The field of metal–organic frameworks 1,2 is developing at an extraordinary pace owing to the enormous structural and chemical diversity and the myriad potential applications in gas storage, separations, catalysis, non-linear optics, luminescence and magnetism.3 After two decades of intense research, the redox, optical and electronic properties of three dimensional framework materials have received relatively limited attention.4 Notable exceptions are the Prussian blue systems, in which the electrochemical properties arising from intervalence charge transfer transitions have been extensively studied,5 in addition to frameworks in which the counter-ion insertion (in particular, lithium intercalation) alters the redox state.6,7 This work has enabled fundamental insights into the conductivity properties of coordination polymers8 and underscores their numerous potential applications in electrocatalysis, solid state sensing and battery technologies.3,4

In general, the aforementioned investigations of the optical and electronic properties of solid materials have relied upon chemical reduction/oxidation of the material, followed by its isolation in a given redox state. This ex situ approach requires that the material possess stable and isolable electronic states; however, in cases where these are not accessible, in situ UV-Vis-NIR spectroelectrochemical (SEC) techniques have proven powerful in elucidating the properties of the redox-accessible states of metals and ligands.9

Herein, we report the development of a simple and robust in situ diffuse reflectance UV-Vis-NIR SEC technique and its application to the redox-active framework [Zn2(NDC)2(DPNI)]

The optical properties of [Zn2(NDC)2(DPNI)]0/−/2− (NDC = 2,7-naphthalene dicarboxylate, DPNI = N,N′-di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide), a redox-active metal–organic framework, have been examined using a simple and robust in situ solid state UV-Vis-NIR spectroelectrochemical technique.

The redox properties of [Zn2(NDC)2(DPNI)] and DPNI were investigated using solid state cyclic voltammetry (CV) in 0.1 M [(n-C4H9)4N]PF6/CH3CN. The framework exhibits a reversible reduction peak at −0.33 V and an irreversible peak at −0.66 V versus Fe(CN)63−/4− which are consistent over two repeat cycles (see Fig. 2). Both redox processes are associated with the reduction of DPNI within the framework in accordance with previous literature reports in the solution state for NDI-type ligands.11 The scan rate dependence of the peak splitting for each redox process revealed that the first reduction from the neutral to developed by Hupp and co-workers (see Fig. 1).10 1,4,5,8-Naphthalenetetracarboxydiimide (NDI) is a well-known organic electron acceptor11 and the electronic properties of many different substituted forms, including DPNI, have been extensively studied in the past.12 Including by solution state SEC.13 In the case of the framework, chemical reduction upon exposure to lithium metal in N,N′-dimethylformamide led to the anion radical form in which the structural integrity was maintained.14

Fig. 1 Perspective view down the (100) direction of [Zn2(NDC)2(DPNI)] highlighting the structure of the DPNI ligand. Only one of the interpenetrating lattices is shown for clarity.10

Fig. 2 Solid state cyclic voltammograms (2 cycles) of (A) [Zn2(NDC)2(DPNI)] (the asterisks denote the redox processes for the internal Fe(CN)63−/4− reference at +0.55 V) and (B) DPNI at 100 mV s−1 in 0.1 M [(n-C4H9)4N]PF6/CH3CN at 298 K. The arrows indicate the direction of the forward scan.
the monoanion species is relatively invariant to the scan rate. The peak splitting increases for the second reduction to the dianion species at high scan rates (up to 1000 mV s⁻¹), suggesting that the charge propagation processes are influenced to some extent by the diffusion of counter-ions through the framework lattice.

The solid state CV of DPNI revealed similar features to [Zn₂(NDC)₂(DPNI)], consistent with the d¹⁰ configuration of the ZnII centre. The reversibility of the first reduction in both cases over two repeat cycles confirms the stability of the ligand and the framework upon addition of one electron to the nitrogen ligand. The absence of a metal–metal bond in the paddlewheel precludes electronic communication between the DPNI ligands situated on opposite ends of the Zn…Zn axis. Hence, the reduction potentials for the framework are approximately the same as those for the DPNI ligand itself.

Previous solution state electrochemical measurements have determined that the NDI core can undergo two reversible reductions. In the present case of solid state electrochemical measurements on the DPNI ligand and framework, the second redox process corresponding to the formation of a dianion species appears to be irreversible due to scavenging of residual oxygen in the cell, or photo-degradation.

The UV-Vis-NIR spectra of DPNI and [Zn₂(NDC)₂(DPNI)] were featureless in the 5000–25 000 cm⁻¹ region, while the absorption bands above 25 000 cm⁻¹ correspond to π → π* transitions within the NDI core.

Solid state SEC studies on the DPNI ligand were conducted on a sample of the powdered material (approximately 1.5 mg covering a circular area with a diameter and thickness of approximately 1.5 mm and 0.5 mm, respectively) which was affixed to the surface of an ITO coated quartz working electrode using a LiClO₄-intercalated polyvinylchloride polymer as a supporting substrate. A conventional three-electrode cell was constructed from Teflon and featured a compartment at its centre containing a 0.1 M [(n-C₄H₉)₄N⁺PF₆⁻]CH₃CN electrolyte. Platinum auxiliary and Ag/Ag⁺ reference electrodes were contained in side-ports of the cell. The spectral response of the material was monitored using a commercially-available Omni-Diff diffuse reflectance probe coupled to a CARY 5E spectrophotometer using fibre optic cables. As the potential was gradually applied in steps of −0.05 V from 0.00 to −1.00 V over 0.5 h, broad bands appeared in the NIR region at 7500 cm⁻¹ and in the UV-Vis region for the reduced species.

Previous solution state SEC experiments by Bond et al. revealed that NDI derivatives undergo significant changes in their UV-Vis spectra upon reduction corresponding to the formation of anion radical species. Using Hartree–Fock PM3 molecular orbital calculations on NDI derivatives, Wasielwski et al. suggested that the lowest energy band in the NIR may be assigned to a D₈h → D₄h transition, however, no experimental data in the region 5000–11 111 cm⁻¹ (2000–900 nm) were reported. In the present case, several broad overlapping bands appear in the UV-Vis region which can be ascribed to HOMO–LUMO transitions. The broadening of the peaks in the solid state SEC experiments compared to those obtained in the solution state could be attributed to a concentration dependence of the DPNI spectra: the powdered material used for solid state measurements represents a sample at high concentration, at which intermolecular π–π stacking interactions are significant.

Solid state SEC investigations were conducted on [Zn₂(NDC)₂(DPNI)] using identical experimental conditions to those described for the DPNI ligand. The formation of the monoaon species was observed at −0.45 V over the course of 0.5 h and was accompanied by the appearance of a band at 23 000 cm⁻¹ (see Fig. 3(A)). Similar transitions were observed for the DPNI ligand in the solution state, and were found to be characteristic for the one-electron reduced anion radical species DPNI⁺⁻. A minor increase in absorbance occurred in the NIR region, in contrast to the broad band observed for the DPNI ligand. Indeed, intermolecular π–π stacking interactions would be reduced in the framework compared with the sample of ligand, suggesting that the origin of the intensity of the NIR band may arise from inter-ligand electronic interactions between the formally neutral and anionic species. The importance of such ligand–ligand interactions has been emphasised previously by Hupp et al.

The application of an increasingly cathodic potential of −0.60 V to [Zn₂(NDC)₂(DPNI)]⁻ revealed a new set of spectral features, including the appearance of a low-intensity band at 16 000 cm⁻¹ and a shift of the UV band to higher energies (see Fig. 3(B)). This spectral response mimics the behaviour observed in solution state experiments on NDI derivatives.
was assigned to their diianion forms.\textsuperscript{11} The existence of an isosbestic point at 15 500 cm\textsuperscript{-1} indicates that the diion species \([\text{Zn}_2(\text{NDC})_2(\text{DPNI})]^2\text{−}\) is stable towards chemical degradation on the timescale of the experiment. By contrast, the second reduction process is irreversible in the CV experiment. This differing behaviour may be attributed to the instability of the framework towards potentials that are cathodic of the maximum reduction peak in CV. Indeed, a further increase in the potential beyond \(-0.60\) V in the SEC experiment led to the appearance of a number of absorption features throughout the entire UV-Vis-NIR region (see Fig. 3(C)) which were attributed to decomposition products of \([\text{Zn}_2(\text{NDC})_2(\text{DPNI})]^2\text{−}\) due to residual oxygen in the SEC cell or photo-degradation.\textsuperscript{15}

Overall, the spectral changes observed during SEC measurements on \([\text{Zn}_2(\text{NDC})_2(\text{DPNI})]\) occurred at similar potentials to those measured in solid state CV measurements, supporting the assigned generation of the framework into its reduced states incorporating the mono- and diianion forms of DPNI. Fig. 4 presents photographic images of the framework through the assigned generation of the framework into its reduced states incorporating the mono- and diianion forms of DPNI. Overall, the spectral changes observed during SEC measurements on \([\text{Zn}_2(\text{NDC})_2(\text{DPNI})]\) occurred at similar potentials to those measured in solid state CV measurements, supporting the assigned generation of the framework into its reduced states incorporating the mono- and diianion forms of DPNI. Fig. 4 presents photographic images of the framework through the surface of the ITO coated quartz working electrode which were obtained using the digital camera incorporated into the external diffuse reflectance probe. The colour of the material varies from yellow in its neutral state to an increasingly intense brown colouration upon formation of the mono- and dianion species. A controlled potential electrolysis experiment on \([\text{Zn}_2(\text{NDC})_2(\text{DPNI})]\) was conducted to examine the proposed structural degradation that occurs upon the application of a potential sufficiently beyond that required for formation of the two-electron dianion species. A potential of \(-1.20\) V was applied to a suspension of the powder in CH\textsubscript{3}CN containing a 0.1 M \([\text{Li}2\text{C}_6\text{H}_5\text{N}_2\text{H}_2\text{N}]\text{PF}_6\) electrolyte for 0.5 h, after which time the solid was isolated by centrifugation and washed with CH\textsubscript{3}CN. A powder X-ray diffraction analysis of the resulting material revealed that the reductive potential rendered the framework amorphous, consistent with the degradation observed during SEC measurements (see Fig. 3(C)).

The development of a simple and robust in situ diffuse reflectance solid state SEC technique has permitted the first investigation of the optical properties of the \([\text{Zn}_2(\text{NDC})_2(\text{DPNI})]\) metal-organic framework as a function of its redox state. A comparison with previous solution state SEC measurements\textsuperscript{11} confirms that the DPNI ligand undergoes reduction to its mono- and dianion forms. The technique employs a commercially-available external diffuse reflectance probe and offers the advantages of requiring a low volume of electrolyte in addition to milligram quantities of the material of interest. An essential criterion for application of this method is that the solid material possesses absorption bands in the UV-Vis-NIR region of the electromagnetic spectrum that vary as a function of the redox state. Notwithstanding this limitation, further development of the SEC cell will extend the technique to measurements on air- and moisture-sensitive redox states of metal–organic frameworks. Potentially wide-ranging applications can also be envisaged for the assessment of the conductive properties of redox-active metal–organic frameworks amongst other solid materials.

This work was supported by the Australian Research Council, The University of Sydney and by the Australian Institute of Nuclear Science & Engineering. We thank Dr Graham Heath and Dr Greg Lumpkin for helpful discussions.

Notes and references