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Suppoting information

Enhanced efficiency and stability of inverted perovskite solar cells by interfacial engineering with alkyl bisphosphonic molecules

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Fig. S1 (a-e) The top-view SEM images and (f-g) corresponding AFM images of perovskite films with and without interfacial treatment. The scale bars represent 500 nm.



Fig. S2 The contact angles of water on perovskite films.



Fig. S3 XRD spectra of perovskite films before and after stored in 50~60%RH atmosphere under AM1.5G illumination.

	J_{sc} / mA cm ⁻²	V _{oc} / V	FF / %	PCE / %	SPO / %
control	20.8	1.05	73.2	16.0	15.4
C ₉	21.9	1.07	73.0	17.1	16.9
C ₁₃	22.4	1.08	74.6	18.1	17.8
C ₁₅	22.1	1.06	74.2	17.4	17.0
C ₁₇	21.6	1.05	73.9	16.8	16.1

Table S1. The detailed photovoltaic parameters of the best performed devices.



Fig. S4 The time-resolved PL spectra of the glass/perovskite/ $PC_{61}BM$ films with and without the interfacial treatment between perovskite and $PC_{61}BM$.



Fig. S5 The c-AFM images of the ITO/perovskite films with and without the interfacial treatment. The mapping area is $1 \ \mu m \times 1 \ \mu m$.



Fig. S6 The moisture and light-stability test for the control devices and the analogues treated with alkyl bisphosphonic molecules in 50~60%RH atmosphere under AM1.5G illumination. The PCE was averaged form 5 devices for each condition.

Theoretical calculation of the alkyl bisphosphonic molecules passivation

The MA₉Pb₄I₁₆⁺ cluster is extracted from the MAPbI₃ crystal structure¹. In the cluster model, there are 4 vacant X site exposed on the surface. We assume the oxygen on the P=O bond of the alkyl bisphosphonic molecules will attached to the exposed X site, passivating the Pb atoms. The geometries of the perovskite cluster attached with the alkyl bisphosphonic molecules (C₉, C₁₃) are optimized using PBE1PBE density functional² along with the Los-Alamos double- ζ pseudopential basis set³ in Gaussian 16 program. The position of MAPbI₃ is kept fixed during the optimization..

Synthesis of the alkyl bisphosphonic molecules

(1) Synthesis route



C9: n=7, C13: n=11, C15: n=13, C17: n=15

(2) Experimental procedure⁴

Tridecae-1,1-diyldiphosphonic acid C_{13} was prepared by the following prosedre. A mixture of tetraisopropyl methylenebisphosphonate (6.88 g, 20.0 mmol) and dry THF (20 mL) was added dropwise to a solution of NaH (1.10 g, 60% in oil, 27.5 mmol) in dry THF (50 mL) followed by stirring under an argon atmosphere at room temperature for 0.5 h. 1-Bromododecane (4.98 g, 20 mmol) in dry THF (20 ml) was added gradually and the mixture was maintained reflux for 24 h. Water was added to the cooled mixture, the product was extracted with DCM, dried over MgSO₄, and the solvent was removed under reduced pressure. The residue was purified by column chromatography. In the next step, the isopropyl protecting groups were removed by refluxing in concentrated hydrochloric acid 24 h yielding C₁₃ (1.50 g, 21.8%) as a white solid. ESI-MS *m/z* 345 [M+1]⁺. ¹H NMR (600 HZ, DMSO): δ 1.97 (t, 1H), 1.71 (m, 2H), 1.45 (m, 2H), 1.25-1.21 (m, 18H), 0.84 (m, 3H). ¹³C NMR (150HZ, DMSO): δ 31.83, 30.55, 29.61~29.25 (9C), 22.62, 14.47. ³¹P NMR: δ 22.17.

The compound C_9 , C_{15} , C_{17} , were prepared as C_{13} from corresponding bromoalkane to give as white solid.

Nonane-1,1-diyldiphosphonic acid C₉, yielding (18.1%). ESI-MS *m/z* 289 [M+1]⁺. ¹H NMR (600 HZ, DMSO): δ1.91 (t, 1H), 1.69 (m, 2H), 1.46 (m, 2H), 1.24 (m, 10H), 0.86 (m, 3H). ¹³C NMR (150HZ, DMSO):31.84, 30.66, 29.39~29.26 (5C), 22.64, 14.49. ³¹P NMR: δ22.04.

Pentadecane -1,1-diyldiphosphonic acid C₁₅, yielding (22.0%). ESI-MS *m/z* 373[M+1]⁺. ¹H NMR (600 HZ, DMSO): δ1.92 (t, 1H), 1.72 (m, 2H), 1.46(m, 2H), 1.18 (m, 24H), 0.84 (m, 3H). ¹³C NMR (150 HZ, DMSO):31.47, 29.27~28.89 (12C), 22.25, 14.03. ³¹P NMR: δ21.92.

Heptadecane-1,1-diyldiphosphonic acid C₁₇, yielding (25.6%). ESI-MS *m/z* 401[M+1]⁺. ¹H NMR (600 HZ, DMSO): δ1.93 (t, 1H), 1.73 (m, 2H), 1.46 (m, 2H), 1.23 (m, 28H), 0.83 (m, 3H). ¹³C NMR (150HZ, DMSO):31.43, 29.23~28.85 (14C), 22.22, 14.03. ³¹P NMR: δ22.18.

Characterization of the alkyl bisphosphonic molecules by NMR spectra

















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