules

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Materials

Microspherical silica particles (5 µm) Nucleosil 300-5 (pore size 30 nm, specific surface area 100 m^2/g) were obtained from Macherey-Nagel GmbH & Co. KG. Germany. Carboxylic acid modified 2.1 µm non-porous silica particles were obtained from microParticles GmbH, Germany. Toluene, 3-(glycidyloxypropyl)trimethoxysilane, glutamic acid (Glu), 1,4-benzenedicarboxylic acid (H_2bdc, 98%) were purchased from Sigma-Aldrich (St Louis, MO, USA). Zirconium chloride (anhydrous) was obtained from Merck (Schuchardt, Germany). Dimethylformamide (DMF) and hydrochloric acid (32%) were purchased from Univar Ajax Finechem, NSW, Australia. HPLC grade *n*-hexane, 2-propanol, and dimethylformamide (all from Sigma-Aldrich, St Louis, MO, USA) were used for packing of stainless steel column and HPLC experiments. Solutions of pure reagents (>99%, Sigma-Aldrich, St Louis, MO, USA) were used as model solutes in chromatographic experiments.

Instrumentation

PXRD measurements were performed on a PAN Analytical X'pert Pro diffractometer fitted with a solid-state PIXcel detector (40 kV, 30 mA, 1° divergence and anti-scatter slits, and 0.3 mm receiver and detector slits) using Cu-K_α (λ = 1.5406 Å) radiation. Scanning electron microscopy (SEM) images of the particles were performed using a FEI Quanta 600 MLA ESEM in the Central Science Laboratory, University of Tasmania (Australia). The particles were sputter-coated with platinum. Nitrogen sorption isotherms were measured using a 3Flex Instrument (Micromeritics Instruments Inc.). Approximately 100 mg of particles were loaded into a glass analysis tube and outgassed for 12 h under vacuum at 120 °C prior to measurement. N_2 adsorption and desorption isotherms were measured at 77 K and data was analysed using BET models to determine the surface area. Pore size distribution curves at the micropore range were obtained using the density functional theory (DFT) model. FT-IR spectra were obtained using a Bruker Vertex 70 infrared spectrometer equipped with an ATR probe. Chromatographic separations were performed using a Water 2490 HPLC system equipped with Water 2487 UV detector (Milford, MA, USA).

Hydrophobicity of UiO-66@SiO_2

Since a new UiO-66@SiO_2 stationary phase was prepared for normal and reversed phase HPLC, it was necessary to assess its hydrophobicity. As discussed in the Section 3.2.3, strong hydrogen bonding was evidenced in RP HPLC, which resulted in extremely strong retention of nitrogen containing compounds (toluidines and anilines). For this reason, standard hydrophobicity tests (such as Engelhardts's, etc.) could not be applied. Instead, information about hydrophobicity of UiO-66@SiO_2 could be obtained by investigating retention dependence on the length of side carbon chain (n_c) in homological compounds. Such dependences for alkyl benzenes and alkyl phenyl ketones are given in Fig. 5S. A clear decrease in retention is observed for both types of solutes with increasing n_c, which indicates relatively low hydrophobicity of UiO-66@SiO_2.

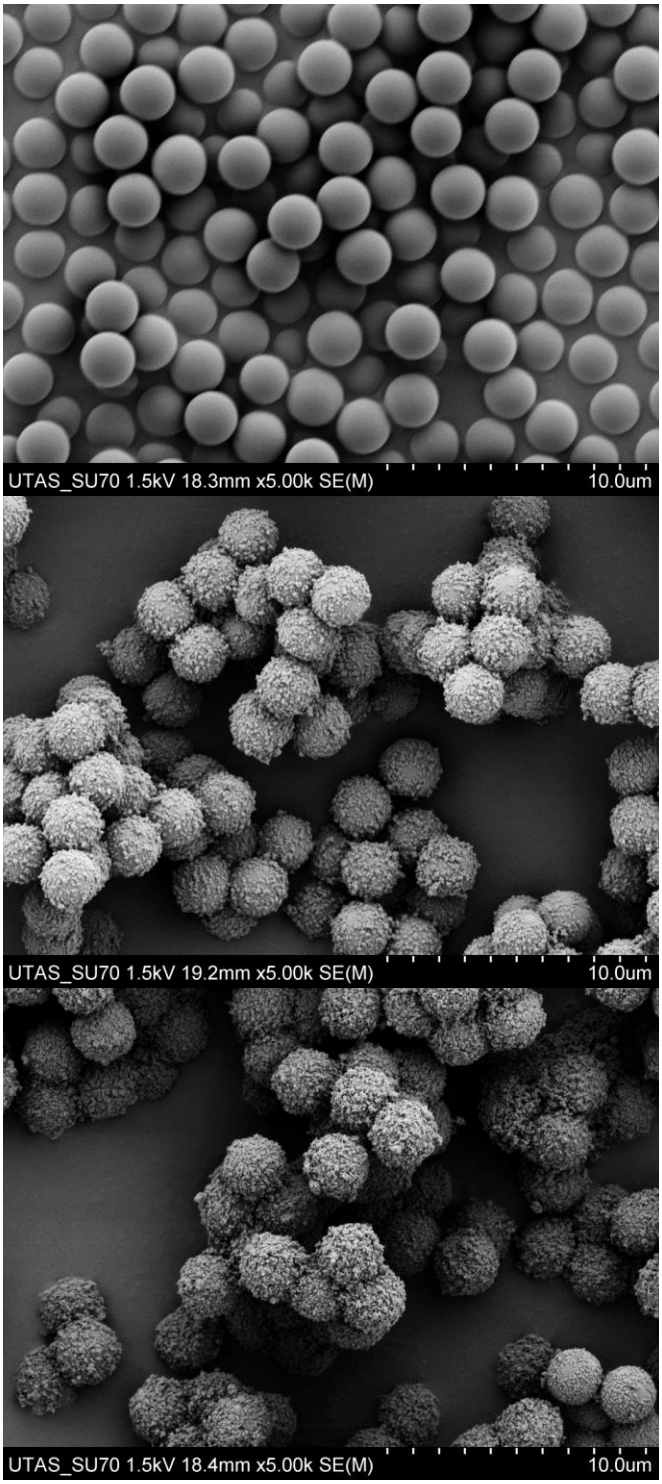

Figure 1S. Scanning electron microscopy images of SiO_2(2.1)-COOH (top), UiO-66(1x)@SiO_2(2.1) (middle) and UiO-66(2x)@SiO_2(2.1) (bottom) particles.

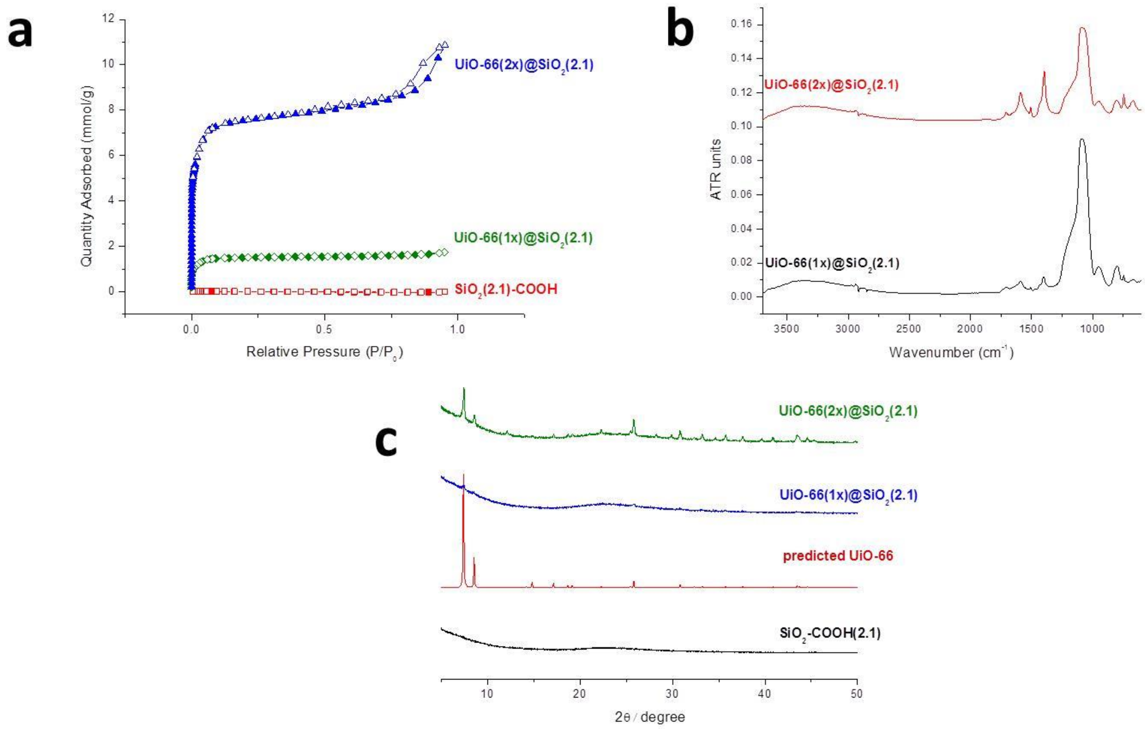

Figure 2S. A) N_2 adsorption (filled) and desorption (open) isotherms at 77 K for SiO_2(2.1)-COOH (red squares), UiO-66(1x)@SiO_2(2.1) (green diamonds) and UiO-66(2x)@SiO_2(2.1) (blue triangles) core-shell particles. B) FT-IR spectra of SiO_2(2.1)@UiO-66(1) (black) and UiO-66(2x)@SiO_2(2.1) (red) core-shell particles. C) PXRD patterns of Upper: SiO_2-COOH(5) (black), predicted UiO-66 (red), synthesized UiO-66 (blue) UiO-66(1x)@SiO_2(5) (orange) and UiO-66(2x)@SiO_2(5) core-shell particles (green) and bottom: SiO_2-COOH(2.1) (black), predicted UiO-66 (red), UiO-66(1x)@SiO_2(2.1) (blue) and UiO-66(2x)@SiO_2(2.1)core-shell particles (green).

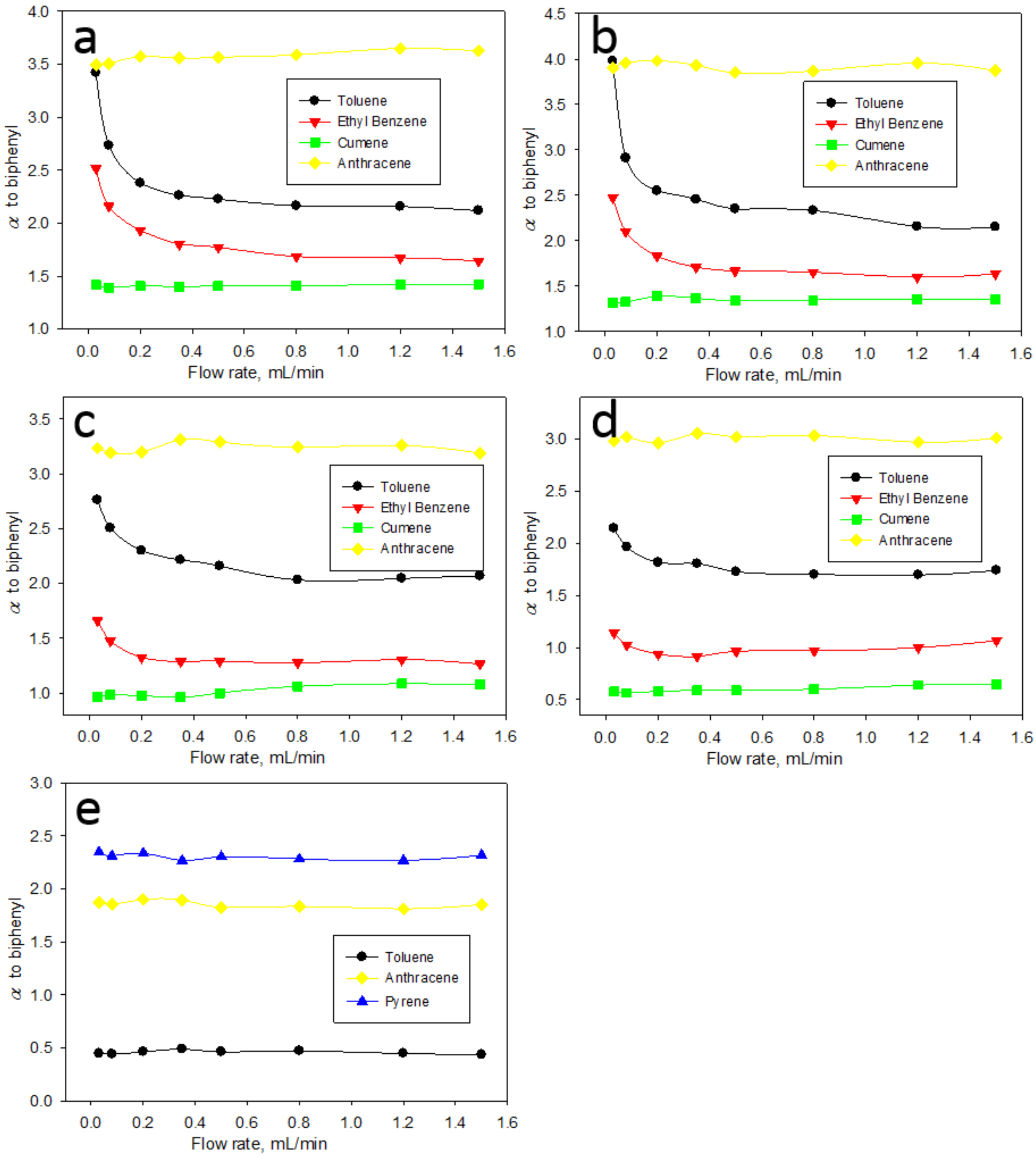

Figure 3S. Influence of the *n*-hexane flow rate on the selectivity of solute retention to biphenyl on UiO-66@SiO_2 columns. 25°C, 2 µL injections of analytes (50 µg/mL) in mobile phase, UV detection at 254 nm. Columns: UiO-66(2x)@SiO_2(5) (a), UiO-66(2x)@SiO_2(2.1) (b), UiO-66(1x)@SiO_2(5) (c), UiO-66(1x)@SiO_2(2.1) (d), SiO_2(5) (e).

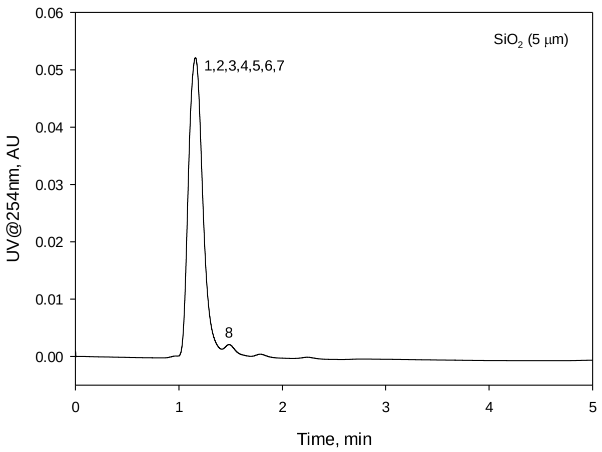

Figure 4S. Separation of a mixture of 8 hydrocarbons using a control 50 mm × 2.1 mm ID unmodified SiO_2(5) column. Mobile phase – 0.2 mL/min of *n*-hexane, 25°C, 2 µL injections of analytes (50 µg/mL) in mobile phase, UV detection at 254 nm. Analytes: 1 – pentyl benzene, 2 – biphenyl, 3 – ethyl benzene, 4 – styrene, 5 – *m*-xylene, 6 – phenyl acetylene, 7 – *o*-xylene, 8 – naphthalene.

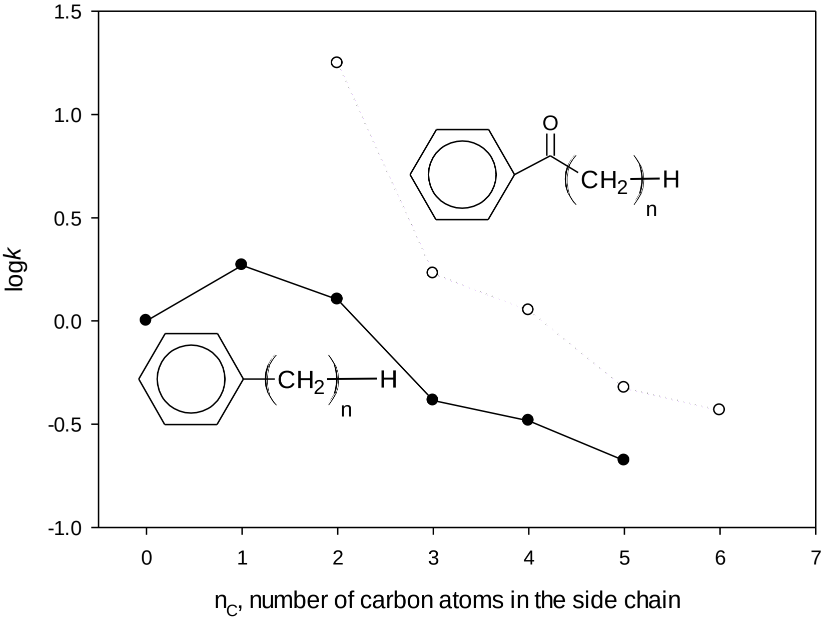

Figure 5S. Influence of the number of the carbon atoms in the side chains of alkyl benzenes and alkyl phenyl ketones on their retention on UiO-66(2x)@SiO_2(5) column. Mobile phase – 0.2 mL/min of *n*-hexane (alkyl benzenes) or 80% *n*-hexane – 20% 2-propanol (alkyl phenyl ketones), 25°C, 2 µL injections of analytes (50 µg/mL) in mobile phase, UV detection at 254 nm.