Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

High Surface Area Sulfur-Doped Microporous Carbons from Inverse Vulcanized Polymers

*Jet-Sing M. Lee, Douglas J. Parker, Andrew I. Cooper, and Tom Hasell**

Department of Chemistry and Materials Innovation Factory, University of Liverpool, Crown Street, Liverpool, L69 7ZD, UK.

E-mail: T.Hasell@liverpool.ac.uk

Gas Sorption: The porous properties of the networks were investigated by nitrogen adsorption and desorption at 77.3 K using an ASAP2420 volumetric adsorption analyser (Micrometrics Instrument Corporation). 1 bar CO_2 and CH_4 isotherms at 298 K and H_2 isotherms at 77.3 K were collected on a Micromeritics ASAP2020 and ASAP2050. 10 bar CO_2 and CH_4 isotherms at 298 K and H_2 isotherms at 77.3 K were collected using a Micromeritics ASAP2050. All samples were degassed at 100 °C for 15 h under vacuum (10^{-5} bar) before analysis.

Pore Structure Analysis: Pore structure properties of the samples were determined via nitrogen adsorption and desorption at 77.3 K using a volumetric technique on an ASAP2420 adsorption analyser (Micromeritics Instrument Corporation). Before analysis, the samples were degassed at 100 °C for 15 h under vacuum (10^{-5} bar).

Brunauer-Emmett-Teller (BET) surface area was obtained in the relative pressure (P/P_0) range of 0.05–0.20, and total pore volume (V_t) was determined from the amount of nitrogen adsorbed at P/P_0 = *ca.* 0.99.

FE-SEM: High resolution imaging of the polymer morphology was achieved using a Hitachi S-4800 cold field emission scanning electron microscope (FE-SEM).

HR-TEM: High-resolution transmission electron microscopy (HR-TEM) was performed using a JEOL 2100FCS microscope, equipped with a Schottky field emission gun, operating at 200 kV. Bright field images were recorded in conventional TEM illumination mode. Chemical analyses were performed by energy dispersive x-ray spectroscopy using a windowless EDAX spectrometer.

TEM specimens were produced by ultrasonically dispersing powder in analytical grade methanol, the suspension was then dropped onto copper mesh grids with holey carbon support films and allowed to dry.

Elemental Analysis: CHN elemental analysis was conducted on a Thermo FlashEA 1112.

PXRD: Powder X-ray diffraction (PXRD) data were collected in transmission mode on loose powder samples held on thin Mylar film in Stainless steel well plates on a Panalytical X'Pert PRO MPD equipped with an high throughput screening (HTS) XYZ stage, X-ray focusing mirror, 1/2 degree divergence slit, 0.04 degree soller slits, 4 mm beam mask and PIXcel detector, using Cu Kα radiation. Data were measured over the range 5-50° 2Θ in 0.013° steps over 60 minutes.

Other Metals studies: Tests were carried out on a range of other metals to determine if the high uptake of mercury on 1K-S-DCPD-750 was a function of the sulfur loading, or merely the higher surface area. 100 ppm solutions (50 ml) of chromium, cobalt, copper, manganese, iron, nickel and mercury were made up from stock solutions respective metal salts (Copper (II) Nitrate Hydrate, Cobalt (II) Nitrate Hexahydrate, Nickel (II) Nitrate Hexahydrate, Chromium (III) Nitrate Nonahydrate, Mercury (II) Chloride, Manganese (II) Chloride Tetrahydrate, and Iron (III) Chloride Hexahydrateand) and de-ionised water. Activated charcoal and 1K-S-DCPD-750 were coarsely ground and screened through a 45 Mesh sieve to ensure that all tests would contain particles no larger than 350 microns. 15 ml plastic vials were loaded with 30 mg of either 1K-S-DCPD-750 or activated charcoal and 12 ml of the chosen metal solution, the tubes were then capped and placed on a roller for 1 hour at room temperature. Multiple metals were tested at a time by conducting tests in parallel. After 1 hour, the vials were removed and stood in a rack to allow the particulates to settle, whilst a 1 ml aliquot was removed for analysis. The samples were diluted by a factor of 10 by adding the 1 ml aliquots each to a vial containing 9 ml of de-ionised water. Samples were analysed along with a water blank and 100 ppm control samples of each metal using the same calibration method on the ICP-OES, with the data being corrected post collection. ICP-OES analysis was conducted using an Agilent 5110.

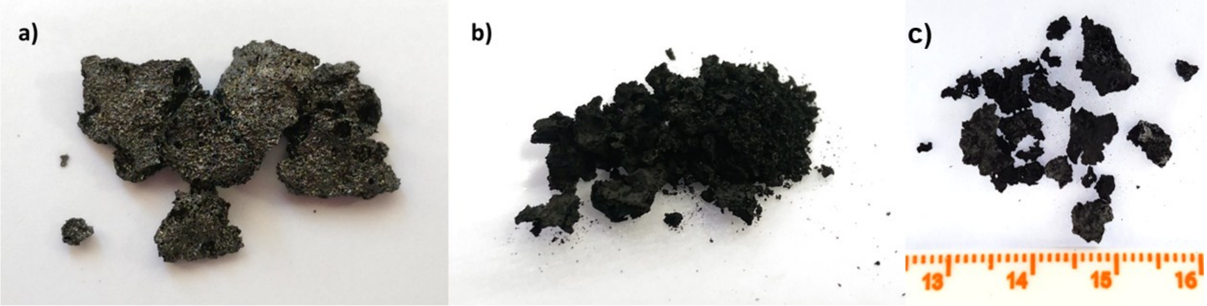

Fig. S1 Photographs of a) directly carbonized S-DCPD resulting in a large grey metallic monolith and b) KOH activated S-DCPD carbon black powder. c) Additional photo of S-DCPD showing scale (graduations are mm) to allow observation of particle size.

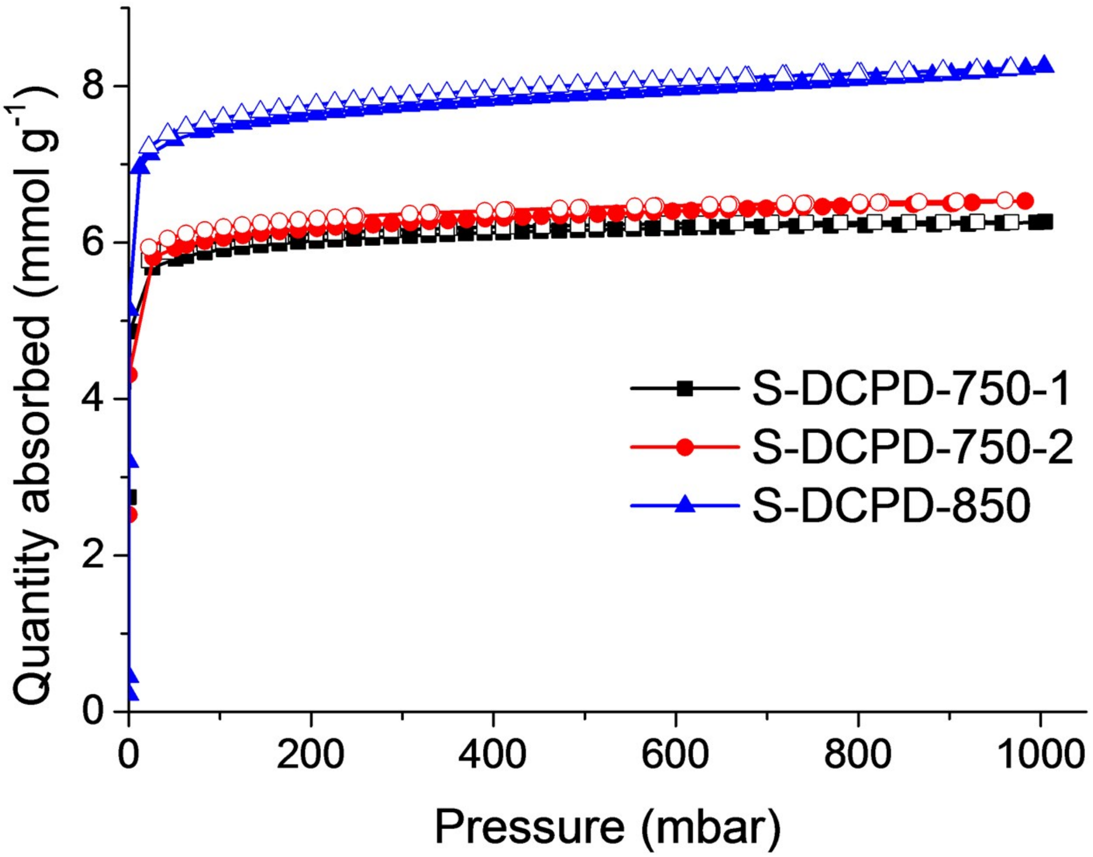

Fig. S2 Nitrogen adsorption–desorption isotherms of directly carbonized S-DCPD at 77.3 K (the adsorption and desorption branches are labelled with filled and empty symbols, respectively).

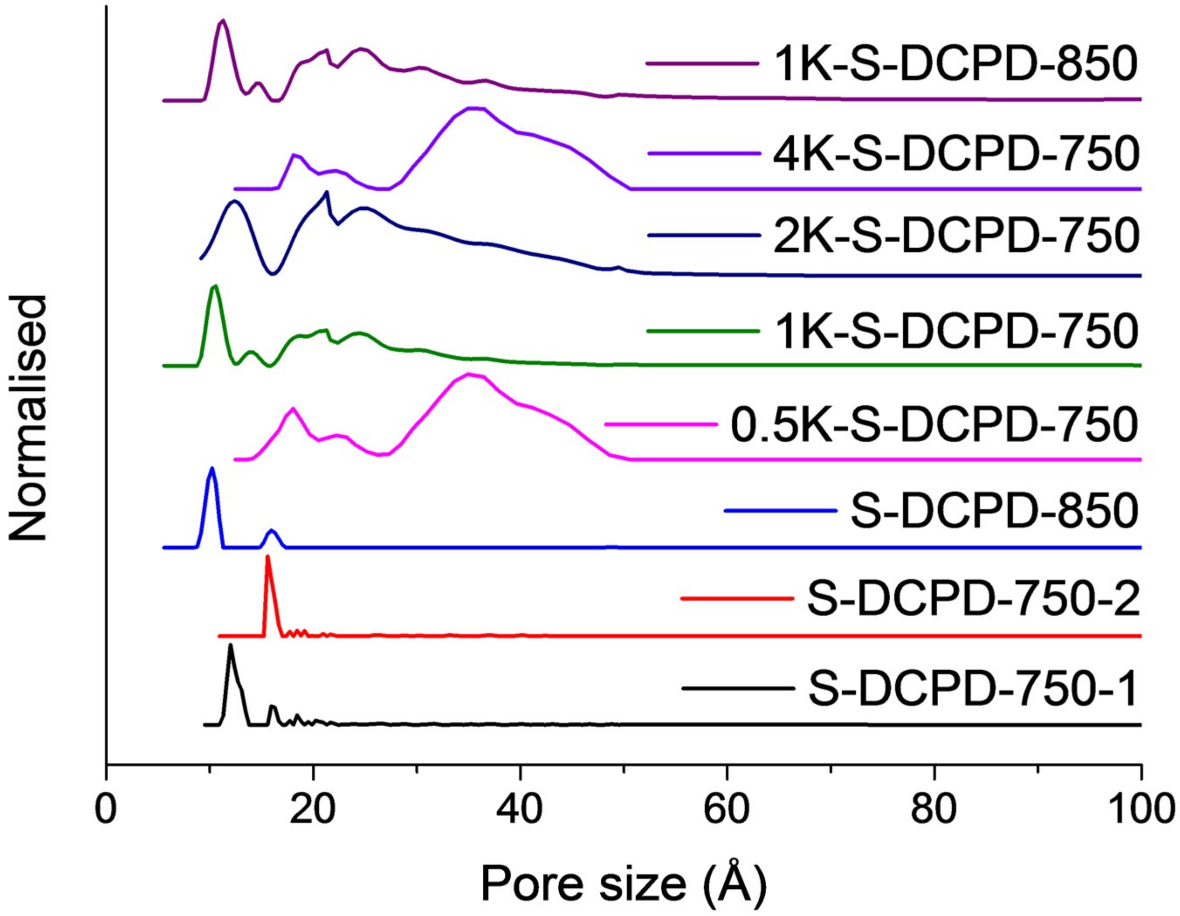

Fig. S3 Pore size distributions of carbonised S-DCPD calculated by non-local density functional theory (NL-DFT), from the nitrogen sorption isotherms. It can be seen that without KOH present as a porogen, only micropores are generated (<2 nm). However, addition of KOH also generates mesopores (2-50 nm), therefore creating hierarchical porosity.

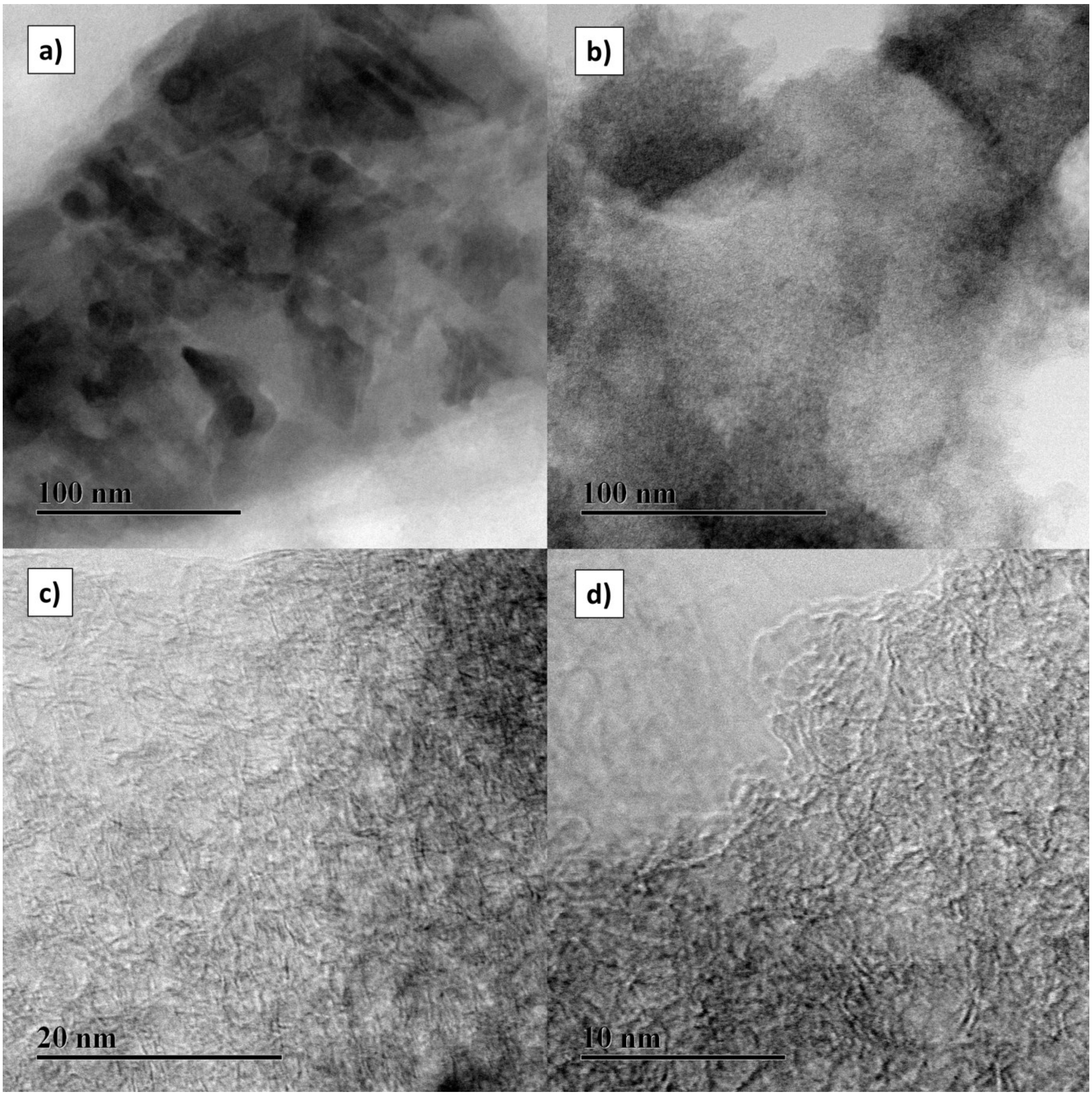

Fig. S4 HR-TEM images of a) S-DCPD-850 and b) 1K-S-DCPD-750 with higher resolution images of 1K-S-DCPD-750 at c) 20 nm and d) 10 nm scale.

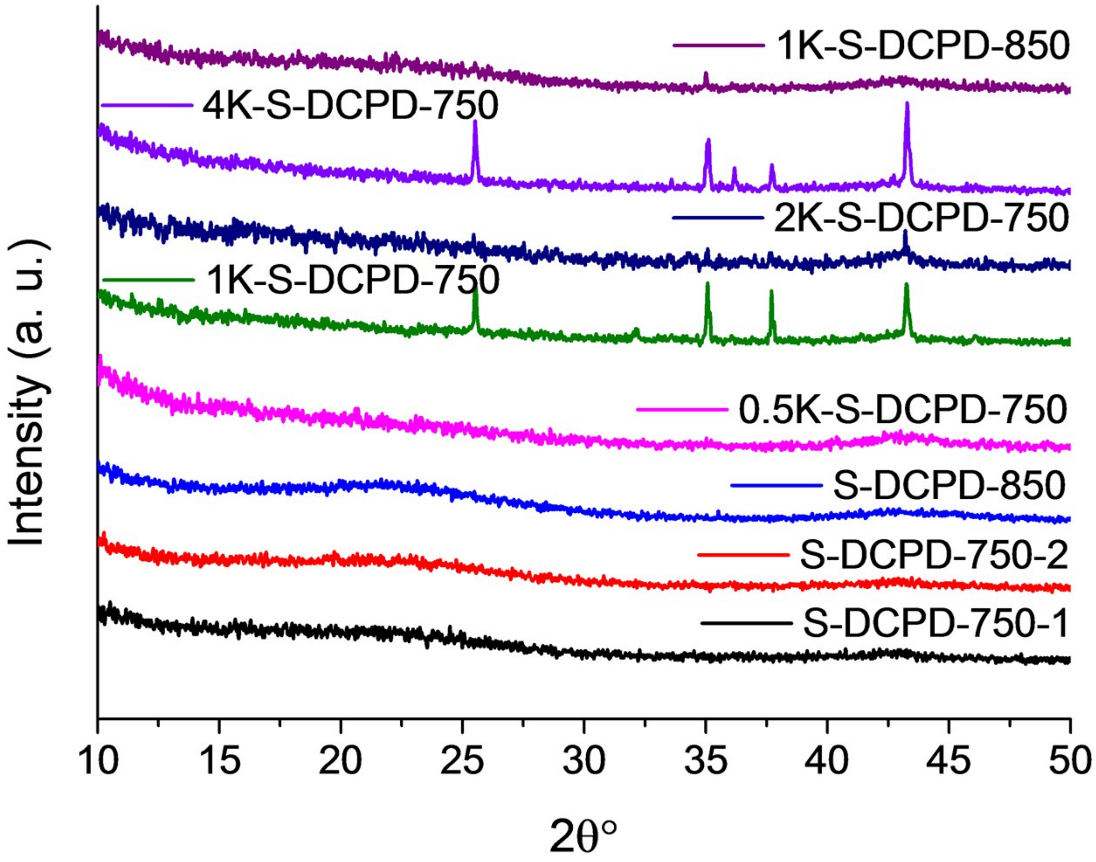

Fig. S5 PXRD patterns of carbonized S-DCPD samples. Samples 1K-S-DCPD-750 and 4K-S-DCPD-750 contain additional alumina peaks associated from the ceramic boat and/or use of pestle and mortar.

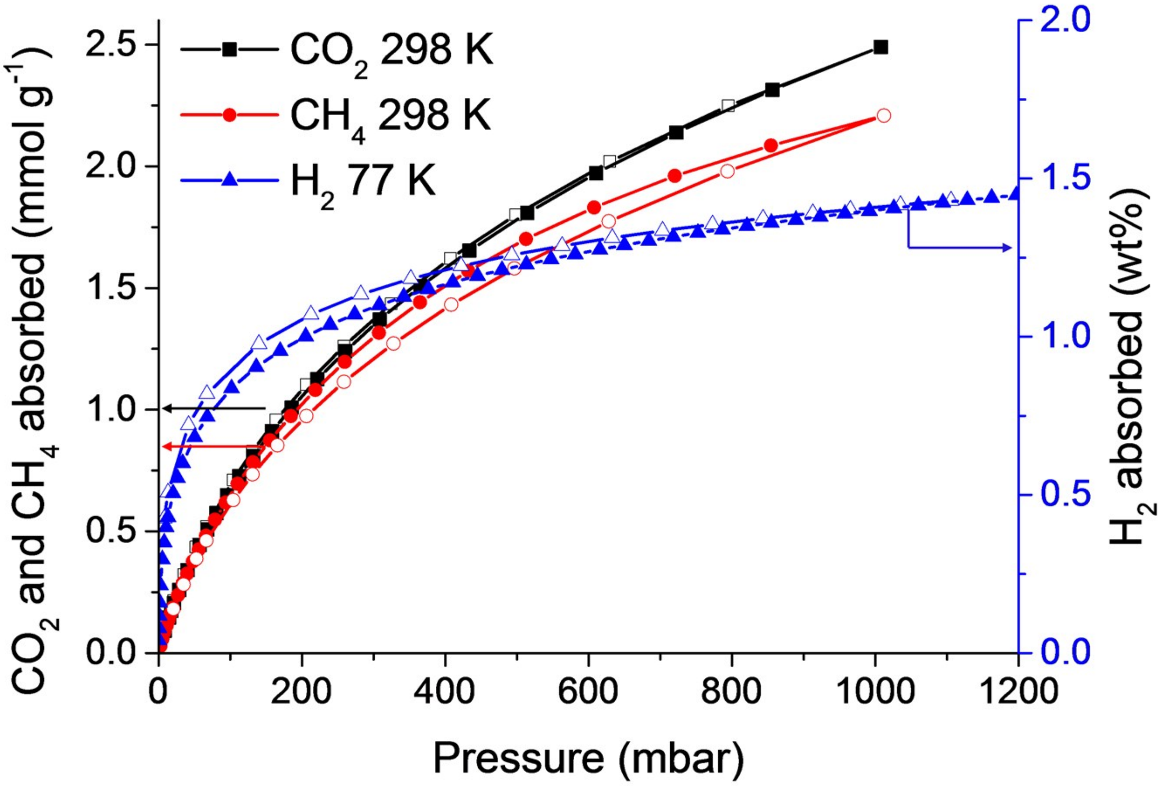

Fig. S6 CO_2 and CH_4 sorption isotherms at 298 K and H_2 sorption isotherms at 77 K of S-DCPD-850 over a pressure range of 0-10 bar.

Table S1 Carbonisation yields and CHNS elemental analysis of S-doped porous carbon products.

Sample	Yield (%)	C	H	S
S-DCPD-750-1	36	75.85	0.66	18.16
S-DCPD-750-2	35	77.25	0.63	17.67
S-DCPD-850	32	81.86	0.50	11.89
0.5K-S-DCPD-750	23	74.91	0.35	13.54
1K-S-DCPD-750	34	74.14	0.55	13.27
2K-S-DCPD-750	14	78.37	0.95	12.77
4K-S-DCPD-750	16	77.98	0.55	12.73
1K-S-DCPD-850	34	69.40	0.87	9.55

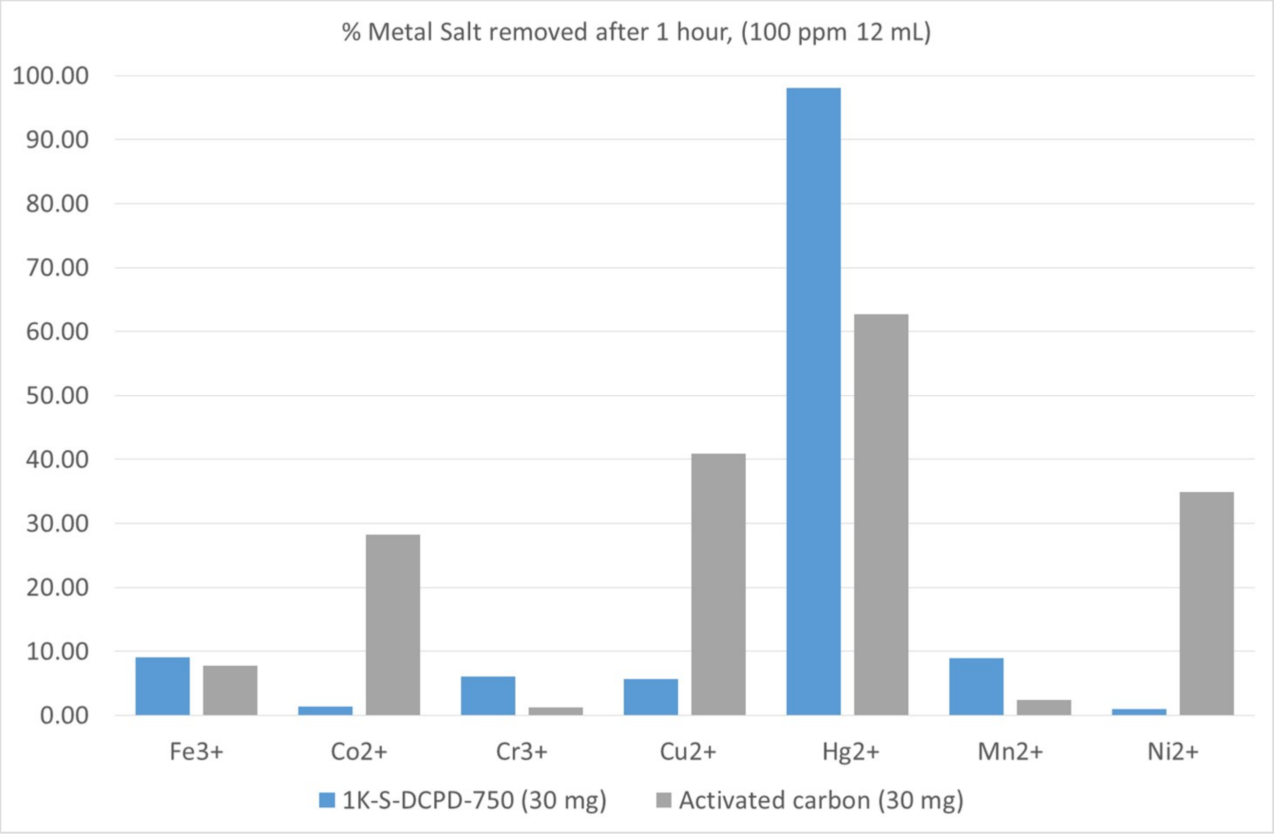

Fig. S7 Metal uptake of 1K-S-DCPD (blue) and activated carbon (grey) for a series of metal salts. The higher uptake of the activated carbon for many of the metals suggests that the higher metal uptake of 1K-S-DCPD-750 for Hg is not merely a function of its higher surface area, but is instead related to the sulfur content having a specific affinity for Hg.