Electronic Supporting Information

Polymerization-Enhanced Optical Anisotropy in Selenites: A Trimeric [$H_2Se_3O_7$] Motif Delivering Large UV Birefringence

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Section S1. Experimental section

Structure determination and refinement. Suitable single crystals were selected under an optical microscope. Single-crystal X-ray diffraction data for $(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$ were collected at room temperature using a Rigaku XtaLAB diffractometer with graphite monochromatic Mo-Kα (λ = 0.71073 Å). The crystal structure was solved with the SHELXTL program package.[1] The atomic coordinates and anisotropic thermal parameters are refined by least-squares plane convergence based on the complete matrix of moments of F^2. Structural analysis was performed with the ADDSYM algorithm from the PLATON software, confirming no additional symmetries.[2]

Characterization of the Powder Sample. Powder X-ray diffraction (PXRD) analysis of the title compound was performed on a Shimadzu XRD-6100 system equipped with a monochromatic Cu-Kα source (λ = 1.5418 Å, 40 kV/30 mA). The angle range of 2θ is 5-50°, with a scanning step width of 0.05° and a scanning time of 0.2 s.

Thermal Behavior Analysis. Thermogravimetric analysis (TGA) was conducted utilizing a Netzsch STA 409 PC in a flowing N_2 atmosphere, with a heating rate of 10 °C/min and a temperature range of 30-800 °C. An empty Al_2O_3 crucible was employed as the reference material.

Infrared and UV-Vis Diffuse Reflectance Spectrum. Infrared spectrum was collected using a Vertex 70 Fourier Transform Infrared (FT-IR) spectrometer with a spectral range of 4000-400 cm^{-1}. KBr was used as a reference material. The crystals were thoroughly mixed and ground with KBr in an agate mortar, and then pressed into clear tablets approximately 1 mm thick and 10 mm in diameter using a specialized tablet press for testing. The UV-visible diffuse reflectance spectrum was recorded in the 200-800 nm range at room temperature using a Shimadzu UV-2600 spectrophotometer with $BaSO_4$ plates as standard (100% reflectance).

Theoretical Calculations. To investigate the band structure and optical properties of the title compounds, density functional theory (DFT)[3] calculations were performed.

To obtain the linear optical properties, the complex dielectric function

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

has been determined in the random phase approximation from the PBE wavefunctions. The imaginary part of the dielectric function due to direct inter-band transitions is given by the expression,

$$\varepsilon_2(\hbar\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{k,v,c}\left|\left\langle\psi_k^c\right|u\cdot r\left|\psi_k^v\right\rangle\right|^2\delta(E_k^c - E_k^v - E)$$

,

where Ω, ω, u, v and c are the unit-cell volume, photon frequencies, the vector defining the polarization of the incident electric field, valence and conduction bands, respectively. The real part of the dielectric function is obtained from ε_2 by a Kramers-Kronig transformation,

$$\varepsilon_1(\omega) = 1 + \left(\frac{2}{\pi}\right)\int_0^{+\infty} d\omega \frac{\omega'^2\varepsilon_2(\omega)}{\omega'^2 - \omega^2}.$$

To ensure energy convergence, a cutoff energy of 750 eV was applied. For $(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$, a Monkhorst-Pack k-point grid of 4 × 4 × 3 was used in the Brillouin zone, while a 6 × 6 × 5 grid was employed for $CsCl(H_2SeO_3)_2$.[4-5] The relevant analyses were performed using Multiwfn for the calculation of polarizability anisotropy.[6]

Table S1. Crystal data and structure refinement for $CsCl(H_2SeO_3)_2$ and $(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$.

Formula	**$CsCl(H_2SeO_3)_2$**	**$(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$**
Formula weight	426.31	408.3
Temperature(K)	293(2)	298.34(10)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	5.3224(2)	8.4541(8)
b (Å)	6.4994(3)	9.9920(5)
c (Å)	6.7116(3)	10.4237(11)
α (deg)	70.800(4)	73.076(7)
β (deg)	88.917(3)	70.505(9)
γ (deg)	79.738(4)	67.811(7)
V (Å^3)	215.552(17)	754.71(13)
Z	1	4
ρ_{calcd} (g/cm^3)	3.284	3.593
μ (mm^{-1})	13.025	14.862
F (000)	192.0	728.0
Goodness-of-fit on F^2	1.020	0.994
Final R indices $(I>2\sigma(I))^a R_1/wR_2$	R_1 = 0.0290, wR_2 = 0.0753	R_1 = 0.0354, wR_2 = 0.0748

$^aR_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2\ (F_o^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $CsCl(H_2SeO_3)_2$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cs1	10000	10000	5000	33.5(2)
Se1	5726.1(8)	6906.4(7)	1686.0(6)	26.56(19)
Cl1	10000	10000	0	29.0(3)
O1	3959(5)	4869(5)	2341(4)	33.3(7)
O2	8652(6)	5058(5)	2344(5)	40.0(8)
O3	5444(6)	7837(5)	3750(4)	34.2(7)
H1	4718.08	3790.59	3284.86	50
H2	9760(120)	5870(100)	1940(90)	60

Table S3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cs1	3808.7(4)	4720.3(4)	3222.2(4)	25.76(12)
Cs2	2908.3(5)	9184.6(4)	4151.5(4)	29.39(12)
Se1	924.3(7)	6088.6(6)	6937.0(6)	20.48(14)
Se2	-919.2(6)	8497.4(5)	2384.0(6)	18.22(14)
Se3	2050.9(6)	7555.5(5)	-269.4(6)	16.39(13)
Se4	5570.1(6)	7793.2(5)	27.5(6)	18.26(14)
Cl1	-1845.8(17)	9597.0(14)	9326.5(16)	26.6(3)
Cl2	4220.1(18)	8840.9(15)	-2904.2(16)	28.5(3)
O1	93(5)	8002(4)	6872(5)	31.7(10)
O2	-389(6)	6064(6)	5972(6)	34.8(11)
O3	2821(5)	5994(4)	5817(4)	27.9(9)
O4	-245(5)	8216(5)	3763(4)	30.6(10)
O5	-2321(5)	7421(4)	3039(4)	24.8(9)
O6	856(5)	7068(4)	1497(4)	27.1(9)
O7	2179(5)	6177(4)	-867(4)	26.3(9)
O8	4107(5)	6764(4)	216(4)	24.6(9)
O9	5623(5)	7380(4)	1650(5)	28.6(9)
O10	7427(5)	6484(4)	-720(5)	28.2(9)
H1	-2828	7515	2455	37
H2	263	8181	7685	48
H3	2070(60)	5440(30)	-250(20)	40
H4	-200	6490	5300	80(40)

Table S4. Selected bond lengths [Å] and angles [°] for $CsCl(H_2SeO_3)_2$.

Se(1)-O(3)	1.679(3)	Se(1)-O(1)	1.696(3)
Se(1)-O(2)	1.751(3)	O(3)-Se(1)-O(1)	103.36(14)
O(1)-Se(1)-O(2)	94.16(14)	O(3)-Se(1)-O(2)	101.01(16)

Table S5. Selected bond lengths [Å] and angles [°] for $(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$.

Se(3)-O(6)	1.624(3)	Se(1)-O(3)	1.626(4)
Se(4)-O(8)	1.819(3)	Se(2)-O(5)	1.739
Se(4)-O(10)	1.734(4)	Se(3)-O(8)	1.794(3)
Se(4)-O(9)	1.632(4)	Se(3)-O(6)	1.804(4)
Se(2)-O(6)	1.836(4)	Se(1)-O(2)	1.740(4)
Se(2)-O(4)	1.630(4)	Se(1)-O(1)	1.759(4)
Se(2)-Se(1)-O(1)	95.5(2)	O(3)-Se(1)-O(2)	103.3(2)
O(3)-Se(1)-O(1)	99.20(19)	O(4)-Se(2)-O(5)	98.9(2)
O(4)-Se(2)-O(6)	99.9(2)	Se(3)-O(6)-Se(2)	120.0(2)
O(9)-Se(4)-O(8)	96.75(18)	O(10)-Se(4)-O(8)	93.02(17)
O(7)-Se(3)-O(8)	97.42(19)	Se(3)-O(8)-Se(4)	124.2(2)
O(8)-Se(3)-O(6)	90.99(19)	O(7)-Se(3)-O(6)	98.9(19)
O(9)-Se(4)-O(10)	103.2(2)	O(5)-Se(2)-O(6)	92.38(18)

Table S6. Calculation of the density (ρ_s) of $[SeO_3]^{2-}$ atoms per unit cell for $CsCl(H_2SeO_3)_2$ and $(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$.

Compounds	n_s	V (Å^3)	ρ_s
$CsCl(H_2SeO_3)_2$	2	215.55	0.0093
$(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$	8	754.7	0.0106

Table S7. The quantity, density, and SCALPs-to-minimum-optical-axis angle (θ) of the $[H_2Se_3O_7]$ trimer and $[H_2SeO_3]$ monomer, and their contribution in $(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$.

Groups	n	ρ	cosθ	ρ*cosθ	Contribution
$[H_2Se_3O_7]$	3	0.00397	0.802	0.00318	73.6%
$[H_2SeO_3]$	2	0.00265	0.431	0.00114	26.4%

Table S8. Space group, band gap and birefringence of most polymerized selenites.

Compounds	Space group	Eg(eV)	Birefringence
$CsGa_3(SeO_3)_2(Se_2O_5)_3$	$P\bar{6}2c$	3.8	0.025@532nm
$CsAl_3(SeO_3)_2(Se_2O_5)_3$	$P\bar{6}2c$	2.66	0.035@532nm
$CsIn_3(SeO_3)_2(Se_2O_5)_3$	$P\bar{6}2c$	3.37	0.038@532nm
$Ga_2(Se_2O_5)_2(HSeO_3)(H_2SeO_3)F$	$Pna2_1$	4.71	0.051@532nm
$Ga(Se_2O_5)(HSeO_3)$	$P2_1/c$	4.34	0.108@532nm
$Gd(NO_3)(Se_2O_5)\cdot 3H_2O$	$P2_12_12_1$	5.53	0.109@1064nm
$(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$ (This work)	**$P\bar{1}$**	**4.2**	**0.188@546 nm**

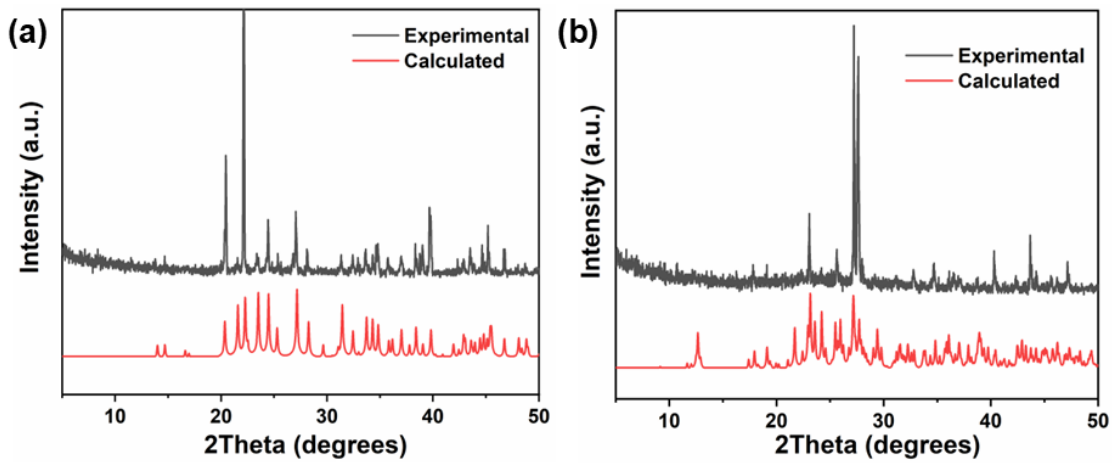

Figure S1. The calculated and experimental XRD patterns of $CsCl(H_2SeO_3)_2$ (a) and $(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$ (b).

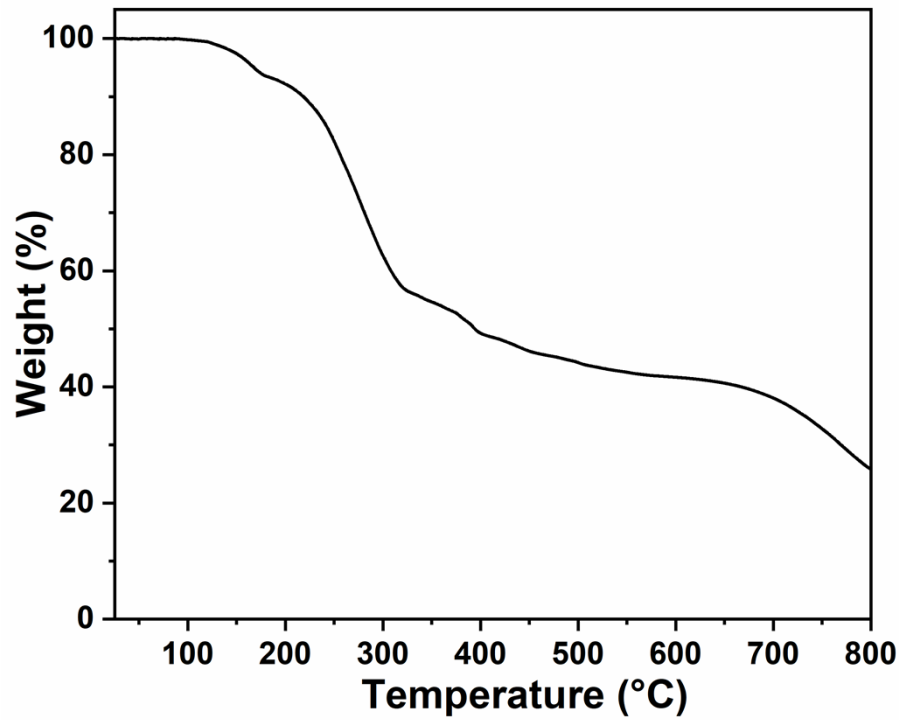

Figure S2. The TGA curve of $(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$.

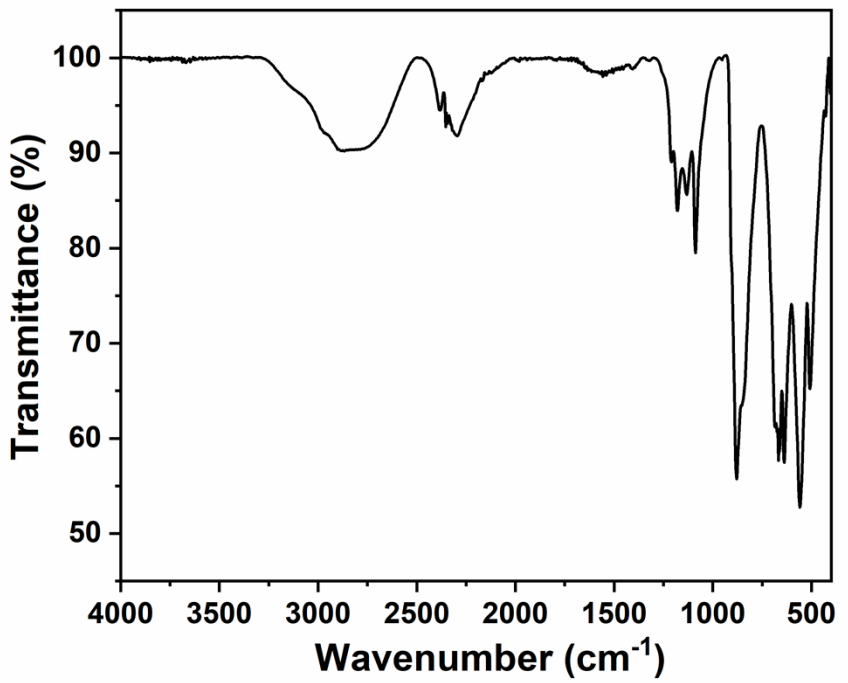

Figure S3. The IR spectrum of $(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$.

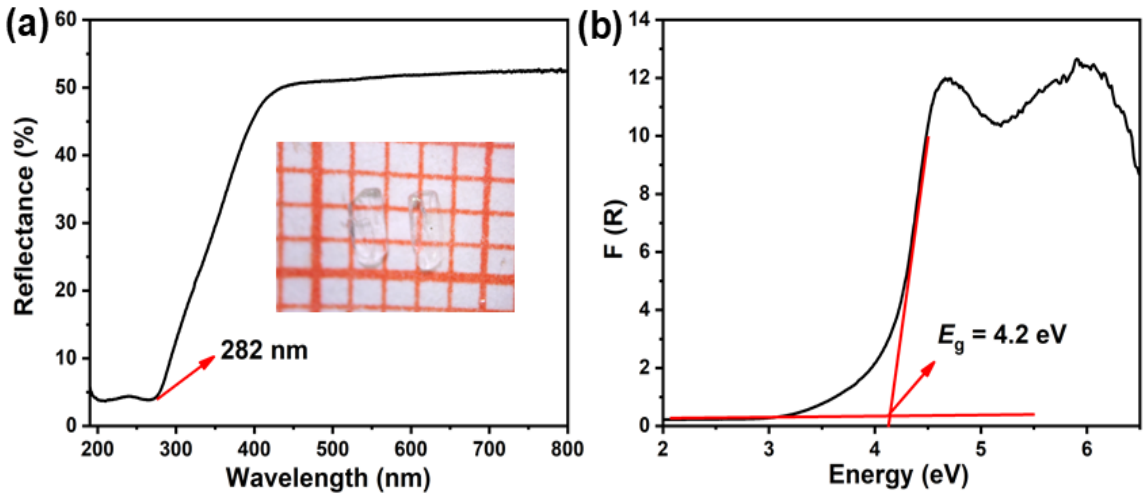

Figure S4. The UV-vis diffuse reflectance spectrum (a) and the bandgap (b) of $(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$. The embedded image shows the single crystals photograph of $(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$ (scale bar: 1 mm).

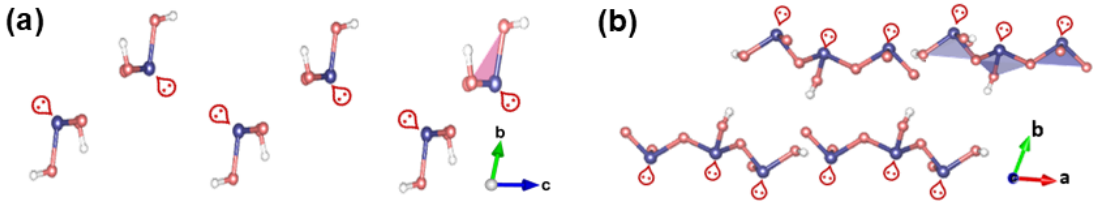

Figure S5. The arrangement of $[H_2SeO_3]$ units along the *a*-axis (a) and the arrangement of $[H_2Se_3O_7]$ trimers along the *c*-axis in $(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$.

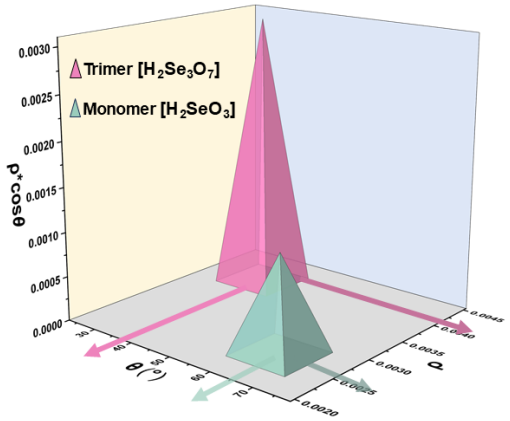

Figure S6. Comparison of the contributions to the birefringence ($\rho \times \cos\theta$) from the monomer $[H_2SeO_3]$ and the trimer $[H_2Se_3O_7]$ in $(CsCl)_2(H_2SeO_3)(H_2Se_3O_7)$. ρ represents the density of the respective selenite monomer or trimer within the unit cell, and θ is the angle between the SCALPs of the selenite groups and the optical axis.

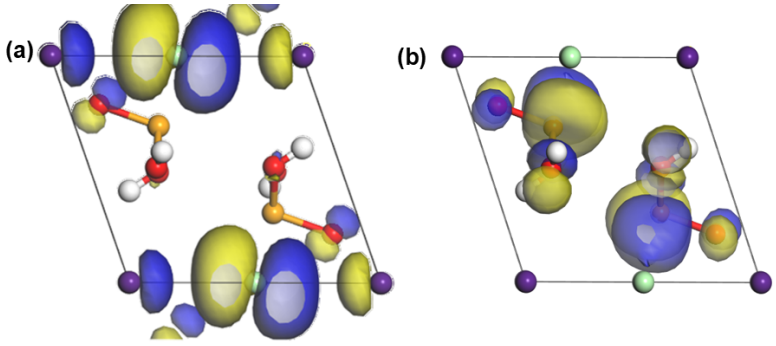

Figure S7. The HOMO-LUMO of $CsCl(H_2SeO_3)_2$.

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