Is it possible to create ternary-like aqueous biphasic systems with deep eutectic solvents?

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12 Pages, 6 Figures, 5 Tables

Table S1. Experimental binodal weight fraction (wt %) data for the systems composed of $[N_{111(2OH)}]$Cl:Glucose + PPG + H_2O at 298.15 K and atmospheric pressure.

$[N_{111(2OH)}]$Cl:Glucose (2:1)	PPG	$[N_{111(2OH)}]$Cl:Glucose (1.1)	PPG	$[N_{111(2OH)}]$Cl:Glucose (1:2)	PPG
0.5	78.5	0.6	78.8	1.1	77.1
1.4	74.9	1.4	74.8	3.2	66.8
2.3	68.5	2.3	68.5	4.4	60.4
2.9	65.0	2.9	65.1	5.3	56.2
3.6	61.8	3.6	61.9	6.3	52.6
4.8	56.4	4.7	56.9	8.2	47.2
5.2	54.3	5.2	54.3	9.0	43.5
6.1	50.1	6.0	50.0	9.7	41.1
6.4	48.0	6.9	44.8	10.5	38.5
6.9	44.8	7.6	42.4	11.9	33.5
7.5	42.4	8.3	38.6	13.1	28.9
7.8	40.4	10.6	32.3	13.9	27.0
8.3	38.6	12.1	29.9	14.6	25.5
8.9	36.2	13.2	27.6	15.5	23.9
9.3	34.0	14.8	24.2	16.6	21.9
10.2	30.8	16.3	21.6	17.6	20.5
11.0	29.1	18.1	18.5	18.8	18.8
12.9	25.5	19.9	15.7	19.8	17.3
13.6	23.6	20.9	15.1	20.1	16.5
16.8	17.8	22.9	13.4	21.6	15.2
19.9	12.1	25.1	13.0	23.4	13.7
23.1	10.8	26.6	11.9	32.4	8.7
25.6	9.7	30.3	10.0	40.0	5.3
26.6	9.2	33.8	8.4	48.6	2.3
29.4	8.5	39.7	7.1		
32.7	7.2	48.0	3.1		

Figure S1. Binodal curves representation as function of glucose concentration in ABS composed of PPG, water and mixtures of [$N_{111(2OH)}$]Cl and glucose at different molar ratios – 2:1 (🟦), 1:1 (●) and 1:2 (▲) – and glucose, PPG and water (▼) at 298 K and atmospheric pressure

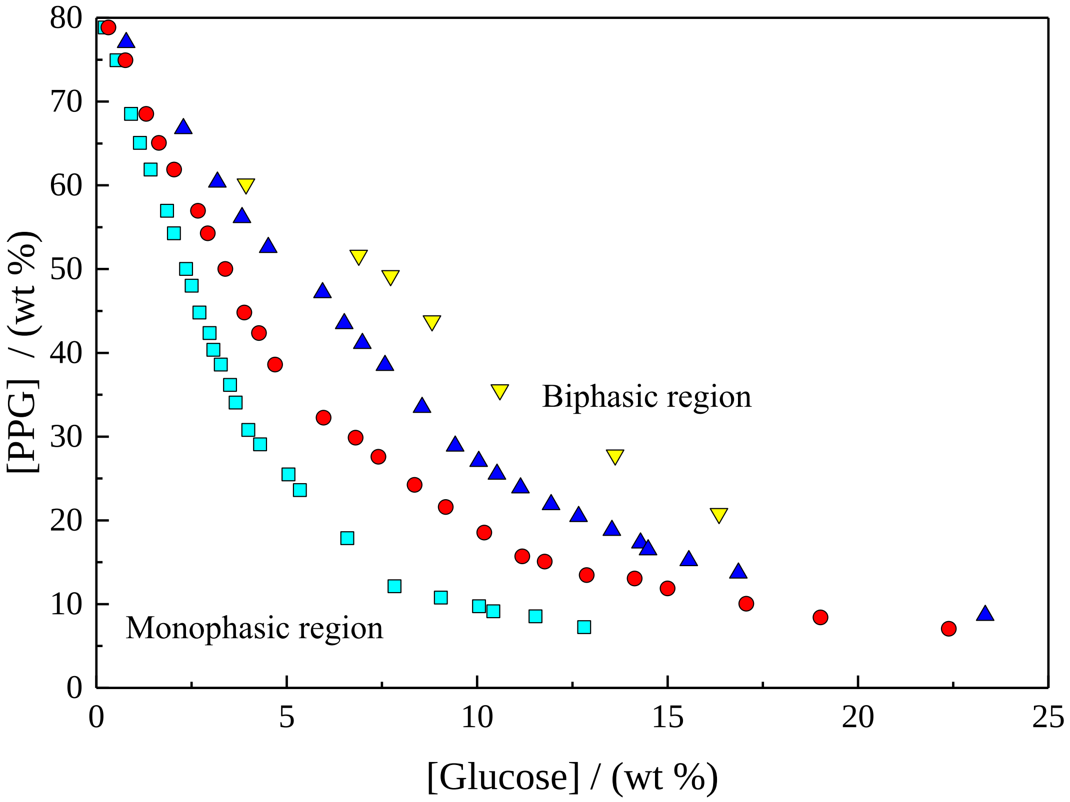

Figure S2. Three-dimensional phase diagram of ABS composed of PPG, water and mixtures of $[N_{111(2OH)}]Cl$ and glucose at different molar ratios — 2:1 (●), 1:1 (●) and 1:2 (●) – $[N_{111(2OH)}]Cl$, PPG, and water (●)^{1} and glucose, and glucose , PPG and water (●) at 298 K and atmospheric pressure.

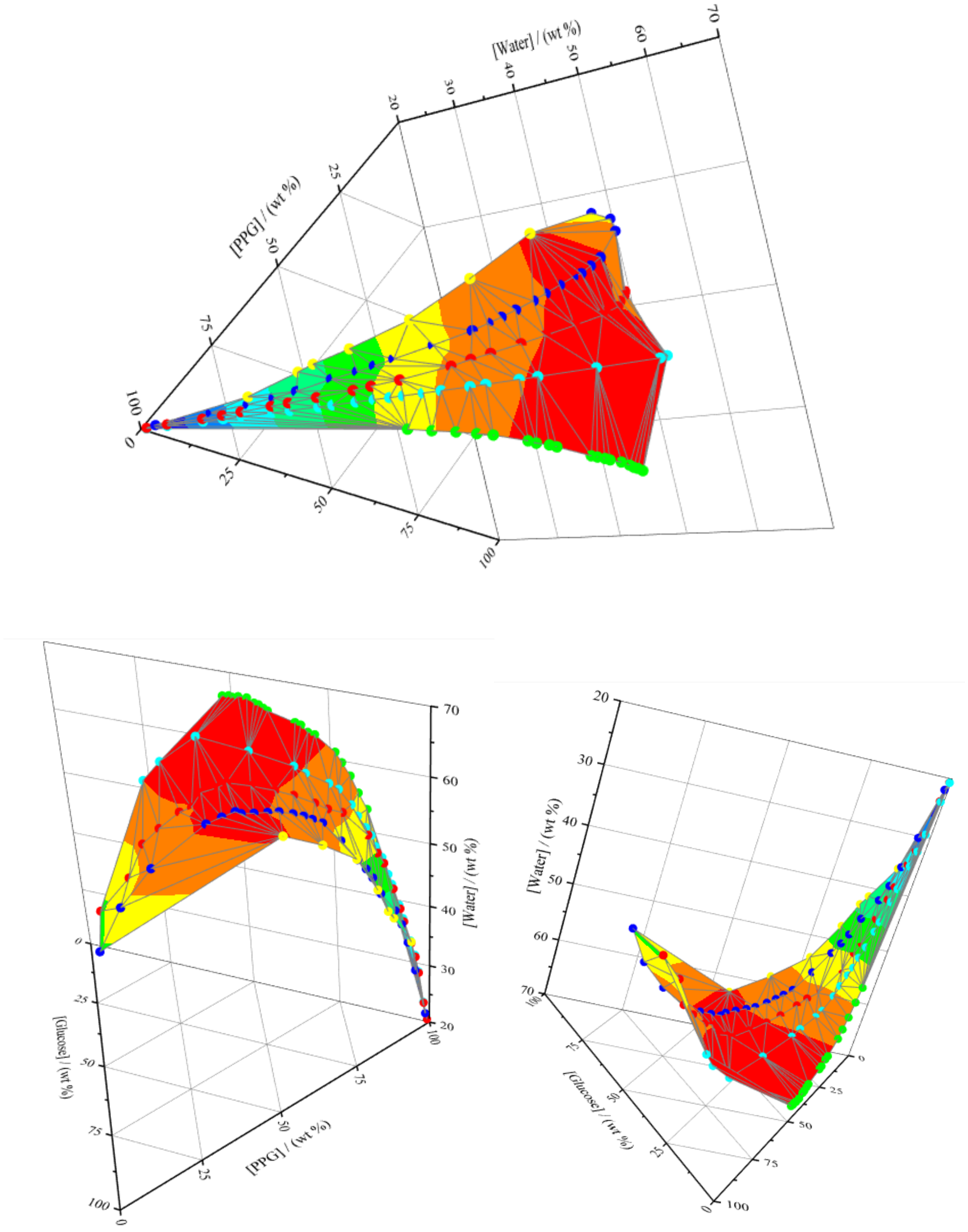

Figure S3. Three-dimensional phase diagram and respective tie-lines (those used in biomolecules partition) of ABS composed of PPG, water and mixtures of $[N_{111(2OH)}]Cl$ and glucose at different molar ratios – 2:1 (●), 1:1 (●) and 1:2 (●) – $[N_{111(2OH)}]Cl$, PPG, and water (●),[1] and glucose, PPG and water (●) at 298 K and atmospheric pressure.

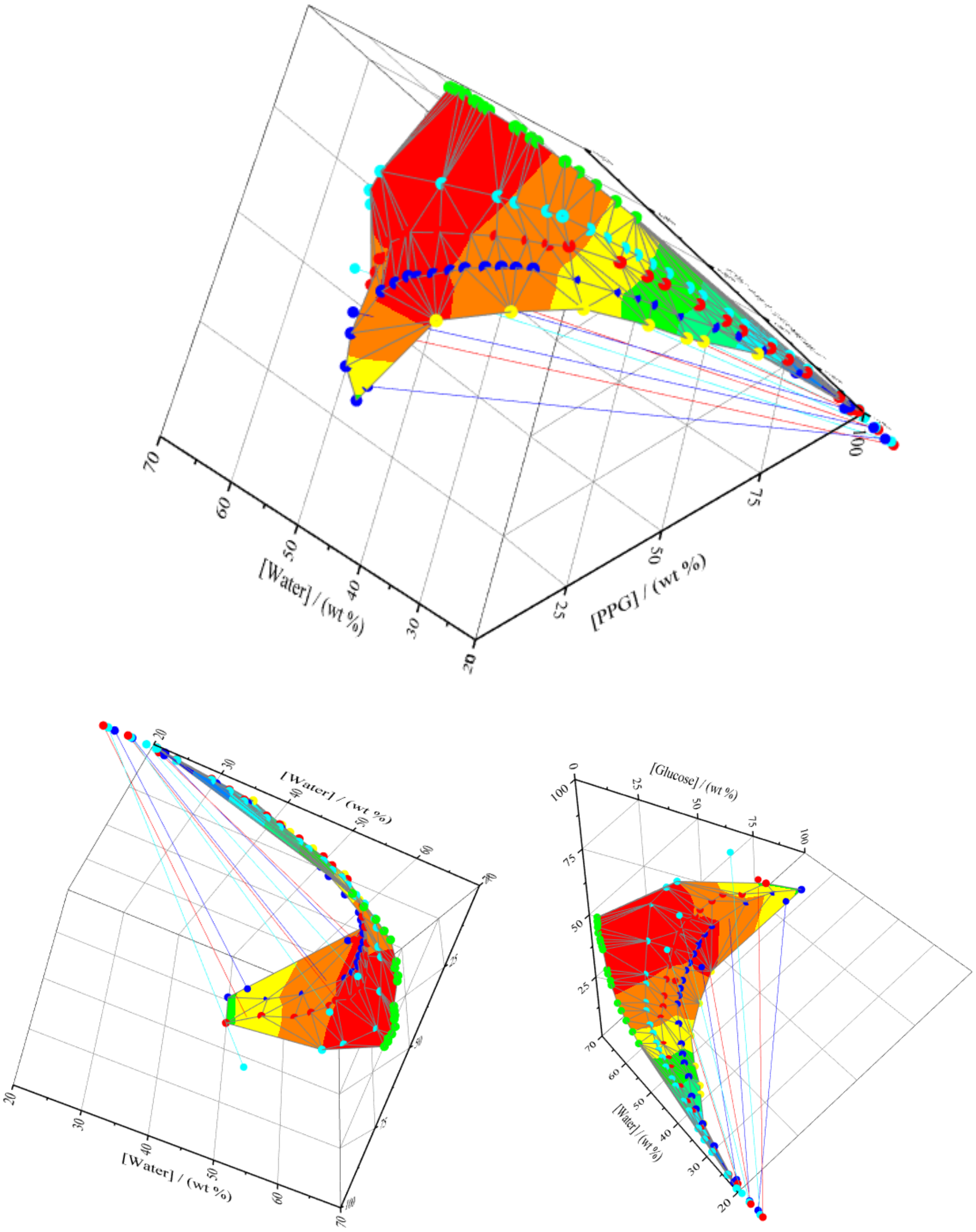

Table S2. Critical point of quaternary systems composed of $[N_{111(2OH)}]Cl$ + glucose or urea (HBD) + PPG + H_2O.

HBA:HBD molar ratio	f	g	R^2	Critical point / wt %	
				$[N_{111(2OH)}]Cl$:HBD	[PPG]
			glucose		
2:1	0.23	76.41	0.77	1.2	76.7
1:1	0.33	72.61	0.89	1.5	73.7
1:2	0.38	71.1	0.77	2.1	71.1
			urea		
2:1	0.24	78.93	0.81	2.6	79.5
1:1	0.30	75.33	0.81	3.4	76.4
1:2	0.27	73.10	0.81	4.3	74.3

Figure S4. Geometrical approach to critical point determination using **Equation 9** for the quaternary system $[N_{111(2OH)}]Cl$ + glucose + PPG + H_2O at 298 K at 1:1 $[N_{111(2OH)}]Cl$:glucose molar ratio. Binodal curve (●), tie-lines overall composition (▲), tie-lines phases composition (■), (−) adjusted binodal data, tie-lines relation (■) and critical point (●).

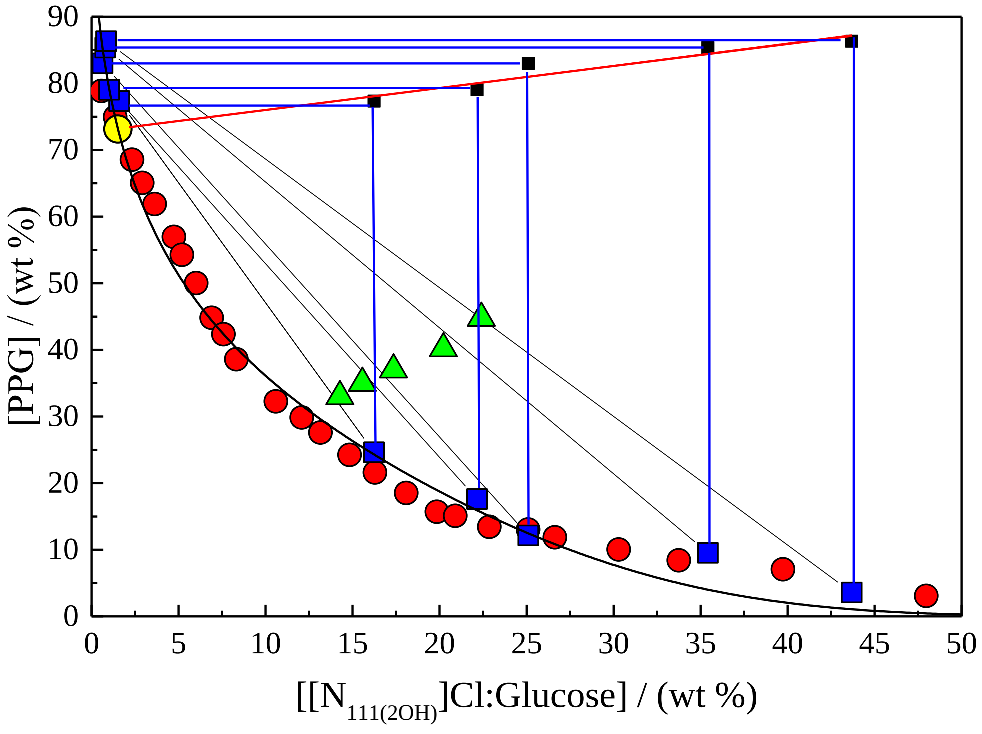

Figure S5. Phase diagrams for the quaternary systems composed of [N$_{111(2OH)}$]Cl + urea + PPG + H_2O at 298 K and different [N$_{111(2OH)}$]Cl:urea molar ratios: (A) 2:1; (B) 1:1; (C) 1:2. Binodal curve (●),[2] tie-line overall composition (▲), tie-line phases composition (■) and critical point (●).

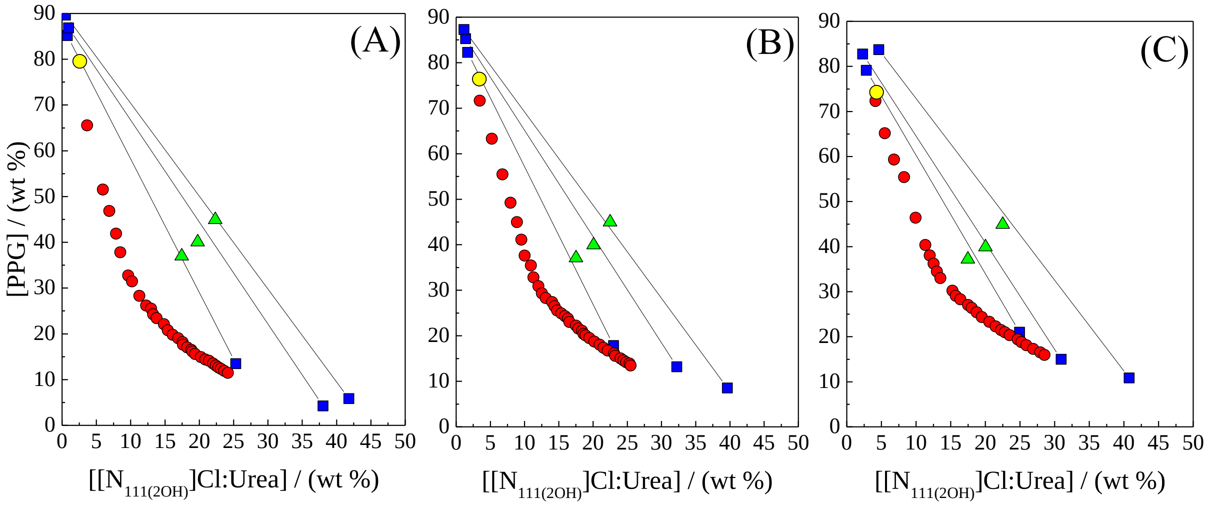

Figure S6. Molar ratio between the HBA ([$N_{111(2OH)}$]Cl) and the HBD (urea) in the coexisting phases of ABS composed of [$N_{111(2OH)}$]Cl + urea + PPG + H_2O (solid lines) and in the initial mixture composition (dashed line): 2:1 (🟦); 1:1 (●); 1:2 (▲).

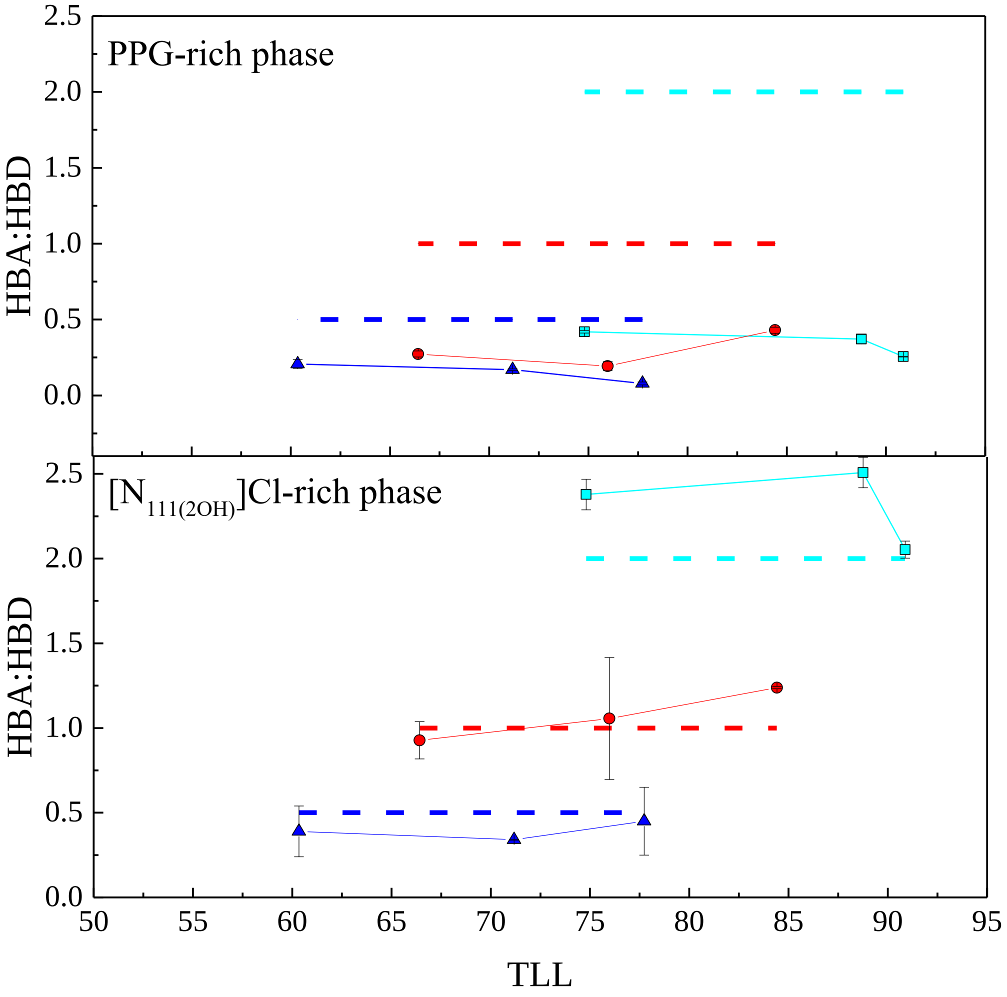

Table S3. Molar ration between the HBA ($[N_{111(2OH)}]Cl$) and the HBD (glucose or urea) in the coexisting phases of ATPS composed of PPG, water and mixtures of $[N_{111(2OH)}]Cl$ and glucose or urea.

HBA:HBD molar ratio	Overall composition / wt %		HBA/HBD (mol/mol)		TLL
	[HBA:HBD]	[PPG]	PPG-rich phase	$[N_{111(2OH)}]Cl$-rich phase	
			Glucose (HBD)		
2:1	14.0	33.0	1.04 ± 0.10	1.39 ± 0.14	62.2
1:1			0.51 ± 0.08	0.89 ± 0.17	53.7
1:2			0.25 ± 0.08	0.39 ± 0.08	56.6
2:1	15.0	35.0	0.68 ± 0.08	1.63 ± 0.12	63.5
1:1			0.67 ± 0.12	0.79 ± 0.11	63.3
1:2			0.45 ± 0.12	0.34 ± 0.07	60.0
2:1	17.5	37.0	0.97 ± 0.23	1.63 ± 0.08	71.0
1:1			0.64 ± 0.08	0.89 ± 0.06	73.0
1:2			0.32 ± 0.09	0.45 ± 0.13	74.1
2:1	20.0	40.0	0.91 ± 0.15	1.81 ± 0.12	81.7
1:1			1.01 ± 0.27	0.89 ± 0.09	79.8
1:2			0.39 ± 0.13	0.52 ± 0.10	81.7
2:1	22.5	45.0	1.31 ± 0.18	1.64 ± 0.15	91.3
1:1			0.85 ± 0.11	0.90 ± 0.08	88.3
1:2			0.32 ± 0.14	0.47 ± 0.06	85.3
			Urea (HBD)		
2:1	17.5	37.0	0.42 ± 0.01	2.38 ± 0.09	74.8
1:1			0.27 ± 0.02	0.93 ± 0.11	66.4
1:2			0.21 ± 0.03	0.61 ± 0.15	60.3
2:1	20.0	40.0	0.37 ± 0.03	2.51 ± 0.09	88.8
1:1			0.19 ± 0.03	1.06 ± 0.36	76.0
1:2			0.17 ± 0.00	0.86 ± 0.00	71.2
2:1	22.5	45.0	0.26 ± 0.00	2.05 ± 0.05	90.9
1:1			0.43 ± 0.02	1.24 ± 0.01	84.4
1:2			0.08 ± 0.01	0.68 ± 0.20	77.7

Table S4. pH measurements and *α* parameter (ratio between the PPG-rich phase and $[N_{111(2OH)}]Cl$-rich phase) of the tie-lines applied to the partition assays for the $[N_{111(2OH)}]Cl$ (HBA) + glucose (HBD) + PPG + H_2O systems at 298.15 K and atmospheric pressure.

HBA:HBD molar ratio	Overall Composition (wt %)		pH		α
	[HBA:HBD]	[PPG]	$[N_{111(2OH)}]Cl$-rich phase	PPG-rich phase	
2:1	14.0	33.0	7.82	7.10	0.25
1:1			7.51	6.88	0.20
1:2			7.23	7.43	0.21
2:1	17.5	37.0	6.94	6.80	0.47
1:1			6.61	7.14	0.55
1:2			6.88	6.70	0.53
2:1	22.5	45.0	7.03	6.77	0.84
1:1			6.92	7.10	0.87
1:2			6.82	6.67	0.88

Table S5. Partition coefficient (*K*) and extraction efficiency (*EE* %) of studied biomolecules in ABS composed of $[N_{111(2OH)}]Cl$ (HBA) + glucose (HBD) + PPG + H_2O systems.

HBA:HBD molar ratio	Overall Composition (wt %)		*K*	*EE* % $[N_{111(2OH)}]Cl$ - rich phase
	[HBA:HBD]	[PPG]		
L-Phenylalanine				
2:1	14.0	33.0	1.41 ± 0.04	84.86 ± 0.37
	17.5	37.0	1.52 ± 0.03	76.44 ± 0.37
	22.5	45.0	1.51 ± 0.08	64.08 ± 1.16
1:1	14.0	33.0	1.27 ± 0.05	86.69 ± 0.48
	17.5	37.0	1.48 ± 0.03	73.05 ± 0.38
	22.5	45.0	1.62 ± 0.04	65.02 ± 0.57
1:2	14.0	33.0	1.33 ± 0.05	86.58 ± 0.42
	17.5	37.0	1.45 ± 0.03	73.27 ± 0.36
	22.5	45.0	1.42 ± 0.02	61.65 ± 0.37
L-Tryptophan				
2:1	14.0	33.0	1.67 ± 0.16	86.83 ± 1.18
	17.5	37.0	3.12 ± 0.26	86.94 ± 0.95
	22.5	45.0	3.60 ± 0.01	81.00 ± 0.06
1:1	14.0	33.0	1.89 ± 0.17	90.59 ± 0.75
	17.5	37.0	2.45 ± 0.19	81.75 ± 1.18
	22.5	45.0	2.90 ± 0.30	76.79 ± 2.12
1:2	14.0	33.0	1.67 ± 0.11	88.96 ± 0.65
	17.5	37.0	2.32 ± 0.03	81.40 ± 0.18
	22.5	45.0	2.06 ± 0.13	70.05 ± 1.28
L-Tyrosine				
2:1	14.0	33.0	0.93 ± 0.08	78.57 ± 1.48
	17.5	37.0	1.36 ± 0.03	74.47 ± 0.47
	22.5	45.0	1.11 ± 0.02	56.80 ± 0.36
1:1	14.0	33.0	0.99 ± 0.02	83.55 ± 0.27
	17.5	37.0	1.25 ± 0.07	69.61 ± 1.12
	22.5	45.0	1.33 ± 0.05	60.36 ± 0.88
1:2	14.0	33.0	0.89 ± 0.02	81.21 ± 0.31
	17.5	37.0	1.17 ± 0.02	68.78 ± 0.44
	22.5	45.0	1.04 ± 0.05	54.11 ± 1.12
Vanillic Acid				
2:1	14.0	33.0	0.27 ± 0.04	51.62 ± 3.51
	17.5	37.0	0.20 ± 0.01	30.46 ± 1.51
	22.5	45.0	0.27 ± 0.05	24.34 ± 3.23
1:1	14.0	33.0	0.23 ± 0.01	54.54 ± 1.21
	17.5	37.0	0.20 ± 0.02	27.20 ± 1.64
	22.5	45.0	0.25 ± 0.03	22.08 ± 1.95
1:2	14.0	33.0	0.26 ± 0.02	55.35 ± 2.31
	17.5	37.0	0.18 ± 0.01	25.50 ± 0.97
	22.5	45.0	0.29 ± 0.00	24.74 ± 0.24

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Gallic Acid				
2:1	14.0	33.0	0.50 ± 0.00	66.26 ± 0.15
	17.5	37.0	0.44 ± 0.00	48.25 ± 0.22
	22.5	45.0	0.70 ± 0.15	45.05 ± 5.19
1:1	14.0	33.0	0.53 ± 0.07	72.88 ± 2.46
	17.5	37.0	0.39 ± 0.01	41.86 ± 0.74
	22.5	45.0	0.52 ± 0.08	37.05 ± 3.53
1:2	14.0	33.0	0.48 ± 0.06	69.79 ± 2.45
	17.5	37.0	0.34 ± 0.02	39.22 ± 1.23
	22.5	45.0	0.50 ± 0.04	35.70 ± 4.33
Caffeine				
2:1	14.0	33.0	0.82 ± 0.01	76.49 ± 0.21
	17.5	37.0	0.61 ± 0.01	56.66 ± 0.22
	22.5	45.0	0.49 ± 0.07	36.69 ± 3.16
1:1	14.0	33.0	0.83 ± 0.06	80.87 ± 1.17
	17.5	37.0	0.70 ± 0.02	56.19 ± 0.56
	22.5	45.0	0.59 ± 0.08	40.10 ± 3.10
1:2	14.0	33.0	0.82 ± 0.07	79.77 ± 1.32
	17.5	37.0	0.75 ± 0.03	58.65 ± 1.05
	22.5	45.0	0.60 ± 0.01	40.57 ± 0.34
Nicotine				
2:1	14.0	33.0	0.44 ± 0.03	63.28 ± 1.71
	17.5	37.0	0.39 ± 0.00	45.48 ± 0.07
	22.5	45.0	0.52 ± 0.09	38.08 ± 4.13
1:1	14.0	33.0	0.45 ± 0.02	69.95 ± 0.90
	17.5	37.0	0.50 ± 0.01	47.80 ± 0.41
	22.5	45.0	0.56 ± 0.01	39.39 ± 0.30
1:2	14.0	33.0	0.48 ± 0.04	69.64 ± 1.80
	17.5	37.0	0.58 ± 0.01	52.42 ± 0.54
	22.5	45.0	0.64 ± 0.01	42.17 ± 0.31

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