Electronic Supplementary Information (ESI) for

Strategically designed metal-free deep-ultraviolet birefringent crystals with superior optical properties

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Table S1. Crystallographic data for $C(NH_2)_3CH_3SO_3$.

Formula	$C(NH_2)_3CH_3SO_3$
Formula weight	155.18
Temperature/K	299.15
Crystal system	monoclinic
Space group	*I*2/*m*
a/Å	10.0029(11)
b/Å	7.3514(5)
c/Å	10.4776(7)
α/°	90
β/°	102.800(7)
γ/°	90
Volume/Å^3	751.33(11)
Z	4
ρ_{calc} g/cm^3	1.372
μ/mm^{-1}	0.382
F(000)	328.0
Crystal size/mm^3	0.392 × 0.378 × 0.058
Radiation	MoKα (λ = 0.71073)
2*θ* range for data collection/°	6.382 to 55.2
Index ranges	-13 ≤ *h* ≤ 12, -9 ≤ *k* ≤ 9, -13 ≤ *l* ≤ 13
Reflections collected	6829
Independent reflections	940 [R_{int} = 0.0735, R_{sigma} = 0.0455]
Data/restraints/parameters	940/0/49
Goodness-of-fit on F^2	1.202
Final *R* indexes [I≥2σ (I)]	R_1 = 0.0680, wR_2 = 0.1393
Final *R* indexes [all data]	R_1 = 0.0775, wR_2 = 0.1432

[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 S2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $C(NH_2)_3CH_3SO_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	***x***	***y***	***z***	$U_{(eq)}$
S1	9534.4(11)	0	2311.7(11)	31.3(3)
O1	872(3)	0	3209(3)	45.4(9)
O2	9207(3)	8361(3)	1522(2)	49.9(7)
C2	8297(7)	0	3290(7)	79(2)
N1	2262(3)	6559(4)	4032(3)	44.8(8)
N2	714(4)	5000	2480(4)	52.9(13)

Table S3. Interatomic distances (Å) for $C(NH_2)_3CH_3SO_3$.

Atom	Atom	Length	Atom	Atom	Length
S1	O1	1.455(3)	S1	C2	1.774(6)
S1	O2[1]	1.451(2)	N1	C1	1.320(3)
S1	O2	1.451(2)	N2	C1	1.327(6)

[1]+X, 2-Y, +Z

Table S4. Bond Angles (˚) for $C(NH_2)_3CH_3SO_3$.

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O1	S1	C2	106.7(3)	O2	S1	C2	106.32(18)
O2	S1	O1	112.37(13)	N1	C1	N1[2]	120.6(4)
O2[1]	S1	O1	112.37(13)	N1[2]	C1	N2	119.7(2)
O2	S1	O2[1]	112.3(2)	N1	C1	N2	119.7(2)
O2[1]	S1	C2	106.32(18)				

[1]+X,2-Y,+Z; [2]+X,1-Y,+Z

Table S5. Hydrogen Bonds for $C(NH_2)_3CH_3SO_3$.

D	H	A	*d*(D-H)/Å	*d*(H-A)/Å	*d*(D-A)/Å	D-H-A/°
N1	H1A	O2[1]	0.79	2.15	2.932(3)	166.2
N1	H1B	O1	0.80	2.13	2.923(3)	171.0
N2	H2	O2[2]	0.81	2.11	2.915(3)	174.8

[1]1/2+X,3/2-Y,1/2+Z; [2]+X,1-Y,+Z

Table S6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for $C(NH_2)_3CH_3SO_3$.

Atom	*x*	*y*	*z*	$U_{(eq)}$
H2A	8571.58	8930	3732.17	94
H2B	7521.68	0	2612.17	94
H1A	2908.85	6549.87	4629.68	54
H1B	1908.85	7479.87	3729.58	54
H2	359.96	4050	2189.84	63

Table S7. Calculated bandgap for $C(NH_2)_3CH_3SO_3$, *β*-/*γ*-$C(NH_2)_3Cl$ and NH_2COF.

	$C(NH_2)_3CH_3SO_3$	*β*-$C(NH_2)_3Cl$	*γ*-$C(NH_2)_3Cl$	NH_2COF
GGA	5.21 eV	4.96 eV	4.93 eV	6.15 eV
HSE06	6.71 eV	6.49 eV	6.51 eV	7.87 eV

Table S8. Birefringence of selected DUV metal-free compounds and metal-containing optical crystals.

	λ_{Cutoff} (nm)	Bandgap (eV)	Δn	Reference
		Metal containing compounds		
α-BaB_2O_4	189	4.96	0.116 [1]	1
$LiBO_2$	164	6.49	0.136 [2]	2
$Ca(BO_2)_2$	169	7.34	0.124 [2]	3
$KF{\cdot}B(OH)_3$	<190	7.63 [a]	0.114 [2]	4
$Na_3F(B_3O_6)_2$	175	7.09	0.102 [3]	5
$Ba_2Mg(B_3O_6)_2$	187	6.63	0.098 [3]	6
$BaZnB_4O_8$	180	6.89	0.14 [4]	7
$LiB_5O_5F_2(OH)_4$	<190	7.99 [a]	0.124 [5]	8
$Rb[B_3O_3F_2(OH)_2]$	<200	7.46 [a]	0.09 [6]	9
$KB_3O_4F_2$	/	6.80 [a]	0.096 [5]	10
$LiNaB_6O_9F_2$	<190	7.47 [a]	0.067 [2]	11
NaB_4O_6F	<180	7.57	0.12 [2]	12
CsB_4O_6F	155	8.01	0.115 [7]	13
$SrB_5O_7F_3$	<180	8.58 [a]	0.07 [2]	14
RbB_4O_6F	<190	7.73 [a]	0.102 [2]	15
$NH_4[LiC_3H(CH_3)O_4]$	<190	7.58 [b]	0.06 [6]	16
$NaZnCO_3(OH)$	200	6.20	0.114 [2]	17
$Li_2CsB_7O_{10}(OH)_4$	<190	6.35	0.0612 [2]	18
$Cs_3[(BOP)_2(B_3O_7)_3]$	165	7.52	0.075 [8]	19
$Sr(NH_2SO_3)_2$	<190	7.32	0.03 [2]	20
$Ba(CH_3SO_3)_2$	159	7.80	0.04 [4]	21
$Ba_3P_3O_{10}Cl$	180	6.89	0.023 [2]	22
		Metal-free compounds		
$NH_4B_4O_6F$	156	7.95	0.1184 [7]	23
$C(NH_2)_3SO_3F$	200	6.20	0.133 [2]	24
GBF1	190	6.53	0.173 [2]	25
GBF2	195	6.36	0.162 [2]	25
$C(NH_2)_3BF_4$	193	6.42	0.113 [3]	26
$(N_2H_6)[HPO_3F]_2$	<200	6.51	0.077 [2]	27
$(NH_4)_4[B_{12}O_{16}F_4(OH)_4]$	<200	7.10	0.116 [6]	28
$(NH_4)_2B_4SO_{10}$	184	6.74	0.056 [2]	29
$SO_2(NH_2)_2$	160	7.75	0.07 [4]	30
NH_3BH_3	<190	7.48	0.055 [9]	31
$C(NH_2)_3CH_3SO_3$	<190	6.71 [a]	0.166 [2]	This work
β-$C(NH_2)_3Cl$	~191	6.49 [a]	0.201[2]	This work
γ-$C(NH_2)_3Cl$	~190	6.51 [a]	0.211[2]	This work
NH_2COF	~159	7.85 [a]	0.241[2]	This work

[a] By HSE06 functional; [b] by PBE0 functional.

[1] @1064 nm; [2] @1064 nm (calculated); [3] @1014 nm; [4] @589.3 nm; [5] @546 nm (calculated); [6] @546 nm; [7] @964.8 nm; [8] @532 nm; [9] @550 nm.

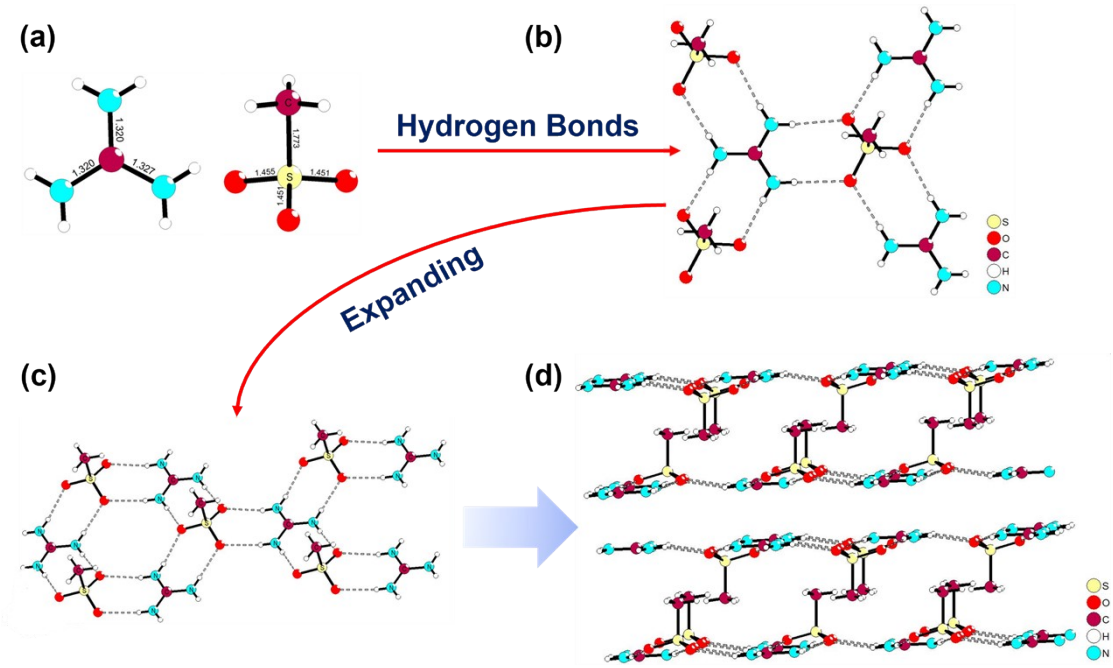

Fig. S1 (a) Functional basic building blocks of $C(NH_2)_3CH_3SO_3$; (b) Hydrogen bonds around $[C(NH_2)_3]^+$ and $CH_3SO_3^-$; (c) Single layer of $[C(NH_2)_3{\cdot}CH_3SO_3]$; and (d) Structures of $C(NH_2)_3CH_3SO_3$.

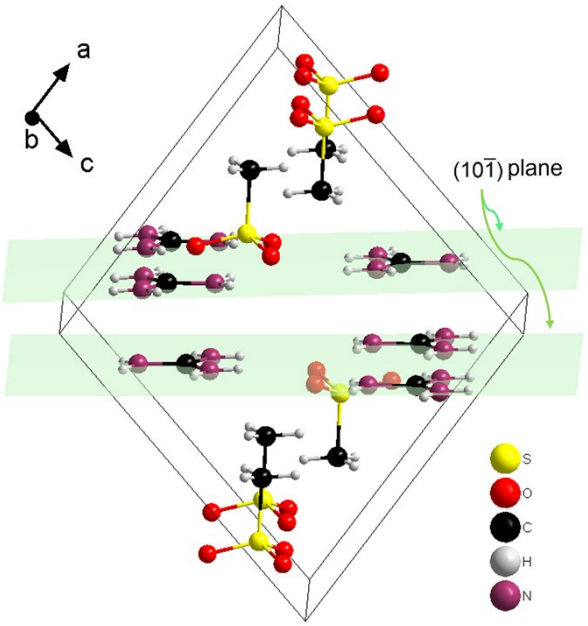

Fig. S2 Crystal plane of $[C(NH_2)_3]^+$ located in the structure of $C(NH_2)_3CH_3SO_3$.

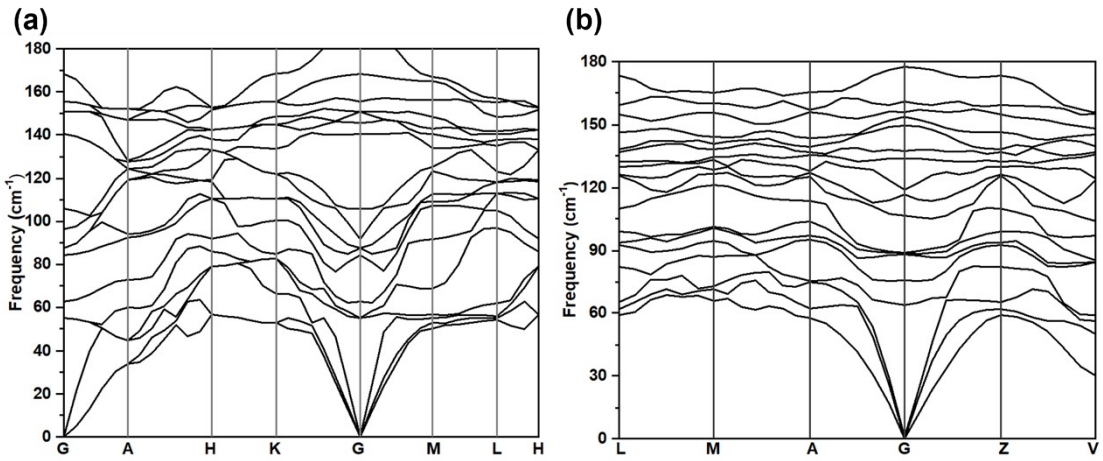

Fig. S3 Phonon dispersion of (a) *β*-$C(NH_2)_3Cl$ and (b) *γ*-$C(NH_2)_3Cl$**.**

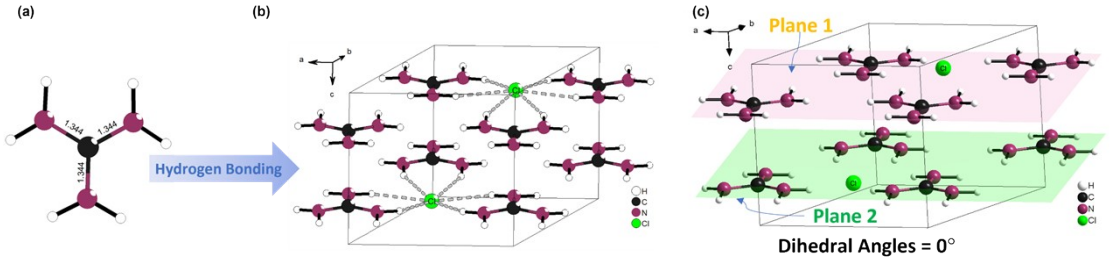

Fig. S4 Ball-and-stick representations of (a) $[C(NH_2)_3]^+$; (b) and (c) Structure of *β*-$C(NH_2)_3Cl$.

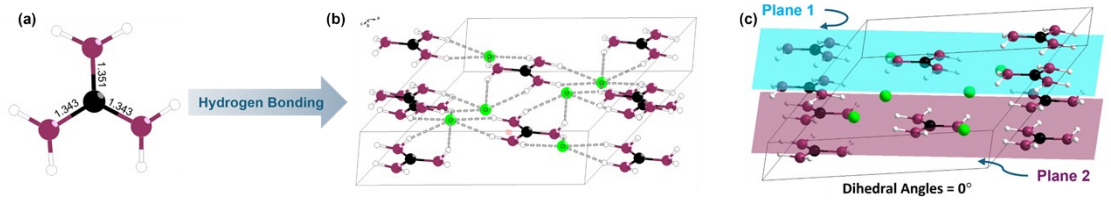

Fig. S5 Ball-and-stick representations of (a) $[C(NH_2)_3]^+$; (b) and (c) Structure of *γ*-$C(NH_2)_3Cl$.

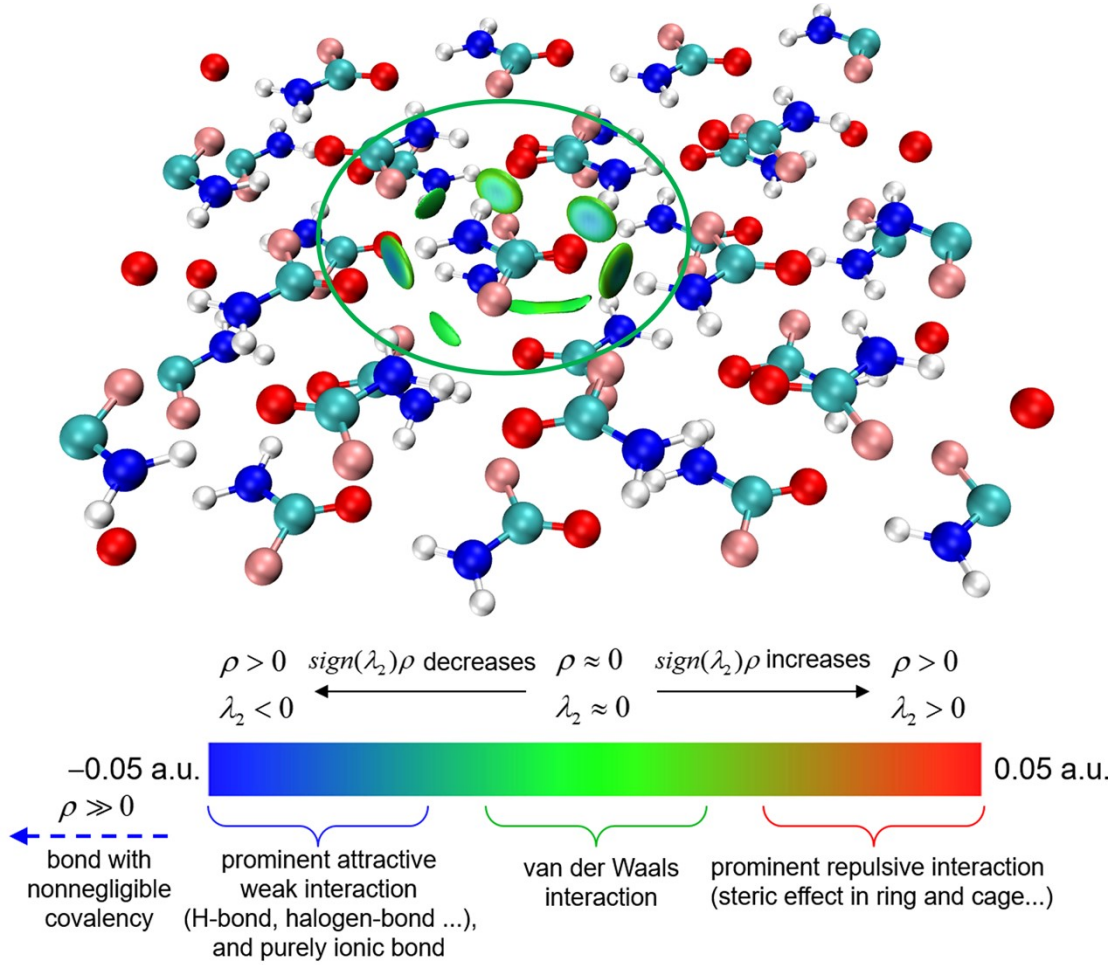

Fig. S6 Independent gradient model based on Hirshfeld partition (IGMH) analyses of NH_2COF.

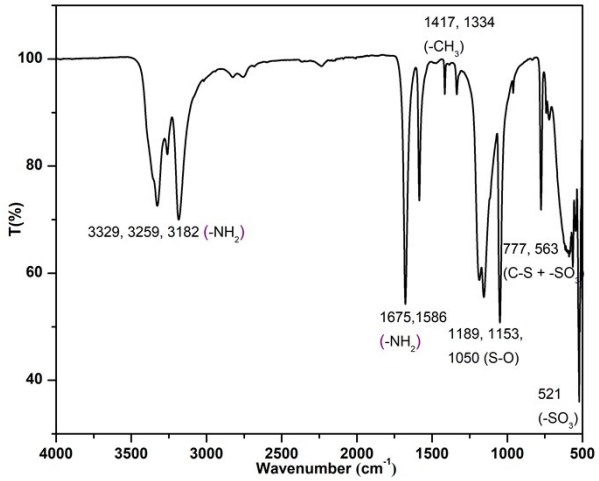

Fig. S7 IR spectrum of $C(NH_2)_3CH_3SO_3$.

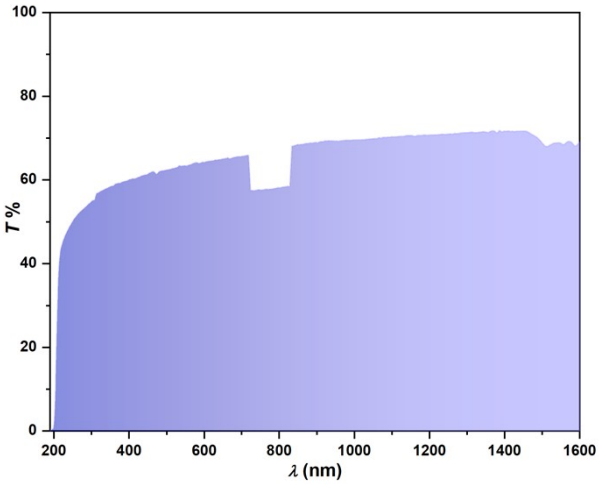

Fig. S8 UV-vis-NIR transmittance spectrum for $C(NH_2)_3CH_3SO_3$.

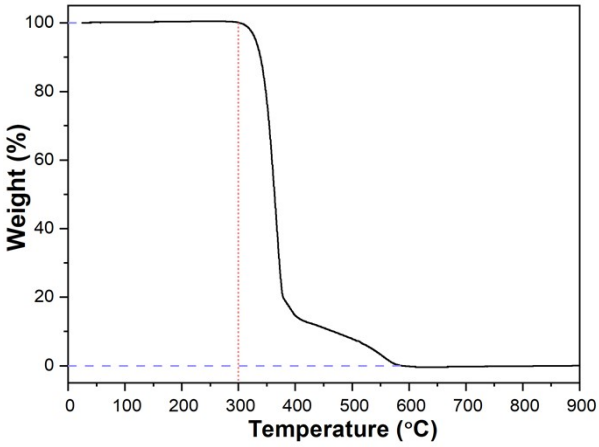

Fig. S9 TGA diagram for $C(NH_2)_3CH_3SO_3$.

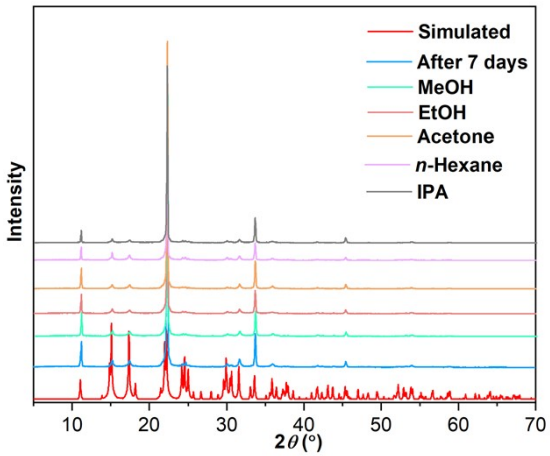

Fig. S10 The chemical stability and air stability test of $C(NH_2)_3CH_3SO_3$.

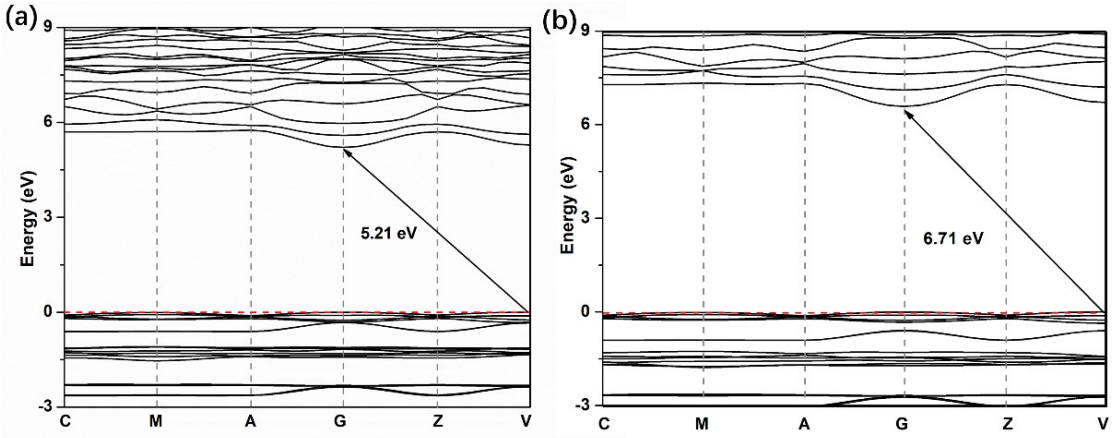

Fig. S11 Calculated band structure by GGA (a) and HSE06 (b) for $C(NH_2)_3CH_3SO_3$.

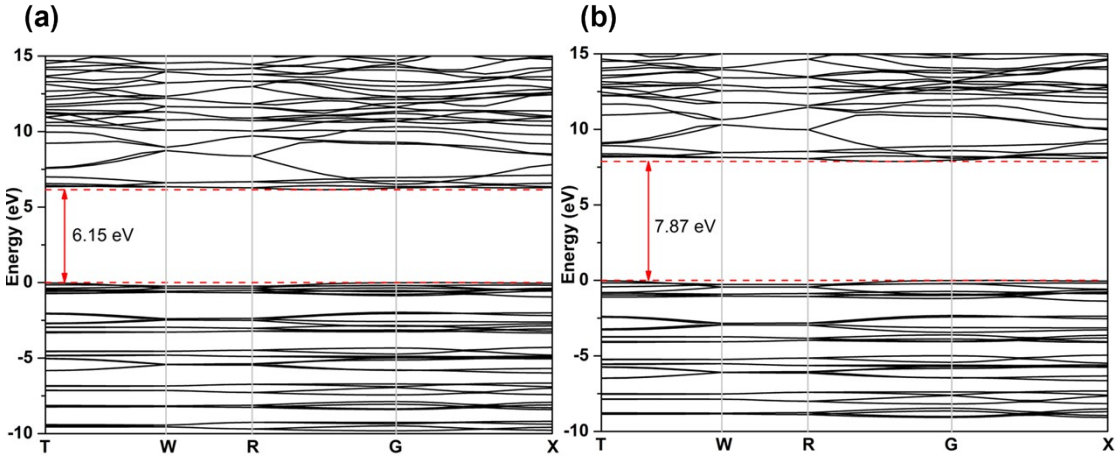

Fig. S12 Calculated band structure by GGA (a) and HSE06 (b) for NH_2COF.

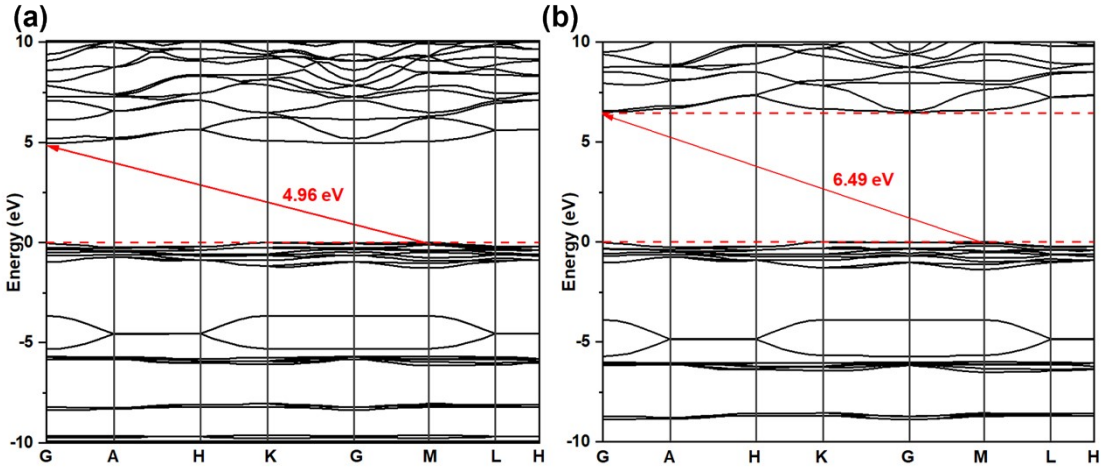

Fig. S13 Calculated band structure by GGA (a) and HSE06 (b) for *β*-$C(NH_2)_3Cl$.

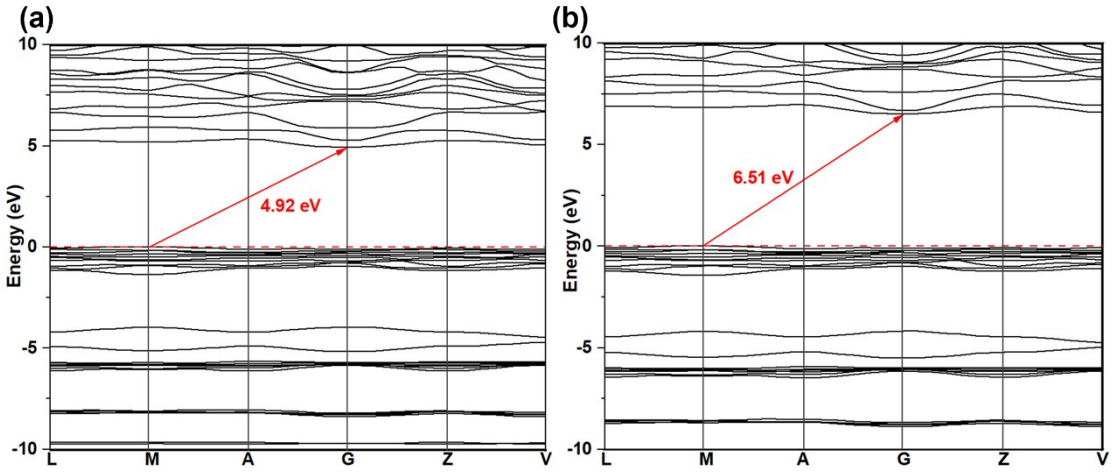

Fig. S14 Calculated band structure by GGA (a) and HSE06 (b) for *γ*-$C(NH_2)_3Cl$.

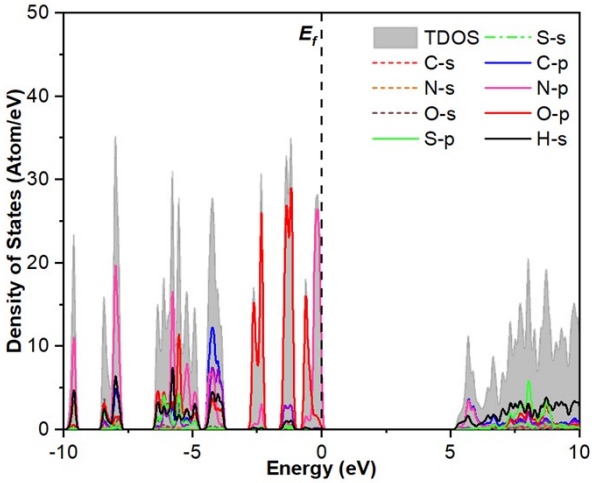

Fig. S15 Density of states for $C(NH_2)_3CH_3SO_3$.

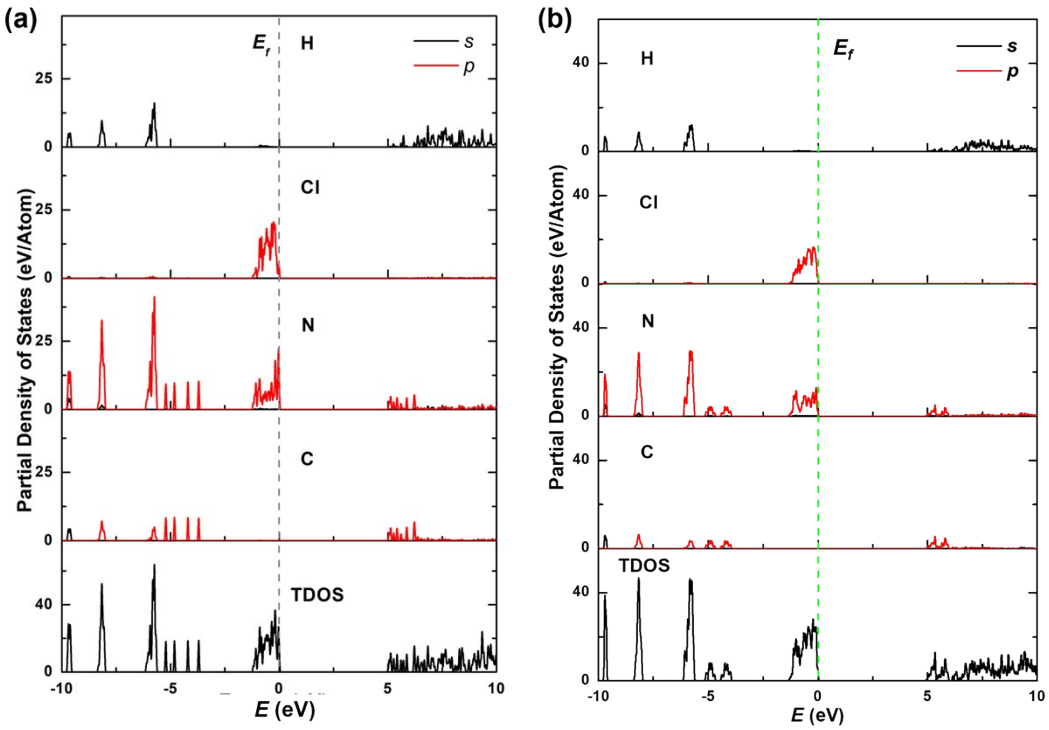

Fig. S16 Density of states for (a) *β*-$C(NH_2)_3Cl$ and (b) γ-$C(NH_2)_3Cl$.

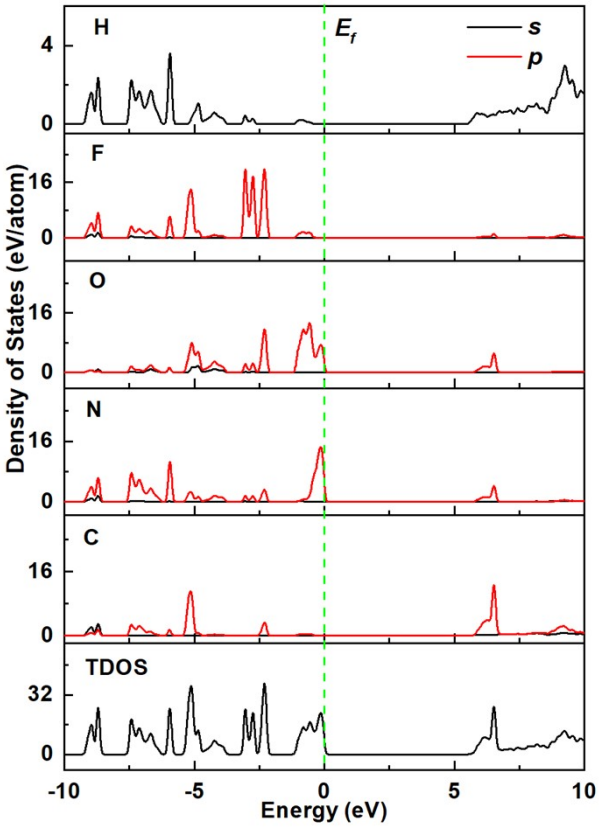

Fig. S17 Density of states for NH_2COF.

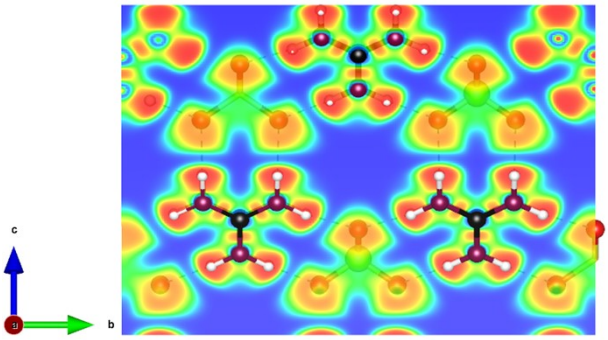

Fig. S18 ELF diagram for $C(NH_2)_3CH_3SO_3$.

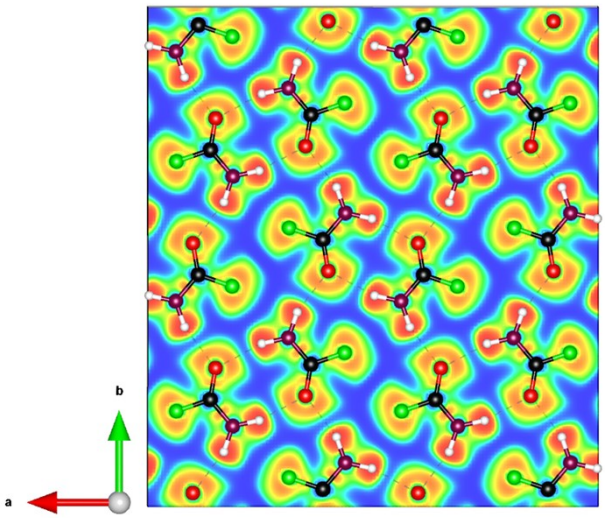

Fig. S19 ELF diagram for NH_2COF.

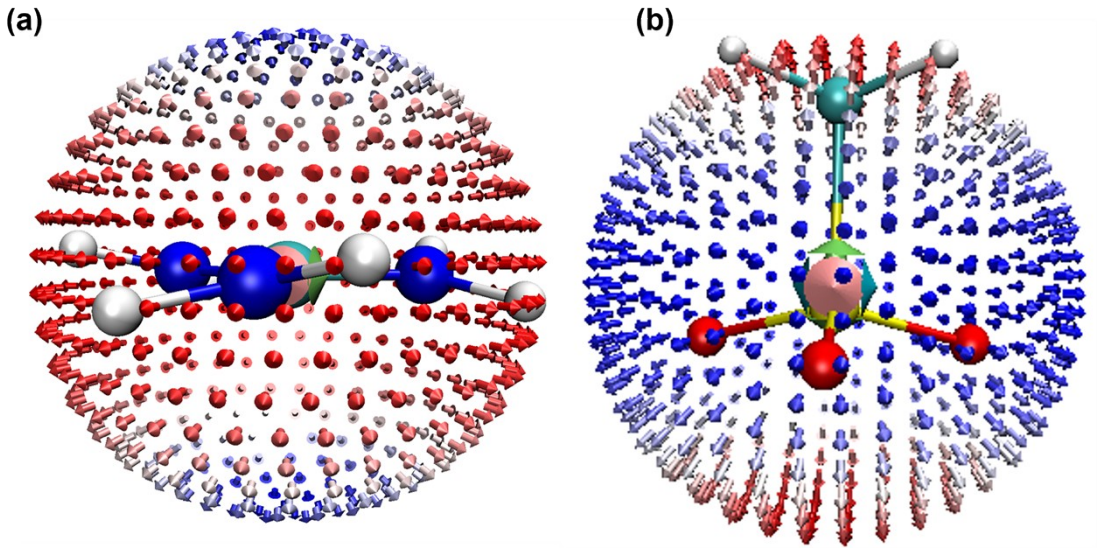

Fig. S20 Unit sphere representations of polarizability for (a) $[C(NH_2)_3]^+$ and (b) $CH_3SO_3^-$ under a static electric field. Longer and redder radial arrows indicate a larger tensor value in the corresponding direction.

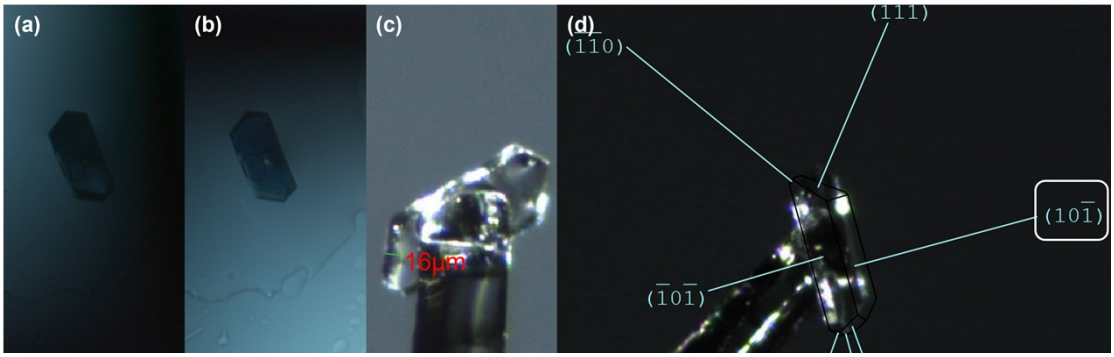

Fig. S21 Birefringence measurement on (10$\bar{1}$) crystal plane of $C(NH_2)_3CH_3SO_3$ crystal. (a) and (b) achieving complete extinction under a polarizing microscope; (c) thickness of selected crystal and (d) crystal orientation observed via the single-crystal XRD.

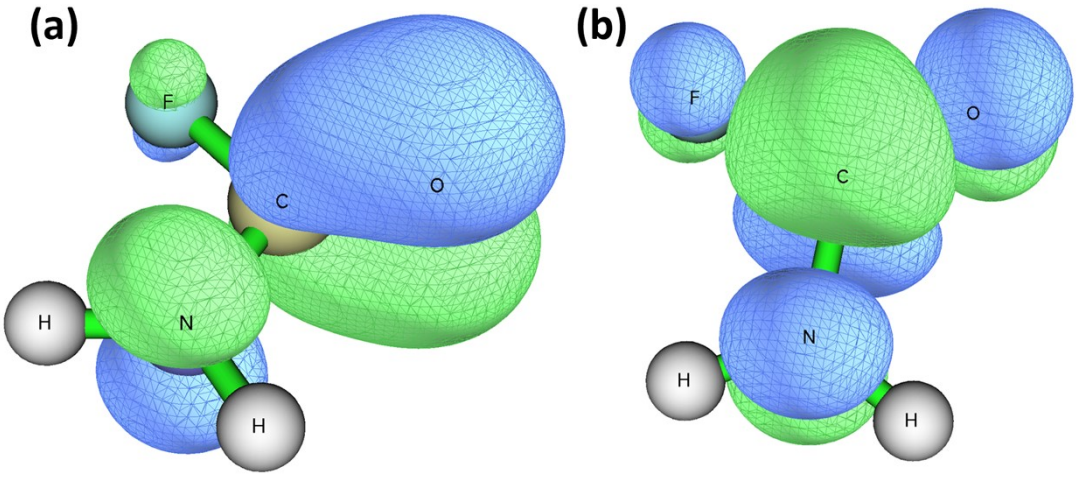

Fig. S22 (a) HOMO energy gap and (b) LUMO energy gap for NH_2COF.

References

1 G. Zhou, J. Xu, X. Chen, H. Zhong, S. Wang, K. Xu, P. Deng and F. Gan, *J. Cryst. Growth*, 1998, **191**, 517–519.

2 F. Zhang, X. Chen, M. Zhang, W. Jin, S. Han, Z. Yang and S. Pan, *Light Sci. Appl.*, 2022, **11**, 0–7.

3 X. Chen, B. Zhang, F. Zhang, Y. Wang, M. Zhang, Z. Yang, K. R. Poeppelmeier and S. Pan, *J. Am. Chem. Soc.*, 2018, **140**, 16311–16319.

4 Y. Li, X. Chen and K. M. Ok, *Chem. Commun.*, 2022, **58**, 8770-8773.

5 H. Zhang, M. Zhang, S. Pan, Z. Yang, Z. Wang, Q. Bian, X. Hou, H. Yu, F. Zhang, K. Wu, F. Yang, Q. Peng, Z. Xu, K. B. Chang and K. R. Poeppelmeier, *Cryst. Growth Des.*, 2015, **15**, 523–529.

6 X. Lv, P. Wang, H. Yu, Y. Hu, H. Zhang, C. Qiu, J. Li, X. Wang, B. Liu and Y. Zhang, *Opt. Mater. Express*, 2019, **9**, 3835.

7 J. Han, K. Liu, L. Chen, F. Li, Z. Yang, F. Zhang, S. Pan and M. Mutailipu, *Chem. - A Eur. J.*, 2023, **29**, 4–10.

8 Z. Chen, H. Zeng, D. Chu, F. Zhang, M. Cheng, Z. Yang and S. Pan, *Sci. China Mater.*, 2022, **2**, 1–6.

9 Z. Chen, F. Li, Y. Liu, C. Cui and M. Mutailipu, *Inorg. Chem.*, 2023, **62**, 14512–14517.

10 B. Cheng, W. Ma, A. Tudi, F. Zhang, Z. Chen, X. Hou, Z. Yang and S. Pan, *Chem. Mater.*, 2023, **35**, 5671–5679.

11 X. Li, Z. Chen, F. Li, F. Zhang, Z. Yang and S. Pan, *Adv. Opt. Mater.*, 2023, **11**, 2202195.

12 Z. Zhang, Y. Wang, B. Zhang, Z. Yang and S. Pan, *Angew. Chem. Int. Ed.*, 2018, **57**, 6577–6581.

13 X. Wang, Y. Wang, B. Zhang, F. Zhang, Z. Yang and S. Pan, *Angew. Chem. Int. Ed.*, 2017, **56**, 14119–14123.

14 M. Mutailipu, M. Zhang, B. Zhang, L. Wang, Z. Yang, X. Zhou and S. Pan, *Angew. Chem. Int. Ed.*, 2018, **57**, 6095–6099.

15 Y. Wang, B. Zhang, Z. Yang and S. Pan, *Angew. Chem. Int. Ed.*, 2018, **57**, 2150–2154.

16 H. Tian, C. Lin, Y. Zhou, X. Zhao, H. Fan, T. Yan, N. Ye and M. Luo, *Angew. Chem. Int. Ed.*, 2023, **62,** e202304858.

17 G. Peng, C. Lin and N. Ye, *J. Am. Chem. Soc.*, 2020, **142**, 20542–20546.

18 J. H. Huang, C. C. Jin, P. L. Xu, P. Gong, Z. Lin, J. W. Cheng and G. Y. Yang, *Inorg. Chem.*, 2019, **58**, 1755–1758.

19 H. Liu, H. Wu, Z. Hu, J. Wang, Y. Wu and H. Yu, *J. Am. Chem. Soc.*, 2023, **145**, 12691–12700.

20 X. Hao, M. Luo, C. Lin, G. Peng, F. Xu and N. Ye, *Angew. Chem. Int. Ed.*, 2021, **60**, 7621–7625.

21 H. Tian, C. Lin, X. Zhao, F. Xu, C. Wang, N. Ye and M. Luo, *CCS Chem.*, 2023, **2**, 1–9.

22 P. Yu, L. M. Wu, L. J. Zhou and L. Chen, *J. Am. Chem. Soc.*, 2014, **136**, 480–487.

23 G. Shi, Y. Wang, F. Zhang, B. Zhang, Z. Yang, X. Hou, S. Pan and K. R. Poeppelmeier, *J. Am. Chem. Soc.*, 2017, **139**, 10645–10648.
24 M. Luo, C. Lin, D. Lin and N. Ye, *Angew. Chem. Int. Ed.*, 2020, **59**, 15978–15981.
25 C. Jin, H. Zeng, F. Zhang, H. Qiu, Z. Yang, M. Mutailipu and S. Pan, *Chem. Mater.*, 2022, **34**, 440–450.
26 M. Mutailipu, J. Han, Z. Li, F. Li, J. Li, F. Zhang, X. Long, Z. Yang and S. Pan, *Nat. Photonics*, 2023, **17**, 694–701.
27 H. Qiu, F. Li, C. Jin, J. Lu, Z. Yang, S. Pan and M. Mutailipu, *Chem. Commun.*, 2022, 5594–5597.
28 C. Jin, F. Li, B. Cheng, H. Qiu, Z. Yang, S. Pan and M. Mutailipu, *Angew. Chem. Int. Ed.*, 2022, **61**, e202203984.
29 Z. Li, W. Jin, F. Zhang, Z. Chen, Z. Yang and S. Pan, *Angew. Chem. Int. Ed.* , 2021, **61**, e202112844.
30 H. Tian, N. Ye and M. Luo, *Angew. Chem. Int. Ed.*, 2022, **61**, e202200395.
31 Y. Zhou, N. He, Z. Lin, X. Shang, X. Chen, Y. Li, W. Huang, M. Hong, S. Zhao and J. Luo, *Small*, 2024, **20**, 1–7.