Supplementary Information

Solar CO₂ Reduction using a Molecular Re(I) Catalyst Grafted on SiO₂ via Amide and Alkyl Amine Linkages

Thomas Fenton, Esraa Ahmad, and Gonghu Li *

Department of Chemistry, University of New Hampshire, Durham, NH 03824, United States * Corresponding author. Email: <u>gonghu.li@unh.edu</u> (G.L.)

Supplementary Figures



Figure S1. Structures of (a) Re-3-SiO₂ featuring an amide linkage, and (b) Re-4-SiO₂ featuring an alkyl amine linkage.



Figure S2. Output spectra of the halogen lamp used in this study without (red trace) and with (black trace) a 420-nm long-pass optical filter.



Figure S3. Diffuse reflectance UV-vis spectra of (a) $Re-3-SiO_2$ and (b) $Re-4-SiO_2$. Barium sulfate was used as the background.



Figure S4. DRIFTS spectra of (a) Re-3-SiO₂ and (b) Re-4-SiO₂. Potassium bromide was used as the background.



Figure S5. DRIFTS spectra of (a) Re-3-SiO₂ and (b) Re-4-SiO₂ in the presence of TEOA and CO₂.



Figure S6. CO production in CO₂ reduction using different heterogenized Re(I) catalysts under simulated solar irradiation (provided by a Xe lamp and an AM1.5 optical filter) in the absence of the Ru(II) photosensitizer. Light intensity was 100 mW/cm².



Figure S7. CO production in CO₂ reduction using (a) Re-3-SiO₂ and (b) Re-4-SiO₂ under visible light using a molecular Ru(II) photosensitizer. Light intensity was 100 mW/cm². The loadings of Re were determined to be 2.7 and 4.2 μ mol per 10 mg of Re-3-SiO₂ and Re-4-SiO₂, respectively.



Figure S8. Difference DRIFTS spectra of (a) Re-3-SiO₂ and (b) Re-4-SiO₂ upon light irradiation in the presence of TEOA and CO₂. The spectra were obtained by subtracting spectra collected before light irradiation (t = 0) from corresponding spectra collected after light irradiation for different times (2, 10, 30, and 60 min).