Supporting Information for

Synergetic Catalysis of Cobalt-based Coordination Polymer for Selective Visible-Light Driven CO_2-to-CO Conversion

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EXPERIMENTAL SECTION

Characterization

The UV-Vis spectra were tested using a Lambda 750 UV/vis/NIR spectrophotometer. The transmission electron microscope images (TEM) were recorded on the Talos F200X, FEI (the acceleration voltage was 200 kV). Scanning electron microscopy (SEM) was performed using Quanta FEG 250, FEI. Photoluminescence spectroscopy (PL) were tested by a (F-7000, Hitachi, Tokyo, Japan) fluorescence spectrophotometer. The electrochemical test was carried out with the CHI 760E electrochemical workstation. The cyclic voltammetry test performed with a three-electrode system, with glassy carbon electrode as working, platinum wire as counter electrode, and $Ag/AgNO_3$ as the reference electrode.

Infrared spectrum testing was conducted using a Frontier Mid-IR FTIR instrument from PerkinElmer, USA. The dynamic light scattering (DLS) tests were detected on a laser-light scattering spectrometer equipped with a digital correlator at 636 nm at a scattering angle of 90°.

Preparation of PEIx-Co nanocomposites.

Co_2L and CoL^1 were prepared according to the literature.[1] PEI-Co was synthesized through the coordination between the amine groups of PEI and cobalt ions. Specifically, PEI (0.055 mmol, 0.068 mmol, 0.082 mmol, 0.096 mmol, 0.11 mmol) was dissolved into 10 mL ethanol, then the solution of cobalt perchlorate (0.20 mmol) in 5 mL ethanol was added slowly under Ar atmosphere and stirred at room temperature for 6h. After that, the precipitate formed was washed with ethanol and centrifuged for five times, and then was dried under vacuum to obtain the brown sample. The catalysts with different ratio of N atom and cobalt were synthesized by adjusting the amount of polyethyleneimine and cobalt perchlorate and labeled as PEI_4-Co (N/Co = 4/1), PEI_5-Co (N/Co = 5/1), PEI_6-Co (N/Co = 6/1), PEI_7-Co (N/Co = 7/1), and PEI_8-Co (N/Co = 8/1), respectively. The exact contents of cobalt in the catalyst were measured by ICP-MS. The results are listed in Table S1.

Photocatalytic reduction of CO_2

Photocatalytic conversions of CO_2 were carried out by adding 0.5 μg photocatalyst PEI_6-Co and 2 mg photosensitizer $[Ru(phen)_3](PF_6)_2$ into 5 mL solution of CH_3CN/H_2O (4:1) and 0.3 M triethanolamine (TEOA) in a quartz bottle. The

photoreaction equipment was sealed by the rubber tube and filled with CO2 for 30 min, then, the photoreaction system was irradiated by a 450 nm LED light (100 $mW \cdot cm^{-2}$, irradiation area 0.8 cm^2). The generated gas products were detected by a GC-2014 (Shimadzu) gas chromatography with a hydrogen flame ionization detector (FID).

Table S1. ICP-MS results for the contents of cobalt in the catalyst

Entry	Catalyst	wt % (Co)
1	PEI_4-Co	11.51
2	PEI_5-Co	10,72
3	PEI_6-Co	10.85
4	PEI_7-Co	9.86
5	PEI_8-Co	9.56

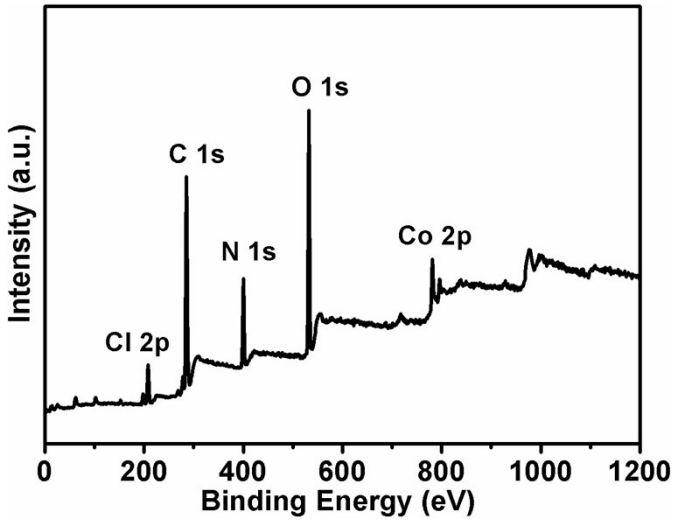

Figure S1. XPS scan of PEI_6-Co.

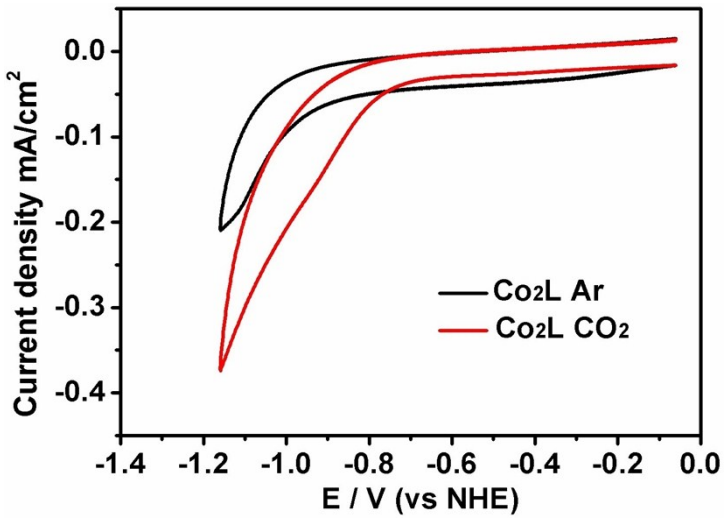

Figure S2. CV curves of 0.5 mM Co_2L in aqueous solution containing 0.1 M $NaHCO_3$ under an Ar (black) and CO_2 atmosphere (red) at 25°C, using a glassy carbon electrode with a scan rate of 100 $mV \cdot s^{-1}$

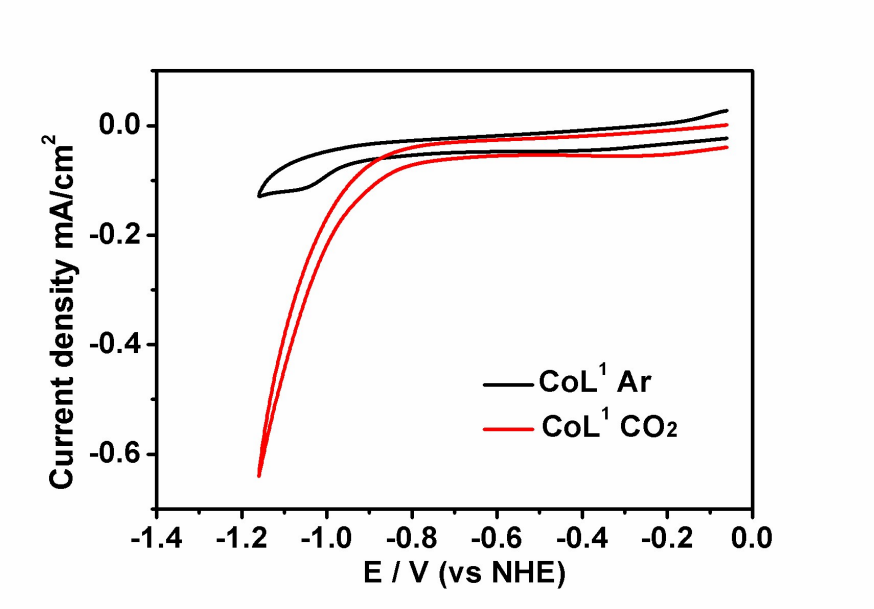

Figure S3. CV curves of 0.5 mM CoL^1 in aqueous solution containing 0.1 M $NaHCO_3$ under an Ar (black) and CO_2 atmosphere (red) at 25°C, using a glassy carbon electrode with a scan rate of 100 $mV \cdot s^{-1}$

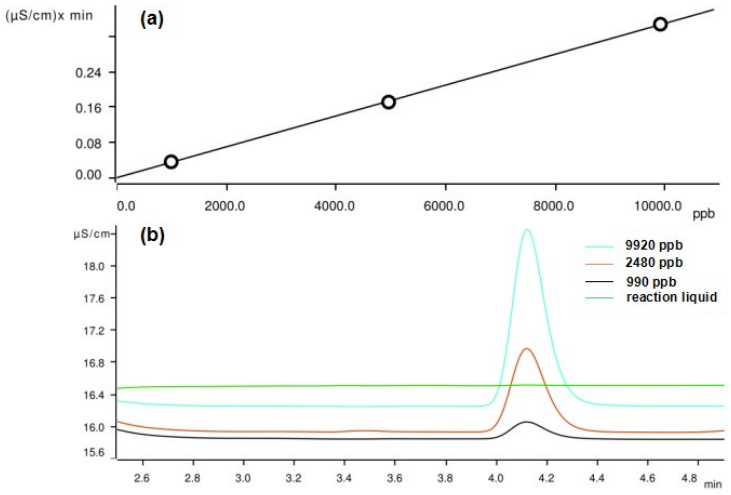

Figure S4. (a) The standard curve of formate, and (b) the ion chromatogram of the reaction liquid, indicating the amount of formed formate is negligible (about 13.7 ppb)

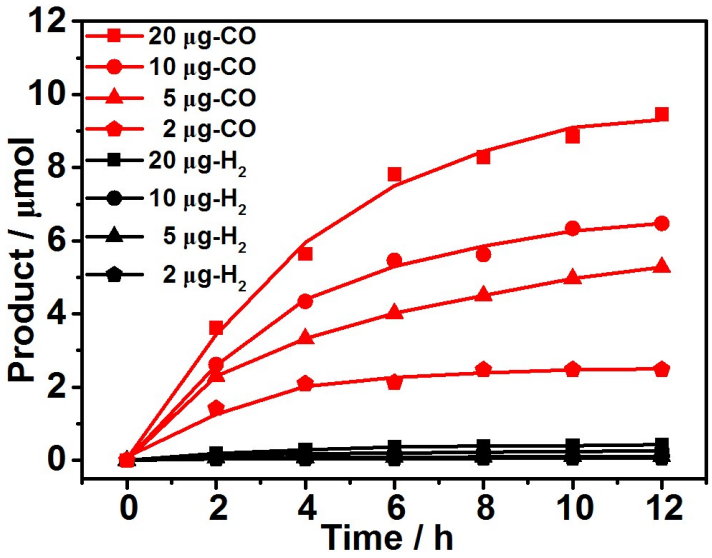

Figure S5. Photocatalytic reduction of CO2 with different amounts of PEI6-Co (2 μg, 5 μg, 10 μg, 20 μg).

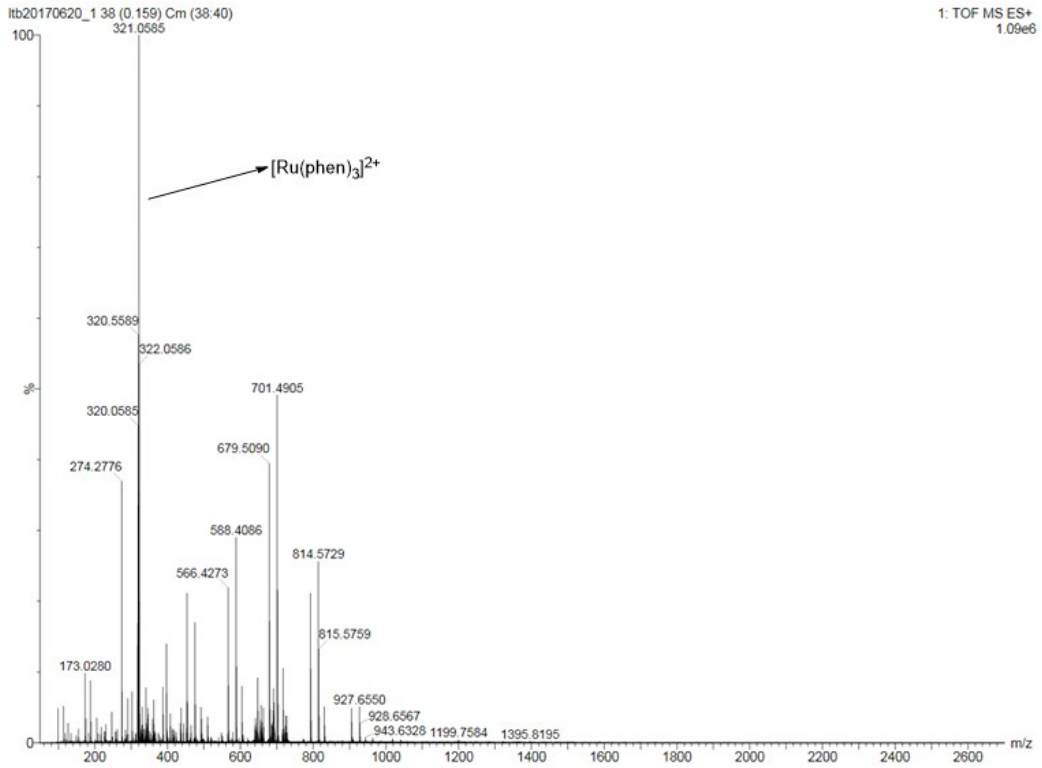

Figure S6. HRMS (ESI) spectrum of $[Ru(phen)_3](PF_6)_2$ before the photoreaction.

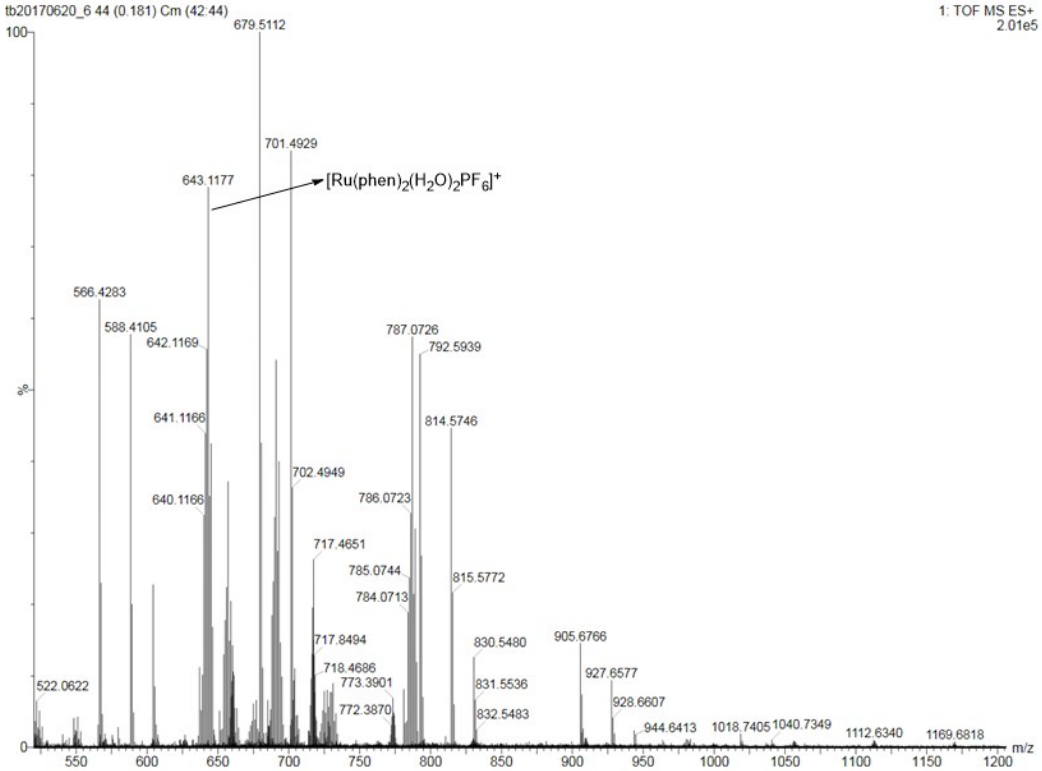

Figure S7. HRMS (ESI) spectrum of $[Ru(phen)_3](PF_6)_2$ after the photoreaction.

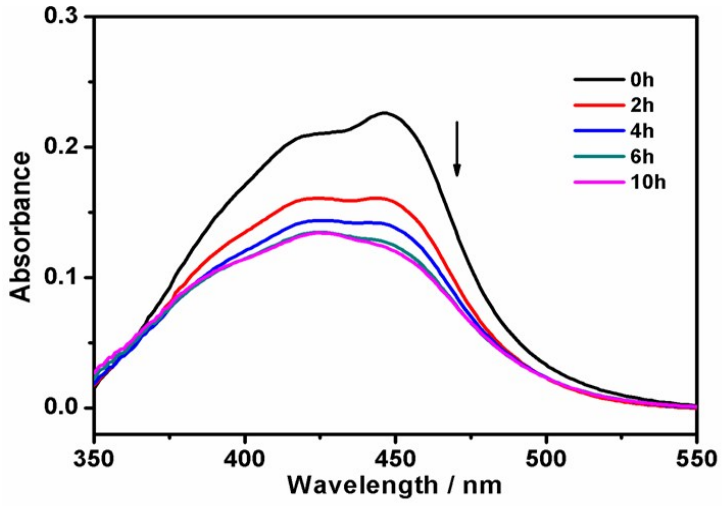

Figure.S8 UV absorption spectrum of phenanthroline quinone at different reaction times.

Reference

(1) Ouyang, T.; Huang, H. H.; Wang, J. W.; Zhong, D. C.; Lu, T. B. A Dinuclear Cobalt Cryptate as a Homogeneous Photocatalyst for Highly Selective and Efficient Visible-Light Driven CO_2 Reduction to CO in CH_3CN/H_2O Solution. *Angew. Chem., Int. Ed.* **2017,** *56*, 738-743.