Supporting Information

Constructing Rhenium complex supported on g-C_3N_4 for Efficient Visible-Light-Driven Photoreduction of CO_2 to CO via a novel Z-scheme Heterojunction

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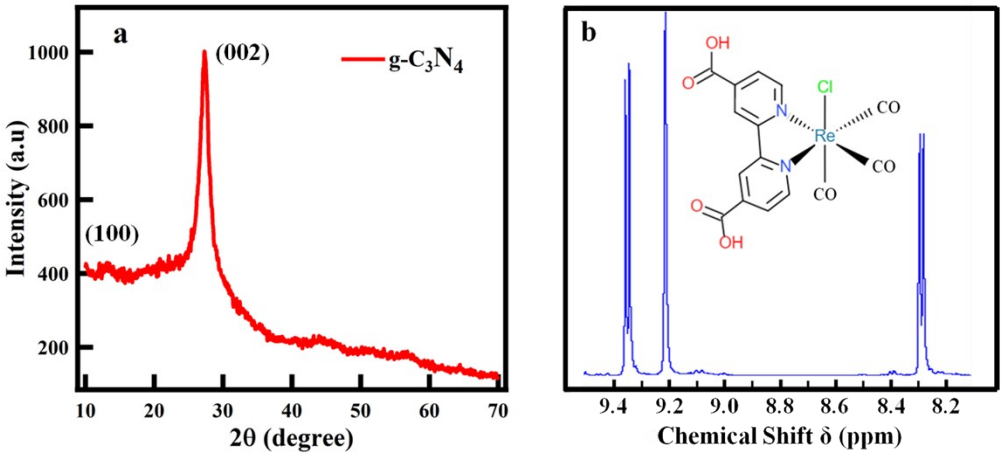

Figure S1: XRD pattern of g-C_3N_4 (a), 1H NMR of Re(bpy-COOH) (b).

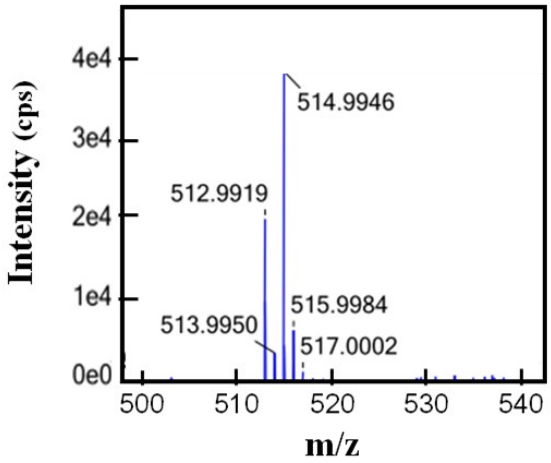

Figure S2. ESI-MS of Re(bpy-COOH) in MeCN under drift voltage at 20 mV.

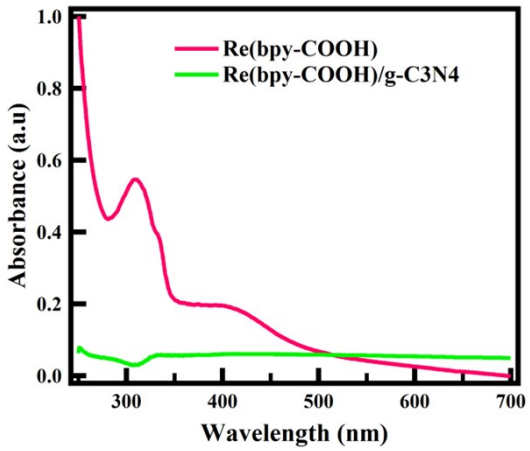

Figure S3: UV/Vis absorption spectrum of Re(bpy-COOH) and Re(bpy-COOH)/g-C_3N_4 in MeCN at room temperature.

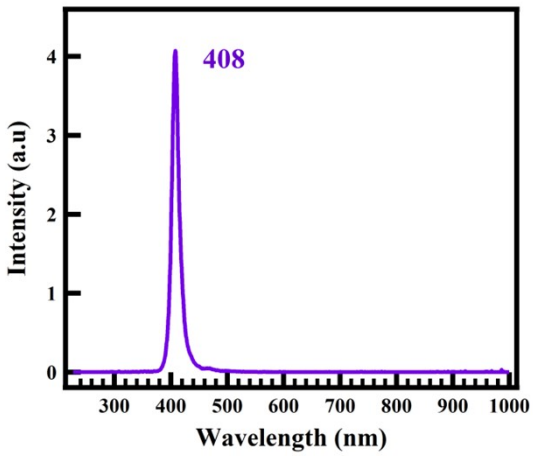

Figure S4: Light source spectrum of the photo-irradiation system used in the experiment (light intensity at a distance of 5 cm and 11 cm are 210W/m^2 and 78W/m^2, respectively).

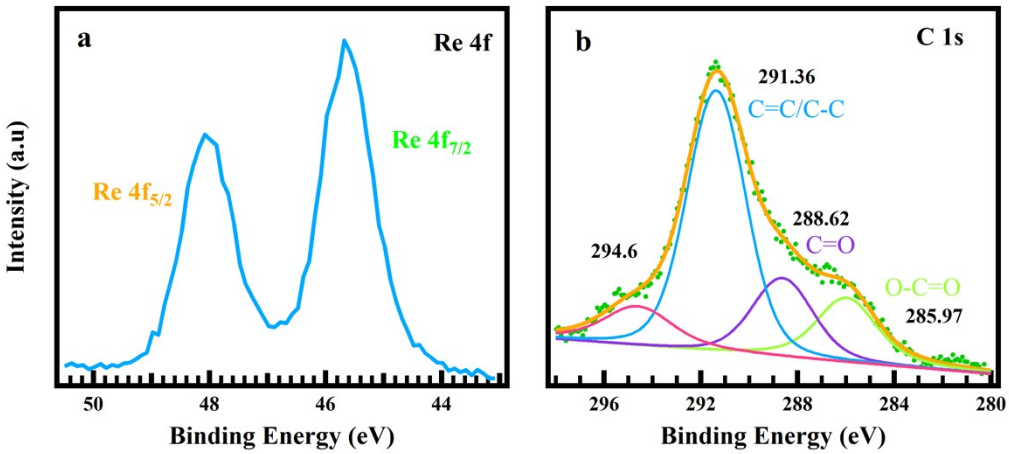

Figure S5: High resolution scan of Re 4f (a) and C 1s (b) of Re(bpy-COOH).

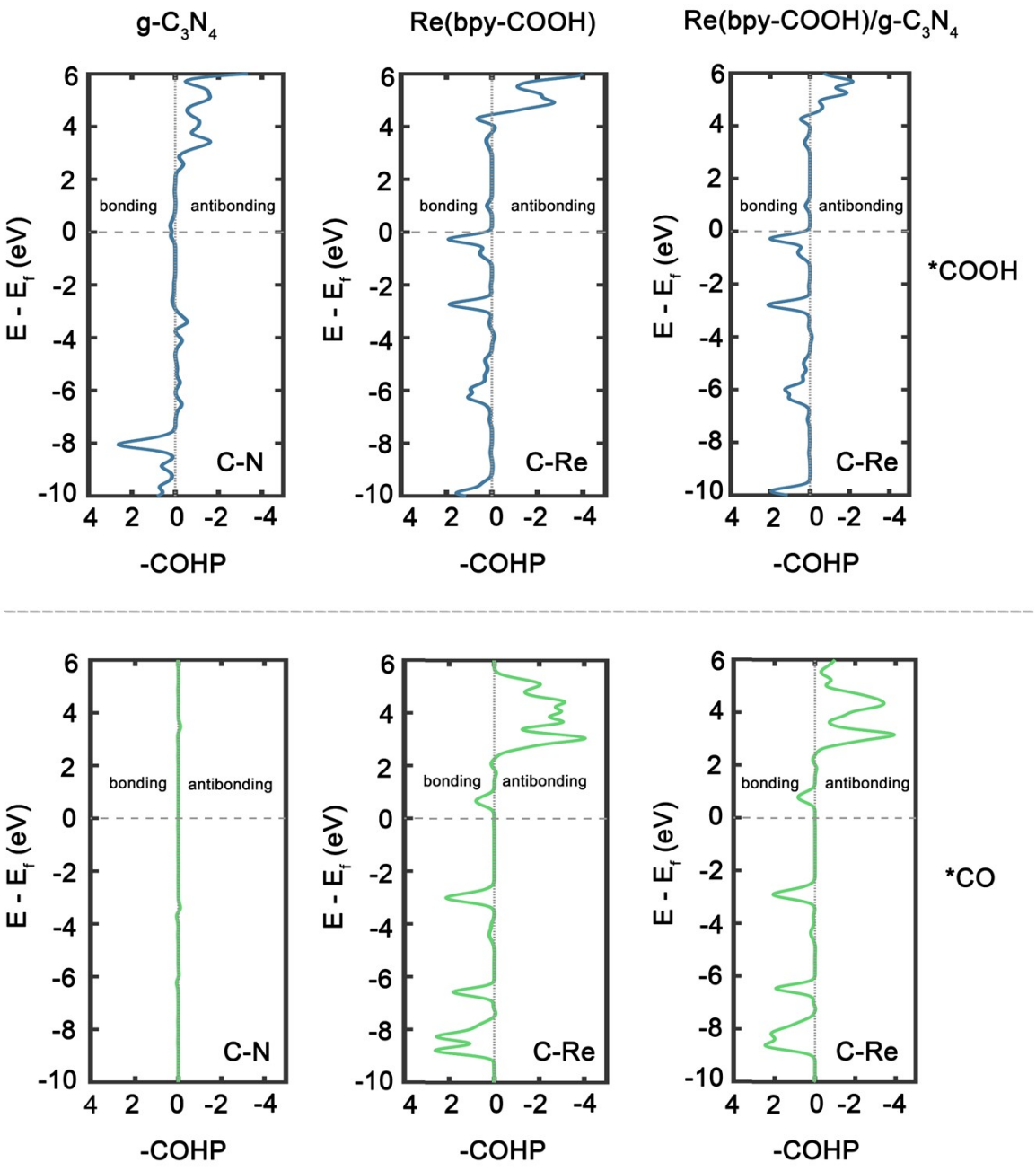

Figure S6. Crystal orbital Hamilton population (COHP) for *COOH (blue) and *CO (green) intermediates in g-C_3N_4 (left panels), Re(bpy-COOH) (middle panels), and Re(bpy-COOH)/g-C_3N_4 (right panels), respectively. Fermi level is shifted to zero. Positive (negative) value of -COHP indicates the bonding (antibonding) interactions. For g-C_3N_4, C-N interaction is considered, while C-Re interaction is for Re(bpy-COOH) and Re(bpy-COOH)/g-C_3N_4.

Table S1: Emission decay parameters of Re(bpy-COOH)/g-C_3N_4 and g-C_3N_4 excited and emitted at the wavelength of 355 nm and 450 nm, respectively.

Materials	A_0	A_1	A_2	A_3	τ_1 (ms)	τ_2 (ms)	τ_3 (ms)	B_1	B_2	B_3	τ (ms)
Re(bpy-COOH)/g-C_3N_4	0.0016	0.8215	0.0880	0.1172	2.8242	10.6930	10.2230	0.8001	0.0857	0.1142	4.3435
g-C_3N_4	0.0051	0.8597	0.0711	0.1349	2.2625	8.0532	8.7477	0.8067	0.0667	0.1266	3.4697

The emission decay curve was fitted by triple- exponential function, as shown in eq. 1. The average lifetime τ and the relative ratio B_i were calculated by following functions (2) and (3), as presented below:

$$f(x) = A_0 + A_1 * \exp\left(-\frac{x}{\tau_1}\right) + A_2 * \exp\left(-\frac{x}{\tau_2}\right) + A_3 * exp(-\frac{x}{\tau_3}) \quad (1)$$

$$\tau = \sum_{i=1}^{3} B_i * \tau_i / \sum_{i=1}^{3} B_i \quad (2)$$

$$B_i = A_i / \sum_{i=1}^{3} A_i \quad (3)$$

Table S2. Mulliken charge and charge transfer between each atom of *COOH, *CO and g-C_3N_4, Re(bpy-COOH), Re(bpy-COOH)/g-C_3N_4, respectively. The positive (negative) value in charge transfer column represents the loss (gain) electron.

	Atoms	**g-C_3N_4**		**Re(bpy-COOH)**		**Re(bpy-COOH)/g-C_3N_4**	
		Mulliken charge	Charge transfer	Mulliken charge	Charge transfer	Mulliken charge	Charge transfer
*COOH	C	-3.34	0.66	-3.96	0.04	-3.87	0.13
	O	-6.54	-0.54	-6.45	-0.45	-6.5	-0.50
	O	-6.59	-0.59	-6.53	-0.53	-6.56	-0.56
	H	-0.48	0.52	-0.57	0.43	-0.55	0.45
	Total		0.05		-0.51		-0.48
*CO	C	-3.61	0.39	-3.89	0.11	-3.83	0.17
	O	-6.38	-0.38	-6.26	-0.26	-6.30	-0.30
	Total		0.01		-0.15		-0.13

Control experiment

The observed CO might include not only from photocatalytic CO2RR but also from CO photo-degradation of Re(bpy-COOH), we conduct photcatalytic activity of Re(bpy-COOH) under Ar gas. The amount of CO production from photocatalytic CO_2 reaction was determined by subtracting the CO produced by Re(bpy-COOH) photo-degradation. (TON_{CO}= $TON_{CO\_PCO2RRexp}$ -$TON_{COphoto\text{-}deg}$) (PCO2RR: photocatalytic CO_2 reduction reaction)

The reaction solution containing Re(bpy-COOH) (0.6 mM) in DMF:TEOA mixed solvent (5:1 v/v) was placed in a visible-light-transparent vial (5mL) and purged with Ar to remove all of air. The reaction vial was irradiated by a light-source system (15 W energy-saving light bulk, center wavelength λ = 408 nm, and light intensity at a distance of 5 cm is 210W/m^2) in the photoreaction box. During irradiation, the solution was being stirred slowly by a magnetic bar and the temperature of the solution was controlled at room temperature by constant temperature system. The gaseous reaction products were identified by gas chromatography (GC Clarus 680-PerkinElmer), which was equipped with TCD detector, molecular sieve column (LxI.D.: 30 m x 0.32 mm), and Ar carrier gas. The CO produced by Re(bpy-COOH) photo-degradation was shown in table S3.

Table S3: The CO produced by Re(bpy-COOH) photo-degradation

Time (minute)	$TON_{COphoto\text{-}deg}$
20	0.323
40	0.364
60	0.398

Time-resolved photoluminescence measurement

For TRPL measurement, the 355-nm laser diode was used as the excitation source. The signals were recorded by using a 0.6-m grating monochromator (Jobin-Yvon HRD1) and then detected by a fast photomultiplier (Hamamatsu model H733, with a rise time of 700 ps). Averaging the multi-pulses at each spectral point using a 1.0 GHz digital oscilloscope (Tektronix DPO 4102B) improved the signal-to-noise ratio.

The emission lifetime of Re(bpy-COOH) was confirmed in nanosecond timescale with the avarage lifetime was 8.22 ns, which reached agreement with the previous report [1].

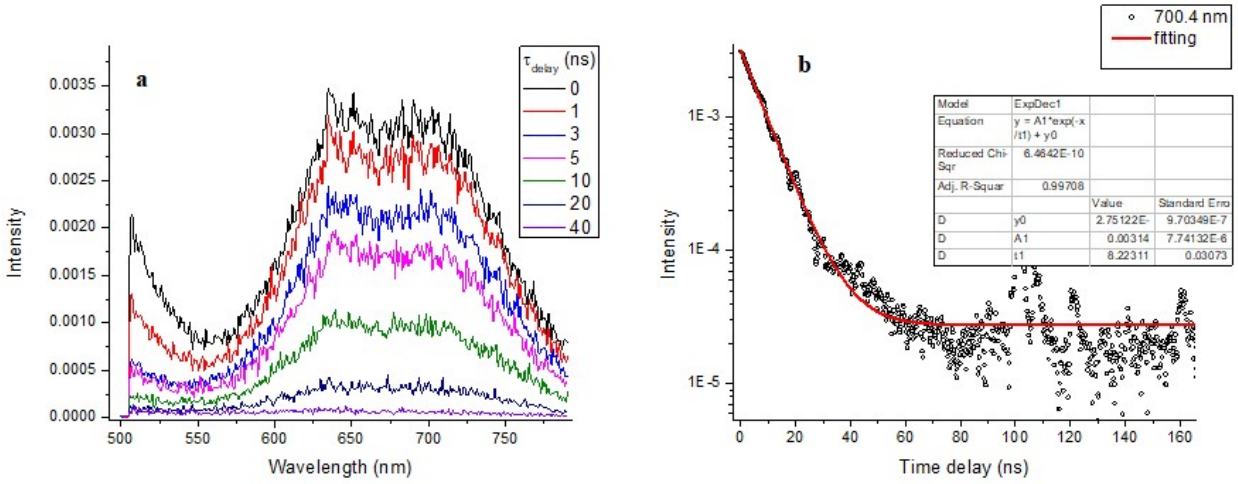

Figure S7. Time-resolved photoluminescence (TRPL) of Re(bpy-COOH) in methanol (a) and emission decay profile of Re(bpy-COOH) (b).

Reference

1. Nahhas, A. El *et al.* Ultrafast excited-state dynamics of [Re(L)(CO)$_3$(bpy)] n complexes: Involvement of the solvent. *J. Phys. Chem. A* **114**, 6361–6369 (2010).