

### *Supporting Information*

## (*t*Bu)<sub>4</sub>M(II)Phthalocyanines (M = Co(II), Ni(II), Mn(II)) Revisited: Self-assembled Nanosheets for Enhanced Electrochemically Catalyzed Hydrogen Evolutions

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### **1 Experimental Sections**

#### **1.1 General**

All reagents and solvents used were of reagent grade and were used as received unless noted otherwise. Cyclic voltammetry was carried out on a Chi-730D electrochemistry station with a three-electrode cell. A glassy carbon disk, a platinum wire and an Ag/AgCl electrode were used as the working, counter and reference electrodes, respectively. An inert nitrogen atmosphere was introduced during all of the electrochemical measurements, which were carried out at room temperature. The UV and visible regions of the electronic absorption spectra were recorded with an HP 8453A diode array spectrophotometer. All solutions reported in this section were firstly degassed and protected with high-purity Ar gas (over 99.99%).

#### **1.2 Direct Preparation of Nanosheets on the rGO surface**

Firstly, 1.0 mg of rGO was mixed with 1 mL of isopropyl alcohol containing 0.2% nafion and the mixture sonicated in an ultrasonic bath for 30 min to produce a homogeneous mixture of concentration 1 mg/mL. The surface of the glassy carbon electrode (GCE,  $\Phi = 3$  cm) was polished with 0.05  $\mu\text{m}$  alumina and rinsed with doubly distilled water in the ultrasonic bath to remove any adhered Al<sub>2</sub>O<sub>3</sub> particles. The electrodes were rinsed with ethanol and dried under

room temperature for ca. 5 min. Then, 4  $\mu\text{L}$  of the rGO/isopropyl alcohol/nafion suspensions were drop cast on the surface of the GC electrode and allowed to dry at room temperature. Then, three metallophthalocyanines were prepared as the mixed solution (concentration is  $C = 1 \text{ mg/mL}$ ). Upon using various organic solvents and sonication (details have been well discussed in the main manuscript), 50  $\mu\text{L}$  aliquots of 0.2 mM dichloromethane solutions of **3** were added dropwise to the rGO/nafion-coated electrodes and dried at room temperature overnight. Before electrocatalytic investigations, the electrodes were stored in MilliQ water in the dark.

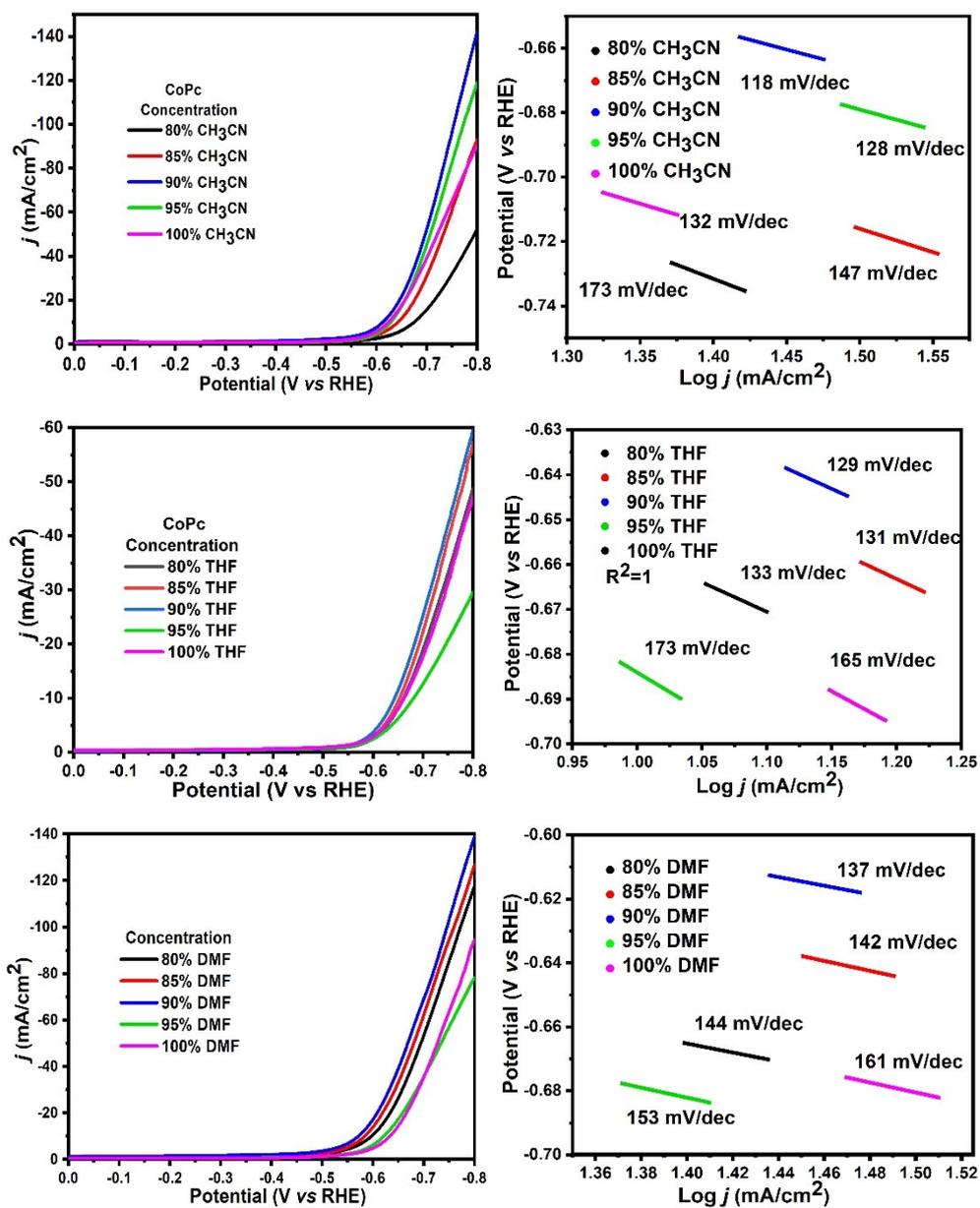


Figure S1 LSV measurement (left) and Tafel Slope (right) of Co(II)(tBu)<sub>4</sub>Pc 1 upon introducing water to various solvents.

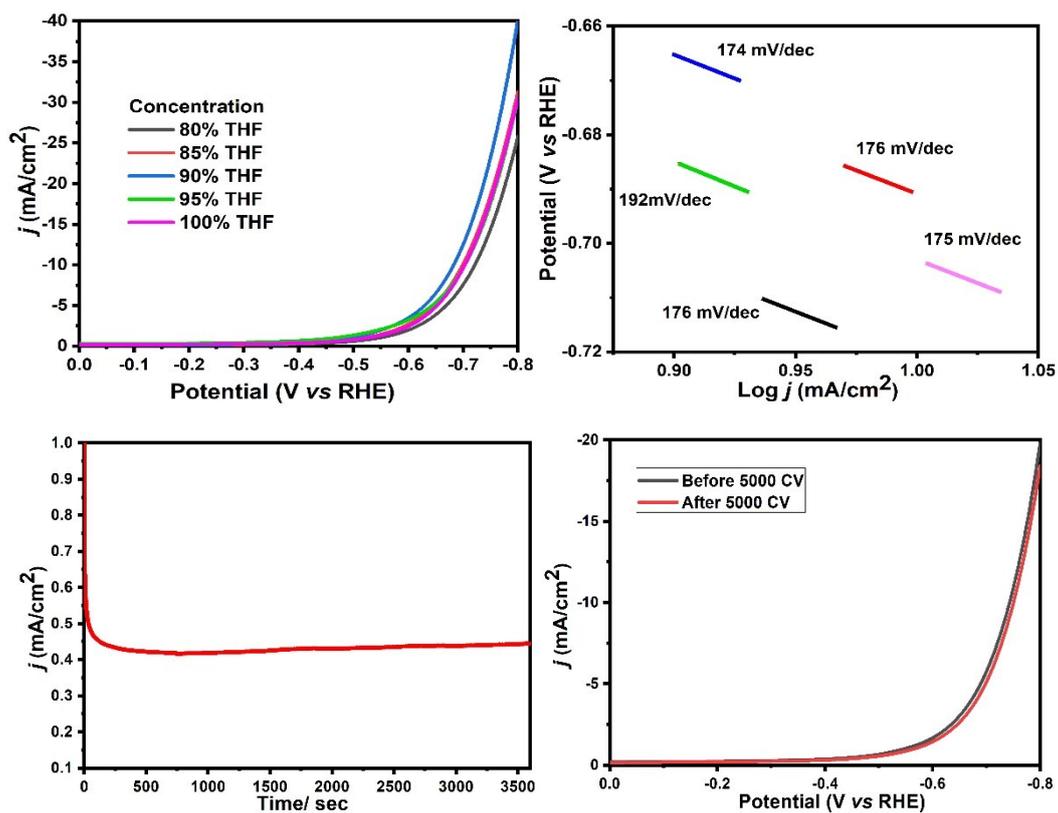


Figure S2 LSV measurement (left) and Tafel Slope (right) of Co(II)(tBu)<sub>4</sub>Pc 1 upon introducing water to THF solution.

**Table S1.** Summary of electrochemically catalyzed hydrogen evolution behaviors of Co(II)Pc **1**, Ni(II)Pc **2** and Cu(II)Pc **3** at different conditions.

No.	Condition	Over potential (V)	Current Density (mA/cm <sup>2</sup> )	Tafel Slop (mV/dec)
<b>Co(II)Pc 1</b>	80% iPA	-0.53	-18.87	133
	85% iPA	-0.53	-22.27	131
	90% iPA	-0.52	-32.22	129
	95% iPA	-0.53	-16.95	173
	100% iPA	-0.53	-24.53	165
	80% THF	-0.61	-3.97	254
	85% THF	-0.61	-5.19	187
	90% THF	-0.61	-6.43	185
	95% THF	-0.61	-4.72	326
	100% THF	-0.61	-3.68	245
	80% CH <sub>3</sub> CN	-0.65	-5.68	173
	85% CH <sub>3</sub> CN	-0.64	-9.12	147
	90% CH <sub>3</sub> CN	-0.62	-12.82	118
	95% CH <sub>3</sub> CN	-0.62	-9.59	128
	100% CH <sub>3</sub> CN	-0.62	-10.94	132
	80% DMF	-0.58	-7.49	144
	85% DMF	-0.58	-10.16	142
	90% DMF	-0.57	-11.67	137
	95% DMF	-0.61	-9.05	163
	100% DMF	-0.62	-8.15	161
<b>Ni(II)Pc 2</b>	80% iPA	-0.40	-15.52	273
	85% iPA	-0.40	-21.13	252
	90% iPA	-0.40	-26.50	186
	95% iPA	-0.40	-18.43	272
	100% iPA	-0.40	-26.97	218
	80% THF	-0.60	-1.94	176
	85% THF	-0.60	-2.64	176
	90% THF	-0.60	-3.65	175
	95% THF	-0.60	-3.46	175
	100% THF	-0.60	-2.70	192
<b>Cu(II)Pc 3</b>	80% THF	-0.63	-3.04	152
	85% THF	-0.63	-3.24	148
	90% THF	-0.62	-3.82	138
	95% THF	-0.63	-2.40	139
	100% THF	-0.63	-2.19	141