Supporting Information

Thermochromism of Metal Ion Complexes of Semiquinone Radical Anions. Control of Equilibria between Diamagnetic and Paramagnetic Species by Lewis Acids

Junpei Yuasa, Tomoyoshi Suenobu, and Shunichi Fukuzumi*

Department of Material and Life Science, Division of Advanced Science and Biotechnology, Graduate School of Engineering, Osaka University, SORST, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan

* To whom correspondence should be addressed.

E-mail: fukuzumi@chem.eng.osaka-u.ac.jp

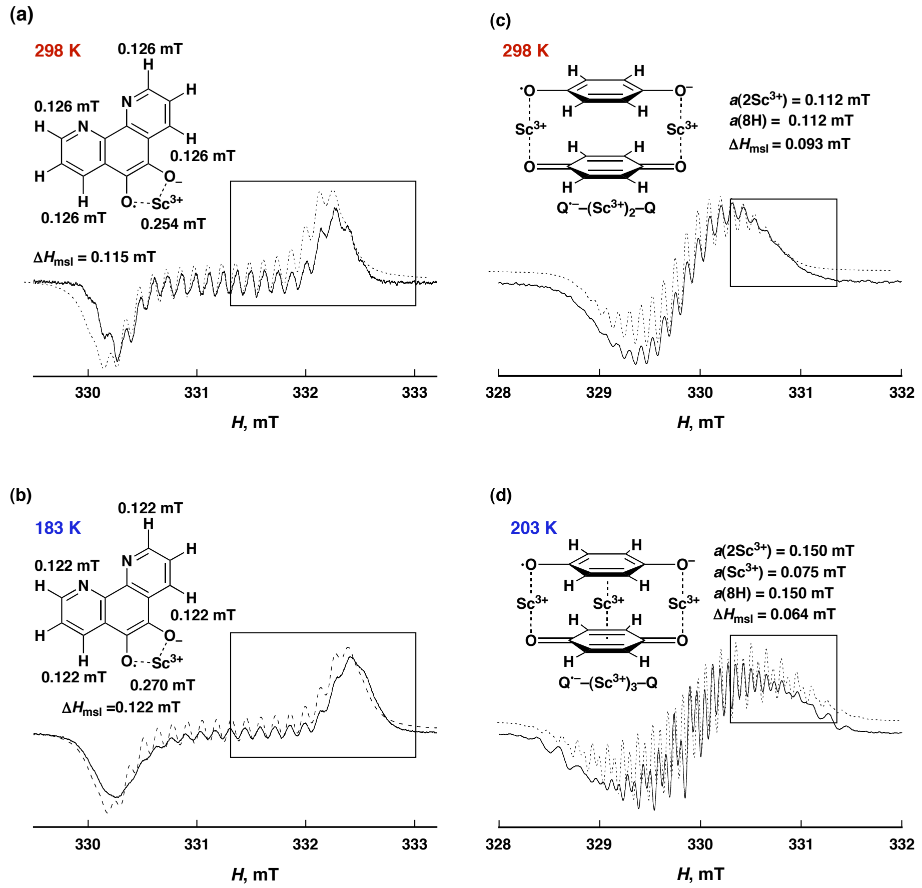

Figure S1. ESR spectra of a deaerated EtCN solution of Me_2Fc (3.6×10^{-4} M) and PTQ (3.9×10^{-4} M) in the presence of $Sc(OTf)_3$ (4.0×10^{-1} M) at (a) 298 K and (b) 183 K. ESR spectra of a deaerated EtCN solution of QH_2 (3.2×10^{-3} M) and Q (1.8×10^{-2} M) in the presence of $Sc(OTf)_3$ (3.2×10^{-1} M) at (c) 298 K and (d) 203 K. Broken lines show the computer simulation spectra. The *hfs* values are given with the structures of metal ion complexes of the radical anions. The boxed areas are magnified and shown in Figures 3c and 3d.

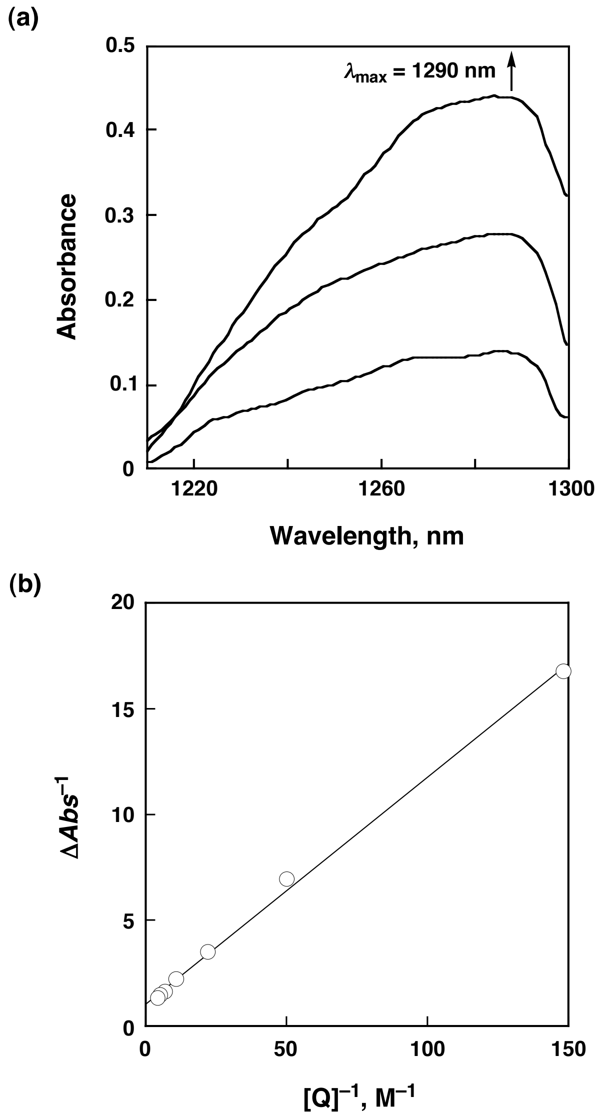

Figure S2. (a) Absorption spectral change of $Q_2^{\bullet-}$ in the NIR region observed by addition of Q (2.0×10^{-2}, 4.5×10^{-2}, and 9.3×10^{-2} M, spectra from bottom to up) to a deaerated MeCN solution of $Q^{\bullet-}$ (5.0×10^{-4} M) at 298 K. (b) Plot of ΔAbs^{-1} vs $[Q]^{-1}$.

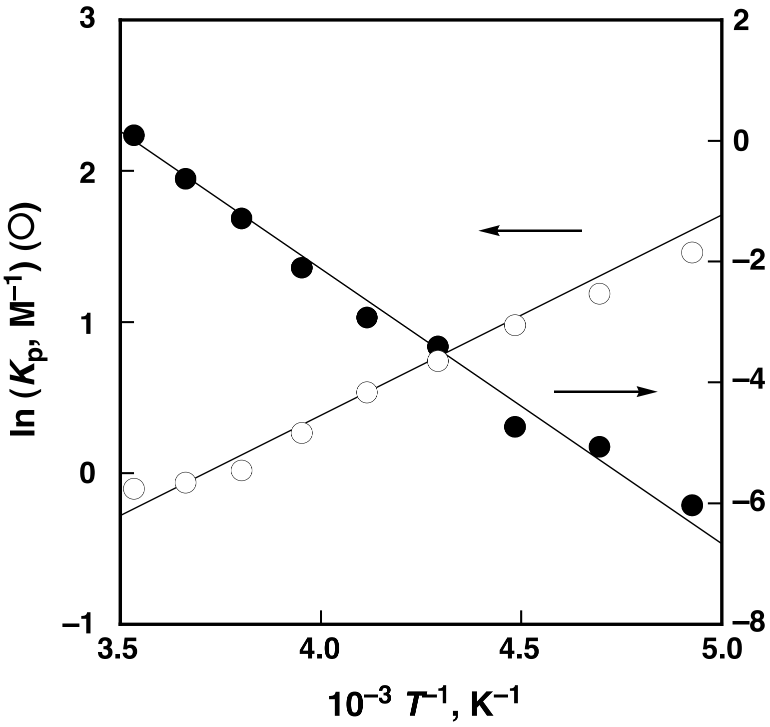

Figure S3. Plots of logarithm of equilibrium constants of the electron-transfer equilibrium (K_{et}, ●) and the proportionation equilibrium (K_p, ○) vs T^{-1}.

K_{et} = $[PTQ^{\bullet -}–Mg^{2+}]^2/\{([Me_2Fc]_0 – [PTQ^{\bullet -}–Mg^{2+}])([PTQ]_0 – [PTQ^{\bullet -}–Mg^{2+}])([Mg^{2+}]_0 – [PTQ^{\bullet -}–Mg^{2+}])\}$

Where, $[Me_2Fc]_0 = 1.7 \times 10^{-3}$ M, $[PTQ]_0 = 1.7 \times 10^{-3}$ M, and $[Mg^{2+}]_0 = 3.3 \times 10^{-3}$ M.

K_p = $4[PTQ^{\bullet -}–Sc^{3+}]^2/\{([Me_2Fc]_0 – [PTQ^{\bullet -}–Sc^{3+}])(2[PTQ]_0 – [PTQ^{\bullet -}–Sc^{3+}] – [Me_2Fc]_0)[Sc^{3+}]_0\}$

Where, $[Me_2Fc]_0 = 3.6 \times 10^{-4}$ M, $[PTQ]_0 = 3.9 \times 10^{-4}$ M, and $[Sc^{3+}]_0 = 1.7 \times 10^{-2}$ M.