Supplementary material

1. Synthesis of bulk polymeric ionic liquids (in the absence of nanoparticles)

The PIL was synthesized according to the procedure developed by J.P. Lindner. Basically, the PIL was readily obtained by aqueous mixing of acetic acid (2 equivalents), hexamethylenediamine, glyoxal solution (40%) and formaldehyde (37%), (each 1 equivalent). A mixture of acetic acid (5.05 g), water (7.33 g) and hexamethylendiamine (4.89 g) was performed until total dissolution. Hexamethylendiamine was melted first at 60°C. On the other hand, a mixture of glioxal solution (40%) (6.10 g) and formaldehyde (37%) (3.41 g) were mixed until total dissolution. Both solutions were mixed in a vessel and placed on a magnetic stirrer during 24 h at 25°C. Finally, a yellowish viscous liquid was obtained. This obtained color was due to side products resulting from a Maillard-type reaction of glyoxal with amines.

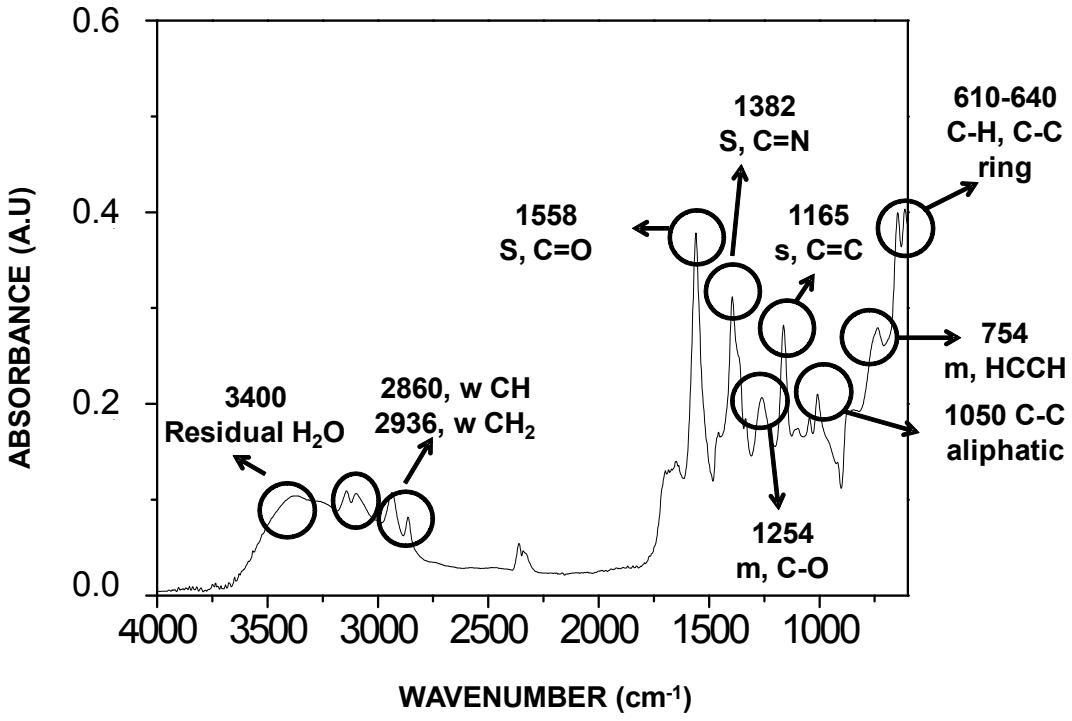

Figure S1. ATR-IR spectrum of bulk polymeric ionic liquid containing a backbone of 6 carbons

The obtained PIL was characterized by IR spectroscopy. Fig. S1 shows the IR spectrum for the PIL based in C6 chain monomer. There was a set of three strong signals between 1600 and 1000 cm^{-1}. The peak at 1558 cm^{-1} corresponded to the C=O stretching of the acetate counterion. The intense peaks at 1382 and 1165 cm^{-1} corresponded to C-N and C-C stretching vibrations of the imidazolium ring and the alkyl chains. The rest of the peaks were of medium or low intensity and corresponded to the other vibration modes of the bonds C-H, C-C, C-O and C=O present in the medium. The bands at 2860 and 2936 cm^{-1} correspond to the asymmetric and symmetric stretching modes of $-CH_2-$ vibrations. This IR spectrum matched in 100% the PIL spectrum available in the literature.

2. XRD measurements

The XRD spectra of the original and resulting material are presented in Figure S2 and discussed in the manuscript.

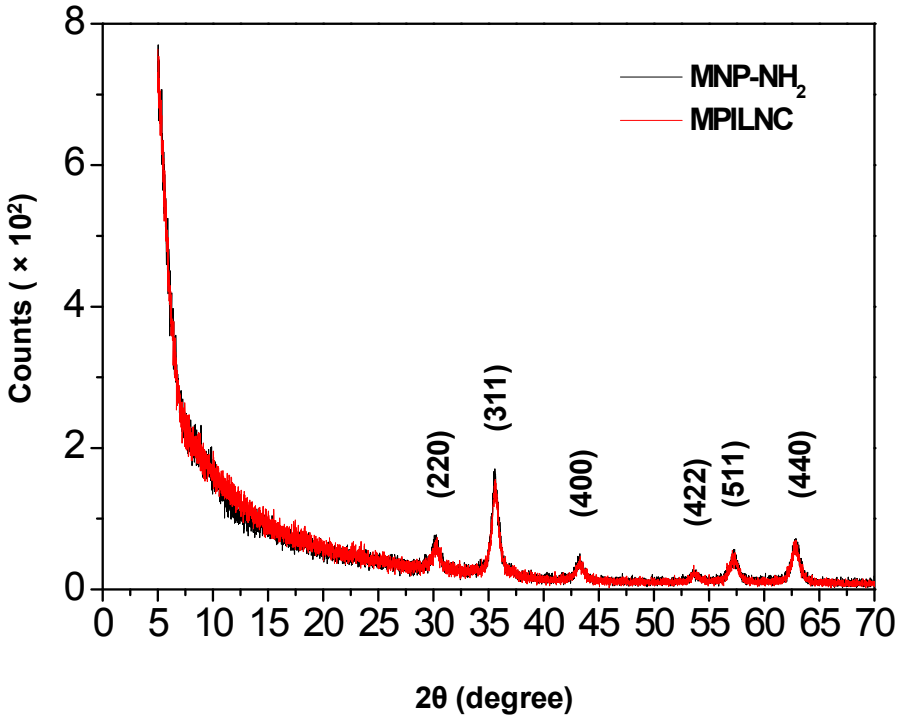

Fig. S2 X-ray diffraction for a) bare MNPs and b) MPILNC

3. Optimization of the extraction

Table S1
Studied variables in the microextraction process, including optimum values as well as the evaluated range.

Variables	Range	Optimum value
pH	2.0-8.0	6.0
Ionic strength (NaCl, g L^{-1})	0-300	0
MPILNC amount (mg)	5-30	5
Agitation type	Vortex-Ultrasound	Vortex
Microextraction time	5-30	5
Eluent	Methanol/Acetic acid 80:20, acetonitrile, Metanol/ammonia 80:20, methanol	Methanol/Acetic acid 80:20
Eluent volume (μL)	100-500	500

4. Extraction procedure

An amount of 5 mg of MPILNC were added to vials. Aliquots of 1.5 mL of aqueous standards or salive samples, containing the analytes were placed in the vials and dispersed for 1 min in a ultrasounds bath (J. P. Selecta, Barcelona, Spain). The dispersion was mechanically stirred in a vortex (IKA®, Staufen, Germany) at 750 r.p.m for 5 min. Further, the MPILNCs enriched with the analytes were separated by means of an external magnet (60 mm × 30 mm × 15 mm and 549.4 N of maximum magnetic force; Supermagnete, Gottmadingen, Germany). The liquid phase was discarded and 500 μL of methanol/acetic acid (80:20) were added. Elution of the analytes was accomplished during 1 min in an ultrasound bath. Then, 20 μL of the methanolic/acetic acid phase were injected in the HPLC-UV/VIS for analytes separation and quantification. Peak area of the chromatographic peaks was used as analytical signal.