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

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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 PbI₂·(L)ₙ 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 PbI₂·(L)ₙ 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 PbI₂·(L)ₙ 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.

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.1–15 In general, there are mainly three methods, including one-step solution deposition,1,4,9,15,19–21 two-step sequential deposition,6,7,24–30 and vacuum deposition,39 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.15–34 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 CH₃NH₃PbI₃, the conventional two-step dipping deposition provides a potential route toward room-temperature and scalable fabrication of perovskite films.6,25 However, when PbI₃ 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 PbI₃ to perovskite during the exposure to CH₃NH₃I solution. The unreacted PbI₃ in the final device will reduce photovoltaic performances and stability.4 These drawbacks make it difficult to fabricate high-quality perovskite films on a planar...
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 PbI$_2$·(ligand)$_x$ or CH$_3$NH$_3$I·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 PbI$_2$·(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 process 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). The kinetic studies of perovskite is still unclear.

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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 PbI$_2$·(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 PbI$_2$·(L)$_x$ films, the nanostructured PbI$_2$·(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)].

$$\text{PbI}_2 (s) + xL (g) \rightarrow \text{PbI}_2 \cdot (L)_x (s)$$

The formation of PbI$_2$·(L)$_x$ intermediates is confirmed by UV-vis spectra and X-ray powder diffraction (XRD). The content of ligand in the PbI$_2$·(L)$_x$ intermediates is estimated from thermogravimetric analysis (TGA) as shown in Fig. S1 in the ESL. 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 PbI$_2$·(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 PbI$_2$·[Py]$_x$ and PbI$_2$·[DMSO]$_x$ is also not long and takes 100 s and 140 s, respectively. However, the complete transformation of PbI$_2$ into the PbI$_2$·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 PbI$_2$·(L)$_x$ intermediates is further confirmed by the XRD pattern (Fig. 2b) and Fourier transform infrared spectra (FTIR) (Fig. S3). After the treatment of initial

![Fig. 1](image-url) (a) Schematics of room-temperature crystallization of the CH$_3$NH$_3$PbI$_3$ film by the ligand-promoted approach. (b) The molecular structure of different ligands.
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°), indicating the formation of the PbI$_2$·(L)$_x$ intermediates. Meanwhile, the (001) peak shifts to a smaller angle after the PbI$_2$·(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 CH$_3$NH$_3$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 PbI$_2$·TBP at 5.87° is smaller than that of PbI$_2$·(DMSO)$_2$ (10.44°) due to the bigger molecular size of TBP (146.07 cm$^3$ mol$^{-1}$) than DMSO (71.43 cm$^3$ mol$^{-1}$). It should be noted that PbI$_2$ coordinated with EDA tends to form a chemically stable stoichiometric complex PbI$_2$·(EDA)$_2$, which shows a totally different XRD pattern from PbI$_2$ and does not convert to the perovskite film.

The morphology of PbI$_2$·(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. Distinguishably, the PbI$_2$·(Py)$_x$ 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 CH$_3$NH$_3$PbI$_3$ as described later. The PbI$_2$·TBP film is also porous, but its morphology is a little disordered (Fig. 3c). The PbI$_2$·(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 PbI$_2$·DMF film undergoes severe structural changes over this time period, exhibiting a coarsening of crystals with micrometer size and voids occur (Fig. 3e). The PbI$_2$·(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 PbI$_2$·(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 PbI$_2$·(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 PbI$_2$·(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 mg ml$^{-1}$), TBP (148 mg ml$^{-1}$), and DEA (<5 mg ml$^{-1}$)) will favor the formation of appropriate PbI$_2$·(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 PbI$_2$·(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 PbI$_2$·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 PbI$_2$·(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 PbI$_2$·(L)$_x$ intermediates into CH$_3$NH$_3$I solution for seconds at room temperature. Through the conversion of PbI$_2$·(L)$_x$ to CH$_3$NH$_3$PbI$_3$, the ligand molecules intercalated in PbI$_2$ are replaced by external CH$_3$NH$_3$I whenever CH$_3$NH$_3$I affinity is higher than that of the intercalated ligands [eqn (2)]

$$\text{PbI}_2\cdot(L)_x(s) + \text{CH}_3\text{NH}_3\text{I(aq)} \xrightarrow{25^\circ C} \text{CH}_3\text{NH}_3\text{PbI}_3(s) + xL(aq)$$

(2)
To compare the reactivity of different ligands, the formation time of the PbI$_2$·(L)$_x$ intermediate and perovskite is set as 60 s and 20 s, respectively. Interestingly, the nanostructure-based PbI$_2$·(Py)$_2$ intermediate is converted into CH$_3$NH$_3$PbI$_3$ completely by immersion in the CH$_3$NH$_3$I solution leaving no residual PbI$_2$ (see Fig. 4). By contrast, pristine PbI$_2$ and other PbI$_2$·(L)$_x$ films (L = TBP and DMF) are incompletely converted into CH$_3$NH$_3$PbI$_3$ with a large amount of PbI$_2$ residue but no PbI$_2$·(L)$_x$ residue, which can be confirmed by the XRD patterns (Fig. 4b). For the extreme case of the PbI$_2$·(EDA)$_2$ film, no conversion to CH$_3$NH$_3$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 CH$_3$NH$_3$I, and thus the EDA molecule is not exchanged by CH$_3$NH$_3$I to form CH$_3$NH$_3$PbI$_3$ crystals. It shall be noted that owing to the strong affinity of DMSO toward PbI$_2$, the PbI$_2$·(DMSO)$_2$ residue is still detected. Therefore, the reactivity of nanostructure-based PbI$_2$·(L)$_x$ intermediates toward CH$_3$NH$_3$I has a great impact on the formation of CH$_3$NH$_3$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 PbI$_2$·(L)$_x$ intermediates is investigated by using SEM. Fig. 5 and S5† show the top-view SEM images of CH$_3$NH$_3$PbI$_3$ films produced from the PbI$_2$·(L)$_x$ intermediates. As expected, the morphology of CH$_3$NH$_3$PbI$_3$ films depends on their starting PbI$_2$ film in the two-step dipping method. The CH$_3$NH$_3$PbI$_3$ films prepared from pristine PbI$_2$ and PbI$_2$·(L)$_x$ intermediates (L = TBP, DMSO, and DMF) are rough with small grains, voids and cracks. Notably, the CH$_3$NH$_3$PbI$_3$ film prepared from PbI$_2$·(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 PbI$_2$·(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 PbI$_2$·(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 ($\Delta H_f$) were conducted based on density functional theory (DFT). Detailed
calculation procedures are provided in the ESI. Fig. S6† shows the crystallographic structures of PbI$_2$ and PbI$_2$·(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, $\Delta H_f$ is the overall energy required for a chemical reaction. Generally, if $\Delta H_f$ is negative, the reaction is exothermic and is more likely to be spontaneous; positive $\Delta H_f$ values correspond to endothermic reactions.\(^*\)

Fig. 6 shows the reaction coordinate diagram of the perovskite formation via different pathways in this study. The corresponding calculated $E_a$ and $\Delta H_f$ 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 CH$_3$NH$_3$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: PbI$_2$·(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 PbI$_2$·(EDA)$_x$ is positive (+0.179 eV), which indicates that PbI$_2$·(EDA)$_x$ is more thermodynamically stable than perovskite. In other words, the formation of perovskite from PbI$_2$·(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 PbI$_2$·(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 PbI$_2$·(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 ITO/NiO/CH$_3$NH$_3$PbI$_3$/C$_60$/bis-C$_60$/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% (PCE$_{avg}$ = 3.86 ± 0.49%). This is because the unreacted PbI$_2$ with a lower valence band edge at the CH$_3$NH$_3$PbI$_3$–NiO interface hinders the hole transfer from the perovskite film to the NiO$_2$ 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% (PCE$_{avg}$ = 15.32 ± 0.91%), which is higher than that reported in a previous study by using room-temperature techniques.\(^4\) The PbI$_2$·TBP and PbI$_2$·(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 PbI$_2$·DMF-based device gives a relatively low $V_{oc}$ of 0.93 V, $J_{sc}$ 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 PbI$_2$·(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 formation significantly enhances the IPCEs in the visible-light region and improves the overall PCEs. The PbI$_2$·TBP-based device exhibits the highest PCE of 11.90%, which is attributed to the improved charge transport and collection efficiency in the perovskite film.
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:

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**Fig. 5** Top-view SEM images of CH$_3$NH$_3$PbI$_3$ films with high magnification from (a) PbI$_2$, (b) PbI$_2$-(Py)$_2$, (c) PbI$_2$-TBP, (d) PbI$_2$-(DMSO)$_2$, and (e) PbI$_2$-DMF on the NiO$_x$/ITO substrate. (f) Top-view SEM image of the PbI$_2$-(EDA)$_2$ film after dipping into CH$_3$NH$_3$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: PbI$_2$ → CH$_3$NH$_3$PbI$_3$; (b) Route B: PbI$_2$ → PbI$_2$-(L)$_x$ → CH$_3$NH$_3$PbI$_3$ (L = Py, TBP, DMSO, and DMF); (c) Route C: PbI$_2$ → PbI$_2$-(L)$_x$ → CH$_3$NH$_3$PbI$_3$ (L = EDA).
good reactivity (i.e. low activation energy and negative formation enthalpy) to form perovskite from PbI$_2$$(L)_x$ intermediates. The activation energy and formation enthalpy of ligands will determine the reactivity of the PbI$_2$$(L)_x$ intermediates toward CH$_3$NH$_3$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 PbI$_2$·(Py)$_2$ and CH$_3$NH$_3$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 PbI$_2$·(DEA)$_2$ and the positive formation enthalpy (+0.179 eV) of perovskite from PbI$_2$·(DEA)$_2$. This reveals the reason why the DEA molecule in PbI$_2$·(DEA)$_2$ cannot be exchanged by CH$_3$NH$_3$I to form CH$_3$NH$_3$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 PbI$_2$·(L)$_x$ intermediates. The nanostructured PbI$_2$·(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 PbI$_2$·(L)$_x$ intermediates. If the solubility of PbI$_2$ in the chemical ligands vapor is very low (e.g., Py and TBP), PbI$_2$·(L)$_x$ intermediates with appropriate nanostructures can be achieved by the treatment of ligand vapors. On the contrary, the morphology of the PbI$_2$·(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 PbI$_2$·(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 PbI$_2$·(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 cm$^3$ mol$^{-1}$), the PbI$_2$ film changes into a uniform and nanoporous PbI$_2$·(Py)$_2$ film with many small holes (Fig. 3b). However, TBP with too large ligand molecular size (146.05 cm$^3$ mol$^{-1}$) makes the morphology of PbI$_2$·TBP films change in an uncontrollable manner (see Fig. 3c).

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### Table 1 - The calculated activation energies and formation energies

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<th>Perovskite formation pathway</th>
<th>Reaction scheme</th>
<th>Activation energy $E_a$ (eV)</th>
<th>Formation enthalpy $\Delta H_f$ (eV)</th>
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<td>Route A</td>
<td>PbI$_2$ → CH$_3$NH$_3$PbI$_3$</td>
<td>1.004</td>
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<td>−0.265</td>
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<td>PbI$_2$·TBP → CH$_3$NH$_3$PbI$_3$</td>
<td>0.787</td>
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<td>PbI$_2$ · (DMSO)$_2$ → CH$_3$NH$_3$PbI$_3$</td>
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<td>PbI$_2$ → PbI$_2$·DMF</td>
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<td>PbI$_2$·DMF → CH$_3$NH$_3$PbI$_3$</td>
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<td>Route B</td>
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<td>0.135</td>
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<td>PbI$_2$ · (EDA)$_2$ → CH$_3$NH$_3$PbI$_3$</td>
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<td>Route C</td>
<td>PbI$_2$ → PbI$_2$·(EDA)$_2$</td>
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<td></td>
<td>PbI$_2$ · (EDA)$_2$ → CH$_3$NH$_3$PbI$_3$</td>
<td>0.722</td>
<td>+0.179</td>
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Fig. 7 (a) J–V curves and (b) IPCEs for the best PVSCs based on different ligands.
perovskite formation, but also to realizing the emerging optoelectronics. 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 PbI2; (ii) a high volatility (or low boiling point); (iii) a low solubility of PbI2; (iv) a small molecular size. Using our room-temperature crystallization of perovskite intermediates, 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.

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 PbI2|(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 PbI2|(L)x toward exchange by CH3NH3I; (ii) a high volatility (or low boiling point); (iii) a low solubility of PbI2|(L)x 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. CH3NH3I was purchased from Dyesol and used as received. PbI2 (99%) and ligands were purchased from Sigma-Aldrich. Bis-C60 surfactant was kindly provided by Prof. Alex Jen. NiOx NCS inks were synthesized according to our previous report.*

Ligand-promoted perovskite formation

The PbI2 precursor was prepared by dissolving 450 mg PbI2 powder in 1 ml DMF, and then spin coated on the substrate at 4000 rpm for 100 s. The PbI2 films were treated with different chemical ligand vapors for different time periods to form PbI2|(L)x films. In particular, the PbI2 films were covered by a glass Petri dish. Around 20 μL of pure ligand was added at the edge of the Petri dish. The ligand vaporized in the Petri dish and reacted with the PbI2 films to form PbI2|(L)x intermediates. The formation of PbI2|(L)x intermediates from the PbI2 solid film is a solid–gas reaction process and does not need the drying process. Then, the formed PbI2|(L)x intermediates were dipped in a solution of 15 mg CH3NH3I 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 NiOx NCS aqueous ink (20 mg ml−1 in deionized water) was spin-coated on pre-cleaned ITO glass to form NiOx films. The resultant NiOx films were used to fabricate devices without the annealing process or other treatments. After that, the perovskite films were formed on the NiOx substrate. For the champion cell, the PbI2 precursor was modified using a formulation of 28 mg PbCl2 and 462 mg PbI2 per ml DMF, and the crystallization of the resulting CH3NH3-PbI2 films was improved by CH3NH2/CH3OH mixed vapor treatment for 1–2 s. Subsequently, the C60/PCBM mixture (12/8 mg ml−1 dissolved in dichlorobenzene) and bis-C60 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 KF3-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 (CuKz radiation, λ = 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).

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

* f_{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.
DFT calculations
All the calculations were carried out using the first principles methods based on DFT. The projector augmented wave potentials36 and Perdew–Burke–Ernzerhof37 functions were implemented using the Vienna Ab initio Simulation Package.4 The orbitals (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. To avoid the conjugate gradient method, all atomic positions were optimized until the atomic forces were lower than 0.005 eV Å$^{-1}$.

Acknowledgements
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References
41 D. Liu and T. L. Kelly, Nat. Photonics, 2014, 8, 133.