



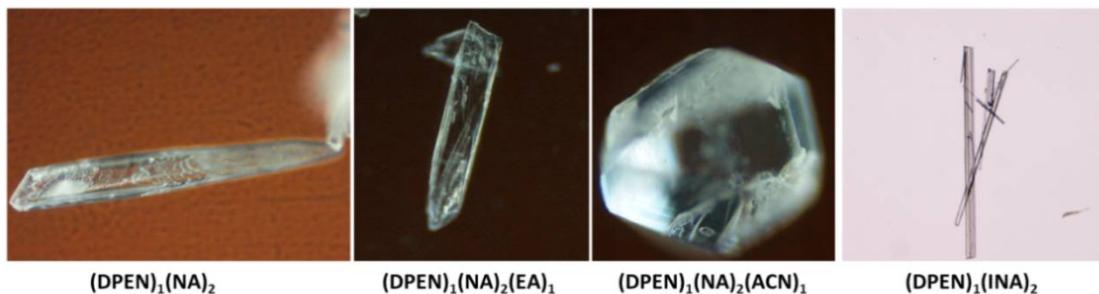
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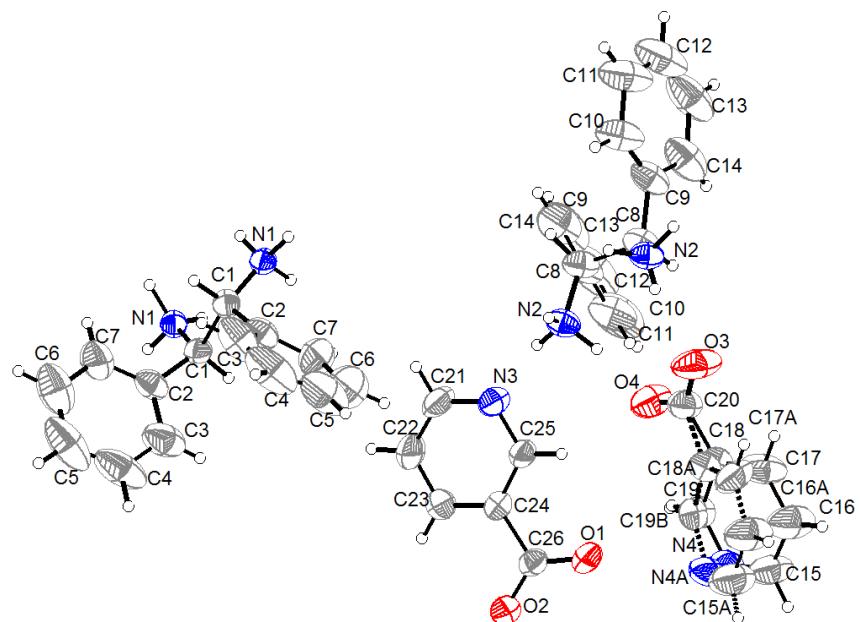
**Supporting information for article:**

**Acid-ammonium heterodimer and N(ammonium)-H $\cdots$ N(pyridine)  
Synthon preference in the salts of nicotinic acid with (1R,2R)-1,2-di-  
phenylethylenediamine**

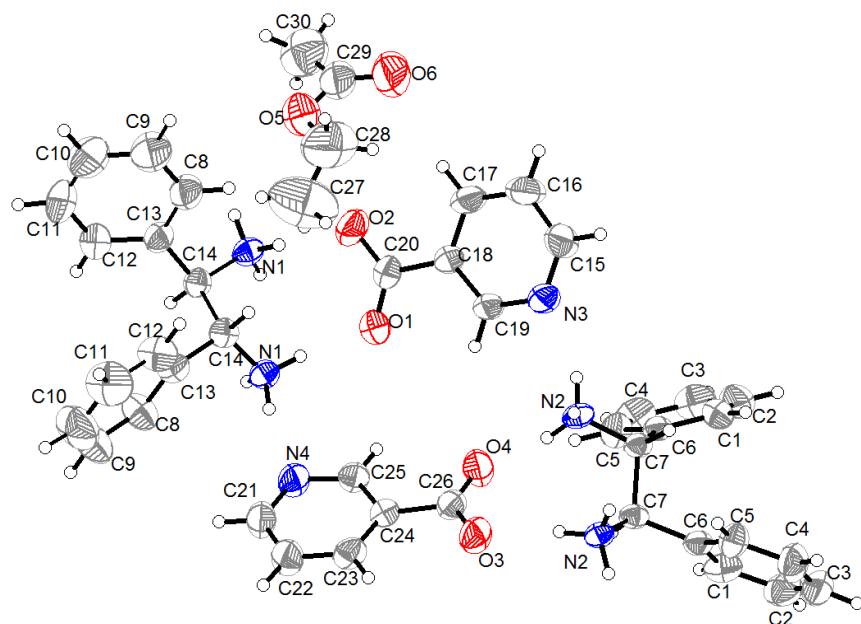
**Yang Han, Qiang Fu, Peng Zhang, Hongyu Guan and Fang Guo**



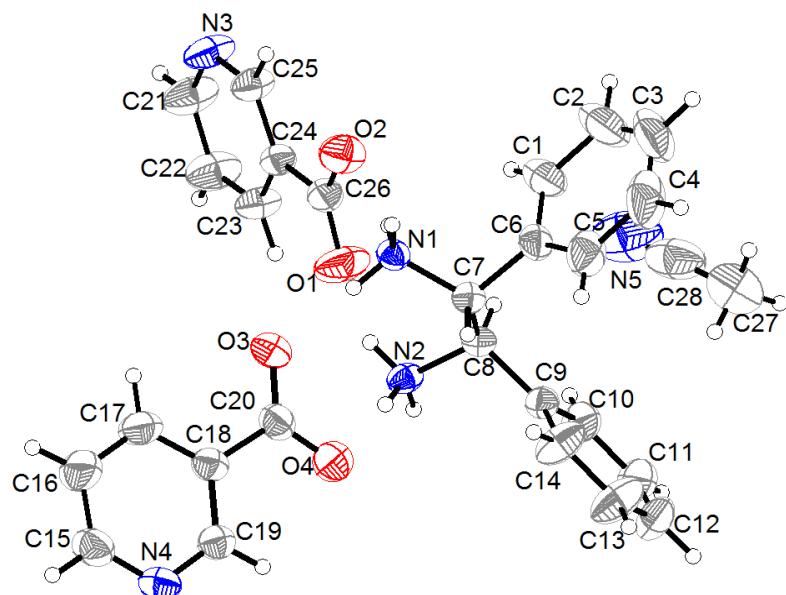
**Figure S1** Polarized light microscopies for four salts



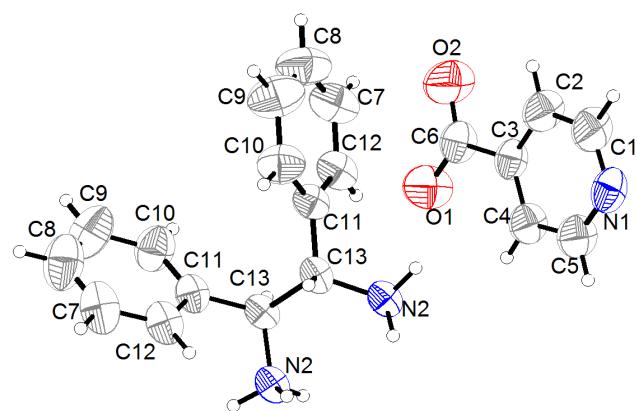
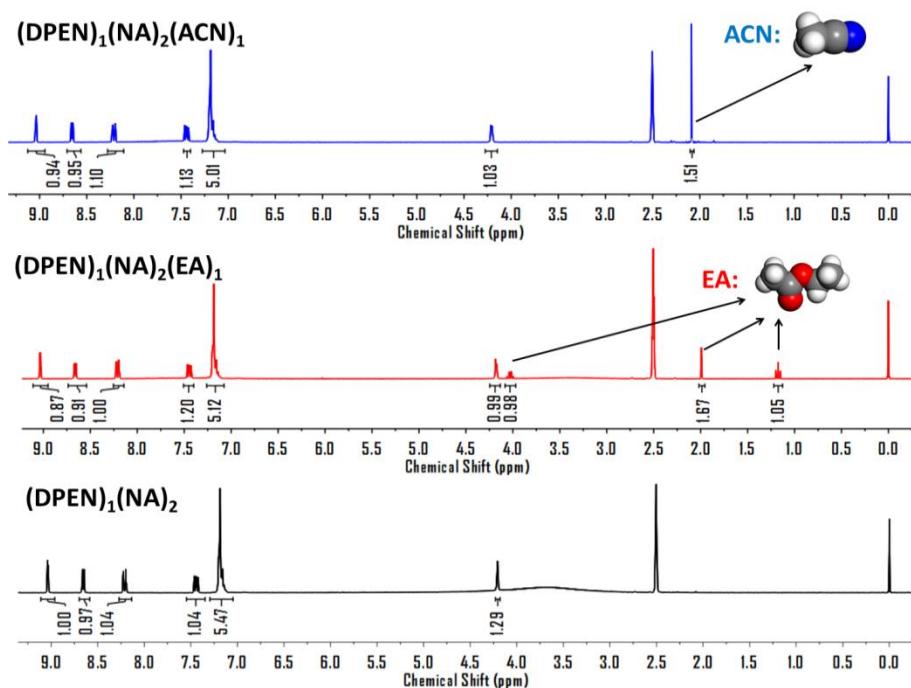
**Figure S2** The Ellipsoid plot of  $(\text{DPEN})_1(\text{NA})_2$

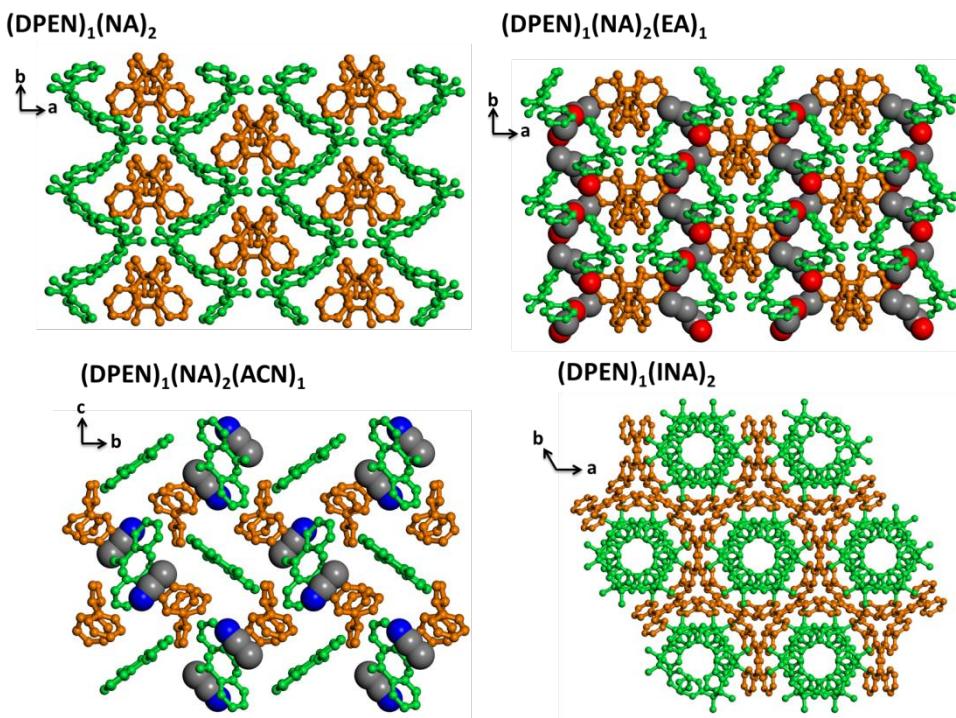


**Figure S3** The Ellipsoid plot of  $(\text{DPEN})_1(\text{NA})_2(\text{EA})_1$

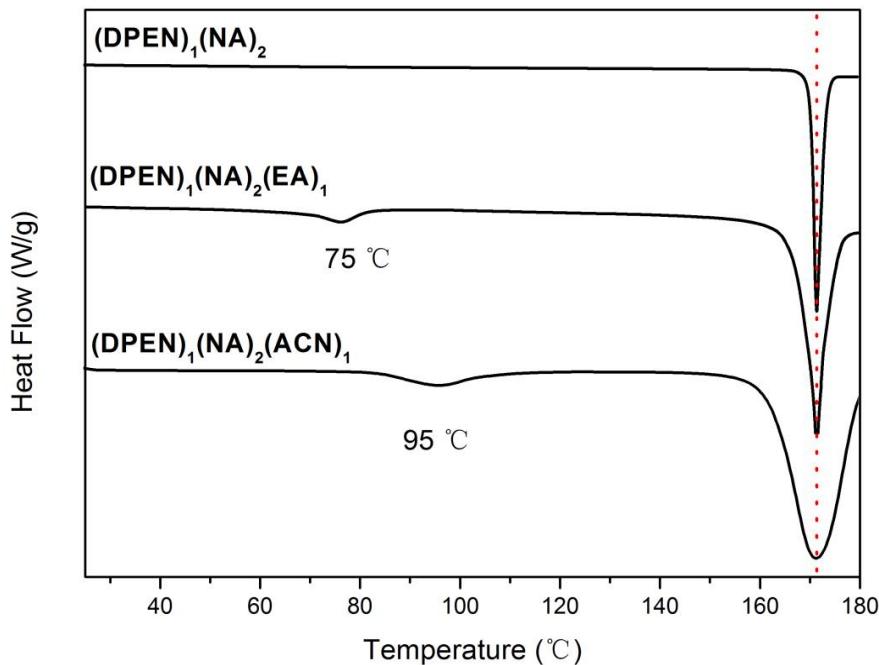


**Figure S4** The Ellipsoid plot of  $(\text{DPEN})_1(\text{NA})_2(\text{ACN})_1$

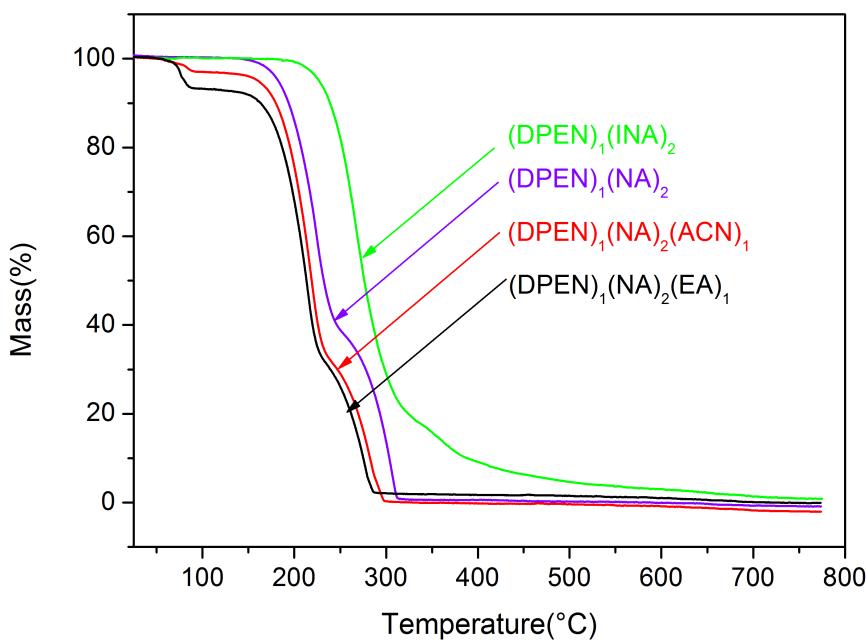
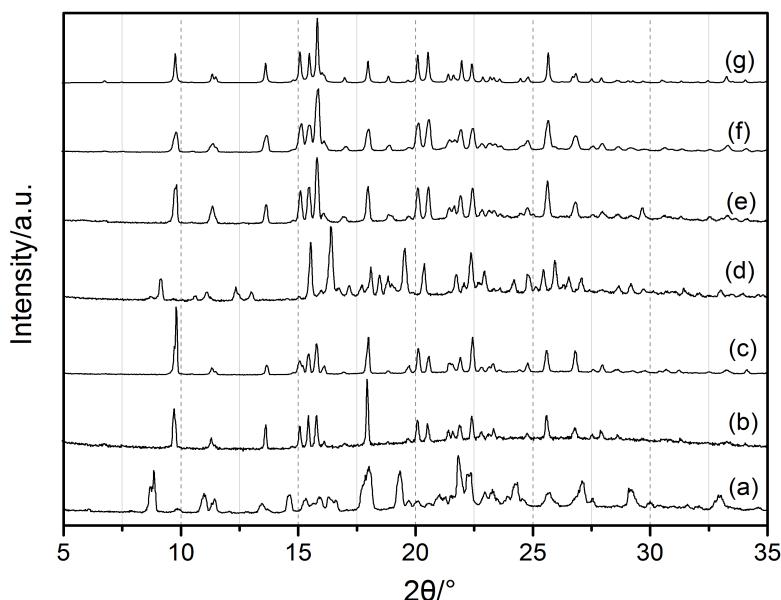
**Figure S5** The Ellipsoid plot of  $(\text{DPEN})_1(\text{INA})_2$ **Figure S6**  $^1\text{H}$ -NMR of NA salts.

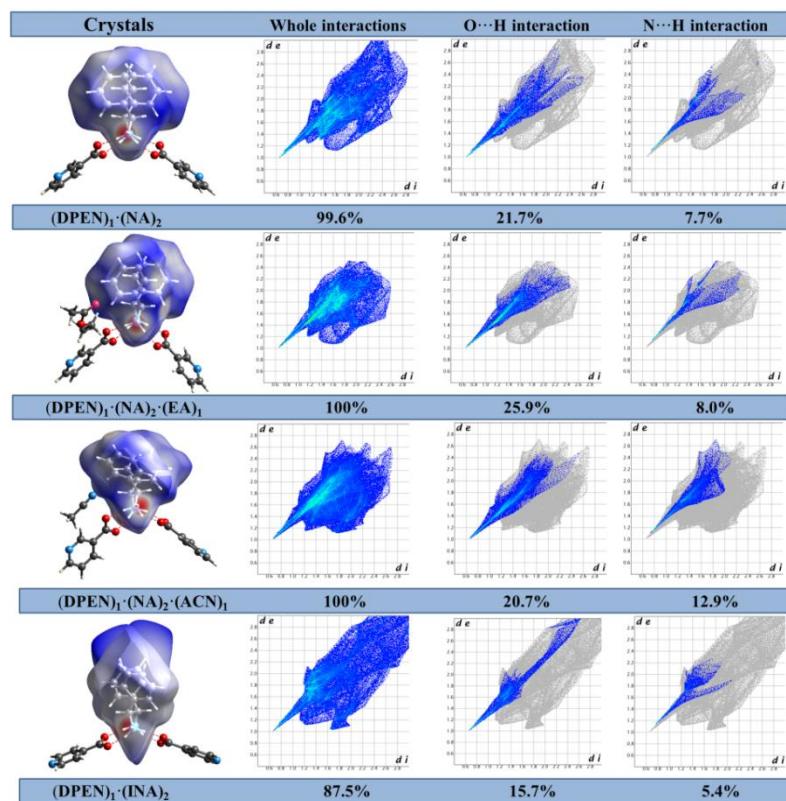
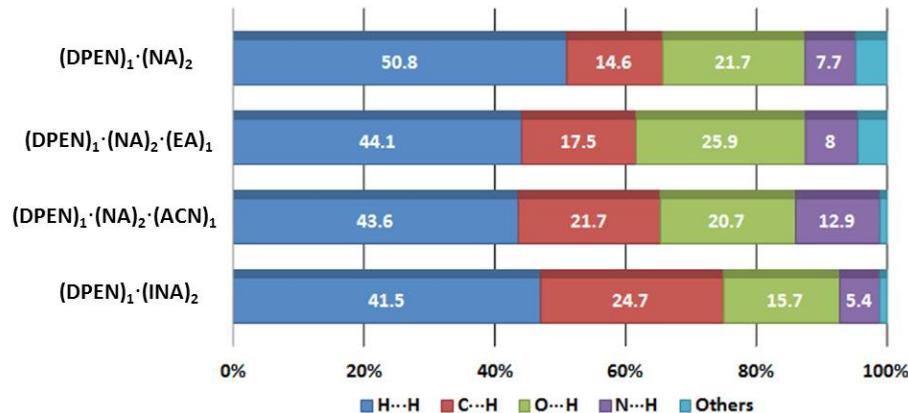


**Figure S7** The 3D structural packing of four salts.



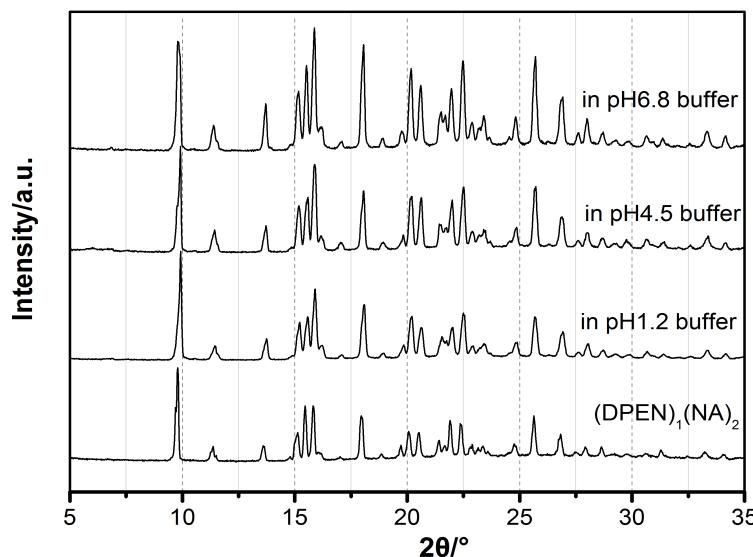
**Figure S8** DSC curves of four salts

**Figure S9** TGA curves of four salts.**Figure S10** PXRD patterns of **(DPEN)<sub>1</sub>(NA)<sub>2</sub>(EA)<sub>1</sub>** (a) at room temperature; (b) heating at 75 °C for half an hour; and (c) immersing **(DPEN)<sub>1</sub>(NA)<sub>2</sub>** into ethyl acetate solutions for two days. PXRD patterns of **(DPEN)<sub>1</sub>(NA)<sub>2</sub>(ACN)<sub>1</sub>** (d) at room temperature; (e) heating at 95 °C for half an hour; (f) immersing **(DPEN)<sub>1</sub>(NA)<sub>2</sub>** into acetonitrile solutions for two days and (g) **(DPEN)<sub>1</sub>(NA)<sub>2</sub>** simulation of PXRD from single crystal structure.

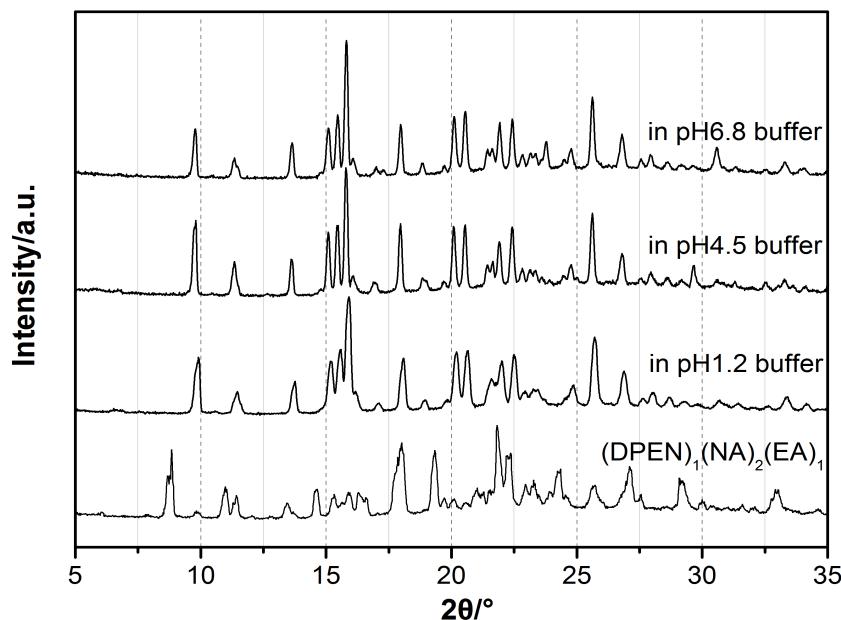
**Figure S11** The Hirshfeld surfaces of four crystals.**Figure S12** Percentage contributions to the Hirshfeld surface area for the various close intermolecular contacts.

Hirshfeld surface (HS) analysis is a relatively intuitive method for the analysis of intermolecular forces. Through 3D Hirshfeld surface maps and 2D fingerprints, combined with the color depth near the map atoms, the size of the spots determines the intermolecular forces and reveals the proportion of different forces between molecules. For HS, intermolecular interactions shorter than the sum of its van der Waals radii can be seen on the surface of the Hirshfeld, for example in the red region of the amine group of the **DPEN** molecule, generally expressed as the site of hydrogen bond formation. The

white areas indicate contact points that are close to Van der Waals' length, and the blue areas indicate longer contact points. As shown in Fig. S11 and S12, we can clearly observe the difference in **DPEN** molecules in the four salt structures mapped to the three-dimensional Hirshfeld surface of  $d_{\text{norm}}$ .



**Figure S13** PXRD patterns for residual solids from  $(\text{DPEN})_1(\text{NA})_2$  solubility experiments.



**Figure S14** PXRD patterns for residual solids from  $(\text{DPEN})_1(\text{NA})_2(\text{EA})_1$  solubility experiments.

**Table S1** Crystallography data of four crystals

Crystal	<b>(DPEN)<sub>1</sub>·(NA)<sub>2</sub></b>	<b>(DPEN)<sub>1</sub>·(NA)<sub>2</sub>·(EA)<sub>1</sub></b>	<b>(DPEN)<sub>1</sub>·(NA)<sub>2</sub>·(ACN)<sub>1</sub></b>	<b>(DPEN)<sub>1</sub>·(INA)<sub>2</sub></b>
Empirical formula	C <sub>26</sub> H <sub>26</sub> N <sub>4</sub> O <sub>4</sub>	C <sub>30</sub> H <sub>33</sub> N <sub>4</sub> O <sub>6</sub>	C <sub>28</sub> H <sub>29</sub> N <sub>5</sub> O <sub>4</sub>	C <sub>26</sub> H <sub>26</sub> N <sub>4</sub> O <sub>4</sub>
Formula weight	458.51	546.61	499.56	458.51
Temperature (K)	273(2)	273(2)	273(2)	293(2)
Crystal size (mm)	0.20×0.16×0.10	0.26×0.24×0.18	0.16×0.14×0.11	0.20×0.18×0.12
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Hexagonal
Space group	C2	C2	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P6 <sub>5</sub> 22
Z	4	4	4	6
a (Å)	23.479(6)	22.9673(11)	11.770(8)	13.854(3)
b (Å)	8.602(2)	8.8676(4)	14.079(10)	13.854(3)
c (Å)	16.899(4)	16.7749(8)	16.502(12)	27.167(8)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	129.963(5)	118.613(2)	90.00	90.00
γ (deg)	90	90.00	90.00	120.00
V (Å <sup>3</sup> )	2616.1(11)	2999.2(2)	2734(3)	4516(2)
Dx (mg.cm <sup>-3</sup> )	1.164	1.208	1.213	1.012
μ (mm <sup>-1</sup> )	0.080	0.090	0.080	0.566
F (000)	968.0	1160.0	1056.0	1452.0
R <sub>int</sub>	0.0250	0.0230	0.0330	0.0611
Total reflns	11704	25955	50039	34749
Unique reflns	6271	7385	6822	2862
Obsd reflns	4303	6427	5953	1940
Goof	1.032	1.060	1.021	1.021
R <sub>f</sub> /wR <sub>f</sub>	0.0596/0.1742	0.0516/0.1518	0.0386/0.1053	0.0421/0.1133
All data R <sub>f</sub> /wR <sub>f</sub>	0.1025/0.2013	0.0607/0.1648	0.0491/0.1307	0.0752/0.1183

**Table S2** Hydrogen bonding in **(DPEN)<sub>1</sub>(NA)<sub>2</sub>**, **(DPEN)<sub>1</sub>(NA)<sub>2</sub>(EA)<sub>1</sub>**, **(DPEN)<sub>1</sub>(NA)<sub>2</sub>(ACN)<sub>1</sub>** and **(DPEN)<sub>1</sub>(INA)<sub>2</sub>**.

	D-H···A	D-H (Å)	D···A (Å)	H···A (Å)	D-H···A (°)	Symmetry Code
<b>(DPEN)<sub>1</sub>(NA)<sub>2</sub></b>	N1-H1B···O1(i)	0.8451(37)	2.6814(52)	1.8567(16)	164.791(314)	x, y, z
	N1-H1C···O2(ii)	1.0398(98)	2.6803(59)	1.6415(90)	176.873(750)	-x+1, y, -z+2
	N2-H2A···O3(iii)	0.7989(48)	2.7236(68)	1.9419(57)	165.854(894)	-x+1, y, -z+1
	N2-H2B···O4(iv)	0.9775(16)	2.6651(66)	1.7044(62)	166.653(580)	x, y, z
	N1-H1A···N3(v)	0.9524(84)	2.8826(13)	1.9367(39)	171.852(498)	-x+1, y, -z+1
	N2-H2C···N4(vi)	0.9875(80)	2.8300(38)	1.8602(13)	166.556(434)	x, y, z
<b>(DPEN)<sub>1</sub>(NA)<sub>2</sub>(EA)<sub>1</sub></b>	N1-H1B···O1(i)	0.9327(99)	2.6664(31)	1.7719(85)	159.671(180)	x, y, z
	N1-H1C···O2(ii)	0.9387(85)	2.7155(31)	1.7767(85)	179.543(812)	-x+1, y, -z+1
	N2-H2A···O3(iii)	1.0006(28)	2.7291(34)	1.7325(26)	173.554(881)	-x+1, y, -z
	N2-H2B···O4(iv)	1.0103(63)	2.6824(28)	1.6764(78)	173.288(197)	x, y, z
	N1-H1A···N3(v)	0.8239(60)	2.8578(47)	2.0428(59)	170.005(817)	x, y, z
	N2-H2C···N4(vi)	0.8839(80)	2.8991(44)	2.0423(79)	163.018(958)	x, y, z
	C8-H8···O5(vii)	0.9300(32)	3.3461(37)	2.6670(26)	130.381(105)	x, y, z
	C7-H7···O6(viii)	0.9800(22)	3.4010(35)	2.5250(37)	148.720(159)	-x+1/2, y-1/2, -z
	C17-H17···O6(ix)	0.9300(19)	3.3040(37)	2.5070(33)	143.940(168)	x, y, z
<b>(DPEN)<sub>1</sub>(NA)<sub>2</sub>(ACN)<sub>1</sub></b>	N1-H1B···O2(i)	0.8894(53)	2.8090(28)	1.9405(50)	164.970(341)	x, y, z
	N2-H2A···O1(ii)	0.8911(42)	2.6428(29)	1.8082(41)	155.014(264)	x, y, z
	N1-H1A···O3(iii)	0.9306(29)	2.7110(26)	1.7901(29)	169.780(133)	x, y, z
	N2-H2B···O4(iv)	0.9163(82)	2.6864(29)	1.7710(82)	176.910(671)	x, y, z
	C7-H7···N5(v)	0.9798(18)	3.3920(45)	2.4800(37)	154.770(123)	-x+1, y-1/2, -z+3/2
	N1-H1C···N4(vi)	0.8999(37)	2.8871(28)	1.9930(37)	172.173(182)	x-1/2, -y+1/2, -z+1
<b>(DPEN)<sub>1</sub>(INA)<sub>2</sub></b>	N2-H2C···N3(vii)	0.8886(38)	2.8470(29)	1.9705(41)	168.602(224)	x+1/2, y+3/2, -z+1
	N2-H2A···O1(i)	0.9707(32)	2.7234(28)	1.7555(26)	174.625(194)	x, x-y, -z+5/6
	N2-H2B···O2(ii)	1.0436(29)	2.6282(45)	1.6271(15)	159.031(533)	y, -x+y, z+1/6
	N2-H2C···N1(iii)	0.9834(42)	2.8844(29)	1.9301(57)	162.880(266)	-y+1, -x+1, -z+7/6

**Table S3** Equilibrium solubility<sup>a</sup> of **(DPEN)<sub>1</sub>·(NA)<sub>2</sub>** and **(DPEN)<sub>1</sub>·(NA)<sub>2</sub>·(EA)<sub>1</sub>** and their salts at 37 °C.

Material	Equilibrium Solubility (mg·mL <sup>-1</sup> )		
	pH 1.2	pH 4.5	pH 6.8
<b>NA</b>	15.318	22.727	31.592
<b>(DPEN)<sub>1</sub>·(NA)<sub>2</sub></b>	58.902	152.235	123.495
<b>(DPEN)<sub>1</sub>·(NA)<sub>2</sub>·(EA)<sub>1</sub></b>	46.921	67.699	90.533

<sup>a</sup> Relative standard uncertainty for solubility values  $\mu_r = 2.5 \times 10^{-2}$ .