

Photochemistry between a ruthenium(II) pyridylimidazole complex and benzoquinone: Simple electron transfer versus proton-coupled electron transfer

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Supporting Information

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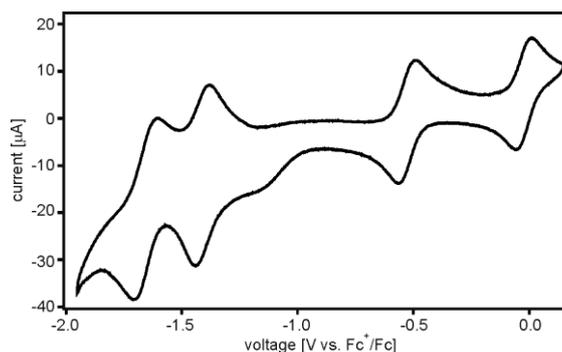


Figure S1. Cyclic voltammogram of complex **1** in dry and de-oxygenated CH₃CN solution showing the reductive side of the entire potential sweep. The prominent reversible waves at 0.0 V vs. Fc⁺/Fc and at -0.51 V vs. Fc⁺/Fc are due to ferrocene and decamethylferrocene, respectively, which were added in small quantities for internal voltage calibration. The waves below -1.0 V vs. Fc⁺/Fc are due to bipyridine reductions. 0.1 M tetrabutylammonium hexafluoride (TBAPF₆) was used as an electrolyte.

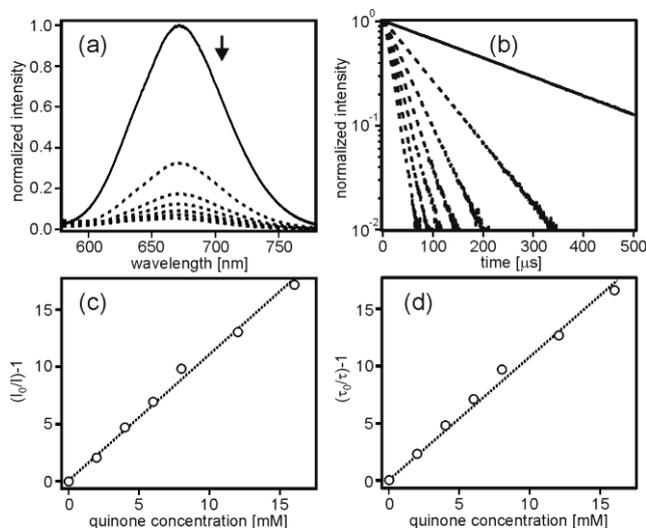


Figure S2. (a) Luminescence spectra of a $\sim 10^{-5}$ M solution of complex **1** in 1:1 (v:v) CH₃CN/D₂O acidified with aqueous DCl to a pH meter reading of 4 measured after excitation at 470 nm; solid trace: solution containing complex **1** only; dashed traces: solutions containing 2 mM, 4 mM, 6 mM, 8 mM, 12 mM, 16 mM benzoquinone concentrations; the data is normalized arbitrarily to a value of 1.0 for the highest intensity. (b) Decays of the luminescence intensities at 670 nm of the solutions from (a) after excitation at 532 nm with laser pulses of ~ 8 ns width. (c) Stern-Volmer plot based on the luminescence intensity data from (a); the dashed line is the result of a linear regression fit (forced to an ordinate of 0) yielding the K_{SV} value of 1129 ± 27 M⁻¹ in Table 2. (d) Stern-Volmer plot based on the luminescence lifetime data from (b); the dashed line is the result of a linear regression fit (forced to an ordinate of 0) yielding the K_{SV} value of 1124 ± 28 M⁻¹ in Table 2.

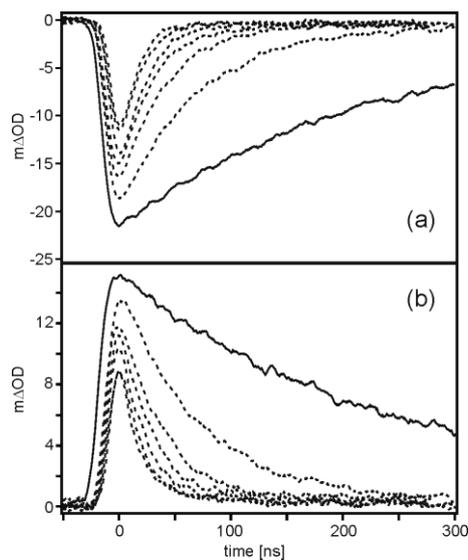


Figure S3. (a) MLCT bleach recoveries observed at 490 nm in transient absorption spectroscopy of complex **1** in de-oxygenated 1:1 (v:v) CH₃CN/H₂O solution after excitation at 532 nm with pulses of ~8 ns width. (b) Temporal evolution of the transient absorption signal at 380 nm in the same solutions. Solid traces: Transients obtained in absence of benzoquinone; dashed traces: transients obtained from solutions with 2 mM, 4 mM, 6 mM, 8 mM, 12 mM, 16 mM of 1,4-benzoquinone.