Electronic Supplementary Information

Acid-promoted hydride transfer from an NADH analogue to a Cr(III)-superoxo complex *via* proton-coupled hydrogen atom transfer

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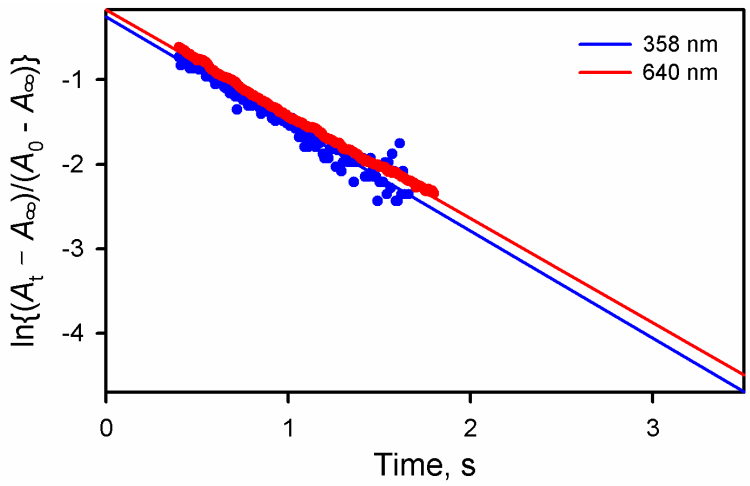

Fig. S1 (a) First-order plot of $\ln\{(A_t - A_\infty)/(A_0 - A_\infty)\}$ against time for the time courses of absorbance at 640 nm due to the decay of $AcrH_2^{\bullet+}$ (red circles) and 358 nm due to the formation of $AcrH^+$ (blue circles) observed in the reaction of $AcrH_2$ (1.0 mM) with **1** (0.050 mM) in the presence of HOTf (10 mM) in MeCN at 233 K (see inset of Fig. 1b in text).

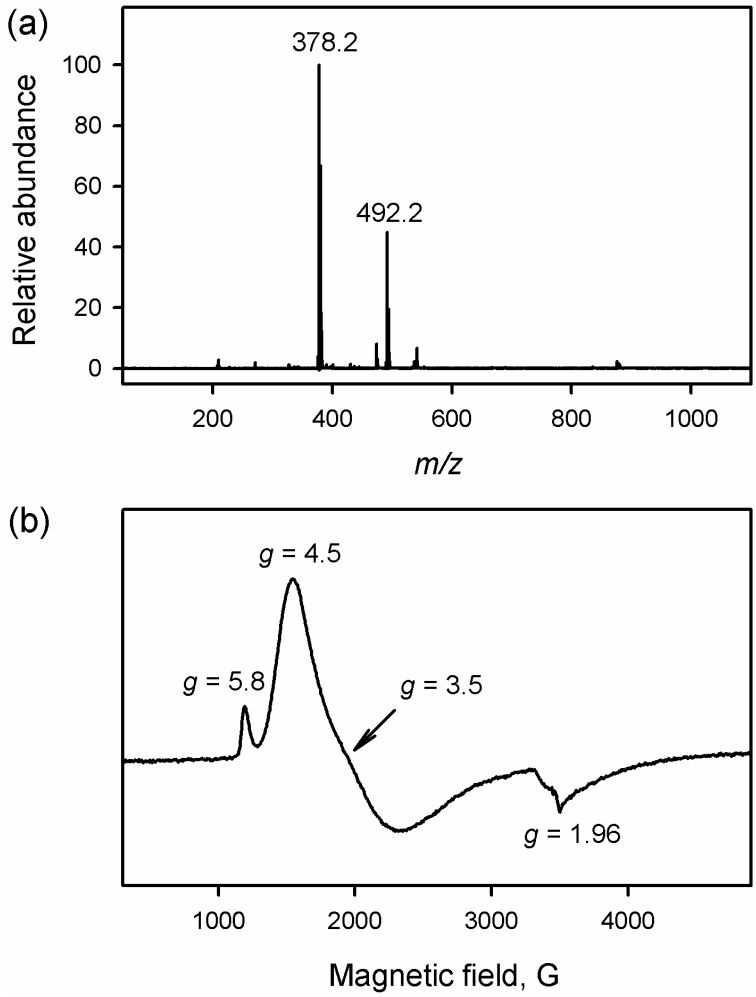

Fig. S2 (a) CSI-MS spectrum of the complete reaction solution obtained in the hydride-transfer reaction from $AcrH_2$ (0.75 mM) by **1** (0.50 mM) in the presence of HOTf (1.3 mM) in MeCN at 233 K. The peaks at *m/z* = 378.2 and 492.2 correspond to $[Cr^{III}(TMC)(Cl_2)]^+$ (*calc. m/z* = 378.1) and $[Cr^{III}(TMC)(Cl)(OTf)]^+$ (*calc. m/z* = 492.1), respectively. (b) X-band EPR spectrum of the complete reaction solution obtained in the oxidation of $AcrH_2$ (0.75 mM) by **1** (0.50 mM) in the presence of HOTf (1.3 mM) in MeCN at 233 K. The spectrum was recorded at 5 K.