

Electronic Supplementary Information

Porosity-Engineered Carbons for Supercapacitive Energy Storage Using Conjugated Microporous Polymer Precursors

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Experimental Section

Materials

1,4-diiodobenzene, 2,5-dibromoaniline, tetrakis(triphenylphosphine)palladium(0), copper(I) iodide, triethylamine, sulphuric acid, sodium sulphate, potassium hydroxide were purchased from Sigma Aldrich. 1,3,5-triethynylbenzene was purchased from TCI America. Toluene was purchased from Fisher Scientific. All chemicals were used as received without any further purification. Triply distilled water was used in all experiments.

Characterisation

XPS: X-ray photoelectron spectroscopy (XPS) were performed in a standard ultrahigh vacuum surface science chamber consisting of a PSP Vacuum Technology electron energy analyser (angle integrating $\pm 10^\circ$) and a dual anode x-ray source. The base pressure of the system was less than 2×10^{-10} mbar, with hydrogen as the main residual gas in the chamber. The XPS measurements were carried out with a Mg K-alpha source (1253.6 eV). The spectrometer was calibrated using Au 4f7/2 at 83.9 eV. The samples were corrected for charging using the adventitious carbon 1s peak to 284.6 eV. The peaks were deconvoluted using the CASA XPS software.

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

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 (Micromeritics Instrument Corporation). Samples were degassed at 120 °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 120 °C for 15 h under vacuum (10^{-5} Bar).

Brunauer-Emmett-Teller (BET) surface area (S_{BET}) 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 $P/P_0 = \text{ca. } 0.99$.

Raman Spectroscopy: Raman spectra were recorded with a Raman microscope (Renishaw inVia), using a 785 nm wavelength laser focussed through an inverted microscope (Leica), via a 50x objective (Leica).

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.

TGA: Thermogravimetric analysis (TGA) was carried out in platinum pans using a Q5000IR analyser (TA instruments) with an automated vertical overhead thermobalance. The samples were heated at 20 °C/min to 1000 °C under nitrogen.

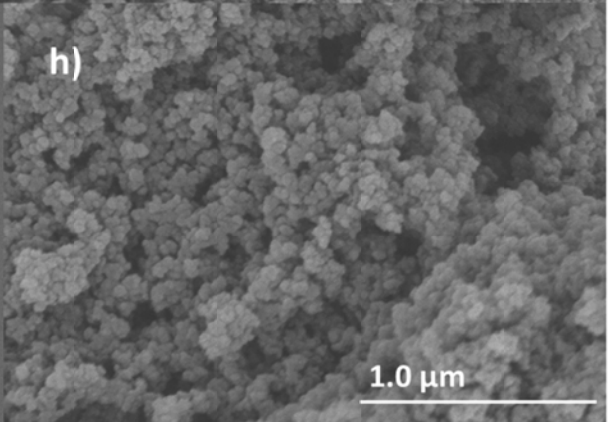
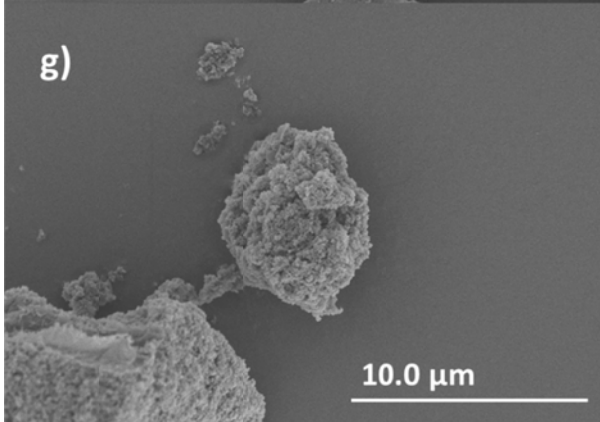
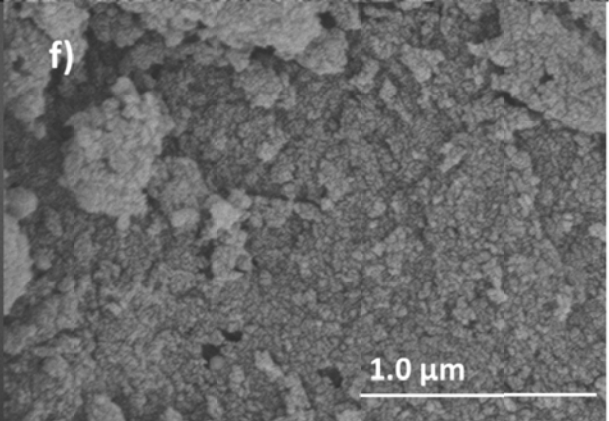
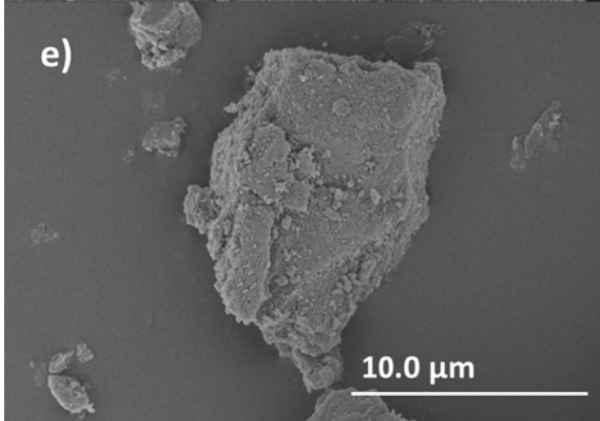
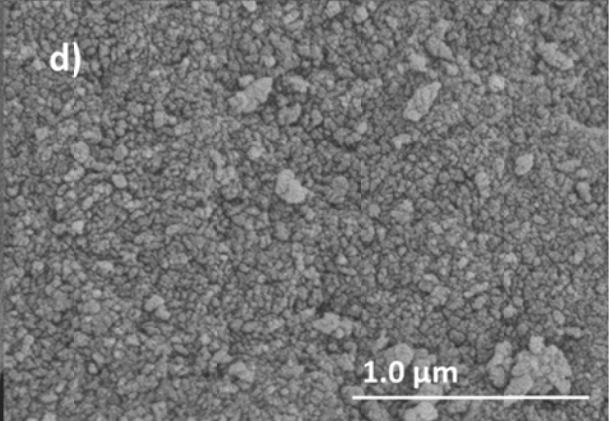
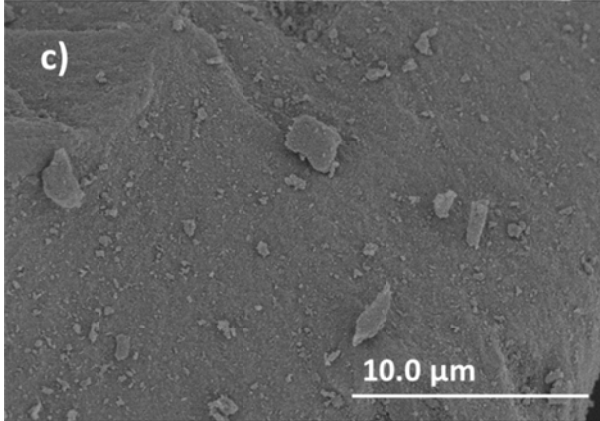
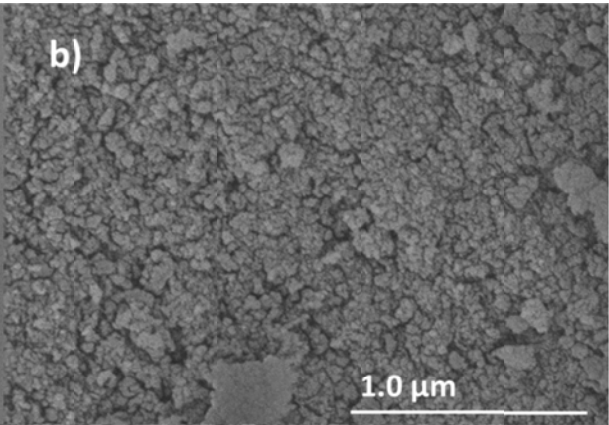
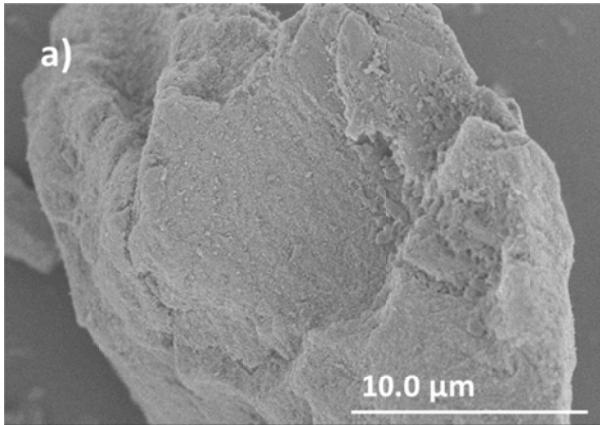
Table S1 Carbonisation yields, surface areas and CHN analysis of pristine and carbonised CMPs.

Sample	Yield (%) [*]	BET (m ² g ⁻¹)	C	H	N
CMP-1	-	737	81.92	3.65	-
CMP-1-NH ₂	-	522	67.18	3.34	2.02
C1-CMP-1	80	608	87.92	0.62	-
C2-CMP-1	70	577	88.51	0.56	-
N1-CMP-1	73	790	85.00	0.59	1.89
N2-CMP-1	49	1139	75.98	0.87	9.07
N3-CMP-1	60	1436	80.79	0.70	7.14

*Yield calculated from final mass against the starting precursor mass.

Table S2 Ratio of nitrogen groups from XPS of N 1s.

Sample	Amount (%)			
	Pyridinic	Pyrrolic	Quaternary	Oxidised
N1-CMP-1	31.15	30.75	35.91	2.19
N2-CMP-1	54.34	28.59	15.21	1.86
N3-CMP-1	52.32	39.90	7.59	0.20



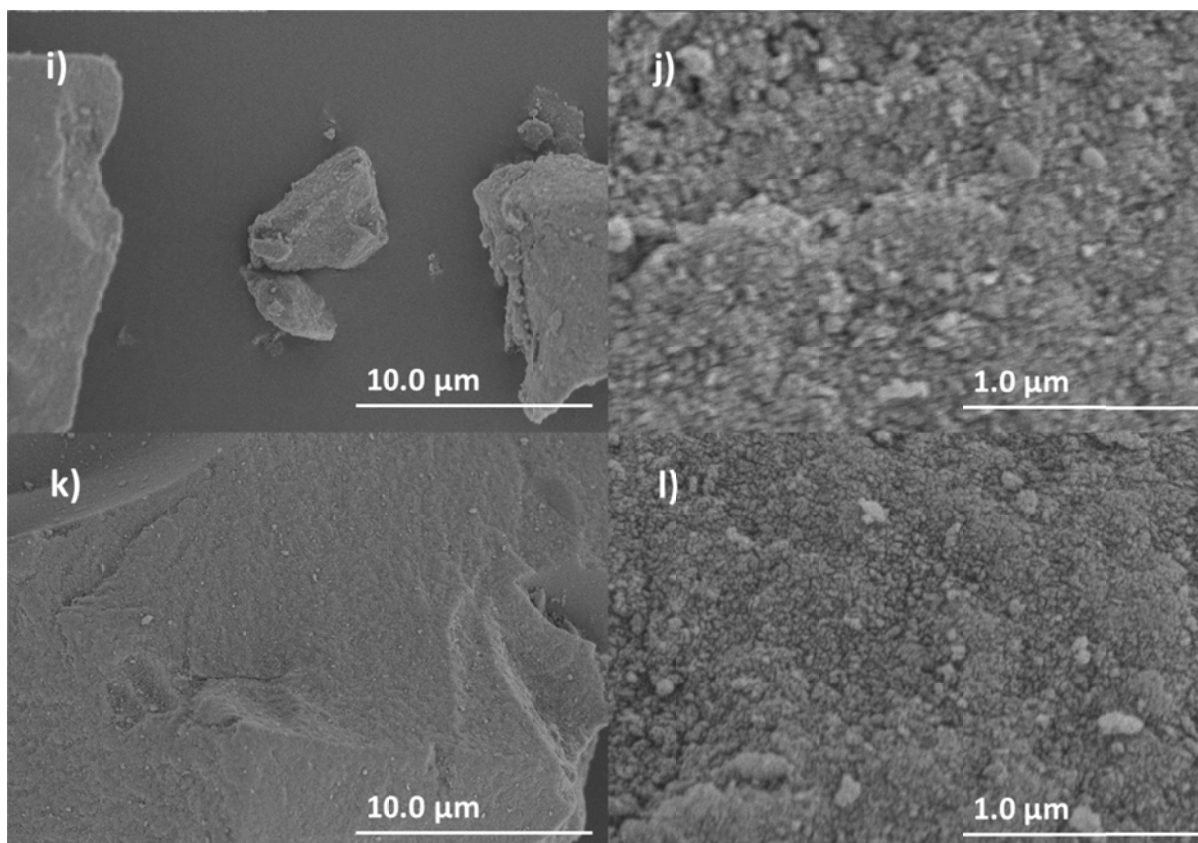


Fig. S1 FE-SEM images of (a, b) CMP-1, (c, d) C1-CMP-1, (e, f) C2-CMP-1, (g, h) N1-CMP-1, (i, j) N2-CMP-1, (k, l) N3-CMP-1 at low and high magnification respectively.

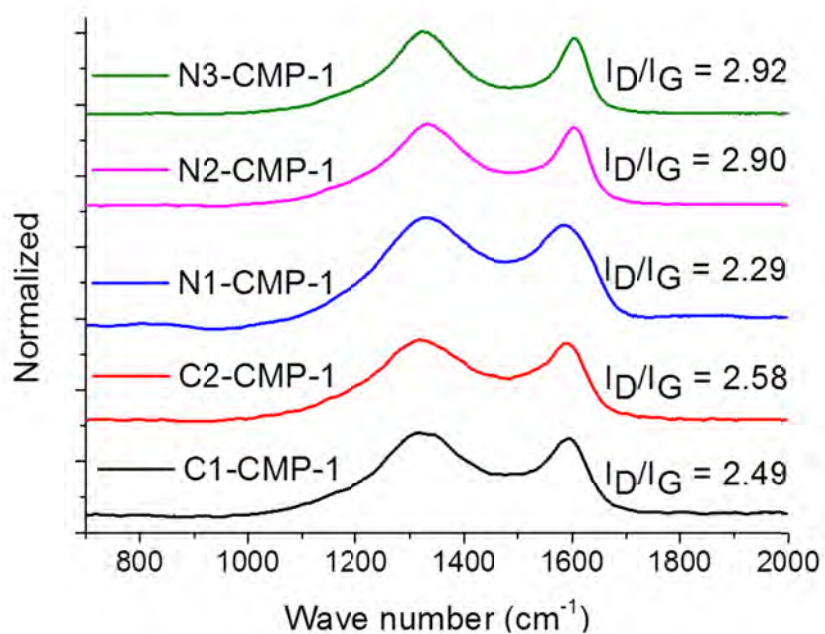


Fig. S2 Raman spectra of carbonised CMPs with peaks at 1350 cm^{-1} and 1596 cm^{-1} assigned to the *D* band and *G* band, respectively.^{1,2}

The L_a crystallite size was estimated from the following equation:³

$$L_a(\text{nm}) = (2.4 \times 10^{-10}) \lambda_l^4 \left(\frac{I_D}{I_G}\right)^{-1} \quad (1)$$

where λ_l is the wavelength of laser in nanometer units and I_D/I_G is the ratio between the D band and G band from Raman spectroscopy.

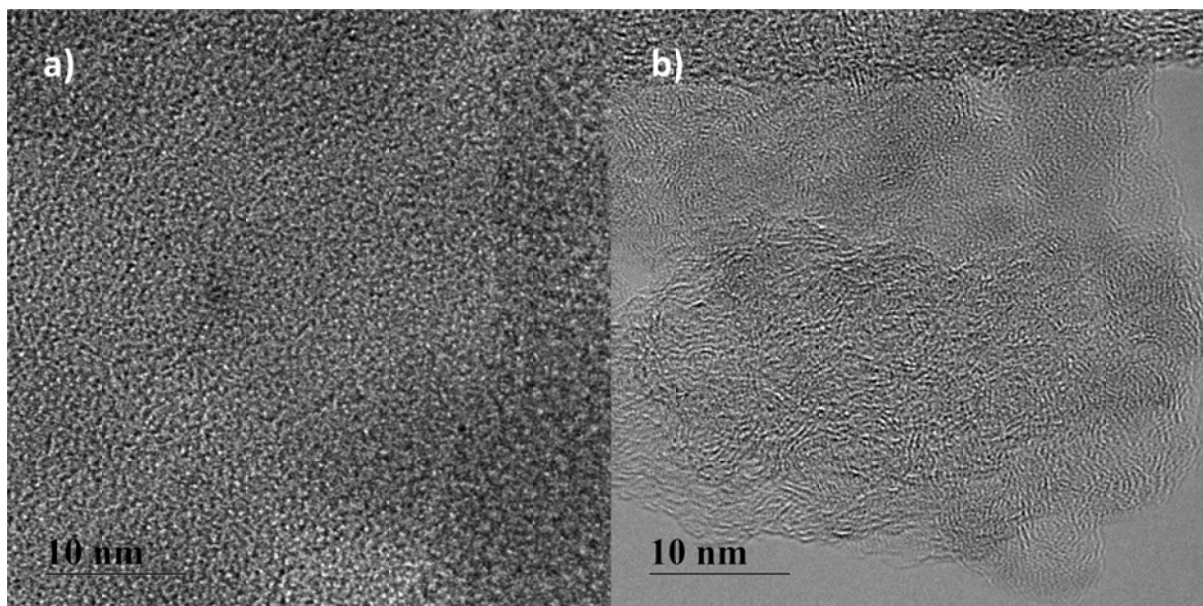


Fig. S3 HR-TEM of (a) CMP-1 and (b) N1-CMP-1.

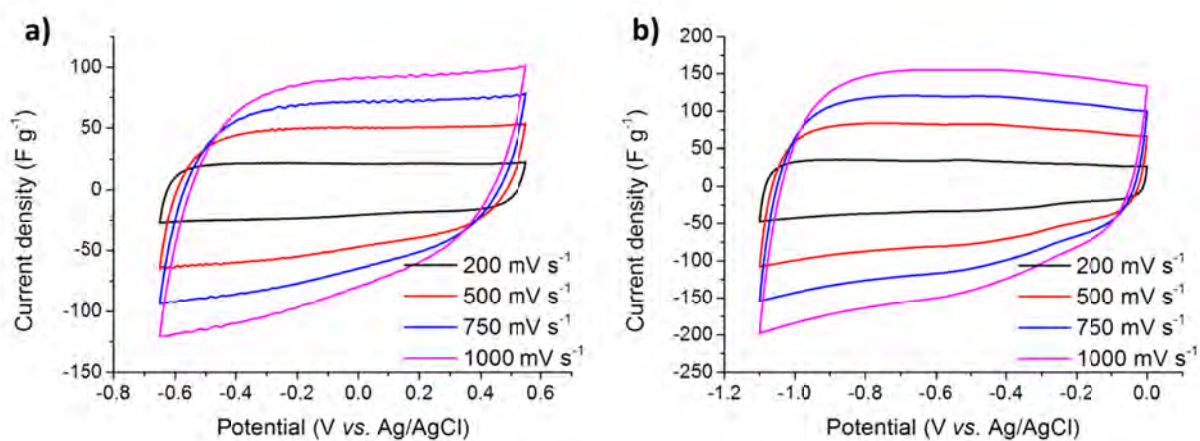


Fig. S4 Cyclic voltammograms of N3-CMP-1 in (a) 1 M Na₂SO₄ and (b) 3 M KOH at high scan rates.

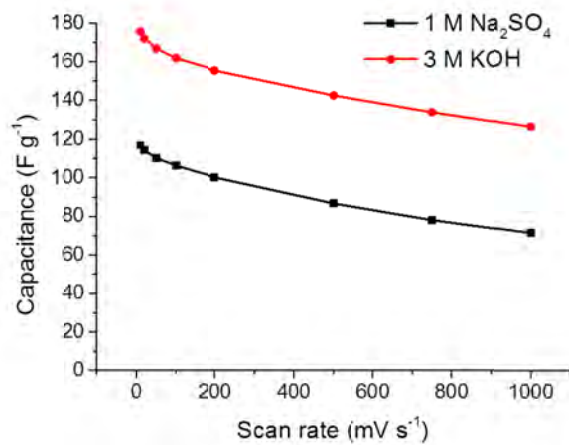


Fig. S5 Specific capacitance of N3-CMP-1 at varying scan rates in 1 M Na₂SO₄ and 3 M KOH.

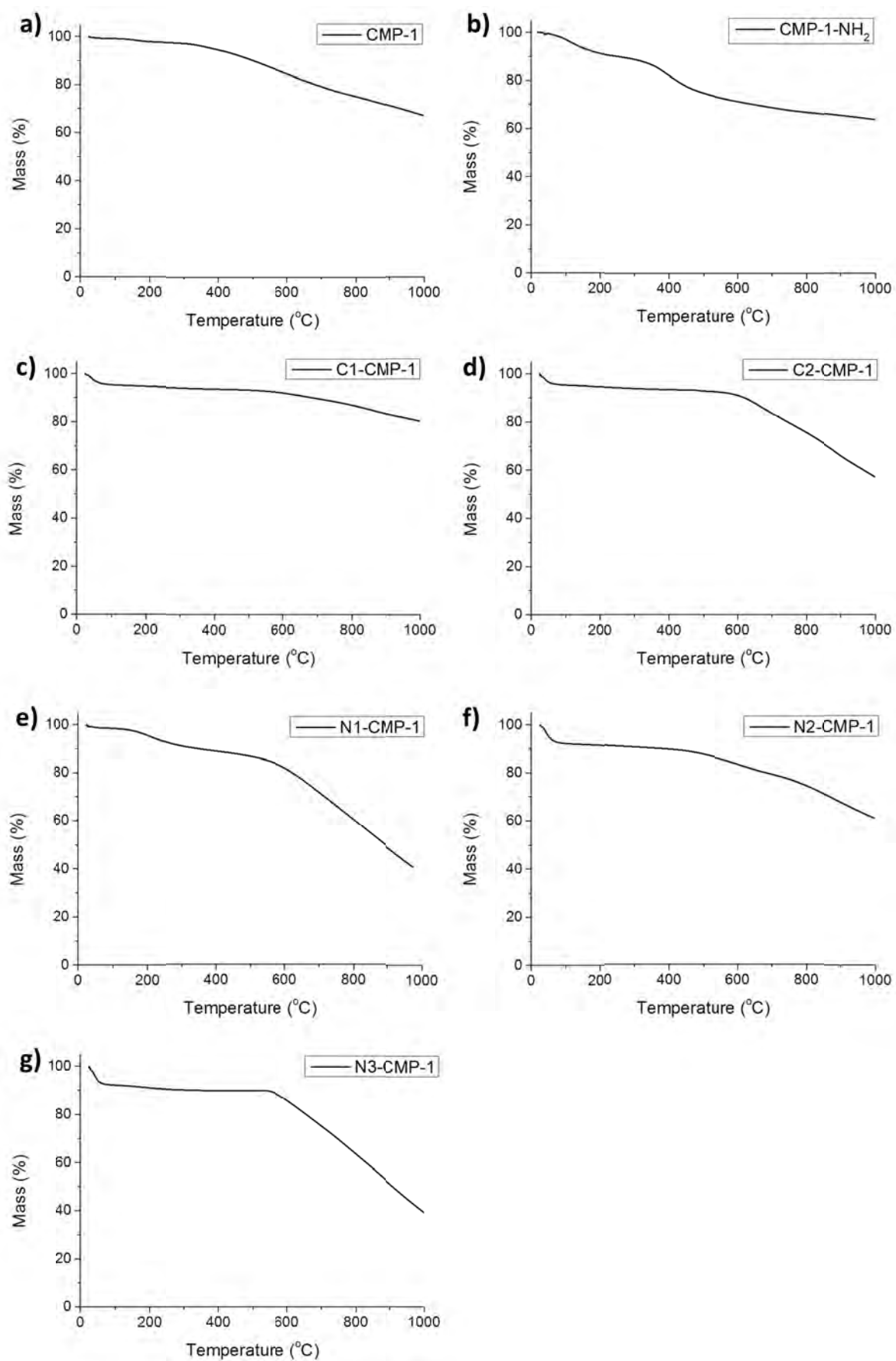


Fig. S6 TGA analysis of (a) CMP-1, (b) CMP-1-NH₂, (c) C1-CMP-1, (d) C2-CMP-1, (e) N1-CMP-1, (f) N2-CMP-1 and (g) N3-CMP-1 measured at a heating rate of 20 °C min⁻¹ under nitrogen flow.

References

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2. D. Mhamane, W. Ramadan, M. Fawzy, A. Rana, M. Dubey, C. Rode, B. Lefez, B. Hannoyer and S. Ogale, *Green Chem.*, 2011, **13**, 1990-1996.
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