

Electronic Supplementary Information

Rapid electrochemically induced linkage isomerism in a
ruthenium(II) polypyridyl complex

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Experimental

Electrochemistry All solutions were prepared from dry acetonitrile (Merck, spectroscopy grade, dried with MS 3 Å) with 0.1 M tetrabutylammonium hexafluorophosphate (Fluka, electrochemical grade) as supporting electrolyte that has been dried in vacuum at 353 K. Before all measurements, oxygen was removed by bubbling the stirred solutions with solvent saturated argon and the samples were kept under argon atmosphere during measurements.

Cyclic voltammetry, differential pulse voltammetry and controlled potential electrolysis were carried out using an Autolab PGSTAT 100 potentiostat with a GPES 4.9 electrochemical interface (Eco Chemie) and a CHI660A electrochemical workstation (CH Instruments) for fast voltammetry. The working electrode was a glassy carbon disc (diameter 3 mm, freshly polished) for voltammetry, a Pt disk microelectrode (CH Instruments, diameter 25 µm, freshly polished with alumina 0.3 µm) for fast voltammetry, or a platinum grid for bulk electrolysis, respectively. A platinum spiral in a compartment separated from the bulk solution by a fritted disk was used as counter electrode. The reference electrode was a non-aqueous Ag/Ag⁺ electrode (CH Instruments, 0.01 M AgNO₃ in acetonitrile) with a potential of -0.08 V vs the ferrocenium/ferrocene (Fc⁺⁰) couple in acetonitrile as an external standard or a silver wire quasi reference electrode (-0.41 V vs Fc⁺⁰) for fast voltammetry. All potentials reported here are vs the Fc⁺⁰ couple. The diffusion coefficient of **1**, $D = 1.0 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$, was obtained from the limiting current in steady state voltammograms relative to a value of $D = 2.6 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ for ferrocene. All electrochemical measurements were done at room temperature (295 K).

Spectroscopy Spectroelectrochemical measurements were made in an OTTLE-type quartz cell with an optical path length of 1 mm. A platinum grid with a size of 10 × 30 mm² and 400 meshes per cm² was used as working electrode. The counter and reference (Ag/Ag⁺) electrodes were of the same type as described in the electrochemistry paragraph. Samples were bubbled for 20 min with solvent saturated argon and transferred to the argon-flushed cell with the argon stream. The spectra were recorded on an UV-Vis diode array spectrophotometer (Hewlett Packard 8435) with the background collected on electrolyte solution in the potential free OTTLE cell. Kinetic measurements were performed on the same spectrophotometer with a temperature controlled sample holder.

Synthesis The compound 1-[6-(2,2'-bipyridyl)]-1-(2-pyridyl)-ethanol and the corresponding heteroleptic ruthenium(II) complex **1** were prepared as reported earlier.¹ ¹H NMR (**1**) (CD₃CN, 298 K): δ 1.75 (s, 3H), 2.53 (s, 3H), 6.63 (s, 1H), 6.87 (ddd, 1H), 7.04-7.12 (m, 3H), 7.18 (m, 1H), 7.33 (ddd, 1H), 7.40 (m, 1H), 7.58 (d, 2H), 7.68 (ddd, 1H), 7.76-7.86 (m, 2H), 8.01 (dt, 1H), 8.08-8.15 (m, 3H), 8.26 (m, 1H), 8.37 (m, 1H), 8.41 (t, 1H), 8.49 (m, 1H), 8.63 (dd, 1H), 8.69 (m, 1H), 8.83 (dd, 1H), 8.89 (d, 1H), 8.99 (d, 1H); MALDI-TOF MS: *m/z* [M-2PF₆⁻-H⁺]⁺ 701.04 (calc. for C₃₉H₃₁N₆ORu: 701.16); elemental analyses calc. (%) for C₃₉H₃₂N₆ORuP₂F₁₂: C 47.23, H 3.25, N 8.47. Found: C 47.14, H 3.37, N 8.43.

Complex **1** (0.010 g, 0.01 mmol) was dissolved in DMF (1 mL) and added in one portion to *t*-BuOK (2.2 mg, 0.02 mmol) and the solution was left stirring for 15 min. Diethylether was added and the resulting solid was filtered off and washed with additional Et₂O to give **2**. ¹H NMR (CD₃CN, 298 K): δ 1.65 (s, 3H), 2.47 (s, 3H), 6.72 (ddd, 1H), 6.83 (ddd, 1H), 6.88-7.00 (m, 4H), 7.07 (dt, 1H), 7.26 (ddd, 1H), 7.41 (d, 2H), 7.49 (m, 1H), 7.56-7.66 (m, 2H), 7.77 (dt, 1H), 8.01 (d, 2H), 8.12-8.22 (m, 2H), 8.30-8.37 (m, 2H), 8.44 (d, 1H), 8.48 (d, 1H), 8.54 (dd, 1H), 8.75 (d, 1H), 8.77 (d, 1H).

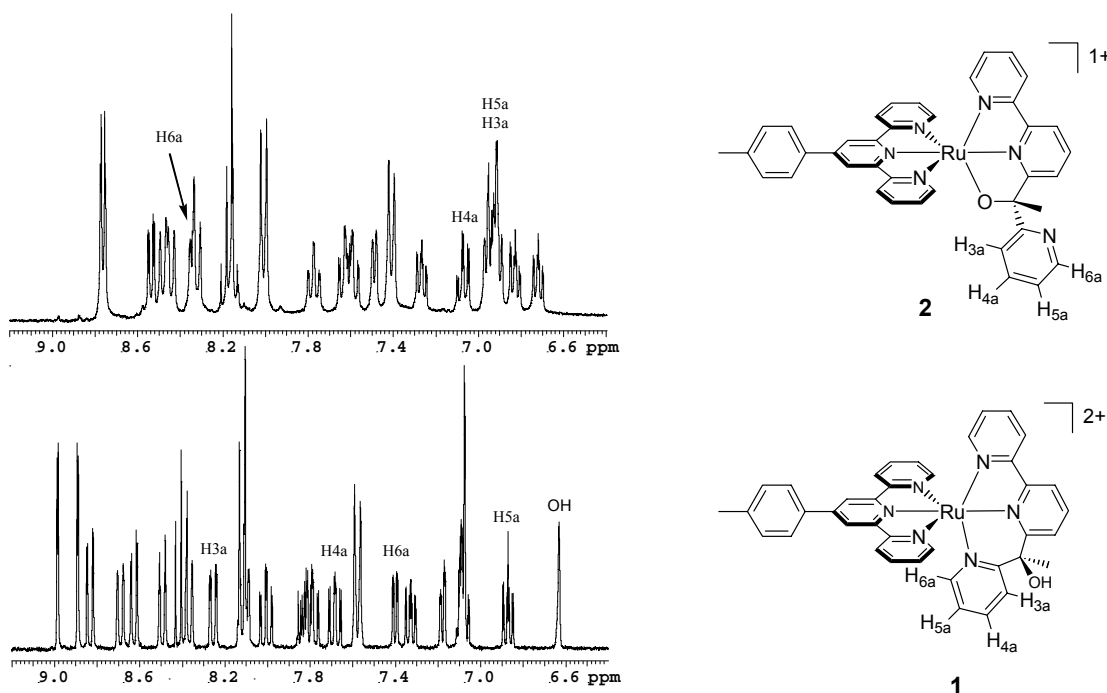


Figure S1. ¹H NMR spectra of **2** and **1** recorded in CD₃CN (300 MHz, 298 K).

¹ M. Abrahamsson, H. Wolpher, O. Johansson, J. Larsson, M. Kritikos, L. Eriksson, P.-O. Norrby, J. Bergquist, L. Sun, B. Åkermark, L. Hammarström, *Submitted*.

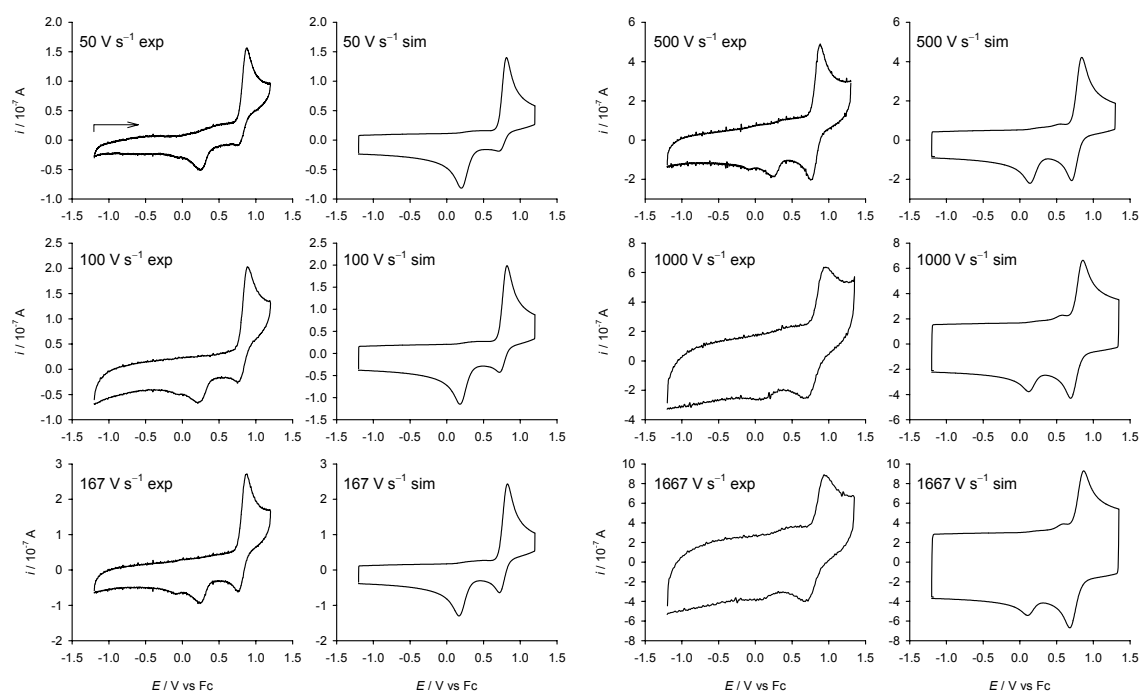


Figure S2. Scan rate dependency of cyclic voltammograms of **1** (5 mM) at a Pt microdisc electrode ($\varnothing = 25 \mu\text{m}$) in CH_3CN with 0.5 M $(n\text{-C}_4\text{H}_9)_4\text{NPF}_6$ and digital simulations according to the square scheme shown in Scheme 2. Experimental (exp) and simulated (sim) voltammograms show the last of six scans. Scan rates and direction as indicated in the graph. Simulation parameters: $[\mathbf{1}] = 5 \times 10^{-3}$ M (the initial concentration of all other species is zero), $D = 1.0 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ was determined for **1** (see Experimental) and the same value was used for all species in the square scheme. $A = 4.91 \times 10^{-6} \text{ cm}^2$, $E_{1/2}(\text{I}) = 0.77 \text{ V}$, $k^0(\text{I}) = 0.2 \text{ cm s}^{-1}$, $\alpha(\text{I}) = 0.5$, $E_{1/2}(\text{II}) = 0.35 \text{ V}$, $k^0(\text{II}) = 0.01 \text{ cm s}^{-1}$, $\alpha(\text{II}) = 0.5$, $k_1 = 600 \text{ s}^{-1}$, $k_2 = 500 \text{ s}^{-1}$, $k_{-1} = k_{-2} = 0.03^{1/2}$. (Within the limits of the estimated k_{-1} and k_{-2} the effect of the back reactions on the simulated voltammograms is negligible.)

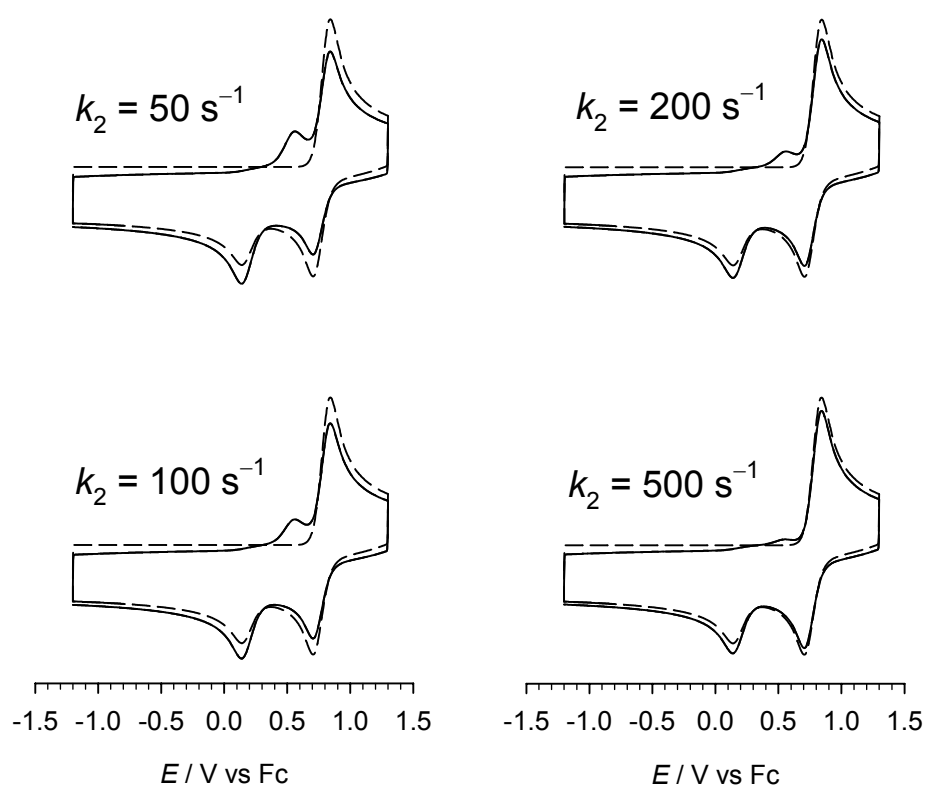


Figure S3. Simulated cyclic voltammograms with a scan rate of $\nu = 500 \text{ Vs}^{-1}$. First scan (--) and scan six (–) for different values of the isomerization rate constant k_2 . All other simulation parameters as in Figure S2. The absence of the anodic peak at 0.5 V in the experimental voltammogram with $\nu = 500 \text{ Vs}^{-1}$ (see Figure S2) indicates $k_2 \geq 500 \text{ s}^{-1}$. The minor peaks at 0.5 V at higher scan rates (see Figure S2) show that k_2 does not substantially exceed the lower limit and thus $k_2 \approx 500 \text{ s}^{-1}$.

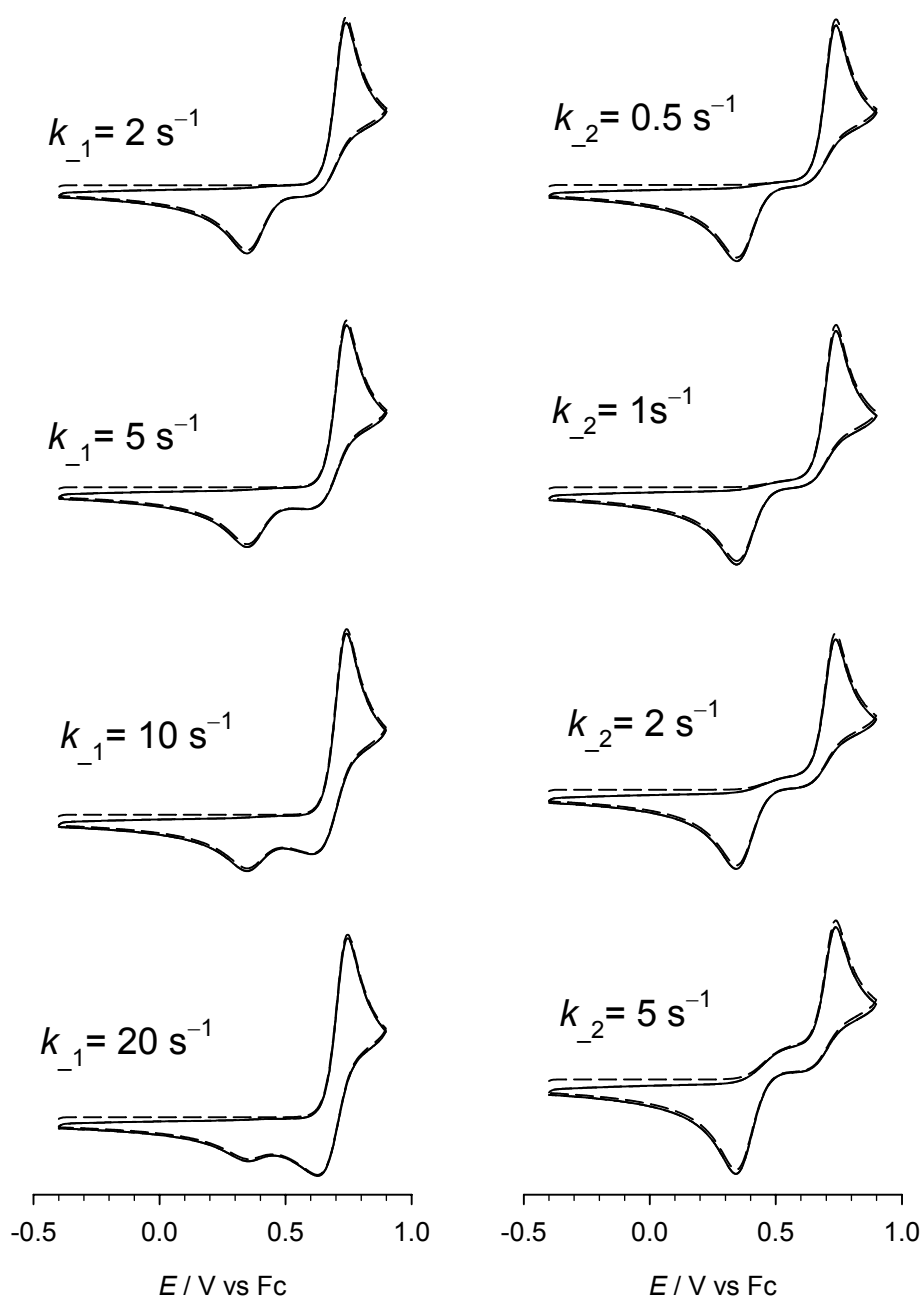


Figure S4. Simulated cyclic voltammograms with a scan rate of $\nu = 0.10 \text{ V s}^{-1}$ on a macro electrode ($\varnothing = 3 \text{ mm}$). First (---) and second (–) scans for different values of the reverse isomerization rate constants k_{-1} (left column) and k_{-2} (right column). The product $k_{-1} k_{-2}$ is always 0.03 s^{-2} as required by the thermodynamic cycle ($\Delta E_{1/2} = 0.06 \log \{(k_1 k_2)/(k_{-1} k_{-2})\}$) and all other simulation parameters are the same as in Figure S2. Comparison with the experimental voltammogram in Figure 1a allows one to estimate upper limits of $k_{-1} \leq 10 \text{ s}^{-1}$ and $k_{-2} \leq 2 \text{ s}^{-1}$.

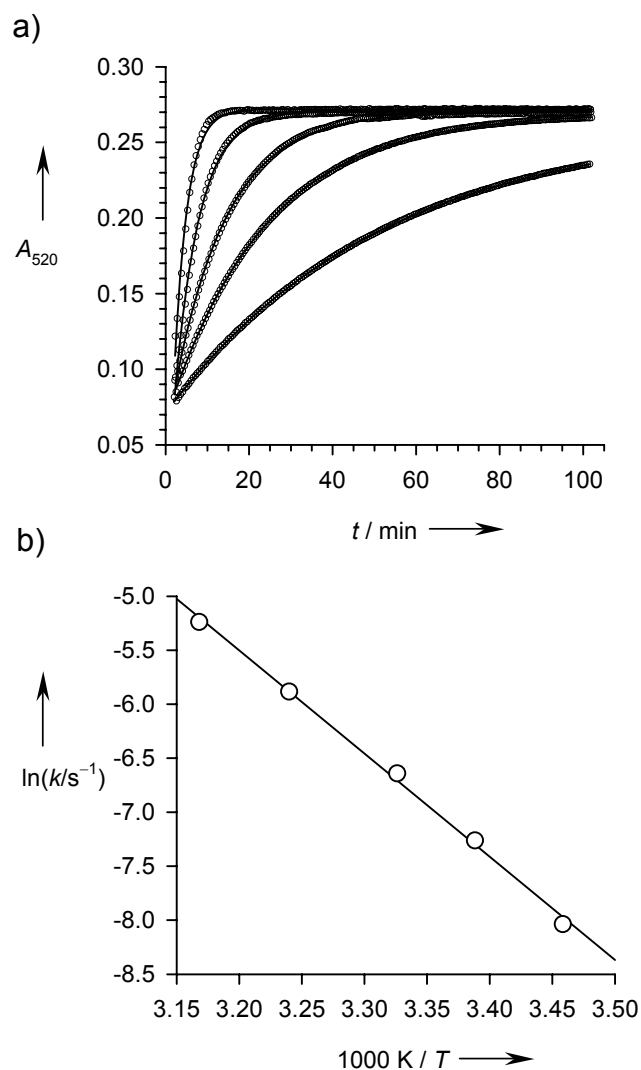


Figure S5. Kinetics of the base induced isomerization reaction. (a) Absorption changes (\circ) and exponential fits ($-$) at 520 nm after addition of NaOMe (2 mM) to a solution of **1** (1.94×10^{-5} M) in MeOH at 289, 295, 300.5, 308.5, and 315.5 K. (b) Arrhenius plot of rate constants from (a) and least square fit with $E_a = 79.4 \text{ kJ mol}^{-1}$ and $\ln(A \text{ s}) = 25.05$.