Supporting Information

Energy Transfer on Two-Dimensional Antenna Enhances Photocatalytic Activity of CO_2 Reduction by Metal-Organic Layers

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General Methods

All the reagents and solvents were commercially available and used without further purification unless otherwise indicated. ^{1}H-NMR spectra were recorded on a Bruker NMR 500 DRX spectrometer and a Bruker 400 MHz DRX spectrometer and referenced to the proton resonance resulting from incomplete deuteration of the D_2O (δ 4.7). Electron microscopy images were obtained on a Tecnai F30 and JEOL 2100 High Resolution Transmission Electron Microscope. The powder X-ray diffraction data were collected on Rigaku diffractometers using Cu Kα radiation sources (λ = 1.54178 Å). The fluorescence spectrums and decay curve were obtained on a Edinburgh Instrument FL980. ICP-MS analysis of samples were performed on an ELAN ICP-DRC-qMS (PerkinElmer, SCIEX, Canada) instrument.

Zr-TCBPE-MOL-Ru and Zr-TCBPE-MOL-Re were prepared by post-modification of Zr-TCBPE-MOL with DMF solution of 3 mM $[H_2BPYDC\text{-}Ru(BPY)_2]Cl_2$ and DMF solution of 1.5 mM $H_2BPYDC\text{-}Re(CO)_3Cl$ with stirring at room temperature. Zr-TCBPE-MOL-BPYDC-Ir was prepared in two steps: first preparing a DMF solution of 5mM $H_2BPYDC\text{-}IrCp^*(NO_3)_2$ by reacting H_2BPYDC with $IrCp^*(NO_3)_2$ that was prepared by treating $Ir_2Cp^*{}_2Cl_4$ dimmer with $AgNO_3$, and then modifying Zr-TCBPE-MOL with $H_2BPYDC\text{-}IrCp^*(NO_3)_2$ at room temperature.

Materials Characterization

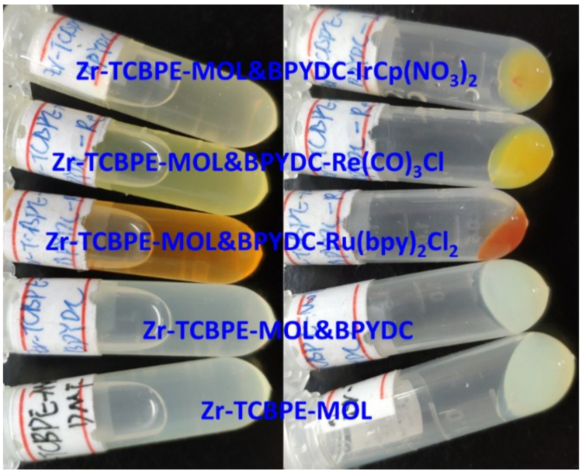

Figure s1 The photo of Zr-TCBPE-MOL and the functionalized MOLs dispersed in DMF(left) and as a solid gel (right)

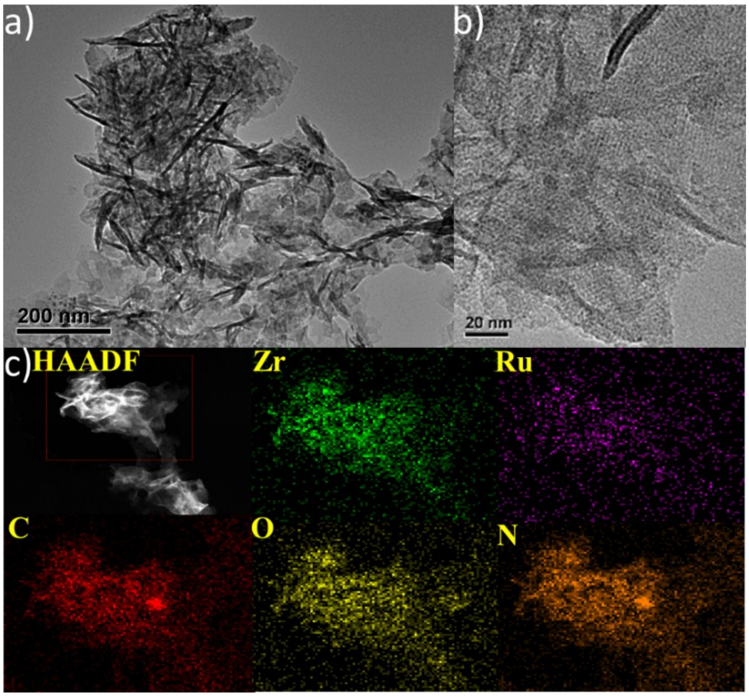

Figure s2 a). The TEM image of Zr-TCBPE-MOL-Ru, b). HRTEM of Zr-TCBPE-MOL-Ru, c). The HAADF image and EDS mapping of Zr-TCBPE-MOL-Ru

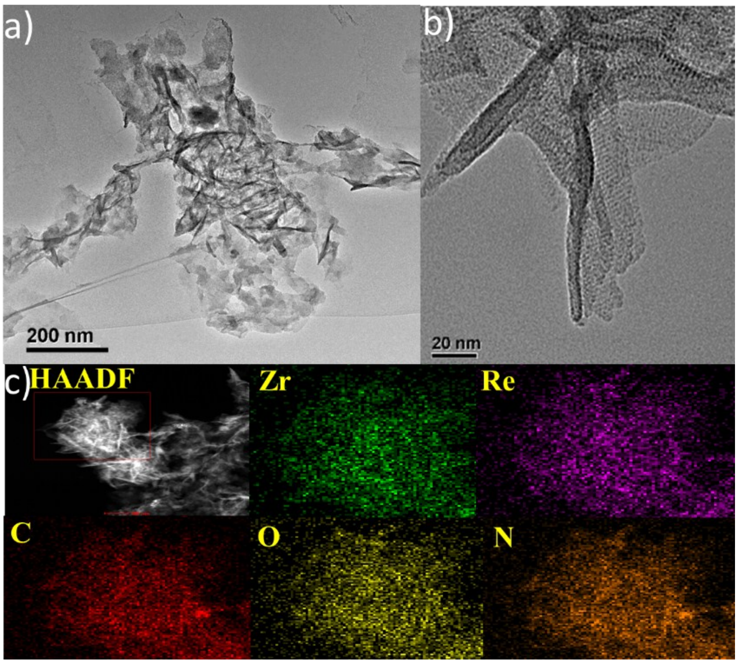

Figure s3 a). The TEM image of Zr-TCBPE-MOL-Re, b). HRTEM of Zr-TCBPE-MOL-Re, c). The HAADF image and EDS mapping of Zr-TCBPE-MOL-Re

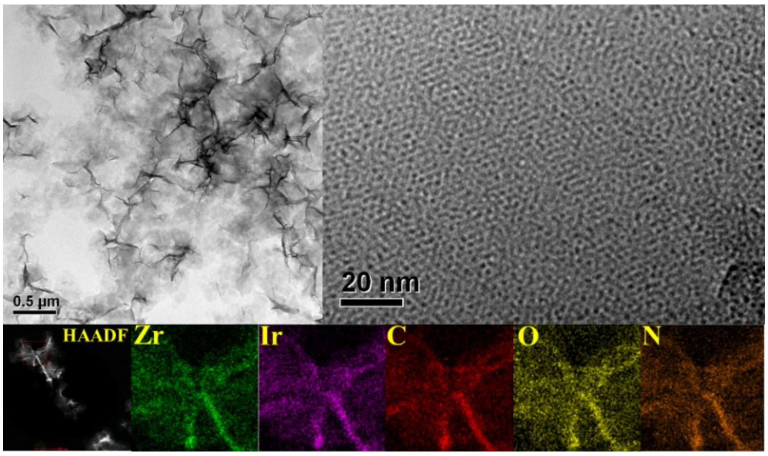

Figure s4 a). The TEM image of Zr-TCBPE-MOL-Ir, b). HRTEM of Zr-TCBPE-MOL-Ir, c). The HAADF image and EDS mapping of Zr-TCBPE-MOL-Ir

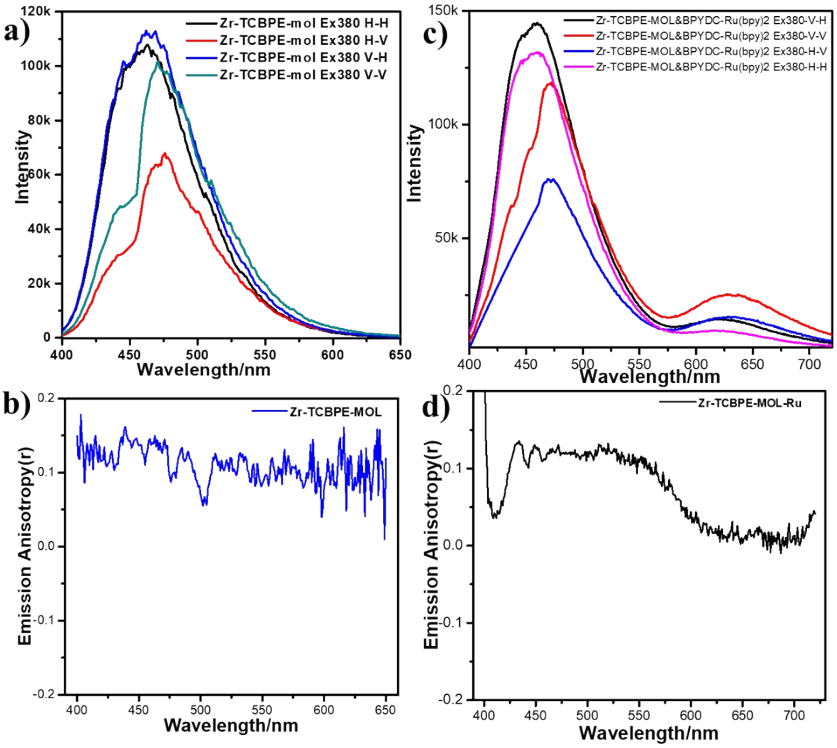

Figure s5 The polarized fluorescence spectrum and corresponding emission anisotropy value of Zr-TCBPE-MOL(a&b) and Zr-TCBPE-MOL-Ru (c&d)

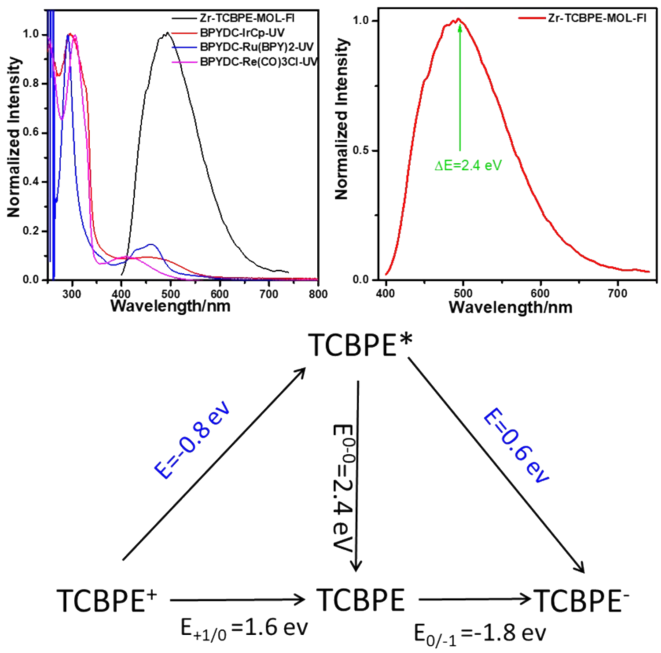

Figure s6 The normalized UV-Vis spectrum of $[H_2BPYDC\text{-}Ru(BPY)_2]Cl_2$, $H_2BPYDC\text{-}Re(CO)_3Cl$, and $[H_2BPYDC\text{-}IrCp^*OH]NO_3$ and the fluorescence spectrum of Zr-TCBPE-MOL, and the redox potential calculation of ligand TCBPE.

The redox potentials of TCBPE should be close to that of the TPE core, which are E_{ox1}=1.6v (vs NHE, TPE^+/TPE^0), E_{ox2}=1.91v (vs NHE, TPE^{2+}/TPE^+) (J. Org. Chem. 2007, 72, 8054-8061) and E_{re1}=-1.8v (vs NHE, TPE^0/TPE^-) (J Electroanal Chem, 1984, 162, 189-206). In the meantime, the fluorescence spectrum of the TCBPE ligand indicates a ΔE value close to 2.4eV. Combining this ground state/excited state energy difference with the redox potentials of the TPE, we can estimate the redox potential of $TCBPE^+/TCBPE^*$ and $TCBPE^*/TCBPE^-$ to be -0.8 V and 0.6 V vs NHE, respectively. These redox potentials are not sufficient for electron transfer to/from $[H_2BPYDC\text{-}Ru(BPY)_2]Cl_2$ (E_{ox1}=1.26v vs NHE for $[H_2BPYDC\text{-}Ru(BPY)_2]^{3+}/[H_2BPYDC\text{-}Ru(BPY)_2]^{2+}$ and E_{re1}=-1.28v vs NHE for $[H_2BPYDC\text{-}Ru(BPY)_2]^{2+}/[H_2BPYDC\text{-}Ru(BPY)_2]^{+}$), $H_2BPYDC\text{-}Re(CO)_3Cl$ (E_{re1}=-0.9v vs NHE for $[H_2BPYDC\text{-}Re(CO)_3]^+/[H_2BPYDC\text{-}Re(CO)_3]^0$), and $[H_2BPYDC\text{-}IrCp^*OH]NO_3$ (E_{ox1}=~1.5v vs NHE $[H_2BPYDC\text{-}IrCp^*(OH)]^+/[H_2BPYDC\text{-}IrCp^*(OH)]^0$, E_{re1}=-1.07v vs $Fc^{+/0}$ $[BPY\text{-}IrCp^*CH_3CN]^{2+}/[BPY\text{-}IrCp^*CH_3CN]^+$).

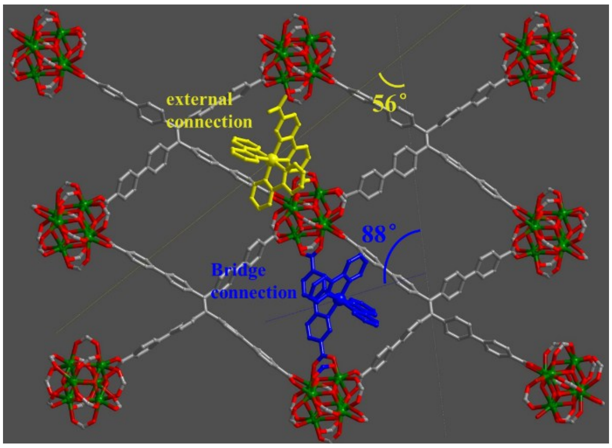

Figure s7 The two possible connection modes of linear dicarboxylate ligands on the MOL

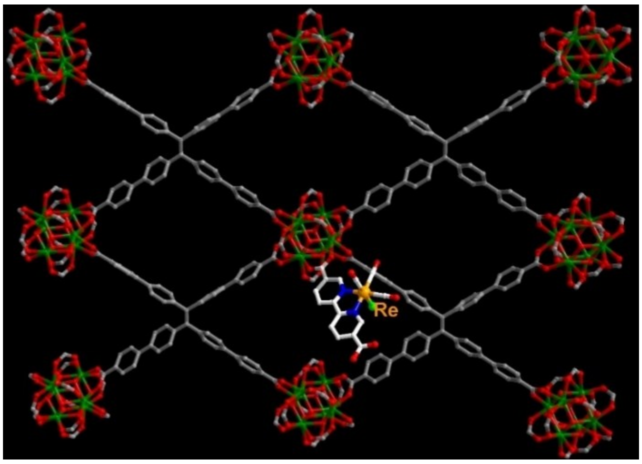

Figure s8 The structure model of Zr-TCBPE-MOL-Re

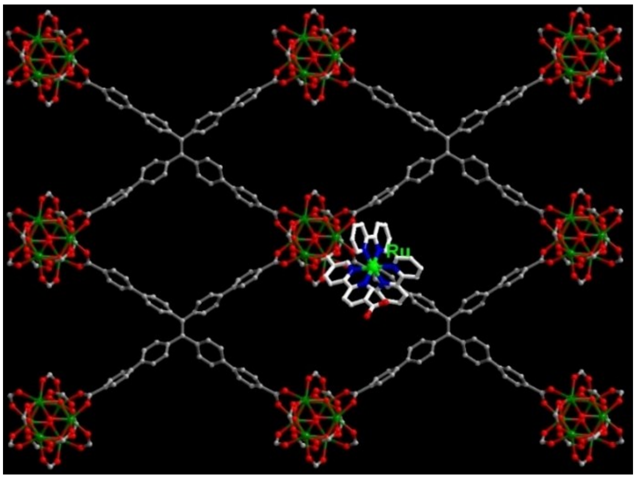

Figure s9 The structure model of Zr-TCBPE-MOL-Ru

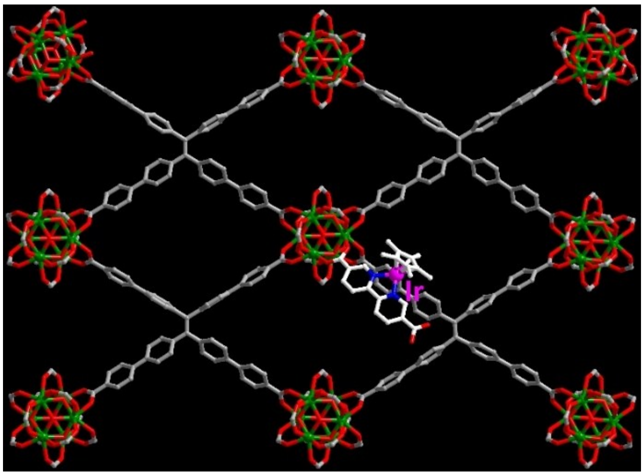

Figure s10 The structure model of Zr-TCBPE-MOL-Ir

Table s1 The ICP-MS analysis of Zr-TCBPE-MOL-Ir and Zr-TCBPE-MOL-Re

Sample[a]	Zr	Re	Ir	Zr_6:Re	Zr_6:Ir
Zr-TCBPE-Re	305.5ppb	17.5ppb	✗	6:1	✗
Zr-TCBPE-Ir	715.6 ppb	✗	19.6 ppb	✗	12.8:1

[a]The samples for ICP-MS analysis were prepared by the following procedure: 2.5 mg of catalyst was put in a teflon reactor, followed by adding 0.6 mL of concentrated HCl and 0.2 mL of concentrated HNO_3 and 0.1 mL of H_2O_2. The teflon reactor was sealed and kept at 160 °C for 5h. After cooling down, the solution was diluted to a total volume of 10 mL. The solution was then diluted for 100 times for the test.

Table s2 The reaction condition and catalysis result of CO_2 reduction

Catalyst		Solvent	Light	Entry
Zr-TCBPE-Ir	2.5 mg	1mL THF and 1mL H_2O	400 nm LED	CO_2&H_2=1:3 1 bar
Zr-TCBPE-Re	35 mg	27 mL MeCN, 1mL TEOA and 1mL H_2O	400 nm LED	CO_2 1 bar

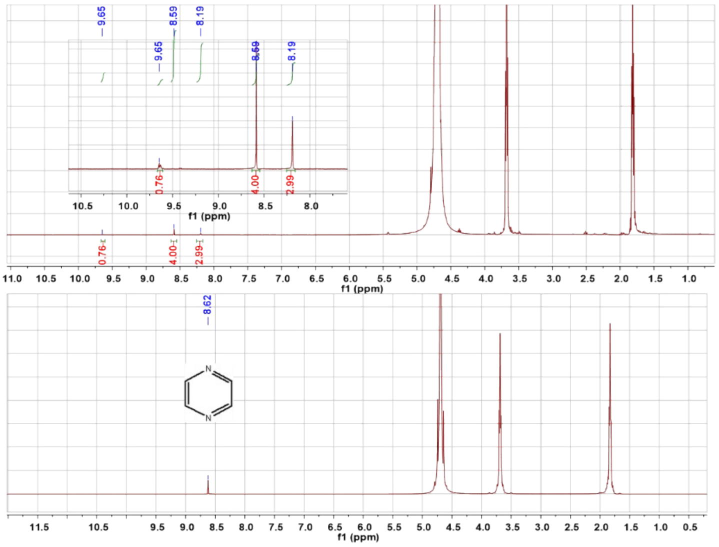

Figure s11 The ^{1}H-NMR of the reaction mixture after catalysis of CO_2 hydrogenation using Zr-TCBPE-MOL-Ir. Pyrazine was added as an internal standard and the solvent was H_2O/D_2O

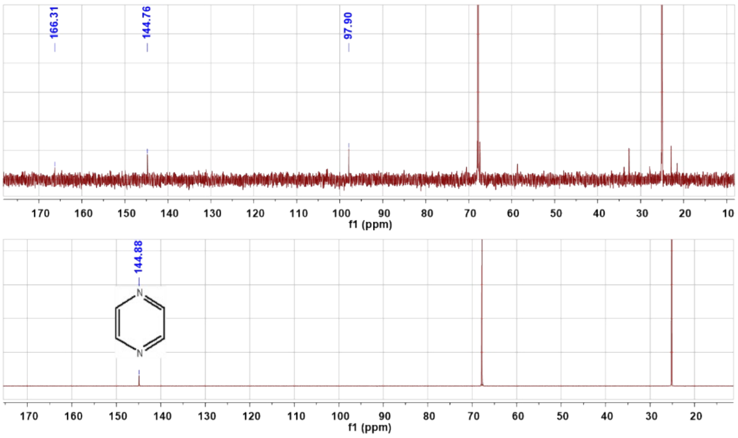

Figure s12 The ^{13}C-NMR of the reaction mixture after catalysis of CO_2 hydrogenation using Zr-TCBPE-MOL-Ir. Pyrazine was added as an internal standard and the solvent was H_2O/D_2O