

Supplementary Information

Zeolitic imidazolate framework dispersions for the fast and highly efficient extraction of organic micropollutants

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Experimental details

Glassware and reagent control for phthalate analysis at low concentrations: In order to avoid phthalate contamination, all glassware was rinsed with acetone, dichloromethane and acetone again, and dried at 573 K for at least 4 h and stored covered with aluminium foil. All reagents were checked in advance for potential phthalate contamination.

Stock standard solutions of the phthalate esters (10 mg/L) were prepared in hexane. Stock intermediate solutions were diluted stepwise in water. Working solutions were prepared daily. All standard solutions were kept in the dark at 253 K and working solutions were stored at 277 K in the refrigerator.

Chromatographic analysis of EPA phthalates: The analysis was performed using a Hewlett–Packard (Agilent Technologies, Palo Alto, CA, USA) HP 7890 series gas chromatography system, with a split/splitless injector and a HP 5973C mass selective detector system. The mass spectrometer was operated in the electron impact (EI) mode (70 eV using helium (99.999%) as the carrier gas at a flow rate of 1 mL/min. Analytes were separated on a 30 m × 0.25 mm i.d. × 0.25 mm film thickness DB5 (methyl 5% phenylpolysiloxane) gas chromatographic column (Agilent Technologies, Palo Alto, CA, USA). The initial GC oven temperature was 323 K (holding 1 min) and it was increased at 303 K/min to 553 K, and then up to 583 K (holding for 4 min) at 288 K/min. The injection volume was 1 μL, which was injected in pulsed splitless mode at a constant temperature of 563 K; pressure pulse: 35 psi and a pulsed time of 0.5 min, using an ultra-inert commercial liner packed with glass wool (Agilent). Later on, the inlet pressure was automatically increased up to a constant flow of 1 mL/min.

The EI ion source, the quadrupole mass analyzer, and the interface temperature were maintained at 503, 423, and 553 K, respectively. The MS is tuned to m/z 69, 219, and 502 for the EI corresponding to perfluorotributylamine. The MS was operated in the total ion current

mode, scanning from m/z 50 to 550 for identification purposes. In order to obtain the highest possible sensitivity, the acquisition was performed in the selected ion monitoring mode. The quantitative ion for each analyte was set as follows: DMP: 163,194; DEP: 149, 177, 222; DBP: 144, 167, 205, 223; BBP: 91, 149, 206; DEHP: 149, 167, 279 and DNOP: 149, 167, 261, 279.

FTIR spectra: Fourier transform infrared spectroscopy of the samples (as KBr pellets) were performed on a Bruker Vertex 80v spectrometer equipped with an MCT cryodetector, working at 3 cm^{-1} resolution.

Electronic microscopy: Particle morphology was analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) using a Hitachi S-3400N microscope operated at 15 kV and a Hitachi ABS microscope operated at 100 kV, respectively. The mean particle size and the size distribution were determined by measuring 200 particles per sample.

¹HNMR spectra: Proton NMR spectra was collected on a Bruker Avance 300 in D₂O solvent.

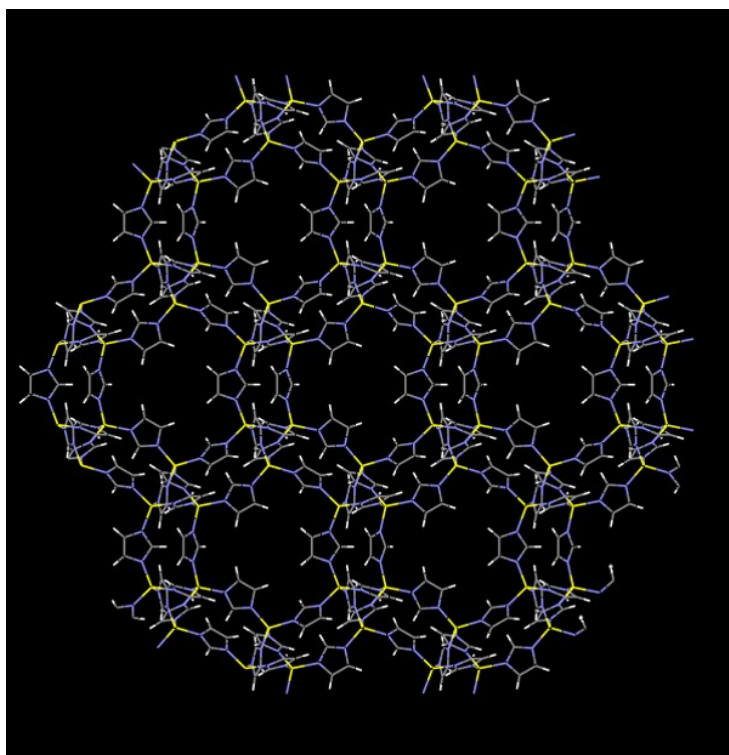
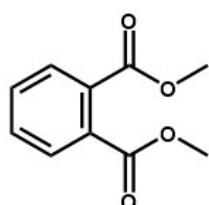
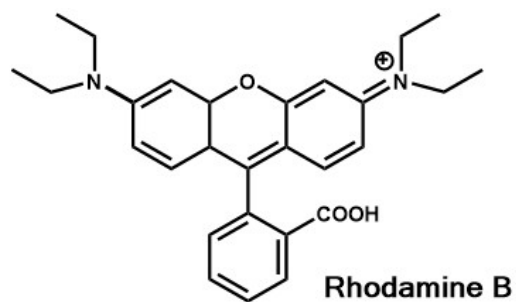
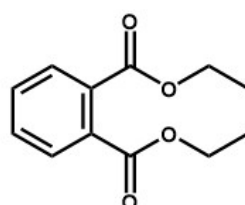


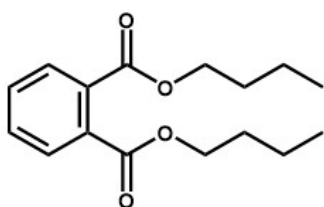
Fig. S1 ZIF-8 structure showing the position of the Zn(II) atoms (yellow) tetrahedrally coordinated by four 2-methylimidazole linkers.



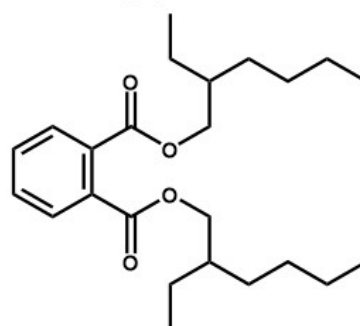
Dimethyl phthalate



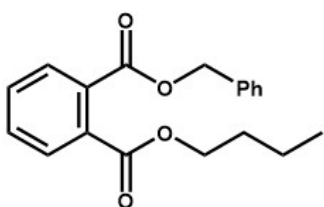
Diethyl phthalate



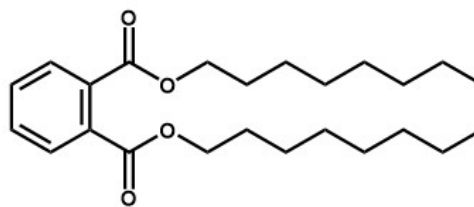
Di-n-butyl phthalate



Bis(2-ethylhexyl)phthalate



Butyl benzyl phthalate



Di-n-octyl phthalate

Fig. S2 Chemical structures of rhodamine B and the phthalate esters extracted.

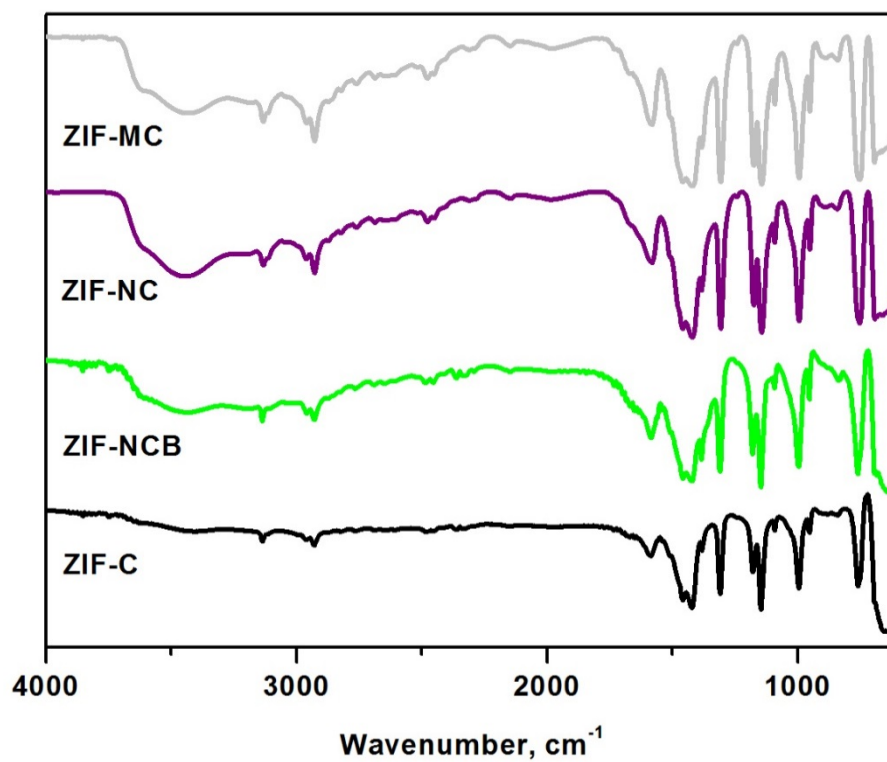


Fig. S3 FT-IR spectra of the prepared ZIF-8 materials. ZIF-NCB, *n*-butylamine modulated nanocrystals. ZIF-NC, nanocrystals. ZIF-MC, formate-modulated microcrystals. ZIF-C, formate-modulated microcrystals prepared at 373 K.

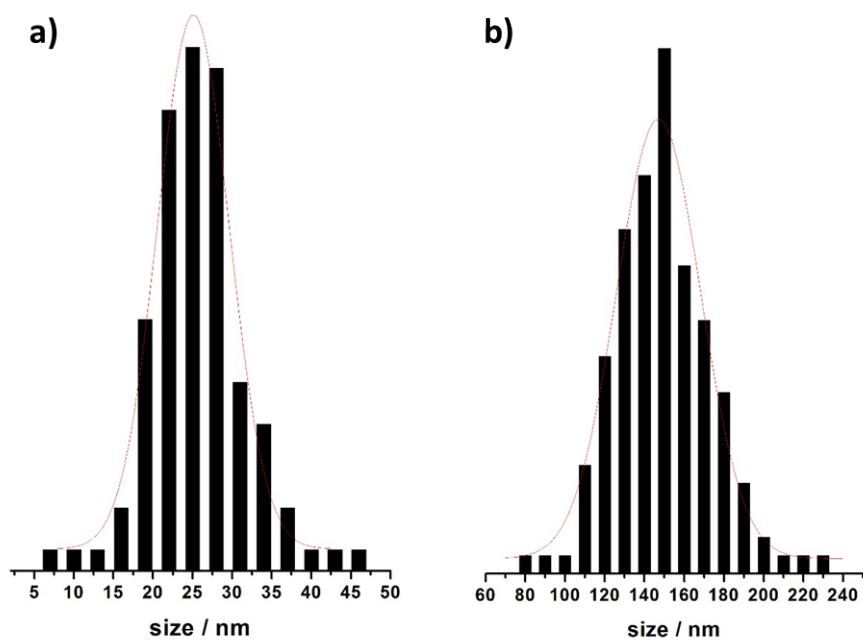


Fig. S4 Size distribution of nanocrystals synthesized a) in the presence of *n*-butylamine (ZIF-NCB), and b) in the absence of modulator (ZIF-NC). The red lines represent Gaussian fits.

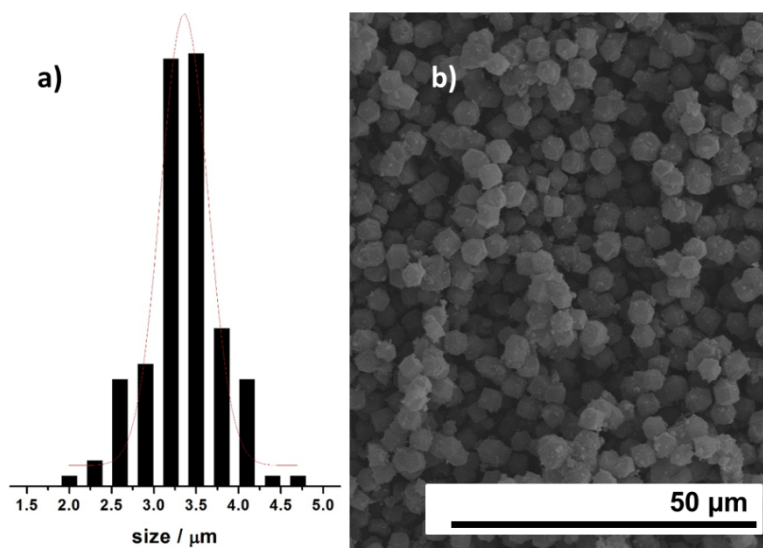


Fig. S5 a) Size distribution of microcrystals prepared using formate at room temperature (ZIF-MC). The red line represents a Gaussian fit. b) SEM image of ZIF-MC microcrystals.

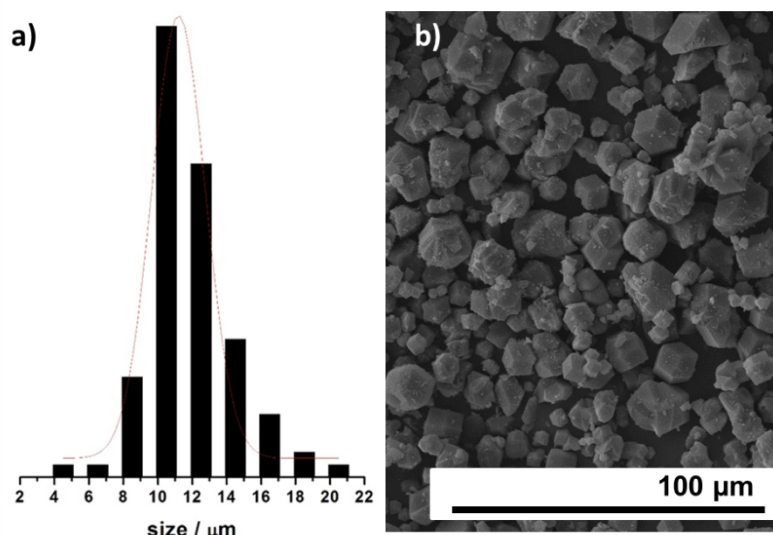


Fig. S6 Size distribution of microcrystals prepared using formate and microwave irradiation (ZIF-C). The red line represents a Gaussian fit. b) SEM image of ZIF-C microcrystals.

Comments to Fig. S4, S5 and S6:

A statistical evaluation of 200 particles (Fig. S4) resulted in an average size of 26 ± 4 and 148 ± 20 nm for ZIF-NCB and ZIF-NC, respectively. In the case of nanocrystals synthesized in the presence of *n*-butylamine, particle size was also estimated from the broadening of the Bragg reflections of the corresponding diffractograms by applying the Scherrer's equation. A value of 28 nm was obtained which is in good agreement with that obtained by analysis of TEM micrographs confirming that the primary particles are crystalline ZIF-8.

The statistical evaluation of the same number of microcrystals prepared using formate as modulator (Fig. S5 and S6) resulted in an average size of 3.3 ± 0.4 and 12 ± 2 μm for ZIF-MC and ZIF-C, respectively.

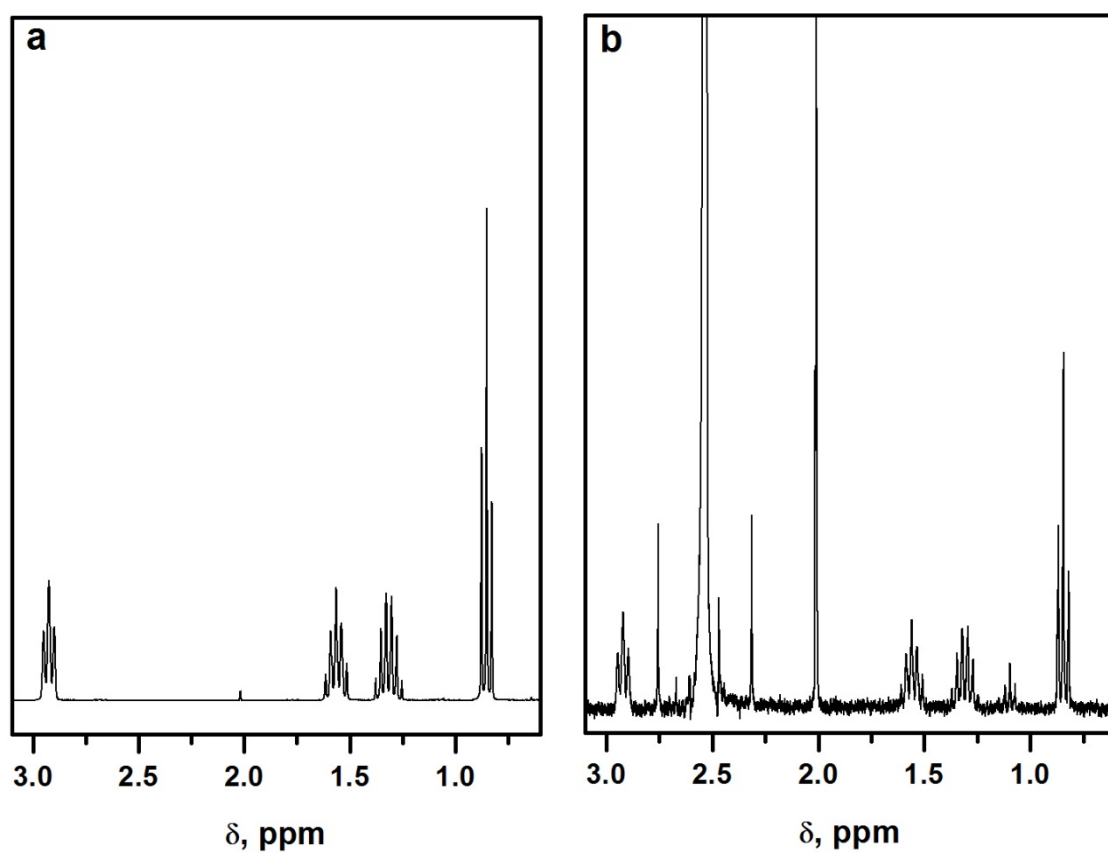


Fig. S7 ¹H NMR spectrum of a) pure *n*-butylamine and b) *n*-butylamine-modulated ZIF-8 nanocrystals (ZIF-NCB) after mineralization in deuterium chloride (2.5 wt. % in D₂O).

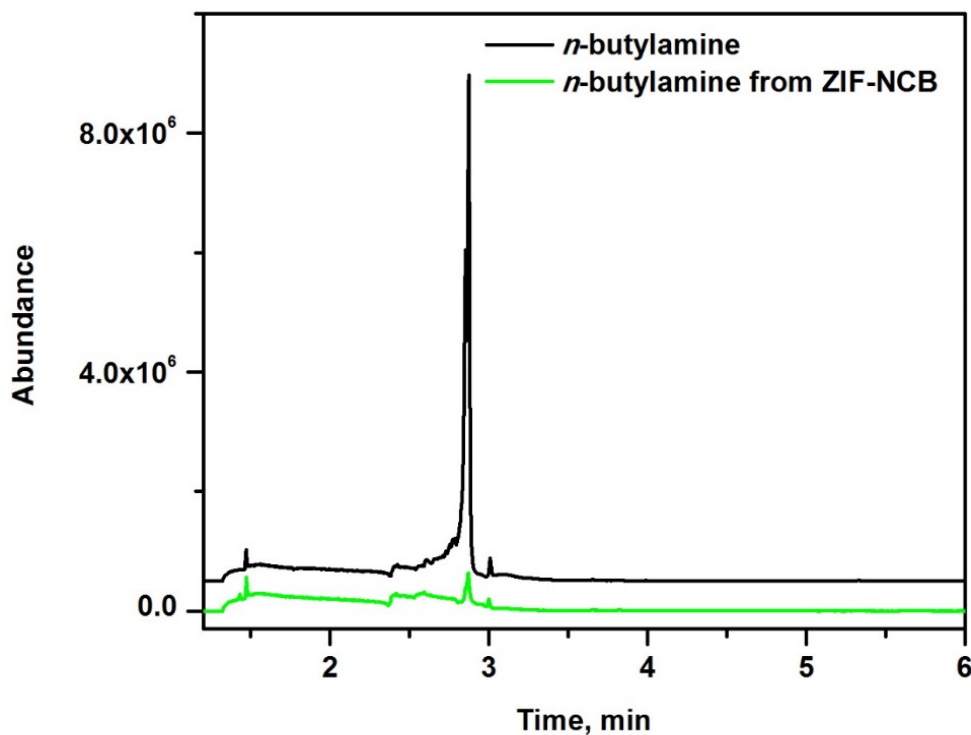


Fig. S8 GC-MS chromatogram of a dispersion of 5 mg of butylamine-modulated ZIF-8 nanocrystals in 2 mL of a dichloromethane/methanol mixture (20/80, v/v%). The dispersion was sonicated for 5 min, and after centrifugation, the supernatant was injected into a GC-MS. The injection of 1 mg/L pure *n*-butylamine in methanol is also shown for comparison purposes.

Comment to Fig. S8: The concentration of the ZIF-8 crystals in the dispersion is 2.5 g/L. According to the NMR results, the concentration of *n*-butylamine that could be potentially released from the crystals to the medium was expected to be in the order of 50-100 mg/L, while the concentration of *n*-butylamine determined in the dispersion medium by GC-MS analysis was 0.05 mg/L. The small concentration of released *n*-butylamine (at trace level) suggests that most of the *n*-butylamine is attached to the ZIF-8 crystals.

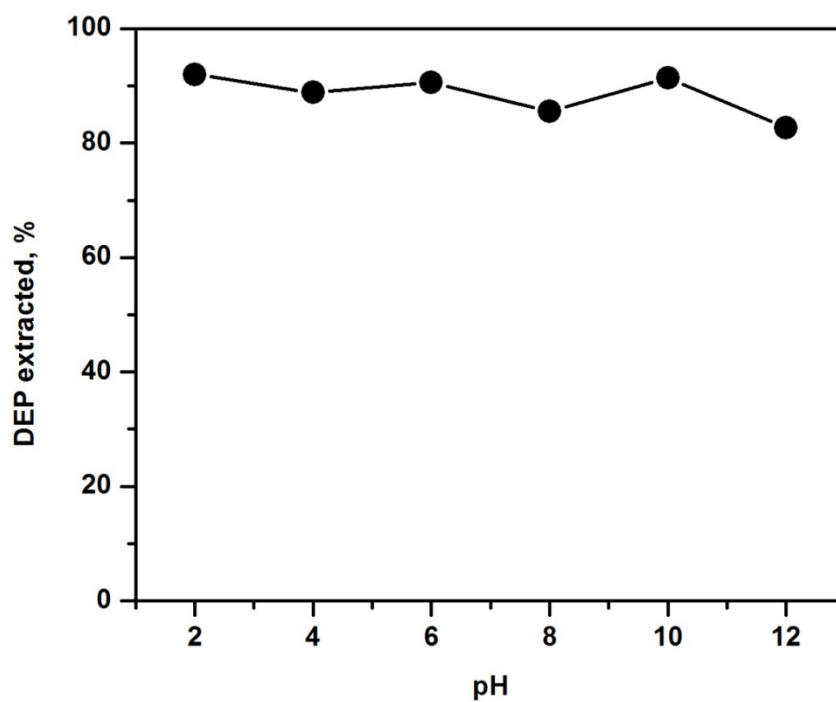


Fig. S9 Effect of pH of the extraction medium on the extraction of DEP using ZIF-8 nanocrystals prepared using *n*-butylamine as modulator agent.

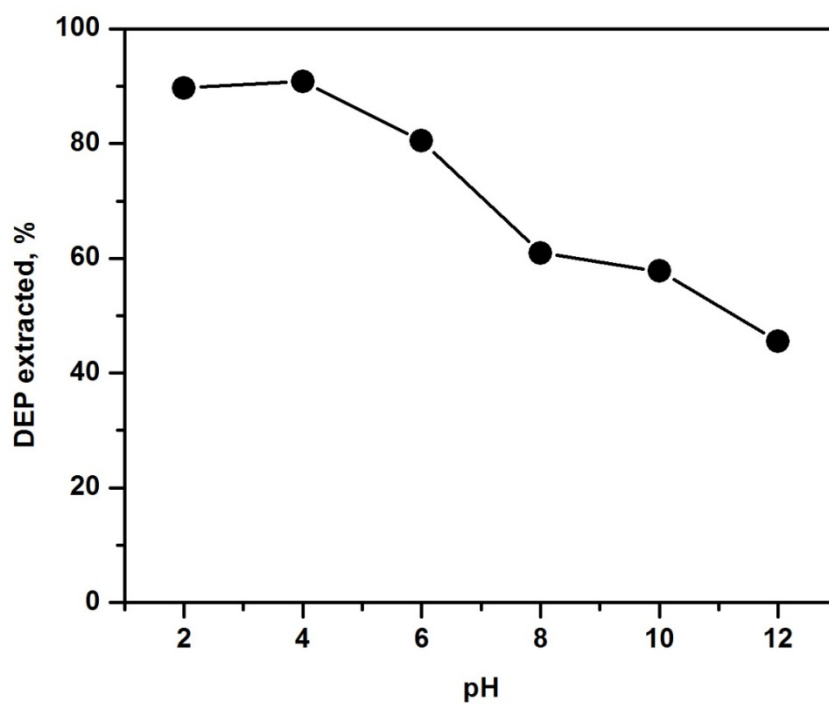


Fig. S10 Effect of pH of the extraction medium on the extraction of DEP using ZIF-8 nanocrystals prepared in the absence of modulator agent. The extraction time was increased to 10 min.

Table S1. Limits of detection of GC-MS methods for the determination of phthalate esters based on different extraction procedures.

Sample preparation	Limit of detection (ng/L)	(Ref)
Automated dispersive liquid-liquid microextraction (batch)	10-20	(1)
Automated dispersive liquid-liquid microextraction (flow)	35-100	(2)
Liquid-liquid extraction	50-100	(3)
Dispersive liquid-liquid microextraction – floating organic drop	20-50	(4)
Stir bar sorptive extraction	2	(5)
Dispersive liquid-liquid microextraction GC-MS	2-8	(6)
Dispersive solvent extraction incorporating porous ZIF-8 crystals	0.08-0.2	This work

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