

**Amine-directed synthesis, valence state control, and optical properties
of two new organic-inorganic tin chlorides**

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Table S1. Hydrogen bonds for compound **1**

| D-H···A ^a | d(D-H) (Å) | d(H···A) (Å) | d(D···A) (Å) | <(DHA) (deg) |
|----------------------|------------|--------------|--------------|--------------|
| N1-H1B···Cl3#1 | 0.98 | 2.12 | 3.078(5) | 166.8 |
| N2-H2···Cl4 | 0.98 | 2.05 | 3.005(8) | 163.9 |

^aSymmetry transformations used to generate equivalent atoms: #1 +X,1-Y,-1/2+Z.

Table S2. Hydrogen bonds for compound **2**

| D-H···A | d(D-H) (Å) | d(H···A) (Å) | d(D···A) (Å) | <(DHA) (deg) |
|-------------|------------|--------------|--------------|--------------|
| N1-H1···Cl1 | 0.98 | 2.52 | 3.234(4) | 129.3 |
| N1-H1···Cl6 | 0.98 | 2.59 | 3.372(4) | 136.7 |
| N2-H2···Cl7 | 0.98 | 2.06 | 3.024(4) | 166.8 |
| N3-H3···Cl7 | 0.98 | 2.10 | 3.062(4) | 168.6 |

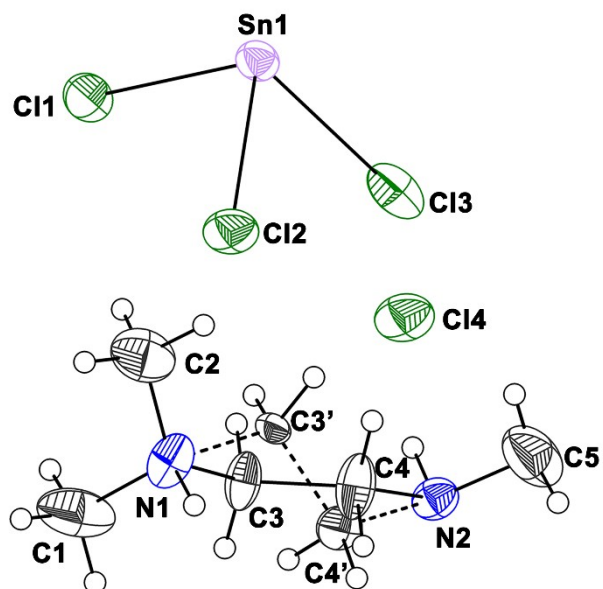


Fig. S1 ORTEP plot of the asymmetric unit of compound **1**, showing the labeling scheme and the 50% probability displacement ellipsoids.

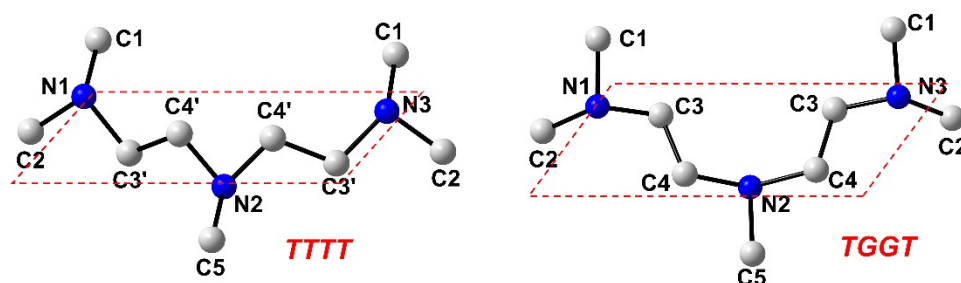


Fig. S2 The *TTTT*- and the *TGGT*- conformations of two different statistical positions of the pmdeta molecules in compound **1**.

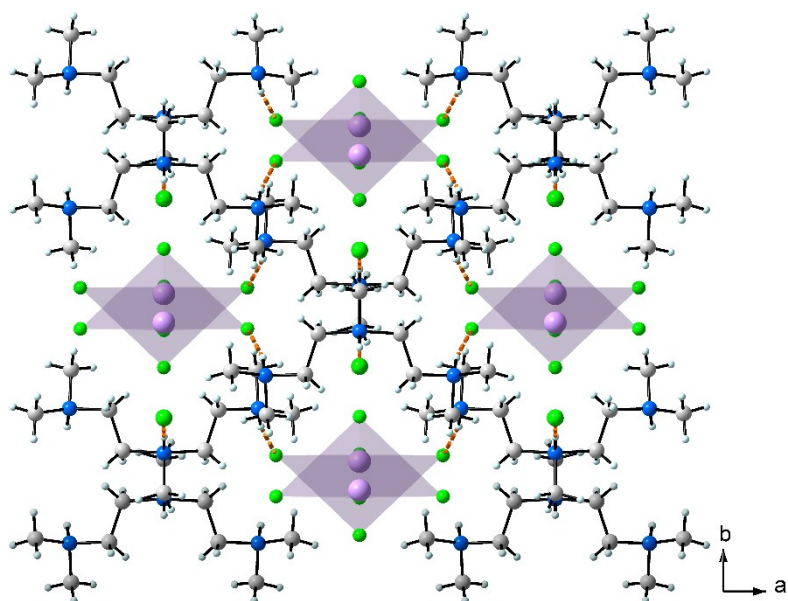


Fig. S3 View of the hydrogen-bonded interaction between organic SDAs and inorganic anions in compound **1**.

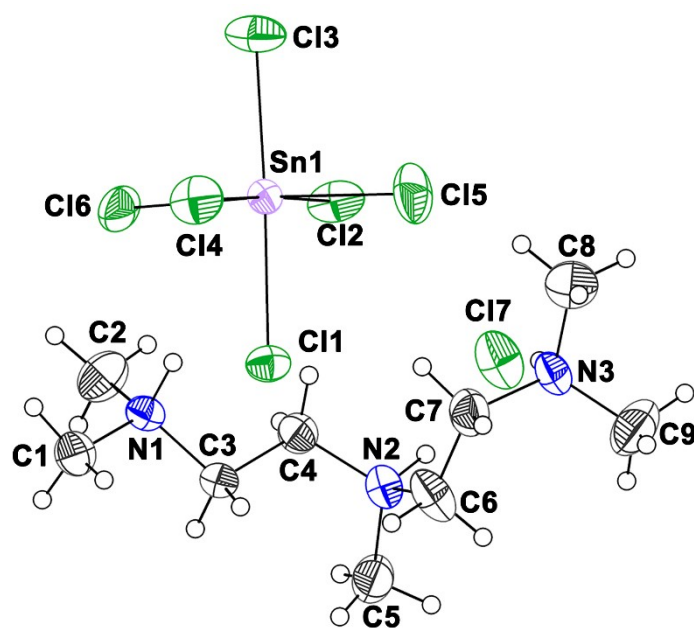


Fig. S4 ORTEP plot of the asymmetric unit of compound **2**, showing the labeling scheme and the 50% probability displacement ellipsoids.

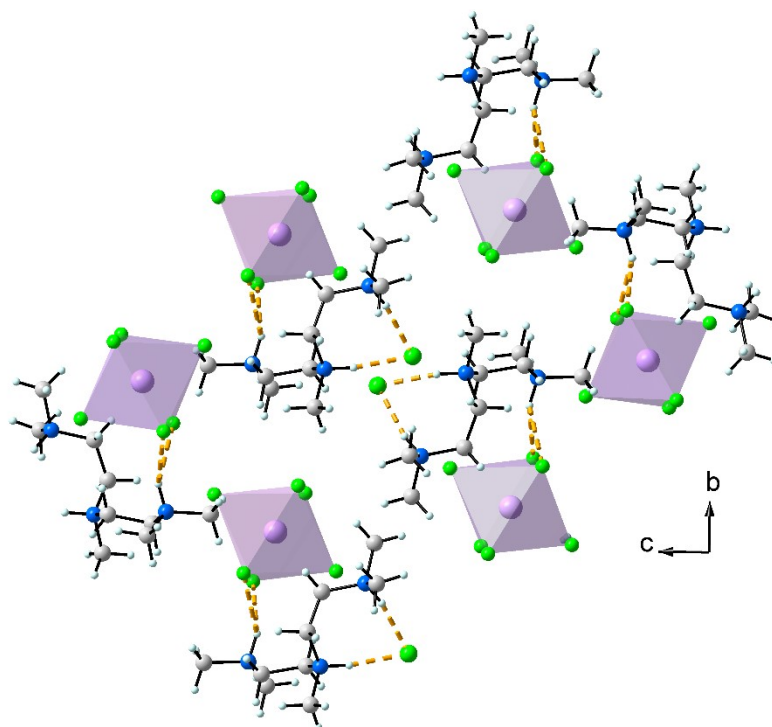


Fig. S5 View of the hydrogen-bonded interaction between organic SDAs and inorganic anions in compound **2**.

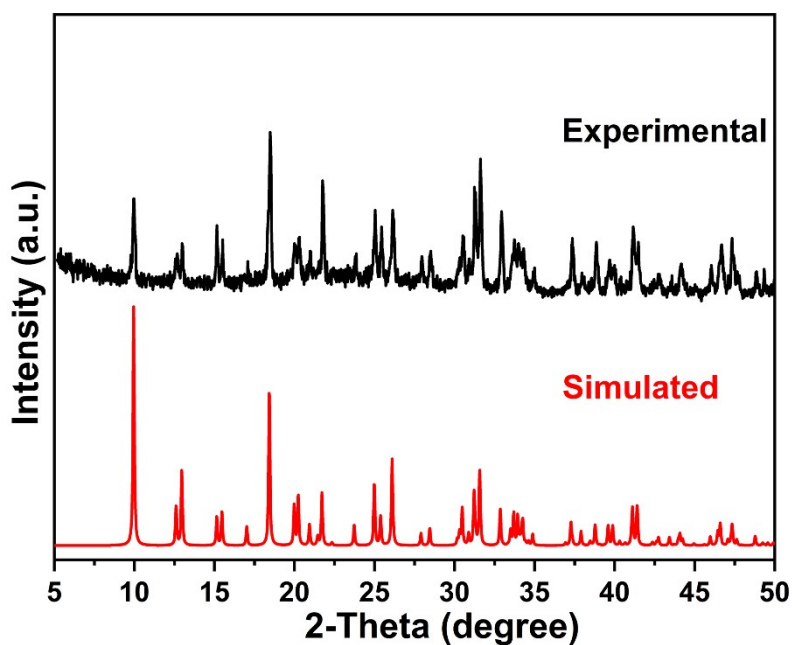


Fig. S6 Experimental and simulated XRD patterns for compound **1**.

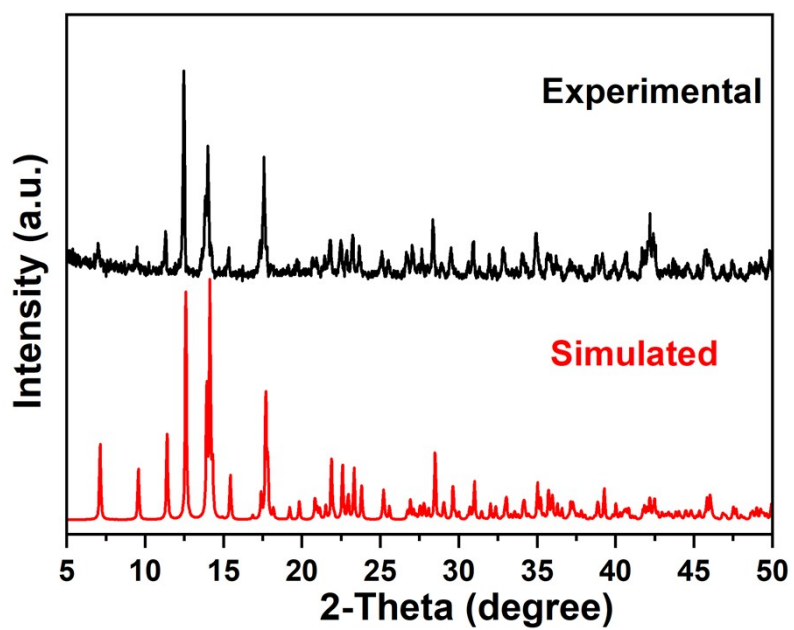


Fig. S7 Experimental and simulated XRD patterns for compound 2.

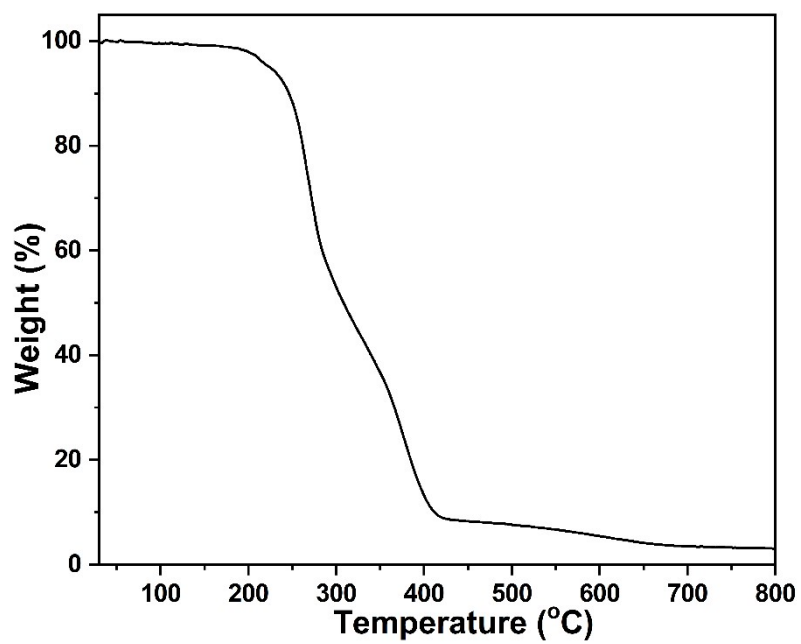


Fig. S8 TGA curve of compound 1 under N₂ atmosphere.

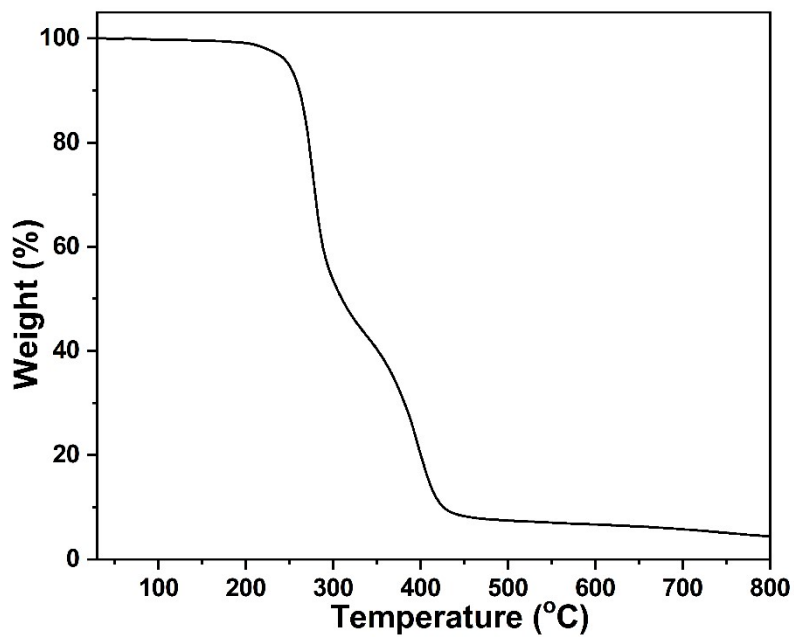


Fig. S9 TGA analysis of compound 2 under N₂ atmosphere.

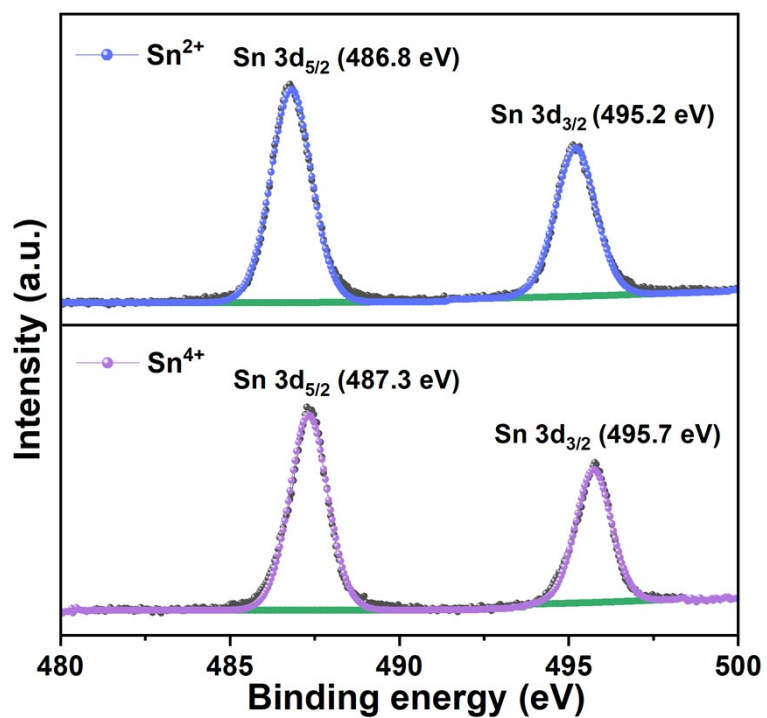


Fig. S10 Sn 3d XPS spectra of compounds 1 (top) and 2 (bottom).

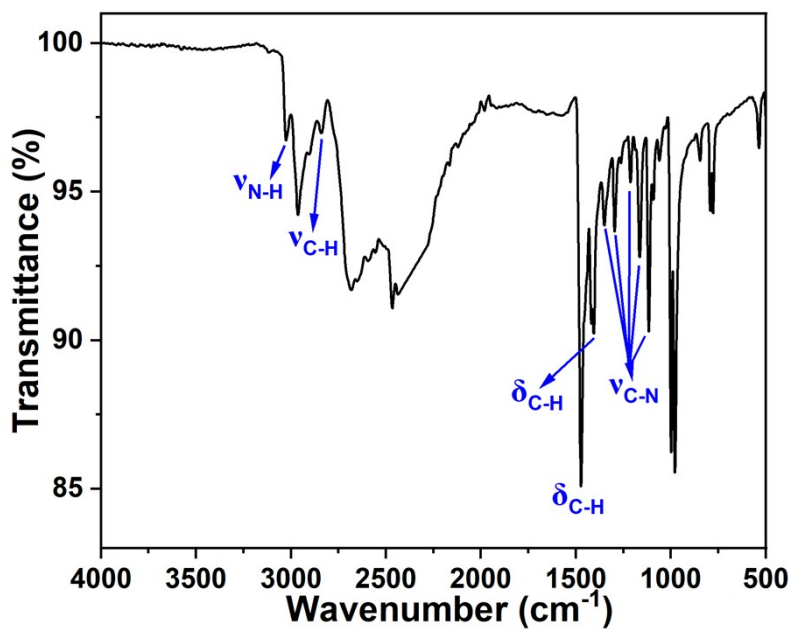


Fig. S11 IR spectrum of compound 1.

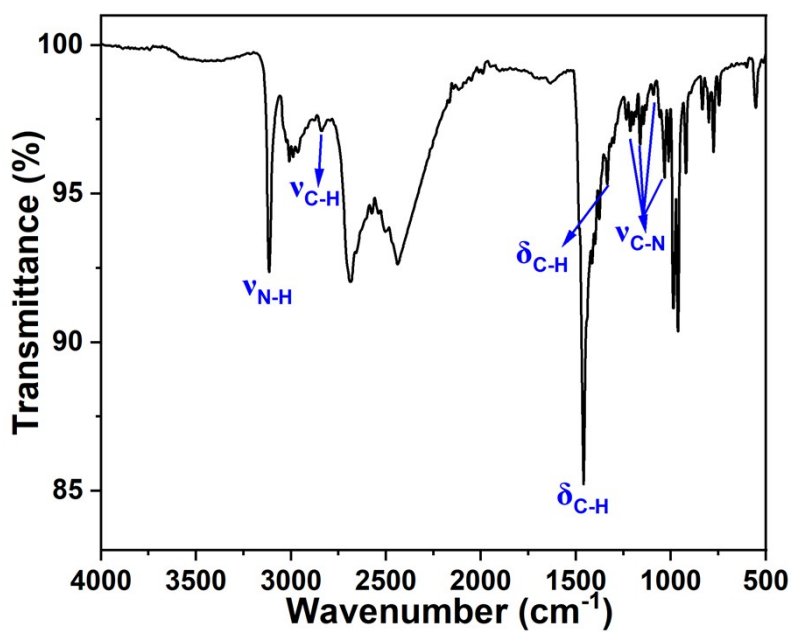


Fig. S12 IR spectrum of compound 2.

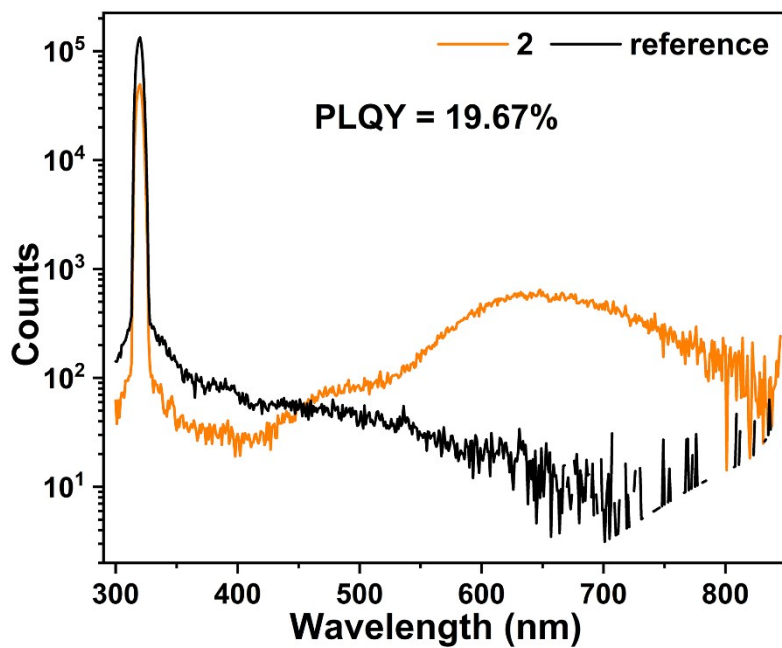


Fig. S13 The PLQY diagram of compound 2.

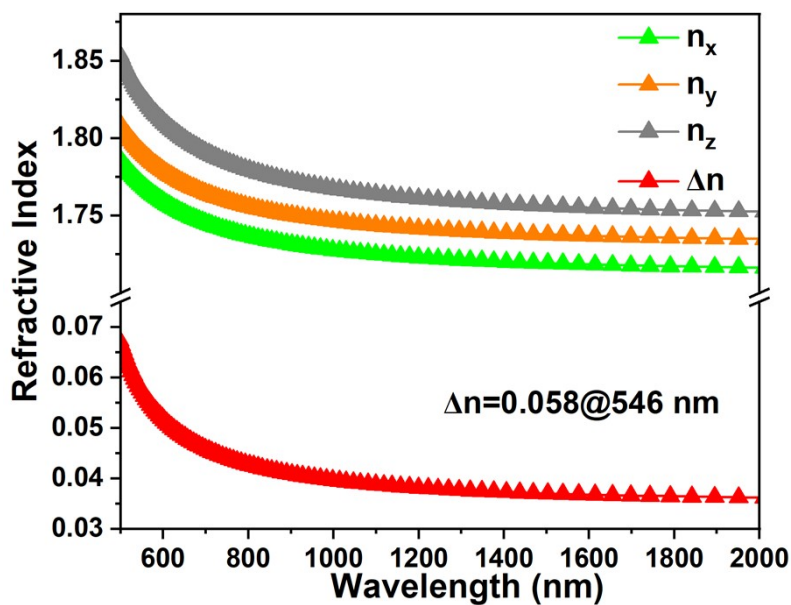


Fig. S14 Calculated dispersion of refractive index curves and birefringence of compound 1.

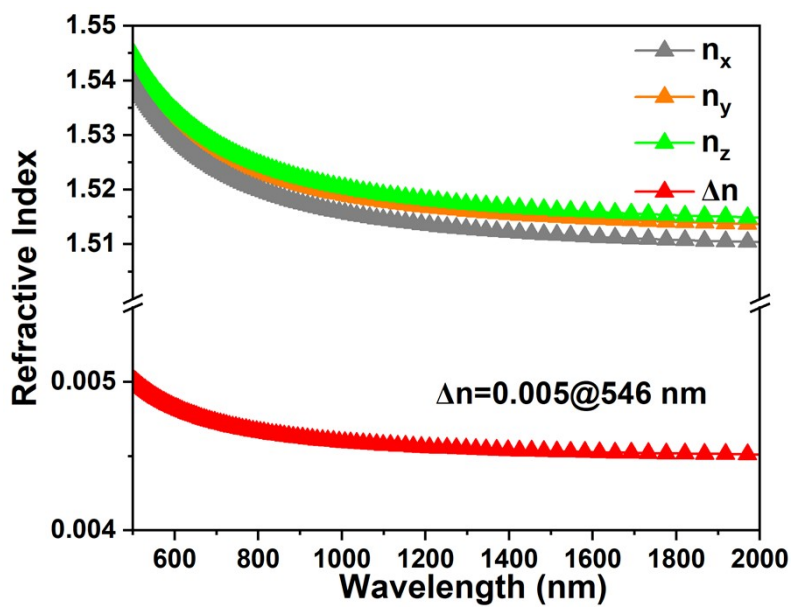


Fig. S15 Calculated dispersion of refractive index curves and birefringence of compound 2.