Supporting Information:

Photochemical Reduction of Carbon Dioxide Using a CN-modified \textit{fac}-Mn(bpy)(CO)$_3$ Catalyst

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Figure S1. The linear fit lines of HCO₂H TON vs. catalyst (complex 1) concentration shows high linearity for both 15 h and 6 h irradiation.
Scan-Rate Dependence Data for Mn(CN) (bpy)(CO)$_3$

Figure S2. Linear plots of anodic and cathodic currents against square root of scan rate of CV for 1.0 mM of complex 1 in 0.1 M TBAPF$_6$ in dry $N,N$-DMF under Ar.
**Figure S3.** Infrared spectra of Mn(bpy)(CO)$_3$(CN) (1) at controlled potentials in dry MeCN-TEOA under CO$_2$. Enlarged spectra of the CO$_2$ peak at around 2337 cm$^{-1}$ shows the decrease in CO$_2$ concentration under catalytic conditions (ca. –1.9 V vs Fc/Fc+) over the course of 5 min. Conditions: 4 mM 1 in 0.1 M TBAPF$_6$/MeCN-TEOA (4 : 1); glassy carbon working electrode, Pt counter electrode, Ag pseudoreference electrode.
Figure S4. Infrared spectra of Mn(bpy)(CO)$_3$(CN) (1) taken at controled potentials in dry $N,N$-DMF-TEOA (4:1) under CO$_2$. Enlarged spectra of the CO$_2$ peak at around 2337 cm$^{-1}$ shows the decrease in CO$_2$ concentration at catalytic potentials (ca. $-1.9$ V vs Fc/Fc+) over the course of 5 min. Conditions: 4 mM 1 in 0.1 M TBAPF$_6$/N,N-DMF-TEOA (4 : 1); glassy carbon working electrode, Pt counter electrode, Ag pseudoreference electrode.
Figure S5. A sample $^1$H NMR spectrum of the worked-up photocatalytic reaction solution of 1 mM 1 under CO$_2$ after 15 h irradiation. The solvent was a N,N-DMF-TEOA (4 : 1 v/v) in CD$_3$CN solution. The ferrocene reference is at 4.13 ppm while formate is observed at 8.50 ppm.
UV-Vis Spectra

Figure S6. UV-Vis spectra of Mn(bpy)(CO)$_3$(CN) (A) in dry MeCN with and without Vkd base in the absence or presence of TEOA; and (B) in dry N,N-DMF with and without Vkd base in the absence or presence of TEOA. Upon the addition of Vkd base to solution in the absence of TEOA, the band at ~370 nm diminished in intensity and broadened. There was a slight diminishment observed with the addition of TEOA only, likely due to a decrease in the concentration of 1 from dilution.