Electrochemically Active Phenylenediamine Probes for Transition Metal Cation Detection

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Supplementary information

The first oxidation process of **1** is fully reversible: the linear dependence of the logarithm of the first peak current (I_{pa}^{I}) versus the logarithm of the scan rate (log ip ~ log v) in the range of 50-1000 mVs^{-1} confirms a diffusion controlled electron transfer process for all compounds, the slope of the curve being close to 0.5.[1] The potential difference between the anodic and cathodic peaks ($\Delta E_p = E_{pa} - E_{pc}$) of the first oxidation wave is close to 60 mV for all studied compounds, confirming reversible one electron transfer.

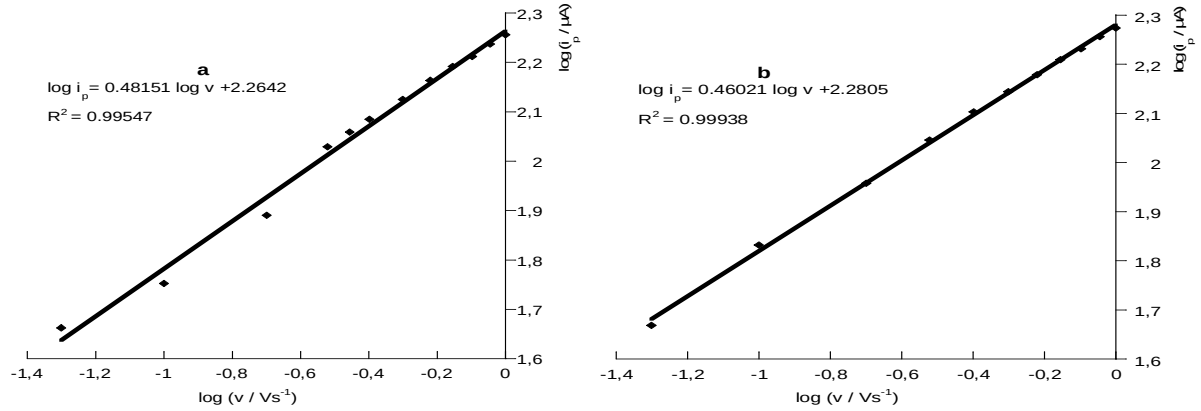

Figure S-1. Variation of the logarithm of the first anodic peak current (I_{pa}^{I}) of compound a) **1a** (4 mM) and b) **1c** (4 mM) as a function of the logarithm of scan rate measured in 0.1M $TBABF_4$ / acetonitrile solution.

[1] R.S. Nicholson, I. Shain, *Anal. Chem*., **1964,** 36, 706-723.

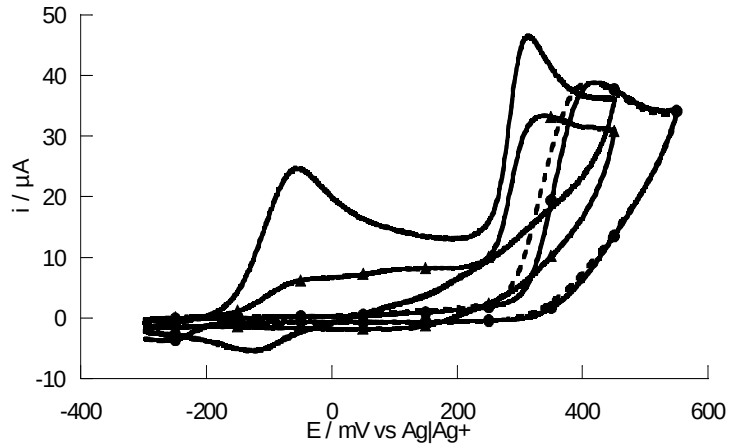

Figure S-2. Cyclic voltammograms of **1a** (2 mM) in the presence of 0, 0.2, 0.5 and1 equiv. of $Zn(ClO_4)_2$. Scan rate: 0.1 Vs^{-1}.

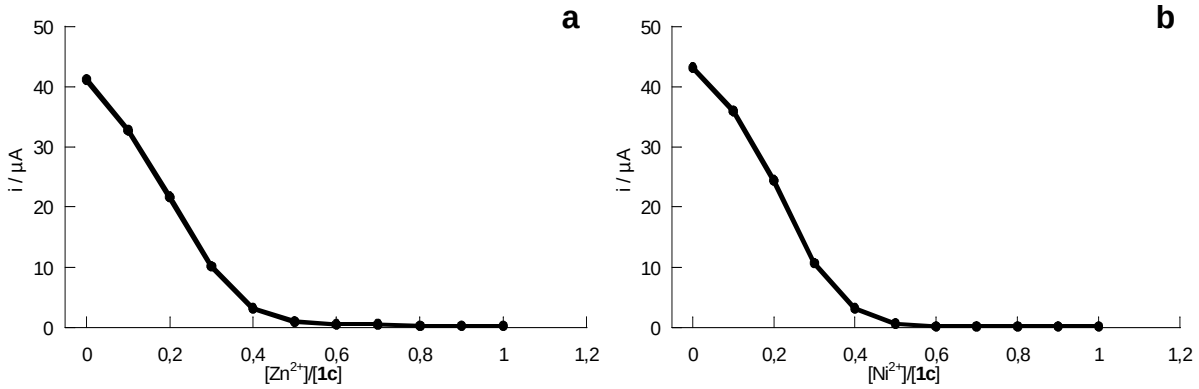

Figure S-3: Variation of the peak current I_{pa} of compound **1c** depending on the relative metal ion concentration of the number of $\mathbf{Zn^{2+}}$ (a) or $\mathbf{Ni^{2+}}$ (b). C = 2 mM.

Selectivity

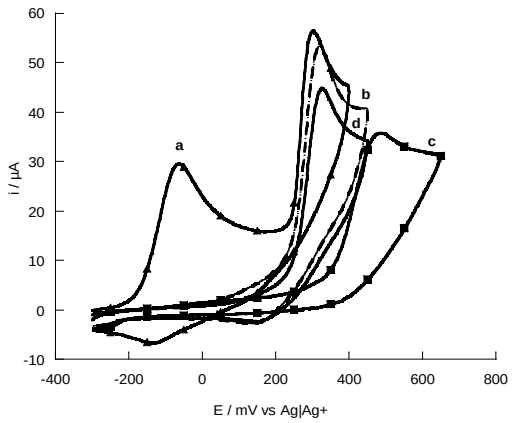

Figure S-4: Cyclic voltammograms of (a) **1a** (2 mM) alone (–▲–) , (b) **1a** in the presence of 1 mM of Cd^{2+} (---), (c) **1a** in the presence of 1 mM of Ni^{2+} (–■–) and (d) solution (b) in the presence of 1 mM of Ni^{2+} (**––**) in 0.1M $TBABF_4$ acetonitrile solution. Scan rate: 0.1Vs^{-1};

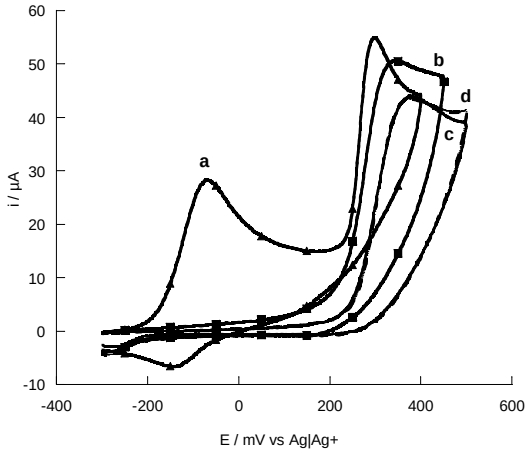

Figure S-5: Cyclic voltammograms of (a) **1a** (2 mM) alone (–▲–) , (b) **1a** in the presence of 1 mM of Cd^{2+} (–■–), (c) **1a** in the presence of 1 mM of Zn^{2+} (**––**) and (d) solution (b) in the presence of 1 mM of Zn^{2+} (**---**) in 0.1M $TBABF_4$ acetonitrile solution. Scan rate: 0.1 Vs^{-1};

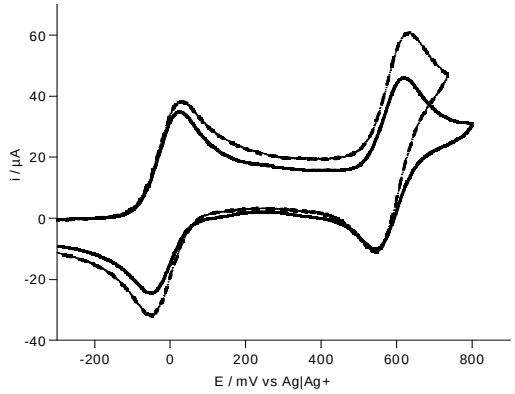

Figure S-6: Cyclic voltammograms of **2a** (2 mM) in the absence (solid line) and presence (dashed line) of 1 equiv. of $Cd(ClO_4)_2$ (2 mM) in 0.1M $TBABF_4$ acetonitrile with a scan rate of 0.1 Vs^{-1}.