

Supplementary Information

Super concentrated HCl in a deep eutectic solvent as media for the integrated leaching and separation of metals from end-of-life lithium-ion batteries

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Figures and Tables

Table S1. Laptop batteries that were dismantled in this work.

Brand	Model name/product ID
HP	43628-141
HP	411462-141
HP	582213-121
HP	9196682
HP	L12L4E01
Samsung	AA – PB9NC6B
Panasonic	CGR – B/8B5AE
Sanyo	BTP – APJ1
Toshiba	PA – 5185U – 1BRS
Toshiba	PA – 3534U – 1BRS
Toshiba	PA – 5185U – 1BRS
LG	LB62115E
Asus	41NR18165
Asus	A41-K53
Asus	A31N1601
Asus	A41 – X550A



Figure S1. SEM-EDS of the black mass from spent cathode materials.

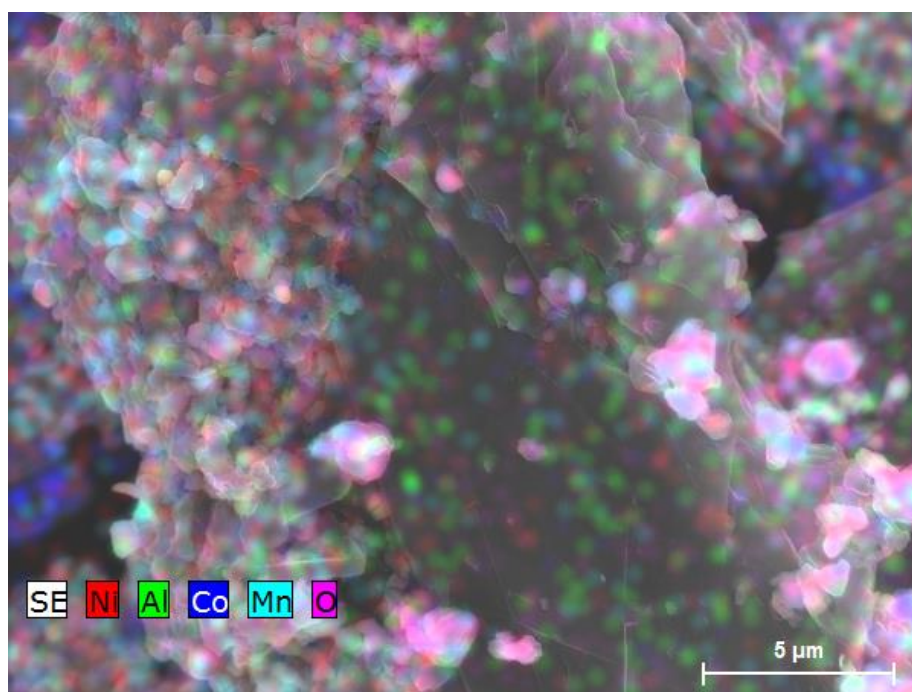
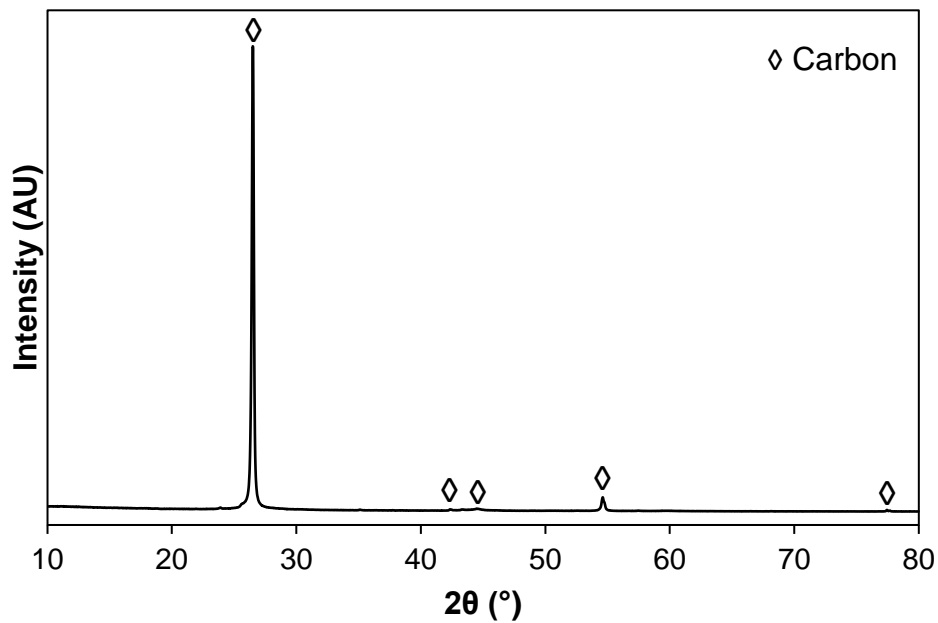


Figure S2. XRD pattern (top) and SEM-EDS (bottom) of the black mass from spent cathode materials after *aqua regia* leaching.

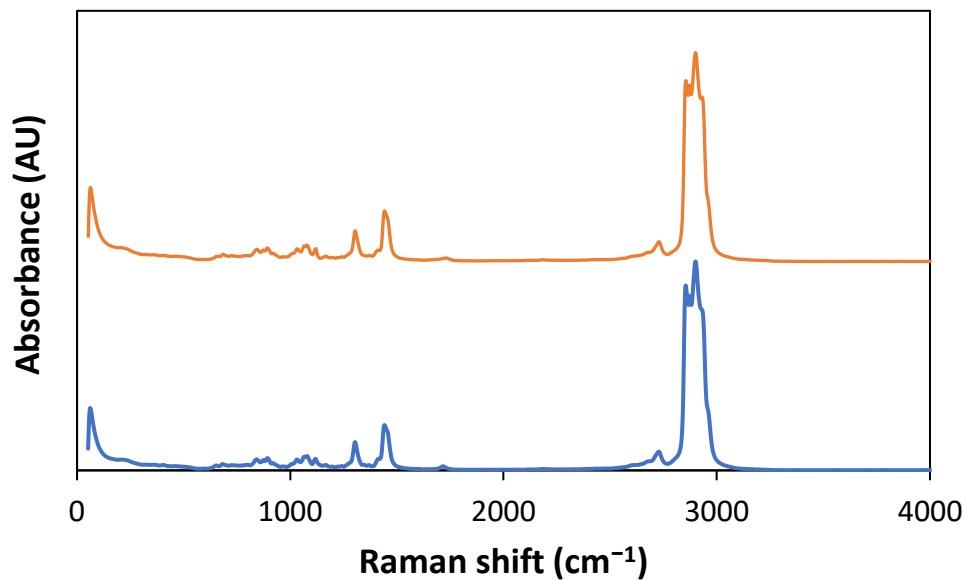


Figure S3. Raman spectra of the TOPO:decanoic acid mixture before (blue line) and after (orange line) contact with HCl 8 mol·L⁻¹.

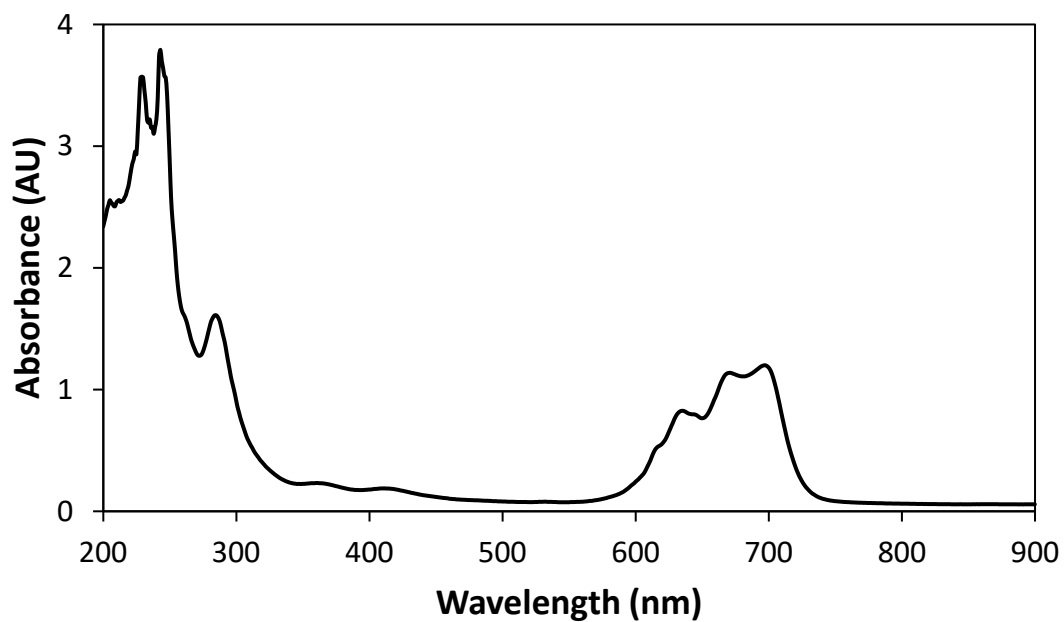


Figure S4. UV-Vis spectra of the DES after metal leaching.

Table S2. Kinetic parameters for Co(II), Ni(II) and Mn(II) at 333 K, 353 K and 373 K (± 1 K) given by all the adjusted empirical models.

	Co(II)			Ni(II)		Mn(II)	
	T (K)	k (min ⁻¹)	R ²	k (min ⁻¹)	R ²	k (min ⁻¹)	R ²
SCM reaction	333	0.002	0.9513	0.0006	0.9997	0.003	0.9545
	353	0.002	0.9773	0.0008	0.9609	0.003	0.9493
	373	0.002	0.9439	0.001	0.8878	0.002	0.9034
SCM diffusion	T (K)	k (min ⁻¹)	R ²	k (min ⁻¹)	R ²	k (min ⁻¹)	R ²
	333	0.0006	0.9973	7.00E-05	0.9626	0.0008	0.9968
	353	0.0013	0.9918	0.0002	0.979	0.0019	0.989
	373	0.0021	0.9594	0.0005	0.9364	0.0025	0.9031
SCM mixed-controlled	T (K)	k (min ⁻¹)	R ²	k (min ⁻¹)	R ²	k (min ⁻¹)	R ²
	333	0.0001	0.9938	0.00001	0.9612	0.0004	0.9896
	353	0.0004	0.9728	0.00004	0.9673	0.0007	0.9903
	373	0.001	0.8074	0.0001	0.9100	0.002	0.6806
	333	0.1	0.8903	0.2	0.8129	0.2	0.9606
	353	0.3	0.8967	0.1	0.6631	0.03	0.9258
	373	0.4	0.9190	0.1	0.7255	0.3	0.9417

Table S3. Leaching conditions and atom efficiency of reported leaching media for spent cathodes, including for our leaching results, inorganic acids, HES based on organic acids and hydrophobic DES. (ChCl – Choline chloride; OxA – oxalic acid; LacA – lactic acid; TosA – p-toluenesulfonic acid; ForA – formic acid; HBTA – benzoyltrifluoroacetone).

Leaching medium	Acid/HBD concentration (mol·L ⁻¹)	Solvent density (kg·L ⁻¹)	Cathode powder (mol·L ⁻¹)	S/L ratio (g L ⁻¹)	Atom efficiency (%)	Ref.
TOPO:decanoic acid (+ 1 mol·L ⁻¹ HCl)	0.9	0.9	0.99	44	(95 ± 6)	This work
ChCl:OxA (1:1)	5.5	1.3	0.25	24	18	[1,2]
ChCl:LacA (2:1)	3.2	1.2	0.20	19	24	[3,4]
ChCl:TosA:H ₂ O (1:1:2)	3.1	1.2	0.31	30	39	[5,6]
ChCl:ForA (1:2)	10.3	1.2	0.25	24	9	[7]
HBTA:TOPO (2:1)	2.6	1.1	0.10	10	16	[6,8]
HNO ₃ + 1.7 v% H ₂ O ₂	1.0	–	0.19	20	78	[9]
H ₂ SO ₄ + 0.075 mol·L ⁻¹ NaHSO ₃	1.0	–	0.19	20	76	[10]
HCl	1.0	–	0.75	44	75	This work

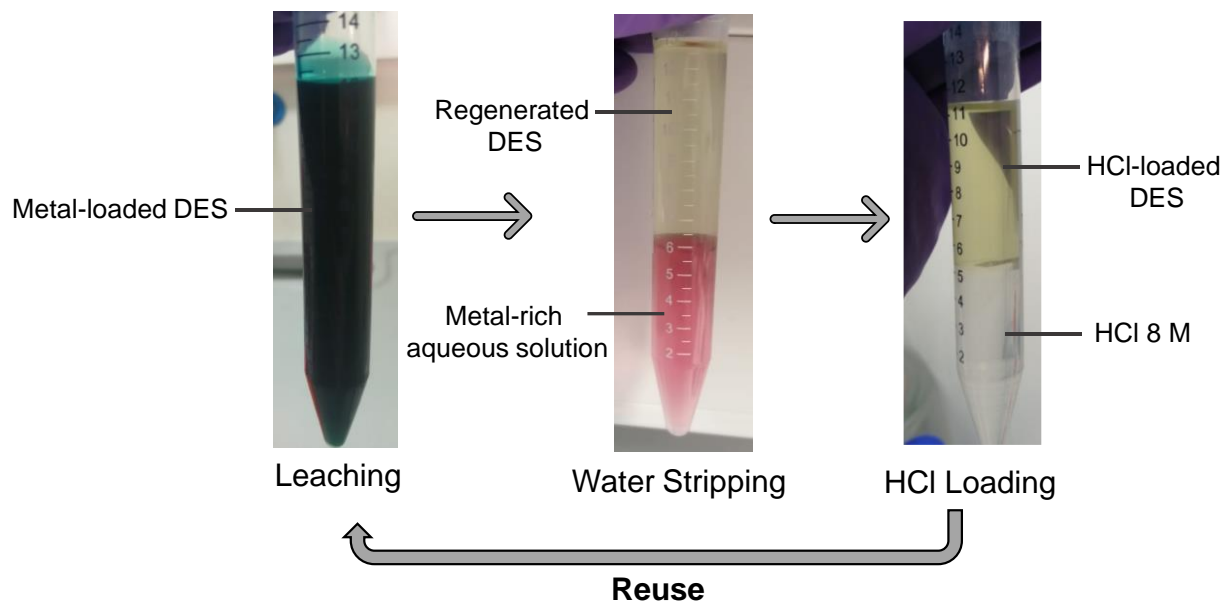


Figure S5. Visual changes of the system throughout the various stages of the process.

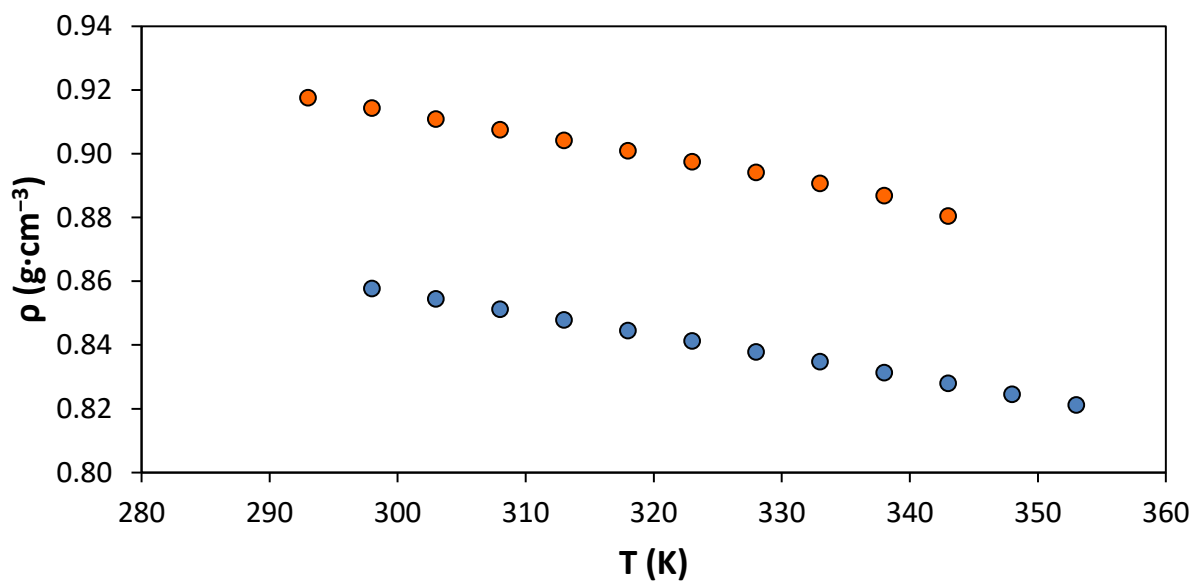


Figure S6. Density of the DES before (blue) and after (orange) metal loading.

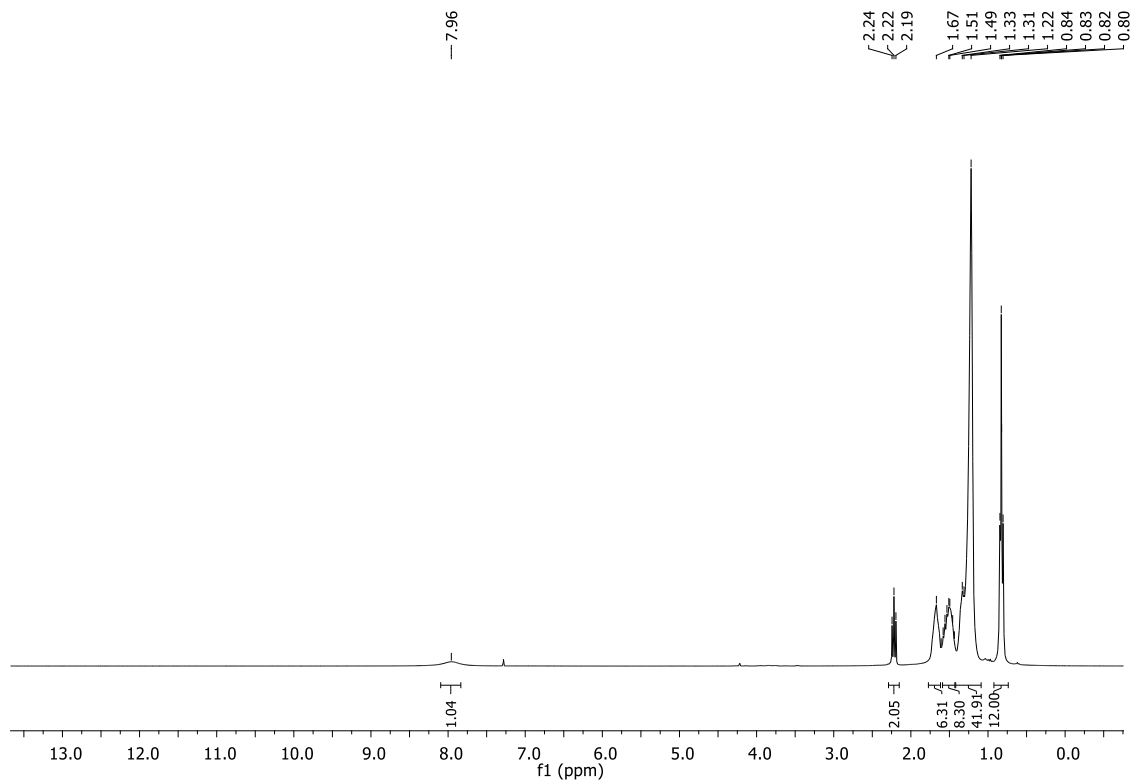
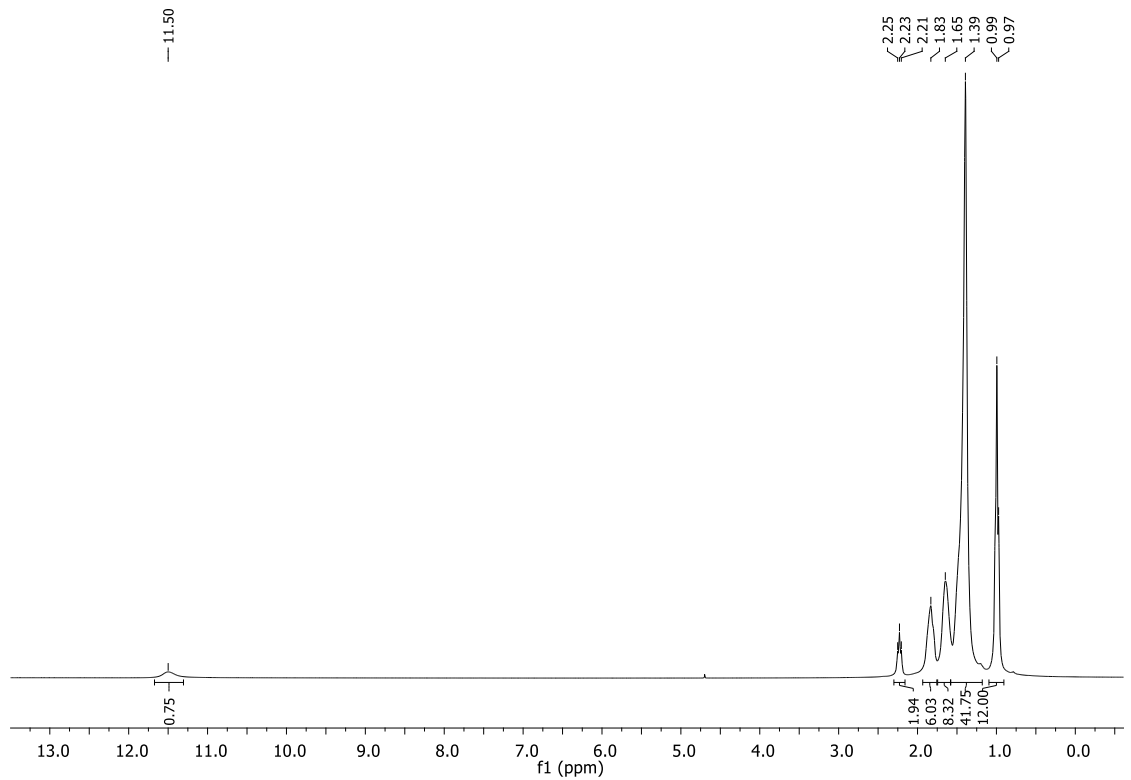


Figure S7. ^1H NMR spectra of TOPO:decanoic acid mixture before (top) and after (bottom) five leaching-stripping cycles.

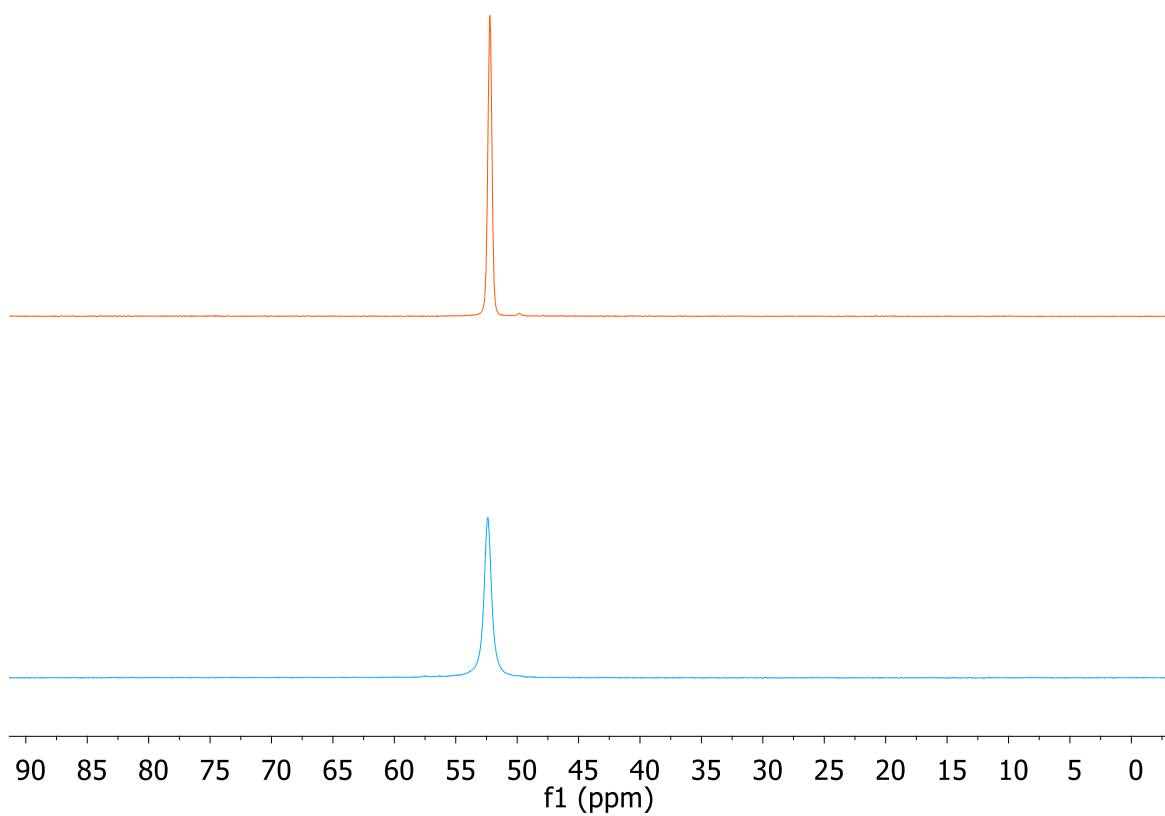


Figure S8. ^{31}P NMR spectra of TOPO:decanoic acid mixture before (blue line) and after (orange line) five leaching-stripping cycles.

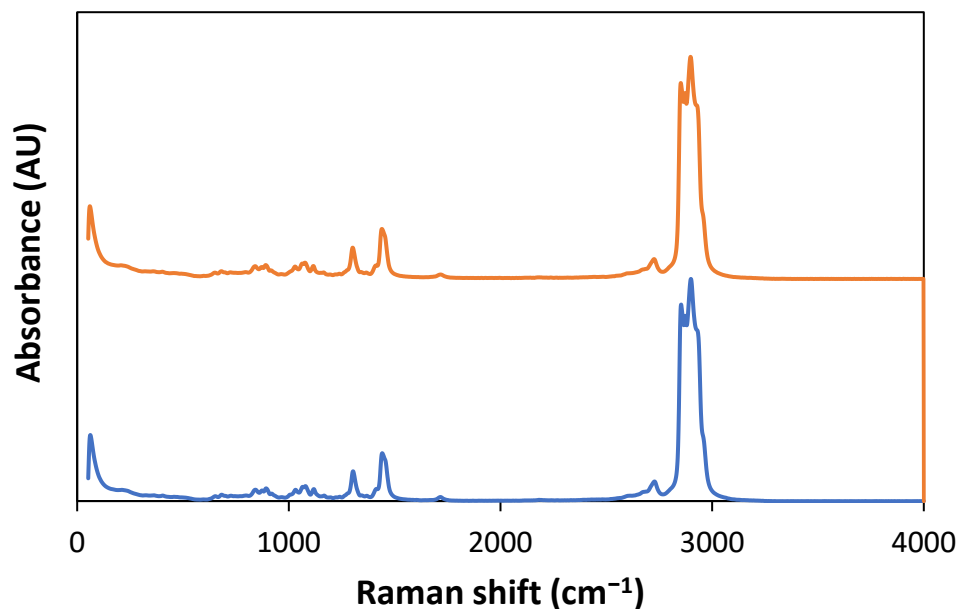


Figure S9. Raman spectra of the TOPO:decanoic acid mixture before (blue line) and after (orange line) five leaching-stripping cycles.

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