

## **The Photocurrent Response in the Perovskite Device Based on Coordination Polymer: Structure, Topology, Band Gap and Matched Energy Level**

**Hai-Qiang Luo,<sup>a</sup> Xiao-Han Xing,<sup>a</sup> Pan Zhang,<sup>a</sup> Zhi-Shuo Yan,<sup>a</sup> Qing-Feng Zhou,<sup>a</sup> Yun Gong<sup>\*a</sup> and Jian-Hua Lin<sup>\*a, b</sup>**

*<sup>a</sup> Department of Applied Chemistry, College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 401331, P. R. China Tel: +86-023-65678932 E-mail: gongyun7211@cqu.edu.cn*

*<sup>b</sup> State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China Tel: +86-010-62753541 E-mail: jhlin@pku.edu.cn*

### **Fabrication of Device Based on FTO/ Compact TiO<sub>2</sub> (cTiO<sub>2</sub>)/ Perovskite CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/ CP 2**

The fabrication of device based on FTO/compact TiO<sub>2</sub> (cTiO<sub>2</sub>)/perovskite CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/ CP 2 is according to the literature method.<sup>1</sup>

Firstly, fluorine doped tin oxide (FTO, 12-14 μS/m) glass substrate was ultrasonic bath washed successively in acetone, ethanol and deionized water for 10 min each.

Secondly, a compact TiO<sub>2</sub> blocking layer was prepared with sol-gel method. The TiO<sub>2</sub> sol-gel used here was prepared by mixing titanium tetraisopropoxide (TTIP) contained solution A (TTIP, ethanol) and acid solution B (ethanol, HCl, H<sub>2</sub>O). 0.1 mL of the sol-gel was dropped onto FTO with the effective area of the TiO<sub>2</sub> film maintained at 1.0 × 1.0 cm<sup>2</sup> through a Scotch tape mask. Then the substrate was calcined at 450 °C for 1 hour in

air. After cooling to room temperature, the surface of the TiO<sub>2</sub> film was further deposited by 0.1 mL of a 40 mM aqueous solution of TiCl<sub>4</sub>. Then the TiCl<sub>4</sub> treated substrate was again calcined at 500 °C for 15 min to obtain the compact TiO<sub>2</sub> layer (cTiO<sub>2</sub>).

Thirdly, 2 mg perovskite (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) (homemade and characterized by powder X-ray diffraction, please see **Fig. S1**) was dissolved in 2 mL N, N'-dimethylformamide (DMF), then 0.1 mL of the perovskite solution was dropped onto the compact TiO<sub>2</sub> surface. The substrate was then dried by an IR lamp on to remove the remaining solvent.

The fourth step is to deposit CP **2** on the above perovskite layer. 2 mg CP **2** was ultrasonicated in 2 mL ethanol, then 0.4 or 0.1 mL of the mixture (CP **2** mass loading: 0.4 mg or 0.1 mg) was dropped on the perovskite and dried by an IR lamp.

The above fabricated FTO/ cTiO<sub>2</sub> / perovskite / CP **2** device was used as the working electrode from the back side for the detection of the photocurrent generation with a platinum foil and a AgCl/Ag electrode as the counter electrode and the reference electrode, respectively. 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution (80 mL) was used as the electrolyte.

**Table S1** Selected bond lengths (Å) and angles (°) for CPs **1-3**

<i>CP 1</i>			
Mn(1)-O(4)#1	2.140(2)	Mn(1)-O(6)	2.263(3)
Mn(1)-O(2)#2	2.163(2)	Mn(1)-O(1)	2.177(3)
O(4)#1-Mn(1)-O(3)#3	96.85(10)	O(4)#1-Mn(1)-O(5)	84.03(9)
O(3)#3-Mn(1)-O(6)	177.80(11)	O(1)-Mn(1)-O(3)#3	92.21(10)
<i>CP 2</i>			
Cd(1)-O(5)	2.274(4)	Cd(1)-O(3)#4	2.493(3)

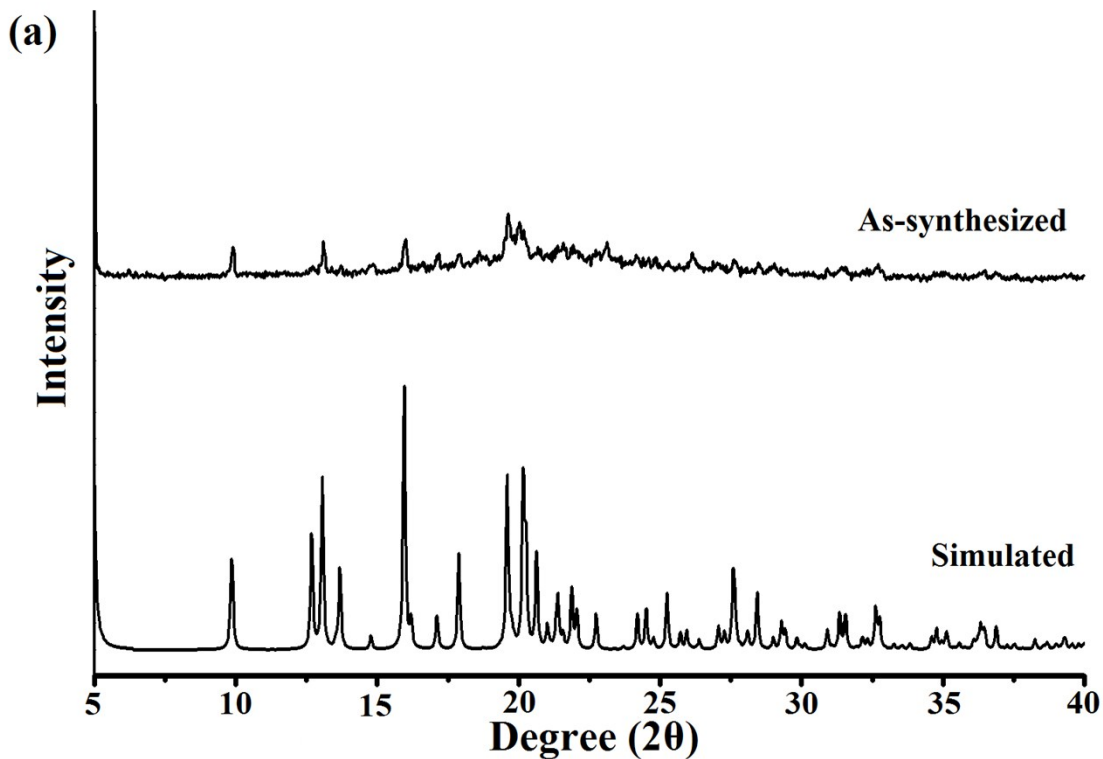
Cd(1)-O(4)#4	2.330(3)	Cd(1)-O(2)#5	2.359(3)
O(2)#5-Cd(1)-O(3)#6	173.35(11)	O(4)#4-Cd(1)-O(3)#4	53.84(12)
O(3)#6-Cd(1)-O(3)#4	97.38(12)	O(2)#5-Cd(1)-O(2)	105.03(12)

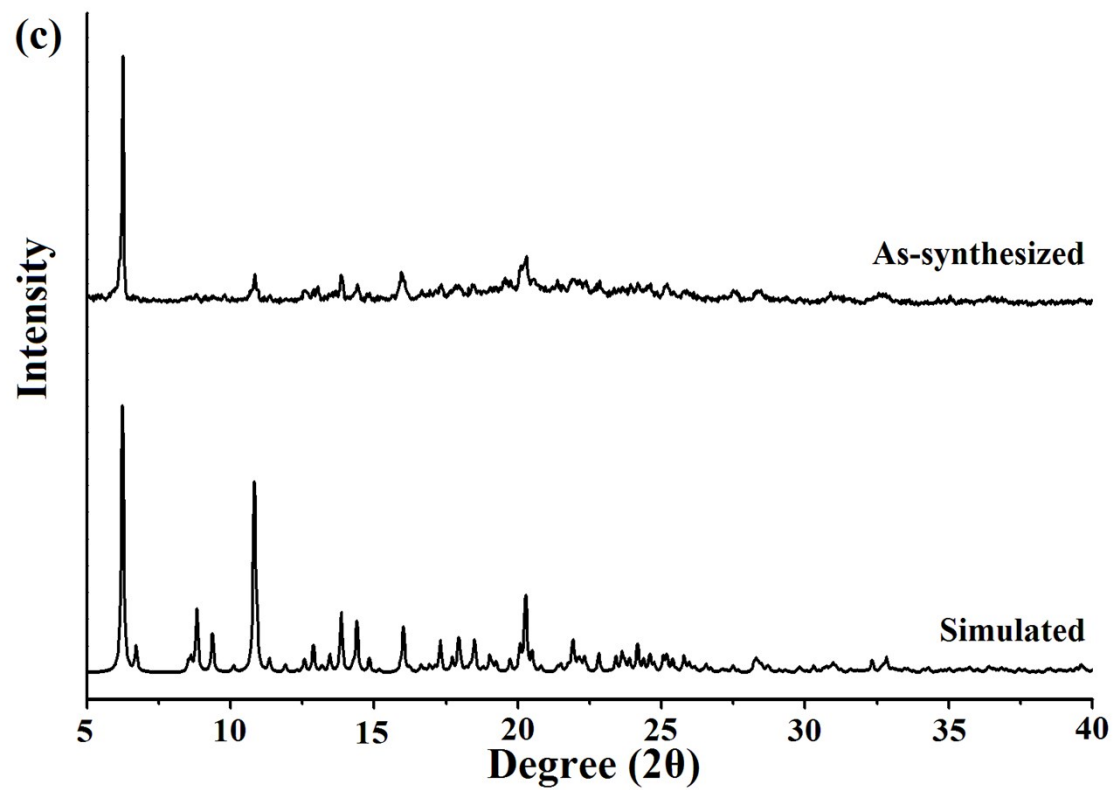
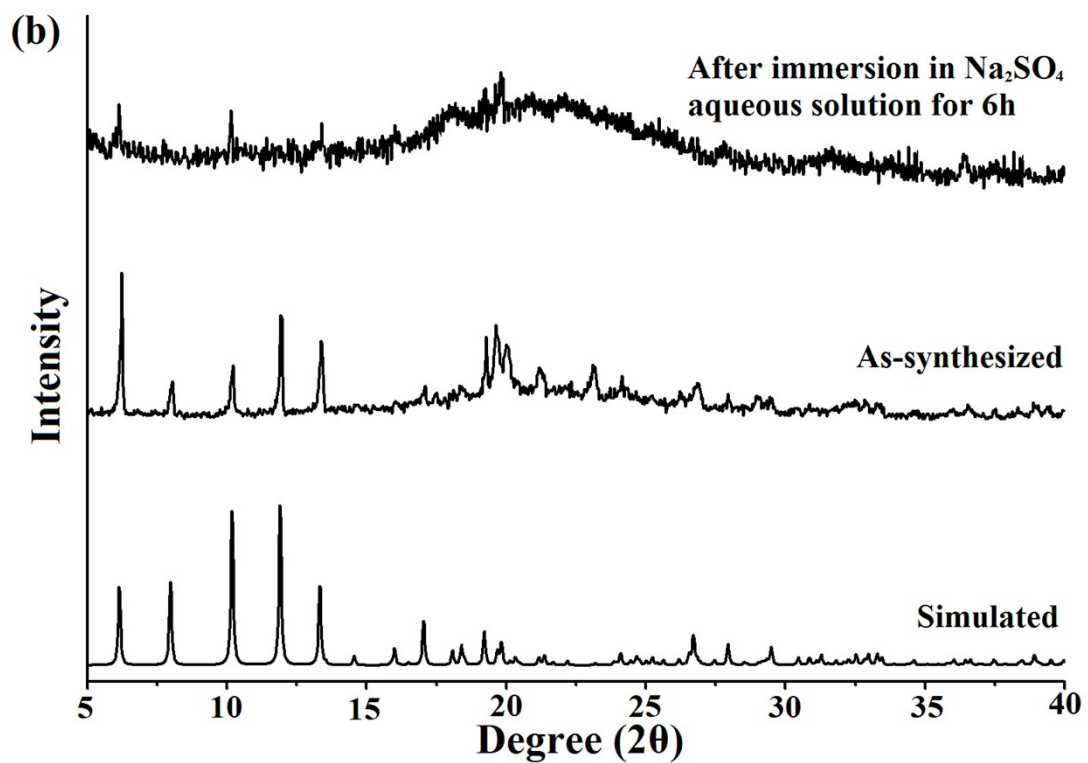
**CP 3**

Mn(1) - O(1)	2.127(3)	Mn(1) - O(9)	2.233(3)
Mn(2)-O(4)#7	2.072(3)	Mn(2)-O(8)	2.324(3)
O(10)-Mn(1)-O(9)	82.23(12)	O(7)-Mn(1)-O(9)	179.05(11)
O(4)#7-Mn(2)-O(8)	101.09(11)	O(10)-Mn(1)-O(7)	96.82(10)

Symmetry transformations used to generate equivalent atoms:

- #1  $-x, -y+1, -z$       #2  $-x, -y+1, -z+1$       #3  $-x, y+1/2, -z+1/2$       #4  $x-1/2, y+1, -z+1/2$   
 #5  $-x+1/2, y+1/2, z$       #6  $-x+1, y+1/2, -z+1/2$       #7  $x-1, y, z$





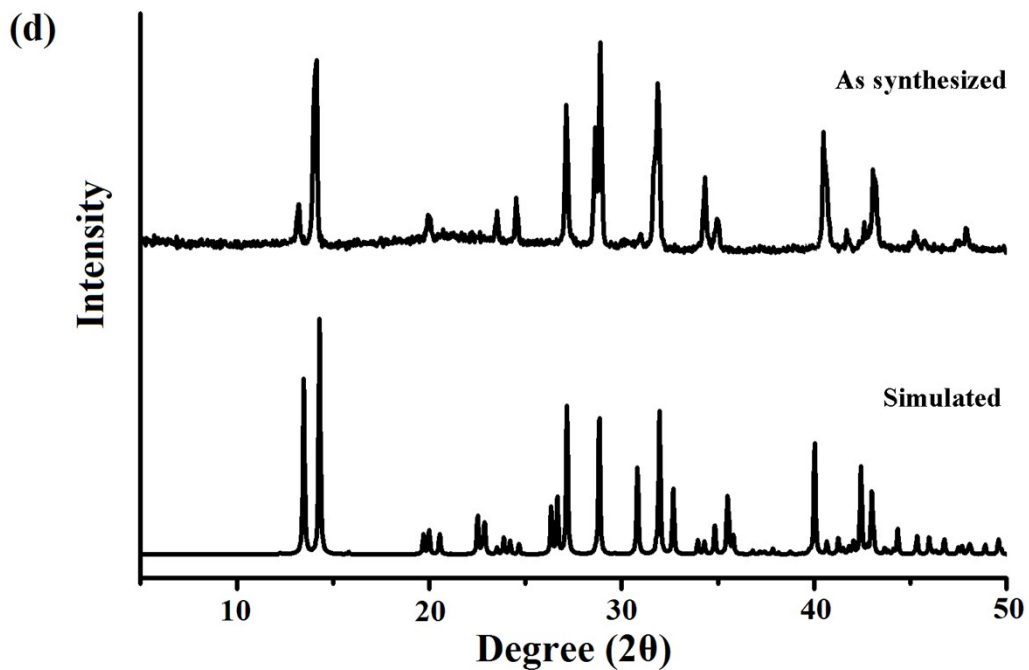


Fig.S1 The PXRD patterns of CPs 1 (a), 2 (b), 3 (c) and the perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (d)

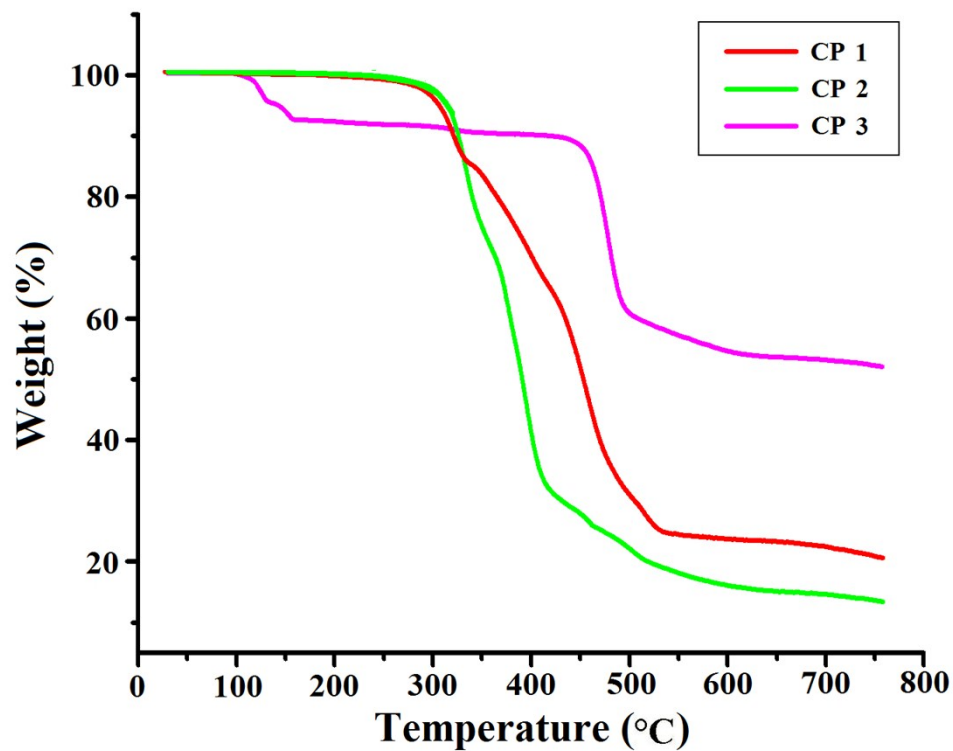
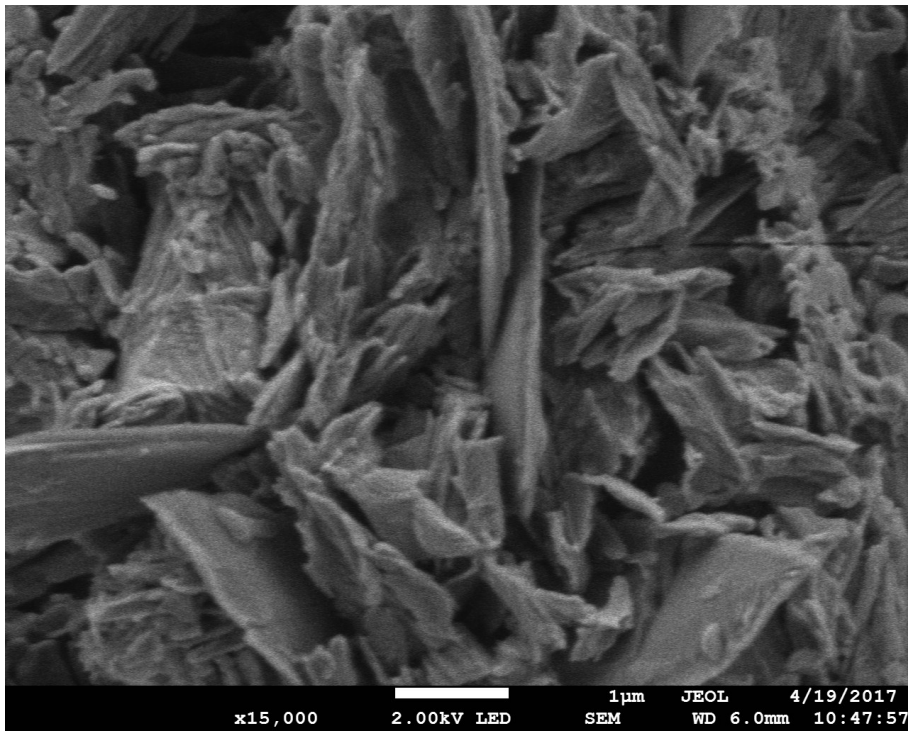
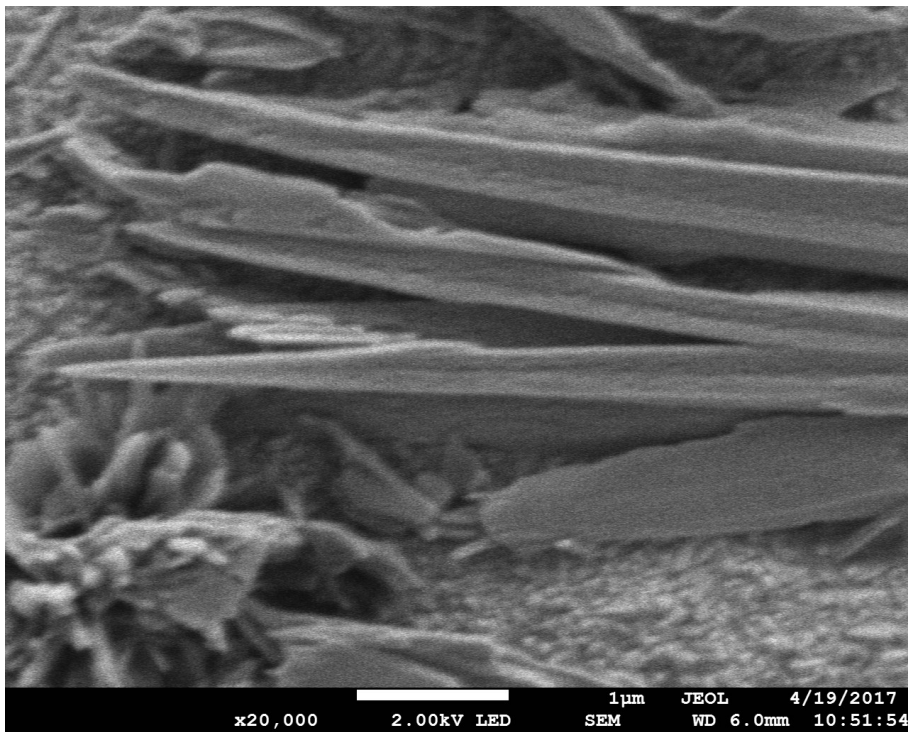


Fig.S2 Thermogravimetric curves of CPs 1 (red), 2 (green) and 3 (pink).

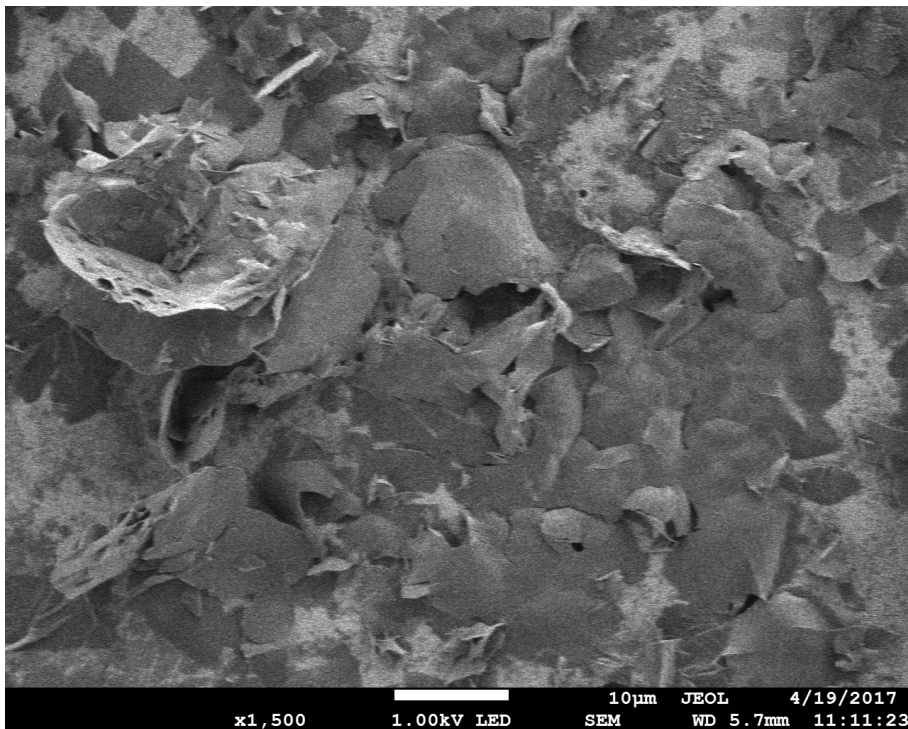
(a)



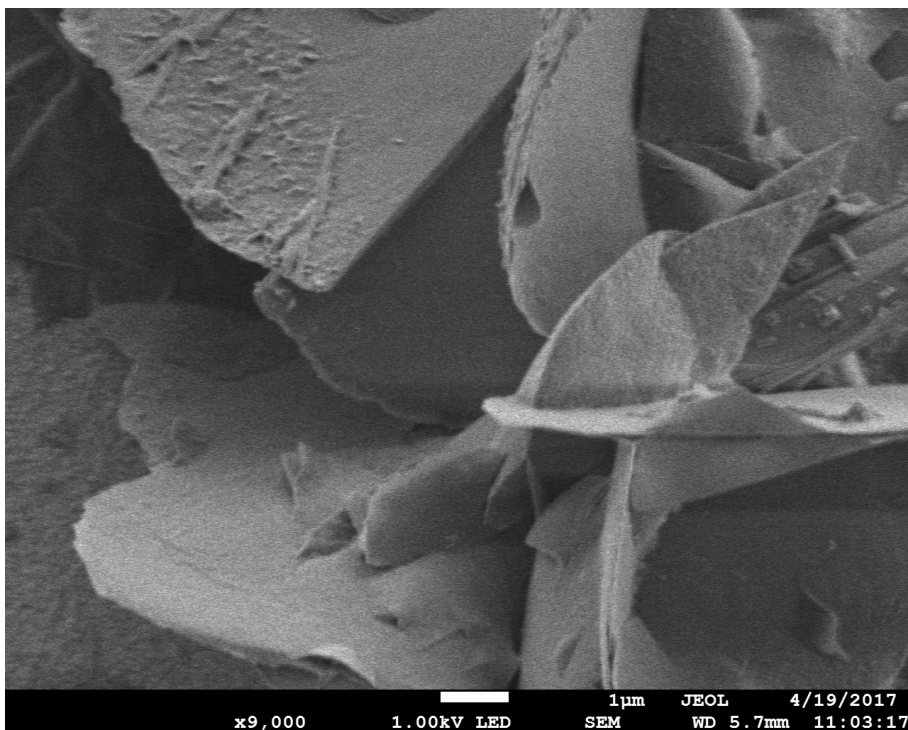
(b)



(c)

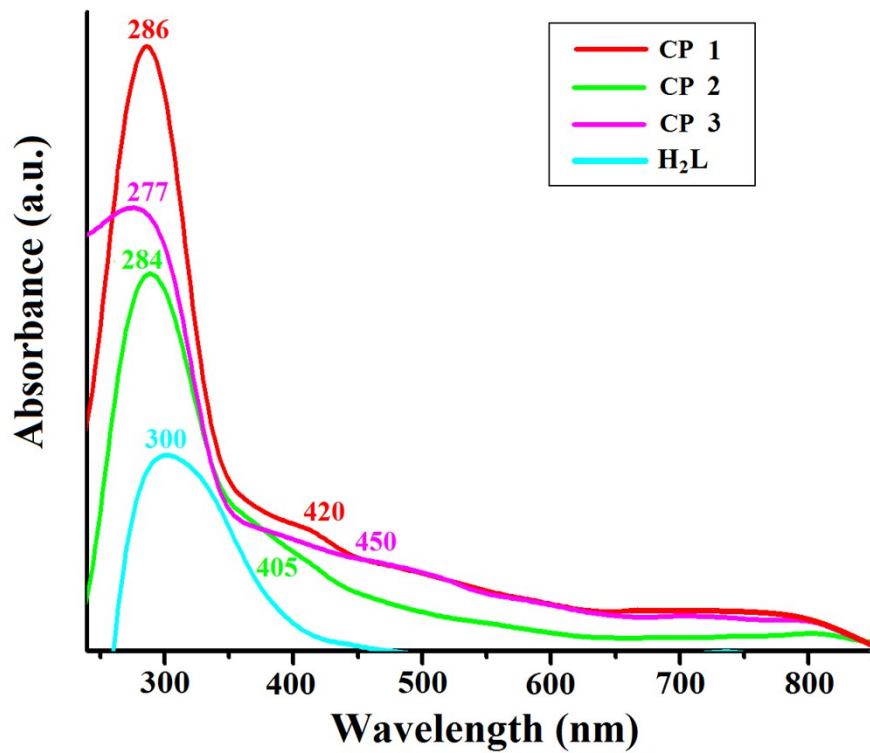


(d)



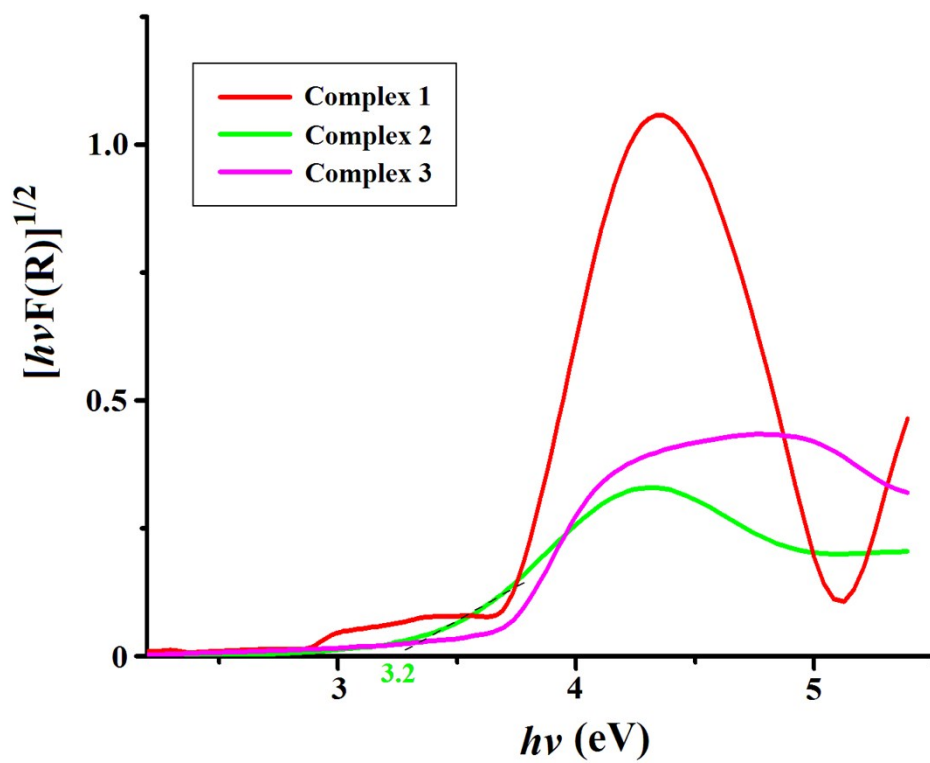
**Fig. S3** The SEM images of CP 2 before (a, b) and after immersion in  $\text{Na}_2\text{SO}_4$  aqueous

solution (c, d).

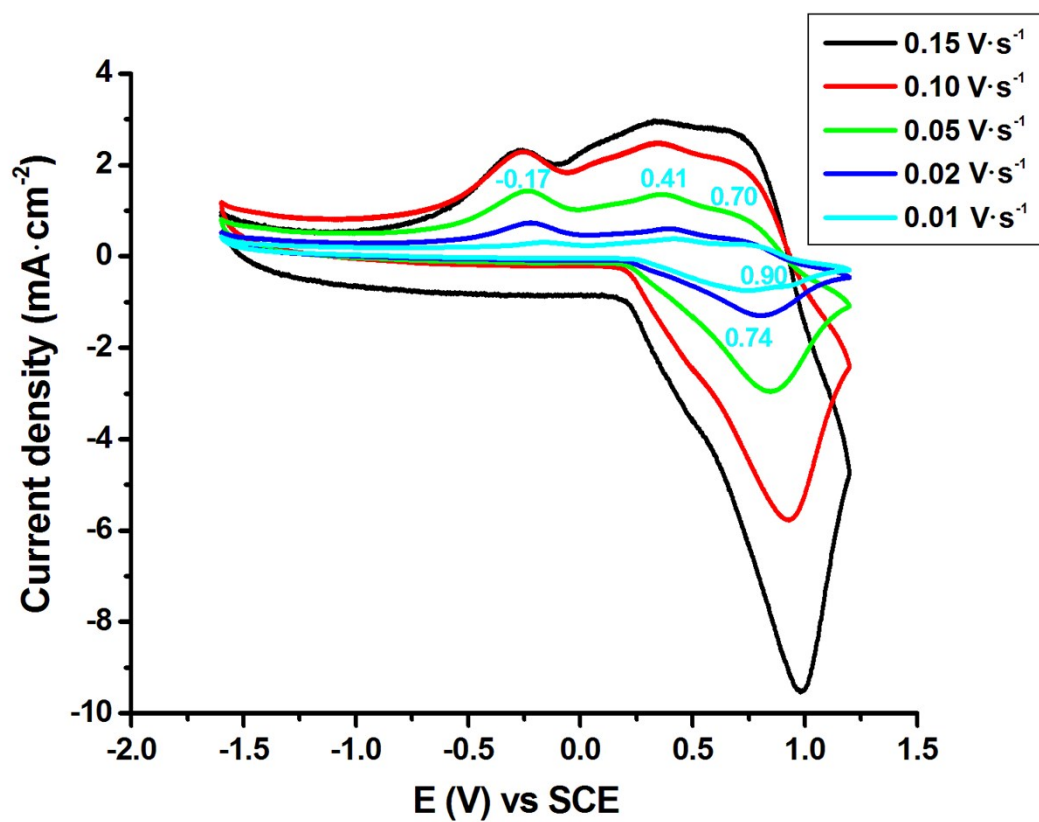


**Fig. S4** UV-vis absorption spectra at room temperature for the free organic ligand **H<sub>2</sub>L** and CPs 1-3.

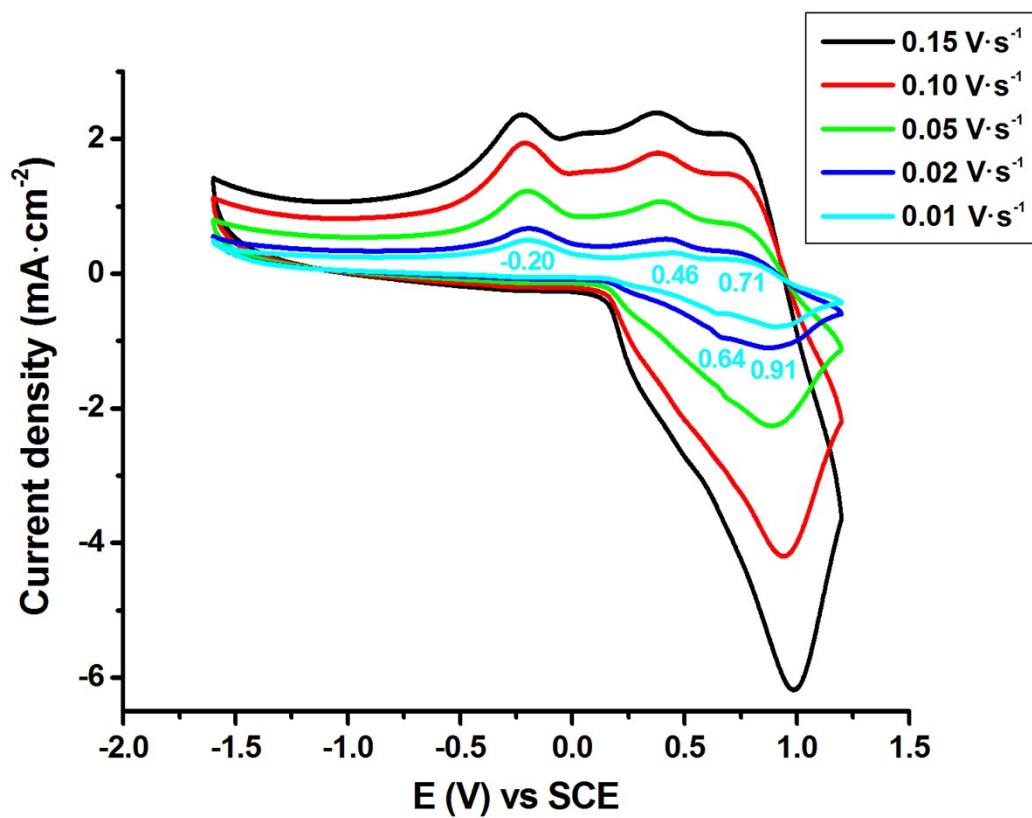




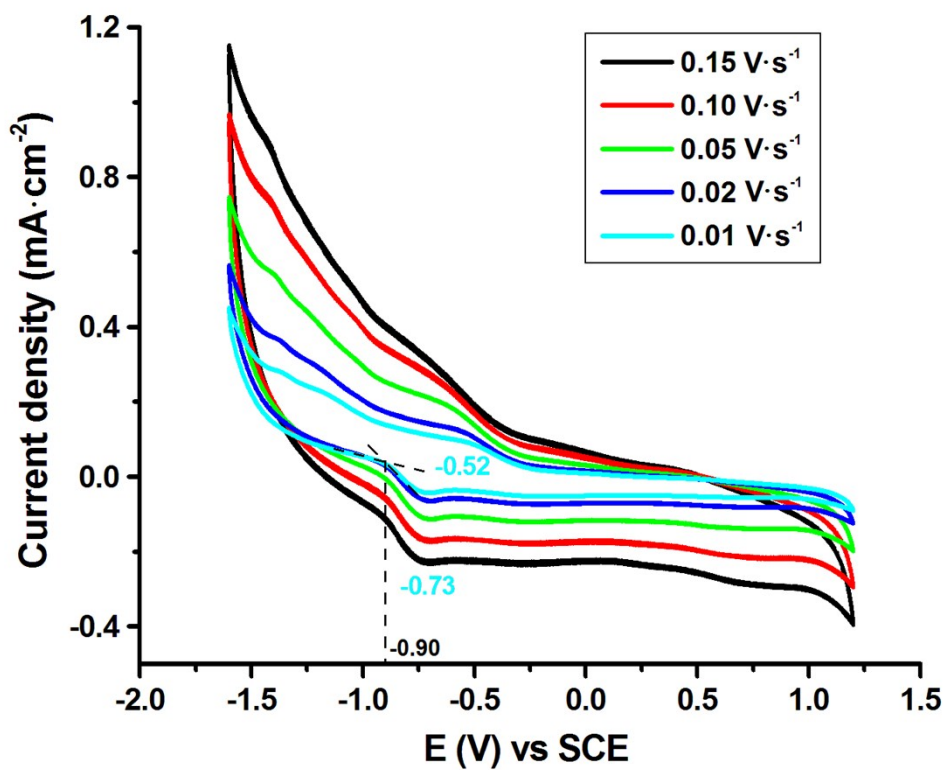
**Fig. S5** The diffuse reflectance spectra (DRS) for CPs 1-3 in the transformed Kubelka-Munk functions.



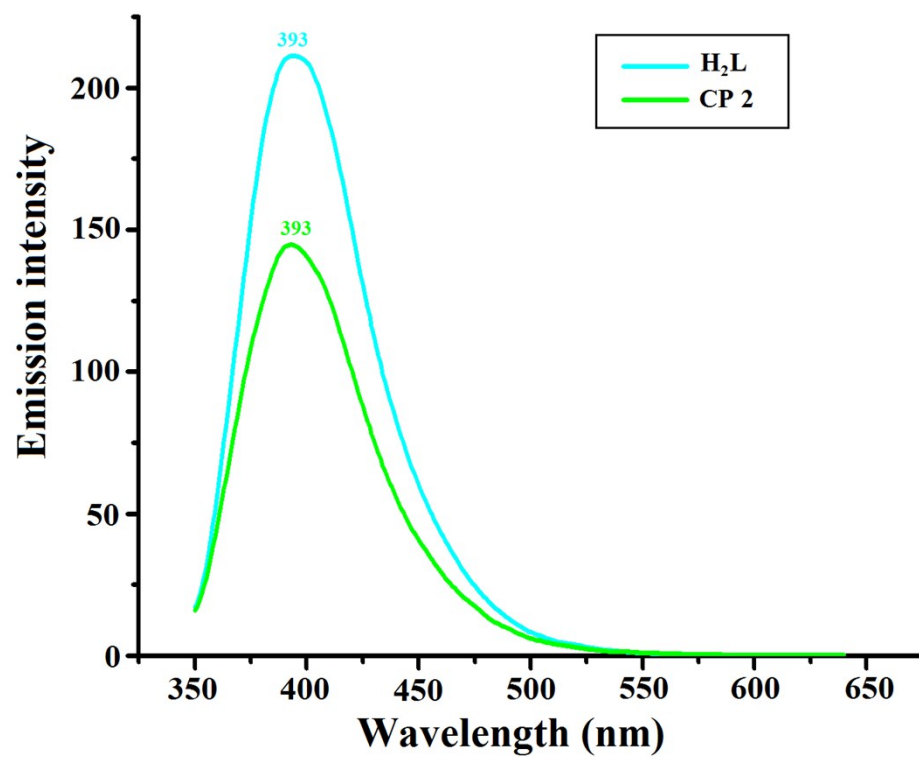
**Fig. S6** CVs of 1-GCE in a 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution (80 mL) in the potential range from -1.6 to 1.2 V vs SCE at different scan rates.



**Fig. S7** CVs of 3-GCE in a 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution (80 mL) in the potential range from -1.6 to 1.2 V vs SCE at different scan rates.

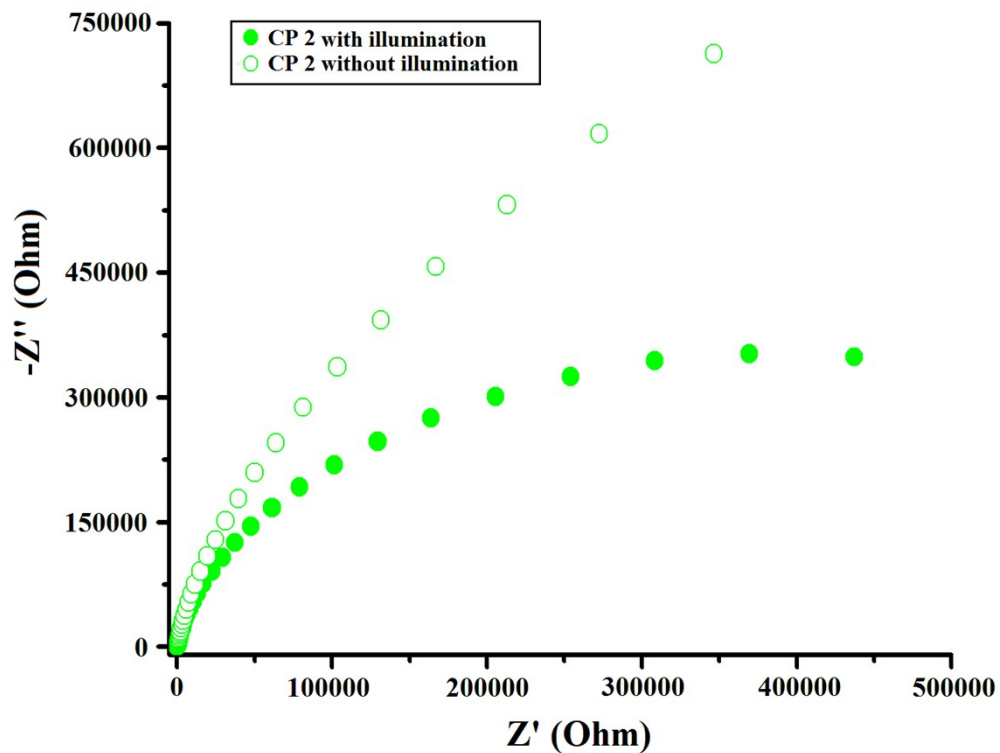


**Fig. S8** CVs of 2-GCE in a 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution (80 mL) in the potential range from -1.6 to 1.2 V vs SCE at different scan rates.



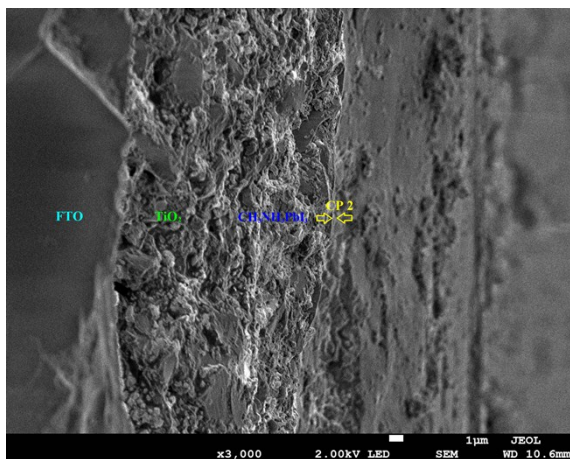
**Fig. S9** Solid-state emission spectra at room temperature for the free ligand H<sub>2</sub>L and CP

2.

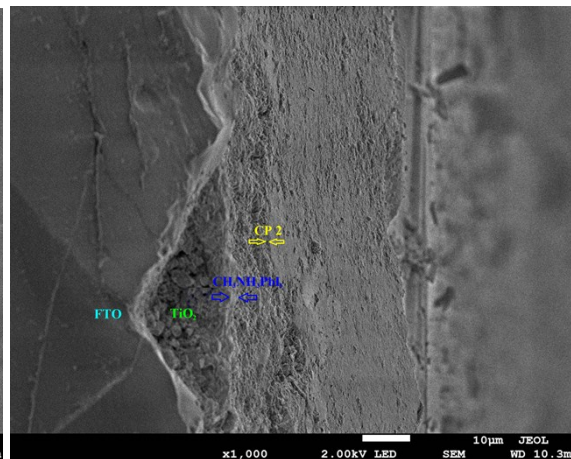


**Fig. S10** Nyquist plots ( $Z'$  vs.  $-Z''$ ) of the three-electrode system at  $E = 0$  V vs AgCl/Ag in  $\text{Na}_2\text{SO}_4$  aqueous solution (0.2 M, 80 mL) in the absence and presence of visible light illumination ( $650 \text{ nm} > \lambda > 350 \text{ nm}$ ) with the CP 2-modified FTO slide as working electrode.

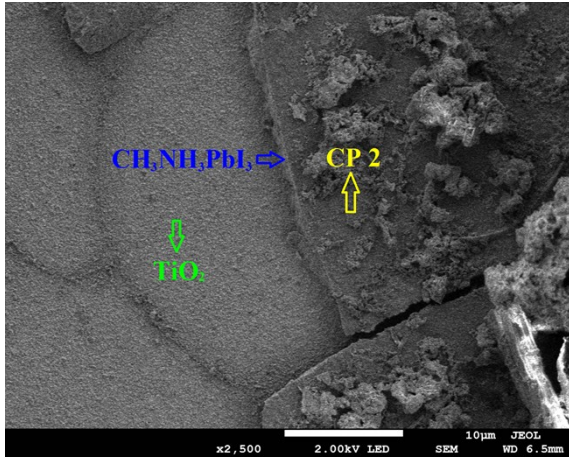
(a)



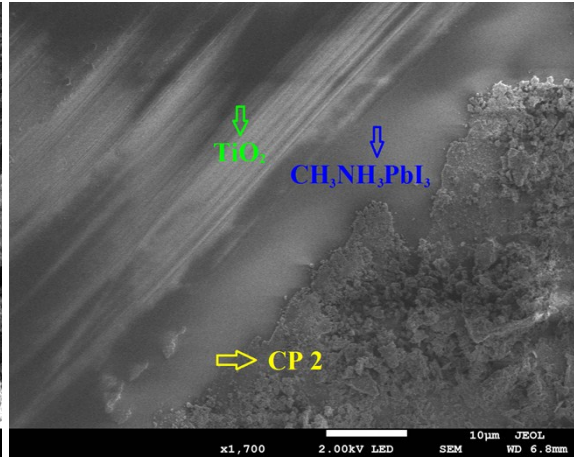
(b)



(c)

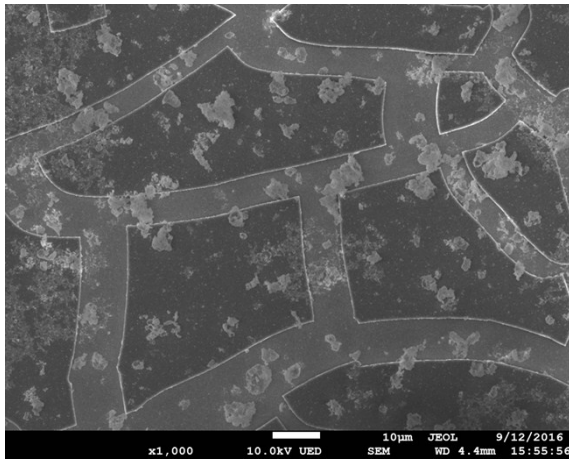


(d)

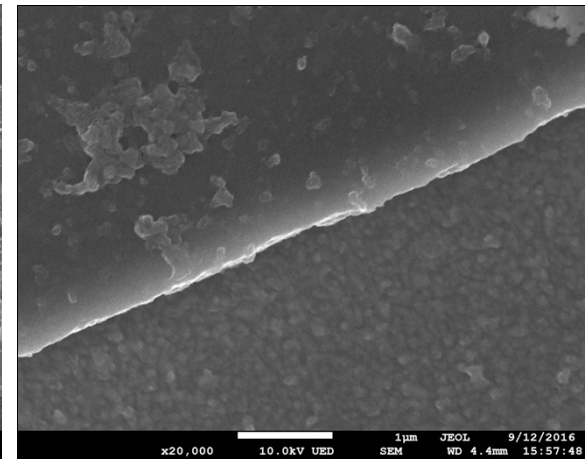


**Fig. S11** Cross-section (a-b) and oblique-view SEM images of FTO /  $\text{TiO}_2$  /  $\text{CH}_3\text{NH}_3\text{PbI}_3$  / CP 2 device (c-d).

(a)

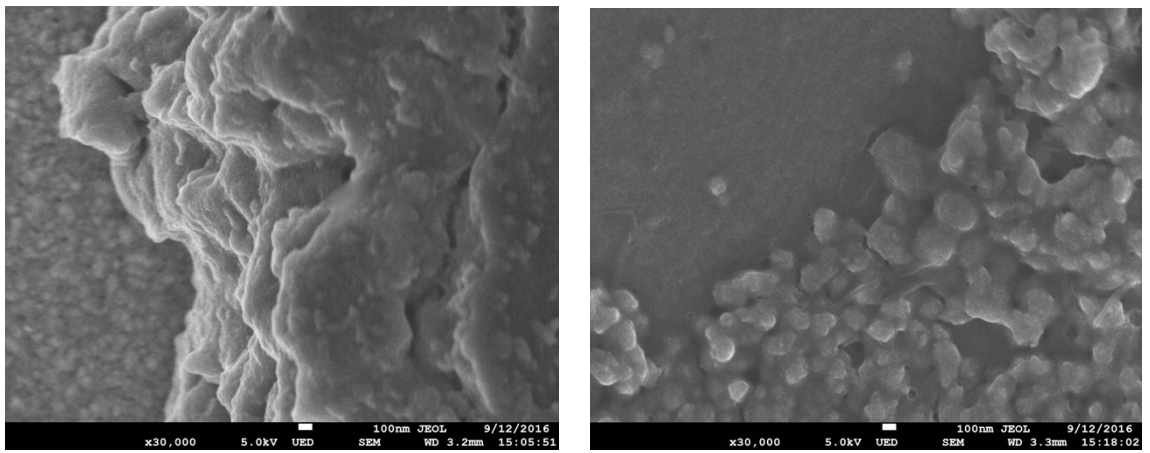
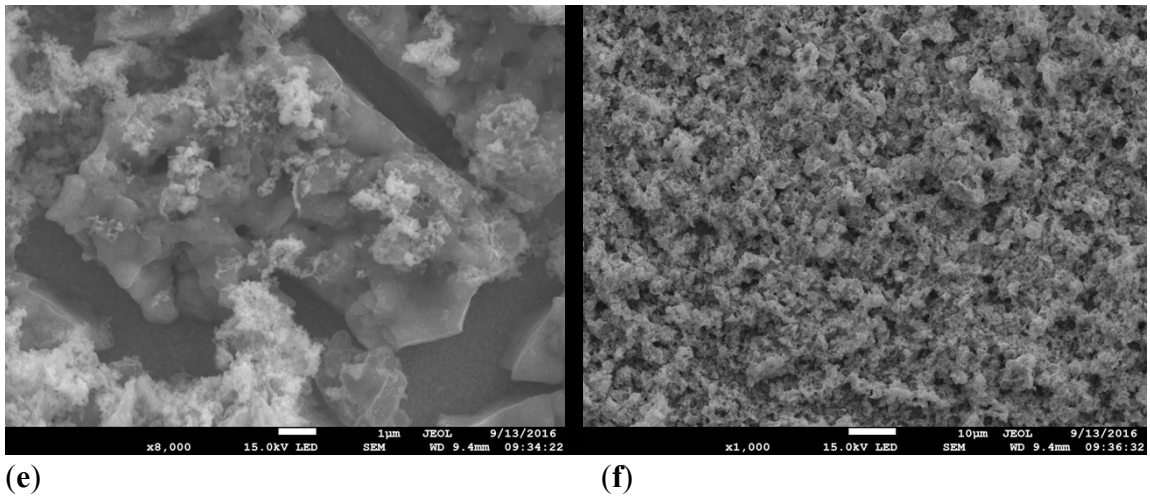


(b)



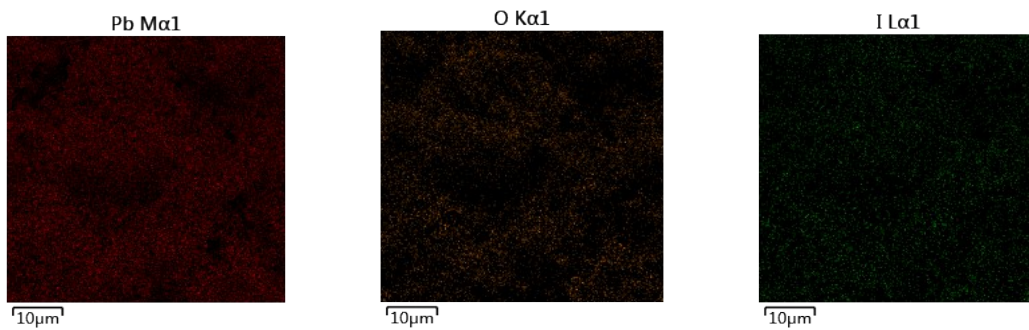
(c)

(d)

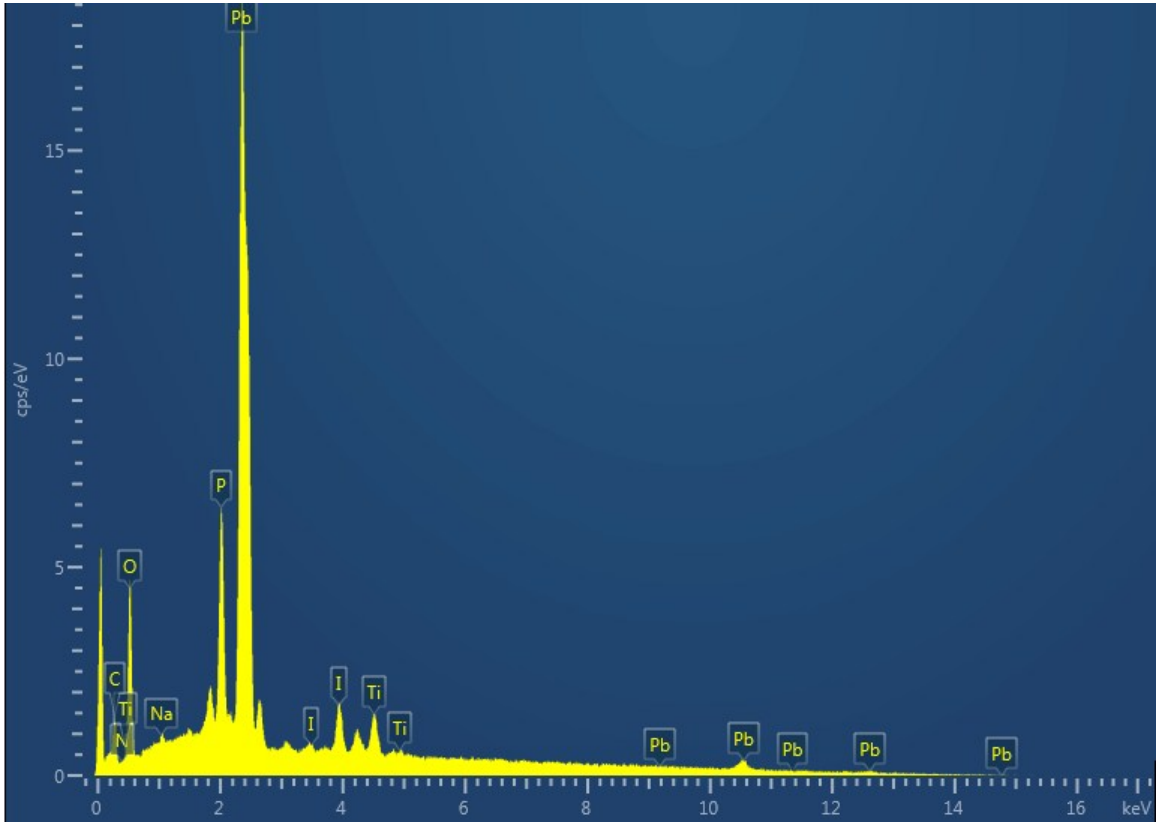
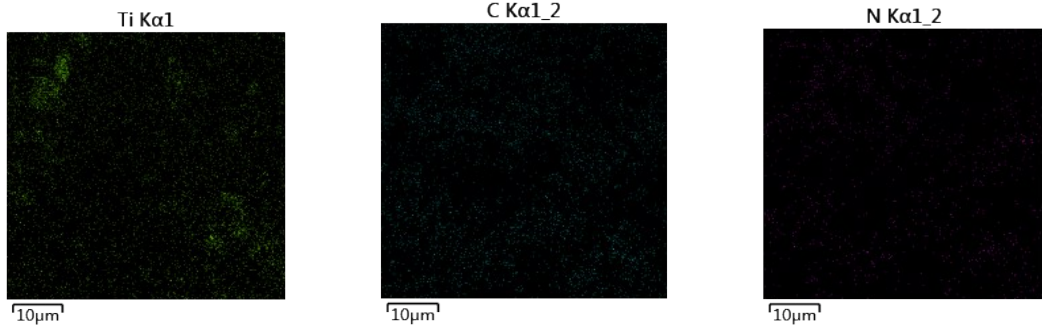


**Fig. S12** Top-view SEM images of the compact  $\text{TiO}_2$  layer (**a**, **b**); the perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$  on the top of the compact  $\text{TiO}_2$  layer (**c**, **d**) and CP 2 (**e**, **f**) on the top of the perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$ .

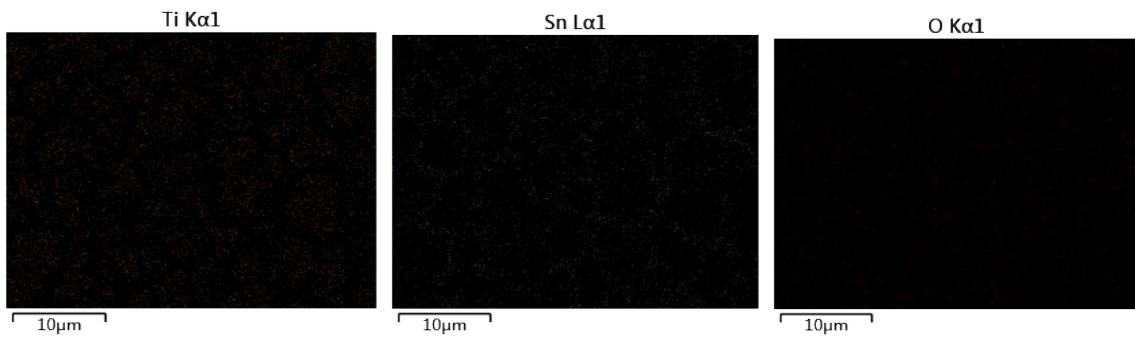
(a)

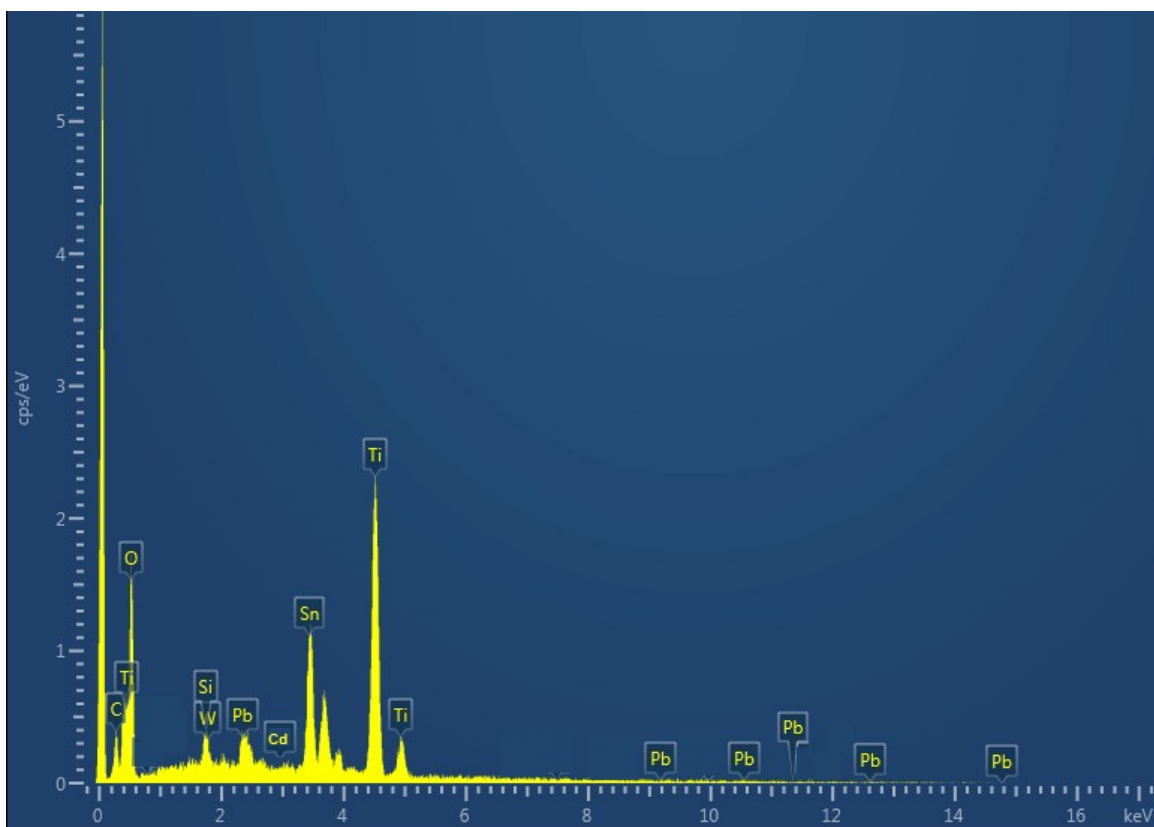
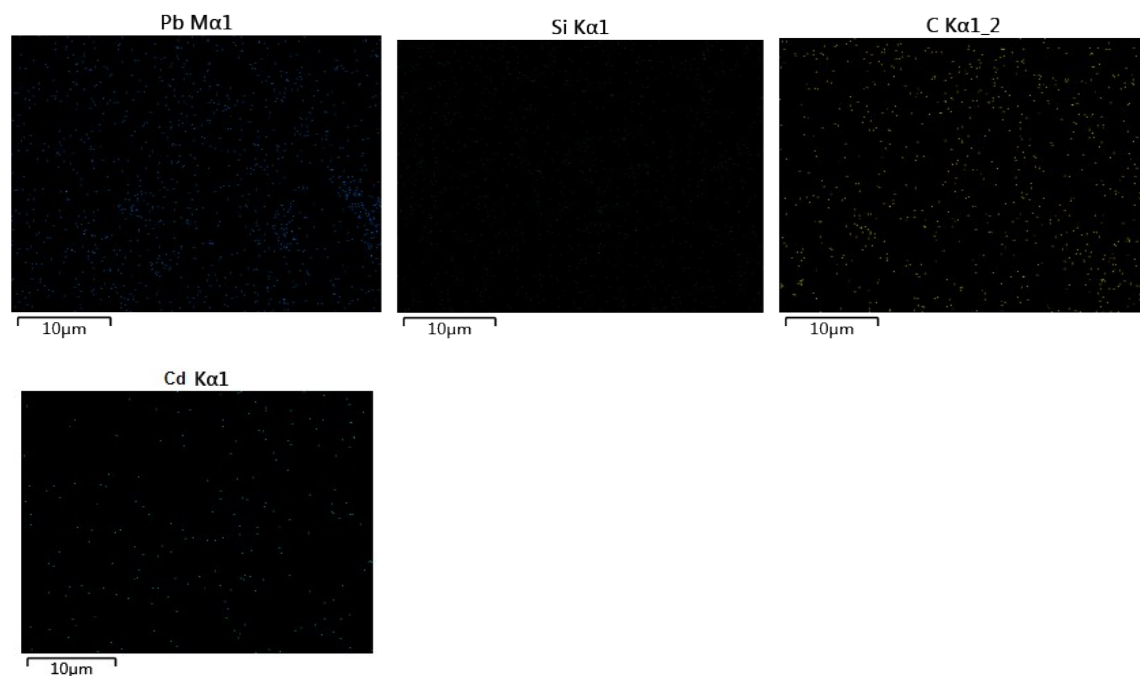






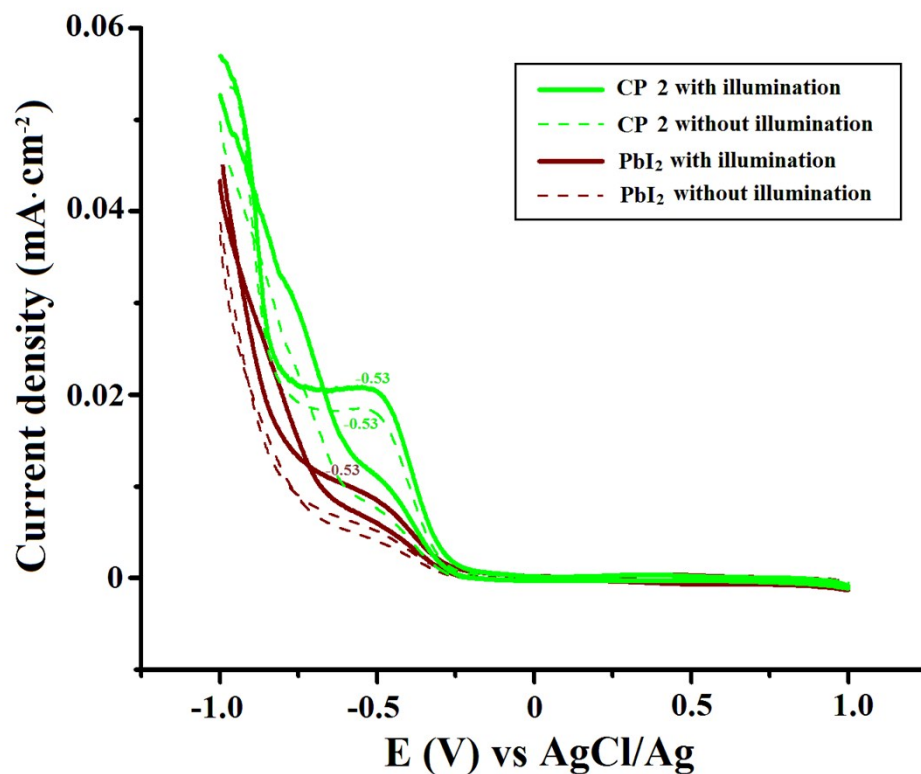
(b)



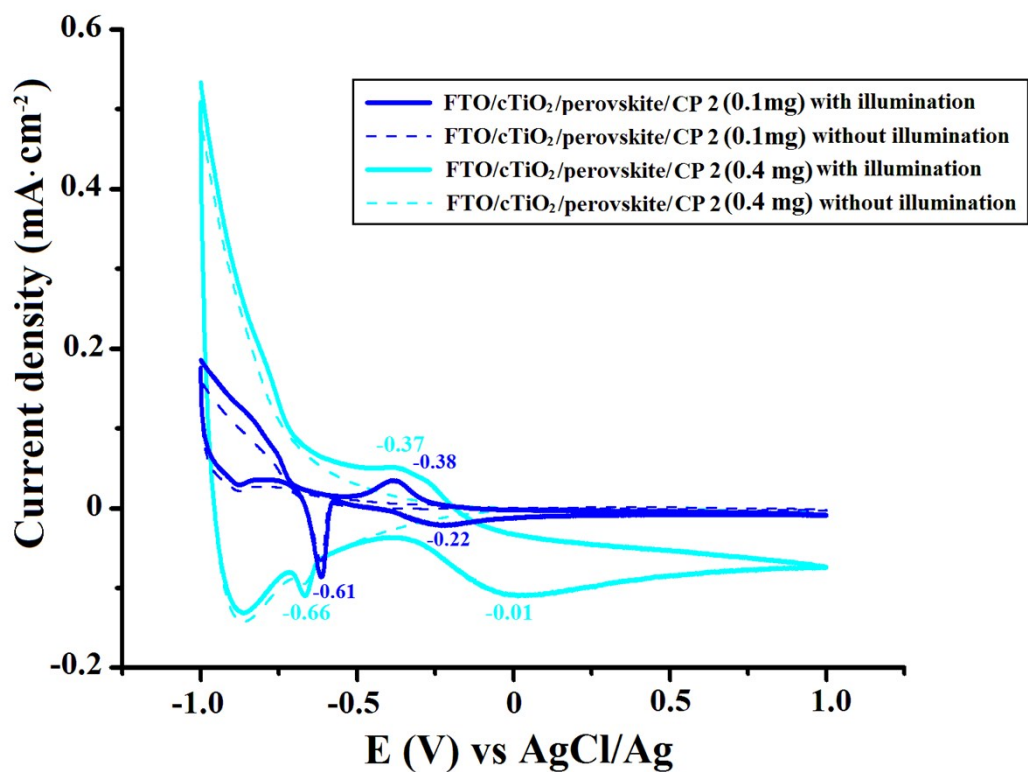


**Fig. S13** Elemental mapping and total element amount of the perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$  on the top of the compact  $\text{TiO}_2$  layer (a) and CP 2 (b) on the top of the perovskite

CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>.



**Fig. S14** CVs of CP 2- or PbI<sub>2</sub> - modified FTO slices in a 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution (80 mL) in the potential range from -1.0 to 1.0 V vs AgCl/Ag at a scan rate of 0.01 V·s<sup>-1</sup> with (solid line) and without (dotted line) the visible light illumination (650 nm > λ > 350 nm).



**Fig. S15** CVs of FTO/cTiO<sub>2</sub>/ perovskite / CP 2 in a 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution (80 mL) from -1.0 to 1.0 V vs AgCl/Ag at 0.01 V·s<sup>-1</sup> with (solid line) and without (dotted line) the visible light illumination (650 nm > λ > 350 nm) at 100 mW·cm<sup>-2</sup>. CP 2 mass loading: 0.4 mg (sapphire) or 0.1 mg (blue).

## Reference

- (a) Chen, S. S.; Lei, L.; Yang, S. W.; Liu, Y.; Wang, Z. S. *ACS Appl. Mater. Interfaces*, **2015**, *7*, 25770; (b) Yue, Y. F.; Umeyama, T.; Kohara, Y.; Kashio, H.; Itoh, M.; Ito, S.; Sivaniah, E.; Imahori, H. *J. Phys. Chem. C*, **2015**, *119*, 22847.