Supplementary Information

Rapid Determination of the Optical and Redox Properties of A Metal-Organic Framework via *in situ* Solid State Spectroelectrochemistry

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Experimental Methods

Synthesis. $[Zn_2(NDC)_2(DPNI)]$ was prepared according to procedures described by Hupp and co-workers and its structure was confirmed by comparison of the powder X-ray diffraction (PXRD) pattern with that previously reported.[1]

Structural Characterisation. Solid samples were structurally characterized by PXRD. Patterns were collected on a PANalytical X'Pert PRO MPD diffractometer with Cu-Kα (1.5406 Å) radiation. The application software was X'Pert Data Collector v2.2f, and the instrument control software was XPERT-PRO v1.9E. PXRD data was collected over 5-50^o 2θ range with a 0.02^o step size and 2^o/min scan rate. Powders were mounted onto reflective discs with an Si (110) surface which were placed into a Bragg-Brentano reflection transmission spinner attachment.

Solid State Electrochemistry. A standard three-electrode cell incorporating a glassy carbon working electrode, a platinum wire counter electrode and a silver wire quasi reference electrode was employed for electrochemical measurements using a BASi Epsilon Electrochemical Analyser. Cyclic voltammograms (CVs) were recorded at at scan rates of 10, 25, 50, 100, 200, 500 and 1000 mVs^{-1} under an argon atmosphere in 0.1 M $[(n\text{-}C_4H_9)_4N](PF_6)$ dissolved in anhydrous CH_3CN. The ferrocene/ferrocenium couple (Fc^0/Fc^+) was used as an internal reference. Powdered samples were mounted onto the working electrode using mechanical immobilization. The electrode was pressed against the powder forming a weakly bound layer of material on its surface which was supported by a $LiClO_4$-intercalated polyvinylchloride (PVC) substrate. The $LiClO_4$-intercalated PVC substrate was prepared by dissolving PVC (0.6 g), polycarbonate (0.6 g) and $LiClO_4$ (0.4 g) in a minimum amount of THF.[2] The solution was applied to a powdered sample immobilised on the working electrode surface and was left to dry overnight yielding a thin polymer layer.

Solid State UV-Vis-NIR Spectroscopy. UV-Vis-NIR diffuse reflectance spectroscopy was used to analyse powdered samples. Spectra were collected on a Varian CARY 5E UV-Vis-NIR spectrophotometer with a Harrick Omni Diff Probe attachment using Varian WinUV software V3.0. The data was recorded from 5000 to 25000 cm^{-1} with a scan rate of 6000 cm^{-1}/min. Samples were supported on a high density filter paper which was also used to provide the background reference.

Solid State UV-Vis-NIR Spectroelectrochemistry (SEC). The diffuse reflectance spectra of the electrogenerated species were collected *in situ* using a Varian CARY 5E UV-Vis-NIR spectrophotometer with a Harrick Omni Diff Probe attachment interfaced to Varian WinUV software V3.0. Redox processes were carried out in a custom built solid state spectroelectrochemical (SEC) cell.

The cell (Fig. S1) comprises of a block of Teflon featuring an electrolyte compartment at the centre. The compartment is connected to the side-ports of the cell which are used to harbor the platinum wire counter and the silver wire reference electrodes. The redox-active solid (~2 mg[1§] covering a circular area with diameter ~1.5 mm and thickness ~0.5 mm) is mechanically immobilised on the underside of the Indium-Tin-Oxide (ITO) coated quartz slide supplied by UQG Optics (25×25×0.15 mm) which is secured into a slot directly above the compartment. In all cases, the $\mathrm{LiClO_4}$-intercalated PVC was used for immobilisation. Strips of 3M Copper Tape foil with conducting adhesive were used to connect the working electrode to the electrode leads from the potentiostat. The cell was filled with 0.1 M $[n\text{-}(\mathrm{C_4H_9})_4\mathrm{N}](\mathrm{PF_6})$ solution in $\mathrm{CH_3CN}$. A silicon O-ring was placed between the central compartment and the working electrode to create a seal when the Omni Diff Probe was placed on it. In order to completely immobilize the working electrode, two strips of adhesive tape were applied along its edges.

The spectroscopic backgrounds were collected from a region of PVC which contained no sample. The potentials were applied using an eDAQ e-corder 410 potentiostat. The potentials of the redox processes determined from electrochemical measurements were used as a guide for SEC experiments. Due to the over-potential of the SEC cell the measurements were carried out by increasing the potential in small increments of -0.05 V. The attainment of steady-state spectra and the decay of the current to a constant minimum served as an indication of a given electron transfer process being in dynamic equilibrium. At this point the potential was increased further to ensure the completion of the redox process.

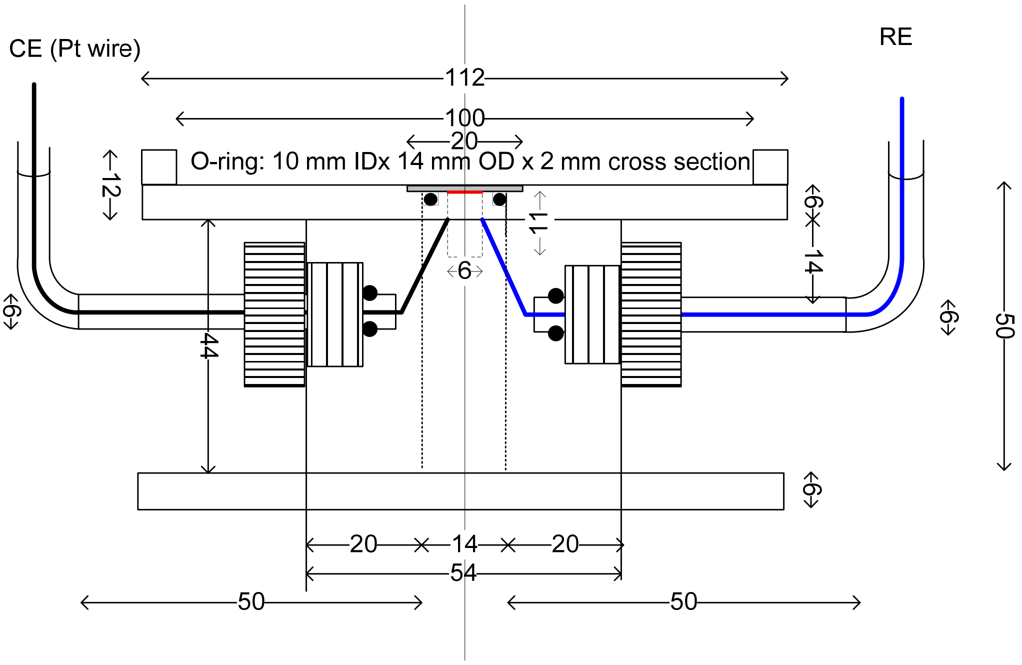
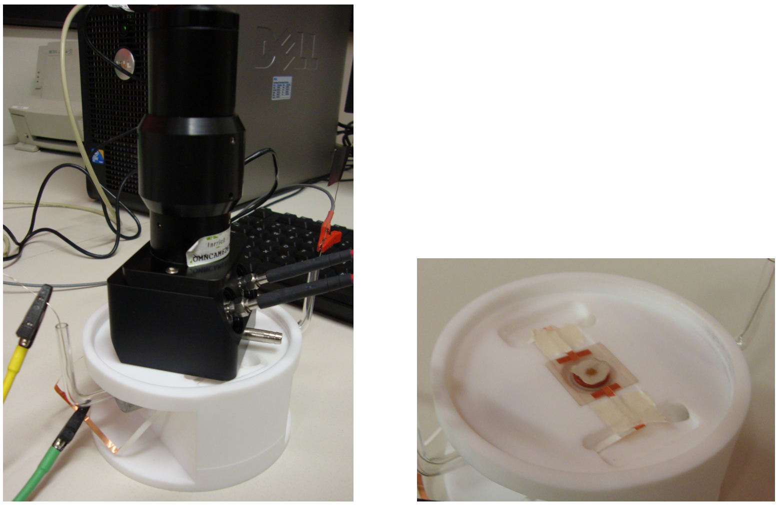


Fig. S1 A schematic diagram (side view) of the solid state SEC cell (CE = counter electrode, RE = reference electrode).

[1§] Mizuguchi et al.[3] report a density of 1.432 Mg m^{-3} for DPNI. Based on the use of ~2 mg of solid on the electrode surface, a more realistic value for the concentration is ~2.5 mol dm^{-3}.



(A) (B)

Fig. S2 The solid state SEC cell: (A) The Omni-Diff probe situated on top of the cell. The electrode leads are connected to the potentiostat. (B) The ITO coated quartz working electrode. The powdered solid is adhered to the underside of the transparent quartz.

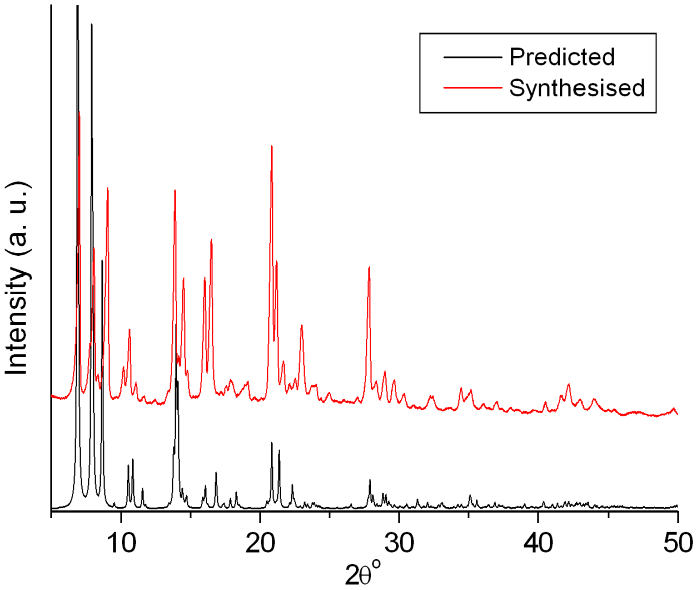


Fig. S3 PXRD pattern of as-synthesised [$Zn_2(NDC)_2(DPNI)$] and its predicted pattern from the crystal structure.[1]

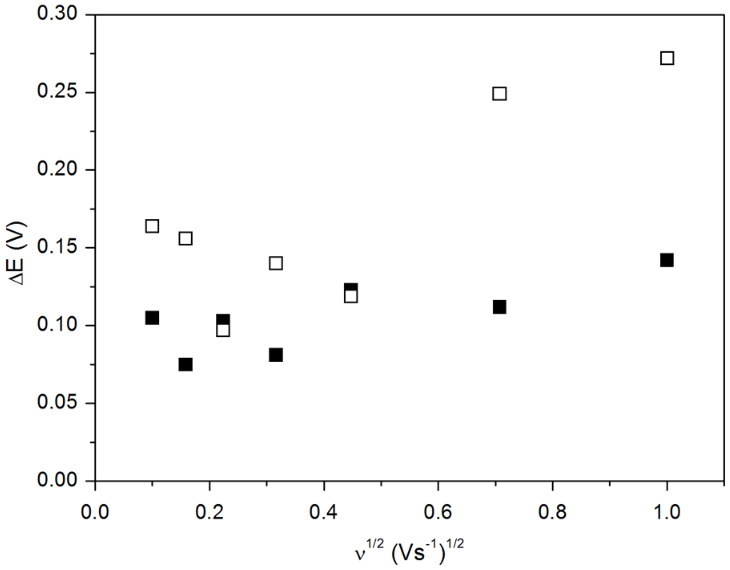


Fig. S4 Dependence of the peak splitting for the first (■) and second (□) reduction processes on the square root of the scan rate ($\nu^{1/2}$). The peak splitting (ΔE) is defined as the potential difference between the redox waves on the forward and reverse potential scans. Note that the return wave for the second reduction process was difficult to distinguish.

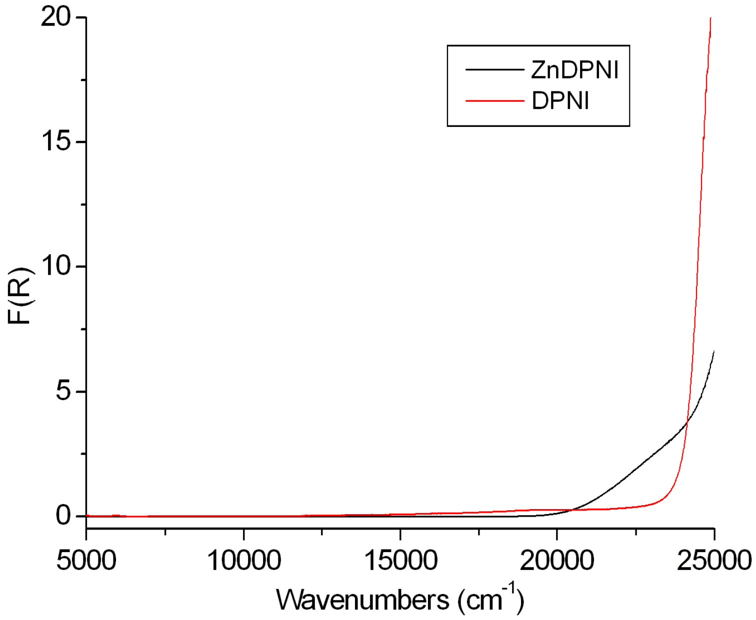


Fig. S5 UV-Vis-NIR diffuse reflectance spectra of $[Zn_2(NDC)_2(DPNI)]$ and DPNI.

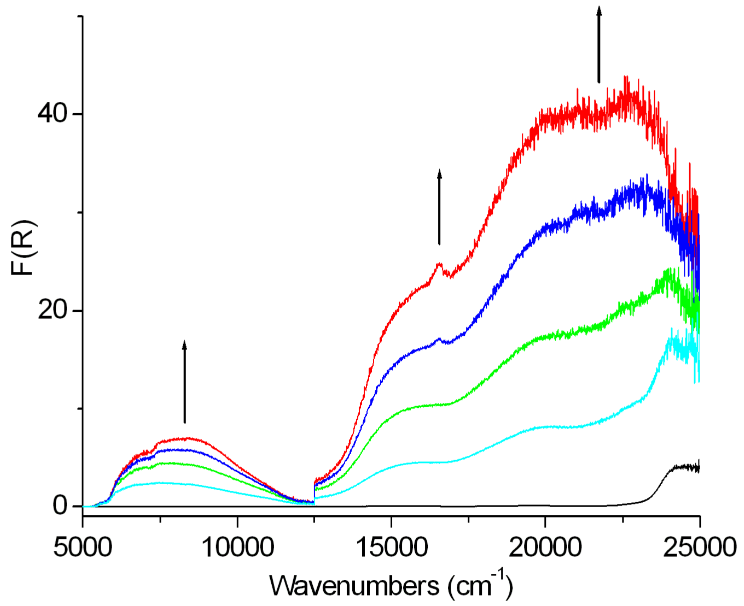


Fig. S6 Solid state SEC data for the DPNI ligand. Arrows indicate the direction of the spectral changes. The discontinuity at 12500 cm^{-1} represents the change in monochromator gratings.

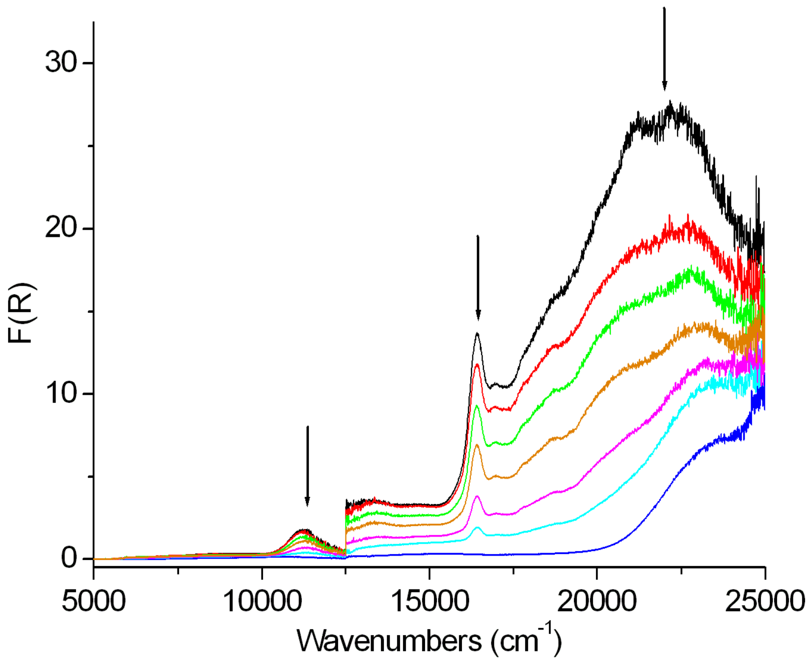


Fig. S7 Solid state SEC data for $[Zn_2(NDC)_2(DPNI)]$ at a potential of 0 V showing the regeneration of the starting spectrum from the dianion state. Arrows indicate the direction of the spectral change. The discontinuity at 12500 cm^{-1} represents the change in monochromator gratings.

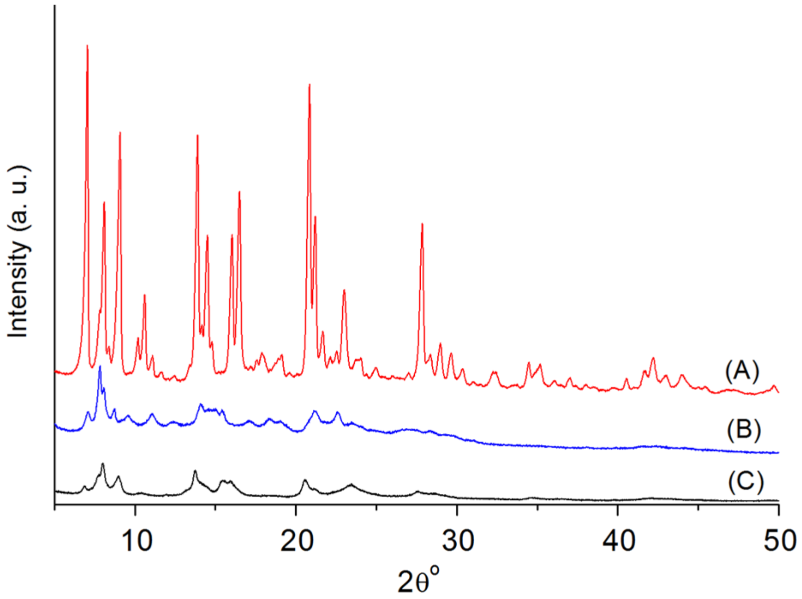


Fig. S8 PXRD pattern of as-synthesised [$Zn_2(NDC)_2(DPNI)$] (A) and the pattern following a controlled potential electrolysis (CPE) experiment at -1.2 V for 0.5 h (B). The latter shows that the material becomes amorphous due to decomposition at potentials sufficiently cathodic of those required for formation of the dianion system. In (C), the potential was set to 0 V for 0.5 h (following CPE at -1.2 V) demonstrating that the crystallinity is not regained by re-oxidation of the material.

References

1. B. Q. Ma, K. L. Mulfort, J. T. Hupp, *Inorg. Chem.*, 2005, **44**, 4912-4914.
2. S. Rajendran, M. R. Prabhu, M. U. Rani, *Int. J. Electrochem. Sci.*, 2008, **3**, 282-290.
3. J. Mizuguchi, T. Makino, Y. Imura, H. Takahashi, S. Suzuki, *Acta Cryst.*, 2005, **E61**, 03044-o3046.