

Supporting Information for

Proton-Coupled Electron Transfer of Ruthenium(III)-
Pterin Complexes: A Mechanistic Insight

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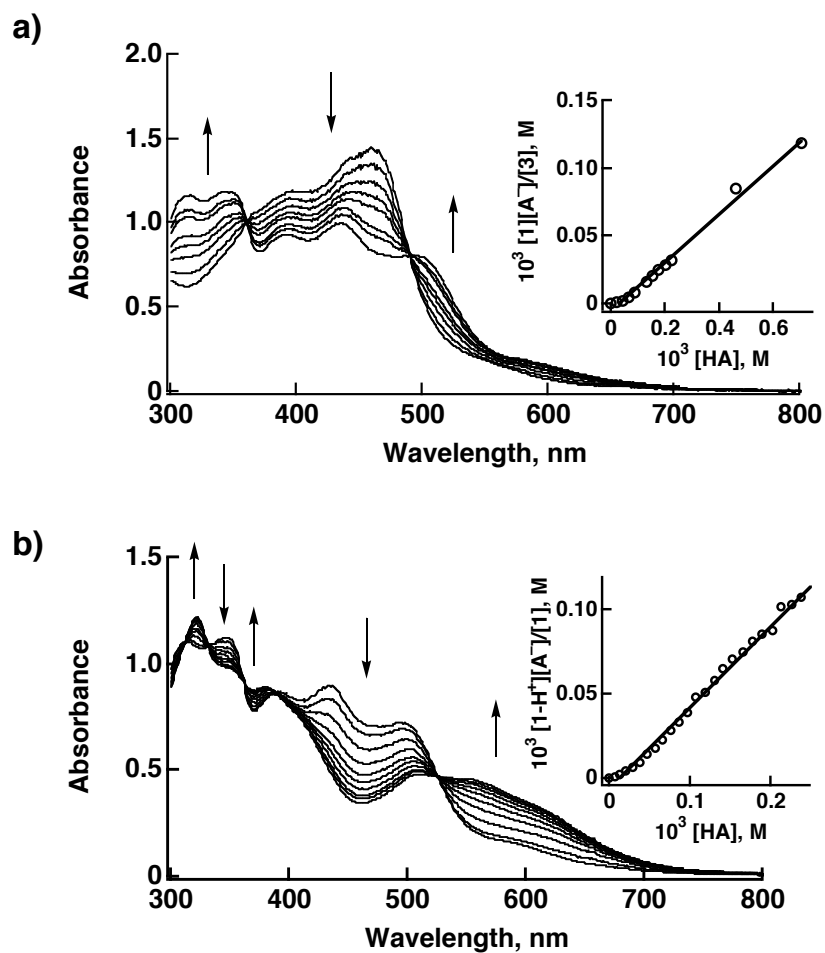


Figure S1. (a) UV-Vis spectral change for the first protonation step of **3** upon addition of HClO₄. Insets are plot of $[1][A]/[3]$ vs. $[HA]$ ($HA = 2,6\text{-dichlorobenzoic acid}$). (b) For the second protonation step of **3** upon addition of HClO₄ for **1**. Insets are plot of $[1-H^+][A]/[1]$ vs. $[HA]$ ($HA = HClO_4$).

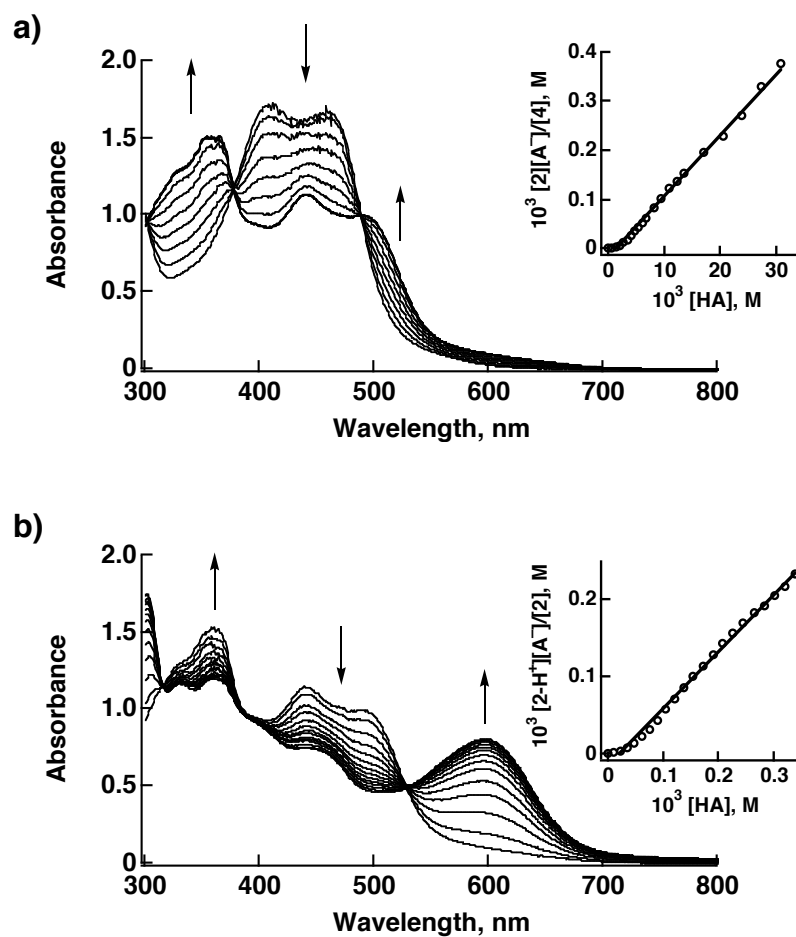


Figure S2. (a) UV-Vis spectral change for the first protonation step of **4** upon addition of HClO_4 . Insets are plot of $[2][A]/[4]$ vs. $[HA]$ ($HA = 2,6\text{-dichlorobenzoic acid}$). (b) For the second protonation step upon addition of HClO_4 for **4**. Insets are plot of $[2\text{-H}^+][A]/[2]$ vs. $[HA]$ ($HA = \text{HClO}_4$).

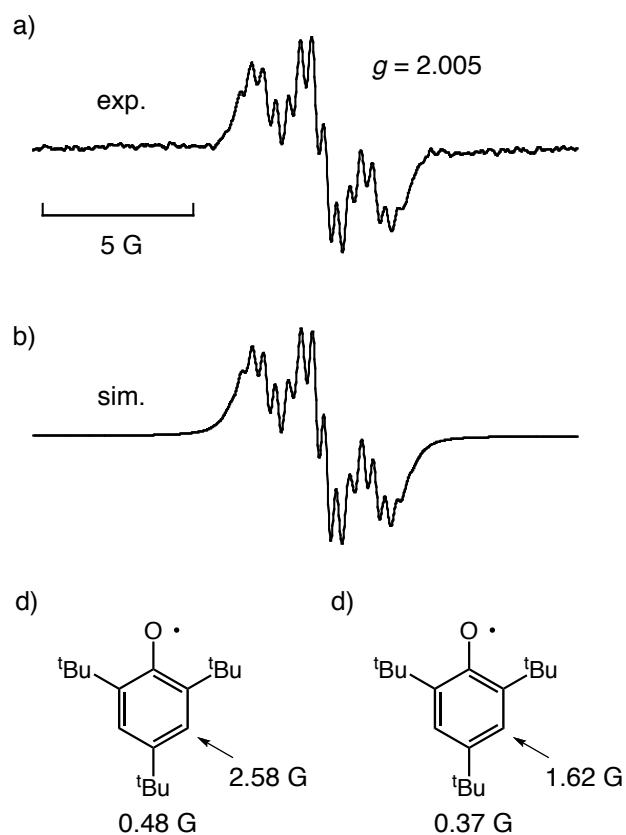


Figure S3. a) Experimental ESR spectrum of 2,4,6-tri-*tert*-butyl phenoxyl radical obtained by the hydrogen atom transfer reaction from 2,4,6-tri-*tert*-butyl phenol to $[\text{Ru}^{\text{III}}(\text{dmp})(\text{TPA})]^{2+}$. b) The computer simulation spectrum with $\Delta H_{\text{msl}} = 1.4$ G. c) Hyperfine coupling constant based on spin density obtained by DFT calculation. d) The hyperfine coupling constants used for the simulation. Values are given in gauss.

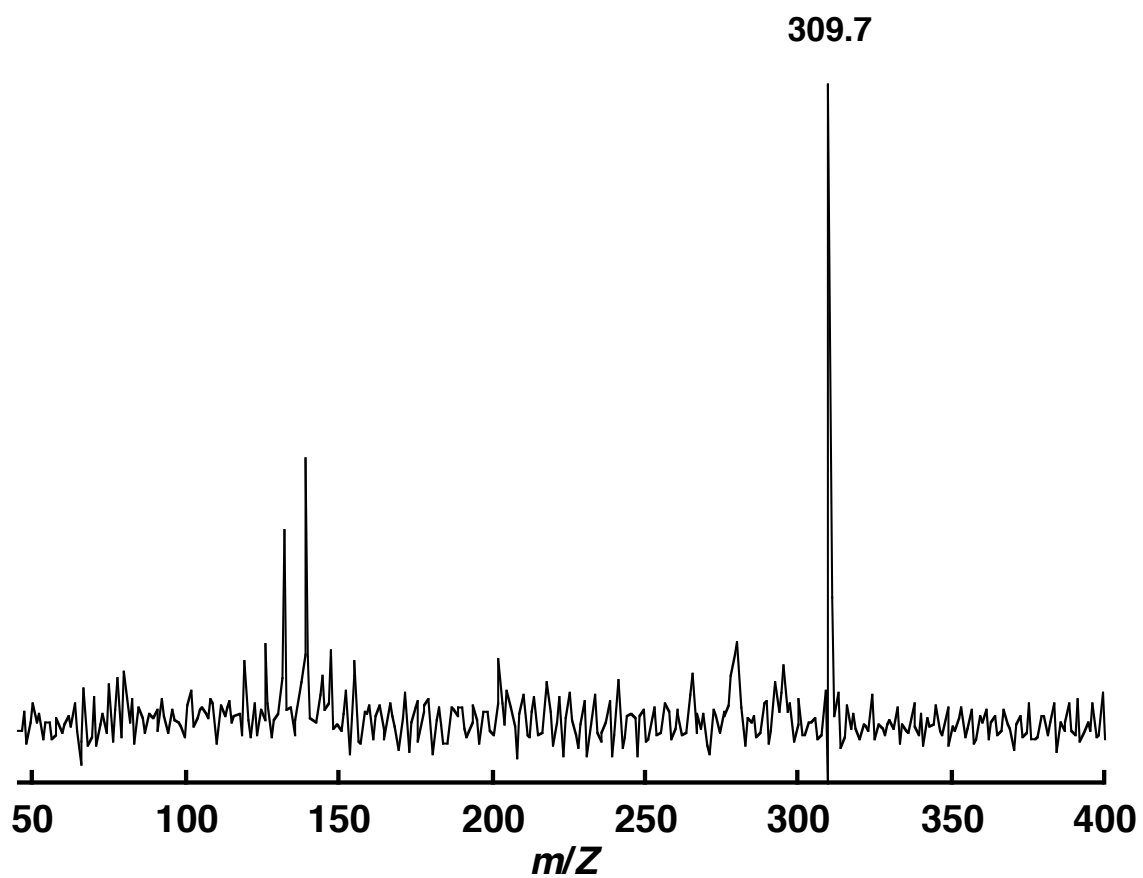


Figure S4. The mass spectrum of reaction mixture obtained by the reaction of 4-nitrophenol with $[\text{Ru}^{\text{III}}(\text{dmp})(\text{TPA})]^{2+}$ in MeCN.