

Electronic Supplementary Information

Hydroxyfluorooxoborate $(\text{NH}_4)[\text{C}(\text{NH}_2)_3][\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$ for exploring the effects of cation substitution on structure and optical properties

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Experimental Section

Reagents and synthesis. Reagents $[\text{C}(\text{NH}_2)_3]_2\text{CO}_3$ (99 %), HF (AR, ≥ 40 %), NH_4HF_2 (99 %), and H_3BO_3 (99 %) were purchased from Aladdin and used as received. $[\text{C}(\text{NH}_2)_3]\text{HF}_2$ was obtained by the spontaneous evaporation of $[\text{C}(\text{NH}_2)_3]_2\text{CO}_3$ and excess HF in a Teflon beaker, and its purity was verified by powder XRD test. $(\text{NH}_4)[\text{C}(\text{NH}_2)_3][\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$ crystals were obtained by the hydrothermal method. $[\text{C}(\text{NH}_2)_3]\text{HF}_2$ (0.435 g, 4.392 mmol), NH_4HF_2 (0.251 g, 4.392 mmol), and H_3BO_3 (0.815 g, 13.176 mmol) were mixed homogeneously and sealed in a Teflon-lined autoclave at 101 °C for 4000 min and then slowly cooled to room temperature with a rate of 2 °C/h. Colorless block crystals of $(\text{NH}_4)[\text{C}(\text{NH}_2)_3][\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$ were obtained. The polycrystalline powder samples for experimental characterization were obtained directly from grinding the as-grown crystals, and its purity was checked by X-ray diffraction (XRD) patterns.

Characterization. Powder XRD data were collected with a Bruker D2 PHASER diffractometer (Cu $K\alpha$ radiation with $\lambda = 1.5418 \text{ \AA}$, $2\theta = 10$ to 70° , scan step width = 0.02° , and counting time = 1 s/step). The single-crystal XRD data were collected on a Bruker D8 Venture diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The intensity, reduction and cell refinement were carried out on Bruker SAINT.¹ All the structures were solved by direct method and refined through the full-matrix least-squares fitting on F^2 with OLEX2 software.² These structures were verified by virtue of ADDSYM algorithm from PLATON.³ Infrared spectroscopy was carried out on a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in the 400-4000 cm^{-1} range. UV-vis-NIR diffuse-reflectance spectroscopy data in the wavelength range of 190-2500 nm were recorded at room temperature using a powder sample of $(\text{NH}_4)[\text{C}(\text{NH}_2)_3][\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$ on a Shimadzu SolidSpec-3700 DUV spectrophotometer.

Calculation details

The electronic structure and optical property were calculated by using the DFT method implemented in the CASTEP package.⁴ During the calculation, the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional was adopted.⁵ Under the norm-conserving pseudopotential (NCP), the following orbital electrons were treated as valence electrons: H:1s¹, B:2s²2p¹, C:2s²2p², N:2s²2p³, O:2s²2p⁴ and F:2s²2p⁵. The kinetic energy cutoffs of 850 eV were chosen, and the numerical integration of the Brillouin zone was performed using a 4 × 4 × 2 Monkhorst-Pack *k*-point sampling. The other calculation parameters and convergent criteria were the default values of the CASTEP code. Although the GGA-PBE method is adequately eligible to describe the electronic structures and optical properties in terms of numerous crystals. In order to give an accurate estimation of the band gap, the HSE06 method with the Pwmat⁶ code was also adopted. During the calculation process, the convergent conditions or parameters were unchanged in the auto setting of the CASTEP code.

Table S1. Crystallographic data and structural refinement parameters of (NH₄)[C(NH₂)₃][B₃O₃F₄(OH)].

Compound	(NH ₄)[C(NH ₂) ₃][B ₃ O ₃ F ₄ (OH)]
Formula weight	251.57
Crystal system	monoclinic
Space group	<i>C2/c</i>
<i>a</i> /Å	15.280(2)
<i>b</i> /Å	8.7593(11)
<i>c</i> /Å	14.8039(18)
<i>α</i> /°	90

$\beta/^\circ$	98.748(9)
$\gamma/^\circ$	90
Volume/ \AA^3	1958.4(5)
Z	8
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.706
μ/mm^{-1}	0.185
$F(000)$	1024.0
Radiation	MoK α ($\lambda = 0.71073$)
2θ range for data collection/ $^\circ$	5.376 to 55.052
Index ranges	$-19 \leq h \leq 19, -11 \leq k \leq 11, -19 \leq l \leq 19$
Reflections collected	31760
Independent reflections	2254 [$R_{\text{int}} = 0.0949, R_{\text{sigma}} = 0.0365$]
Data/restraints/parameters	2254/0/150
Goodness-of-fit on F^2	1.069
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0407, wR_2 = 0.0930$
Final R indexes [all data]	$R_1 = 0.0571, wR_2 = 0.1067$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.40/-0.25

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) and bond valence sum (BVS) for $(\text{NH}_4)[\text{C}(\text{NH}_2)_3][\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$	BVS
B1	7132.4(12)	4161(2)	5815.3(13)	27.1(4)	3.07
B2	8690.8(12)	4893(2)	6116.1(14)	28.6(4)	3.08
B3	7523.5(13)	6611(2)	6567.0(14)	28.6(4)	3.01
O1	6894.6(8)	5395.6(14)	6266.6(10)	34.2(3)	1.85
O2	7981.6(7)	3942.9(14)	5660.5(9)	31.8(3)	1.83
O3	8422.0(8)	6169.8(15)	6576.7(10)	39.3(4)	1.78
O4	6490.7(8)	3110.9(15)	5506.2(10)	34.0(3)	2.41
F1	9247.3(8)	3953.3(14)	6763.5(9)	49.4(3)	0.65
F2	9252.6(8)	5310.2(17)	5480.8(9)	53.4(4)	0.70
F3	7407.3(9)	7067.6(15)	7455.7(9)	51.9(4)	0.70
F4	7305.0(10)	7946.0(15)	6006.5(11)	63.8(4)	0.65
C1	4493.2(12)	4987(2)	6306.5(13)	32.9(4)	-
N1	4703.9(12)	3625(2)	6031.6(15)	51.7(5)	-
N2	3703.4(11)	5221(2)	6535.7(14)	47.3(5)	-
N3	5068.5(10)	6114.7(19)	6342.8(13)	42.3(4)	-
N4	6109.8(11)	10215(2)	6480.5(12)	34.4(4)	-

Table S3. Selected bond lengths (Å) and angles (deg.) for (NH₄)[C(NH₂)₃][B₃O₃F₄(OH)].

Bond	Length	Bond	Length
C(1)-N(1)	1.317(2)	B(2)-O(3)	1.403(2)
C(1)-N(2)	1.318(2)	B(2)-F(1)	1.439(2)
C(1)-N(3)	1.318(2)	B(2)-F(2)	1.414(2)
B(1)-O(1)	1.350(2)	B(3)-O(1)	1.458(2)
B(1)-O(2)	1.365(2)	B(3)-O(3)	1.424(2)
B(1)-O(4)	1.372(2)	B(3)-F(3)	1.411(2)
B(2)-O(2)	1.449(2)	B(3)-F(4)	1.443(2)
Type	Angle	Type	Angle
N(1)-C(1)-N(2)	119.78(18)	O(3)-B(2)-F(2)	111.68(15)
N(1)-C(1)-N(3)	119.93(17)	F(1)-B(2)-O(2)	107.80(15)
N(3)-C(1)-N(2)	120.29(18)	F(2)-B(2)-O(2)	109.00(15)
B(1)-O(2)-B(2)	120.29(14)	F(2)-B(2)-F(1)	103.51(14)
B(1)-O(1)-B(3)	121.45(14)	O(3)-B(3)-O(1)	113.21(14)
B(2)-O(3)-B(3)	124.37(14)	O(3)-B(3)-F(4)	111.35(16)
O(1)-B(1)-O(2)	121.97(15)	F(3)-B(3)-O(1)	108.72(15)
O(1)-B(1)-O(4)	118.10(15)	F(3)-B(3)-O(3)	108.98(15)
O(2)-B(1)-O(4)	119.93(16)	F(3)-B(3)-F(4)	104.82(15)
O(3)-B(2)-O(2)	115.50(14)	F(4)-B(3)-O(1)	109.39(15)
O(3)-B(2)-F(1)	108.61 (15)		

Table S4. Hydrogen Bonds for (NH₄)[C(NH₂)₃][B₃O₃F₄(OH)].

D-H···A	d(D-A)/Å	D-H···A/°
N(3)-H(7)···O(1)	2.879(2)	160.7
N(3)-H(6)···F(1) ¹	2.895(2)	163.2
O(4)-H(1)···O(2) ²	2.699(17)	175.3
N(4)-H(5)···F(4)	2.858(2)	177.2

¹-1/2+X,1/2+Y,+Z; ²3/2-X,1/2-Y,1-Z

Table S5. Anisotropic displacement parameters (\AA^2) for $(\text{NH}_4)[\text{C}(\text{NH}_2)_3][\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	26.6(8)	34.5(9)	39.0(10)	0.0(7)	8.6(7)	1.0(7)
N1	39.3(9)	34.2(9)	86.1(15)	-9.8(9)	23.3(10)	-1.9(7)
N2	29.9(8)	48.7(10)	67.0(12)	-7.7(9)	18.8(8)	-2.2(7)
N3	27.5(8)	33.3(8)	68.3(12)	-5.9(8)	13.5(8)	0.5(6)
N4	27.0(8)	44.4(9)	32.0(8)	4.5(7)	4.4(6)	-1.6(7)
B1	21.5(8)	29.7(9)	30.8(10)	-2.9(7)	6.0(7)	-1.2(7)
B2	19.2(8)	32.0(9)	35.0(10)	-5.9(8)	5.1(7)	-0.7(7)
B3	24.2(9)	24.6(9)	38.4(10)	-5.3(8)	8.7(8)	0.2(7)
O1	20.8(6)	32.1(7)	51.9(8)	-12.2(6)	11.3(5)	-2.1(5)
O2	20.8(6)	34.8(7)	40.5(7)	-13.7(5)	6.2(5)	-2.2(5)
O3	23.1(6)	32.8(7)	62.1(9)	-17.5(6)	5.7(6)	-1.0(5)
O4	23.0(6)	37.6(7)	41.9(7)	-12.2(6)	7.5(5)	-6.0(5)
F1	42.5(7)	47.3(7)	53.3(7)	-7.2(6)	-10.5(6)	13.0(5)
F2	40.8(7)	76.3(9)	47.9(7)	-13.4(6)	20.8(6)	-21.2(6)
F3	54.8(7)	57.8(8)	48.5(7)	-22.0(6)	24.2(6)	-14.7(6)
F4	60.3(9)	43.6(8)	83.0(11)	13.6(7)	-4.5(7)	3.1(6)

Table S6. Real-space atom-cutting analysis of calculated birefringence in $(\text{NH}_4)[\text{C}(\text{NH}_2)_3][\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$.

Cut unit	Birefringence(@1064nm)
None	0.101
$[\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$	0.0919
$[\text{C}(\text{NH}_2)_3]$	0.0445
NH_4^+	0.1008

Figure S1. X-ray powder diffraction patterns of experimental and calculated results for $(\text{NH}_4)[\text{C}(\text{NH}_2)_3][\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$.

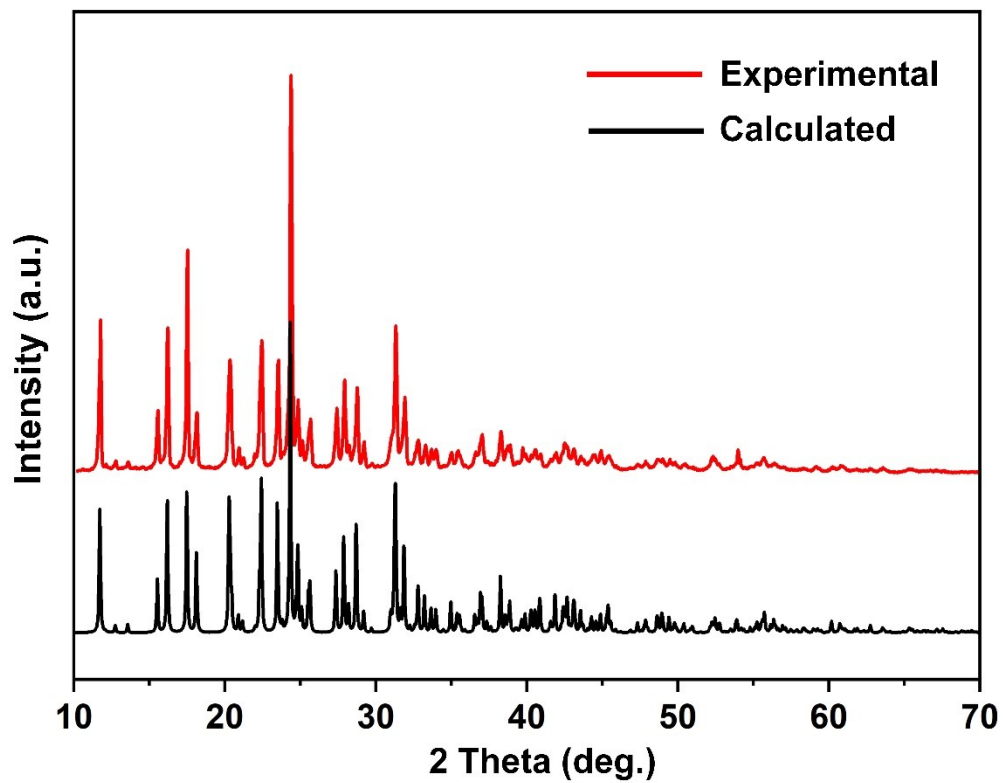


Figure S2. FT-IR spectrum of $(\text{NH}_4)[\text{C}(\text{NH}_2)_3][\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$.

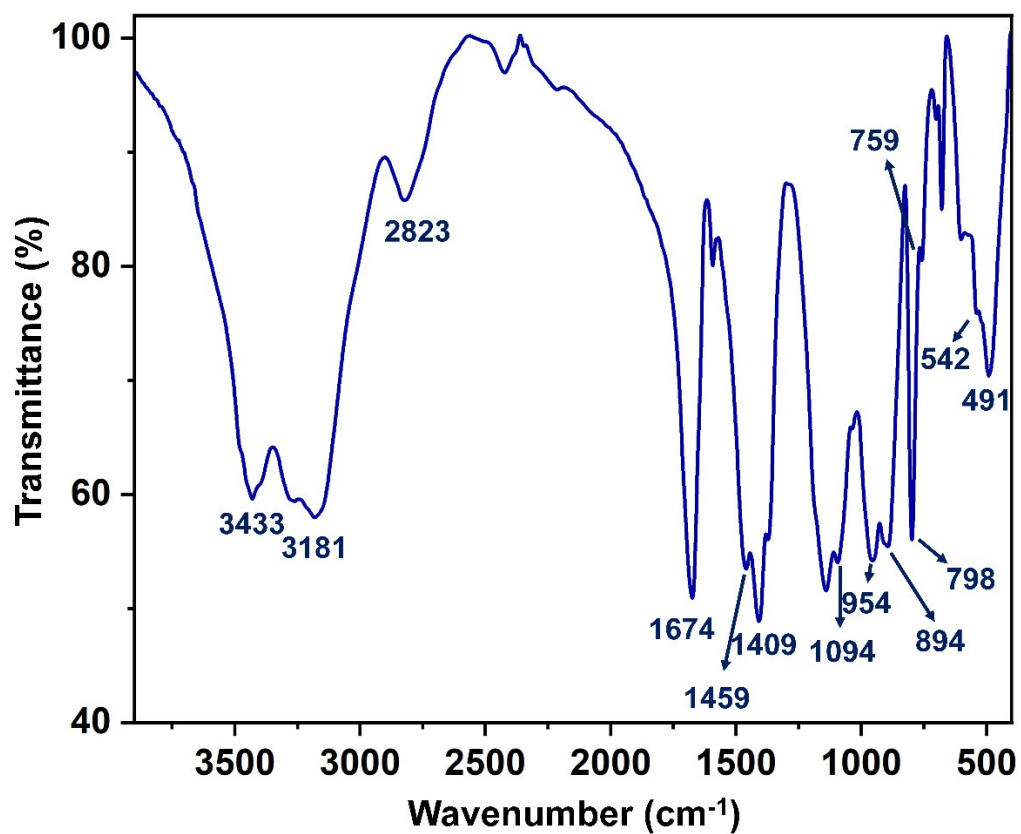


Figure S3. UV-VIS-NIR spectrum of $(\text{NH}_4)[\text{C}(\text{NH}_2)_3][\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$.

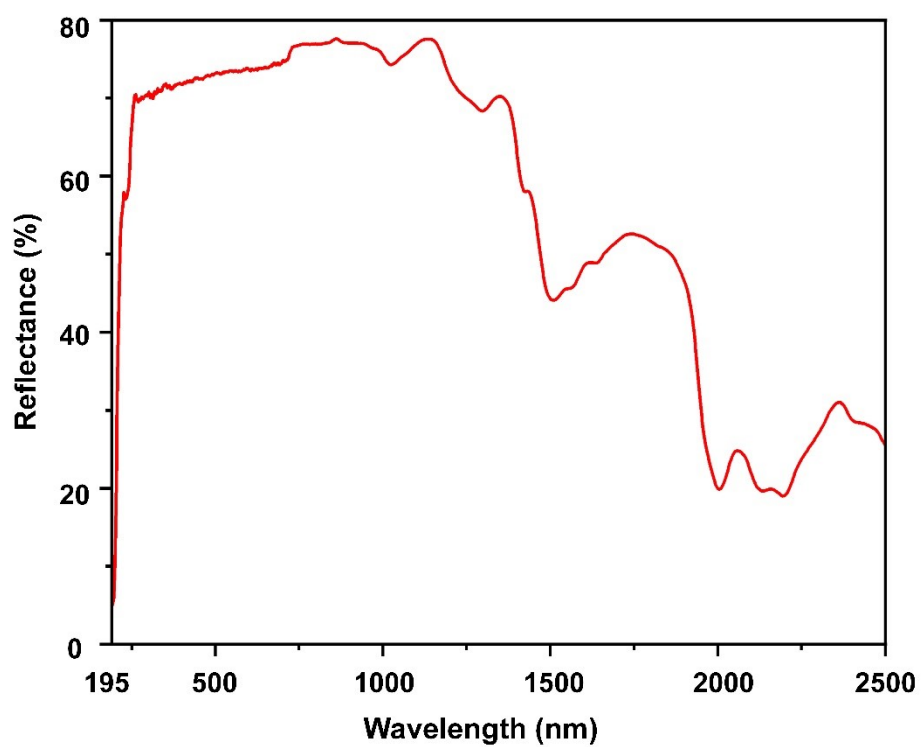


Figure S4. The TG–DSC curves of $(\text{NH}_4)[\text{C}(\text{NH}_2)_3][\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$.

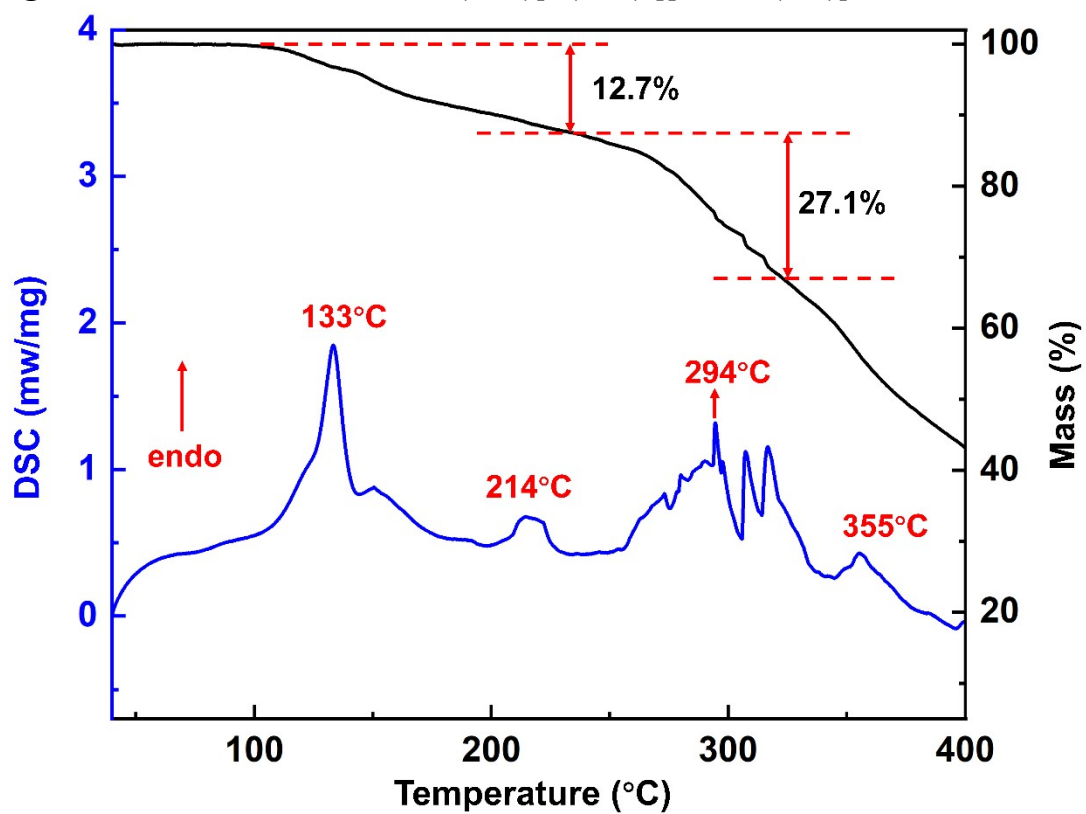


Figure S5. The total and partial density of states of $(\text{NH}_4)[\text{C}(\text{NH}_2)_3][\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$.

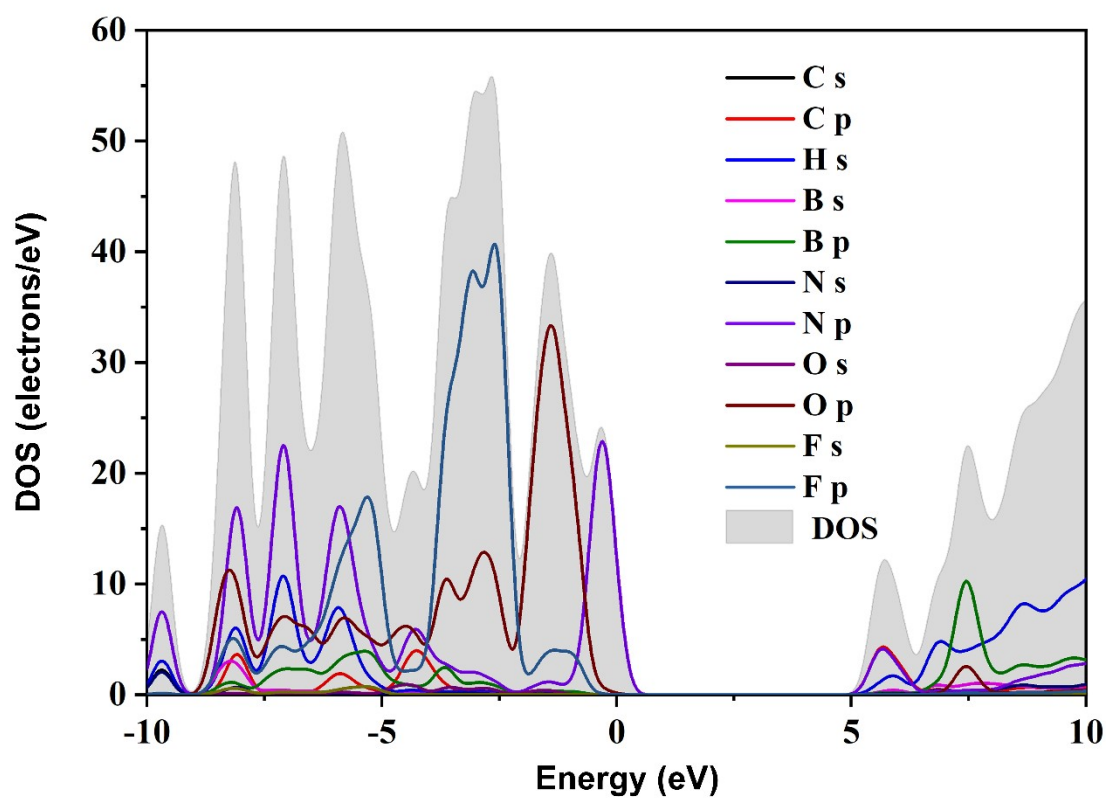


Figure S6. The electronic structure of $(\text{NH}_4)[\text{C}(\text{NH}_2)_3][\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$ based on GGA method.

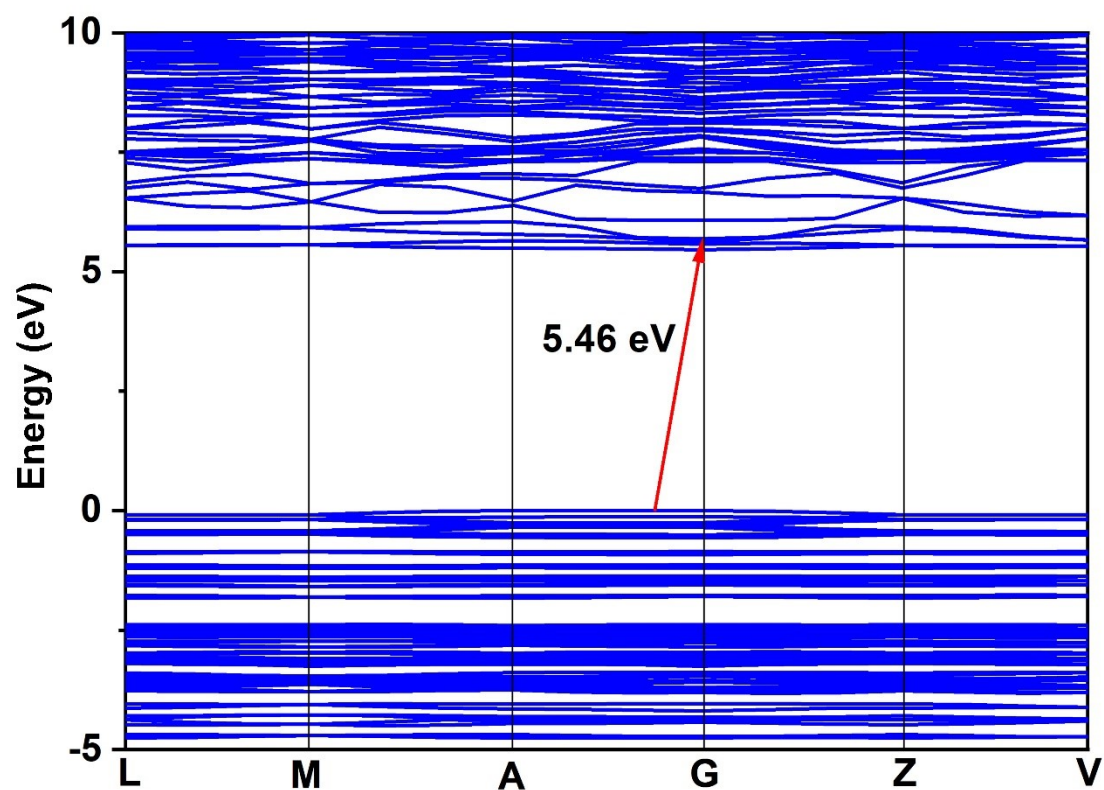
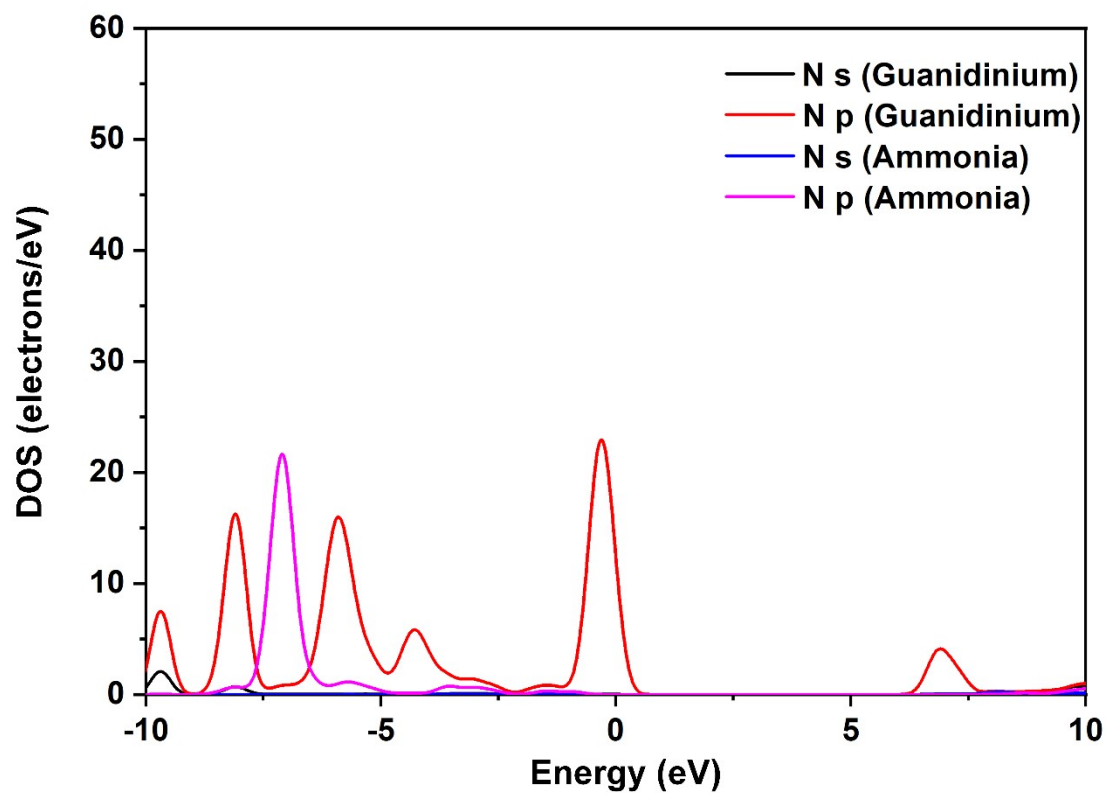


Figure S7. The partial density of states of N atoms in $(\text{NH}_4)[\text{C}(\text{NH}_2)_3][\text{B}_3\text{O}_3\text{F}_4(\text{OH})]$.



References

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