Coordination polymer based perovskite device: matched energy levels and photocurrent enhancement in the absence or presence of methanol Sen Lv,^a Ze Yuan Wang,^a Xu Gu,^a Chong Zhang,^a Yun Gong ^{*a} and Jian-Hua Lin ^{*a,} ^b

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Fabrication of Composite Electrode Based on FTO/ TiO₂ /Perovskite CH₃NH₃PbI₃/ CP 2

The fabrication of device based on FTO/ TiO_2 /perovskite $CH_3NH_3PbI_3$ / CP **2** is according to the literature method. ¹

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

Secondly, a compact TiO₂ blocking layer was prepared with sol-gel method. The TiO₂ sol-gel used here was prepared by mixing titanium tetraisopropoxide (TTIP) contained solution A (TTIP, ethanol) and acid solution B (ethanol, HCl, H₂O). 0.1 mL of the sol-gel was dropped onto FTO with the effective area of the TiO₂ film maintained at 1.0×1.0 cm² 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 TiO₂ film was further deposited

by 0.1 mL of a 40 mM aqueous solution of $TiCl_4$. Then the $TiCl_4$ treated substrate was again calcined at 500 °C for 15 min to obtain the compact TiO_2 layer.

Thirdly, 2 mg perovskite (CH₃NH₃PbI₃) (homemade and characterized by powder Xray diffraction, please see **Fig. S1**) was dissolved in 2 mL N, N'-dimethylformamide (DMF), then 0.3 mL of the perovskite solution was dropped onto the compact TiO_2 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 0.3 mL of the mixture was dropped on the perovskite and dried by an IR lamp.

The above fabricated FTO/ TiO₂ / perovskite / CP device was used as the working electrode with a platinum foil and a AgCl/Ag electrode as the counter electrode and the reference electrode, respectively. The photocurrent–time (I–t) curve of the CP-based perovskite was measured by a light irradiation from the back side under a constant potential of -0.1 V vs AgCl/Ag at room temperature. The area irradiated was maintained at 1.0×1.0 cm². 0.2 M Na₂SO₄ solution with or without 0.5 M CH₃OH (80 mL) was used as the electrolyte.

Table S1 Selected bond lengths (Å) and angles (°) for CPs 1 and 2

CP 1			
Co(1)-O(3)#1	2.093(4)	Co(1)-O(9)	2.170(4)
Co(1)-N(1)	2.200(5)	Co(2)-O(10)	2.066(4)
Co(2)-O(6)	2.297(4)	Co(2)-N(3) #2	2.093(4)
O(3)#1-Co(1)-O(3)	180.0(2)	O(3)-Co(1)-O(9)#1	88.87(14)

O(9)-Co(1)-N(1)	87.65(17)	N(1)-Co(1)-N(1)#1	180.0(3)
O(11)-Co(2)-O(12)	172.30(15)	O(10)-Co(2)-O(12)	84.89(17)
N(3)#2-Co(2)-O(12)	87.66(18)	N(3)#2-Co(2)-O(5)	151.40(17)
<i>CP 2</i>			
Zn(1)-O(8)	1.964(4)	Zn(1)-O(6)	2.241(4)
Zn(1)-O(5)	2.117(3)	Zn(1)-N(1)	2.041(3)
O(8)-Zn(1)-O(6)	152.43(14)	O(5)-Zn(1)-O(6)	59.13(14)
N(1)-Zn(1)-O(5)	120.56(15)	N(1)-Zn(1)-O(6)	96.95(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y, -z #2 -x+1, -y+2, -z+1

D	Н	А	D…A distance	H…A distance	∠D–H…A
CP 1					
N2	H2	O4#1	2.956	2.140	158
N4	H4	O1#1	2.842	2.020	159
09	H9C	O4#2	2.734	1.880	180
O10	H10C	O1#3	2.695	1.850	176
O10	H10D	O5#4	2.808	1.960	176
011	H11C	O2#4	2.683	1.850	168
011	H11D	O6#5	2.945	2.110	169
012	H12C	O2#4	2.810	1.960	173
CP 2					

Table S2 Distances (Å) and angles (°) of the selected hydrogen bonds for CPs 1 and 2

N2	H2	O9#6	2.994	2.15	167
03	H3	O4#7	2.581	1.77	173
08	H8C	O2#1	2.686	1.84	173
08	H8D	O10#1	2.653	1.81	172

Symmetry transformations used for generating equivalent atoms:

#1: x, 1+y, z; #2: -x, -y, -z; #3: 1-x, -y, 1-z; #4: -x, -y, 1-z; #5: 1-x, 1-y, 1-z; #6: -1/2+x, 1/2+y, z; #7 1-x, -y, -z.

Table S3 The centroid-centroid (CC) distance (Å) and perpendicular (P) distance (Å) involving $\pi \cdots \pi$ stacking interactions for CPs 1 and 2

Plane	Plane	CC distance	P distance
CP 1			
N3/C21-C25	C10A-C15A	3.798(3)	3.476(2)
C3-C8	C28B-C33B	3.933(4)	3.428(2)
C3-C8	C28D-C33D	3.683(4)	3.667(2)
CP 2			
N1/C16-C20	C3E-C8E	3.647(3)	3.415(2)

Symmetry transformations used to generate equivalent atoms:

A x, 1+y, z B -1+x, -1+y, z D x, -1+y, z E -1/2+x, 1/2+y, z





Fig. S1 The PXRD patterns of CPs 1 (a), 2 (b) and the perovskite CH₃NH₃PbI₃ (c)



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



Fig. S3 UV-vis absorption spectra at room temperature for the free organic ligands H_3L1 , L and CPs 1-2.



Fig. S4 The diffuse reflectance spectrum (DRS) for CP **2** in the transformed Kubelka– Munk functions.



Fig. S5 CVs of the bare GCE in a $0.2 \text{ M Na}_2\text{SO}_4$ solution (80 mL) in the potential range from -1.6 to 1.2 V vs SCE at different scan rates.



Fig. S6 CVs of L-GCE in a $0.2 \text{ M} \text{ Na}_2\text{SO}_4$ solution (80 mL) in the potential range from - 1.6 to 1.2 V vs SCE at different scan rates.



Fig. S7 CVs of H_3L1 -GCE in a 0.2 M Na₂SO₄ solution (80 mL) in the potential range from -1.6 to 1.2 V vs SCE at different scan rates.



Fig. S8 CVs of **1-GCE** in a $0.2 \text{ M} \text{ Na}_2\text{SO}_4$ solution (80 mL) in the potential range from - 1.6 to 1.2 V vs SCE at different scan rates.



Fig. S9 CVs of 2-GCE in a $0.2 \text{ M Na}_2\text{SO}_4$ solution (80 mL) in the potential range from - 1.6 to 1.2 V vs SCE at different scan rates.



Fig. S10 Solid-state emission spectra at room temperature for the free ligands H_3L1 , L and CP 2 (slit width = 5 nm).



Fig. S11 Nyquist plots (Z' vs. -Z'') of the three-electrode systems at E = -0.1 V vs AgCl/Ag in Na₂SO₄ aqueous solution (0.2 M, 80 mL) in the absence and presence of visible light illumination (650 nm > λ > 350 nm) with the CP **2**-modified FTO slides as working electrodes.



Fig. S12 CVs of 2-FTO in a 0.2 M Na₂SO₄ solution (80 mL) with or without 0.5 M MeOH in the absence (dotted line) and presence (solid line) of the visible light illumination (650 nm > λ > 350 nm, 100 mW·cm⁻²) in the potential range from -1.0 to 1.3 V vs AgCl/Ag at a scan rate of 0.01 V·s⁻¹ (The black arrows indicate the scan directions).









Fig. S13 Top-view SEM images of the TiO_2 layer (a), $CH_3NH_3PbI_3$ layer on the top of TiO_2 layer (b) and CP 2 layer on the top of $CH_3NH_3PbI_3$ for the FTO/ TiO_2 / $CH_3NH_3PbI_3$ / CP 2 device (c).





(b)





(c)





Fig. S14 EDS and elemental mappings of the TiO_2 layer (**a**), $CH_3NH_3PbI_3$ layer on the top of TiO_2 layer (**b**) and CP **2** layer on the top of $CH_3NH_3PbI_3$ for the FTO/ TiO_2 / $CH_3NH_3PbI_3$ / CP **2** device (**c**).



(b)



Fig. S15 Cross-section (a) and oblique-view SEM images for the FTO/ TiO_2 / $CH_3NH_3PbI_3/CP 2$ device (b).



Fig. S16 CVs of FTO/TiO_2 / perovskite / CP 2 in a 0.2 M Na₂SO₄ solution (80 mL) with or without 0.5 M MeOH in the absence (dotted line) and presence (solid line) of the

visible light illumination (650 nm > λ > 350 nm, 100 mW·cm⁻²) in the potential range from -1.0 to 1.3 V vs AgCl/Ag at a scan rate of 0.01 V·s⁻¹ (The black arrows indicate the scan directions).



Fig. S17 CVs of **Pt-FTO** in a 0.2 M Na₂SO₄ solution (80 mL) with or without 0.5 M MeOH in the potential range from -1.0 to 1.3 V vs AgCl/Ag at a scan rate of 0.01 V·s⁻¹ (The black arrows indicate the scan directions).



Fig. S18 CV of **Pt-FTO** without illumination in a 0.2 M Na₂SO₄ solution (80 mL) containing 0.5 M MeOH and CVs of FTO/TiO₂/ perovskite / CP **2** in the absence and presence of methanol at 0.01 V·s⁻¹ irradiated by the visible light (650 nm > λ > 350 nm, 100 mW·cm⁻²) (The black arrows indicate the scan directions).

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.