

Electronic Supplementary Information

Surface modification of carbon and metal electrodes with bistable molecular redox switches by click and amide coupling

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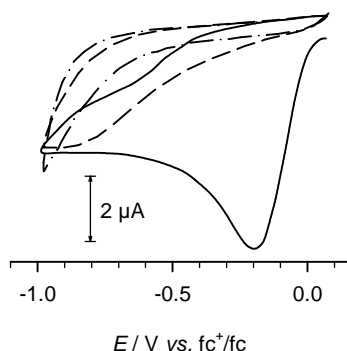


Figure S-1. Cyclic voltammograms (0.2 Vs^{-1}) of $\text{NO}_2\text{-Ph-N}_2^+$ (0.5 mM in acetonitrile with 0.1 M TBAPF₆) on Pt electrode (diam.: 2 mm), scans 1 (—), 2 (---) and 3 (-•-).

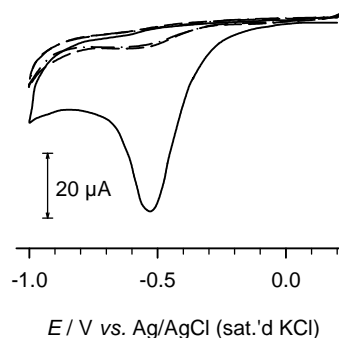


Figure S-2. Cyclic voltammograms (0.2 Vs^{-1}) of a $\text{NO}_2\text{-Ph}$ -modified glassy carbon electrode (diam.: 3 mm) in 0.25 M H_2SO_4 , scans 1 (—), 2 (---) and 3 (-•-).

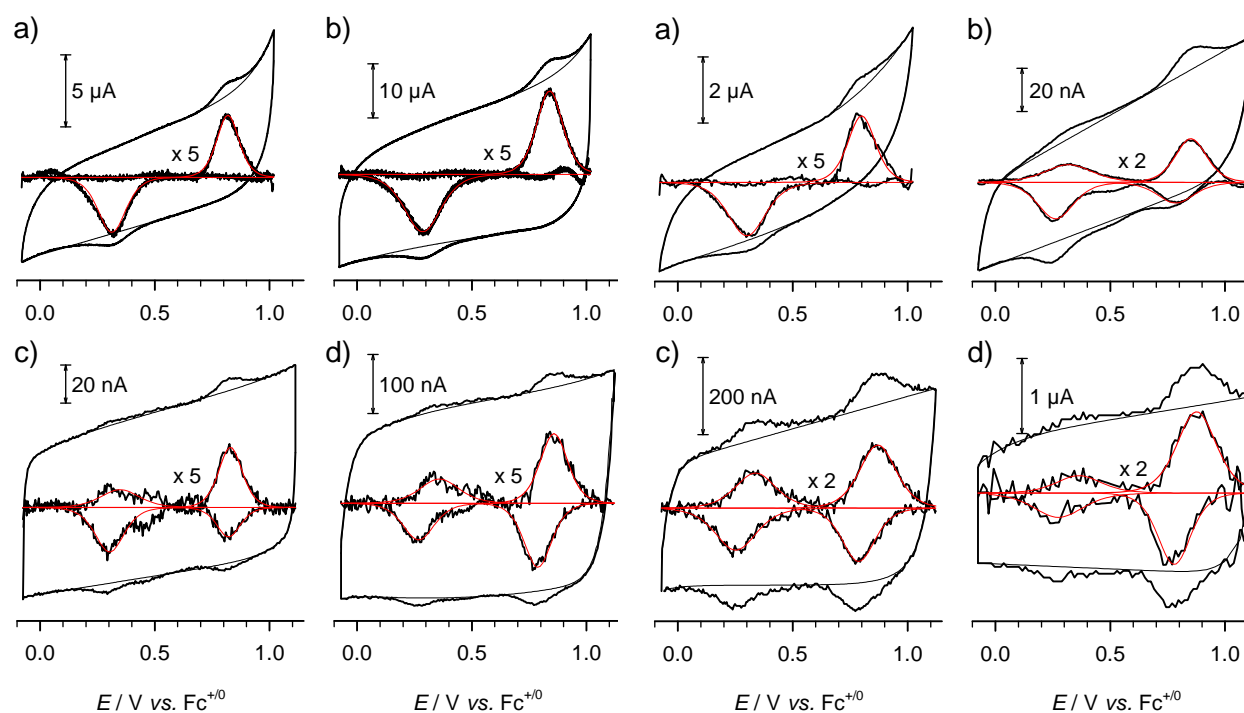


Figure S-3. Cyclic voltammograms of Pt electrodes (electrode diam.: 2 mm (a), 25 μm (b-d)) modified by grafting of $\text{N}_2^+\text{-Ph-NO}_2$, -NO_2 to -NH_2 reduction, and subsequent amide coupling of complex **2**. Capacitive background (thin lines) and faradaic peaks (red) fitted to background subtracted current. Scan rate: 5 Vs^{-1} (a), 20 Vs^{-1} (b), 500 Vs^{-1} (c), 2000 Vs^{-1} (d).

Figure S-4. Cyclic voltammograms of Pt electrodes (electrode diam.: 2 mm (a, b), 25 μm (c-d)) modified by grafting of $\text{N}_2^+\text{-Ph-COOH}$ and subsequent amide coupling of complex **1**. Capacitive background (thin lines) and faradaic peaks (red) fitted to background subtracted current. Scan rate: 2 Vs^{-1} (a), 200 Vs^{-1} (b), 2000 Vs^{-1} (c), 10000 Vs^{-1} (d).

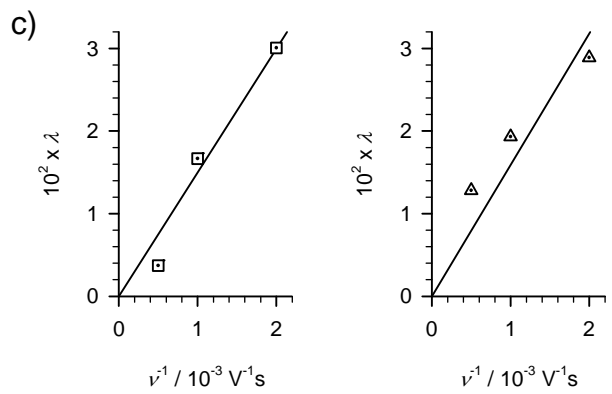
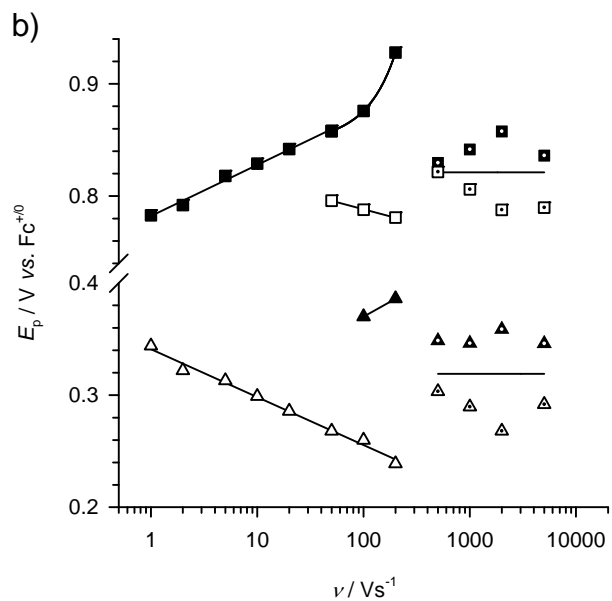
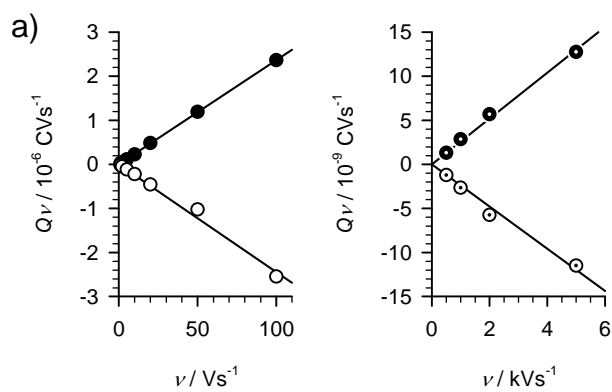


Figure S-5. Scan rate dependent CV parameters of Pt electrodes (2 mm diam. and 25 μm diam. (dotted symbols)) modified by grafting of N_2^+ -Ph- NO_2 , - NO_2 to - NH_2 reduction, and subsequent amide coupling of complex **2**. (a) Total anodic (●) and cathodic (○) peak. (b) Peak potentials of the $\text{Ru}^{\text{III/II}}(\text{N}_6)$ (■, □) and $\text{Ru}^{\text{III/II}}(\text{N}_5\text{O})$ (▲, △) couples. (c). Kinetic parameters obtained from reverse/forward peak current ratios $i_{\text{pc}}(\text{N}_6)/i_{\text{pa}}(\text{N}_6)$ (□) and $i_{\text{pa}}(\text{N}_5\text{O})/i_{\text{pc}}(\text{N}_5\text{O})$ (△).

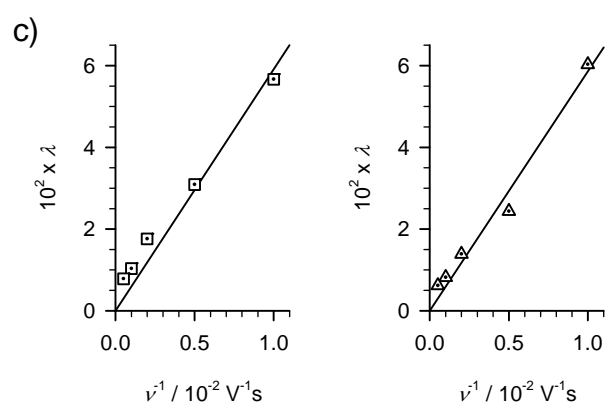
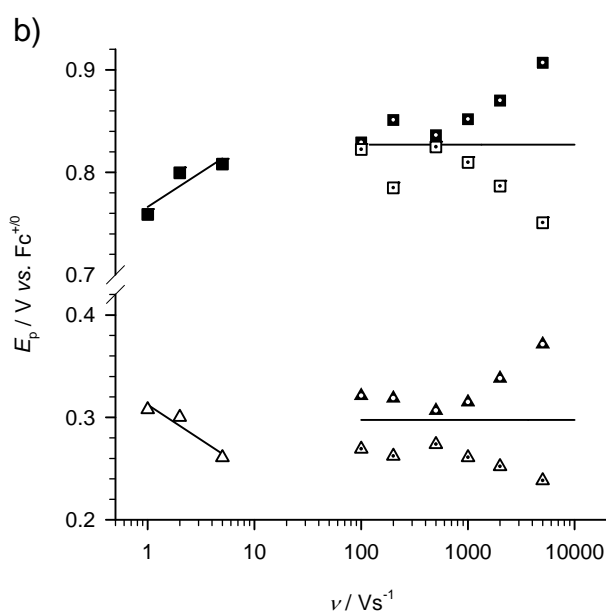
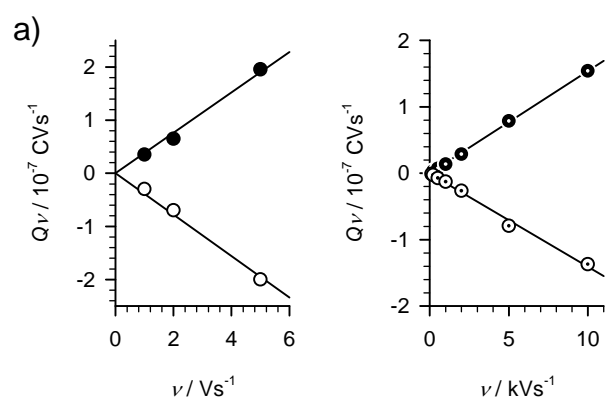


Figure S-6. Scan rate dependent CV parameters of Pt electrodes (2 mm diam. and 25 μm diam. (dotted symbols)) modified by grafting of N_2^+ -Ph-COOH and subsequent amide coupling of complex **1**. (a) Total anodic (●) and cathodic (○) peak. (b) Peak potentials of the $\text{Ru}^{\text{III/II}}(\text{N}_6)$ (■, □) and $\text{Ru}^{\text{III/II}}(\text{N}_5\text{O})$ (▲, △) couples. (c). Kinetic parameters obtained from reverse/forward peak current ratios $i_{\text{pc}}(\text{N}_6)/i_{\text{pa}}(\text{N}_6)$ (□) and $i_{\text{pa}}(\text{N}_5\text{O})/i_{\text{pc}}(\text{N}_5\text{O})$ (△).