Lead—Porphyrin Metal—Organic Framework: Gas Adsorption Properties and Electrocatalytic Activity for Water Oxidation

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Synthesis of Pb-TCPP

A mixture of H_6TCPP (5.0 mg, 0.006 mmol) and $PbCl_2$ (8.0 mg, 0.03 mmol) in a mixed solvent of DMF (1.0 mL) and $HClO_4$ (1 d) was heated to 130 ℃ in a 4 mL glass tube for 3 days. Deep brownish crystals of **Pb-TCPP** were filtered, washed with DMF and EtOH, and dried at room temperature. Yield: 25%, based on H_6TCPP. This complex could also be isolated by the different reported method [1].

Experiment for electrochemical measurements

The glassy carbon electrode (GCE) as work electrode with the diameter of 4.0 mm (Gamry Reference 600 Instruments, USA) was polished with alumina slurry and cleaned with ethanol and DI water. A conventional three-electrode system was used with SCE (saturated KCl) as the reference electrode and Pt foil as counter electrode. The potential values are corrected to the reverse hydrogen electrode (RHE) according the equation E(RHE)=E (SCE)+0.245+0.0591pH V. Typically, 5.0 mg of sample and 20.0 μL Nafion solution (5 wt%) were dispersed in mixed solution containing deionized water and ethanol with volume ratio of 1:1 by sonicating for 1 h to form a homogeneous ink. Then 5.0 μL of the dispersion was loaded onto a glassy carbon electrode. The cathodic current density was calculated by the geometric area of GCE which is 0.1256 cm^2. Prior to each electrochemical measurement, the electrolyte solution was purified with O_2 for 30 min to saturate the electrolyte and the O_2 flow was maintained over the solution during the test. Linear sweep voltammogram curves were examined in 1 M KOH (pH=14), 0.1M KOH (pH=13) and 0.2M PBS (pH=7.4) solution for electro-catalysts, respectively, The scan rate is 20 $mV \cdot s^{-1}$ and the scan region ranges from 0 to 0.8 V vs SCE, AC impedance spectra for different electro-catalysts at overpotential of 0.65 V vs SCE from 145 to 0.1 Hz with an AC voltage of 5 mV.

Calculation method of the turnover frequency (TOF)

The mass activity ($A \cdot g^{-1}$) was calculated on the basis of the catalyst loading m = 0.199 mg cm^{-2} and the measured current density j ($mA \cdot cm^{-2}$) at η = 1.2 V vs RHE by

$$mass\ activity = \frac{j}{m}$$

TOF was calculated on the basis of the catalyst loading m = 0.199 mg cm^{-2}, and the measured current density j ($mA \cdot cm^{-2}$) at η = 1.2 V vs RHE by

$$TOF = Jg\frac{A}{4nF}$$

j is the measured currenat density ($mA \cdot cm^{-2}$) at η = 1.2 V vs RHE, A is the geometric area of the PG electrode, n is the mole number of the coated catalysts, and F is the Faraday constant (96 500 $C \cdot mol^{-1}$)[2].

A suitable crystal was selected and tested on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2[3], the structure was solved with the structure solution program using and refined with the ShelXL refinement package using Least Squares minimisation.

Table SI1. Crystal data and structure refinement for **Pb-TCPP**.

Empirical formula	$C_{28}H_{23}N_3O_5Pb$
Formula weight	688.68

Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.0356(2)
b/Å	7.08902(10)
c/Å	28.1674(4)
α/°	90
β/°	99.7997(14)
γ/°	90
Volume/Å^3	2958.49(8)
Z	4
ρ_{calc}mg/mm^3	1.546
m/mm^{-1}	11.407
F(000)	1336.0
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection	12.55 to 134.13°
Index ranges	$-17 \le h \le 13$, $-7 \le k \le 8$, $-32 \le l \le 33$
Reflections collected	10588
Independent reflections	5268 [R_{int} = 0.0270, R_{sigma} = 0.0330]
Data/restraints/parameters	5268/210/337
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0530, wR_2 = 0.1481
Final R indexes [all data]	R_1 = 0.0558, wR_2 = 0.1507
Largest diff. peak/hole / e Å^{-3}	2.81/-1.39

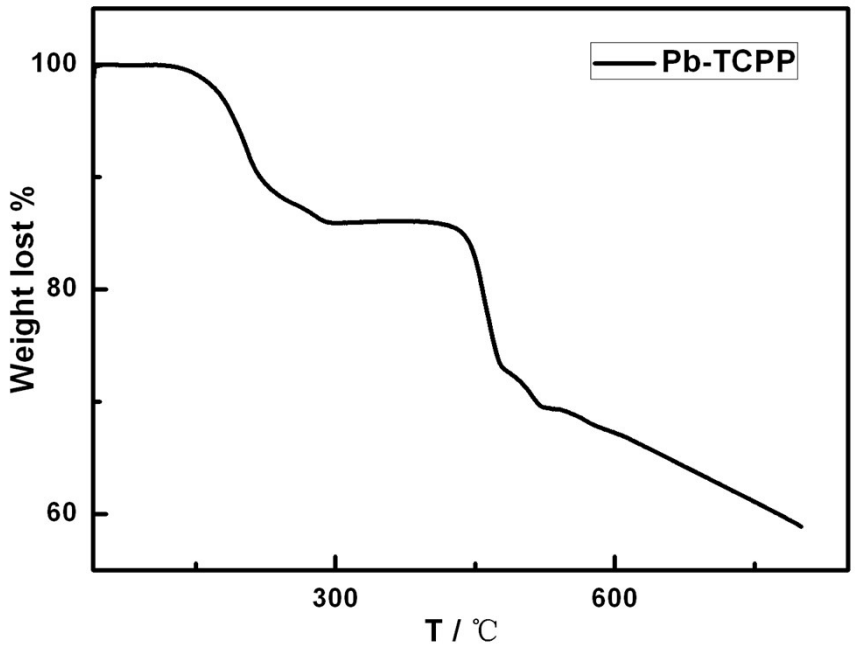

Figure SI1. TGA curve of **Pb-TCPP**.

References

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