Electronic Supplementary Information for Dalton Transactions

Electronic Supplementary Information

for

Photoinduced Four- and Six-Electron Reduction of Mononuclear Ruthenium Complexes Having NAD^+ Analogous Ligands

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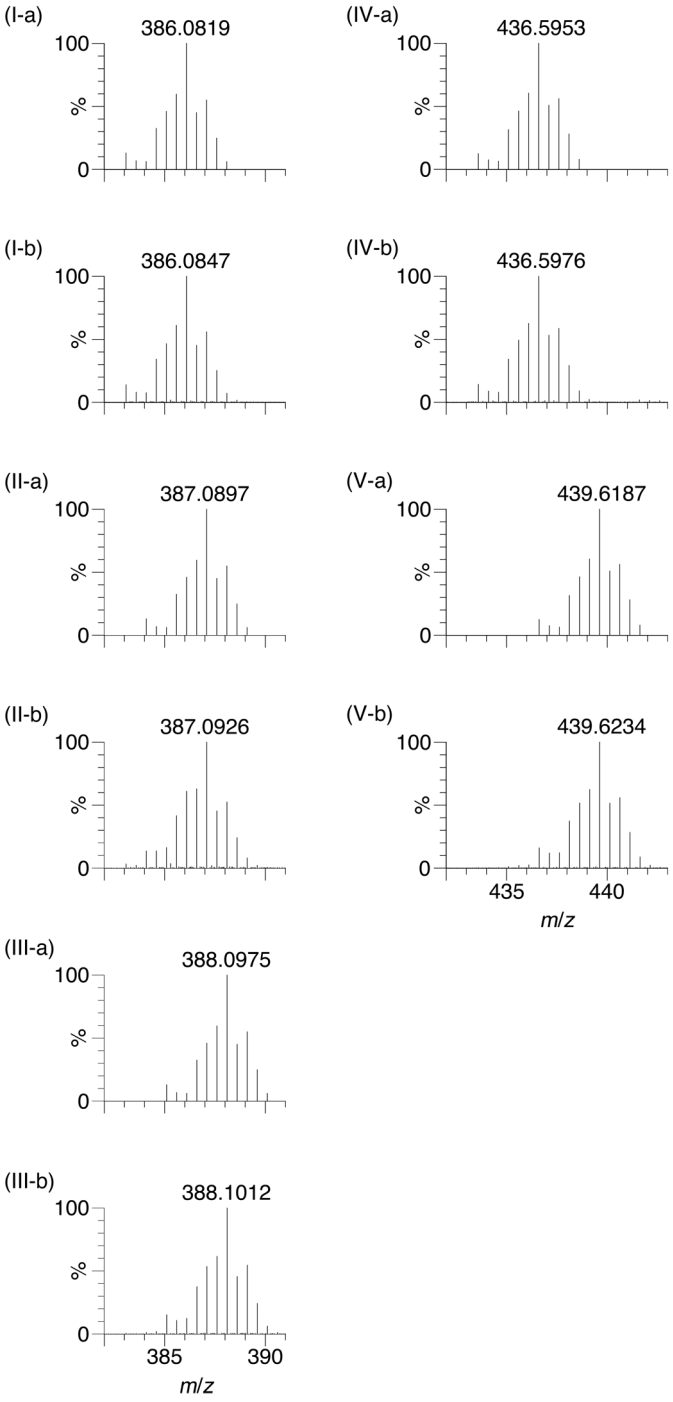

Fig. S1 HR-ESI-MS spectra of $[\mathbf{2}]^{2+}$ (I), $[\mathbf{2}\bullet H_2]^{2+}$ (II), $[\mathbf{2}\bullet H_4]^{2+}$ (III), $[\mathbf{3}]^{2+}$ (IV), and $[\mathbf{3}\bullet H_6]^{2+}$ (V); (a) Simulation and (b) Experimental.

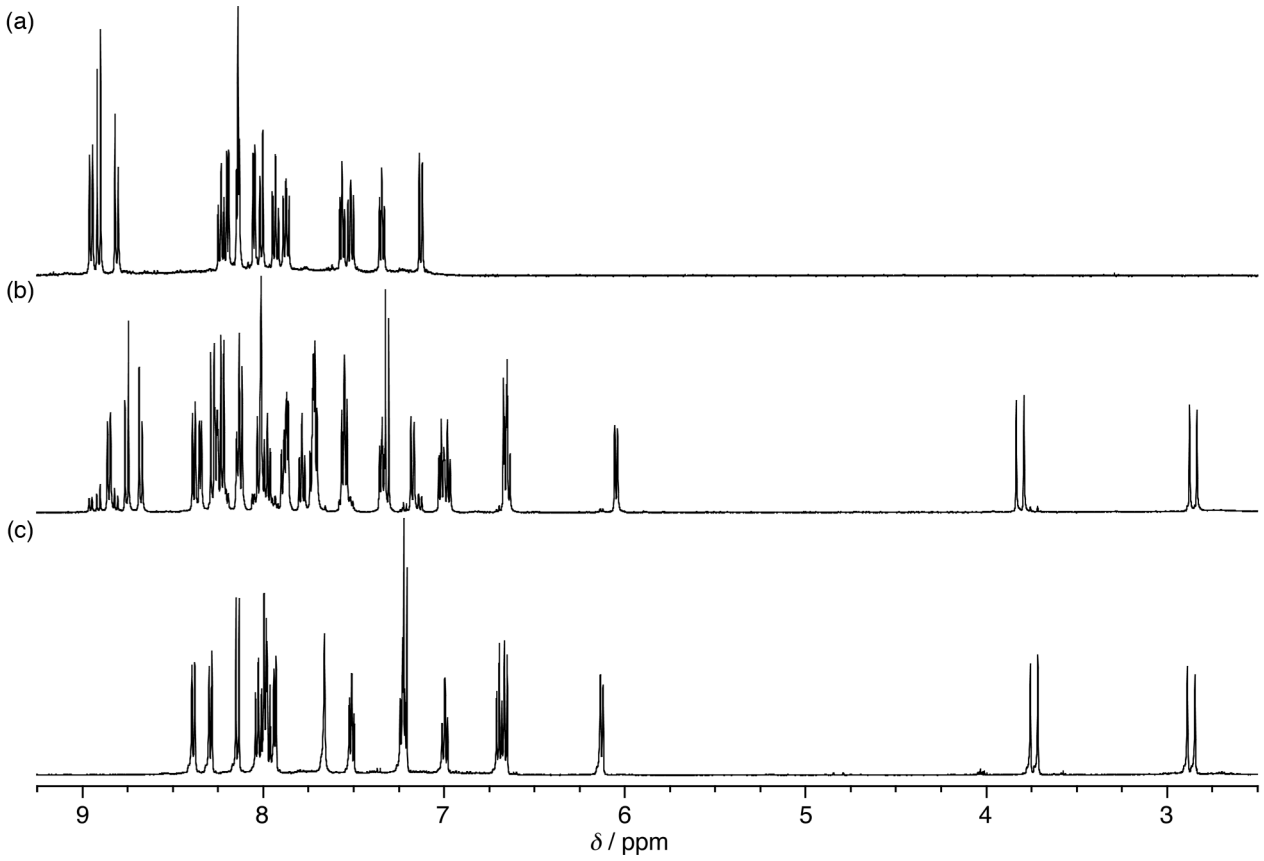

Fig. S2 ^{1}H NMR of (a) $[\mathbf{2}]^{2+}$, (b) $[\mathbf{2}\bullet H_2]^{2+}$ and (c) $[\mathbf{2}\bullet H_4]^{2+}$ in CD_3CN.

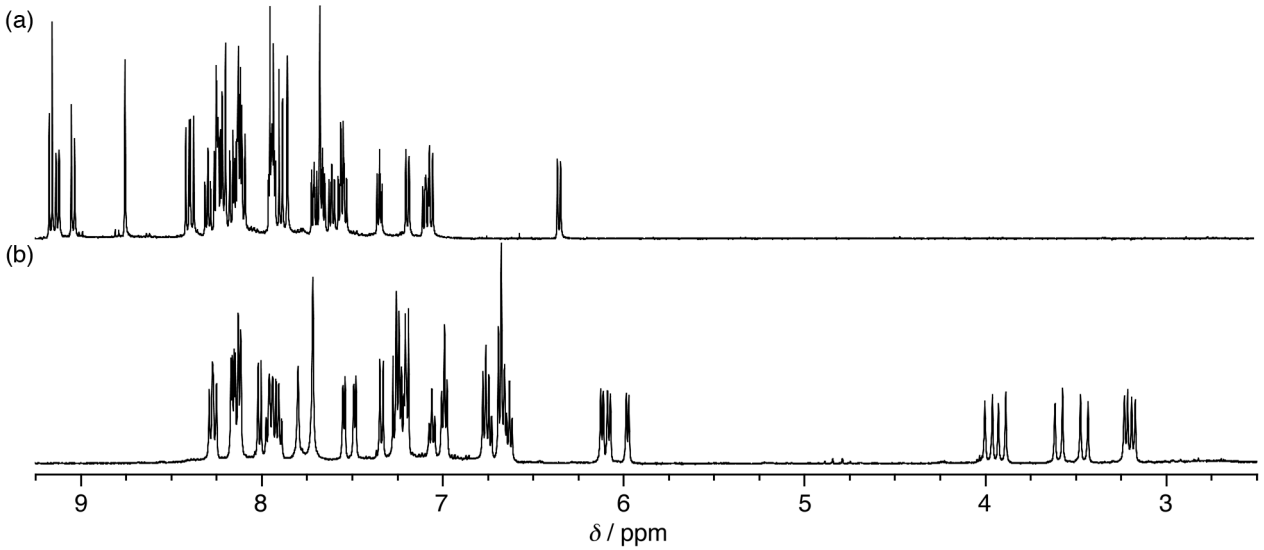

Fig. S3 ^{1}H NMR spectra of (a) $[\mathbf{3}]^{2+}$ and (b) $[\mathbf{3}\bullet H_6]^{2+}$ in CD_3CN.

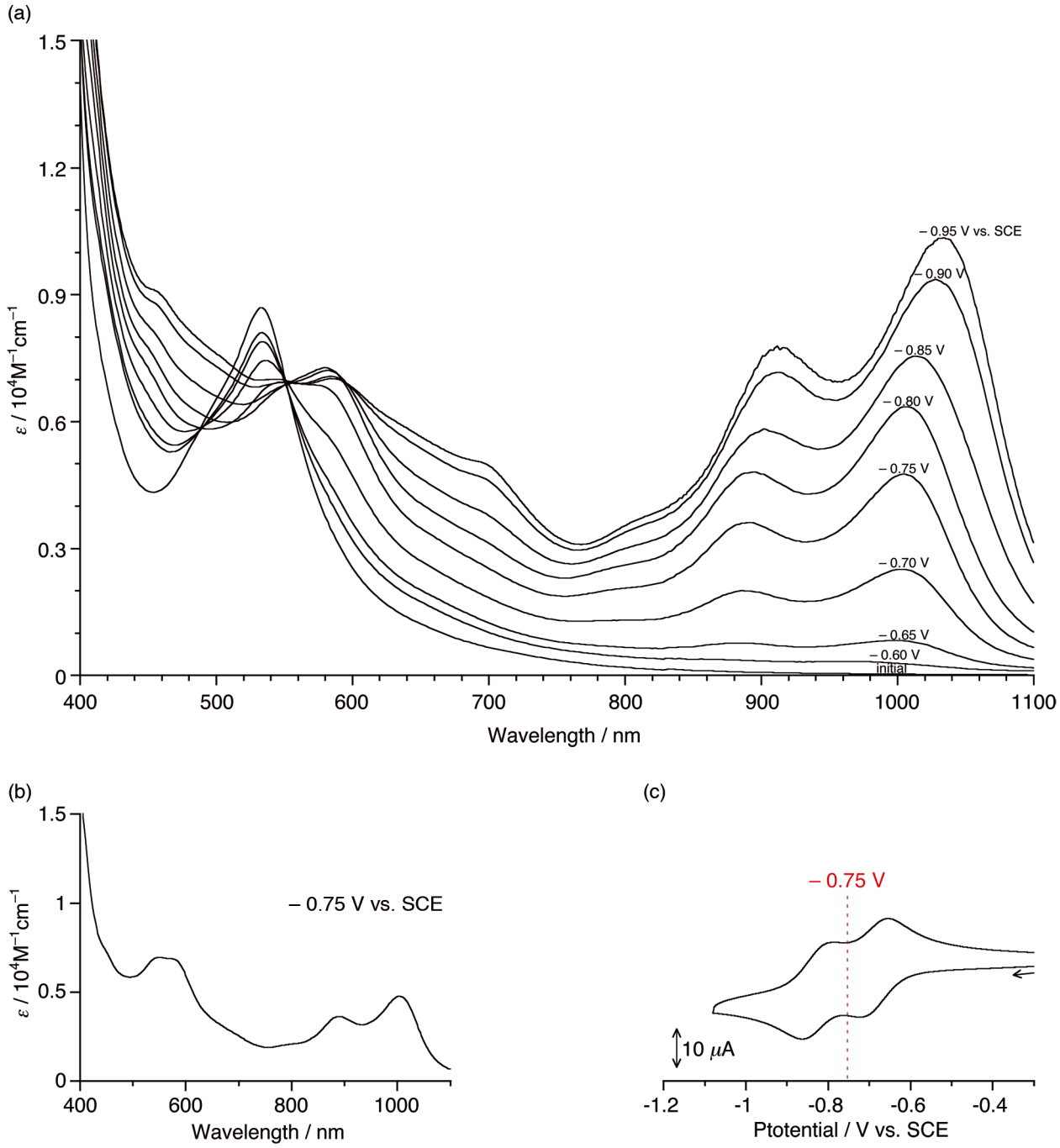

Fig. S4 (a) The electronic absorption spectra of $[\mathbf{2}]^{2+}$ under the electrolysis at various potentials in CH_3CN containing 0.1 M *n*-Bu_4NPF_6. (b) The spectrum measured at –0.75 V is consistent with that of $[\mathbf{2}]^{2+}$ after irradiation of visible light for 10 min. in dry CH_3CN/TEA (Fig. 5(a)). Based on (c) the cyclic voltammogram of $[\mathbf{2}]^{2+}$ in CH_3CN, electrolysis of the complex at –0.75 V evidently generates $[Ru(bpy)(pbn)(pbn^{\bullet-})]^{+}$ in the solution.

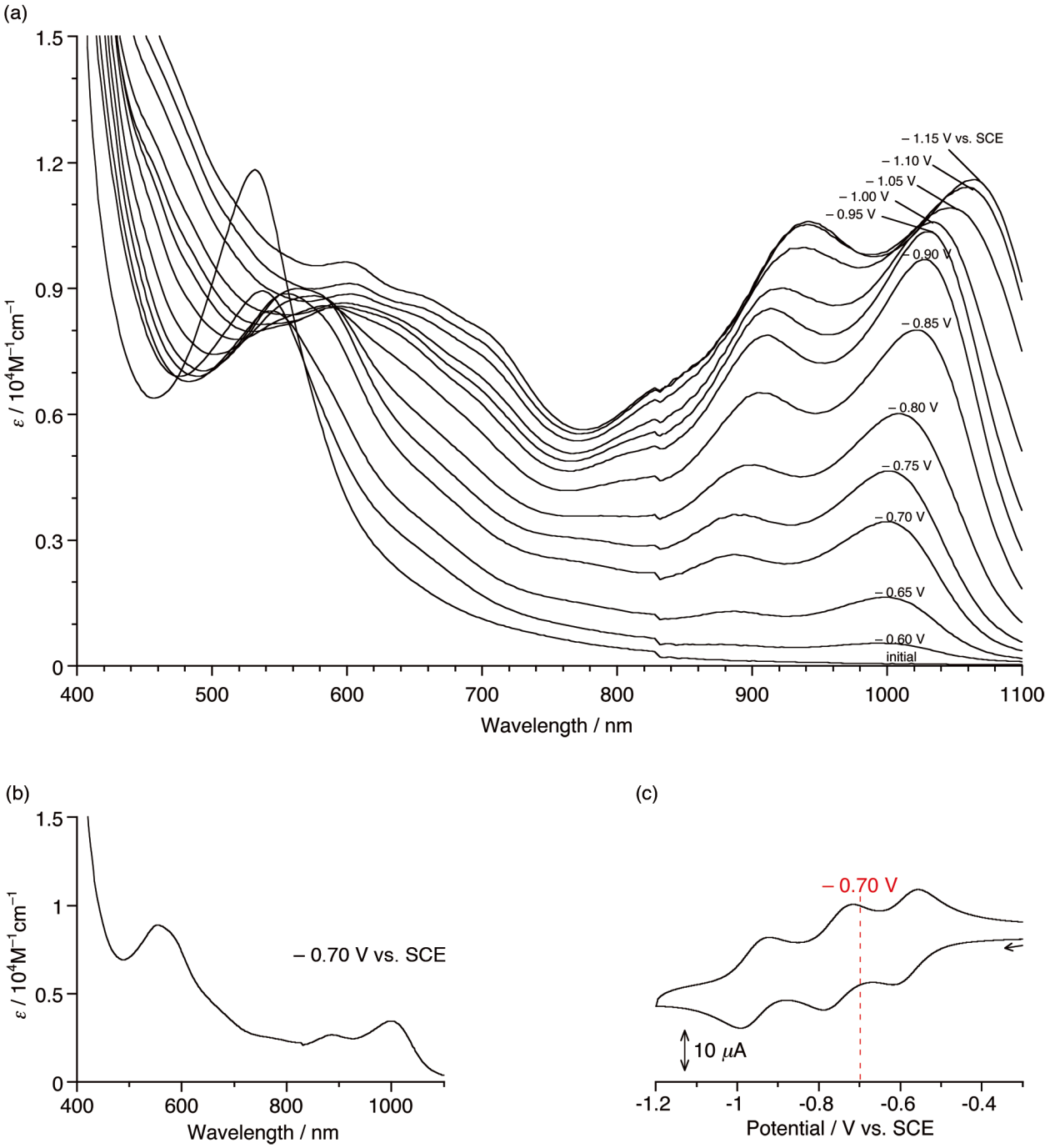

Fig. S5 (a) The electronic absorption spectra of $[\mathbf{3}]^{2+}$ under the electrolysis at various potentials in CH_3CN containing 0.1 M *n*-Bu_4NPF_6. (b) The spectrum measured at –0.70 V is consistent with that of $[\mathbf{3}]^{2+}$ after irradiation of visible light for 10 min. in dry CH_3CN/TEA (Fig. 5(b)). Based on (c) the cyclic voltammogram of $[\mathbf{3}]^{2+}$ in CH_3CN, electrolysis of the complex at –0.70 V evidently generates $[Ru(pbn)_2(pbn^{\bullet-})]^{+}$ in the solution.

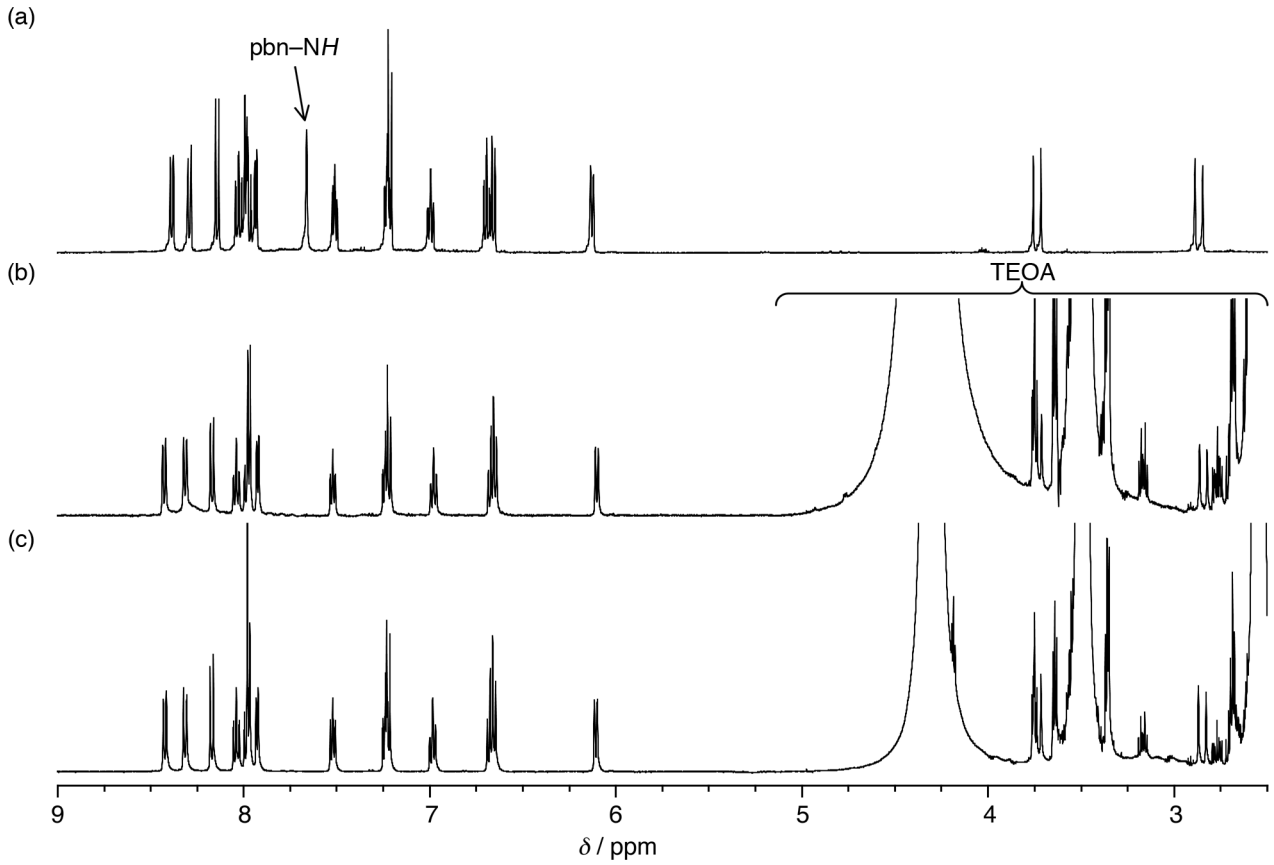

Fig. S6 ^{1}H NMR spectra of $[\mathbf{2}\bullet H_4]^{2+}$ produced (a) by the reduction of $[\mathbf{2}]^{2+}$ with $Na_2S_2O_4$, (b) by the photochemical reduction of $[\mathbf{2}]^{2+}$ and (c) that of $[\mathbf{2}\bullet H_2]^{2+}$ in CD_3CN/TEOA under visible light.

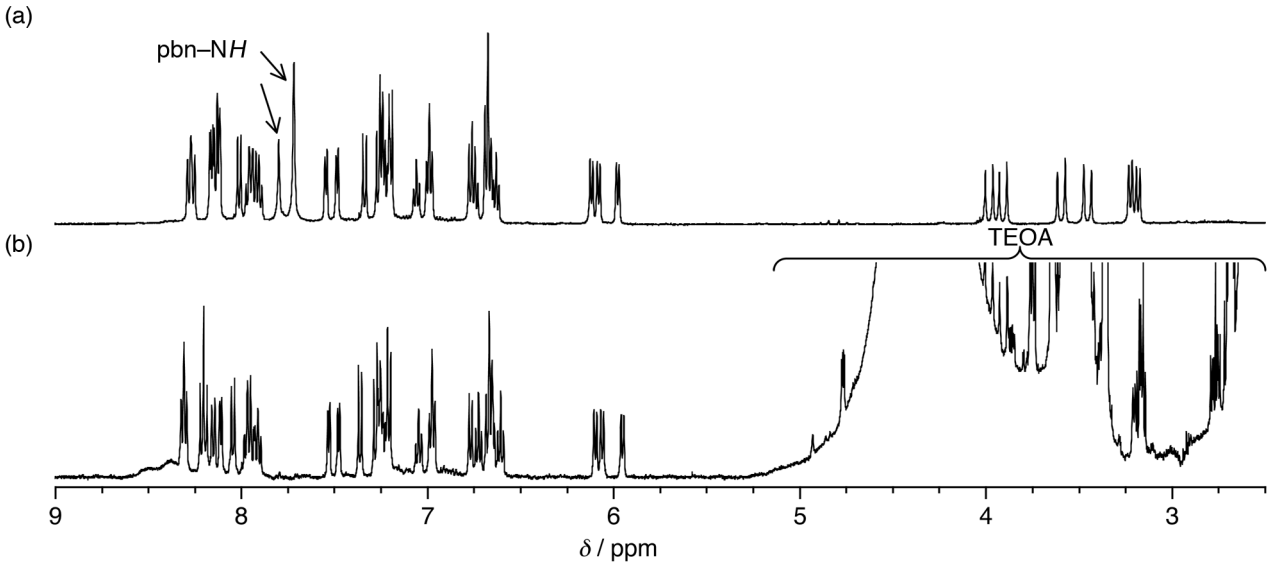

Fig. S7 ^{1}H NMR spectra of $[\mathbf{3}\bullet H_6]^{2+}$ produced (a) by the reduction of $[\mathbf{3}]^{2+}$ with $Na_2S_2O_4$ and (b) by the photochemical reduction of $[\mathbf{3}]^{2+}$ in CD_3CN/TEOA under visible light.