Supporting Information

A[N(SO_2NH_2)$_2$] (A=Na, K, Rb, and Cs): Enhancing Birefringence of Non π-Conjugated Deep-Ultraviolet Crystals *via* Novel Dimeric Disulfonamide [N(SO_2NH_2)$_2$]$^-$ Groups

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Experimental

Reagents

$SO_2(NH_2)_2$ (Adamas, >98.0%), NaOH (Greagent, ≥98.0%), KOH (Greagent, ≥95.0%), $CsOH·H_2O$ (Adamas, 99.0%), RbF (Adamas, 99.0%) and Ammonium Hydroxide (Greagent 25-28%) were used as received.

Synthesis

The synthesis of $A[N(SO_2NH_2)_2]$ compounds (A =Na, K, Cs, Rb) was achieved through a slow evaporation method from aqueous solution under optimized conditions. The overall reaction is shown below:

$$AOH+2[NH_2\text{-}SO_2\text{-}NH_2] \rightarrow A[\ NH_2\text{-}SO_2\text{-}N\text{-}SO_2\text{-}NH_2]+H_2O+NH_3\uparrow$$

$[SO_2(NH_2)_2]$ and NaOH (KOH, RbF or $CsOH·H_2O$) in a 1:2 molar ratio was added to 100 mL glass beakers containing 20 mL deionized water. Moreover, add 20 mL of ammonium hydroxide to the $Na[N(SO_2NH_2)_2]$ beaker and add an appropriate amount of NaOH to the $Rb[N(SO_2NH_2)_2]$ beaker. After several days of evaporation at 45 °C, $A[N(SO_2NH_2)_2]$ (A =Na, K, Cs, Rb) crystals can be obtained.

Single crystal X-ray diffraction

Transparent bulk single crystals of $A[N(SO_2NH_2)_2]$ (A = Na, K, Rb, and Cs) were selected and put on the loop for the single-crystal structure determination. All of the data were collected by a Bruker D8 Venture diffractometer equipped using Mo Kα radiation (λ= 0.71073 Å) at room temperature. And the collected data were integrated by the SAINT program. The structure was resolved using the direct method, and the structure was optimized by full-matrix least-squares techniques using the program suite SHELXTL on F^2.[1] The single-crystal data were handled with OLEX2 software, and check the symmetry of the refined structures by PLATON, and no higher symmetries were found.[2]

Powder X-ray diffraction (XRD)

On a Rigaku Smart Lab 9kW diffractometer equipped with graphite monochromatic Cu Kα radiation (λ = 1.5418 Å), powder XRD patterns were characterized. The scanning angle range (2θ) for the test was from 10 to 70° and the scan step width and rate were 0.02° and 1 s/step, respectively.

Thermogravimetric (TG) analysis

The thermal behavior of $A[N(SO_2NH_2)_2]$ (A = Na, K, Rb, and Cs) were performed using a 209F3A TG analyzer (NETZSCH Instruments). The sample of ~10 mg was enclosed in an alumina crucible and heated from 40 to 700 °C at a rate of 10 °C/min. The measurements were carried out in an atmosphere of flowing Ar.

Infrared (IR) spectroscopy

To favourably verify the structural units, the infrared (IR) spectroscopy was recorded in the wavelength range of 400−4000 cm^{-1} at room temperature using Nicolet iS50 FT-IR spectrometer with ATR.

Energy-dispersive X-ray spectroscopy (EDS) analysis

Microprobe elemental analyses and elemental distribution maps were conducted using an energy-dispersive X-ray spectroscope (EDS) coupled with a field-emission scanning electron microscope (Quanta FEG 250) manufactured by FEI.

Transmittance spectroscopy

The transmittance spectrum for $A[N(SO_2NH_2)_2]$ (A = Na, K, Rb, and Cs) crystal without polishing was collected on PerkinElmer Lamda-950 UV–vis–NIR spectrophotometer ranging from 190 to 1600 nm with a scan step width of 1 nm.

Birefringence measurements

The birefringence of $A[N(SO_2NH_2)_2]$ (A = Na, K, Rb, and Cs) were measured using an Eclipse E200MV polarizing microscope. The wavelength of the light source was 546 nm. The birefringence was determined according to the following equation:

$$\Delta R(\text{retardation}) = \Delta n \times d$$

Here, ΔR represents the optical path difference, Δn represents the birefringence, and d denotes the thickness of the crystal.

Theoretical calculations

The first-principles calculations for $A[N(SO_2NH_2)_2]$ (A = Na, K, Rb, and Cs) were performed using the CASTEP package based on density functional theory (DFT). [3-4] The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional was adopted to describe the exchange–correlation energy.[3] The optimized norm-conserving pseudopotentials in the Kleinman–Bylander form was used for all the elements (Na $2s^22p^63s^1$, K $3s^23p^64s^1$, Rb $4s^24p^65s^1$, Cs $5s^25p^66s^1$, S $3s^23p^4$, O $2s^22p^4$, N $2s^22p^3$, and H $1s^1$) to model the effective interaction between atom cores and valence electrons.[5] The high kinetic energy cutoffs for $A[N(SO_2NH_2)_2]$ (A = Na, K, Rb, and Cs) were set as 750 eV, 750 eV, 750 eV, and 750 eV, respectively. The dense Monkhorst–Pack k-point meshes in the Brillouin zones were set to 3 × 2 × 1, 1 × 2 × 1, 1 × 2 × 1, and 2 × 1 × 1, respectively. Because of the discontinuity of exchange–correlation energy, the band gaps calculated using GGA-PBE were usually underestimated. A scissor operator was applied to make the calculated band gaps match the measured values for the optical properties' calculations.

Table S1. Crystallographic data of $A[N(SO_2NH_2)_2]$ (A=Na, K, Rb, and Cs)

Formula	$Na[N(SO_2NH_2)_2]$	$K[N(SO_2NH_2)]$	$Rb[N(SO_2NH_2)_2]$	$Cs[N(SO_2NH_2)_2]$
Formula weight	197.17	213.28	259.65	307.09
Temperature/K	293	293	293	293
Crystal system	Triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	5.2132(11)	9.268(6)	9.6096(17)	7.1310(18)
b/Å	8.4779(18)	5.782(4)	5.7879(10)	10.448(3)
c/Å	14.130(3)	11.971(7)	12.217(2)	10.171(3)
α/°	104.982(8)	90	90	90
β/°	97.466(9)	93.55(3)	94.418(7)	96.385(13)
γ/°	93.339(9)	90	90	90
Volume/$Å^3$	595.4(2)	640.3(7)	677.5(2)	753.1(4)
Z	4	4	4	4
$\rho_{(calc)}g/cm^3$	2.200	2.213	2.546	2.714
μ/mm^{-1}	0.921	1.44	7.885	5.447
F(000)	400	432	504	576
Theta range for data collection/°	2.498 to 27.550	2.700 to 27.593	2.601 to 27.503	2.808 to 27.530
Index ranges	-6<=h<=6, -11<=k<=10, -18<=l<=18	-12 ≤ h ≤ 12, -7 ≤ k ≤ 7, -14 ≤ l ≤ 15	-12 ≤ h ≤ 12, -7 ≤ k ≤ 7, -15 ≤ l ≤ 15	-7 ≤ h ≤ 9, -13 ≤ k ≤ 13, -12 ≤ l ≤ 12
Reflections collected / unique	20072 / 2730 [$R_{(int)}$ = 0.0679]	3782 / 1450 [$R_{(int)}$ = 0.0747]	7665 / 1566 [$R_{(int)}$ = 0.0624]	14207 / 1724 [$R_{(int)}$ = 0.0592]
Data/restraints/parameters	2730 / 0 / 214	1450/0/108	1566/0/108	1724 / 0 / 108
GOOF on F^2	1.075	0.986	1.044	1.035
R_1, wR_2 [I>=2σ (I)]	0.0340, 0.0774	0.0461, 0.0919	0.0306, 0.0660	0.0161, 0.0412
R_1, wR_2 [all data]	0.0422,0.0808	0.0810, 0.1072	0.0444, 0.0710	0.0181, 0.0416
Largest diff. peak/hole / e $Å^{-3}$	0.421 and -0.450	0.436 and -0.543	0.416 and -0.404	0.720 and -0.334

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

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for $A[N(SO_2NH_2)_2]$ (A=Na, K, Rb, and Cs). Ueq is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

$Na[N(SO_2NH_2)_2]$

Atom	x	y	z	U(eq)
Na(1)	8287(2)	-1253(1)	3862(1)	27(1)
Na(2)	-2808(2)	-801(1)	1464(1)	25(1)
S(1)	-1543(1)	2643(1)	311(1)	17(1)
S(2)	-974(1)	5323(1)	1967(1)	16(1)

S(3)	3149(1)	960(1)	3144(1)	17(1)
S(4)	6072(1)	2549(1)	4966(1)	17(1)
O(1)	-2031(4)	1494(2)	870(2)	30(1)
O(2)	-3005(4)	2287(2)	-673(1)	27(1)
O(3)	-1336(4)	4334(2)	2641(1)	27(1)
O(4)	-2108(4)	6868(2)	2198(2)	27(1)
O(5)	486(4)	276(2)	2864(2)	28(1)
O(6)	5106(4)	-165(2)	2958(1)	28(1)
O(7)	7707(4)	1271(2)	5082(1)	24(1)
O(8)	5347(4)	3495(3)	5884(1)	33(1)
N(1)	1517(5)	2579(3)	155(2)	25(1)
N(2)	-2079(4)	4471(3)	838(2)	17(1)
N(3)	2154(4)	5586(3)	2015(2)	23(1)
N(4)	3542(6)	2208(3)	2461(2)	28(1)
N(5)	3361(4)	1935(3)	4283(2)	19(1)
N(6)	7759(6)	3688(4)	4493(2)	34(1)

$K[N(SO_2NH_2)_2]$

Atom	x	y	z	U(eq)
K(1)	11036(1)	3657(2)	6762(1)	34(1)
S(1)	7570(1)	2044(2)	4936(1)	22(1)
S(2)	5424(1)	2889(2)	6387(1)	22(1)
O(1)	8499(3)	3702(5)	5524(2)	33(1)
O(2)	7634(3)	2007(5)	3736(2)	32(1)
O(3)	6137(3)	1397(5)	7220(2)	34(1)
O(4)	3880(3)	2802(5)	6303(2)	30(1)
N(1)	8115(5)	-509(8)	5354(4)	33(1)
N(2)	5909(3)	2400(5)	5165(3)	22(1)
N(3)	5829(5)	5514(7)	6791(3)	28(1)

$Rb[N(SO_2NH_2)_2]$

Atom	x	y	z	U(eq)
Rb(1)	6025(1)	8532(1)	1721(1)	33(1)
S(1)	7494(1)	7956(2)	4960(1)	25(1)
S(2)	5462(1)	7097(2)	6384(1)	25(1)
O(1)	7555(3)	8051(4)	3792(2)	35(1)
O(2)	8383(3)	6271(4)	5520(2)	36(1)
O(3)	6190(3)	8538(5)	7203(2)	40(1)
O(4)	3963(2)	7194(4)	6318(2)	36(1)
N(1)	8049(4)	10477(6)	5402(3)	37(1)
N(2)	5893(3)	7602(5)	5179(2)	25(1)
N(3)	5852(3)	4446(5)	6752(2)	28(1)

$Cs[N(SO_2NH_2)_2]$

Atom	x	y	z	U(eq)
Cs(1)	2651(1)	6555(1)	4915(1)	30(1)
S(1)	4049(1)	4084(1)	8011(1)	25(1)
S(2)	1432(1)	2170(1)	7925(1)	23(1)
O(1)	3849(3)	4112(2)	6584(2)	38(1)
O(2)	5921(2)	4302(2)	8673(2)	38(1)
O(3)	-32(2)	3122(1)	7763(2)	34(1)
O(4)	1071(2)	1068(2)	8708(2)	37(1)
N(1)	2777(3)	5279(2)	8446(2)	35(1)
N(2)	3387(2)	2760(2)	8573(2)	24(1)
N(3)	1612(3)	1614(2)	6439(2)	35(1)

Table S3. Bond Lengths and bond Angles for $A[N(SO_2NH_2)_2]$ (A=Na, K, Rb, and Cs)

$Na[N(SO_2NH_2)_2]$

Na(1)-O(4)#4	2.450(2)	O(1)-S(1)-O(2)	116.15(12)
Na(1)-O(5)#3	2.484(2)	O(1)-S(1)-N(1)	106.09(14)
Na(1)-O(6)	2.339(2)	O(1)-S(1)-N(2)	113.71(12)
Na(1)-O(7)#2	2.407(2)	O(2)-S(1)-N(1)	105.64(13)
Na(1)-O(7)	2.439(2)	O(2)-S(1)-N(2)	104.78(12)
Na(1)-O(8)#1	2.728(3)	N(2)-S(1)-N(1)	110.19(12)
Na(2)-O(1)	2.344(2)	O(3)-S(2)-O(4)	114.35(12)
Na(2)-O(2)#5	2.433(2)	O(3)-S(2)-N(2)	115.20(11)
Na(2)-O(4)#6	2.482(2)	O(3)-S(2)-N(3)	104.56(13)
Na(2)-O(5)	2.387(2)	O(4)-S(2)-N(2)	105.28(11)
Na(2)-O(6)#7	2.450(2)	O(4)-S(2)-N(3)	111.84(12)
S(1)-O(1)	1.435(2)	N(2)-S(2)-N(3)	105.40(12)
S(1)-O(2)	1.4443(19)	O(5)-S(3)-O(6)	116.84(12)
S(1)-N(1)	1.641(2)	O(5)-S(3)-N(4)	105.54(14)
S(1)-N(2)	1.594(2)	O(5)-S(3)-N(5)	104.56(12)
S(2)-O(3)	1.4439(19)	O(6)-S(3)-N(4)	105.58(14)
S(2)-O(4)	1.4462(19)	O(6)-S(3)-N(5)	113.04(11)
S(2)-N(2)	1.587(2)	N(5)-S(3)-N(4)	111.11(13)
S(2)-N(3)	1.623(2)	O(7)-S(4)-O(8)	113.90(12)
S(3)-O(5)	1.4369(19)	O(7)-S(4)-N(5)	115.21(12)
S(3)-O(6)	1.4395(19)	O(7)-S(4)-N(6)	104.33(15)
S(3)-N(4)	1.627(3)	O(8)-S(4)-N(5)	103.04(12)
S(3)-N(5)	1.594(2)	O(8)-S(4)-N(6)	110.59(16)
S(4)-O(7)	1.4463(19)	N(5)-S(4)-N(6)	109.88(14)
S(4)-O(8)	1.447(2)	S(2)-N(2)-S(1)	121.73(13)
S(4)-N(5)	1.581(2)	S(4)-N(5)-S(3)	122.03(13)
S(4)-N(6)	1.593(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1 #2 -x+2,-y,-z+1 #3 x+1,y,z #4 x+1,y-1,z #5 -x-1,-y,-z #6 x,y-1,z #7 x-1,y,z #8 -x,-y,-z #9 x-1,y+1,z #10 x,y+1,z

$K[N(SO_2NH_2)_2]$

K(1)-O(4)#2	3.331(3)	S(2)-N(3)	1.629(4)
K(1)-O(4)#4	2.770(3)	O(4)-S(2)-O(3)	116.08(18)
K(1)-O(2)#5	2.738(3)	O(4)-S(2)-N(2)	105.61(18)
K(1)-O(2)#3	2.872(3)	O(4)-S(2)-N(3)	105.4(2)
K(1)-O(1)#3	3.185(4)	O(3)-S(2)-N(2)	112.77(18)
K(1)-O(1)	2.701(3)	O(3)-S(2)-N(3)	105.3(2)
K(1)-O(3)#2	2.891(3)	N(2)-S(2)-N(3)	111.59(19)
S(1)-O(2)	1.441(3)	O(2)-S(1)-O(1)	115.81(17)
S(1)-O(1)	1.443(3)	O(2)-S(1)-N(2)	105.90(18)
S(1)-N(2)	1.593(3)	O(2)-S(1)-N(1)	105.1(2)
S(1)-N(1)	1.629(4)	O(1)-S(1)-N(2)	112.61(18)
S(2)-O(4)	1.430(3)	O(1)-S(1)-N(1)	106.7(2)
S(2)-O(3)	1.447(3)	N(2)-S(1)-N(1)	110.4(2)
S(2)-N(2)	1.582(3)	S(2)-N(2)-S(1)	121.0(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+5/2,y-1/2,-z+3/2 #2 -x+3/2,y+1/2,-z+3/2 #3 -x+2,-y+1,-z+1 #4 x+1,y,z #5 x+1/2,-y+1/2,z+1/2 #6 -x+3/2,y-1/2,-z+3/2 #7 -x+2,-y,-z+1 #8 x-1,y,z #9 x-1/2,-y+1/2,z-1/2

$Rb[N(SO_2NH_2)_2]$

Rb(1)-O(1)#1	3.038(3)	S(2)-N(3)	1.634(3)
Rb(1)-O(1)	2.840(2)	O(1)-S(1)-O(2)	115.60(16)
Rb(1)-O(1)#3	3.528(3)	O(1)-S(1)-N(1)	104.92(18)
Rb(1)-O(2)#4	2.835(2)	O(1)-S(1)-N(2)	106.61(15)
Rb(1)-O(2)#1	3.251(3)	O(2)-S(1)-N(1)	106.4(2)
Rb(1)-O(3)#2	3.093(3)	O(2)-S(1)-N(2)	112.27(15)
Rb(1)-O(4)#5	2.933(2)	N(2)-S(1)-N(1)	110.78(17)
Rb(1)-O(4)#2	3.443(3)	O(3)-S(2)-N(2)	112.93(15)
S(1)-O(1)	1.434(2)	O(3)-S(2)-N(3)	105.29(16)
S(1)-O(2)	1.435(2)	O(4)-S(2)-O(3)	116.54(16)
S(1)-N(1)	1.631(3)	O(4)-S(2)-N(2)	105.84(15)
S(1)-N(2)	1.595(3)	O(4)-S(2)-N(3)	105.07(17)
S(2)-O(3)	1.442(3)	N(2)-S(2)-N(3)	110.93(16)
S(2)-O(4)	1.438(2)	S(2)-N(2)-S(1)	120.23(16)
S(2)-N(2)	1.587(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,y+1/2,-z+1/2 #2 -x+1,-y+2,-z+1 #3 -x+3/2,y-1/2,-z+1/2 #4 x-1/2,-y+3/2,z-1/2 #5 x+1/2,-y+3/2,z-1/2 #6 -x+1,-y+1,-z+1 #7 x+1/2,-y+3/2,z+1/2 #8 x-1/2,-y+3/2,z+1/2

$Cs[N(SO_2NH_2)_2]$

Cs(1)-O(1)#2	3.1434(18)	S(2)-N(3)	1.633(2)
Cs(1)-O(1)	3.1285(16)	O(1)-S(1)-O(2)	116.59(11)
Cs(1)-O(2)#3	3.3161(16)	O(1)-S(1)-N(1)	105.07(11)
Cs(1)-O(3)#1	3.5629(17)	O(1)-S(1)-N(2)	112.25(9)

Cs(1)-O(3)#4	3.1418(15)	O(2)-S(1)-N(1)	105.49(11)
Cs(1)-O(4)#5	3.1581(16)	O(2)-S(1)-N(2)	105.50(9)
Cs(1)-O(4)#1	3.1764(18)	N(2)-S(1)-N(1)	111.86(10)
S(1)-O(1)	1.4390(16)	O(3)-S(2)-N(2)	111.71(9)
S(1)-O(2)	1.4463(16)	O(3)-S(2)-N(3)	105.70(10)
S(1)-N(1)	1.6333(19)	O(4)-S(2)-O(3)	116.36(10)
S(1)-N(2)	1.5871(16)	O(4)-S(2)-N(2)	106.42(9)
S(2)-O(3)	1.4394(15)	O(4)-S(2)-N(3)	105.25(11)
S(2)-O(4)	1.4372(16)	N(2)-S(2)-N(3)	111.26(10)
S(2)-N(2)	1.5992(17)	S(1)-N(2)-S(2)	117.97(9)

Symmetry transformations used to generate equivalent atoms: #1 -x,y+1/2,-z+3/2 #2 -x+1,-y+1,-z+1 #3 -x+1,y+1/2,-z+3/2 #4 -x,-y+1,-z+1 #5 x,-y+1/2,z-1/2 #6 x,-y+3/2,z-1/2 #7 -x+1,y-1/2,-z+3/2 #8 -x,y-1/2,-z+3/2 #9 x,-y+1/2,z+1/2 #10 x,-y+3/2,z+1/2

Table S4. Anisotropic displacement parameters (Å^2×10^3) for A[N(SO_2NH_2)$_2$] (A = Na, K, Rb, and Cs). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 a^{*2} U11 + ... + 2 h k a* b* U12].

Na[N(SO_2NH_2)$_2$]

	U11	U22	U33	U23	U13	U12
Na(1)	25(1)	27(1)	27(1)	7(1)	1(1)	7(1)
Na(2)	28(1)	24(1)	21(1)	6(1)	1(1)	-1(1)
S(1)	18(1)	16(1)	15(1)	3(1)	1(1)	-1(1)
S(2)	17(1)	15(1)	16(1)	3(1)	4(1)	1(1)
S(3)	12(1)	17(1)	20(1)	4(1)	0(1)	0(1)
S(4)	19(1)	18(1)	14(1)	5(1)	2(1)	2(1)
O(1)	46(1)	19(1)	27(1)	10(1)	9(1)	-1(1)
O(2)	28(1)	31(1)	16(1)	1(1)	-3(1)	-3(1)
O(3)	36(1)	27(1)	18(1)	9(1)	6(1)	-4(1)
O(4)	29(1)	19(1)	29(1)	0(1)	5(1)	6(1)
O(5)	15(1)	34(1)	33(1)	7(1)	-2(1)	-6(1)
O(6)	25(1)	31(1)	25(1)	2(1)	2(1)	13(1)
O(7)	22(1)	26(1)	28(1)	12(1)	1(1)	7(1)
O(8)	43(1)	42(1)	14(1)	2(1)	5(1)	16(1)
N(1)	21(1)	26(1)	26(1)	3(1)	4(1)	5(1)
N(2)	19(1)	17(1)	15(1)	4(1)	1(1)	2(1)
N(3)	17(1)	29(1)	20(1)	5(1)	-1(1)	-3(1)
N(4)	30(1)	31(1)	25(1)	13(1)	1(1)	-4(1)
N(5)	16(1)	23(1)	19(1)	4(1)	4(1)	3(1)
N(6)	26(1)	34(2)	50(2)	25(1)	4(1)	-5(1)

K[N(SO_2NH_2)$_2$]

	U11	U22	U33	U23	U13	U12
K(1)	23(1)	49(1)	30(1)	4(1)	2(1)	-1(1)
S(1)	21(1)	28(1)	19(1)	-1(1)	2(1)	-3(1)
S(2)	19(1)	28(1)	19(1)	4(1)	2(1)	-1(1)
O(1)	26(2)	40(2)	35(2)	-11(1)	-1(1)	-8(1)
O(2)	37(2)	41(2)	18(2)	0(1)	4(1)	-6(1)
O(3)	37(2)	45(2)	22(2)	18(1)	3(1)	10(2)
O(4)	22(2)	34(2)	33(2)	-1(1)	5(1)	-2(1)
N(1)	36(3)	36(2)	28(2)	3(2)	5(2)	5(2)
N(2)	19(2)	29(2)	18(2)	0(1)	0(1)	-2(1)
N(3)	19(2)	36(2)	27(2)	-2(2)	-5(2)	0(2)

Rb[N(SO_2NH_2)$_2$]

	U11	U22	U33	U23	U13	U12
Rb(1)	22(1)	50(1)	28(1)	3(1)	1(1)	-2(1)
S(1)	22(1)	31(1)	21(1)	1(1)	2(1)	4(1)
S(2)	18(1)	32(1)	25(1)	-6(1)	2(1)	0(1)
O(1)	41(2)	44(2)	21(1)	1(1)	6(1)	6(1)
O(2)	24(1)	49(2)	34(1)	10(1)	0(1)	10(1)
O(3)	36(2)	53(2)	30(1)	-17(1)	5(1)	-8(1)
O(4)	18(1)	42(2)	48(2)	-1(1)	7(1)	3(1)
N(1)	40(2)	38(2)	35(2)	-6(2)	8(2)	-7(2)
N(2)	20(1)	31(2)	24(1)	0(1)	-2(1)	5(1)
N(3)	25(2)	33(2)	26(2)	2(1)	0(1)	2(1)

Cs[N(SO_2NH_2)$_2$]

	U11	U22	U33	U23	U13	U12
Cs(1)	29(1)	29(1)	33(1)	0(1)	0(1)	-2(1)
S(1)	24(1)	25(1)	26(1)	4(1)	2(1)	0(1)
S(2)	22(1)	24(1)	24(1)	2(1)	2(1)	1(1)
O(1)	47(1)	42(1)	27(1)	8(1)	7(1)	-1(1)
O(2)	26(1)	38(1)	50(1)	4(1)	-2(1)	-5(1)
O(3)	24(1)	34(1)	43(1)	-2(1)	-2(1)	8(1)
O(4)	41(1)	31(1)	41(1)	10(1)	7(1)	-5(1)
N(1)	34(1)	25(1)	45(1)	-2(1)	-1(1)	6(1)
N(2)	23(1)	23(1)	24(1)	4(1)	-1(1)	1(1)
N(3)	40(1)	38(1)	27(1)	-7(1)	3(1)	0(1)

Table S5. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for $A[N(SO_2NH_2)_2]$ (A = Na, K, Rb, and Cs).

$Na[N(SO_2NH_2)_2]$

Atom	x	y	z	U(eq)
H(1A)	2090(80)	3530(50)	50(30)	50(11)
H(1B)	2380(80)	2450(50)	630(30)	44(11)
H(3A)	2570(70)	6160(40)	1660(30)	39(10)
H(3B)	2900(70)	5930(40)	2560(30)	33(10)
H(4A)	2320(80)	2850(50)	2530(30)	53(12)
H(4B)	4920(80)	2610(50)	2530(30)	46(12)
H(6A)	9060(90)	3390(50)	4320(30)	61(14)
H(6B)	7150(70)	4350(50)	4340(30)	39(11)

$K[N(SO_2NH_2)_2]$

Atom	x	y	z	U(eq)
H1A	7480(80)	-1630(110)	5080(60)	110(30)
H1B	8240(50)	-350(80)	5900(40)	18(14)
H3A	6640(40)	5560(60)	6900(30)	2(10)
H3B	5510(60)	6220(80)	6380(40)	31(16)

$Rb[N(SO_2NH_2)_2]$

Atom	x	y	z	U(eq)
H1A	7570(50)	11570(80)	5150(40)	45(14)
H1B	8280(50)	10400(80)	6030(40)	52(14)
H3A	5520(40)	3580(60)	6220(30)	18(9)
H3B	6670(50)	4240(80)	6900(40)	55(15)

$Cs[N(SO_2NH_2)_2]$

Atom	x	y	z	U(eq)
H(1A)	8010(70)	7880(60)	43(18)	3980(50)
H(1B)	7510(70)	9090(50)	40(13)	3430(50)
H(2A)	7020(70)	4620(50)	42(16)	710(50)
H(2B)	8230(70)	4970(60)	53(19)	1790(60)

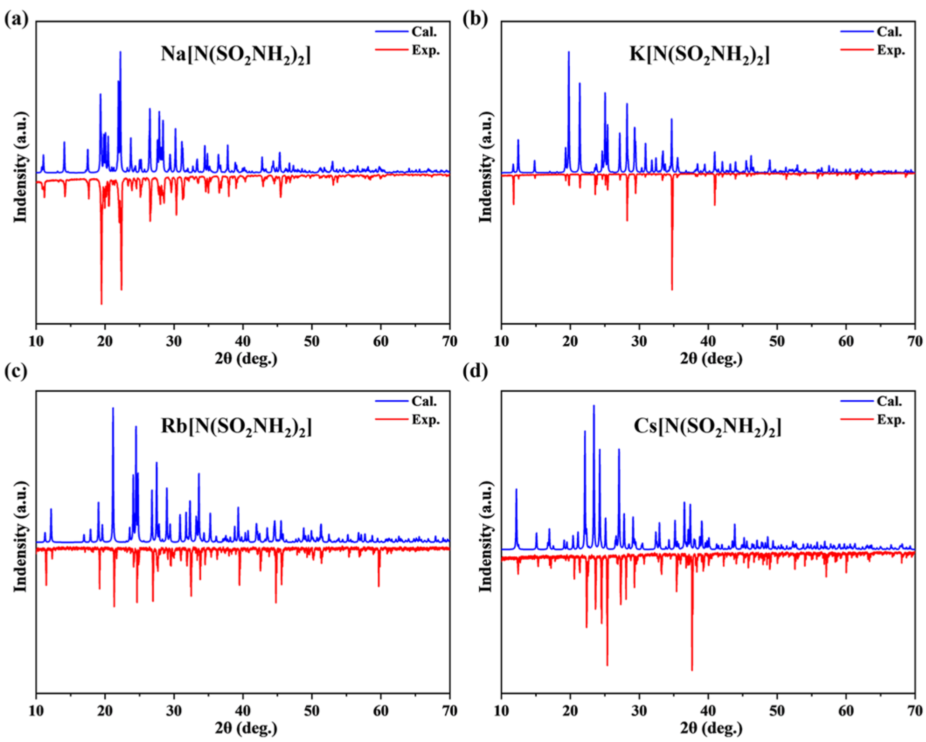

Figure S1. The calculated (blue line) and experimental (red line) PXRD patterns of $A[N(SO_2NH_2)_2]$ (A = Na, K, Rb, and Cs).

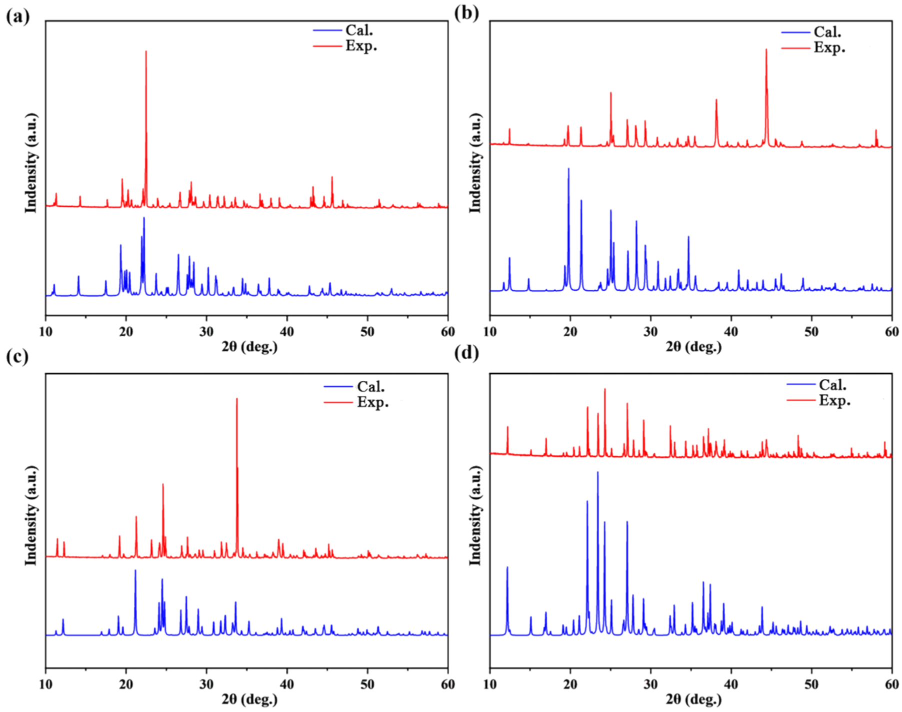

Figure S2. Calculated and experimental powder XRD patterns of $A[N(SO_2NH_2)_2]$ (A = Na, K, Rb, and Cs) (a-d) crystals stored for nearly one year.

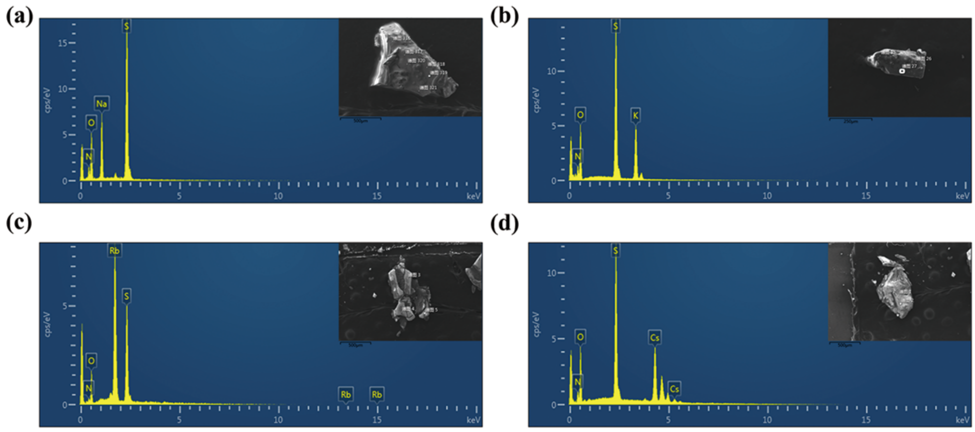

Figure S3. Energy-dispersive X-ray spectroscope (EDS) analysis for $A[N(SO_2NH_2)_2]$ (A = Na, K, Rb, and Cs).

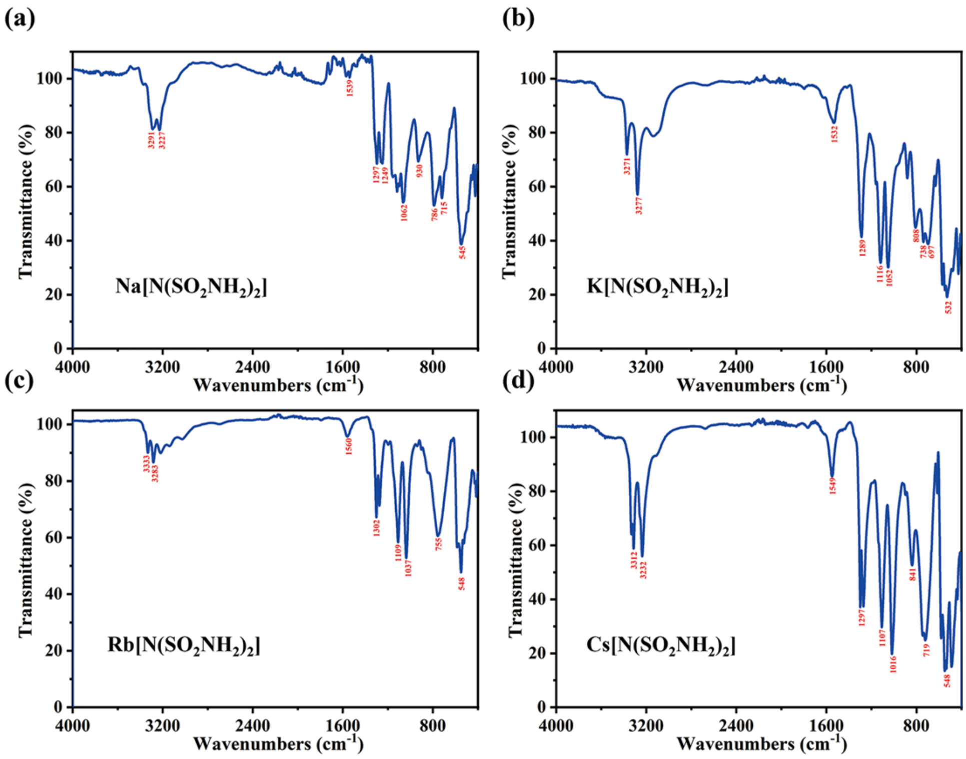

Figure S4. The IR spectrum of $A[N(SO_2NH_2)_2]$ (A = Na, K, Rb, and Cs).

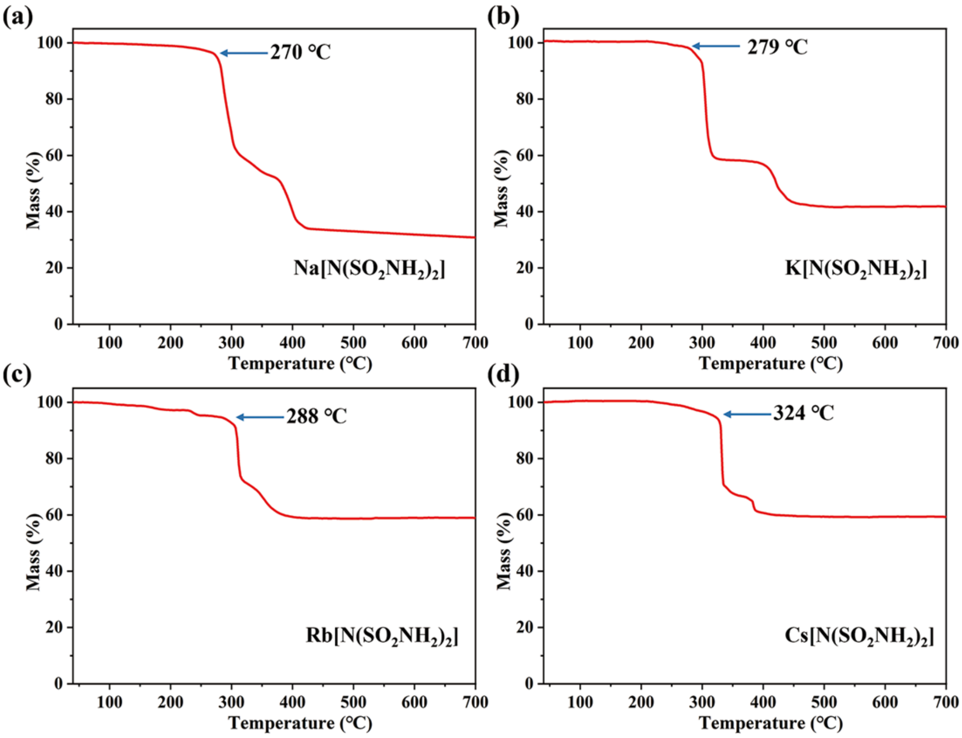

Figure S5. The TG curves of A[N(SO_2NH_2)$_2$] (A = Na, K, Rb, and Cs).

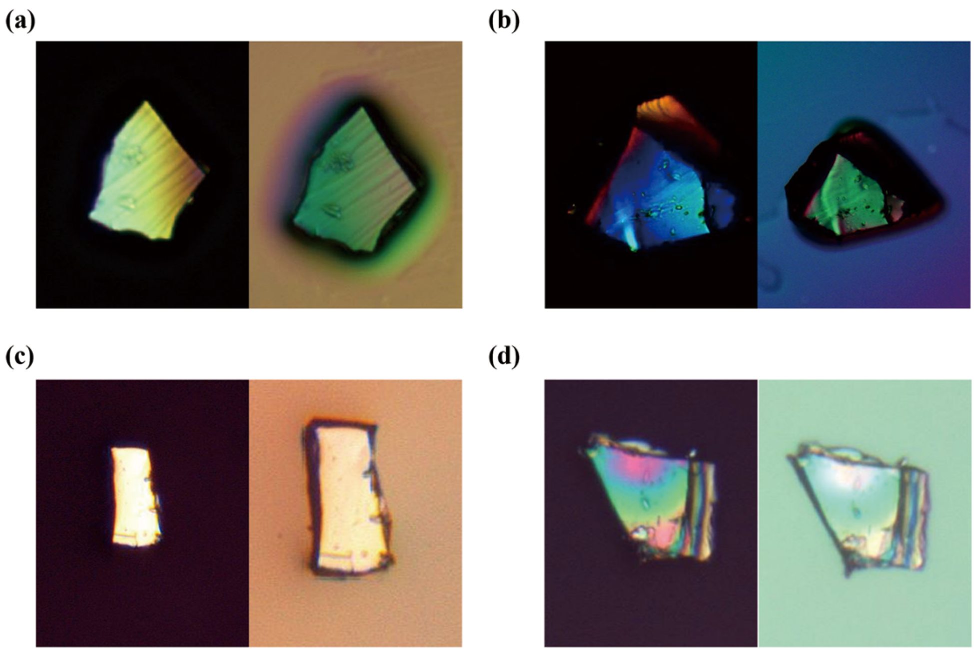

Figure S6. The photographs of crystals of A[N(SO_2NH_2)$_2$] (A = Na, K, Rb, and Cs).

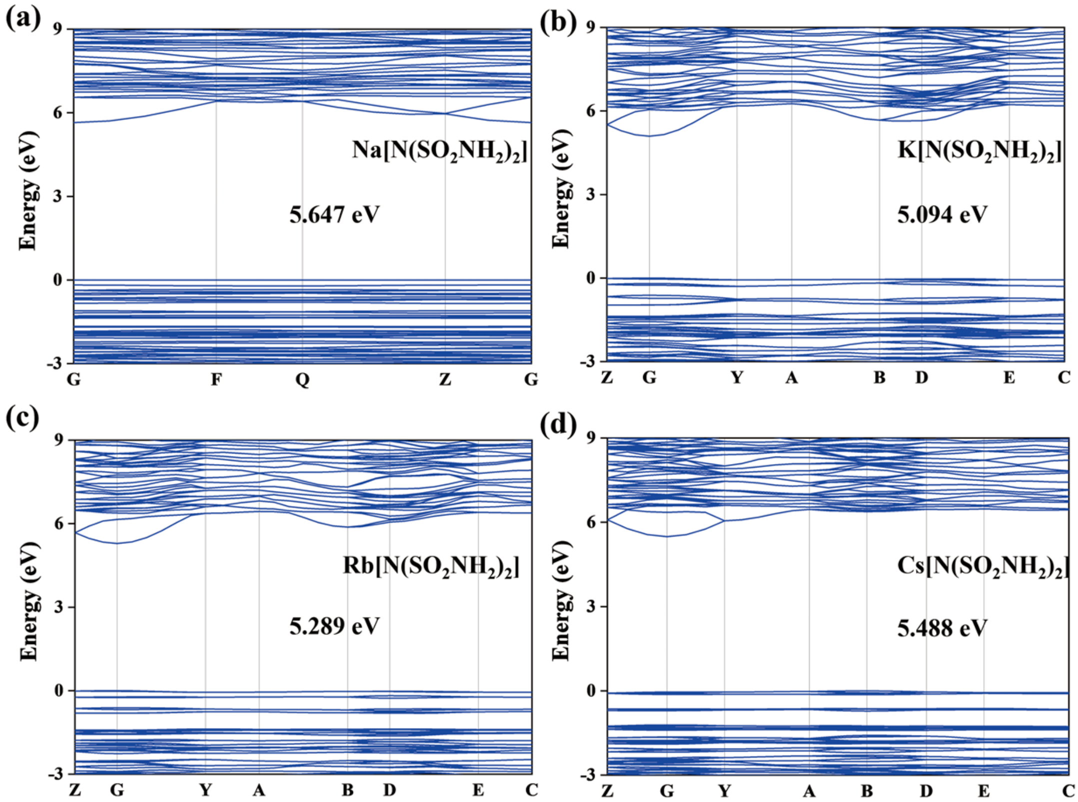

Figure S7. Band structures of compounds for $A[N(SO_2NH_2)_2]$ (A = Na, K, Rb, and Cs).

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