

Tetraviologen calix[4]resorcine as a mediator of the electrochemical reduction of $[\text{PdCl}_4]^{2-}$ for the production of Pd^0 nanoparticles

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Experimental

The investigation was carried out using the methods of CV, electrolysis, dynamic light scattering (DLS), NMR spectroscopy and Atomic force microscopy (AFM).

The cyclic voltammograms were recorded on a P-30S potentiostat in inert atmosphere (nitrogen) in the 60% aqueous DMF/0.1 M NaCl (NaClO_4) media. The working electrode was a GC disc electrode ($d = 3.4$ mm) pressed into Teflon. The electrode was cleaned by mechanical polishing before each measurement. Platinum wire was a counter electrode. The potentials were measured relative to the saturated calomel electrode (SCE), $E_f(\text{Fc}/\text{Fc}^+) = +0.41$ V. The temperature was 295 K. The diffusion nature of the peak currents i_p was proven using the theoretical shape of the voltammogram and the linear dependence $i_p - \nu^{1/2}$ and the adsorption nature was substantiated by the presence of an adsorption maximum and the linear dependence $i_p - \nu$ by varying the potential scan rate from 10 to 200 mV/s.

The electrolysis was carried out in a three electrode diaphragm (porous glass) cell in a potentiostatic mode under an inert gas (nitrogen) at room temperature ($T = 295$ K) using a P-30S potentiostat. During the electrolysis, the solution was stirred with a magnetic stirrer. GC tissue was the working electrode ($S = 12.6$ cm²); platinum wire was a counter electrode; and SCE was the reference electrode. The solution during the electrolysis were controlled by CV on the indicator GC disc electrode ($d = 3.4$ mm). For electrolysis, the working solution (20 mL) was prepared by dissolving of MVCA- $\text{C}_5^{8+} \cdot 8\text{Cl}^-$ (18.4 mg, $C = 0.5$ mM), PdCl_2 (5.3 mg, $C = 1.5$ mM), and supporting salt (0.1 M NaCl) in 60% aqueous DMF. A solution of the supporting electrolyte was poured into the auxiliary space.

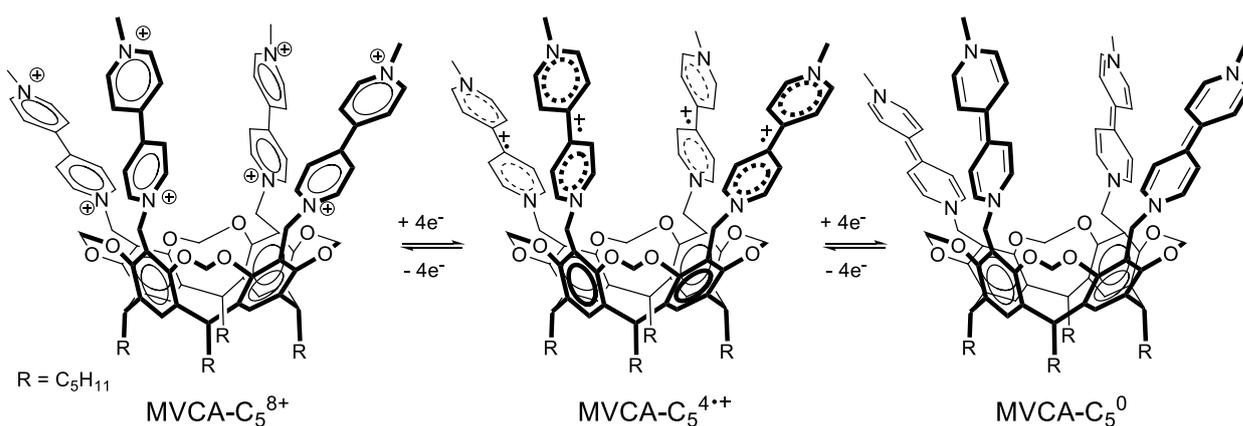
DLS measurements were performed by Malvern Instrument Zetasizer Nano. The measured autocorrelation functions were analyzed by Malvern DTS software.

The ^1H NMR experiments were carried out using a Bruker Avance III 400 spectrometer operating at a frequency of 400 MHz at room temperature. The samples were dissolved in D_2O –DMF- d_7 (60 vol. % DMF- d_7).

The investigation of the surface of samples was carried out by intermittent contact mode AFM using Scanning Probe Microscope MultiMode V (Veeco).

$\text{MVCA-C}_5^{8+} \cdot 8\text{Cl}^-$ were synthesized by the literature procedure [1]. The salts PdCl_2 , NaCl and DMF were used as purchased without additional purification. All the salts dissociate well in the solvents used, therefore, our discussion of experimental data used mainly ions. Water for the experiment was twice distilled.

Scheme and Figures



Scheme S1 Reversible electrochemical reduction of MVCA-C_5^{8+} .

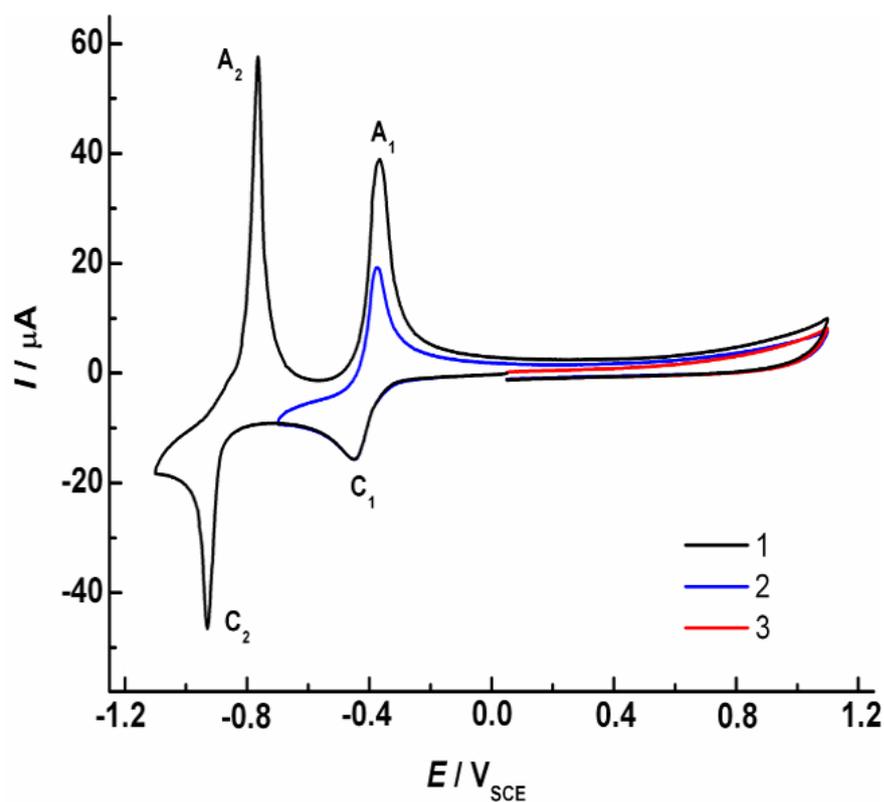


Figure S1 CV of MVCA-C₅⁸⁺ (0.5 mM) in 60% DMF / 0.1 M NaCl media using the glassy carbon electrode at scan rate of 100 mV/s: (1, 2) cathodic and (3) anodic areas.

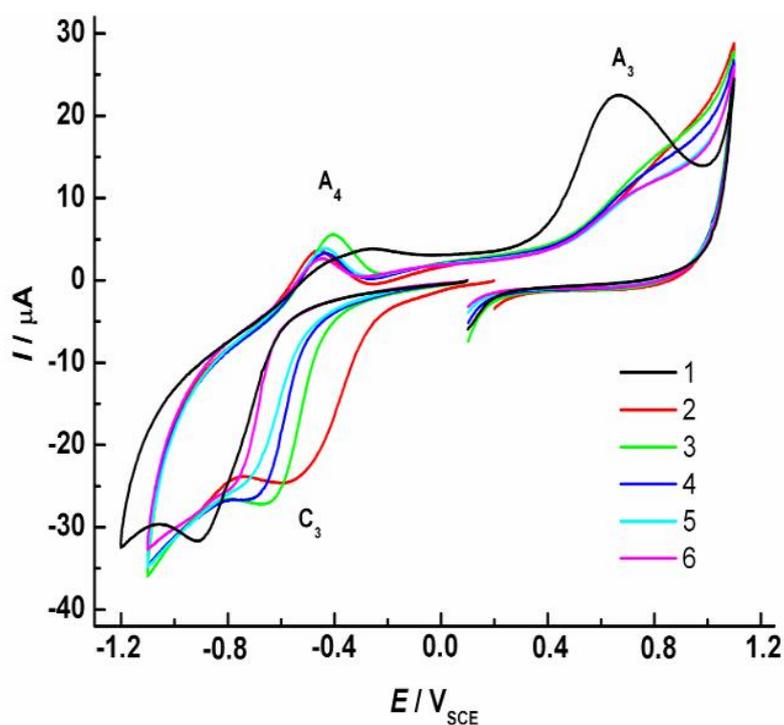


Figure S2 CV of PdCl₂ (1.5 mM) (1) in 60% DMF / 0.1 M NaCl, (2-6) in 60% DMF/0.1M NaClO₄ in the presence of NaCl: (2) 0 mM; (3) 3.0 mM; (4) 7.5 mM; (5) 15 mM; (6) 30.0 mM using the glassy carbon electrode at scan rate of 100 mV/s.

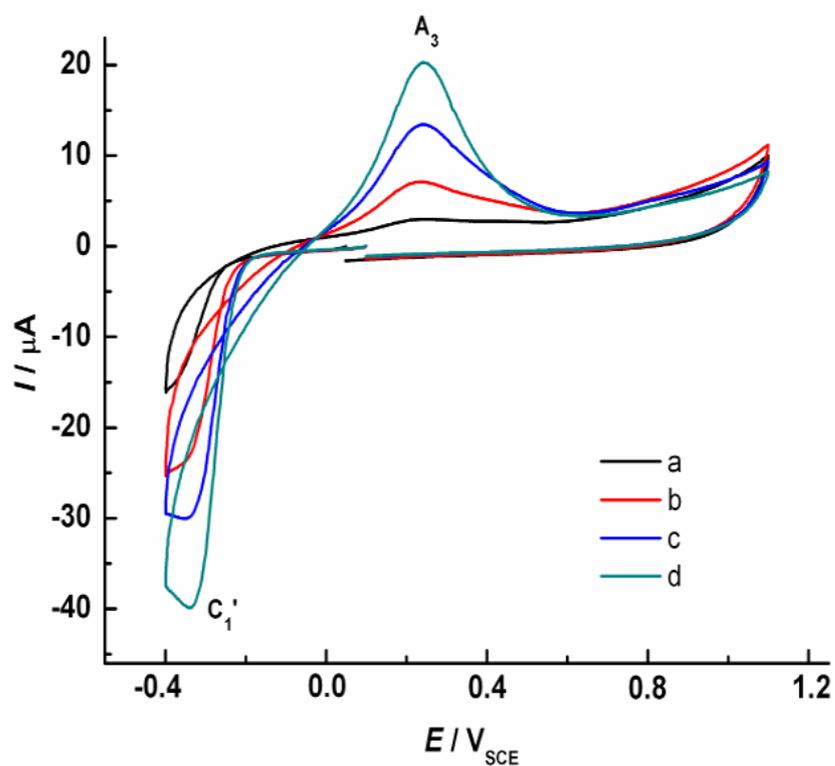


Figure S3 CV of the system MVCA-C₅⁸⁺ (0.5 mM) + PdCl₂ in 60% DMF / 0.1 M NaCl media using the glassy carbon electrode at scan rate of 100 mV/s, C(PdCl₂) = 1 mM (a); 1.5 mM (b); 2.0 mM (c); 2.5 mM (d).

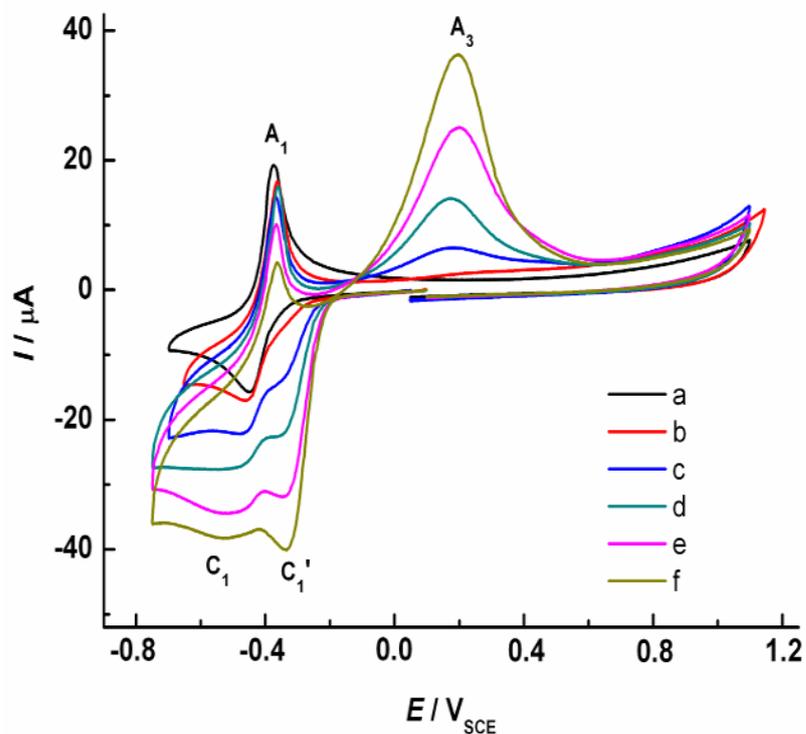


Figure S4 CV of the system MVCA-C₅⁸⁺ (0.5 mM) + PdCl₂ in 60% DMF / 0.1 M NaCl media using the glassy carbon electrode at scan rate of 100 mV/s, C(PdCl₂) = 0 mM (a); 0.5 mM (b); 1.0 mM (c); 1.5 mM (d); 2.0 mM (e); 2.5 mM (f).

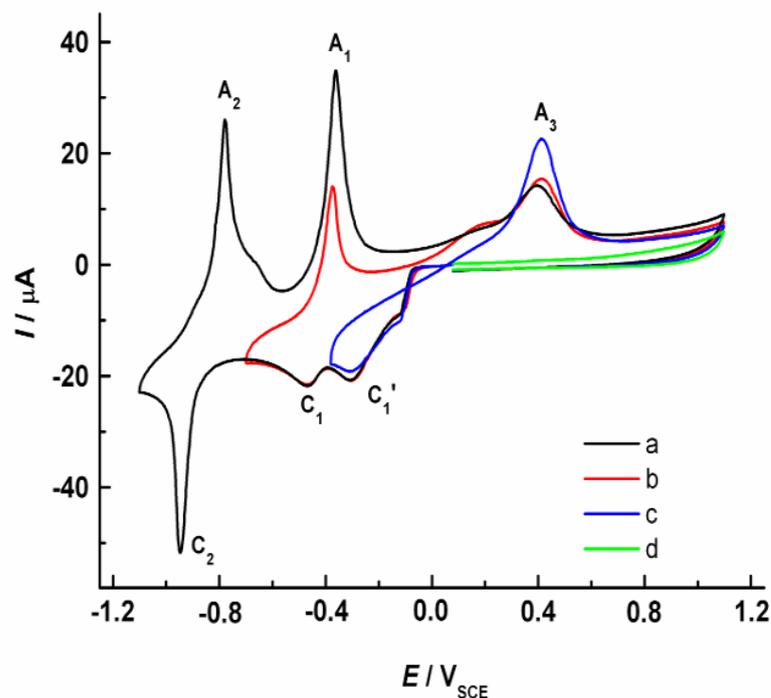


Figure S5 CV of the system MVCA-C₅⁸⁺ (0.5 mM) + PdCl₂ (1.5 mM) recorded in the electrolysis cell before electrolysis in 60% DMF / 0.1 M NaCl media using the glassy carbon electrode at scan rate of 100 mV/s.

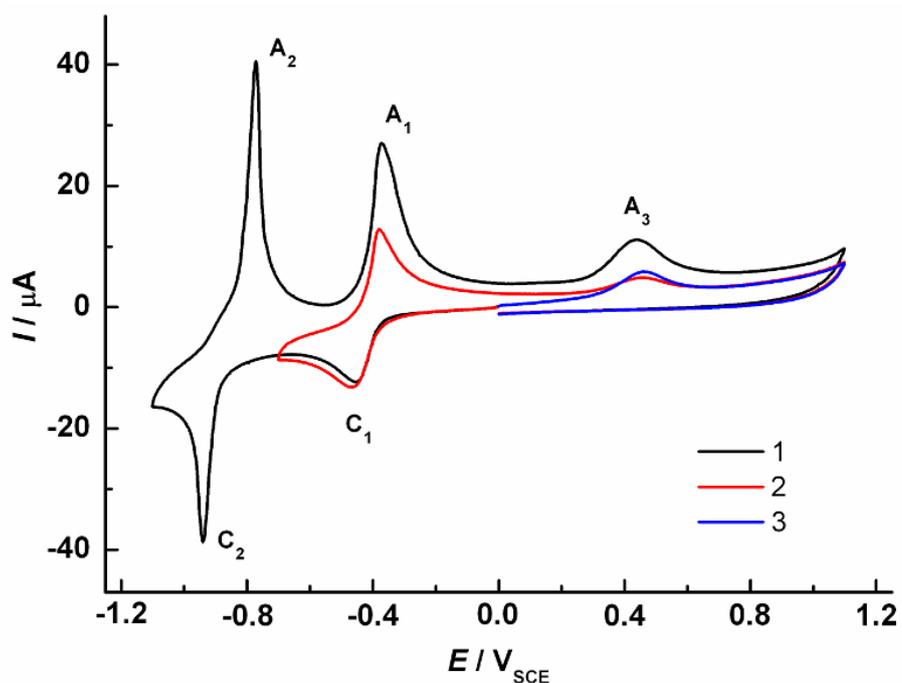


Figure S6 CV of the system MVCA-C₅⁸⁺ (0.5 mM) + PdCl₂ (1.5 mM) recorded in the electrolysis cell after electrolysis at $E = -0.6$ V ($Q = 2F/\text{mole PdCl}_2$) in 60% DMF / 0.1 M NaCl media using the glassy carbon electrode at scan rate of 100 mV/s with the potential scan in (1, 2) negative and (3) positive directions.

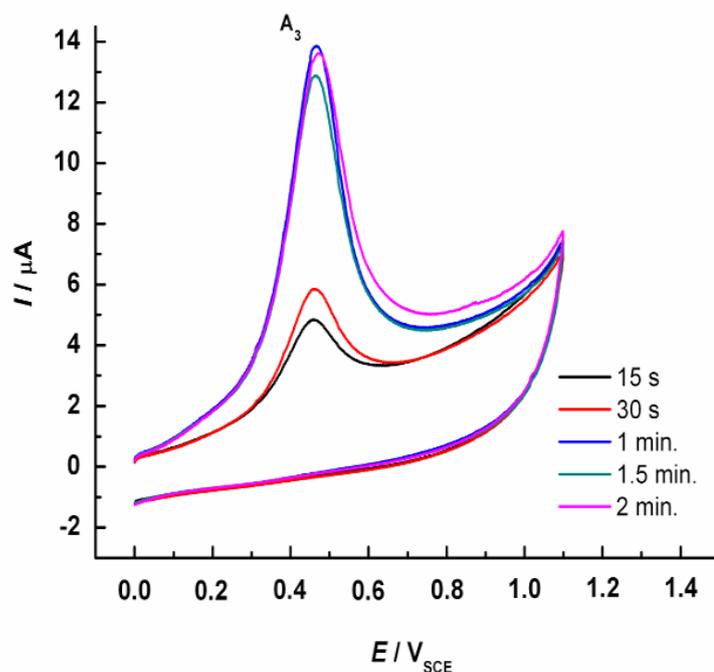


Figure S7 CV of the system MVCA-C₅⁸⁺ (0.5 mM) + PdCl₂ (1.5 mM) recorded in the electrolysis cell after electrolysis at $E = -0.6$ V ($Q = 2F/\text{mole PdCl}_2$) in 60% DMF / 0.1 M NaCl media using the glassy carbon electrode at scan rate of 100 mV/s depending on incubation time the indicator electrode the solution.

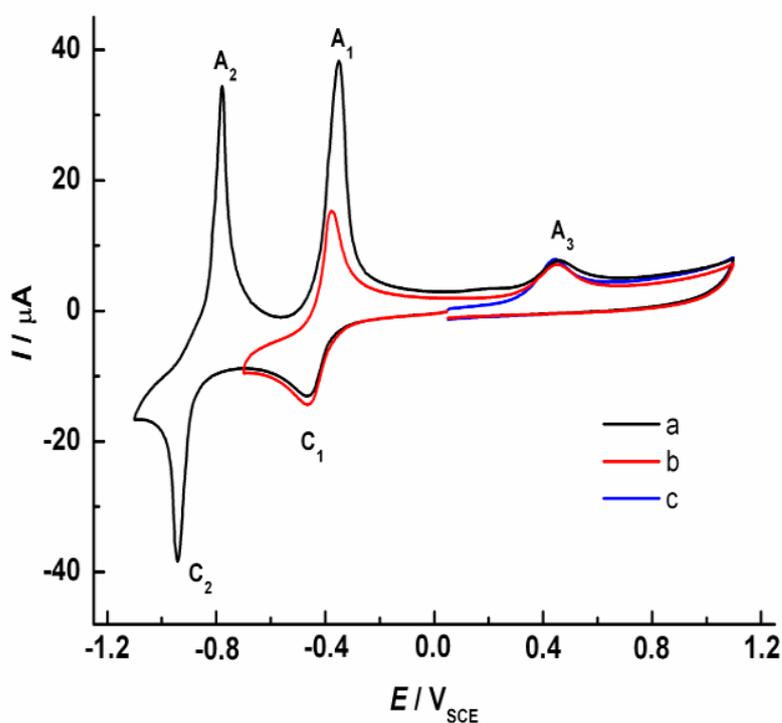


Figure S8 CV of the system MVCA-C₅⁸⁺ (0.5 mM) + PdCl₂ (1.5 mM) recorded in the electrolysis cell after electrolysis at $E = -0.6$ V ($Q = 2F/\text{mole PdCl}_2$) and an oxidation with air in 10 min in 60% DMF / 0.1 M NaCl media using the glassy carbon electrode at scan rate of 100 mV/s with the potential scan in (a, b) negative and (c) positive directions.

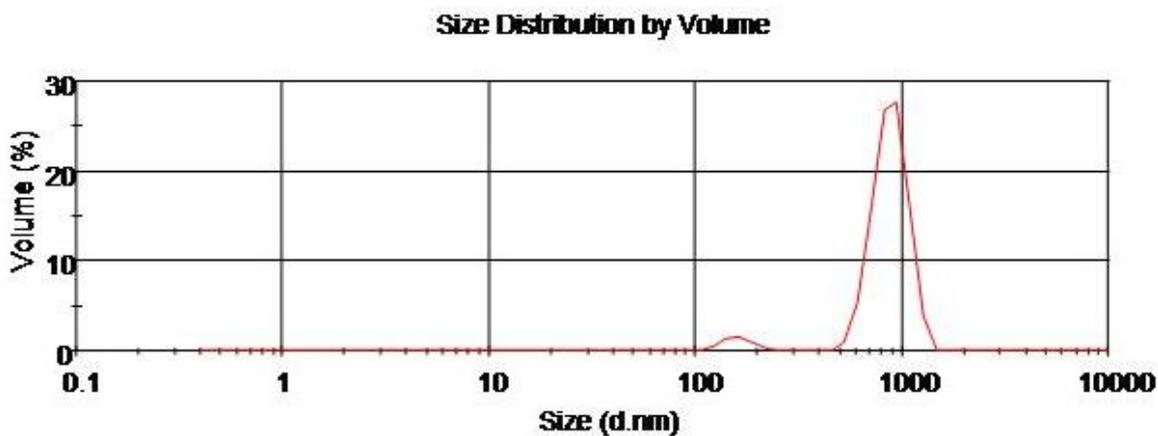


Figure S9 The volume distribution of the $(\text{Pd}^0)_m$ particles size (DLS data).

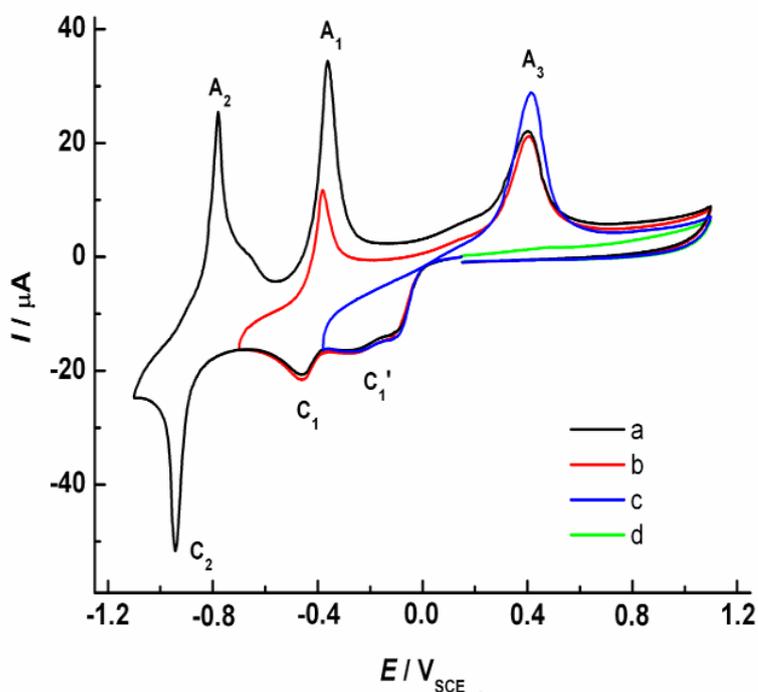


Figure S10 CV of the system MVCA-C_5^{8+} (0.5 mM) + PdCl_2 (1.5 mM) recorded in the electrolysis cell after electrolysis at $E = -0.6$ V ($Q = 2\text{F/mole PdCl}_2$) and the re-oxidation at $E = 0.6$ V ($Q = 2\text{F/mole PdCl}_2$) in 60% DMF / 0.1 M NaCl media using the glassy carbon electrode at scan rate of 100 mV/s with the potential scan in (a, b,c) negative and (d) positive directions.

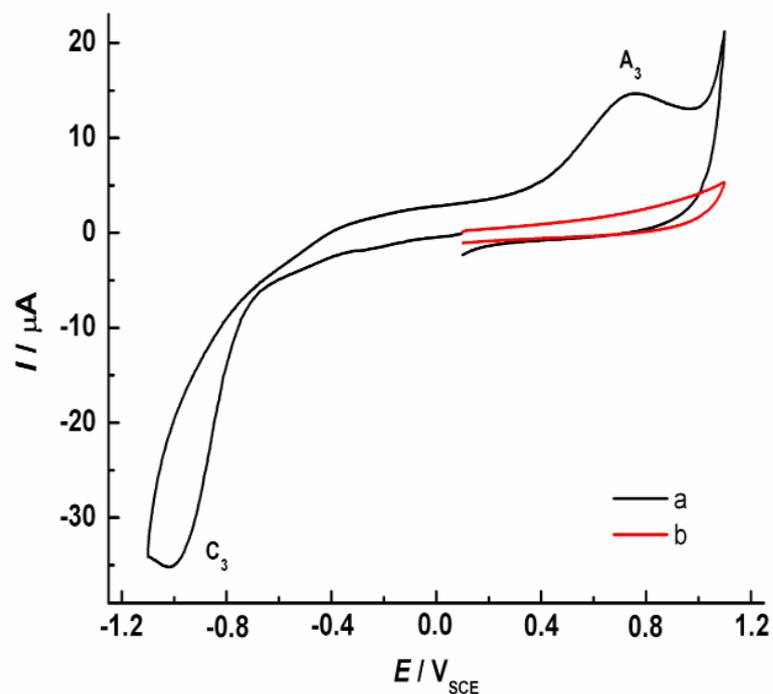


Figure S11 CV of PdCl₂ (1.5 mM) recorded in the electrolysis cell before electrolysis in 60% DMF / 0.1 M NaCl media using the glassy carbon electrode at scan rate of 100 mV/s with the potential scan in (a) negative and (b) positive directions.

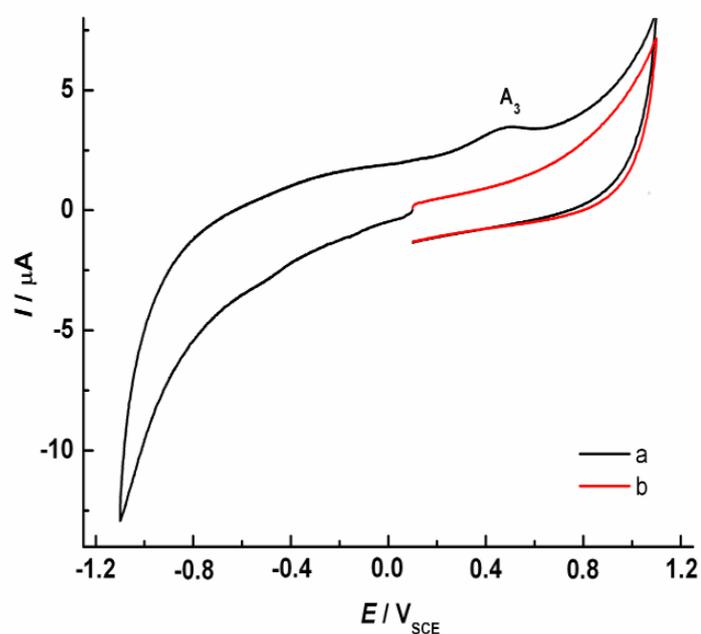


Figure S12 CV of PdCl₂ (1.5 mM) recorded in the electrolysis cell after electrolysis at $E = -1.0$ V ($Q = 2F/\text{mole PdCl}_2$) in 60% DMF / 0.1 M NaCl media using the glassy carbon electrode at scan rate of 100 mV/s with the potential scan in (a) negative and (b) positive directions.

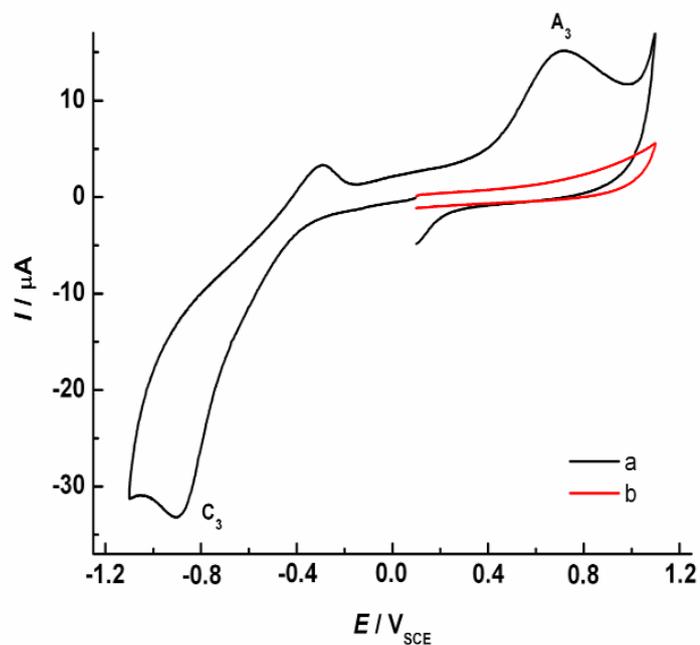


Figure S13 CV of PdCl₂ (1.5 mM) recorded in the electrolysis cell after electrolysis at $E = -1.0$ V ($Q = 2F/\text{mole PdCl}_2$) and the re-oxidation at $E = 0.6$ V ($Q = 2F/\text{mole PdCl}_2$) in 60% DMF / 0.1 M NaCl media using the glassy carbon electrode at scan rate of 100 mV/s with the potential scan in (a) negative and (b) positive directions.

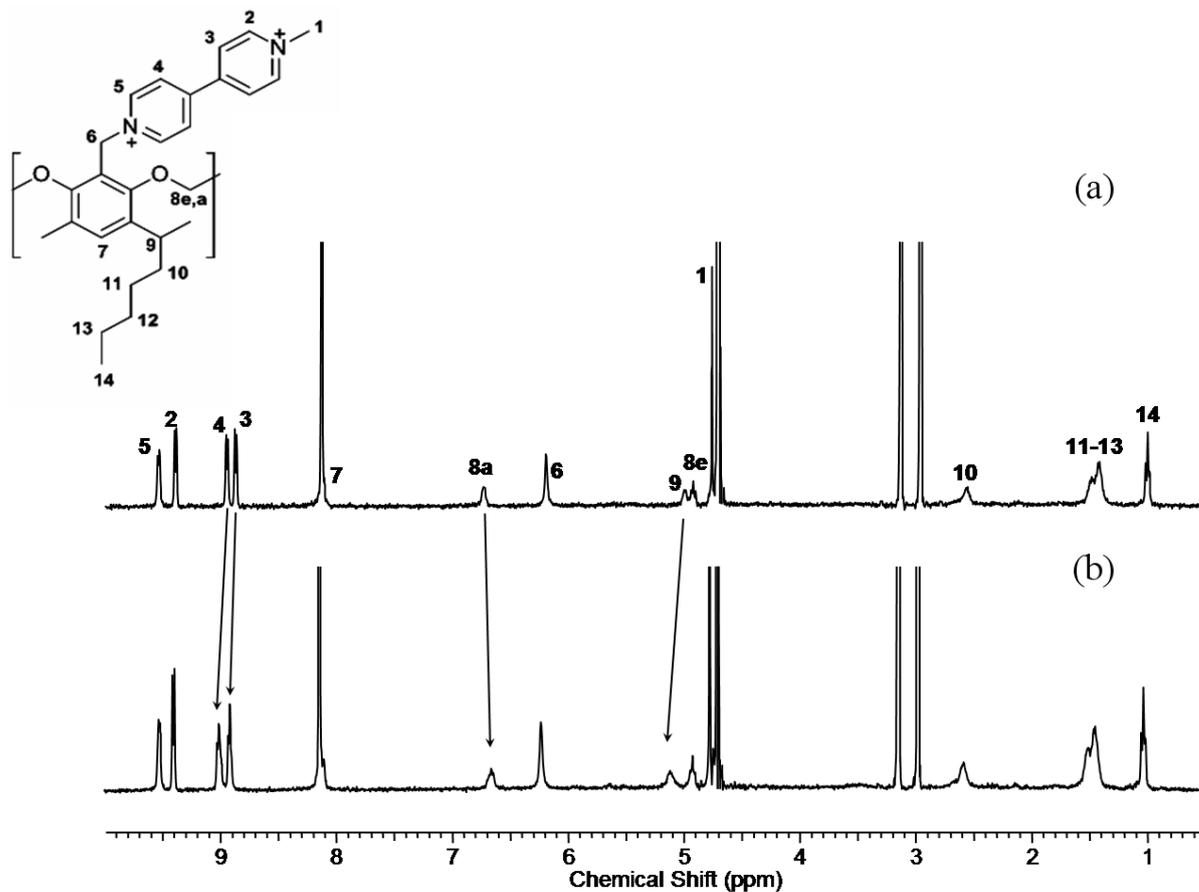


Figure S14 ¹H NMR spectra of (a) MVCA-C₅⁸⁺ (0.5 mM); (b) MVCA-C₅⁸⁺ (0.5 mM) + PdCl₂ (1.5 mM) in 0.1 M NaCl solution in DMF-*d*₇ – D₂O (60% DMF-*d*₇).