

Voltammetric reduction and re-oxidation of solid coordination polymers of dihydroxybenzoquinone

Brendan F. Abrahams,^{*a} Alan M. Bond^b, Thanh Hai Le^b, Laura J. McCormick^a,
Ayman Nafady^b, Richard Robson^{*a} and Nguyen Vo^b

^a School of Chemistry, University of Melbourne, Parkville, Victoria 3010, Australia.
Fax: +61 3 8344 0341; Tel: +61 3 9347 5180; E-mail: bfa@unimelb.edu.au;
r.robson@unimelb.edu.au.

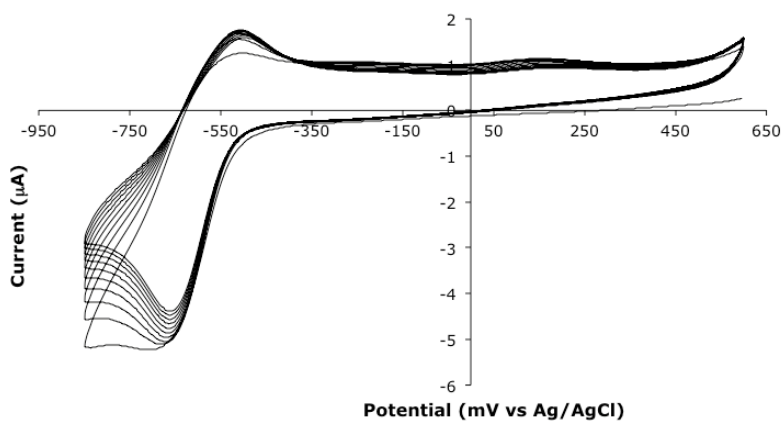
^b School of Chemistry, Monash University, Clayton, Victoria 3800, Australia.

Supplementary Information

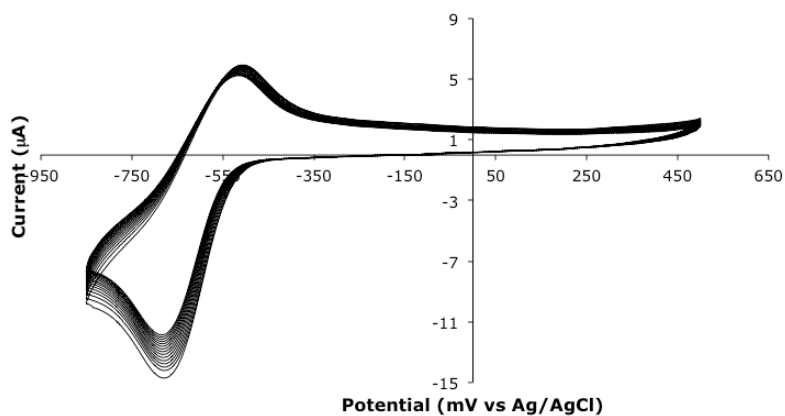
- I Cyclic voltammograms of (PMePh₃)₂Cd₂(dhbq)₃ (**3**) (Figure S1) (PMePh₃)₂Mn₂(dhbq)₃ (**4**) (Figure S2) and H₂dhbq (**1**) (Figure S3) in a range of electrolytes.
- II Details of controlled electrolysis experiments on indium-tin oxide electrodes.
- III *Ex situ* infra-red spectra of (PMePh₃)₂Cd₂(dhbq)₃ (**3**) on an ITO electrode surface.
- IV Powder diffraction pattern of (PMePh₃)₂Cd₂(dhbq)₃ (**3**)

I Cyclic voltammograms of $(\text{PMePh}_3)_2\text{Cd}_2(\text{d}hbq)_3$ (3) (Figure S1) $(\text{PMePh}_3)_2\text{Mn}_2(\text{d}hbq)_3$ (4) (Figure S2) and $\text{H}_2\text{d}hbq$ (1) (Figure S3) in a range of electrolytes.

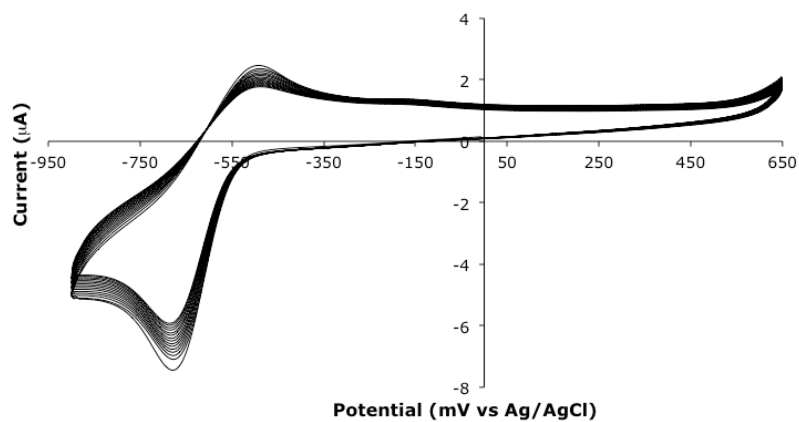
a)



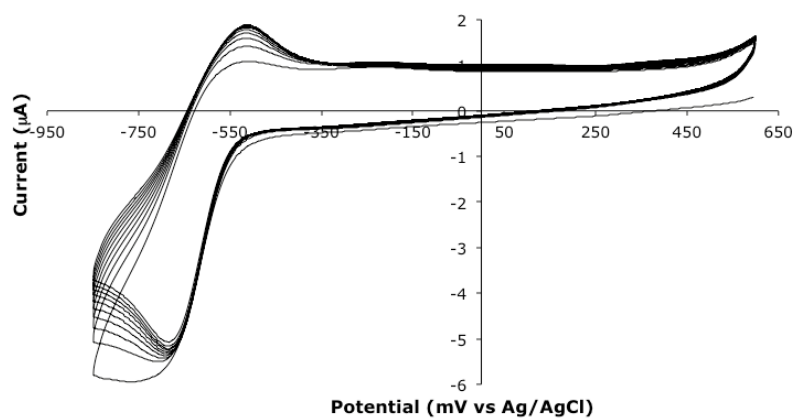
b)



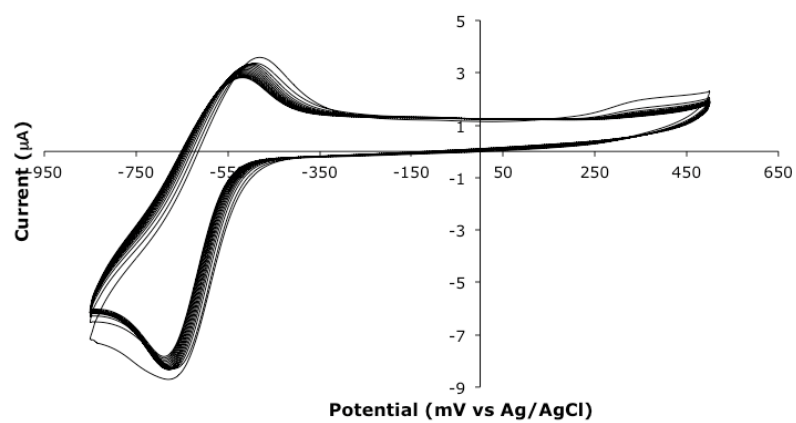
c)



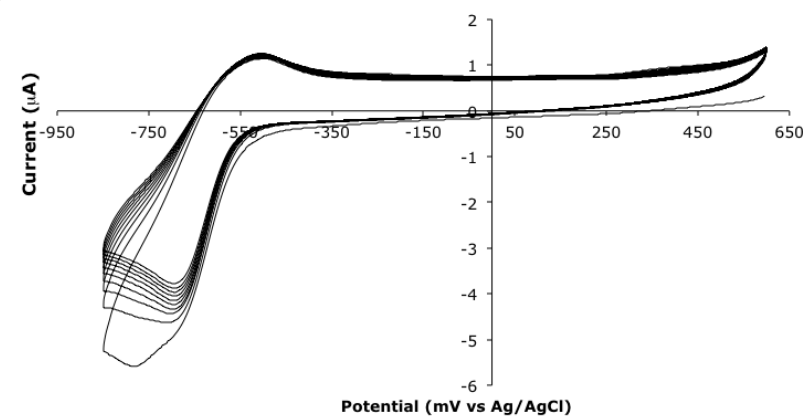
d)



e)



f)



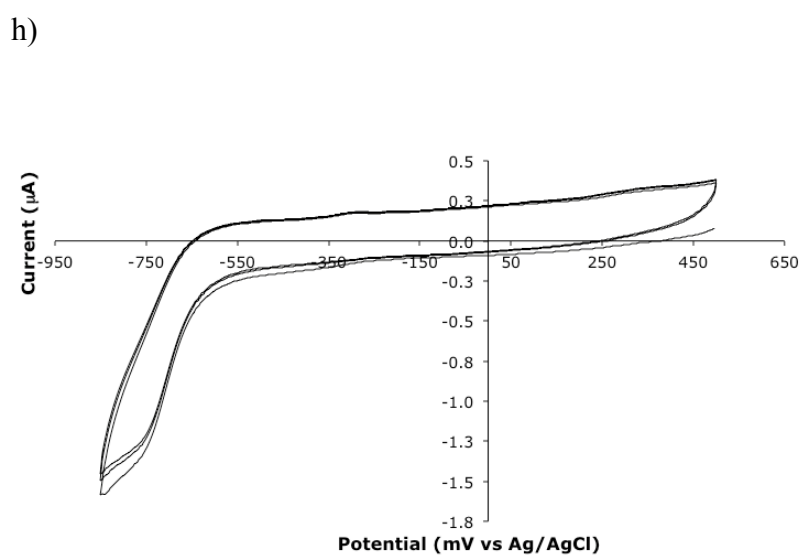
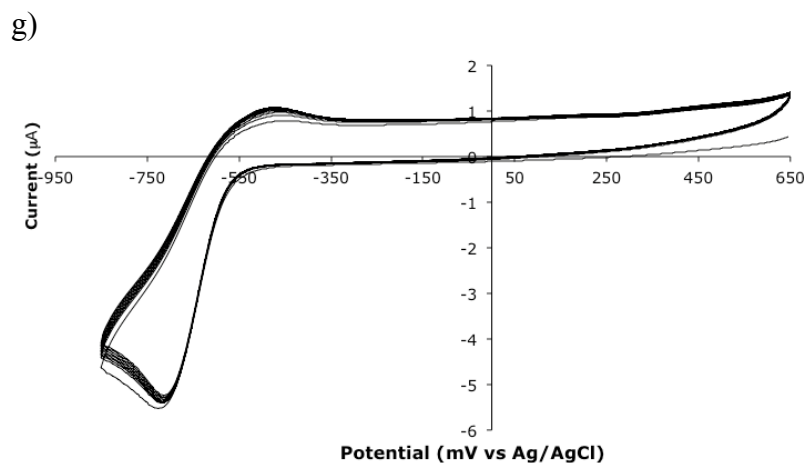


Figure S1: Cyclic voltammograms obtained with a scan rate 100 mVs^{-1} of a $(\text{PMePh}_3)_2\text{Cd}_2(\text{dhbq})_3$ (**3**)-modified 1.5 mm diameter GC electrode in contact with 0.1 M aqueous electrolyte solutions of **a)** LiClO_4 , **b)** NaCl , **c)** KCl , **d)** NMe_4Cl , **e)** NEt_4Cl , **f)** NPr_4Br , **g)** NBu_4Br and **h)** PMePh_3Br .

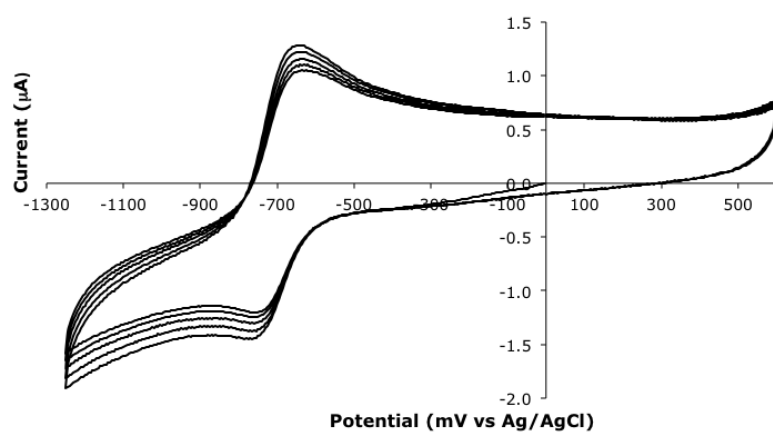


Figure S2: Cyclic voltammogram obtained with a scan rate of 100 mVs^{-1} of a $(\text{PMePh}_3)_2\text{Mn}_2(\text{d}hbq)_3$ (**4**)-modified 1.5 mm diameter GC electrode in contact with a 0.1 M aqueous electrolyte solution of NaClO_4 .

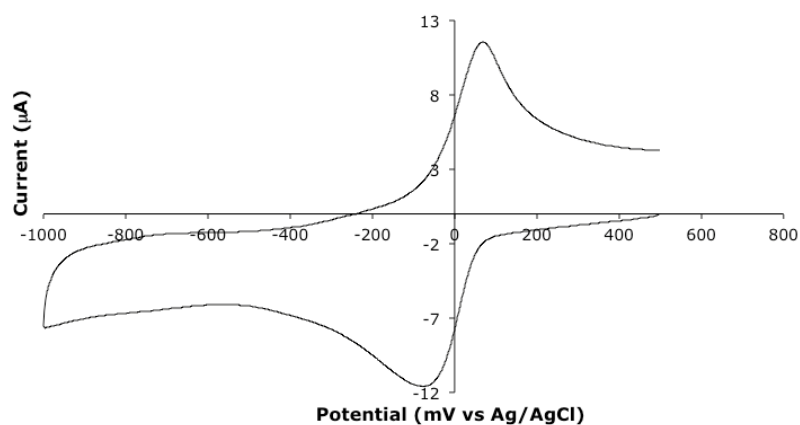


Figure S3: Cyclic voltammogram of 2 mM H_2dwbq in 0.1 M aqueous KCl with a scan rate of 100 mVs^{-1} .

II Details of controlled potential electrolysis experiments.

We have demonstrated that it is possible to perform repeated cycles of reduction and oxidation on the $(\text{PMePh}_3)_2\text{Cd}_2(\text{d}hbq)_3$ sample on the voltammetric time scale (100 mVs^{-1}) when microgram quantities of the solid are attached to a glassy carbon electrode. In order to investigate the stability of the reduced compound on the longer seconds time scale we performed controlled potential electrolysis experiments with the potential held for designated periods of time. The supporting electrolyte used in these experiments was NBu_4Br .

Figure S4 presents the results of a series of experiments where the potential of a GC modified electrode is held at -900 mV for between 1 and 120 s, followed by scanning the potential in the positive direction at a scan rate of 100 mVs^{-1} . At times longer than 5s, it is clearly evident that a new process emerges at approx. -500 mV vs. Ag/AgCl . This new process was confirmed to be a result of the stripping of Cd metal from the surface that occurs at a potential of -500 mV . Clearly, reduced $(\text{PMePh}_3)_2\text{Cd}_2(\text{d}hbq)_3$ is unstable on these 5s or longer time scale experiments.

An infra-red spectrum of the deep red $(\text{PMePh}_3)_2[\text{Cd}_2(\text{d}hbq)_3]$ adhered to an optically transparent indium-tin oxide (ITO) electrode surface (Figure S5a) shows characteristic bands associated with the coordinated d**h**bq and methyltriphenylphosphonium. After immersion of the chemically modified electrode into the $0.1 \text{ M NBu}_4\text{Br}$ aqueous electrolyte solution and exhaustive reduction with the potential held at -900 mV , followed by removal of the electrode from the solution, major changes are apparent in the infra-red spectrum (Figure S5b). We also note that the electrolyte solution is now alkaline, consistent with dissociation and then protonation of the non-coordinated ligand. The implication of the controlled potential experiments is that on this longer time scale, the coordination polymer undergoes dissociation.

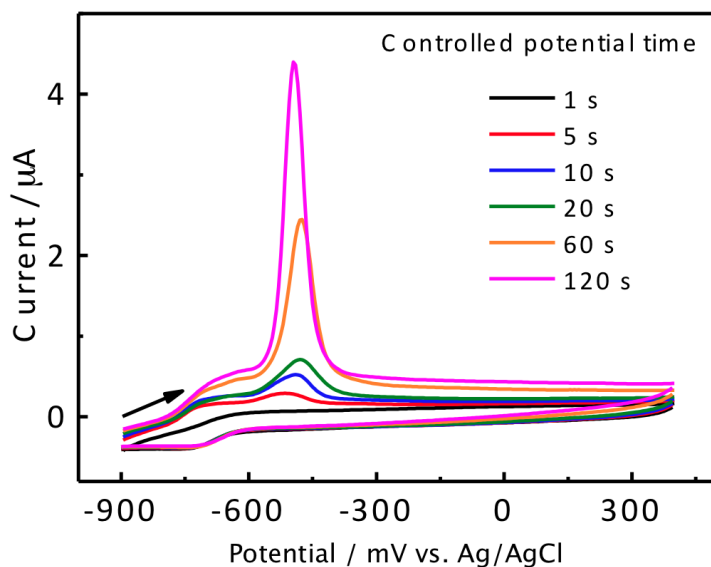
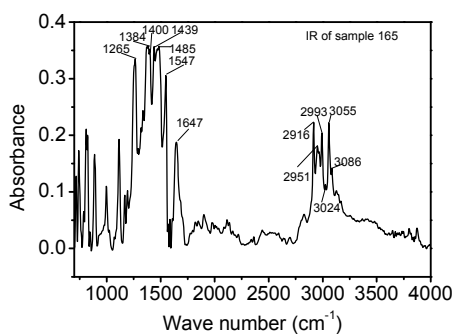


Figure S4: Results of controlled potential electrolysis experiments obtained with a $(\text{PMePh}_3)_2\text{Cd}_2(\text{d}hbq)_3$ (**3**)-modified 1 mm diameter GC electrode in contact with 0.1 M NBu_4Br aqueous electrolyte solution. In these experiments the potential was initially held at -900 mV for periods of time ranging from 1 to 120 s and then scanned at a rate of 100 mVs^{-1} in the positive direction.

III *Ex situ* infra-red spectra of $(\text{PMePh}_3)_2\text{Cd}_2(\text{d}h\text{bq})_3$ (3) on an ITO electrode surface.

a)



b)

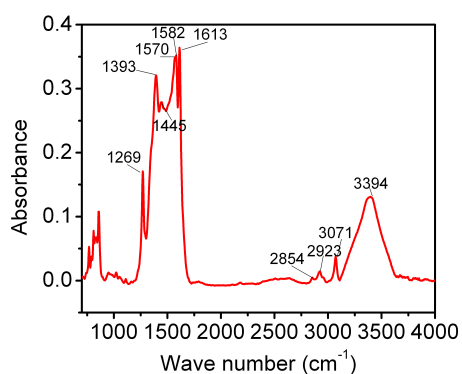
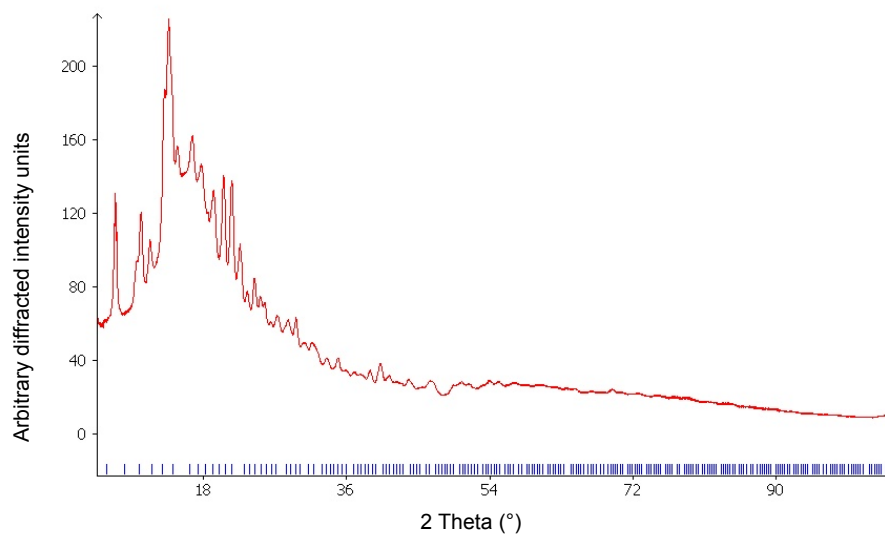


Figure S5. *Ex situ* infra-red spectra of $(\text{PMePh}_3)_2\text{Cd}_2(\text{d}h\text{bq})_3$ (3) on an ITO electrode surface a) before immersion in 0.1 M NBu_4Br aqueous electrolyte solution, b) after holding the potential at -900 mV and undertaking exhaustive electrolysis

IV Powder diffraction pattern of $(\text{PMePh}_3)_2\text{Cd}_2(\text{dhbq})_3$ (**3**)

a)



b)

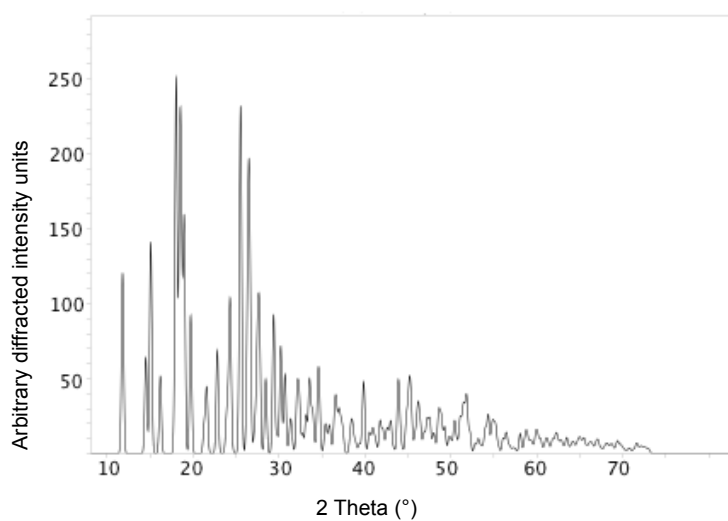


Figure S6 Powder diffraction pattern of $(\text{PMePh}_3)_2\text{Cd}_2(\text{dhbq})_3$ (**3**) a) measured data b) calculated data from single crystal structure determination.