Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

Enhancing Selective CO_2 Adsorption via Chemical Reduction of a Redox-Active Metal-Organic Framework

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Table S1. Crystallographic information for Zn(NDC)(DPMBI)·2DMF

Formula	$C_{40}H_{34}N_6O_{10}Zn$
Mw (g mol^{-1})	824.10
Crystal System	Orthorhombic
Space Group	*Pbcn*(#60)
a (Å)	25.91510(10)
b (Å)	14.17440(10)
c (Å)	20.60420(10)
V (Å^3)	7568.56(7)
Z	8
T (K)	150(2)
λ (Å)	1.5418
μ (mm^{-1})	1.478
D_c (g cm^{-3})	1.446
R1 (F)	0.0523
wR2(F^2)	0.1749

$R1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$

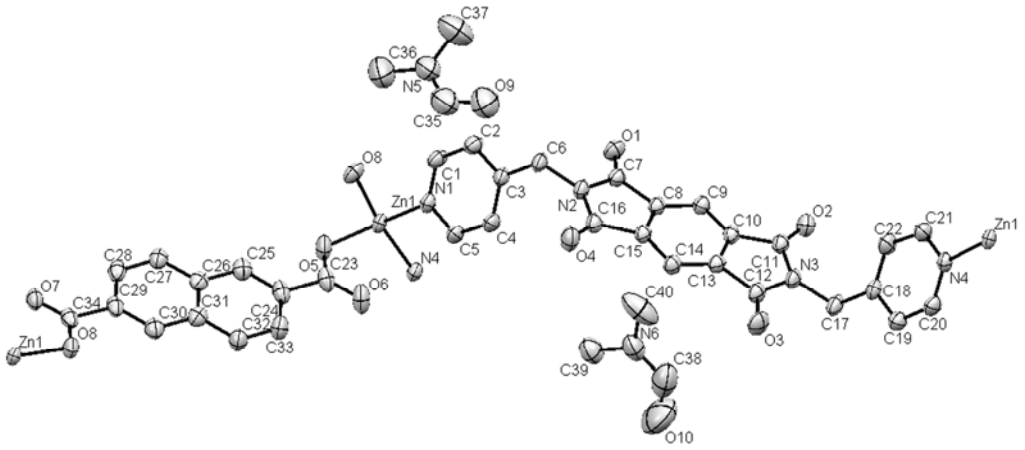


Fig. S1 An ORTEP depiction of the asymmetric unit of Zn(NDC)(DPMBI)·2DMF with the thermal ellipsoids drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

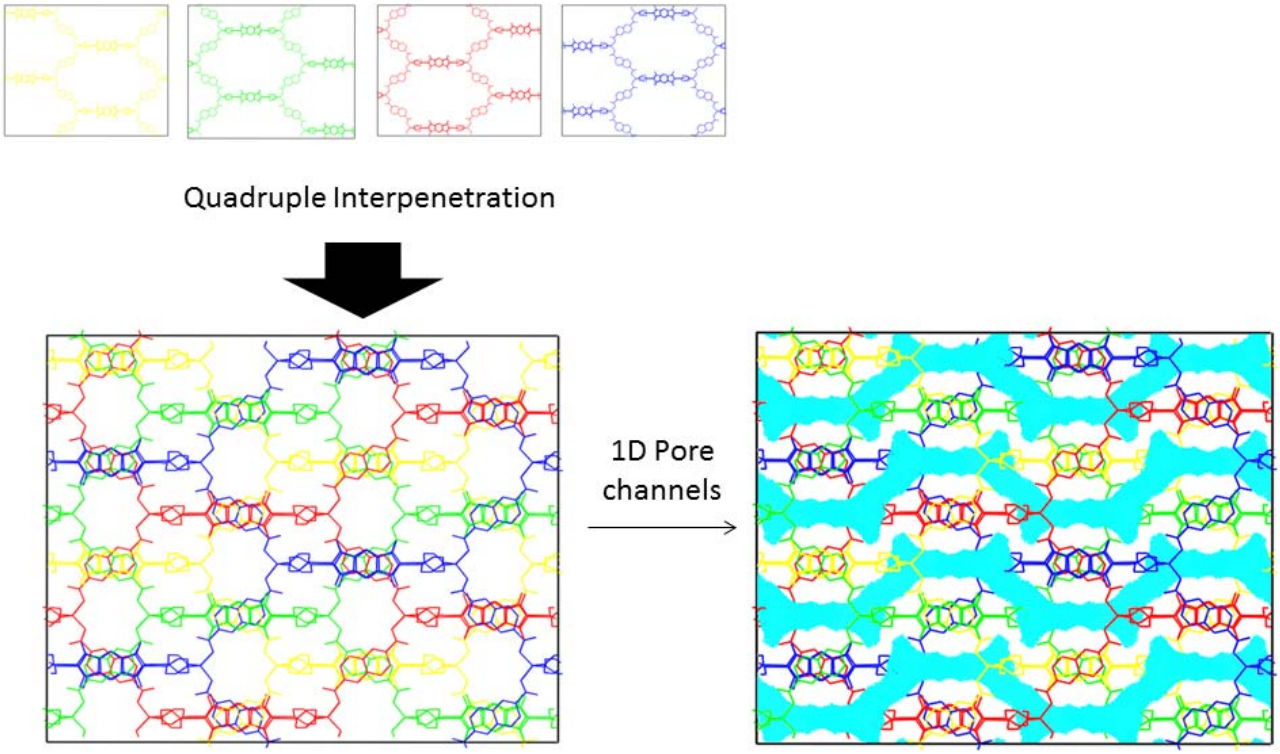


Fig. S2 Pore size analysis of the quadruply interpenetrated framework Zn(NDC)(DPMBI). The one dimensional channels in the desolvated material are depicted in cyan at right.

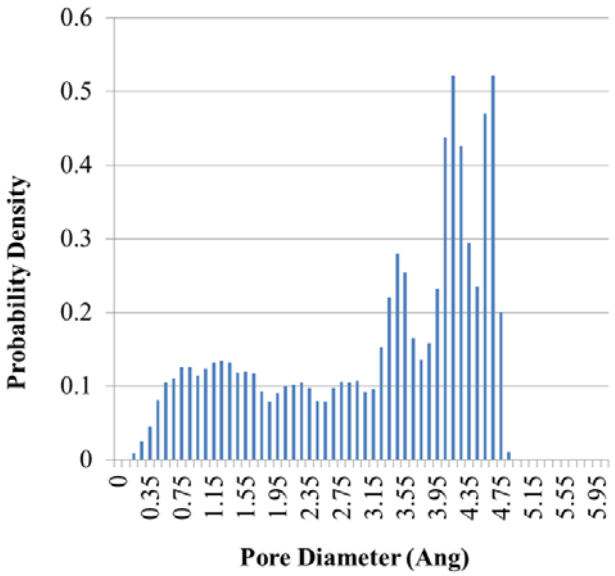


Fig. S3 Pore size analysis of the framework Zn(NDC)(DPMBI) obtained using the RASPA Package (D. Dubbeldam, S. Calero, D. E. Ellis and R. Q. Snurr, RASPA 1.0, Northwestern University, Evanston, 2008).

Activation of Zn(NDC)(DPMBI)

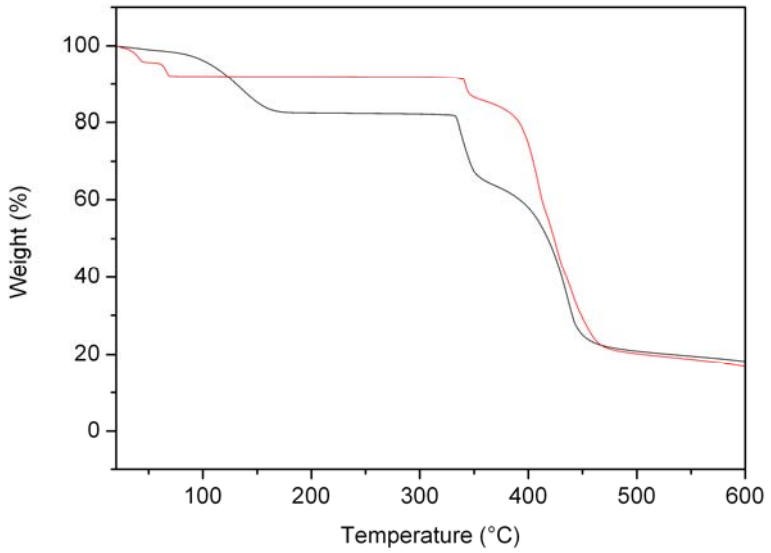


Fig. S4 TGA data for the as-synthesised Zn(NDC)(DPMBI) (black) and Zn(NDC)(DPMBI) solvent-exchanged with methanol (red). The step at 150 ºC in the as-synthesised sample is attributed to DMF.

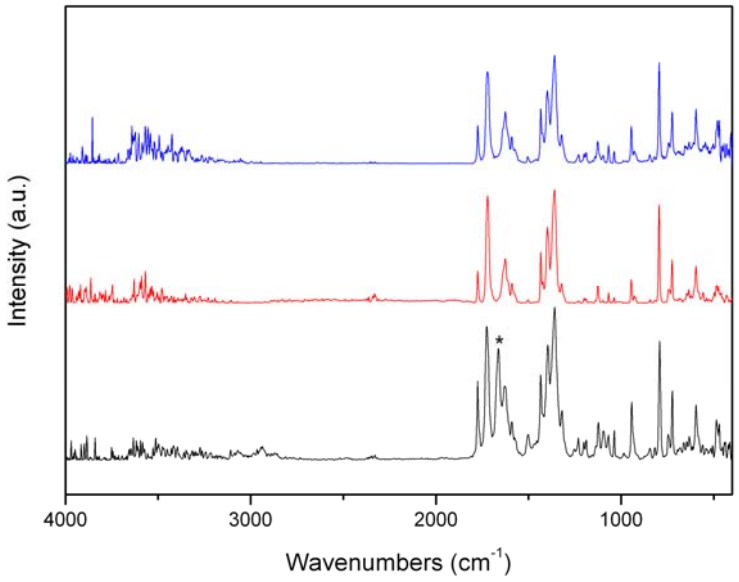


Fig. S5 FTIR spectra of the as-synthesised Zn(NDC)(DPMBI) (black), Zn(NDC)(DPMBI) solvent-exchanged with methanol (red) and Zn(NDC)(DPMBI) activated at 110 °C under vacuum (blue). The DMF carbonyl stretching band is indicated by an asterisk.

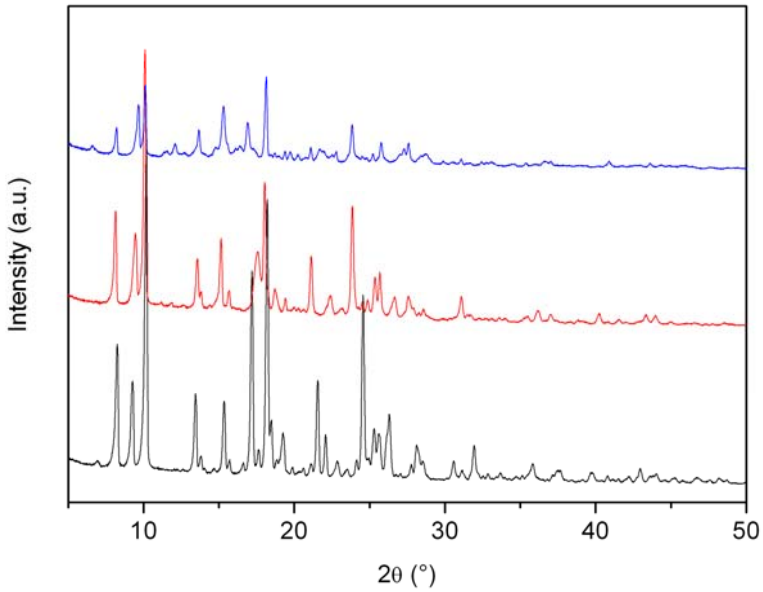


Fig. S6 PXRD comparison of as-synthesised Zn(NDC)(DPMBI) (black) and Zn(NDC)(DPMBI) solvent-exchanged with methanol (red) and heating at 110 °C under vacuum (blue).

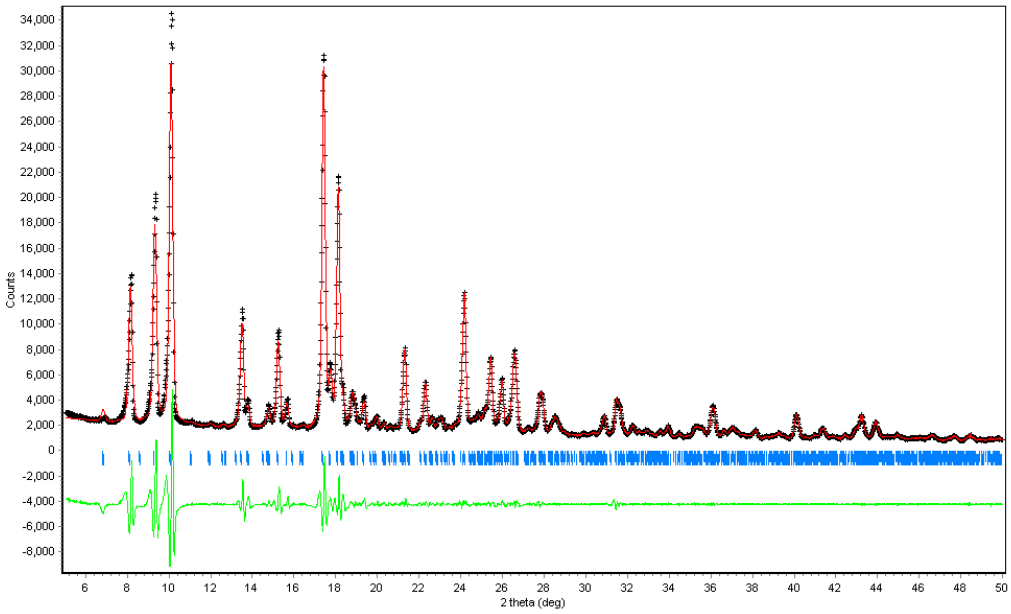


Fig. S7 Le Bail refinement of the bulk as-synthesised Zn(NDC)(DPMBI). The black crosses represent the PXRD pattern of the bulk material, the calculated pattern is represented by the red line, the blue markers are indicative of reflections expected for the Pbcn(#60) space group and the green line represents differences between the experimental and calculated data.

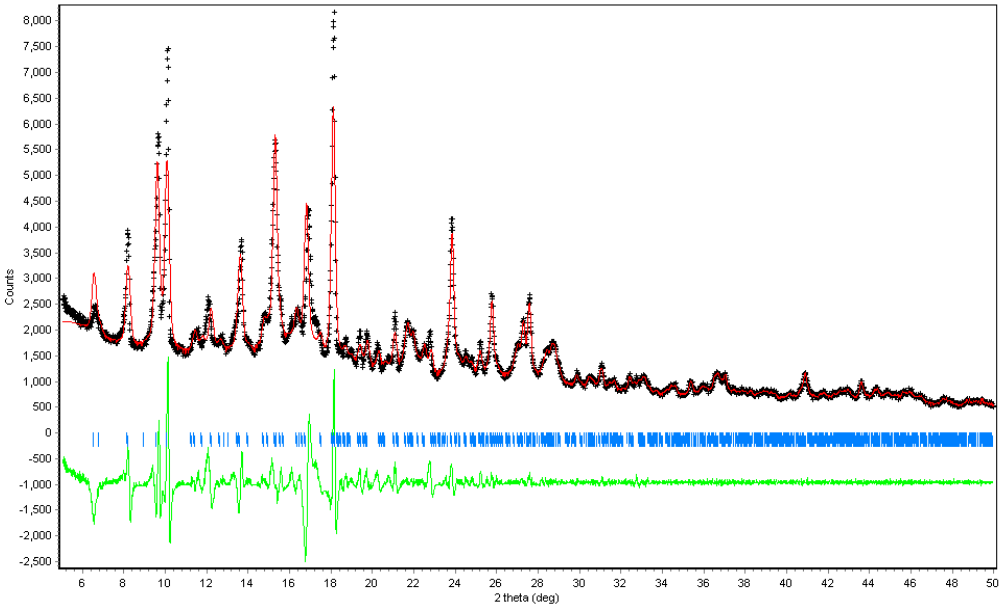


Fig. S8 Le Bail refinement of the activated Zn(NDC)(DPMBI). The black crosses represent the PXRD pattern of the bulk material, the calculated pattern is represented by the red line, the blue markers are indicative of reflections expected for the Pbcn(#60) space group and the green line represents differences between the experimental and calculated data.

Chemical Reduction of Zn(NDC)(DPMBI)

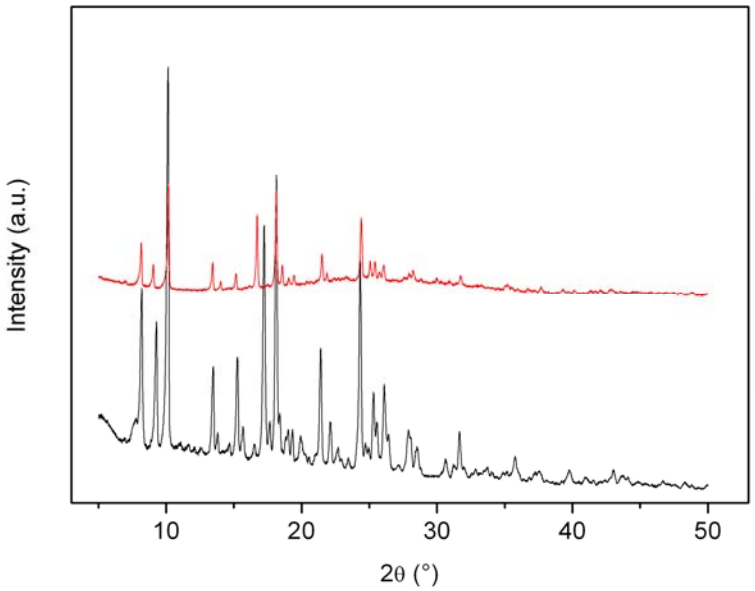


Fig. S9 PXRD overlay of Zn(NDC)(DPMBI) (black) and Zn(NDC)(DPMBI)·$Na_{0.109}$ (red) demonstrating a lowering of crystallinity due to framework reduction.

Table S2. Le Bail fitted cell parameters (in Å) for the neutral and chemically reduced frameworks.

Zn(NDC)(DPMBI) species	*a*	*b*	*c*
Neutral	25.893(7)	14.470(4)	20.672(7)
0.109 Na^+/Zn^{2+}	25.815(4)	14.104(3)	20.429(3)
0.233 Na^+/Zn^{2+}	25.799(4)	14.100(3)	20.492(3)
0.367 Na^+/Zn^{2+}	26.004(3)	14.038(1)	20.276(1)
0.378 Na^+/Zn^{2+}	25.792(5)	13.909(3)	20.268(3)

Detection of the Pyromellitic Radical

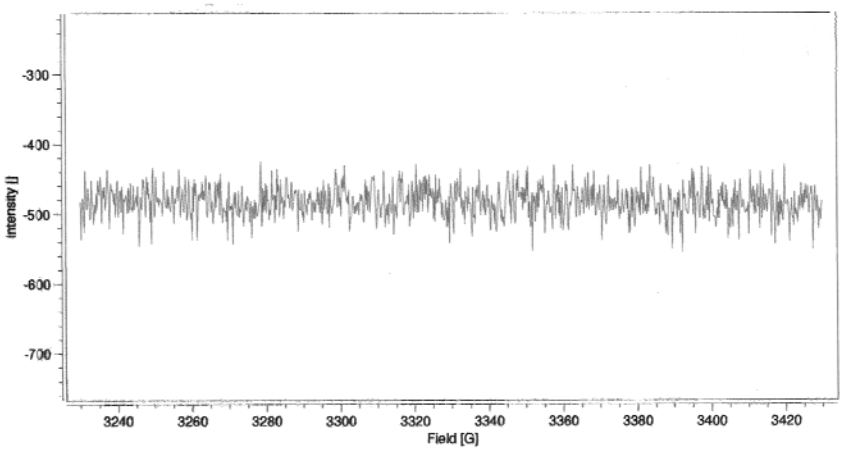


Fig. S10 X-band EPR spectrum of powdered Zn(NDC)(DPMBI) at 298 K.

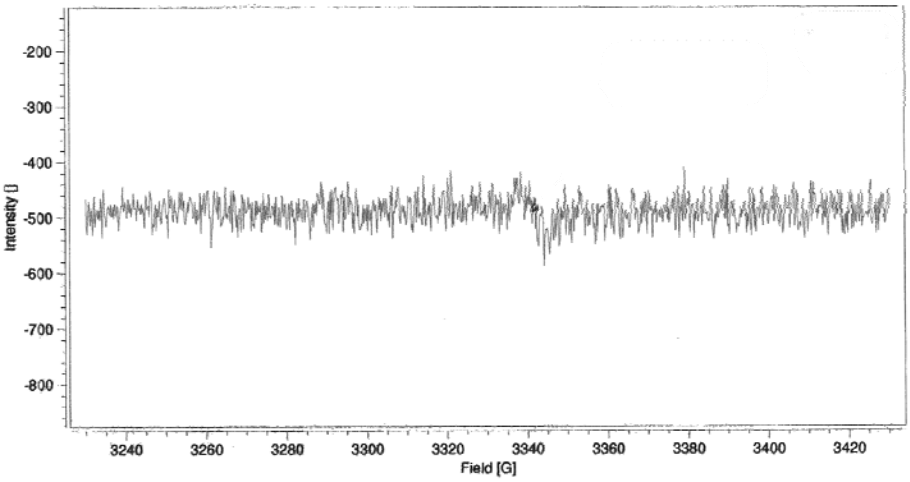


Fig. S11 X-band EPR spectrum of powdered Zn(NDC)(DPMBI)·$Na_{0.109}$ at 298 K.

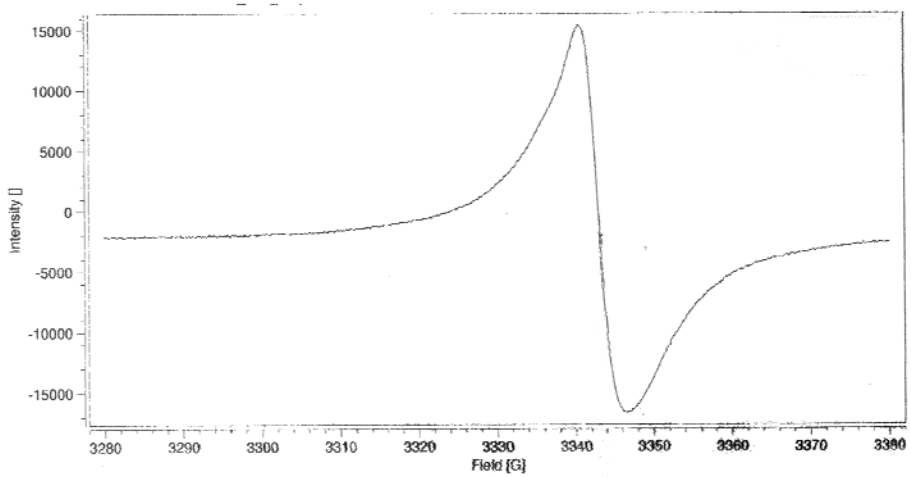


Fig. S12 X-band EPR spectrum of powdered Zn(NDC)(DPMBI)·$Na_{0.233}$ at 298 K.

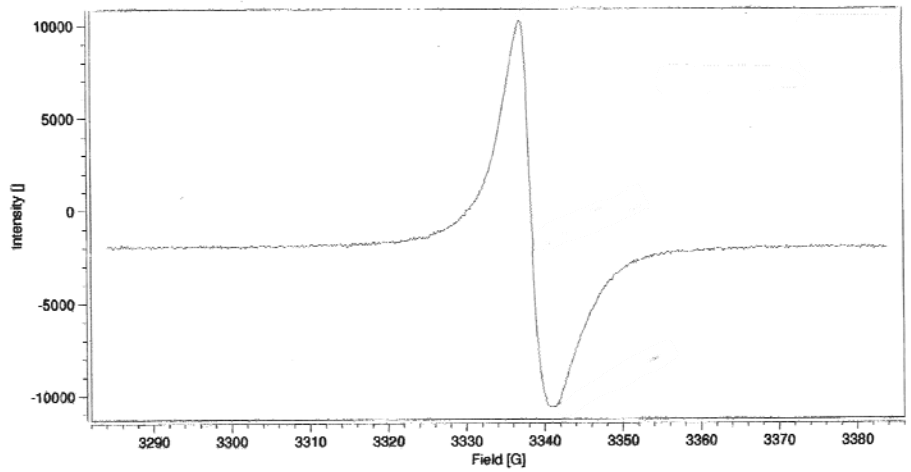


Fig. S13 X-band EPR spectrum of powdered EPR spectrum of Zn(NDC)(DPMBI)·$Na_{0.367}$ at 298 K.

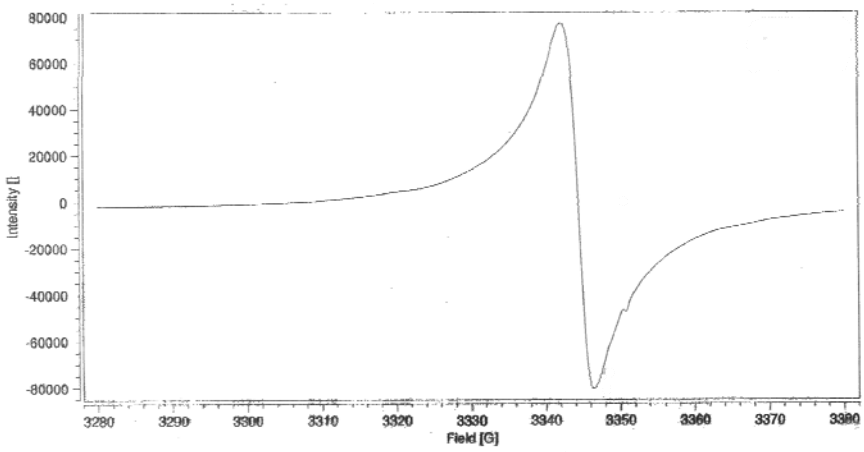


Fig. S14 X-band EPR spectrum of powdered EPR spectrum of Zn(NDC)(DPMBI)·$Na_{0.378}$ at 298 K.

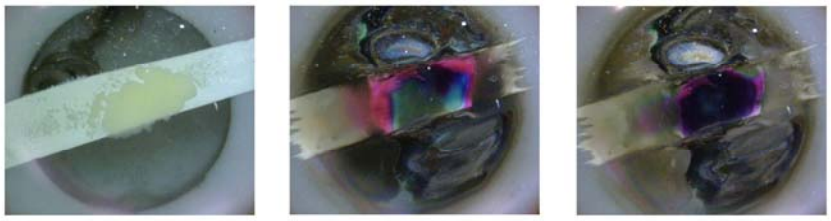
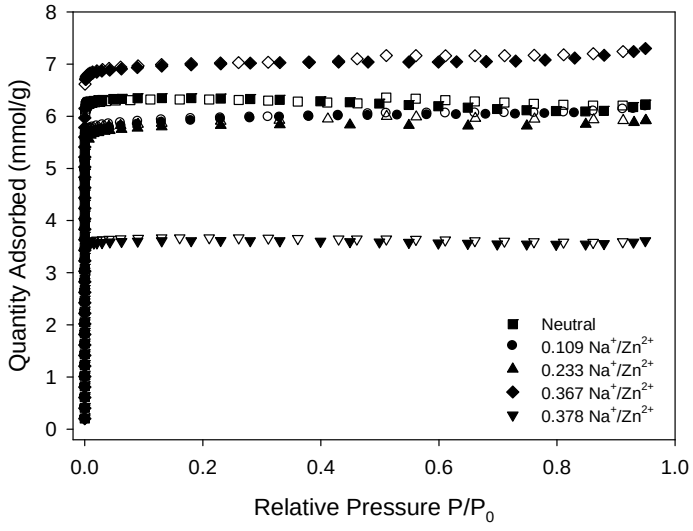
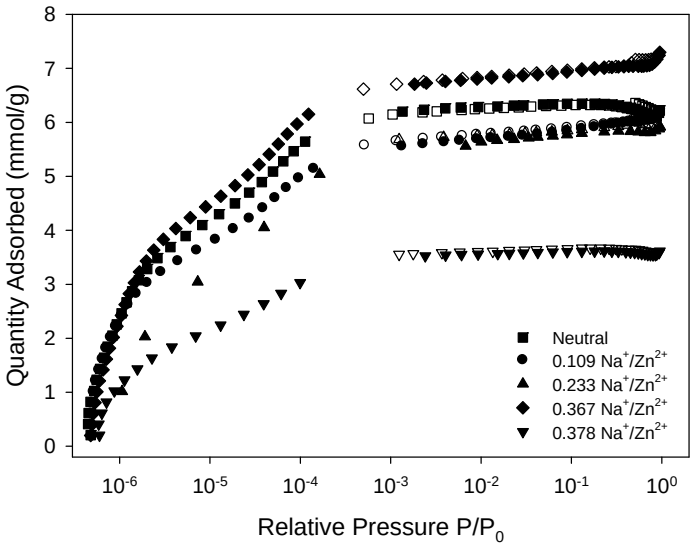


Fig. S15 Photographic image of the colour change of the solid Zn(NDC)(DPMBI) material at the transparent ITO-Quartz working electrode. The image at far left shows the neutral material (0 V) and the two images to the right show the colour changes as a potential of -2.20 V is applied to the cell.



(a)



(b)

Fig. S16 (a) Nitrogen isotherms for the neutral Zn(NDC)(DPMBI) and its reduced analogues at 77 K (filled symbols = adsorption, open symbols = desorption). The logarithmic plot in **(b)** shows the adsorption behaviour in the low pressure region 10^{-7}-10^{-4} P/P_0.

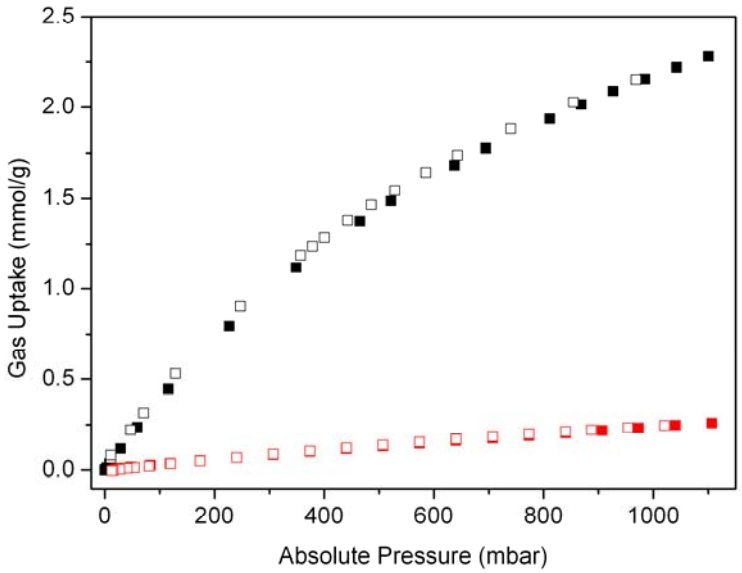


Fig. S17 CO_2 (black) and N_2 (red) adsorption (filled squares) and desorption (open squares) isotherms of Zn(NDC)(DPMBI) at 298 K.

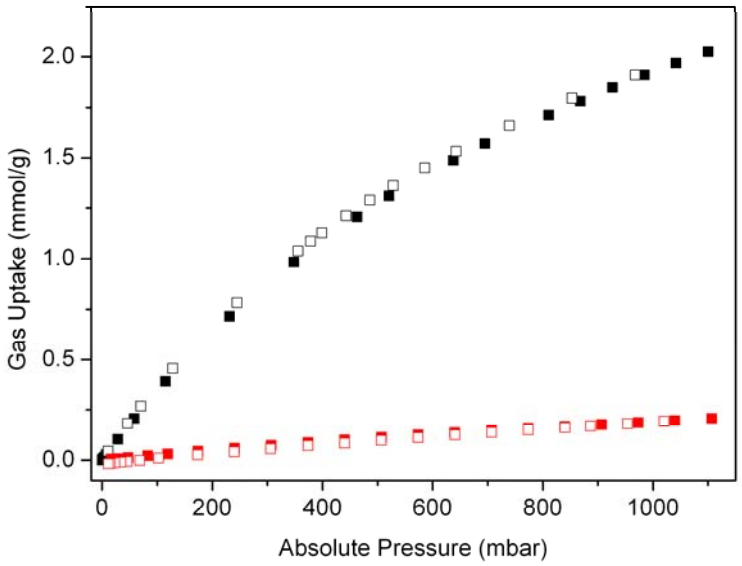


Fig. S18 CO_2 (black) and N_2 (red) adsorption (filled squares) and desorption (open squares) isotherms of Zn(NDC)(DPMBI)·$Na_{0.109}$ at 298 K.

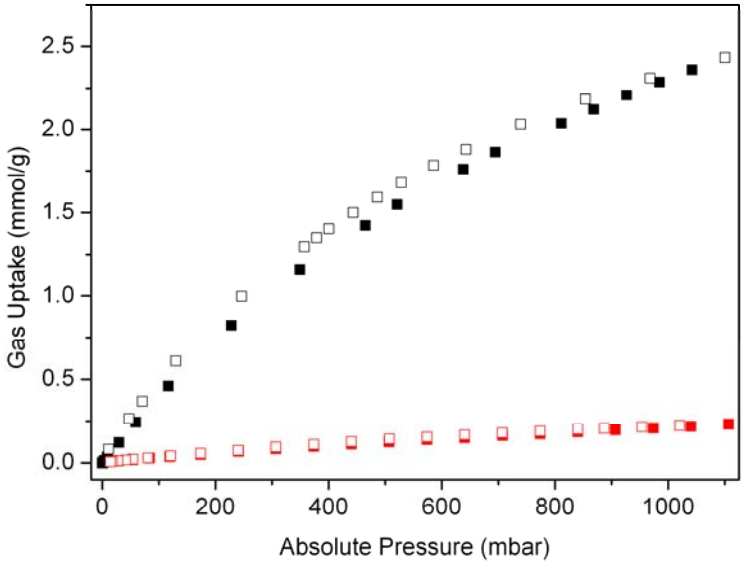


Fig. S19 CO_2 (black) and N_2 (red) adsorption (filled squares) and desorption (open squares) isotherms of Zn(NDC)(DPMBI)·$Na_{0.233}$ at 298 K.

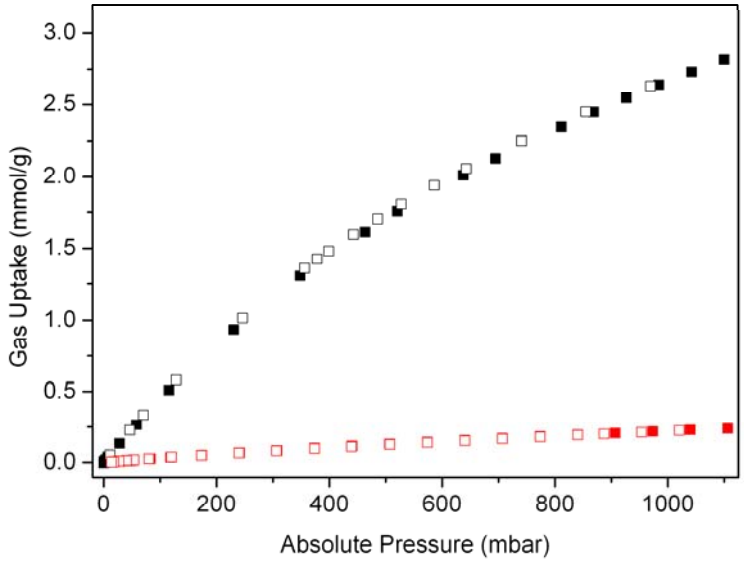


Fig. S20 CO_2 (black) and N_2 (red) adsorption (filled squares) and desorption (open squares) isotherms of Zn(NDC)(DPMBI)·$Na_{0.367}$ at 298 K.

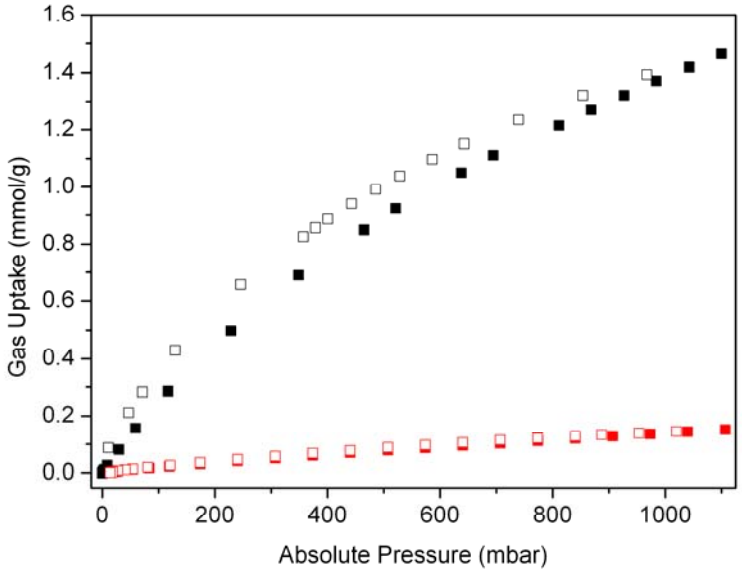


Fig. S21 CO_2 (black) and N_2 (red) adsorption (filled squares) and desorption (open squares) isotherms of Zn(NDC)(DPMBI)·$Na_{0.378}$ at 298 K.

IAST Selectivity Calculations

Table S3. Fitted parameters using single-site Langmuir-Freundlich (SSLF) equation.

Zn(NDC)(DPMBI) species		$N_{A,sat}$ mol kg^{-1}	$k_{i,A}$ $mbar^{-1}$	$n_{i,A}$ dimensionless
Neutral	CO_2	4.38	0.000956	1.00
	N_2	4.56	0.000097	0.917
0.109 Na^+/Zn^{2+}	CO_2	4.01	0.00097	0.99
	N_2	0.74	0.00042	0.97
0.233 Na^+/Zn^{2+}	CO_2	5.16	0.00092	0.98
	N_2	1.89	0.000321	0.86
0.367 Na^+/Zn^{2+}	CO_2	6.41	0.000842	0.97
	N_2	0.99	0.000364	0.96
0.378 Na^+/Zn^{2+}	CO_2	3.57	0.00107	0.92
	N_2	2.59	0.00013	0.88