Optimizing Optical Anisotropy in Low-Dimensional Structures via Intralayer Hydrogen Bonding Modulation and Anionic Substitution

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Table of contents

1. Experimental Section

1.1. Synthesis and Crystal Growth

The reactants, $C_4H_5N_3$ (≥ 99 %), H_3PO_4 (≥ 85 % in H_2O), HBF_4 (≥ 40 % in H_2O), CF_3SO_3H (≥ 98 % in H_2O), NH_2SO_3H (≥ 99 %), CH_3SO_3H (≥ 70 % in H_2O), $C_4H_6O_4$ (≥ 99 %), and H_3BO_3 (≥ 99) were purchased from Aladdin Chemistry Aladdin Chemical Industry Co., Ltd., and used without further purification. Single crystals of all seven compounds were obtained using a solvent diffusion method. A (1:1) molar ratio of $C_4H_5N_3$ along with H_3PO_4 and $C_4H_6O_4$ in 20 mL (3:water + 2:ethanol) solvent for **I-1** and **III** while (1:1) molar ratio of $C_4H_5N_3$ along with HBF_4, CF_3SO_3H, NH_3SO_3, CH_3SO_3H and H_3BO_3 for **I-2**, **II-1**−**II-3** and **IV** were dissolved in 20 mL ethanol solvent in a clean beaker while stirring using magnetic stirrer until the solution became clear, filtered it to remove any suspended impurities. Then the solution was covered by parafilm and we made small holes to control the evaporation rate and kept it undisturbed at ambient temperature to evaporate. Good optical quality cocrystals of centimeter-sized and millimeter-sized single crystals were harvested from the mother solution within several weeks.

1.2. Characterization

Single crystals of **I-1**−**I-2**, **II-1**−**II-3**, **III**, and **IV** used in the single-crystal X-ray diffraction (XRD) data measurement were separated under a polarization contrast microscope. Single-crystal XRD data were collected at room temperature by a Bruker D8 Venture CMOS X-ray diffractometer with Mo Kα radiation (λ = 0.71073 Å). Intensity corrections for Lorentz and polarization effects were performed with the SAINT program.[1] The structure solution and parameter refinement (full-matrix least-squares against F^2) were performed by using the SHELX-14 suite on olex2 software with anisotropic displacement parameters for all atoms.[2] The structural data were also inspected for possible missing symmetries using the PLATON program and no higher symmetries were found.[3] The summary of the key crystallographic parameters of the crystals **I-1**−**I-2**, **II-1**−**II-3**, **III**, and **IV** is provided in Table S1. The final refined atomic positions and selected bond distances and angles are given in Table S3. The polycrystalline powder samples of **I-1**−**I-2**, **II-1**−**II-3**, **III**, and **IV** were acquired by grinding the as-grown crystals directly. The purity of these samples was subsequently validated through X-ray diffraction analysis. Powder XRD measurements were performed on Bruker D2 Advance X-ray diffractometer using monochromated Cu Kα radiation (λ = 1.5418 Å, 2θ = 5 to 70 °, scan step width = 0.02 °, and counting time = 1 s/step). The powder XRD patterns for **I-1**−**I-2**, **II-**

1−**II-3**, **III**, and **IV** are shown in Figure S1, and it is clear that the experimental profiles are in line with the simulated ones. Elemental analyses were measured using an energy dispersive X-ray spectrometer (Oxford, X-Max 50) operated at 5 kV was utilized for examining the EDS spectrum at room temperature using a scanning electron microscope with field emission scanning electronic microscope (FE-SEM, JEOL JSM-7610F Plus, Japan) (Figure S12). The NETZSCH STA 449C thermal analysis instrument was used to test the thermal habit of **I-1**−**I-2**, **II-1**−**II-3**, **III**, and **IV**. The test conditions were performed by heating the polycrystalline powder samples from 40 to 600 °C at a constant rate of 5 °C/min under a flowing nitrogen atmosphere (Figure S3). Infrared (IR) spectra were recorded on a Shimadzu IR Affinity-1 IR spectrometer ranging from 4000 to 400 cm^{-1} to verify functional groups. The spectral resolution is about 1 cm^{-1}. The samples were pressed into discs (1 mg of the sample and 200 mg of KBr) (Figure S4). UV-vis-NIR diffuses reflectance spectra were measured with a Shimadzu SolidSpec-3700 DUV spectrophotometer in the wavelength range of 200-2000 nm (Figure S2). The spectral resolution is about 0.1 nm. The Kurtz–Perry method was employed for powder second harmonic generation (SHG) measurements of **A-1** and **B-1** using a Q-switched Nd: YVO4 solid-state laser with an incident wavelength of 1064 nm. Before measurements, polycrystalline samples of the aforementioned compounds were finely ground into powder and divided into six different particle size ranges (20−38, 38−55, 55−88, 88−105, 105−150, 150−200, and 200−250 μm). Additionally, microcrystalline KDP samples were sieved into the same particle size ranges and used as references for SHG. Subsequently, all microcrystalline samples were placed between microscope cover glass slides with a diameter of 6 mm and secured with 1 mm thick tape.[4] Birefringence measurements were conducted using a ZEISS Axio Scope polarizing microscope equipped with a Berek compensator. Small crystals were carefully chosen for measurement at a wavelength of 546 nm. The birefringence was calculated using the equation (1).

$$R = |N_e - N_o| = \Delta n \times T \quad (1)$$

where R denotes the optical path difference, Δn represents the birefringence, and T signifies the thickness of the crystal (Figure S11). Molecular Hirshfeld surfaces and related 2D fingerprint plots of **I-1**−**I-2**, **II-1**−**II-3**, **III**, and **IV** were produced using a CIF file to analyze the crystal structures generated by the Crystal Explorer program. The normalized contact distance (d_{norm}) depends on the atom's *di* and *de* (the distance from Hirshfeld surface to the nearest nucleus inside and outside, respectively) as well as the van der Waals radii of the atoms given by the equation (2).

$$d_{norm} = \frac{d_i - r_i^{vdw}}{r_i^{vdw}} + \frac{d_e - r_e^{vdw}}{r_e^{vdw}} \quad (2)$$

Where r_i^{vdw} and r_e^{vdw} are the van der Waals radii of the atoms internal and external to the surface, respectively (Figure S7) .

1.3. Theoretical Calculations

The electronic structure calculations were performed by first-principles calculation in the CASTEP package, with the norm-conserving pseudopotentials (NCPs).[5] The Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was applied for the exchange-correlation potential.[6] The interactions between the core and valence electrons were represented by the norm-conserving pseudopotentials, and the following valence configurations were regarded: C, $2s^2 2p^2$; N, $2s^2 2p^3$; H, $1s^1$; F, $2s^2 2p^5$; S, $3s^2 3p^4$; O, $2s^2 2p^4$; P, $3s^2 3p^3$; B, $2s^2 2p^1$. The kinetic energy cutoffs of **I-1**−**I-2**, **II-1**−**II-3**, **III** were set as 750, 850, 850, 600, 830 and 750 eV in the Brillouin zone.[7] The Monkhorst–Pack k-point meshes of **I-1**−**I-2**, **II-1**−**II-3**, **III** were set as 6×3×1, 7×2×5, 3×3×3, 2×4×5, 5×2×2 and 4×1×3. Because of the discontinuity of exchange-correlation energy, the calculated band gaps by GGA-PBE were usually underestimated. A scissor operator was adopted to shift all the conduction bands to match the calculated band gaps with the measured value for the optical properties calculations. A post-processing tool, namely, the SHG-density was performed to further explore the contribution of atoms or groups to the SHG response based on the SOS method through CASTEP package.[8-9]

The orbitals and polarizability anisotropy for $[C_4H_5N_3]$, $[C_4H_6N_3]^+$, $[H_2PO_4]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$, $[NH_2SO_3]^-$,$[CH_3SO_3]^-$, $[C_4H_6O_4]$ units at the molecular level were calculated using DFT method implemented in the Gaussian09 package[10] B3LYP (Becke, three-parameter, Lee-Yang-Parr) exchange-correlation functional[11] with the Lee–Yang– S7 Parr correlation functional at the 6-31G(d,p) basis set in Gaussian was being employed.

Table S1. Crystal data and structure refinement for **APZ**, **I-1**, **I-2**, and **II-1.**

Empirical formula	**[APZ] $C_4H_5N_3$**	**I-1 $[(C_4H_6N_3)(H_2PO_4)]$**	**I-2 $[(C_4H_6N_3)(BF_4)$**	**II-1 $[(C_4H_5N_3)(C_4H_6N_3)(CF_3SO_3)]$**
Formula weight	95.11	193.10	182.93	340.30
Temperature [K]	298	298	298	298
Crystal system	monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group (number)	$P2_1/c$	$P2_12_12_1$	$P2_1/n$	$P\text{-}\bar{1}$
a /Å	6.2804(12)	4.4906(4)	4.9961(5)	8.658(3)
b / Å	10.2328(14)	8.7661(11)	20.906(2)	8.791(3)
c / Å	7.3769(12)	19.496(2)	7.0582(6)	9.477(3)
α /°	90	90	90	71.944(12)
β /°	93.117(7)	90	102.398(3)	81.828(12)
γ /°	90	90	90	83.043(12)
Volume / Å^3	473.38(14)	767.45(14)	720.03(12)	676.6(4)
Z	4	4	4	2
ρ_{calc} / g·cm^{-3}	1.335	1.671	1.687	1.670
μ / mm^{-1}	0.091	0.339	0.178	0.299
F(000)	200.0	400.0	368.0	348.0
Crystal size/mm^3	0.154 × 0.131 × 0.112	0.24 × 0.194 × 0.187	0.206 × 0.184 × 0.154	0.213 × 0.185 × 0.171
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ range (°)	6.496 to 50.68	6.25 to 55.002	6.224 to 55.156	4.548 to 50.68
Index ranges	$-7 \le h \le 7$, $-12 \le k \le 12$, $-8 \le l \le 8$	$-5 \le h \le 5$, $-11 \le k \le 11$, $-24 \le l \le 24$	$-6 \le h \le 6$, $-27 \le k \le 27$, $-9 \le l \le 9$	$-10 \le h \le 10$, $-10 \le k \le 10$, $-11 \le l \le 11$
Reflections collected	2736	5621	17178	8971
Independent reflections	841 [R_{int} = 0.0645, R_{sigma} = 0.0677]	1727 [R_{int} = 0.0834, R_{sigma} = 0.0819]	1659 [R_{int} = 0.0975, R_{sigma} = 0.0476]	2462 [R_{int} = 0.0703, R_{sigma} = 0.0598]
Completeness	96.9 %	98.4 %	99.7 %	99 %
Data / Restraints / Parameters	841/0/64	1727/2/111	1659/0/109	2462/0/204
Goodness-of-fit on F^2	1.074	1.054	1.070	1.084
Final R indexes [$I \ge 2\sigma(I)$][a]	R_1 = 0.0603, wR_2 = 0.1641	R_1 = 0.0473, wR_2 = 0.1061	R_1 = 0.0476, wR_2 = 0.1237	R_1 = 0.0494, wR_2 = 0.1292
Final R indexes [all data][a]	R_1 = 0.0814, wR_2 = 0.1883	R_1 = 0.0531, wR_2 = 0.1133	R_1 = 0.0567, wR_2 = 0.1358	R_1 = 0.0640, wR_2 = 0.1461
Largest peak/hole [e·Å^{-3}]	0.14/-0.14	0.25/-0.32	0.27/-0.29	0.48/-0.41
Flack X parameter	/	-0.11(15)	/	/

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S1. Crystal data and structure refinement for **II-2**, **II-3**, **III**, **IV.**

Empirical formula	**II-2 [$(C_4H_6N_3)(NH_2SO_3)$]**	**II-3 [$(C_4H_6N_3)(CH_3SO_3)$]**	**III [$(C_4H_5N_3)_2(C_4H_6O_4)$]**	**IV [$(C_4H_5N_3)(H_3BO_3)_2$]**
Formula weight	192.20	191.21	308.31	218.78
Temperature [K]	298	298	298	298
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group (number)	*C*2/*c*	$P2_1/c$	$P2_1/c$	$P2_1/c$
a /Å	23.329(2)	5.1632(8)	5.3958(6)	10.2656(14)
b / Å	8.9732(6)	10.2883(17)	19.471(2)	3.7235(5)
c / Å	7.4927(6)	15.253(3)	6.9453(7)	13.2934(19)
α /°	90	90	90	90
β /°	101.254(3)	93.922(5)	104.630(5)	107.188(5)
γ /°	90	90	90	90
Volume / Å^3	1538.3(2)	808.4(2)	706.02(13)	485.43(12)
Z	8	4	2	2
ρ_{calc} / g·cm^{-3}	1.660	1.571	1.450	1.497
μ / mm^{-1}	0.395	0.372	0.112	0.132
F(000)	800.0	400.0	324.0	228.0
Crystal size/mm^3	0.184 × 0.162 × 0.144	0.185 × 0.141 × 0.12	0.22 × 0.186 × 0.162	0.154 × 0.132 × 0.112
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ range (°)	7.012 to 54.944	4.78 to 50.69	4.184 to 55.084	4.154 to 50.752
Index ranges	$-30 \le h \le 28$, $-10 \le k \le 11$, $-9 \le l \le 9$	$-6 \le h \le 6$, $-12 \le k \le 12$, $-16 \le l \le 18$	$-7 \le h \le 7$, $-25 \le k \le 25$, $-9 \le l \le 9$	$-12 \le h \le 12$, $-4 \le k \le 4$, $-16 \le l \le 16$
Reflections collected	5566	4225	7097	3009
Independent reflections	1730 [R_{int} = 0.0539, R_{sigma} = 0.0520]	1470 [R_{int} = 0.0495, R_{sigma} = 0.0551]	1605 [R_{int} = 0.0717, R_{sigma} = 0.0526]	854 [R_{int} = 0.0381, R_{sigma} = 0.0375]
Completeness	98.5 %	99.2 %	99.6 %	95.1 %
Data / Restraints / Parameters	1730/0/110	1470/0/107	1605/0/100	854/1/65
Goodness-of-fit on F^2	1.087	1.114	1.034	1.180
Final *R* indexes [$I \ge 2\sigma(I)$][a]	R_1 = 0.0392, wR_2 = 0.0980	R_1 = 0.0477, wR_2 = 0.0981	R_1 = 0.0441, wR_2 = 0.1077	R_1 = 0.0481, wR_2 = 0.1026
Final *R* indexes [all data][a]	R_1 = 0.0485, wR_2 = 0.1034	R_1 = 0.0685, wR_2 = 0.1109	R_1 = 0.0628, wR_2 = 0.1264	R_1 = 0.0554, wR_2 = 0.1061
Largest peak/hole [e·Å^{-3}]	0.27/-0.38	0.22/-0.32	0.31/-0.22	0.15/-0.15

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma$

Table S2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **I-1**–**I-2**, **II-1**–**II-3**, **III** and **IV.** U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor**.**

I-1 [$(C_4H_6N_3)(H_2PO_4)$]				
Atom	***x***	***y***	***z***	$U_{(eq)}$
P(1)	6377(2)	10960.6(10)	5726.3(5)	15.5(3)
N(1)	7167(8)	6686(4)	5871.7(18)	25.7(8)
N(2)	2017(8)	6878(4)	7287.9(18)	25.2(8)
N(3)	4402(7)	4767(3)	6403.5(16)	19.1(7)
C(1)	5248(9)	6236(4)	6340.0(18)	17.9(8)
C(2)	3939(10)	7273(4)	6818(2)	22.3(8)
C(3)	1220(11)	5368(4)	7318(2)	24.5(8)
C(4)	2398(9)	4327(5)	6879(2)	21.7(8)
O(1)	5185(6)	10574(3)	4989.2(14)	23.2(6)
O(2)	8749(6)	9807(3)	5896.9(14)	20.5(6)
O(3)	3749(6)	10798(3)	6237.6(13)	21.8(6)
O(4)	7419(6)	12595(3)	5751.2(15)	20.9(6)
I-2 [$(C_4H_6N_3)(BF_4)$				
Atom	***x***	***y***	***z***	$U_{(eq)}$
B(1)	-815(4)	4249.2(9)	2148(3)	35.1(4)
N(1)	6129(3)	4435.2(8)	6876(2)	48.5(4)
N(2)	3154(3)	3813.3(7)	8194.6(19)	39.2(4)
N(3)	3352(4)	2875.5(8)	5539(2)	53.8(4)
C(1)	4699(3)	3908.9(8)	6893(2)	36.0(4)
C(2)	1706(4)	3263.2(9)	8229(3)	46.1(4)
C(3)	1828(5)	2805.9(10)	6917(3)	53.4(5)
C(4)	4707(4)	3404.1(9)	5535(3)	43.6(4)
F(1)	1716(2)	4279.6(6)	1656.3(17)	53.5(3)
F(3)	-453(3)	4305.4(8)	4127.0(17)	67.4(4)
F(2)	-2488(3)	4738.2(6)	1257.0(19)	63.4(4)
F(4)	-2047(3)	3677.7(6)	1537(2)	71.1(4)
II-1 [$(C_4H_5N_3)(C_4H_6N_3)(CF_3SO_3)$]				
Atom	***x***	***y***	***z***	$U_{(eq)}$
S1	7004.0(8)	3674.7(9)	-226.9(7)	41.4(3)
N1	12455(3)	1944(3)	2451(3)	52.8(7)
N2	11340(3)	1239(3)	4898(3)	40.8(6)
N3	9117(3)	3789(3)	4195(3)	41.0(6)
N4	6070(3)	1801(3)	-5884(3)	51.2(7)
N5	5407(3)	1245(3)	-3344(2)	43.4(6)
N6	3191(3)	3800(3)	-3785(3)	42.9(6)
C1	11338(3)	2224(3)	3494(3)	36.5(6)
C2	10215(4)	1565(4)	5913(3)	48.1(7)
C3	9116(4)	2818(4)	5604(3)	46.2(7)
C4	10186(3)	3509(3)	3146(3)	41.3(6)
C5	8501(4)	2011(4)	-5(3)	52.1(8)
C6	5159(3)	2157(3)	-4736(3)	34.4(6)
C7	4545(4)	1650(4)	-2217(3)	51.4(8)
C8	3438(4)	2921(4)	-2403(3)	48.8(7)
C9	4016(3)	3458(3)	-4952(3)	39.2(6)
O1	7711(3)	4823(3)	223(3)	62.7(7)
O2	5704(3)	2947(3)	754(2)	64.4(7)
O3	6842(3)	4138(3)	-1786(2)	54.2(6)
F1	8757(3)	1393(3)	1408(2)	97.9(9)

F2	9845(2)	2464(3)	-797(3)	84.1(7)
F3	8119(3)	854(3)	-463(3)	82.5(7)
II-2 [$(C_4H_6N_3)(NH_2SO_3)$]				
Atom	***x***	***y***	***z***	$U_{(eq)}$
S(1)	5805.3(2)	3354.8(5)	4169.8(6)	24.7(2)
N(1)	5870.7(8)	8998.7(18)	3305(2)	35.3(4)
N(2)	7148.5(9)	9136(2)	6881(2)	40.5(5)
N(3)	6454.8(7)	7093.2(17)	4775(2)	29.9(4)
N(4)	5280.6(7)	3061.4(18)	5318(2)	29.7(4)
C(1)	6325.7(9)	8542(2)	4516(3)	27.6(4)
C(2)	6707.3(9)	9555(2)	5632(3)	33.2(5)
C(3)	7245.3(10)	7649(3)	7115(3)	40.6(5)
C(4)	6905.8(10)	6628(2)	6076(3)	35.5(5)
O(1)	5714.2(7)	4819.5(14)	3304.6(19)	35.0(4)
O(2)	5730.0(7)	2170.3(15)	2824.2(19)	34.1(4)
O(3)	6340.2(6)	3271.6(16)	5495.1(19)	36.6(4)
II-3 [$(C_4H_6N_3)(CH_3SO_3)$)]				
Atom	***x***	***y***	***z***	$U_{(eq)}$
S(1)	-4380.9(15)	6204.1(8)	6508.5(5)	38.0(3)
N(1)	2064(5)	7984(3)	8201.9(19)	49.4(8)
N(2)	1060(5)	5797(3)	8284.4(16)	39.8(7)
N(3)	-2820(5)	6346(3)	9350.7(18)	46.5(7)
C(1)	647(6)	7042(3)	8493(2)	37.0(7)
C(2)	-382(7)	4822(3)	8593(2)	44.3(8)
C(3)	-2292(7)	5099(4)	9118(2)	47.2(9)
C(4)	-1413(5)	7264(2)	9052.4(15)	42.7(8)
C(5)	-6494(5)	6504(2)	5596.8(15)	43.4(8)
O(1)	-2036(4)	5667(3)	6183.4(17)	57.2(7)
O(2)	-4004(5)	7438(2)	6959.6(17)	60.6(8)
O(3)	-5668(5)	5247(2)	7040.2(15)	49.8(7)
III [$(C_4H_5N_3)_2(C_4H_6O_4)$]				
Atom	***x***	***y***	***z***	$U_{(eq)}$
N(1)	8073(2)	554.4(7)	6351(2)	27.7(4)
N(2)	3985(2)	880.8(7)	4691(2)	22.6(3)
N(3)	5323(3)	2249.0(7)	5545(2)	26.3(3)
C(1)	6340(3)	1055.3(8)	5738(2)	20.7(4)
C(2)	2326(3)	1395.8(9)	4082(3)	26.2(4)
C(3)	2955(3)	2072.9(9)	4490(3)	28.0(4)
C(4)	6988(3)	1752.6(8)	6168(3)	23.2(4)
C(5)	4903(3)	989.7(8)	10179(2)	21.2(4)
C(6)	5893(3)	266.4(8)	10591(2)	22.9(4)
O(1)	6597(2)	1445.4(6)	11095.8(19)	28.3(3)
O(2)	2803(2)	1137.5(6)	9145.7(19)	28.8(3)
IV [$(C_4H_5N_3)(H_3BO_3)_2$]				
Atom	***x***	***y***	***z***	$U_{(eq)}$
B(1)	9042(3)	7603(8)	3595(2)	32.6(7)
N(1)	4445.5(14)	7524(4)	3084.4(11)	51.4(13)
N(2)	6029.7(14)	5889(4)	4566.4(11)	44.3(6)
C(1)	4721.5(14)	6410(4)	4036.2(11)	42.6(7)
C(2)	6300.8(14)	4499(4)	5520.7(11)	44.8(7)
O(1)	8323.8(18)	5818(5)	2721.2(13)	44.3(6)
O(2)	10341.2(16)	8704(5)	3712.1(12)	40.1(6)
O(3)	8474.5(17)	8305(5)	4379.5(13)	44.2(6)

Table S3. Bond lengths and bond angles for **I-1**–**I-2**, **II-1**–**II-3**, **III** and **IV.**

I-1 [$(C_4H_6N_3)(H_2PO_4)$]			
P(1)-O(1)	1.570(3)	N(2)-C(3)	1.373(5)
P(1)-O(2)	1.506(3)	N(3)-C(1)	1.349(5)
P(1)-O(3)	1.551(3)	N(3)-C(4)	1.348(5)
P(1)-O(4)	1.508(3)	C(1)-C(2)	1.428(5)
N(1)-C(1)	1.316(5)	C(3)-C(4)	1.358(6)
N(2)-C(2)	1.305(5)		
O(2)-P(1)-(O1)	107.36(15)	C(4)-N(3)-C(1)	121.6(3)
O(2)-P(1)-(O3)	109.54(16)	N(1)-C(1)-N(3)	122.3(4)
O(2)-P(1)-(O4)	114.28(17)	N(1)-C(1)-C(2)	122.1(3)
O(3)-P(1)-(O1)	108.01(16)	N(3)-C(1)-C(2)	115.6(3)
O(4)-P(1)-(O1)	109.88(15)	N(2)-C(2)-C(1)	124.1(4)
O(4)-P(1)-(O3)	107.62(16)	C(4)-C(3)-N(2)	121.3(4)
C(2)-N(2)-(C3)	117.2(3)	N(3)-C(4)-C(3)	120.1(4)
I-2 [$(C_4H_6N_3)(BF_4)$]			
B(1)-F(1)	1.383(2)	N(2)-C(2)	1.362(2)
B(1)-F(3)	1.374(2)	N(3)-C(3)	1.366(3)
B(1)-F(2)	1.383(2)	N(3)-C(4)	1.296(2)
B(1)-F(4)	1.370(2)	C(1)-C(4)	1.426(2)
N(1)-C(1)	1.314(2)	C(2)-C(3)	1.341(3)
N(2)-C(1)	1.336(2)		
F(1)-B(1)-F(2)	110.34(14)	C(4)-N(3)-C(3)	117.61(16)
F(3)-B(1)-F(1)	108.86(15)	N(1)-C(1)-N(2)	121.83(15)
F(3)-B(1)-F(2)	109.50(15)	N(1)-C(1)-C(4)	122.24(16)
F(4)-B(1)-F(1)	109.52(14)	N(2)-C(1)-C(4)	115.92(16)
F(4)-B(1)-F(3)	110.28(15)	C(3)-C(2)-N(2)	119.13(17)
F(4)-B(1)-F(2)	108.34(15)	C(2)-C(3)-N(3)	122.04(18)
C(1)-N(2)-C(2)	121.75(15)	N(3)-C(4)-C(1)	123.54(16)
II-1 [$(C_4H_5N_3)(C_4H_6N_3)(CF_3SO_3)$]			
S(1)-C(5)	1.814(3)	N(5)-C(7)	1.330(4)
S(1)-O(1)	1.438(3)	N(6)-C(8)	1.331(4)
S(1)-O(2)	1.431(2)	N(6)-C(9)	1.324(4)
S(1)-O(3)	1.429(2)	C(1)-C(4)	1.403(4)
N(1)-C(1)	1.340(4)	C(2)-C(3)	1.353(4)
N(2)-C(1)	1.344(3)	C(5)-F(1)	1.319(4)
N(2)-C(2)	1.339(4)	C(5)-F(2)	1.325(4)
N(3)-C(3)	1.344(4)	C(5)-F(3)	1.315(4)
N(3)-C(4)	1.319(4)	C(6)-C(9)	1.403(4)
N(4)-C(6)	1.346(3)	C(7)-C(8)	1.365(4)
N(5)-C(6)	1.346(3)		
O(1)-S(1)-C(5)	102.73(16)	N(3)-C(3)-C(2)	118.9(3)
O(2)-S(1)-C(5)	102.30(15)	N(3)-C(4)-C(1)	120.6(3)
O(2)-S(1)-O(1)	116.07(16)	F(1)-C(5)-S(1)	110.8(2)
O(3)-S(1)-C(5)	102.93(14)	F(1)-C(5)-F(2)	108.0(3)
O(3)-S(1)-O(1)	114.09(15)	F(2)-C(5)-S(1)	111.7(2)
O(3)-S(1)-O(2)	115.87(15)	F(3)-C(5)-S(1)	112.4(2)
C(2)-N(2)-C(1)	116.6(2)	F(3)-C(5)-F(1)	107.9(3)

C(4)-N(3)-C(3)	119.6(2)	F(3)-C(5)-F(2)	105.8(3)
C(7)-N(5)-C(6)	117.2(2)	N(4)-C(6)-N(5)	117.7(2)
C(9)-N(6)-C(8)	120.5(2)	N(4)-C(6)-C(9)	122.2(2)
N(1)-C(1)-N(2)	118.3(2)	N(5)-C(6)-C(9)	120.1(2)
N(1)-C(1)-C(4)	121.4(3)	N(5)-C(7)-C(8)	123.6(3)
N(2)-C(1)-C(4)	120.2(2)	N(6)-C(8)-C(7)	118.6(3)
N(2)-C(2)-C(3)	124.0(3)	N(6)-C(9)-C(6)	120.0(3)
II-2 [$(C_4H_6N_3)(NH_2SO_3)$]			
S(1)-N(4)	1.6487(16)	N(2)-C(3)	1.358(3)
S(1)-O(1)	1.4625(13)	N(3)-C(1)	1.340(2)
S(1)-O(2)	1.4519(13)	N(3)-C(4)	1.353(3)
S(1)-O(3)	1.4371(15)	C(1)-C(2)	1.424(3)
N(1)-C(1)	1.320(3)	C(3)-C(4)	1.353(3)
N(2)-C(2)	1.304(3)		
O(1)-S(1)-N(4)	108.45(8)	C(1)-N(3)-C(4)	121.64(17)
O(2)-S(1)-N(4)	104.12(8)	N(1)-C(1)-N(3)	121.92(18)
O(2)-S(1)-O(1)	111.26(8)	N(1)-C(1)-C(2)	122.14(18)
O(3)-S(1)-N(4)	105.32(9)	N(3)-C(1)-C(2)	115.94(18)
O(3)-S(1)-O(1)	112.61(8)	N(2)-C(2)-C(1)	123.52(19)
O(3)-S(1)-O(2)	114.38(9)	C(4)-C(3)-N(2)	121.8(2)
C(2)-N(2)-C(3)	117.64(18)	N(3)-C(4)-C(3)	119.41(19)
II-3 [$(C_4H_6N_3)(CH_3SO_3)$)]			
S(1)-C(5)	1.736(3)	N(2)-C(2)	1.354(4)
S(1)-O(1)	1.449(2)	N(3)-C(3)	1.364(4)
S(1)-O(2)	1.450(2)	N(3)-C(4)	1.294(4)
S(1)-O(3)	1.464(2)	C(1)-C(4)	1.427(4)
N(1)-C(1)	1.310(4)	C(2)-C(3)	1.343(5)
N(2)-C(1)	1.340(4)		
O(1)-S(1)-C(5)	106.73(14)	C(4)-N(3)-C(3)	117.9(3)
O(1)-S(1)-O(2)	114.07(16)	N(1)-C(1)-N(2)	121.7(3)
O(1)-S(1)-O(3)	110.79(14)	N(1)-C(1)-C(4)	122.7(3)
O(2)-S(1)-C(5)	106.31(15)	N(2)-C(1)-C(4)	115.6(3)
O(2)-S(1)-O(3)	112.15(15)	C(3)-C(2)-N(2)	119.6(3)
O(3)-S(1)-C(5)	106.22(13)	C(2)-C(3)-N(3)	121.6(3)
C(1)-N(2)-C(2)	121.7(3)	N(3)-C(4)-C(1)	123.6(3)
III [$(C_4H_5N_3)_2(C_4H_6O_4)$]			
N(1)-C(1)	1.344(2)	C(2)-C(3)	1.373(2)
N(2)-C(1)	1.339(2)	C(5)-C(6)	1.508(2)
N(2)-C(2)	1.340(2)	C(5)-O(1)	1.3169(19)
N(3)-C(3)	1.347(2)	C(5)-O(2)	1.2126(19)
N(3)-C(4)	1.316(2)	C(6)-C(6)#1	1.510(3)
C(1)-C(4)	1.415(2)		
C(1)-N(2)-C(2)	116.64(14)	N(3)-C(3)-C(2)	120.53(16)
C(4)-N(3)-C(3)	117.83(15)	N(3)-C(4)-C(1)	121.56(15)
N(1)-C(1)-C(4)	120.95(14)	O(1)-C(5)-C(6)	111.60(13)
N(2)-C(1)-N(1)	118.49(15)	O(2)-C(5)-C(6)	124.56(15)
N(2)-C(1)-C(4)	120.56(14)	O(2)-C(5)-O(1)	123.83(15)
N(2)-C(2)-C(3)	122.88(15)	C(5)-C(6)-C(6)#1	113.06(16)

Symmetry transformations used to generate equivalent atoms:
#1 1-X,-Y, 2-Z

IV $[(C_4H_5N_3)(H_3BO_3)_2]$			
B(1)-O(1)	1.353(3)	N(2)-C(1)	1.3336
B(1)-O(2)	1.359(3)	N(2)-C(2)	1.3213
B(1)-O(3)	1.362(3)	C(1)-C(2)#1	1.389(3)
N(1)-C(1)	1.2811		
O(1)-B(1)-O(2)	120.9(2)	N(1)-C(1)-N(2)	117.6
O(1)-B(1)-O(3)	120.3(2)	N(1)-C(1)-C(2)#1	121.57(12)
O(2)-B(1)-O(3)	118.8(2)	N(2)-C(1)-C(2)#1	120.63(12)
C(2)-N(2)-C(1)	117.3	N(2)-C(2)-C(1)#1	122.11(12)

Symmetry transformations used to generate equivalent atoms:
#1 1-X,1-Y, 1-Z

Table S4. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameter (Å^2×10^3) for **I-1**–**I-2**, **II-1**–**II-3**, **III** and **IV.**

I-1 [$(C_4H_6N_3)(H_2PO_4)$]				
Atom	***x***	***y***	***z***	$U_{(eq)}$
H(1A)	7946.24	6018.13	5586.31	31
H(1B)	7671.74	7653.73	5844.01	31
H(3)	5177.47	4077.61	6127.94	23
H(2)	4502.26	8315.96	6792.09	27
H(3A)	-182.39	5044.28	7652.19	29
H(4)	1807.76	3288.6	6906.79	26
H(3B)	1859.33	10373.79	6147.5	70(20)
H(4A)	8427.92	13251.74	5436.23	200(50)
I-2 [$(C_4H_6N_3)(BF_4)$				
Atom	***x***	***y***	***z***	$U_{(eq)}$
H(1A)	6087.56	4730.02	7718.73	58
H(1B)	7107.46	4485.02	6021.83	58
H(2)	3072.78	4106.88	9033.62	47
H(2A)	646.34	3205.4	9149.25	55
H(3)	844.9	2429.7	6947.84	64
H(4)	5741.08	3456.98	4596.42	52
II-1 [$(C_4H_5N_3)(C_4H_6N_3)(CF_3SO_3)$]				
Atom	***x***	***y***	***z***	$U_{(eq)}$
H(1A)	12886.19	982.75	2779.91	63
H(1B)	12039.19	2029.95	1651.81	63
H(4A)	6324.7	784.25	-5632.11	61
H(4B)	5561.2	2069.15	-6652.51	61
H(6)	2489.9	4597.55	-3921.06	52
H(2)	10185.58	888.29	6887.78	58
H(3)	8371.3	3003.85	6355.11	70(11)
H(4)	10176.77	4169.79	2167.72	50
H(7)	4704.59	1033.65	-1248.12	62
H(8)	2868.82	3165.44	-1581.75	59
H(9)	3840(40)	4090(40)	-5960(40)	51(9)
II-2 [$(C_4H_6N_3)(NH_2SO_3)$]				
Atom	***x***	***y***	***z***	$U_{(eq)}$
H(1A)	5641.93	8344.63	2639.48	42
H(1B)	5796.23	9957.53	3163.68	42
H(3)	6241.01	6427.45	4081.77	36
H(4A)	4984.83	2819.26	4665.12	45
H(4B)	5262.33	3755.26	5995.72	45
H(2)	6636.71	10592.89	5457.51	40
H(3A)	7559.75	7317.28	8031.99	49
H(4)	6983.38	5594.38	6259.02	43
II-3 [$(C_4H_6N_3)(CH_3SO_3)$)]				
Atom	***x***	***y***	***z***	$U_{(eq)}$
H(1A)	3295.78	7811.23	7868.33	59
H(1B)	1761.68	8775.73	8344.73	59
H(2)	2273.57	5613.69	7945.38	48
H(2A)	-51.03	3964.24	8443.19	53
H(3)	-3278.14	4424.89	9327.62	57
H(4)	-1762.19	8116.1	9211.2	51
H(5A)	-6829.59	5708.9	5280.2	65
H(5B)	-5725.69	7123.3	5221.5	65
H(5C)	-8094.59	6847	5784.4	65

III $[(C_4H_5N_3)_2(C_4H_6O_4)]$				
Atom	***x***	***y***	***z***	$U_{(eq)}$
H(1A)	7648.88	123.23	6061.78	33
H(1B)	9632.18	657.63	7041.68	33
H(2)	639.98	1287.83	3334.81	31
H(3)	1710.61	2419.88	4024.13	34
H(4)	8664.62	1865.23	6924.74	28
H(6A)	6155.74	168.44	12027.7	27
H(6B)	7576.24	230.34	10273.4	27
H(1)	6010.04	1842.73	10815.06	42
IV $[(C_4H_5N_3)(H_3BO_3)_2]$				
Atom	***x***	***y***	***z***	$U_{(eq)}$
H(1A)	5100.89	7911.68	2806.5	62
H(1B)	3602.69	7892.18	2715.9	62
H(1C)	4485.29	7597.28	3464.7	62
H(2)	7214.99	4113.18	5912.3	54
H(1)	8826.42	5367.85	2349.57	66
H(2A)	10664.43	9602.88	4305.11	60
H(3)	7734.8	7235.53	4258.43	66

Table S5. Hydrogen Bonds for **I-1**–**I-2**, **II-1**–**II-3**, **III** and **IV.**

I-1 [$(C_4H_6N_3)(H_2PO_4)$]				
D–H···A	$d_{D–H}$ **(Å)**	$d_{H···A}$ **(Å)**	$d_{D–A}$ **(Å)**	**D–H–A (°)**
N(1)–H(1A)···O(1)#1	0.88	2.05	2.929(4)	172.7
N(1)–H(1B)···O(2)	0.88	1.95	2.828(4)	173.4
N(3)–H(3)···O(4)#2	0.88	1.80	2.660(4)	164.9
C(2)–H(2)···O(3)	0.95	2.45	3.292(5)	147.2
O(3)–H(3B)···O(2)#3	0.94	1.56	2.497(4)	171.5
O(4)–H(4A)···O(1)#4	0.96	1.54	2.490(4)	172.6

Symmetry transformations used to generate equivalent atoms:
#1 1/2+X,3/2-Y,1-Z; #2 +X,-1+Y,+Z; #3 -1+X,+Y,+Z; #4 1/2+X,5/2-Y,1-Z

I-2 [$(C_4H_6N_3)(BF_4)$				
D–H···A	$d_{D–H}$ **(Å)**	$d_{H···A}$ **(Å)**	$d_{D–A}$ **(Å)**	**D–H–A (°)**
N(1)–H(1A)···F(1)#1	0.86	2.34	2.995(2)	133.2
N(1)–H(1A)···F(2)#2	0.86	2.36	3.010(2)	133.1
N(1)–H(1A)···F(2)#3	0.86	2.45	3.086(2)	131.8
N(1)–H(1B)···F(3)#4	0.86	2.03	2.859(2)	162.2
N(2)–H(2)···F(1)#5	0.86	2.13	2.8619(17)	142.1
N(2)–H(2)···F(2)#2	0.86	2.44	3.080(2)	132.2
N(2)–H(2)···F(4)#3	0.86	2.83	2.994(2)	92.4
C(2)–H(2A)···F(1)#5	0.93	2.84	3.219(2)	105.9
C(3)–H(3)···F(4)#6	0.93	2.59	3.174(2)	121.7

Symmetry transformations used to generate equivalent atoms:
#11-X,1-Y,1-Z; #2 -X,1-Y,1-Z; #3 1+X,+Y,1+Z; #4 1+X,+Y,+Z; #5 +X,+Y,1+Z;
#6 1/2+X,1/2-Y,1/2+Z

II-1 [$(C_4H_5N_3)(C_4H_6N_3)(CF_3SO_3)$]				
D–H···A	$d_{D–H}$ **(Å)**	$d_{H···A}$ **(Å)**	$d_{D–A}$ **(Å)**	**D–H–A (°)**
N(1)–H(1A)···N(5)#1	0.86	2.28	3.118(3)	165.2
N(1)–H(1B)···O(1)#2	0.86	2.80	3.172(4)	107.7
N(4)–H(4A)···N(2)#1	0.86	2.55	3.262(4)	140.9
N(4)–H(4B)···O(2)#3	0.86	2.33	3.080(4)	146.5
N(6)–H(6)···N(3)#4	0.86	1.85	2.705(3)	176.1
C(2)–H(2)···F(1)#5	0.93	2.33	3.161(4)	148.3
C(8)–H(8)···O(1)#4	0.93	2.46	3.266(4)	145.2
C(8)–H(8)···F(2)#6	0.93	2.71	3.277(4)	120.1
C(9)–H(9)···O(3)#7	0.97(3)	2.32(3)	3.286(4)	171(3)

Symmetry transformations used to generate equivalent atoms:
#1 2-X,-Y,-Z; ; #2 2-X,1-Y,-Z; #3 +X,+Y,-1+Z; #4 1-X,1-Y,-Z; #5 2-X,-Y,1-Z; #6 1-X,1-Y,1-Z;
#7 1-X,1-Y,-1-Z

II-2 [$(C_4H_6N_3)(NH_2SO_3)$]				
D–H···A	$d_{D–H}$ **(Å)**	$d_{H···A}$ **(Å)**	$d_{D–A}$ **(Å)**	**D–H–A (°)**
N(1)–H(1A)···N(4)#1	0.88	2.18	3.020(2)	159.3
N(1)–H(1A)···O(3)#1	0.88	2.89	3.269(2)	107.7
N(1)–H(1B)···O(2)#2	0.88	2.00	2.879(2)	173.0
N(3)–H(3)···O(1)	0.88	1.91	2.760(2)	161.6
N(3)–H(3)···O(3)#1	0.88	2.76	3.183(2)	111.3
N(4)–H(4A)···O(2)#3	0.79	2.32	3.094(2)	164.9
N(4)–H(4B)···O(1)#4	0.81	2.24	2.960(2)	148.0
C(4)–H(4)···O(3)	0.95	2.57	3.283(3)	132.4

Symmetry transformations used to generate equivalent atoms:
#1 +X,1-Y,-1/2+Z; #2 +X,1+Y,+Z; #3 1-X,+Y,1/2-Z; #4 +X,1-Y,1/2+Z

II-3 [$(C_4H_6N_3)(CH_3SO_3)$)]

D–H···A	$d_{D–H}$ (Å)	$d_{H···A}$ (Å)	$d_{D–A}$ (Å)	D–H–A (°)
N(1)–H(1A)···O(2)#1	0.86	2.07	2.925(4)	174.2
N(1)–H(1B)···O(1)#2	0.86	2.08	2.916(4)	165.0
N(1)–H(1B)···O(3)#2	0.86	2.62	3.019(4)	109.5
N(2)–H(2)···O(3)#1	0.86	1.84	2.686(3)	168.2
C(5)–H(5C)···O(1)#3	0.96	2.48	3.175(3)	129.1

Symmetry transformations used to generate equivalent atoms:
#1 1+X,+Y,+Z; #2 -X,1/2+Y,3/2-Z; #3 -1+X,+Y,+Z

III [$(C_4H_5N_3)_2(C_4H_6O_4)$]

D–H···A	$d_{D–H}$ (Å)	$d_{H···A}$ (Å)	$d_{D–A}$ (Å)	D–H–A (°)
N(1)–H(1A)···N(2)#1	0.88	2.15	3.027(2)	171.2
N(1)–H(1B)···O(2) #2	0.88	2.16	3.0114(18)	162.1
C(2)–H(2)···O(1)#3	0.95	2.36	3.260(2)	158.5
O(1)–H(1)···N(3)#4	0.84	1.81	2.6359(18)	168.8

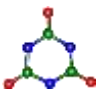
Symmetry transformations used to generate equivalent atoms:
#1 1-X,-Y,1-Z; #2 1+X,+Y,+Z; #3 -1+X,+Y,-1+Z; #4 +X,1/2-Y,1/2+Z

IV [$(C_4H_5N_3)(H_3BO_3)_2$]

D–H···A	$d_{D–H}$ (Å)	$d_{H···A}$ (Å)	$d_{D–A}$ (Å)	D–H–A (°)
N(1)–H(1A)···N(1)#1	0.87	2.44	2.867(2)	110.6
N(1)–H(1A)···N(1)#2	0.87	2.21	2.867(2)	131.9
N(1)–H(1B)···O(1)#2	0.87	2.18	2.989(2)	154.3
N(1)–H(1C)···N(2)	0.50	1.92	2.237	124.0
O(1)–H(1)···O(2)#3	0.83	1.95	2.770(2)	167.2
O(2)–H(2A)···O(3)#4	0.83	1.88	2.708(2)	175.5
O(3)–H(3)···N(2)	0.83	1.98	2.746(2)	153.8

Symmetry transformations used to generate equivalent atoms:
#1 1-X,-1/2+Y,1/2-Z;#2 1-X,1/2+Y,1/2-Z; #3 2-X,-1/2+Y,1/2-Z; #4 2-X,2-Y,1-Z

Table S6. NLO properties comparison among inorganic and metal-free organic fundamental building units.

Groups	Structures	Polarizability Anisotropy (δ)	Hyperpolarizability ($\|\beta_{max}\|$)	HOMO-LOMO *Eg*(eV)
$[BO_3]^{2-}$		9.18	15.71	8.39
$[CO_3]^{2-}$		12.49	23.87	8.02
$[NO_3]^{2-}$		17.35	22.61	6.06
$[C(NH_2)_3]^{+}$		19.91	72.13	8.74
$[B_3O_6]^{3-}$		28.9	62.5	8.3
$[C_3O_3N_3]^{3-}$		51.2	175.2	6.4
$[HC_3O_3N_3]^{2-}$		53.6	250.3	6.6
$[H_2C_3O_3N_3]^{-}$		52.6	195.9	6.7
$[H_3C_3O_3N_3]$		54.4	112.9	5.9
$[H_2C_3N_3S_3]^{-}$		119	768	6.16
$[HC_3N_3S_3]^{2-}$		120	1112	6.12

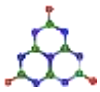
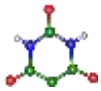
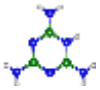
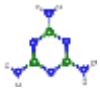
$[C_6N_7O_3]^{3-}$		111.82	413.05	5.25
$[C_6N_7(NH_2)_3]$		131.60	529.95	4.87
$[H_2C_4N_2O_3]^{2-}$		55.6	190.5	6.0
$[H_3C_4N_2O_3]^{-}$		54.4	112.9	5.9
$[C_3H_7N_6]^{+}$		64.4	287.0	6.5
$[C_3H_8N_6]^{2+}$		57.2	196.36	6.04
$[C_3H_6N_6]^{2+}$		65.72	178.21	6.67
$[C_5H_6ON]^{+}$		51.4	230.1	6.4
$[C_4H_7N_3]^{2+}$		43	97.92	5.14
$[C_4H_6N_3]^{+}$		46.88	165.6	5.25
$[C_4H_5N_3]$		47.1	262.92	5.51
$[C_4H_6N_3]^{+}$		43.71	160.96	4.92
$[C_4H_5N_3]$		48.48	208.6	5.15

Table S7. Comparisons of title compounds with known semi-organic crystals.

Sr. No	Compound	Space group	λ_{cutoff}/nm	Birefringence	Ref
1.	$[C(NH_2)_3]_2(HPO_4)(H_2O)]$	$P\bar{4}2_1c$	220	0.014@532 nm	[12]
2.	$[(C(NH_2)_3)_2Zn(HPO_3)_2]$	$Fdd2$	194	0.030@1064 nm	[13]
3.	$[C(NH_2)_3]_2(PO_3F)]$	Cm	194	0.039@532 nm	[14]
4.	$[C(NH_2)_3]_3(PO_4)(2H_2O)]$	$Pna2_1$	250	0.055@546 nm	[15]
5.	$[C(NH_2)_3]_2(SO_3S)]$	$P6_3mc$	254	0.073@546 nm	[16]
6.	$[C(NH_2)_3(ClO_4)]$	$R3m$	200	0.076@1064 nm	[17]
7.	$[C(NH_2)_3]_6(PO_4)_2(3H_2O)]$	Cc	205	0.078 @546nm	[18]
8.	$[C(NH_2)_3(SbF_4)]$	$P2_12_12_1$	241	0.08@532 nm	[19]
9.	$[(C_3N_6H_7)_3(HgCl_5)]$	$P\bar{1}$	290	0.093@1064 nm	[20]
10.	$[C(NH_2)_3(H_2PO_2)]$	$Pnma$	201	0.10 @532 nm	[21]
11.	$[(CN_4H_7)(CH_3SO_3)]$	$P2_1/n$	198	0.102 @1064 nm	[22]
12.	$[C(NH_2)_3(BF_4)]$	$R3m$	193	0.11@1064 nm	[23]
13.	$[C(NH_2)_3(SO_3F)]$	$R3m$	200	0.133@1064 nm	[24]
14.	$[C(NH_2)_3(CH_3SO_3)]$	$C2/m$	195	0.137 @ 1064 nm	[22]
15.	$[C(NH_2)_3(CF_3SO_3)]$	$C2/c$	182	0.139@1064 nm	[22]
16.	$[(CN_4H_7)(CF_3SO_3)]$	$P\bar{1}$	183	0.141@1064 nm	[22]
17.	$[C(NH_2)_3(NO_3)]$	Cm	269	0.143@1064 nm	[25]
18.	$[(C_4H_6N_3)(H_2PO_4)]$ **I-1**	$P2_12_12_1$	366	0.145 @546 nm	This work
19.	$[Lu_5(C_3N_3O_3)(OH)_{12}]$	$P\bar{6}2m$	235	0.148@800 nm	[26]
20.	$[Y_5(C_3N_3O_3)(OH)_{12}]$	$P\bar{6}2m$	225	0.149@800 nm	[26]
21.	$[(C_3N_6H_7)_2(SiF_6)(H_2O)]$	$P2_1/n$	220	0.152@550 nm	[27]
22.	$[RbLi(HC_3N_3O_3)(2H_2O)]$	$Pna2_1$	239	0.18@514 nm	[28]
23.	$[KLi(HC_3N_3O_3)(2H_2O)]$	$Pna2_1$	237	0.186@514 nm	[29]
24.	$[K_3Pb(H_2C_3N_3O_3)_5(H_2O)_6]$	$C2/m$	255	0.193 @532nm	[30]
25.	$[RbNa(HC_3N_3O_3)(2H_2O)]$	$Pna2_1$	266	0.194@589 nm	[31]
26.	$[(C_3H_7N_6)_6(H_2PO_4)_4(HPO_4)(4H_2O)]$	$P2_1$	N/A	0.220@1064 nm	[32]
27.	$[NaRb_{0.86}Cs_{0.14}(HC_3N_3O_3)(2H_2O)]$	$Pna2_1$	N/A	0.238@532 nm	[33]
28.	$[Sr_{0.5}(H_2C_6N_7O_3](4H_2O)]$	$Fdd2$	304	0.239@1064 nm	[34]
29.	$(C_3N_6H_7)(C_3N_6H_6)HgCl_3$	$P2_1$	278	0.246@1064 nm	[20]
30.	$[(C_4H_5N_3)(H_3BO_3)_2]$ **IV**	$P2_1/c$	340	0.248 @546 nm*	This work
31.	$[(C_3N_6H_7)(C_3N_6H_6)(ZnCl_3)]$	$P2_1$	236	0.255@1064 nm	[35]
32.	$2(C_3H_7N_6)(2Cl)(H_2O)]$	$Cmc2_1$	245	0.277@546 nm	[36]
33.	$[LiCl(H_3C_3N_3O_3)]$	$R3m$	215	0.28@800 nm	[37]
34.	$[NaCs_3(H_2C_3N_3O_3)_4(3H_2O)$	$Pmn2_1$	227	0.29@514 nm	[38]
35.	$[(C_3H_8N_6)(SnCl_4)]$	$Pna2_1$	334	0.294@550 nm	[39]
36.	$[K_2Sn_2(C_2O_4)_2F_2(H_2O)]$	$P2_1/c$	310	0.301@546 nm	[40]
37	$[RbLi(H_2C_3N_3O_3)_2(2H_2O)]$	$P2_1/m$	N/A	>0.30	[41]
38.	$[CsLi(H_2C_3N_3O_3)_2(2H_2O)]$	$P2_1/m$	N/A	>0.30	[41]
39.	$[Ba_2Pb(C_3N_3O_3)_2]$	$R\bar{3}$	264	0.31@800 nm	[42]
40.	$[(C_3N_6H_7)(CH_3SO_3)(H_2O)]$	$P\bar{1}$	233	0.31@546 nm	[43]
41.	$[(C_3H_8N_6)(PbBr_4)]$	$P2_1/c$	374	0.322@550 nm	[44]
42.	$[K_2Pb(H_2C_3N_3O_3)_4(4H_2O)]$	Cm	277	0.325@532 nm	[30]
43.	$[\beta\text{-}(C_3H_7N_6)_2Cl_2(H_2O)]$	$C2/m$	230	0.33@550 nm	[45]
44.	$[(C_3N_6H_7)(NH_2SO_3)]$	$P\bar{1}$	206	0.340@546 nm	[46]
45.	$[C_{10}H_{10}ClNO_3]$	$P2_1/c$	N/A	0.345 @550 nm	[47]
46.	$[Ba_2Ca(C_3N_3O_3)_2]$	$R\bar{3}$	230	0.345@800 nm	[48]
47.	$[Li_2(HC_3N_3O_3)]$	$P2_1/c$	N/A	0.345@532 nm	[33]
48	$[K_2(HC_3N_3O_3)]$	$Cmcm$	240	0.35@800 nm	[49]
49.	$[K_{0.5}In_{0.5}(H_2C_6N_7O_3)_2(9H_2O)]$	$P\bar{1}$	306	0.35@1064 nm	[50]
50.	$[Ba_2Mg(C_3N_3O_3)_2]$	$R\bar{3}$	225	0.351@800 nm	[48]
51.	$[Rb_2Ca(H_2C_3N_3O_3)_4(4H_2O)]$	$C2/m$	231	0.362@800 nm	[51]
52.	$[NaRb_3(H_2C_3N_3O_3)_4(3H_2O)]$	$Pmn2_1$	230	0.368@1064 nm	[52]
53.	$[(C_3N_6H_7)(BF_4)(H_2O)$	$P\bar{1}$	244	0.37@546 nm	[43]
54.	$[K_2Ca(H_2C_3N_3O_3)_4(4H_2O)]$	$C2/m$	233	0.371@800 nm	[51]
55.	$[Ca_3(C_3N_3O_3)_2]$	$R3c$	N/A	0.372@589 nm	[53]

56.	$[Sr_3(C_3N_3O_3)_2]$	$R3c$	420	0.374@589 nm	[54]
57.	$[K_2Mg(H_2C_3N_3O_3)_4(4H_2O)]$	$C2/m$	230	0.376@800 nm	[51]
58.	$[(C_3H_7N_6)F(H_2O)]$	$C2/m$	220	0.38@550 nm	[55]
59.	$[(C_3N_6H_7)_2SbF_5(H_2O)]$	$P\bar{1}$	220	0.38@550 nm	[56]
60.	$[(Cs_2Mg(H_2C_3N_3O_3)_4(10H_2O)]$	$P\bar{1}$	234	0.391@800 nm	[51]
61.	$[(Rb_2(HC_3N_3O_3)]$	$Cmcm$	N/A	0.4@532 nm	[33]
62.	$[K_4(HC_3N_3S_3)_2(H_2O)]$	$P2_12_12_1$	406	0.402@ 550 nm	[57]
63.	$[C_3N_6H_7]_2[B_3O_3F_4(OH)]$	$P\bar{1}$	240	0.440@546 nm	[58]
64.	$[K_3(C_6N_7O_3)(2H_2O)]$	Cc	N/A	0.446@1064 nm	[59]
65.	$[(C_4H_6N_3)(NH_2SO_3)]$ **II-2**	$C2/c$	350	0.452@546nm	This work
66.	$[(C_4H_6N_3)(BF_4)]$ **I-2**	$P21/n$	370	0.489@546nm	This work
67.	$[(C_4H_5N_3)(C_4H_6N_3)(CF_3SO_3)]$ **II-1**	$P\bar{1}$	362	0.49@546 nm	This work
68.	$[(C_5H_5NO)(Sb_2OF_4)]$	Cm	270	0.513@546 nm	[60]
69.	$[(C_4H_6N_3)(CH_3SO_3)]$ **II-3**	$P2_1/c$	360	0.594@546 nm	This work
70.	$[Cd(H_2C_6N_7O_3)_2(8H_2O)]$	$P2_1$	310	0.60@550 nm	[61]
71.	$[C_6N_7(NH_2)_3(H_3PO_4)]$	$R3c$	300	0.609@1064 nm	[62]
72.	$[(C_4H_5N_3)_2(C_4H_6O_4)]$ **III**	$P2_1/n$	364	0.658@546 nm	This work

*Represent the experimental birefringence

Table S8. Comparisons of title compounds with known semi-organic compounds in their corresponding families.

Sr. No	Compound	Space group	λ_{cutoff}/nm	Birefringence	Ref
		Phosphates			
1.	$[C(NH_2)_3]_2(HPO_4)(H_2O)]$	$P\bar{4}2_1c$	220	0.010@532 nm	[12]
2.	$[C(NH_2)_3]_6(PO_4)_2(3H_2O)]$	Cc	205	0.077@546nm	[18]
3.	$[C(NH_2)_3(H_2PO_2)]$	$Pnma$	201	0.085@532nm	[21]
4.	$[(C_4H_6N_3)(H_3PO_4)]$ **I-1**	$P2_12_12_1$	366	0.145@546 nm	This work
5.	$[(C_3H_7N_6)_6(H_2PO_4)_4(HPO_4)(4H_2O)]$	$P2_1$	N/A	0.220@1064 nm	[32]
6.	$[(C_5H_6ON)(H_2PO_4)]$	$P2_12_12_1$	246	0.250@1064 nm	[63]
7.	$[(C_4H_6N_3)(H_2PO_3)]$	$P2_1$	346	0.275@1064 nm	[64]
8.	$[(C_4H_6N_3)(H_2PO_2).(H_2O)]$	$P\bar{1}$	328	0.349@1064 nm	[65]
		Fluoroborates/Fluorooxoborates			
9.	$[(NH_4)_3(PO_3F)(BF_4)]$	$P2_1/m$	190	0.012@1064 nm	[66]
10.	$[C(NH_2)_3(BF_4)]$	$R3m$	193	0.120@546nm	[23]
11.	$[(C_4H_6N_3)(BF_4)]$	$P2_1/n$	333	0.127@1064 nm	[65]
12.	$[C(NH_2)_3]_2[B_3O_3F_4(OH)]$	$P1$	190	0.161@1064 nm	[67]
13.	$[C(NH_2)_3][B_3O_3F_2(OH)_2]$	$P1$	195	0.173@1064 nm	[67]
14.	$[(C_3N_2H_5)B_3O_3F_2(OH)_2$	$P\bar{1}$	207	0.205@546 nm	[68]
15.	$[(C_3N_6H_7)(BF_4)\cdot(H_2O)]$	$P\bar{1}$	244	0.37@546 nm	[43]
16.	$[C_3N_6H_7]_2[B_3O_3F_4(OH)]$	$P\bar{1}$	240	0.440@546 nm	[69]
17.	$[(C_4H_6N_3)(BF_4)]$ **I-2**	$P2_1/n$	370	0.489 @546nm	This work
		Triflates			
18.	$[(C_4H_7N_3)(CF_3SO_3)_2]$	$P2_12_12_1$	324	0.063@1064 nm	[65]
19.	$[C(NH_2)_3(CF_3SO_3)]$	$C2/c$	182	0.139@1064 nm	[22]
20.	$[(CN_4H_7)\,(CF_3SO_3)]$	$P\bar{1}$	183	0.141@1064 nm	[22]
21.	$[(C_4H_5N_3)(C_4H_6N_3)(CF_3SO_3)]$ **II-1**	$P\bar{1}$	362	0.490@546 nm	This work
		Sulfamates			
22.	$[(C_4H_6N_3)(NH_2SO_3)]$	Cm	350	0.220@546 nm	[70]
23.	$[(C_4H_6N_3)(NH_2SO_3)]$	$P2_1/n$	333	0.241@1064 nm	[65]
24.	$[(C_3N_6H_7)(NH_2SO_3)]$	$P\bar{1}$	206	0.340 @546 nm	[46]
25.	$[(C_4H_6N_3)(NH_2SO_3)]$ **II-2**	$C2/c$	350	0.452@546 nm	This work
		Methane sulfonates			
26.	$[(CN_4H_7)(CH_3SO_3)]$	$P2_1/n$	198	0.102@1064 nm	[22]
27.	$[C(NH_2)_3(CH_3SO_3)]$	$C2/m$	195	0.137@1064 nm	[22]
28.	$[(C_5H_6NO)(CH_3SO_3)]$	$Pna2_1$	252	0.202@546 nm	[71]
29.	$[(C_3N_6H_7)(CH_3SO_3)(H_2O)$	$P\bar{1}$	233	0.310@546 nm	[43]
30.	$[(C_4H_5N_3)(C_4H_6N_3)(CH_3SO_3)]$	$P2_1/c$	330	0.320@1064 nm	[65]
31.	$[(C_4H_6N_3)(CH_3SO_3)]$ **II-3**	$P2_1/c$	360	0.594@ 546 nm	This work
		Succinate			
32.	$[(C_4H_5N_3)_2(C_4H_6O_4)]$ **III**	$P2_1/c$	364	0.658@546 nm	This work

Table S9. Assignments of the IR peaks for **I-1**−**I-2**, **II-1**−**II-3**, **III**, and **IV.**

Mode description	I-1	I-2	II-1	II-2	II-3	III	IV	Ref
$\upsilon(NH_2)$	3329	3329	3334	3311	3316	3394	3391	
υ_s(C=N)	1687	1659	1657	1677	1668	1696	-	[72-74]
υ_s(C=C)	-			1640		1636	1610	
υ(P=O)	1111,1219							[64,74]
δ (O−P−O)	497, 561							
υ_s(B−F)		703						
υ_{as}(B−F)		1071						[75]
δ (B−F)		529						
υ_s(S=O)			1016	1005	1004			
υ_{as}(S=O)			634	636	1042			[22]
υ_s(C−F)			1263		630			
δ (C−F)			812					
δ_s(CH3)					1371			
δ_{as}(CH3)					1421			[71]
υ(S−C)					776			
υ(C=O)						1544		
υ_{as}(COO)						1704		[73]
$\upsilon_{as}(BO_3)$							1442,1522	
$\delta(BO_3)$							548	[76]

$\boldsymbol{\upsilon}$= stretching, $\boldsymbol{\upsilon_s}$= symmetrical Stretching, $\boldsymbol{\upsilon_{as}}$= asymmetrical stretching, δ= bending vibrations, δ_s=symmetric bending vibrations, δ_{as}=*a*symmetric bending vibrations.

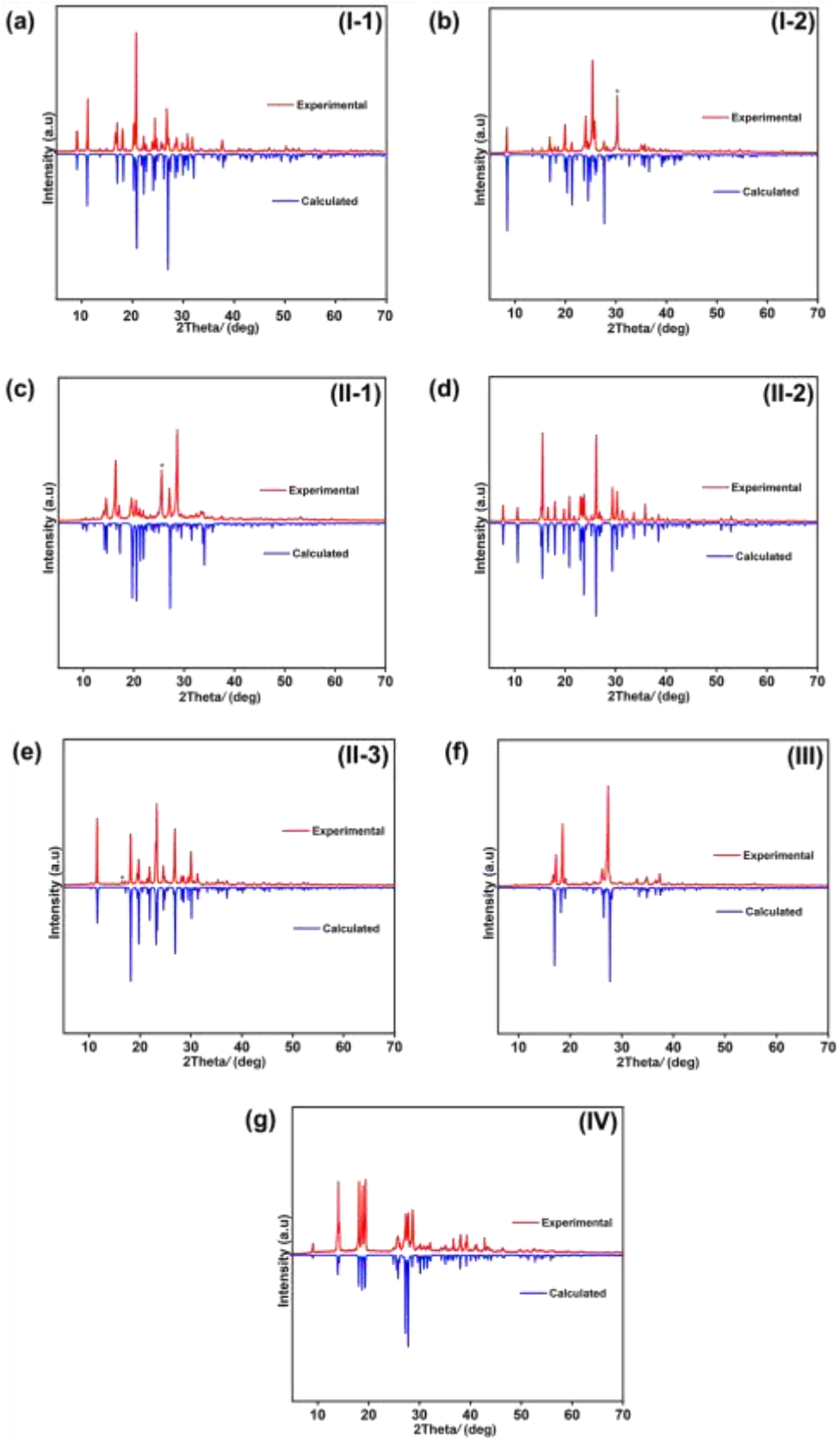


Figure S1. The powder XRD patterns of **I-1**−**I-2**, **II-1**−**II-3**, **III**, and **IV.**

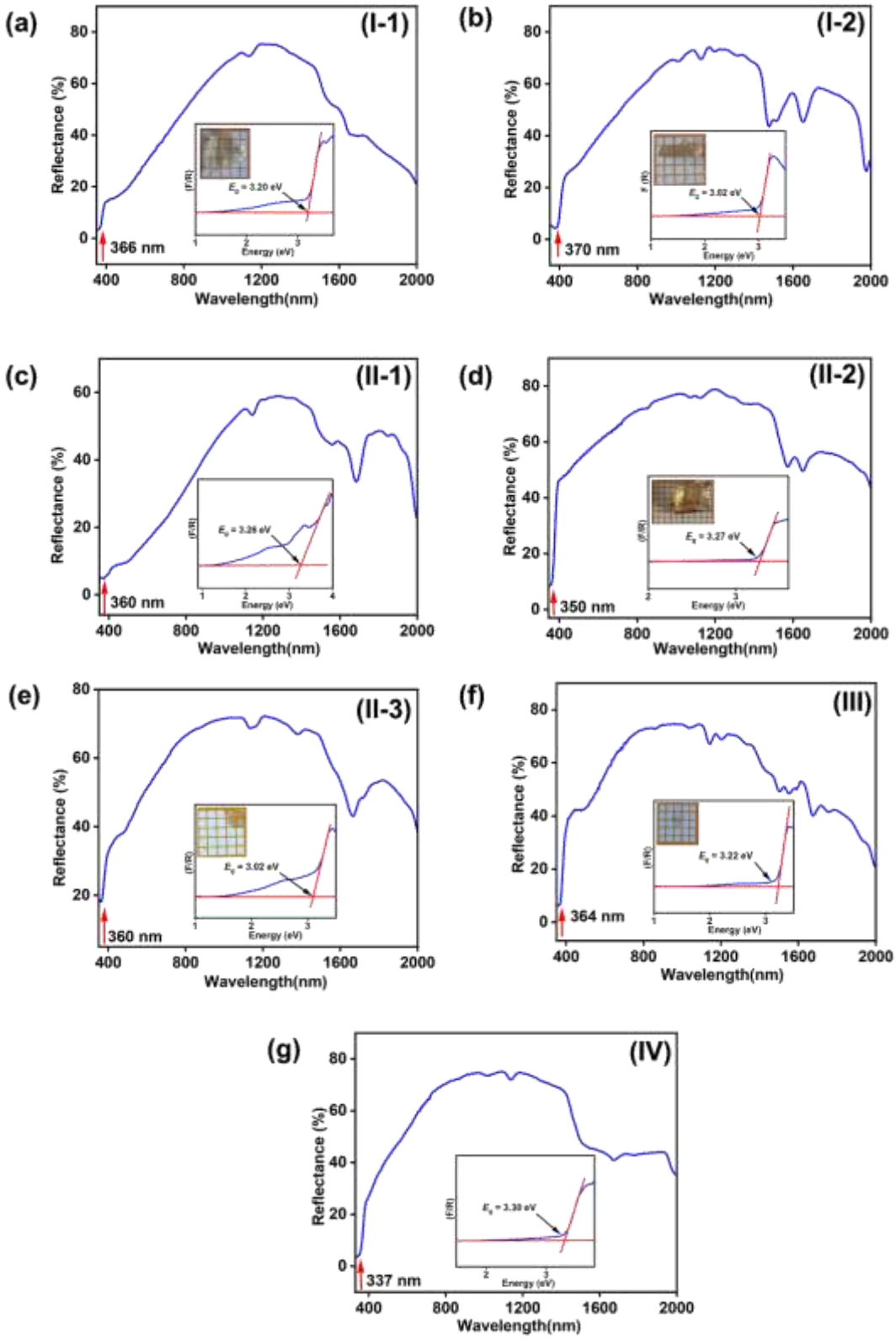


Figure S2. UV-vis-NIR diffuse reflectance spectra and their corresponding experimental band gaps of **I-1**−**I-2**, **II-1**−**II-3**, **III**, and **IV.**

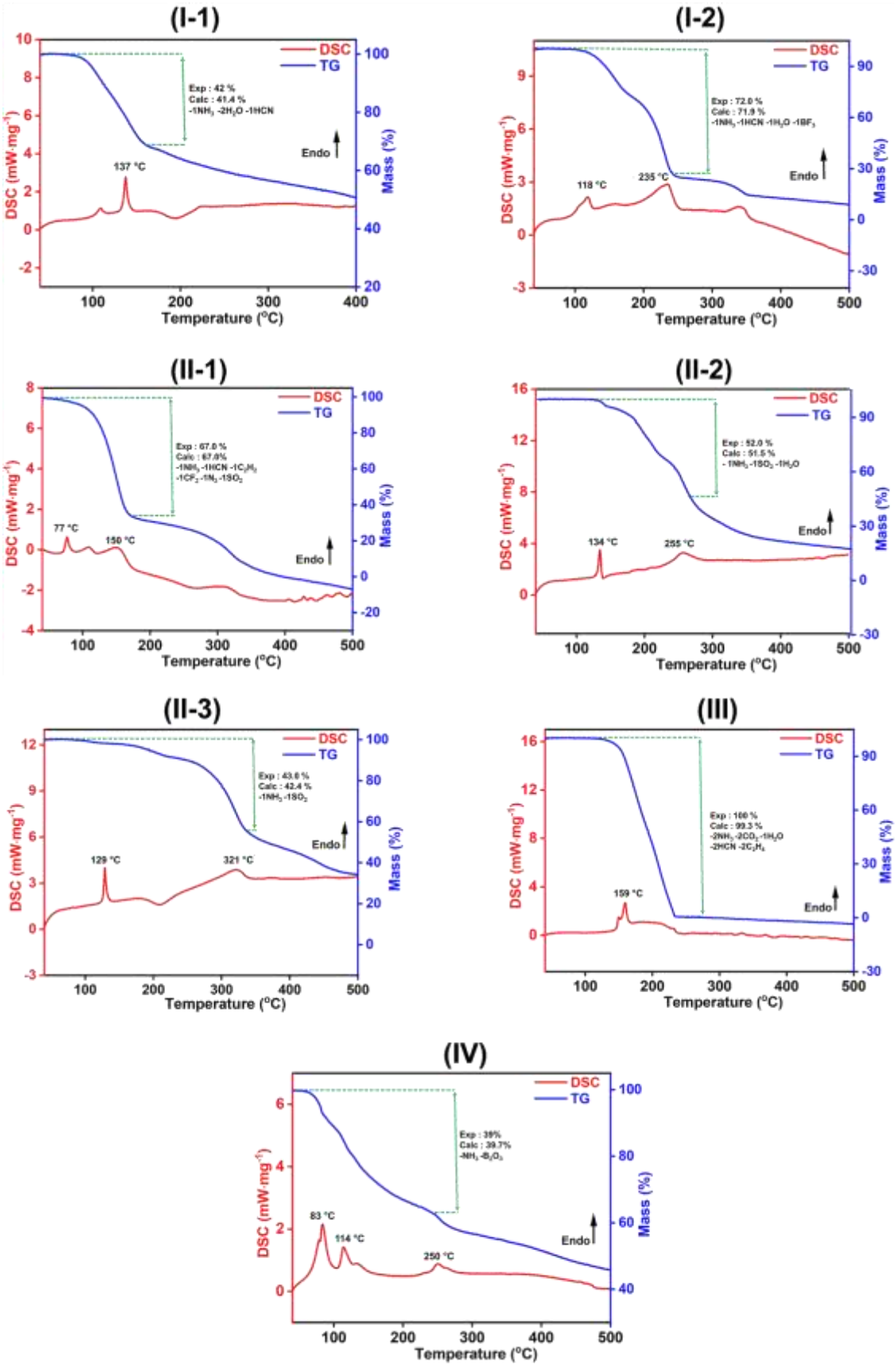


Figure S3. The differential scanning calorimetry (DSC) and thermogravimetry (TG) curves for **I-1**−**I-2**, **II-1**−**II-3**, **III**, and **IV.**

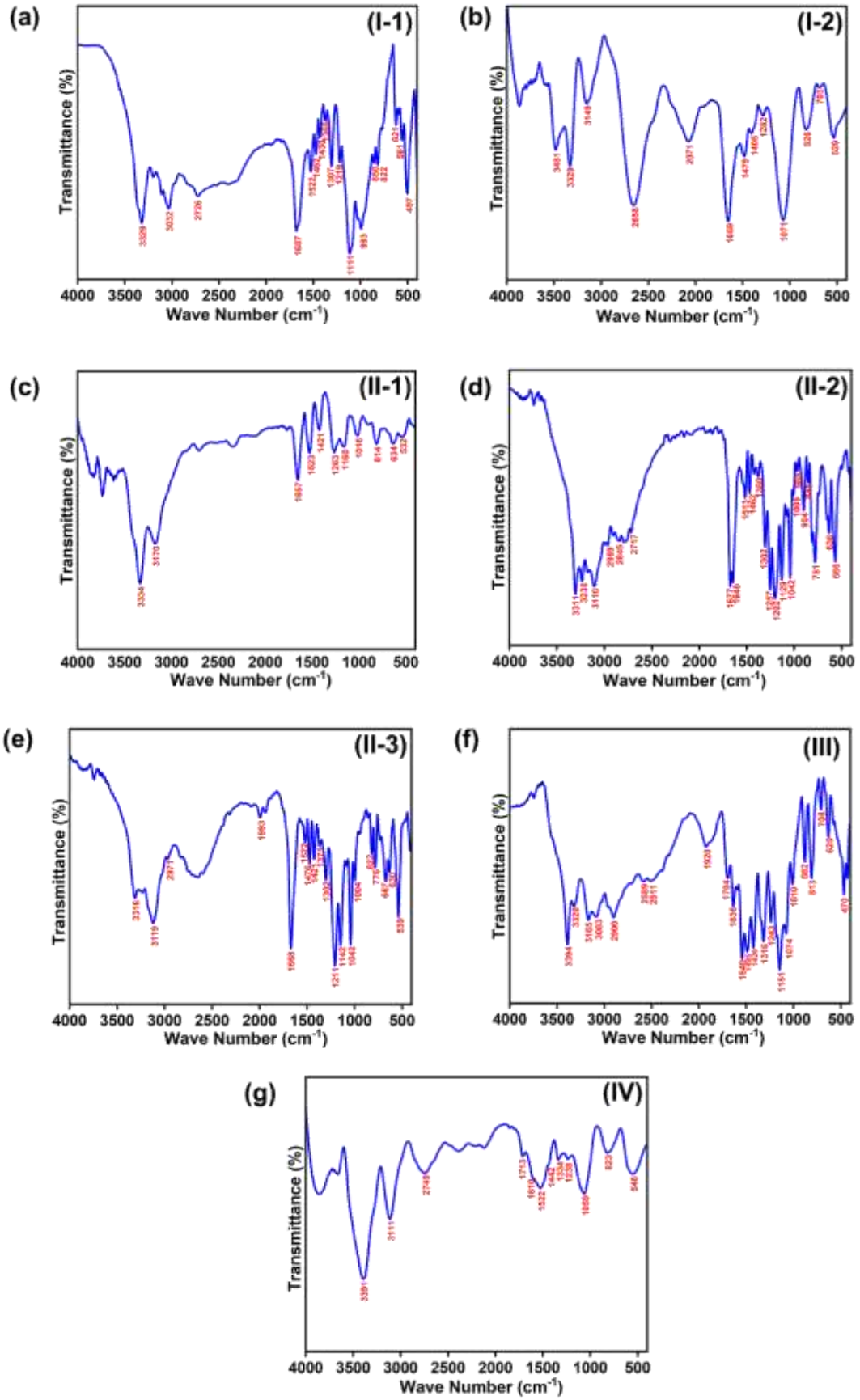
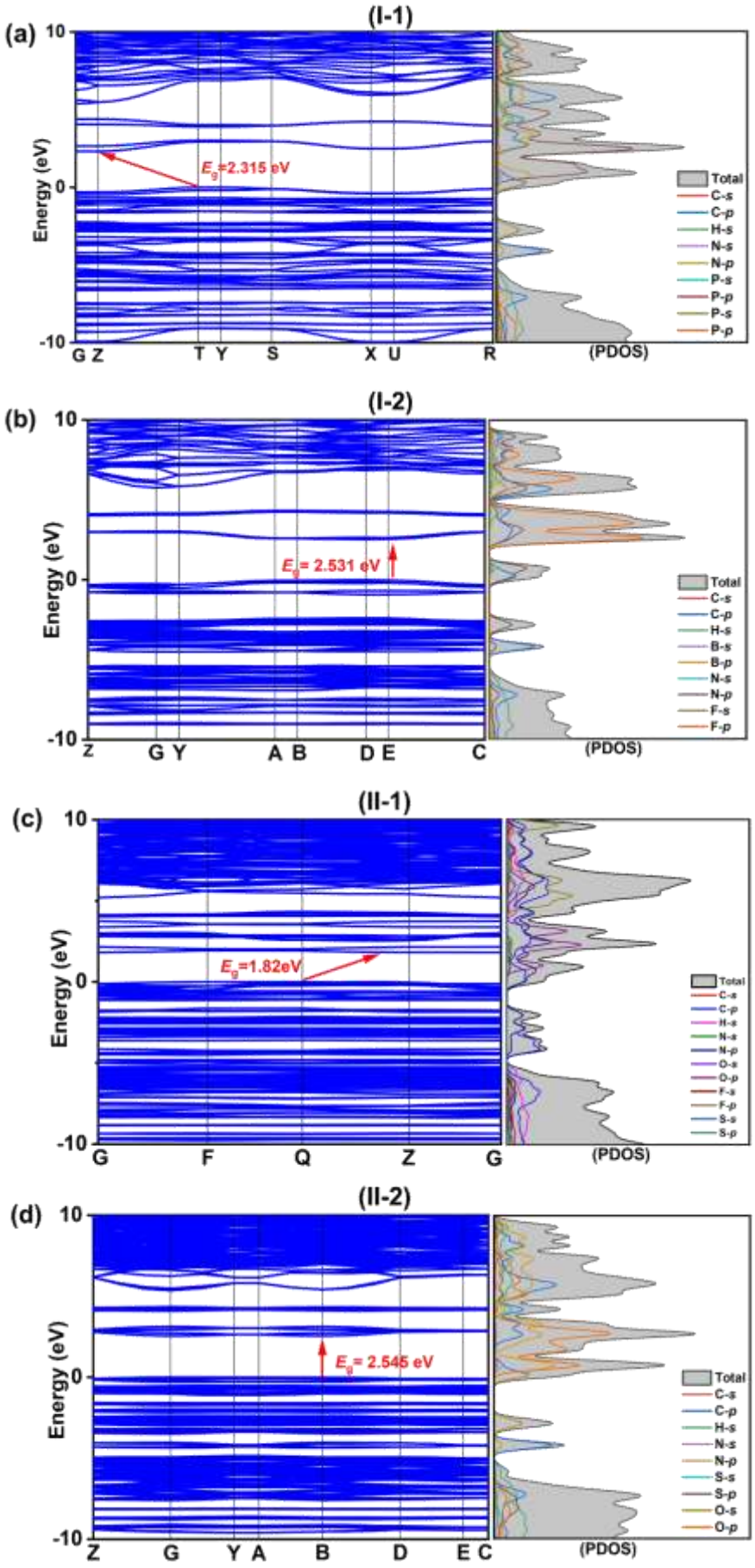


Figure S4. IR spectra for **I-1**−**I-2**, **II-1**−**II-3**, **III**, and **IV**.


(I-1)
(a)
Energy (eV)
E_g=2.315 eV
G Z T Y S X U R
(PDOS)
Total
C-s
C-p
H-s
N-s
N-p
P-s
P-p
P-s
P-p
(I-2)
(b)
Energy (eV)
E_g= 2.531 eV
Z G Y A B D E C
(PDOS)
Total
C-s
C-p
H-s
B-s
B-p
N-s
N-p
F-s
F-p
(II-1)
(c)
Energy (eV)
E_g=1.82eV
G F Q Z G
(PDOS)
Total
C-s
C-p
H-s
N-s
N-p
O-s
O-p
F-s
F-p
S-s
S-p
(II-2)
(d)
Energy (eV)
E_g= 2.545 eV
Z G Y A B D E C
(PDOS)
Total
C-s
C-p
H-s
N-s
N-p
S-s
S-p
O-s
O-p

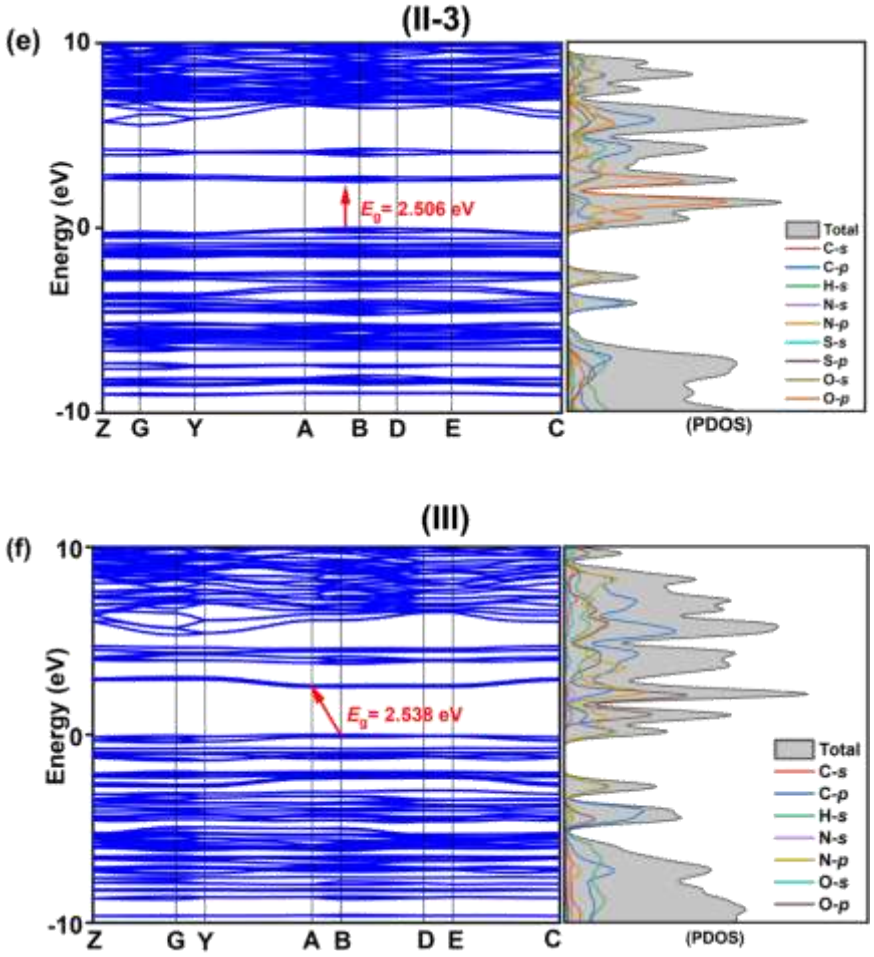


Figure S5. The calculated band gaps and partial densities of states for **I-1**−**I-2**, **II-1**−**II-3**, and **III**.

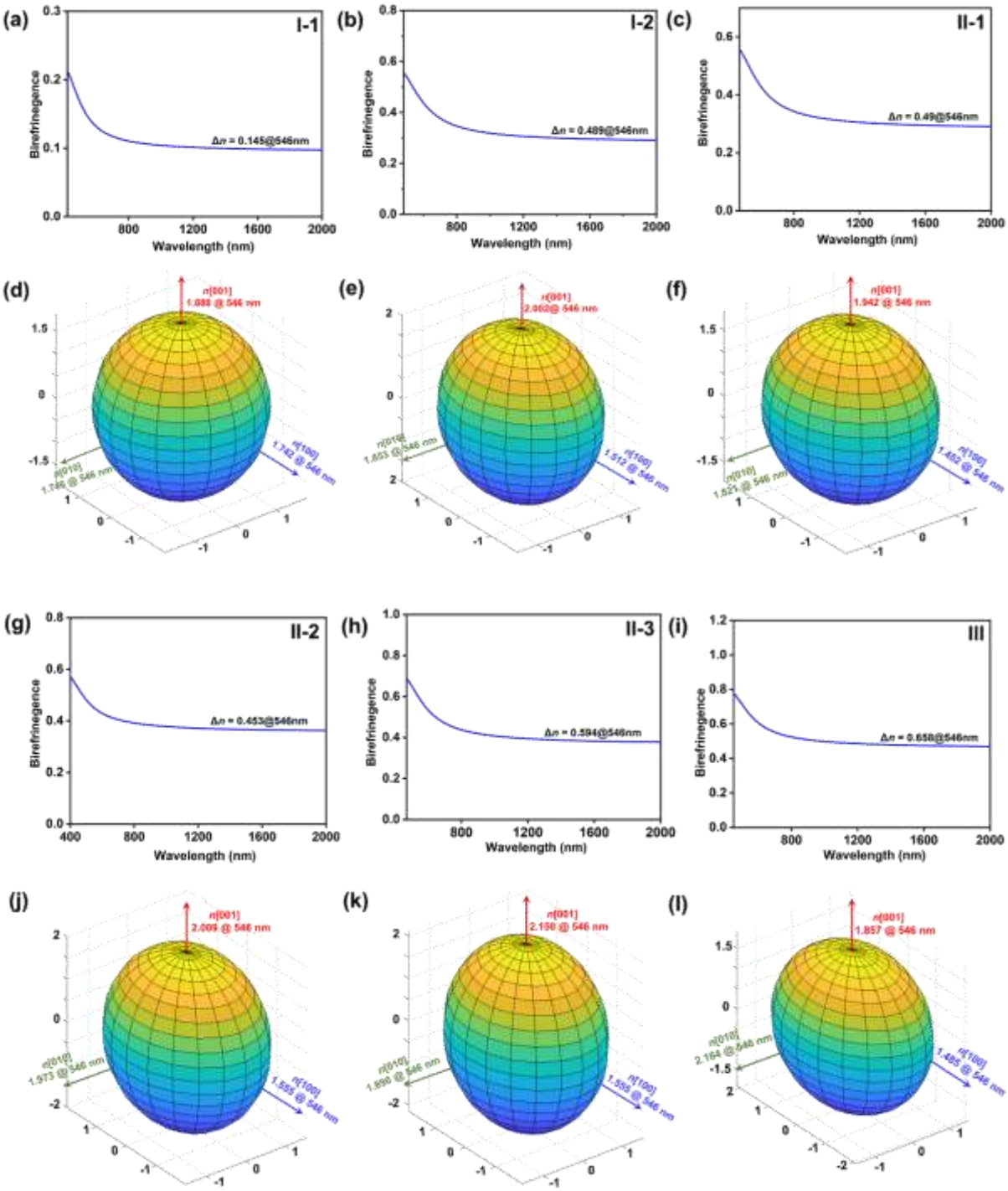
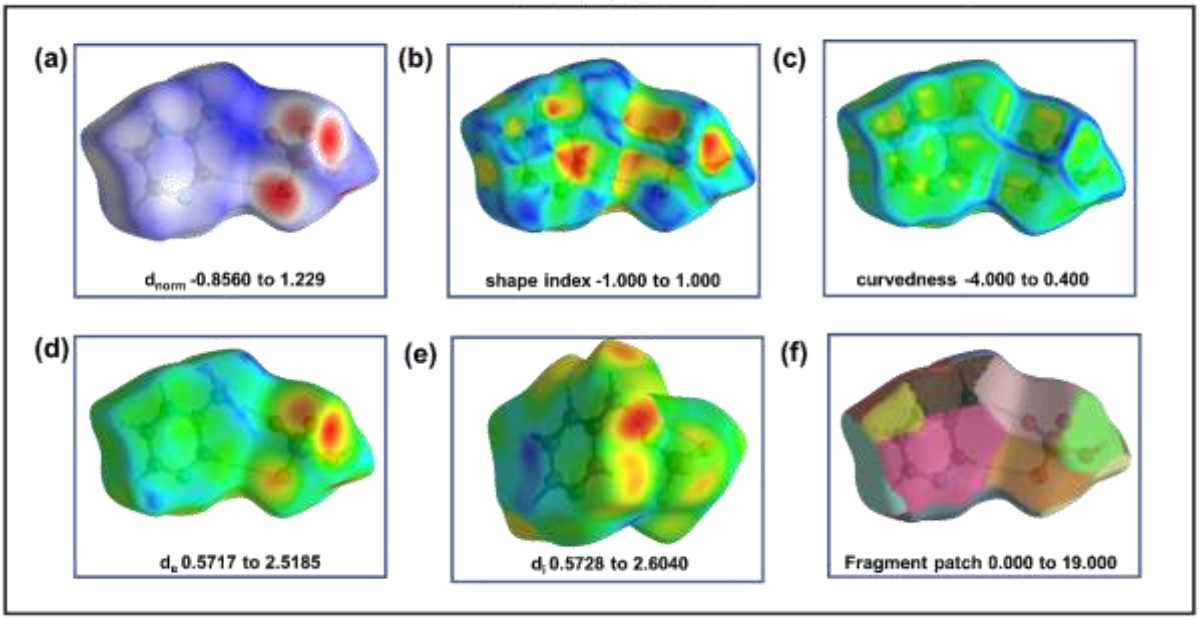
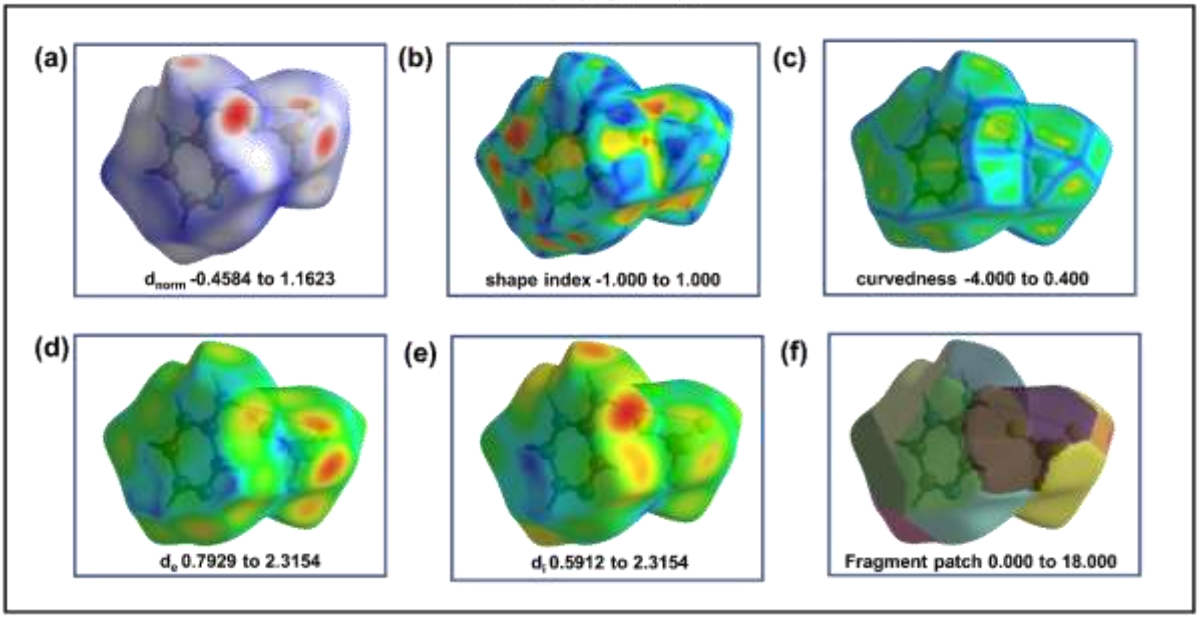


Figure S6. Calculated birefringence and triaxial ellipsoid of three refractive indices along crystallographic axes for **I-1**−**I-2**, **II-1**−**II-3**, and **III**.

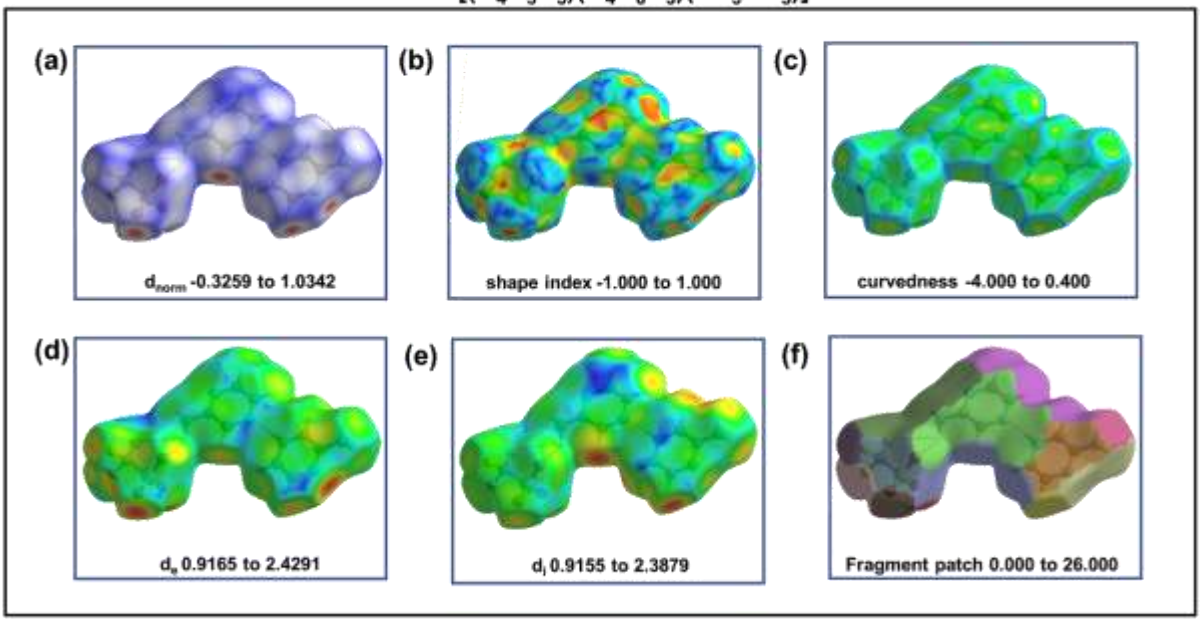
I-1 $[(C_4H_6N_3)(H_2PO_4)]$



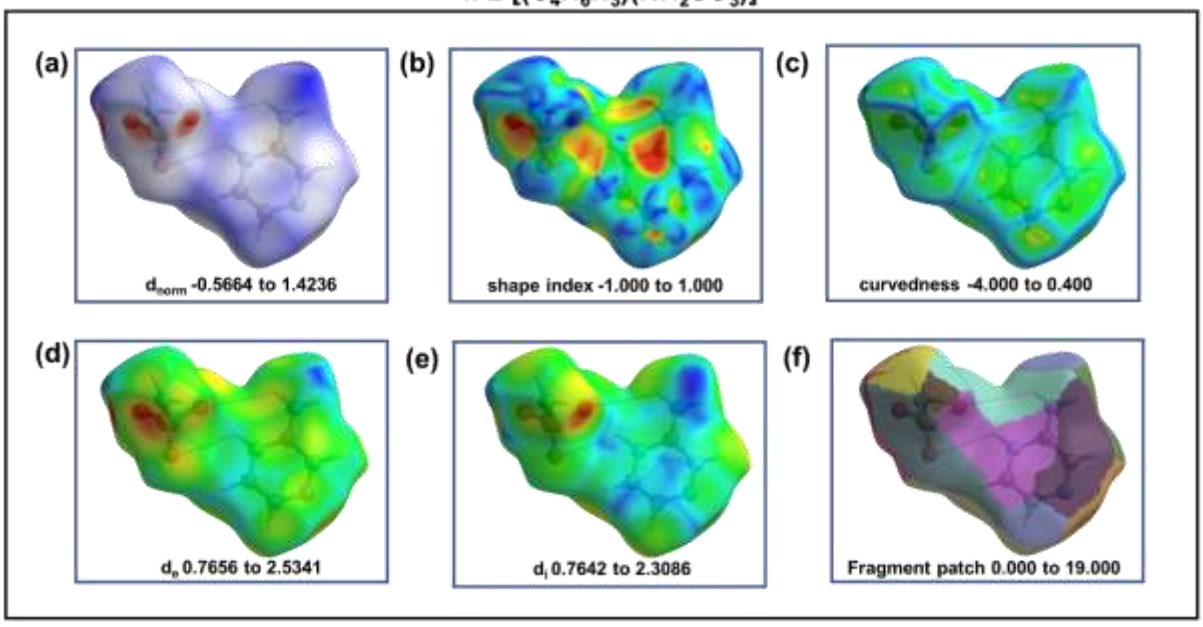
I-2 $[(C_4H_6N_3)(BF_4)]$



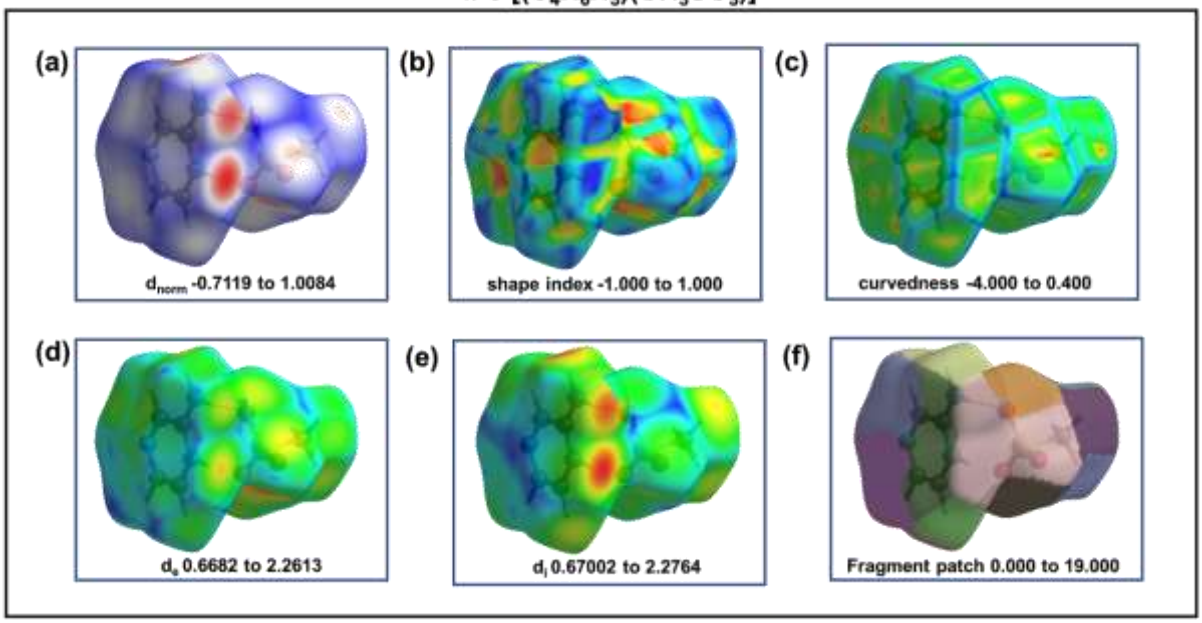
II-1 [$(C_4H_5N_3)(C_4H_6N_3)(CF_3SO_3)$]



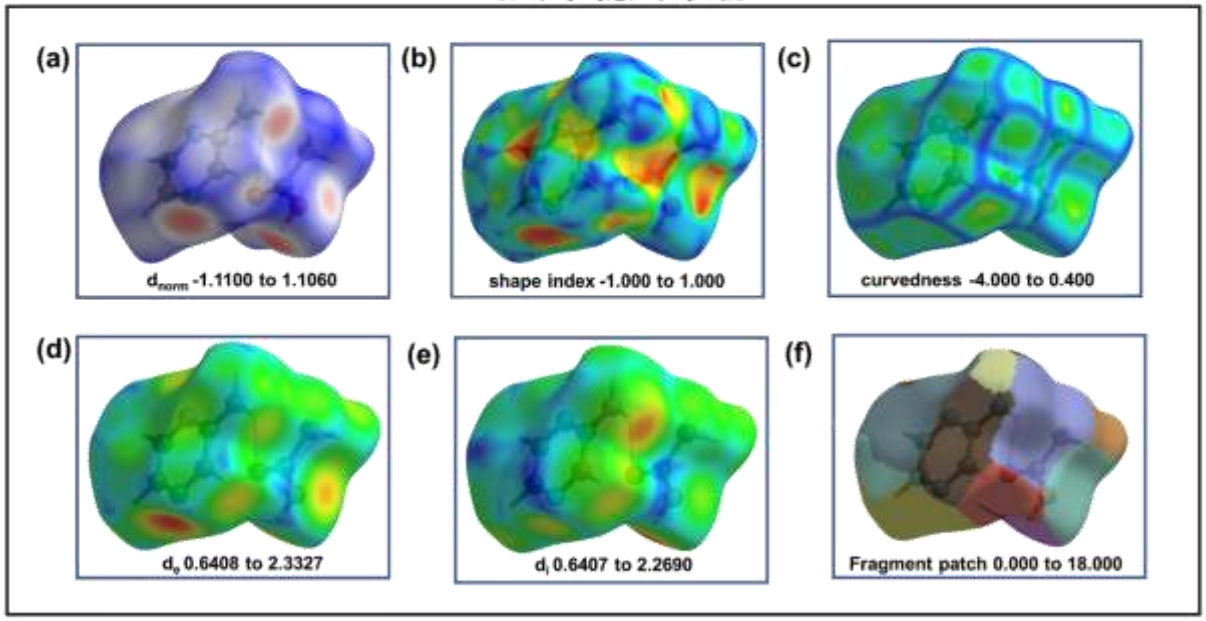
II-2 [$(C_4H_6N_3)(NH_2SO_3)$]



II-3 [$(C_4H_6N_3)(CH_3SO_3)$]



III [$(C_4H_5N_3)_2(C_4H_6O_4)$]



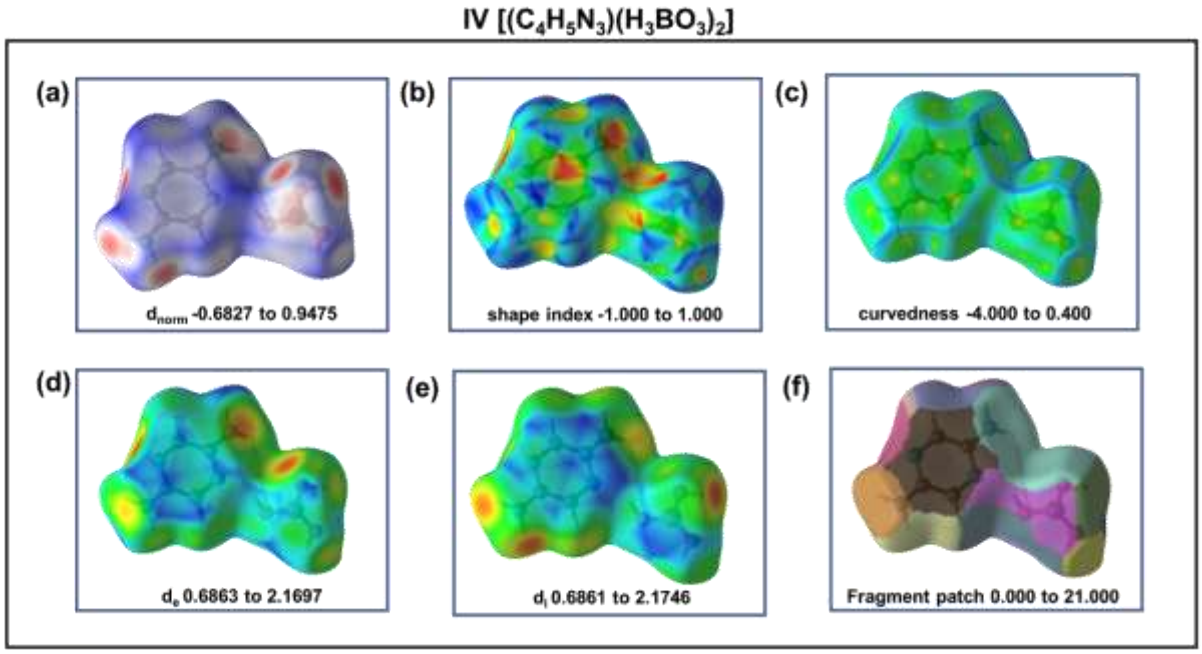
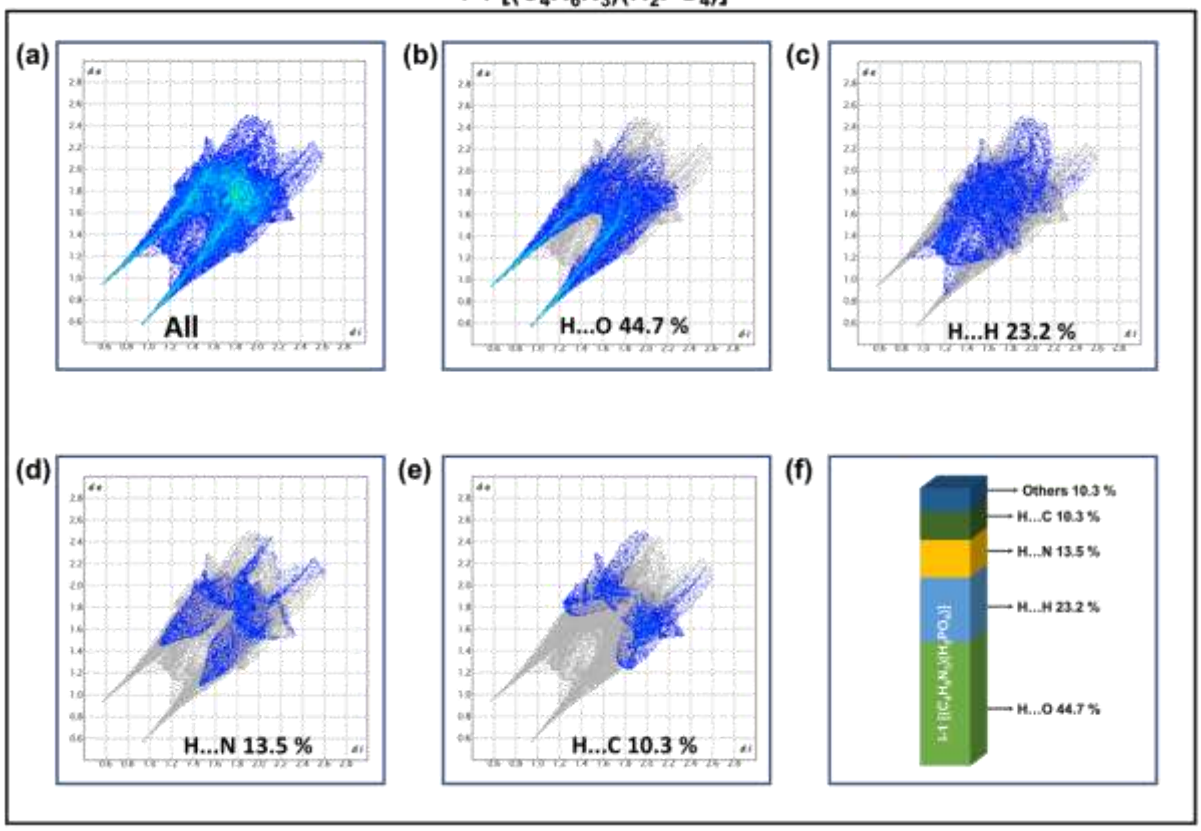
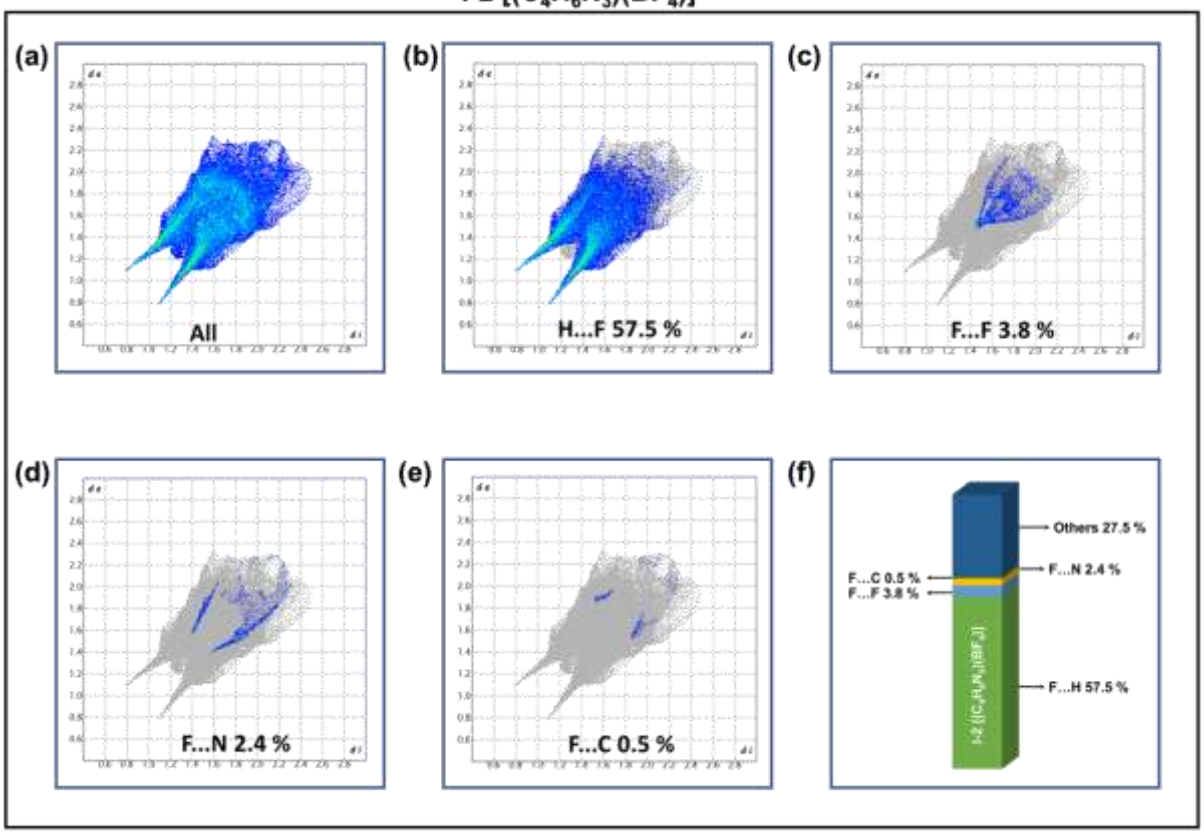


Figure S7. Visualization of hirshfeld surfaces: d_{norm} (a), shape index (b), curvedness (c) d_e (d), d_i (e), and fragment patch for **I-1**−**I-2**, **II-1**−**II-3**, **III**, and **IV.**

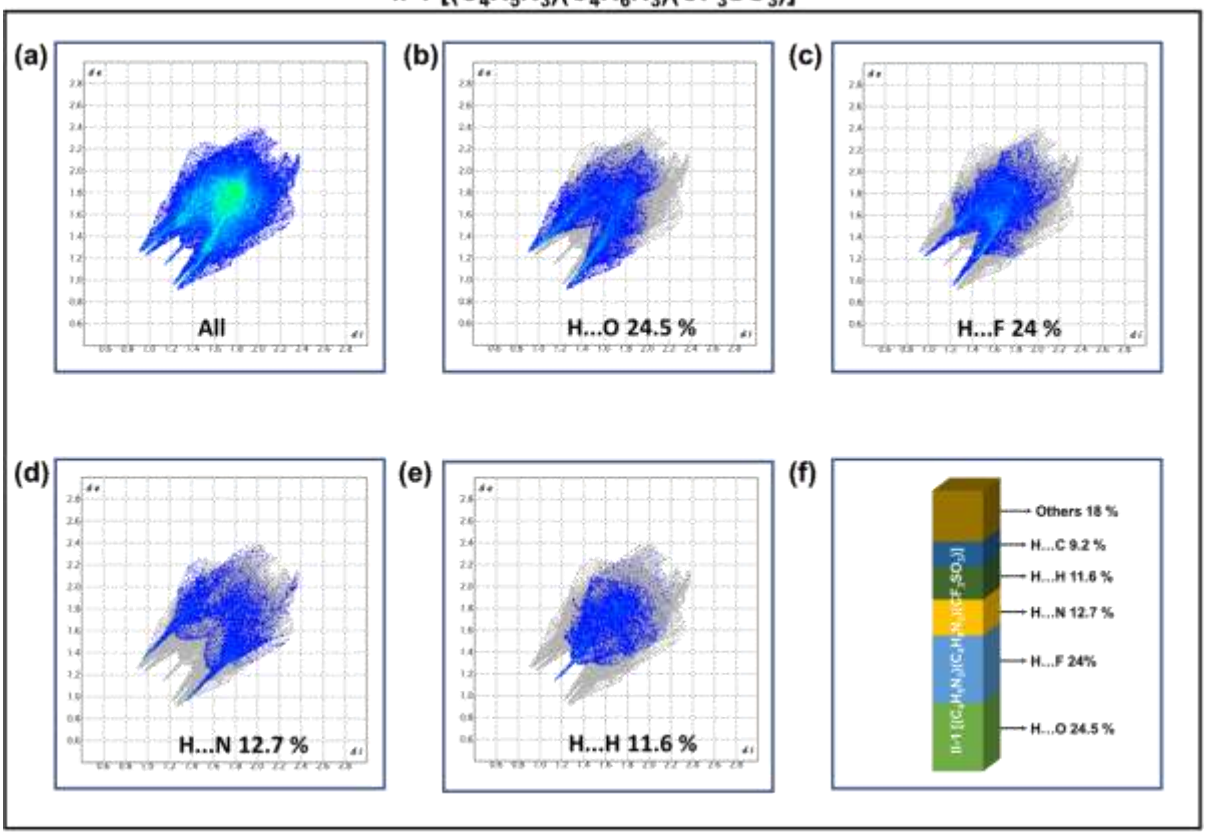
I-1 [$(C_4H_6N_3)(H_2PO_4)$]



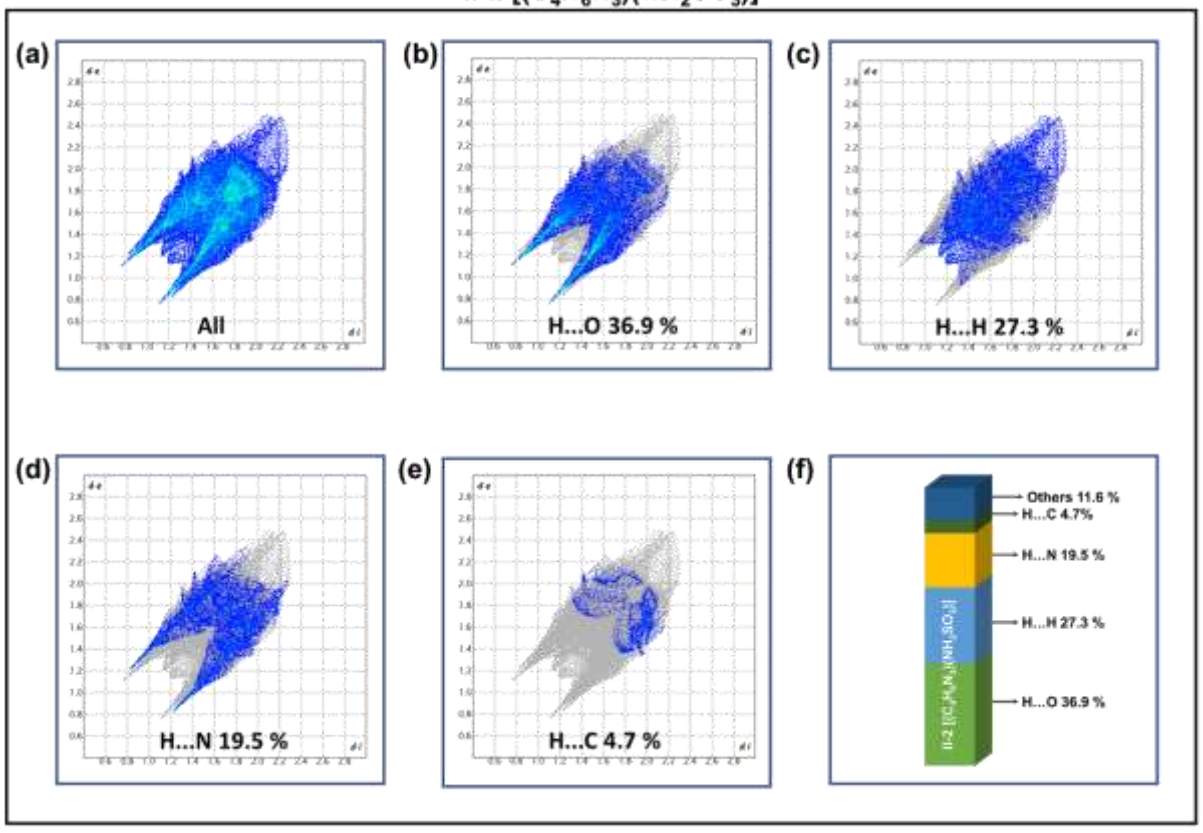
I-2 [$(C_4H_6N_3)(BF_4)$]



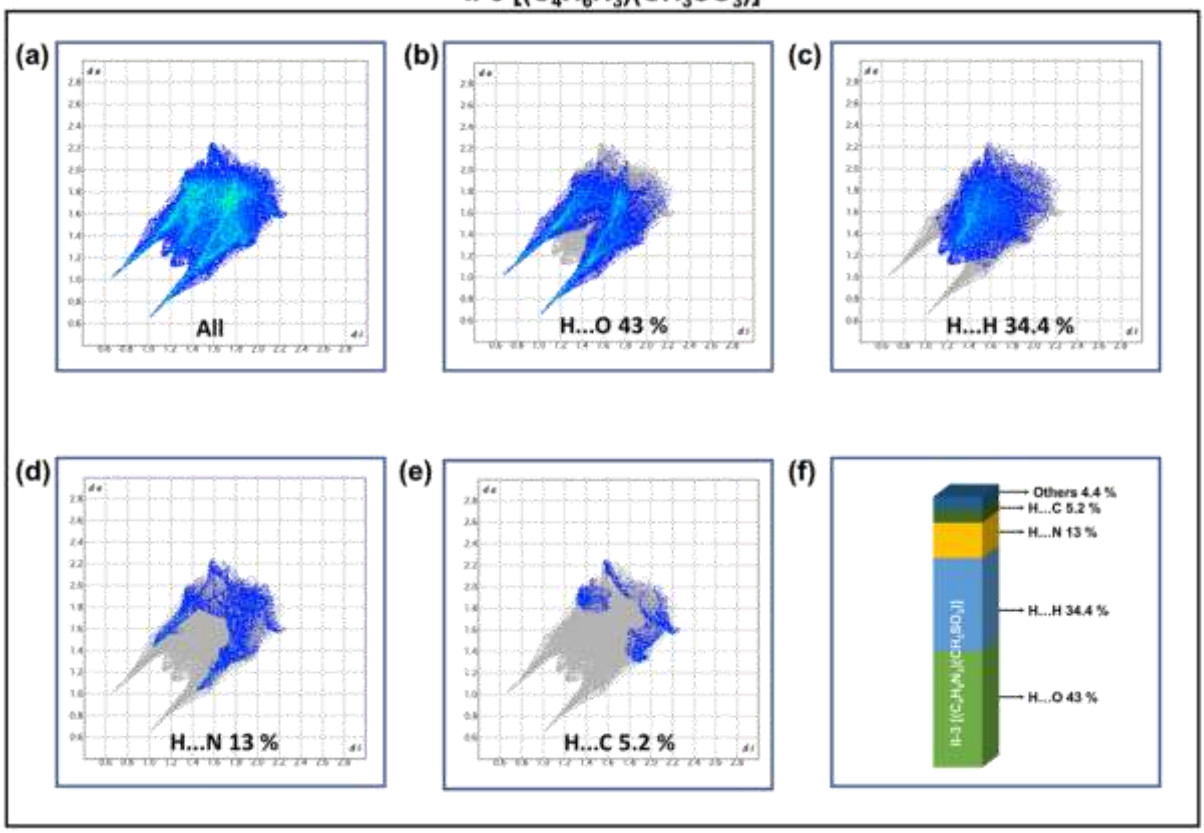
II-1 [$(C_4H_5N_3)(C_4H_6N_3)(CF_3SO_3)$]



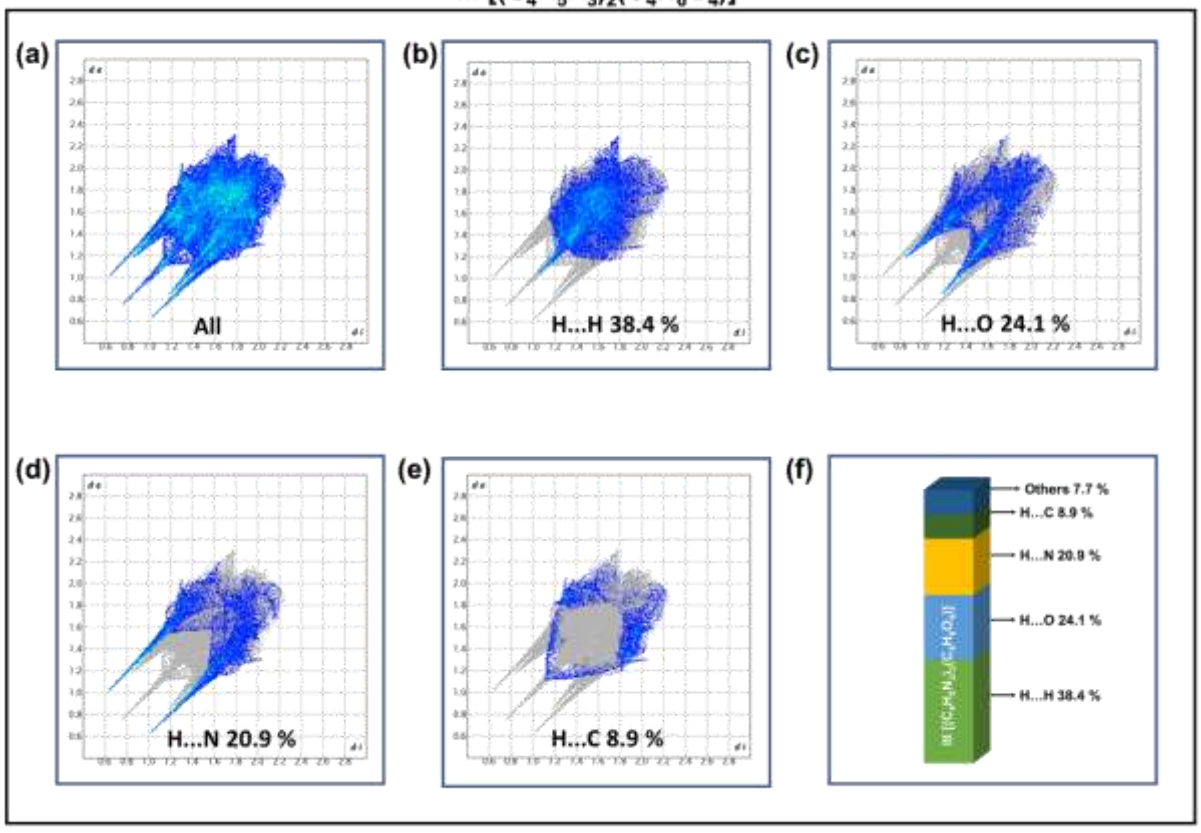
II-2 [$(C_4H_6N_3)(NH_2SO_3)$]



II-3 [$(C_4H_6N_3)(CH_3SO_3)$]



III [$(C_4H_5N_3)_2(C_4H_6O_4)$]



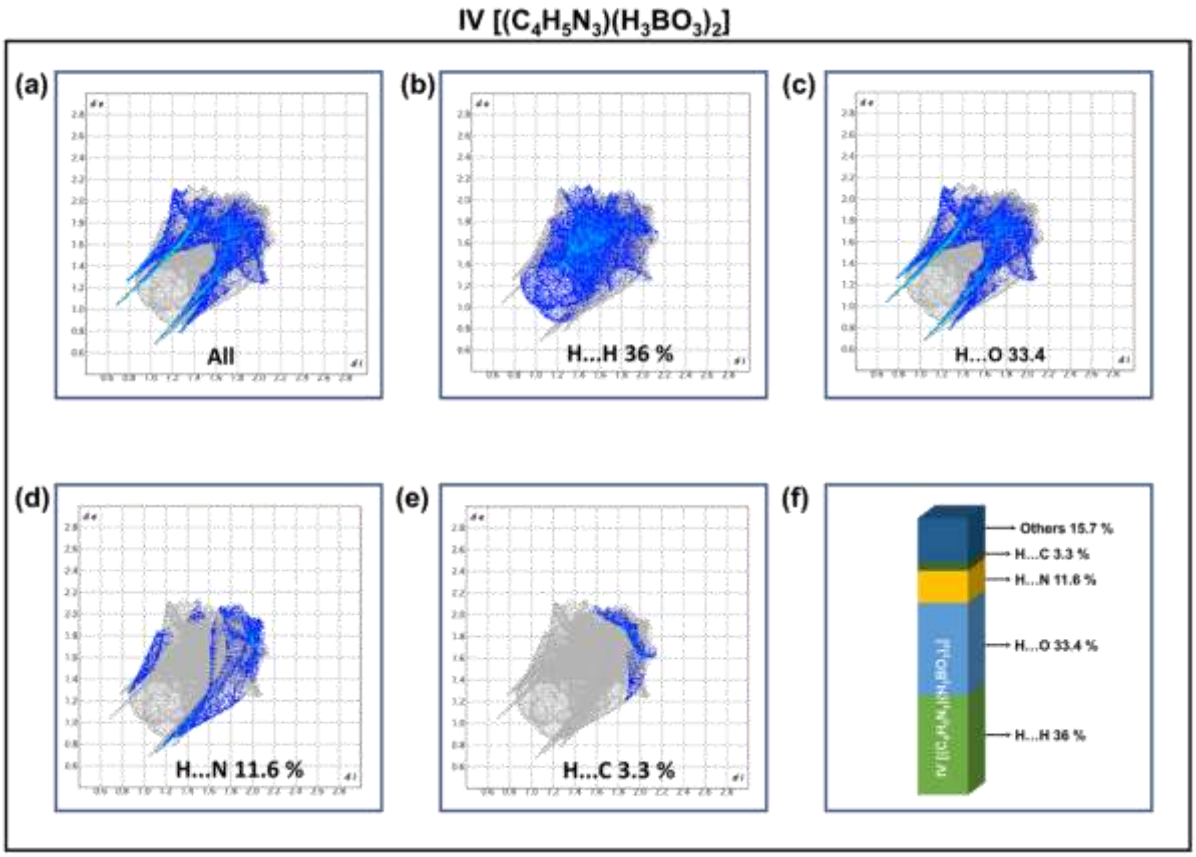
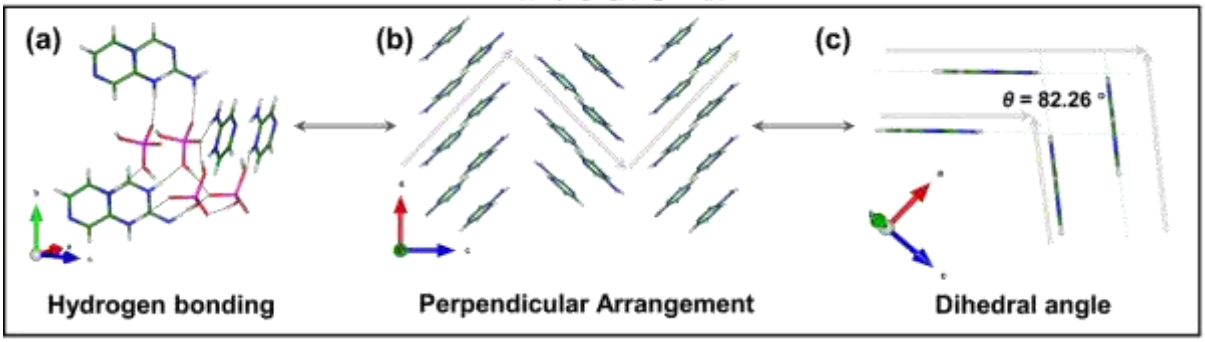
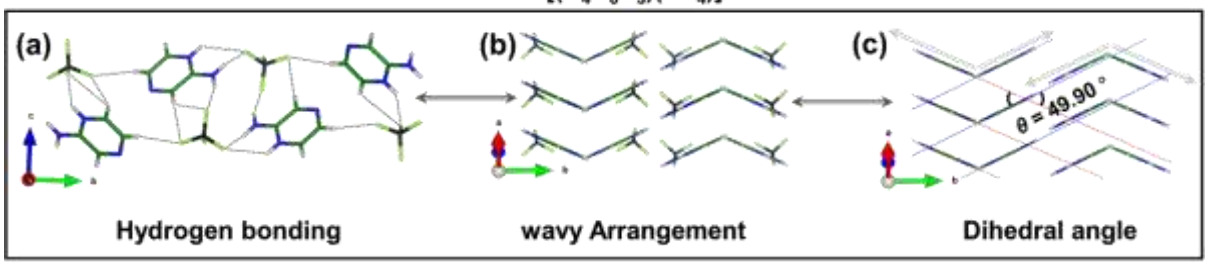


Figure S8. Visualization of 2D fingerprint plots for overall interactions and individual interactions of atom types in crystal packing of **I-1**−**I-2**, **II-1**−**II-3**, **III**, and **IV**.

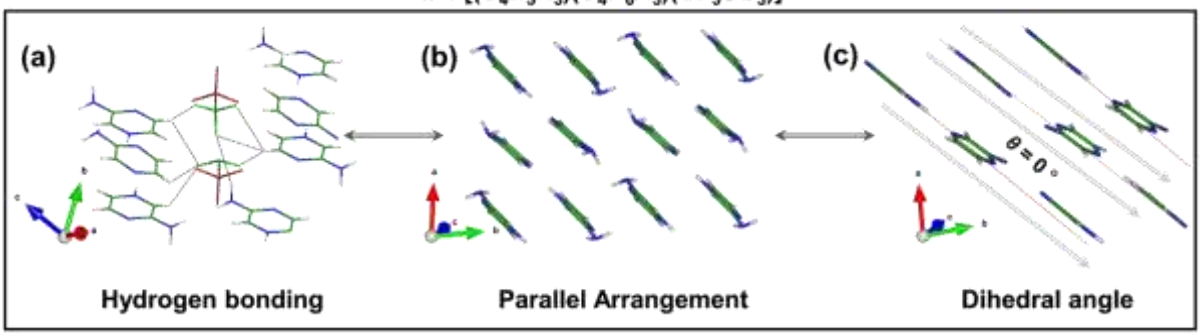
I-1 [$(C_4H_6N_3)(H_2PO_4)$]



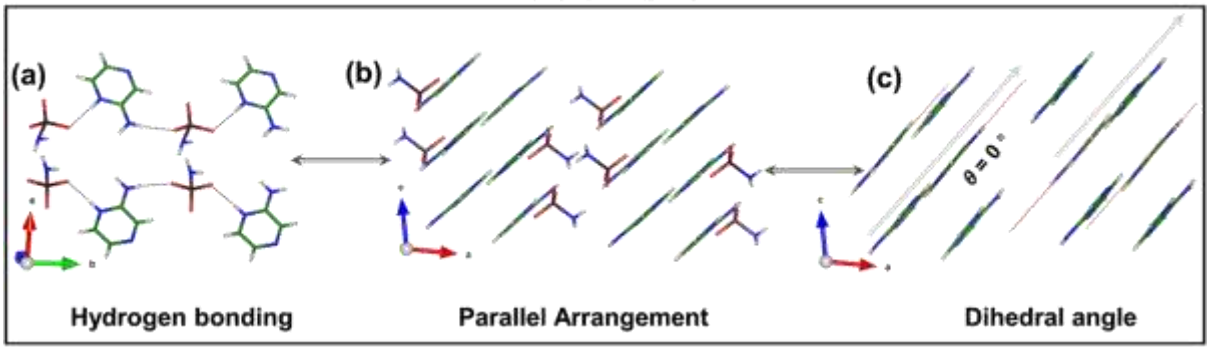
I-2 [$(C_4H_6N_3)(BF_4)$]



II-1 [$(C_4H_5N_3)(C_4H_6N_3)(CF_3SO_3)$]



II-2 [$(C_4H_6N_3)(NH_2SO_3)$]



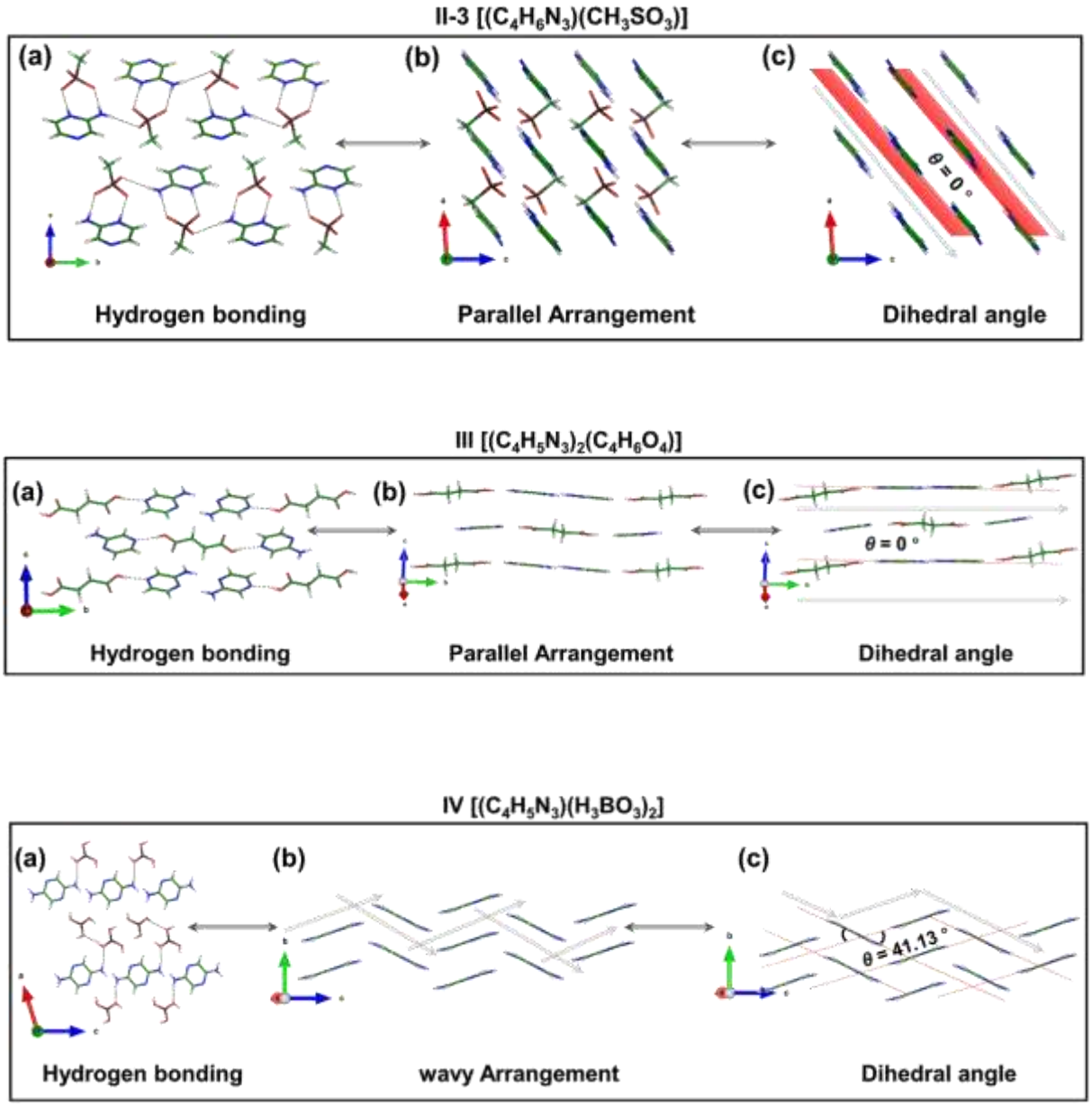


Figure S9. Visualization of hydrogen bonding, spatial arrangement, and dihedral angle of **I-1**−**I-2**, **II-1**−**II-3**, **III**, and **IV**.

We attempted various approaches, adjusting temperature, ratios, and solvent composition, to synthesize this compound without disorder; however, all efforts have been unsuccessful.

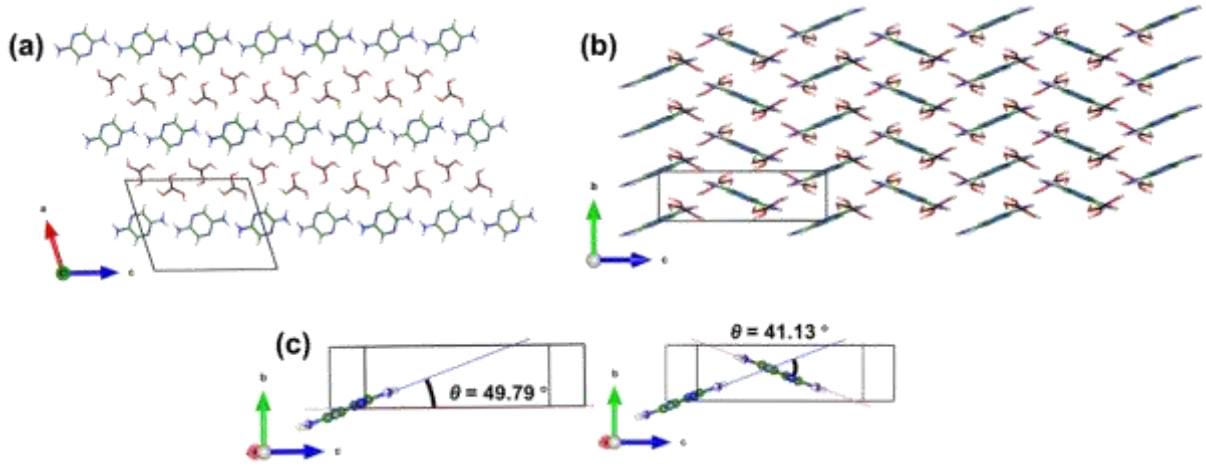


Figure S10. Crystal packing of **IV** along the a and b axis (a,b), and dihedral angle (γ) of [APZ] along (010) plane and angles between π-conjugated units (c).

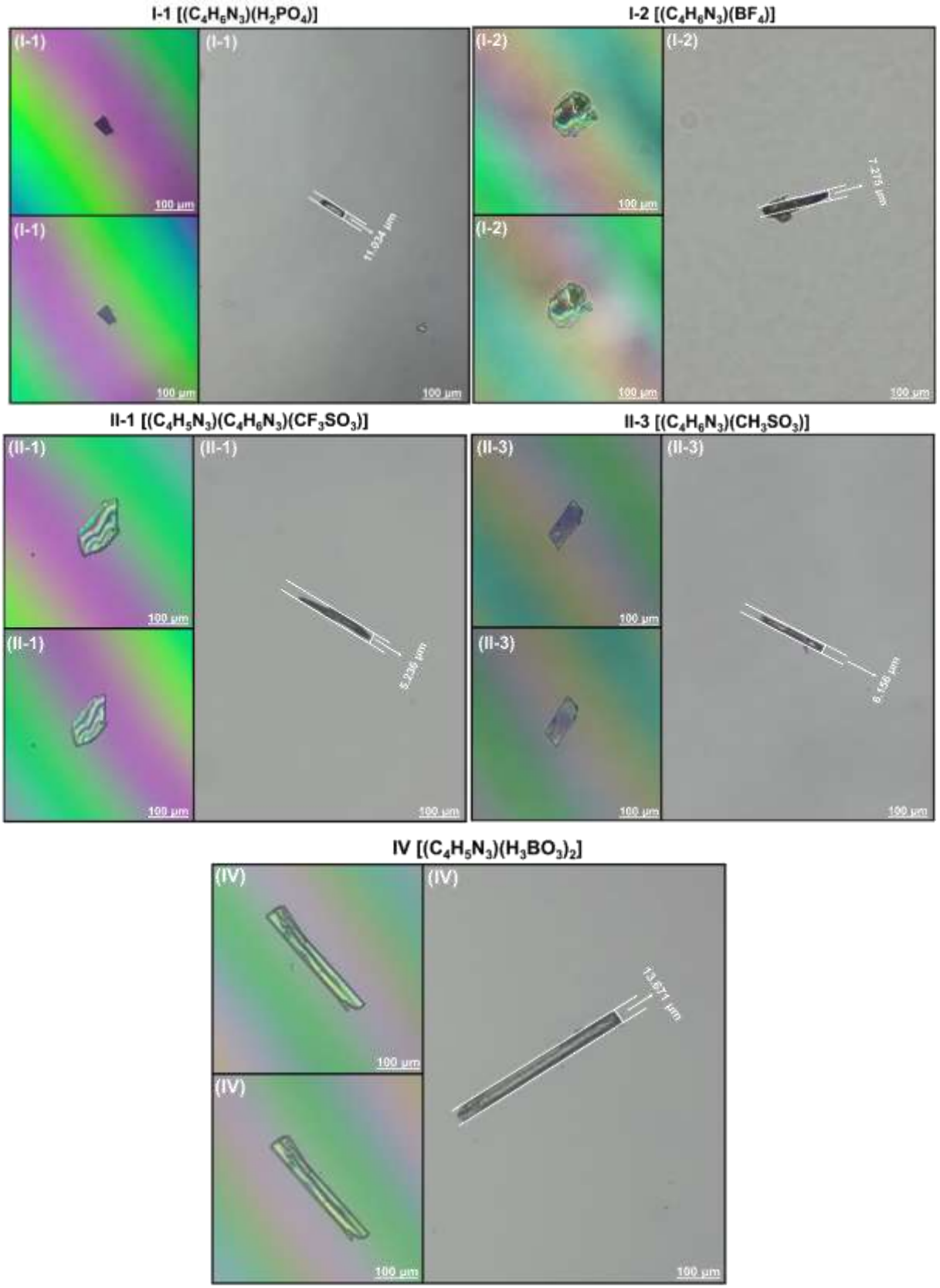


Figure S11. Birefringence measurements under the polarizing microscope and the thickness for **I-1**−**I-2**, **II-1**, **II-3**, and **IV**.

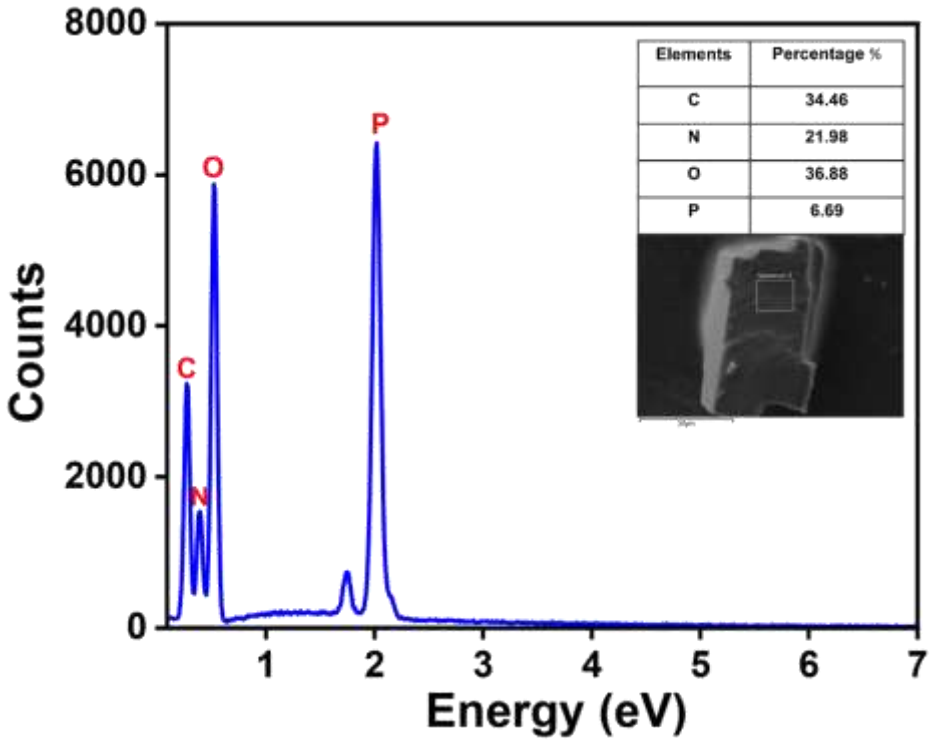


Figure S12. Energy dispersive X-ray spectroscopy (EDS) analysis of **I-1.**

Given the propensity of NCS crystal structures to exhibit second-harmonic generation (SHG). The SHG effect was measured on polycrystalline samples by Kurtz-Perry method at a wavelength of 1064 nm, using KDP as the reference.[4] However, upon testing **I-1**, the SHG signal was negligible. It can be attributed to the perpendicular arrangement of fundamental structural components $[APZ]^+$ within crystal structure, which effectively cancel out frequency-doubling effect. This finding was further substantiated by SHG-weighted electron density analysis,[77] which provide insights into the origin of the SHG effects. The majority of SHG-weighted electron clouds are concentrated around the C-C, and C-N bonds, as well as C and N atoms, confirming that the $[APZ]^+$ units are the primary determinants of the SHG response.

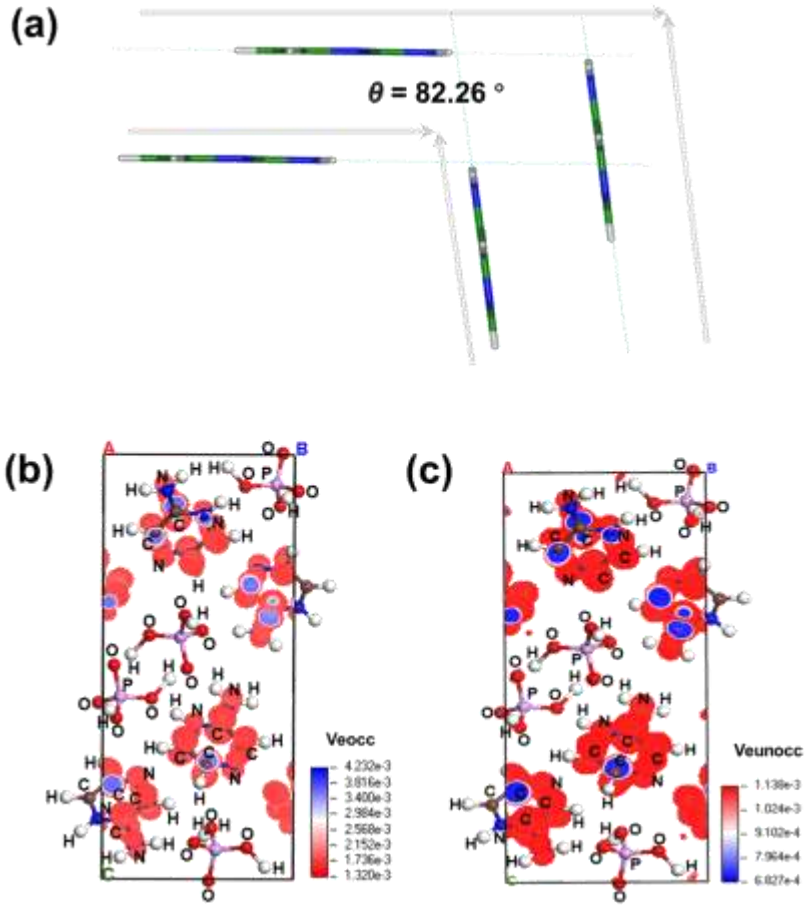


Figure S13. Spatial Arrangement of functional units in **I-1** (a), SHG-weighted densities for occupied and unoccupied electronic states in **I-1** (b,c).

References

(1) *SAINT, Version 7.60A,* Bruker Analytical X-ray Instruments, Inc. Madison, WI, **2008**.

(2) G. M. Sheldrick, *SHELXTL*; Bruker AXS Inc.: Madison, WI, **2008**.

(3) A. L. Spek, Single-crystal Structure Validation with the Program PLATON. *J. Appl. Crystallogr.* **2003**, *36*, 7.

(4) S. K. Kurt, T. T. Perry. *J. Appl. Phys.* **1968**, *39*, 3798-3813.

(5) S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, M. C. Payne, Z. *Kristallog. Cryst. Mater*. **2005**, *220*, 567– 570.

(6) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.

(7) J. H. Monkhorst, J. D. Pack, *Phys. Rev. B.* **1976**, *13*, 5188.

(8) C. Aversa, J. E. Sipe, *Phys. Rev. B.* **1995**, *52*, 14636–14645.

(9) S. N. Rashkeev, W. R. L. Lambrecht, B. Segall, *Phys. Rev. B.* **1998**, *57*, 3905–3919.

(10) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G .E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr. , J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, *Revision A.02*, Gaussian, Inc., Wallingford CT **2009**.

(11) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem*. **1994**, *98*, 11623-11627.

(12) I. Němec, I. Matulková, P. Held, J. Kroupa, P. Němec, D. Li, L. Bohatý, P. Becker, *Opt. Mater.* **2017**, *69*, 420–431.

(13) J. Zhang, X. Zhang, Y. Wang, K. Wu, B. Zhang, *Inorg. Chem.* **2022**, *61*, 18622–18628.

(14) L. Xiong, J. Chen, J. Lu, C.-Y. Pan, L.-M. Wu, *Chem. Mater.* **2018**, *30*, 7823–7830.

(15) H. Zhang, D. Jiao, X. Li, C. He, X. Dong, K. Huang, J. Li, X. An, Q. Wei, G. Wang, *Small.* **2024**, *20*, 2401464.

(16) Y. Liu, X. Liu, Z. Xiong, B. Liu, J. Xu, L. Li, S. Zhao, Z. Lin, M. Hong, J. Luo, *Inorg. Chem.* **2021**, *60*, 14544–14549.

(17) Y. Song, M. Luo, D. Lin, C. Lin, Z. Wang, X. Long, N. Ye, *ACS Omega.* **2021**, *6*, 9263–9268.

(18) C. Wu, X. Jiang, Z. Wang, H. Sha, Z. Lin, Z. Huang, X. Long, M. G. Humphrey, C. Zhang, *Angew. Chem. Int. Ed.* **2021**, *60*, 14806–14810.

(19) M. Zhang, B. Zhang, D. Yang, Y. Wang, *Inorg. Chem.* **2021**, *60*, 18483–18489.

(20) Z. Bai, J. Lee, H. Kim, C. L. Hu, K. M. Ok, *Small.* **2023**, *19*, 2301756.

(21) M. Xia, M. Mutailipu, F. Li, Z. Yang, S. Pan, *Cryst. Growth Des.* **2021**, *21*, 1869–1877.

(22) H. Zhou, M. Cheng, D. Chu, X. Liu, R. An, S. Pan, Z. Yang, *Angew. Chem. Int. Ed.* **2024**, *63*, e202413680.

(23) M. Mutailipu, J. Han, Z. Li, F. Li, J. Li, F. Zhang, X. Long, Z. Yang, S. Pan, *Nat. Photonics.* **2023**, *17*, 694–701.

(24) M. Luo, C. Lin, D. Lin, N. Ye, *Angew. Chem. Int. Ed.* **2020**, *59*, 15978–15981.

(25) P. Vivek, G. S. Kumar, A. Steephen, R. M. Jauhar, A. Suvitha, M. Rekha, M. Kowsalya, N. Karunagaran, R. Arunkumar, *J. Mater. Sci. Mater. Electron.* **2021**, *32*, 4493–4504.

(26) X. Meng, X. Zhang, Q. Liu, Z. Zhou, X. Jiang, Y. Wang, Z. Lin, M. Xia, *Angew. Chem. Int. Ed.* **2023**, *62*, e202214848.

(27) Y. Shen, Y. Zhou, X. Xue, H. Yu, S. Zhao, J. Luo, *Inorg. Chem. Front.* **2022**, *9,* 5226-5230.

(28) X. Meng, F. Liang, K. Kang, J. Tang, T. Zeng, Z. Lin, M. Xia, *Inorg. Chem.* **2019**, *58*, 11289-11293.

(29) D. Lin, M. Luo, C. Lin, F. Xu, N. Ye, *J. Am. Chem. Soc.* **2019**, *141*, 3390-3394.

(30) Y. Chen, C. Hu, Z. Fang, J. Mao, *Inorg. Chem. Front.* **2021**, *8*, 3547-3555.

(31) Y. Song, D. Lin, M. Luo, C. Lin, Q. Chen, N. Ye, *Inorg. Chem. Front.* **2020**, *7*, 150-156.

(32) S.-F. Li, L. Hu, Y. Ma, F.-F. Mao, J. Zheng, X.-D. Zhang, D. Yan, *Inorg. Chem.* **2022**, *61*, 10182-10189.

(33) J. Lu, Y.-K. Lian, L. Xiong, Q.-R. Wu, M. Zhao, K.-X. Shi, L. Chen, L.-M. Wu, *J. Am. Chem. Soc.* **2019**, *141*, 16151-16159.

(34) X. Du, F. Wang, F. Liang, Z. Hu, Y. Wu, X. Zhang, *Inorg. Chem. Front.* **2023**, *10*, 5979-5985.
(35) L. Liu, Z. Bai, L. Hu, D. Wei, Z. Lin, L. Zhang, *J. Mater. Chem. C.* **2021**, *9*, 7452-7457.
(36) L. Liu, C.-L. Hu, Z. Bai, F. Yuan, Y. Huang, L. Zhang, Z. Lin, *Chem. Commun.* **2020**, *56*, 14657-14660.
(37) F. Liang, N. Wang, X. Liu, Z. Lin, Y. Wu, *Chem. Commun.* **2019**, *55*, 6257-6260.
(38) X. Meng, F. Liang, J. Tang, K. Kang, Q. Huang, W. Yin, Z. Lin, M. Xia, *Eur. J. Inorg. Chem.* **2019**, *2019*, 2791-2795.
(39) W. Huang, X. Wu, B. Ahmed, Y. Li, Y. Zhou, H. Wang, Y. Song, X. Kuang, J. Luo, S. Zhao, *Inorg. Chem. Front.* **2023**, *10*, 2039-2044.
(40) L. Ren, L. Cheng, X. Zhou, J. Ren, L. Cao, L. Huang, X. Dong, Y. Zhou, D. Gao, G. Zou, *Inorg. Chem. Front.* **2023**, *10*, 5602-5610.
(41) X. Meng, F. Liang, J. Tang, K. Kang, T. Zeng, W. Yin, R. Guo, Z. Lin, M. Xia, *Inorg. Chem.* **2019**, *58*, 8948–8952.
(42) K. Kang, F. Liang, X. Meng, J. Tang, T. Zeng, W. Yin, M. Xia, Z. Lin, B. Kang, *Inorg. Chem.* **2019**, *58*, 9553-9556.
(43) H. Jia, D. Xu, Z. Li, M. Arif, Y. Jiang, X. Hou, *Inorg. Chem. Front.* **2024**, *11*, 8331-8338.
(44) W. Huang, X. Zhang, Y. Li, Y. Zhou, X. Chen, X. Li, F. Wu, M. Hong, J. Luo, S. Zhao, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202746.
(45) Y. Shen, L. Ma, G. Dong, H. Yu, J. Luo, *Inorg. Chem. Front.* **2023**, *10*, 2022-2029.
(46) D. Dou, Q. Shi, Y. Bai, C. Chen, B. Zhang, Y. Wang, *Mater. Chem. Front.* **2023**, *7*, 5924-5931.
(47) S. Z. Hao Chen, Bo Chen , Yaoguo Shen, Junhua Luo, *Inorg. Chem. Front.* **2023**, *10*, 3293.
(48) Z. Li, F. Liang, Y. Guo, Z. Lin, J. Yao, G. Zhang, W. Yin, Y. Wu, C. Chen, *J. Mate. Chem. C.* **2018**, *6*, 12879-12887.
(49) N. Wang, F. Liang, Y. Yang, S. Zhang, Z. Lin, *Dalton Trans.* **2019**, *48*, 2271-2274.
(50) L. Zhang, F. Wang, X. Zhang, F. Liang, Z. Hu, Y. Wu, *Cryst. Growth Des.* **2024**, *24*, 627-631.
(51) X. Meng, F. Liang, K. Kang, J. Tang, Q. Huang, W. Yin, Z. Lin, M. Xia, *Dalton Trans.* **2019**, *48*, 9048-9052.
(52) M. Aibibula, L. Wang, S. Huang, *ACS Omega.* **2019**, *4*, 22197-22202.
(53) M. Kalmutzki, M. Ströbele, F. Wackenhut, A. J. Meixner, H. J. Meyer, *Angew. Chem. Int. Ed.* **2014**, *53*, 14260-14263.
(54) M. Kalmutzki, M. Ströbele, F. Wackenhut, A. J. Meixner, H. J. Meyer, *Inorg. Chem.* **2014**, *53*, 12540-12545.
(55) Y. Shen, L. Ma, G. Dong, H. Yu, J. Luo, *Inorg. Chem. Front.* **2023**, *10*, 2022-2029.
(56) Y. Shen, B. Chen, H. Chen, J. Luo, *Inorg. Chem.* **2022**, *61*, 14242-14246.
(57) Q. Xu, Y. Liu, Q. Wu, L. Hou, Y. Li, L. Li, Z. Lin, S. Zhao, J. Luo, *Sci. China Mater.* **2023**, *66*, 3271-3277.
(58) C. Jin, F. Li, Z. Yang, S. Pan, M. Mutailipu, *J. Mater. Chem. C.* **2022**, *10*, 6590-6595.
(59) X. Zhang, X. Du, J. Wang, F. Wang, F. Liang, Z. Hu, Z. Lin, Y. Wu, *ACS Appl. Mater. Interfaces.* **2022**, *14*, 53074-53080.
(60) L. Qi, X. Jiang, K. Duanmu, C. Wu, Z. Lin, Z. Huang, M. G. Humphrey, C. Zhang, *J. Am. Chem. Soc.* **2024**, *146*, 9975–9983.
(61) Y. Li, X. Zhang, J. Zheng, Y. Zhou, W. Huang, Y. Song, H. Wang, X. Song, J. Luo, S. Zhao, *Angew. Chem. Int. Ed.* **2023**, *62*, e202304498.
(62) R. Wei, H. Huang, D. Yang, Y. Wang, B. Zhang, *Adv. Opt. Mater.* **2024**, DOI:10.1002/adom.202401814.
(63) J. Lu, X. Liu, M. Zhao, X. Bin Deng, K. X. Shi, Q. R. Wu, L. Chen, L. M. Wu, *J. Am. Chem. Soc.* **2021**, *143*, 3647–3654.
(64) Z. P. Zhang, X. Liu, X. Liu, Z. W. Lu, X. Sui, B. Y. Zhen, Z. Lin, L. Chen, L. M. Wu, *Chem. Mater.* **2022**, *34*, 1976–1984.
(65) M. Arif, X. Liu, Z. Li, H. Jia, Y. Jiang, Z. Yang, X.Hou, S. Pan, *Adv. Opt. Mater.* **2025**, DOI: 10.1002/adom.202402327.
(66)H. Qiu, W. Cai, Z. Yang, Y. Liu, M. Mutailipu, S. Pan, *ACS Org. Inorg. Au* **2021**, *1*, 6–10.
(67)C. Jin, H. Zeng, F. Zhang, H. Qiu, Z. Yang, M. Mutailipu, S. Pan, *Chem. Mater.* **2022**, *34*, 440–450.
(68) C. Hu, C. Shen, H. Zhou, J. Han, Z. Yang, K. R. Poeppelmeier, F. Zhang, S. Pan, *Small. Struct.* 2024, **5**, 240029.
(69) C. Jin, F. Li, Z. Yang, S. Pan, M. Mutailipu, *J. Mater. Chem. C* **2022**, *10*, 6590–6595.

(70) D. Dou, Q. Shi, H. Li, B. Zhang, D. Yang, Y. Wang, *Adv. Sci.* 2024, **11**, 2401325.
(71) Z. Zhang, X. Liu, R. Wang, S. Zhao, W. He, H. Chen, X. Deng, L. Wu, Z. Zhou, L. Chen, *Angew. Chem. Int. Ed.* **2024**, *136*, e202408551.
(72) M. Kloda, I. Matulková, I. Císařová, P. Becker, L. Bohatý, P. Němec, R. Gyepes, I. Němec, *Crystals.* **2019**, *9*, 403.
(73) S. Thangarasu, V. Siva, S. Athimoolam, S. A. Bahadur, *J. Theor. Comput. Chem.* **2018**, *17*, 1850021.
(74) S. Thangarasu, S. Suresh Kumar, S. Athimoolam, B. Sridhar, S. Asath Bahadur, R. Shanmugam, A. Thamaraichelvan, *J. Mol. Struct.* **2014**, *1074*, 107–117.
(75) S. Manivannan, S. Dhanuskodi, K. Kirschbaum, S. K. Tiwari, Cryst. Growth Des. **2005**, *5*, 1463–1468.
(76) J. Fan, Z. Yan, Z. Chen, H. Li, Z. Yang, F. Zhang, S. Pan, *Sci. China Chem.* **2024**, DOI: 10.1007/s11426-024-2170-6.
(77) M. H. Lee, C. H. Yang, J. H. Jan, *Phys. Rev. B.* **2004**, *70*, 1–11.