Supporting Information

Rhenium-Modified Porous Covalent Triazine Framework for Highly Efficient Photocatalytic Carbon Dioxide Reduction in Solid-Gas System

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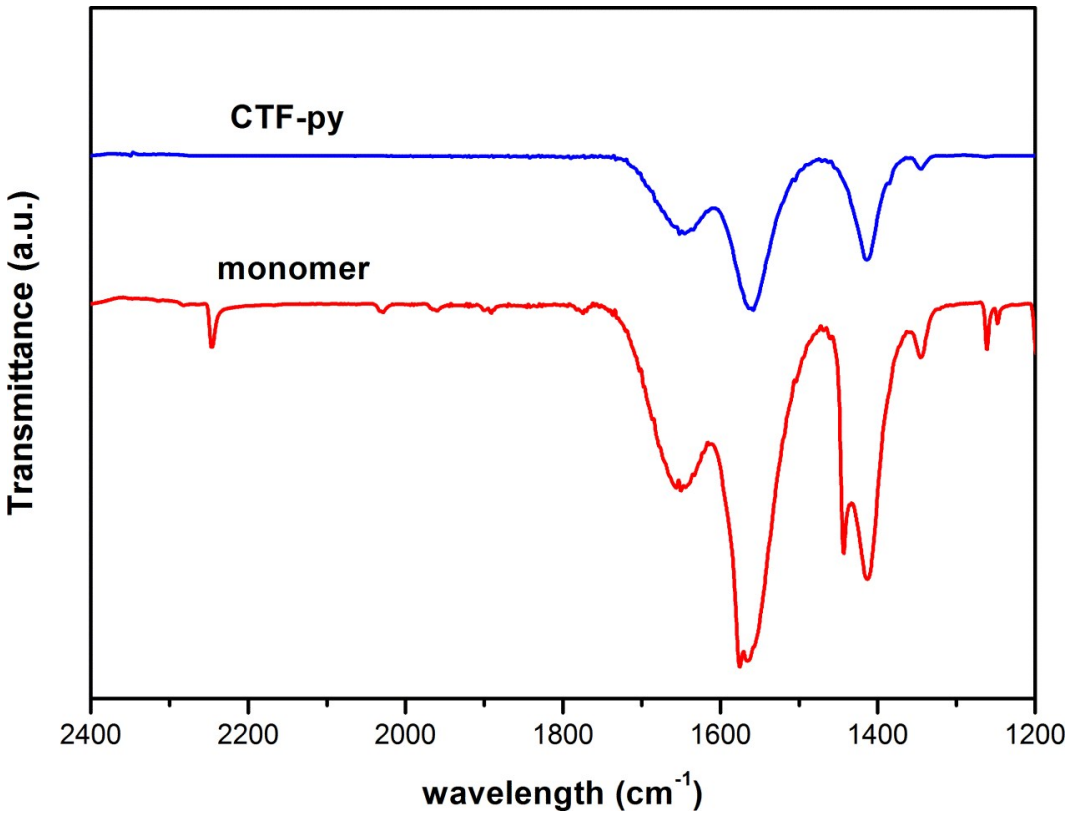

Fig. S1 IR spectrum of CTF-py and monomer (2,6-dicyanopyridine).

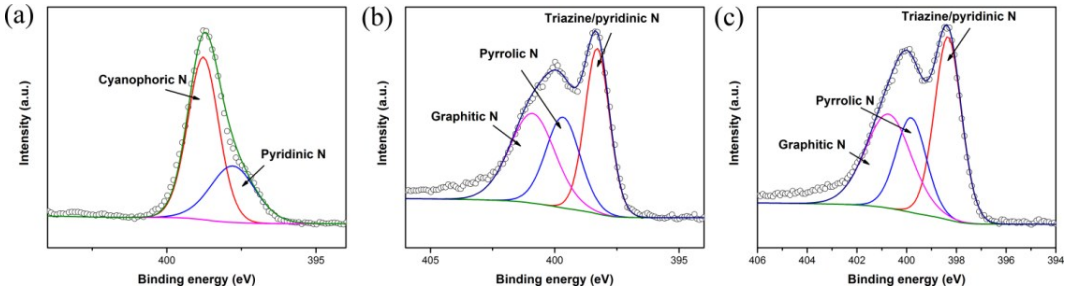

Fig. S2 (a-c) XPS survey, N 1s spectra of monomer, CTF-py, and Re-CTF-py.

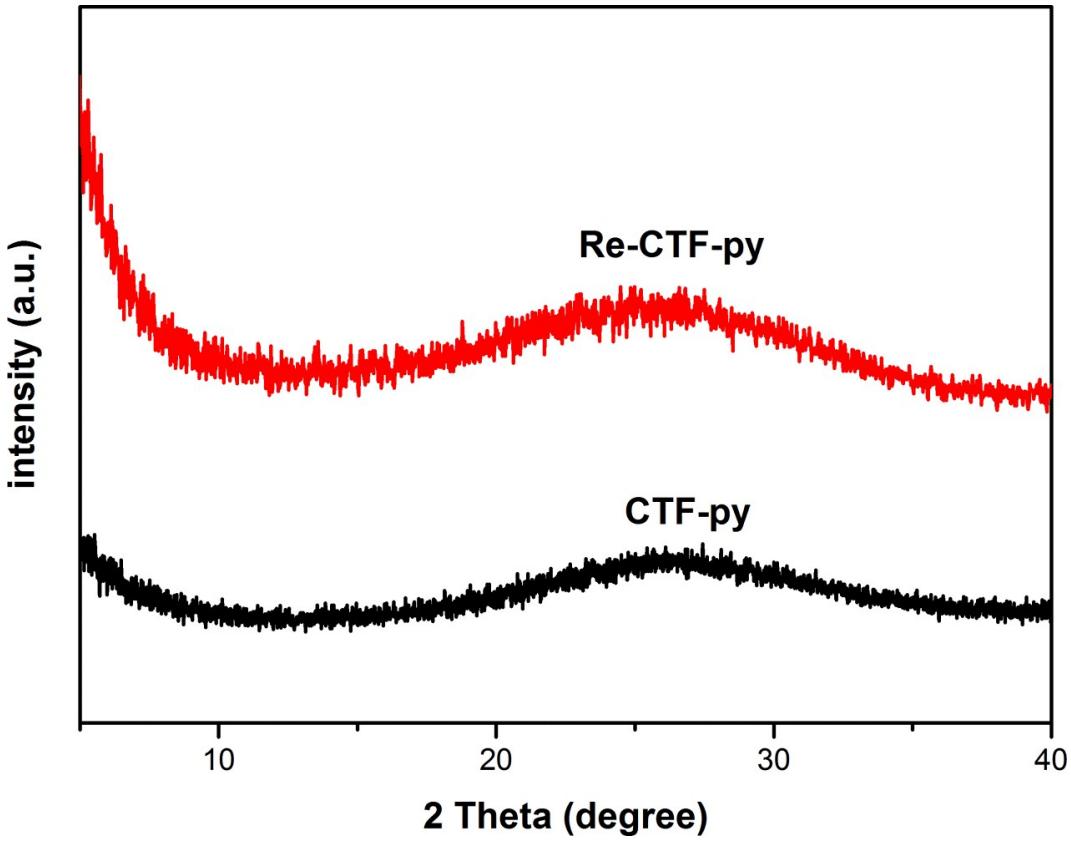

Fig. S3 PXRD of CTF-py and Re-CTF-py.

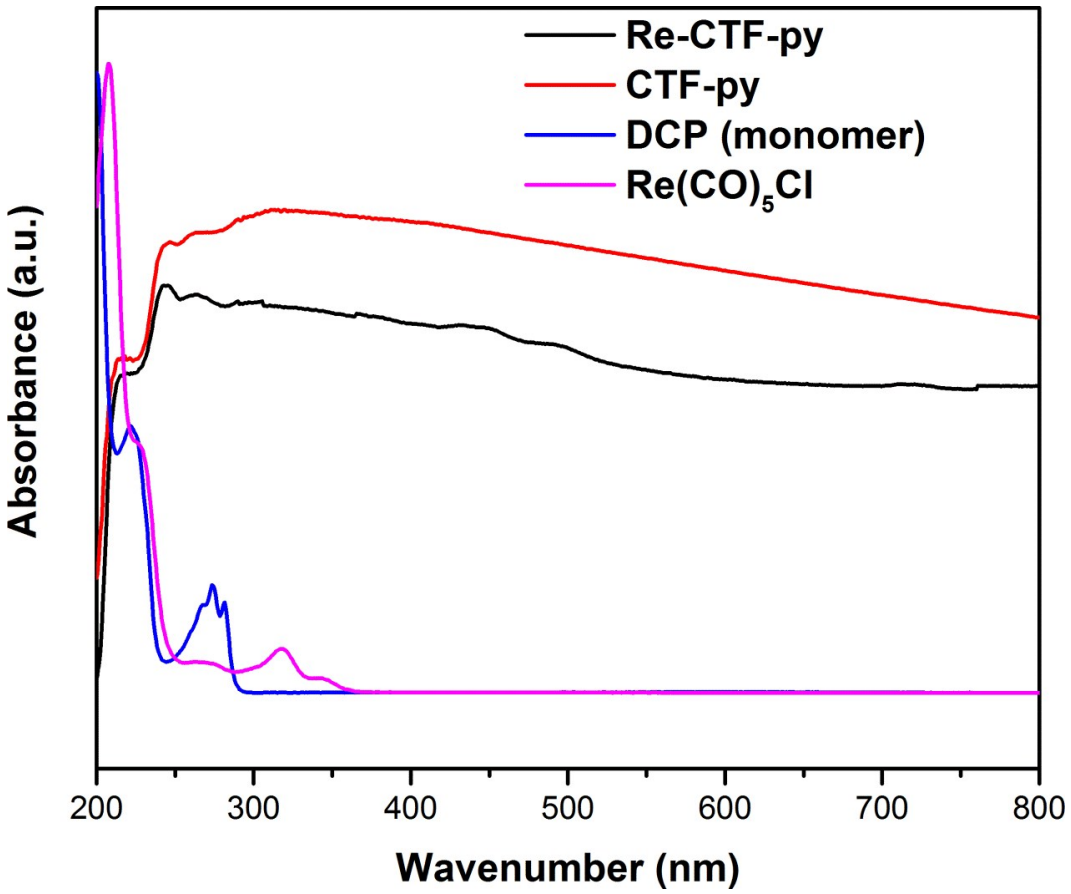

Fig. S4 UV-Vis absorbance spectra of Re-CTF-py, CTF-py, DCP (momomer) and $Re(CO)_5Cl$.

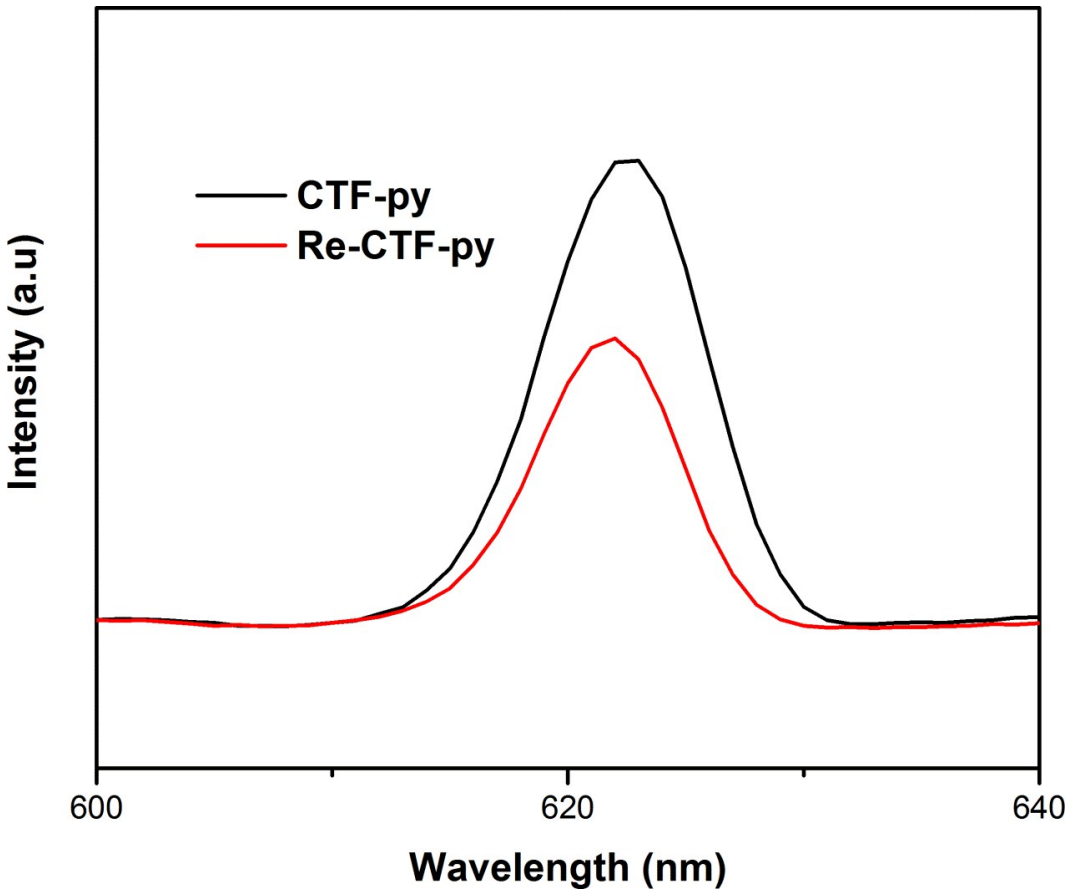

Fig. S5 Photoluminescence spectra of CTF-py and Re-CTF-py under 508 nm excitation at room temperature.

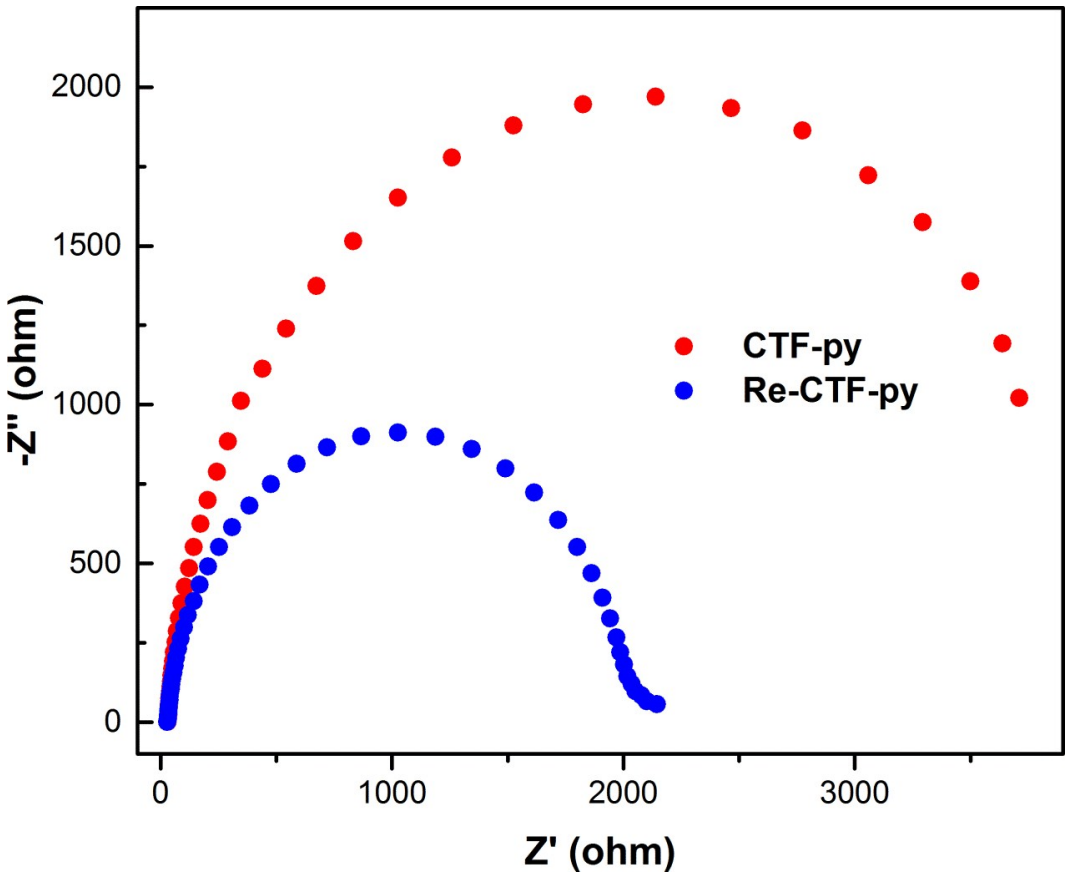

Fig. S6 EIS Nyquist plots obtained at an AC voltage with an amplitude of 5 mV over the frequency range from 10^{5} to 10^{-1} Hz for monomer, CTF-py and Re-CTF-py.

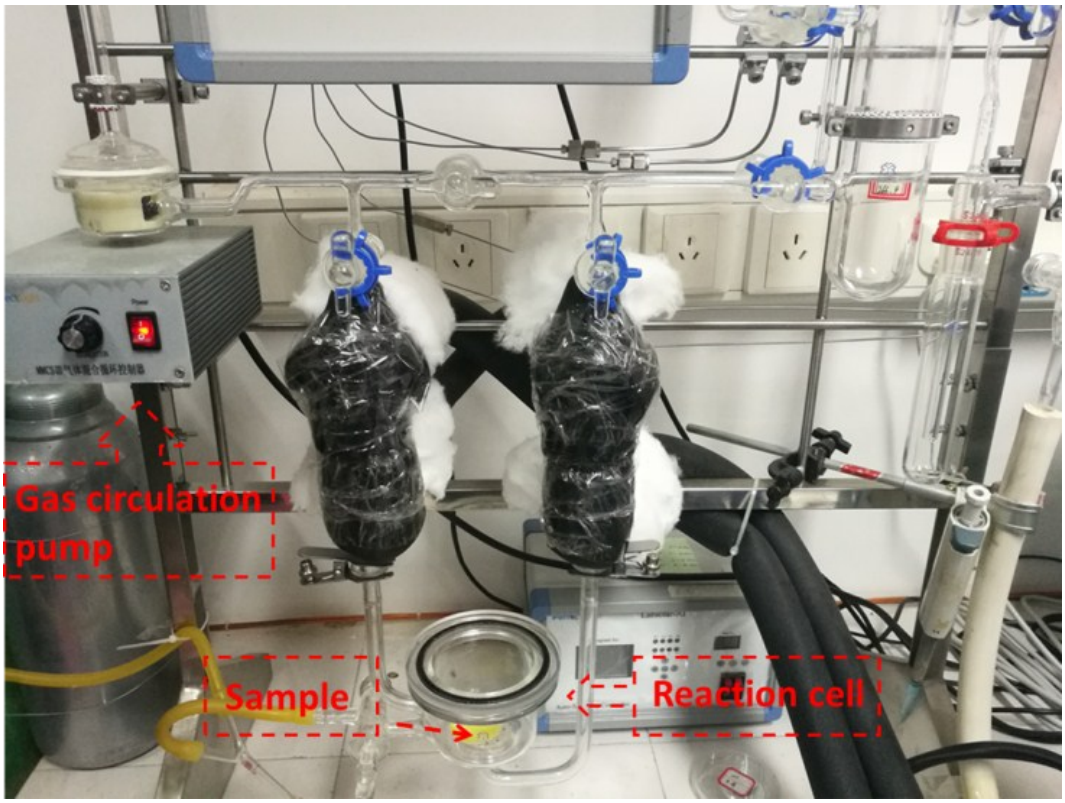

Fig. S7 Solid-gas system.

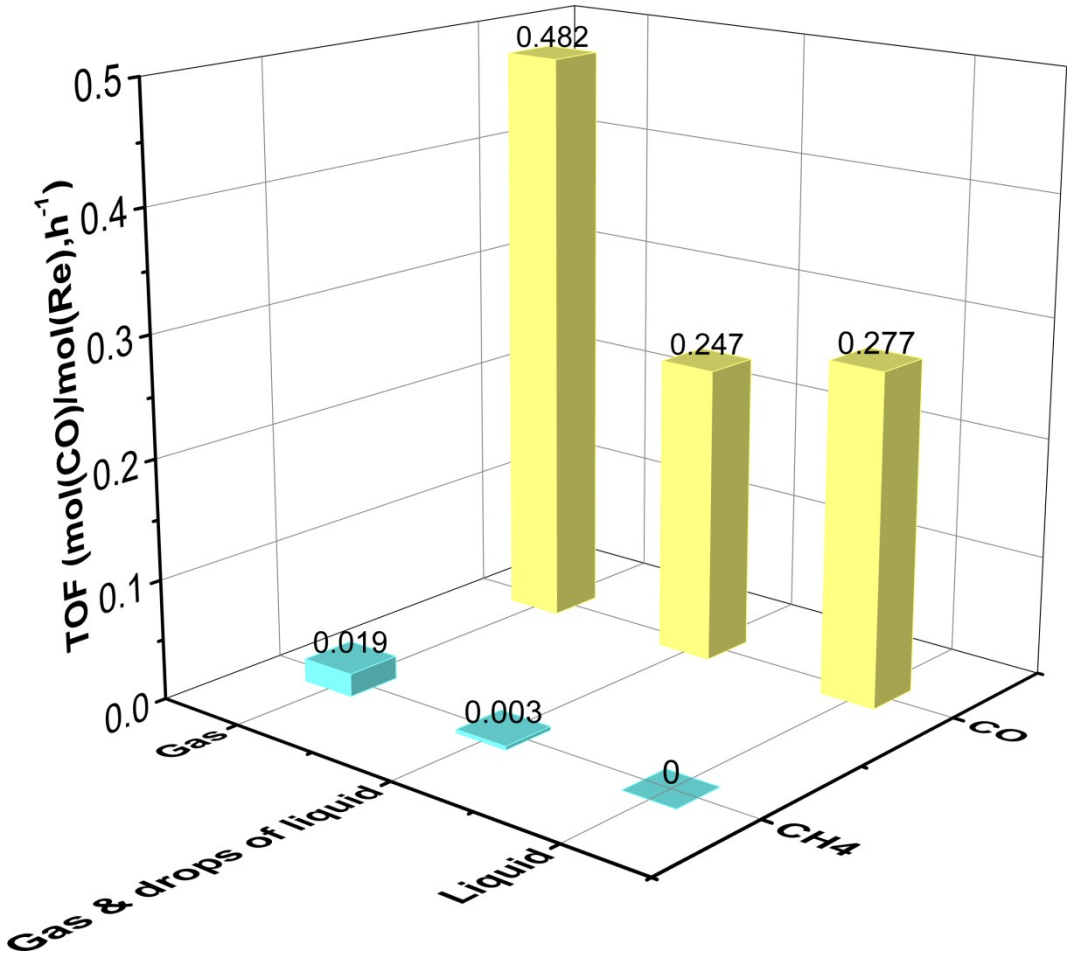

Fig. S8 The photocatalytic CH4 and CO evolution rate of Re-CTF-py in different condition.

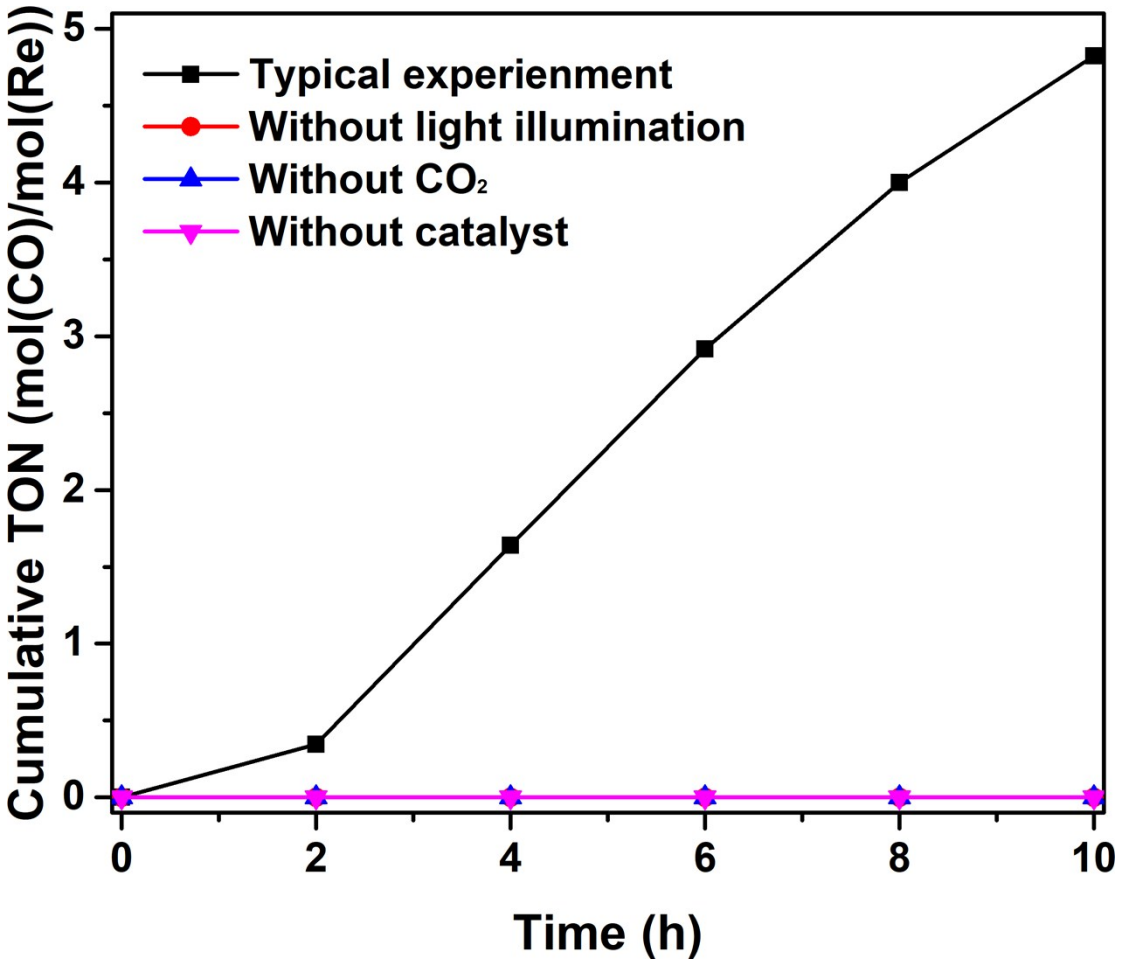

Fig. S9 Time course of CO evolution in different reaction condition. General reaction condition: 2 mg catalyst, 2 mL mixed solution of MeCN/TEOA (4/1), 0.8 atm CO_2, 10 h.

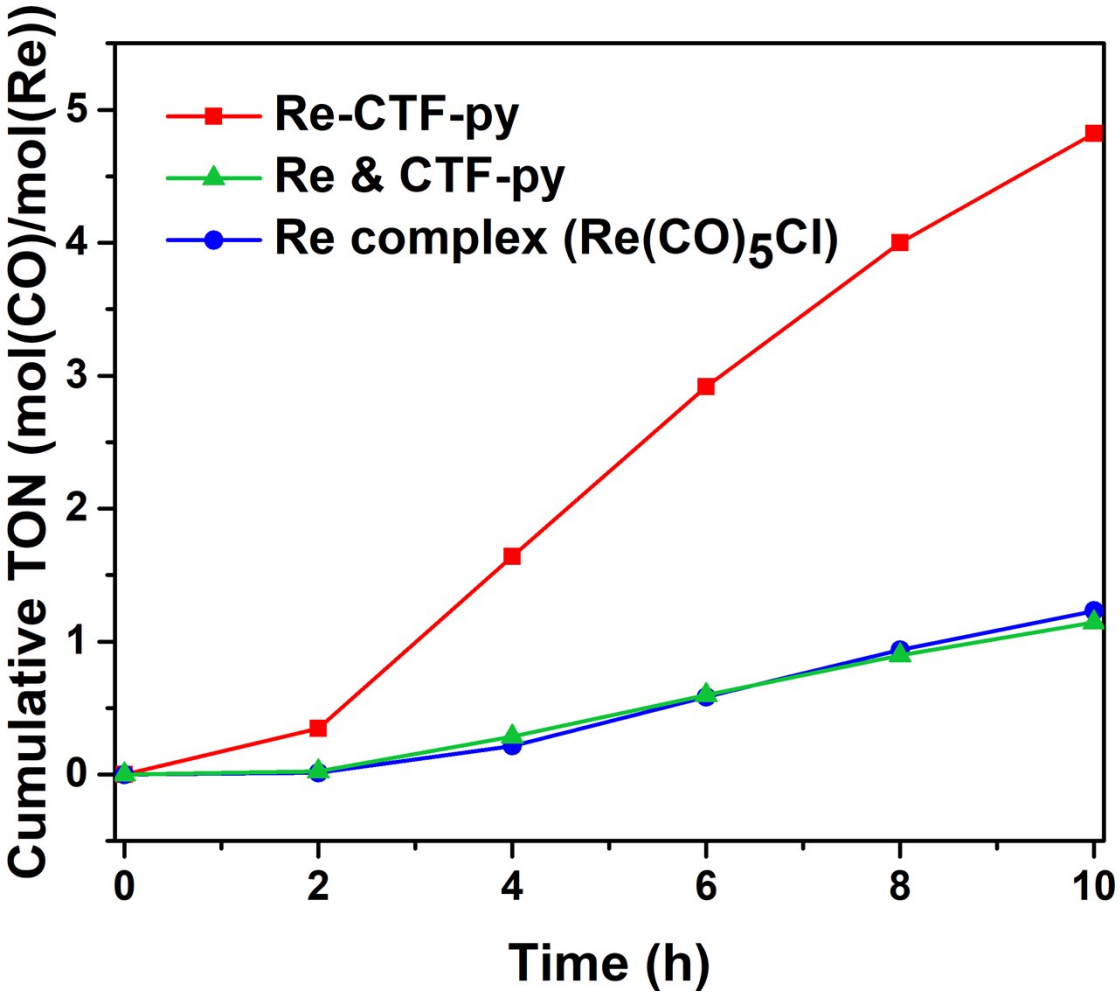

Fig. S10 TON of CO evolution over Re-CTF-py, $Re(CO)_5Cl$ and the physical mixture of CTF-py and $Re(CO)_5Cl$ (Re & CTF-py) in solid-gas system.

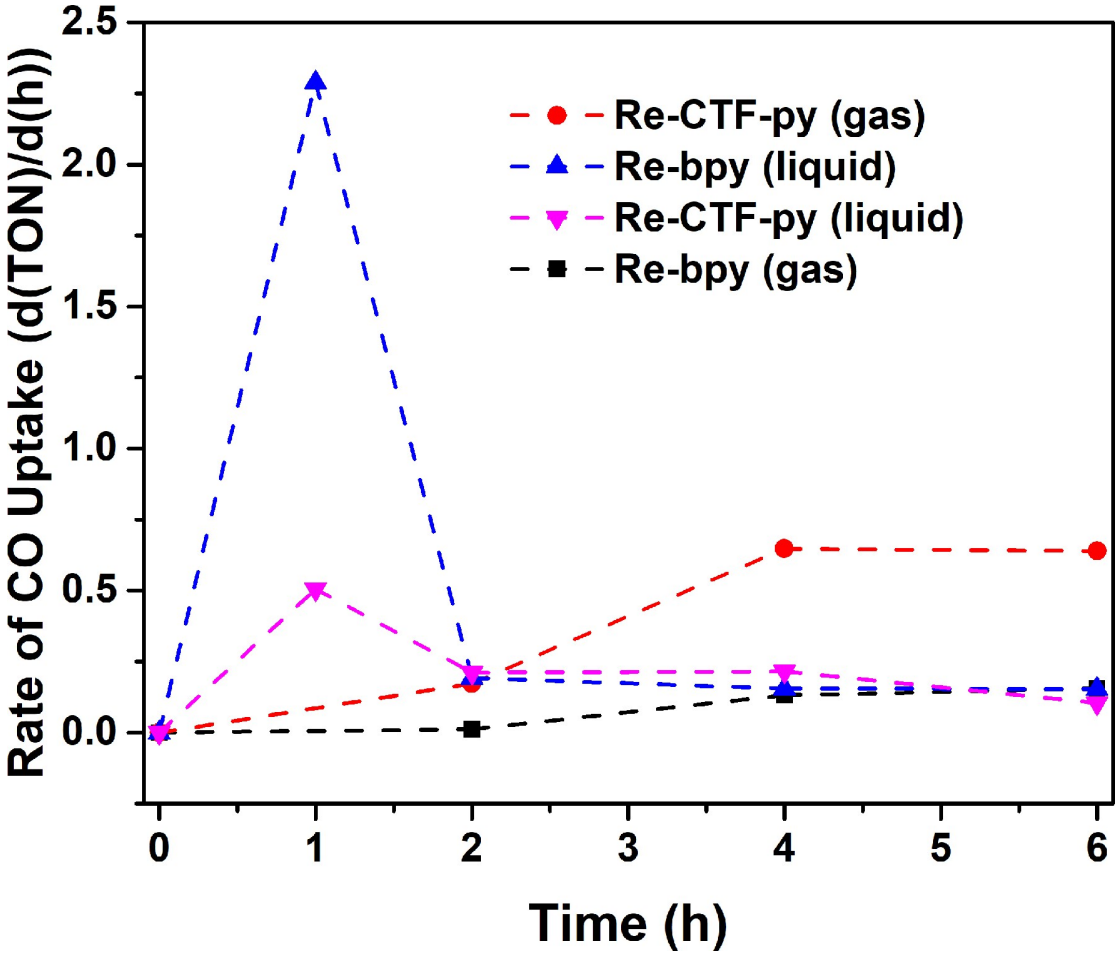

Fig. S11 Photocatalytic activity of Re-bpy and Re-CTF-py in solid-gas and liquid-gas systems.

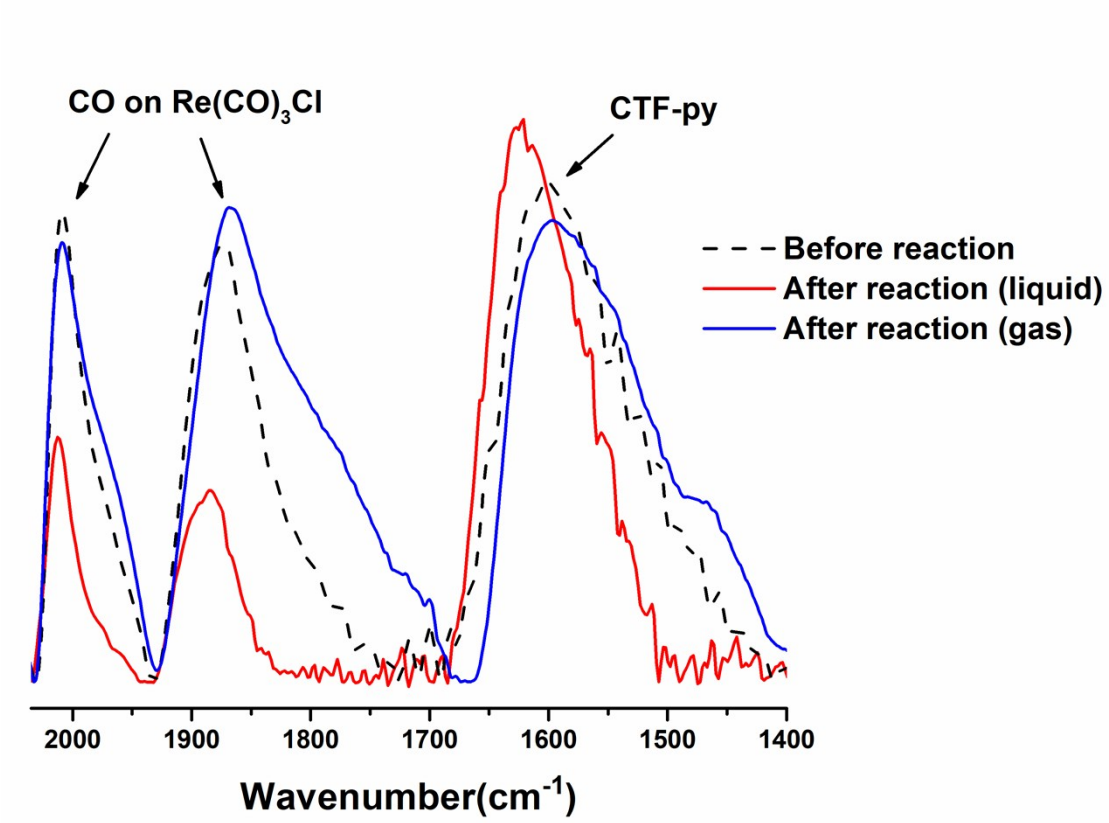

Fig. S12 IR spectrum of Re-CTF-py in different condition: before reaction, after solid-liquid reaction and after solid-gas reaction.

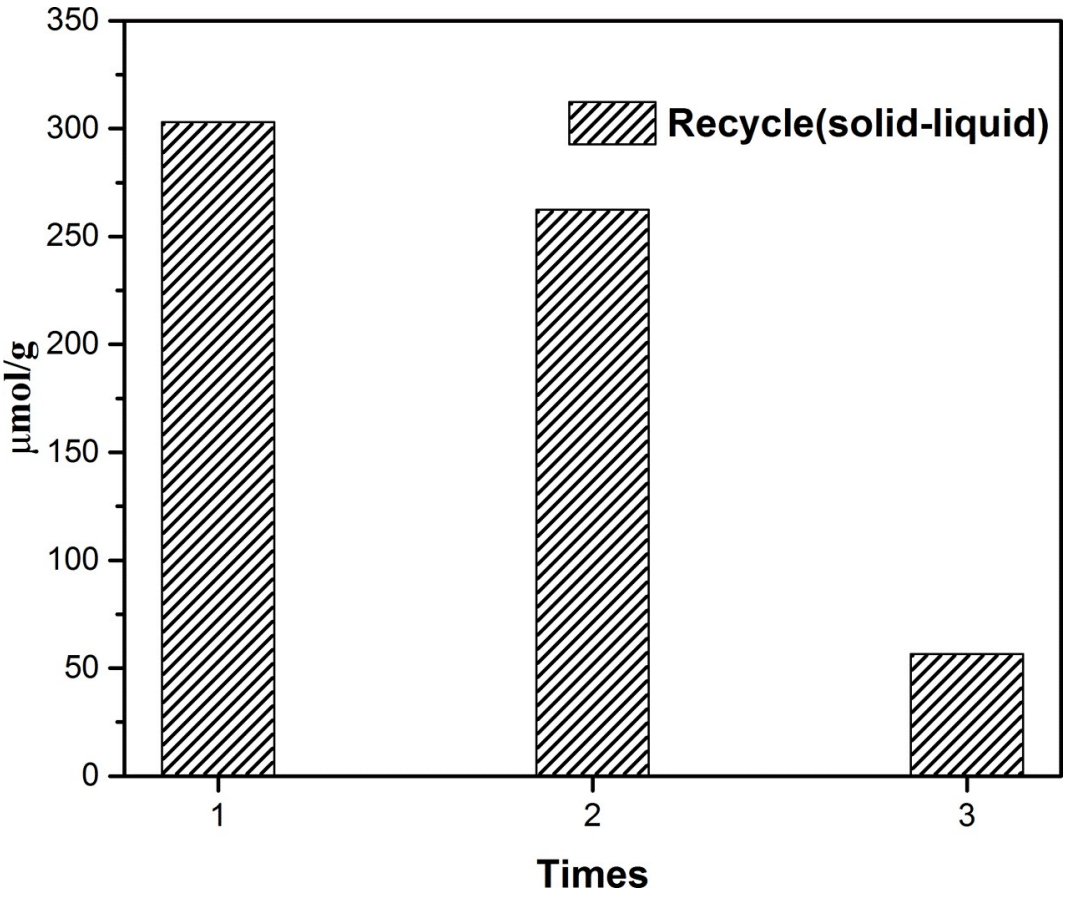

Fig. S13 Recycle of Re-CTF-py in solid-liquid system. Reaction conditions: 2 mg catalyst, 20mL mixed solution of MeCN/TEOA (4/1), 1 atm CO_2, 1h.

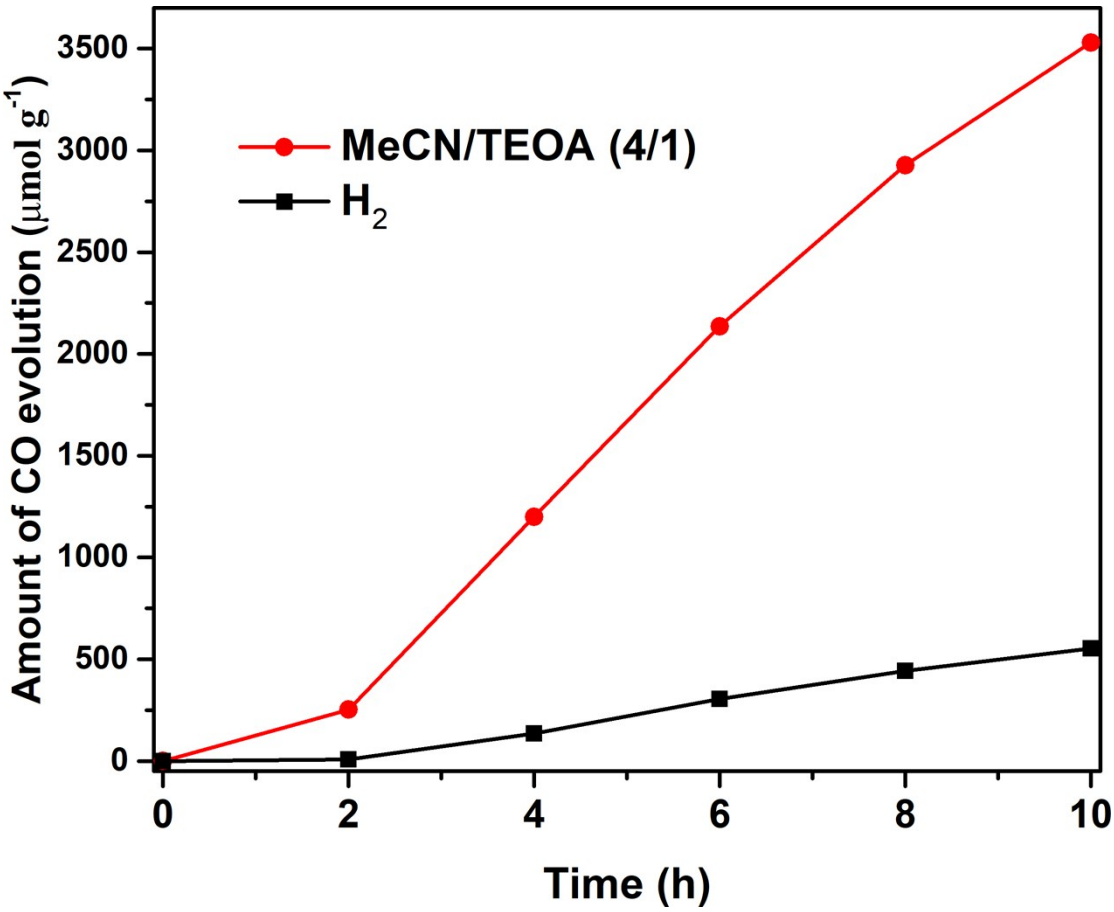

Fig. S14 Photocatalytic activity of using H_2 or TEOA as a sacrificial agent.

Table S1. C/N ratio of CTF-py and Re content of Re-CTF-py.

Materials	**C/N**	**Theoretical Value (C/N)**	**Re**	**Theoretical Value (Re)**
CTF	3.7	2.3	0%	0%
Re-CTF	4.0	2.6	13.63%	21.96%

Table S2. Photocatalytic ability of Re-CTF-py compared to other porous framework system for CO_2 reduction. Re-CTF-py showed much higher TOF values when compared to various heterogeneous systems.

Name	Photosensitizer	Solvent	TOF (h^{-1})	Reference
MOF-253-Ru(CO)$_2$Cl	None	MeCN/TEOA	0.363	*Chem. Commun.* 2015, 51, 2645
NH$_2$-MIL-101(Fe)	None	MeCN/TEOA	0.05	*ACS Catal.* 2014, 4, 4254
NH$_2$-MIL-53(Fe)	None	MeCN/TEOA	0.013	*ACS Catal.* 2014, 4, 4254
NH$_2$-MIL-888(Fe)	None	MeCN/TEOA	0.008	*ACS Catal.* 2014, 4, 4254
{Cd$_2$[Ru(dcbpy)$_3$]·12H$_2$O}$_n$	None	MeCN/TEOA	0.231	*J. Mater. Chem. A* 2015, 3, 15764
{Cd[Ru(4,4-dcbpy)$_2$(bpy)]·3(H$_2$O)}$_n$	None	MeCN/TEOA	0.172	*Inorg. Chem. 2015, 54, 8375*
Re-CTF-py	None	MeCN/TEOA	0.482	*This work*