

# Understanding and Mapping the Assembly of a Family of Trimeric Polyoxometalates: Transition Metal Mediated Wells-Dawson ( $M_{18}$ )-Trimers

Thomas Boyd, Scott G. Mitchell, Haralampos N. Miras, De-Liang Long and Leroy Cronin\*

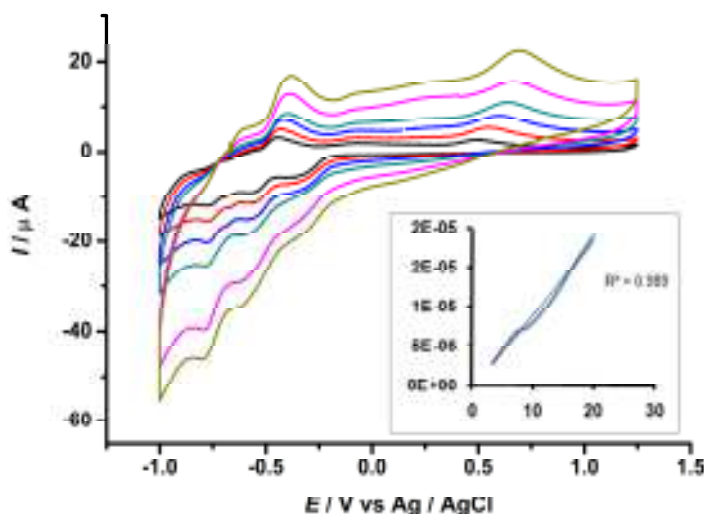
WestCHEM, Department of Chemistry, University of Glasgow, Joseph Black Building, University Avenue, Glasgow, UK, G12 8QQ.

Fax: +44 (0) 141 330 4888; Tel: +44 (0) 141 330 6650;

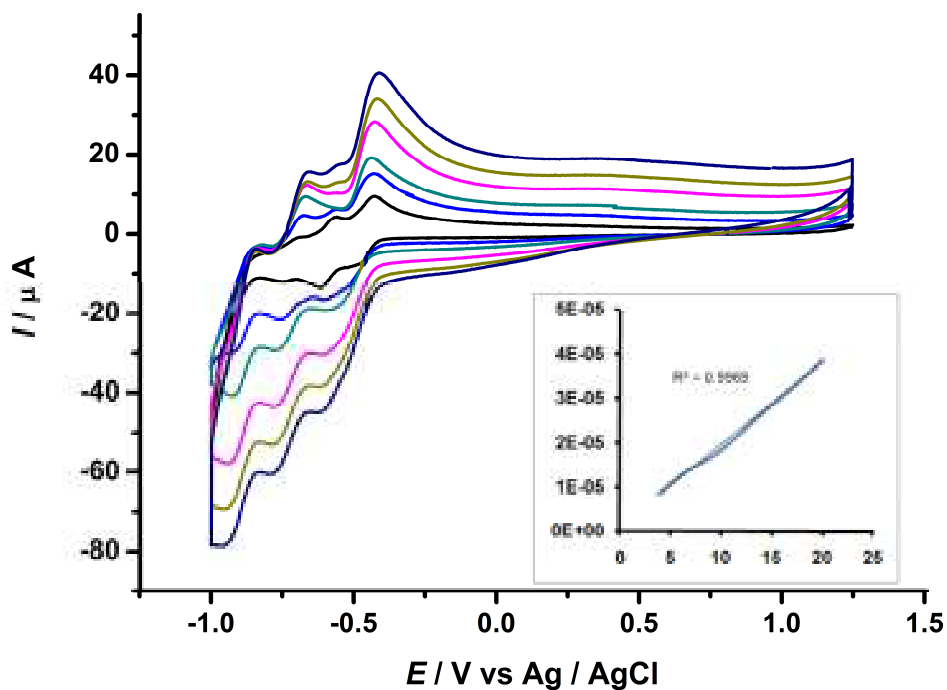
E-mail: [L.Cronin@chem.gla.ac.uk](mailto:L.Cronin@chem.gla.ac.uk); [www.croninlab.com](http://www.croninlab.com)

## Supplementary Information

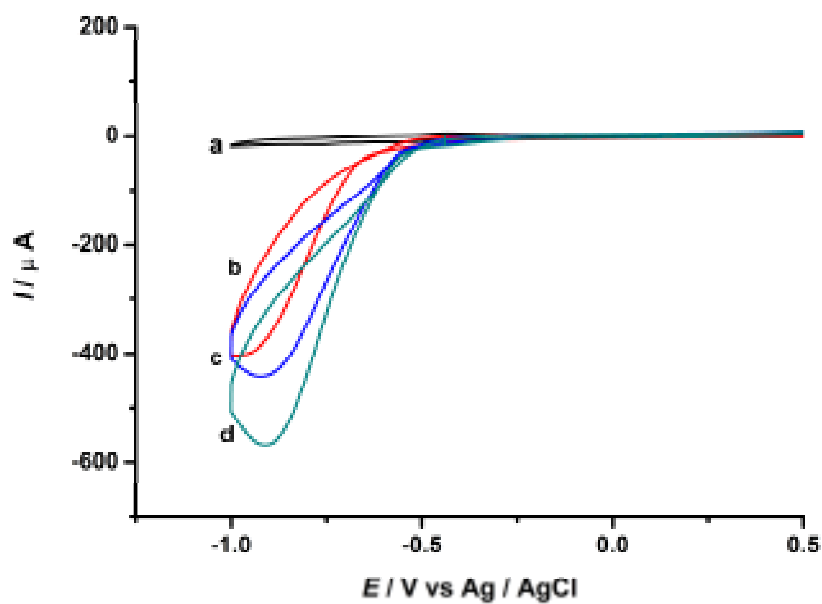
The cyclic voltammograms of both compounds at different scan rates (see Figures S1 and S2) showed that the peak currents were proportional to the square root of the scan rate, indicating that the redox processes are diffusion-controlled in the 15 – 300 mV/sec region of scan rate. This study shows the direct effect that the electropositive transition hetero metals have on the W-centred redox couples. In the case of compounds **1**, **3** and **4**, the observed redox couples were shown to be shifted towards more negative potentials, reflecting the difficulty in reducing the clusters following the trend  $Co^{3+} > Fe^{2+} > Ni^{2+}$ . Also, this data is consistent with the general electrochemical behaviour of the majority of the polyoxometalates whose W-waves depend on the pH and on the buffering strength of the electrolyte.<sup>1-3</sup> Figures S3 and S4 show the effect of  $NO_2^-$  reduction. Table S1 is a summary of the structural information for compounds **1-4** depicted in Fig. 4 of the manuscript.



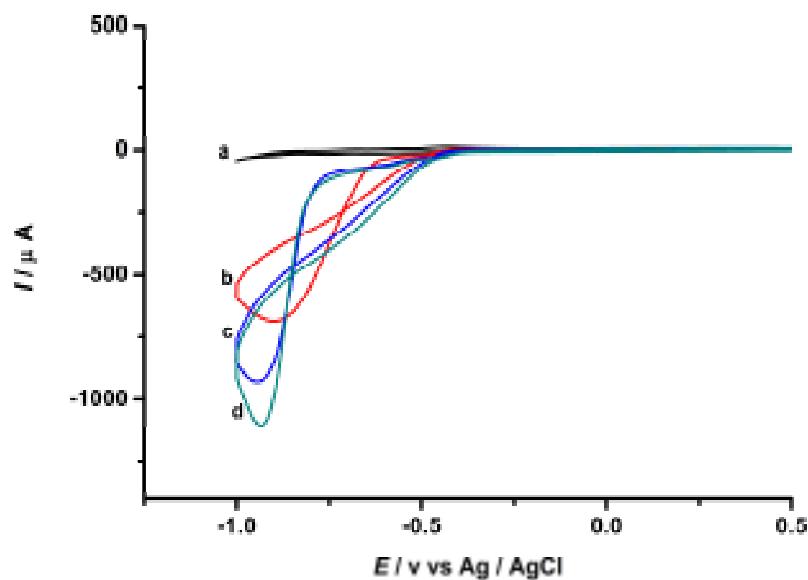
**Fig. S1** Cyclic voltammograms of compound **3** at scan rates (from inner to outer) 15, 25, 50, 100, 200 and 300 mV/sec. The inset represents the dependence of the current intensity as a function of the square root of the scan rate.



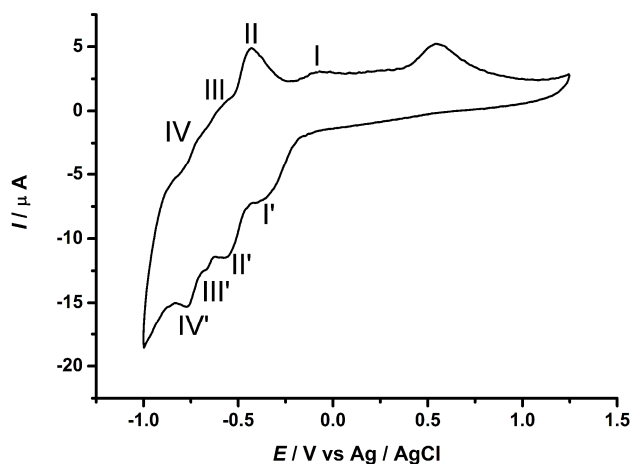
**Fig. S2** Cyclic voltammograms of compound 4 at scan rates (from inner to outer) 15, 25, 50, 100, 200 and 300 mV/sec. The inset represents the dependence of the current intensity as a function of the square root of the scan rate.



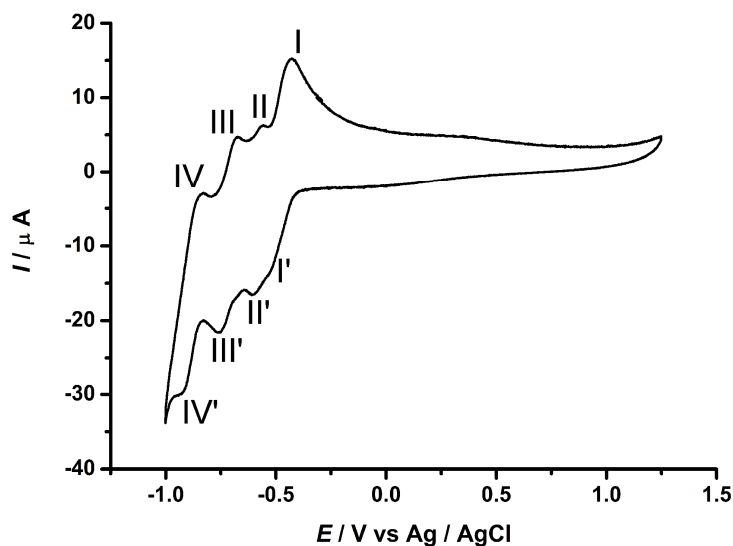
**Fig. S3** CVs of 3 addressing just the first redox processes of the W centers, in the absence of  $\text{NO}_2^-$  (black line) and after addition of a specific amount of  $\text{NO}_2^-$ ; C = a) 0, b) 5, c) 7 mM and d) 10 mM.



**Fig. S4** CVs of **4** addressing just the first redox processes of the W centres, in the absence of  $\text{NO}_2^-$  (black line) and after addition of specific amount of  $\text{NO}_2^-$ ; C = a) 0, b) 5, c) 7 mM and d) 10 mM



**Fig. S5** Cyclic voltammograms of **3** ( $1 \times 10^{-3}$  M) in aqueous 0.2 M  $\text{Na}_2\text{SO}_4$  of 1 M  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  buffer solution. The scan rate was  $25 \text{ mV s}^{-1}$ , the working electrode was glassy carbon (3 mm) and the reference electrode was Ag/AgCl.



**Fig. S6** Cyclic voltammograms of **4** ( $1 \times 10^{-3}$  M) in aqueous 0.2 M  $\text{Na}_2\text{SO}_4$  of 1 M  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  buffer solution. The scan rate was  $50 \text{ mV s}^{-1}$ , the working electrode was glassy carbon (3 mm) and the reference electrode was Ag/AgCl

	1a	2a	3a	4a	Avg.
a (Å)	1.823	1.835	1.902	1.828	1.847 (±0.055)
b (Å)	1.875	1.817	1.911	1.855	1.864 (±0.047)
c (Å)	1.874	1.904	1.897	1.852	1.882 (±0.030)
$\alpha$ (°)	150.00	149.41	145.30	150.45	148.79 (±3.49)
$\beta$ (°)	151.87	156.51	146.33	149.88	151.15 (±5.36)
$\gamma$ (°)	147.81	150.39	145.47	146.58	147.56 (±2.83)
z (Å)	6.815	6.747	6.614	6.725	6.723 (±0.109)

**Table S1** Average bond distances, angles and minimum cavity size of the central core in polyoxoanions **1a-4a**.

- 1 L. H. Bi, E.-B. Wang, J. Peng, R. D. Huang, L. Xu and C. W. Hu, *Inorg. Chem.*, 2000, **39**, 671.
- 2 I. M. Mbomekalle, B. Keita, L. Nadjo, P. Berthet, W. A. Neiwert, C. L. Hill, M. D. Ritorto and T. M. Anderson, *Dalton Trans.*, 2003, 2646.
- 3 B. Keita, Y.W. Lu, L. Nadjo, R. Contant, *Eur. J. Inorg. Chem.*, 2000, 567; M. Sadakane and E. Steckhan, *Acta Chem. Scand.*, 1999, **53**, 837.