Printable high-efficiency organic ionic photovoltaic materials discovered by high-throughput first-principle calculations

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Highlights
- Ionic-type high-efficiency organic photovoltaic materials have been identified
- The advantages of organic and perovskite solar cells are integrated
- High dielectric constant (27.03) and high efficiency (28.7%) are predicted
Printable high-efficiency organic ionic photovoltaic materials discovered by high-throughput first-principle calculations

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SUMMARY
Printable solar cells are promising for low cost and large-scale production. As the two main classes of printable solar cells, organic and perovskite solar cells show distinct advantages and apparent drawbacks. The latter stand as major obstacle toward their commercialization. It is amazing if the advantages of organic and perovskite solar cells are integrated since some of them are complementary. Here, we report ionic-type high-efficiency photovoltaic materials which achieve this goal. We explore 46,388 organic materials from the Crystallography Open Database by extensive quantum mechanical calculations. Through photovoltaic-functionality-directed materials screening, we identify 5 organic ionic-type photovoltaic materials. They show the merits of nontoxic, high dielectric constant (27.03), high theoretical efficiency (28.7%), and superior thermal stability. Our findings propose ionic-type photovoltaic materials, which may surpass traditional organic and perovskite materials and open the door to next-generation printable solar cells.

INTRODUCTION
In recent years, printable solar cells have attracted lots of attention owing to the merits1 such as low-cost fabrication process, mechanical flexibility, solution processability, etc. These merits enable multiple advanced applications such as smart textiles, window shades, tents, and even consumer packaging. As the two main classes of printable solar cells, organic and perovskite solar cells show distinct advantages and apparent drawbacks. The latter hinder their commercial process.

Organic solar cells have the advantages of nontoxicity, lightweight, and easily recycling (electrode). The major obstacle limiting commercial production of organic solar cells is the low dielectric constant ($\varepsilon \approx 3–4$) of molecular-type organic materials. Low dielectric constant offers less screening between charges and leads to stronger interactions (excitons),7 which result in large binding energies ($\approx 0.5$ eV)8 and aggravate geminate as well as bimolecular recombination. Bulk heterojunctions are used to produce a driving force to dissociate excitons. The energy offsets needed for bulk heterojunction to ensure efficient exciton dissociation lead to a voltage loss of ~0.3 eV in practice.7 Besides, to achieve efficient exciton splitting at interfaces, complex interpenetrating networks of donor and acceptor materials are required, which cause instabilities in interfaces, and make morphology optimization intricate. As a result, the highest reported certified efficiency for a single-junction organic solar cell is only 19.2%,9 while large-area photovoltaic systems require high-performance solar cells with efficiency of 20%, which usually is 5% lower than the certified efficiency of small-area devices from the laboratory.

Perovskite solar cells show the advantage of high efficiency. It originates from the outstanding optical properties of ionic-type perovskite materials, such as appropriate bandgap ($\approx 1.5$ eV), high dielectric constant ($\varepsilon \approx 70$),10 high absorption coefficient, high mobility, etc. The high dielectric constant results in low exciton binding energy ($\approx 2$ meV) and enables single-component device structure. As a result, perovskite solar cells show extremely rapid increase of efficiencies,5,7 which increase from 3.8% in 20099 to as high as 25.7% recently10 in a single-junction cell. However, perovskite solar cells show apparent drawbacks of toxicity, difficulty recycling, and serious stability issue due to ion migration, perovskite decomposition, and so on.11

It is amazing if the advantages of organic solar cells and perovskite solar cells are integrated. On one hand, the low-cost, nontoxic, and solution-processed organic materials should retain to enable solution
processability. On the other hand, the high dielectric constant and ionic-type characters of perovskite materials should be absorbed to enable high efficiency. Stability issue should also be checked after materials screening. An important previous work has illustrated the utility of dielectric properties as a screen for identifying photovoltaic semiconductors. Therefore, it is promising to design organic ionic-type photovoltaic materials with high dielectric constant, which may surpass traditional organic and perovskite materials. However, this goal is long-term hindered by high costs and time-consuming procedures of synthesis, and unclear structure-property relationship.

High-throughput computational method has become a powerful tool in materials design and structure-property relationship discovery since 1995. They have been extensively used in inorganic solar cell materials search, perovskite materials design, as well as small-molecule organic photovoltaic materials discovery. The concept is simple yet powerful: build a large database containing existing and hypothetical materials, and then intelligently screen the materials step by step with desired properties (descriptors). These descriptors are often calculated by ab initio codes. However, previous work for prediction of organic photovoltaics materials stays in molecular level, while the bulk properties of their corresponding crystals are often different, which play a key role in the photoelectric properties of devices.

Here, we report high-throughput discovery of high-efficiency organic ionic photovoltaic materials from organic crystal database. These materials combine the advantages of organic and perovskite solar cells. We explore 46,388 organic crystal materials from the Crystallography Open Database (COD) cataloged using Pymatgen. We use bandgap, carrier effective mass, dielectric constant, and absorption coefficient as distinct descriptors. Through photovoltaic-functionality-directed materials screening, we identify 5 promising candidate materials, of which the highest dielectric constant research 27.03 and the simulated theoretical maximum solar cell efficiency research 28.7%. All of the 5 candidate materials are nontoxic organic ionic-type materials. The large dielectric constants of the identified materials can be attributed to large Born effective charges. Electronic properties calculations of the optimum material reveal that high efficiency originates from strong optical absorption (\(\alpha > 10^5 \text{ cm}^{-1}\)), owing to high joint density of states (JDOS). Lp states contribute significantly to both valence band maximum (VBM) and conduction band minimum (CBM) of the electronic density of states. Furthermore, ab initio molecular dynamics simulations show excellent thermal stability of the candidate materials. We also identify a useful rule for designing high-efficiency organic photovoltaic materials, i.e., by designing polyiodide or tellurium-iodine hybrid organic ionic materials. Our findings provide promising materials for next-generation printable solar cells.

RESULTS AND DISCUSSION

High-throughput calculations

It is noticed that there are plentiful of unexplored materials in organic materials database. In this study, we get an initial pool of 468,310 structures from the COD database. To filter out organic crystal structures, we exclude wrong, fractional, inorganic, and similar structures by Pymatgen. Afterward, 259,242 organic structures are left. Considering that commercial solar cells should be environmentally friendly and cheap. We exclude structures containing toxic elements (Cd, Hg, and Pb) and elements with low abundance. In consideration of the computation cost, we select structures with 1–100 atoms in their primitive cell, as shown in Figure 1A. Thus, we have 46,388 organic materials in our database. These structures are representative as shown in Figure S1.

We use four descriptors to downselect high-efficiency organic photovoltaic materials from the initial list by ab initio calculations, including suitable bandgap, light carrier effective mass, high dielectric constant, and high absorption coefficient. Benchmark calculations of these descriptors show good theory-experiment agreement as shown in Figure S2 and Tables S1–S4.

Firstly, we calculate the bandgaps of all these structures in the level of PBE functional, as shown in Figure 1B. According to the Shockley-Queisser (S-Q) limit, the optimum bandgap for semiconductor adopted in solar cells is 1.34 eV, whose limiting photovoltaic energy conversion efficiency for a single-junction solar cell is 33.7%. And considering that PBE functional tend to underestimate bandgap, we select materials with bandgap between 0.1 and 2.0 eV. There are 12,965 structures in this scope.

Secondly, efficient photovoltaic materials should have high as well as balanced electron and hole mobility. Mobility \(\mu\) is related to mean free time \(\tau\) and effective mass of carrier \(m^*\) by \(\mu = q\tau/m^*\). Since the
computation of \( n \) is expensive, here we only calculate \( m^* \). As shown in Figure 1C, we select structures satisfying \( m_e^* < 3 m_0 \) and \( m_h^* < 3 m_0 \), where \( m_0 \) is the mass of electron. After selection, we get 853 structures.

Thirdly, we calculate the static dielectric constant, which is the sum of two parts, i.e., electronic contribution and ionic contribution. We select structures with \( \varepsilon > 5 \) as shown in Figure 1D. There are 252 structures meeting this metric. From here on, we recalculate the bandgap, carrier effective mass, and dielectric constant with higher precision. The HSE06 hybrid functional is used to remedy the bandgap and spin-orbit coupling (SOC) effect is also taken into account. Finally, we pick out 5 candidate structures with suitable bandgap (0.8–2.0 eV), small carrier effective mass (\( m^* < 2 m_0 \)), and high dielectric constant (\( \varepsilon > 10 \)).

**Photovoltaic properties**

To evaluate the photovoltaic performance of the candidate materials, we further calculate the optical absorption coefficients. For comparison and to validate our results, we also calculate the absorption coefficients of MAPbI\(_3\) (Pnma) and CdTe. The calculated absorption coefficient of MAPbI\(_3\) and CdTe is in line with previous work.\(^ {15,20,21} \) As shown in Figure 2A, the 5 candidate materials exhibit large intensity of band-edge optical transitions. The absorption coefficients are larger than \( 10^5 \) cm\(^{-1}\), approaching \( 10^6 \) cm\(^{-1}\), which are as high as, or even larger than the counterpart of MAPbI\(_3\). And the absorption coefficient of CdTe is much lower when the photon energy is below 3 eV.

Finally, to estimate the theoretical limit of power conversion efficiency for the 5 candidate materials, we calculate the spectroscopic limited maximum efficiency (SLME) as a function of film thickness at AM1.5G solar spectrum. SLME is an improved model based on S-Q limit, which takes the absorption coefficient and thickness of films into consideration. As shown in Figures 2B and S3, the predicted efficiencies of all the 5 candidate are larger than 20% when the film thickness exceeds 100 nm, which are larger than that of MAPbI\(_3\) and CdTe. When the thickness increases from 100 nm to 1 \( \mu \)m, their efficiencies increase slower than MAPbI\(_3\) and CdTe. When the thickness is increased to 1 \( \mu \)m, the SLMEs of the candidate materials are lower than that of MAPbI\(_3\), but are larger than or comparable to the counterpart of CdTe.

We summarize the optical properties of the 5 candidate materials in Table 1. Our results are in line with previous experimental values, which reported a direct bandgap of MAPbI\(_3\) to be 1.5 eV.\(^ {22} \) The static dielectric constant of MAPbI\(_3\) is reported to be \( \sim 70 \), and the exciton binding energy is of order 2 meV.\(^ {6} \) The
effective masses of MAPbI$_3$ calculated in this work are identical to previous work,$^{23}$ which estimates $m_\text{h}^*$ and $m_\text{e}^*$ to be 0.23 $m_0$ and 0.29 $m_0$. These results validate our calculation results. As listed in Table 1, the highest SLME of our candidate materials at 0.5 $\mu$m is 28.3%, which is higher than that of CdTe (24.6%), but slightly smaller than that of MAPbI$_3$ (30.7%). And the SLME reaches as high as 28.7% for compound 4311112$^{27}$ when the thickness reaches 1 $\mu$m. What’s more important, the reported crystal color of compound 2015623 and 2200111 are red-purple and green-black, indicating that they are promising for photovoltaic applications.

The calculated binding energies of the 5 candidate materials are lower than 10 meV as shown in Table 1. For comparison, the exciton binding energy of Y6 is reported to be 100–250 meV.$^{25}$ What’s more important, these binding energies are smaller than the thermal kinetic energy at room temperature ($k_B T = 26$ meV). Therefore, the candidate materials will generate Wannier-Mott excitons rather than Frenkel excitons, just as the situation in perovskite solar cells. In that case, energy offset is not required, and single-component device structures are feasible.

**Structural and electronic properties**

It is quite essential to investigate the origin of the excellent photovoltaic performance from aspects of crystal structure and electronic properties for the candidate materials. Surprisingly, we find that all of them are ionic crystals, unlike typical organic photovoltaic materials, which are molecular crystals. And all of them contain iodine ions. Specifically, compound 7218348,$^{26}$ 2015623,$^{27}$ and 2200111$^{28}$ are polyiodide, and 4311112 and 4311113 are tellurium-iodine hybrid compounds, which can be formulated as (C$_4$H$_8$TeI$_7$)$_2$C$_2$I$_{20}$ and (C$_4$H$_8$TeI$_7$)$_2$(TeI$_3$)$_2$(I$_7$)$_4$. Iodine ions may play an important role in improving the dielectric constants due to its large electronegativity (2.66 in Pauling scale) and appropriate ionic radius (2.06 Å).

**Table 1. Optical properties of the candidate materials**

| ID     | Formula     | Bandgap (eV) | Effective Mass ($m_0$) | Effective Mass ($m_0^*$) | Dielectric Constant | Binding Energy (meV) | Direct/Indirect | SLME (0.5 $\mu$m/1 $\mu$m) |
|--------|-------------|--------------|------------------------|--------------------------|---------------------|----------------------|------------------|--------------------------|
| 4311112| C$_4$H$_8$I$_6$Te$_2$ | 1.24         | 0.46                   | 0.28                     | 17.69               | 8                    | D                | 28.3/28.7                |
| 4311113| C$_4$H$_8$I$_6$Te$_2$ | 1.25         | 0.48                   | 0.39                     | 24.48               | 5                    | I                | 27.5/27.8                |
| 7218348| C$_4$H$_8$I$_6$I$_4$N$_4$ | 0.87         | 1.81                   | 0.46                     | 22.71               | 10                   | D                | 26.6/26.7                |
| 2015623| C$_4$H$_8$Bi$_2$I$_2$N$_2$ | 1.22         | 0.23                   | 0.18                     | 27.03               | 2                    | I                | 26.7/27.0                |
| 2200111| C$_4$H$_8$I$_5$N         | 1.29         | 1.29                   | 0.25                     | 19.21               | 8                    | D                | 23.9/24.1                |
| MAPbI$_3$| CH$_3$NPbI$_3$       | 1.77         | 0.29                   | 0.22                     | 88.05               | 0.2                  | D                | 30.7/31.8                |
| CdTe   | CdTe         | 0.50         | 0.58                   | 0.05                     | 15.39               | 26                   | D                | 24.6/27.1                |
The large dielectric constants of the identified materials can be attributed to large Born effective charges, as shown in Table S5. The enhanced Born effective charges lead to dominant lattice contribution in the static dielectric constant. The trend of calculated Born effective charge is consistent with projected density of states (PDOS), as shown in Figure S4. The PDOS near VBM and CBM of these 3 polyiodides are contributed by I p states. As to tellurium-iodine hybrid compounds, the PDOS near VBM are composed of I p states. The PDOS near CBM are composed of I p and Te p states. We therefore propose a useful rule for designing high-efficiency organic photovoltaic materials, i.e., by designing polyiodide or tellurium-iodine hybrid organic ionic materials.

Among the 5 candidate materials, compound 4311112 shows suitable bandgap (1.58 eV), light effective mass of hole (0.46 $m_0$) and electron (0.28 $m_0$), which are comparable to that of MAPbI$_3$. The light carrier effective mass and high dielectric constant together lead to small exciton binding energy (8 meV). And its SLME is the highest among the 5 candidate materials, which make it a promising photovoltaic material.

The crystal structure of compound 4311112 is shown in Figure 3A. There are two kinds of basic units in this structure. The Te$_2$I$_{10}^2$- anion forms two octahedral structure connected through the edge. The C$_4$H$_8$TeI$^+$ cation forms a five-membered ring. It is a direct bandgap structure as shown in Figure 3B. Figure 3C shows that the density of states near VBM and CBM are significantly larger than the counterpart of MAPbI$_3$ and CdTe, leading to higher JDOS (Figure 3D), and therefore, stronger optical absorption coefficients. The PDOS near VBM are mainly composed of I p states (Figure S4). And the PDOS near CBM are composed of I p and Te p states. These results imply that the hybrid of tellurium and iodine contributes significantly to the optical properties.

Compound 4311112 is synthesized in 2004 by reaction of Te$_4$ with Ph$_3$P. It is necessary to figure out the difference in optical properties between Te$_4$ and compound 4311112. We therefore calculate the bandgap, carrier effective mass, and dielectric constant of Te$_4$ (Pnma). The bandgaps of Te$_4$ in the level of PBE and HSE06 + SOC are 1.77 and 2.05 eV. The effective mass of hole and electron is 1.83 $m_0$ and 1.66 $m_0$. The static dielectric constant is calculated to be 7.41. These results demonstrate the superior optical properties of compound 4311112 than that of Te$_4$. 

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**Figure 3. Crystal structure and electronic properties of compound 4311112**

(A) Crystal structure, (B) band structure, (C) density of states, and (D) joint density of states of compound 4311112 are compared with MAPbI$_3$ and CdTe.

See also Figure S4.
Thermal stability

Stability is very important for solar cells. Here, we focus on the thermal stability. We conduct \textit{ab initio} molecular dynamics simulations at 500, 1,000, and 1,500 K for compound 4311112 and MAPbI$_3$. To investigate the dynamical behavior, we calculate the mean square displacement (MSD) for each simulation. As shown in Figure 4, compound 4311112 remains solid at 500 and 1,000 K. At 1,500 K, it shows fluid behavior since the MSDs increase monotonously. The situation is different for MAPbI$_3$. At 500 K, MAPbI$_3$ remains solid, but the MSD of iodine keeps increasing. Furthermore, when the temperature is increased to 1,000 K, I atoms diffuse dramatically. And the MSDs of other elements also increase. These results are in line with halide ion migration observed by experiments. At 1,500 K, MAPbI$_3$ shows typical fluid behavior. These simulations indicate that the thermal stability of compound 4311112 is superior than that of MAPbI$_3$, which is beneficial for commercial production.

Conclusion

We have identified 5 candidate materials as ionic-type high-efficiency photovoltaic materials through extensive high-throughput first-principle calculations. These materials combine the advantages of organic and perovskite solar cells. They are organic ionic-type materials, which show the merits of nontoxic, high dielectric constant (27.03), and high theoretical efficiency (28.7%). Electronic properties calculations reveal that polyiodide or tellurium-iodine hybrid play an important role in their dielectric constant and photovoltaic properties. Among the 5 candidate materials, compound 4311112 shows comparable efficiency to MAPbI$_3$. \textit{Ab initio} molecular dynamics simulations further demonstrate its superior thermal stability. These results indicate that compound 4311112 is most promising for single-component printable solar cells. Our findings point out that organic ionic photovoltaic materials may surpass traditional organic and perovskite materials and open the door to next-generation printable solar cells.

Limitations of the study

Further investigations are needed, for example, we have not considered the defect properties, and intensive experiments are needed to identify our results. Other stability properties (such as light soaking stability) and robustness should also be checked.

STAR Methods

Detailed methods are provided in the online version of this paper and include the following:

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- Materials availability
- Data and code availability

METHOD DETAILS
- Ab initio parameters
- Electronic properties calculation methods
- Theoretical efficiency estimation

SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.105639.

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AUTHOR CONTRIBUTIONS
Conceptualization, P.H. and S.L.; Methodology, P.H.; Software, P.H.; Validation, P.H., J.Y., D.H., and S.L.; Formal Analysis, P.H. and S.L.; Investigation, P.H.; Resources, P.H.; Data Curation, P.H.; Writing - Original Draft, P.H. and S.L.; Writing - Review & Editing, P.H., J.Y., D.H., and S.L.; Visualization, P.H.; Supervision, S.L.; Project Administration, S.L.; Funding Acquisition, P.H. and S.L.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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STAR METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Deposited data | Gražulis et al., 2012 | http://www.crystallography.net/cod/ |
| COD | | |
| Software and algorithms | | |
| VASP | Version 5.4.4 | https://www.vasp.at/ |
| Pymatgen | Version 2020.10.9 | https://pymatgen.org/ |
| SL3ME | Version 1.0 | https://github.com/ldwillia/SL3ME |
| VASPKIT | Version 1.4 | https://vaspkit.com/ |

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the Lead Contact, Shirong Lu (lushirong@cigit.ac.cn).

Materials availability
This study did not generate new unique reagents.

Data and code availability
All data reported in this paper will be shared by the lead contact upon request.

This study did not report original code.

Any additional information required to reanalyze the data reported in this work paper is available from the lead contact upon request.

METHOD DETAILS

Ab initio parameters
The organic crystal structures are screened from COD by Pymatgen. First principle calculations are performed within the framework of density functional theory (DFT) using the VASP plane-wave code, where the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation density functional and frozen-core all-electron projector-augmented wave (PAW) potentials are adopted. The electronic wave functions are expanded in a plane-wave basis set with a kinetic energy cutoff of 520 eV. Brillouin zone sampling is performed on k-meshes with a reciprocal space resolution of \( 2\pi \times 0.032 \text{ Å}^{-1} \). For band gap, carrier effective mass and absorption coefficient calculations, the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional is used since PBE functional underestimates the band gap. The spin-orbit coupling (SOC) effect is also taken into account.

Electronic properties calculation methods
Static dielectric constants and Born effective charge are calculated by means of density functional perturbation theory (DFPT). Effective mass is calculated at the bands extrema using finite difference method by Effective mass calculator (EMC). Exciton binding energy is calculated by \[ E_b = m^* R_v / m_e^* \] where \( R_v \) is Rydberg energy and \( m^* \) is the reduced exciton mass \((1 / m^* = 1 / m_e^* + 1 / m_h^*)\). Ab initio molecular dynamics simulations are performed in the canonical (NVT) ensemble applying a Nose thermostat by using VASP. The system sizes are 80 atoms for compound 4311112 and 48 atoms for MAPbI3. The Gamma point is adopted for brillouin zone sampling. A time step of 0.5 fs is selected.
Theoretical efficiency estimation

To evaluate the photovoltaic performance of the selected materials, the theoretical maximum solar cell efficiency, i.e., “spectroscopic limited maximum efficiency (SLME)"\textsuperscript{36,37} is calculated. The transition dipole moment (TDM) and JDOS are calculated by VASPKit.\textsuperscript{38}