

SUPPORTING INFORMATION

Separation of metals using *in situ* formation of DES-DES biphasic systems

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Materials

The reagents listed in **Table S1** were used to prepare the biphasic DES-DES systems in this work. The metal salts used to prepare spiking solutions for metal partition studies are listed in **Table S2**. All reagents were used as received. Choline chloride was dried prior to use in a vacuum line prior to use and stored in a desiccator.

Table S1. Reagents used for DES preparation.

Reagent	CAS	Minimum purity	Supplier
Trioctylphosphine oxide (TOPO)	78-50-2	99%	Thermo Scientific
Choline chloride (ChCl)	67-48-1	99%	Thermo Scientific
Malonic acid (MA)	141-82-2	99.7%	Sigma Aldrich
Levulinic acid	123-76-2	98%	Sigma Aldrich
Propionic acid	79-09-4	99%	Acros Organics
Butyric acid	107-92-6	99%	Sigma Aldrich
Lactic acid	50-21-5	85%	Sigma Aldrich
Acetic acid	64-19-7	99%	JMGS

Table S2. Salts used for partition study.

Salt	CAS	Minimum purity	Supplier
FeCl ₃ ·6H ₂ O	10025-77-1	99%	Merck
CoCl ₂ ·6H ₂ O	7791-13-1	99%	Merck
NiCl ₂ ·6H ₂ O	7791-20-0	97%	BDH Chemicals
CuCl ₂	7447-39-4	98%	BDH Chemicals
GaCl ₃	13450-90-3	99.99%	Acros Organics
LaCl ₃	10099-58-8	99.99%	Alfa Aesar
AuCl ₃ ·3H ₂ O	16961-25-4	99.9%	Sigma Aldrich
InCl ₃	10025-82-8	98.0%	Sigma Aldrich
ZnCl ₂	7646-85-7	98.0%	Merck

Total Reflection X-ray Fluorescence (TXRF) required the use of Triton™ X-100 from Merck, polyvinyl alcohol (PVA, 87-90%) and an yttrium standard for ICP (1000 ± 4 mg/L), both from Sigma-Aldrich. All chemicals were used as received without further purification. Ultrapure, double distilled water, passed through a reverse osmosis system and was further treated with a Milli-Q plus 185 water purification apparatus, (18.2 MΩ.cm at 298 K) was used for all experiments.

Methodology

System preparation

The ternary TOPO-ChCl-organic acid systems were prepared by combining the appropriate amount of each in glass vials and mixing at 400 rpm, in a thermostatic bath maintained at 333 K for 3 h. The mixtures were left undisturbed overnight to allow for phase separation. Six different organic acids were used in TOPO-ChCl systems as hydrogen bond donors. Namely, malonic, levulinic, propionic, butyric, lactic and acetic acid. **Figure S1** shows the systems as prepared.

Phase diagrams

The phase equilibrium of the ternary TOPO-ChCl-MA systems was investigated by preparing a series of mixture points containing 10 to 80 mol.% of TOPO, ChCl and MA. All systems were prepared gravimetrically using a Mettler Toledo XS205 analytical balance with an accuracy of ± 0.00001 g. Each mixture point was heated at 333 K under agitation for 3h and rested overnight at room temperature before visual evaluation.

NMR

After separation of the phases, the tie-line of the TOPO-ChCl-MA system for four mixture points with overall composition provided in **Tables S10** and **S11**, two without and with the addition of 10 wt.% H₂O respectively, were determined by ¹H nuclear magnetic resonance spectroscopy (¹H-NMR). The NMR spectra were recorded on a Bruker Avance III NMR spectrometer. The choline-rich and TOPO-rich phases were diluted in deuterated water and chloroform, respectively, and 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid (TSP) was added as an internal standard. In the upper phase, in both the water and water-free analyses, the TOPO shifts range from 0.88 to 1.66 ppm. This

indicates that the signals of TOPO are free of interferences from the other components, as the choline chloride (ChCl) and malonic acid signals are in the ranges of 3.30 to 4.24 ppm and 3.17 to 13.82 ppm, respectively. The integration of the signals spans the entire TOPO molecule in all phases. In the case of malonic acid, two shifts were observed, at 3.23 and 12.36 ppm.; the signal at 3.23 ppm was selected because of its greater intensity and relative insensitivity to the water content (the signal at 12.36 ppm disappears in the presence of H₂O). The shift at approximately 3.34 ppm was used for the quantification of ChCl and deconvoluted from that of the nearby malonic acid. For the systems with 10 wt.% water, the same methodology was followed as for the systems without added water, considering shift dislocation due to the presence of the latter in the choline chloride-rich phase.

To validate the analysis, the density of the phases was gravimetrically determined using an analytical balance and compared - in the case of the system without water - to the predicted density obtained from the H-NMR phase compositions. Estimated NMR densities are available in **Table S10** and have an error of estimation below 1% for both top and bottom phases.

Raman

Raman spectroscopy was used to complement the composition of the phases. Samples of the TOPO and ChCl-rich phases were collected from a system with overall composition $x_{\text{TOPO}} = 0.1$, $x_{\text{MA}} = 0.5$ and $x_{\text{ChCl}} = 0.4$ and used without dilution. After phase separation, the individual phases were analyzed by Raman spectroscopy using a confocal Raman-AFM-SNOM microscope WITec alpha300 RAS+. A Nd:YAG laser operating at 532 nm laser with the power set to 32 mW and a 50x objective. The Raman spectrum of each phase was acquired 10 times with 2 sec each acquisition. The interface was analyzed via Raman imaging by placing droplets of each phase approximately 1 cm apart on a glass slide, which were left to spread and come into contact before sweep scanning a 150 by 150 μm section (150 \times 150 points per grid, 0.01 sec). Raman image was produced by raster scanning the laser beam over the sample and by accumulating a full Raman spectrum at each pixel (in total 22500 spectra), with a spatial resolution of approximately 580 nm. Raman image (**Figure 1E**) was constructed by integrating the absolute area underneath the Choline Raman band at 712 cm^{-1} (assigned to the C-N symmetric stretching mode) using WITec software (Project 5.3+).

UV-VIS

Analysis was performed using a Molecular Devices SpectraMax® iD3 UV-VIS spectrophotometer equipped with a 96-well microplate reader. The absorbance was measured from 230 to 1000 nm with a 1 nm step. A blank measurement (containing all reagents except the analyte) was included for baseline correction.

Viscosity

The viscosity of the DES phases (general system composition of $x_{\text{TOPO}} = 0.1$, $x_{\text{MA}} = 0.5$, $x_{\text{ChCl}} = 0.4$ with and without 10 wt.% added H₂O) was determined after phase separation at 298 K using a SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter. Measurements were performed at 1 bar and 298 K.

Karl Fischer

Water content was determined using a Metrohm Eco Karl Fisher titrator. Titration was performed using Hydranal™ Titrant 5, and water content was calculated using the volume of consumed titrant and the sample weight.

Metal quantification

Metal quantification was performed using a Picofox S2 TXRF spectrometer (Bruker Nano, Billerica, MA, USA) equipped with a molybdenum X-ray source. The X-ray tube was operated at 50 kV and 600 μ A. All carriers were first pre-treated with 10 μ L of a silicon solution in isopropanol and dried at 353 K for 15 min. Samples were diluted in an aqueous solution containing 1 wt.% PVA, 1 wt.% Triton™ X-100, and 20 wt.% ethanol, and spiked with a known concentration of YCl_3 . Ten microliters of each solution containing the metals and the YCl_3 standard were added onto a clean carrier and dried on a hot plate at 353 K for 15 min. Spectra acquisition time was set at 240 s.

Metal Partition

The metal partition coefficients for DES-DES TOPO-ChCl-MA systems are calculated following **Equations 1**. The separation factor $\alpha_{Mi/Mj}$ of two metals *i* and *j* is calculated through **Equation 2**. Partition coefficients are available in **Tables S13** to **S15**.

$$D_M = \frac{[M]_{TOPO}}{[M]_{ChCl}} \#(1)$$

$$\alpha_{Mi/Mj} = \frac{D_{Mi}}{D_{Mj}} \#(2)$$

Aqueous solutions of each target metal were prepared by dissolving the respective chlorinated salts in **Table S2** in ultrapure water. Each salt was carefully weighed so that each aqueous solution contained 0.5 mol/L of the respective metals. For the partition tests, DES-DES biphasic System 1 ($x_{TOPO} = 0.1$, $x_{MA} = 0.5$, $x_{ChCl} = 0.4$), 2 g each, were spiked using 8 μ L of each metal solution. The test vials were then placed in a rotating vertical shaker and mixed at 60 RPM for 8 hours, before leaving undisturbed overnight to allow for phase separation. The two DES phases were then individually collected using a syringe and placed in separate sample vials. The metal content in each phase was then measured by TXRF, as described above. The effect of water content on metal partition was studied by adding 10 to 36 wt% H_2O to System 1. The metal spiking, phase separation and quantification procedures were performed as described above. In **Table S15**, System 1 is compared with a system containing a TOPO-rich phase with the composition in **Table S10** and a NaCl solution containing $[Cl^-] = 4.65$ M, mimicking System 1 ChCl-rich phase concentration. In this case, a phase ratio of 1:2 organic to aqueous was used (total system volume 1.5 mL). The systems were spiked using the same conditions as the previous metal partition studies and left to settle overnight.

Metal Partition Kinetics

The kinetics of metal partition from the ChCl-MA phase to the TOPO-MA phase were studied in the following way: A volume of ternary biphasic system ($x_{TOPO} = 0.1$, $x_{MA} = 0.5$, $x_{ChCl} = 0.4$) was prepared as described above and allowed to settle for several hours before collecting the individual phases using a syringe. Each kinetic test was prepared by spiking 1 mL of the ChCl-rich phase using 8 μ L of each metal solution, similarly to the procedure followed for the metal partition tests. After thorough

mixing in a 30 RPM overhead shaker, 0.67 mL of the TOPO phase was added. The mixture was then returned to the overhead shaker, at the same speed, for the time required for each test ($t = 0.5 - 10$ min). After the appropriate time elapsed, the vials were centrifuged at 12000 RPM for 10 seconds to promote phase separation. Samples of each phase were then collected using a micropipette and analyzed by TXRF, as described above.

Metal Stripping from TOPO-rich phase and reuse

Stripping of metals from the TOPO-rich phase was studied by preparing a volume of ternary biphasic system ($x_{\text{TOPO}} = 0.1$, $x_{\text{MA}} = 0.5$, $x_{\text{ChCl}} = 0.4$) as described above. The biphasic systems were allowed to settle before separating the individual phases using a syringe. Aqueous solutions of pH 2 sulfuric acid, 0.1 mol.L⁻¹ oxalic acid, 1 mol.L⁻¹ and 5 mol.L⁻¹ hydrochloric acid were prepared. For each test, 2 mL of the TOPO-rich phase was spiked using 16 μL of 0.5 mol.L⁻¹ solutions of FeCl₃, GaCl₃, InCl₃ and AuCl₃. After thorough mixing, 4 mL of acid solution was added. The biphasic DES-dilute acid systems were mixed at 30 RPM in an overhead shaker for 1 hour before allowing to settle overnight. Samples of each phase were then collected for TXRF using a syringe.

The reuse of the TOPO-rich phase was investigated by transferring 10 mL of TOPO-ChCl-MA system ($x_{\text{TOPO}} = 0.1$, $x_{\text{MA}} = 0.5$, $x_{\text{ChCl}} = 0.4$) to a separating funnel. The system was spiked with 20 μL of 0.5 mol.L⁻¹ solutions of each metal of interest. After thorough mixing, the system was left to separate. The bottom, ChCl-rich phase was drained. The same volume of pristine ChCl-rich phase was added back to the separating funnel and spiking again. This procedure was repeated three times, collecting samples of TOPO-rich phase for TXRF metal quantification after each stripping step.

Results

Organic acid screening

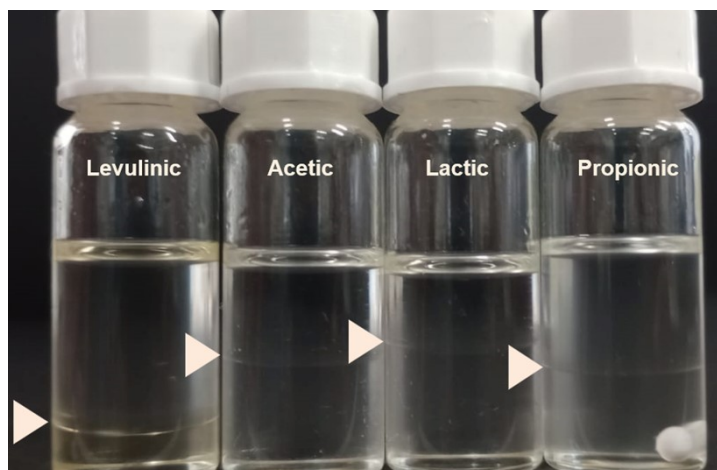


Figure S1. Visual appearance of binary DES-DES systems containing TOPO, ChCl and an organic acid. From left to right, levulinic acid, acetic acid, lactic acid and propionic acid. Arrows point to the interface. System composition varies between all systems.

Table S3. Composition and visual observation of the TOPO-ChCl-Levulinic acid system at 298K under ambient conditions (SL – solid-liquid system, LL – liquid-liquid system).

x_{TOPO}	$x_{\text{Levulinic acid}}$	x_{ChCl}	Phase
0.1	0.5	0.4	SL
0.3	0.4	0.3	SL
0.3	0.5	0.2	LL
0.2	0.4	0.4	LL
0.4	0.4	0.2	SL
0.2	0.5	0.3	LL
0.2	0.6	0.2	LL

Table S4. Composition and visual observation of the TOPO-ChCl-Lactic acid system at 298K under ambient conditions (LL – liquid-liquid system).

x_{TOPO}	$x_{\text{Lactic acid}}$	x_{ChCl}	Phase
0.1	0.5	0.4	LL

Table S5. Composition and visual observation of the TOPO-ChCl-Acetic acid system at 298K under ambient conditions (SL – solid-liquid system, LL – liquid-liquid system).

x_{TOPO}	$x_{\text{Acetic acid}}$	x_{ChCl}	Phase
0.1	0.5	0.4	SL

0.1 0.6 0.3 LL

Table S6. Composition and visual observation of the TOPO-ChCl-Propionic acid system at 298K under ambient conditions (SL – solid-liquid system, LL – liquid-liquid system).

x_{TOPO}	$x_{\text{Propionic acid}}$	x_{ChCl}	Phase
0.1	0.5	0.4	SL
0.1	0.6	0.3	SL
0.2	0.5	0.3	SL
0.2	0.6	0.2	SL
0.1	0.4	0.5	SL
0.3	0.4	0.3	SL
0.5	0.4	0.1	SL
0.3	0.5	0.2	SL
0.2	0.6	0.2	SL
0.1	0.7	0.2	LL
0.3	0.4	0.3	SL
0.1	0.8	0.1	LL
0.2	0.7	0.1	LL

Table S7. Composition and visual observation of the TOPO-ChCl-Butyric acid system at 298K under ambient conditions (SL – solid-liquid system, LL – liquid-liquid system).

x_{TOPO}	$x_{\text{Butyric acid}}$	x_{ChCl}	Phase
0.1	0.5	0.4	SL
0.1	0.6	0.3	SL
0.3	0.5	0.2	SL
0.2	0.5	0.3	SL
0.1	0.4	0.5	SL
0.1	0.3	0.6	SL
0.3	0.3	0.4	SL
0.5	0.3	0.2	SL
0.3	0.4	0.3	SL
0.2	0.6	0.2	SL
0.1	0.7	0.2	SL
0.3	0.6	0.1	SL
0.2	0.7	0.1	SL
0.1	0.8	0.1	LL

Phase diagrams

Table S8. Composition and phase distribution of the TOPO-ChCl-MA system without H₂O at 298K under ambient conditions (S – solid system; SL – solid-liquid system, LL – liquid-liquid system).

x_{TOPO}	x_{MA}	x_{ChCl}	Phase
0.8	0.1	0.1	S
0.6	0.1	0.3	S
0.6	0.3	0.1	SL
0.4	0.1	0.5	S
0.4	0.3	0.3	SL
0.4	0.5	0.1	LL
0.2	0.1	0.7	S
0.2	0.3	0.5	SL
0.2	0.5	0.3	LL
0.2	0.7	0.1	SL
0.1	0.1	0.8	S
0.1	0.3	0.6	SL
0.1	0.5	0.4	LL
0.1	0.7	0.2	SL
0.1	0.8	0.1	SL
0.5	0.4	0.1	LL
0.3	0.4	0.3	LL
0.1	0.4	0.5	LL
0.3	0.6	0.1	SL
0.1	0.6	0.3	SL

Table S9. Composition (not considering water) and phase distribution of the TOPO-ChCl-MA system with 10 wt.% H₂O at 298K under ambient conditions (S – solid system; SL – solid-liquid system, LL – liquid-liquid system).

x_{TOPO}	x_{MA}	x_{ChCl}	Phase
0.6	0.3	0.1	LL
0.4	0.3	0.3	LL
0.2	0.3	0.5	LL
0.2	0.7	0.1	LL
0.1	0.3	0.6	LL
0.1	0.7	0.2	SL
0.1	0.8	0.1	SL
0.3	0.6	0.1	LL
0.1	0.6	0.3	LL
0.1	0.2	0.7	LL
0.3	0.2	0.5	LL
0.5	0.2	0.3	LL
0.7	0.2	0.1	LL
0.1	0.1	0.8	S
0.3	0.1	0.6	S
0.5	0.1	0.4	S
0.8	0.1	0.1	S
0.4	0.5	0.1	LL
0.2	0.5	0.3	LL
0.1	0.5	0.4	LL
0.5	0.4	0.1	LL
0.3	0.4	0.3	LL
0.1	0.4	0.5	LL

Tie-lines

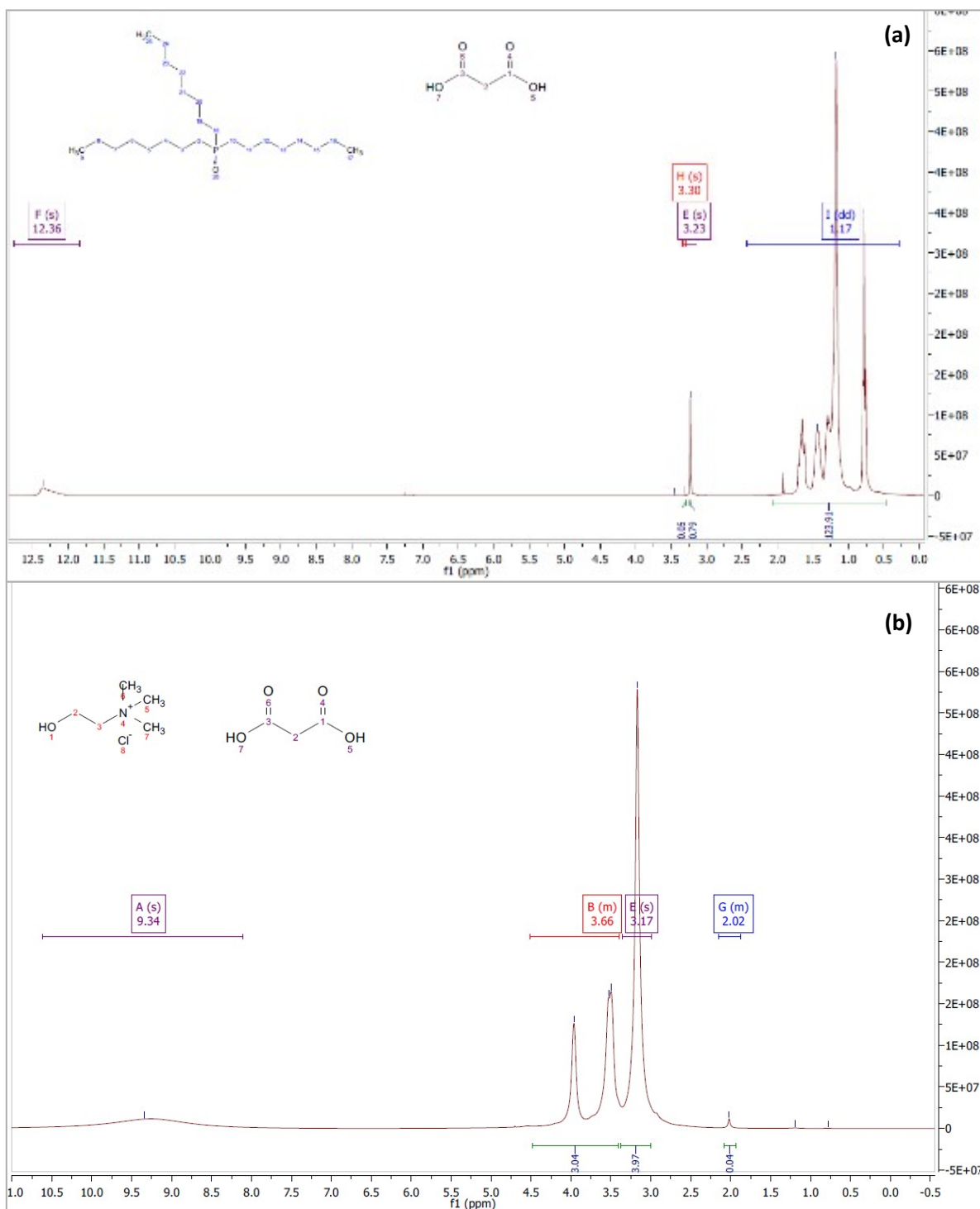


Figure S2. $^1\text{H-NMR}$ spectra of the TOPO/Malonic Acid/Choline Chloride system with mole fractions of 0.1/0.5/0.4. (a) Top phase. (b) Bottom phase.

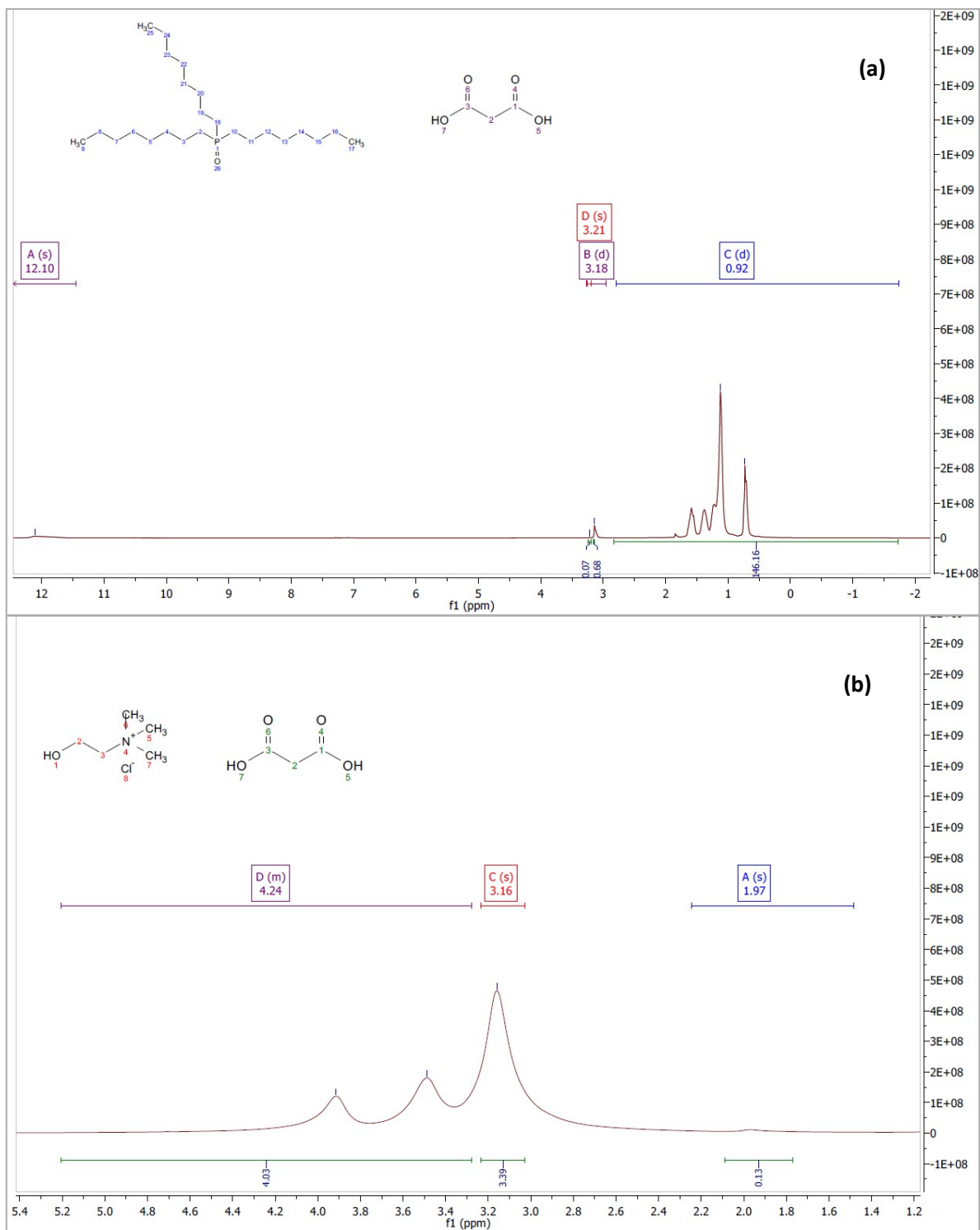


Figure S3. $^1\text{H-NMR}$ spectra of the TOPO/Malonic Acid/Choline Chloride System with mole fractions of 0.3, 0.4 and 0.3. (a) Top phase. (b) Bottom phase.

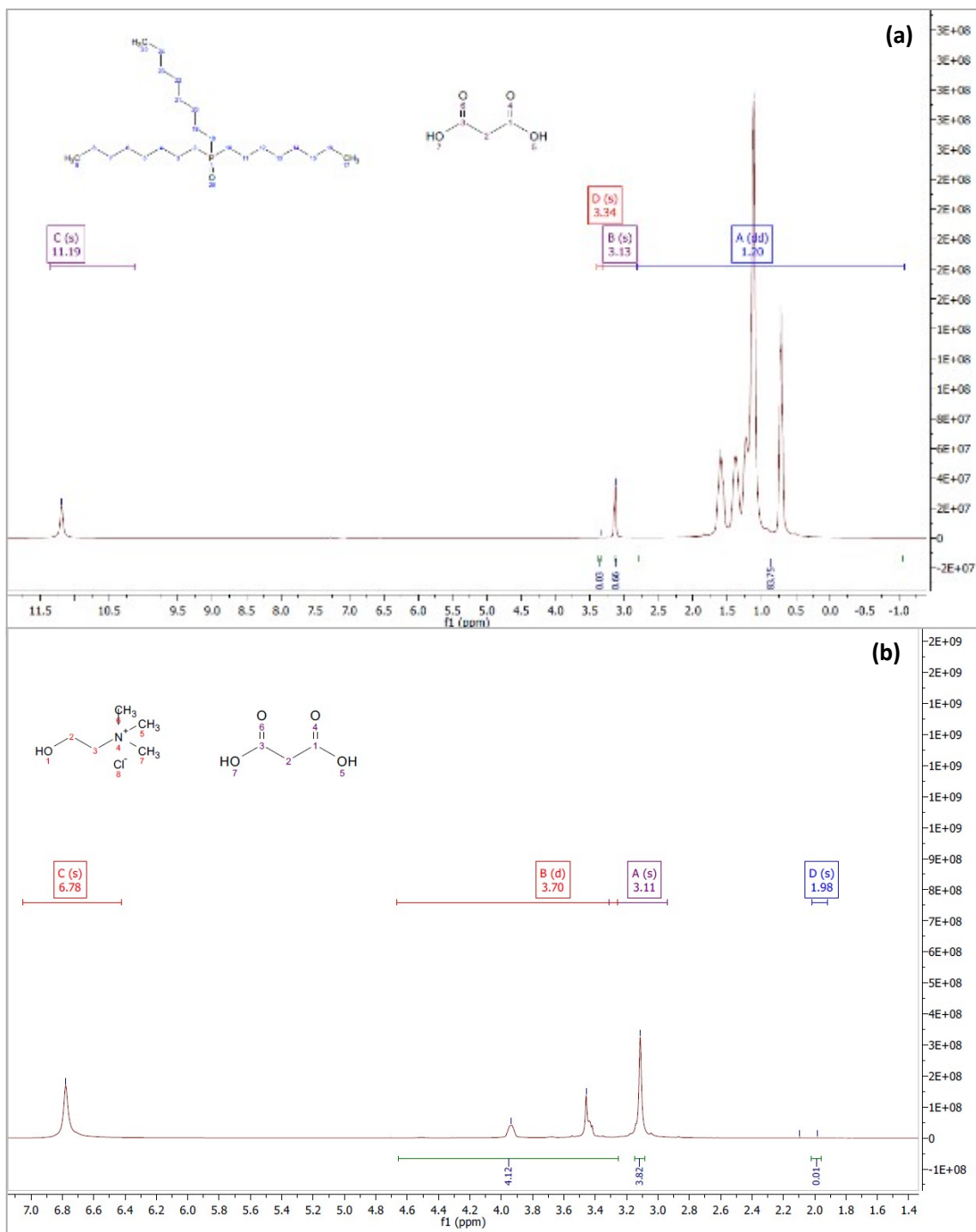


Figure S4. $^1\text{H-NMR}$ spectra of the TOPO/Malonic Acid/Choline Chloride system with mole fractions of 0.1, 0.5 and 0.4 in the presence of 10% H_2O . (a) Top phase. (b) Bottom phase.

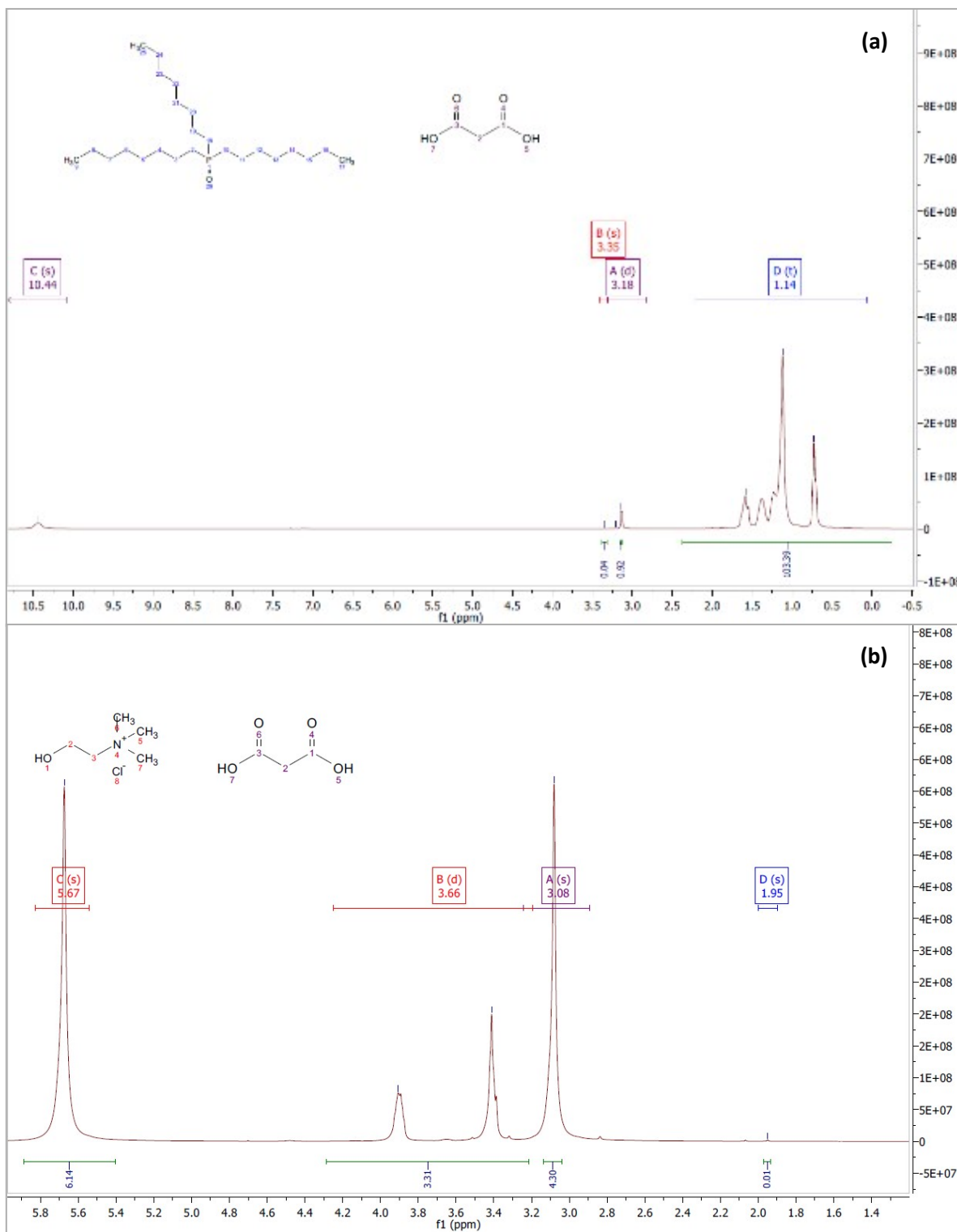


Figure S5. $^1\text{H-NMR}$ spectra of the TOPO/Malonic Acid/Choline Chloride system with mole fractions of 0.3, 0.4 and 0.3 in the presence of 10% H_2O . (a) Top phase. (b) Bottom phase.

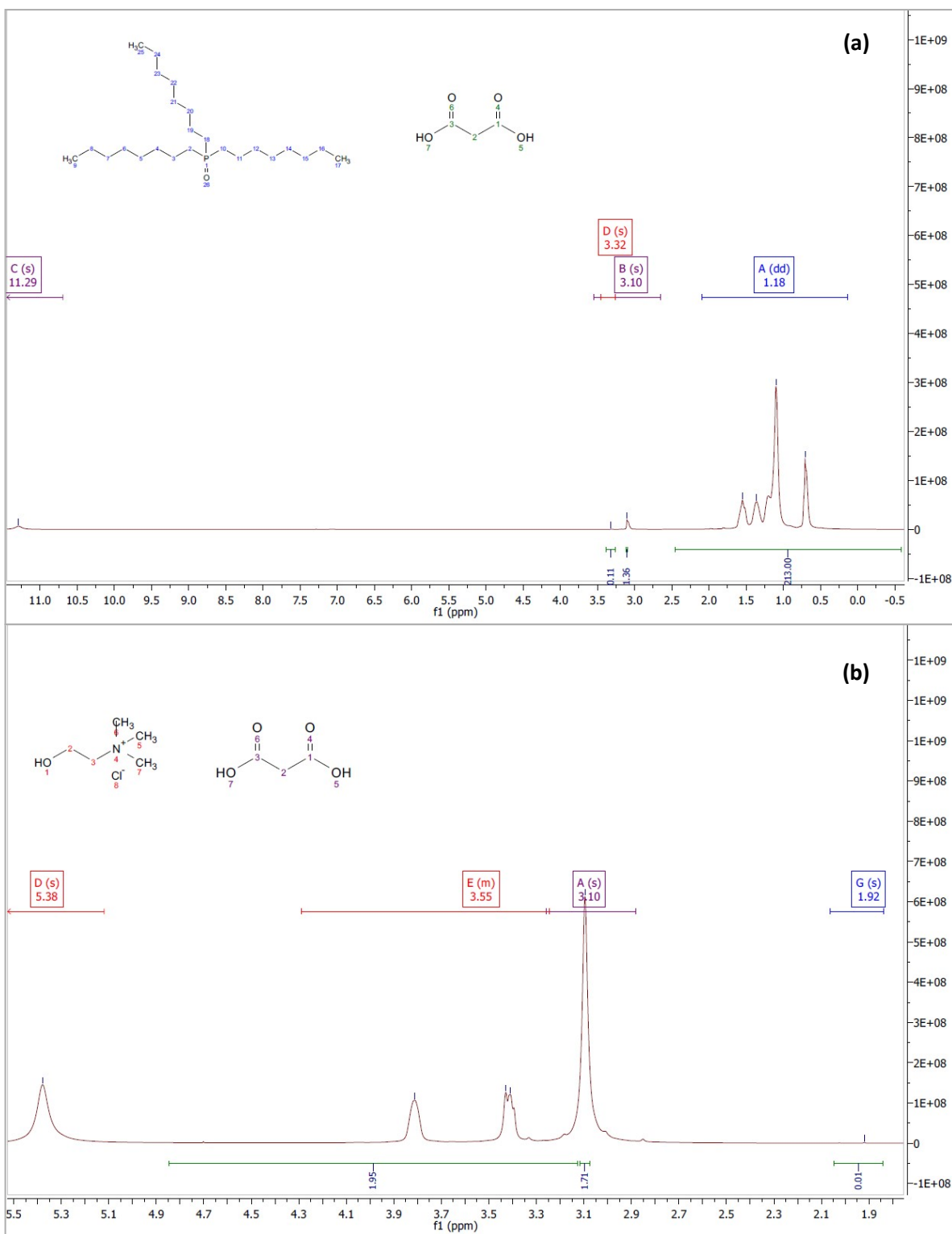


Figure S6. $^1\text{H-NMR}$ spectra of the TOPO/Malonic Acid/Choline chloride system with mole fractions of 0.1, 0.2 and 0.7 in the presence of 10% H_2O . (a) Top phase. (b) Bottom phase.

Table S10. $^1\text{H-NMR}$ determined tie-Line composition, density (in $\text{g}\cdot\text{mL}^{-1}$), and viscosity (in $\text{mPa}\cdot\text{s}$) of the ternary TOPO-ChCl-MA system without H_2O after phase separation. The density was measured gravimetrically and $\Delta\rho$ represents the difference between the measured and predicted density from $^1\text{H-NMR}$ composition. All measurements were performed at 298K and 1 bar.

System	Phase	x_{TOPO}	x_{MA}	x_{ChCl}	ρ (measured)	ρ (NMR predicted)	$\Delta\rho$	η (mPa.s)
1	Overall	0.1000	0.4999	0.4001	-	-	-	-
	Bottom	0.0003	0.5662	0.4335	1.2758	1.2823	0.5%	1023.1
	Top	0.8912	0.1023	0.0065	0.9481	0.9553	0.8%	150.57
2	Overall	0.2998	0.4003	0.2999	-	-	-	-
	Bottom	0.0010	0.4564	0.5426	1.2020	1.1972	0.4%	-
	Top	0.9154	0.0767	0.0079	0.9291	0.9364	0.8%	-

Table S11. $^1\text{H-NMR}$ determined tie-line composition, density (in $\text{g}\cdot\text{mL}^{-1}$), and viscosity (in $\text{mPa}\cdot\text{s}$) of the TOPO-ChCl-MA system with 10% H_2O after phase separation. The density was measured gravimetrically. All measurements were performed at 298K and 1 bar.

System	Phase	x_{TOPO}	x_{MA}	x_{ChCl}	ρ (measured)	η (mPa.s)
System 1 + 10% H_2O	Overall	0.0998	0.5002	0.4000	-	-
	Bottom	0.0001	0.4811	0.5189	1.2230	83.327
	Top	0.8709	0.1235	0.0056	0.9644	236.91
System 2 + 10% H_2O	Overall	0.3001	0.4013	0.2986	-	-
	Bottom	0.0001	0.5650	0.4349	1.1598	-
	Top	0.8568	0.1372	0.0060	0.9744	-

The tie-lines indicate the near absence of TOPO in the ChCl-rich phase, with an average TOPO molar fraction of $x_{\text{TOPO}} < 0.001$. ChCl contamination in the TOPO-rich phase is also found comparably low: $x_{\text{ChCl}} = 0.007$ on average. The addition of 10 wt.% H_2O has a negligible effect on the tie-lines. MA was found to partition preferentially to the ChCl phase, forming a binary DES with composition within the reported liquid region. However, the TOPO-rich phase is relatively depleted in MA, forming a mixture whose composition lies outside the reported miscible region. During the duration of this study, no recrystallization of the TOPO-rich phase was observed. The reported binary TOPO-MA system was measured under an inert and moisture-free atmosphere.¹ In this work, systems were prepared under ambient conditions, the average water content in the TOPO-rich phase was $x_{\text{H}_2\text{O}} = 0.056$ (0.3 wt.%) and $x_{\text{H}_2\text{O}} = 0.204$ (1.3 wt.%) in the “dry” and 10 wt.% H_2O systems respectively. Similarly to the thymol – H_2O system, in which the melting point of thymol decreased by approximately 40K for $x_{\text{H}_2\text{O}} \approx 0.1$, the existence of a liquid TOPO-rich phase is assigned to the presence of extra water molecules in the system in addition to MA.²

The presence of small water concentrations in the system allows for a more forgiving biphasic system formation while also enabling easier handling and processing of the system. A significant

reduction of the ChCl-rich phase viscosity from 1023 mPa.s to a manageable 83.3 mPa.s was observed upon addition of 10 wt.% H₂O (Tables S10-11). Interestingly, an increase in the viscosity of the TOPO-rich top phase was observed upon addition of 10 wt.% water, from 150.6 mPa.s to 236.9. This is assigned to the partial deprotonation of MA in the system, facilitated by the introduction of water, and the increase of ionic components in the phase.

Raman analysis

Table S12. Experimental Raman band positions (wavenumber, cm⁻¹) for TOPO^{3,4}, malonic acid⁵ and Choline chloride^{6,7} with the corresponding vibrational mode assignments.

Wavenumber (cm ⁻¹)	Vibrational modes
TOPO	
1444	ν(P-O)
1308	δ(CH ₃)
1119	ν(P=O)
Malonic acid	
1728	ν(C=O) of -COOH
1406	δ(CH ₂)
916	γ(C-C-C)
Choline	
956	ν _{assym} (CN)
918	ρ(CH ₂)
763	ν _{sym} (CN) for the <i>trans</i> conformations of the O-C-C-N+ backbone
712	ν _{sym} (CN) for the <i>gauche</i> conformations of the O-C-C-N+ backbone

ρ: rocking mode; ν: stretching mode (bonding vibrations); δ: bending mode (deformation vibrations); γ: out-of-plane deformation vibration

Metal partition – system composition, kinetics, and influence of water content

Table S13. Average partition coefficient, D_M , in the TOPO-ChCl-MA systems of different compositions across two separate measurements. System compositions are available in **Table S10** and **Table S11**.

System	Fe(III)	Co(II)	Ni(II)	Cu(II)	Ga(III)	La(III)	Au(III)	In(III)	Zn(II)
System 1 - dry	164.75	0.03	0.0047	0.03	368.99	20.59	48.85	0.10	8.97
System 1 + 10% H ₂ O	191.59	0.15	0.0008	0.06	3458.42	0.27	51.21	-	-
System 2 - dry	106.51	0.10	0.0003	0.04	4463.52	0.62	3.44	-	-
System 2 + 10% H ₂ O	34.98	0.09	0.0006	0.10	453.33	0.04	14.45	-	-
System 3 + 10%	218.04	0.07	0.0046	0.03	4740.65	11.37	35.21	-	-

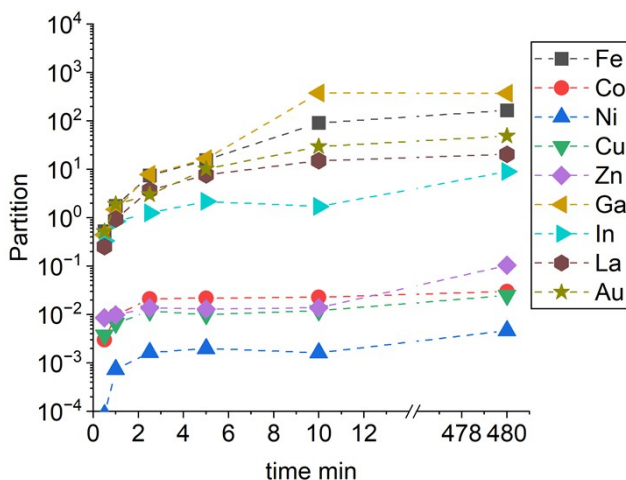


Figure S7. Partition coefficient, D_M , as a function of time, in a TOPO-ChCl-MA system ($x_{\text{TOPO}} = 0.1$, $x_{\text{ChCl}} = 0.5$, $x_{\text{MA}} = 0.4$). Time is measured after addition of the TOPO-rich phase and mixing in a 30 RPM overhead shaker at 298 K.

Table S14. Partition coefficient, D_M , as a function of time, in a TOPO-ChCl-MA system ($x_{\text{TOPO}} = 0.1$, $x_{\text{ChCl}} = 0.5$, $x_{\text{MA}} = 0.4$). Time is measured after addition of the TOPO-rich phase and mixing in a 30 RPM overhead shaker at 298 K.

Time (min)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Ga(III)	In(III)	La(III)	Au(III)
0.5	0.5	0.003	0.0001	0.004	0.009	0.4	0.3	0.3	0.5
1.0	1.8	0.010	0.0007	0.007	0.010	1.5	0.8	0.9	1.9
2.5	7.5	0.021	0.0017	0.012	0.014	7.8	1.2	3.7	3.0
5.0	15.7	0.022	0.0020	0.010	0.013	16.5	2.2	7.7	10.2

10	91.9	0.023	0.0016	0.012	0.014	375.8	1.7	15.1	29.5
480	164.8	0.030	0.0047	0.025	0.105	369.0	9.0	20.6	48.8

Table S15. Average partition coefficient, D_M , in DES-DES systems ($x_{\text{TOPO}} = 0.1$, $x_{\text{ChCl}} = 0.5$, $x_{\text{MA}} = 0.4$) with increasing added H_2O (10 to 36 wt.%) across two separate measurements.

Added H_2O wt.%	Fe(III)	Co(II)	Ni(II)	Cu(II)	Ga(III)	La(III)	Au(III)
0%	164.75	0.03	0.0047	0.03	368.99	20.59	48.85
10%	191.59	0.15	0.0008	0.06	3458.42	0.27	51.21
18%	279.90	0.13	0.0012	0.23	2576.76	0.09	90.01
23%	91.72	0.04	0.0012	0.09	554.23	0.04	163.88
31%	32.77	0.02	0.0019	0.07	96.25	0.05	93.60
36%	15.98	0.01	0.0004	0.05	38.19	0.06	110.89

Table S16. Average partition coefficient, D_M , in TOPO-MA-NaCl system (organic: $x_{\text{TOPO}} = 0.9$, $x_{\text{MA}} = 0.1$; aqueous: 4.65 mol/L NaCl) across two separate measurements.

	Fe(III)	Co(II)	Ni(II)	Cu(II)	Ga(III)	La(III)	Au(III)	In(III)	Zn(II)
NaCl	128.70	0.14	0.0007	1.00	1147.06	0.04	242.87	434.78	24.05

UV-VIS Spectra

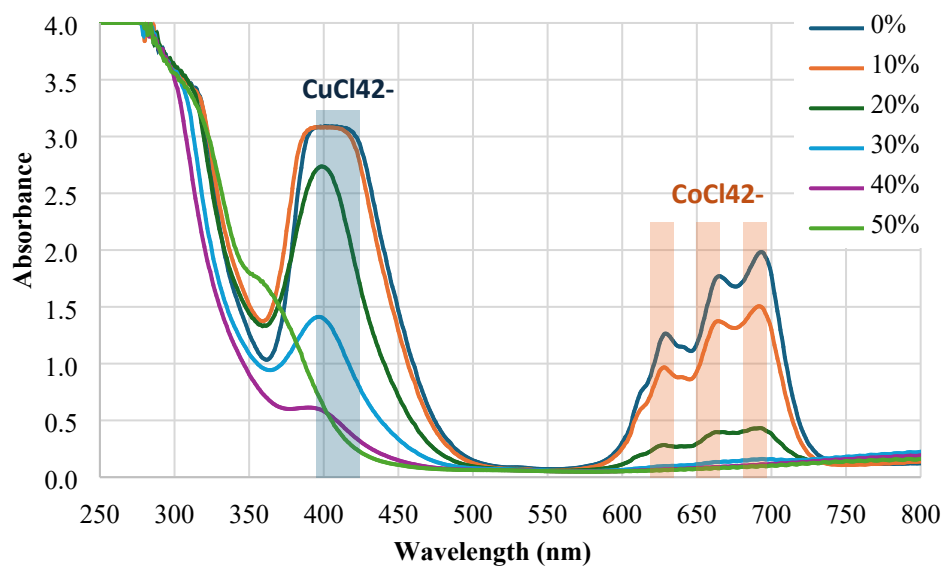


Figure S8. UV-VIS spectra of the ChCl-rich phase of System 1 ($x_{\text{TOPO}} = 0.1$, $x_{\text{MA}} = 0.5$, $x_{\text{ChCl}} = 0.4$) with increasing added water from 0 wt.% to 36 wt.%. $[\text{CuCl}_4]^{2-}$ and $[\text{CoCl}_4]^{2-}$ peak assignments based on Liu et al. and Uchikoshi et al.^{8,9}

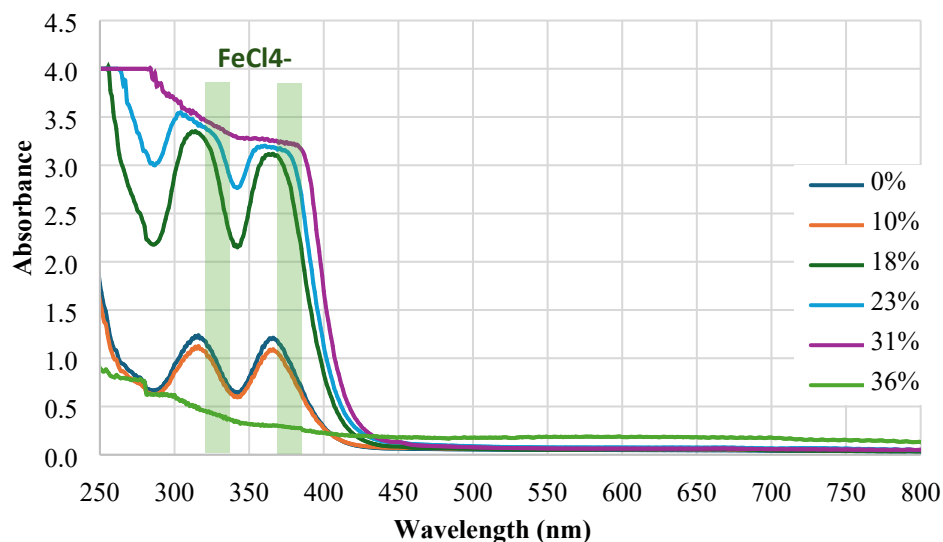


Figure S9. UV-VIS spectra of the TOPO-rich phase of System 1 ($x_{\text{TOPO}} = 0.1$, $x_{\text{MA}} = 0.5$, $x_{\text{ChCl}} = 0.4$) with increasing added water from 0 wt.% to 36 wt.%. $[\text{FeCl}_4]^-$ bands assignment based on Liu et al.¹⁰

Metal stripping and system reuse

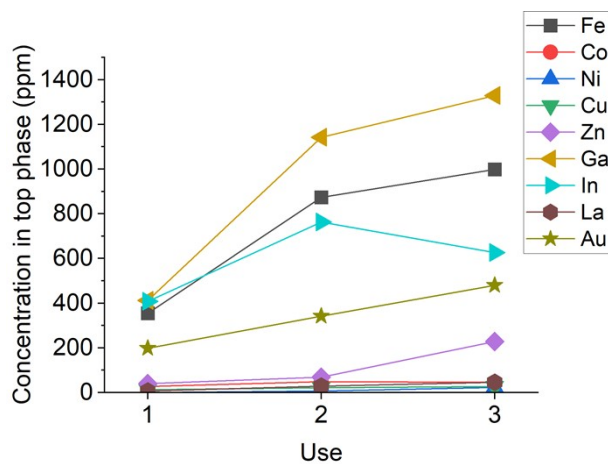


Figure S10. Concentration of metals (in ppm) after each use of TOPO-rich phase to strip metals from the ChCl phase. A constant system composition of $x_{\text{TOPO}} = 0.1$, $x_{\text{ChCl}} = 0.5$, $x_{\text{MA}} = 0.4$.

Table S17. Concentration of metals (in ppm) after each use of TOPO-rich phase to strip metals from the ChCl phase.

Use	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Ga(III)	In(III)	La(III)	Au(III)
1	354.5	27.3	0.05	13.6	39.7	412.8	408.4	7.7	198.6
2	873.9	49.2	7.73	21.4	69.5	1142.3	762.3	28.8	342.5
3	998.1	45.6	22.85	27.8	228.2	1328.8	627.1	45.8	479.7

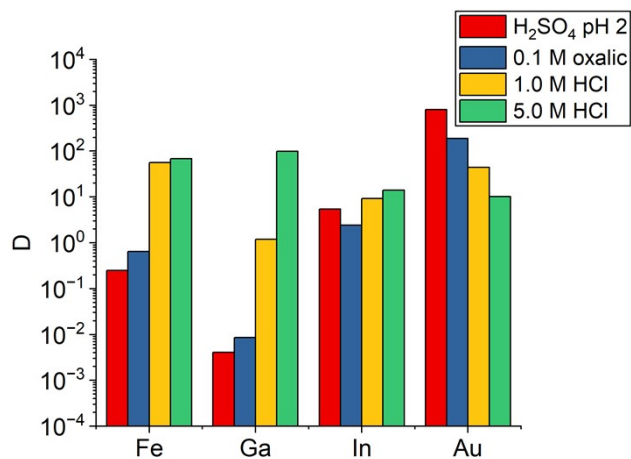


Figure S11. Partition coefficient, D_M , after stripping with aqueous solutions of sulfuric, oxalic, and hydrochloric acid. An organic:aqueous ratio of 1:2 was used. Samples were mixed using an overhead shaker at 30 RPM for 1 hour before leaving to settle overnight.

Table S18. Partition coefficient, D_M , after stripping with aqueous solutions of sulfuric, oxalic, and hydrochloric acid. An organic:aqueous ratio of 1:2 was used. Samples were mixed using an overhead shaker at 30 RPM for 1 hour before leaving to settle overnight.

System	Fe(III)	Ga(III)	In(III)	Au(III)
H₂SO₄ @ pH 2	0.25	0.004	5.41	804.45
0.1 M oxalic	0.64	0.009	2.44	190.13
1 M HCl	55.97	1.190	9.23	44.20
5 M HCl	68.36	99.167	14.15	10.12

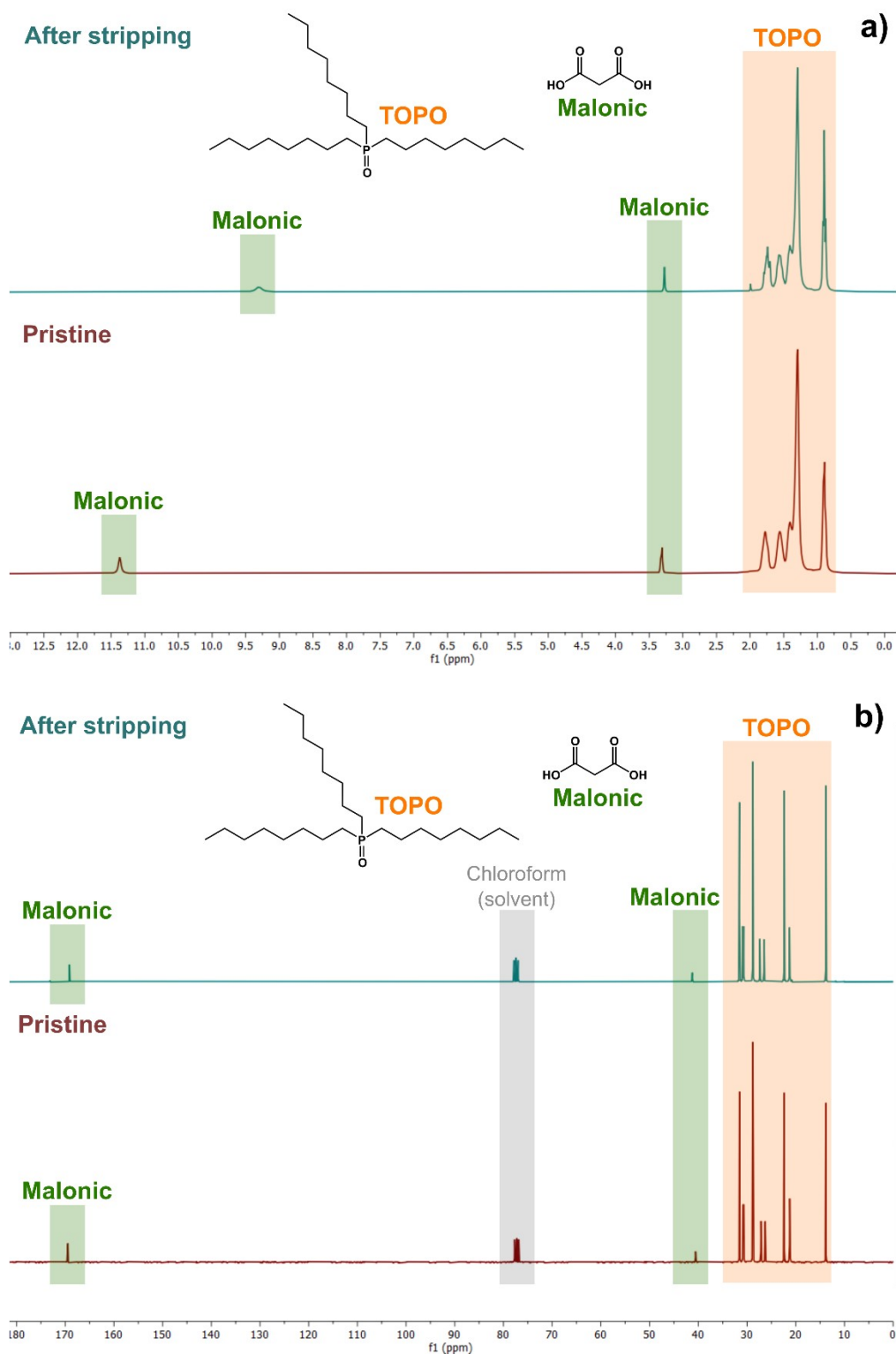


Figure S12. ^1H -NMR (a) and ^{13}C -NMR (b) of TOPO-rich phase of TOPO-ChCl-MA system ($x_{\text{TOPO}} = 0.1$, $x_{\text{ChCl}} = 0.5$, $x_{\text{MA}} = 0.4$), pristine and after stripping with aqueous solution of sulfuric acid in a 1:2 organic:aqueous ratio. Samples were mixed using an overhead shaker at 30 RPM for 1 hour before leaving to settle overnight.

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