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Molecular pseudo-halogen engineering enables remarkable birefringence enhancement in hybrid perovskites

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Hybrid perovskites have emerged as promising candidates for birefringent crystals due to their structural diversity. Conventional strategies to enhance birefringence often rely on incorporating highly π -conjugated organic components; however, it remains challenging to achieve both high birefringence (>0.3) and large single crystal growth. Herein, we present a pseudo-halogen engineering method that also enables giant birefringence enhancement. By substituting halogen Cl^- with polar pseudo-halogen $(\text{SCN})^-$, we designed and synthesized a one-dimensional hybrid perovskite, namely $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$, which exhibits a high birefringence of $\Delta n_{\text{exp}} = 0.37@550 \text{ nm}$, more than 12 times that of isostructural $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ ($\Delta n_{\text{exp}} = 0.03@550 \text{ nm}$). This birefringence value not only surpasses those of all commercial birefringent crystals, but also is even higher than those of many hybrid perovskites composed of π -conjugated cations. Moreover, large single crystals of $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ were readily grown by the facile evaporation method. First-principles calculations reveal that the remarkable birefringence enhancement originates from a tens-of-times increase in polarizability anisotropy of the distorted $\text{Cd}(\text{SCN})_6$ octahedra compared to their $\text{CdCl}_5 \cdot \text{H}_2\text{O}$ counterparts. This work provides a novel molecular-level strategy towards designing high-performance birefringent crystals for polarized optics.

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1. Introduction

When light passes through an optically anisotropic crystal, it splits into two distinct rays, which are orthogonally polarized and travel at different speeds, namely, the ordinary and extraordinary rays.^{1–3} This phenomenon enables birefringent crystals to modulate polarized light, making them indispensable in various polarized optical devices, such as polarizers, wave plates, mirrors, phase compensators, *etc.*^{4–6} High birefringence is highly desirable, as it allows for the fabrication of more compact and efficient devices.^{7–9} From the viewpoint of practical applications, it is also critical that large single crystals of these materials are easy to grow.¹⁰ However, commercial birefringent crystals have long been limited to inorganic oxides and fluorides, which typically exhibit relatively small birefringence,^{11–16} such as MgF_2

($0.011@532 \text{ nm}$),¹¹ LiNbO_3 ($0.074@546 \text{ nm}$),¹² $\alpha\text{-BaB}_2\text{O}_4$ ($0.122@532 \text{ nm}$),¹³ CaCO_3 ($0.172@532 \text{ nm}$),¹⁴ and YVO_4 ($0.209@532 \text{ nm}$).¹⁵ Moreover, it remains difficult to grow pure single crystals for some materials, like CaCO_3 . These limitations have spurred the necessity to explore new birefringent crystals with superior comprehensive properties.

Recently, hybrid perovskites have emerged as promising candidates for birefringent crystals due to their rich structural diversity.^{5,17–21} To enhance the birefringence, researchers have explored various strategies, one of which involves applying external thermal stimuli to induce structural phase transitions. However, the amplitude of birefringence enhancement by such physical means is relatively limited. For example, Sun *et al.* synthesized a two-dimensional (2D) tri-layered hybrid perovskite, namely $(\text{CH}_3\text{NH}_3)_2[(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{NH}_3]_2\text{Pb}_3\text{Cl}_{10}$, whose in-plane birefringence slightly improved from $\Delta n_{\text{exp}} = 0$ to $\Delta n_{\text{exp}} = 0.01@546 \text{ nm}$ upon cooling.¹⁸

It is widely acknowledged that macroscopic birefringence is strongly correlated with the polarizability anisotropy of crystal structures. On this basis, the other common effective strategies involve chemical modification, that is, introducing highly delocalized π -conjugated cations with inherent anisotropy of polarizability between the in-plane and out-of-plane directions.^{17,21} In 2022, our group reported a new 2D layered hybrid perovskite, $(\text{C}_3\text{N}_6\text{H}_8)\text{PbBr}_4$, *via* the introduction of π -conjugated

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organic cations $(C_3N_6H_8)^+$.¹⁷ This birefringent crystal has a high birefringence of 0.322@550 nm, mainly attributed to π -conjugated $(C_3N_6H_8)^+$. Although such large π -conjugated cations can significantly enhance the birefringence, the resultant birefringent crystals are typically limited to micron-scale sizes, seriously hindering their practical applications.

In this work, by employing a non- π -conjugated, cheap organic component, *N,N*-dimethylpiperazine, we successfully synthesized and reported two novel hybrid perovskites, namely $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ and $(C_6N_2H_{15})Cd(SCN)_3$, which feature similar 1D $[CdCl_3 \cdot H_2O]_\infty$ and $[Cd(SCN)_3]_\infty$ perovskite chains, constructed by $CdCl_5 \cdot H_2O$ and distorted $Cd(SCN)_6$ octahedra. Interestingly, there is a distinct birefringence gap between $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ ($\Delta n_{exp} = 0.03@550$ nm) and $(C_6N_2H_{15})Cd(SCN)_3$ ($\Delta n_{exp} = 0.37@550$ nm), respectively. In other words, the birefringence has been improved by more than 12 times *via* the chemical substitution of halogen Cl^- ions with polar pseudo-halogen thiocyanide. The transparent crystal of $(C_6N_2H_{15})Cd(SCN)_3$ with dimensions up to $17 \times 4 \times 2$ mm³ has been successfully grown.

2. Results and discussion

Polycrystalline samples of $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ and $(C_6N_2H_{15})Cd(SCN)_3$ were synthesized by the facile solution method. Large single crystals of $(C_6N_2H_{15})Cd(SCN)_3$ were successfully grown by slow evaporation from its solution (Fig. S1). Their phase purities were confirmed by powder X-ray diffraction (XRD) analysis, as demonstrated in Fig. S2, in which experimental patterns match well with the simulated ones. Besides, the powder XRD patterns of $(C_6N_2H_{15})Cd(SCN)_3$ remained highly consistent over time (Fig. S3) even after a month of air exposure, indicating that $(C_6N_2H_{15})Cd(SCN)_3$ has good air stability.

Single-crystal XRD analysis revealed that both $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ and $(C_6N_2H_{15})Cd(SCN)_3$ crystallize in the monoclinic space group $P2_1/c$ (no. 14) (see detailed crystallographic information listed in Tables S1–S5). As shown in Fig. 1a and b, in both compounds, central Cd^{2+} ions exhibit similar octahedral coordination environments. In $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$,

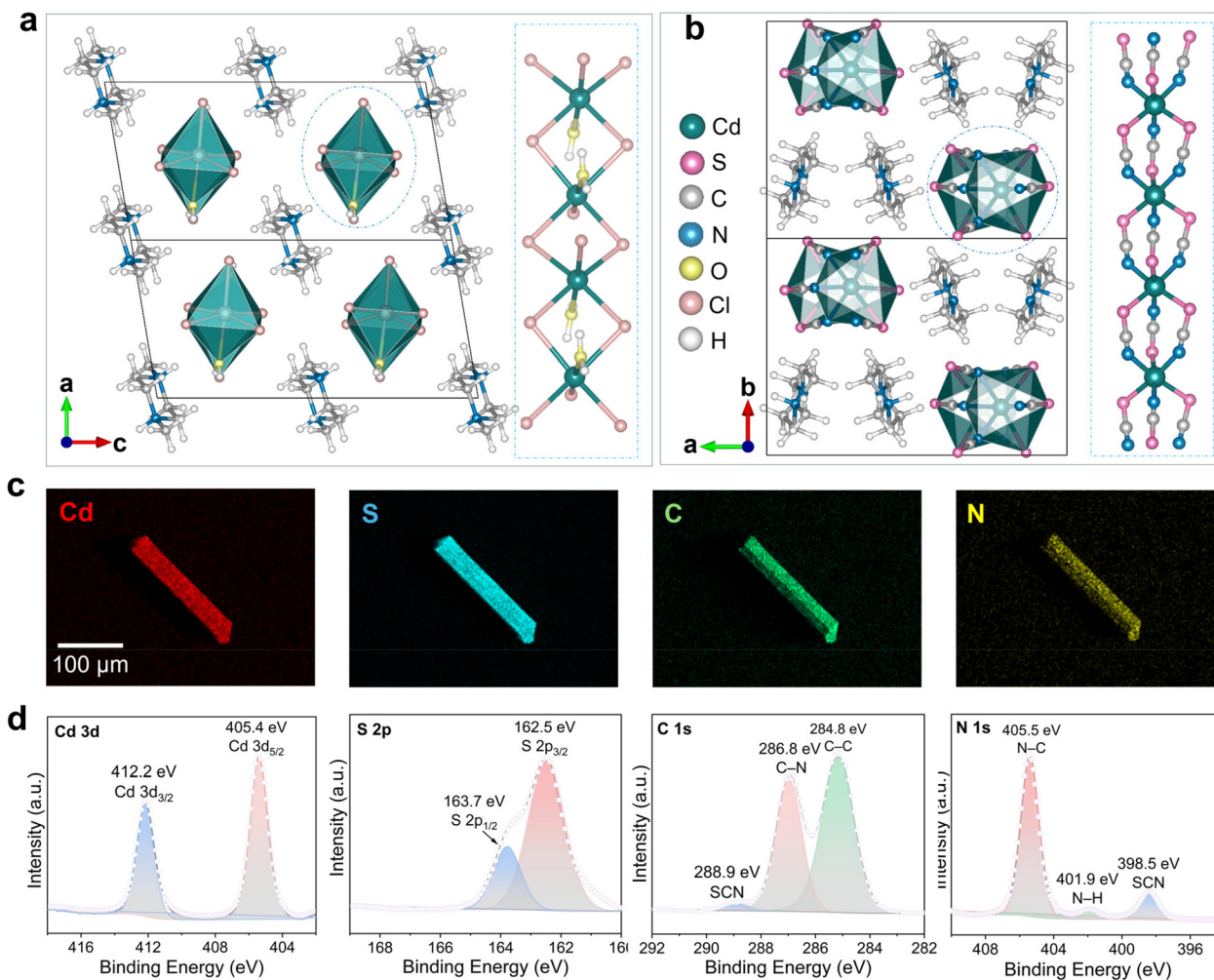


Fig. 1 Structural and compositional analyses of $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ and $(C_6N_2H_{15})Cd(SCN)_3$. (a) The crystal structure of $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ viewed along the *b*-axis. (b) The crystal structure of $(C_6N_2H_{15})Cd(SCN)_3$ viewed along the *c*-axis. (c) Scanning electron microscopy elemental mapping for $(C_6N_2H_{15})Cd(SCN)_3$. (d) XPS fine spectra for Cd 3d, S 2p, C 1s, and N 1s in $(C_6N_2H_{15})Cd(SCN)_3$.

each Cd^{2+} is coordinated by one H_2O and five Cl^- , forming $\text{CdCl}_5\cdot\text{H}_2\text{O}$ octahedra (Fig. S4), while in $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$, six $(\text{SCN})^-$ ligands coordinate with Cd^{2+} to form twisted $\text{Cd}(\text{SCN})_6$ octahedra (Fig. S4). These octahedra are further interconnected with each other to construct similar 1D perovskite frameworks of $[\text{Cd}(\text{SCN})_3]_\infty$ and $(\text{CdCl}_3\cdot\text{H}_2\text{O})_\infty$ chains (Fig. 1a and b). The organic *N,N*-dimethylpiperazine cations reside between the infinite $(\text{CdCl}_3\cdot\text{H}_2\text{O})_\infty$ and $[\text{Cd}(\text{SCN})_3]_\infty$ chains, keeping the overall structural balance. In $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6\cdot 2\text{H}_2\text{O}$, Cd–Cl bonds fall in the length range of 2.5640(6)–2.6622(6) Å, and Cd–O bond lengths are 2.4265(16) Å (Table S4). Similarly, in $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$, Cd–S bond lengths fall in the range of 2.6453(6) Å to 2.8280(6) Å, and Cd–N bond distances vary between 2.2450(2) Å and 2.3636(19) Å (Table S4). In addition, $(\text{SCN})^-$ ligands adopt an almost linear geometry with angles ranging from 177.9(2)° to 179.7(2)° (Table S5). According to previous reports, all these bond lengths and bond angles are reasonable.^{22,23} Notably, in the crystal structure of $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$, the $(\text{SCN})^-$ ligands basically align along the *c*-axis, which means it should exhibit larger optical anisotropy along the *c* axis than that along the *a*-axis and *b*-axis. This structural arrangement is beneficial for large birefringence. Moreover, $[\text{Cd}(\text{SCN})_3]_\infty$ chains realize basically an optimal parallel arrangement, further improving the overall birefringence performance of $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$.

Energy dispersive X-ray spectroscopy mapping confirms the expected composition and uniform distribution within the crystal (Fig. 1c and Fig. S5 and 6). In addition, X-ray photoelectron spectroscopy (XPS) was further employed to investigate the chemical composition of $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ (Fig. S7 and Fig. 1d), in which C 1s, N 1s, S 2p, and Cd 3d signals were clearly observed. The fine XPS spectrum of Cd 3d exhibits two peaks at approximately 412.2 eV and 405.4 eV, which correspond to Cd 3d_{3/2} and Cd 3d_{5/2}, respectively.²⁴ In the fine spectrum of S 2p, there are two major peaks at about 162.5 eV and 163.7 eV, coming from 2p_{3/2} and 2p_{1/2}.²⁵ As for the C 1s spectrum, the peak at 284.8 eV belongs to C–C from the adventitious C. The other peaks at 286.8 eV and 288.9 eV derive from the C of the organic cation *N,N*-dimethylpiperazine and C of $(\text{SCN})^-$.²⁵ The fine spectrum of N 1s contains three peaks at 398.5 eV, 401.9 eV, and 405.4 eV, in which the strongest peak at 405.4 eV is related to C–N. Other binding energies located at 398.5 eV and 401.9 eV are attributed to the N of $(\text{SCN})^-$ and N–H bonding.²⁵ Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy of $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6\cdot 2\text{H}_2\text{O}$ and $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ were conducted in the spectral range between 4000 and 400 cm^{-1} (Fig. S8 and S9). Some strong and sharp peaks corresponding to characteristic bending and stretching vibrations of the organic cation *N,N*-dimethylpiperazine could be observed. In addition, the sharp absorption signals at about 2098/2121 cm^{-1} in FTIR spectroscopy and 2099/2122 cm^{-1} in Raman spectroscopy correspond to vibrations of $(\text{SCN})^-$.²⁶

The thermal properties of $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6\cdot 2\text{H}_2\text{O}$ and $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ were analyzed using differential thermal and thermogravimetric analyses (Fig. S10), which show that

$(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ remains thermally stable up to 519 K, whereas $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6\cdot 2\text{H}_2\text{O}$ exhibits lower thermal stability of about 373 K. The UV-visible-near-infrared diffuse reflectance spectra of $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6\cdot 2\text{H}_2\text{O}$ and $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ were recorded from 200 nm to 800 nm, respectively (Fig. S11). Based on the Kubelka–Munk function,²⁷ the calculated absorption data indicate that the bandgap of $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6\cdot 2\text{H}_2\text{O}$ is about 4.38 eV, while that of $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ is about 3.69 eV.

To investigate the structural anisotropic characteristics of $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$, angle-resolved polarized Raman spectroscopy (ARPRS) was performed, whose measurement schematic diagram is illustrated in Fig. 2a. The incident laser was initially polarized using the linear polarizer, while a half-wave plate was then introduced into the shared optical path to adjust the polarization directions. The intensity of Raman vibrations follows the relation:

$$I \propto |e_i \times R \times e_s|^2$$

where *R* is the Raman tensor, and e_i and e_s represent the unit polarization vectors of the incident and scattered signal, respectively. Given that $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ crystallizes in the monoclinic space group $P2_1/c$ (no. 14), only the A_g and B_g vibrational modes contribute to Raman activities. Their respective Raman tensors are expressed as:²⁸

$$R(A_g) = \begin{bmatrix} b & 0 & d \\ 0 & c & 0 \\ d & 0 & a \end{bmatrix}$$

$$R(B_g) = \begin{bmatrix} 0 & f & 0 \\ f & 0 & e \\ 0 & e & 0 \end{bmatrix}$$

Accordingly, the intensities of Raman vibrations on the (010) plane in the parallel and perpendicular polarization configurations for $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ can be described by:²⁹

$$I(A, \parallel) \propto d \sin 2\theta + (a - b) \sin^2 \theta + b$$

$$I(B, \parallel) \propto 0$$

$$I(A, \perp) \propto 2d \cos 2\theta + (a - b) \sin 2\theta$$

$$I(B, \perp) \propto 0$$

Herein the θ denotes the angle between the *b*-axis and the polarization direction of the incident light.

Fig. 2b and c display the 2D false-color contour ARPRS maps of $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ under parallel and perpendicular polarization configurations, as rotation angles change from 0° to 360°. The observed periodic changes of Raman vibrations reflect the strongly anisotropic nature of molecular vibrations in $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$. Fig. 2d and e depict the polar plots showing polarization-resolved intensity variation of the Raman mode intensity at 2096 cm^{-1} . In both polarization configurations, this peak exhibits a characteristic two-lobed shape, agreeing well with the theoretical expressions.

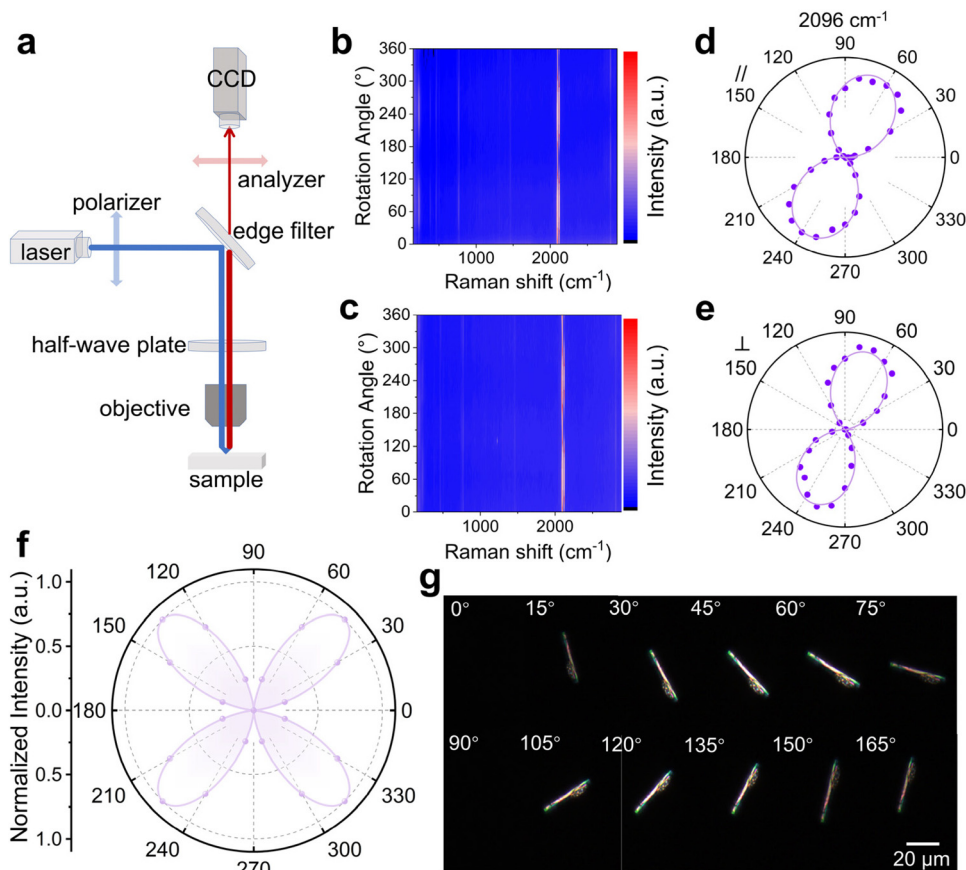


Fig. 2 The anisotropic investigation of $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$. (a) The schematic diagram of ARPRS measurement. 2D contour color maps of polarized Raman intensity under (b) parallel- and (c) perpendicular-polarization configurations for $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$. The polar plots showing polarized Raman intensity at 2096 cm^{-1} under (d) parallel- and (e) perpendicular-polarization configurations for $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$. (f) The normalized fitted polar plots showing the relationship between the transmitted light intensity and the rotation angle. (g) Transmitted images under cross polarized light in increments of 15° from 0° to 165° for $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$.

To reveal the anisotropic optical behavior of $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ and $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$, we further carried out polarization-resolved optical microscopy measurement. As shown in Fig. 2g and Fig. S12, the brightness changes periodically every 45° with the rotation of both tested single crystals. This phenomenon is consistent with the normalized fitted polar plots showing the relationship between the transmitted light intensity and the rotation angle (Fig. 2f), which clearly displays the in-plane optical anisotropy for the refraction of both structures.

The schematic diagram of the orthogonally polarized microscope is illustrated in Fig. 3a. When a beam of light passes through an optically anisotropic crystal along the non-optical-axis direction, it splits into two orthogonally polarized beams: the ordinary ray (o-ray) and the extraordinary ray (e-ray). These two beams exhibit different refractive indices due to the crystal's anisotropy, thereby generating birefringence. As shown in Fig. 3b and e, the original interference color of $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ and $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ is first-order blue and third-order pink under the orthogonally polarized light, respectively, corresponding to the optical path

difference of $0.60\text{ }\mu\text{m}$ and $1.54\text{ }\mu\text{m}$. Both the measured single crystals could achieve complete extinction by using a Berek compensator when rotated clockwise and counterclockwise (Fig. 3c, d, f, and g). The thicknesses for the tested single crystals are $21.1\text{ }\mu\text{m}$ for $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ and $4.3\text{ }\mu\text{m}$ for $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ (Fig. S13). Based on the single-crystal XRD analyses, the measured samples correspond to the (10–2) plane for $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ (Fig. S14a) and the (010) crystal plane for $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ (Fig. S14b), which are the only natural crystal planes suitable for measurement. Therefore, according to the birefringence calculation formula provided in the SI,³⁰ the observed birefringence values were determined to be about $\Delta n_{(10-2)\text{exp}} = 0.03@550\text{ nm}$ for $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ and about $\Delta n_{(010)\text{exp}} = 0.37@550\text{ nm}$ for $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$.

The wavelength-dependent refractive indices at angles from 0° to 360° for the tested (10–2) and (010) crystal planes of $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ and $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ were obtained and are shown in Fig. S15. The changes in refractive indices at $\lambda = 550\text{ nm}$ are further presented in polar plots (Fig. 3h and k). From the ellipsoidal fitting drawn with the solid line, the

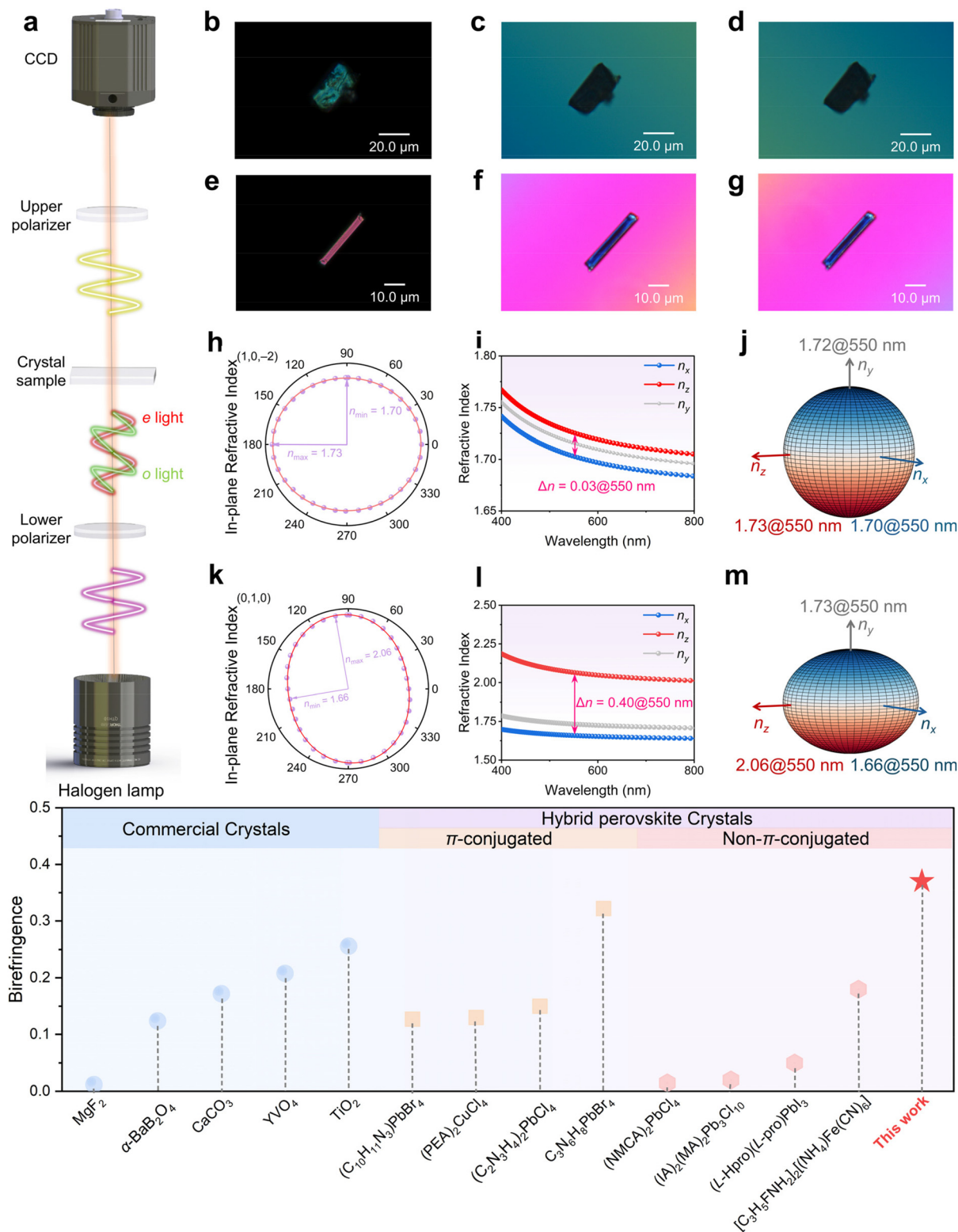


Fig. 3 Birefringence properties of $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ and $(C_6N_2H_{15})Cd(SCN)_3$. (a) Schematic diagram of the polarized microscopy method. Original interference color of the crystal sample under the orthogonally polarized light of (b) $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ and (e) $(C_6N_2H_{15})Cd(SCN)_3$. Complete extinction of (c and d) $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ and (f and g) $(C_6N_2H_{15})Cd(SCN)_3$ achieved by clockwise and counterclockwise rotation of the compensator. Polar plots of calculated refractive indices at $\lambda = 550$ nm in different directions for the (10–2) plane of $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ (h) and the (010) plane of $(C_6N_2H_{15})Cd(SCN)_3$ (k). The solid lines are fit to guide the eyes. Theoretically calculated refractive indices and birefringence of (j) $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ and (l) $(C_6N_2H_{15})Cd(SCN)_3$. Triaxial ellipsoid of three principal refractive indices of (j) $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ and (m) $(C_6N_2H_{15})Cd(SCN)_3$ at $\lambda = 550$ nm. (n) Comparison of the birefringence of $(C_6N_2H_{15})Cd(SCN)_3$ with that of representative commercial birefringent crystals and some reported hybrid perovskite birefringent crystals.

maximum refractive index and minimum refractive index at $\lambda = 550$ nm were determined. The calculated birefringence values for the (10–2) plane of $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ and the (010) plane of $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ are $\Delta n_{(10-2)\text{cal}} = 0.03@550$ nm and

$\Delta n_{(010)\text{cal}} = 0.40@550$ nm, which match well with the experimental results, $\Delta n_{(10-2)\text{exp}} = 0.03@550$ nm and $\Delta n_{(010)\text{exp}} = 0.37@550$ nm. Considering that both $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ and $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$ crystallize in the monoclinic space

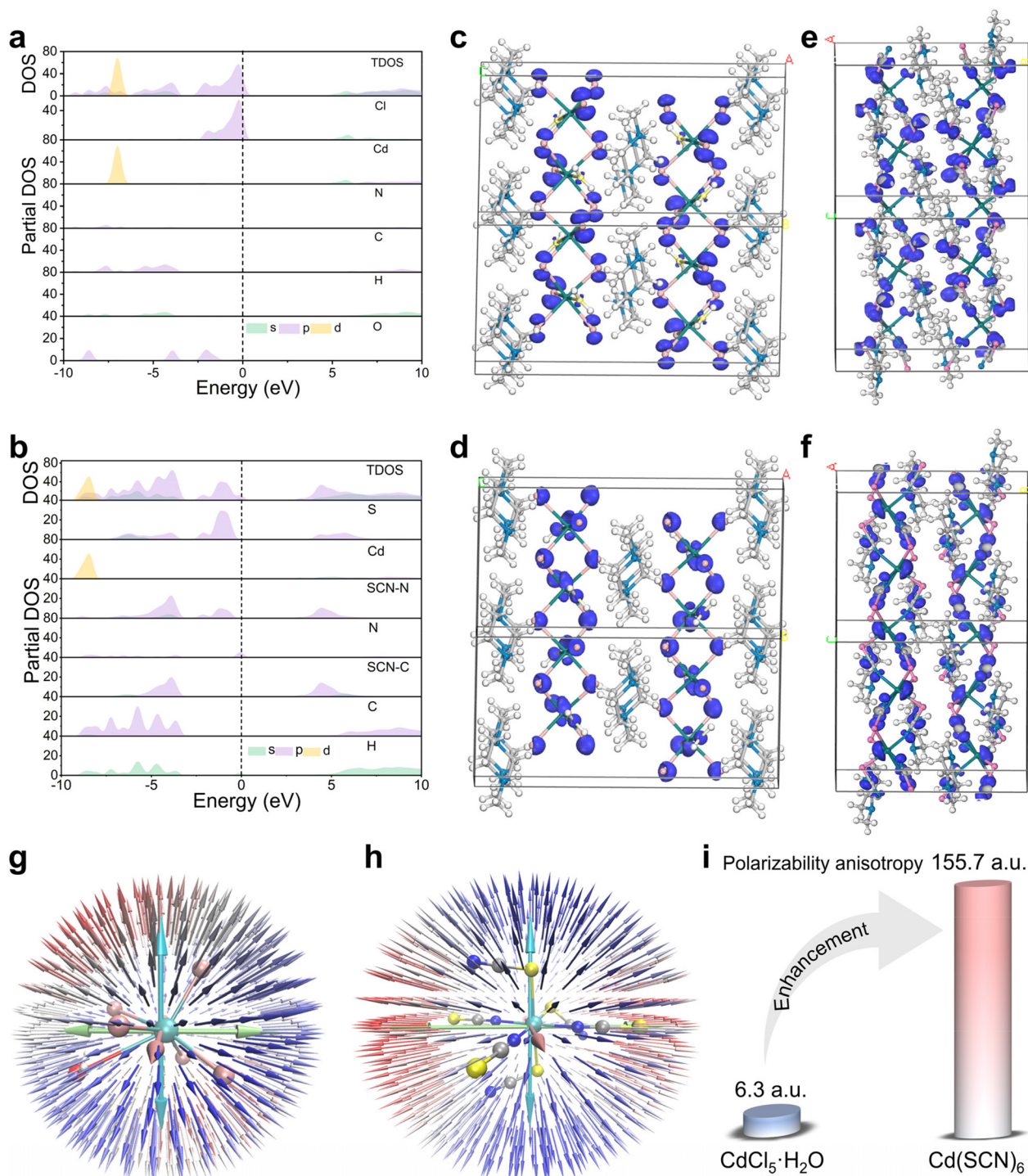


Fig. 4 Theoretical calculations of $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ and $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$. Total and partial DOS of (a) $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ and (b) $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$. The HOMO of (c) $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ and (e) $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$. The LUMO of (d) $(\text{C}_6\text{N}_2\text{H}_{16})\text{Cd}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ and (f) $(\text{C}_6\text{N}_2\text{H}_{15})\text{Cd}(\text{SCN})_3$. The unit sphere representation map of the polarizability tensor of (g) $\text{CdCl}_5 \cdot \text{H}_2\text{O}$ and (h) $\text{Cd}(\text{SCN})_6$. (i) The comparison of the polarizability anisotropy between $\text{CdCl}_5 \cdot \text{H}_2\text{O}$ and $\text{Cd}(\text{SCN})_6$.

group $P2_1/c$ (no. 14), one of their three principal optical axes aligns with the crystallographic b -axis, while the other two are located within the (010) crystal plane. As demonstrated in Fig. 3i and l, the overall birefringence of $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ and $(C_6N_2H_{15})Cd(SCN)_3$ is calculated to be about $\Delta n_{cal} = 0.03@550 \text{ nm}$ and $0.40@550 \text{ nm}$. In addition, the triaxial ellipsoid corresponding to the three principal refractive indices at $\lambda = 550 \text{ nm}$ also exhibits significant difference in optical anisotropy (Fig. 3j and m). Clearly, compared to $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$, the birefringence of $(C_6N_2H_{15})Cd(SCN)_3$ has increased more than 12 times by the chemical substitution of halogen Cl^- ions with pseudo-halogen $(SCN)^-$. Remarkably, the birefringence of $(C_6N_2H_{15})Cd(SCN)_3$ represents almost the largest value among reported hybrid perovskites without π -conjugated cations, exceeding that of recently reported $(IA)_2(MA)_2Pb_3Cl_{10}$,¹⁸ $(L\text{-Hpro})(L\text{-pro})PbI_3$,³¹ $(NMCA)_2PbCl_4$,³² and $[C_3H_5FNH_2]_2[(NH_4)Fe(CN)_6]$.³³ Furthermore, it is also comparable to those of numerous hybrid perovskite birefringent crystals containing π -conjugated cations, including $(C_{10}H_{11}N_3)PbBr_4$,³⁴ $C_3N_6H_8PbBr_4$,¹⁷ $(PEA)_2CuCl_4$,⁵ and $(C_2N_3H_4)_2PbCl_4$.¹⁹

To understand the significant difference in birefringence between $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ and $(C_6N_2H_{15})Cd(SCN)_3$, the first-principles calculations were performed by using the CASTEP package based on density functional theory.^{35,36} Electronic band structure analyses reveal that $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ features an indirect band gap of 4.58 eV (Fig. S16a), while $(C_6N_2H_{15})Cd(SCN)_3$ has a direct band gap of 3.58 eV (Fig. S16b), both of which align well with the experimental result (4.38 eV and 3.69 eV). Fig. 4a and b show the total and partial density of states (DOS) of $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ and $(C_6N_2H_{15})Cd(SCN)_3$. For $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$, the upper valence bands near the Fermi level are mainly derived from Cl 3p orbitals and the bottom of conduction bands predominantly consists of Cd 5s orbitals, suggesting that $CdCl_5 \cdot H_2O$ polyhedra significantly influence the optical properties of $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$, while the contribution from the N,N -dimethylpiperazine cations remains minimal. In contrast, for $(C_6N_2H_{15})Cd(SCN)_3$, the upper valence bands near the Fermi level are predominantly composed of S 2p orbitals and SCN-N 2p orbitals. The bottom of conduction bands is mainly contributed by SCN-N 2p orbitals, SCN-C 2p orbitals, and S 2p orbitals together with a small amount of Cd 5s orbitals. This indicates that $Cd(SCN)_6$ polyhedra play a dominant role in the optical properties of $(C_6N_2H_{15})Cd(SCN)_3$, while the contribution from the N,N -dimethylpiperazine cations is negligible. To further elucidate these contributions, the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) were also calculated. Fig. 4c and d demonstrate that the HOMO and LUMO for $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ are mainly influenced by Cl 3p orbitals, O 2p orbitals, and Cd 5s orbitals. As presented in Fig. 4e and f, the HOMO of $(C_6N_2H_{15})Cd(SCN)_3$ is mainly occupied by SCN-N 2p orbitals and S 2p orbitals, while the LUMO consists of SCN-N 2p orbitals, SCN-C 2p orbitals, and Cd 5s orbitals.

Despite both $CdCl_5 \cdot H_2O$ and $Cd(SCN)_6$ adopting similar octahedral configurations, why does $(C_6N_2H_{15})Cd(SCN)_3$

exhibit much larger birefringence than $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$? Since macroscopic birefringence is closely related to the microscopic polarizability of functional groups, we calculated the polarizability tensors of $CdCl_5 \cdot H_2O$ and $Cd(SCN)_6$ octahedra.^{37,38} As demonstrated in Table S6, the polarizability tensor of $CdCl_5 \cdot H_2O$ remains almost the same along different directions with $\alpha_{xx} = 210.1 \text{ a.u.}$, $\alpha_{yy} = 212.5 \text{ a.u.}$, and $\alpha_{zz} = 207.1 \text{ a.u.}$ In contrast, in $Cd(SCN)_6$, the components of the polarizability tensor aligned with the polar $(SCN)^-$ chain direction ($\alpha_{xx} = 536.1 \text{ a.u.}$) are significantly larger than those of other directions ($\alpha_{yy} = 399.7 \text{ a.u.}$ and $\alpha_{zz} = 372.3 \text{ a.u.}$). In order to further visualize these differences, we plotted the unit sphere representation map of $CdCl_5 \cdot H_2O$ and $Cd(SCN)_6$ polyhedra.³⁷⁻³⁹ As shown in Fig. 4g and h, the lengths of large bidirectional arrows represent the total magnitude of polarizability along the X, Y, and Z directions, while the small arrows indicate the changes in dipole moment induced by an external electric field applied from the molecular center. The nearly spherical distribution for $CdCl_5 \cdot H_2O$ reflects its isotropic polarizability nature. In contrast, the polarizability tensor of $Cd(SCN)_6$ along the polar $(SCN)^-$ chain direction is significantly larger than those along other directions, indicating pronounced polarizability anisotropy. Quantitatively, the polarizability anisotropy ($\Delta\alpha$) of $Cd(SCN)_6$ reaches 155.7 a.u., which is considerably larger than that of $CdCl_5 \cdot H_2O$ ($\Delta\alpha = 6.3 \text{ a.u.}$) (Fig. 4i). Moreover, the 1D $Cd(SCN)_3$ chains are arranged in parallel within the crystal structure of $(C_6N_2H_{15})Cd(SCN)_3$, which facilitates the effective superposition of polarizability anisotropy, further inducing large optical birefringence of $(C_6N_2H_{15})Cd(SCN)_3$.

3. Conclusions

In summary, we present a polar pseudo-halogen substitution strategy that significantly enhances the birefringence of hybrid perovskites by over an order of magnitude—from 0.03@550 nm for $(C_6N_2H_{16})Cd_2Cl_6 \cdot 2H_2O$ to 0.37@550 nm for isostructural $(C_6N_2H_{15})Cd(SCN)_3$. Theoretical calculations and structural analyses confirm that the pronounced birefringence gap arises from the substantial increase in polarizability anisotropy induced by replacing halide Cl^- ions with pseudo-halogen $(SCN)^-$. Such a birefringence value of $(C_6N_2H_{15})Cd(SCN)_3$ exceeds those of all commercial birefringent crystals and ranks almost the highest among those for reported hybrid perovskites with non- π -conjugated organic cations. Combining the outstanding birefringence performance and ease of growth of large single-crystals of $(C_6N_2H_{15})Cd(SCN)_3$, this work establishes a scalable chemical design paradigm for developing outstanding birefringent crystals in the future.

Author contributions

All authors have given approval to the final version of the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

Experimental and characterization details are given in the article and supplementary information (SI). The Supplementary Information includes Experimental Section, XPS Analysis, Powder XRD, FTIR, Raman, Angle-resolved Polarized Raman, UV-Vis-NIR Diffuse Reflectance Spectroscopy, Birefringence Tests, Theoretical Calculations. See DOI: <https://doi.org/10.1039/d5qi02592c>.

CCDC 2467217 ((C₆N₂H₁₅)Cd(SCN)₃) and 2467218 ((C₆N₂H₁₆)Cd₂Cl₆·2H₂O) contain the supplementary crystallographic data for this paper.^{40a,b}

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