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PAPER

Discovery of a new type of organic ferroelectric materials in natural biomass dehydroabietylamine Schiff bases†

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Three kinds of Schiff bases, 5-chlorosalicylidene dehydroabietylamine (CIDHA), 5-bromosalicylidene dehydroabietylamine (BrDHA) and 5-nitrosalicylidene dehydroabietylamine (NODHA), have been prepared and characterized by elemental analyses, IR, circular dichroism (CD), and X-ray structural analyses. Ferroelectric, dielectric and NLO properties are reported for the first time in cheap natural biomass resource dehydroabietylamine derivatives and their ferroelectric properties can be easily tuned through the substituents of the aromatic aldehyde. With the increase in electron-withdrawing properties of the substituents from -Br to -Cl and then $-NO_2$, the P_s values or the ferroelectric properties gradually increased.

Introduction

Ferroelectricity is one of the major subjects in the field of materials science due to its wide applications in ferroelectric random-access memories (FeRAM), switchable nonlinear optical devices, electro-optical devices, and light modulators.¹ Since the discovery of ferroelectricity in Rochelle salt in 1920, many efforts have been ongoing towards the design and synthesis of noncentrosymmetric ferroelectric compounds.²⁻⁴ But much of the attention in this field has been focused on developing ferroelectric and high-dielectric inorganic or inorganic-organic hybrid compounds such as KH₂PO₄ (KDP), BaTiO₃, LiNbO₃, CaCu₃Ti₄O₁₂ and triglycine sulfate (TGS) etc.⁵ To the best of our knowledge, pure organic ferroelectrics, especially low-molecularmass organic ferroelectrics, still remain sparse.⁶ However, ferroelectric materials based on organic compounds may be particularly important in organic electronics. One of the merits of low-molecular-mass organic compounds is applicability with solution and/or dry processes such as spin-coating, spray-on, inkjet printing and vapor-phase deposition techniques. This would be also advantageous in the fabrication of flexible, lightweight, large-area, low-cost organic devices. Therefore, allorganic electronic and photonic devices have gained great interest.7 Recently, we have reported a new type of ionic

ferroelectric based on Schiff base nickel coordination complexes with polarization values higher than KDP.8 As an extension of our interest in molecular ferroelectric materials, we turned to the ferroelectric properties of pure organic compounds.

Biomass resources have attracted great interest in both industry and fundamental research, not only because of their abundance and biodegradation ability, but also due to their special structures containing several chiral centers.9 Dehydroabietylamine is a naturally occurring enantiomeric pure diterpenic amine with the hydrophanthrene structure.¹⁰ The chirality in the dehydroabietylamine molecule prompts us to study the ferroelectric property of this compound. In this paper, we report the crystal structures, ferroelectric, dielectric and NLO properties of dehydroabietylamine Schiff bases (CIDHA, BrDHA and NODHA, Scheme 1). To the best of our knowledge, it is the first time that ferroelectricity was discovered in cheap natural biomass resource dehydroabietylamine derivatives.

Experimental section

General materials and methods

All reagents and solvents were purchased from commercial sources and used as received. Elemental analyses for C, H, and N were performed on a CHN-O-Rapid analyzer and an Elementar Vario MICRO analyzer. The IR spectra were taken on a Bruker Vector 22 FT-IR spectrometer with KBr discs in the 4000-400 cm⁻¹ range. The ¹H NMR spectra were recorded with a Bruker DRX 500 spectrometer at 500 MHz. The CD spectra were recorded on a JASCO J-810 Spectropolarimeter. The electric hysteresis loops were recorded on a Ferroelectric Tester Precision Premier II made by Radiant Technologies, Inc. The temperature dependence of the dielectric constant and dielectric loss at

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[†] Electronic supplementary information (ESI) available: E-P hysteresis of powdered samples, leakage currents. X-Ray crystallographic files (CIF) for BrDHA and NODHA. CCDC reference numbers 806391 and 806392. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/c0jm03461d



Scheme 1 Synthesis of dehydroabietylamine Schiff bases.

10⁰–10⁶ Hz frequencies were measured using a dielectric impedance analyzer, Concept 80 system (Novocontrol, Germany).

Synthesis of dehydroabietylamine Schiff bases

CIDHA. A mixture of dehydroabietylamine (10 mmol, 2.85 g), 5-chlorosalicylaldehyde (10 mmol, 1.56 g) and methanol (200 ml) was refluxed for 2 h, and then cooled to room temperature. The precipitate was collected and dried under vacuum. The product was then dissolved in methanol and the solution was left to stand undisturbed. Upon slow evaporation at room temperature for several days, yellow single crystals of the title compound were collected. m.p.= 451 K. FT-IR (KBr, cm⁻¹): 2929(s), 1634(s), 1606(m), 1574(m), 1482(s). Anal. Calcd. for C₂₇H₃₄ClNO: C, 76.48, H, 8.08, N, 3.30. Found: C, 76.43, H, 8.23, N, 3.47%. ¹H NMR (500 MHz, CDCl₃): δ 8.267 (s, 1H, CH=N), 6.903–7.284 (m, 6H, Ph), 3.464–3.540 (m, 2H, N–CH₂), 1.071–2.855 (m, 24H, aliphatic cyclo).

BrDHA. BrDHA was synthesized by a similar method to **CIDHA** except 5-bromosalicylaldehyde was used instead of 5-chlorosalicylaldehyde. m.p.= 457 K. FT-IR (KBr, cm⁻¹): 2928 (s), 1632(s), 1602(m), 1570(m), 1478(s). Anal. Calcd. for C₂₇H₃₄BrNO: C, 69.22, H, 7.32, N, 2.99. Found: C, 69.01, H, 7.20, N, 2.87%. ¹H NMR (500 MHz, CDCl₃): δ 8.257 (s, 1H, CH=N), 6.902–7.403 (m, 6H, Ph), 3.459–3.539 (m, 2H, N–CH₂), 1.070–2.843 (m, 24H, aliphatic cyclo).

NODHA. NODHA was prepared by a similar method to **CIDHA** except 5-nitrosalicylaldehyde was used instead of 5-chlorosalicylaldehyde. m.p.= 469–470 K. FT-IR (KBr, cm⁻¹): 2927(s), 1639(s), 1615(m), 1543(m), 1478(w). Anal. Calcd. for $C_{27}H_{34}N_2O_3$: C, 74.62, H, 7.89, N, 6.45. Found: C, 74.48, H, 7.76, N, 6.37%. ¹H NMR (500 MHz, CDCl₃): δ 8.267 (s, 1H, CH=N), 6.903–7.284 (m, 6H, Ph), 3.464–3.540 (m, 2H, N–CH₂), 1.071–2.855 (m, 24H, aliphatic cyclo).

X-Ray crystallography

Diffraction intensities for **CIDHA**, **BrDHA** and **NODHA** were collected at 293(2) K on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using SADABS.¹¹ The structures were solved by direct methods and refined with the full-matrix least-squares technique using

SHELXS-97 and SHELXTL-97 programs, respectively.¹² Anisotropic thermal parameters were applied to all nonhydrogen atoms. The H atoms were positioned geometrically and treated as riding on their parent atoms, with C–H distances of 0.97 Å (methylene) and 0.96 Å (methyl). Crystal data as well as details of data collection and refinement for the compounds are summarized in Table 1. The structure of **CIDHA** has been reported by others previously.¹³

Results and discussion

Crystal structural descriptions

Due to the structural similarity of **CIDHA**, **BrDHA** and **NODHA**, only **BrDHA** will be discussed in detail as an example. As shown in Fig. 1a and 1b, **BrDHA** contains four crystallographically distinct six-membered rings (A, B, C and D). The two rings A and D are planar and the dihedral angle between them is $104.2(3)^{\circ}$. Whereas rings B or C are not planar, and the internal torsion angles indicated that a half-chair and a chair conformation were adopted by them, respectively. **BrDHA** contains three chiral centers in the C9, C13 and C14 atoms, with *R*, *S* and *R* absolute configurations, respectively. There is an intramolecular O–H…N hydrogen bond; the O1–H1, H1…N1, O1… N1 distances and O1–H1…N1 angle are 1.05 Å, 1.54 Å, 2.570(6) Å and 162.6°, respectively.

NODHA has a similar crystal structure to **BrDHA** (Fig. 2), but there is a non-classical intermolecular C–H···O hydrogen bond besides an intramolecular O–H···N hydrogen bond. The O3–H3, H3···N1, O3···N1 distances and O3–H3···N1 angle are 0.82 Å, 1.81 Å, 2.544(4) Å and 148.8°, respectively. The C8–H8B, H8B··· O1, C8···O1 distances and C8–H8B···O1 angle are 0.97 Å, 2.41 Å, 3.146(5) Å and 132.4°, respectively. Its symmetry code is: -x, y-1/2, -z.

Circular dichroism (CD) spectra

To confirm the optical activity of **CIDHA**, **BrDHA** and **NODHA**, the circular dichroism (CD) spectra were measured in methanol solutions (Fig. 3). **CIDHA** exhibits negative Cotton effects at *ca*. $\lambda_{max} = 220$, 253 and 331 nm and a positive signal at *ca*. $\lambda_{max} = 210$ nm; **BrDHA** exhibits negative Cotton effects at *ca*. $\lambda_{max} = 213$, 254 and 325 nm and a positive signal at *ca*. $\lambda_{max} = 221$ nm. Similarly, **NODHA** exhibits negative Cotton effects at *ca*. $\lambda_{max} = 260$ and 387 nm and a positive signal at *ca*. $\lambda_{max} = 222$ nm.

Table 1	Crystal data	and structure	refinements for	CIDHA,	BrDHA	and NOD	HA
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Compound	CIDHA	BrDHA	NODHA	
Empirical formula	C ₂₇ H ₃₄ ClNO	C ₂₇ H ₃₄ BrNO	C ₂₇ H ₃₄ N ₂ O ₃	
Formula weight	424.00	468.46	434.56	
Crystal system	Monoclinic	Monoclinic	Monoclinic	
Space group	$P2_1$	$P2_1$	$P2_1$	
alÅ	11.249 (2)	11.264 (4)	11.1580 (17)	
b/Å	6.1790 (12)	6.189 (2)	6.2046 (10)	
c/Å	17.276 (4)	17.301 (6)	17.347 (3)	
β (°)	103.04 (3)	102.785 (7)	101.490 (3)	
VÅ ³	1169.8 (4)	1176.2 (8)	1176.9 (3)	
Ζ	2	2	2	
$D_c/Mg m^{-3}$	1.204	1.323	1.226	
θ range [°]	10-13	2.69-20.72	2.40-19.22	
Collected reflections	2657	6409	7421	
Unique reflections	2526	4196	4172	
Parameters	275	275	295	
T/K	293 (2)	293 (2)	293 (2)	
$R_1 [I > 2\sigma(I)], wR_2 (all data)^a$	0.061, 0.16	0.053, 0.119	0.047, 0.099	
GOF	1.06	1.02	0.99	
Flack parameter	0.07 (18)	-0.010(13)	0.1(1)	



Fig. 1 (a, top) Crystal structure of **BrDHA** (30% probability thermal ellipsoids). (b, bottom) The ring conformations of **BrDHA** (30% probability thermal ellipsoids, H atoms omitted for clarity).



Fig. 2 Crystal structure of NODHA (30% probability thermal ellipsoids).

Ferroelectric and nonlinear optical properties

As CIDHA, BrDHA and NODHA crystallize in a chiral polar space group $(P2_1)$, belonging to the polar point (C_2) , their second



Fig. 3 Circular dichroism (CD) spectra of ClDHA, BrDHA and NODHA in methanol solutions.

nonlinear optical and ferroelectric properties were examined. The second-order nonlinear optical effects were determined on a LAB130 Pulsed Nd:YAG laser according to the principle proposed by Kurtz and Perry,¹⁴ and preliminary studies of powder samples of CIDHA, BrDHA and NODHA showed second harmonic generation (SHG) efficiency with approximately 0.5, 0.4 and 1.2 times that of urea, respectively. This implied that the three compounds were all dipolar active compounds.

The ferroelectric behaviors of CIDHA, BrDHA and NODHA were also examined given that point group C_2 was one of the ten polar point groups required for ferroelectric materials.¹⁵ Under the symmetry operation of 2-fold screw axes, the components of the dipole vector are cumulative along the *b* axis and cancellative along other axes. Therefore, the three compounds may have a significant ferroelectric effect along the *b* axis for the single crystal samples. The ferroelectric properties were investigated at room temperature with single crystal samples and recorded on

a Ferroelectric Tester Precision Premier II made by Radiant Technologies, Inc. The ferroelectric measurements along the polar b axis revealed obvious hysteresis loops for all the three compounds. The hysteresis loops of BrDHA are shown in Fig. 4 as an illustrative example and the others are given in Fig. S1 in the ESI.[†] The summarized results (Table 2) indicated that all the three compounds indeed displayed obvious ferroelectric behavior with remnant polarization (P_r) between 31.8 and 34.5 μ C cm⁻², and coercive field (E_c) between 2.63–4.73 kV cm⁻¹. The saturation spontaneous polarization (P_s) was between 44.3 and 86.5 μ C cm⁻², which was close to that of typical inorganic single crystal ferroelectric materials such as BaTiO₃,¹⁶ PbTiO₃¹⁷ etc. More importantly, as shown in Table 2, the P_s values are directly related to the substituents of the aromatic aldehydes. With the increase in electron-withdrawing properties of the substituents from -Br to -Cl and then $-NO_2$, the P_s values or the ferroelectric properties gradually increased. This provides us a useful message that the ferroelectricity of dehydroabietylamine Schiff bases can be easily tuned through the variation of the substituents of the aromatic aldehydes.

To further confirm the ferroelectricity of CIDHA, BrDHA and NODHA, the ferroelectric properties of powdered samples in pellets were also investigated at room temperature (Fig. S2 in the ESI[†]). The observed hysteresis loops and the low leakage currents (less than 10⁻⁷ A cm⁻²; Fig. S3 in the ESI[†]) indicated that the three compounds indeed display obvious ferroelectric behavior and the observed hysteresis loops were clearly due to ferroelectricity. The saturation spontaneous polarization (P_s) of powdered samples are much smaller than the corresponding single crystal samples, the reason should be due to the irregular arrangement of the polar direction in powdered samples. In addition, the leakage currents of single crystal samples are also lower than 10⁻⁷ A cm⁻² (Fig. S4 in ESI[†]).

Dielectric properties

Polarization (µC/cm²

20

-20

-40

-60

Due to the structural similarity of the three compounds, only CIDHA was selected to investigate the dielectric properties. The temperature dependence of the dielectric constant and dielectric loss of CIDHA were measured at various frequencies in the range of 10°-106 Hz. A dielectric constant peak appears at about 390 K

5.00kV/cm

5.71kV/cm

6.07kV/cm

6 43kV/cm

6.79kV/cm

7.14kV/cr

4

-6



ò 2 4

Table 2 Ferroelectric measurement results for single crystal samples along the b axis

Compound	$P_{\rm s}$ (µC cm ⁻²)	$P_{\rm r}~(\mu{\rm C~cm^{-2}})$	$E_{\rm c}~({\rm kV~cm^{-1}})$
CIDHA	44.3–74.5	44.3–74.5	2.63–4.73
BrDHA	49.4–69.0	31.8–45.9	3.28–4.63
NODHA	61.5–86.5	38.2–52.5	2.81–3.63

indicating the presence of a phase transition (Fig. 5a). The peak slightly moves toward lower temperature and the height decreases with increasing frequency. As shown in Fig. 5b, a relaxation process was also observed, indicating that dielectric loss changes with temperature at different frequencies.

Conclusions and perspectives

In this paper, three dehydroabietylamine Schiff bases have been synthesized by using dehydroabietylamine and aromatic aldehydes with different electron-withdrawing substituents. The ferroelectric, dielectric and NLO properties are reported for the first time in cheap natural biomass resource dehydroabietylamine derivatives. The results demonstrate that the ferroelectricity can be tuned through the substituents of the aromatic aldehyde. With the increase in electron-withdrawing properties of the



Fig. 5 (a, top) Temperature dependence of the dielectric constant ϵ' (real part) of CIDHA at various frequencies (10º-106 Hz). (b, bottom) Temperature dependence of the dielectric loss ϵ''/ϵ' , where ϵ'' and ϵ' are the imaginary and real parts of the dielectric constant for CIDHA, at various frequencies (10º-106 Hz).

substituents from –Br to –Cl and then –NO₂, the P_s values or the ferroelectric properties gradually increased. It can be predicted that these properties can be further improved by replacing the substituents with groups with higher electron-withdrawing properties, such as –F, –CF₃ *etc.* or with multiple electron-withdrawing groups. Further studies on the improvement of the ferroelectricity of pure organic compounds are still under way in our laboratory.

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