

# Synthesis of $Zr_4(\text{embonate})_6$ -Cobalt Based Superstructure for Photocatalytic Hydrogen Production

Qian Teng <sup>a,b</sup>, Yan-Ping He <sup>a,\*</sup>, Shu-Mei Chen <sup>b</sup> and Jian Zhang <sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China. E-mail: hyp041@163.com, and zhj@fjirsm.ac.cn

<sup>b</sup> College of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, China.

## Experimental section

**Materials and instrumentation:** All reagents were purchased commercially and used without further purification. PTC-101(Zr) as a starting material of  $Zr_4L_6$  cages was massively synthesized by the method reported in our previous work.<sup>1</sup> Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. Powder XRD was recorded on a Rigaku Dmax/2500 X-ray diffractometer operating at 40 kV and 100 mA, using Cu-K $\alpha$  or Ga-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$  or  $1.3405 \text{ \AA}$ ). The patterns were scanned over an angular range of 3-45° (2 theta) with a step length of 0.05° (2 theta). The UV diffuse reflection data were recorded at room temperature using a powder sample with BaSO<sub>4</sub> as a standard (100% reflectance) on a PerkinElmer Lambda-950 UV spectrophotometer. Steady-state PL spectra are investigated by a fluorescent spectrophotometer (Edinburgh, FLS980). PL spectra are scanned on a photoluminescence spectrometer under an excitation wavelength of 370 nm. Thermogravimetric (TGA) analysis is performed on a Netzsch STA449F3 analyzer at a heating rate of 10°C / min from ambient temperature to 800 °C under a nitrogen gas atmosphere. Mott-Schottky measurements are conducted at frequencies of 1000 and 3000 Hz in the potential range from -1 to 1 V using ZAHNER IM6 electrochemical analyzer in a standard three-electrode cell, with working electrode (ITO), reference electrode Ag/AgCl (KCl saturated) and counter electrode platinum plate. Surface chemical analyses were performed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher, ESCALAB 250Xi). Magnetic properties were measured on a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms (Variable-temperature magnetic susceptibilities were measured at 2-300 K at 2000 Oe field).

**Synthesis of (anion)[Co(II)Co(III)(Zr<sub>4</sub>L<sub>6</sub>)<sub>0.5</sub>(bidpe)<sub>2.5</sub>(H<sub>2</sub>O)<sub>6</sub>]·Guest (PTC-318).** PTC-101(Zr) (80 mg, 0.02 mmol), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (30 mg, 0.10 mmol) and 4,4'-bis(imidazolyl)diphenyl ether (bidpe, 15 mg, 0.05 mmol) were dissolved to 6 mL of DMF/H<sub>2</sub>O (2:4 v/v) mixed solvents. The mixture was heated at 60 °C for 3 days. Yellow crystals of **PTC-318** were obtained. Yield: 61% based on PTC-101(Zr).

**X-ray Crystallography.** Crystallographic data of **PTC-318** was collected on a Supernova single crystal diffractometer equipped with graphite-monochromatic Cu-K $\alpha$  or Ga-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$  or  $1.3405 \text{ \AA}$ ) at 100 K. Absorption correction was

applied using SADABS.<sup>2</sup> Structure was solved by direct method and refined by full-matrix least-squares on  $F^2$  using SHELXTL.<sup>3</sup> In these structures, some cations/anions and free guest molecules were highly disordered and could not be located. The diffused electron densities resulting from these residual cations/anions and guest molecules were removed from the data set using the SQUEEZE routine of PLATON<sup>4</sup> and refined further using the data generated. Crystal data and details of data collection and refinement of **PTC-318** were summarized in Table S1.

**Photocatalytic H<sub>2</sub> evolution test.** The photocatalytic generation of H<sub>2</sub> was carried out in a 25 mL Pyrex reactor and irradiated under a 300 W (PLS-SXE300D) Xe lamp with a 420 nm cutoff filter. Crystals of **PTC-318** (10 mg) were added to the mixed solution of CH<sub>3</sub>CN/H<sub>2</sub>O (5 mL, v/v = 4:1, containing 10mg BIH as a sacrificial agent) as photocatalysts, and then stirred by using a magnetic stirrer. After degassing with high-purity N<sub>2</sub> to remove dissolved O<sub>2</sub> for 30 min, the reaction is performed under the irradiation of a 300-W Xe lamp with a 420 nm cutoff filter. The generated gas products were analyzed by a gas chromatography analyzer (FULI 9790II), equipped with the flame ionization detector (FID) and thermal conductivity detector (TCD). Each reaction was repeated three times to ensure the reliability of the experiment data.

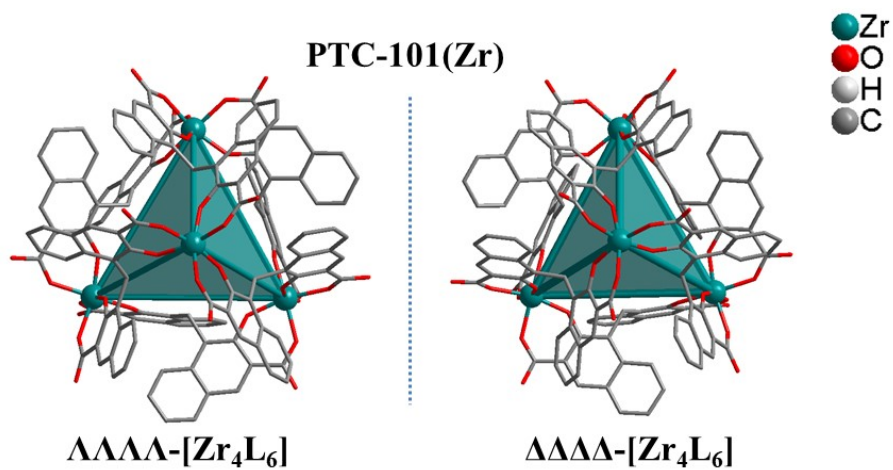
**Electrochemical measurement.** An ITO glass with 0.196 cm<sup>2</sup> deposition area is used as the support for the working electrode. The sample suspensions are prepared by dispersing 5 mg of **PTC-318** in the solution containing 985 uL ethanol and 15  $\mu$ L Nafion followed by ultrasonication in 20 °C for 30 min. Then, 20  $\mu$ L of the suspension is pipetted onto the ITO in four times and dried at ambient temperature, which is used as the working electrode. Na<sub>2</sub>SO<sub>4</sub> solution aqueous solution (0.5 M, pH = 6.6) is used as electrolyte solution.

## References:

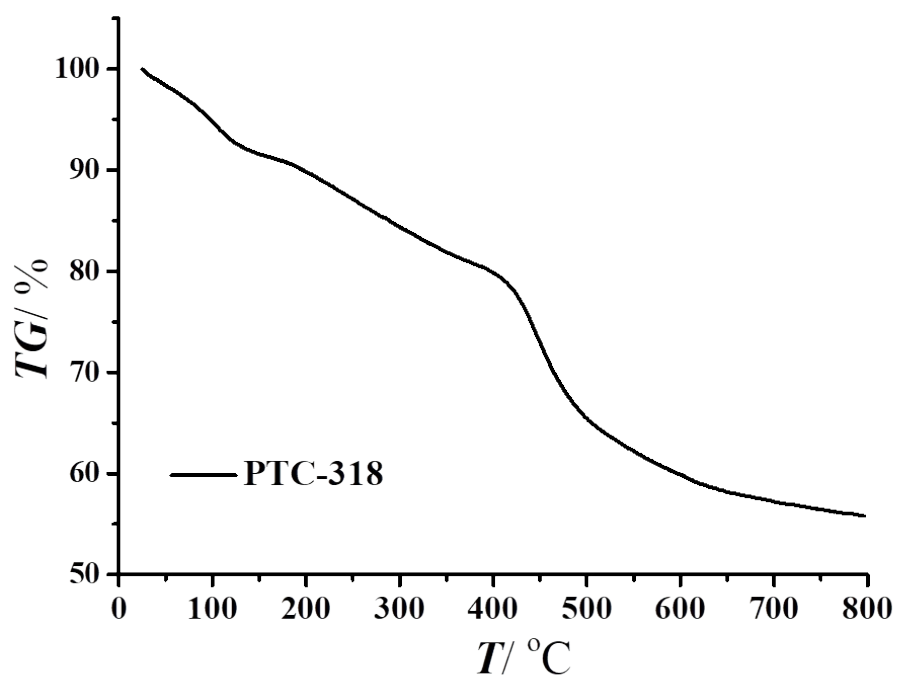
- [1] Y.-P. He, L.-B. Yuan, G.-H. Chen, Q.-P. Lin, F. Wang, L. Zhang and J. Zhang, *J. Am. Chem. Soc.*, 2017, **139**, 16845–16851.
- [2] G. M. Sheldrick, SADABS, Program for area detector adsorption correction. *Institute for Inorganic Chemistry*, University of Göttingen, Göttingen (Germany), 1996.
- [3] G. M. Sheldrick, SHELXL-2014/7: *A Program for Structure Refinement*, University of Göttingen, Göttingen, Germany, 2014.
- [4] P. van der Sluis, A. L. Spek, *Acta Cryst. A*, 1990, **46**, 194–201.

**Table S1.** Crystallographic Data and Structure Refinement Details for **PTC-318**.

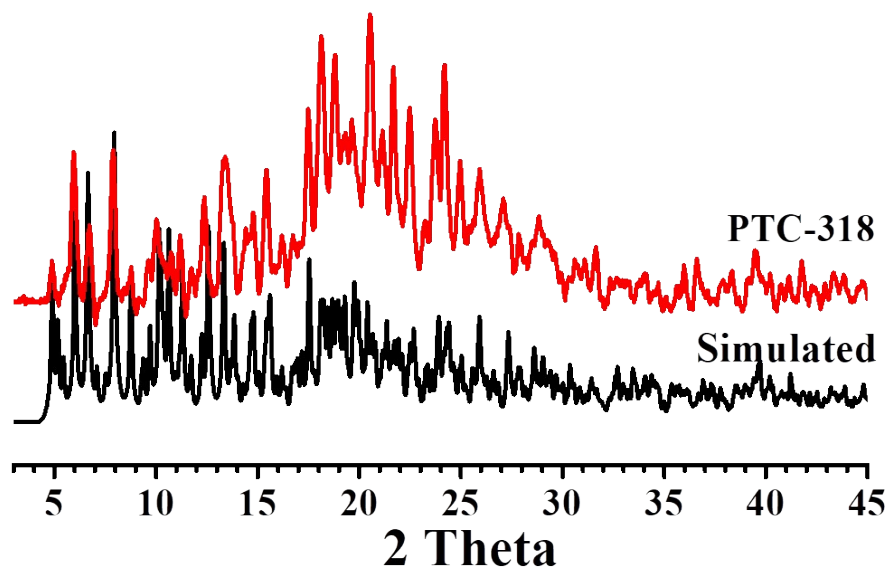
<b>Compounds</b>	<b>PTC-318</b>
CCDC	2175124
Formula	C <sub>228</sub> H <sub>172</sub> Co <sub>4</sub> N <sub>22</sub> O <sub>55</sub> Zr <sub>4</sub>
Formula weight	4700.47
Crystal system	Monoclinic
Space group	<i>C2/c</i>
<i>a</i> (Å)	29.2228 (4)
<i>b</i> (Å)	23.4628 (3)
<i>c</i> (Å)	33.6913 (4)
$\alpha$ (°)	90
$\beta$ (°)	105.9570(10)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	22210.3(5)
<i>Z</i>	4
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.406
$\mu$ (Mo/Cu <i>Ka</i> ) (mm <sup>-1</sup> )	3.052
<i>F</i> (000)	9608
Temperature (K)	100.00(10)
Theta min, max (deg)	3.275, 44.130
Tot., uniq. Data	63137, 12480
Observed data [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	9717
<i>R</i> <sub>int</sub>	0.0477
Data/restraints/parameters	12480/166/1400
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.1023, 0.2685
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.1260, 0.2940
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.976



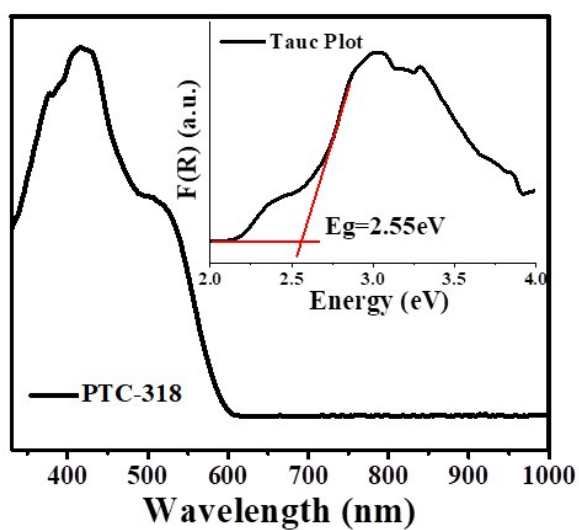
**Figure S1.** Structures of the  $\Delta\Delta\Delta\Delta$ -[Zr<sub>4</sub>L<sub>6</sub>] and  $\Lambda\Lambda\Lambda\Lambda$ -[Zr<sub>4</sub>L<sub>6</sub>] isomers in PTC-101(Zr).



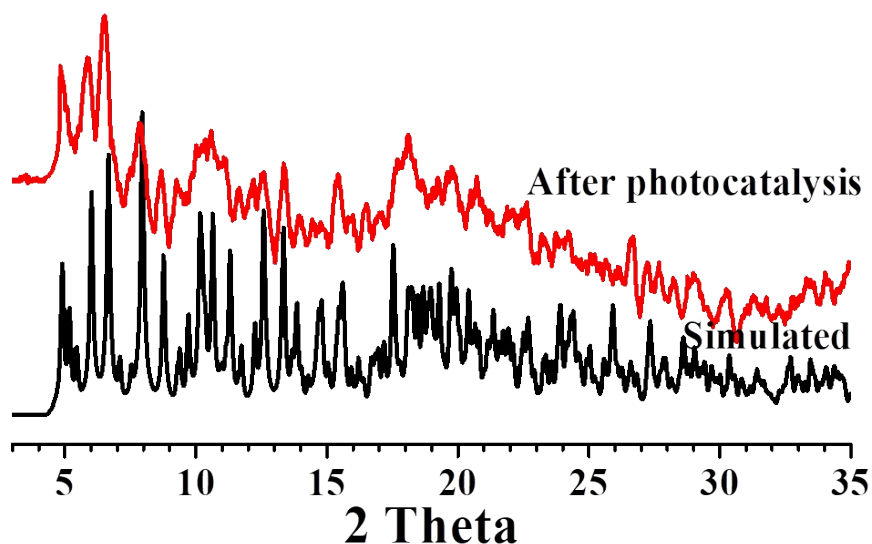
**Figure S2.** TGA curve of PTC-318.



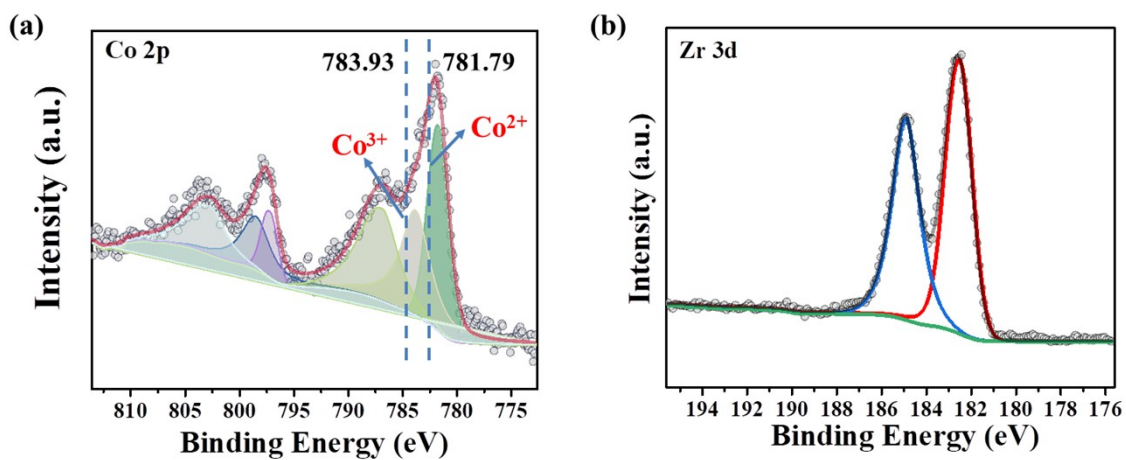
**Figure S3.** PXRD patterns of simulated from the single-crystal data of PTC-318 (black) and as-synthesized PTC-318 (red).



**Figure S4.** UV-vis absorption spectrum of PTC-318 and its Kubelka-Munk-transformed reflectance spectrum.

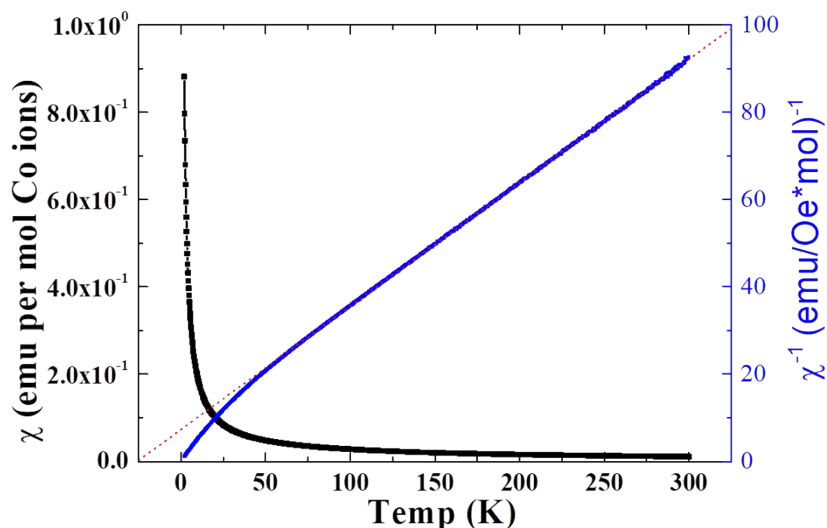


**Figure S5.** PXRD patterns of simulated from the single-crystal data of **PTC-318** (black) and the sample of **PTC-318** (red) after catalytic test.



**Figure S6.** High-resolution XPS spectra of **PTC-318**.

To investigate the electronic structure of the composite sample, X-ray photoelectron spectroscopy (XPS) measurements were carried out. As shown in the Co 2p curves of **PTC-318**, the metal peaks of **PTC-318** are located at different binding energies (781.79 and 783.93 eV), indicating that the valence states of their metal ions are different and have obvious differences.



**Figure S7.** The temperature dependence of molar magnetic susceptibility  $\chi(T)$  for compound **PTC-318** was measured at the magnetic field of 2000 Oe (plot of  $\chi$  versus T). The inverse susceptibility  $\chi^{-1}$  (blue line) and corresponding linear temperature fit (red dashed line) are also plotted to determine the effective moment for Co ions.

We also measured the temperature dependence of the magnetic susceptibility ( $\chi$ ) of our sample (**PTC-318**) in a magnetic field of  $H=2000$  Oe. In the zero-field-cooling (ZFC) and the field-cooling (FC) measurements, no essential difference was observable. As shown in Figure S7,  $\chi(T)$  increases monotonically upon cooling, showing a typical paramagnetic behavior. The good linear behavior can be observed in the corresponding plot of the temperature dependent inverse susceptibility ( $\chi^{-1}$ ) in Figure S7 above 50 K. A Curie-Weiss fit ( $\chi=C/(T-\theta_{C-W})$ ) yields a negative Curie-Weiss temperature ( $\theta_{C-W}=-25.9$  K), suggesting the presence of mainly weak antiferromagnetic exchange interactions between Co ions in this compound.<sup>1</sup> The fitted effective moment is about  $5.35 \mu_B$  per Co ion. This value is much larger than the spin-only value of  $\text{Co}^{2+}$  ( $3.87 \mu_B$ ) or  $\text{Co}^{3+}$  ( $4.90 \mu_B$ ), large orbital moment contributions must be considered. According to the previous studies on the magnetic properties of  $3d$  group ions, our results are between the usual  $\text{Co}^{2+} 3d^6$  configuration ( $5.40 \mu_B$ ) and the  $\text{Co}^{2+} 3d^7$  one ( $4.80 \mu_B$ ),<sup>2</sup> suggesting the valence state of Co ion in our sample is +3 and +2.

#### References:

- [1] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, p.285, Oxford, 1952.
- [2] R. Kubo and T. Nagamiya, p.453, *Solid State Physics*, McGraw-Hill, New York, 1969.