Electronic Supplementary Information

Organic-solvent-free electromembrane extraction based on semi-interpenetrating polymer networks

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Table S1 Comparison between the traditional existing EME and the organic-solvent-free semi-IPN EME system in this study.

SLM		Mw	Water solubility (g/L) [a]	Boiling point (°C) [a]	Toxicity [a]	Reusability	Degradation half-life [a]	Safety [a]
Type	Organic solvent							
Nitroaromatis /benzene derivatives	2-NPOE [1]	251	0.006 [b]	351 [b]	Ecotoxicity, carcinogenicity, mutagenicity. [3-5]	n.r.	n.r.	n.r.
	Toluene [2]	92	0.526	111	Ecotoxicity: Morone saxatilis, LC50, 7.3 mg/L; Acute toxicity: Mouse, LD50, 59 mg/kg (ip);	n.r.	2 d	Flammable; Irritant.
Aliphatic alcohols	1-Heptanol [6]	116	1.67	175	Ecotoxicity: Alburnus alburnus, LC50, 45 mg/L; Acute toxicity: Rat, LD50, 500 mg/kg (oral); Severe eye irritation;	n.r.	28 h	Irritant;
	1-Octanol [6]	130	0.54	196	Ecotoxicity: Pimephales promelas, LC50, 13.5 mg/L; BCF: 44; Acute toxicity: Mouse, LD50, 69 mg/kg (iv); Severe eye irritation;	n.r.	27 h	Irritant;
	1-Nonanol [6]	144	0.14	213	Ecotoxicity: Pimephales promelas, LC50, 5.7 mg/L; Toxic to aquatic life with long lasting effects; BCF:160; Acute toxicity: Rabbit, LC50, 15 mg/kg (iv); Skin and eye irritation;	n.r.	28 h	Irritant;
Ketones	2-Octanone [7]	128	0.899	173	Ecotoxicity: Pimephales promelas, LC50, 36 mg/L; Acute toxicity: Rat, LD50, 800 mg/kg (ip); Severe eye irritation; Possible CNS depression to human.	n.r.	1.6 d	Flammable;
	2-nonanone [8]	142	0.371	195	Acute toxicity: Rat, LD50: 3200 mg/kg (oral); Skin and eye irritation.	n.r.	n.r.	Highly flammable; Irritant.
	2-Undecanone [9]	170	0.24	232	Ecotoxicity: Pimephales promelas, LC50, 1.5 mg/L; Very toxic to aquatic life.	n.r.	1.2 d	n.r.
	6-Undecanone [8]	170	0.05	228	Toxic to aquatic life with long lasting effects; Acute toxicity: Mouse, LD50:117 mg/kg (iv); Skin and eye irritation;	n.r.	n.r.	Flammable; Irritant.
Alkylated phosphates /phosphites	DEHPi [10]	305	0.006 [b]	309 [b]	BCF:410; Acute toxicity: Rabbit, LD50, 100 mg/kg (iv); Skin, eye and respiratory tract irritation.	n.r.	5.9 h	Corrosive; Irritant. Heating produces toxic fumes
	DEHP [10]	322	2.1 [b]	393 [b]	Ecotoxicity: water flea, LC50, 27.2 mg/L; Acute toxicity: Rat, LD50, 50 mg/kg (ip); Prolonged contact to human may cause severe burns;	n.r.	5.9 h	Corrosive; Irritant. Heating produces toxic fumes.
	TBoEP [10]	399	1.1	414 [b]	Ecotoxicity: Japanese Medaka, LC50, 6.8mg/L (24h); Acute toxicity: Mouse, LD50, 180 mg/kg (iv); Neurotoxicity; Developmental or reproductive toxicity; Skin, eye and respiratory tract irritation.	n.r.	3 h; 93-95 d (hydrolysis, pH 5-9)	Irritant; Heating produces toxic fumes.
	TBP [10]	266	0.28	289	Ecotoxicity: Goldfish, LC50: 8.8 mg/L; BCF:30-35; Acute toxicity: Rat, LD50, 100 mg/kg (iv); Endocrine disrupting effect; Neurotoxicity; Skin, eye and respiratory irritation; Probable oral lethal dose to human: 0.5-5 g/kg.	n.r.	4.4 h; 9.9-11.5 y (pH 9-5)	Irritant; Corrosive; Heating produces toxic fumes.
Aliphatic nitriles	Dodecanenitrile [11]	181	0.071 [b]	277	Very toxic to aquatic life with long lasting effects; Skin irritation;	n.r.	n.r.	Irritant;
	2,3,4,5,6-Pentafluorobenzonitrile [11]	193	0.005 [b]	162	Skin and eye irritation.	n.r.	n.r.	Flammable; Irritant.
	o-Tolunitrile [11]	117	0.64 [b]	205	Harmful to aquatic life with long lasting effects; Acute toxicity: Mouse, LD50, 700mg/kg (ip);	n.r.	n.r.	Flammable; irritant.
Phthalates	Diallyl phthalate [11]	246	0.182	290	Ecotoxicity: Green algae, EC50, 5.3mg/L (48h); BCF:61; Acute toxicity: Rat, LD50: 656 mg/kg (oral); Hamster ovary cytogenetic mutation, 200 mg/L; Teratogenic, carcinogenicity, mutagenicity, reproductive and developmental toxicity, under restriction in EU and China.	n.r.	6.9 h; 1 y (hydrolysis, pH 7)	Irritant;
	Diisobutyl phthalate [11]	278	0.031 [b]	296	Ecotoxicity: Pimephales promelas, LC50, 0.9mg/L; BCF:240; Endocrine disrupting and genotoxic effect to human cells (DNA damage, 216 μmol/L);	n.r.	1.2 d; 5 y (hydrolysis, pH 7)	Combustible; Fire produce toxic fumes.
	Diethyl Phthalate [11]	222	1.08 [b]	295	Ecotoxicity: Opossum shrimp, LC50,10.3mg/L; BCF: 117 (bluegill sunfish); Acute toxicity: Rat, LC50 >4.64 mg/L(inhalation); Germ cell mutagenicity; Eye and respiratory irritation.	n.r.	4.6 d; 106 d (hydrolysis, pH 8)	Irritant; Heating emits acrid smoke.
	Dibutyl phthalate [11]	278	0.01	340	Ecotoxicity: Zebrafish, LC50, 2.2 mg/L; BCF:176 (Cyprinus carpio); Very toxic to aquatic life; Acute toxicity: Mouse, LD50: 720 mg/kg(iv); Reproductive toxicity, endocrine disrupting effects;	n.r.	42 h; 3.4 y (hydrolysis, pH 7)	Heating emits acrid fumes.
	Benzyl butyl phthalate [11]	312	0.003	370	Ecotoxicity: Pimephales promelas, LC50, 2.1 mg/L (48h); Very toxic to aquatic life with long lasting effects; Endocrine disruptor, carcinogenicity, reproductive toxicity and neurotoxicity; A teratogens; A possibly human carcinogen (U.S. EPA IRIS);	n.r.	35 h; 1.4 y (hydrolysis, pH 7)	Heating emits irritating fumes.
Ionic liquid	1-Hexyl-3-methylimidazolium-hexafluorophosphate [12]	312	7.5	n.r.	Skin, respiratory, eye irritation or damage.	n.r.	n.r.	n.r.
PIM	2-NPOE, ionic liquid, DCM [13]	DCM: 85	13	40	Ecotoxicity: Daggerblade Grass Shrimp, LC50, 108.5 mg/L(48h); Acute toxicity: Mouse, LD50,437mg/kg (ip); Animal: liver, lung, gland tumors (inhalation); Skin, eyes irritation, chemical burns; A probably carcinogenic to human.	n.r.	160 d; 1.5 y (hydrolysis, 25°C)	Release toxic chloride fumes.
semi-IPN	**Free**	≥4000	<0.015	>300 [b]	Acute toxicity: Rat, LD50 >40 g/kg (oral); Very low toxicity or non-toxicity, easy access.	8 times	n.r.	Non-flammable and non-irritating

2-NPOE: 2-nitrophenyl octyl Ether; DEHPi: bis(2-ethylhexyl) hydrogen phosphite; DEHP: di(2-ethylhexyl) phosphate; TBoEP: tris(2-butoxyethyl) phosphate; TBP: tributyl phosphate; Mw: Molecular weight; DCM: dichloromethane; Degradation half-life: It refers to the estimated half-life of the gas-phase organic solvent in the atmosphere

through reaction with photochemically-produced hydroxyl radicals; BCF: bioconcentration factor; CNS: Central Nervous System; EC50: concentration for 50% of maximal effect; ip: intraperitoneal; iv: intravenous; n.r. means not reported. [a] https://pubchem.ncbi.nlm.nih.gov/ (January 7, 2021); [b] https://scifinder.cas.org (January 7, 2021).

Table S2 The corresponding amount of PPG4000 and TDI for semi-IPN and IPN membrane with different cross-linking degrees.

TDI (μL) / Crosslinkage / PPG (g)	semi-IPN (0%)	IPN (25%)	IPN (50%)	IPN (100%)
PPG2000 (2.0 g)	0	*	*	142.2
PPG3000 (2.0 g)	0	*	*	94.8
PPG4000 (2.0 g)	0	17.7	35.5	71.1

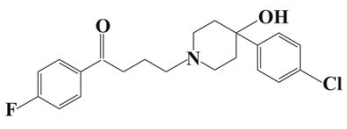
* means not synthesized.

Table S3 Thermal profiles of the semi-IPN membranes before and after EME.

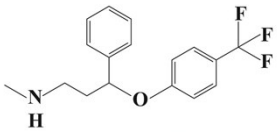
Samples		PPG molecular weights	20% Weight loss in Temperature (°C)	Δ Temperature (°C)	Char yield at 500 °C (%)
semi-IPN$_2$	Before EME	2000	260	68	0.80
	After EME	2000	328		0.73
semi-IPN$_3$	Before EME	3000	230	30	-0.85
	After EME	3000	260		-0.02
semi-IPN$_4$	Before EME	4000	243	-5	0.00
	After EME	4000	238		0.00

Table S4 EME recoveries and the percentage decrease in recovery rate (PDIRR) compared to 0 day for model basic drugs (1.0 mg L^{-1}) as a function of ambient storage time of the semi-IPN$_4$ membrane.

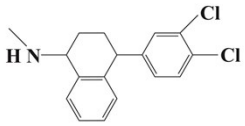
	0 day	0.5 day		1 day		2 days		4 days		8 days	
	Recovery (%)	Recovery (%)	PDIRR (%)	Recovery (%)	PDIRR (%)	Recovery (%)	PDIRR (%)	Recovery (%)	PDIRR (%)	Recovery (%)	PDIRR (%)
HAL	70.45	77.01	-9.30	64.18	8.90	63.17	10.33	64.15	8.94	62.58	11.18
FLU	83.14	81.33	2.17	78.15	5.99	72.66	12.61	75.38	9.33	79.66	4.19
SER	94.01	96.91	-3.08	89.70	4.59	86.33	8.17	87.96	6.43	86.14	8.37



Haloperidol (HAL)
(log P=3.8, pKa=8.0)

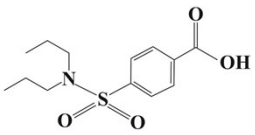


Fluoxetine (FUL)
(log P=3.9, pKa=10.1)

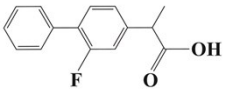


Sertraline (SER)
(log P=5.1, pKa=9.5)

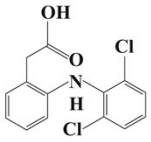
Scheme S1 Chemical structures, log P and pKa values of the model basic analytes.



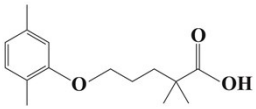
Probenecid (PRO)
(log P=2.4, pKa=3.5)



Flurbiprofen (FBP)
(log P=3.9, pKa=4.4)



Diclofenac sodium (DIC)
(log P=4.3, pKa=4.0)



Gemfibrozil (GEM)
(log P=4.4, pKa=4.4)

Scheme S2 Chemical structures, log P and pKa values of the model acidic analytes.

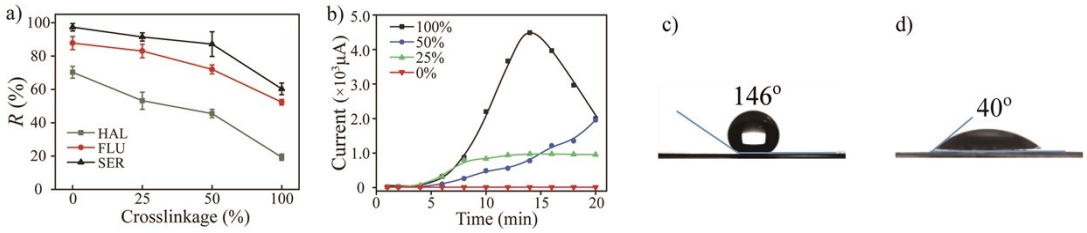


Fig. S1 Performance of membranes with different degrees of crosslinking. a) EME efficiency of IPN membrane synthesized by PPG4000 with different crosslinking degree (0%, 25%, 50%, 100%) for three basic drugs with concentration of 1.0 mg L^{-1}. b) Extraction current at each crosslinking degree during EME. EME was conducted for 20 min with 10 mM TFA as acidic solvents of donor and acceptor solution. The extraction voltage was 100 V. c) The contact angle of water droplet on the neat PP network/support. d) The contact angle of water droplet on the smooth polypropylene membrane.

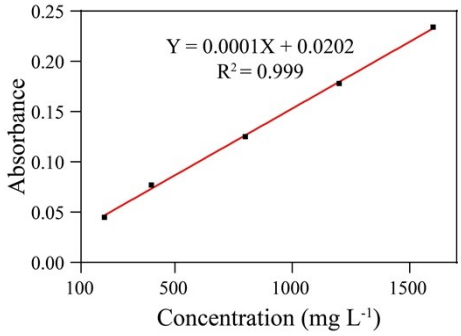


Fig. S2 Linear results for detection of PPG2000. The absorbance set at 570 nm. (The absorbance at 570 nm of the reaction solution was 0.147, according to the standard curves, the mass of the leaked PPG2000 from semi-IPN_2 was 1.52 mg. The PPG2000 on the membrane before EME was 3.26 mg by subtracting the mass of the neat pp support (0.67 mg) from the mass of semi-IPN_2 (3.93 mg). PPG2000 leakage in solution was calculated to be 47 %.)

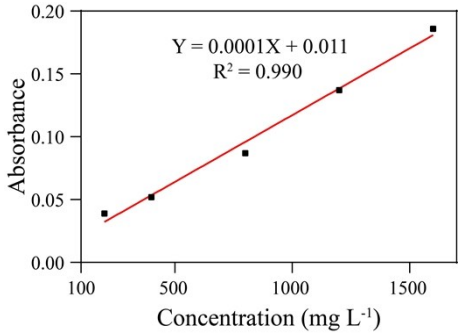


Fig. S3 Linear results for detection of PPG3000. The absorbance set at 570 nm. (The absorbance at 570 nm of the reaction solution was 0.079, according to the standard curves, the mass of the leaked PPG3000 from semi-IPN_3 was 0.816 mg. The PPG3000 on the membrane before EME was 3.68 mg by subtracting the mass of the neat pp support (0.57 mg) from the mass of semi-IPN_3 (4.25 mg). PPG3000 leakage in solution was calculated to be 22 %.)

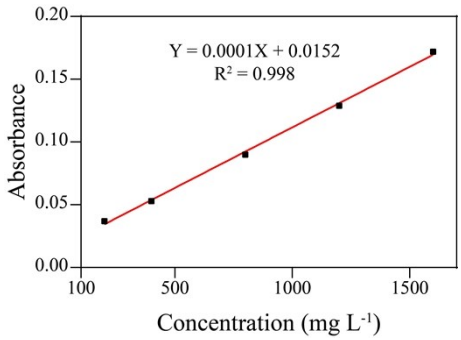


Fig. S4 Linear results for detection of PPG4000. The absorbance set at 570 nm. (The absorbance at 570 nm of the reaction solution was 0.051, according to the standard curves, the mass of the leaked PPG4000 from semi-IPN_4 was 0.42 mg. The PPG4000 on the membrane before EME was 4.13 mg by subtracting the mass of the neat pp support (0.65 mg) from the mass of semi-IPN_4 (4.78 mg). PPG4000 leakage in solution was calculated to be 10 %.)

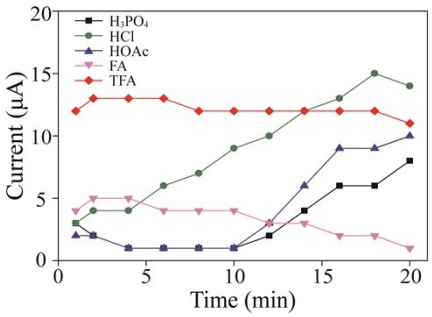


Fig. S5 The EME current of each acid (10 mM H_3PO_4, HCl, HOAc, FA, TFA) as donor and acceptor solution for basic drugs. EME was conducted for 20 min and the extraction voltage was 100 V.

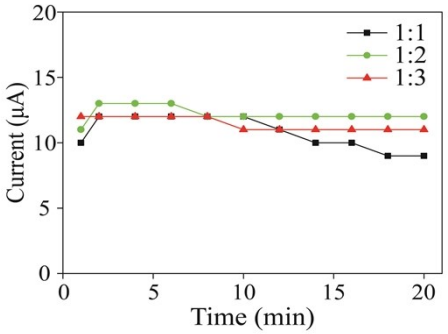


Fig. S6 The EME current of the basic drugs spiked urine samples with different dilution (1:1, 1:2, 1:3). EME was conducted for 20 min with 10 mM TFA as acceptor solution and the extraction voltage was 100 V.

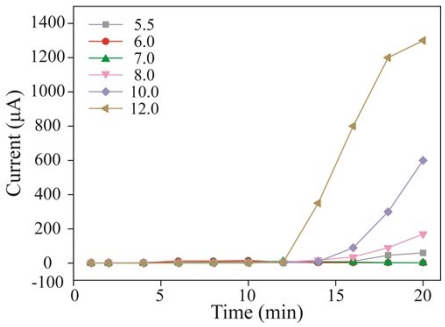


Fig. S7 The EME current of the four acidic analytes with concentration of 1.0 mg L^{-1} at different pH value of the donor solution (pH at 5.5, 6.0, 7.0, 8.0, 10.0, 12.0). Donor solutions of different pH values were adjusted by HCl (pH at 1.0) or NaOH (pH at 13.0) solution. EME was conducted for 20 min with NaOH (pH at 12.0) as basic solvent of acceptor solution. The extraction voltage was 100 V.

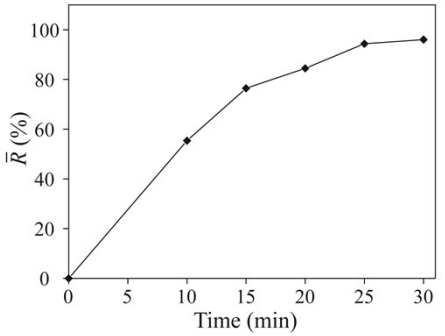


Fig. S8 Extraction time on the average recoveries of the acid analytes with a concentration of 1.0 mg L^{-1}.

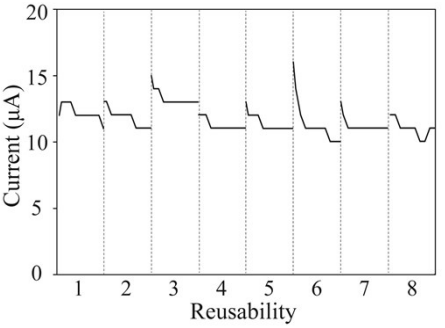


Fig.S9 The EME current of each cycle. EME was conducted for 20 min with 10 mM TFA as acidic solvent of the donor and acceptor solution and the extraction voltage was 100 V in each cycle.

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