

Supplementary Information

Highly porous aerogels based on imine chemistry: syntheses and sorption properties

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Experimental section

Materials and method. Chemicals and solvents were obtained from commercial sources and used as received without further purification. Tetrakis-(4-aminophenyl)methane¹ and 1,3,5-benzenetricarboxaldehyde² were synthesized as reported previously. Adsorption measurements were performed using a Quantachrome Autosorb-iQ₂ analyzer. Prior to analysis, the aerogels were degassed at 100 °C for 12 h to remove solvent molecules. ¹³C cross-polarization magic angle spinning NMR spectra were recorded in a Varian Inova 500 NB Superconducting Fourier Transform NMR spectrometer operating at spinning rate 10 kHz. Scanning electron microscopy (SEM) images were collected on a Hitachi S-4800 Cold Field Emission Scanning Electron Microscope. Before measurement, the aerogel sample was dispersed in ethanol with the aid of sonication, put on aluminum foil, and sputter coated with gold. Transmission electron microscopy (TEM) investigations were carried out on a FEI Tecnai G2 Spirit 120 kV transmission electron microscope. The aerogel sample was dispersed in ethanol with the aid of sonication and mounted on a carbon coated copper grid. Particle sizes were measured on a Brookhaven-Elektroskop-Omni instrument. Rheological measurement was performed on an AR-G2 Stress-Controlled Rheometer (TA Instruments) equipped with steel parallel-plate geometry (40 mm diameter) at 25 °C. The frequency sweep was obtained from 0.01 rad s⁻¹ to 100 rad s⁻¹ at a constant strain of 1%.

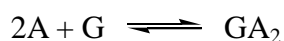
Preparation of imine aerogels. Typical procedure: To a solution of tetrakis-(4-aminophenyl)methane (22.6 mg, 0.060 mmol) in water (2 mL), AcOH (0.5 mL) was added dropwise whilst stirring to form a solution. Biformyl (60 μL, excess, 40% w/w aq. soln.) was added and stirred for 15 min at room temperature. The resulting solution was heated in a closed vial at 80 °C to obtain an opaque dark red gel after 30 min. The resulting gel was further aged at 80 °C for 5 days. The gel was subsequently washed with anhydrous THF at room temperature. THF was replaced every day by fresh solvent and solvent exchange was finished after 3 days. Then the gel was washed with anhydrous EtOH for 3 days in similar way. The solvent in the

exchanged gel was next extracted with subcritical CO₂(l) in a 0.75 L high pressure stainless-steel Soxhlet extractor to obtain A1B1-0.030 aerogel (56.1 mg).

Solid-phase microextraction (SPME). The general procedures for SPME analyses were described previously.³ For BTEX/Phenols, headspace extraction was performed. The 40 mL sample vial was sealed with a septum with 10 mL sample solution of BTEX/Phenols inside. The concentration of sample solutions is 1 ppm. A magnetic stirrer (1000 rpm) was used for agitation. The coated fiber end was exposed to the gas phase for extraction for 10 min, and then the fiber was inserted into the GC inlet for desorption and analysis. For PAHs/OCPs, the fiber was immersed into the sample solution whilst stirring (1500 rpm) for 30 min. The concentration of PAHs sample solutions is 100 ppb and the concentration of OCPs sample solutions is 120 ppb. After extraction, the fiber was inserted into the GC injector for desorption and analysis. For BTEX, the fiber was kept at 250 °C for 1 min for desorption. For Phenols, the fiber was kept at 260 °C for 1 min for desorption. For PAHs/OCPs, the fiber was kept at 260 °C for 5 min for desorption.

Pseudo-second-order kinetic model⁴

The pseudo-second-order kinetic model has been applied widely in the use of sorbents and biosorbents to treat polluted aqueous effluents containing dyes/organics or metal ions. Toluene adsorption from aqueous solution may be represented in the following way:



where A and G are active sites on the gel matrix and guest molecules, respectively. The sorption may be attributed to favourable π - π interactions between guest benzene molecules and the aromatic framework.

If the pseudo-second-order kinetic model holds true and it is assumed that the sorption capacity is proportional to the number of active sites occupied on the sorbent, the rate law for the sorption is expressed as:

$$\frac{dq_t}{dt} = k_2(q_0 - q_t)^2$$

where q_t and q_e are the amount of the adsorbate adsorbed at time t and at equilibrium, respectively. k_2 stands for the pseudo-second-order rate constant of adsorption.

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated rate law can be written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (1)$$

1. P. Ganesan, X. Yang, J. Loos, T. J. Savenije, R. D. Abellon, H. Zuilhof and E. J. R. Sudhölter, *J. Am. Chem. Soc.*, 2005, **127**, 14530-14531.
2. P. Pandey, A. P. Katsoulidis, I. Eryazici, Y. Y. Wu, M. G. Kanatzidis and S. T. Nguyen, *Chem. Mater.*, 2010, **22**, 4974–4979.
3. L. Li, S. Xiang, S. Cao, J. Zhang, G. Ouyang, L. Chen and C. Y. Su, *Nat. Commun.*, 2013, **4**, 1774.
4. Y. S. Ho and G. McKay, *Process Biochemistry*, 1999, **34**, 451–465.

Table S1 Porosity properties of imine aerogels with various aldehyde precursors.

aerogel	S_{BET} /m ² g ⁻¹	V_{t} /cm ³ g ⁻¹	V_{meso} /cm ³ g ⁻¹	V_{micro} /cm ³ g ⁻¹
A1B1-0.030	1021	1.10	0.78	0.31
A1B2-0.075	822	1.58	1.37	0.21
A1B3-0.0125	727	4.21	3.95	0.24
A1B4-0.0125	281	3.13	3.06	0.08
A1B5-0.017	63	1.39	0.13	0.01

^a S_{BET} is the BET-specific surface area; ^b V_{t} is the total specific pore volume; ^c V_{meso} is the specific mesopore volume calculated from adsorption isotherm using the BJH method; ^d V_{micro} is the specific micropore volume calculated using the SF method.

Table S2 Porosity properties of A1B2 aerogels with various A1 precursor concentrations.

	c / mol L ⁻¹	S_{BET} /m ² g ⁻¹	V_{t} /cm ³ g ⁻¹	V_{meso} /cm ³ g ⁻¹	V_{micro} /cm ³ g ⁻¹
A1B2-0.017	0.017	619	1.03	1.13	0.26
A1B2-0.050	0.050	810	0.82	0.58	0.23
A1B2-0.075	0.075	822	1.58	1.37	0.21
A1B2-0.100	0.100	737	1.47	1.28	0.20

^a S_{BET} is the BET-specific surface area; ^b V_{t} is the total specific pore volume; ^c V_{meso} is the specific mesopore volume calculated from adsorption isotherm using the BJH method; ^d V_{micro} is the specific micropore volume calculated using the SF method.

Table S3 Repeatability of porosity properties of A1B1 aerogels.

Times	S_{BET} /m ² g ⁻¹	V_{t} /cm ³ g ⁻¹	V_{meso} /cm ³ g ⁻¹	V_{micro} /cm ³ g ⁻¹
1 st	1021	1.10	0.78	0.31
2 nd	1009	1.18	0.90	0.29
3 rd	1047	1.23	0.97	0.30
$\bar{\chi} \pm \bar{\sigma}$	1026 ± 14	1.17 ± 0.05	0.88 ± 0.07	0.30 ± 0.01

^a S_{BET} is the BET-specific surface area; ^b V_{t} is the total specific pore volume; ^c V_{meso} is the specific mesopore volume calculated from adsorption isotherm using the BJH method; ^d V_{micro} is the specific micropore volume calculated using the SF method.

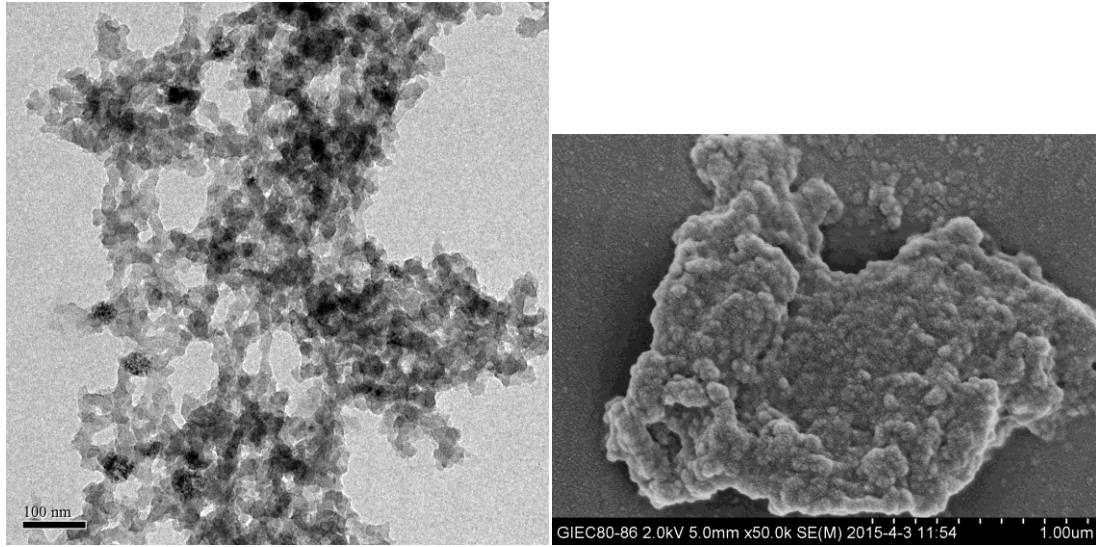


Fig. S1 Additional TEM and SEM images of A1B1-0.030 aerogel.

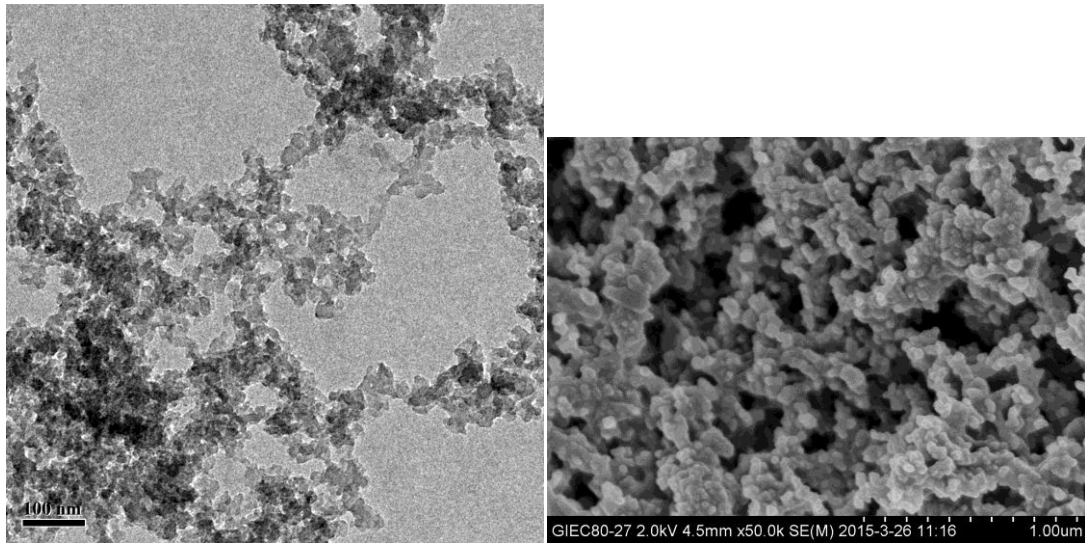


Fig. S2 Additional TEM and SEM images of A1B2-0.075 aerogel.

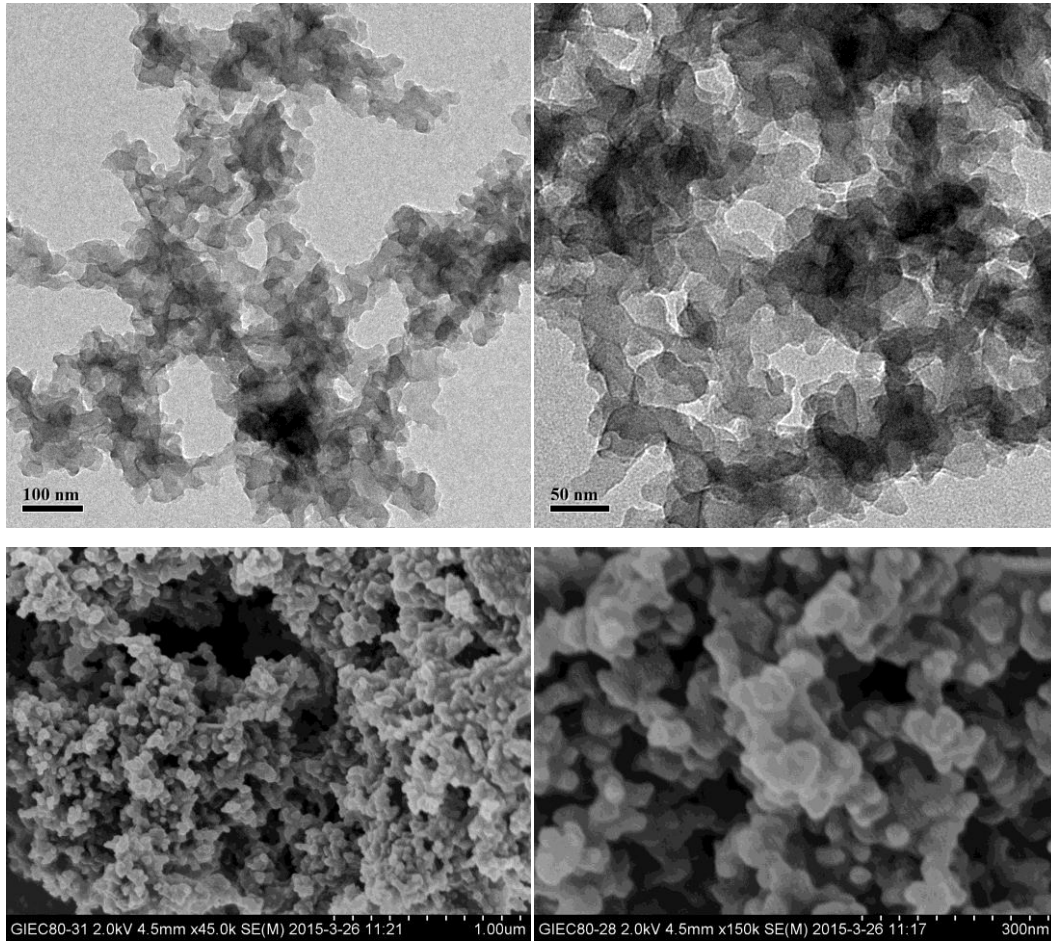


Fig. S3 TEM and SEM images of A1B3-0.0125 aerogel.

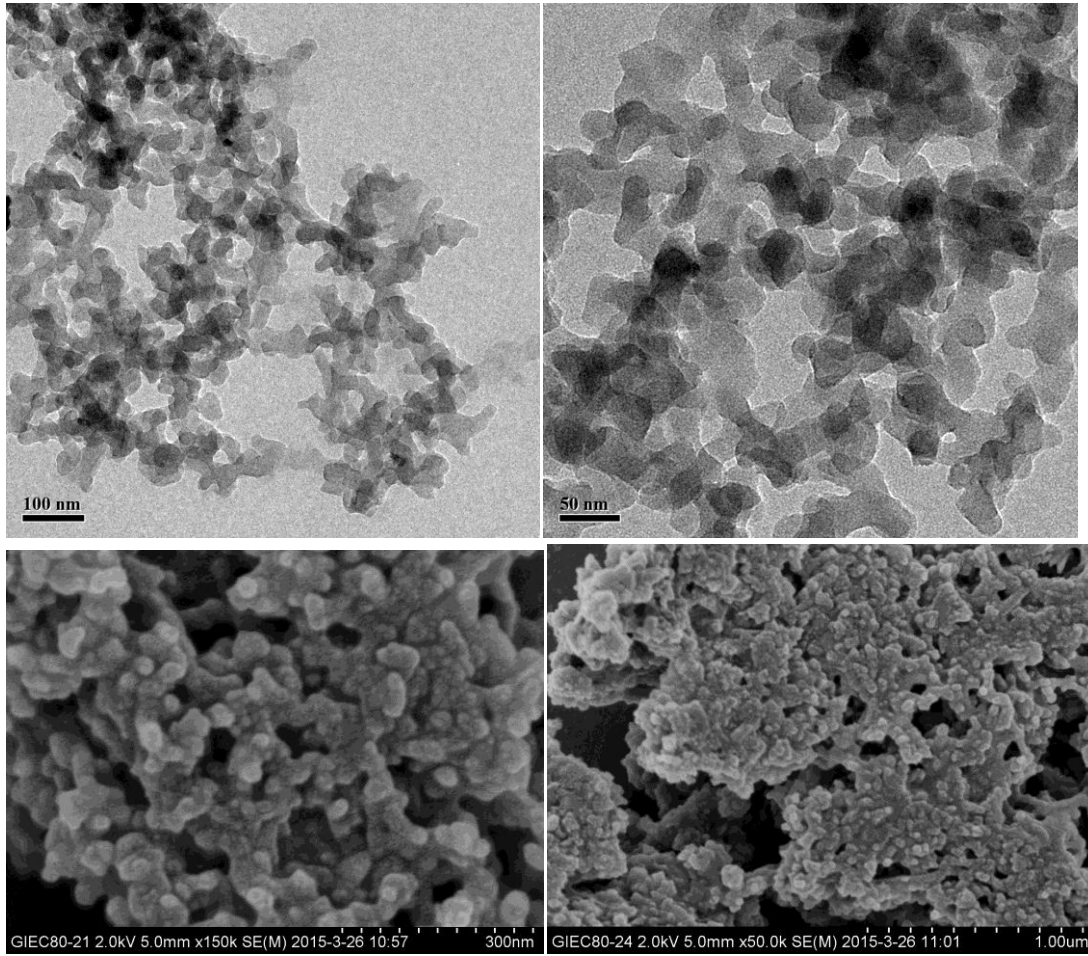


Fig. S4 TEM and SEM images of A1B4-0.0125 aerogel.

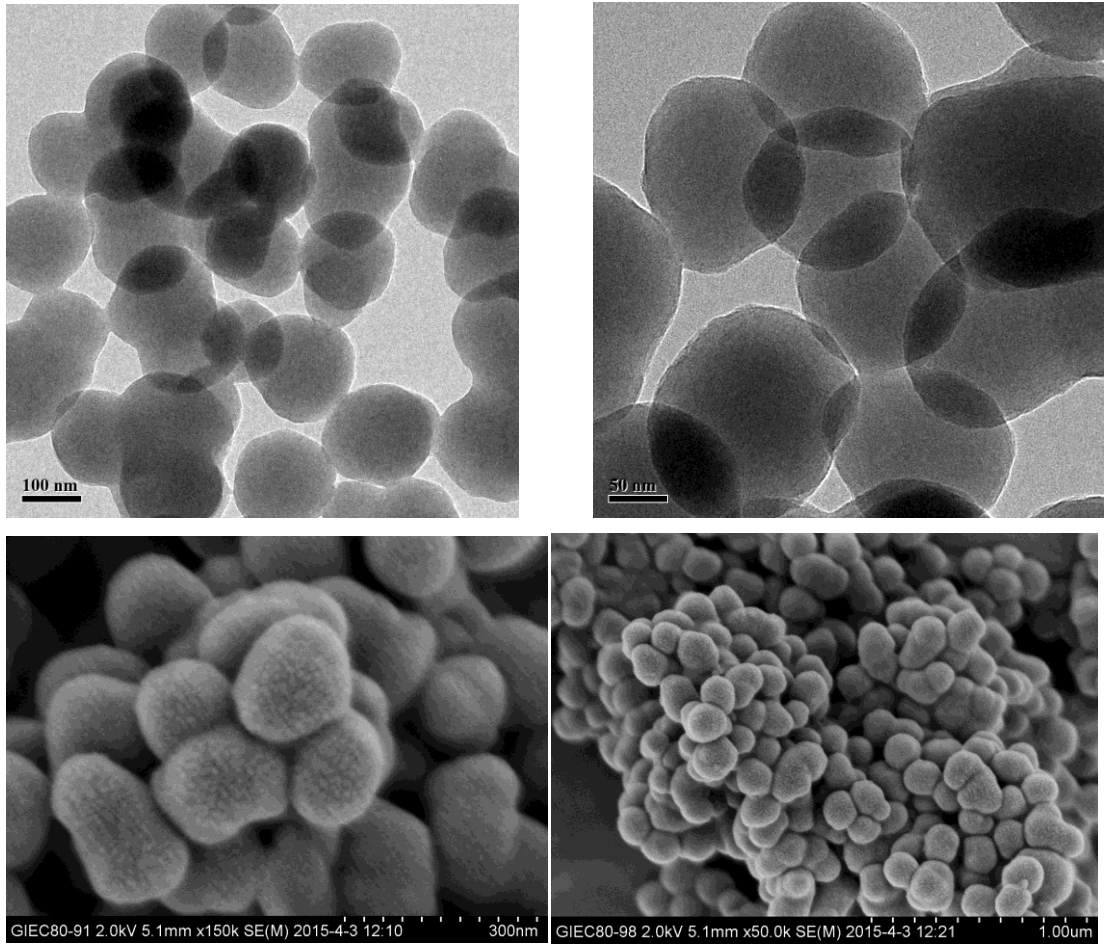
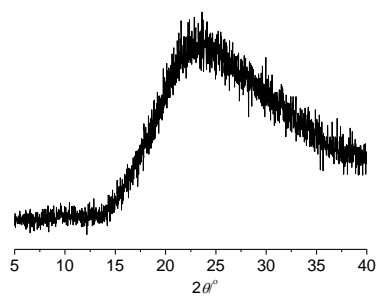
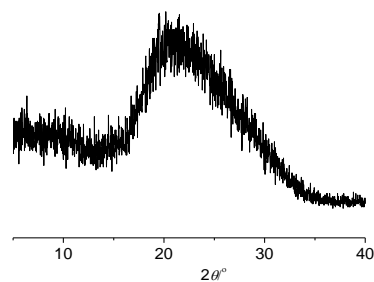


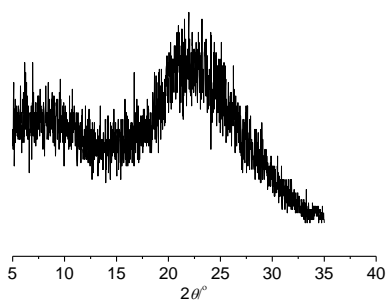
Fig. S5 TEM and SEM images of A1B5-0.017 aerogel.



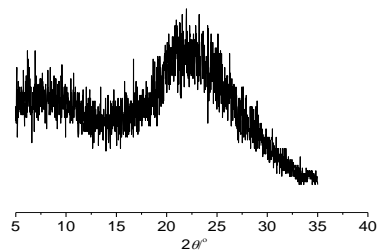
a



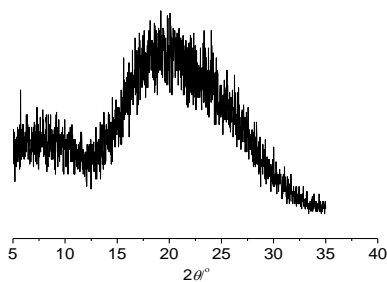
b



c



d



e

Fig. S6 XRPD patterns of a) A1B1-0.030, b) A1B2-0.075, c) A1B3-0.0125, d) A1B4-0.0125 and e) A1B5-0.017 aerogels.

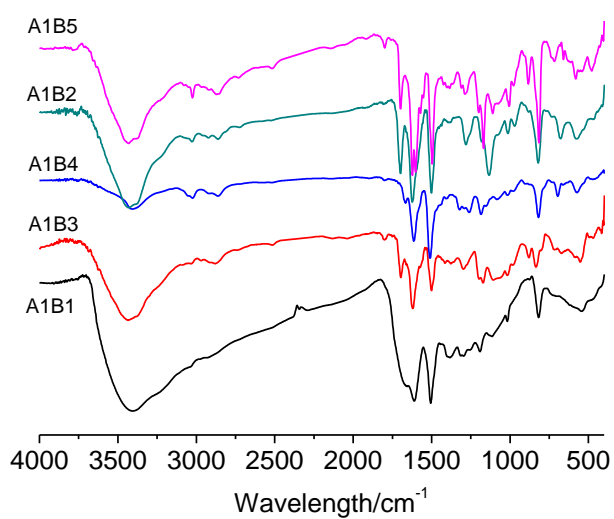


Fig. S7 FT-IR spectra of A1B1-0.030, A1B2-0.075, A1B3-0.0125, A1B4-0.0125 and A1B5-0.017 aerogels.

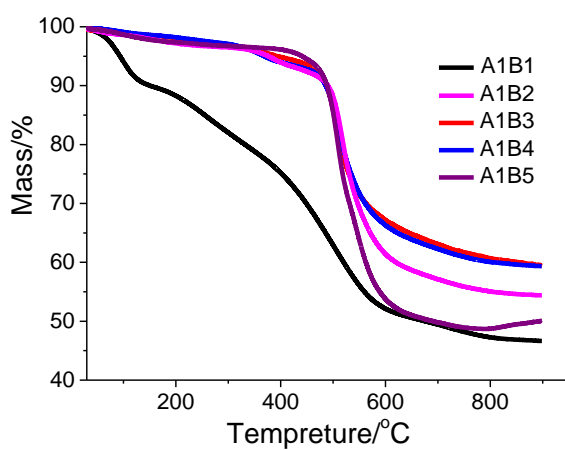


Fig. S8 TG curves of A1B1-0.03, A1B2-0.075, A1B3-0.0125, A1B4-0.0125 and A1B5-0.017 aerogels.

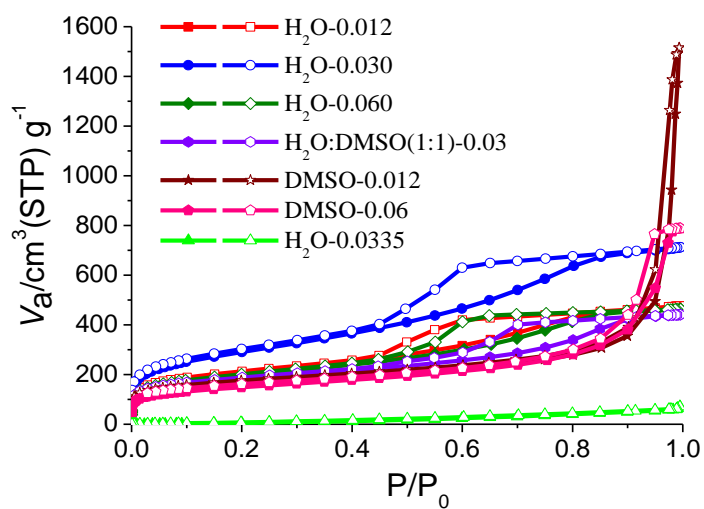


Fig. S9 N₂ adsorption and desorption isotherms at 77 K of A1B1 aerogels prepared from aqueous and DMSO solutions with various concentrations.

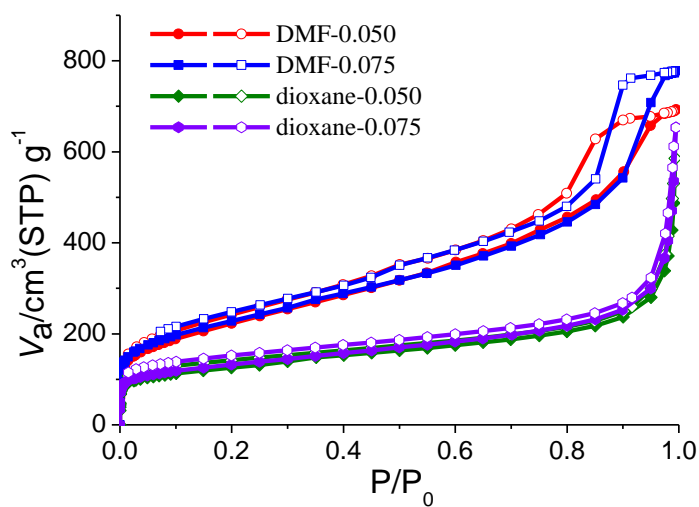


Fig. S10 N₂ adsorption and desorption isotherms at 77 K of A1B2 aerogels prepared from DMF and 1,4-dioxane solutions with various concentrations.

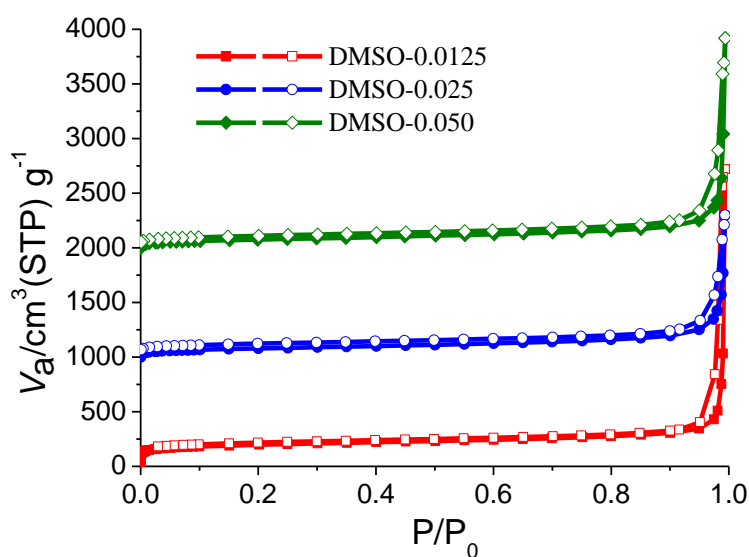


Fig. S11 N₂ adsorption and desorption isotherms at 77 K of A1B3 aerogels prepared from DMSO solutions with various concentrations. For clarity, the isotherms of A1B3-DMSO-0.025 and A1B3-DMSO-0.050 are offset by 1000 and 2000 cm³(STP) g⁻¹, respectively.

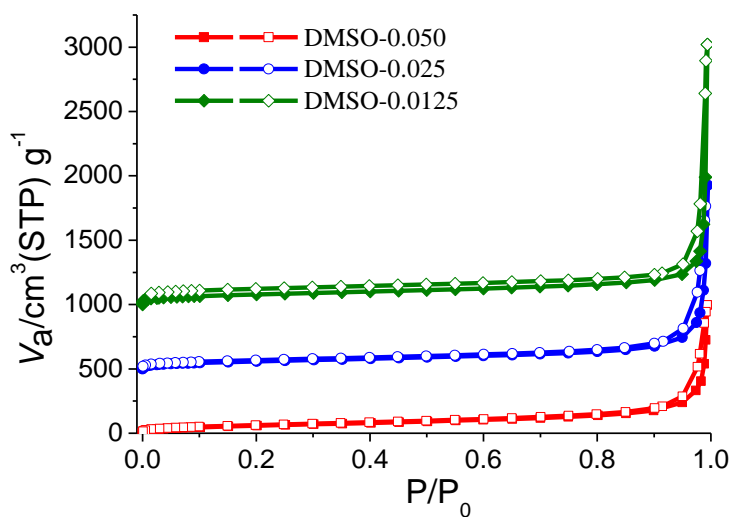


Fig. S12 N₂ adsorption and desorption isotherms at 77 K of A1B4 aerogels prepared from DMSO solutions with various concentrations. For clarity, the isotherms of A1B4-DMSO-0.025 and A1B4-DMSO-0.0125 are offset by 500 and 1000 cm³(STP) g⁻¹, respectively.

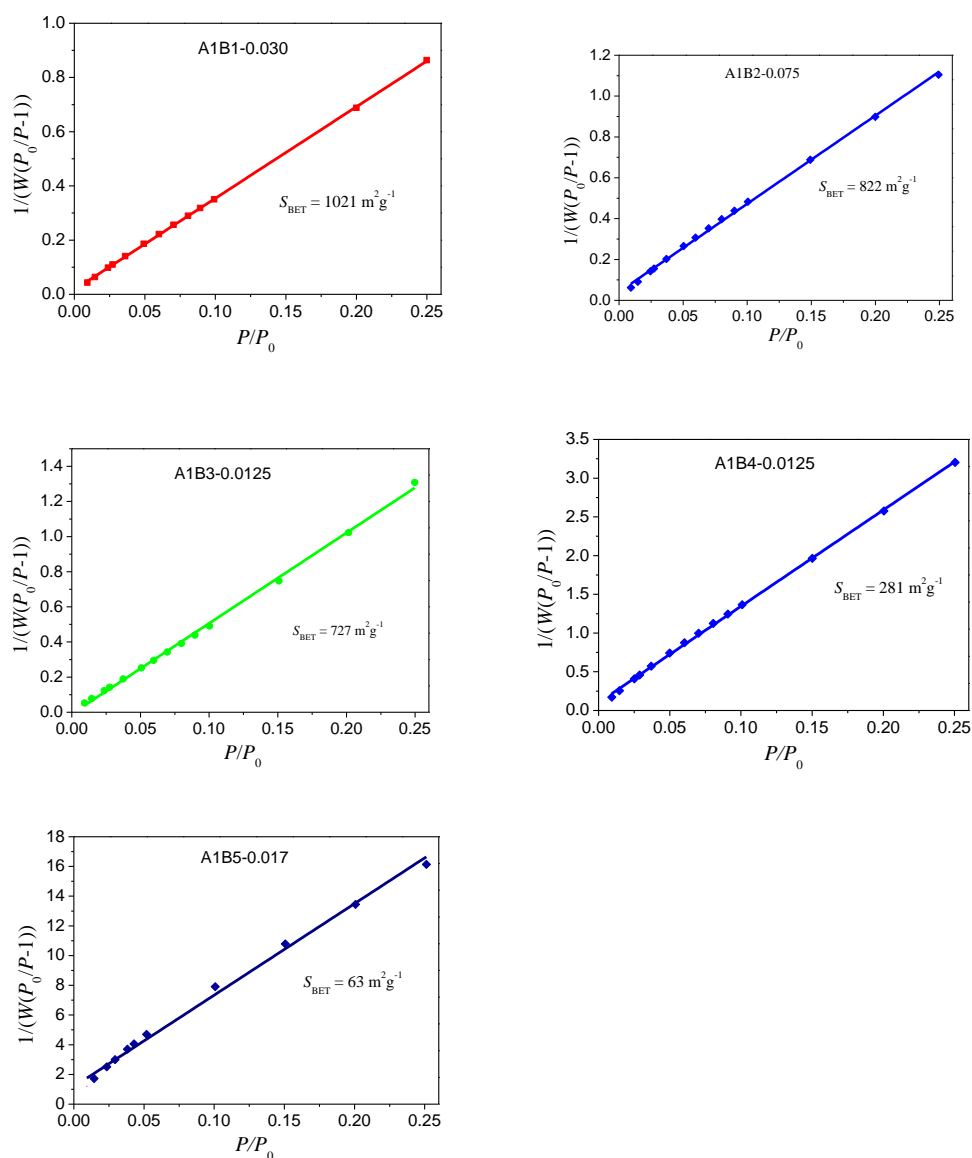


Fig. S13 BET surface area plots calculated from the isotherms for various imine aerogels with different precursor aldehydes, A1B1-0.030, A1B2-0.075, A1B3-0.0125, A1B4-0.0125 and A1B5-0.017.

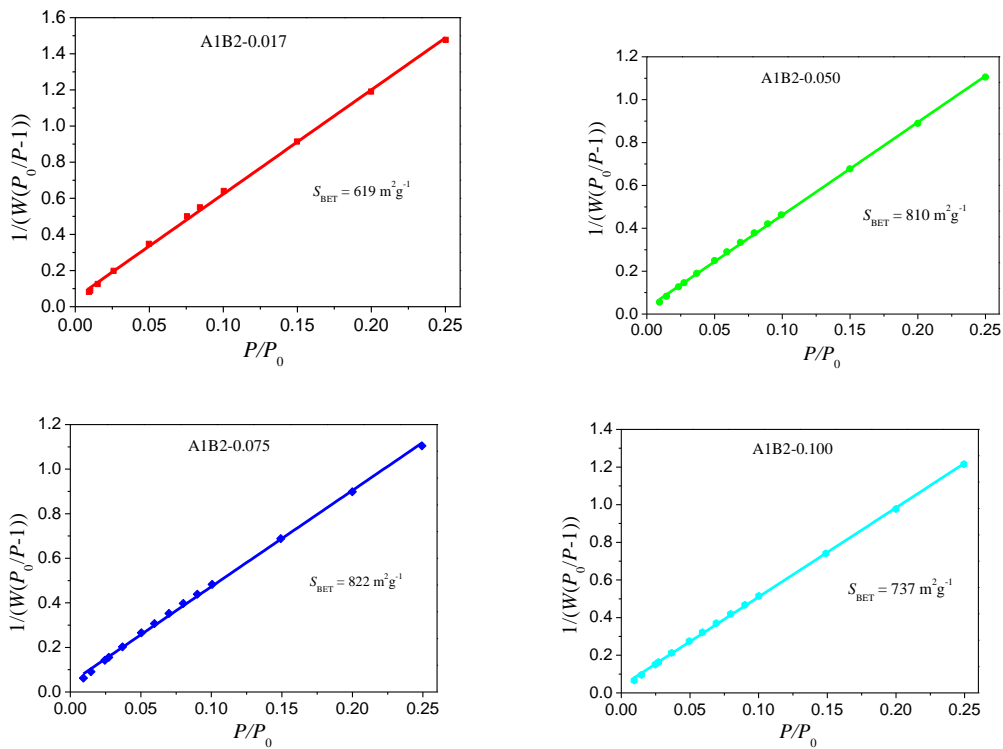


Fig. S14 BET surface area plots calculated from the isotherms for A1B2 aerogels with different precursor concentrations ($c_{A1} = 0.017, 0.050, 0.075$ and 0.100 mol L^{-1}).

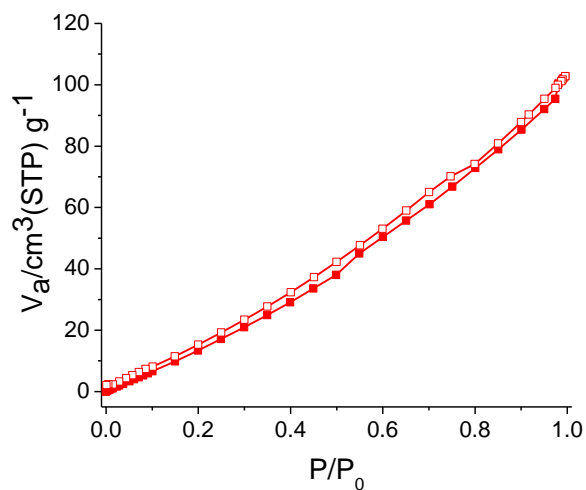


Fig. S15 N_2 adsorption and desorption isotherms at 77 K of A1B1-0.03 xerogel.

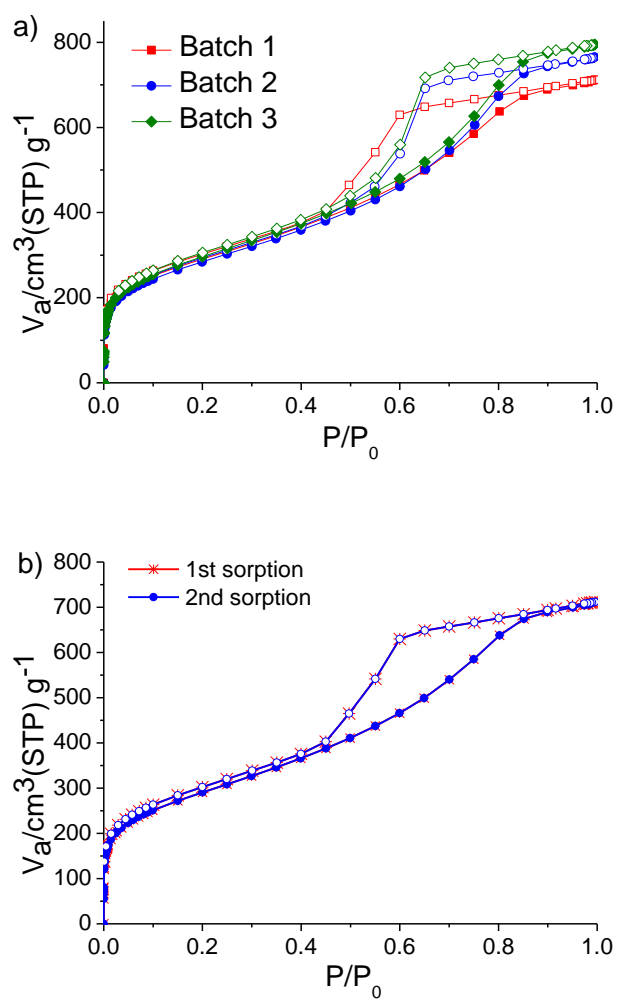


Fig. S16 N_2 adsorption and desorption isotherms at 77 K of A1B1 aerogels, a) prepared in three parallel batches, and b) repeatability for the same sample.

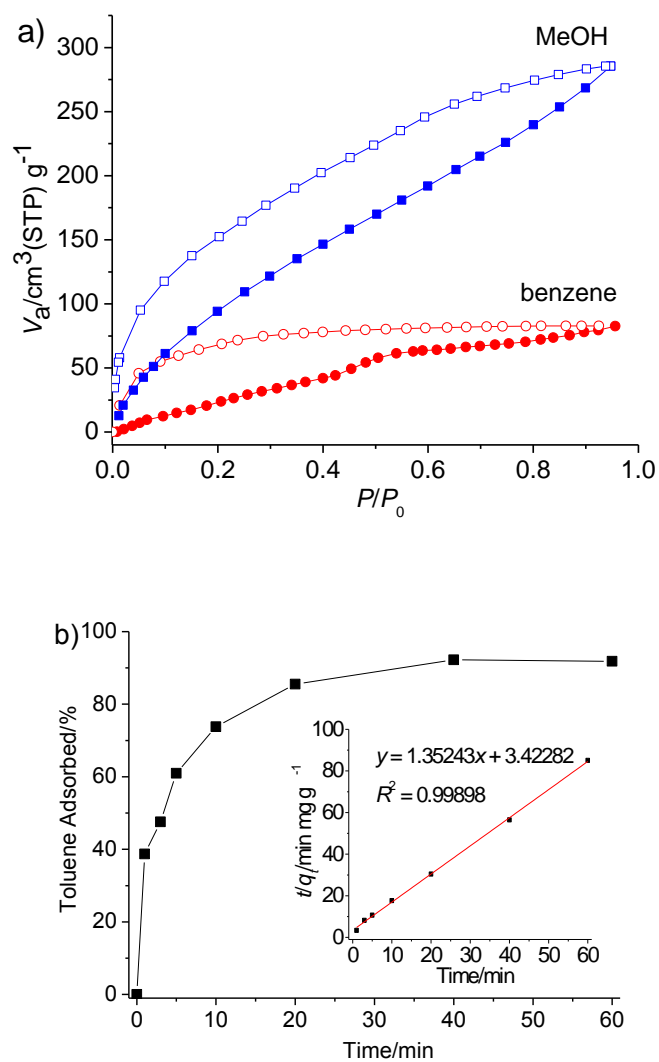


Fig. S17 a) Vapour sorption isotherms of benzene and methanol for A1B1-0.030 aerogel at 298 K (Filled shapes represent adsorption and open shapes represent desorption), and b) kinetic curve for the toluene adsorption by A1B1-0.030 aerogel (69.0 mg) in 25 mL of toluene aqueous solution (initial concentration = 0.023 mol L^{-1}) at room temperature. Inset: pseudo-second-order kinetic plot.

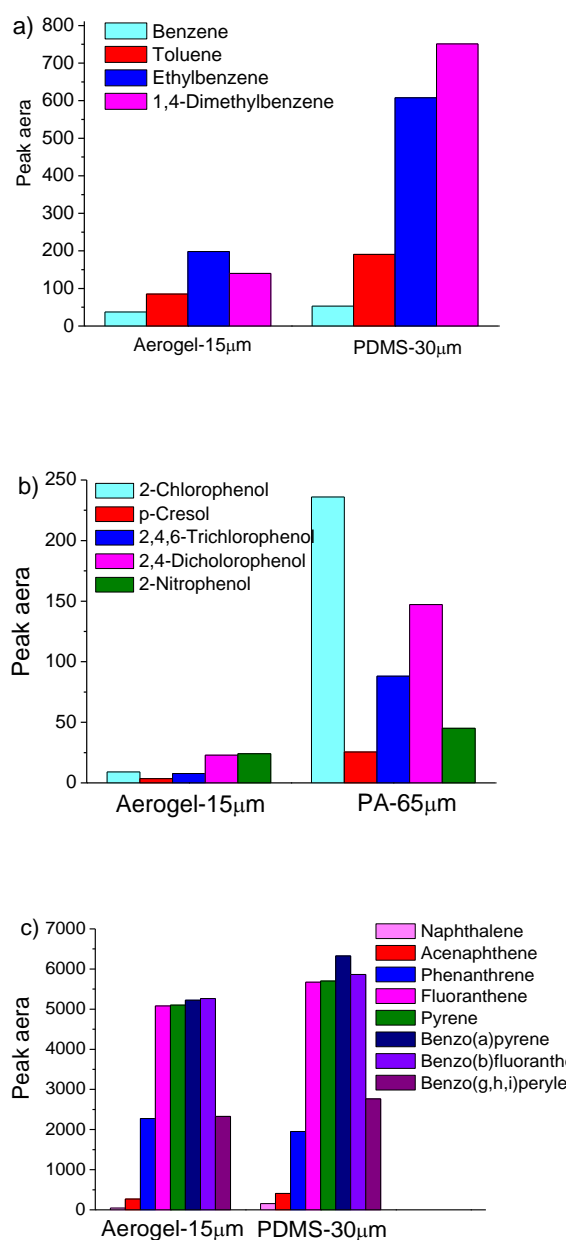


Fig. S18 Extraction contrast profiles with 15/40 µm A1B1-0.03 aerogel-coated fibres, commercial 30 µm PDMS fibres and commercial 65 µm PA fibres, a) BTEX, b) Phenols, c) PAHs and d) OCPs.