Electronic Supporting Information

Separate Mechanisms of Ion Oligomerization Tune the Physicochemical Properties of n-Butylammonium Acetate: Cation-Base Clusters *vs.* Anion-Acid Dimers

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1. Thermal data for $[C_4NH_3][OAc]$

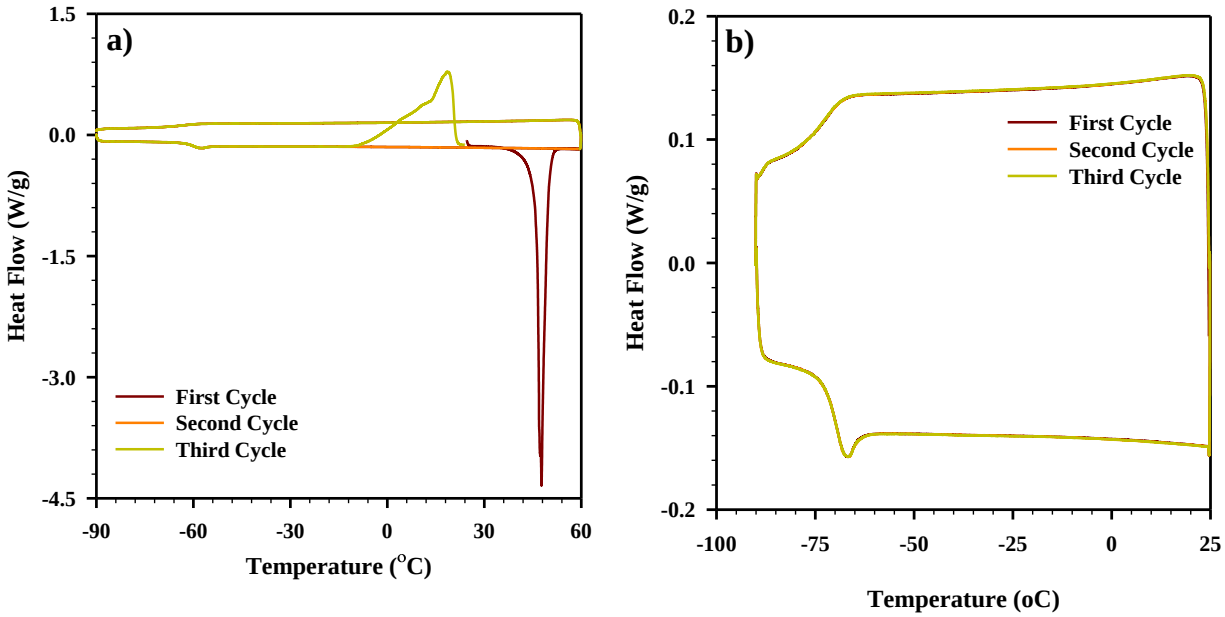

Figure S1. DSC of **a)** crystalline $[C_4NH_3][OAc]$, and **b)** liquid $[C_4NH_3][OAc]$. Dark brown line: First cycle; Orange line: Second cycle; Lime green line: Third cycle.

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2. Water content of the mixtures

Table S1. Water content of the mixtures.

Mole fraction of HOAc or C_4NH_2 (χ) in the mixtures	Mixtures of $[C_4NH_3][OAc]$ + HOAc		Mixtures of $[C_4NH_3][OAc]$ + C_4NH_2	
	Water content (ppm)	Mole of water per mole mixture	Water content (ppm)	Mole of water per mole mixture
0	3687.3	0.027	4147.5	0.030
0.10	4307.8	0.030	5147.9	0.036
0.20	4768.0	0.031	4645.2	0.031
0.33	4384.2	0.027	5017.4	0.032
0.50	4542.3	0.024	4573.3	0.026
0.67	3627.4	0.017	3689.6	0.019
0.80	3072.9	0.013	3113.4	0.015
0.90	2665.9	0.010	2734.9	0.012
1.0	1165.0	0.004	1018.1	0.004

3. Thermal data of the mixtures

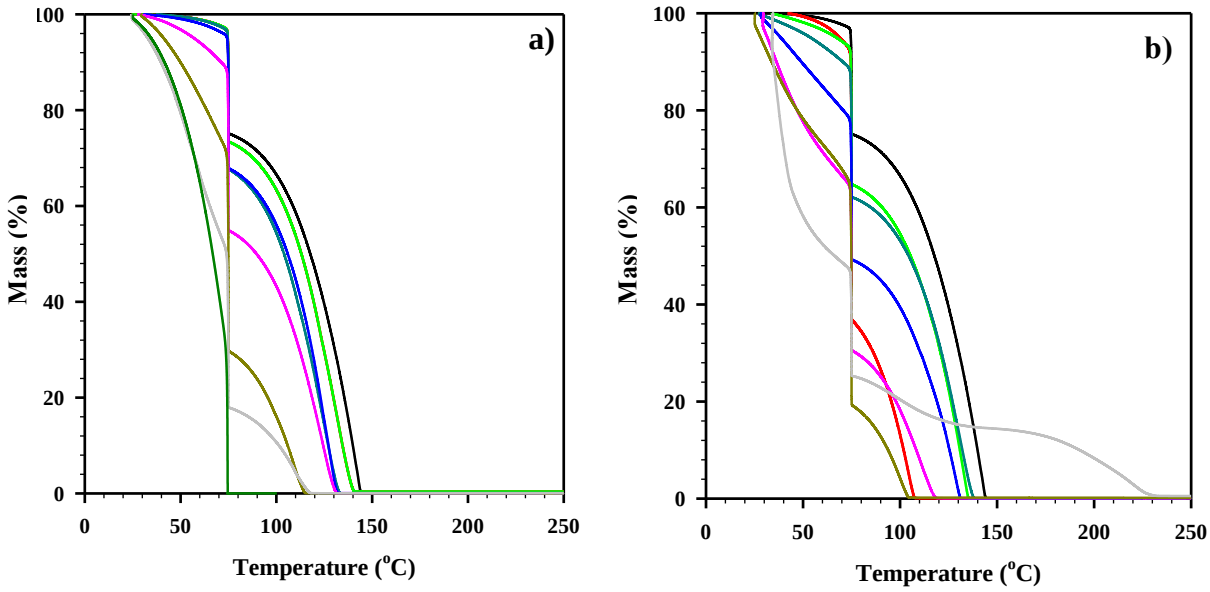

Figure S2. TGA of the mixtures of **a)** $[C_4NH_3][OAc]$ + HOAc, and **b)** $[C_4NH_3][OAc]$ + C_4NH_2, with χ = **0** ($[C_4NH_3][OAc]$), **0.10**, **0.20**, **0.33**, **0.50**, **0.67**, **0.80**, **0.90**, and **1.0**.

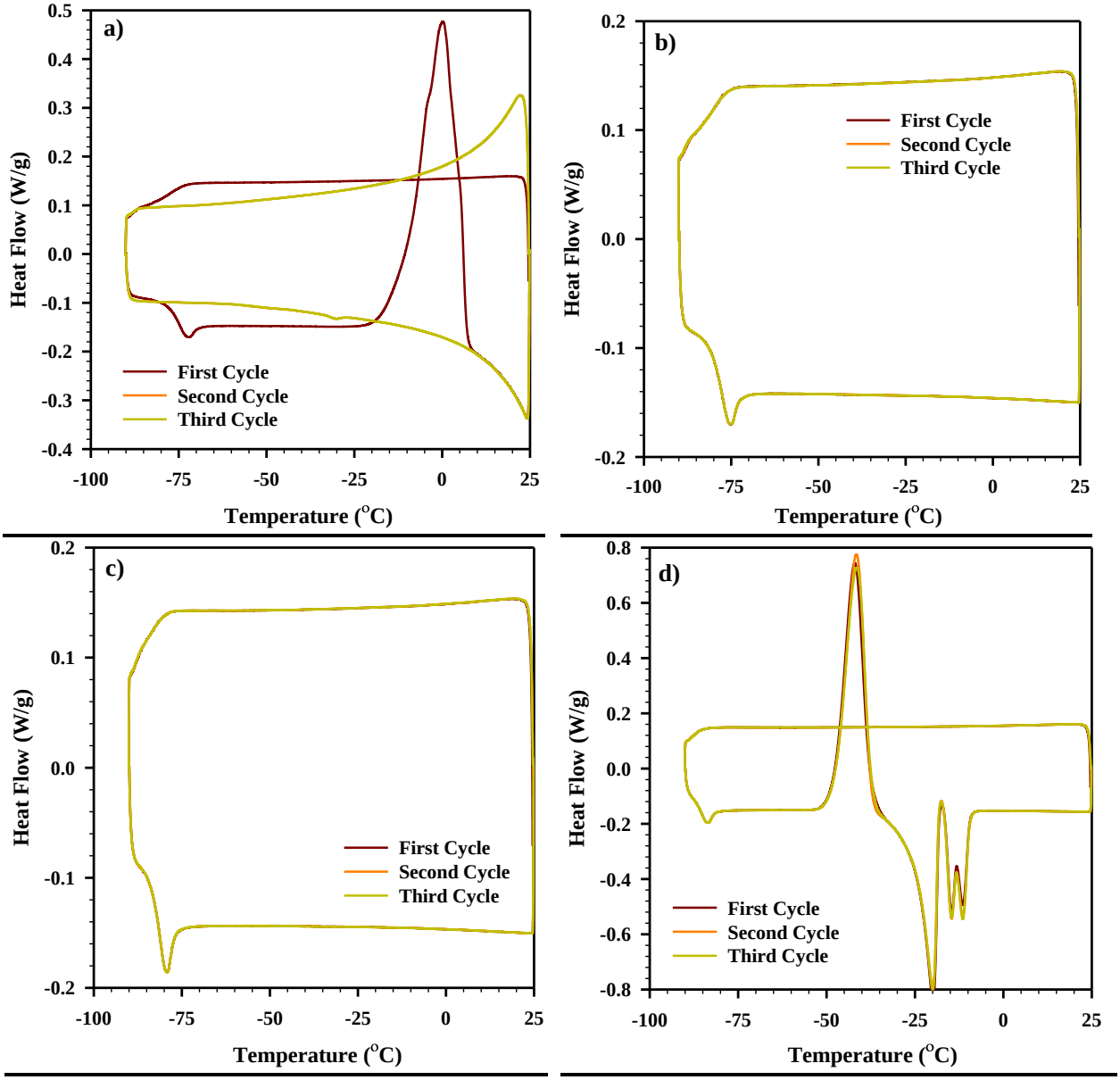

Figure S3. DSC of $[C_4NH_3][OAc]$ + HOAc **a)** χ_{HOAc} =0.1, **b)** χ_{HOAc} =0.2, **c)** χ_{HOAc} =0.33, and **d)** χ_{HOAc} =0.5. Dark brown line: First cycle; Orange line: Second cycle; Lime green line: Third cycle.

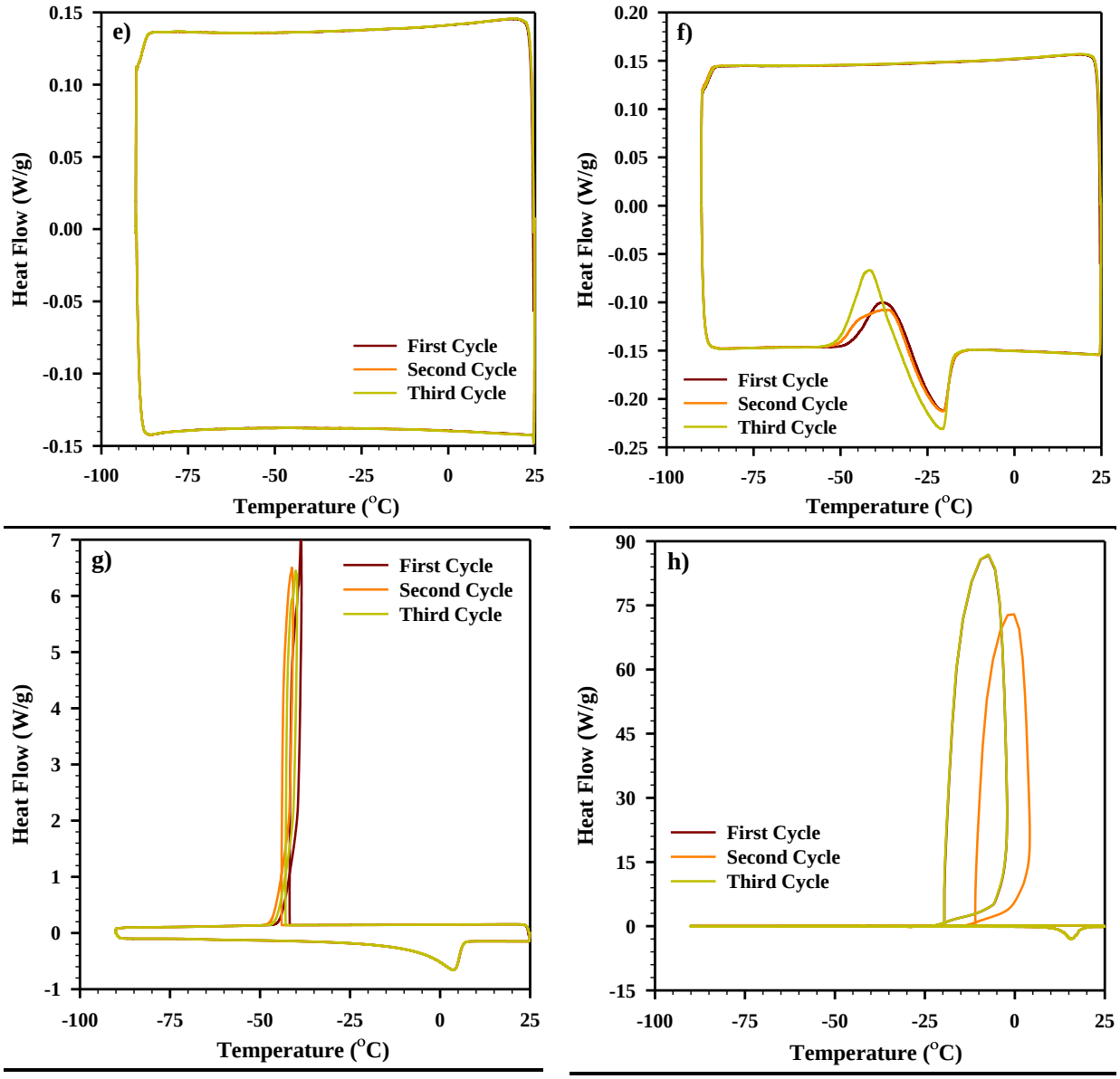

Figure S3 (cont.). DSC of $[C_4NH_3][OAc]$ + HOAc **e)** χ_{HOAc} =0.67, **f)** χ_{HOAc} =0.8, **g)** χ_{HOAc} =0.9, and **h)** HOAc (χ_{HOAc} =1). Dark brown line: First cycle; Orange line: Second cycle; Lime green line: Third cycle.

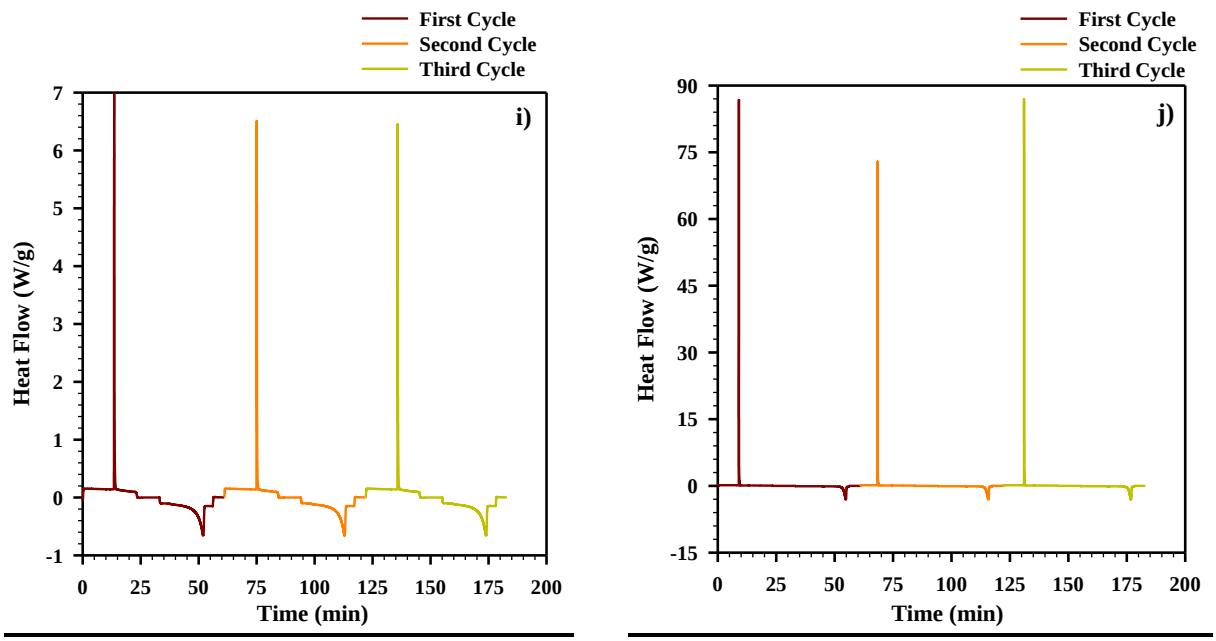

Figure S3 (cont.). Heat Flow of $[C_4NH_3][OAc]$ + HOAc vs. time **i)** χ_{HOAc} =0.9, and **j)** HOAc (χ_{HOAc} =1). Dark brown line: First cycle; Orange line: Second cycle; Lime green line: Third cycle.

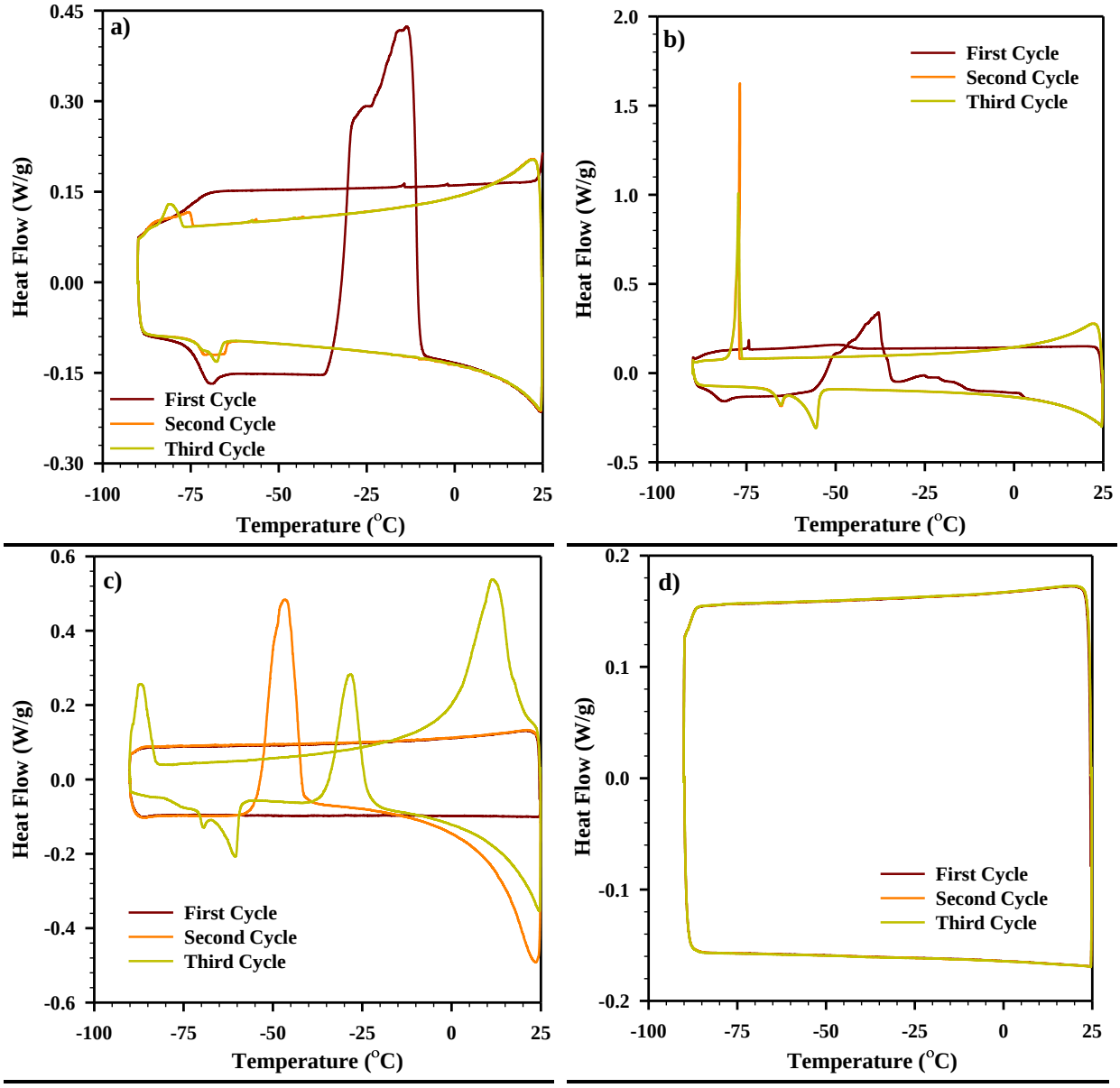

Figure S4. DSC of $[C_4NH_3][OAc] + C_4NH_2$ **a)** χ_{C4NH2} =0.1, **b)** χ_{C4NH2} =0.2, **c)** χ_{C4NH2} =0.33, and **d)** χ_{C4NH2} =0.5. Dark brown line: First cycle; Orange line: Second cycle; Lime green line: Third cycle.

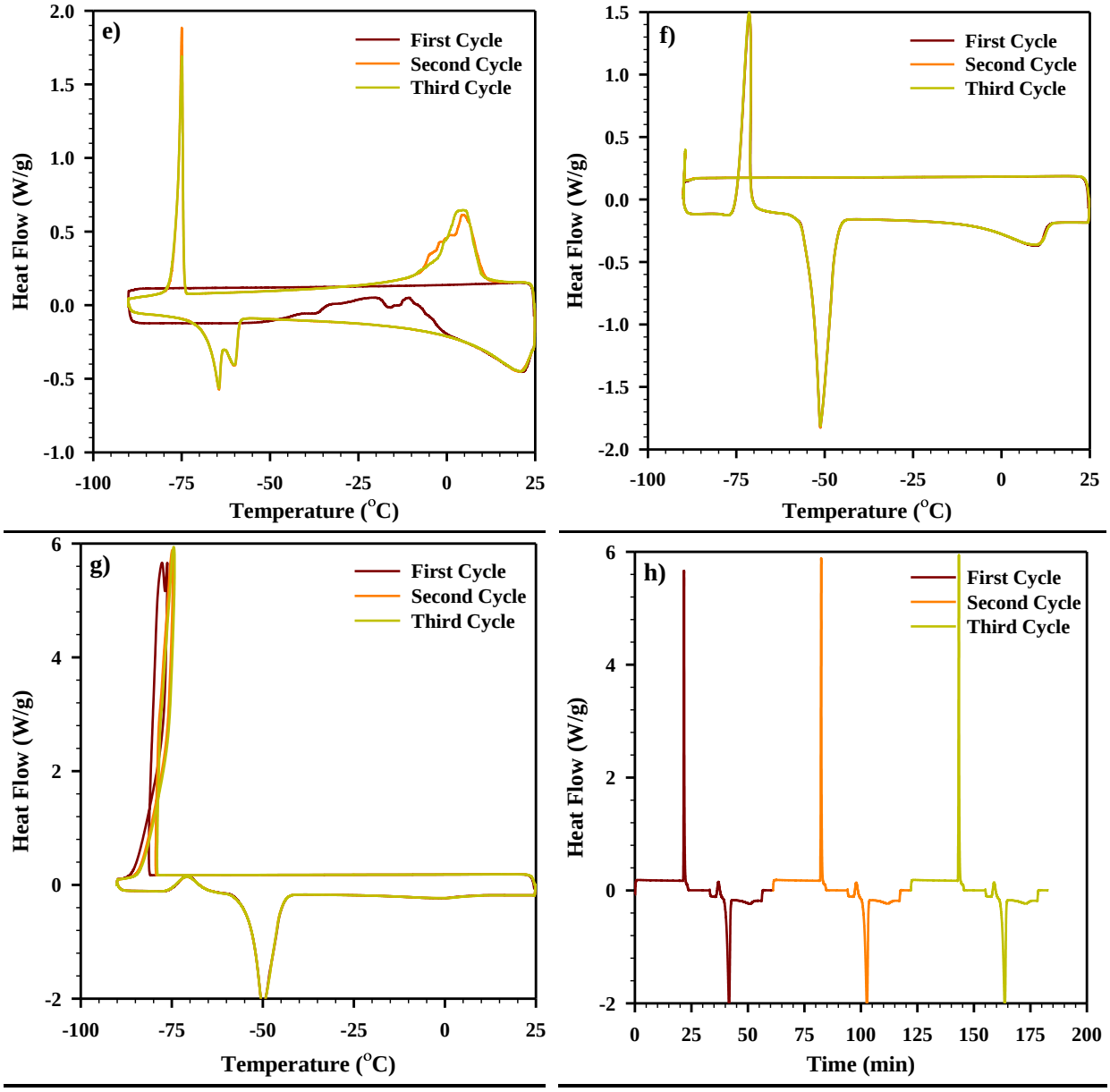

Figure S4 (cont.). DSC of $[C_4NH_3][OAc]$ + C_4NH_2 **e)** χ_{C4NH2} =0.67, **f)** χ_{C4NH2} =0.8, and **g)** χ_{C4NH2} =0.9. (The DSC of C_4NH_2 (χ_{C4NH2} =1) was not recorded due to its volatility at room temperature). **h)** Heat Flow of $[C_4NH_3][OAc]$ + C_4NH_2 (χ_{C4NH2} =0.9) vs. time. Dark brown line: First cycle; Orange line: Second cycle; Lime green line: Third cycle.

4. ^{1}H NMR spectra

$[C_4NH_3][OAc]$ + HOAc system:

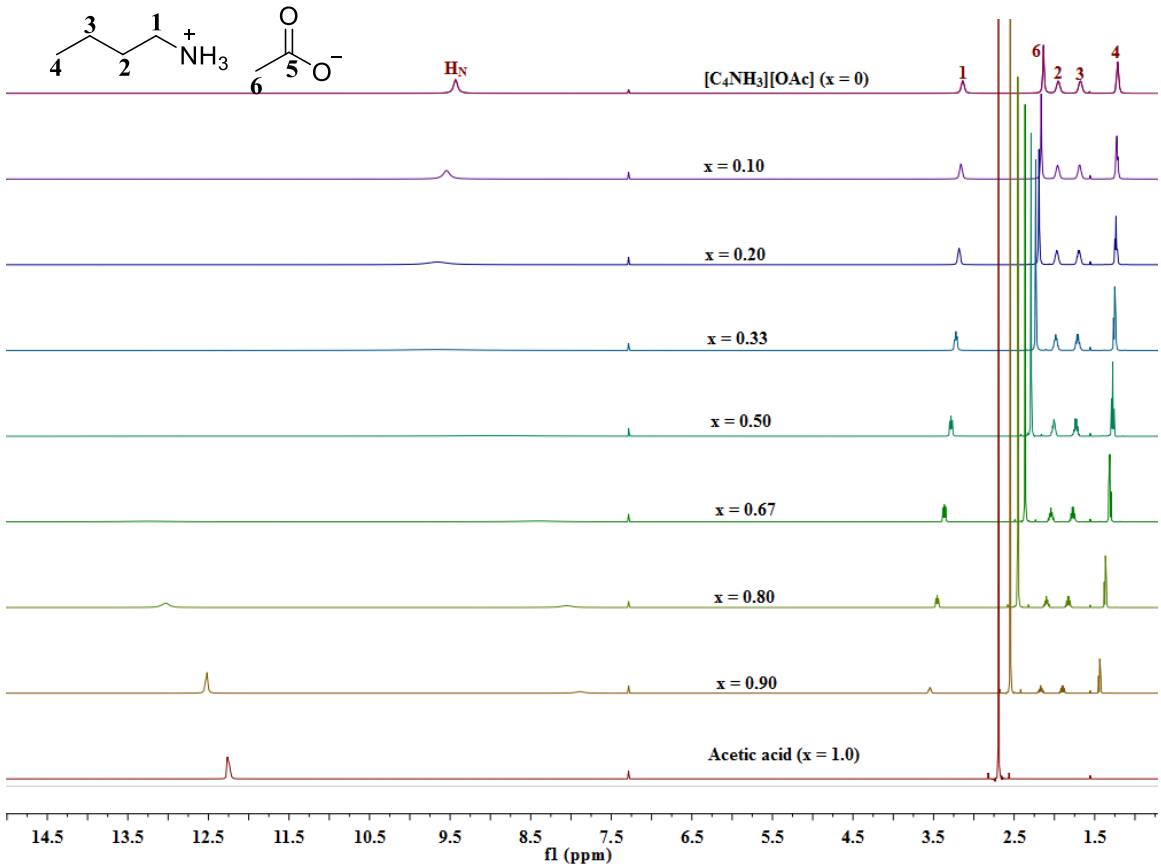

Figure S5. ^{1}H NMR spectra of the mixtures of $[C_4NH_3][OAc]$ + HOAc using $CDCl_3$ as external lock at 25 °C (H_N represents the protons on nitrogen).

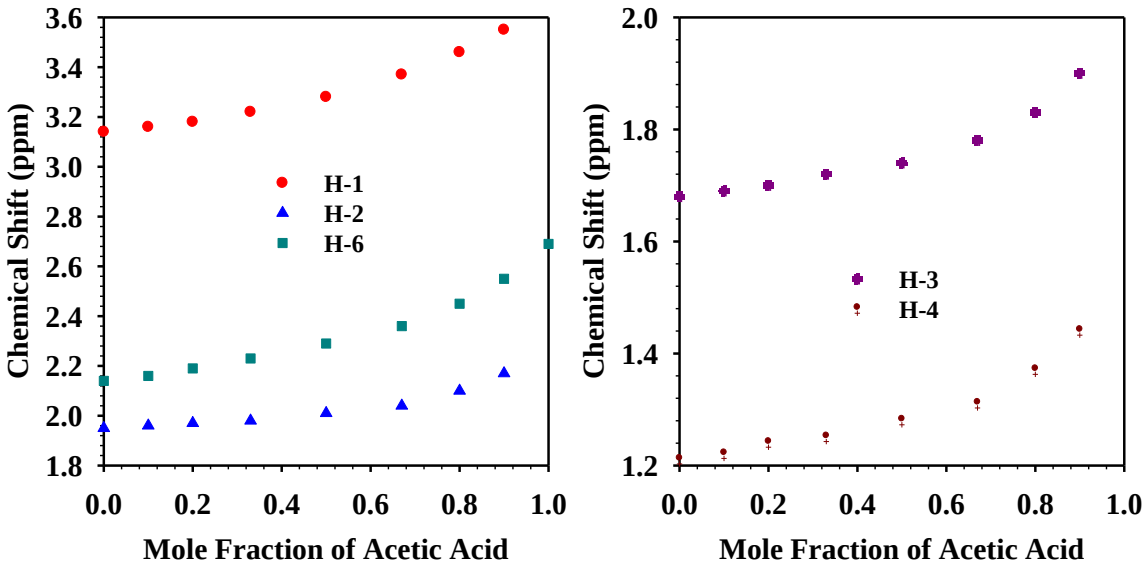

Figure S6. ^{1}H NMR chemical shifts of H-1, H-2, H-3, H-4, and H-6 of the $[C_4NH_3][OAc]$ + HOAc mixtures as a function of HOAc concentration.

$[C_4NH_3][OAc]$ + C_4NH_2 system:

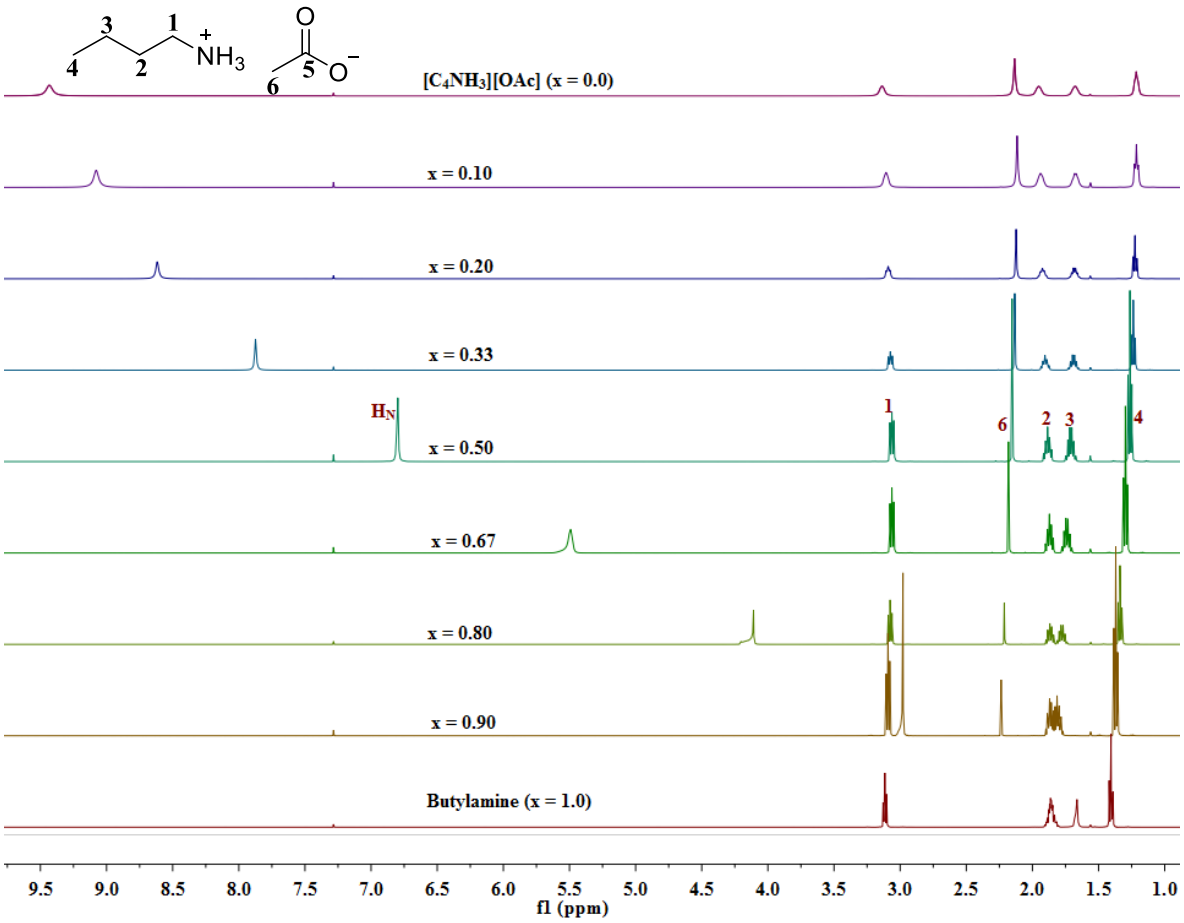

Figure S7. ^{1}H NMR spectra of the mixtures of $[C_4NH_3][OAc]$ + C_4NH_2 using $CDCl_3$ as external lock at 25 °C (H_N represents the protons on nitrogen).

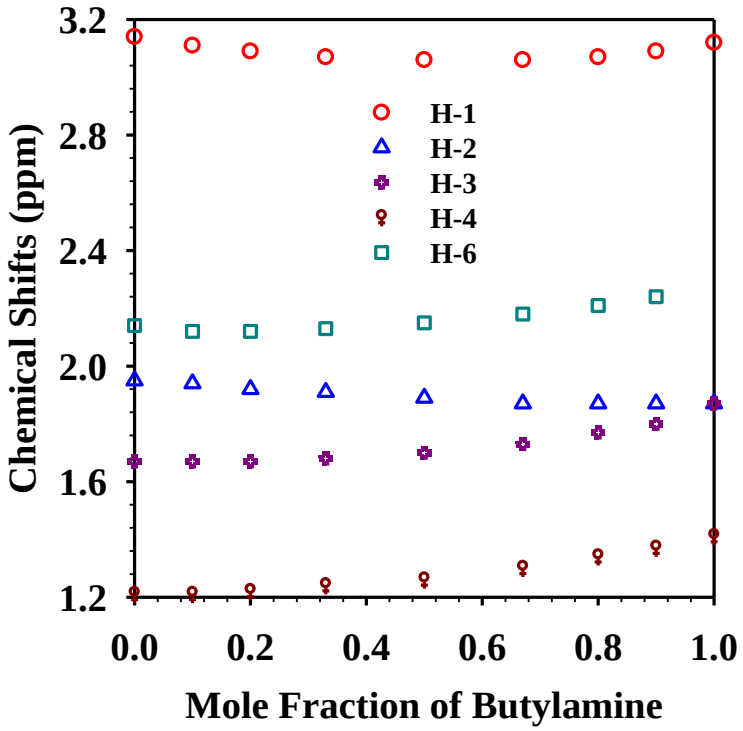

Figure S8. ^{1}H NMR chemical shifts of H-1, H-2, H-3, H-4, and H-6 of the $[C_4NH_3][OAc]$ + C_4NH_2 mixtures as a function of C_4NH_2 concentration.

5. FT-IR spectra

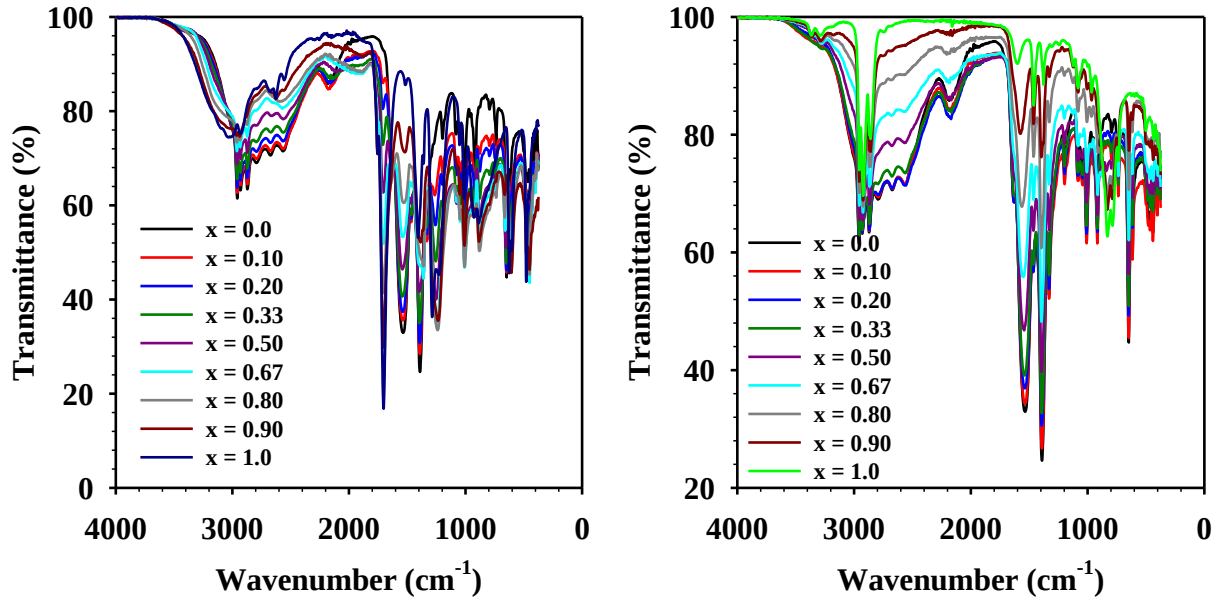

Figure S9. FT-IR spectra of the mixtures of $[C_4NH_3][OAc]$ + HOAc (left) and the mixtures of $[C_4NH_3][OAc]$ + C_4NH_2 (right). (x in the legends represents mole fraction of HOAc or C_4NH_2 in the mixtures.)

6. Solubilities of organics and pharmaceuticals in the mixtures

Table S2. Solubilities of organics in the mixtures.

χ	Solubilities (mol/mol mixture)							
	$[C_4NH_3][OAc]$ + HOAc mixtures*				**$[C_4NH_3][OAc]$ + C_4NH_2 mixtures***			
	Benzene	**EtOAc**	**Heptane**	**Et_2O**	**Benzene**	**EtOAc**	**Heptane**	**Et_2O**
0	0.93	0.65	0.05	0.31	0.93	0.65	0.05	0.31
0.10	1.54	0.88	0.06	0.67	1.13	0.66	0.13	0.38
0.20	2.96	2.61	0.06	0.80	1.43	0.76	0.15	0.45
0.33	Miscible	Miscible	0.07	1.25	2.02	1.20	0.16	0.52
0.50	Miscible	Miscible	0.08	8.66	3.43	1.65	0.24	0.79
0.67	Miscible	Miscible	0.07	Miscible	11.99	2.97	0.43	1.32
0.80	Miscible	Miscible	0.05	Miscible	Miscible	6.88	0.74	1.99
0.90	Miscible	Miscible	0.06	Miscible	Miscible	Miscible	1.29	3.46
1.0	Miscible	Miscible	0.12	Miscible	Miscible	Miscible	Miscible	Miscible

*Miscible: The solution was still clear when the mole ratio of the organic solvent to the IL mixture reached 25:1. *Abbreviations*: EtOAc: ethyl acetate; Et_2O: diethyl ether.

Table S3. Solubilities of active pharmaceutical ingredients in the mixtures.

χ	Solubilities (mol/mol mixture)							
	$[C_4NH_3][OAc]$ + HOAc mixtures*				**$[C_4NH_3][OAc]$ + C_4NH_2 mixtures***			
	IL (mol/mol mixture)	**HOAc** (mol/mol mixture)	**Ibuprofen** (mol/mol mixture)	**HOAc + Ibuprofen** (mol Ibu+HOAc/mol $[OAc]^-$)	**IL** (mol/mol mixture)	**C_4NH_2** (mol/mol mixture)	**Lidocaine** (mol/mol mixture)	**C_4NH_2 + Lidocaine** (mol Lid+ C_4NH_2/mol base)
0	1	**0**	0.15	0.15	1	**0**	0.06	0.06
0.10	0.9	**0.10**	0.80	0.9	0.9	**0.10**	0.08	0.18
0.20	0.8	**0.20**	1.37	1.57	0.8	**0.20**	0.10	0.3
0.33	0.67	**0.33**	1.04	1.37	0.67	**0.33**	0.13	0.46
0.50	0.5	**0.50**	0.72	1.22	0.5	**0.50**	0.28	0.78
0.67	0.33	**0.67**	0.43	1.1	0.33	**0.67**	0.45	1.12
0.80	0.2	**0.80**	0.21	1.01	0.2	**0.80**	0.68	1.48
0.90	0.1	**0.90**	0.19	1.09	0.1	**0.90**	0.78	1.68
1.0	0	**1.0**	0.23	1.23	0	**1.0**	0.93	1.93

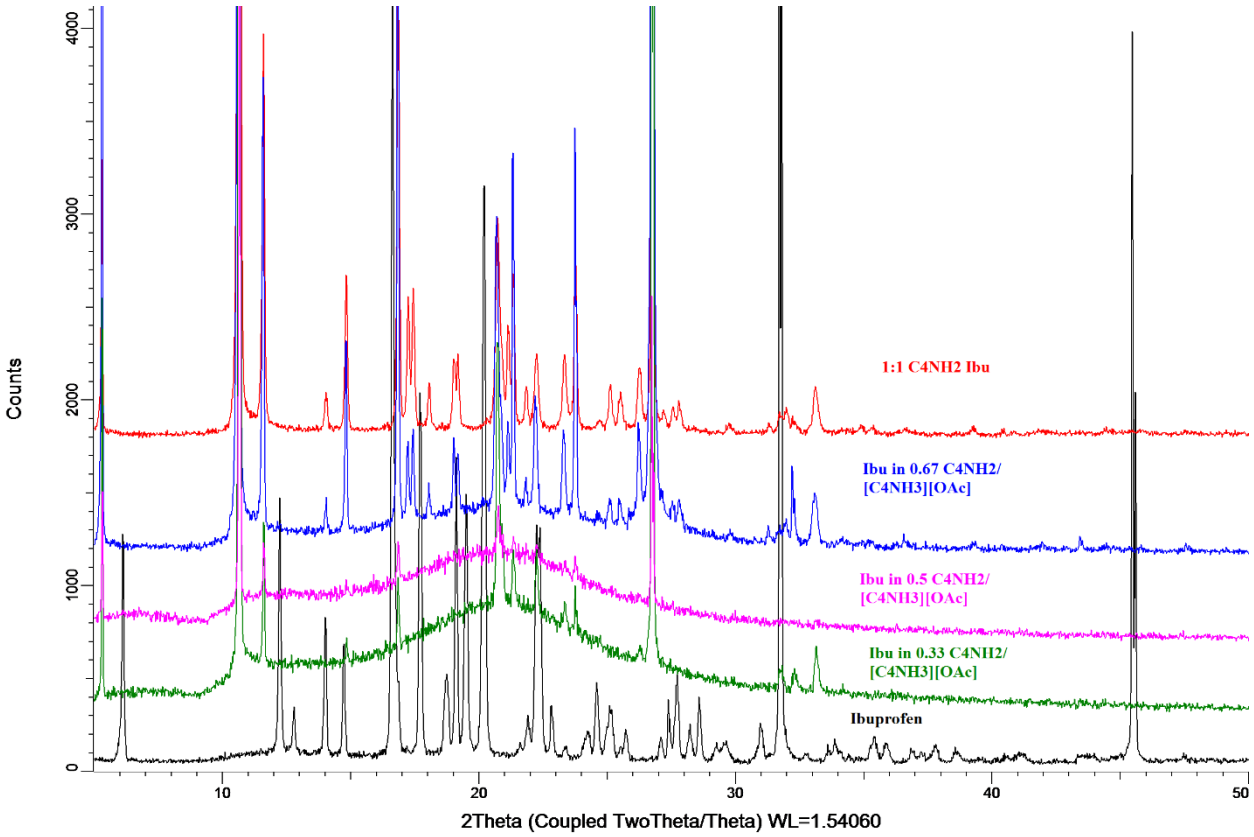

Figure S10. PXRD diffractograms of solids obtained when ibuprofen was added to $[C_4NH_3]$ or to mixtures of $[C_4NH_3][OAc] + C_4NH_2$.

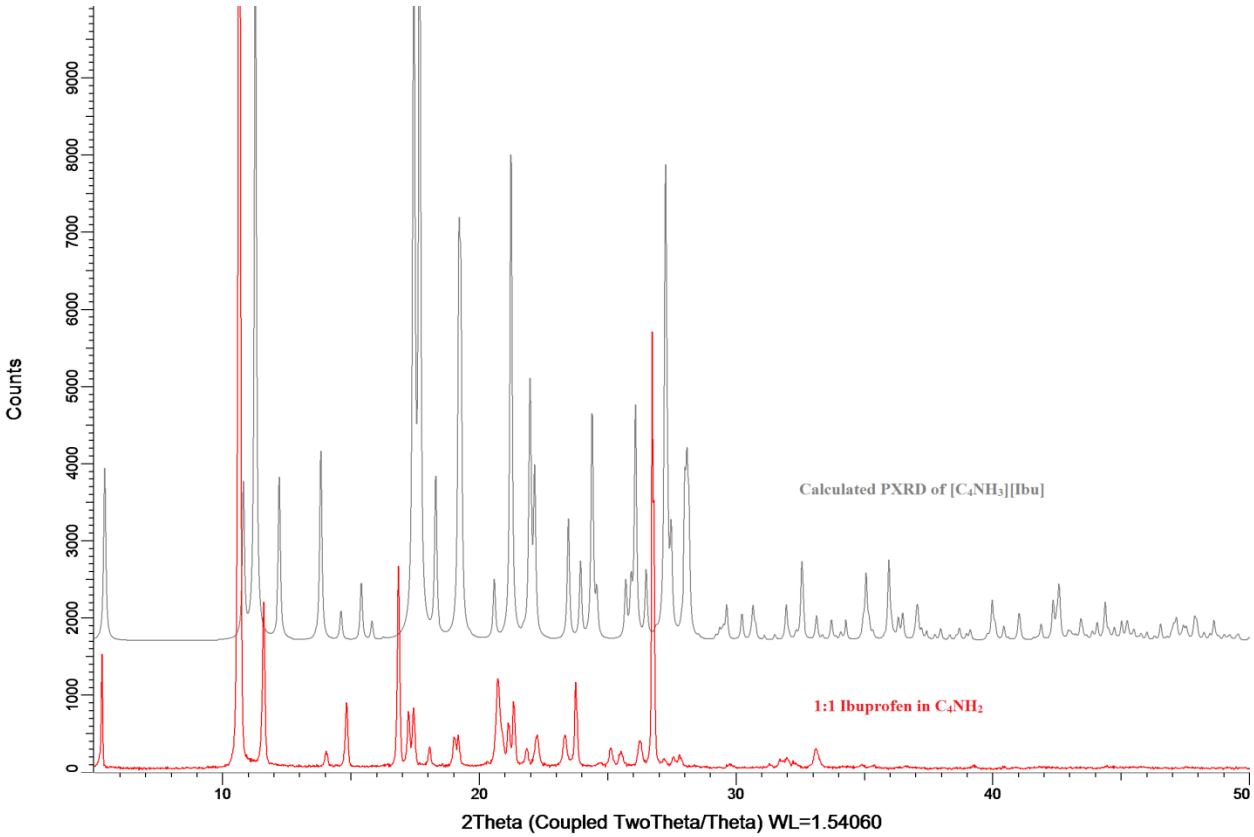

Figure S11. Comparison of measured PXRD of 1:1 C_4NH_2 + Ibuprofen with calculated PXRD pattern of $[C_4NH_3][Ibu]$.

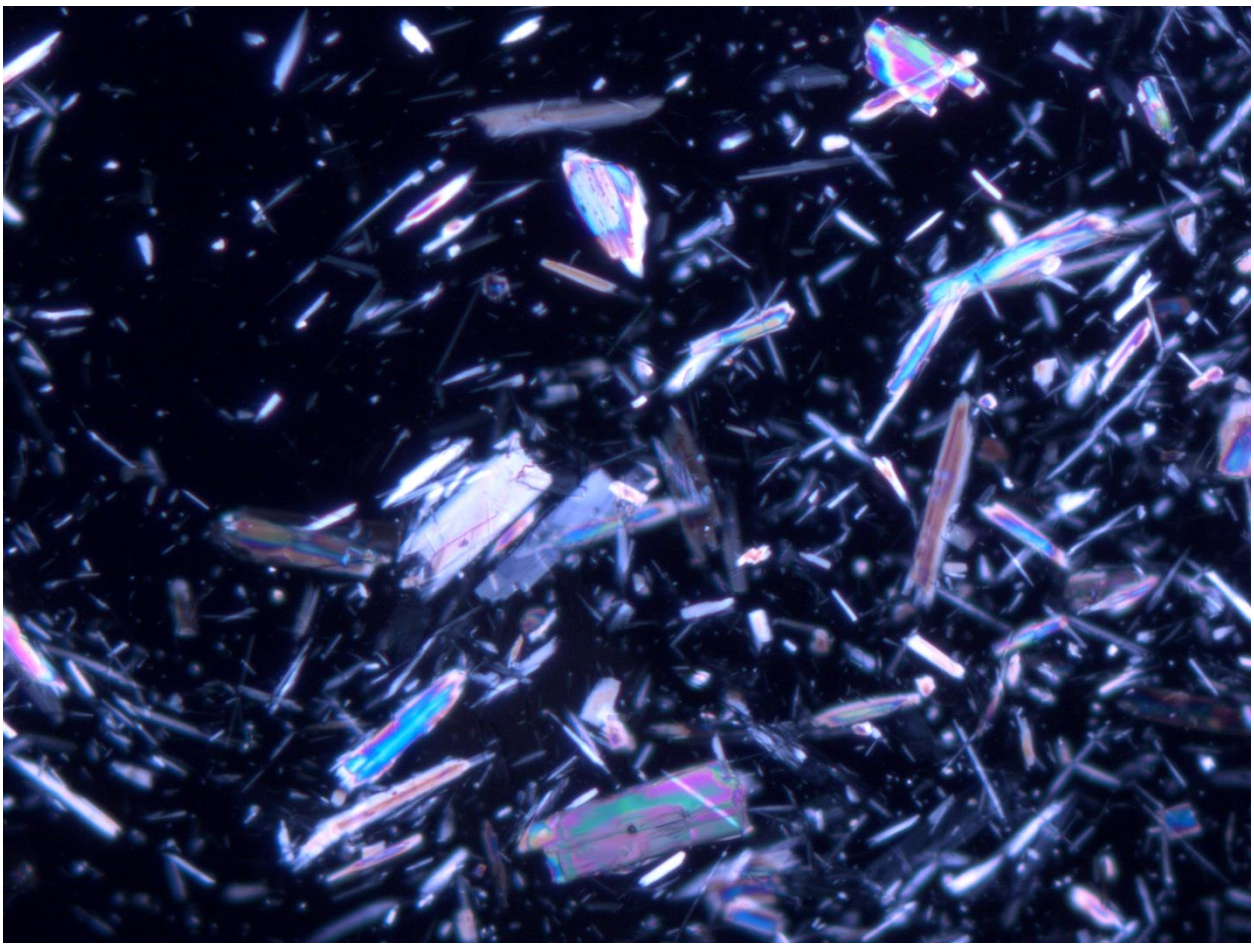

Figure S12. Optical microscope image of crystalline 1:1 ibuprofen in C_4NH_2.

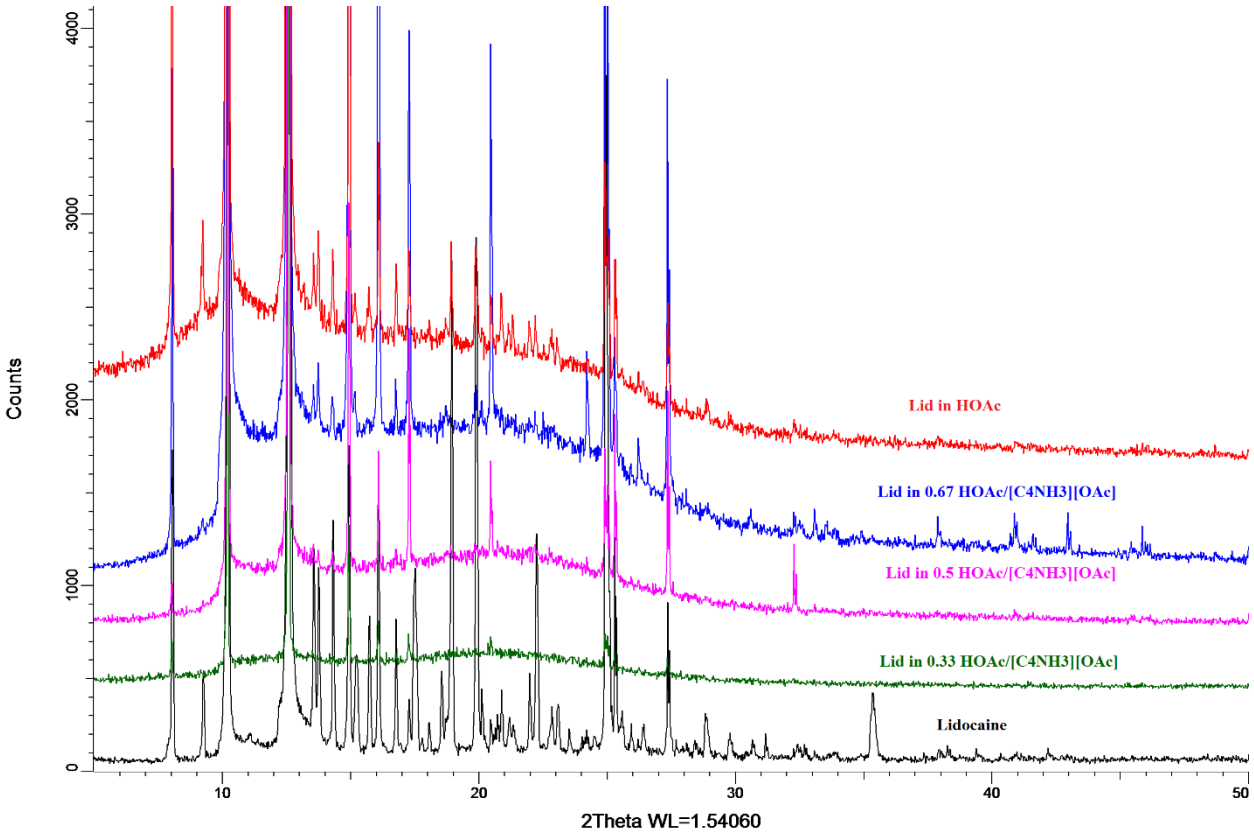

Figure S13. PXRD diffractograms of solids obtained when lidocaine was added to HOAc or to mixtures of $[C_4NH_3][OAc]$ + HOAc.