Condensed π -Molecular Arrangement for

-C₂H₄SO₃⁻ Armed Naphtalenediimide

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Experimental Section

General. UV-vis-NIR spectra (200-3000 nm) in solution and IR spectra (400-4000 cm⁻¹) on KBr pellets were measured using PerkinElmer Lambda 750 and Thermo Fisher Scientific Nicolet 6700 FT-IR spectrophotometers, respectively. Elemental analyses were measured on Microcoder JM10 (J Science Lab. Co. Ltd). Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) were conducted using a Rigaku Thermo plus TG8120 thermal analysis station and a Mettler DSC1-T unit with an Al₂O₃ reference at a heating and cooling rate of 5 K min⁻¹ under N₂-flow. Temperature-dependent powder X-ray diffraction patterns (PXRD) were obtained using a Rigaku Rint-Ultima diffractometer with Cu K α radiation at λ =1.54185Å within the temperature range of 298-498 K. The temperature-dependent dielectric constants were measured with the two-probe AC impedance method from 100 Hz to 1 MHz using a Hewlett-Packard HP4194A and a cryostat temperature controller. The electrical contacts were prepared using gold paste (Tokuriki 8560) to attach the 25-µm \$\phi\$ gold wires to the 3-mm \$\phi\$ compressed pellet. An atomic force microscope (Hitachi AFM5000) was used to observe the surface morphologies of salts 1-4. Thin films were prepared by drop casting method using aqueous solution onto mica substrate or n-doped silicon substrate (n-Si/SiO₂) with silicon oxide film (200 nm) and drying at 393 K.

Preparations of [(CH₃)₂NH₂⁺]₂(ESNDI^{2–}). One equivalent of naphthalene-1,4,5,8-tetracarboxylic acid dihydrate (210 mg, 784 μ mol) and 1.8 equivalent of taurine (175 mg, 1.40 mmol) was dissolved in DMF (10 mL) and stirred for 39 h at 150 °C.⁷⁰ The reaction mixture was cooled to 25 °C, and the precipitate was collected by filtration and washed three times with DMF and three times with diethyl ether. The precipitate was dried in vacuo to afford 364 mg (631 μ mol, 90% yield) of reddish-brown crystalline powder. ¹H NMR (400 MHz,

DMSO- d_6) δ -8.67 (s, 4H); 8.16 (s, 4H); 4.35-4.31 (m, 4H); 2.80-2.76 (m, 4H); 2.55 (s, 12H); IR (KBr, cm⁻): 3440 (br), 3083 (w), 3023 (m), 2978 (m), 2780 (m), 1704 (m), 1662 (s), 1585 (w), 1459 (m), 1384 (m), 1345 (m), 1269 (m), 1238 (m), 1218 (m), 1193 (s), 1054 (m), 1040 (m), 1011 (w), 767 (m), 539 (m). Elemental analysis. Calcd. for C₁₈H₁₂N₂O₁₀S₂•2(C₆H₁₆N₂): C, 46.15; H, 4.93; N, 9.78. Found: C, 45.88; H, 4.80; N, 9.81.

Preparations of (Na⁺)₂(EPNDI^{2–})•4.0(H₂O) (1). One equivalent of $[(CH_3)_2NH_2^+]_2(ESNDI^{2–})$ (502 mg, 876 µmol)) and two equivalents of sodium acetate (143 mg, 1.75 mmol.) were dissolved in distilled water (60 mL) and stirred at 25°C for 2 hours. 250 mL of ethanol was added to the solution, and the resultant precipitates were collected by filtration and vacuum dried. The crude product was suspended in 15 mL of distilled water and stirred at 100 °C. The solution was allowed to stand overnight at 25°C, the precipitates were collected by filtration and the resulting solid was dried in vacuo to give 356 mg (594 µmol, 68% yield) of yellow-green crystalline powder. ¹H NMR (400 MHz, D₂O) δ -8.65 (s, 4H); 4.55 (t, *J* = 7.1 Hz, 4H); 3.32 (t, *J* = 7.4 Hz, 4H); IR (KBr, cm⁻¹): 3482 (br), 1711 (s), 1669 (m), 1584 (w), 1462 (w), 1383 (w), 1375 (m), 1353 (w), 1338 (w), 1300 (w), 1252 (m), 1218 (s), 1188 (m), 1156 (m), 1049 (m), 770 (w), 751(w), 578 (w), 511 (w); Elemental analysis. Calcd. for C₁₈H₁₂N₂O₁₀S₂Na₂•4(H₂O): C, 36.13; H, 3.37; N, 4.68. Found: C, 35.83; H, 3.32; N, 4.68.

Preparations of (K⁺)₂(**EPNDI**^{2–})•1.0(H₂**O**) (2). One equivalent of $[(CH_3)_2NH_2^+]_2(ESNDI^{2-})$ (502 mg, 877 µmol)) and two equivalents of potassium acetate (174 mg, 1.77 mmol.) were dissolved in distilled water (60 mL) and stirred at 25°C for 2 hours. 150 mL of ethanol was added to the solution, and the resultant precipitates were collected by filtration and vacuum dried. The crude product was suspended in 25 mL of distilled water and stirred at 100 °C. The solution was allowed to stand overnight at 25°C, the precipitates were collected by filtration and the resulting

solid was dried in vacuo to give 273 mg (489 µmol, 56% yield) of yellow-green crystalline powder. ¹H NMR (400 MHz, D₂O) δ -8.70 (s, 4H); 4.56 (t, *J* = 7.4 Hz, 4H); 3.32 (t, *J* = 7.4 Hz, 4H); IR (KBr, cm⁻¹): 3464 (br), 3084 (w), 1704 (m), 1667 (s), 1584 (w), 1457 (w), 1379 (w), 1344 (s), 1259 (w), 1246 (m), 1215 (s), 1189 (s), 1099 (w), 1053 (m), 1039 (s), 1011 (w), 819 (w), 800 (w), 767 (w), 634 (w), 535 (m), 521 (w), 445 (w), 411 (w). Elemental analysis. Calcd. for C₁₈H₁₂N₂O₁₀S₂K₂: C, 38.70; H, 2.17; N, 5.01. Found: C, 38.48; H, 2.30; N, 5.01.

Preparations of (Rb⁺)₂(**EPNDI**^{2–}) (**3**). One equivalent of $[(CH_3)_2NH_2^+]_2(ESNDI^{2-})$ (503 mg, 877 µmol) and two equivalent of rubidium acetate (258 mg, 1.79 mmol.) was dissolved in distilled water (60 mL) and stirred at 25°C for 2 hours. 50 mL of ethanol and 50 mL of propanol were added to the solution, and the resultant precipitates were collected by filtration and vacuum dried. The crude product was suspended in 37 mL of distilled water and stirred at 100 °C. The solution was allowed to stand overnight at 25°C, the precipitates were collected by filtration and the resulting solid was dried in vacuo to give 273 mg (388 µmol, 44% yield) of yellow-green crystalline powder. ¹H NMR (400 MHz, D₂O) δ -8.70 (s, 4H); 4.53 (t, *J* = 7.4 Hz, 4H); 3.28 (t, *J* = 7.4 Hz, 4H); IR (KBr, cm⁻¹): 3352 (w), 1703 (m), 1662 (s), 1585 (m), 1459 (m), 1444 (w), 1383 (m), 1343 (m), 1268 (m), 1255 (m), 1237 (m), 1196 (s), 1097 (w), 1053 (m), 1038 (m), 1009 (m), 879 (w), 816 (w), 799 (m), 767 (m), 641 (w), 540 (m), 525 (w), 414 (w). Elemental analysis. Calced. for C₁₈H₁₂N₂O₁₀S₂Rb₂: C, 33.19; H, 1.86; N, 4.30; Found: C, 33.08; H, 1.92; N, 4.30.

Preparations of $(Cs^+)_2(EPNDI^{2-})$ (4). One equivalent of $[(CH_3)_2NH_2^+]_2(ESNDI^{2-})$ (503 mg, 877 µmol) and two equivalent of cesium acetate (340 mg, 1.77 mmol.) was dissolved in distilled water (120 mL) and stirred at 25°C for 2 hours. 100 mL of ethanol was added to the solution, and the resultant precipitates were collected by filtration and vacuum dried. The crude product was suspended in 40 mL of distilled water and stirred at 100 °C. The solution was allowed to stand

overnight at 25°C, the precipitates were collected by filtration and the resulting solid was dried in vacuo to give 312 mg (420 μ mol, 48% yield) of yellow-green crystalline powder. ¹H NMR (400 MHz, D₂O) δ -8.70 (s, 4H); 4.53 (t, *J* = 7.4 Hz, 4H); 3.28 (t, *J* = 7.4 Hz, 4H); IR (KBr, cm⁻¹): 3354 (w), 1703 (m), 1662 (s), 1583 (m), 1458 (m), 1442 (w), 1382 (m), 1347 (m), 1265 (m), 1252 (m), 1236 (m), 1196 (s), 1097 (w), 1052 (m), 1036 (m), 1008 (m), 877 (w), 815 (w), 797 (m), 766 (m), 640 (w), 539 (m), 526 (w), 414 (w). Elemental analysis. Calced. for C₁₈H₁₂N₂O₁₀S₂Cs₂: C, 28.97; H, 1.62; N, 3,75. Found: C, 28.84; H, 1.68; N, 3.75.

Preparations of single crystals. Single crystals **2** were grown by mixing an aqueous solution of $[(CH_3)_2NH_2^+]_2(ESNDI^{2^-})$ (23 mM, 200 µL) with potassium chloride solution (94 mM, 100 µL), where ethanol vapor was diffused at 25°C. Anhydrous single crystal $(K^+)_2(ESNDI^{2^-})$ (2') was prepared by dehydration of single crystal **2**, prepared by the method described above. Single crystal **2** was fixed at the end of a glass capillary with epoxy resin and leaving it at 57 °C for 110 min and 97 °C for 10 min under nitrogen flow to produce dehydrated single crystals **2**'. Single crystals **3** were grown by vapor diffusion of ethanol in an aqueous solution of **3** (2.2 mM, 300 µL) at 25 °C. Single crystals **4** were grown by mixing an aqueous solution of $(CH_3)_2NH_2^+]_2(ESNDI^{2^-})$ (23 mM, 200 µL) with a cesium acetate solution (94 mM 100 µL) and allowed to stand at 25°C.

Crystal structure determination. The crystallographic data were collected using a Rigaku RAPID-II diffractometer equipped with a rotating anode, fitted with a multilayer confocal optic, using Cu K α ($\lambda = 1.54187$ Å) radiation from a graphite monochromator. Structural refinements were performed using the full-matrix least-squares method on F^2 . Calculations were performed using the Crystal Structure software packages. All parameters were refined using anisotropic temperature factors, except for those of the hydrogen atoms. Temperature-dependent powder

X-ray diffraction (PXRD) patterns were collected using a Rigaku Rint-Ultima III diffractometer with Cu K α radiation at $\lambda = 1.54187$ Å.

Crystal	2 •1.0(H ₂ O)	2'	3	4
Chemical formula	$C_{18}H_{14}K_2O_{11}S_2$	$C_{18}H_{12}K_2O_{10}S_2$	$C_{18}H_{12}Rb_2O_{10}S_2$	$C_{18}H_{12}Cs_2O_{10}S_2$
Formula weight	576.63	558.62	651.36	746.23
<i>T</i> , K	100	300	100	100
Space group	<i>P</i> -1 (#2)	<i>P</i> 2 ₁ / <i>c</i> (#14)	<i>P</i> 2 ₁ / <i>c</i> (#14)	<i>P</i> 2 ₁ / <i>c</i> (#14)
<i>a</i> , Å	5.58699(10)	17.381(15)	17.6025(4)	17.9643(4)
b, Å	6.06438(11)	7.430(6)	7.56017(17)	7.74901(19)
<i>c</i> , Å	15.7629(3)	7.862(7)	7.8108(2)	7.9121(2)
α , deg	89.525(6)	_	_	_
β , deg	81.652(7)	93.796(11)	96.151(7)	97.552(7)
γ, deg	76.562(5)	_	_	_
V, Å ³	513.77(2)	1013.2(15)	1033.46(5)	1091.86(5)
Ζ	1	2	2	2
$D_{\text{calc}}, \text{g} \cdot \text{cm}^{-3}$	1.857	1.831	2.093	2.270
μ , cm ⁻¹	0.6636	0.6670	0.8608	2.8368
Reflections measured	6036	10017	11264	12094
Independent reflections	1840	1828	1854	1981
Reflections used	1840	1828	1854	1981
R _{int}	0.0871	0.3268	0.0652	0.0871
$R_1^{\ a}$	0.0409	0.1939	0.0339	0.0309
R _{all}	0.0427	0.2889	0.0376	0.0324

Table S1. Crystal data, data collection, and reduction parameters for salts 2–4.

$R_{\rm w}({\rm F_2})^{a}$	0.1027	0.5029	0.0947	0.0751
GOF	1.132	1.112	1.197	1.050
CCDC	2308338	2308337	2308340	2308339

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}| \text{ and } R_{w} = (\Sigma \omega (|F_{o}| - |F_{c}|)^{2} / \Sigma \omega F_{o}^{2})^{1/2}.$

Theoretical calculation. The transfer integrals (*t*) between the LUMOs of **ESNDI**^{2–} in all crystals were calculated within the tight-binding approximation using the extended Hückel molecular orbital method, where the LUMOs of protonated **H2ESNDI** were used as the basis functions.⁷⁸ Semiempirical parameters for Slater-type atomic orbitals were obtained from the literature. The *t* values between each pair of molecules were assumed to be proportional to the overlap integral (*S*) via the equation t = -10S eV.

H₂O sorption behavior of salts 1 and 2. H₂O adsorption-desorption isotherms at 273 and 298 K for powder 1' and 2' were measured using a MicrotracBEL BELSORP-max II. H₂O used for the sorption measurements was degassed by freezing to remove dissolved gases before measurement. Samples 1 and 2 were vacuum heated at 200 °C for 12 h at a pressure of 1.42×10^{-5} Pa to completely remove H₂O molecules.

Flash-photolysis time-resolved microwave conductivity measurements. The thin films of salts 1–4 were fabricated by drop-cast method onto quartz substrates (9 × 40 mm², 1 mm thick) and dried under ambient condition, whereas dehydrated thin film of 2' were obtained by thermal annealing at 400 K. Charge carrier mobility was evaluated by flash-photolysis time-resolved microwave conductivity (FP-TRMC) under Ar-saturated conditions at 290 K. Charge carriers were injected into the materials via photo-ionization with a third harmonic generation ($\lambda = 355$ nm) of a Spectra Physics model INDI-HG Nd:YAG laser pulses at 10 Hz with a pulse duration of ca. 5 ns. The photon density of a 355 nm pulse was modulated from $4.8 \times 10^{15} \sim 6.1 \times 10^{15}$

photons cm⁻² pulse⁻¹. The microwave frequency and power were set at ~9.1 GHz and 3 mW, respectively, and guided into a microwave cavity. The *Q*-factor of the microwave cavity loaded with the sample was ~2200 at 290 K depending on the temperature, and the substrate with the compound films was set at the point of electric field maximum. The reflected power of the probing microwave, picked up by a GaAs crystal–diode with Schottky–barriers (rise time < 1 ns), was monitored by a Tektronics model TDS3054 digital oscilloscope. The observed change in the reflected microwave power (ΔP_r) was normalized with the steady reflection of the microwave from the cavity (P_r), and converted directly into the product of a photo carrier generation yield (ϕ) and the sum of photo-generated electron/hole mobilities ($\Sigma \mu$),

$$\phi \sum \mu = \frac{1}{e \cdot I_0 \cdot F_{\text{Light}}} \cdot \frac{1}{A} \cdot \frac{\Delta P_{\text{r}}}{P_{\text{r}}}$$
(S1)

where ε , *A*, *I*₀, and *F*_{light} are elementary charge, sensitivity factor (S⁻¹ cm), incident photon density of the excitation laser (photon cm⁻²), and filling factor (cm⁻¹), respectively. The value of *F*_{light} was calculated based on the overlap of the area of photo-carrier injection (presumed to be proportional to the absorbance of excitation light by the sample film) with electric field strength distribution in the cavity derived from a calculation code of CST Microwave Studio from AET Inc.



Figure S1. TG charts of salts 1, 2', 3, and 4.



Figure S2. DSC charts of salt 1 (Na⁺), 2 (K⁺), 3 (Rb⁺), and 4 (Cs⁺).



Figure S3. Transfer integrals of 2D layer of NDIs in salts 1 (Na⁺), 2 (K⁺), 3 (Rb⁺), and 4 (Cs⁺).



Figure S4. Calculation of the LUMO band of salt 4 using the tight-binding approximation assuming a partially occupied state of Fermi energy $E_F = 0.15$.



Figure S5. Calculation of the LUMO band of salt 1 using the tight-binding approximation assuming a partially occupied state of Fermi energy $E_F = 0.15$.



Figure S6. Calculation of the LUMO bands of a) hydrated **2** and b) anhydrous **2'** using the tight-binding approximation assuming a partially occupied state of Fermi energy $E_F = 0.15$.



Figure S7. Calculation of the LUMO band of salt 3 using the tight-binding approximation assuming a partially occupied state of Fermi energy $E_F = 0.15$.



Figure S8. TG charts and H₂O re-adsorption process of salt **1**. i) Hydrated crystal **1**, ii) **1'** with H₂O adsorbed in air, iii) **1'** exposed to distilled H₂O vapor by standing overnight in a vial at 298 K.



Figure S9. TG charts and H₂O re-adsorption process of salt **2**. i) **2'** with H₂O adsorbed in air and ii) **2'** exposed to distilled H₂O vapor by standing overnight in a vial at 298 K.



Figure S10. Dielectric response of salt **2**. a) *T*- and *f*-dependent imaginary parts of dielectric constant ε_2 . b) *T*-dependent Cole-Cole plots.



Figure S11. Dielectric response of salt **2**'. a) *T*- and *f*-dependent imaginary parts of dielectric constant ε_2 . b) *T*-dependent Cole-Cole plots.



Figure S12. Dielectric response of salt 1. *T*- and *f*-dependent a) real part ε_1 and b) imaginary parts of dielectric constant ε_2 . c) *T*-dependent Cole-Cole plots. d) $\ln(\tau) - T^{-1}$ plot.



Figure S13. Dielectric response of salt **1**'. *T*- and *f*-dependent a) real part ε_1 and b) imaginary parts of dielectric constant ε_2 . c) *T*-dependent Cole-Cole plots. d) $\ln(\tau) - T^{-1}$ plot.



Figure S14. Dielectric response of salt **3**. a) *T*- and *f*-dependent imaginary parts of dielectric constant ε_2 . b) *T*-dependent Cole-Cole plots.



Figure S15. Dielectric response of salt 4. *T*- and *f*-dependent imaginary parts of dielectric constant ε_2 .



Figure S16. POM images of thin films a) **1** (a,e), **2** (b, f), **3** (c, d), and **4** (d, h). Images of a)-d) are a magnification of ×164 and e)-h) are a magnification of ×2940.



Figure S17. AFM images of thin films a) **1** (a,e), **2** (b, f), **3** (c, d), and **4** (d, h). Images of a)-d) are a scan range at $20 \times 20 \ \mu\text{m}^2$ and e)-h) are a scan range at $2 \times 2 \ \mu\text{m}^2$.



Figure S18. XRD patterns of **1**. Powder of **1** (iv), thin film of anhydrous **1**' (iii), thin film of hydrous **1** (ii), and the simulated pattern based on single crystal X-ray analysis at 100 K (i).



Figure S19. XRD patterns of **4**. Thin film (ii) and the simulated pattern based on single crystal X-ray analysis at 100 K (i).