Electronic Supplementary Information for

A Techno-Economic Approach to Guide the Selection of Flow Recyclable Ionic Liquids for Nanoparticle Synthesis

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Table S1 Ten IL solvents that were evaluated for the Pt nanoparticle synthesis that did not yield isolable, phase pure Pt nanoparticles.

1	trihexyltetradecylphosphonium bis(trifluoromethanefulonate)imide
2	trihexyltetradecylphosphonium decanoate
3	trihexyltetradecylphosphonium dicyanamide
4	trihexyltetradecylphosphonium bromide
5	trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate
6	1-butyl-3-methylimidizolium hexafluorophosphate
7	1-butyl-3-methylimidizolium tetrafluoroborate
8	1-butyl-3-methylimidizolium dicyanamide
9	1-butyl-1-methylpyrrolidinium dicyanamide
10	1-butyl-2-methylpyridinium tetrafluoroborate

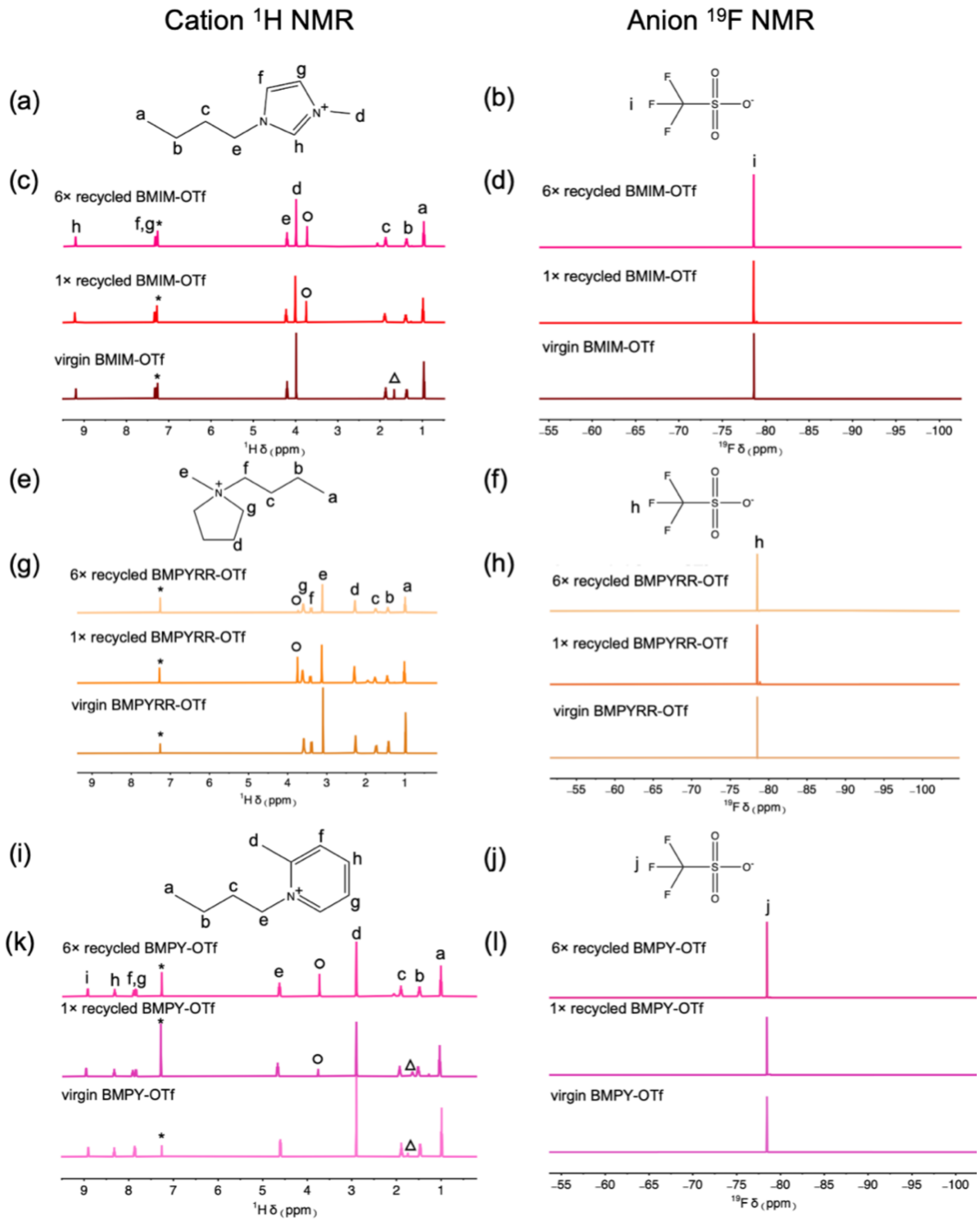

Fig. S1 Structures of the (a) $BMIM^+$ cation and the (b) OTf^- anion with labeled solution (c) ^{1}H NMR and (d) ^{19}F NMR spectra of virgin, 1×, and 6× recycled IL solvent. Structures of the (e) $BMPYRR^+$ cation and the (f) OTf^- anion with labeled solution (g) ^{1}H NMR and (h) ^{19}F NMR spectra of virgin, 1×, and 6× recycled IL solvent. Structures of (i) $BMPY^+$ cation and the (j) OTf^- anion with labeled solution (k) ^{1}H NMR and (l) ^{19}F NMR spectra of virgin, 1×, and 6× recycled IL solvent. The open triangle (Δ) denotes water at 1.56 ppm. The open circle (○) denotes ethylene glycol at 3.70 ppm. Asterisks (*) represent the residual nondeuterated solvent peak of chloroform.

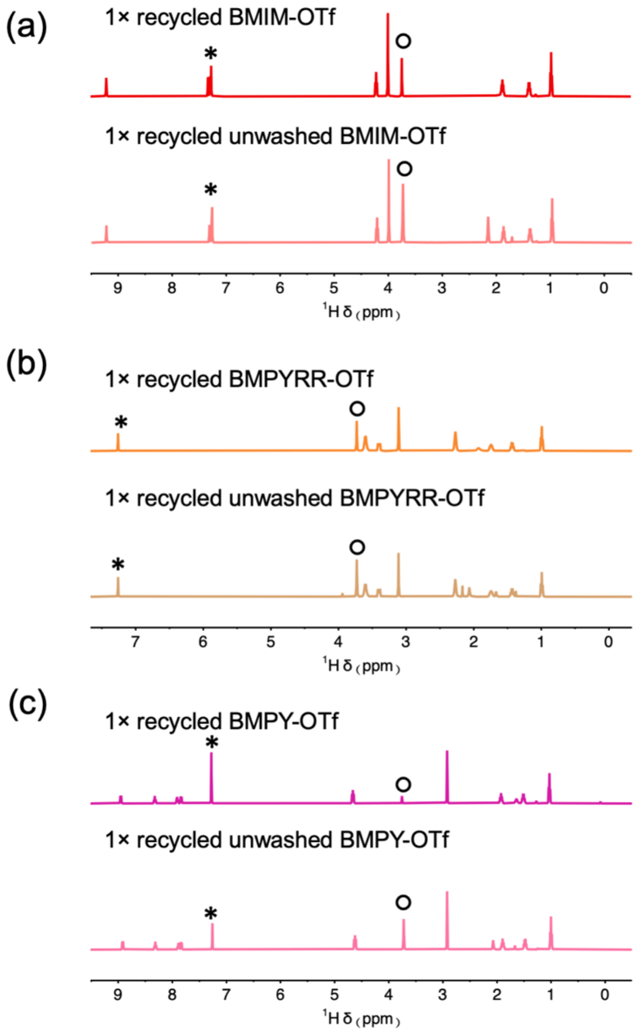

Fig. S2 Solution ^{1}H NMR spectra of 1× recycled (a) BMIM-OTf, (b) BMPYRR-OTf, and (c) BMPY-OTf before and after purification. The open circle (○) denotes ethylene glycol at 3.70 ppm, which decreases comparing the before and after spectra. Asterisks (*) represent the residual nondeuterated solvent peak of chloroform.

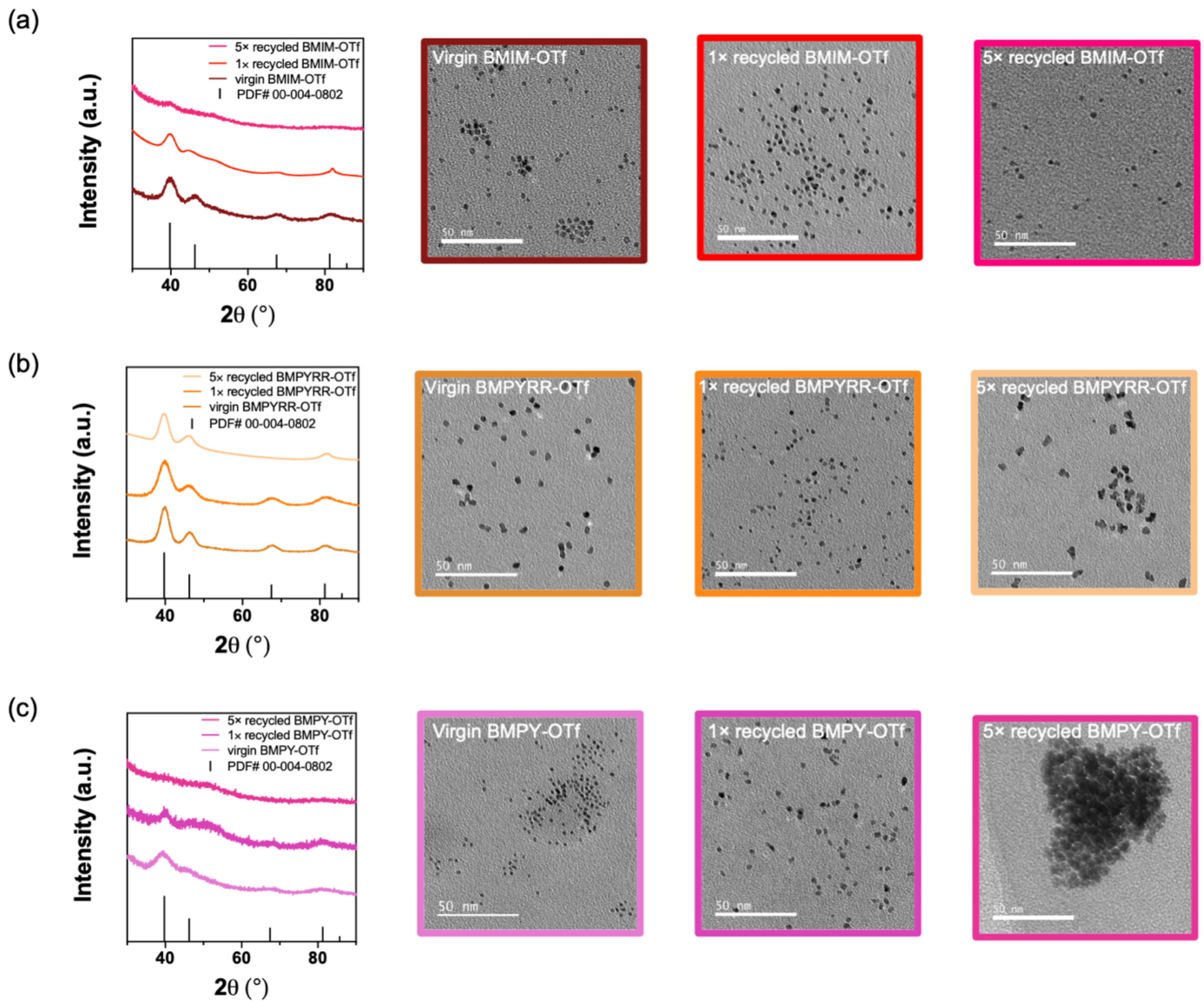

Fig. S3 Powder XRD patterns and TEM images of Pt nanoparticles synthesized in virgin, 1×, and 5× recycled (a) BMIM-OTf, (b) BMPYRR-OTf, and (c) BMPY-OTf.

Techno-Economic Analysis Details

In the assumptions, "base" denotes the base case for analysis, while "high" and "low" indicate the high and low values used for that parameter in sensitivity analysis, respectively. Note that, for some parameters, a higher parameter value translates to lower material cost.

Assumptions: General

Table S2 Assumptions for cost analysis: economic and processing cost.

Economic	
Pricing Basis Year	2016
Currency	U.S. Dollars ($)
CapEx & OpEx Factors Processing Cost	
Production Scale (Finished Material)[a]	500,000 kg/year
Operating Hours per Year	8760 h
On-Stream Factor[b]	90%

Plant Life	10 years
Selling Margin: Return on Capital Investment (pre-tax)	25%/year
Labor Rate (including benefits)	$48/h

[a] The production scale is relatively arbitrary for this synthesis, which uses equipment that "scales out not up," meaning that costs scale linearly with production volume. The variation in cost with changing scale was found to be only on the order of 1%. The production scale in this instance was chosen to align with other estimates on supported Pt catalysts using CatCost.

[b] Fraction of operating hours in which product is being made, with the remainder maintenance downtime. Operating labor is charged even during downtime.

Assumptions: Raw Materials

Table S3 Assumptions for cost analysis: raw materials.

General Factors	
Losses Due to Waste/Spoilage	3%
Materials Prices[a]	
Pt metal (2018 USD)[b]	Base $840/oz t, High $1,030/oz t, Low $770/oz t
K_2PtCl_4[c]	Base $11,683.92/kg
Ethylene glycol	$52.01
BMIM-NTf_2	$189.24/kg
BMIM-OTf	$187.30/kg
BMPYRR-NTf_2	$424.48/kg
BMPYRR-OTf	$290.69/kg
BMPY-NTf_2	$383.16/kg
BMPY-OTf	$409.06/kg
Polyvinylpyrrolidone (PVP)	$52.01/kg
0.1 M HNO_3	$0.02/kg
Carbon Support (2017 dollars)[2]	$20/kg
Acetone	$1.87/kg
Ethanol	$1.33/kg
Hexane	$0.64/kg

[a] Prices were determined through a survey of public and proprietary sources of both contracts and commodity prices. The prices reflect the authors' judgement of reasonable scenarios for high purity (99+%) gases, water, etc., but will not be applicable for all situations. All prices are given in 2016 USD except where noted.

[b] Prices for Pt were determined by a survey of the spot prices on infomine.com, rounded to the nearest $10/oz t, from the two-year period ending 07/30/2019. Prices from this survey were treated as being in 2018 USD to approximate the 2017–2019 time range. A baseline Pt price of $840/oz t was assumed, with the two-year high ($1030/oz t) and low ($770/oz t) as scenarios. Prices were escalated to 2016 USD using the U.S. Bureau of Labor Statistics Chemical Producer Price Index.

[c] The price of K_2PtCl_4 was unreasonably low when determined by extrapolation from Sigma Aldrich lab-scale pricing ($6,680/kg), so the price was estimated using the value of Pt content as a proxy. The Pt content in K_2PtCl_4 is 46.998% by mass. Using the baseline price of $840/oz t for Pt ($27,006.63/kg and $24,860.46/kg after escalating from 2018 to 2016 dollars), the price for K_2PtCl_4 is obtained as 46.998% × $24,860.46/kg = 11,683.92/kg (2016 USD).

Assumptions: Synthesis & Recycling

Table S4 Assumptions for cost analysis: 0.5 wt% NP-Pt/C material.

General	
Synthesis Yield, ethylene glycol + virgin BMIM-NTf_2	36%
Synthesis Yield, ethylene glycol + recycled BMIM-NTf_2	38%
Synthesis Yield, ethylene glycol + virgin BMIM-OTf	14%
Synthesis Yield, ethylene glycol + recycled BMIM-OTf	70%
Synthesis Yield, ethylene glycol + virgin BMPYRR-NTf_2	98%
Synthesis Yield, ethylene glycol + recycled BMPYRR-NTf_2	98%
Synthesis Yield, ethylene glycol + virgin BMPYRR-OTf	94%
Synthesis Yield, ethylene glycol + recycled BMPYRR-OTf	160%
Synthesis Yield, ethylene glycol + virgin BMPY-NTf_2	24%
Synthesis Yield, ethylene glycol + recycled BMPY-NTf_2	31%
Synthesis Yield, ethylene glycol + virgin BMPY-OTf	10%
Synthesis Yield, ethylene glycol + recycled BMPY-OTf	68%
Recycling Yield for BMIM-NTf_2[a]	91%
Recycling Yield for BMIM-OTf[a]	65%
Recycling Yield for BMPYRR-NTf_2[a]	94%
Recycling Yield for BMPYRR-OTf[a]	70%
Recycling Yield for BMPY-NTf_2[a]	90%
Recycling Yield for BMPY-OTf[a]	68%
CapEx & OpEx Factors Parameters: Synthesis	
Synthesis Scale[b]	0.195 g K_2PtCl_4/batch
Production Rate Per Reactor System (for CapEx)	2 batches/h
Operators Per Reactor System (for OpEx)	1
Active Glassware Quantity Per Reactor System[c]	48
Spares: Glassware[d]	5:1 spares:active (base quantity × 6)
Spares: Equipment (pumps, tubing, separators, etc.)	1:2 spares:active (base quantity × 1.5)
Electricity Consumption[e]	0.19 kWh/batch
CapEx & OpEx Factors Parameters: IL Recycling	
Recycling Scale[f]	0.96 L IL/batch
Production Rate Per Recycling System (for CapEx)	One batch every shift (8 hours)
Operators Per Recycling System (for OpEx)	0[f]
Electricity Consumption[e]	0.58 kWh/batch

[a] Defined as volume of IL recovered after recycling steps divided by volume of IL added initially in synthesis.

[b] Based on the 5× scale used in the optimized IL recycling procedure. This scale was confirmed to preserve yield and product quality.

[c] The quantity of glassware in active use. Assuming a 24-hour cleaning cycle and 2 reactions per hour with 24/7 operation, 48 flasks would be needed. Spares/replacement due to breakage accounted for separately.

[d] This quantity of spare glassware purchased (capitalized) at the start of operations is roughly equivalent to a 20%/year replacement rate.

[e] The electricity consumption of the synthesis (hot plate/stirrer) and IL recycling (syringe pump, vacuum pump and hot plate) procedures was measured using a Kill-a-Watt power meter on a per-batch basis. Power consumption for a synthesis batch was measured as 0.19 kWh. For a recycling batch and flow workups, the hotplate contributes 0.11 kWh and the vacuum pump (190 W), which was assumed to be shared between four recycling batches during the 1 h drying step of the recycling procedure, or 0.05 kWh. Power consumption for the syringe pumps was measured as 0.05 kWh per pump (6.8 W), on an 8 h operation basis, regardless of infusion or withdrawal mode.

[f] We have assumed that an operator would be able to complete the recycling and purifying process (3× washes the continuous flow recycler) in as little as 15 min of hands-on time spaced throughout the day. Manifolds can be used to split the IL infusion stream and acidified water infusion stream into 20 parallel operation lines,[3] and the washed IL products from the corresponding 20 recyclers can be collected to 20 individual syringes driven by two syringe pumps in withdrawal mode with two 10-syringe holder racks. The parallel processes could recycle all of the IL needed for a day's syntheses (48 mL/synthesis batch × 20 synthesis batches/day = 960 mL/day) in one recycling batch per day. Therefore, the additional labor requirements for the recycling step can be already included in the daily duties of the synthesis reactor operators.

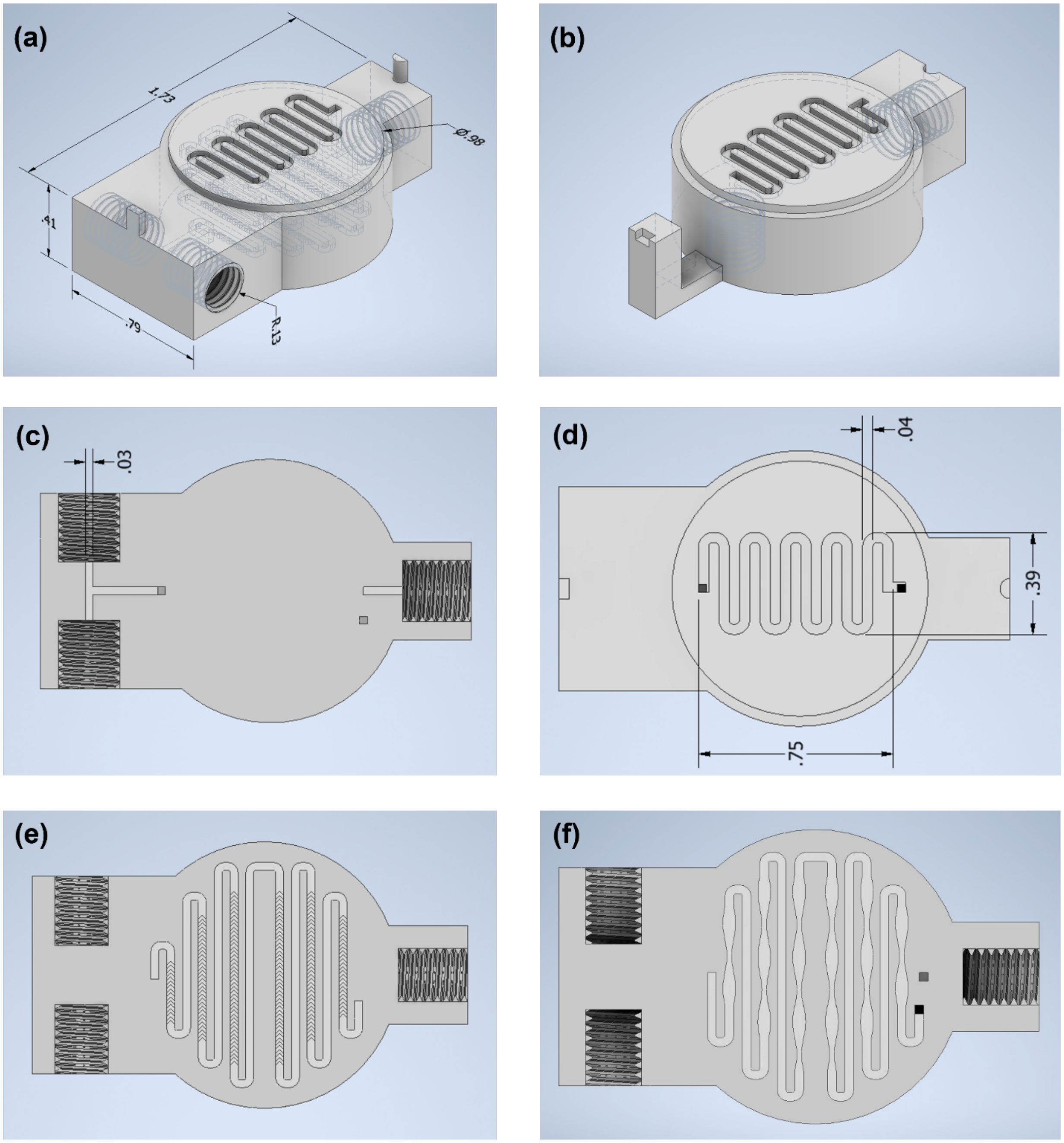

Fig. S4 Drawings and details of the 3D-printed recycler. All measurements are in the unit of inches. (a) upper part of the recycler, containing an IL inlet, a water inlet, and a wastewater outlet. (b) Lower part of the recycler, containing an IL washed product outlet. (c) Cross section of the upper part showing a T-shaped junction in the inlet. (d) Bottom view of the upper part showing the membrane separation area. (e) Cross section of the upper part showing the herringbones in the channel. (f) Cross section of the upper part showing the wavy channels.

References

1. S. García, J. J. Buckley, R. L. Brutchey, and S. M. Humphrey, *Inorganica Chimica Acta*, 2014, **422**, 65-69.
2. F. G. Baddour, L. Snowden-Swan, J. D. Super, K. M. Van Allsburg, *Org. Process Res. Dev.* 2018, **22**, 1599–1605.
3. L. Wang; L. R. Karadaghi; R. L. Brutchey; N. Malmstadt *Chem Commun.*, 2020, **56**, 3745-3748.