Supporting Information

$[(Me)_2NH_2]_{0.75}[Ag_{1.25}SnSe_3]$: A Three-dimensionally Microporous Chalcogenide Exhibiting Framework Flexibility Upon Ion-exchange

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1. More Structural details

The intensity data were collected on a Rigaku SCXmini CCD diffractometer for **1, 1Cs, 1Rb** and a Rigaku Mercury CCD diffractometer for **1NH$_4$** with graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å) at room temperature. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX97 program package.[1] The hydrogen atoms attached to the C and N atoms in compound **1** were located at geometrically calculated positions, and the restraints (DFIX, ISOR and SIMU) were applied on C and N atoms to obtain chemical-reasonable models for disordered dimethylammonium ions. The Cs1 ion in compound **1Cs** showed positional disorder and was refined split into three non-equivalent positions Cs1A, Cs1B and Cs1C, respectively, while the Cs2 ion was half-occupied. The water molecules are also half-occupied. The hydrogen atoms of the water molecules were not added. In the structure of **1Rb**, the Rb1 ion showed positional disorder and was refined split into two non-equivalent positions Rb1A and Rb1B, respectively, while the Rb2 ion was half-occupied. The residual dimethylammounium cations in **1Cs** and **1Rb** could not be found in the difference Fourier maps, therefore were not included in the structure refinements. In the structure of 1NH$_4$, the hydrogen atoms were not added, and the restraints (DFIX and SIMU) were applied on C and N atoms to obtain chemical-reasonable models for the disordered dimethylammonium ion. The empirical formulae for **1Cs**, **1Rb**, and **1NH$_4$** were calculated based on the TGA, EA and EDS results. The crystal data and structure refinement details are listed in Table S1. The selected bond lengths and angles of compounds **1**, **1Cs**, **1Rb**, and **1NH$_4$** are listed in Table S2.

[1] G. M. Sheldrick, *SHELXS97 and SHELXL97*, University of Göttingen, Germany, **1997**.

Table S1 Crystallographic data for compound **1** and the ion-exchanged products

	1	**1Cs**	**1Rb**	**1NH$_4$**
Formula	$[(Me)_2NH_2]_{0.75}[Ag_{1.25}SnSe_3]$	$[Me_2NH_2]_{0.05}Cs_{0.70}[Ag_{1.25}SnSe_3]\cdot 0.25H_2O$	$[Me_2NH_2]_{0.10}Rb_{0.65}[Ag_{1.25}SnSe_3]\cdot 0.75H_2O$	$[Me_2NH_2]_{0.25}(NH_4)_{0.50}[Ag_{1.25}SnSe_3]\cdot 0.5H_2O$
Empirical formula	$C_{1.50}H_6Ag_{1.25}N_{0.75}Se_3Sn$	$C_{0.10}H_{0.90}Ag_{1.25}Cs_{0.70}N_{0.05}O_{0.25}Se_3Sn$	$C_{0.20}H_{2.30}Ag_{1.25}N_{0.10}O_{0.75}Rb_{0.65}Se_3Sn$	$C_{0.50}H_5Ag_{1.25}N_{0.75}O_{0.50}Se_3Sn$
Crystal Size (mm)	0.25×0.16×0.14	0.16×0.14×0.12	0.11×0.10×0.09	0.07×0.06×0.05
Crystal system	tetragonal	tetragonal	tetragonal	tetragonal
Space group	*P-42$_1$m*	*P-42$_1$m*	*P-42$_1$m*	*P-42$_1$m*
a (Å)	13.8051(8)	13.9886(8)	13.998(2)	13.9087(6)
c (Å)	9.6707(9)	8.8534(13)	8.6852(17)	8.8618(7)
V (Å^3)	1843.0(2)	1732.4(3)	1701.9(5)	1714.33(17)
Z	8	8	8	8
μ (mm^{-1})	17.113	21.097	22.227	18.400
F(000)	1848	2025	1960	1824
θ range (°)	2.57 to 27.46	2.72 to 27.47	2.76 to 27.49	2.73 to 27.46
Reflections measured	14465	13505	13288	13455
Independent reflections	2228	2105	2066	2056
Observed Reflection [$I>2\sigma(I)$]	2068	1886	1771	1973
Temperature (K)	293	293	293	293
ρ_{calc}/g cm^{-3}	3.784	4.526	4.403	4.029
Parameter	86	84	84	84
R_{int}	0.0538	0.0598	0.0888	0.0648
R_1, wR_2 [$I>2\sigma(I)$]$^{a, b}$	0.0366, 0.0799	0.0520, 0.1423	0.0639, 0.1399	0.0465, 0.0910
GOF	1.074	1.081	1.084	1.152
Largest diff. Peak and hole/e Å^{-3}	1.037, -1.006	2.021, -1.583	1.066, -1.083	0.961, -1.018

^{a} $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, ^{b} $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$

Table S2. Selected bond lengths (Å) and angles (°) for **1** and the ion-exchanged products **1NH$_4$**, **1Cs**, and **1Rb**.

	1	**1NH$_4$**		**1Cs**	**1Rb**
Sn(1)-Se(1)	2.4861(10)	2.4795(13)	Sn(1)-Se(1)	2.4804(16)	2.480(2)
Sn(1)-Se(2)	2.5064(11)	2.5040(14)	Sn(1)-Se(2)	2.5048(16)	2.501(2)
Sn(1)-Se(3)	2.5795(12)	2.5756(15)	Sn(1)-Se(3)	2.5809(19)	2.575(2)
Sn(1)-Se(4)	2.5595(11)	2.5701(14)	Sn(1)-Se(4)	2.5777(18)	2.570(2)
Ag(1)-Se(2)#1	2.5950(12)	2.5823(15)	Ag(1)-Se(2)#1	2.5782(18)	2.582(2)
Ag(1)-Se(1)	2.6281(13)	2.6151(17)	Ag(1)-Se(1)	2.620(2)	2.610(3)
Ag(1)-Se(2)#2	2.6554(13)	2.6687(17)	Ag(1)-Se(2)#2	2.672(2)	2.678(3)
Ag(1)-Ag(1)#1	3.1826(17)	3.208(2)	Ag(1)-Ag(1)#1	3.185(2)	3.208(3)
Ag(1)-Ag(1)#2	3.2414(16)	3.208(2)	Ag(1)-Ag(1)#2	3.221(3)	3.185(3)
Ag(1)-Ag(1)#3	3.2414(16)	3.228(2)	Ag(1)-Ag(1)#3	3.221(3)	3.185(3)
Ag(2)-Se(1)#1	2.6759(10)	2.6888(12)	Ag(2)-Se(1)	2.7022(15)	2.7012(19)
Ag(2)-Se(1)#4	2.6759(10)	2.6888(12)	Ag(2)-Se(1)#1	2.7022(15)	2.7012(19)
Ag(2)-Se(1)#5	2.6759(10)	2.6888(12)	Ag(2)-Se(1)#4	2.7022(15)	2.7012(19)
Ag(2)-Se(1)	2.6759(10)	2.6888(12)	Ag(2)-Se(1)#5	2.7022(15)	2.7012(19)
Se(1)-Sn(1)-Se(2)	119.59(4)	120.46(5)	Se(1)-Sn(1)-Se(2)	120.35(6)	120.31(7)
Se(1)-Sn(1)-Se(4)	108.84(4)	108.68(6)	Se(1)-Sn(1)-Se(4)	109.39(7)	109.77(9)
Se(2)-Sn(1)-Se(4)	108.72(5)	106.61(6)	Se(2)-Sn(1)-Se(4)	107.49(8)	105.97(10)
Se(1)-Sn(1)-Se(3)	114.21(5)	113.13(6)	Se(1)-Sn(1)-Se(3)	112.99(8)	112.06(10)
Se(2)-Sn(1)-Se(3)	106.95(4)	109.17(6)	Se(2)-Sn(1)-Se(3)	107.87(8)	110.18(10)
Se(4)-Sn(1)-Se(3)	95.85(3)	95.72(4)	Se(4)-Sn(1)-Se(3)	95.87(5)	95.49(7)
Se(2)#1-Ag(1)-Se(1)	123.55(5)	124.35(6)	Se(2)#1-Ag(1)-Se(1)	126.26(8)	125.40(9)
Se(2)#1-Ag(1)-Se(2)#2	116.98(4)	119.30(5)	Se(2)#1-Ag(1)-Se(2)#2	118.06(6)	119.79(7)
Se(1)-Ag(1)-Se(2)#2	114.76(4)	110.94(5)	Se(1)-Ag(1)-Se(2)#2	109.90(6)	108.83(8)
Se(1)#1-Ag(2)-Se(1)#4	105.209(19)	99.45(2)	Se(1)#1-Ag(2)-Se(1)#4	99.23(2)	98.67(3)
Se(1)#1-Ag(2)-Se(1)	118.38(4)	132.18(6)	Se(1)#1-Ag(2)-Se(1)	132.77(7)	134.30(8)
Se(1)#4-Ag(2)-Se(1)	105.209(19)	99.45(2)	Se(1)#4-Ag(2)-Se(1)	99.23(2)	98.67(3)
Se(1)#1-Ag(2)-Se(1)#5	105.209(19)	99.45(2)	Se(1)#1-Ag(2)-Se(1)#5	99.23(2)	98.67(3)
Se(1)#4-Ag(2)-Se(1)#5	118.38(4)	132.18(6)	Se(1)#4-Ag(2)-Se(1)#5	132.79(7)	134.30(8)
Se(1) -Ag(2)-Se(1)#5	105.209(19)	99.45(2)	Se(1)-Ag(2)-Se(1)#5	99.23(2)	98.67(3)
Ag(1)-Se(1)-Ag(2)	97.87(4)	87.76(4)	Ag(1)-Se(1)-Ag(2)	86.36(5)	85.38(7)
Sn(1)-Se(1)-Ag(2)	103.02(3)	96.50(4)	Sn(1)-Se(1)-Ag(2)	97.02(5)	95.81(6)
Sn(1)-Se(1)-Ag(1)	83.06(4)	84.56(5)	Sn(1)-Se(1)-Ag(1)	84.38(6)	85.49(7)
Ag(1)#1-Se(2)-Ag(1)#3	76.24(4)	75.30(6)	Ag(1)#1-Se(2)-Ag(1)#3	75.65(7)	74.49(8)
Sn(1)-Se(2)-Ag(1)#1	104.35(4)	106.35(5)	Sn(1)-Se(2)-Ag(1)#1	106.02(6)	106.38(8)
Sn(1)-Se(2)-Ag(1)#3	96.81(4)	94.25(5)	Sn(1)-Se(2)-Ag(1)#3	94.69(6)	93.33(7)
Symmetry codes: #1 -*x*, -*y*, *z*; #2 *y*, -*x*, -*z*+1; #3 -*y*, *x*, -*z*+1; #4 -*y*, *x*, -*z*+2; #5 *y*, -*x*, -*z*+2.			Symmetry codes: #1 -*x*+1, -*y*+1, *z*; #2 -*y*+1, *x*, -*z*+1; #3 *y*, -*x*+1, -*z*+1; #4 *y*, -*x*+1, -*z*; #5 -*y*+1, *x*, -*z*.		

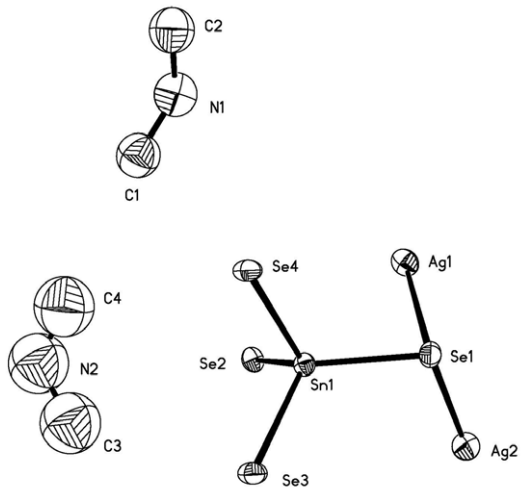

Fig. S1 *ORTEP* plot showing the crystallographically asymmetric unit in the compound **1**; thermal ellipsoids are given at the 30% probability level.

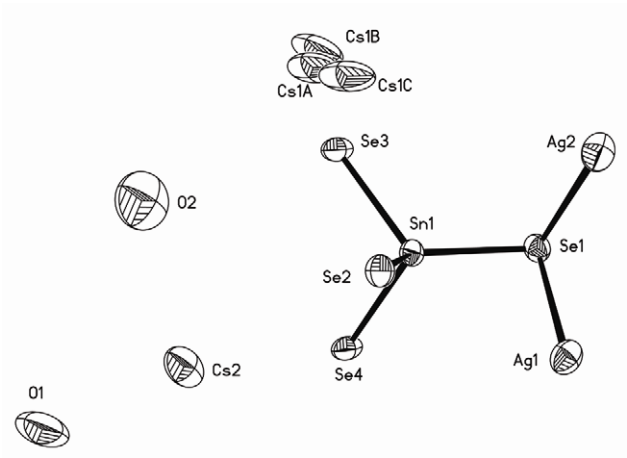

Fig. S2 *ORTEP* plot showing the crystallographically asymmetric unit in the compound **1Cs**; thermal ellipsoids are given at the 30% probability level.

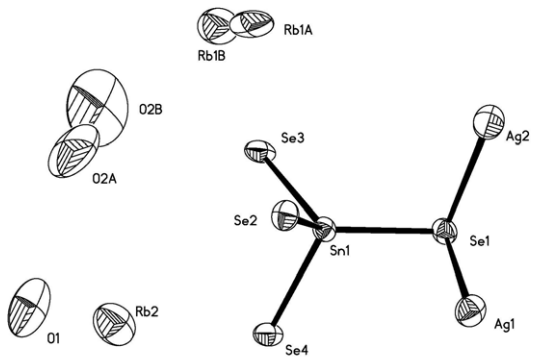

Fig. S3 *ORTEP* plot showing the crystallographically asymmetric unit in the compound **1Rb**; thermal ellipsoids are given at the 30% probability level.

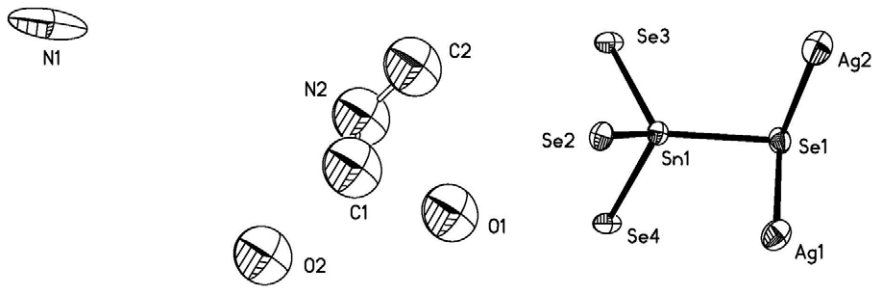

Fig. S4 *ORTEP* plot showing the crystallographically asymmetric unit in the compound **1NH$_4$**; thermal ellipsoids are given at the 30% probability level.

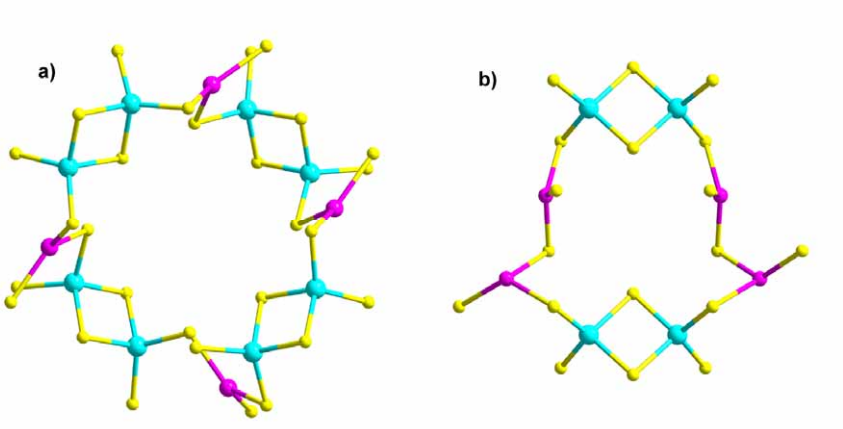

Fig. S5 View of (a) the 24-membered ring window of the channel in the compound **1** along the *c* axis, and (b) the 16-membered ring window of the channel along the [110] direction. The Sn, Ag, Se atoms are drawn as turquoise, pink, and yellow balls, respectively.

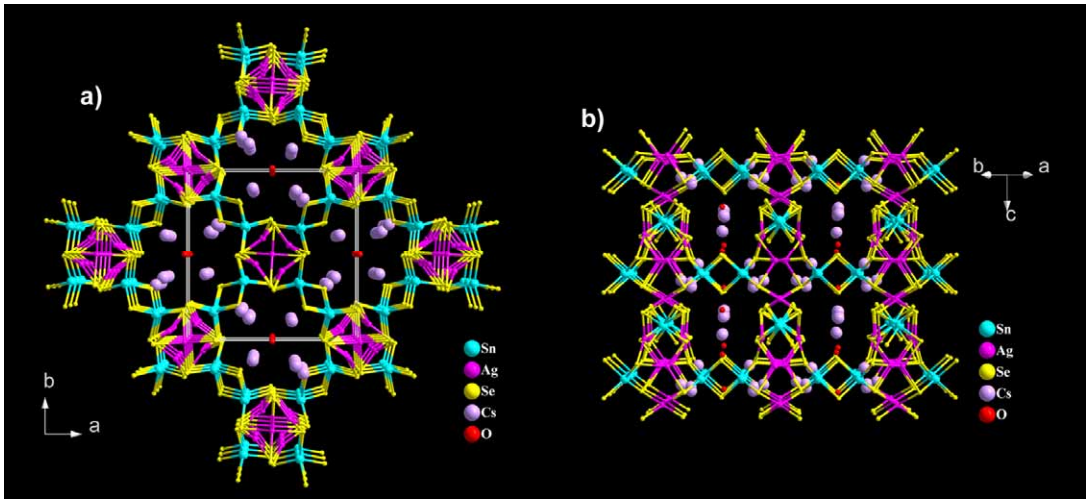

Fig. S6 View of the structure of Cs-exchanged product (**1Cs**) along the *c* axis (a) and [110] direction (b).

2. Physical measurements

All chemicals employed in this study were analytical reagents and commercially available without further purification, except that AgCl was synthesized by the reaction of $AgNO_3$ and KCl. Microprobe elemental analyses were performed by using a field-emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy-dispersive X-ray spectroscope (EDS, Oxford INCA). C, H and N analyses were performed on a German Elementary Vario EL III instrument. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku MiniFlex Ⅱ using Cu*Kα* radiation. Optical diffuse reflectance spectra were measured at room temperature with a Perkin-Elmer Lambda 900 UV/Vis spectrophotometer. A $BaSO_4$ plate was used as a standard (100% reflectance). The absorption spectra were calculated from reflectance spectra by using the Kubelka–Munk function: $a/S = (1-R)^2/2R$,[1] where a is the absorption coefficient, S is the scattering coefficient which is practically independent of wavelength when the particle size is larger than 5 μm, and R is the reflectance. Thermogravimetric analyses were carried out using crystalline samples loaded in Al_2O_3 crucibles with a NETZSCH STA 449F3 unit at a heating rate of 5 °C/min under a nitrogen atmosphere.

[1] W. M. Wendlandt, H. G. Hecht, *Reflectance Spectroscopy*, Interscience, New York, **1966**.

2a). Elemental analyses

Table S3. Elemental analyses of **1** and the ion-exchange products

Exchanged Cations	EDS result	N, C, H, analysis (%) (Calc.)	Estimated formula	Exchange yield (%)
compound **1**	$Ag_{1.24}SnSe_{2.83}$	1.86, 3.43, 1.02 (2.00, 3.42, 1.14)	/	/
Cs^+	$Sn_{0.94}Ag_{1.18}Se_3Cs_{0.70}$	0.3<, 0.3<, 0.3< (0.12 0.20 0.15)	$[SnAg_{1.25}Se_3][Me_2NH_2]_{0.05}Cs_{0.70}$ $\cdot 0.25H_2O$	93
Rb^+	$Ag_{1.32}SnSe_{3.19}Rb0_{.65}$	0.3< 0.5, 0.62 (0.25, 0.43, 0.41)	$[Me_2NH_2]_{0.10}Rb_{0.65}[Ag_{1.25}SnSe_3]$ $\cdot 0.75H_2O$	87
NH_4^+	/	1.81, 1.08, 0.72 (2.02, 1.16, 0.97)	$[Me_2NH_2]_{0.25}(NH_4)_{0.50}[Ag_{1.25}Sn$ $Se_3]\cdot 0.5H_2O$	67

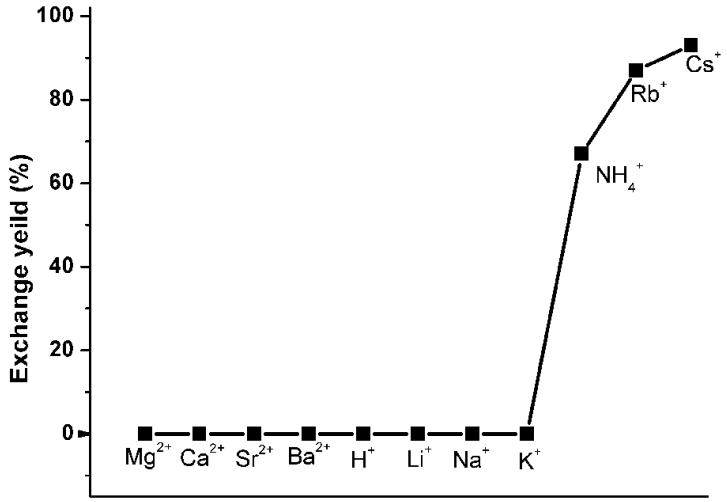

Fig. S7. The Cs^+, Rb^+, K^+, Na^+, Li^+, H^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+} and NH_4^+ ion-exchanged yields for the single ion-exchange experiments are plotted.

Table S4. Elemental analysis results for various single-ion-exchanged products‡

Exchanged Cation	EDS result
K^+	$Ag_{1.40}SnSe_{3.30}$
Na^+	$Ag_{1.37}SnSe_{2.90}$
Li^+	$Ag_{1.32}SnSe_{3.15}$
Ba^{2+}	$Ag_{1.28}SnSe_{3.21}$
Sr^{2+}	$Ag_{1.23}SnSe_{3.20}$
Ca^{2+}	$Ag_{1.33}SnSe_{3.09}$
Mg^{2+}	$Ag_{1.37}SnSe_{2.90}$

‡ The results of TGA and EA for the H^+ exchanged products are in accordance with those of the pristine, indicating that no H^+ was exchanged.

2b) PXRD

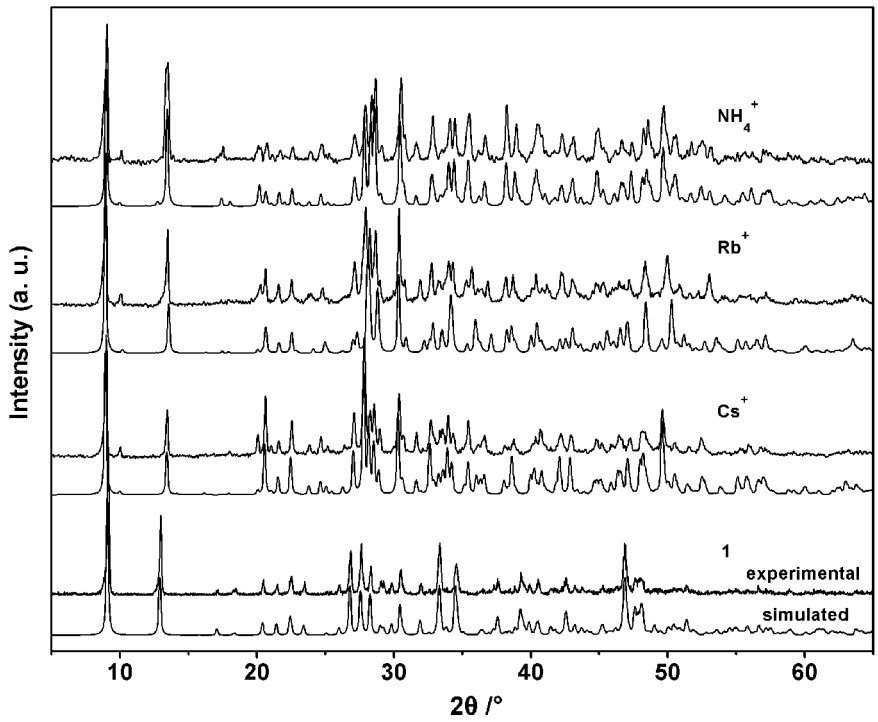

Fig. S8. The experimental PXRD patterns of the pristine compound **1**, Cs^+, Rb^+ and NH_4^+-exchanged products (top) are comparable with the simulated PXRD patterns (bottom) calculated from the respective single crystal X-ray data of **1**, **1Cs**, **1Rb** and **1NH$_4$**.

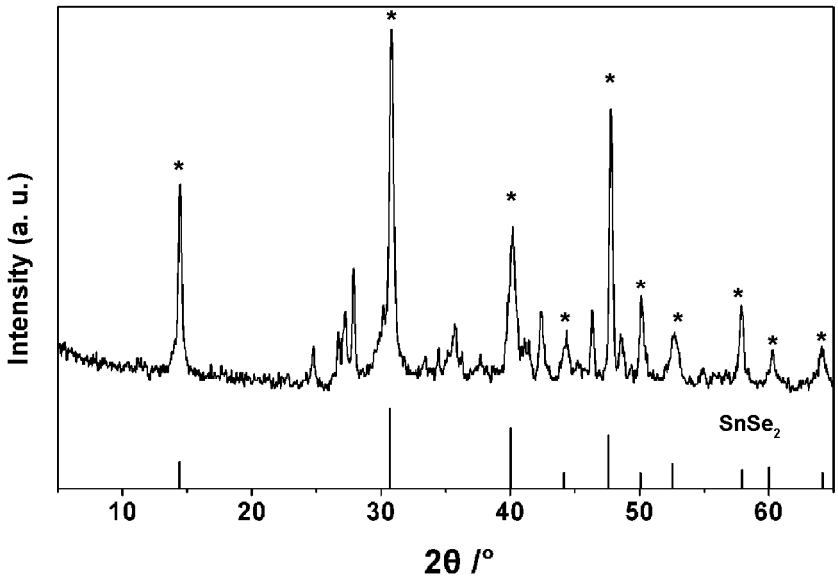

Fig. S9 The PXRD pattern for the post-TGA residue of compound **1** after heated to 320 °C, identified as a mixture of $SnSe_2$ and an indefinite powder.

2c) Optical absorption properties

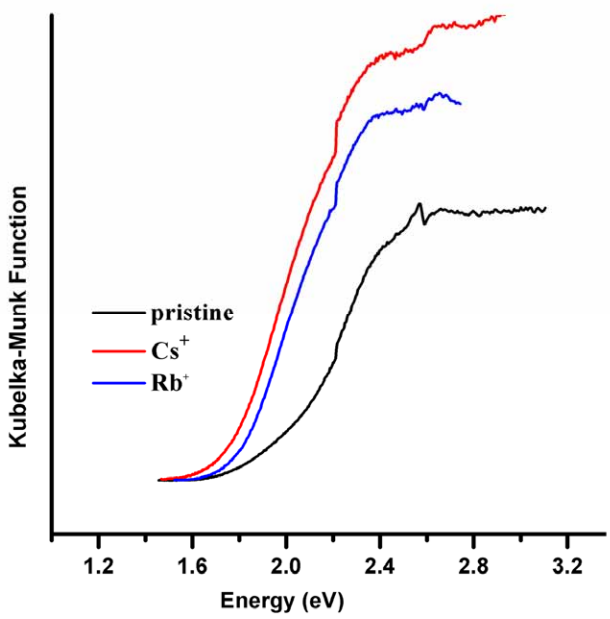

Fig. S10 Optical absorption spectra for the pristine compounds **1**, Cs^+ and Rb^+-exchanged products.

2d) TGA

The ion-exchange properties of **1** were further confirmed by thermogravimetric analyses (Fig. S11, and Tables S5). The thermal stabilities of **1** and ion-exchanged products were investigated on crystalline samples in a N_2 atmosphere from ~20 to 320℃. The TGA curve of **1** showed an obvious weight loss of 11.8% from 200-270℃, which could be attributed to the loss of dimethylammonium ions and the H_2Se molecule (calcd. 12.2%). The post-TGA residue of **1** was identified as a mixture of $SnSe_2$ and an indefinite powder by powder X-ray diffraction (Fig. S9). The TGA curves of the Cs^+- and Rb^+-exchanged products displayed respective weight losses of solvents/water, unexchanged dimethylammonium ions and H_2Se molecules, while the weight losses of NH_4^+-exchanged products included lattice water, NH_4^+, unexchanged diemethylammonium ions, and H_2Se, respectively. All the observed weight losses of ion-exchanged products are close to the theoretical values. These results further support the ion-exchange properties of **1**.

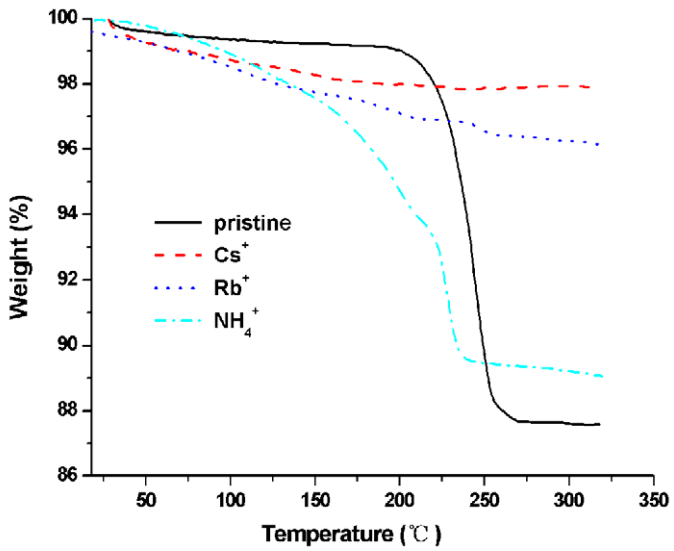

Fig. S11 TGA curves of the products before and after the ion-exchange experiments.

Table S5. Detailed reports on the TGA results of the Cs^+-, Rb^+- and NH_4^+-exchanged products.

Exchanged cation	**Estimated formula**	**Experimental** weight loss at ~20-320°C	**Calculated** weight loss
Pristine	$[(Me)_2NH_2]_{0.75}[Ag_{1.25}SnSe_3]$	11.8% (0.75 Me_2NH_2+ 0.375 H_2Se)	12.3%
Cs^+	$[Me_2NH_2]_{0.05}Cs_{0.70}[Ag_{1.25}SnSe_3]\cdot 0.25H_2O$	1.4% (water)	0.8%
		0.4% (Me_2NH_2+ H_2Se)	0.4%
Rb^+	$[Me_2NH_2]_{0.10}Rb_{0.65}[Ag_{1.25}SnSe_3]\cdot 0.75H_2O$	1.9 % (0.75 H_2O)	2.4%
		1.3% (0.1 Me_2NH_2 + 0.05 H_2Se)	1.5%
NH_4^+	$[Me_2NH_2]_{0.25}(NH_4)_{0.50}[Ag_{1.25}SnSe_3]\cdot 0.5H_2O$	1.4% (0.5 H_2O)	1.7%
		4.8% (0.5 NH_4 + 0.25 H_2Se)	5.6%
		4.6% (0.25 Me_2NH_2 + 0.125 H_2Se)	4.1%

3. Dehydration and re-hydration process

Single crystal x-ray analyses and elemental analyses indicated that the ion-exchanged products **1Cs**, **1Rb**, and **1NH$_4$** all contain a small amount of lattice water molecules. To investigate if they are thermal stable after dehydration process, the crystalline samples of **1Cs** and **1Rb** were loaded in Al_2O_3 crucibles and were heated in a NETZSCH STA 449F3 unit at a heating rate of 5 °C/min from room temperature (~20 °C) to 170 °C in a N_2 atmosphere, and then were kept in the unit at 170°C for 20 minutes to assure the removal of lattice water molecules. After cooled to room temperature, the powder x-ray diffraction experiments were performed on the residuals, which indicated that both the residuals of **1Cs** and **1Rb** after dehydration are still crystalline and the framework structures remain intact after the lattice water molecules being removed. Then the residuals were re-hydrated by immersed in water for six hours. TGA from room temperature (~20 °C) to 170 °C for the re-hydrated samples clearly suggested that the water molecules completely came back to the lattices of **1Cs** and **1Rb**, indicating the reversibility of the dehydration and re-hydration processes. All the results were depicted in Figs. S12 to S15.

To explore if the **1NH$_4$** compound is stable after removing lattice water molecules and partial NH_4 ions, the crystalline sample of **1NH$_4$** was loaded in Al_2O_3 crucibles and were heated in a NETZSCH STA 449F3 unit at a heating rate of 5 °C/min from room temperature (~20 °C) to 200 °C in a N_2 atmosphere, and then were kept in the unit at 200°C for 20 minutes (Fig. S16). After cooled to room temperature, the powder x-ray diffraction experiment was performed on the residue, which showed extra peaks compared to that of the **1NH$_4$** (Fig. S17). This suggested that **1NH$_4$** is unstable after removal of lattice water molecules and partial NH_4 ions.

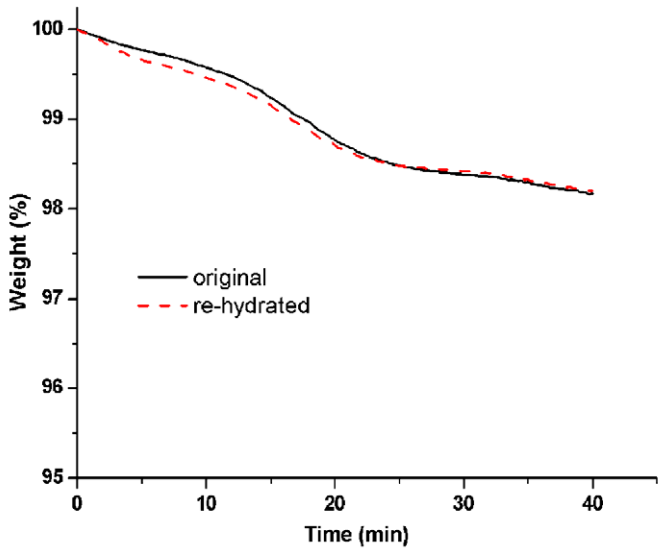

Fig. S12 The TG curves for the dehydration-rehydration processes of **1Cs**. The black curve showed the dehydration process of the original sample **1Cs.** The red curve showed the dehydration process of the rehydrated sample of **1Cs** after immersed in water for six hours.

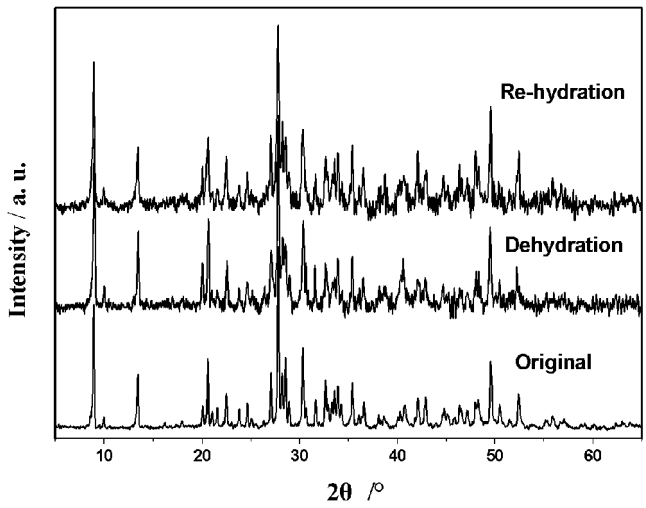

Fig. S13 Comparison of the PXRD patterns of **1Cs** (bottom), dehydrated **1Cs** after heated at 170 °C for approximate 20 mins (middle) and the rehydrated **1Cs** after immersed in water for six hours (top).

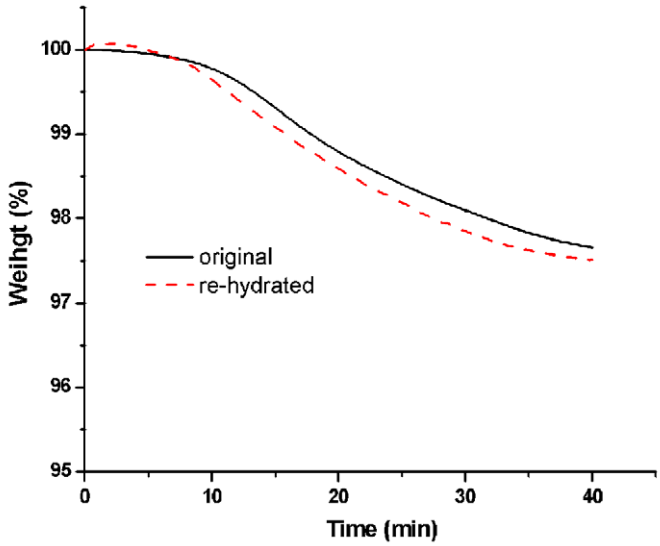

Fig. S14 The TG curves for the dehydration-rehydration processes of **1Rb**. The black curve showed the dehydration process of the original sample **1Rb**. The red curve showed the dehydration process of the rehydrated sample of **1Rb** after immersed in water for six hours.

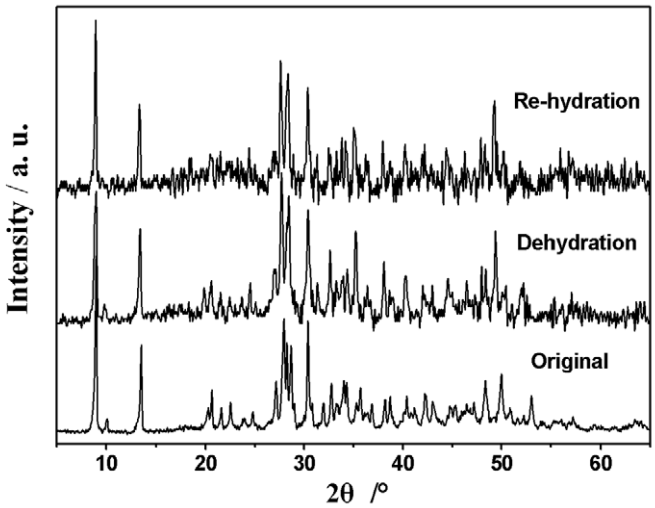

Fig. S15 Comparison of the PXRD patterns of **1Rb** (bottom), dehydrated **1Rb** after heated at 170 °C for approximate 20 mins (middle) and the rehydrated **1Rb** (top) after immersed in water for six hours.

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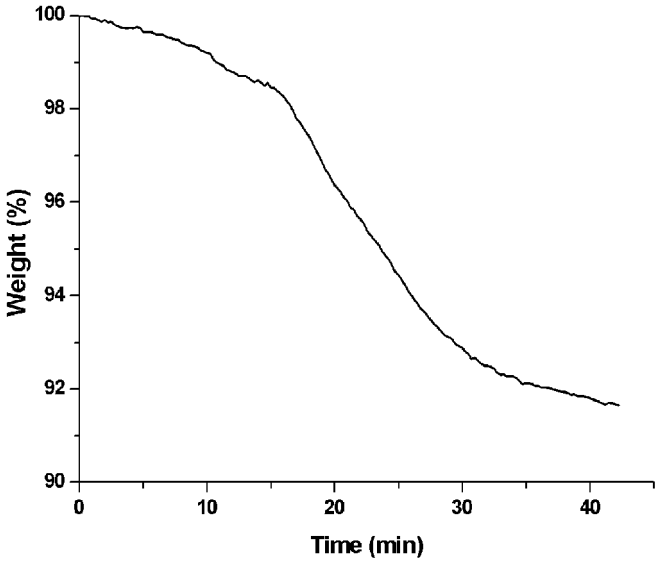

Fig. S16 TG curve showing the removal of H_2O and partial NH_4^+ of **1NH$_4$** by heating at 200 °C for approximate 20 minutes.

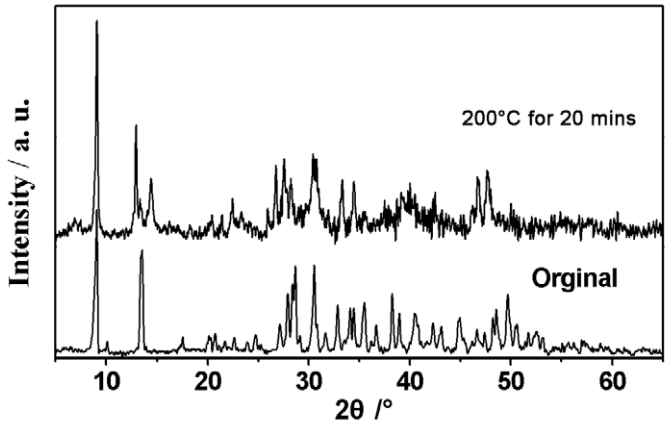

Fig. S17 Comparison of the room temperature PXRD patterns of **1NH$_4$** (bottom) and that of the residue of **1NH$_4$** right after heated at 200 °C for approximate 20 minutes (top).