Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Protic Ionic Liquids (PILs) Nanostructure and Physicochemical Properties: Development of High-Throughput Methodology for PIL Creation and Property Screens

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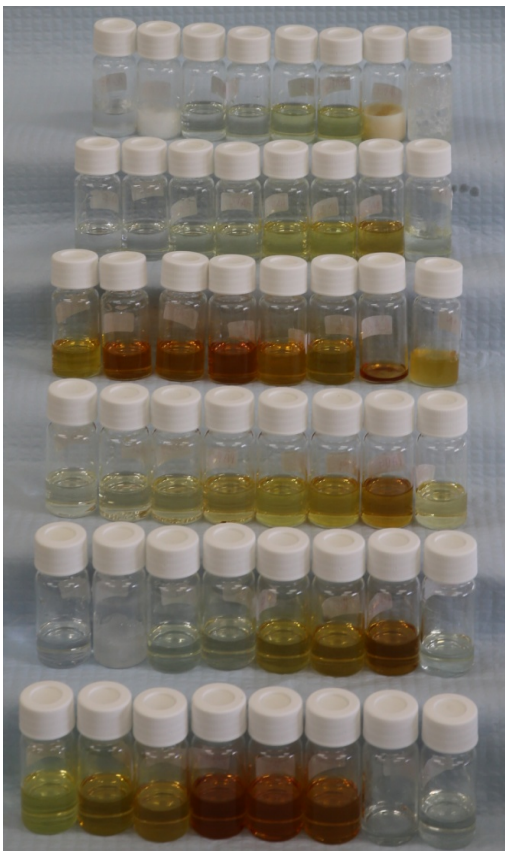


Figure S1. Visual appearance of the 48 acid-base combinations. Left to right the acids are formate, acetate, propanoate, pentanoate, hexanoate, heptanoate, octanoate and nitrate. From bottom to top the amines are ethanolamine, ethylamine, propylamine, pentylamine, hexylamine and octylamine.

Table S1. Amine-methanol stock solutions.

Amine	Volume of amine (ml)	Volume of methanol (ml)
Ethylamine	19.61	9.80
Propylamine	18.56	9.28
Pentylamine	21.06	10.53
Hexylamine	21.76	10.88
Octylamine	23.05	11.52
Ethanolamine	16.27	8.14

Table S2. Volumes dispensed by the Chemspeed robot into each vial for batch 1 and batch 2 of the amine+methanol stocks listed in Table S1, and the acids. All volumes are in ml and are $\pm$ 0.05ml.

Reactor	Ethylamine	Propylamine	Pentylamine	Hexylamine	Octylamine	Ethanolamine	Formate*	Nitrate*	Acetate*	Proponate*	Pentanoate*	Hexanoate*	Heptanoate*	Octanoate*
BATCH 1														
1	7.87						2.13							
2	6.90							3.10						
3	7.13								2.88					
4	6.55									3.46				
5		7.62					2.38							
6		6.59						3.41						
7		6.83							3.17					
8		6.21								3.79				
9			7.98				1.73							
10			7.35					2.65						
11			7.56						2.44					
12			7.02							2.98				
13				7.96			1.54							
14				7.57				2.43						
15				7.76					2.24					
16				7.25						2.75				
17					8.00		1.23							
18					7.97			2.03						
19					7.94				1.81					
20					7.70					2.31				
21						7.03	2.97							
22						5.88		4.13						
23						6.14			3.86					
24						5.47				4.52				
Reactor	Ethylamine	Propylamine	Pentylamine	Hexylamine	Octylamine	Ethanolamine	Formate*	Nitrate*	Acetate*	Proponate*	Pentanoate*	Hexanoate*	Heptanoate*	Octanoate*

BATCH 2														
1	5.62										4.39			
2	5.27											4.74		
3	4.98												5.02	
4	4.70													5.30
5		5.26									4.73			
6		4.91										5.09		
7		4.63											5.37	
8		4.35												5.65
9			6.15								3.85			
10			5.81									4.19		
11			5.53										4.47	
12			5.25											4.75
13				6.42							3.58			
14				6.09								3.92		
15				5.81									4.19	
16				5.54										4.47
17					6.93						3.07			
18					6.62							3.38		
19					6.36								3.64	
20					6.10									3.90
21						4.51					5.49			
22						4.16						5.84		
23						3.89							6.12	
24						3.62								6.38

* Acid was delivered in a “dropwise” manner by using a dispense rate of 0.1 mL/min. This resulted in acid addition over 40-60 minutes depending on the total volume.

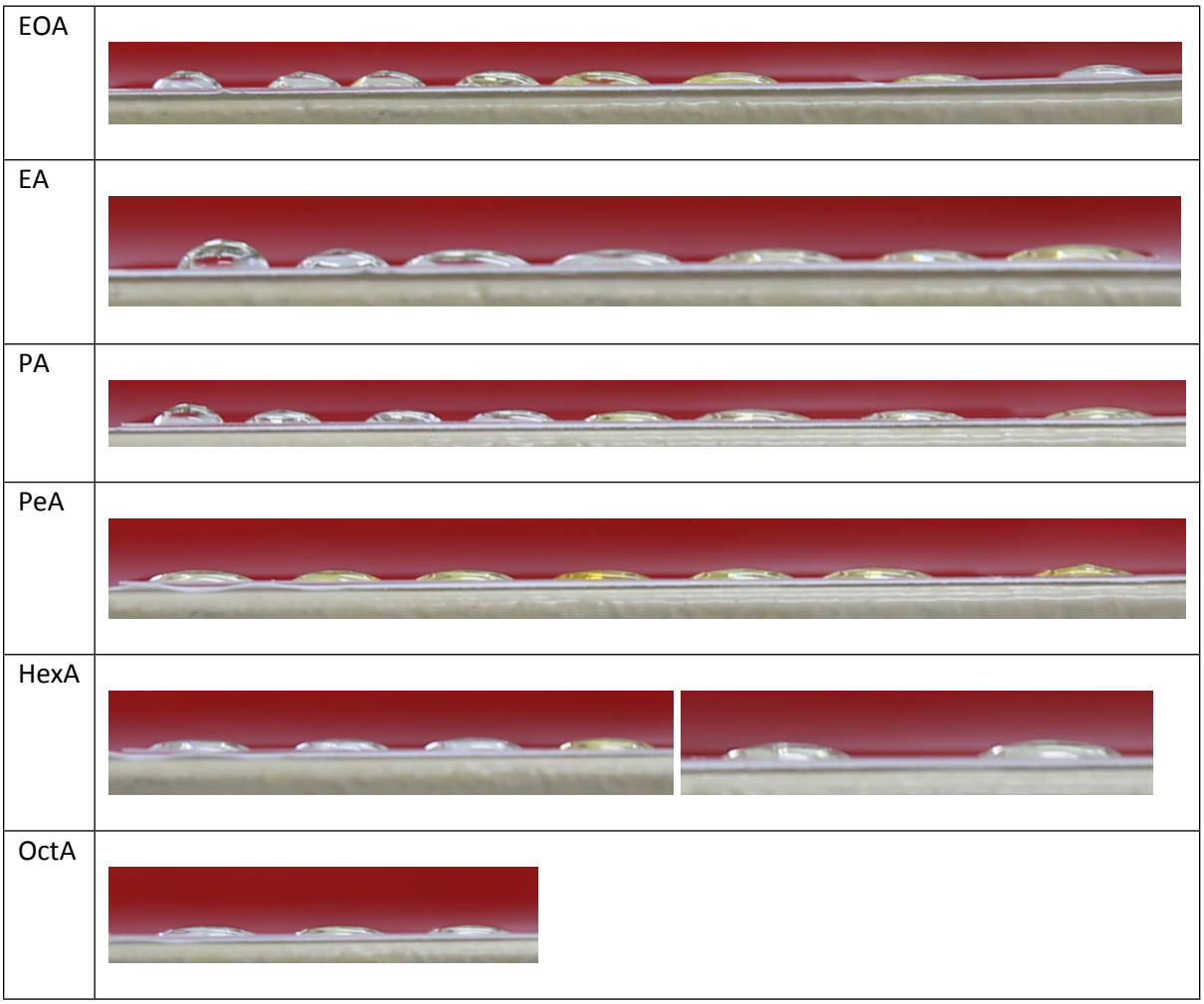


Figure S2. Photographs of the side profiles of the droplets for each liquid acid-base combination on glass slides. The amines are listed on the left hand side. From left to right the acids are nitrate, formate, propanoate, pentanoate, hexanoate, heptanoate and octanoate. Samples which were solid or gel are omitted from the series, so that only those which are categorised as 'liquid' and light blue in Figure 3 are included.

Table S3. Peak positions and corresponding correlation distances from the SAXS/WAXS patterns of the acid-base combinations. SAXS/WAXS patterns were acquired at 25 °C unless otherwise stated.

PIL	**peak 1 (Å^{-1})**	**peak 2 (Å^{-1})**	**d_1(Å)**	**d_2(Å)**
EAF	0.78[d]	1.69	8.07	3.72
EAA [a]	0.68[d]	1.55	9.24	4.05
EAP	0.63	1.55	10.04	4.05
EAPe	0.46	1.51	13.53	4.16

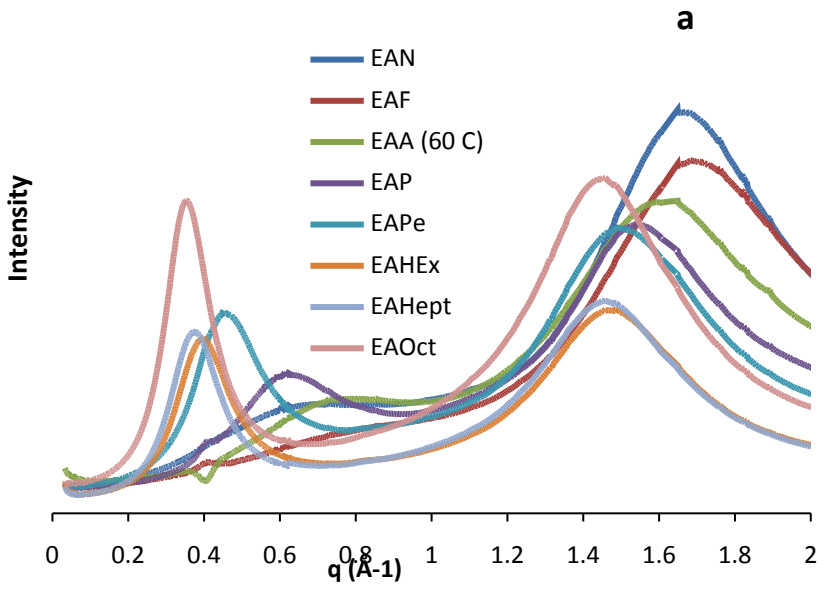
EAH	0.40	1.48	15.60	4.26
EAHep	0.38	1.46	16.55	4.30
EAO	0.36	1.45	17.48	4.32
EAN	0.67[d]	1.66	9.40	3.77
PAF	0.58[d]	1.62	10.87	3.89
PAA	0.64	1.55	9.79	4.05
PAP	0.50	1.49	12.64	4.21
PAPe	0.50	1.49	12.64	4.21
PAH	0.45	1.48	13.93	4.25
PAHep	0.41	1.46	15.25	4.30
PAO	0.39	1.45	16.25	4.33
PAN	0.53	1.62	11.88	3.87
PeAF	0.41	1.54	15.25	4.08
PeAA	0.47	1.50	13.27	4.18
PeAP	0.50	1.48	12.48	4.25
PeAPe	0.46	1.46	13.59	4.30
PeAH	0.44	1.46	14.25	4.30
PeAHep	0.41	1.44	15.18	4.36
PeAN [a]	0.39	1.51	16.07	4.15
HAF	0.37	1.51	16.93	4.15
HAA	0.42	1.48	15.00	4.23
HAP	0.46	1.47	13.66	4.28
HAPe	0.44	1.46	14.20	4.31
HAH	0.42	1.45	14.99	4.35
HAHep	0.40	1.44	15.73	4.38
HAO [a]	0.37	1.37	16.98	4.59
HAN [a]	[b]	1.44	[b]	4.36
OAF [a]	[b]	1.41	[b]	4.46
OAA [a]	0.33	1.42	19.04	4.42
OAP	0.39	1.45	16.16	4.33
OAPe	0.39	1.44	16.07	4.36
OAH	0.38	1.44	16.63	4.38
OAHep [a]	0.37	1.40	17.18	4.48
OAO [a]	0.36	1.40	17.52	4.50
EOAF	[c]	1.65	[c]	3.80
EOAA	0.68 [d]	1.53	9.24	4.11
EOAP	0.54	1.54	11.63	4.07
EOAPe	0.40	1.51	15.61	4.16
EOAH	0.36	1.49	17.38	4.22
EOAHep	0.34	1.47	18.61	4.26
EOAN	[c]	1.66	[c]	3.77

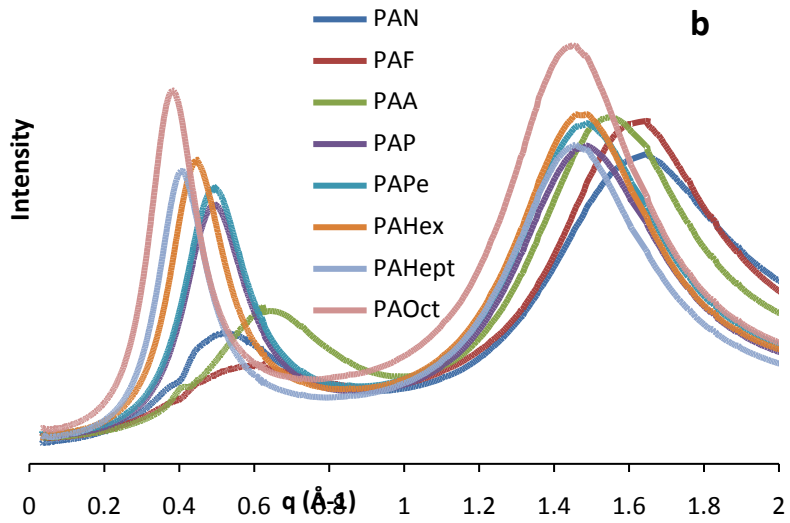
[a] Data acquired at 60 °C, [b] At 25 and 60 °C OctAF and HAN each had one intense, sharp peak at low q at 0.31 and 0.36 $Å^{-1}$ respectively, attributed as a liquid crystalline lamellar phase, [c] No low q peak observable, [d] Peak poorly defined.

Table S4. Peak positions and corresponding correlation distances from the SAXS/WAXS patterns of a selection of the precursor acids. SAXS/WAXS patterns were acquired at 25 °C.

Acid	peak 1 ($Å^{-1}$)	peak 2 ($Å^{-1}$)	d_1(Å)	d_2(Å)
formic	[a]	1.76		3.58
acetic	0.93	1.54	6.76	4.07
propionic	0.79	1.45	7.95	4.32
hexanoic	0.50	1.42	12.62	4.43
heptanoic	0.46	1.41	13.76	4.47

[a] No low q peak observable





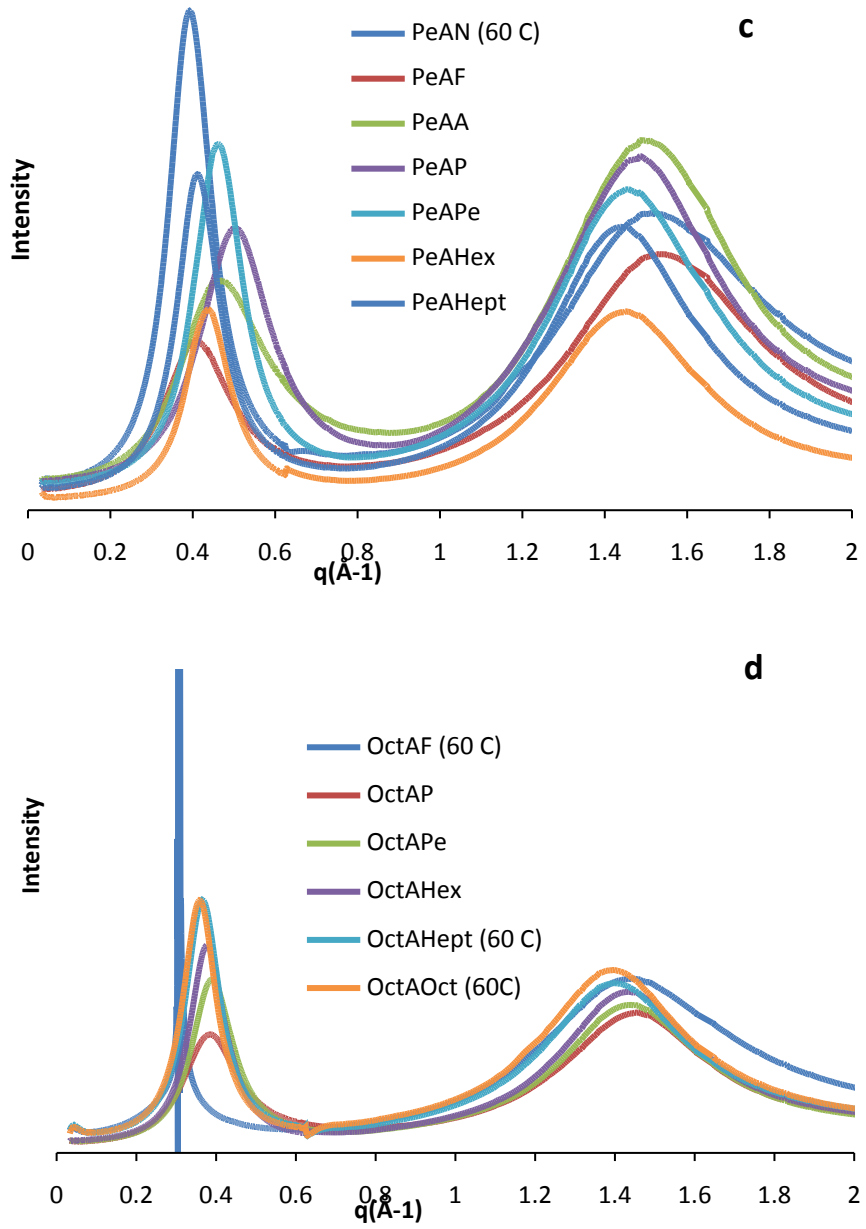


Figure S3. SAXS/WAXS patterns for the PIL series with the same cation paired with the different anions for a) ethylammonium, b) propylammonium, c) pentylammonium and d) octylammonium. All patterns acquired at 25 °C unless otherwise stated. The sharp peak present for OctAF has been truncated.