## Supporting Information

## Halide Anion–Fullerene $\pi$ Noncovalent Interactions: *n*-Doping and Halide Anion Migration Mechanism in *p-i-n* Perovskite Solar Cells

Xuan Sun,<sup>†,‡</sup> Luyi Ji,<sup>†,‡</sup> Weiwei Chen,<sup>†</sup> Xia Guo,<sup>||</sup> Huanhuan Wang,<sup>†</sup> Ming Lei,<sup>\*,†</sup> Qi

Wang\*,<sup>†</sup> and Yongfang  $Li^{\parallel,\$}$ 

<sup>†</sup>Department of Chemistry, Zhejiang University, Hangzhou 310027, China \*Email: leiming@zju.edu.cn

<sup>1</sup>Laboratory of Advanced Optoelectronic Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

<sup>§</sup>Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China



Fig. S1 Cyclic voltammogram of PCBANBr (a) and PCBANCl (b)  $(1.33 \times 10^{-4} \text{ M})$  in BMIH  $(1.23 \times 10^{-2} \text{ M}, \text{ supporting electrolyte})$  DMSO solution under nitrogen atmosphere at a scan rate of 0.05 V/s.



**Fig. S2** AgBr and AgCl precipitation test respectively for the generation of Br<sup>-</sup> and Cl<sup>-</sup> during electrochemical reduction (in the absence of support electrolyte BMIH) of PCBANBr (a) and PCBANCl (b) DMSO aqueous solution. The results indicated that partial oxidation of Br<sup>-</sup> and Cl<sup>-</sup> occurred due to the n-doping and that Br<sup>-</sup> and Cl<sup>-</sup> were dissolved in the solution during reduction.

(Left) PCBANBr DMSO aqueous solution: (1) added AgNO<sub>3</sub> aqueous solution before electrochemical reduction as a control. (2) after electrochemical reduction. (3) AgI precipitation generated when added AgNO<sub>3</sub> aqueous solution to the electrolyte solution.

(Right) PCBANCI DMSO aqueous solution: (1) added AgNO<sub>3</sub> aqueous solution before electrochemical reduction as a control. (2) after electrochemical reduction. (3) AgI precipitation generated when added AgNO<sub>3</sub> aqueous solution to the electrolyte solution.



**Fig. S3** *In situ* UV-vis-NIR absorption spectra of PCBANBr (a) and PCBANCl (b) at different times during the reduction  $(1.33 \times 10^{-4} \text{ M PCBANI } 1.84 \times 10^{-2} \text{ M BMIH in}$  deoxygenated super dry DMSO using a Pt wire working electrode) at -0.60 V *vs.* SCE.



Fig. S4 EPR measurements of PCBANBr (a) and PCBANCl (b).