ELECTRONIC SUPLEMENTARY INFORMATION

Design and characterization of new hydrophobic eutectic solvents based on metal-extracting ligands

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FIGURES

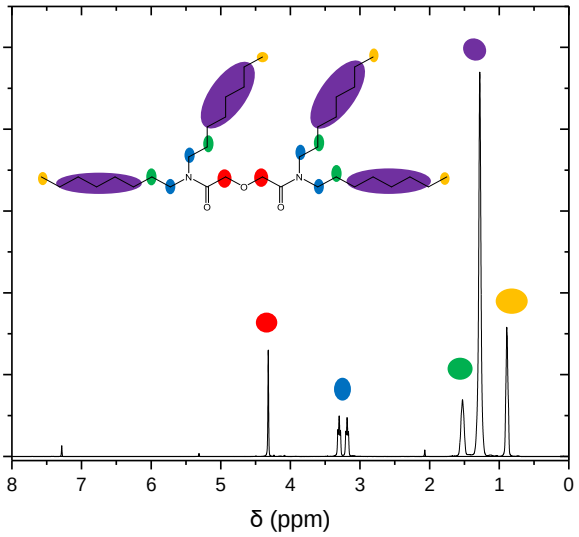

Figure S1. ^{1}H-NMR spectrum of the synthesized TODGA along with the corresponding peak assignments. ^{1}H NMR (400MHz, $CDCl_3$ δ): 4.29-4.34 (4H; -C*H*$_2$-O), 3.34-3.14 (8H; -C*H*$_2$-N), 1.59-1.46 (8H; -C*H*$_2$- CH_2-N),1.36-1.20(40H), 0.94-0.84 (12H; -C*H*$_3$)

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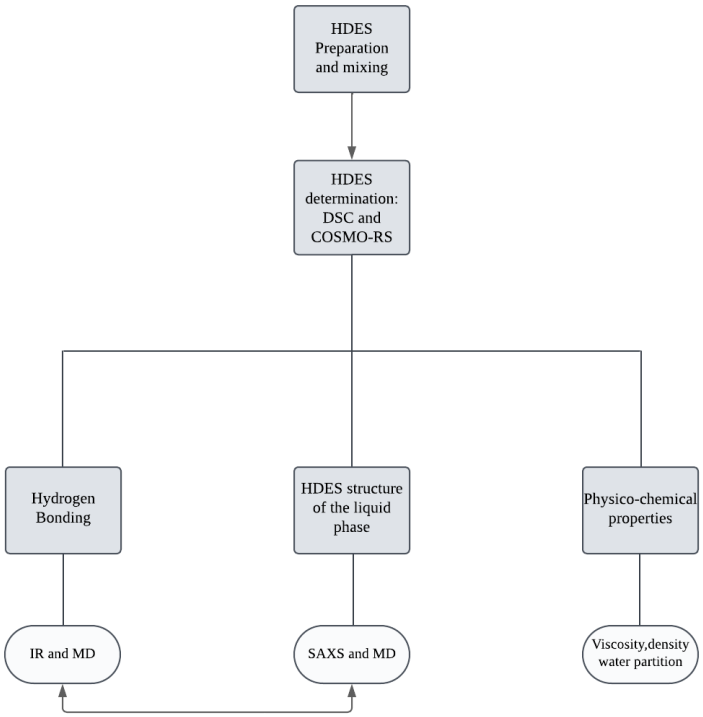

Figure S2. Experimental workflow ~~Worflow for the experiments done~~

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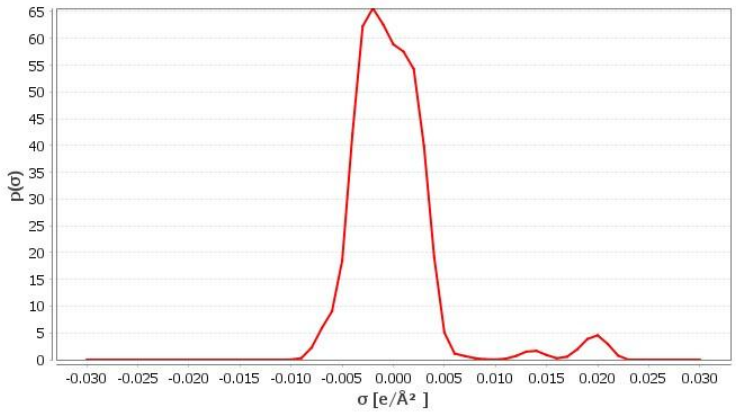

Figure S3. Sigma profile of TOPO based on COSMO-RS optimized structure shown in **Table S2**.

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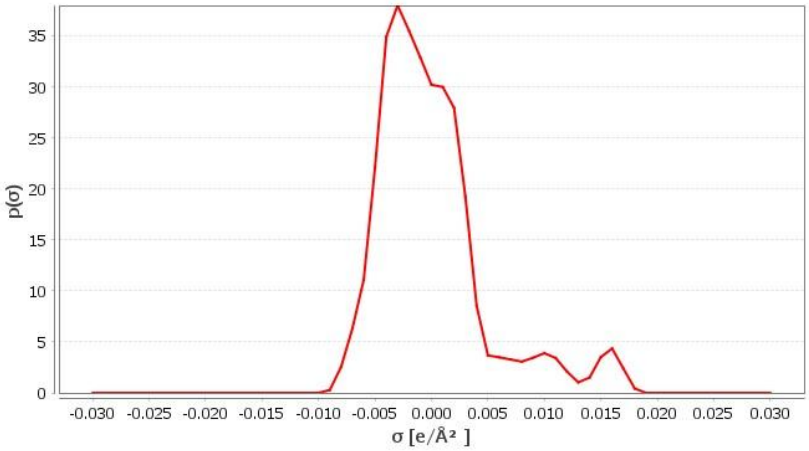

Figure S4. Sigma profile of TBP based on COSMO-RS optimized structure shown in **Table S2**.

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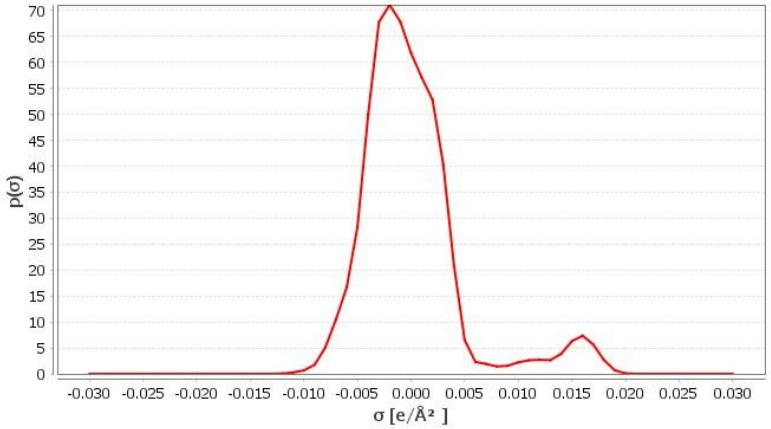

Figure S5. Sigma profile of DMDOHEMA based on COSMO-RS optimized structure shown in **Table S2**.

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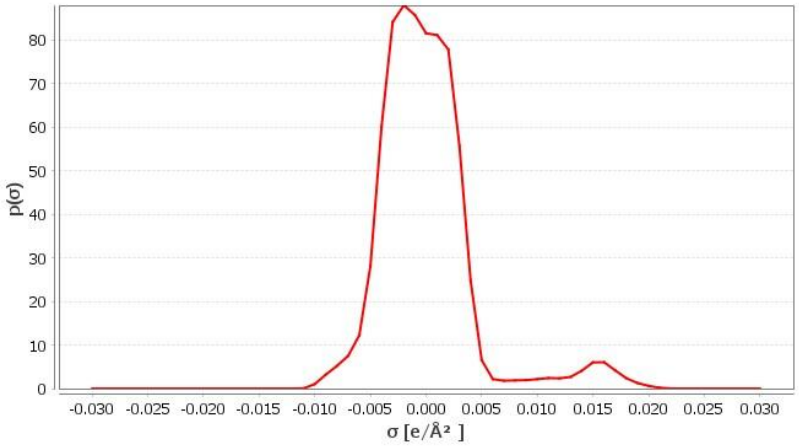

Figure S6. Sigma profile of TODGA based on COSMO-RS optimized structure shown in **Table S2**.

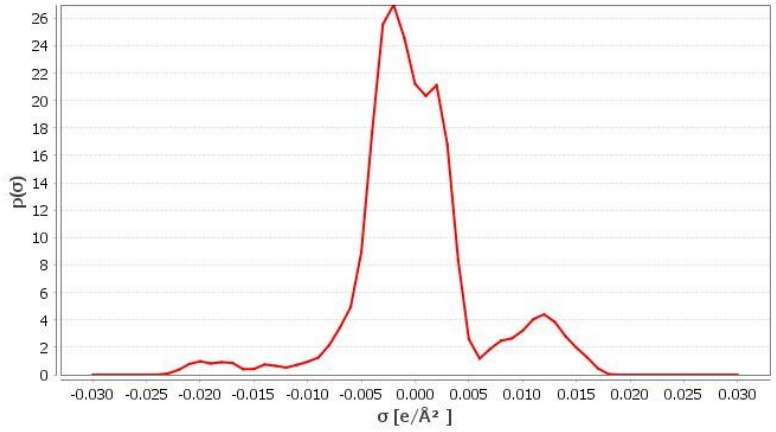

Figure S7. Sigma profile of DecA based on COSMO-RS optimized structure shown in **Table S2**.

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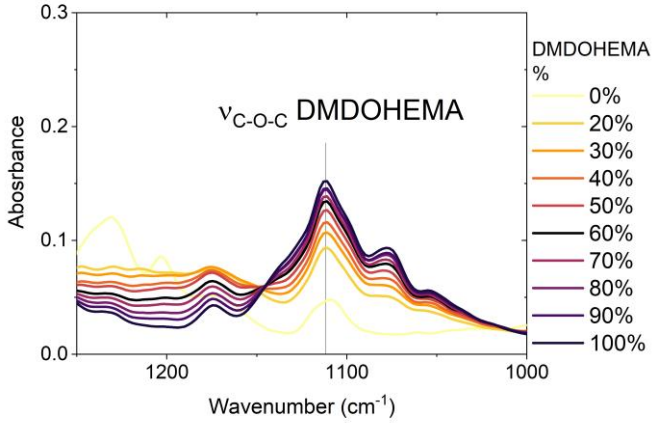

Figure S8. Infrared spectra of DMDOHEMA + DecA as a function of the DMDOHEMA molar fraction focusing on the ether vibration.

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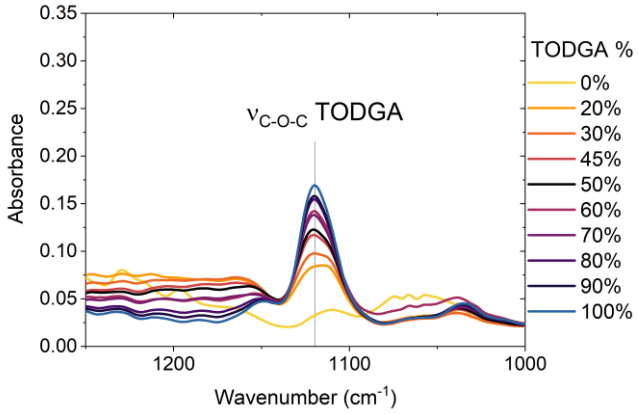

Figure S9. Infrared spectra of TODGA + DecA as a function of the TODGA molar fraction focusing on the ether vibration.

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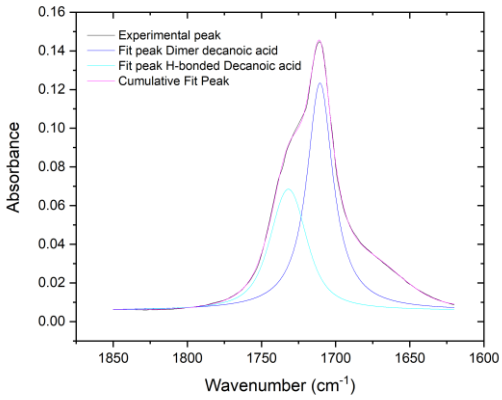

Figure S10. Example of the Gaussian deconvolution procedure followed for the DecA C=O vibration in the TOPO+DecA eutectic system at x_{TOPO} = 0.3.

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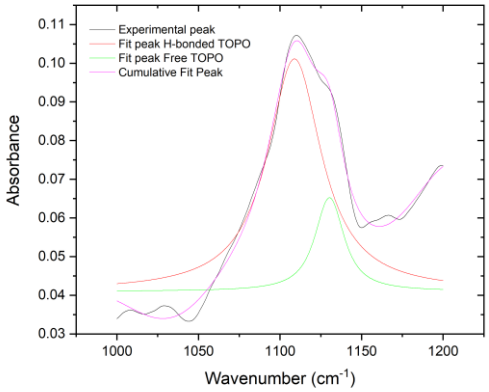

Figure S11. Example of the Gaussian deconvolution procedure followed for the TOPO P=O vibration in the TOPO+DecA eutectic system at x_{TOPO} = 0.3.

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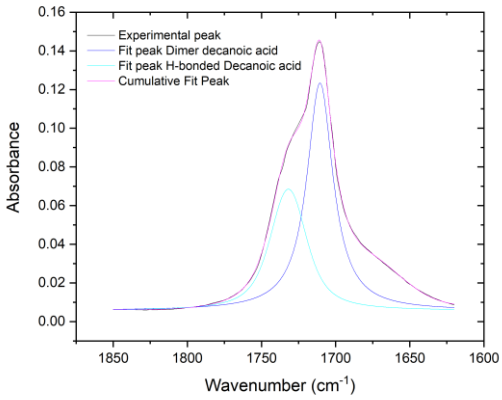

Figure S12. Example of the Gaussian deconvolution procedure followed for the DecA C=O vibration in the TBP+DecA eutectic system at x_{TBP} = 0.3.

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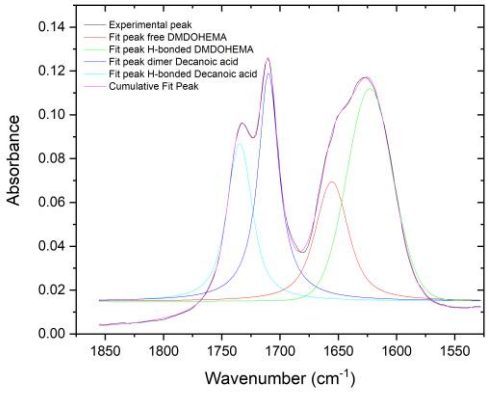

Figure S13. Example of the Gaussian deconvolution procedure followed for the DMODHEMA and DecA C=O vibration in the DMDOHEMA+DecA eutectic system at $x_{DMDOHEMA}$ = 0.3.

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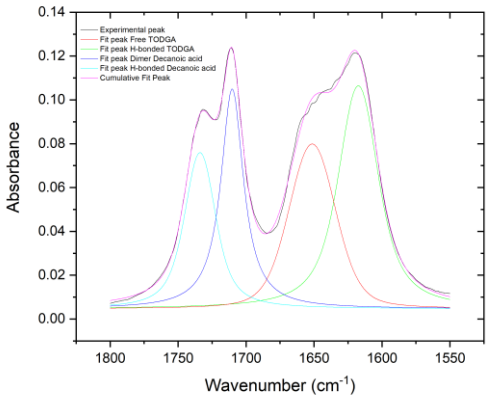

Figure S14. Example of the Gaussian deconvolution procedure followed for the TODGA and DecA C=O vibration in the TODGA+DecA eutectic system at x_{TODGA} = 0.3.

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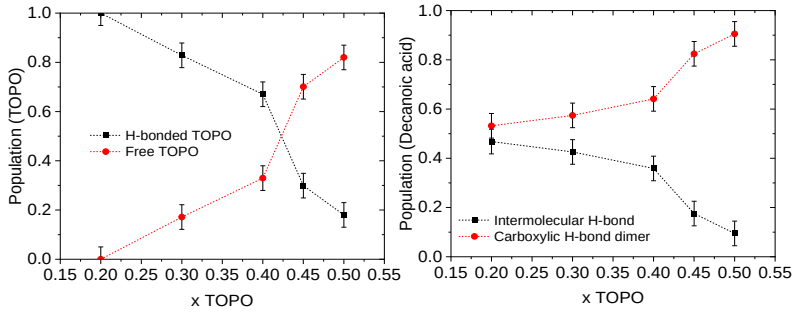

Figure S15. Distribution of hydrogen bonded TOPO (left) and DecA (right) species in the TOPO+DecA eutectic as a function of the composition. The relative population was derived from the integration of the FTIR bands presented in **Figure 3a** of the manuscript. Only compositions liquid at room temperature were investigated.

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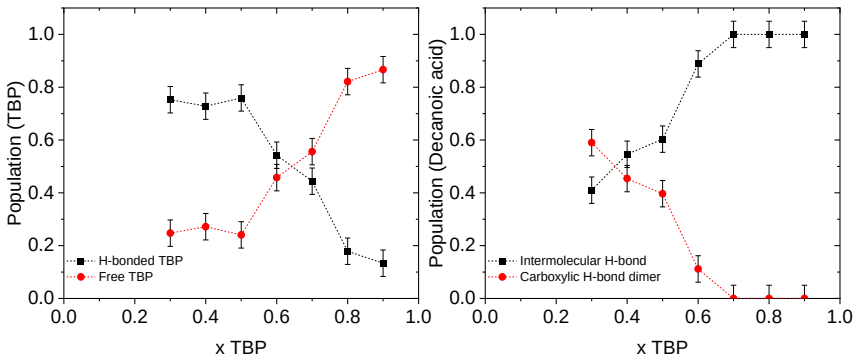

Figure S16. Distribution of hydrogen bonded TBP (left) and DecA (right) species in the TBP+DecA eutectic as a function of the composition. The relative population was derived from the integration of the FTIR bands presented in **Figure 3b** of the manuscript. Only compositions liquid at room temperature were investigated.

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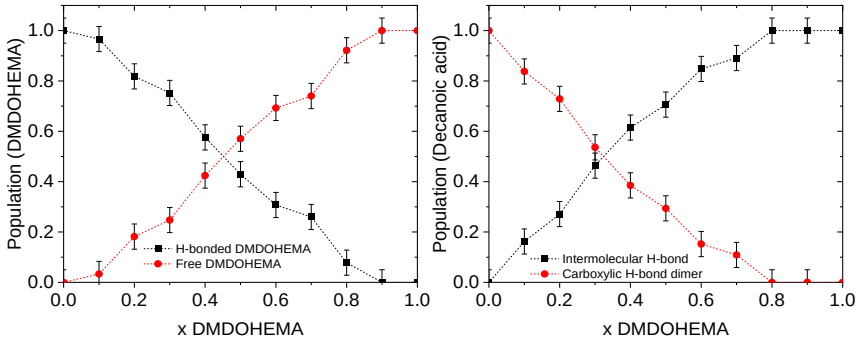

Figure S17. Distribution of hydrogen bonded DMDOHEMA (left) and DecA (right) species in the DMDOHEMA+DecA eutectic as a function of the composition. The relative population was derived from the integration of the FTIR bands presented in **Figure 3c** of the manuscript. Only compositions liquid at room temperature were investigated. Octanoic acid instead of decanoic acid was used to determine the population at $x_{DMDOHEMA}$=0.

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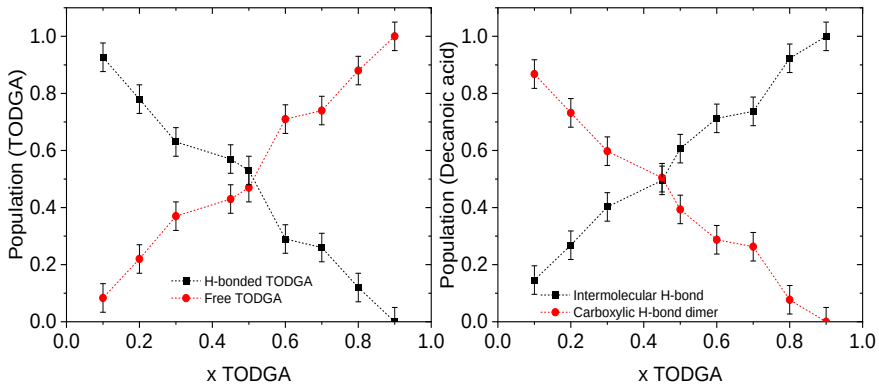

Figure S18. Distribution of hydrogen bonded TODGA (left) and DecA (right) species in the TODGA+DecAeutectic as a function of the composition. The relative population was derived from the integration of the FTIR bands presented in **Figure 3d** of the manuscript. Only compositions liquid at room temperature were investigated. Octanoic acid instead of decanoic acid was used to determine the population at x_{TODGA}=0.

Formatado: Realce

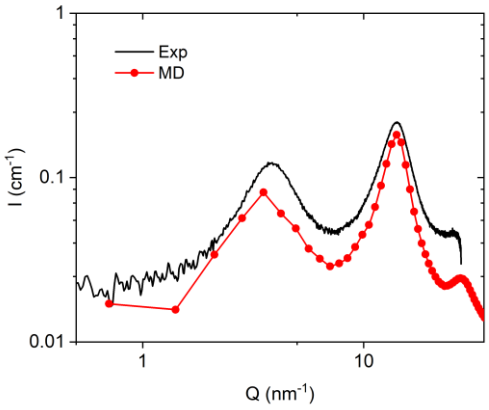

Figure S19. Comparison between the experimental and molecular dynamics SAXS spectra for TOPO+DecA (x_{DecA} = 0.7).

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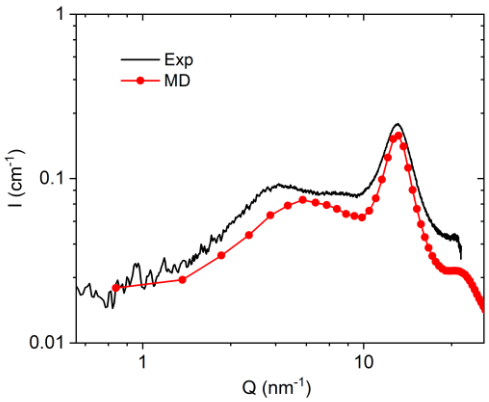

Figure S20. Comparison between the experimental and molecular dynamics SAXS spectra for TBP+DecA (x_{DecA} = 0.7).

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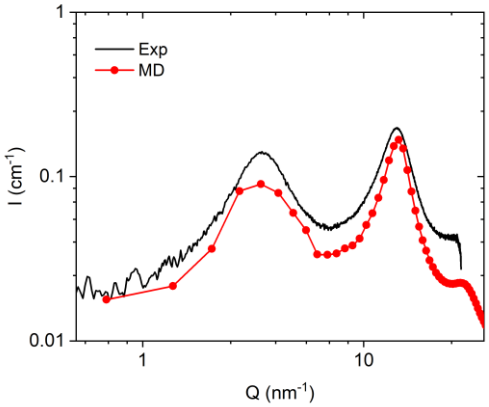

Figure S21. Comparison between the experimental and molecular dynamics SAXS spectra for DMDOHEMA+DecA (x_{DecA} = 0.7)

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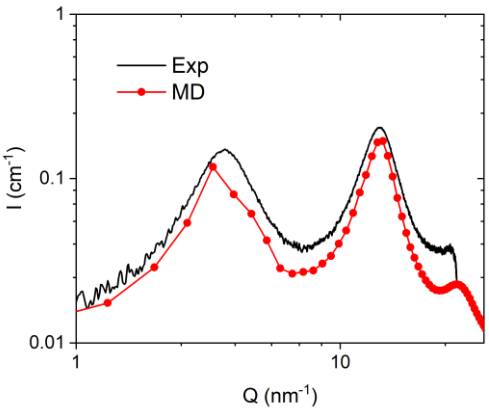

Figure S22. Comparison between the experimental and molecular dynamics SAXS spectra for TODGA+DecA (x_{DecA} = 0.7).

Formatado: Realce

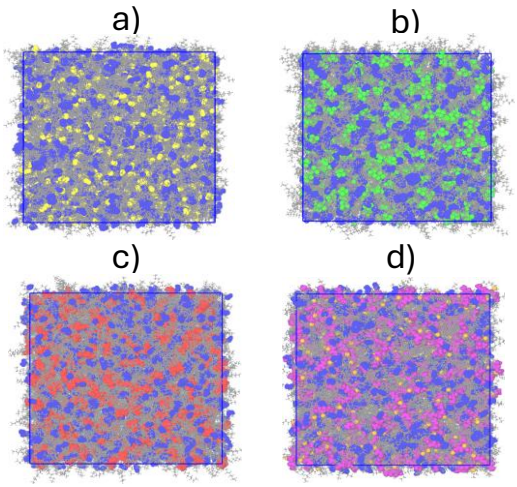

Figure S23. Snapshot of the final equilibration step for the systems composed of a) TOPO, b) TBP, c) TODGA, and d) DMODHEMA with DecA at 298 K for a fixed composition of x_{DecA}=0.7.Color code: yellow – TOPO (P=O), green - TBP (PO_4), red - TODGA polar head purple - DMDOHEMA polar head, orange - ether O of DMDOHEMA, grey - alkyl chains.

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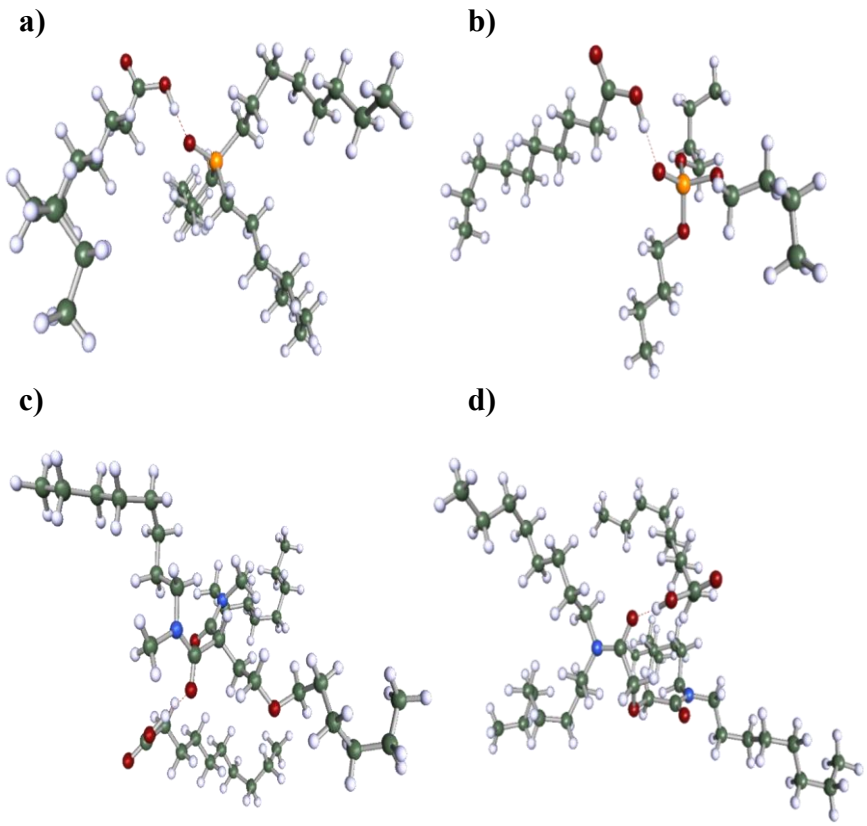

Figure S24. Optimized geometries (COSMO solvation model) of the interaction pairs recognized by COSMO-RS as most probable to occur in the a) TOPO+DecA, b) TBP+DecA, b) DMODHEMA+DecA, and d) TODGA+DecA.

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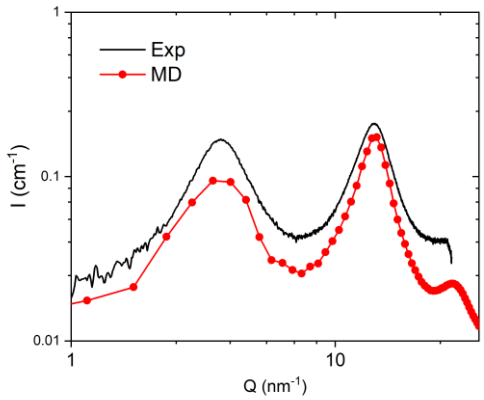

Figure S25. Comparison between the experimental and molecular dynamics SAXS spectra for TODGA+DecA (x_{DecA} = 0.55).

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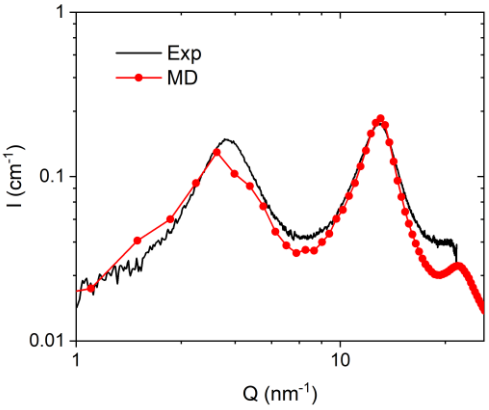

Figure S26. Comparison between the experimental and molecular dynamics SAXS spectra for TODGA+DecA (x_{DecA} = 0.3).

Formatado: Realce

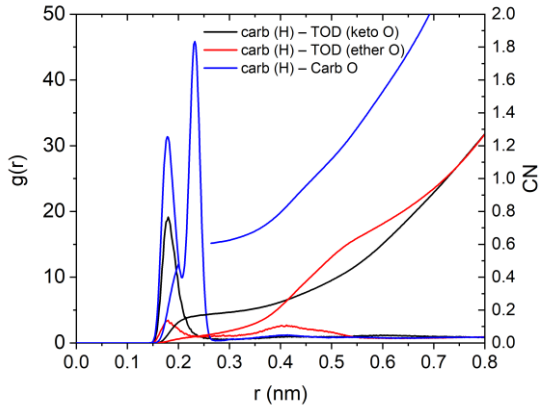

Figure S27. Radial distribution function and coordination number between DecA (carboxylic acid H as reference atom) and TODGA (carbonyl) for a composition of x_{TODGA}= 0.30. The second g(r) peak at 0.24 nm for the DecA– DecA interaction (in blue) corresponds to the intramolecular H-O distance and was corrected in the estimation of the coordination number (CN).

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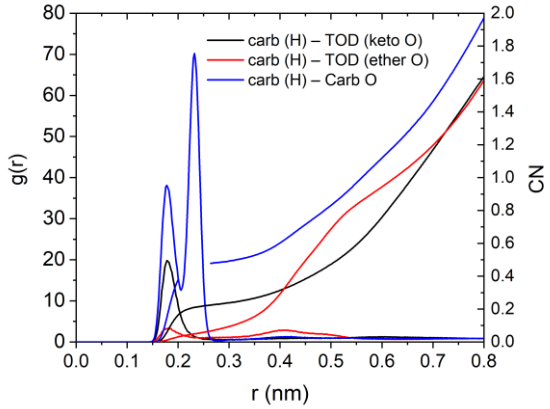

Figure S28. Radial distribution function and coordination number between DecA (carboxylic acid H as reference atom) and TODGA (carbonyl) for a composition of x_{TODGA}= 0.45. The second g(r) peak at 0.24 nm for the DecA– DecA interaction (in blue) corresponds to the intramolecular H-O distance and was corrected in the estimation of the coordination number (CN).

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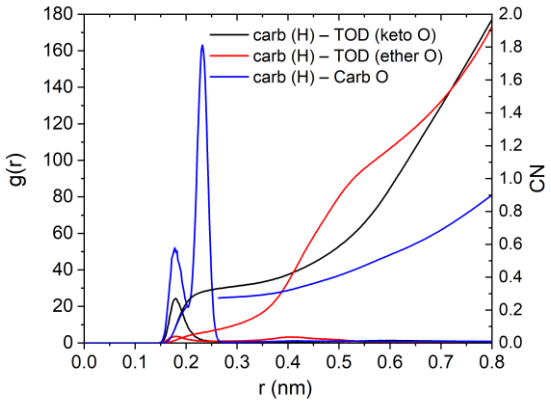

Figure S29. Radial distribution function and coordination number between DecA (carboxylic acid H as reference atom) and TODGA (carbonyl) for a composition of x_{TODGA}= 0.70. The second g(r) peak at 0.24 nm for the DecA – DecA interaction (in blue) corresponds to the intramolecular H-O distance and was corrected in the estimation of the coordination number (CN).

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TABLES

Table S1. Melting temperature (K), eutectic temperature (K) and activity coefficient for the different systems used as a function of the decanoic acid molar fraction.

TOPO(1)/DecA(2)

x_{DecA}	$T_{melting}$	$T_{eutectic}$	γ_1	γ_2
0.0	325.87		1.00	
0.1	324.65		1.03	
0.2	322.90		1.03	
0.3	313.78	253.76/258.18	0.62	
0.4	304.34	250.95/257.57	0.37	
0.5	284.08	252.93/258.03	0.09	
0.6	261.78	250.91/254.92	0.01	
0.7	280.02	254.85		0.55
0.8	289.48	254.42		0.70
0.9	298.25	253.04		0.88
1.0	304.75			1

TBP(1)/DecA(2)

x_{DecA}	$T_{melting}$	$T_{eutectic}$	γ_1	γ_2
0.0	194.15		1.00	
0.1	/	187.10	/	/
0.2	194.43	189.89		0.01
0.3	237.78	196.84		0.15
0.4	256.05	214.49		0.32
0.5	271.50	225.14		0.53
0.6	283.08	227.31		0.71
0.7	289.38	226.31		0.81
0.8	294.31	225.53		0.88
0.9	300.46	236.29		0.96
1.0	304.75			1.00

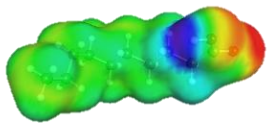
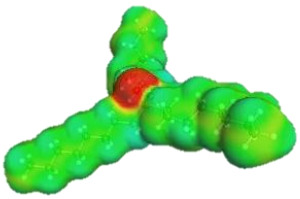
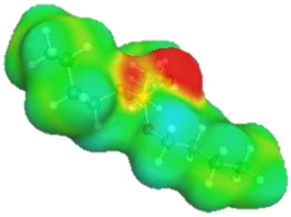
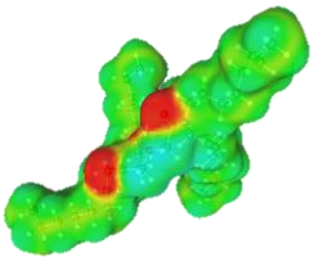
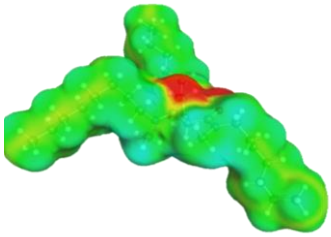
DMDOHEMA(1)/DecA(2)

x_{DecA}	$T_{melting}$	$T_{eutectic}$	γ_1	γ_2
0.0	282.2	/	1	
0.1	281.9	260.65	0.999	
0.2	279.9	261.75	1.0047	
0.3	276.7	260.55	0.991	
0.4	274.3	257.55	/	
0.5	272.8	254.75	1.04	
0.6	278.7	268.05		0.6036
0.7	287.4	267.85		0.7424
0.8	292.8	267.75		0.812
0.9	297.8	267.35		0.869
1	304.75	/		1

TODGA(1)/DecA(2)

x_{DecA}	$T_{melting}$	$T_{eutectic}$	γ_1	γ_2
0.0	284.39		1	
0.1	283.39	269.74	/	
0.2	278.71	/	1.20	
0.3	277.6	269.9	0.863	
0.4	273.89	266.32	0.8348	
0.5	265.138	/		0.459
0.55	272.32	266.347		0.496
0.7	284.09	268.11		0.527
0.8	293.55	269.28		1.027
0.9	302.22	/		1.022
1.0	304.75	/		1

Table S2. Electron density surface of DecA, TOPO, TBP, DMDOHEMA and TODGA obtained with COSMOtherm, blue: polar HBD zone, green: apolar zone, red: polar HBA zone.

Accronym	COSMO electron density surface representation
DecA	
TOPO	
TBP	
TODGA	
DMDOHEMA	

Gaussian deconvolution

$$\%\, Dimers = \frac{Area\ peak\ near\ 1710\ cm^{-1}}{Area\ peak\ near\ 1730\ cm^{-1} + Area\ peak\ near\ 1710\ cm^{-1}}$$

$$\%\, Intermolecular\ H-Bonding = 1 - \%Dimers$$

Table S3. Area, peak center, Full width at half maximum for the carboxyl area of decanoic acid, used for the Gaussian deconvolution

System	Area	Peak center (cm^{-1})	FWHM
TOPO DecA , x_{TOPO} = 0.3	1,46	1731	27,4
TOPO DecA , x_{TOPO} = 0.3	1,97	1710	16,7
TBP DecA, x_{TBP} = 0.3	3,9	1710	21,3
TBP DecA, x_{TBP} = 0.3	2,5	1731	29,2
TODGA DecA , x_{TODGA} = 0.3	3,6	1711	23,2
TODGA DecA , x_{TODGA} = 0.3	2,4	1735	24,2
DMDOHEMA DecA , $x_{DMDOHEMA}$ = 0.3	0,7	1709	13,7
DMDOHEMA DecA , $x_{DMDOHEMA}$ = 0.3	0,65	1735	18,5
TODGA DecA , x_{TODGA} = 0.45	1.6	1711	39,5
TODGA DecA , x_{TODGA} = 0.45	1,6	1731	26,9
TODGA DecA , x_{TODGA} = 0.7	0,5	1701	18,6
TODGA DecA , x_{TODGA} = 0.7	1,4	1730	29,1

Table S4. Comparison between the experimental and calculated density for the systems investigated by molecular dynamics (MD) simulations

System	x_{DecA}	**MD density ($g.cm^{-3}$)**	**Experimental Density ($g.cm^{-3}$)**
TOPO + DecA	0.70	0.889	0.886
TBP + DecA	0.70	0.933	0.925
DMDOHEMA + DecA	0.70	0.915	0.913
TODGA + DecA,	0.70	0.904	0.907
TODGA + DecA,	0.55	0.903	0.905
TODGA + DecA,	0.30	0.902	0.904