

Supporting Information for:

An Outer-Sphere Two-Electron Platinum Reagent

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Experimental:

All reagents were obtained from Pressure Chemical, Aldrich or Acros, and used as received. Tetrahydrofuran (THF) was distilled from Na(s) and benzophenone. ^1H NMR spectra were recorded at room temperature using a Bruker AC 250 MHz spectrometer.

[Pt(tpy)(pip₂NCN)][BF₄] (1(BF₄⁻)): A mixture of silver tetrafluoroborate (0.077 g, 0.40 mmol) and Pt(pip₂NCN)Cl (0.20 g, 0.40 mmol) in 35 ml of acetone was allowed to stir for 30 minutes at room temperature. The resulting precipitate was removed by vacuum filtration through celite. After addition of tpy (0.093 g, 0.40 mmol), the filtrate was allowed to stir for 18 hours, and the solvent was removed by rotary-evaporation. The red solid was dissolved in CH₂Cl₂ and ether was added to induce precipitation. The product was washed with ether and dried. Yield 0.22 g, 70%. Anal. Calcd. for [C₃₃H₃₈N₅Pt][BF₄] · ½CH₂Cl₂: C, 48.53; H, 4.74; N, 8.45. Found: C, 48.55; H, 4.72; N, 8.32. ^1H NMR (CDCl₃, δ): 1.06 (8H, m, CH₂), 1.21 (4H, m, CH₂), 2.27 (8H, m, CH₂), 3.65 (4H, s, CH₂), 7.15 (3H, m, CH), 7.37 (2H, t, CH), 8.13 (2H, d with Pt satellites, J_{Pt-H}=50 Hz, CH), 8.28 (2H, t, CH), 8.44-8.69 (5H, m, CH). Variable temperature ^1H NMR studies show no evidence of fluxional behavior from 232 K to 298 K.

[Pt(tpy)(pip₂NCNH₂)][PF₆]₃ (2(PF₆⁻)₃): A mixture of silver tetrafluoroborate (0.077 g, 0.40 mmol) and Pt(pip₂NCN)Cl (0.20 g, 0.40 mmol) in 35 ml of acetone was allowed to stir for 30 minutes at room temperature. The resulting precipitate was removed by vacuum filtration through celite. After addition of tpy (0.093 g, 0.40 mmol), the filtrate was allowed to stir for 18 hours. 1 M HNO₃ was added dropwise until the red solution turned bright yellow. Water (20

ml) was added and the volume was reduced to ~20 ml by rotary evaporation. The mixture was filtered and 3 ml of concentrated aqueous NH_4PF_6 was added to precipitate the product. The yellow solid was collected by vacuum filtration, washed with ether and dried under vacuum. Yield 0.29 g, 63%. Anal. Calcd. for $[\text{C}_{33}\text{H}_{40}\text{N}_5\text{Pt}][\text{PF}_6]_3$: C, 34.87; H, 3.55; N, 6.16. Found: C, 35.26; H, 3.44; N, 6.35. ^1H NMR (CD_3CN , δ): 1.50 (12H, m, CH_2), 2.80 (4H, m, CH_2), 2.27 (4H, m, CH_2), 4.63 (4H, d, CH_2), 6.88 (2H, broad, NH), 7.47-7.61 (5H, m, CH), 7.93 (2H, d with Pt satellites, $J_{\text{Pt-H}}=48$ Hz, CH), 8.30-8.56 (7H, m, CH).

Pt(COD)(dmph)Cl: $\text{Pt}(\text{COD})\text{Cl}_2$ (1.0 g, 2.7 mmol) was dissolved in THF (80 ml) and cooled to -70 °C. After addition of a solution of 2,6-dimethylphenylmagnesium bromide (16 ml of a 1.0 M solution in THF, 16.2 mmol), the mixture was allowed to warm to room temperature over 4 hours. A concentrated solution of NH_4Cl (15 ml) was added, and the THF layer was separated. The water layer was extracted with ether (2 x 50 ml), and the combined organic layers were dried over MgSO_4 , filtered, and roto-evaporated to dryness. The yellow residue was dissolved in CHCl_3 and hexanes was added to induce precipitation. Yield: 0.936 g, 79 %. Anal. Calcd. for $\text{C}_{16}\text{H}_{21}\text{PtCl} \cdot \frac{1}{2} \text{CHCl}_3$: C, 39.43; H, 4.11. Found: C, 39.55; H, 4.34; ^1H NMR (CDCl_3 , δ) 2.20-2.70 (14H, m, CH_2 and CH_3); 4.43 (2H, m, CH, $J_{\text{Pt-H}}=74$ Hz); 5.79 (2H, m, CH, $J_{\text{Pt-H}}=31$ Hz); 6.83 (3H, m, CH).

[Pt(tpy)(dmph)][BF₄]: A mixture of silver tetrafluoroborate (0.044 g, 0.225 mmol) and $\text{Pt}(\text{COD})(\text{dmph})\text{Cl}$ (0.10 g, 0.225 mmol) in 30 mL of acetone was allowed to stir for 30 minutes at room temperature. The resulting AgCl precipitate was removed by vacuum filtration through celite. After addition of tpy (0.053 g, 0.225 mmol) the solution was allowed to stir overnight in the dark. The solution was evaporated to dryness, and the residue was dissolved in a minimum of CHCl_3 (~ 20 ml). Diethyl ether (75 ml) was added to induce precipitation of the yellow solid. Yield: 0.120 g, 86 %. Anal. Calcd. for $[\text{C}_{23}\text{H}_{20}\text{N}_3\text{Pt}][\text{BF}_4] \cdot \frac{1}{2} \text{CHCl}_3$: C, 41.51; H, 3.04; N,

6.18. Found: C, 41.47; H, 3.10; N, 6.02.; ^1H NMR (CDCl_3 , δ) 2.52 (6H, s, CH_3); 6.99-7.09 (3H, m, CH); 7.48 (2H, m, CH); 8.16 (2H, with Pt satellites, $J_{\text{Pt-H}}=51$ Hz); 8.31 (2H, t, CH); 8.48-8.59 (3H, m, CH); 8.66 (2H, d, CH).

X-ray crystallography. SMART v5.622 and SAINT v6.02A programs were used for data collection and data processing, respectively (Bruker Analytical X-ray Instruments, Inc., Madison, WI). SADABS v.2.03 was used for the application of semi-empirical absorption and beam corrections, and SHELXTL v6.1 was used for the structure solution and generation of figures and tables (G. M. Sheldrick, University of Goettingen, Germany and Bruker Analytical X-ray Instruments, Inc., Madison, WI). Neutral-atom scattering factors were used as stored in this package.

Yellow plate-shaped crystals of $\mathbf{2}(\text{Cl}^-)_3 \cdot 4\text{H}_2\text{O}$ were grown by slow evaporation of an acetone solution of **1** containing excess $\text{HCl}(\text{aq})$. For X-ray examination and data collection, a suitable crystal, approximate dimensions 0.38 x 0.24 x 0.06 mm, was mounted on the tip of a glass fiber with epoxy resin. Intensity data were collected on a standard Siemens SMART 1K CCD diffractometer using graphite-monochromated Mo $\text{K}\alpha$ radiation, $\lambda=0.71073\text{\AA}$. The data frames were processed using the program SAINT. The data were corrected for decay, Lorentz and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of the Patterson method in SHELXTL v6.1 and the difference Fourier technique and refined by full-matrix least squares on F^2 for data out to 0.8 \AA resolution. Non-hydrogen atoms were refined with anisotropic displacement parameters. Weights were assigned as $w^{-1}=[\sigma^2(F_o^2) + (0.0658P)^2 + 21.0649P]$ where $P=0.33333F_o^2+0.66667F_c^2$. The NH hydrogen atoms were located directly while the remaining hydrogen atoms were included in calculated positions and treated with a riding model. Hydrogen atom isotropic displacement parameters were assigned as a times U_{eq} of the adjacent

atom where $a=1.5$ for -OH, and 1.2 for all others. One of the chloride ions is disordered (occupancy set at 0.5). The molecule crystallizes with 4 waters, one of which is disordered (occupancy set at 0.5). The refinement converged with crystallographic agreement factors of $R1=5.27\%$, $wR2=14.05\%$ for 6615 reflections with $I>2\sigma(I)$ ($R1=6.44\%$, $wR2=14.60\%$ for all data) and 433 variable parameters. The highest residual peaks are all near the disordered atoms, however the best model obtained is reported here.

Figure S1 shows a fully labeled ORTEP diagram of **2**. For clarity, all H atoms have been omitted with the exception of those bonded to the N(amine) atoms.

Cyclic Voltammetry. Acetonitrile was distilled over CaH_2 . Data were obtained using a standard three-electrode cell and a CV50w potentiostat from Bioanalytical Systems. Scans were collected in acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6). TBAPF_6 was recrystallized twice from methanol and dried in a vacuum oven prior to use. All scans were recorded using a platinum wire auxiliary electrode, a Ag/AgCl reference electrode, and a 0.79 mm^2 gold working electrode. Between scans, the working electrode was polished with $0.05 \text{ }\mu\text{m}$ alumina, rinsed with distilled water and wiped dry using a Kimwipe. Reported potentials are referenced against Ag/AgCl. Peak currents (i_p) and half-peak potentials ($E_{p/2}$) were estimated with respect to the extrapolated baseline current as described elsewhere (P. T. Kissinger; W. R. Heineman, *J. Chem. Edu.* **1983**, 60, 702-706). The values of $(E_{pc}+E_{pa})/2$, which is an approximation of the formal potential for a redox couple, are referred to as E° . Passed charge (Q) during the sweep was estimated by integrating the current from $E^\circ+150 \text{ mV}$ to $E^\circ-150 \text{ mV}$. Calculated averages are reported as average value plus-or-minus 2σ .

Figure S2 shows the dependence of the CV of $[\text{Pt}(\text{tpy})(\text{pip}_2\text{NCN})][\text{BF}_4]$ (**1**(BF_4^-)) on scan rate for the oxidation process ($E^\circ=0.4 \text{ V}$). Similar results were obtained using a solution of **2**(PF_6^-)₃) and two equivalents of tetrabutylammonium hydroxide. The oxidation is less reversible

using platinum ($i_{pc}/i_{pa}=0.93$, $\Delta E_p=160$ mV, 0.25 V/s) or glassy carbon electrodes ($i_{pc}/i_{pa}=0.75$, $\Delta E_p=300$ mV, 0.25 V/s), or CH₂Cl₂ solvent ($i_{pc}/i_{pa}=0.72$, $\Delta E_p=320$ mV, 0.25 V/s, gold electrode, 0.1 mM TBAPF₆).

For the first reduction process ($E^\circ=-0.98$ V), ΔE_p is essentially invariant (59 ± 6 mV) for scan rates ranging from 0.02 to 2.5 V/s, as expected for a reversible one-electron process. Outside this range (0.01-0.015 and 5.1-25.6 V/s), the process is less reversible. As the scan rate increases from 5.1 to 25.6 V/s, ΔE_p increases from 66 to 88 mV, as expected from uncompensated resistance effects and the onset of slow electron-transfer kinetics relative to the scan rate. Below 0.01 V/s, the anodic and cathodic peak maxima were not resolved. From 0.02 to 2.5 V/s, the average ratio of cathodic charge (Q_c) to the anodic charge (Q_a) is 3.8 ± 1.7 for fourteen measurements. For the faster scan rates over this range, Q_c/Q_a lies near 3.0, as predicted for a chemically reversible process (*e.g.*, $Q_c/Q_a=2.9$, 2.5 V/s). With decreasing scan rate, the ratio increases (*e.g.*, $Q_c/Q_a=5.7$, 0.02 V/s), as expected for the onset decomposition of the reduced complex on these slow timescales. The variation and deviation of Q_c/Q_a with respect to the predicted ratio of 3.0 is partially a result of uncertainty in background current corrections.

Figure S3 shows the CV in acetonitrile of [Pt(tpy)(pip₂NCNH₂)] [PF₆]₃ (**2**(PF₆⁻)₃) in acetonitrile solution. Protonation of the piperdyl groups results in irreversible oxidation near 0.4 V accompanied by electrode fouling. This process may involve the platinum center as observed for **1**, but protonation slows overall kinetics and also causes increased surface adsorption.

Figure S4 shows the CV of [Pt(tpy)(dmph)] [BF₄] in acetonitrile solution. An adsorption wave occurs near 0.8 V on a gold electrode. The current is insensitive to concentration, and this feature is absent when using a glassy carbon electrode.

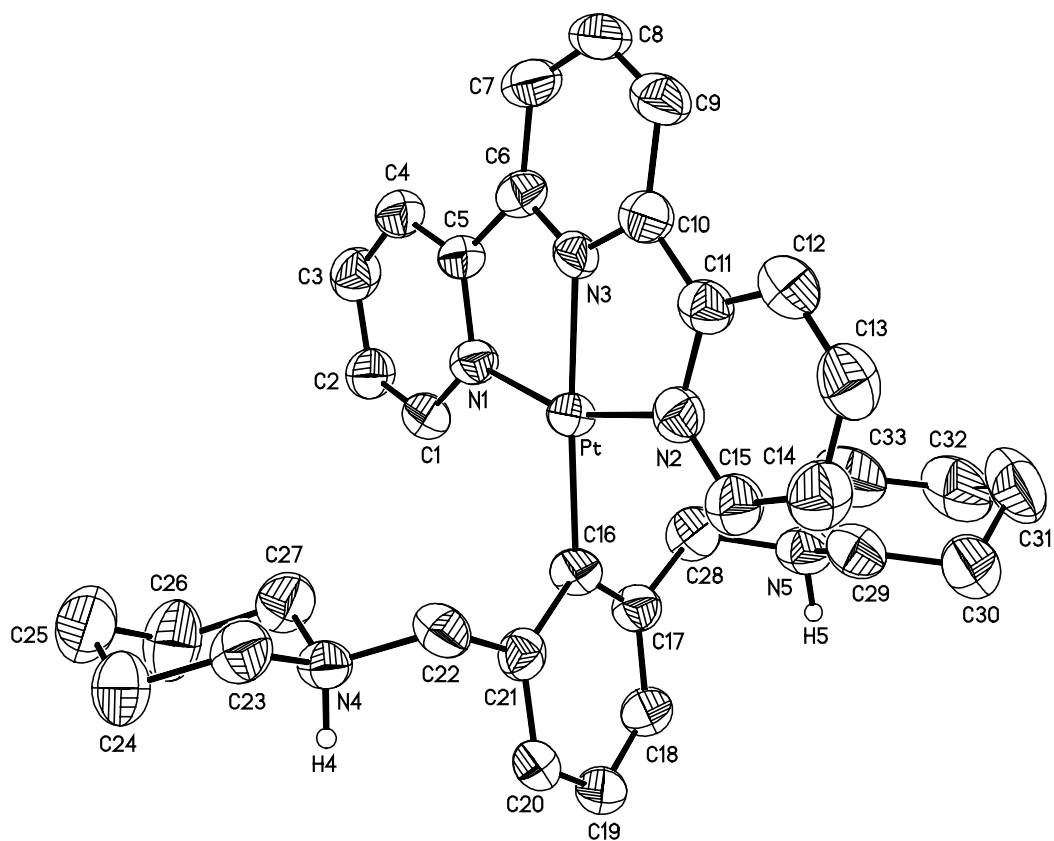


Figure S1. ORTEP diagram of $\text{Pt}(\text{tpy})(\text{pip}_2\text{NCNH}_2)^{3+}$ (**2**). For clarity, all H atoms have been omitted with the exception of those bonded to N(amine) atoms.

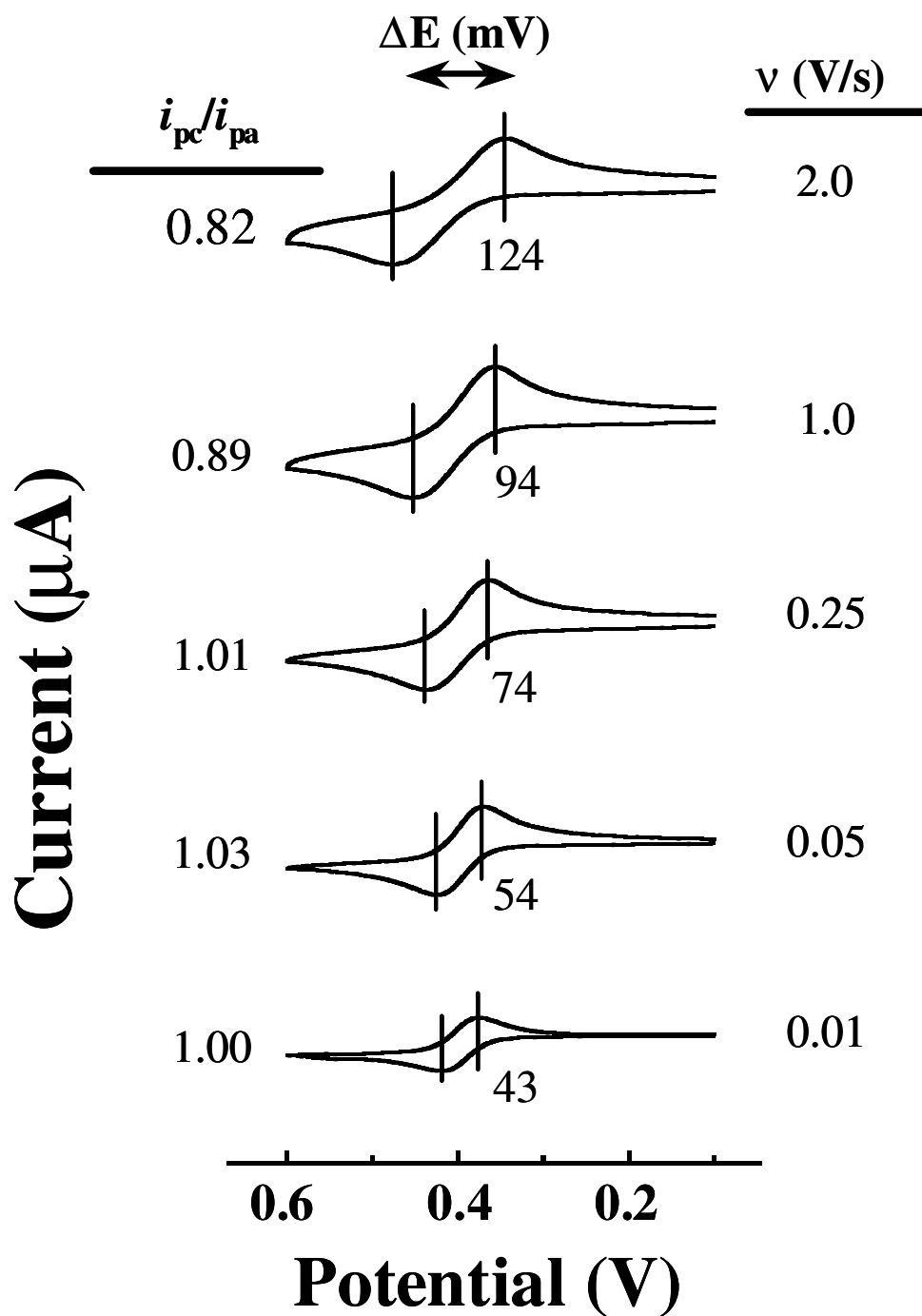


Figure S2. Dependence of cyclic voltammogram of $[\text{Pt}(\text{tpy})(\text{pip}_2\text{NCN})][\text{BF}_4]$ ($\mathbf{1}(\text{BF}_4^-)$) in acetonitrile on scan rate (0.1 M TBAPF_6). Scans are scaled by factors of 1 (2.0), 1.33 (1.0), 2 (0.25), 3 (0.05), and 4 (0.01 V/s), respectively.

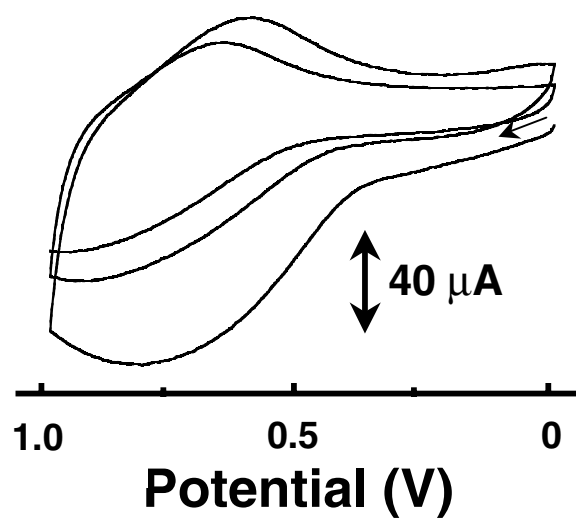


Figure S3. CV of **2** in acetonitrile (0.1 M TBAPF₆, 0.25 V/s), 2.5 cycles between 0 and 1.0 V.

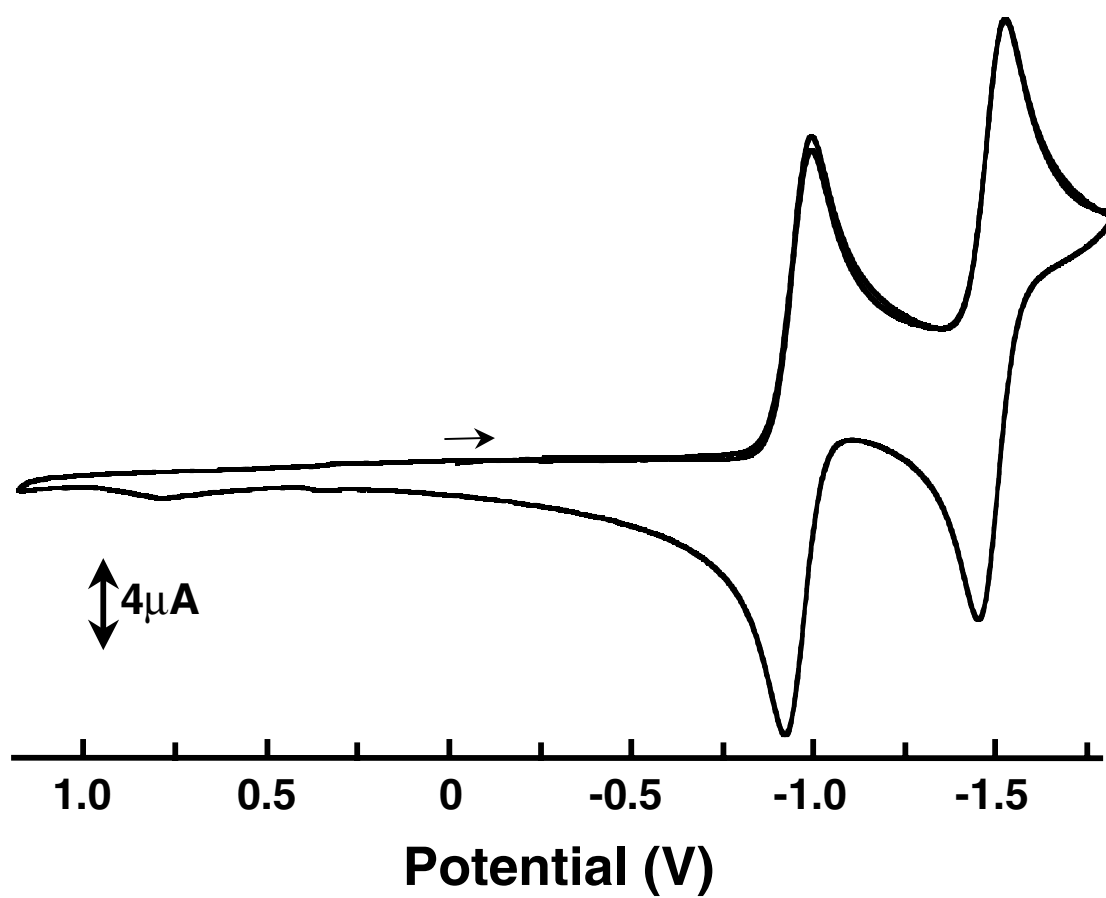


Figure S4. CV of $\text{Pt}(\text{tpy})(\text{dmph})^+$ in acetonitrile (0.1 M TBAPF_6 , 0.25 V/s).