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 $[2]^{2+}$ (I), $[2\cdot\text{H}_2]^{2+}$ (II), $[2\cdot\text{H}_4]^{2+}$ (III), $[3]^{2+}$ (IV), and $[3\cdot\text{H}_6]^{2+}$ (V); (a) Simulation and (b) Experimental.
**Fig. S2** $^1$H NMR of (a) $[2]^{2+}$, (b) $[2\cdot H_2]^{2+}$ and (c) $[2\cdot H_4]^{2+}$ in CD$_3$CN.

**Fig. S3** $^1$H NMR spectra of (a) $[3]^{2+}$ and (b) $[3\cdot H_6]^{2+}$ in CD$_3$CN.
Fig. S4  (a) The electronic absorption spectra of [2]^{2+} under the electrolysis at various potentials in CH$_3$CN containing 0.1 M $n$-Bu$_4$NPF$_6$.  (b) The spectrum measured at −0.75 V is consistent with that of [2]^{2+} after irradiation of visible light for 10 min. in dry CH$_3$CN/TEA (Fig. 5(a)).  Based on (c) the cyclic voltammogram of [2]^{2+} in CH$_3$CN, electrolysis of the complex at −0.75 V evidently generates [Ru(bpy)(pbn)(pbn−)]$^+$ in the solution.
Fig. S5 (a) The electronic absorption spectra of $[3]^{2+}$ under the electrolysis at various potentials in CH$_3$CN containing 0.1 M $n$-Bu$_4$NPF$_6$. (b) The spectrum measured at $-0.70$ V is consistent with that of $[3]^{2+}$ after irradiation of visible light for 10 min. in dry CH$_3$CN/TEA (Fig. 5(b)). Based on (c) the cyclic voltammogram of $[3]^{2+}$ in CH$_3$CN, electrolysis of the complex at $-0.70$ V evidently generates $[\text{Ru(pbn)}_2(pbn^-)]^+$ in the solution.
Fig. S6 $^1$H NMR spectra of [2•H$_4$]$^{2+}$ produced (a) by the reduction of [2]$^{2+}$ with Na$_2$S$_2$O$_4$, (b) by the photochemical reduction of [2]$^{2+}$ and (c) that of [2•H$_2$]$^{2+}$ in CD$_3$CN/TEOA under visible light.

Fig. S7 $^1$H NMR spectra of [3•H$_6$]$^{2+}$ produced (a) by the reduction of [3]$^{2+}$ with Na$_2$S$_2$O$_4$ and (b) by the photochemical reduction of [3]$^{2+}$ in CD$_3$CN/TEOA under visible light.