Supporting information

Discovery and characterization of new crystal forms of bio-based nylon 4F salt

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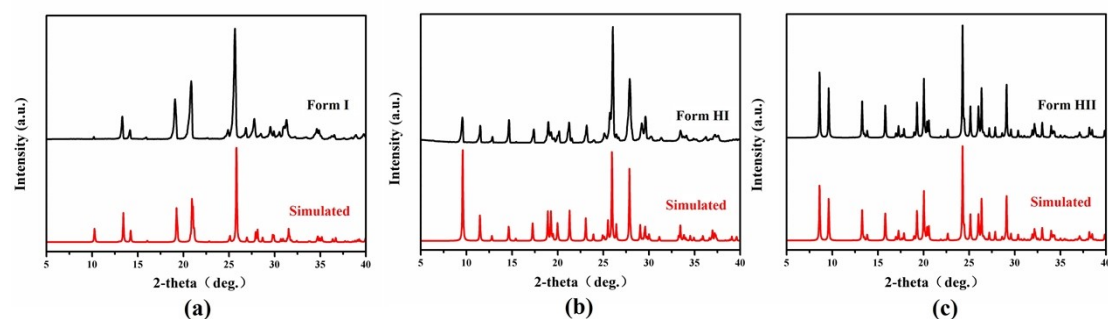
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Figure S1. Comparison of PXRD patterns with the simulated patterns from SCXRD for three forms of nylon 4F salt.
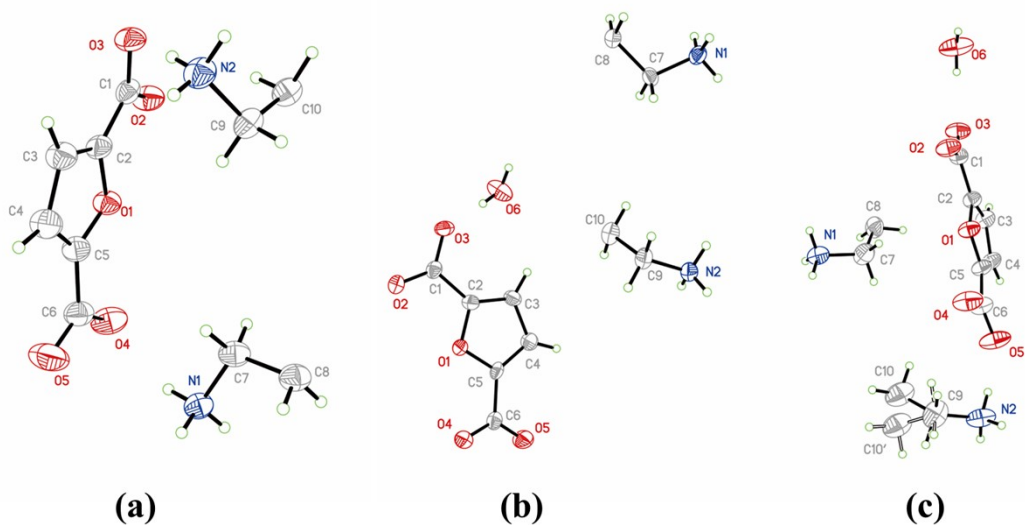
Figure S2. The asymmetric unit ORTEP diagrams of three crystal forms of nylon 4F monomer salt crystal forms, showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level: Form I (a) Form HI (b) and Form HII (c).
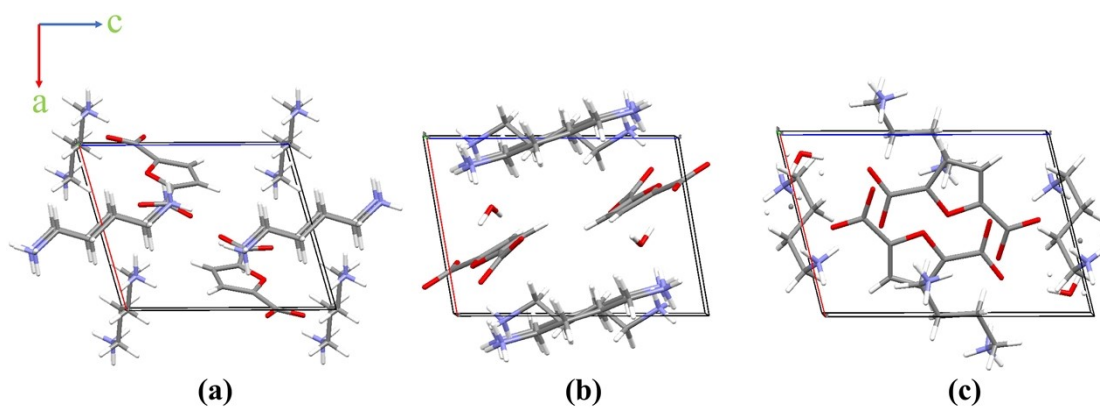

Figure S3. Packing diagrams of the nylon 4F monomer salt: Form I (a) Form HI (b) and Form HII (c).

**Table S1.** Hydrogen bonds data of three crystal forms of nylon 4F monomer salt.

Form I

D−H···A	D(D-H) / Å	d(H···A) / Å	d(D···A)/ Å	<DHA
N1−H1A···O2	0.890(3)	1.893(2)	2.779(4)	173.3(2)
N1−H1B···O4	0.890(3)	2.041(3)	2.853(4)	151.2(2)
N1−H1C···O3	0.890(3)	2.053(3)	2.932(4)	169.0(2)
N1−H1C···O2	0.890(3)	2.519(2)	2.971(4)	112.1(2)
N2−H2A···O5	0.890(3)	2.121(4)	2.937(5)	152.1(2)
N2−H2A···O4	0.890(3)	2.356(3)	3.154(4)	149.3(2)
N2−H2B···O5	0.891(3)	1.922(3)	2.758(4)	155.7(2)
N2−H2C···O3	0.890(3)	2.061(3)	2.924(4)	163.3(2)

Form HI

D−H...A	D(D-H) / Å	d(H···A) / Å	d(D···A)/ Å	<DHA
N1−H1A···O6	0.890(3)	2.220(3)	3.074(4)	160.6(2)
N1−H1C···O3	0.890(3)	1.852(3)	2.741(4)	177.1(2)
N1−H1B···O4	0.890(3)	2.077(3)	2.956(5)	169.0(2)
N2−H2A···O6	0.890(4)	2.028(4)	2.915(4)	174.1(2)
N2−H2B···O4	0.890(3)	2.051(3)	2.878(4)	154.0(2)
N2−H2C···O2	0.890(3)	1.958(3)	2.795(4)	156.0(2)
N2−H2C···O1	0.890(3)	2.415(2)	2.998(4)	123.4(2)
O6−H6A···O3	0.850(3)	1.896(3)	2.742(4)	174.1(3)
O6−H6B···O5	0.859(10)	1.889(17)	2.712(4)	160(3)

Form HII

D−H···A	D(D-H) / Å	d(H···A) / Å	d(D···A)/ Å	<DHA
N1−H1A···O4	0.890(3)	1.995(2)	2.885(3)	178.6(2)
N1−H1C···O2	0.890(3)	2.057(2)	2.942(3)	172.8(2)
N1−H1B···O3	0.890(3)	1.945(2)	2.829(3)	172.4(2)
N2−H2A···O2	0.890(2)	1.949(2)	2.829(3)	169.7(2)
N2−H2B···O6	0.890(3)	2.104(2)	2.922(3)	152.2(2)
N2−H2C···O5	0.890(3)	1.900(3)	2.783(4)	171.7(2)
O6−H6A···O3	0.850(2)	2.015(2)	2.864(3)	177.1(1)
O6−H6B···O5	0.850(2)	1.908(2)	2.757(3)	177.1(2)

Table S2. Torsion angles (°) data of the nylon 4F monomer salt three crystal forms.

Form I		Form HI		Form HII	
C8#1-C8-C7-N1	177.3(3)	N1-C7-C8-C8#1	-178.4 (4)	N1-C7-C8-C8#1	64.1(5)
N2-C9-C10-C10#2	177.4(3)	N2-C9-C10-C10#2	-179.7 (4)	N2-C9-C10-C10#2	66.4(9)
C5-O1-C2-C3	-0.5(3)	C5-O1-C2-C3	-0.8 (4)	C5-O1-C2-C3	1.0(3)
C5-O1-C2-C1	-179.9(2)	C5-O1-C2-C1	177.4 (3)	C5-O1-C2-C1	178.2(2)
C4-O3-C2-O1	-0.2(4)	O1-C2-C3-C4	0.4 (4)	O1-C2-C3-C4	-0.8(3)
C4-C3-C2-C1	179.0(3)	C1-C2-C3-C4	-177.3 (4)	C1-C2-C3-C4	-177.2(3)
O2-C1-C2-O1	10.3(4)	O2-C1-C2-O1	2.0(5)	O2-C1-C2-O1	5.4(4)
O3-C1-C2-O1	-168.3(2)	O3-C1-C2-O1	-179.4(3)	O3-C1-C2-O1	-174.0(2)
O2-C1-C2-C3	-168.9(3)	O2-C1-C2-C3	179.5(4)	O2-C1-C2-C3	-178.3(3)
O3-C1-C2-C3	12.5(5)	O3-C1-C2-C3	-1.9(6)	O3-C1-C2-C3	2.2(5)
C2-O1-C5-C4	1.0(3)	C2-O1-C5-C4	0.8(4)	C2-O1-C5-C4	-0.7(3)
C2-O1-C5-C6	-178.7(2)	C2-O1-C5-C6	177.5(3)	C2-O1-C5-C6	179.0(3)
C4-C5-C6-O5	1.3(5)	C4-C5-C6-O5	-18.5(6)	C4-C5-C6-O5	3.3(5)
O1-C5-C6-O5	-179.1(3)	O1-C5-C6-O5	165.7(3)	O1-C5-C6-O5	-176.4(3)
C4-C5-C6-O4	-178.3(3)	C4-C5-C6-O4	159.3(4)	C4-C5-C6-O4	-177.3(3)
O1-C5-C6-O4	1.3(4)	O1-C5-C6-O4	-16.5(5)	O1-C5-C6-O4	3.0(4)
O1-C5-C4-C3	-1.1(4)	C3-C4-C5-O1	-0.5(4)	C3-C4-C5-O1	0.2(3)
C6-C5-C4-C3	178.5(3)	C3-C4-C5-C6	-176.6(4)	C3-C4-C5-C6	-179.4(3)
C2-C3-C4-C5	0.8(4)	C2-C3-C4-C5	0.1(4)	C2-C3-C4-C5	0.4(3)

Form HII (continued)	
N2-C9-C10'-C10'#2	-66(2)
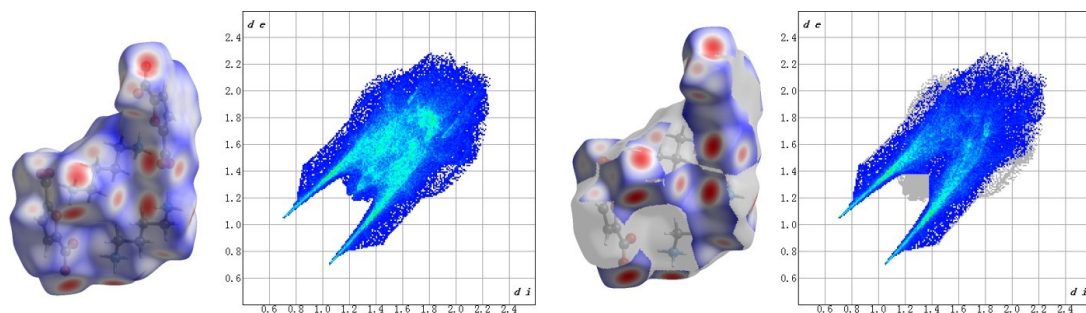
(a) All···All
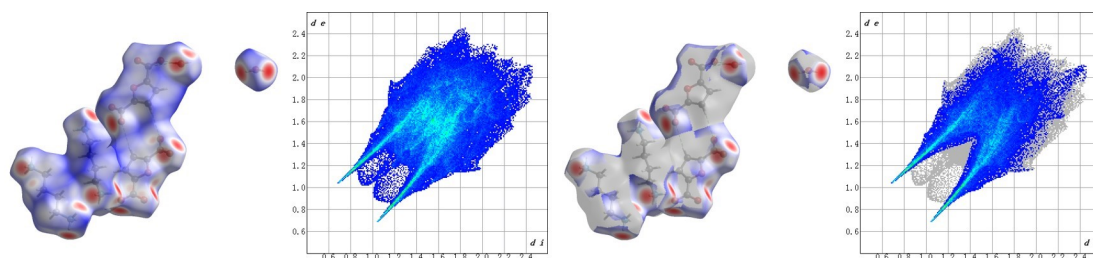
(b) H···O/O···H (54.7%)
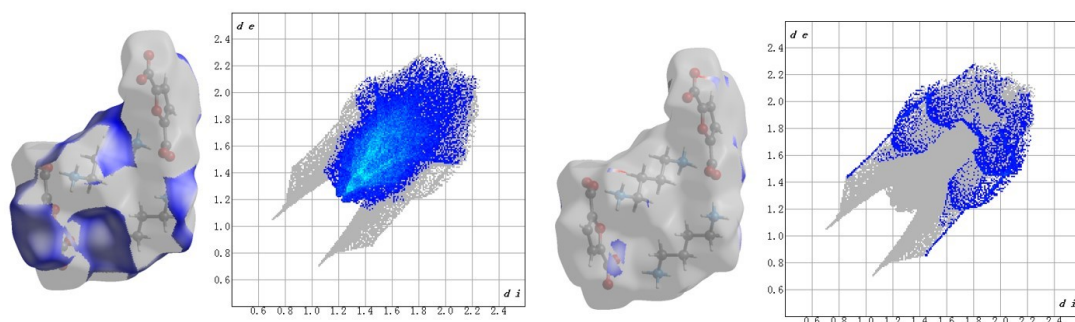
(c) H···H (33.9%)

(d) H···C/C···H (4.2%)
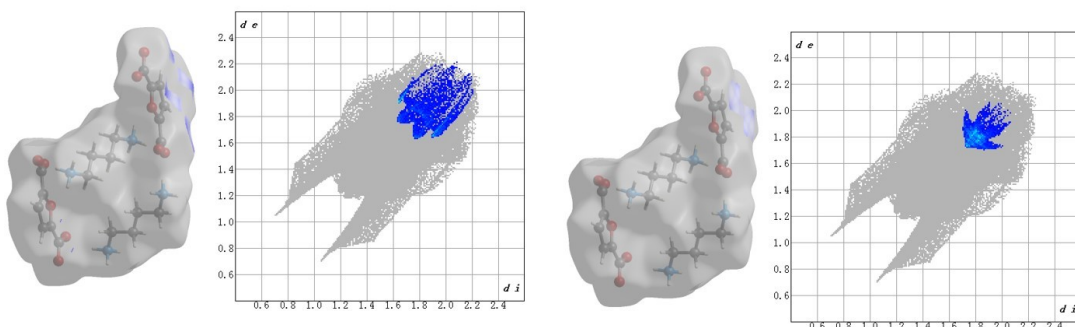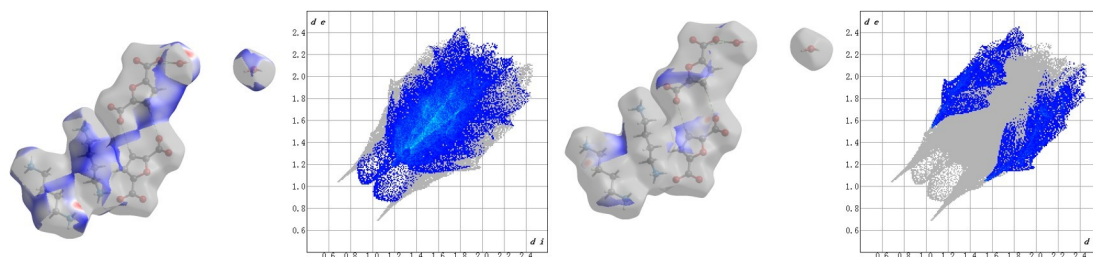
(e) O···C/C···O (3.6%)

(f) C···C (3.2%)

Figure S4. Hirshfeld surfaces of the Form I and its corresponding fingerprint plots.
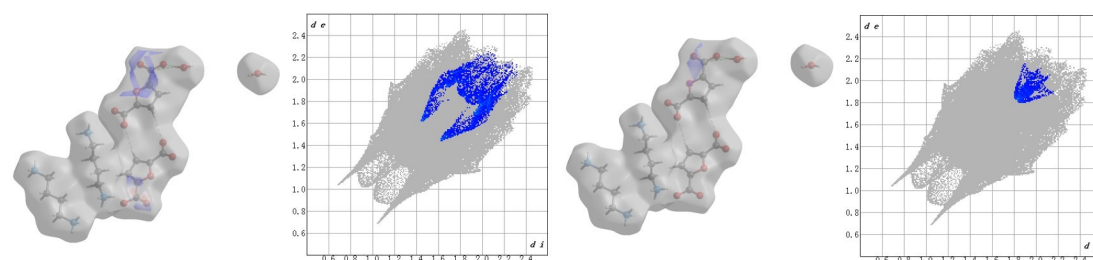
(a) All···All
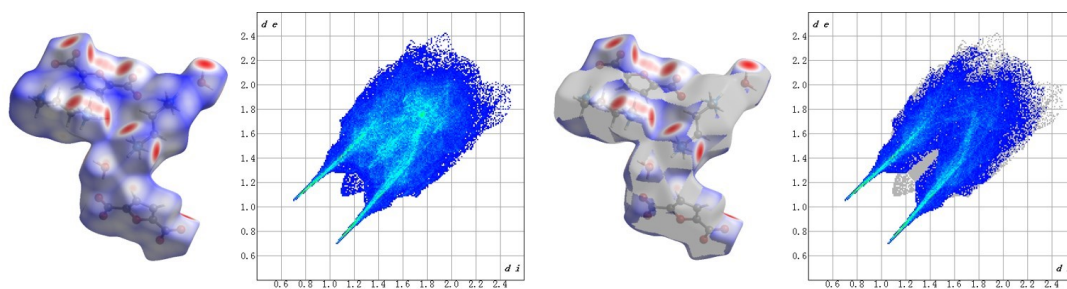
(b) H···O/O···H (50.8%)

(c) H···H (30.1%)
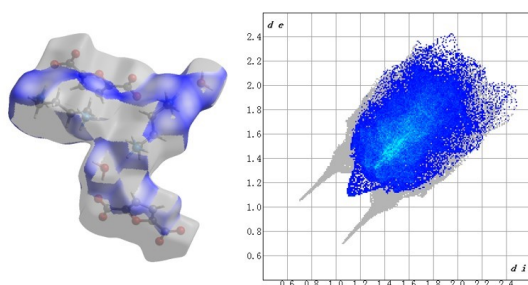
(d) H···C/C···H (9.8%)

(e) O···C/C···O (4.3%)

(f) C···C (1.1%)

Figure S5. Hirshfeld surfaces of the Form HI and its corresponding fingerprint plots.

(a) All···All

(b) H···O/O···H (50.1%)

(c) H···H (37.6%)
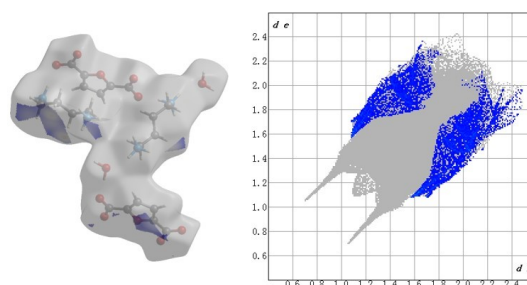
(d) H···C/C···H (5.9%)

(e) O···C/C···O (4.1%)

(f) C···C (1.6%)

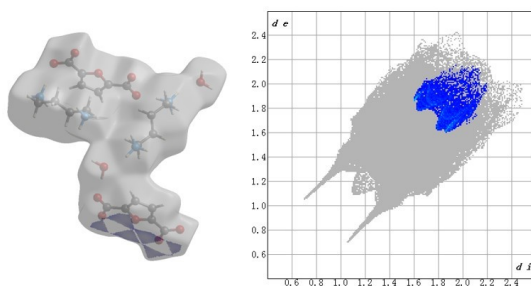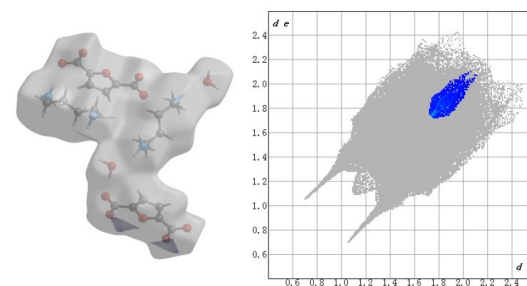**Figure S6.** Hirshfeld surfaces of the Form HII and its corresponding fingerprint plots.

Form I
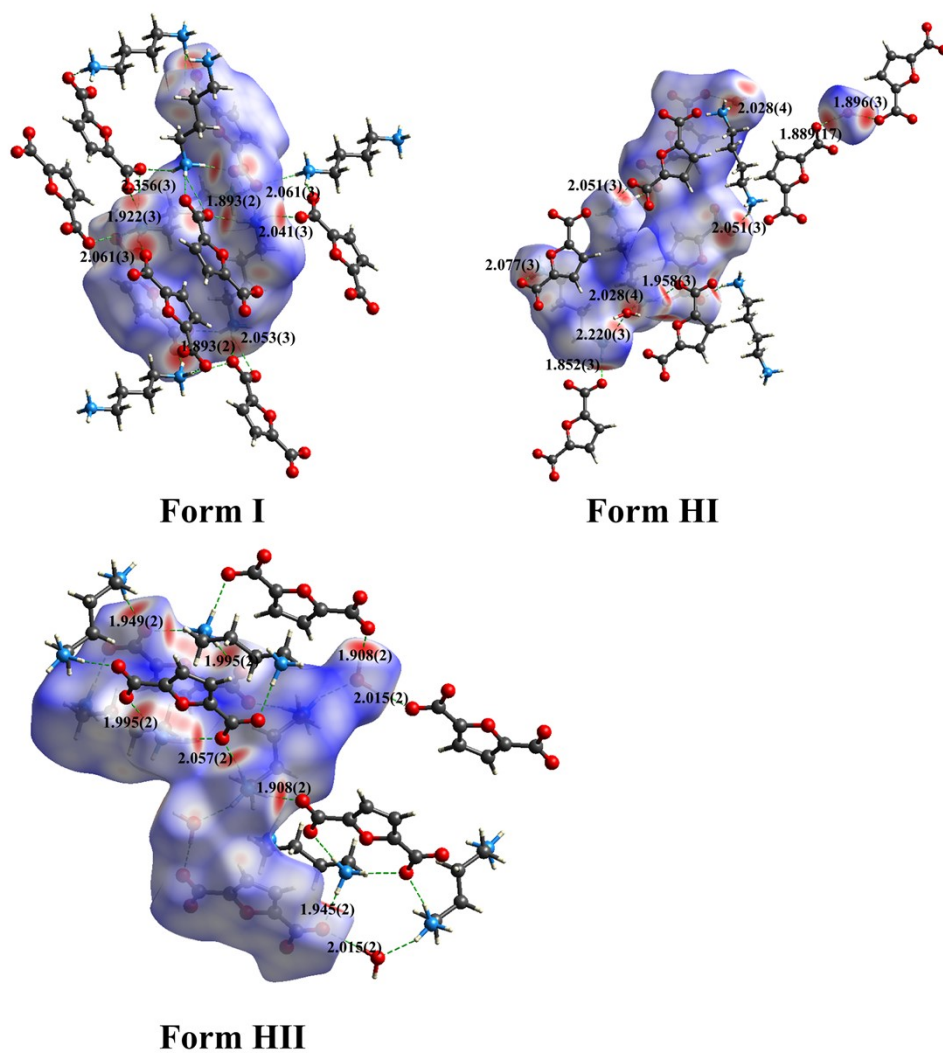
Form HI

Form HII

Figure S7. The distance of hydrogen-bond contacts of three forms of nylon 4F salt in Figure 5.

Table S3. Experimental mole fraction solubility of nylon 4F monomer salt Form I (x_1) and calculated CNIBS/RS mole fraction solubility (x^{calcd}) in binary solvent mixtures of water + ethanol.

T/K	x_2	$10^4 x_1$	$10^4 x^{calcd}$	$10^2(x_1 - x^{calcd})/x_1$
283.15	0.7	2.4480	2.4482	-0.0093
	0.75	1.1717	1.1698	0.1687
	0.8	0.5516	0.5576	-1.0927
	0.85	0.2726	0.2643	3.0443
	0.9	0.1196	0.1240	-3.6661
	0.95	0.0574	0.0573	0.1585
293.15	0.7	2.8781	2.8803	-0.0764
	0.75	1.5054	1.4932	0.8106
	0.8	0.6728	0.6989	-3.8767
	0.85	0.3408	0.3211	5.7719
	0.9	0.1611	0.1592	1.1681
	0.95	0.0909	0.0946	-4.1449
303.15	0.7	3.6498	3.6188	0.8498
	0.75	1.8596	1.8796	-1.0742
	0.8	0.8442	0.9134	-8.2050
	0.85	0.5041	0.4676	7.2275
	0.9	0.4192	0.2879	31.3249
	0.95	0.1772	0.2468	-39.2395

Table S4. Parameters of the CNIBS/RS model for the solubility of nylon 4F monomer salt Form I in water and binary solvent mixtures of water + ethanol.

T/K	B_1	B_2	B_3	B_4	B_5	R-Square	10^2RMSD
283.15	10.5390	-9.4878	-14.0963	16.0359	-6.6444	0.9999	0.4626
293.15	-21.6454	71.1574	-12.4050	-111.7530	72.0655	0.9990	1.4368
303.15	-29.8683	101.0490	-35.8501	-129.0101	92.6181	0.9967	7.0200

Table S5. Parameters of the modified Apelblat model for nylon 4F monomer salt in pure water.

solvent	A	B	C	R-Square	10^6RMSD
Pure water	58.4332	-3510.2090	-8.6256	0.9940	3.2648