## Development of highly efficient supramolecular $CO_2$ reduction photocatalysts with high turnover frequency and durability

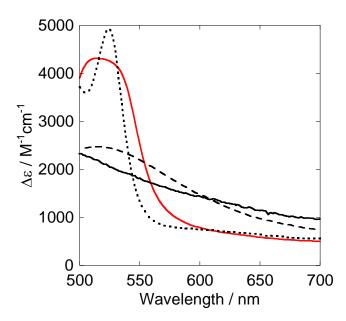
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**Electronic Supplementary Information** 

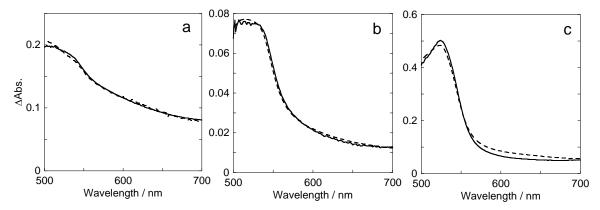
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**Figure S1.** UV-Vis absorption spectra of the OER species in an Ar-saturated CH<sub>3</sub>CN solution containing 0.1 M Et<sub>4</sub>NBF<sub>4</sub> at room temperature obtained by flow electrolysis method: **Ru** (red line), **Re**(**FPh**)<sup>a</sup> (black solid line), **Re**(**Ph**)<sup>a</sup> (black broken line), and **Re**(**OEt**) (black dotted line). <sup>a</sup>H. Tsubaki, A. Sugawara, H. Takeda, B. Gholamkhass, K. Koike and O. Ishitani, *Res. Chem. Intermed.*, 2007, **33**, 37-48.



**Figure S2.** UV-Vis absorption spectra of the reaction solutions during irradiation (solid line): (a, 400 s) **Ru-Re(FPh)**; (b, 680 s) **Ru-Re(Ph)**; (c, 1490 s) **Ru-Re(OEt)**, and simulated spectrum using the spectra of the OER species of the corresponding mononuclear complexes shown in Figure S1 (broken line). The reaction condition was same to that in Figure 2.

**Video S1.** Vigorous production of CO bubbles: a  $CO_2$  saturated DMF - TEOA (5:1 v/v) solution containing BNAH (0.1 M) and **Ru-Re(FPh)** (0.3 mM) was irradiated at > 420 nm using a 500-W high pressure mercury lamp.

**Video S2.** Observation of the solution containing  $\mathbf{Ru}$  instead of  $\mathbf{Ru}$ - $\mathbf{Re}(\mathbf{FPh})$  during irradiation: a  $CO_2$  saturated DMF - TEOA (5:1 v/v) solution containing BNAH (0.1 M) and  $\mathbf{Ru}$  (0.3 mM) was irradiated at > 420 nm using a 500-W high pressure mercury lamp.