Electronic Supplementary Information

Helical ammonium halide framework constituting polar conglomerate crystals of 2-ethylanilinium chloride

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Supplementary data for 1

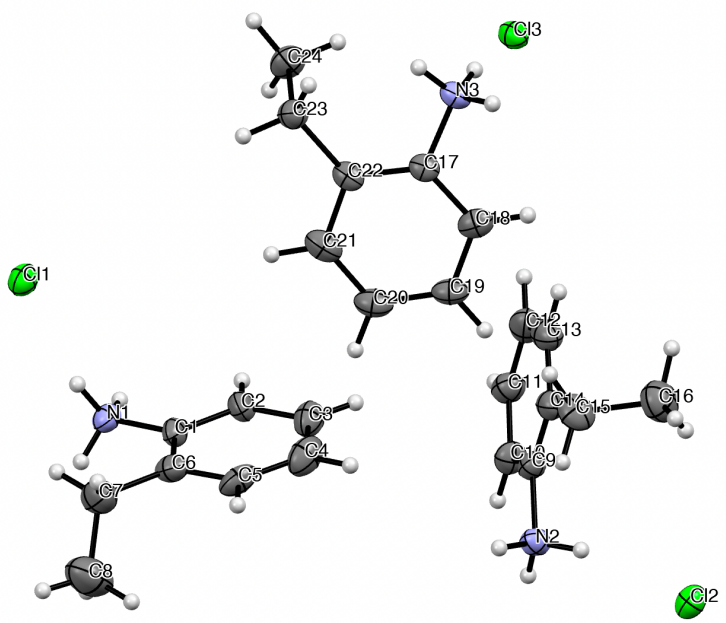

Fig. S1 ORTEP drawing of the asymmetric unit of **1** at the 50% probability level (CCDC deposit number 2386826). Color: C grey, N blue, and Cl green. This figure was produced by the checkCIF report of the International Union of Crystallography.

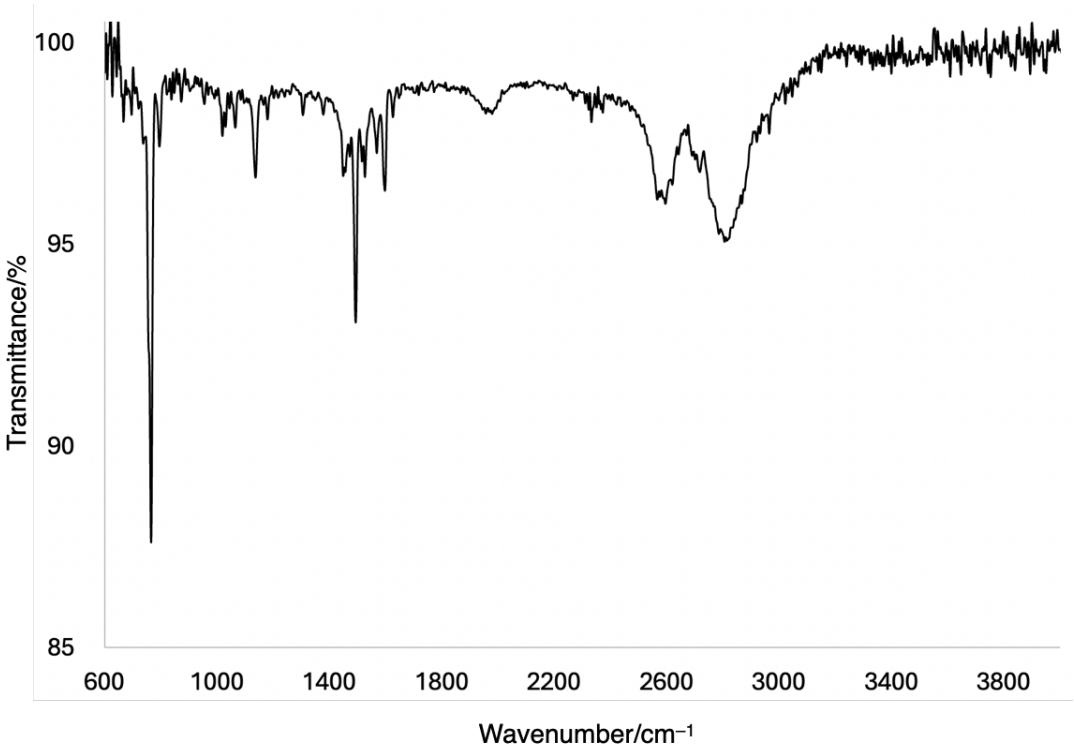

Fig. S2 FTIR spectrum of **1** (ATR, rt).

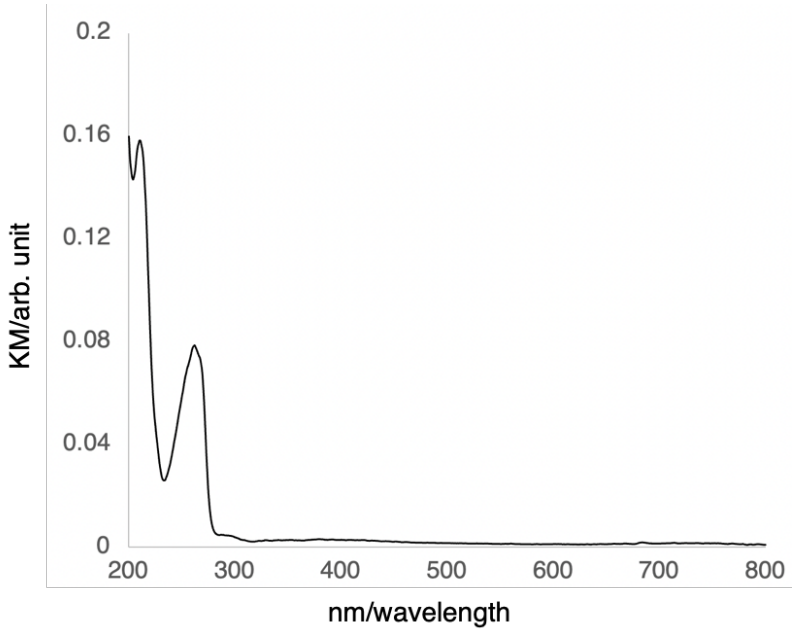

Fig. S3 DRUV spectrum (rt) of **1** diluted with $BaSO_4$ (5 wt%).

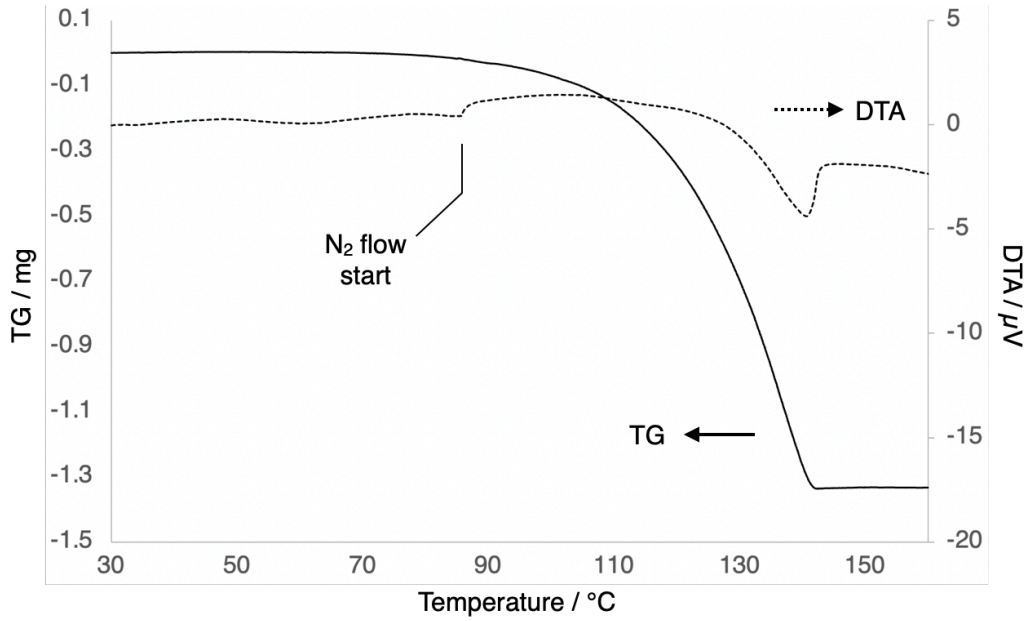

Fig. S4 TG-DTA curves for **1** (heating at 2 °C/min). N_2 flow was started in the middle of the measurement. Solid and dotted lines represent TG and DTA curves, respectively.

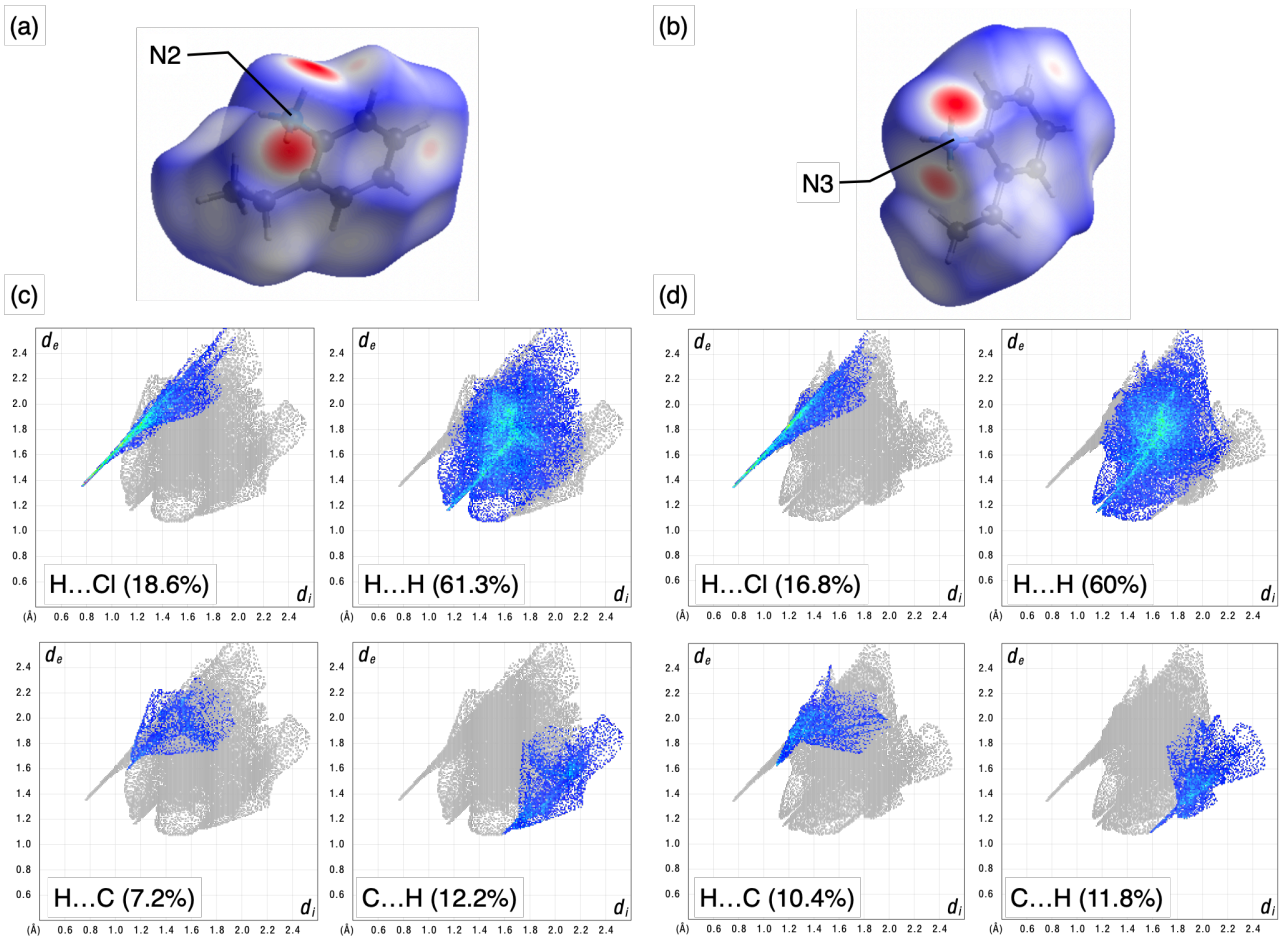

Fig. S5 (a),(b) Hirshfeld surfaces, mapped with d_{norm}, of the 2-ethylanilinium cations with the N2 or N3 atoms, and (c),(d) their 2D fingerprint plots, where the d_i and d_e values are the closest internal and external distances from given points on the Hirshfeld surface.

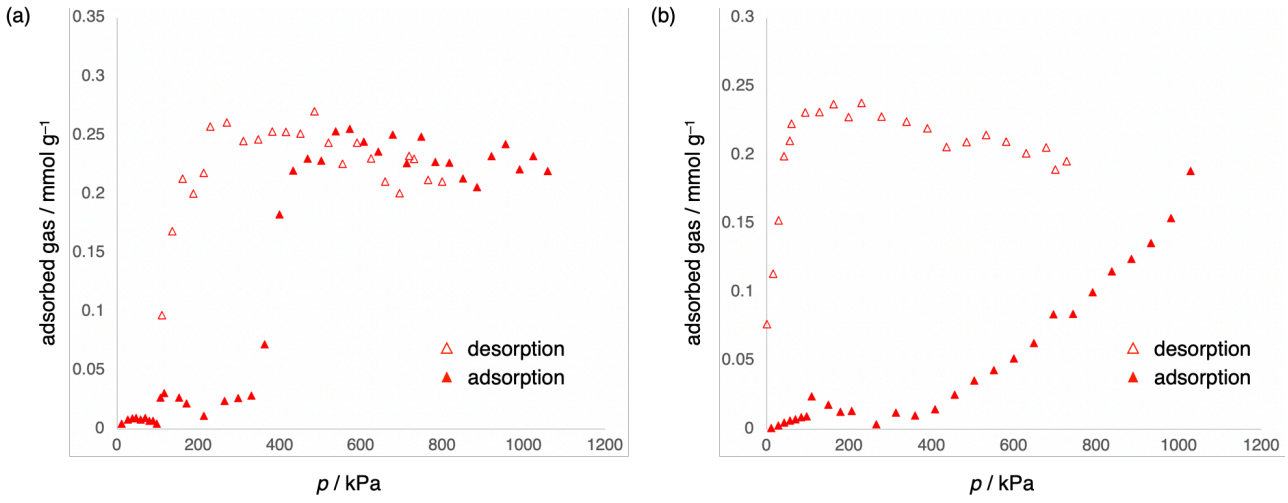

Fig. S6 H_2 adsorption isotherms for crystals of **1** at (a) 77 K and (b) 298 K under high pressure. Full and open symbols represent adsorption and desorption, respectively.

Discussion on hydrogen adsorption

The porosity of **1** was first calculated to be 7.6% by a void analysis on the Mercury program using the contact surface with a probe radius of 0.7 Å (approx. grid spacing = 0.7 Å) (Fig. S7a). The porosity of the continuous pores in the helices was then estimated to be 3.6% by the analysis, in which isolated small cavities were eliminated by placing virtual substituents on the program (Fig. S7b). Considering the porosity (0.036 cm^3/cm^3) and the relative density estimated from the crystal structure (1.186 g/cm^3), the pore volume is calculated to be 0.03 cm^3/g. Given that approximately 0.2 mmol/g of hydrogen is adsorbed to **1** under high pressure, hydrogen adsorption per the unit pore volume is estimated to be 6.7 $mmol/cm^3$ for **1**.

In the case of MOF-5 with a pore volume of 1.27 cm^3/g,[1] MOF-5 crystals adsorb 22 or 0.5 mmol/g of H_2 at 77 K or rt, respectively, at 20 bar.[2] Therefore, hydrogen adsorption per the unit pore volume of MOF-5 is estimated to be 17 or 0.39 $mmol/cm^3$ at 77 K or rt, respectively, under high pressure.

The amounts of hydrogen adsorption per the unit volume for **1** and MOF-5 are roughly comparable to each other as discussed above, supporting that continuous narrow pores in **1** may contribute to hydrogen adsorption. By contrast, hysteresis-like baheviors shown in Fig. S6 are not discussed in this study because the amount of hydrogen adsorbed to **1** was very small.

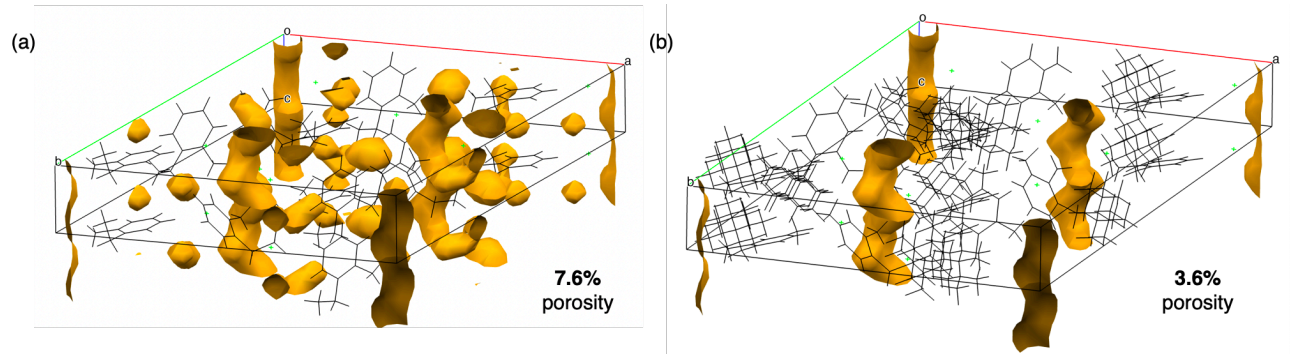

Fig. S7 Voids detected in the crystal structure of (a) **1** and (b) **1** with virtual substituents. Note that a probe radius of 0.7 Å was used for the calculation.

Preparation of 1 using hydrochloric acid

Procedure

Hydrochloric acid (20 wt%, 0.20 mL, 1.1 mmol) was carefully added to 2-ethylaniline (148 mg, 1.2 mmol), and colorless powder immediately precipitated was diluted with diethyl ether (ca. 10–15 mL). After several minutes, the precipitate was collected and washed by filtration, and then dried in vacuo to afford 2-ethylanilinium chloride (**1**) as colorless needles (134 mg, 0.85 mmol, 77%).

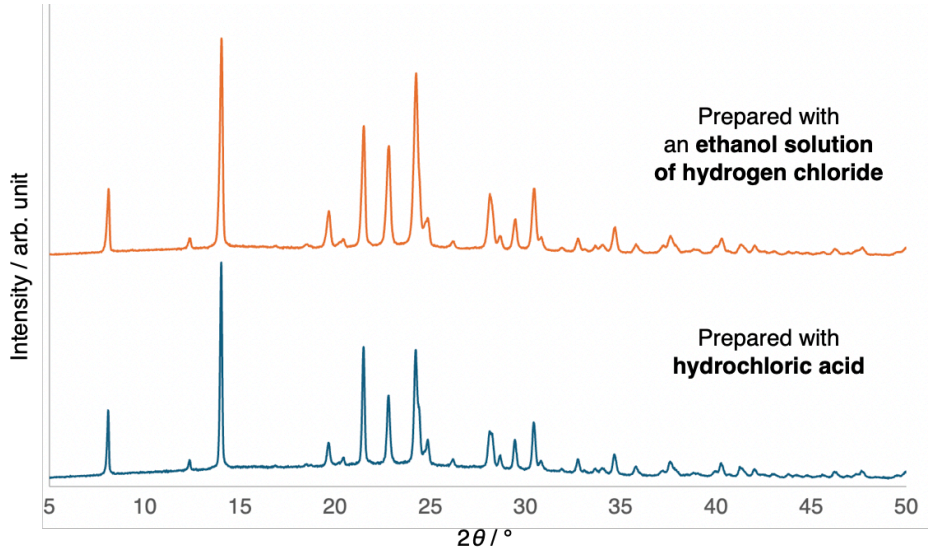

Fig. S8 PXRD patterns (CuKα, rt) of **1** prepared with hydrochloric acid (bottom) and an ethanol solution of hydrogen chloride (top).

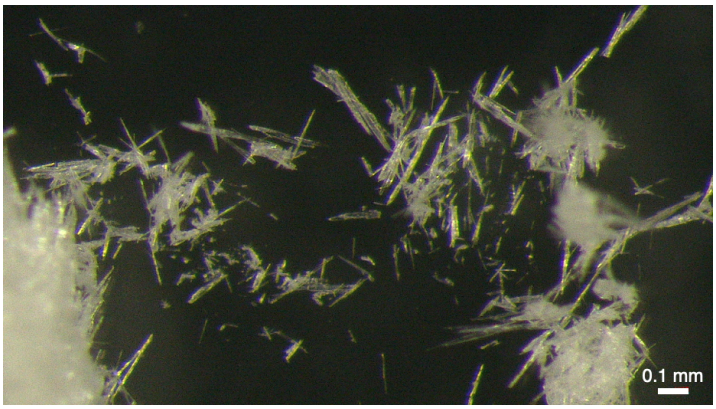

Fig. S9 Photographs of crystals of **1** prepared with hydrochloric acid.

Procedures and experimental data for mixed crystals

Preparation of crystals of anilinium chloride

An ethanol solution of hydrogen chloride (1.0 mol/L, 1.7 mL, 1.7 mmol) was carefully added to aniline (160 mg, 1.7 mmol). To the mixture was added diethyl ether until precipitation occurred (ca. 15–20 mL). After several minutes, the precipitate was collected and washed by filtration, and then dried in vacuo to afford colorless crystals (158 mg).

Preparation of crystals of 2-ethylanilinium and anilinium chloride (1:2.2)

An ethanol solution of hydrogen chloride (1.0 mol/L, 1.0 mL, 1.0 mmol) was carefully added to a mixture of 2-ethylaniline (38 mg, 0.31 mmol) and aniline (55 mg, 0.59 mmol). To the mixture was added diethyl ether until precipitation occurred (ca. 12–15 mL). After several minutes, the precipitate was collected and washed by filtration, and then dried in vacuo to afford colorless crystals (88 mg).

Preparation of crystals of 2-ethylanilinium and anilinium chloride (1:0.97)

An ethanol solution of hydrogen chloride (1.0 mol/L, 1.0 mL, 1.0 mmol) was carefully added to a mixture of 2-ethylaniline (60 mg, 0.50 mmol) and aniline (42 mg, 0.45 mmol). To the mixture was added diethyl ether until precipitation occurred (ca. 12–15 mL). After several minutes, the precipitate was collected and washed by filtration, and then dried in vacuo to afford colorless crystals (100 mg).

Preparation of crystals of 2-ethylanilinium and anilinium chloride (1:0.37)

An ethanol solution of hydrogen chloride (1.0 mol/L, 1.0 mL, 1.0 mmol) was carefully added to a mixture of 2-ethylaniline (78 mg, 0.64 mmol) and aniline (24 mg, 0.26 mmol). To the mixture was added diethyl ether until precipitation occurred (ca. 12–15 mL). After several minutes, the precipitate was collected and washed by filtration, and then dried in vacuo to afford colorless crystals (99 mg).

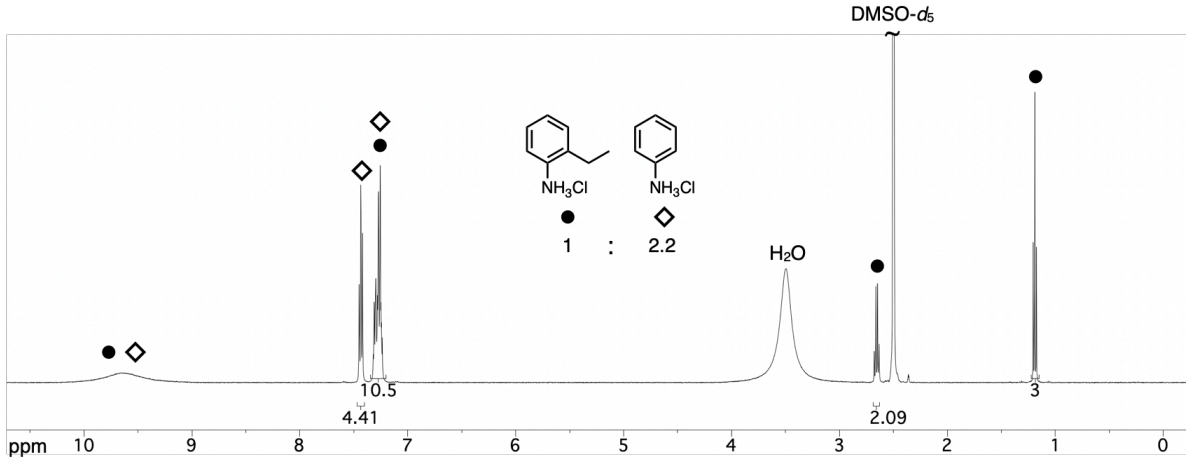

Fig. S10 ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 300 K) of a digested solution of crystals (2-ethylanilinium: anilinium = 1:2.2).

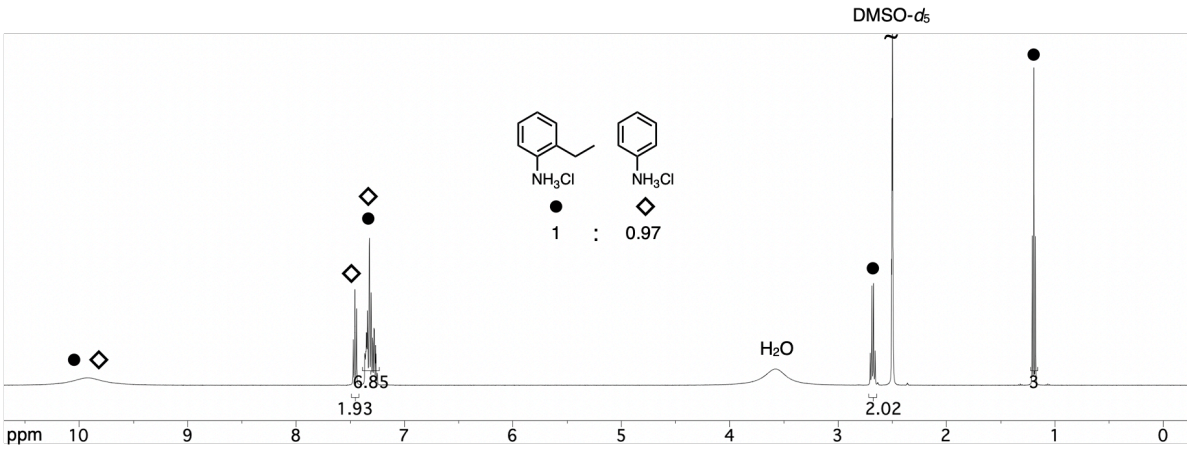

Fig. S11 ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 300 K) of a digested solution of crystals (2-ethylanilinium: anilinium = 1:0.97).

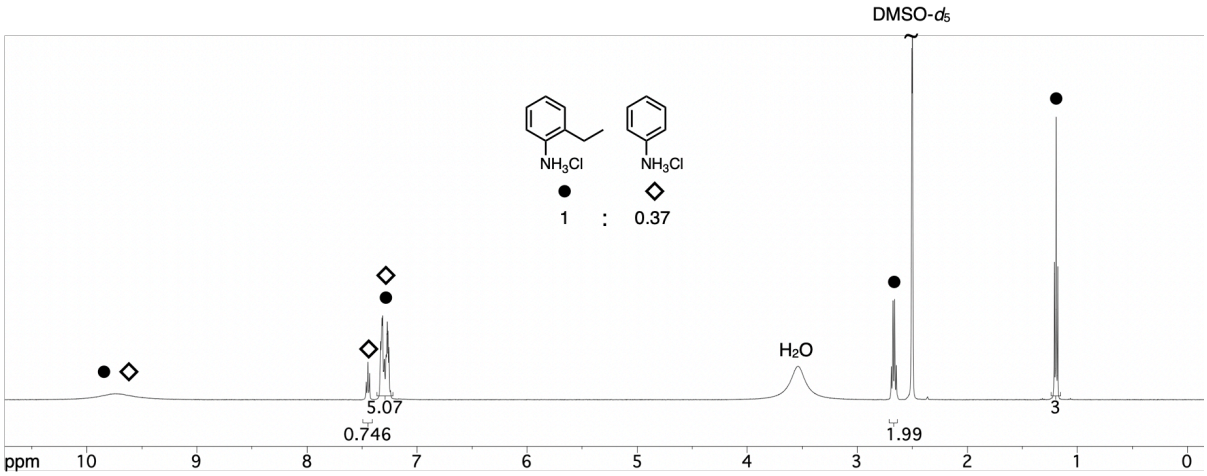

Fig. S12 ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 300 K) of a digested solution of crystals (2-ethylanilinium: anilinium = 1:0.37).

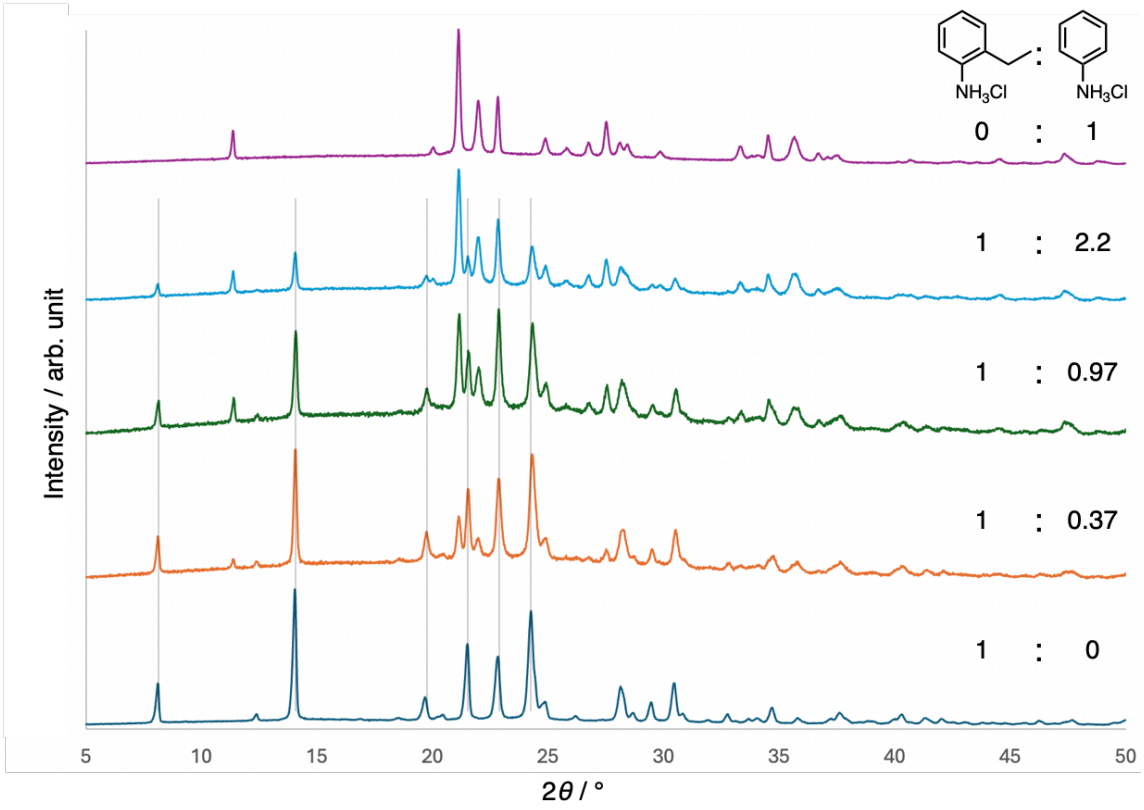

Fig. S13 PXRD patterns (CuKα, rt) of 2-ethylanilinium chloride (bottom), anilinium chloride (top) and crystals containing them with the molar ratio shown in the figure, which were estimated by ^{1}H NMR analysis of the crystals dissolved in DMSO-d_6.

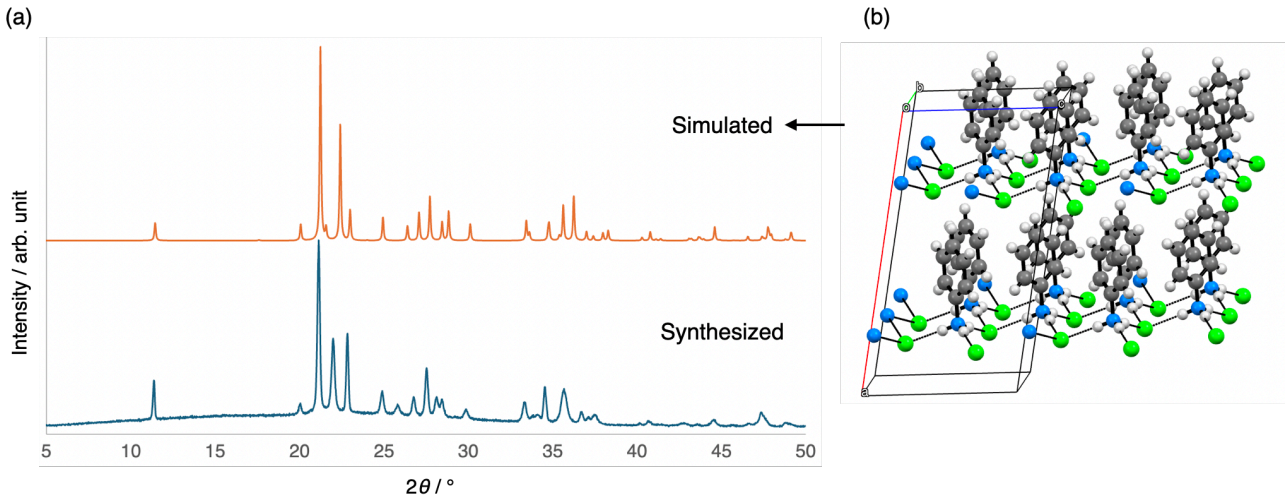

Fig. S14 (a) PXRD pattern (CuKα, rt) of anilinium chloride synthesized in this study (bottom) and the simulated pattern of a reported crystal structure of anilinium chloride (CCDC 299875),[3] whose packing structure is shown in (b).

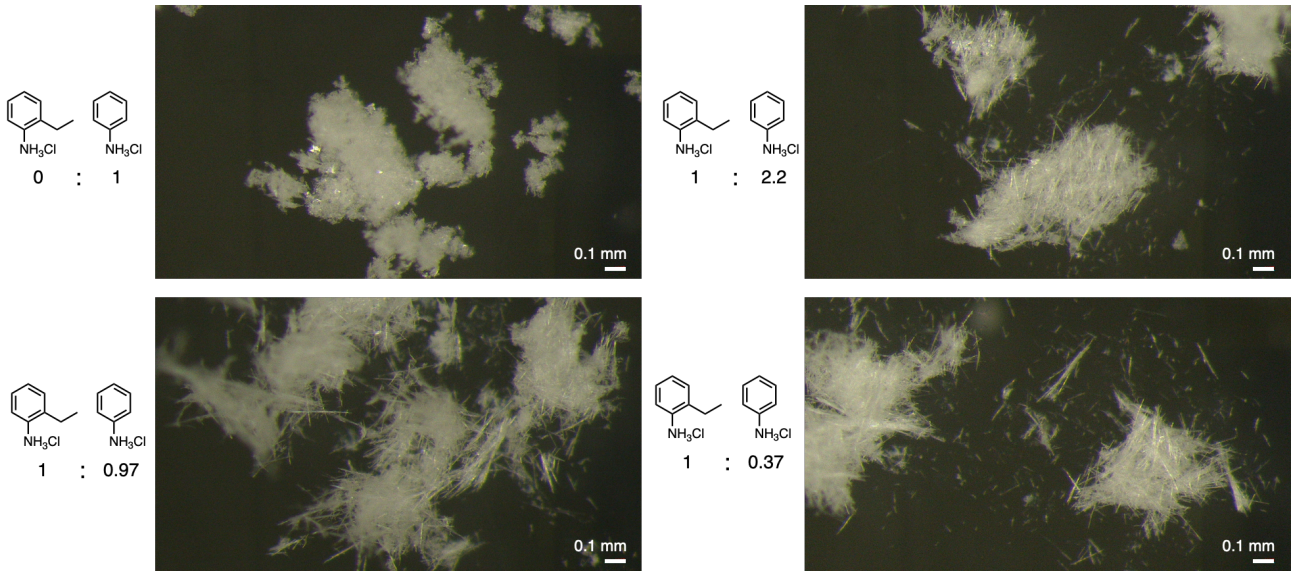

Fig. S15 Photographs of crystals containing 2-ethylanilinium and/or anilinium chloride. The molar ratios shown here were estimated by ^{1}H NMR analysis of the crystals dissolved in DMSO-d_6.

Preparation of crystals of o-toluidinium chloride

An ethanol solution of hydrogen chloride (1.0 mol/L, 1.0 mL, 1.0 mmol) was carefully added to *o*-toluidine (106 mg, 0.99 mmol). To the mixture was added diethyl ether until precipitation occurred (ca. 15–20 mL). After several minutes, the precipitate was collected and washed by filtration, and then dried in vacuo to afford colorless crystals (127 mg).

Preparation of crystals of 2-ethylanilinium and o-toluidinium chloride (1:2.5)

An ethanol solution of hydrogen chloride (1.0 mol/L, 1.0 mL, 1.0 mmol) was carefully added to a mixture of 2-ethylaniline (39 mg, 0.32 mmol) and *o*-toluidine (72 mg, 0.67 mmol). To the mixture was added diethyl ether until precipitation occurred (ca. 15–20 mL). After several minutes, the precipitate was collected and washed by filtration, and then dried in vacuo to afford colorless crystals (97 mg).

Preparation of crystals of 2-ethylanilinium and o-toluidinium chloride (1:0.84)

An ethanol solution of hydrogen chloride (1.0 mol/L, 1.0 mL, 1.0 mmol) was carefully added to a mixture of 2-ethylaniline (58 mg, 0.48 mmol) and *o*-toluidine (51 mg, 0.48 mmol). To the mixture was added diethyl ether until precipitation occurred (ca. 15–20 mL). After several minutes, the precipitate was collected and washed by filtration, and then dried in vacuo to afford colorless crystals (98 mg).

Preparation of crystals of 2-ethylanilinium and o-toluidinium chloride (1:0.55)

An ethanol solution of hydrogen chloride (1.0 mol/L, 1.1 mL, 1.1 mmol) was carefully added to

a mixture of 2-ethylaniline (80 mg, 0.66 mmol) and *o*-toluidine (50 mg, 0.47 mmol). To the mixture was added diethyl ether until precipitation occurred (ca. 15–20 mL). After several minutes, the precipitate was collected and washed by filtration, and then dried in vacuo to afford colorless crystals (109 mg).

Preparation of crystals of 2-ethylanilinium and o-toluidinium chloride (1:0.29)

An ethanol solution of hydrogen chloride (1.0 mol/L, 1.0 mL, 1.0 mmol) was carefully added to a mixture of 2-ethylaniline (91 mg, 0.75 mmol) and *o*-toluidine (29 mg, 0.27 mmol). To the mixture was added diethyl ether until precipitation occurred (ca. 15–20 mL). After several minutes, the precipitate was collected and washed by filtration, and then dried in vacuo to afford colorless crystals (102 mg).

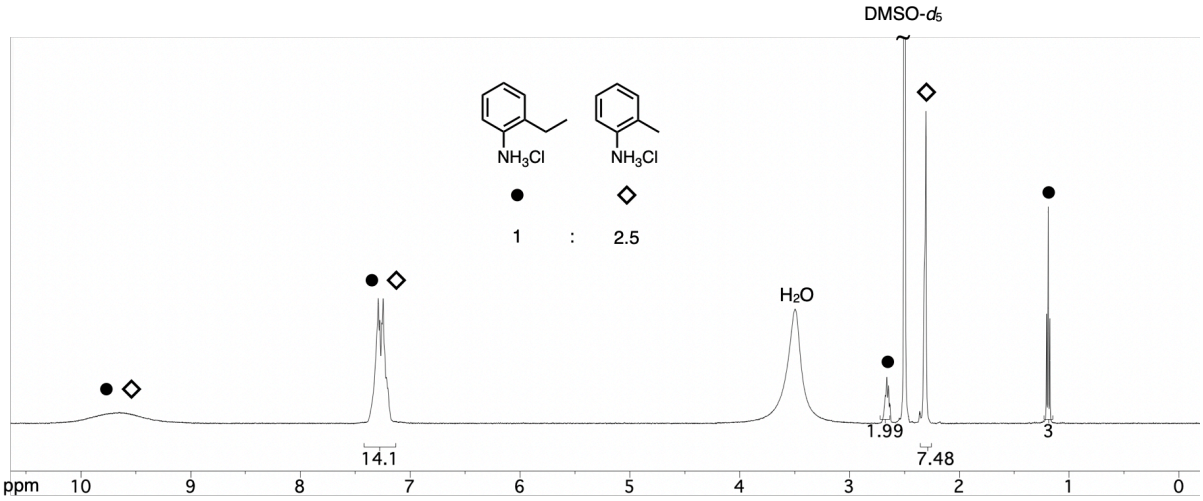

Fig. S16 ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 300 K) of a digested solution of crystals (2-ethylanilinium:*o*-toluidinium = 1:2.5).

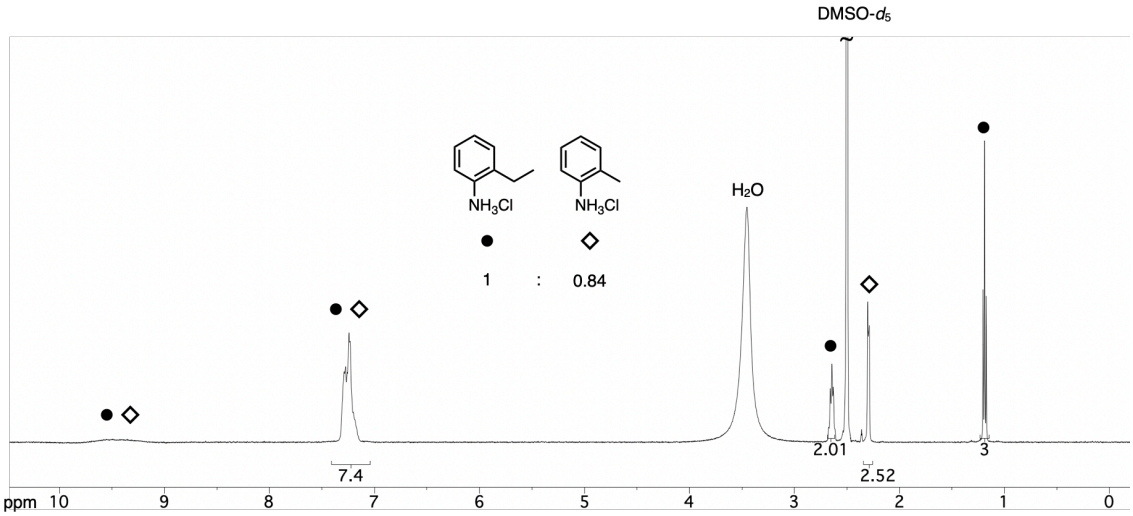

Fig. S17 ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 300 K) of a digested solution of crystals (2-ethylanilinium:*o*-toluidinium = 1:0.84).

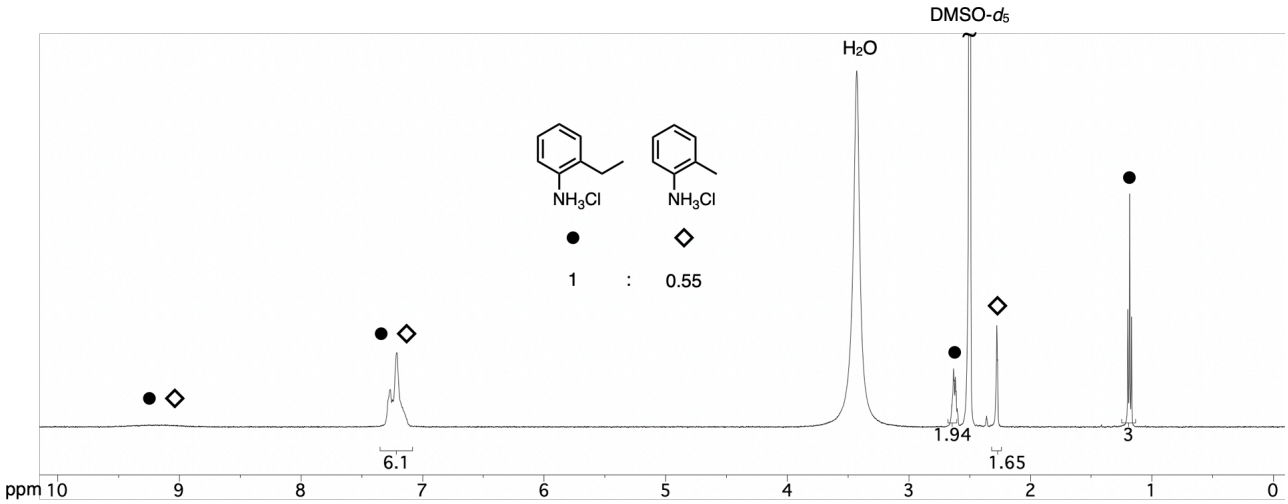

Fig. S18 ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 300 K) of a digested solution of crystals (2-ethylanilinium:*o*-toluidinium = 1:0.55).

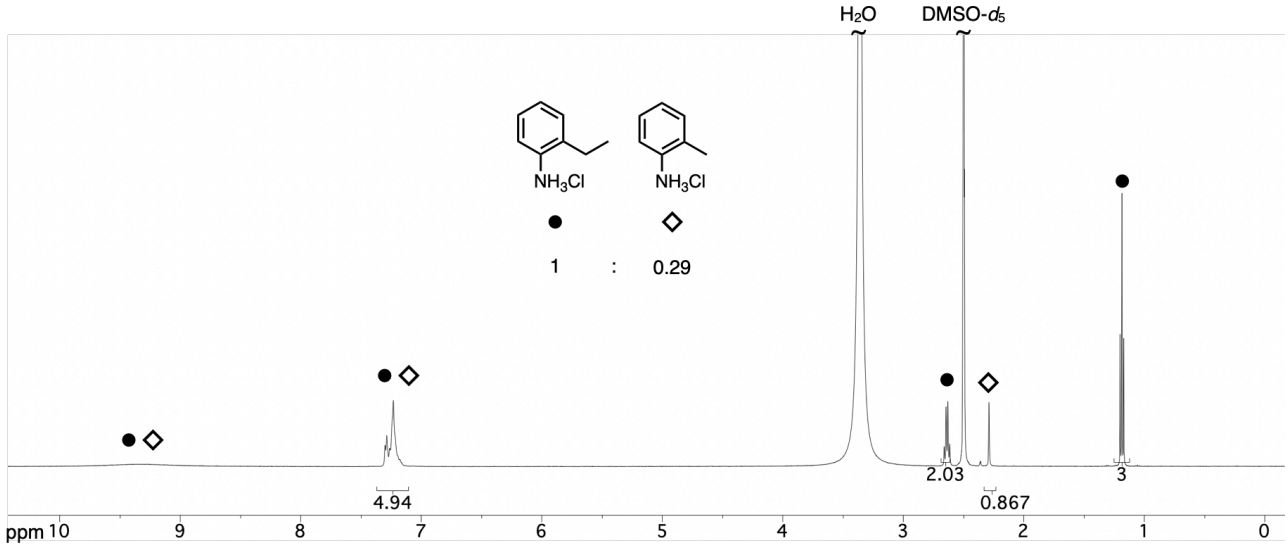

Fig. S19 ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 301 K) of a digested solution of crystals (2-ethylanilinium:*o*-toluidinium = 1:0.29).

Fig. S20 PXRD patterns (CuKα, rt) of 2-ethylanilinium chloride (bottom), o-toluidinium chloride (top) and crystals containing them with the molar ratio shown in the figure, which were estimated by ^{1}H NMR analysis of the crystals dissolved in DMSO-d_6.

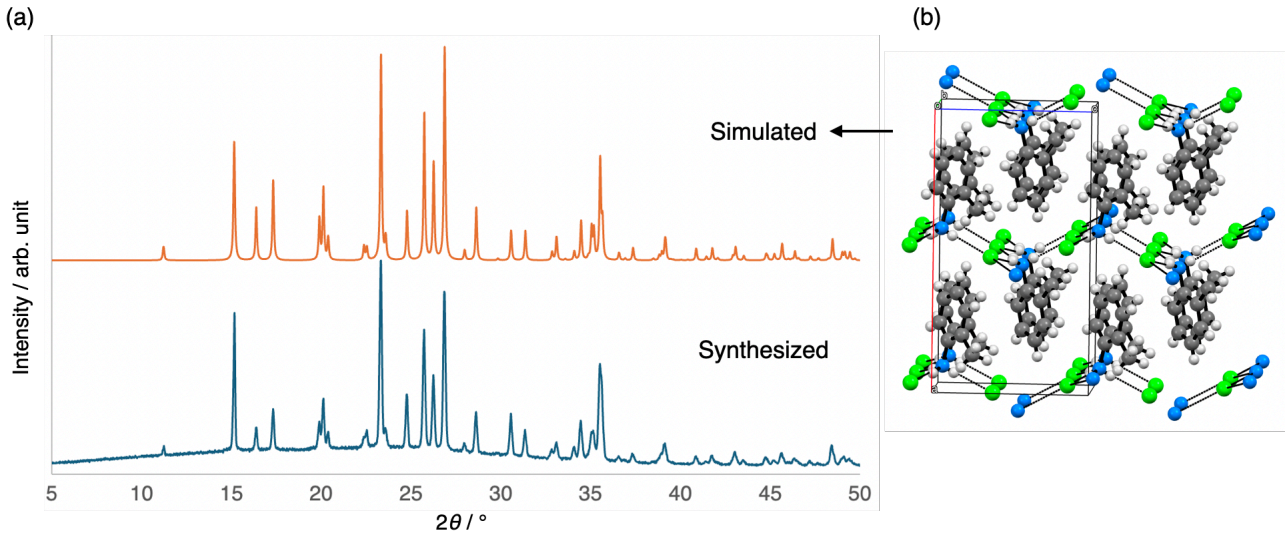

Fig. S21 (a) PXRD pattern (CuKα, rt) of *o*-toluidinium chloride synthesized in this study (bottom) and the simulated pattern of a reported crystal structure of *o*-toluidinium chloride (CCDC 239818),[4] whose packing structure is shown in (b).

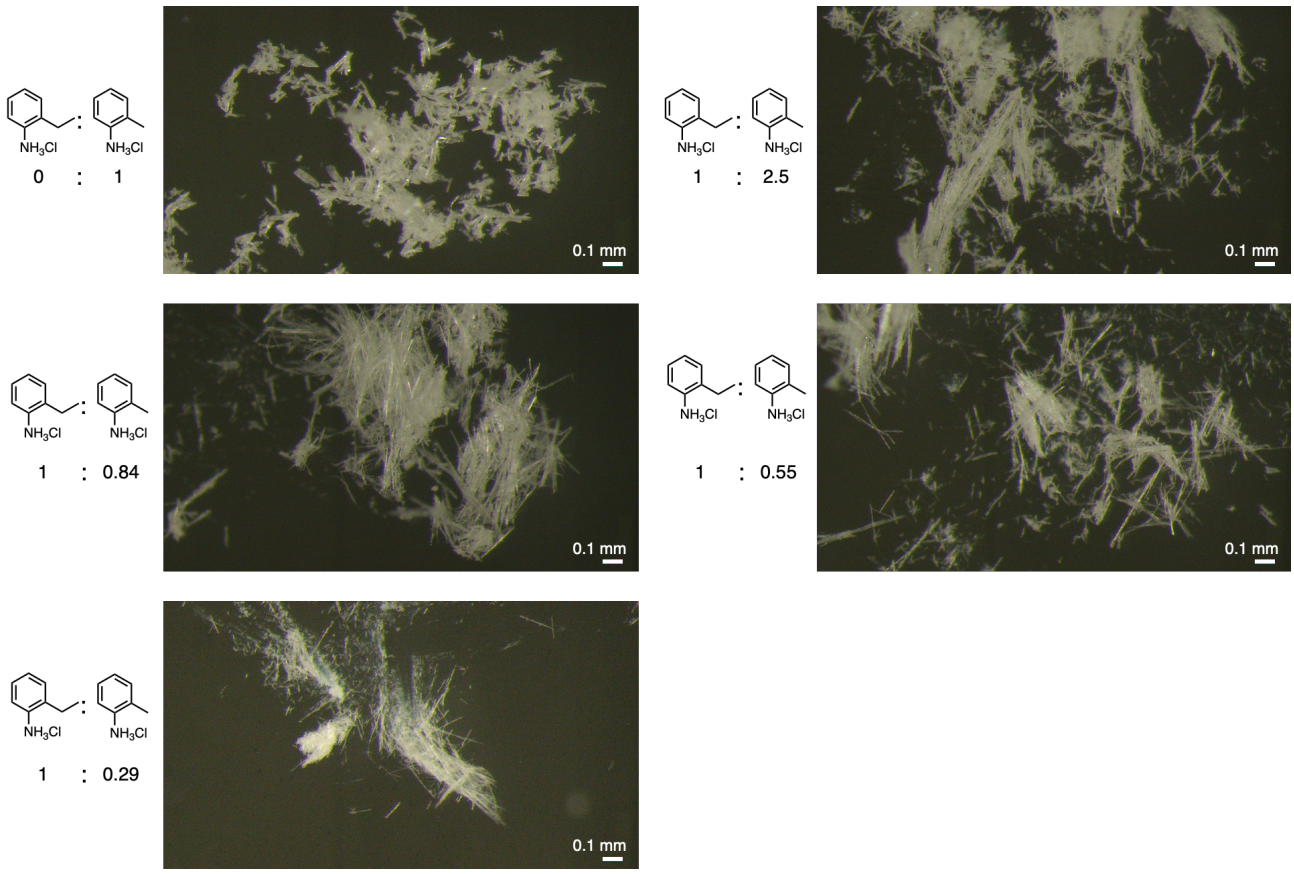

Fig. S22 Photographs of crystals containing 2-ethylanilinium and/or *o*-toluidinium chloride. The molar ratios shown here were estimated by ^{1}H NMR analysis of the crystals dissolved in DMSO-d_6.

Preparation of crystals of 2-isopropylanilinium chloride

An ethanol solution of hydrogen chloride (1.0 mol/L, 1.0 mL, 1.0 mmol) was carefully added to 2-isopropylaniline (136 mg, 1.0 mmol). To the mixture was added diethyl ether (ca. 15–20 mL). However, no precipitation occurred.

Preparation of crystals of 2-ethylanilinium and 2-isopropylanilinium chloride (1:0.17)

An ethanol solution of hydrogen chloride (1.0 mol/L, 1.0 mL, 1.0 mmol) was carefully added to a mixture of 2-ethylaniline (61 mg, 0.50 mmol) and 2-isopropylaniline (66 mg, 0.49 mmol). To the mixture was added diethyl ether until precipitation occurred (ca. 30–40 mL). After several minutes, the precipitate was collected and washed by filtration, and then dried in vacuo to afford colorless crystals (8.9 mg).

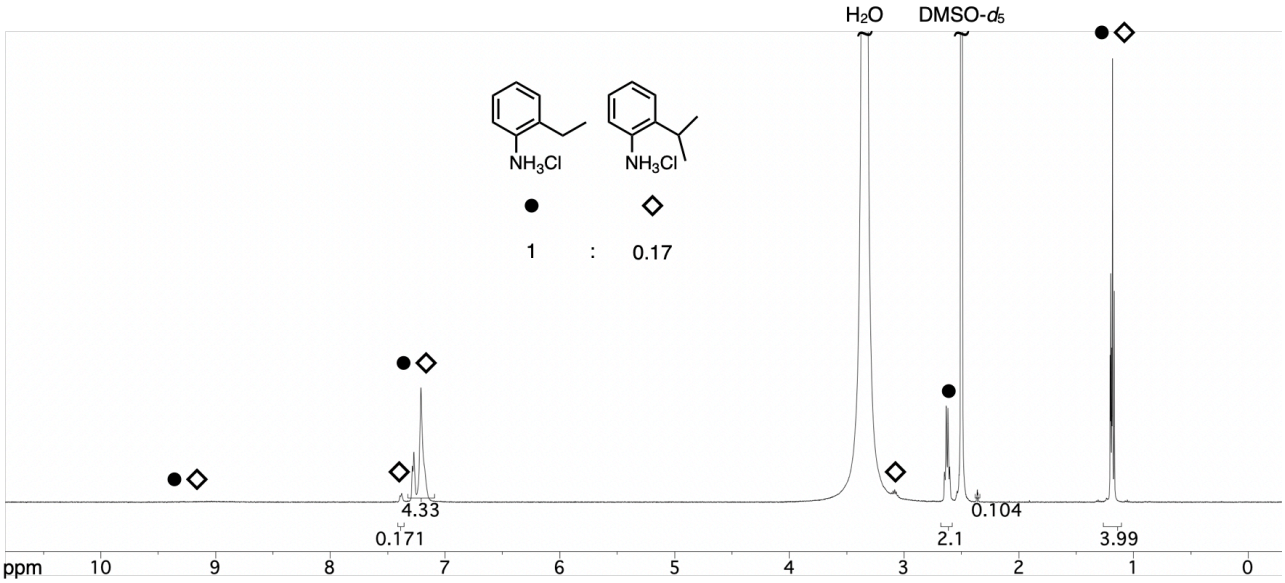

Fig. S23 ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 300 K) of a digested solution of crystals (2-ethylanilinium:2-isopropylanilinium = 1:0.17).

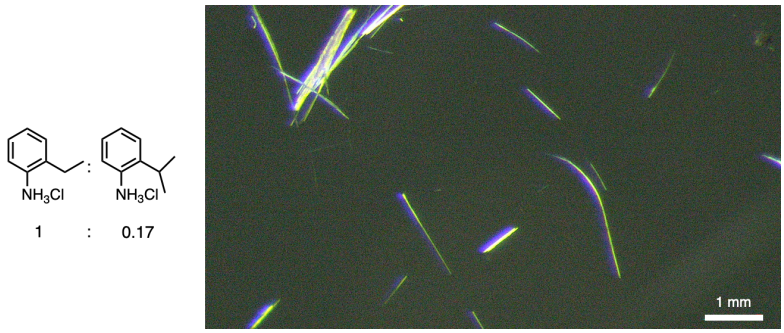

Fig. S24 Photographs of crystals containing 2-ethylanilinium and 2-isopropylanilinium chloride. The molar ratio shown here was estimated by ^{1}H NMR analysis of the crystals dissolved in DMSO-d_6.

References

1. Y. Ming, J. Purewal, D. Liu, A. Sudik, C. Xu, J. Yang, M. Veenstra, K. Rhodes, R. Soltis, J. Warner, M. Gaab, U. Müller and D. J. Siegel, *Microporous Mesoporous Mater.*, 2014, **185**, 235–244.
2. B. Schmitz, U. Müller, N. Trukhan, M. Schubert, G. Férey and M. Hirscher, *ChemPhysChem*, 2008, **9**, 2181–2184.
3. K. M. Anderson, A. E. Goeta, K. S. B. Hancock and J. W. Steed, *Chem. Commun.*, 2006, 2138–2140.
4. P. McArdle, K. Gilligan, D. Cunningham, R. Dark and M. Mahon, *CrystEngComm*, 2004, **6**, 303–309.