

**Supporting Information for**

**Promoting charge separation in composite of  $\delta$ -CsPbI<sub>3</sub> and covalent organic frameworks**

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**EXPERIMENTAL SECTION**

**Chemical reagents**

All reagents were commercially purchased and used without further purification. TaPt, TP and  $\delta$ -CsPbI<sub>3</sub> were purchased from Zhengzhou Alfa. Chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>), triethanolamine (TEOA), ethanol, acetic acid, dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), tetrahydrofuran (THF), 1,3,5-trimethylbenzene, and 1,4-dioxane were purchased from Chengdu Kolon.

**Preparation of  $\delta$ -CsPbI<sub>3</sub>@TAPT-TP-COF**

The  $\delta$ -CsPbI<sub>3</sub>@TAPT-TP-COF was synthesized by the solvothermal method. Certain amount of  $\delta$ -CsPbI<sub>3</sub> powder were ultrasonically dispersed in mixed solvent of 1 mL 1,3,5-trimethylbenzene and 1 mL 1,4-dioxane in a high-pressure glass tube. Then, 12 mg TP, 17.8 mg TAPT and 200  $\mu$ L acetic acid were dissolved in the solution by sonication. After evacuation, the glass tube was heated at 120 °C for 12 h. Then, the precipitate was collected by centrifuging, washing with CH<sub>2</sub>Cl<sub>2</sub>, THF and ethanol three times, and finally, dried at 60 °C overnight.

**Preparation of Pt@ $\delta$ -CsPbI<sub>3</sub>@TAPT-TP-COF**

10 mg of  $\delta$ -CsPbI<sub>3</sub>@TAPT-TP-COF was homogeneously dispersed in 20 mL mixed solvent of 1,3,5-trimethylbenzene and 1,4-dioxane (V/V=1:1) containing certain amount of H<sub>2</sub>PtCl<sub>6</sub> (Figure 1a). After evacuation, the solution was illuminated by using 300 W xenon lamp for 30 min. Then, the precipitate was collected by

centrifuging, washing with CH<sub>2</sub>Cl<sub>2</sub>, THF and ethanol three times, and finally, dried at 60 °C overnight.

### **Characterization**

The composition of the materials was tested by X-ray powder diffraction (X-ray diffractometer, DX2700) with a diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) at 50 kV and 200 mA in the  $2\theta$  range of 20-80° at a scanning rate of 10° min<sup>-1</sup>. The chemical composition and structural details further were analyzed by X-ray photoelectron spectroscopy spectra (XPS, Thermo V4105) using monochromatized Al K $\alpha$  excitation. The microstructure and morphology were confirmed by scanning electron microscope images (SEM, Apreo 2C, Thermo), transmission electron microscope images (TEM, JEM-2100F) and energy-dispersive spectroscopy mapping images (EDS). Physical properties were analyzed by nitrogen adsorption isotherms (ASAP-2460) and thermogravimetric analysis (TGA, DSC2). Optical properties were tested by UV-vis diffuse reflectance spectra (DRS, UV-3600, Shimadzu) detecting absorption over the range of 300-800 nm, photoluminescence spectrometer (PL, F-7000, Hitachi) and fluorescence lifetime (FL, F-7000, Hitachi) with an excitation wavelength of 210 nm.

The electrochemical impedance spectroscopy (EIS), Mott-Schottky plot (MS), and time-resolved photo-current response (PTR) tests were performed using a standard three-electrode system with an electrochemical workstation (CHI660E, Shanghai). 5 mg catalyst was ultrasonically dispersed in mixed solvent of 125  $\mu\text{L}$  ethanol and 375  $\mu\text{L}$  deionized water by sonication for 30 min. Subsequently, 10  $\mu\text{L}$  5 wt% nafion solution was added to the above suspension solution. Finally, 40  $\mu\text{L}$  obtained suspension solution was evenly dropped onto a 1 cm  $\times$  1 cm conductive glass to make a working electrode. During the experiments, AgCl/Ag and Pt electrodes were used as the reference electrode and counter electrode, respectively, and Na<sub>2</sub>SO<sub>4</sub> solution (0.1 M) was used as the electrolyte solution. Among then, EIS experiments were performed under the dark with a frequency range from 1 Hz to 100 k Hz, and the applied voltage was 0 vs. OCP (open-circuit potential). M-S experiments were measured at 500, 1000, and 1500 Hz frequencies under the dark. When doing

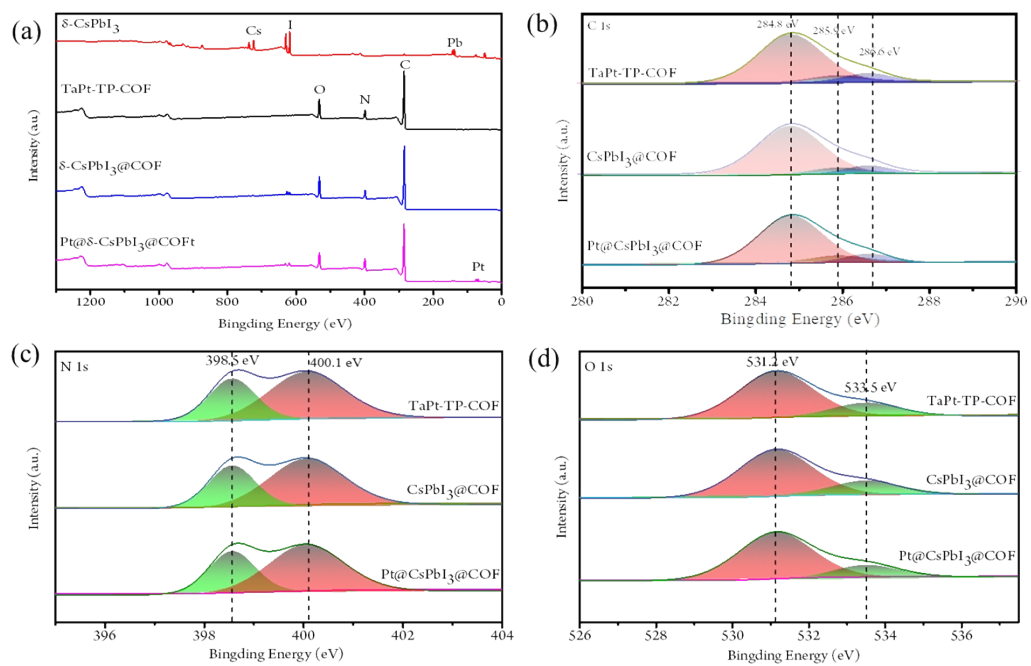
the PTR tests, turn off the light every 20s. Current density-potential (J-V) curves tests were performed by an electrochemical workstation (CHI660E, Shanghai). Ag/AgCl (with saturated KCl aqueous solution), Pt sheet and Na<sub>2</sub>SO<sub>4</sub> solution (0.1 M) were the reference electrode, the counter electrode and the electrolyte solution, respectively. The polarization curves were obtained using the linear sweep voltammetry (LSV) technique with a scan rate of 10mV/s<sup>-1</sup>, including hydrogen evolution reaction and oxygen evolution reaction.

### **SPV measurement**

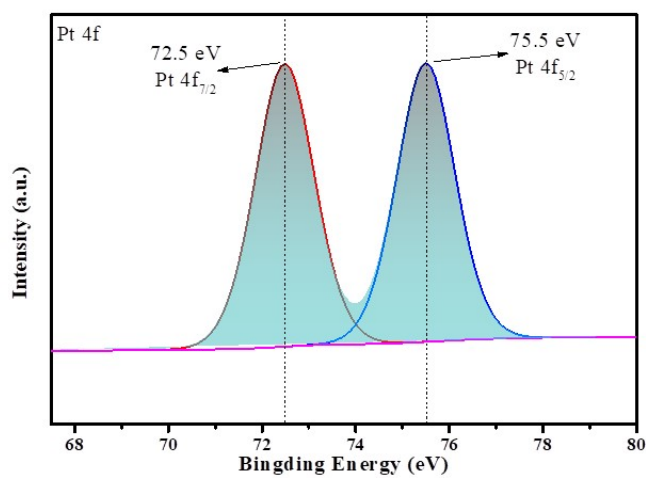
The surface photovoltage (SPV) spectroscopic measurement system consists of a source of monochromatic light, a sample cell, a computer, and a lock-in amplifier (CEL-SPS1000) with a light chopper (SR540). A low chopping frequency of 24 Hz was used. A 500 W xenon lamp (CHF-XM-500 W, Global Xenon Lamp Power) and a grating monochromator (Omni-5007, Zolix) provide monochromatic light. The samples were studied without further treatment during the SPV measurements, and the photovoltaic cell was a structure of fluorine-doped tin oxide (FTO)-sample-FTO.

### **Photocatalytic activity testing**

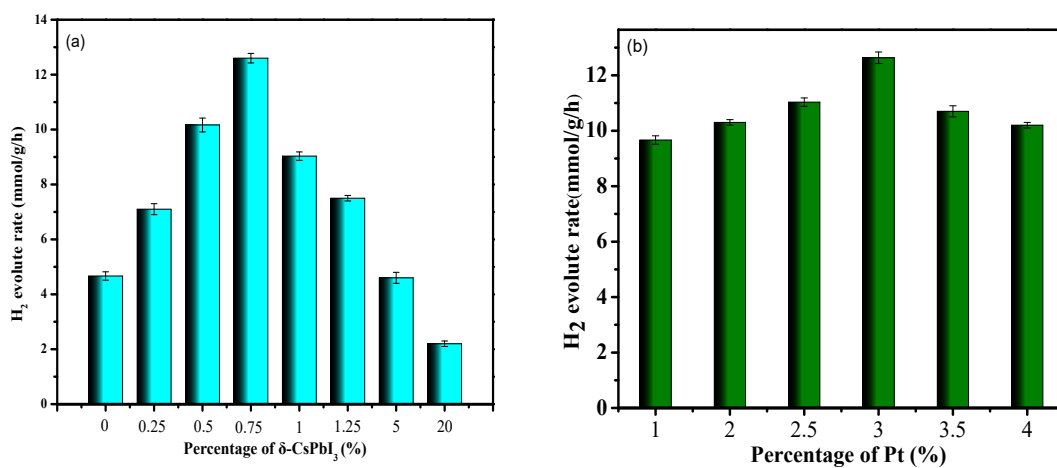
10 mg photocatalyst was ultrasonically dispersed in 200 mL 10% triethanolamine (TEOA) solution. After the air was removed, the solution was irradiated using a 300 W xenon lamp (Ceralux 300BF) equipped with an AM 1.5 G filter (100 mW/cm<sup>2</sup>). During the reaction, the temperature was kept at room temperature and the H<sub>2</sub> evolution rate was measured by gas chromatography (SPSIC, GC-112AT). Test results were averaged over four hours.



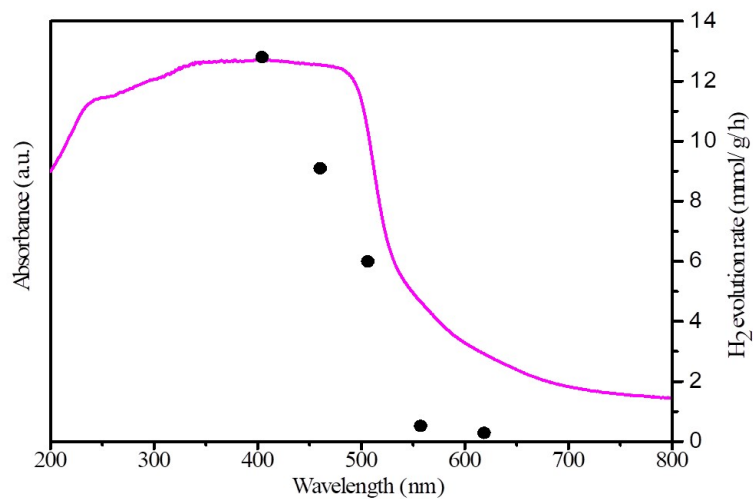
**Fig. S1** The XPS survey scan (a) and C 1s (b), N 1s (c), and O 1s (d) high resolution XPS spectra of samples.



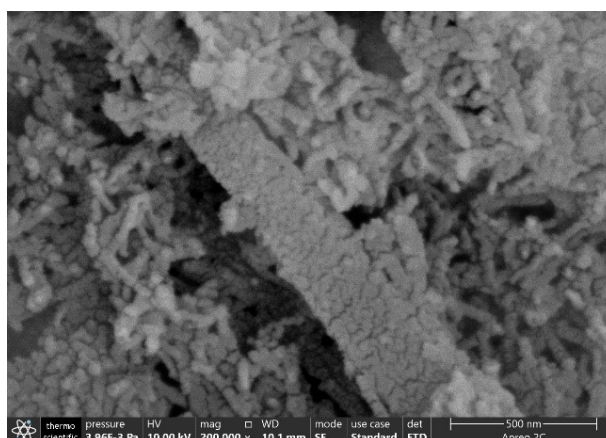
**Fig. S2** The Pt 4f high resolution XPS spectra of Pt@ $\delta$ -CsPbI<sub>3</sub>@TaPt-TP-COF.



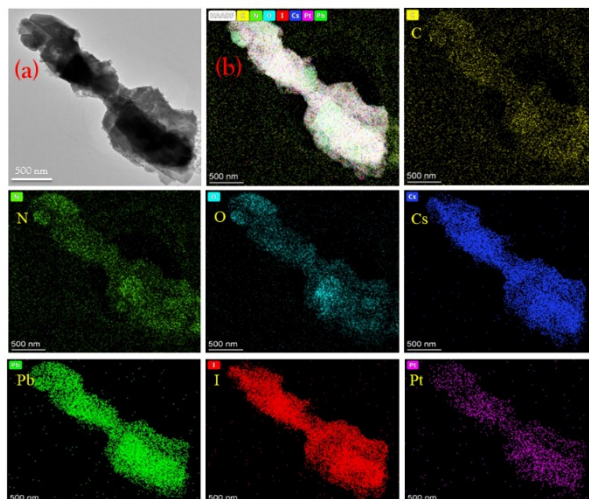
**Fig. S3** H<sub>2</sub> evolution rates of Pt@δ-CsPbI<sub>3</sub>@TaPt-TP-COF with different amount of δ-CsPbI<sub>3</sub> and 3wt% Pt (a), different amount of Pt and 0.75wt% δ-CsPbI<sub>3</sub> (b).



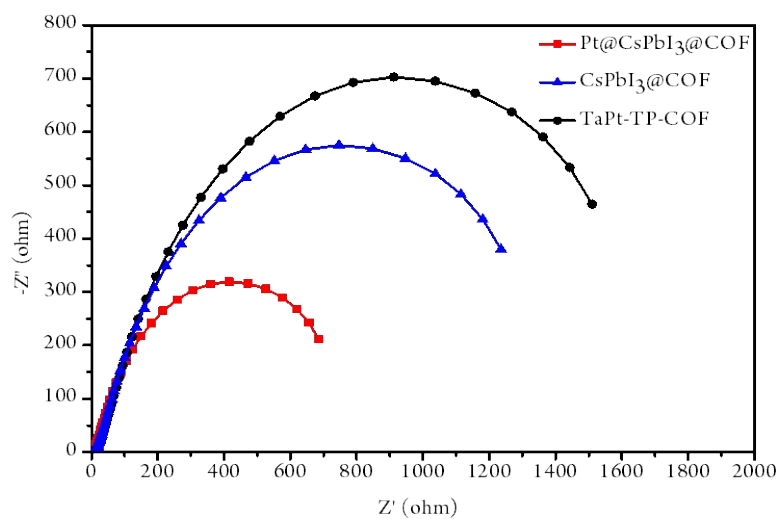
**Fig. S4** The wavelength dependence H<sub>2</sub> evolution of Pt@δ-CsPbI<sub>3</sub>@TaPt-TP-COF.



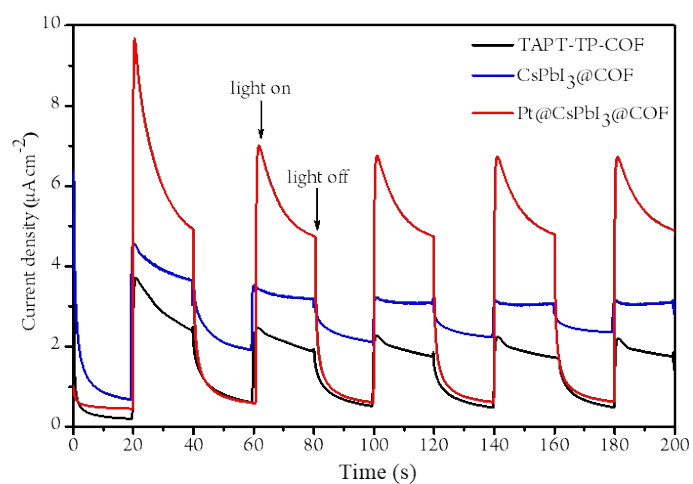
**Fig. S5** The SEM image of Pt@δ-CsPbI<sub>3</sub>@TaPt-TP-COF after reaction.



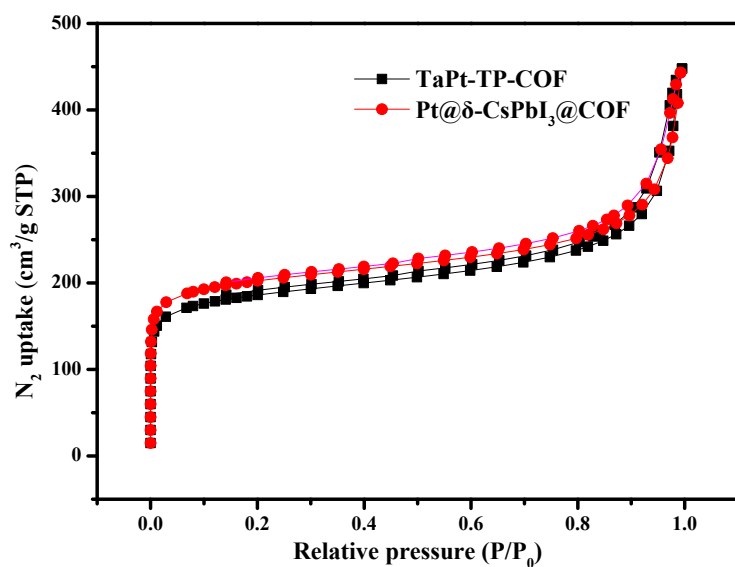
**Fig. S6** The TEM image and element mapping of Pt@ $\delta$ -CsPbI<sub>3</sub>@TaPt-TP-COF after reaction.



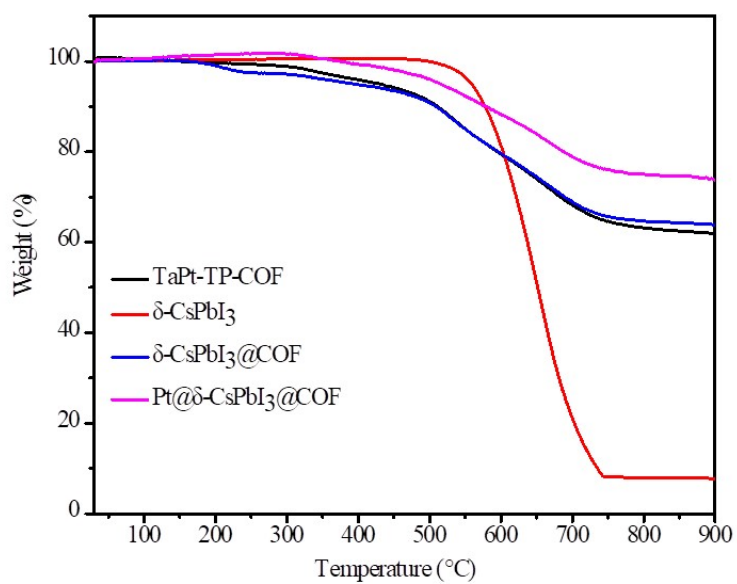
**Fig. S7** The electrochemical impedance spectrum of samples.



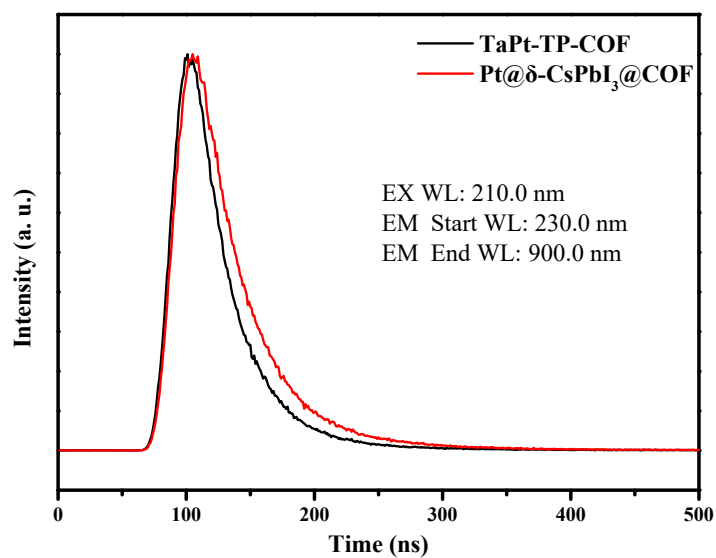
**Fig. S8** The transient photocurrent of samples.



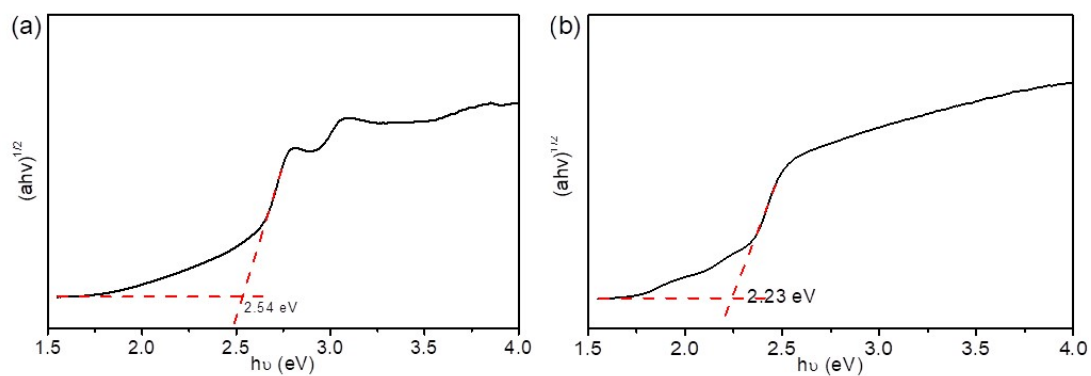
**Fig. S9** The N<sub>2</sub> adsorption-desorption isotherms of TaPt-TP-COF and Pt@ $\delta$ -CsPbI<sub>3</sub>@TaPt-TP-COF.



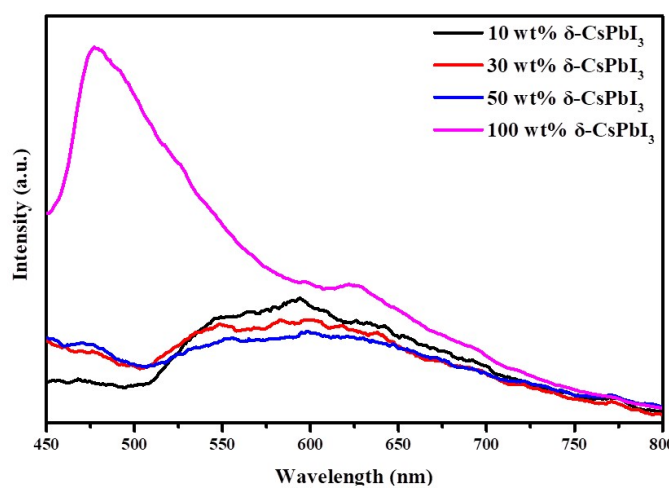
**Fig. S10** TGA curves of the samples.



**Fig. S11** The transient fluorescence spectra of TaPt-TP-COF and Pt@ $\delta$ -CsPbI<sub>3</sub>@TaPt-TP-COF.

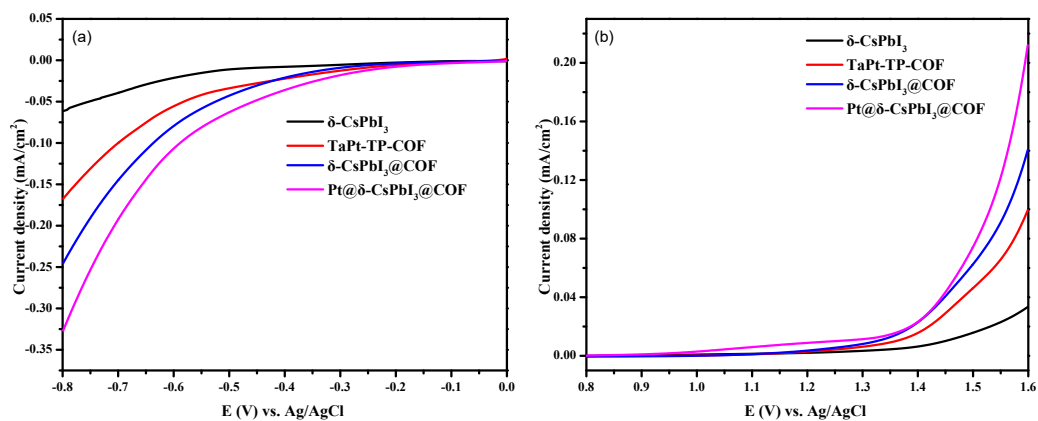


**Fig. S12** The tauc plots of  $\delta$ -CsPbI<sub>3</sub> (a) and TaPt-TP-COF (b).

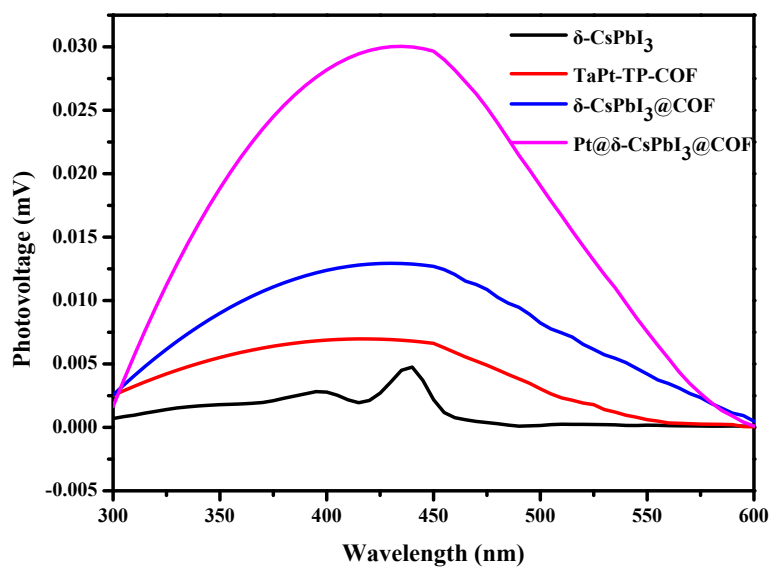


**Fig. S13** Photoluminescence spectra of  $\delta$ -CsPbI<sub>3</sub> and  $\delta$ -CsPbI<sub>3</sub>@TaPt-TP-COF with different amount of  $\delta$ -CsPbI<sub>3</sub>.





**Fig. S14** J-V curves of the electrodes made of the different materials: (a) Hydrogen evolution reaction; (b) Oxygen evolution reaction.



**Fig. S15** SPV spectra of the different materials.