Lyotropic liquid crystalline phases of anisotropic nanoparticles of organic–inorganic metal halide perovskites: photoluminescence from self-assembled ordered microstructures of semiconductors

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A simple method (which could be completed within 60 minutes at 298 K) was developed to transform layered organic–inorganic metal halide perovskites into colloidal lyotropic liquid crystalline dispersions with microscopic structural orderliness as well as semiconducting properties and photoluminescence. Experimentally, hexagonal-shaped mesogenic nanoplatelets of two-dimensional lead iodide perovskites \((\text{R-NH}_3)_2\text{PbI}_4\) were synthesized by antisolvent-induced rapid microcrystallization and stabilized by surfactants, and self-assembled into discotic–nematic phases with optical anisotropy and greenish-blue fluorescence. Combining the stimuli-responsive, light-interactive, and reconfigurable ordered structures of liquid crystals with the adjustable semiconductivity of hybrid perovskites, these photoluminescent soft anisotropic materials may be used for polarized light emission or detection.

With light-emission, light-modulation, and stimuli-responsive features, luminescent liquid crystals could be applied in many areas such as polarized light sources and polarized light detection systems. Various types of luminescent substances exhibit lyotropic or thermotropic liquid crystalline behaviors, including but not limited to organic molecules, polymers, coordination compounds, supramolecular systems with aggregation-induced emission properties, \(\text{CdSe}\) nanorods, dye-functionalized nanoparticles, and lanthanide-doped \(\text{NaYF}_4\) nanocrystals. The preparation of organic luminescent mesogens usually needs specially designed molecular structures as well as complicated synthesis and purification methods. On the other hand, for many inorganic luminescent mesogens, it is difficult to precisely and continuously adjust their emission wavelengths over the whole visible light range. Therefore, the systematic and low-cost development of liquid crystalline materials with highly adjustable luminescence is desired.

A promising class of semiconductors that may significantly broaden the scope of high-performance luminescent liquid crystals is two-dimensional organic–inorganic metal halide perovskites. They are crystalline compounds with the chemical formula \((\text{R-NH}_3)_2\text{BX}_4\) where \(\text{R-NH}_3\) is an organic ammonium cation, \(B\) is a divalent metal cation such as lead, tin, or manganese, and \(X\) is a halide anion. Having the ability to incorporate large-sized organic spacers including long aliphatic chains, bulky conjugated systems containing multiple aromatic rings, and molecules with chirality, two-dimensional perovskites could be easily functionalized to achieve different optical properties including linearly-polarized luminescence, circularly-polarized light detection, etc.

In this study, a simple experimental method was developed to prepare lyotropic liquid crystalline dispersions of colloidal nanoparticles of two-dimensional hybrid organic–inorganic lead iodide perovskites, where the whole synthetic process could be completed within 60 minutes at room temperature, and the products exhibited strong optical anisotropy as well as semiconducting properties (e.g., photoluminescence) characteristic of lead halide perovskites. Specifically, hexagonal-shaped colloidal nanoplatelets with high aspect ratios (diameter to thickness ratios larger than 20) were synthesized by mixing-precipitation of precursor solutions of perovskites in nonpolar antisolvents. As sterically stabilized by long aliphatic chains of non-ionic surfactants, the nanoplatelets could be concentrated beyond the threshold level to form lyotropic liquid crystalline phases by self-assembly. These results indicate a time-saving approach to the systematic design and quick development of luminescent semiconducting liquid crystals.

In this research, bis[[4-(trifluoromethyl)phenyl]methanammonium] tetraiodoplumbate(u) was selected as the model material. It has a two-dimensional structure with an interlayer spacing distance of about 1.7925 nanometers between adjacent inorganic perovskite pseudo-planes as revealed by single-crystal
X-ray diffraction data (Scheme 1 and Fig. S1, ESI†).18 Through an antisolvent-induced rapid microcrystallization process accompanied by the \textit{in situ} grafting of surfactants, where an \textit{N},\textit{N}-dimethylformamide solution (0.1 mL) containing the precursors of organic–inorganic lead iodide perovskites, \textit{i.e.}, [4-(trifluoromethyl)phenyl]methanamine hydroiodide (2.0 mol $\text{L}^{-1}$) and lead(II) iodide (1.0 mol $\text{L}^{-1}$), was mixed with a relatively large volume of chlorobenzene (10.0 mL) containing \textit{cis}-9-octadecenoic acid (3.17 mmol $\text{L}^{-1}$) and \textit{cis}-1-amino-9-octadecene (3.04 mmol $\text{L}^{-1}$) under high-speed stirring (3000 revolutions per minute), a colloidal dispersion of perovskite nanoparticles could be obtained. As one of the most important preconditions for lyotropic liquid crystallinity, stabilization of the mesogenic nanoparticles was achieved through the elimination of polar solvents and residual ionic impurities by ultracentrifugation as well as the post-synthesis grafting of a higher density of surfactant molecules, giving orange- to yellow-colored homogeneous semi-transparent dispersions with long-term (more than 60 days) stability (Fig. 1a, b and Fig. S2, ESI†).

The perovskite mesogens are hexagonal-plate-shaped nanoparticles as revealed by scanning electron microscopy (SEM) (Fig. 2a) and atomic force microscopy (AFM) (Fig. 2b). They have diameters ranging from 100 to 400 nm and thicknesses of 5 to 10 nm (Fig. S3 and S4, ESI†), showing aspect ratios larger than 20, which are comparable to the values of some typical liquid crystalline colloidal substances such as cellulose nanocrystals.19 The diameters of perovskite nanoplatelets

**Scheme 1** Schematic illustration of the self-assembled structures, crystallographic structures and light-emission feature of the lead iodide perovskite liquid crystals involved in this study.

**Fig. 1** Photographs of a perovskite liquid crystal (100 mg $\text{L}^{-1}$ in $\text{C}_6\text{H}_5\text{Cl}$) sealed in a vertically-placed quartz cuvette with an optical path length of 1 mm and an interior width of 10 mm. This liquid crystal was sequentially observed with reflected white light (a), with transmitted white light (b), with transmitted white light between crossed polarizers (c), and under 395 nm UV irradiation (d).

**Fig. 2** SEM (a) and AFM (b) images showing the geometries of mesogenic perovskite nanoplatelets. Scale bars: (a) 500 nm, (b) 50 nm.
increased when higher concentrations of oleic acid and oleylamine were used during the microcrystallization process (Fig. S5, ESI†), indicating the feasibility of morphological control of the mesogens. In dispersions at high concentrations (about 100 mg per 1 mL), anisotropic structures with strong optical birefringence were observed between two perpendicularly oriented linear polarizers using transmitted white light (Fig. 1c). Based on their size polydispersity, two-dimensional geometrical features, and large diameter-to-thickness ratios, these mesogenic nanoplatelets would adopt unidirectional orientations with a face-to-face parallel alignment, forming discotic–nematic phases (Scheme 1) similar to the hierarchical superstructures generated by other types of plate-shaped mesogens.20 The gravitational sedimentation of birefringent microdomains (generally referred to as “tactoids”) to the bottom part of the dispersion is a common behavior of lyotropic systems (Fig. S6, ESI†), which is caused by the slightly higher mass density of liquid crystalline microphases than isotropic regions as mesogenic nanoparticles adopting ordered arrangements in tactoids are able to occupy space more efficiently than nanoparticles with disordered random orientations.21,22

The lyotropic liquid crystallinity of colloidal perovskite nanoplatelets was confirmed by polarized optical microscopy (POM) between two crossed linear polarizers (Fig. 3a and Fig. S7, ESI†), where liquid crystalline tactoidal microphases could be observed as birefringent stripes. When multiple tactoids with their director fields in different directions moved together and subsequently merged into larger-sized anisotropic microdomains through a coalescence mechanism (Fig. S8, ESI†), topological defects would be generated near the original boundary interfaces of the parent tactoids (Fig. 3b).

Under ultraviolet light irradiation (wavelength of about 395 nm), the (4-CF$_3$-C$_6$H$_4$-CH$_2$NH$_3$)$_2$PbI$_4$ liquid crystals exhibited greenish-blue light emission (Fig. 1d), which indicates the preservation of the semiconducting features of this lead iodide perovskite. The optical properties of perovskite liquid crystals were further analyzed by using ultraviolet-visible (UV-Vis) absorption spectroscopy as well as photoluminescence (PL) spectroscopy, revealing an absorption peak at 501 nm, an emission wavelength of 505 nm, and a narrow full width at half maximum (FWHM) of about 21 nm (Fig. 4). The small Stokes shift is characteristic of free-excitonic emissions. The photoluminescence quantum yield (PLQY) of this liquid crystal was measured to be about 0.2%.

The influences of synthesis conditions (e.g., grafting of surfactants) on the chemical compositions and crystallographic structures of the mesogenic nanoplatelets were also evaluated. Using SEM with energy-dispersive X-ray spectroscopy (EDXS), the elemental mapping of a typical hexagonal-plate-shaped perovskite nanocrystal was conducted (Fig. 5a), confirming the existence of lead and iodine atoms of the inorganic perovskite octahedral units, as well as fluorine and nitrogen atoms of the trifluoromethyl-substituted organic ammonium spacer cations. Powder X-ray diffraction (PXRD) analysis of the nanoplatelets showed a series of periodically spaced diffraction peaks (with the first peak at 2θ of about 4.94°) corresponding to the (h00) lattice planes of the two-dimensional perovskite as

![Fig. 3](image1.png) POM images showing the anisotropic microphases (a) and topological defects (b) in perovskite liquid crystals. Scale bars: (a) 200 μm, (b) 100 μm.

![Fig. 4](image2.png) Normalized UV-Vis absorption, PL excitation (emission at 505 nm) and PL emission (excitation wavelength at 372 nm) spectra of the (4-CF$_3$-C$_6$H$_4$-CH$_2$NH$_3$)$_2$PbI$_4$ perovskite liquid crystals.
crystallographic structures of bulk organic–inorganic metal halide perovskites could be easily obtained.

In conclusion, a low-cost and simple synthesis method has been developed for preparing luminescent semiconducting liquid crystals of two-dimensional organic–inorganic lead iodide perovskites. This method should be applicable to various types of two-dimensional and quasi-two-dimensional perovskites since they share similar chemical and structural characteristics. Through this approach, a large family of semiconducting liquid crystals with luminescence or other unique physical properties might be systematically created based on the compositional versatility of metal halide perovskites.

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Conflicts of interest

There are no conflicts to declare.

Notes and references