Colloidal Lyotropic Liquid Crystalline Phases of Two-Dimensional Nanoparticles of Layered Hybrid Organic-Inorganic Metal Halide Perovskites

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ABSTRACT

Lyotropic liquid crystals are fluids with macroscopic anisotropic structures formed by the self-assembly of nonspherically-symmetric mesogenic molecules or nanoparticles. Here, lyotropic liquid crystalline phases with discotic-nematic orderings were observed in colloidal dispersions of hexagonal-shaped nanoplatelets of two-dimensional layered hybrid organic-inorganic metal halide perovskites (with formula A_2BX_4 where A^{1+} is an organic ammonium cation, B^{2+} is a divalent metal cation, and X^{1-} is a halide anion) synthesized via microcrystallization by mixing precursor solutions with antisolvents containing surfactants, which showed semiconducting properties such as blue to green photoluminescence. As nanocrystalline perovskites are compositionally (transition metals like manganese, copper or europium as octahedral unit centers, mixed halides, organic spacers with chirality, etc.), microscopic structurally (three-, two-, or one-dimensional), and geometrically (nanosheets or nanorods) adjustable, liquid crystals with different phase behaviors and physical features (e.g., paramagnetism) may be systematically developed using this method.

Key Words: self-assembly, ordered phases, two-dimensional nanoparticles, organic-inorganic perovskites, semiconducting nanomaterials

INTRODUCTION

Lyotropic liquid crystals, which are dispersions with long-range collective anisotropic structures formed by the self-assembly of geometrically nonspherical (rod-shaped or plate-shaped) molecules or nanoparticles, have been systematically studied since the discovery of optical birefringence in vanadium pentoxide sols in 1925 by Zocher.¹ During the past 95 years, various types of organic molecules, polymers, biomaterials, and nanoparticles have been observed to exhibit lyotropic liquid crystalline behaviors in water or other solvents, such as tobacco mosaic viruses,² polypeptides,³ deoxyribonucleic acids,⁴ collagens,⁵ cellulose nanocrystals,⁶ graphene oxide nanosheets,^{7,8} Sunset Yellow FCF,⁹ as well as many inorganic nanorods or nanodisks.¹⁰⁻¹² Different hierarchical orderings, including nematic, smectic, discotic, columnar, and chiral nematic phases may be obtained with lyotropic liquid crystals, and these ordered microstructures can be transferred to other matrix materials by co-assembly processes or template synthesis,¹³ endowing them with unique optical,¹⁴⁻¹⁷ thermal,¹⁸ mechanical,¹⁹ mesoporous,²⁰⁻²⁴ or stimuli-responsive properties.²⁵⁻²⁷

One of the major obstacles that limited the application of lyotropic liquid crystals is the difficulty to adjust the intrinsic physical properties (energy band gaps, magnetism, spontaneous polarization, chirality, etc.) of mesogenic organic molecules or nanoparticles by chemical modifications. Unfortunately, for colloidal nanoparticles, which are the most commonly used type of lyotropic mesogens, in many situations only a minimal degree of compositional changes can be introduced onto their surfaces (by grafting of functional groups) without destroying their rod-like or plate-like anisotropic shapes. Moreover, chemical treatments usually have negative influences on the net charges and/or grafted polymers on the surfaces of colloidal nanoparticles, which may undermine their ability to form stable homogeneous dispersions and therefore liquid crystalline phases in solvents.

A promising class of materials that may significantly broaden the scope of lyotropic liquid crystals would be two-dimensional layered hybrid organic-inorganic metal halide perovskites. These are highly crystalline organometallic compounds (with the general chemical formula A_2BX_4 , where the A site may be an organic ammonium cation or a monovalent alkali metal cation, the B site is usually a divalent metal cation such as lead or manganese, and the X site is a halide anion) in which corner-sharing octahedral metal halide units (BX_6^{4-}) assemble into negatively-charged flat pseudo-planes (BX_4^{2-}) parallel-aligned and periodically spaced

with positively-charged interlayer organic ammonium cations (A^+) arranged between every two adjacent pseudo-planes.²⁸⁻³² Not like in three-dimensional perovskites,³³⁻³⁶ where the sizes of organic spacers are strictly restricted by the Goldschmidt tolerance factor so that they can fit in the rigid cages surrounded by eight metal halide octahedra, in the crystal lattices of two-dimensional perovskites there is greater spatial freedom to incorporate larger-sized organic cations ranging from long aliphatic chains to bulky conjugated molecules containing multiple aromatic rings.³⁷⁻³⁹ This structural flexibility enables easy functionalization of two-dimensional perovskites by selecting appropriate combinations of the A, B, and X parts, through which a large family of perovskites can be systematically synthesized to achieve different intrinsic physical characteristics including but not limited to photoluminescence,⁴⁰⁻⁴³ photovoltaic effects,⁴⁴ optoelectronic responses,⁴⁵ paramagnetism,⁴⁶ ferromagnetism,⁴⁷ ferroelectricity,⁴⁸⁻⁵⁰ and chirality.⁵¹⁻⁵⁴

Figure 1. (A) Crystal structure of the 2D perovskite $(4\text{-CF}_3\text{-C}_6\text{H}_4\text{-CH}_2\text{NH}_3)_2\text{PbI}_4$ as revealed by single-crystal X-ray diffraction analysis.⁵⁵ The lead atoms are depicted in black, iodine atoms in red, nitrogen atoms in blue, fluorine atoms in green, carbon atoms in brown, and hydrogen atoms in yellow. (B) SEM image of the as-synthesized perovskite nanoplatelets. (C) AFM image showing a hexagonal nanoplatelet with an edge-to-edge width of 225 to 235 nm and a thickness of 8.0 to 8.5 nm. (D-G) Photographs of a liquid crystalline dispersion of perovskite nanoplatelets (100 mg per mL 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 (**D**), with transmitted white light (**E**), with transmitted white light between two perpendicularly oriented linear polarizers (**F**), and under 395-nm-wavelength ultraviolet irradiation (**G**). (**H**) POM image showing the optical birefringence of this dispersion observed between crossed linear polarizers. (**I**) UV-Vis absorption (left red curve) and PL emission (right blue curve; excitation wavelength of 350 nm) spectra of the perovskite liquid crystal.

In this research, an experimental method for preparing lyotropic liquid crystalline dispersions of colloidal nanoparticles of two-dimensional organic-inorganic metal halide perovskites was developed. Specifically, hexagonal-shaped nanoplatelets with high aspect (diameter to thickness) ratios (>20) were synthesized by mixing-precipitation of the precursor solutions of perovskites in nonpolar antisolvents (**Figure 1A-C**). As sterically stabilized by long aliphatic chains from non-ionic surfactants, the perovskite nanoplatelets could be concentrated beyond the threshold level to form lyotropic liquid crystalline phases by self-assembly, exhibiting both the intrinsic semiconducting properties of organic-inorganic perovskites and hierarchical orderliness of the liquid crystalline structures (**Figure 1D-I and Scheme 1**).

Scheme 1. A schematic illustration of the face-to-face parallel self-assembly of perovskite nanoplatelets in the discotic nematic liquid crystalline phase.

RESULTS AND DISCUSSIONS

A lead(II) iodide perovskite, bis[[4-(trifluoromethyl)phenyl]methan ammonium} tetraiodoplumbate(II) was

selected as the model material in this research, which is abbreviated as $(\text{CF}_3\text{-PMA})_2\text{PbI}_4$ hereinafter. It has a two-dimensional structure with an interlayer spacing distance of around 1.79252 nanometers between adjacent inorganic perovskite pseudo-planes as revealed by single-crystal X-ray diffraction analysis (Figure 1A and Figure S1).⁵⁵ Through a rapid antisolvent-induced microcrystallization process accompanied by the *in-situ* grafting of surfactants, where an N,N-dimethylformamide solution containing the precursors of organic-inorganic metal halide perovskites was mixed with a relatively large volume of chlorobenzene containing oleic acid and oleylamine under high-speed stirring, a colloidal dispersion of two-dimensional nanoparticles with high diameter-to-thickness ratios was synthesized, the stabilization of which could be achieved by elimination of polar solvents and residual ionic impurities through ultracentrifugation as well as post-synthesis grafting of a higher density of surfactant molecules on the surfaces of nanoparticles by redispersion in chlorobenzene with higher concentrations of oleic acid and oleylamine. Toluene and ethyl acetate can also work as antisolvents in these experiments, while chlorobenzene was selected here for its relatively high boiling point.

The hexagonal-plate-shaped nanoparticles of two-dimensional perovskite $(\text{CF}_3\text{-PMA})_2\text{PbI}_4$ have diameters ranging from 100 to 200 nm and thicknesses of 5 to 10 nm as measured by scanning electron microscopy (SEM) (Figure 1B and Figure S2) and atomic force microscopy (AFM) (Figure 1C and Figure S3), showing high aspect ratios of 20 to 40, which are comparable to the values of some typical colloidal lyotropic liquid crystalline mesogens like cellulose nanocrystals.⁵⁶⁻⁵⁹ At higher concentrations (about 100 mg per 1 mL), the perovskite nanoplatelets self-assembled into anisotropic structures, giving orange- to yellow-colored semi-transparent dispersions (Figure 1D,E and Figure S4) exhibiting high optical birefringence observable between two perpendicularly oriented linear polarizers with transmitted light (Figure 1F). According to the remarkable size polydispersity, two-dimensional geometrical features and large diameter-to-thickness ratios of these mesogenic perovskite nanoplatelets, they would form a discotic nematic liquid crystalline phase by self-assembly, where the nanoplatelets are unidirectionally oriented with a face-to-face parallel alignment (Scheme 1) similar to the hierarchical superstructures formed by other types of plate-shaped mesogens.⁶⁰⁻⁶⁴ The gravitational sedimentation of bright birefringent microdomains (generally referred to as "tactoids") to the bottom part of the dispersion is a common behavior of lyotropic systems (Figure S5), which is caused by the slightly higher mass density of liquid crystalline tactoids than isotropic phases as mesogenic nanoparticles adopting ordered alignment in tactoids are able to occupy space more efficiently

than nanoparticles with disordered random orientations.⁶⁵⁻⁶⁹ Moreover, when irradiated with ultraviolet light (wavelength of around 395 nm), the colloidal suspensions of $(\text{CF}_3\text{-PMA})_2\text{PbI}_4$ nanoplatelets showed intensive greenish-blue photoluminescence characteristic of this two-dimensional lead iodide perovskite (Figure 1G).

Figure 2. (A) POM image showing the formation of topological defects in a liquid crystalline dispersion of perovskite nanoplatelets. (B) The coalescence of multiple liquid crystalline microphases.

The self-assembly of perovskite nanoplatelets in colloidal dispersions was further examined by polarized optical microscopy (POM) between two crossed linear polarizers (Figure 1H and Figure S6), where liquid crystalline tactoidal microphases were observed as bright long stripes with lengths from 500 to 2000 μm and widths from 200 to 500 μm . When multiple tactoids with their director fields in different directions moved together and then subsequently merged into larger-sized liquid crystalline microdomains through a coalescence mechanism, topological defects would be generated near the original boundary interfaces of the parent tactoids (Figure 2A,B and Figure S7). These thermodynamically unstable topological defects might be eliminated by the reorientation of mesogenic nanoplatelets during the relaxation process of the colloidal system, which tends to minimize the elastic potential energy of the ordered phases.⁷⁰

The lyotropic liquid crystalline dispersions of two-dimensional organic-inorganic perovskite nanoplatelets successfully preserved the excellent intrinsic semiconducting properties of the bulk crystals. As measured by ultraviolet-visible (UV-Vis) absorption spectroscopy and photoluminescence (PL) spectroscopy, liquid

crystals formed by $(\text{CF}_3\text{-PMA})_2\text{PbI}_4$ nanoplatelets exhibited greenish-blue light emission at a wavelength of 505 nm (Figure 1I), which is slightly red-shifted in comparison to the 484 nm blue photoluminescence of spin-coated and thermally-annealed thin films prepared from the same perovskite precursor solution that was used to synthesize the mesogenic nanoplatelets (Figure S8). This decrease in the energy band gap is probably due to the partial release of the structural distortions (e.g, the reduced in-plane lead-iodide-lead bond angles in inorganic PbI_4^{2-} perovskite pseudo-layers) in the crystal lattice as chemical bonds may have more spatial freedom in nanoparticles than in bulk crystals.⁷¹

Figure 3. (A) SEM micrograph of a hexagonal-plate-shaped mesogenic nanocrystal of the two-dimensional perovskite $(4\text{-CF}_3\text{-C}_6\text{H}_4\text{-CH}_2\text{NH}_3)_2\text{PbI}_4$. The distributions of lead ($\text{M}\alpha_1$; B), iodine ($\text{L}\alpha_1$; C), fluorine ($\text{K}\alpha_1$; D), and nitrogen ($\text{K}\alpha_1$; E) atoms in this nanocrystal were revealed by SEM-EDXS elemental mapping. (F) PXRD patterns obtained by simulations based on the single-crystal X-ray crystallography data (upper blue curve) of $(4\text{-CF}_3\text{-C}_6\text{H}_4\text{-CH}_2\text{NH}_3)_2\text{PbI}_4$ and by experimental measurement of a spin-coated and vacuum-dried thin film of a lyotropic liquid crystalline dispersion of the perovskite nanoplatelets (lower red curve).

The chemical composition of the as-synthesized mesogenic nanoplatelets was qualitatively analyzed using scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (SEM-EDXS), where by the elemental mapping of a typical hexagonal-shaped perovskite nanocrystal (Figure 3A), the existence of

lead and iodine atoms of the inorganic perovskite octahedral units (Figure 3B,C), as well as fluorine and nitrogen of the trifluoromethyl-substituted organic ammonium cations was clearly revealed (Figure 3D,E). Crystallographic structures of these nanoplatelets were characterized by powder X-ray diffraction (PXRD) analysis, showing a series of periodically spaced diffraction peaks (with the first peak at 2-theta of about 4.94 degrees) corresponding to the (h00) lattice planes of the two-dimensional perovskite (CF₃-PMA)₂PbI₄ as confirmed by the simulated PXRD patterns based on the single-crystal X-ray diffraction data (Figure 3F). It should be noted that the surfactants, especially oleylamine molecules may enter the crystal lattices of the thin nanoplatelets to form intercalation layers between adjacent inorganic perovskite pseudo-planes, resulting in a significant increase in the interlayer spacing distance,⁷² which could be detected as a new low-angle X-ray diffraction peak at two-theta of 2.82 to 2.85 degrees (Figure S9), indicating an elongated distance of around 3.10 to 3.13 nm compared with the original value of about 1.79 nm. The intercalated crystalline phases became dominant when high concentrations of surfactants were used to stabilize the colloidal nanoplatelets (e.g., more than 100 mmol/L oleylamine and oleic acid) (Figure S9). Nevertheless, by adjusting the chemical properties and amounts of surfactant molecules, mesogenic nanoparticles that exhibit sufficiently good colloidal stability while preserving the original crystallographic structures of bulk organic-inorganic metal halide perovskites would be easily synthesized.

In conclusion, a low-cost and simple synthesis method has been developed for preparing lyotropic liquid crystalline dispersions of colloidal nanoplatelets of two-dimensional hybrid organic-inorganic metal halide perovskites, which would 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 lyotropic liquid crystals with the mesogenic nanoparticles possessing excellent semiconducting properties or other unique physical features might be systematically created based on the compositional versatility of organic-inorganic perovskites. For example, energy band gaps could be adjusted with doping elements or quasi-two-dimensional structures,^{73,74} ferroelectricity and nonlinear optical effects would be achieved with noncentrosymmetric crystal lattices, paramagnetism and ferromagnetism may be realized with manganese, copper or europium as octahedral unit centers, and chirality (either in crystal lattices or in self-assembled superstructures) might be introduced by using chiral organic spacer molecules or chiral surfactants. The transformation of perovskites into liquid crystalline mesogens also enables them to form homogeneous mixtures with other lyotropic liquid crystals, colloids or polymers, providing a new method

to fabricate perovskite-derived composite functional nanomaterials in the forms of free-standing films, organogels, aerogels, monoliths, fibers, or microspheres possessing both the intrinsic physical properties of organic-inorganic perovskites and the microscopic hierarchical orderliness from the liquid crystalline superstructures.^{75,76}

EXPERIMENTAL METHODS

Materials

Lead(II) iodide (99 %, Sigma-Aldrich), [4-(trifluoromethyl)phenyl]methanamine hydroiodide (> 98.0 %, TCI Chemicals), N,N-dimethylformamide (anhydrous, 99.8 %, Sigma-Aldrich), cis-9-octadecenoic acid (oleic acid; > 99 %, Sigma-Aldrich), cis-1-amino-9-octadecene (oleylamine; > 98 %, Aldrich), chlorobenzene (anhydrous, 99.8 %, Sigma-Aldrich), and cyclohexane (anhydrous, 99.5 %, Sigma-Aldrich) were used as received.

Characterization

Field emission scanning electron spectroscopy and energy-dispersive X-ray spectroscopy were performed on a Hitachi Regulus 8230 Ultra-high Resolution Scanning Electron Microscope. Atomic force microscopy was conducted on a Bruker Dimension Icon atomic force microscope with ScanAsyst. Samples for SEM and AFM observations were prepared by spin-coating the colloidal liquid crystalline dispersions of perovskite nanoplatelets (about 100 mg per mL in chlorobenzene) onto flat silicon (111) surfaces at a spinning speed of 6000 RPM for 60 seconds followed by thermal annealing at 373 K for 10 minutes. Excess surfactants on the samples were removed by immersion in a large volume of cyclohexane for 30 minutes then dried in a nitrogen or argon atmosphere. Powder X-ray diffraction patterns were collected on a Bruker D8 ADVANCE diffractometer using Cu-K α radiation (wavelength of 0.15406 nm). Photoluminescence spectroscopy was performed on a Hitachi F-4600 Fluorescence Spectrophotometer with an excitation wavelength of 350 nm and the perovskite liquid crystalline dispersion was sealed in a quartz cuvette with an optical path length of 1 mm. Ultraviolet-visible absorption spectroscopy was conducted on a PerkinElmer LAMBDA 25 UV-Vis Spectrophotometer, and the liquid crystal was sandwiched between two parallel glass slides separated by a distance of about 100 micrometers.

Synthesis of Colloidal Lyotropic Liquid Crystals of Two-Dimensional Organic-Inorganic Perovskites

Unless otherwise stated, all experiments in this study were conducted at room temperature (about 298 K). In a typical experiment, two-dimensional perovskite nanoplatelets of $(\text{CF}_3\text{-PMA})_2\text{PbI}_4$ were synthesized by slowly adding an N,N-dimethylformamide solution (0.1 mL) of 4-(trifluoromethyl)benzylammonium iodide (2 mol/L) and lead(II) iodide (1 mol/L) into a chlorobenzene solution (10.0 mL) of cis-9-octadecenoic acid (oleic acid, 3.17 mmol/L) and cis-1-amino-9-octadecene (oleylamine, 3.04 mmol/L) over a period of about 60 seconds at a stirring speed of 3000 revolutions per minute. The perovskite nanoplatelets were isolated as yellow-colored solids by high-speed ultracentrifugation (about $100,000 \text{ m/s}^2$ for 15 minutes at 283 K) then immediately redispersed in another chlorobenzene solution (10.0 mL) containing cis-9-octadecenoic acid (3.17 mmol/L) and cis-1-amino-9-octadecene (3.04 mmol/L) by sonication at 273 K, where a highly stable colloidal dispersion has been formed. Perovskite nanoplatelets were separated from this dispersion by ultracentrifugation (about $100,000 \text{ m/s}^2$ for 60 minutes at 283 K) again (it should be noted that an amount of the perovskite nanoplatelets could not be isolated as solids after this step, instead they form yellow-colored transparent organogels between the solid-state precipitates and the supernatant solution), then the solids were redispersed in a chlorobenzene solution (1.0 mL) containing cis-9-octadecenoic acid (31.7 mmol/L) and cis-1-amino-9-octadecene (30.4 mmol/L) by sonication at 273 K, by which a lyotropic liquid crystalline phase of $(\text{CF}_3\text{-PMA})_2\text{PbI}_4$ perovskite nanoplatelets (with a concentration of about 100 mg per 1.0 mL) could be obtained.

ACKNOWLEDGMENT

This study was financially supported by the Suzhou Institute of Nano-Tech and Nano-Bionics. The author gratefully acknowledges Li-Li Li for her assistance with SEM and EDXS measurements, Yan-Ru Zheng for her help with AFM characterizations, and Prof. Ting Zhang for kindly providing access to a spin-coating system as well as other instruments.

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SUPPORTING INFORMATION FOR

Colloidal Lyotropic Liquid Crystalline Phases of Two-Dimensional Nanoparticles of Layered Hybrid Organic-Inorganic Metal Halide Perovskites

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Figure S1. Crystal structure of two-dimensional lead iodide perovskite $(4\text{-CF}_3\text{-C}_6\text{H}_4\text{-CH}_2\text{NH}_3)_2\text{PbI}_4$ obtained by single-crystal X-ray diffraction analysis and viewed from different directions (Ref 55). The lead atoms are depicted in black, iodine atoms in red, nitrogen atoms in blue, fluorine atoms in green, carbon atoms in brown, and hydrogen atoms in yellow.

Figure S2. SEM images of the mesogenic perovskite nanoplatelets.

Figure S3. AFM image showing the size and thickness of a representative perovskite nanoplatelet.

Figure S4. Photograph of a colloidal lyotropic liquid crystalline dispersion of perovskite nanoplatelets (at a concentration of about 100 mg per mL).

Figure S5. Photographs taken with transmitted white light and crossed polarizers showing the enrichment of birefringent liquid crystalline microdomains near the bottom part of a colloidal dispersion of perovskite nanoplatelets (enlarged from **Figure 1F**).

Figure S6. POM images showing liquid crystalline microphases in a dispersion of perovskite nanoplatelets.

Figure S7. POM images showing the coalescence of multiple liquid crystalline microphases and formation of topological defects in a colloidal dispersion of perovskite nanoplatelets.

Figure S8. Ultraviolet-visible absorption (plotted in red) and photoluminescence emission (plotted in blue) spectra of a colloidal liquid crystalline dispersion (**A**) as well as a spin-coated and thermally annealed thin film (**B**) of the two-dimensional lead iodide perovskite $(4\text{-CF}_3\text{-C}_6\text{H}_4\text{-CH}_2\text{NH}_3)_2\text{PbI}_4$ used in this research.

Figure S9. (A,B) Powder X-ray diffractions patterns obtained by simulations according to the single-crystal X-ray crystallography data of $(4\text{-CF}_3\text{-C}_6\text{H}_4\text{-CH}_2\text{NH}_3)_2\text{PbI}_4$. (C,D) PXR patterns of a $(4\text{-CF}_3\text{-C}_6\text{H}_4\text{-CH}_2\text{NH}_3)_2\text{PbI}_4$ thin film prepared from the precursor solution by spin-coating and thermal annealing. (E,F) PXR patterns of mesogenic perovskite nanoplatelets used in this study. (G,H) PXR patterns of colloidal nanoparticles prepared with higher concentrations of oleic acid and oleylamine (more than 100 mmol/L).