



Cite this: DOI: 10.1039/c6ta09845b

Room temperature formation of organic–inorganic lead halide perovskites: design of nanostructured and highly reactive intermediates†

Hong Zhang,^a Dan Li,^c Jiaqi Cheng,^a Francis Lin,^b Jian Mao,^a Alex K.-Y. Jen,^b Michael Grätzel^d and Wallace C. H. Choy^{*a}

Recently, organic–inorganic lead halide perovskites have been intensively studied for use in solar cells because of their low cost and high performance. Most of the efficient perovskite solar cells (PVSCs) need layer-dependent high-temperature treatment for each layer of the multilayered structures, increasing the fabrication complexity. In addition, high temperature processes hinder their applications in flexible devices. Therefore, it is highly desirable to develop room-temperature processed methods for controllably forming perovskite films which can simplify the complicated device process and promote emerging flexible device technologies. In this work, we propose a room-temperature scheme of ligand-promoted formation of high quality perovskite films through the judicious design of nanostructured $\text{PbI}_2 \cdot (\text{L})_x$ intermediates, where L denotes the ligand. The high quality perovskite films are free of pinholes and impurities, and have high crystallinity. Using our room-temperature crystallization of perovskite films, we have fabricated highly efficient room-temperature solution-processed PVSCs with a power conversion efficiency (PCE) of 17.21% (the current best PVSCs based on perovskite fabricated at room temperature have a PCE of <16%). Meanwhile, we have experimentally investigated the effects of different ligands on building the nanostructured $\text{PbI}_2 \cdot (\text{L})_x$ intermediates, and thus the purity, morphology, and optoelectronic performances of the resultant perovskite films. Through thermodynamic and kinetic studies, we theoretically study the reactivity of nanostructured $\text{PbI}_2 \cdot (\text{L})_x$ intermediates, thus elucidating the possible mechanism of ligand-promoted perovskite formation. Furthermore, with the experimental and theoretical studies, we establish the selection rules for identifying ideal ligands for the formation of high-quality perovskite films. This work offers a fundamental understanding of ligand effects on the formation of perovskite films for the future design of high-performance and low-cost perovskite-based optoelectronic devices.

Received 14th November 2016
Accepted 27th December 2016

DOI: 10.1039/c6ta09845b

www.rsc.org/MaterialsA

Introduction

Organic–inorganic lead halide perovskites have been intensively studied for forming optoelectronic devices (e.g., thin-film solar cells,^{1–15} light-emitting diodes,^{16,17} and photodetectors¹⁸) due to their low cost and high performance. The growth of perovskite films is a critical step to produce high efficiency and stable perovskite-based optoelectronic devices.^{1–12} In general, there are

mainly three methods, including one-step solution deposition,^{1–4,9–13,19–23} two-step sequential deposition,^{6,7,24–30} and vacuum deposition,³¹ to prepare the hybrid perovskite film. However, most of the approaches reported so far require tedious high-temperature sintering or annealing processes.^{1–9,19–30} Thermal annealing for extended periods is known to cause perovskite decomposition, which degrades device performance, reproducibility, and stability.^{32–34} It is still challenging to fabricate room-temperature processed high-quality perovskite films, owing to a trade-off between processing temperature and device performance.

Considering $\text{CH}_3\text{NH}_3\text{PbI}_3$, the conventional two-step dipping deposition provides a potential route toward room-temperature and scalable fabrication of perovskite films.^{6,7,35} However, when PbI_2 is deposited on a flat substrate, it tends to form a layered and dense film. Therefore, there is a concern of the incomplete conversion of PbI_2 to perovskite during the exposure to $\text{CH}_3\text{NH}_3\text{I}$ solution. The unreacted PbI_2 in the final device will reduce photovoltaic performances and stability.⁶ These drawbacks make it difficult to fabricate high-quality perovskite films on a planar

^aDepartment of Electrical and Electronic Engineering, The University of Hong Kong, Pok Fu Lam Road, Hong Kong, China. E-mail: chchoy@eee.hku.hk

^bDepartment of Materials Science & Engineering, University of Washington, Seattle, Washington 98195, United States

^cKey Laboratory of Luminescence and Optical Information, Ministry of Education, School of Science, Beijing Jiaotong University, Beijing 100044, China

^dLaboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, School of Basic Sciences, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ta09845b

substrate by the conventional sequential deposition method. Although organic ligands (*e.g.*, dimethyl sulfoxide (DMSO), *N,N'*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP)) have been reported to control the crystallization of perovskite by forming $\text{PbI}_2 \cdot (\text{ligand})_x$ or $\text{CH}_3\text{NH}_3\text{I}$ -ligand- PbI_2 intermediates,^{36–39} high temperature thermal annealing is still utilized to remove the ligands for forming pure perovskite crystals. In addition, the intrinsic effect of ligands on the crystallization kinetics of perovskite is still unclear.

In this work, we propose a room-temperature scheme of ligand-promoted formation of high-quality perovskite films through facile design of nanostructured and highly reactive $\text{PbI}_2 \cdot (\text{L})_x$ intermediates. Different representative ligands with different features (molecular size, volatility, solubility, and reactivity) are experimentally investigated to unravel the ligand effects on the film quality (*e.g.*, purity), morphology (*e.g.*, pinhole), and optoelectronic properties of perovskites. The mechanism of ligand-promoted perovskite formation is theoretically elucidated through the thermodynamic and chemical kinetic studies. With the experimental and theoretical studies, a selection rule for identifying ideal ligands for the formation of high-quality perovskite films is established. Using our room-temperature crystallization of perovskite films, highly efficient room-temperature solution-processed PVSCs with a PCE of 17.21% (the current best PVSCs based on perovskite fabricated at room temperature have a PCE of <16%) have been fabricated.

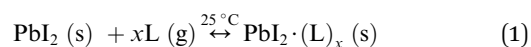
Results and discussion

Ligand-promoted perovskite formation at room temperature

Traditionally, the layered and dense PbI_2 film cannot completely transform into perovskite in a short time, which is detrimental to the device performance and continuous large-scale production of perovskite-based optoelectronic devices. To address this issue, we propose a room-temperature ligand-promoted approach for forming perovskite films. Interestingly, we find that the judicious selection of ligands greatly facilitates the conversion of PbI_2 to highly pure pinhole-free perovskite films at room temperature. Fig. 1a shows the procedure of our

new scheme of ligand-promoted formation of perovskite films at room temperature. The ligand-promoted formation of perovskite films mainly contains two stages, namely (I) ligand-induced formation of nanostructure-based $\text{PbI}_2 \cdot (\text{L})_x$ intermediates (L = ligand) and (II) perovskite film formation facilitated by ligand exchange reactions. Fig. 1a shows the procedure of conventional sequential deposition and our new scheme of ligand-promoted formation of perovskite films at room temperature. To unveil the mechanism of ligand-promoted perovskite formation, five representative ligands with different features (molecular size, volatility, solubility, and reactivity) were investigated. The features and molecular structures of these ligands are shown in Table S1† and Fig. 1b, respectively.

Regarding stage I of ligand-induced formation of nanostructure-based $\text{PbI}_2 \cdot (\text{L})_x$ films, the nanostructured $\text{PbI}_2 \cdot (\text{L})_x$ intermediates are easily synthesized *in situ* by solid-gas reactions between the PbI_2 film and chemical ligand vapors at room temperature [eqn (1)].



The formation of $\text{PbI}_2 \cdot (\text{L})_x$ intermediates is confirmed by UV-vis spectra and X-ray powder diffraction (XRD). The content of ligand in the $\text{PbI}_2 \cdot (\text{L})_x$ intermediates is estimated from thermogravimetric analysis (TGA) as shown in Fig. S1 in the ESI.† As shown in Fig. 2a and Table S1,† the volatility of the ligand has a significant effect on the conversion rate of the PbI_2 film to $\text{PbI}_2 \cdot (\text{L})_x$ intermediates. Owing to the volatility of DMF and EDA whose boiling point is also low with a value of 153 °C and 116 °C respectively, the yellow-colored PbI_2 films change to colorless films (see Fig. S2†) within 50 s upon exposure to their vapors. (The conversion rate was monitored by UV-vis spectra). Meanwhile, the formation of colorless $\text{PbI}_2 \cdot (\text{Py})_2$ and $\text{PbI}_2 \cdot (\text{DMSO})_2$ is also not long and takes 100 s and 140 s, respectively. However, the complete transformation of PbI_2 into the $\text{PbI}_2 \cdot \text{TBP}$ intermediate takes a longer time of 300 s due to the low volatility of TBP (higher boiling point of 197 °C).

The formation of $\text{PbI}_2 \cdot (\text{L})_x$ intermediates is further confirmed by the XRD pattern (Fig. 2b) and Fourier transform infrared spectra (FTIR)²⁴ (Fig. S3†). After the treatment of initial

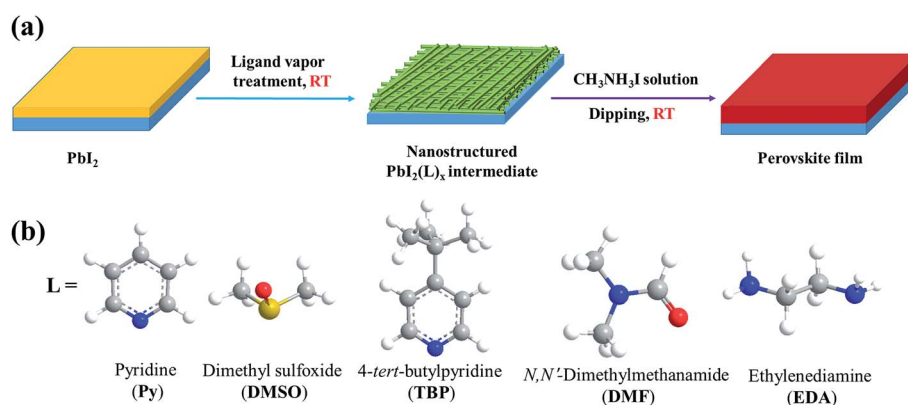


Fig. 1 (a) Schematics of room-temperature crystallization of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film by the ligand-promoted approach. (b) The molecular structure of different ligands.

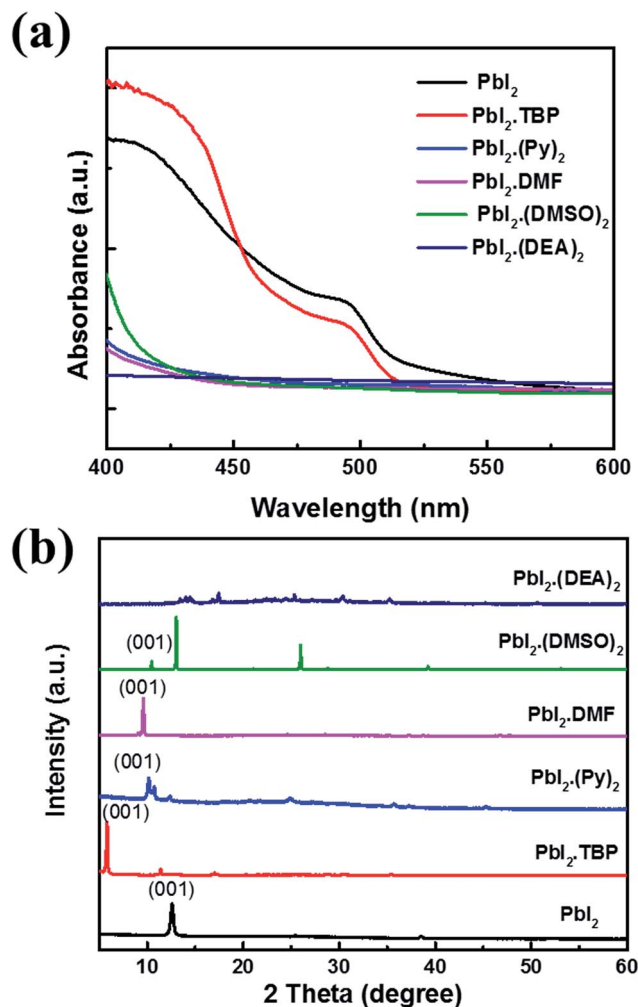


Fig. 2 (a) UV-vis spectra and (b) XRD patterns of different $\text{PbI}_2\cdot(\text{L})_x$ intermediates.

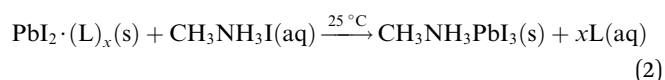
PbI_2 films with the vapor of various ligands (except for EDA), the films not only exhibit Bragg peaks associated with PbI_2 crystal (001) planes at 12.55° , but also show other new peaks at lower angles ($<12.55^\circ$), indicating the formation of the $\text{PbI}_2\cdot(\text{L})_x$ intermediates. Meanwhile, the (001) peak shifts to a smaller angle after the $\text{PbI}_2\cdot(\text{L})_x$ formation. This is because the intercalation of PbI_2 with ligand molecules produced an expansion of interlayer space along the crystal *c*-axis, which is beneficial to the substitution of $\text{CH}_3\text{NH}_3\text{I}$ as will be described later. In addition, the extent of the (001) peak shift is associated with the molecular size (see Table S1†). For instance, as shown in Fig. 2b, the (001) peak of $\text{PbI}_2\cdot\text{TBP}$ at 5.87° is smaller than that of $\text{PbI}_2\cdot(\text{DMSO})_2$ (10.44°) due to the bigger molecular size of TBP ($146.07\text{ cm}^3\text{ mol}^{-1}$) than DMSO ($71.43\text{ cm}^3\text{ mol}^{-1}$). It should be noted that PbI_2 coordinated with EDA tends to form a chemically stable stoichiometric complex $\text{PbI}_2\cdot(\text{EDA})_2$, which shows a totally different XRD pattern from PbI_2 and does not convert to the perovskite film.

The morphology of $\text{PbI}_2\cdot(\text{L})_x$ intermediates will significantly affect the formation of perovskite and thus will be studied

carefully by using a scanning electron microscope (SEM; Fig. 3 and S4†). The untreated PbI_2 forms dense platelet shaped crystals (Fig. 3a), whose layered structure impairs their complete conversion to perovskite.^{6,7} Distinguishably, the $\text{PbI}_2\cdot(\text{Py})_2$ film shows a uniform and nanoporous morphology with many small holes as shown in Fig. 3b, which is very useful for ensuring the complete conversion to $\text{CH}_3\text{NH}_3\text{PbI}_3$ as described later. The $\text{PbI}_2\cdot\text{TBP}$ film is also porous, but its morphology is a little disordered (Fig. 3c). The $\text{PbI}_2\cdot(\text{DMSO})_2$ film also shows a porous morphology with hundreds of nanometer sized holes and is formed by stacked small nanosheets (Fig. 3d). Notably, the process of forming the $\text{PbI}_2\cdot\text{DMF}$ film undergoes severe structural changes over this time period, exhibiting a coarsening of crystals with micrometer size and voids occur (Fig. 3e). The $\text{PbI}_2\cdot(\text{EDA})_2$ film is dense with some cracks (Fig. 3f). Such a large change of morphology is not good for forming high quality perovskite films.

Regarding the control of the morphology of $\text{PbI}_2\cdot(\text{L})_x$ intermediates, the solubility and molecular size of ligands should be taken into account. On one hand, the solubility of PbI_2 in the ligands (see Table S1†) plays an important role in building the nanostructured $\text{PbI}_2\cdot(\text{L})_x$ intermediates. If the solubility of PbI_2 in the chemical ligand vapors is very high, *i.e.* DMF (475 mg ml^{-1}) and DMSO (595 mg ml^{-1}), the morphology of the $\text{PbI}_2\cdot(\text{L})_x$ intermediates changes significantly on a large scale (micrometer scale) by the ligand vapors. On the contrary, the ligands with low solubility (*e.g.*, Py ($<5\text{ mg ml}^{-1}$), TBP (148 mg ml^{-1}), and DEA ($<5\text{ mg ml}^{-1}$)) will favor the formation of appropriate $\text{PbI}_2\cdot(\text{L})_x$ nanostructures, which is critical to obtain pinhole-free perovskite films (see the discussion of perovskite film morphology in the later section). On the other hand, the insertion of ligands with different molecular sizes into the interlayer spaces of PbI_2 produced an expansion of interlayer space along the crystal *c*-axis, which brings a volume expansion from initial PbI_2 into nanostructured $\text{PbI}_2\cdot(\text{L})_x$ intermediates. The volume expansion can be beneficial to the conversion of perovskite. However, too large ligand molecular size such as TBP may make the morphology of $\text{PbI}_2\cdot\text{TBP}$ films change in an uncontrollable manner (see Fig. 3c). Consequently, by using our approach of exposing the PbI_2 film to ligand vapors with high volatility, low solubility, and small molecular size, nanostructure-based $\text{PbI}_2\cdot(\text{L})_x$ intermediates can easily form in a controllable manner, which will favor the formation of high quality perovskite films.

In stage II of perovskite film formation facilitated by ligand exchange reactions, room-temperature crystallized perovskite films are fabricated by dipping the as-formed nanostructure-based $\text{PbI}_2\cdot(\text{L})_x$ intermediates into $\text{CH}_3\text{NH}_3\text{I}$ solution for seconds at room temperature. Through the conversion of $\text{PbI}_2\cdot(\text{L})_x$ to $\text{CH}_3\text{NH}_3\text{PbI}_3$, the ligand molecules intercalated in PbI_2 are replaced by external $\text{CH}_3\text{NH}_3\text{I}$ whenever $\text{CH}_3\text{NH}_3\text{I}$ affinity is higher than that of the intercalated ligands [eqn (2)].



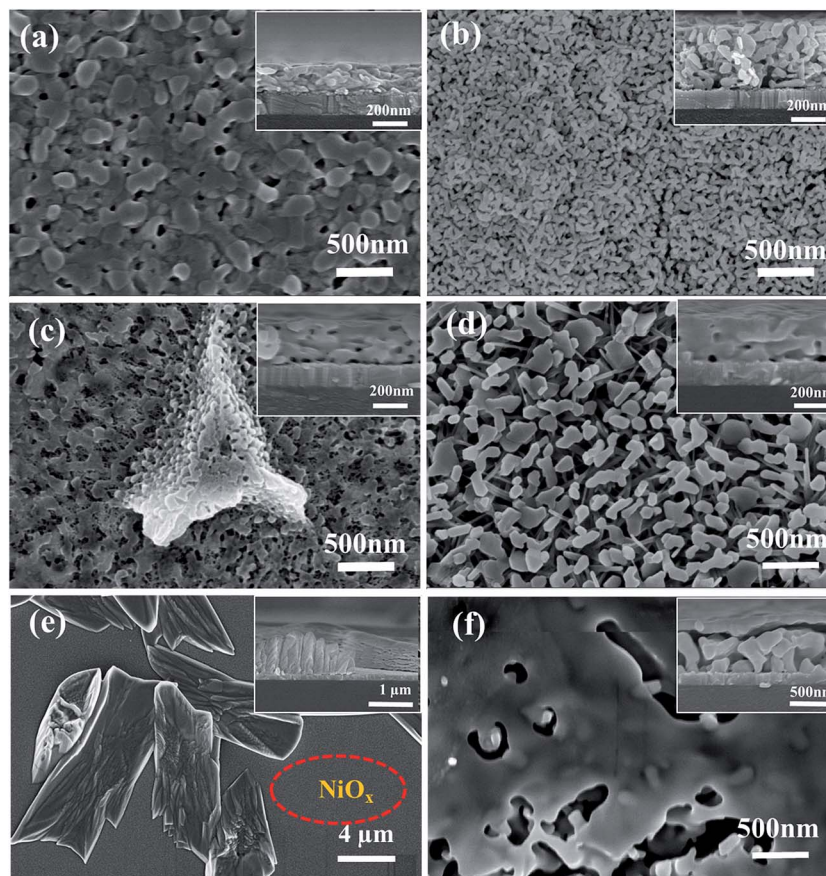


Fig. 3 Top-view and cross-sectional (inset) SEM images of $\text{PbI}_2 \cdot (\text{L})_x$ intermediates with high magnification in which (a) is untreated PbI_2 , (b) is $\text{PbI}_2 \cdot (\text{Py})_2$, (c) is $\text{PbI}_2 \cdot \text{TBP}$, (d) is $\text{PbI}_2 \cdot (\text{DMSO})_2$, (e) is $\text{PbI}_2 \cdot \text{DMF}$ and (f) is $\text{PbI}_2 \cdot (\text{EDA})_2$ film.

To compare the reactivity of different ligands, the formation time of the $\text{PbI}_2 \cdot (\text{L})_x$ intermediate and perovskite is set as 60 s and 20 s, respectively. Interestingly, the nanostructure-based $\text{PbI}_2 \cdot (\text{Py})_2$ intermediate is converted into $\text{CH}_3\text{NH}_3\text{PbI}_3$ completely by immersion in the $\text{CH}_3\text{NH}_3\text{I}$ solution leaving no residual PbI_2 (see Fig. 4). By contrast, pristine PbI_2 and other $\text{PbI}_2 \cdot (\text{L})_x$ films ($\text{L} = \text{TBP}$, DMSO , and DMF) are incompletely converted into $\text{CH}_3\text{NH}_3\text{PbI}_3$ with a large amount of PbI_2 residue but no $\text{PbI}_2 \cdot (\text{L})_x$ residue, which can be confirmed by the XRD patterns (Fig. 4b). For the extreme case of the $\text{PbI}_2 \cdot (\text{EDA})_2$ film, no conversion to $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite is witnessed by the light absorption (Fig. 4a) and XRD measurements (Fig. 4b), indicating that the affinity of EDA toward PbI_2 is higher than that of $\text{CH}_3\text{NH}_3\text{I}$, and thus the EDA molecule is not exchanged by $\text{CH}_3\text{NH}_3\text{I}$ to form $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals. It shall be noted that owing to the strong affinity of DMSO toward PbI_2 , the $\text{PbI}_2 \cdot (\text{DMSO})_2$ residue is still detected.³⁶ Therefore, the reactivity of nanostructure-based $\text{PbI}_2 \cdot (\text{L})_x$ intermediates toward $\text{CH}_3\text{NH}_3\text{I}$ has a great impact on the formation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films.

The morphology of perovskite films has been widely reported to have a great influence on the optoelectronic properties of perovskite. The morphology of perovskite films prepared from different $\text{PbI}_2 \cdot (\text{L})_x$ intermediates is investigated by using SEM. Fig. 5 and S5† show the top-view SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_3$

films produced from the $\text{PbI}_2 \cdot (\text{L})_x$ intermediates. As expected the morphology of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films depends on their starting PbI_2 film in the two-step dipping method.^{6,7} The $\text{CH}_3\text{NH}_3\text{PbI}_3$ films prepared from pristine PbI_2 and $\text{PbI}_2 \cdot (\text{L})_x$ intermediates ($\text{L} = \text{TBP}$, DMSO , and DMF) are rough with small grains, voids and cracks. Notably, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film prepared from $\text{PbI}_2 \cdot (\text{Py})_2$ exhibits a uniform and pinhole-free morphology and hundreds of nanometer sized grains for high performance optoelectronic devices.

Consequently, we demonstrate that by introducing nanostructured $\text{PbI}_2 \cdot (\text{L})_x$ intermediates with an appropriate reactivity and morphology, highly pure and pinhole-free perovskite films can be formed at room temperature through the ligand-promoted perovskite formation including the two stages of the ligand-induced nanostructured $\text{PbI}_2 \cdot (\text{L})_x$ intermediate formation and ligand-facilitated perovskite film formation.

Mechanisms of ligand-promoted perovskite formation

Regarding the role of ligands, we further studied the reaction mechanisms of ligand-promoted perovskite formation through thermodynamic and kinetic studies. Theoretical calculations of activation energies (E_a) and formation enthalpies (ΔH_f) were conducted based on density functional theory (DFT). Detailed

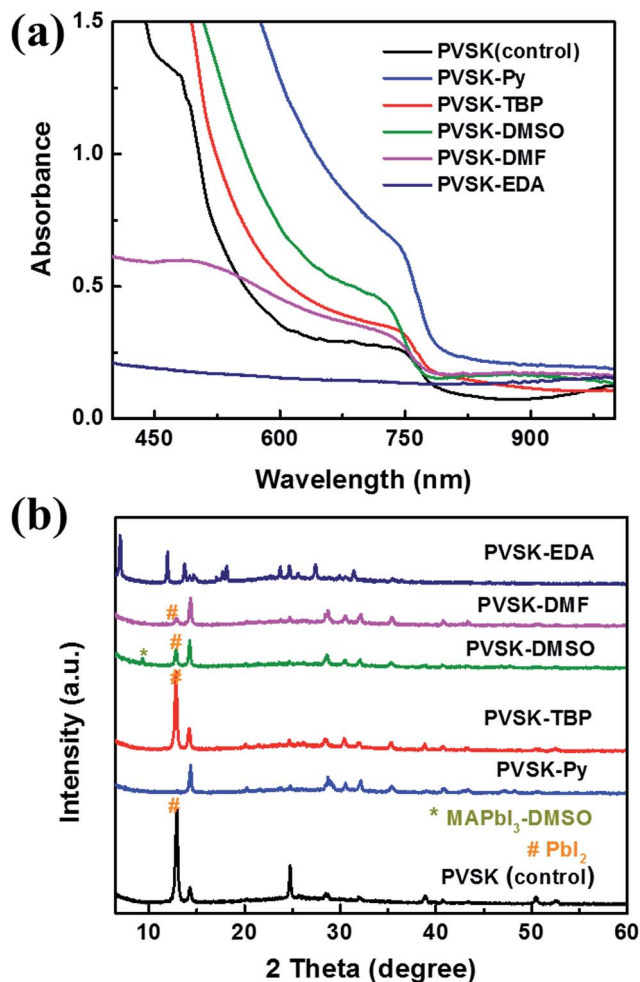


Fig. 4 (a) UV-vis spectra and (b) XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films prepared from $\text{PbI}_2 \cdot (\text{L})_x$ intermediates. The PVSK refers to $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. To compare the reactivity of different ligands, the duration of $\text{PbI}_2 \cdot (\text{L})_x$ intermediates and PVSK formation is 60 s and 20 s in both cases, respectively.

calculation procedures are provided in the ESI. Fig. S6† shows the crystallographic structures of PbI_2 and $\text{PbI}_2 \cdot (\text{L})_x$ intermediates. The E_a of a reaction can be considered as the height of the potential barrier separating two minima of potential energy (of the reactants and products of a reaction). According to Hess's law, ΔH_f is the overall energy required for a chemical reaction. Generally, if ΔH_f is negative, the reaction is exothermic and is more likely to be spontaneous; positive ΔH_f values correspond to endothermic reactions.⁴⁰

Fig. 6 shows the reaction coordinate diagram of the perovskite formation *via* different pathways in this study. The corresponding calculated E_a and ΔH_f are summarized in Table 1. In the conventional pathway (Route A, Fig. 6a), the formation of perovskite needs to overcome a large energy barrier ($E_a = 1.004$ eV). The formation enthalpy is negative (-0.433 eV) for $\text{CH}_3\text{NH}_3\text{PbI}_3$, which is more thermodynamically stable as compared to PbI_2 . Interestingly, in our ligand-promoted pathway (Fig. 6b), the formation of perovskite undergoes two-stage reactions: $\text{PbI}_2 \cdot (\text{L})_x$ formation and perovskite formation. Both the E_{a1} and E_{a2}

of Route B (see Table 1) are lower than that of the conventional pathway, and thus favor the perovskite formation. Regarding Route C, as shown in Fig. 6c, the formation enthalpy of perovskite from $\text{PbI}_2 \cdot (\text{EDA})_2$ is positive ($+0.179$ eV), which indicates that $\text{PbI}_2 \cdot (\text{EDA})_2$ is more thermodynamically stable than perovskite. In other words, the formation of perovskite from $\text{PbI}_2 \cdot (\text{EDA})_2$ is discouraged. In this route, ligands (*e.g.*, EDA) inhibit the formation of perovskite. The calculation results also corroborated well our experimental results above that perovskite cannot be formed from $\text{PbI}_2 \cdot (\text{EDA})_2$ (see Fig. 4).

Through the thermodynamic and kinetic studies, we theoretically show the reaction mechanism that (a) our proposed ligand-promoted perovskite formation distinctly changes from the conventional single pathway with a large activation energy into a two-stage reaction pathway with lower activation energies which favors the formation of perovskite; (b) the ligand-inhibited pathway shows no transformation of perovskite, owing to the positive formation enthalpy ($\Delta H_f > 0$) of perovskite from $\text{PbI}_2 \cdot (\text{L})_x$ intermediates.

Ligand effects on the optoelectronic properties of perovskite

We further investigated the optoelectronic properties of the perovskite prepared from different ligands. We fabricated room-temperature solution-processed perovskite solar cells (PVSCs) with the structure of $\text{ITO}/\text{NiO}_x/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{C}_{60}/\text{bis-C}_{60}/\text{Ag}$. Fig. 7a shows the current density–voltage (J – V) curves for the best PVSCs based on different ligands. The photovoltaic parameters of PVSCs are summarized in Table 2.

As shown in Table 2 and Fig. 7a, the control PVSC (prepared from the pristine PbI_2 film) shows poor performance with $V_{oc} = 0.92$ V, $J_{sc} = 10.63$ mA cm^{-2} , FF = 0.46, and PCE = 4.52% ($\text{PCE}_{\text{avg}} = 3.86 \pm 0.49\%$). This is because the unreacted PbI_2 with a lower valence band edge at the $\text{CH}_3\text{NH}_3\text{PbI}_3$ – NiO_x interface hinders the hole transfer from the perovskite film to the NiO_x layer (see Fig. S7†), leading to the low V_{oc} , FF, and PCE. Encouragingly, the use of ligands significantly promotes the transformation of the perovskite film and thus improves the photovoltaic metrics. Notably, the Py-based PVSC with a high-quality perovskite film shows an attractive photovoltaic performance with $V_{oc} = 1.06$ V, $J_{sc} = 22.59$ mA cm^{-2} , FF = 0.72, and PCE = 17.21% ($\text{PCE}_{\text{avg}} = 15.32 \pm 0.91\%$), which is higher than that reported in a previous study by using room-temperature techniques.⁴¹ The $\text{PbI}_2 \cdot \text{TBP}$ and $\text{PbI}_2 \cdot (\text{DMSO})_2$ films also provide an improvement in photovoltaic performances, yielding an average PCE of 11.90% and 9.60%, respectively. However, owing to the non-uniform and impure perovskite film with many pinholes, the $\text{PbI}_2 \cdot \text{DMF}$ -based device gives a relatively low V_{oc} of 0.93 V, a J_{sc} of 18.48 mA cm^{-2} , and a FF of 0.54, resulting in a modestly enhanced PCE from 4.52% to 9.40%. The improvement is dominated by the increased FF and J_{sc} , which is attributed to the promoted transformation of the perovskite layer. Differently, owing to the lack of perovskite, the $\text{PbI}_2 \cdot (\text{EDA})_2$ -based device depicts no photovoltaic performance.

Fig. 7b shows the incident photon-to-current conversion efficiencies (IPCEs) of our PVSCs. Compared with the control PVSC, the introduction of ligands in the stage of perovskite

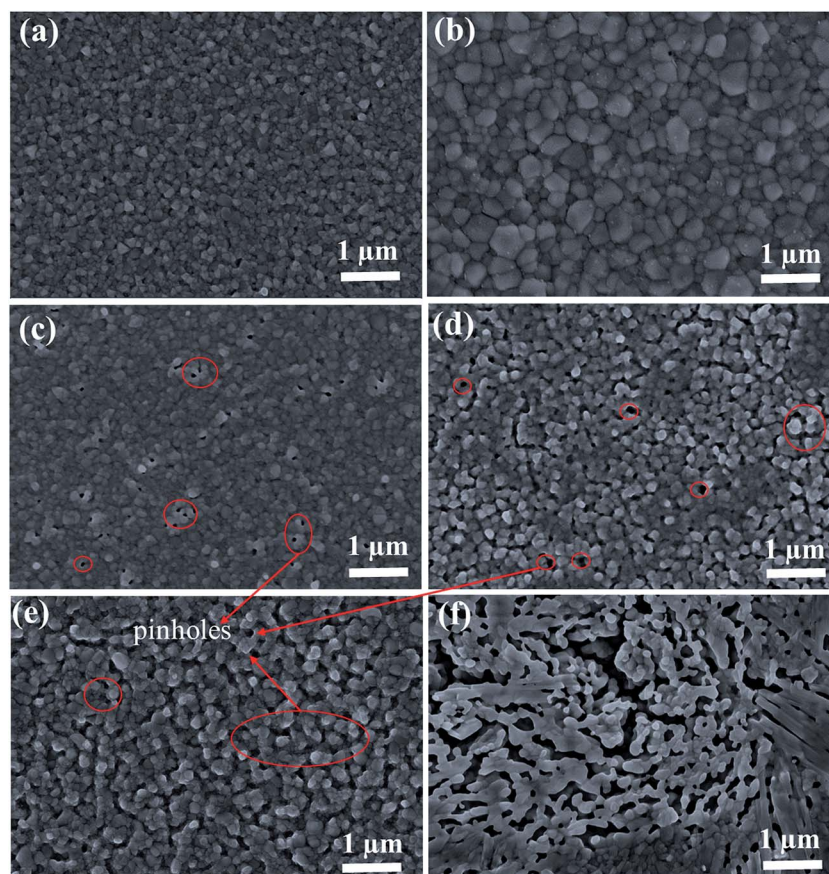


Fig. 5 Top-view SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films with high magnification from (a) PbI_2 , (b) $\text{PbI}_2 \cdot (\text{Py})_2$, (c) $\text{PbI}_2 \cdot \text{TBP}$, (d) $\text{PbI}_2 \cdot (\text{DMSO})_2$, and (e) $\text{PbI}_2 \cdot \text{DMF}$ on the NiO_x/ITO substrate. (f) Top-view SEM image of the $\text{PbI}_2 \cdot (\text{EDA})_2$ film after dipping into $\text{CH}_3\text{NH}_3\text{I}$ solution with high magnification. The dipping time is 20 s in both cases.

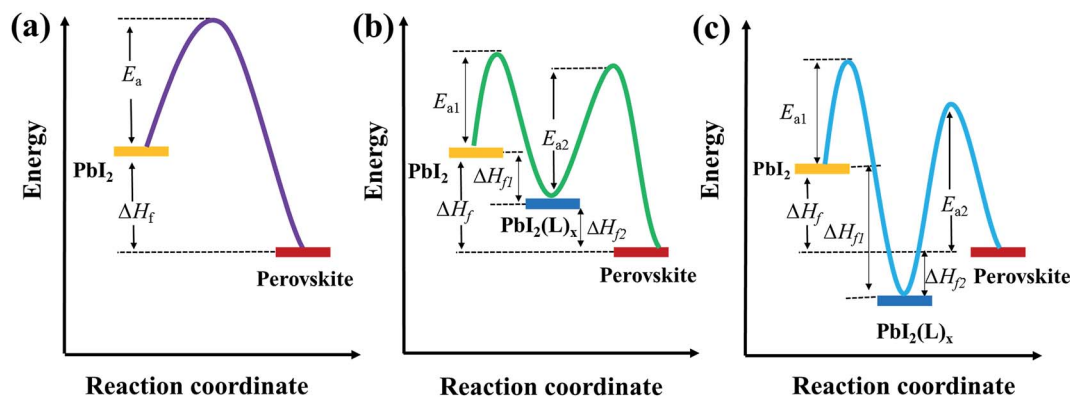


Fig. 6 The reaction coordinate diagram of the ligand-promoted perovskite formation. (a) Route A: $\text{PbI}_2 \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3$; (b) Route B: $\text{PbI}_2 \rightarrow \text{PbI}_2 \cdot (\text{L})_x \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3$ ($\text{L} = \text{Py}, \text{TBP}, \text{DMSO}, \text{and DMF}$); (c) Route C: $\text{PbI}_2 \rightarrow \text{PbI}_2 \cdot (\text{L})_x \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3$ ($\text{L} = \text{EDA}$).

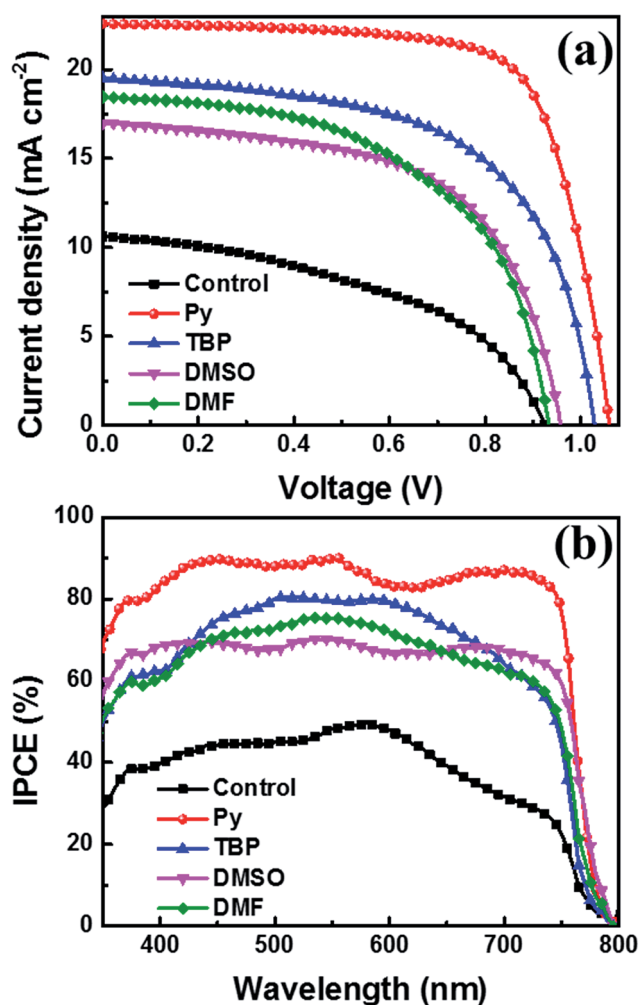
formation greatly improves the IPCE from 350 nm to 800 nm. The maximum IPCE increases in the order control < DMSO < DMF < TBP < Py, in good agreement with the J_{sc} trend. The Py-based PVSC shows the best IPCE performance among the five devices, accounting for its highest J_{sc} . Consequently, it is clearly seen that the features of ligands have a great impact on the optoelectronic properties of the perovskite films, and thus the photovoltaic performance of PVSCs.

Ligand selection rules

On the basis of the theoretical and experimental studies, we conclude that the features of ligands (volatility, solubility, reactivity, and molecular size) have a great impact on the formation mechanism and film quality of perovskite, and thus the performance of optoelectronic devices. The ideal ligands should simultaneously have:

Table 1 The calculated activation energies and formation energies

Perovskite formation pathway	Reaction scheme	Activation energy E_a (eV)	Formation enthalpy ΔH_f (eV)
Route A	$\text{PbI}_2 \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3$	1.004	−0.433
Route B	$\text{PbI}_2 \rightarrow \text{PbI}_2 \cdot (\text{Py})_2$	0.095	−0.400
	$\text{PbI}_2 \cdot (\text{Py})_2 \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3$	0.741	−0.033
	$\text{PbI}_2 \rightarrow \text{PbI}_2 \cdot \text{TBP}$	0.064	−0.265
	$\text{PbI}_2 \cdot \text{TBP} \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3$	0.787	−0.168
	$\text{PbI}_2 \rightarrow \text{PbI}_2 \cdot (\text{DMSO})_2$	0.135	−0.422
	$\text{PbI}_2 \cdot (\text{DMSO})_2 \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3$	0.826	−0.001
	$\text{PbI}_2 \rightarrow \text{PbI}_2 \cdot \text{DMF}$	0.095	−0.294
	$\text{PbI}_2 \cdot \text{DMF} \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3$	0.821	−0.139
Route C	$\text{PbI}_2 \rightarrow \text{PbI}_2 \cdot (\text{EDA})_2$	0.135	−0.612
	$\text{PbI}_2 \rightarrow \text{PbI}_2 \cdot (\text{EDA})_2 \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3$	0.722	+0.179

Fig. 7 (a) J - V curves and (b) IPCEs for the best PVSCs based on different ligands.

(1) good reactivity (*i.e.* low activation energy and negative formation enthalpy) to form perovskite from $\text{PbI}_2 \cdot (\text{L})_x$ intermediates. The activation energy and formation enthalpy of ligands will determine the reactivity of the $\text{PbI}_2 \cdot (\text{L})_x$

intermediates toward $\text{CH}_3\text{NH}_3\text{I}$, and thus the formation and purity of perovskite, which has been supported and described by our DFT calculations. For instance, from our results above, high quality perovskite films can be easily formed using the ligand exchange reaction between $\text{PbI}_2 \cdot (\text{Py})_2$ and $\text{CH}_3\text{NH}_3\text{I}$, owing to its low activation energy (0.741 eV) and negative formation enthalpy (−0.033 eV). However, the strong affinity of DEA toward PbI_2 leads to the formation of thermodynamically stable $\text{PbI}_2 \cdot (\text{DEA})_2$ and the positive formation enthalpy (+0.179 eV) of perovskite from $\text{PbI}_2 \cdot (\text{DEA})_2$. This reveals the reason why the DEA molecule in $\text{PbI}_2 \cdot (\text{DEA})_2$ cannot be exchanged by $\text{CH}_3\text{NH}_3\text{I}$ to form $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals at room temperature.

(2) High volatility (or low boiling point). The volatility of ligands has a great effect on the conversion rate of the PbI_2 film to $\text{PbI}_2 \cdot (\text{L})_x$ intermediates. The nanostructured $\text{PbI}_2 \cdot (\text{L})_x$ intermediates can be readily formed when the PbI_2 film is exposed to ligands with high volatility (or low boiling point) as we discussed above (see Table S1†).

(3) Low solubility of PbI_2 . The solubility of PbI_2 in the ligands (see Table S1†) also plays an important role in building the nanostructured $\text{PbI}_2 \cdot (\text{L})_x$ intermediates. If the solubility of PbI_2 in the chemical ligands vapor is very low (*e.g.*, Py and TBP), $\text{PbI}_2 \cdot (\text{L})_x$ intermediates with appropriate nanostructures can be achieved by the treatment of ligand vapors. On the contrary, the morphology of the $\text{PbI}_2 \cdot (\text{L})_x$ intermediate will change too vigorously into large scale (micrometer scale) structures by the ligand vapors with high solubility (*e.g.*, DMF and DMSO).

(4) Small molecular size. The molecular size of ligands will affect the morphology of $\text{PbI}_2 \cdot (\text{L})_x$ intermediates, and thus perovskite film quality and device performances. The insertion of small ligands into the interlayer spaces of PbI_2 brings a substantial morphology change into nanostructured $\text{PbI}_2 \cdot (\text{L})_x$ intermediates in a controllable manner, which will contribute to the formation of high-quality perovskite films. For example, after the treatment of Py with small molecular size (79.89 cm³ mol^{−1}), the PbI_2 film changes into a uniform and nanoporous $\text{PbI}_2 \cdot (\text{Py})_2$ film with many small holes (Fig. 3b). However, TBP with too large ligand molecular size (146.05 cm³ mol^{−1}) makes the morphology of $\text{PbI}_2 \cdot \text{TBP}$ films change in an uncontrollable manner (see Fig. 3c).

Table 2 The photovoltaic parameters of PVSCs based on different ligands^a

Ligand	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF	Average PCE (best) (%)
Control	0.92 ± 0.01	9.73 ± 0.92	0.43 ± 0.02	3.86 ± 0.49 (4.52)
Py	1.01 ± 0.02	22.00 ± 0.41	0.69 ± 0.04	15.32 ± 0.91 (17.21)
TBP	1.03 ± 0.01	18.05 ± 1.06	0.60 ± 0.04	11.04 ± 0.93 (11.90)
DMSO	0.97 ± 0.02	16.53 ± 0.79	0.56 ± 0.03	9.02 ± 0.55 (9.60)
DMF	0.92 ± 0.01	16.54 ± 1.52	0.55 ± 0.03	8.33 ± 0.59 (9.40)
EDA	—	—	—	—

^a J_{sc} is the short-circuit photocurrent density; V_{oc} is the open-circuit voltage; FF is the fill factor; PCE is the power conversion efficiency.

Conclusions

In summary, we have demonstrated a new strategy to form highly crystalline and pure perovskite films at room temperature through the judicious design of nanostructured $PbI_2 \cdot (L)_x$ intermediates. Different representative ligands with different features are experimentally investigated to unravel the ligand effects on the formation kinetics, morphology, and optoelectronic properties of perovskite. Furthermore, we have also theoretically investigated the mechanisms of ligand-promoted perovskite formation through dynamics and kinetics. With the experimental and theoretical studies, we have identified the ideal ligands for the formation of high-quality perovskite films. In addition, we conclude the ligand selection rules including (i) good reactivity (low activation energy and negative formation enthalpy) of $PbI_2 \cdot (L)_x$ toward exchange by CH_3NH_3I ; (ii) a high volatility (or low boiling point); (iii) a low solubility of PbI_2 ; (iv) and a small molecular size. Using our room-temperature crystallization of perovskite films, we have fabricated highly efficient room-temperature solution-processed PVSCs with a power conversion efficiency (PCE) of 17.21%. This work contributes not only to understanding the mechanisms of ligand-promoted perovskite formation, but also to realizing the emerging flexible perovskite optoelectronics.

Experimental

Materials

All the chemicals and materials were purchased and used as received unless otherwise noted. CH_3NH_3I was purchased from Dyesol and used as received. PbI_2 (99%) and ligands were purchased from Sigma-Aldrich. Bis- C_{60} surfactant was kindly provided by Prof. Alex Jen. NiO_x NCs inks were synthesized according to our previous report.⁸

Ligand-promoted perovskite formation

The PbI_2 precursor was prepared by dissolving 450 mg PbI_2 powder in 1 ml DMF, and then spin coated on the substrate at 4000 rpm for 100 s. The PbI_2 films were treated with different chemical ligand vapors for different time periods to form $PbI_2 \cdot (L)_x$ films. In particular, the PbI_2 films were covered by a glass Petri dish. Around 20 μ L of pure ligand was added at the edge of the Petri dish. The ligand vaporized in the Petri dish and reacted with the PbI_2 films to form $PbI_2(L)_x$ intermediates. The

formation of $PbI_2(L)_x$ intermediates from the PbI_2 solid film is a solid-gas reaction process and does not need the drying process. Then, the formed $PbI_2(L)_x$ intermediates were dipped in a solution of 15 mg CH_3NH_3I per ml 2-propanol for 20 s, rinsed with 2-propanol and dried naturally.

Solar cell fabrication

ITO-coated glass substrates were cleaned and then ultraviolet-ozone treated for 20 min. Then, the NiO_x NCs aqueous ink (20 mg ml⁻¹ in deionized water) was spin-coated on pre-cleaned ITO glass to form NiO_x films. The resultant NiO_x films were used to fabricate devices without the annealing process or other treatments. After that, the perovskite films were formed on the NiO_x substrate. For the champion cell, the PbI_2 precursor was modified using a formulation of 28 mg $PbCl_2$ and 462 mg PbI_2 per ml DMF, and the crystallization of the resulting CH_3NH_3 - PbI_3 films was improved by CH_3NH_2/CH_3OH mixed vapor treatment for 1–2 s. Subsequently, the $C_{60}/PCBM$ mixture (12/8 mg ml⁻¹ dissolved in dichlorobenzene) and bis- C_{60} surfactant (2 mg ml⁻¹ in 2-propanol) were sequentially deposited by spin coating at 1000 rpm for 120 s and 3000 rpm for 30 s, respectively. Finally, the device was completed with the evaporation of Ag contact electrodes (120 nm) through a shadow mask. The active area of this electrode was fixed at 6 mm². All devices were fabricated in a glove box.

Measurement and characterization

Simulated AM 1.5 sunlight was generated using a Newport AM 1.5 G solar simulator (100 mW cm⁻²), calibrated with an ISO 17025-certified KG3-filtered silicon reference cell. The spectral mismatch factor was calculated to be less than 1%. The J - V curves were recorded from 0 V to 1.1 V using a Keithley 2650 apparatus, scan rate being 0.10 V s⁻¹. SEM images were recorded using a LEO 1530 scanning electron microscope. The crystal phases were investigated by using a Siemens D5005 X-ray diffraction system (CuK α radiation, $\lambda = 1.54056$ Å). Transmittance measurements were performed under a dark ambient environment by using spectroscopic ellipsometry (Woollam). The thermal analysis was performed through TGA (TGA/SDT851, Switzerland) at a heating rate of 10 °C min⁻¹ in a temperature range of 25 °C to 400 °C under a nitrogen atmosphere. The FTIR spectra were recorded using a Fourier transform infrared spectrometer (Bruker Tensor 27).

DFT calculations

All the calculations were carried out using the first principles methods based on DFT. The projector augmented wave potentials⁴² and Perdew–Burke–Ernzerhof⁴³ functions were implemented using the Vienna Ab initio Simulation Package.⁴⁴ The orbitals Pb (5d, 6s, 6p), I (5s, 5p), C (2s, 2p), N (2s, 2p), H (1s), O (2s, 2p), and S (3s, 3p) were treated as valences in the calculation. The wave functions were expanded in plane waves with a kinetic energy cut-off of 500 eV. A *k*-point set generated by the $15 \times 15 \times 11$ Monkhorst–Pack mesh was employed. For partial occupancies, the Gaussian smearing method was adopted. The convergence criterion of the self-consistent calculations for ionic relaxations was 10^{-5} eV between two consecutive steps. With the conjugate gradient method, all atomic positions were optimized until the atomic forces were lower than $0.005 \text{ eV } \text{\AA}^{-1}$.

Acknowledgements

This work was supported by the University Grant Council of the University of Hong Kong (Grant 104003113), the General Research Fund (Grant HKU7118 13), the Collaborative Research Fund (Grants C7045-14E, CUHK1/CRF/12 G) from the Research Grants Council of Hong Kong Special Administrative Region, China, and Grant CAS14601 from CAS-Croucher Funding Scheme for Joint Laboratories. AKYJ acknowledges the support from the Office of Naval Research (N00014-14-1-0170) and the Asian Office of Aerospace R&D (FA2386-11-1-4072). We acknowledge the help from Dr Li Zhou for her help in XRD and TGA measurements. We also acknowledge the help from Ms. Y.T. Huang and Dr Tony Feng for their help in FTIR measurements.

References

- 1 M. Grätzel, *Nat. Mater.*, 2014, **13**, 838.
- 2 A. Mei, X. Li, L. Liu, Z. Ku, T. Liu, Y. Rong, M. Xu, M. Hu, J. Chen, Y. Yang, M. Grätzel and H. Han, *Science*, 2014, **345**, 295.
- 3 M. Saliba, T. Matsui, K. Domanski, J.-Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J.-P. Correa-Baena, W. R. Tress, A. Abate, A. Hagfeldt and M. Grätzel, *Science*, 2016, **354**, 206.
- 4 Z.-K. Wang, X. Gong, M. Li, Y. Hu, J.-M. Wang, H. Ma and L.-S. Liao, *ACS Nano*, 2016, **10**, 5479.
- 5 G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar and T. C. Sum, *Science*, 2013, **342**, 344.
- 6 H. Zhang, J. Mao, H. He, D. Zhang, H. L. Zhu, F. Xie, K. S. Wong, M. Grätzel and W. C. H. Choy, *Adv. Energy Mater.*, 2015, **5**, 1501354.
- 7 J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Grätzel, *Nature*, 2013, **499**, 316.
- 8 H. Zhang, J. Cheng, F. Lin, H. He, J. Mao, K. S. Wong, A. K. Y. Jen and W. C. H. Choy, *ACS Nano*, 2016, **10**, 1503.
- 9 H. Zhou, Q. Chen, G. Li, S. Luo, T.-b. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu and Y. Yang, *Science*, 2014, **345**, 542.
- 10 Y. Zhao and K. Zhu, *J. Am. Chem. Soc.*, 2014, **136**, 12241.
- 11 Z. Zhu, Y. Bai, X. Liu, C.-C. Chueh, S. Yang and A. K. Y. Jen, *Adv. Mater.*, 2016, **28**, 6478.
- 12 X. Li, D. Bi, C. Yi, J.-D. Décoppet, J. Luo, S. M. Zakeeruddin, A. Hagfeldt and M. Grätzel, *Science*, 2016, **353**, 58.
- 13 W. Chen, Y. Wu, Y. Yue, J. Liu, W. Zhang, X. Yang, H. Chen, E. Bi, I. Ashraful, M. Grätzel and L. Han, *Science*, 2015, **350**, 944.
- 14 http://www.nrel.gov/ncpv/images/efficiency_chart.jpg, accessed June, 2016.
- 15 W. E. I. Sha, X. Ren, L. Chen and W. C. Choy, *Appl. Phys. Lett.*, 2015, **106**, 221104.
- 16 H. Cho, S.-H. Jeong, M.-H. Park, Y.-H. Kim, C. Wolf, C.-L. Lee, J. H. Heo, A. Sadhanala, N. Myoung, S. Yoo, S. H. Im, R. H. Friend and T.-W. Lee, *Science*, 2015, **350**, 1222.
- 17 X. Zhang, H. Lin, H. Huang, C. Reckmeier, Y. Zhang, W. C. H. Choy and A. L. Rogach, *Nano Lett.*, 2016, **16**, 1415.
- 18 H. L. Zhu, J. Cheng, D. Zhang, C. Liang, C. J. Reckmeier, H. Huang, A. L. Rogach and W. C. H. Choy, *ACS Nano*, 2016, **10**, 6808.
- 19 M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt and M. Grätzel, *Energy Environ. Sci.*, 2016, **9**, 1989.
- 20 D.-Y. Son, J.-W. Lee, Y. J. Choi, I.-H. Jang, S. Lee, P. J. Yoo, H. Shin, N. Ahn, M. Choi, D. Kim and N.-G. Park, *Nat. Energy*, 2016, **1**, 16081.
- 21 W. Ke, C. Xiao, C. Wang, B. Saparov, H.-S. Duan, D. Zhao, Z. Xiao, P. Schulz, S. P. Harvey, W. Liao, W. Meng, Y. Yu, A. J. Cimaroli, C.-S. Jiang, K. Zhu, M. Al-Jassim, G. Fang, D. B. Mitzi and Y. Yan, *Adv. Mater.*, 2016, **28**, 5214.
- 22 P.-W. Liang, C.-Y. Liao, C.-C. Chueh, F. Zuo, S. T. Williams, X.-K. Xin, J. Lin and A. K. Y. Jen, *Adv. Mater.*, 2014, **26**, 3748.
- 23 M. Xiao, F. Huang, W. Huang, Y. Dkhissi, Y. Zhu, J. Etheridge, A. Gray-Weale, U. Bach, Y. B. Cheng and L. Spiccia, *Angew. Chem.*, 2014, **126**, 10056.
- 24 F. Li, C. Bao, W. Zhu, B. Lv, W. Tu, T. Yu, J. Yang, X. Zhou, Y. Wang, X. Wang, Y. Zhou and Z. Zou, *J. Mater. Chem. A*, 2016, **4**, 11372.
- 25 H. Zhang, Y. Shi, F. Yan, L. Wang, K. Wang, Y. Xing, Q. Dong and T. Ma, *Chem. Commun.*, 2014, **50**, 5020.
- 26 D. Bi, W. Tress, M. I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J.-P. Correa Baena, J.-D. Decoppet, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel and A. Hagfeldt, *Sci. Adv.*, 2016, **2**, e1501170.
- 27 C.-H. Chiang and C.-G. Wu, *Nat. Photon.*, 2016, **10**, 196.
- 28 Z. Xiao, Q. Dong, C. Bi, Y. Shao, Y. Yuan and J. Huang, *Adv. Mater.*, 2014, **26**, 6503.
- 29 W. Zhu, C. Bao, B. Lv, F. Li, Y. Yi, Y. Wang, J. Yang, X. Wang, T. Yu and Z. Zou, *J. Mater. Chem. A*, 2016, **4**, 12535.
- 30 W. S. Yang, J. H. Noh, N. J. Jeon, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok, *Science*, 2015, **348**, 1234.
- 31 M. Liu, M. B. Johnston and H. J. Snaith, *Nature*, 2013, **501**, 395.
- 32 G. E. Eperon, V. M. Burlakov, P. Docampo, A. Goriely and H. J. Snaith, *Adv. Funct. Mater.*, 2014, **24**, 151.
- 33 A. Dualeh, N. Tétreault, T. Moehl, P. Gao, M. K. Nazeeruddin and M. Grätzel, *Adv. Funct. Mater.*, 2014, **24**, 3250.

- 34 C. Bi, Y. Shao, Y. Yuan, Z. Xiao, C. Wang, Y. Gao and J. Huang, *J. Mater. Chem. A*, 2014, **2**, 18508.
- 35 S. T. Williams, A. Rajagopal, C.-C. Chueh and A. K. Y. Jen, *J. Phys. Chem. Lett.*, 2016, **7**, 811.
- 36 Y. Wu, A. Islam, X. Yang, C. Qin, J. Liu, K. Zhang, W. Peng and L. Han, *Energy Environ. Sci.*, 2014, **7**, 2934.
- 37 J. Cao, X. Jing, J. Yan, C. Hu, R. Chen, J. Yin, J. Li and N. Zheng, *J. Am. Chem. Soc.*, 2016, **138**, 9919.
- 38 Y. Jo, K. S. Oh, M. Kim, K.-H. Kim, H. Lee, C.-W. Lee and D. S. Kim, *Adv. Mater. Interfaces*, 2016, 1500768.
- 39 X. B. Cao, Y. H. Li, F. Fang, X. Cui, Y. W. Yao and J. Q. Wei, *RSC Adv.*, 2016, **6**, 70925.
- 40 J. Mao, H. Zhang, H. He, H. Lu, F. Xie, D. Zhang, K. S. Wong and W. Choy, *RSC Adv.*, 2015, **5**, 73760.
- 41 D. Liu and T. L. Kelly, *Nat. Photonics*, 2014, **8**, 133.
- 42 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953.
- 43 J. P. Perdew and K. Burke, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 44 G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758.