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TIPS-benzene-based two-dimensional perovskites

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A novel triisopropylsilylethynyl (TIPS)-benzene-based amine and two-dimensional organic–inorganic hybrid perovskites comprising TIPS-benzene-based ammoniums are synthesized. The applicability of TIPS-based component ions to the crystal lattice of perovskites is demonstrated for the first time, promoting the development of TIPS chemistry, chemical materials that leverage TIPS moiety characteristics, and perovskite materials.

Acenes with silylethynyl moieties, particularly triisopropylsilylethynyl (TIPS), exhibit prominent functions in diverse applications.[1–16] In particular, silylethynyl moieties act as functional spacers in various applications.[1,2] For instance, silylethynyl moieties can function as effective spacers in acenes for transistors, allowing prominent carrier transfer properties.[1,2] Moreover, for exciton fission and fusion, which are bimolecular reactions, the silylethynyl moieties presumably allow a preferable orientation between the molecules.[3–13] For example, for the triplet–triplet annihilation (*i.e.*, triplet exciton fusion), TIPS groups allow a preferable orientation between TIPS-anthracene molecules and lead to highly efficient photon upconversion.[3] Furthermore, TIPS groups have prominent affinities for organic moieties, thereby allowing high solubility in various solvents and enabling specific functions such as singlet fission in solutions, which converts a singlet exciton into two triplet excitons.[14–16] Therefore, the development of TIPS chemistry, chemical materials that leverage the characteristics of TIPS moieties, will impact materials science.

One possible perspective of TIPS chemistry is its incorporation into organic–inorganic perovskite materials. Perovskite materials consisting of organic ammoniums, lead cations, and halogen anions for the *A*-, *B*-, and *X*-sites in perovskite crystals, respectively, have attracted attention owing to their exceptional semiconductor properties and potential applications, including solar cells.[17–25] Hence, the combination of TIPS chemistry with perovskite materials is of interest. So far, only a few reports have demonstrated multilayer architectures that combine TIPS-acenes with perovskites.[26–28] However, physical separation between the layers and the low interfacial density at the TIPS-acene/perovskite interface likely limit their functional potential. Moreover, notably, the incorporation of ionic TIPS moieties into the crystal lattice of perovskite materials has not yet been achieved; demonstrating applicability of various organic component ions into perovskite crystals also are instrumental in terms of development of perovskite materials. Therefore, the synthesis of TIPS-acene-based perovskite materials will promote the development of both TIPS chemistry and perovskite materials.

In this study, a novel TIPS-benzene-based amine was synthesized to develop novel TIPS-benzene-based perovskite materials (Fig. 1), revealing the applicability of TIPS-based component ions to the crystal lattice of perovskite materials for the first time.

Perovskite materials can be categorized into three-dimensional (3D) perovskites, which are used primarily as photoabsorbers in solar cells, and two-dimensional (2D) perovskites,[24,25,29–37] which exhibit quantum confinement effects and can be used in various applications. Various organic ammonium cations can be used in 2D perovskite materials.[30,31] Therefore, this study investigated the applicability of TIPS-acene-based materials in the development of 2D perovskite materials.

Phenylethylammonium (PEA), a representative phenyl-type ammonium for 2D perovskite components,[24,29,32] possesses an ethyl chain that provides preferable physical space for stacking into Pb-I slabs in perovskites.[38–40] Accordingly, a PEA-based TIPS amine and the corresponding ammonium salts were developed in this study. 4-(triisopropylsilylethynyl)-2-phenylethylamine, a TIPS-benzene ethylamine (TIPS-PEA), was successfully synthesized (see SI for the synthesis method and characterization results). Fig. 2 shows the optical properties of the TIPS-PEA in hexane. In the excitation spectrum, the TIPS-PEA exhibited a peak at 317 nm, and its energy gap was estimated as 3.79 eV from the extrapolation of the tail. The emission spectra showed peaks at 323, 339, and 357 nm for the (0–0), (0–1), and (0–2) peaks, respectively.

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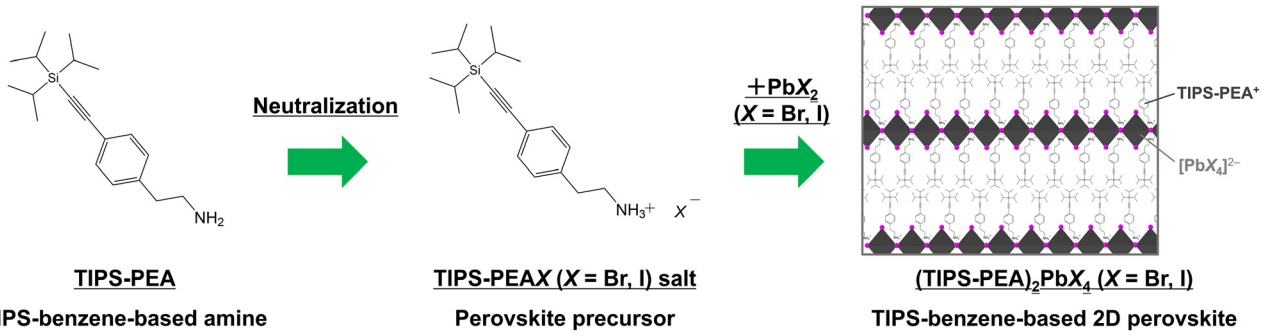

Fig. 1 Schematic of TIPS-benzene-based 2D perovskite synthesis.

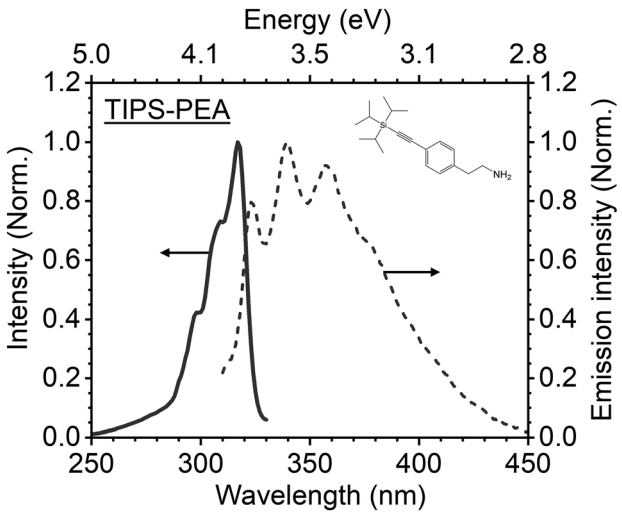

Fig. 2 Optical properties of TIPS-PEA (solid line: excitation spectra at 340 nm, dashed line: emission spectra excited at 295 nm).

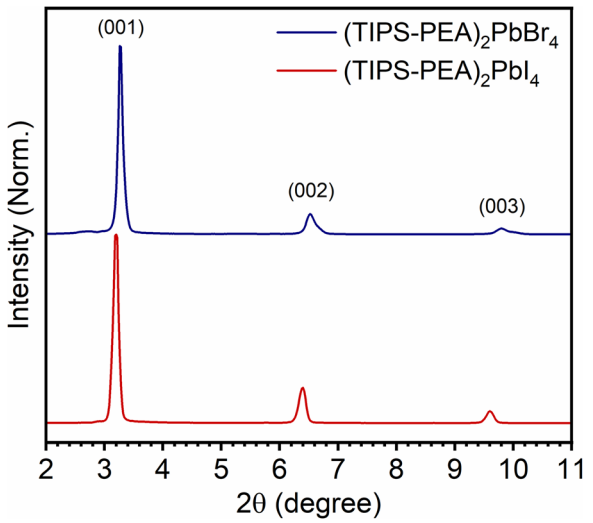

Fig. 3 XRD patterns of TIPS-benzene-based 2D perovskites.

As-synthesized TIPS-PEA was applied to components of a novel series of 2D perovskite materials. Neutralization of TIPS-PEA (amine) with hydrobromic acid (HBr) and hydriodic acid (HI) successfully formed the corresponding ammonium bromide (TIPS-PEABr) and iodide (TIPS-PEAI) (Fig. 1, see SI for detailed neutralization processes).[38,41–43] TIPS-PEABr and TIPS-PEAI were mixed with $PbBr_2$ and PbI_2, respectively, in *N*,*N*-dimethylformamide solvent at a molar ratio of 2 : 1 and used as precursors for the perovskite materials. Spin coating of the solutions led to the formation of the corresponding 2D perovskites, $(TIPS\text{-}PEA)_2PbBr_4$ and $(TIPS\text{-}PEA)_2PbI_4$, whose Pb slab number is one (n = 1) (Fig. 1).

Fig. 3 shows the XRD patterns of TIPS-benzene-based 2D perovskites $(TIPS\text{-}PEA)_2PbBr_4$ and $(TIPS\text{-}PEA)_2PbI_4$. For $(TIPS\text{-}PEA)_2PbBr_4$, the XRD peaks at 3.26°, 6.52°, and 9.78°, corresponding to (001), (002), and (003), respectively, were clearly observed. Similarly, the XRD peaks at 3.20°, 6.40°, and 9.60°, corresponding to the (001), (002), and (003) planes, respectively, were observed for $(TIPS\text{-}PEA)_2PbI_4$. These clear XRD peaks indicate that layered structures of $(TIPS\text{-}PEA)_2PbBr_4$ and $(TIPS\text{-}PEA)_2PbI_4$ were successfully formed.[30,31] The *d*-spacing values for the (001) planes of $(TIPS\text{-}PEA)_2PbBr_4$ and $(TIPS\text{-}PEA)_2PbI_4$ were estimated as 27.1 and 27.6 Å, respectively. The obtained *d*-spacing values for the TIPS-PEA-based 2D perovskites (*i.e.*, 27.1–27.6 Å) are in accordance with the size of TIPS-PEA (Fig. S1, see SI for the details). These *d*-spacing values were considerably larger than those of $(PEA)_2PbBr_4$ (16.5 Å)[33] and $(PEA)_2PbI_4$ (16.5 Å),[34,35] the corresponding 2D perovskites without TIPS groups, and among Pb-based 2D perovskites in general. The prominent affinity of TIPS groups, represented by the high solubility of TIPS-containing materials, facing each other in the interlayer, presumably allowed such large interlayer spaces in the presence of the relatively bulky TIPS groups within the 2D perovskites.

The optical properties of the TIPS-benzene-based 2D perovskites were investigated. Fig. 4 shows the absorption and emission spectra of $(TIPS\text{-}PEA)_2PbBr_4$ and $(TIPS\text{-}PEA)_2PbI_4$. For $(TIPS\text{-}PEA)_2PbBr_4$, an excitonic absorption peak was observed at 385 nm, while its emission peak was observed at 398 nm (Fig. 4a). Meanwhile, $(TIPS\text{-}PEA)_2PbI_4$ exhibited an excitonic absorption peak at 490 nm and an emission peak at 510 nm (Fig. 4b). The $(TIPS\text{-}PEA)_2PbI_4$ retained approximately 80% of its photoluminescence (PL) intensity under a continuous

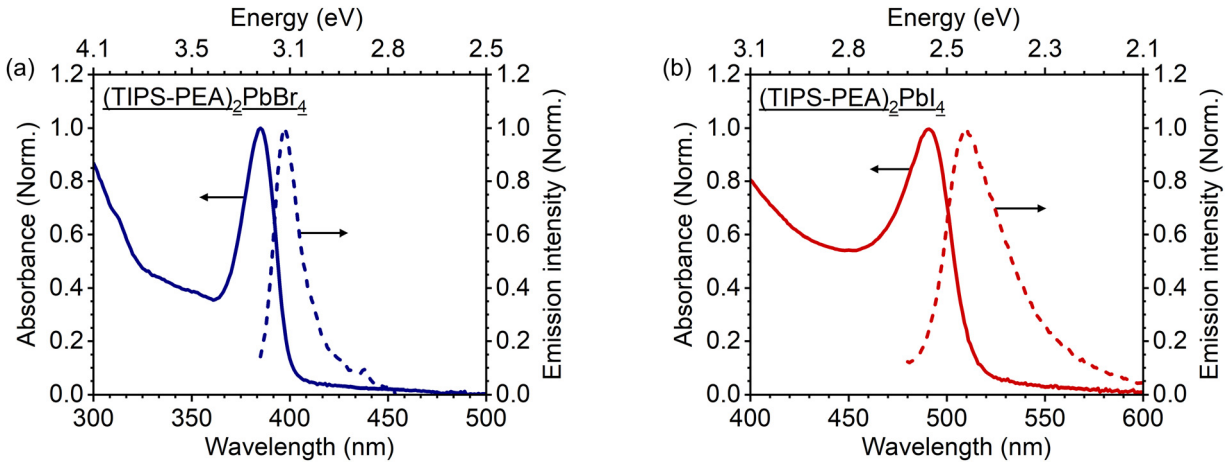

Fig. 4 Optical properties of TIPS-benzene-based 2D perovskites (a) $(TIPS\text{-}PEA)_2PbBr_4$, (b) $(TIPS\text{-}PEA)_2PbI_4$; solid line: absorption spectra, dashed line: emission spectra excited at 350 nm and 450 nm for $(TIPS\text{-}PEA)_2PbBr_4$ and $(TIPS\text{-}PEA)_2PbI_4$.

excitation in ambient air for over 3 h (Fig. S2). Although the large *d*-spacings of TIPS-PEA-based 2D perovskites, observed in XRD patterns, might stem from the formation of 2D structures with multiple Pb-*X* (*X* = Br, I) slabs, the relatively high optical energies support the formation of 2D perovskites with mono Pb-*X* (*X* = Br, I) slabs ($n = 1$).

The conventional $(PEA)_2PbX_4$ (*X* = Br, I) samples, which are the corresponding 2D perovskite without a TIPS group, exhibited red-shifted optical properties to TIPS-PEA-based ones in this work owing to the larger *d*-spacings of the $(TIPS\text{-}PEA)_2PbX_4$ (*X* = Br, I) structures, leading to higher quantum confinement of the Pb-*X* slabs. In particular, an excitonic absorption peak at 402 nm and an emission peak at 412 nm for $(PEA)_2PbBr_4$,[33,37] while excitonic absorption peak at 517 nm and emission peak at 528 nm for $(PEA)_2PbI_4$.[34–36] Therefore, the larger *d*-spacings of the TIPS-PEA-based 2D perovskites can be advantageous for manipulating optical energies and strengthening the quantum confinement effects.

Furthermore, PL lifetime of the $(PEA)_2PbI_4$ strongly supports the successful formation of the 2D perovskites; the PL lifetime of $(PEA)_2PbI_4$ was estimated to be 0.45 ± 0.01 ns (Fig. S3). This short PL lifetime is stemmed from emission directly *via* exciton not *via* charge separations, indicating the strong quantum confinement effects, which the 2D perovskite structures allow.

In conclusion, organic–inorganic hybrid perovskite materials consisting of the corresponding TIPS-benzene-based ammoniums (*viz.*, $(TIPS\text{-}PEA)_2PbBr_4$ and $(TIPS\text{-}PEA)_2PbI_4$) were successfully synthesized. This is the first study to report the incorporation of TIPS-based component ions into the crystal lattices of perovskite materials. Despite the bulky TIPS moiety, 2D perovskites with the TIPS-benzene-based spacer, resulting in relatively large *d*-spacings, were successfully formed, presumably exploiting the prominent affinity of TIPS moieties for each other. Further optimization of materials processing, including thin-film fabrication and single-crystal growth, will be pursued in future work to evaluate performance in a variety of applications. In particular, these 2D perovskites can be applied to passivators for perovskite outer surfaces (Fig. S4)[44] and singlet–triplet exciton conversions,[45] which are under investigation. Notably, this work reveals the applicability of TIPS-based component ions in the crystal lattice of perovskite materials, which will pave the way for further development of both TIPS chemistry and perovskite materials—only allowed by their unique combination.

Author contributions

Naoyuki Nishimura: conceptualization, project administration, investigation, resources, formal analysis, visualization, writing – original draft, writing – review & editing. Takurou N. Murakami: funding acquisition, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: experimental section, structural calculations of TIPS-PEA and the 2D perovskites, PL Stability of TIPS-PEA-based 2D perovskite, PL lifetime of TIPS-PEA-based 2D perovskite, supporting data for TIPS-PEA-based 2D perovskite formation, and NMR spectra. See DOI: https://doi.org/10.1039/d6cc01157h.

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