A green metal-organic framework to monitor water contaminants

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The CIM-80 material (aluminum(III)-mesaconate) has been synthetized in high yield through a novel green procedure involving water and urea as co-reactants. The CIM-80 material exhibit good thermal estability with a working range from RT to 350 °C with a small contraction upon desolvation; moreover, this material is stable in water at different pH values (1 -10) for at least one week, and shows a LC50 value higher than 2 mg·mL-1. The new material has been tested in a microextraction methodology for the monitoring of up to 22 water pollutants, presenting little environmental impact: total waste per analysis being 20 mg of CIM-80 and 500 µL of acetonitrile. The analytical performance of the CIM-80 in the microextraction strategy is similar to that of the MIL-53(Al) or even better for several pollutants. The average extraction efficiencies range from ~20% for heavy polycyclic aromatic hydrocarbons to ~70-100% for the lighter ones. In the case of the emerging contaminants, the average extraction efficiency can reach values up to 70% for triclosan and carbamazepine.

1. Introduction

The monitoring of water quality undoubtedly provides empirical evidence to support decisions regarding health protection versus environmental issues [1,2]. The frequent detection of pharmaceuticals, drugs, endocrine disrupting phenols, personal care products, and other contaminants, has become a global problem due to their potential to cause undesirable ecological and human health effects [3]. Conventional environmental monitoring strategies are, paradoxically, also of environmental concern because they require the use of large amounts of halogenated organic solvents in the environmental sample preparation, thus generating enormous amounts of toxic wastes [4]. Alternatives have arisen to replace conventional approaches [5], mainly by utilizing microextraction techniques (that minimize and even eliminate the requirements of such solvents in the extraction step of the monitoring method) [6], or by incorporating novel materials as successful extraction agents able to replace organic solvents or conventional sorbents [7,8].

Metal-organic frameworks (MOFs) clearly merit citation among novel materials starting to be used in monitoring methods [9-11], particularly in microextraction monitoring methods such as solid-phase microextraction (SPME) [12] or in miniaturized solid phase extraction in its dispersive mode (D-µSPE) [13,14]. D-µSPE is gaining a lot of attention nowadays from an environmental-friendly point of view, because its requirements of sorbents are really low (usually between 2-500 mg) and due to its simplicity. The method only requires proper dispersion of the sorbent in the aqueous sample (stirring, vortex…) to ensure the trapping of the contaminants by the sorbent material [15], followed by separation of the sorbent and further elution of the trapped analytes to be determined with the proper analytical technique. This way, D-µSPE can be utilized easily in laboratories worldwide without the need of expensive instrumentation to accomplish monitoring.

A number of properties of MOFs makes these materials almost ideal candidates for D-µSPE: good thermal and mechanical stability, uniform structured nanoscale cavities, uniform pore topologies, high adsorption affinity, and structural tuneability. The possibility of performing in pore functionalization and outer-surface modifications have made MOFs attractive as highly versatile materials with task-specific properties [16]. Recent studies have tried to correlate the structure of MOFs with that of pollutants intended to be monitored, with the goal of targeting MOFs for selective monitoring [9,17,18]. Such studies pointed out the difficulties in predicting the adsorption of a target analyte (for analytes initially present in a water media) into a specific MOF material. In any case, the MOF's flexibility, the presence of unsaturated metal sites, large pore volumes, and a hydrophobic environment around the pores seem to be adequate characteristics when intending a MOF as generic sorbent for environmental monitoring [19].

A step forward in the utilization of MOFs for water monitoring clearly requires the utilization of: (a) MOFs with high water stability and (b) greener MOFs in such microextraction methods. That is, the use of MOFs prepared following green chemistry routes (milder synthetic procedures and absence of toxic organic solvents) [20]. By incorporating MOFs prepared with greener strategies into D-µSPE monitoring methods, it is possible to avoid the paradoxical situation currently existing with environmental monitoring methods.

The MOF MIL-53(Al) has shown wide extraction capabilities for different contaminants, and thus it can be considered as a generic sorbent in D-µSPE [9,17]. Green synthetic procedures have been developed to prepare MIL-53(Al), but they still need high temperatures and complex procedures to activate the material [21]. To expand its extraction performance while improving its synthesis in terms of greenness, we have decided to use the mesaconate ligand, which includes a methyl functionalization in the fumaric acid. The aluminum(III)-mesaconate MOF (CIM-80) is a porous material with a crystal structure similar to that of MIL-68, good thermal and water stability and a synthetic procedure completely green without employing any organic solvent and short reaction times. At the time preparing this manuscript, this material has been reported with a similar green synthetic approach [20].

To evaluate the performance of this greener CIM-80 as novel sorbent in D-µSPE to monitor waters, 22 different pollutants are selected for being representative analytes of different families. The D-µSPE method is completely optimized and validated with CIM-80; while comparing its analytical performance to that of MIL-53(Al) and other materials.

2. Experimental

2.1 Chemicals, reagents and materials

Aluminum nitrate nonahydrate (98%), mesaconic acid (99%), trimethylamine (>99%), urea (99%), and Na2CO3 (99%), were purchased from Sigma-Aldrich (Steinheim, Germany) and used for synthetizing the CIM-80. Dimethylformamide (99.9%) of high-performance liquid chromatography (HPLC) grade was acquired to Fluka-Sigma Aldrich (Steinheim, Germany). The following reagents were used to prepare the buffer: KCl, acquired to Panreac (Barcelona, Spain); and sodium acetate, acetic acid, and KH2PO4, with pro-analysis purity, acquired to Merck (Darmstadt, Germany).

Carbamazepine (99.0%), methylparaben (95.5%), and atrazine (99.1%), were purchased to Sigma-Aldrich; progesterone (>99.99%) and triclosan (>99.99%) were obtained from US Pharmacopoeia Reference Standard (Basel, Switzerland); estrone (>99.99%) was purchased to European Pharmacopoeia Reference Standard (Strasburg, France); and benzophenone (99%) was supplied by Alfa Aesar (Karlsrube, Germany). All these compounds were acquired as solid products. They were used to prepare individual standard solutions in acetonitrile (ACN). A standard solution with polycyclic aromatic hydrocarbon (PAHs) in ACN was supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany), at a concentration of 10 mg·L-1. The main characteristics of the studied contaminants are shown in Table S1 of the Electronic Supplementary Material (ESM). Working standard solutions of all contaminants were prepared in ultrapure water.

Deionized water (Milli-Q, ultrapure grade) was obtained by a water purification system A10 MiliPore® (Watford, UK). ACN HiPerSolv Chromanorm liquid chromatography grade was purchased from VWR (Llinars del Vallés, Spain). Ultrapure water and ACN were used as mobile phases in ultra-high performance liquid chromatography (UHPLC). ACN was also required in the elution steps of D-µSPE. Methanol (MeOH) and isopropanol (>99%), supplied by Sigma-Aldrich, were used also as elution solvents. UHPLC mobile phases were always filtered with Durapore® membrane filters of 0.45 µm, supplied by Sigma-Aldrich.

Syringe filters Millex® Durapore® of polyvinylidene fluoride (PVDF) of 0.2 µm were purchased from Sartorius Stedim Biotech (Goettingen, Germany). They were used to filtrate all samples and standards before any UHPLC analysis.

The D-µSPE procedure required Pyrex® centrifuge tubes (Staffordshire, UK) with dimensions of 10×1.4 cm and volume of 15 mL. Solvothermal reactors of Teflon and stain steel autoclaves supplied by Parr Instrument Company (Moline, IL, USA) were used in the synthesis of the MOFs.

2.2 Instruments and equipment

A vortex from Reax-Control Heidolph GMBH (Schwabach, Germany), and an ultrasounds bath KM (Shenzhen Codyson Electrical Co., Ltd. Shenzhen, China) were utilized in the D-µSPE procedure.

Phase identification of the synthetized CIM-80 was carried out by X-ray powder diffraction on a X'Pert Diffractometer (Panalytical, Netherlands) operating with Bragg–Brentano geometry. Data collection was carried out using Cu Kα radiation (λ = 1.5418 Å) over the angular range from 5.01° to 80.00° with a total exposure time of 30 min. High resolution powder diffraction patterns were measured at the BL04-MSPD beamline [22] of ALBA synchrotron (Barcelona, Spain), at 17.5 keV (= 0.70815 Å) equipped with the Mythen-II detector (Dectris) in the 0.37-43.2°angular range.

The microscopic morphology of the material was examined by a JSM6300 scanning electron microscope (SEM) from JEOL (Tokyo, Japan); supporting the material on a flat surface and silver cover. The surface area and pore volume of adsorbents were measured on a Gemini V 2365 Model (Micromeritics, Norcross, GA, USA) surface area analyzer at 77 K in the range 0.02 ≤ P/P0 ≤ 1.00. The Brunauer, Emmett and Teller (BET) method was used to calculate the surface area. Thermogravimetric analysis (TG/TDA) was carried out in a Perkin Elmer Pyris Diamond TGA/DTA equipment.

The UHPLC was the 1260 Infinity model from Agilent Technologies (Santa Clara, USA). Its quaternary pumps resist 600 bar. The instrument was equipped with a Rheodyne 7725i injection valve and an injection loop of 5 µL. The UV-Vis detector was a ProStar 325 LC Varian (Palo Alto, CA, USA), operating at 220 nm for the emerging pollutants studied. A multichannel fluorescence detector (FD) 1260 Infinity model from Agilent Technologies was also used. This detector operates with the program included in Table S2 of the ESM for the group of PAHs studied. The UHPLC and the FD were controlled with the C.01.04 version of the OpenLab CDS ChemStation software (Agilent), whereas the UV-Vis data treatment was carried out with the 6.41 version LC Workstation software (Varian).

The separation of the PAHs was carried out using a Zorbax Eclipse PAHs column (1.8 µm, 50×4.6 mm) also from Agilent Technologies. The rest of target analytes were separated with a C18 Kinetex column (1.7 µm, 100×2.1 mm) supplied by Phenomenex (Torrance, CA, USA). The column thermostat was kept at 25°C in both cases. Figures S1 and S2 of the ESM include a representative chromatogram obtained under optimum conditions with a standard solution, together with the specific group of conditions required for each separation.

2.3 Synthesis of [Al(mesaconate)OH]·3H2O CIM-80

The synthesis of CIM-80 was optimized and the best procedure requires a mixture of mesaconic acid (1 mmol; 130 mg) and Al(NO3)3·9H2O (1 mmol; 375 mg) in 15 mL in deionized water containing 0.5 mmol of urea (30 mg), under constant stirring for 20 min. Then, the clear solution is transferred to a 23 mL Teflon lined stainless steel autoclave and kept at 150°C for 3 h. Afterwards, the autoclave is cooled down to room temperature, and the obtained white product is isolated by filtration, washed with water, and air dried at 50°C. Yield: 60% (based on Al). IR (cm-1): 3400 (broad), 1587s, 1408s, 1375m, 1305w, 993m, 916w, 812m, 658s, 619m, 481s. Elemental Analysis for C5H12O8Al (227.13 g/mol): calcd.: 26.4%, H 5.3%; found: C 26.8%, H 5.7%.

Figure 1. Powder X-ray diffraction patterns at different temperatures of the CIM-80 compound.

2.4 D-µSPE-UHPLC procedure with CIM-80 as extraction sorbent of contaminants

The D-µSPE method using CIM-80, followed by UHPLC-UV-Vis or UHPLC-FD depending on the group of contaminants, was optimized properly. Under optimum conditions, 10 mL of water are put in contact with 20 mg of CIM-80 (previously activated at 150°C overnight) in Pyrex® centrifuge tubes. The mixture is then subjected to vortex stirring during 3 min, followed by centrifugation during 5 min at 2739 ×g. The supernatant aqueous phase is then carefully removed by decantation. Afterwards, 500 µL of elution solvent are added to the MOF remaining in the tube (which contains the trapped contaminants). Elution solvents tested were MeOH, ACN and isopropanol. Vortex is then applied for 3 min, followed again by centrifugation during 5 min at 2739×g. The supernatant (eluate containing the contaminants initially trapped by the MOF) is sampled using a Pasteur pipette, filtered through 0.2 µm PVDF syringe filters, and directly injected in UHPLC-UV or UHPLC-FD.

3. Results and Discussion

3.1 Synthesis, structure and stability of CIM-80

The synthesis of [Al(mes)OH] in water has been recently reported to consist of the microwave heating at 90°C of a mixture in water of aluminum(III) nitrate, mesaconic acid and sodium hydroxide [20]. We have developed an alternative route using urea as base and conventional heating, in an attempt to obtain single crystals to determine the crystal structure. Different reaction times (from 1.5 h to 32 h) were tested at a given temperature of 150°C (the higher reaction temperature is needed to ensure the decomposition of urea gradually, thus releasing NH_3 in the medium). At 1.5 h, there is no product in the reactor, but from 3 h to 32 h the CIM-80 is the product formed (Figure S3), and only an increment of 15% yield is achieved at the highest reaction time, but sadly no single crystals were obtained. In Figure S4 is depicted a detailed view of the CIM-80 crystallites with maximum size of ca. 10 µm, but these 'single' crystals seem to be formed of various twin components, precluding their use in SCXRD. In order to keep the synthesis as green as possible, we established 3 h of reaction time as the optimum.

The crystal structure of CIM-80 consists of a kagome-like MIL-68 framework with two different type of channels: large hexagonal and small triangular pores of 6 and 2 Å diameters, with the methyl groups of the mesaconic acid directed towards the large pores [20]. After activation at 150°C, and reduced pressure overnight, the N_2 adsorption isotherm at 77 K leads to a BET surface area for this material of 891 $m^2 \cdot g^{-1}$. This value is close to the reported value of 1040 $m^2 \cdot g^{-1}$. The volume of micropore is 0.46 $cm^3 \cdot g^{-1}$, which is also in agreement with the value of 0.47 $cm^3 \cdot g^{-1}$ obtained from the poreblazer software [23].

The thermal stability of the material has been studied through TG/DTA analysis and temperature dependent X-ray diffraction. The TG shows a 25% weight loss below 100°C that has been assigned to three crystallization water molecules. After that, the material does not show any process up to 400°C, when the decomposition starts (see Fig S5 of the ESM). The crystallinity of CIM-80 was studied as a function of temperature (see Figures 1 and S6), observing well defined peaks in all the powder diffraction patterns up to 200°C (the maximum temperature reached in the experiment), although some variations in the peak intensities were found. The evolution of the cell volume with the temperature was studied from the fitting of the powder patterns at different temperatures (see Figures 2 and S7). It is observed a reduction in the cell volume up to 100°C, indicating that the release of the crystallization water molecules produces a small contraction of the pores (0.4% of the cell volume). Above 100°C, the cell volume increases as it is expected, and when the sample is cooled down again to room temperature, the cell volume is smaller than the hydrated one since the water molecules are not recovered in the process. The thermal expansion parameter calculated is 13.1 MK^{-1}, which is within the range of other metal-organic materials [24].

We are interested in the application of this material as an extractant in different water samples, and thus we have tested the stability of the material at working conditions. The CIM-80 material is stable in water and after two weeks immersed in water, the material does not show signs of degradation or loss of crystallinity. CIM-80 was also tested in waters at different pH values (1, 5, 10) keeping the material for one week immersed in the solution. No significate changes are observed in the powder patterns, supporting the robustness of the framework (see Figure S8). Since the analytical methodology includes a vortex agitation step, the CIM-80 was subjected to 8 min of vortex in water keeping its integrity (see Figure S8).

The cytotoxicity of the MOF CIM-80 was evaluated following a strategy previously reported for other MOFs [25], with details of the procedure included in Fig. S9 of the ESM. The LC_{50} value obtained was higher than 2 $mg \cdot mL^{-1}$, which was the maximum value tested in the study. Therefore, it is possible to work with relatively high values of CIM-80 without provoking cytoxicity issues. Other LC_{50} values reported for MOFs are, for example, 0.70-1.10 $mg \cdot mL^{-1}$ for MIL-100 or 0.02-0.10 $mg \cdot mL^{-1}$ for ZIF-8 [26], clearly supporting the greenness of this MOF.

Figure 2. Cell volume variation with the temperature upon heating. The contraction is associated with the solvent loss. The red dashed line indicates the fitting of the data to get the expansion coefficient.

3.2 Evaluation of the analytical extraction performance of CIM-80 in D-µSPE-UHPLC

Up to 22 analytes, including conventional contaminants such as PAHs [10,27,28] and emerging contaminants such as preservatives, UV filters or drugs [19] have been selected as target compounds (Table S1 of the ESM) to evaluate the ability of the designed MOF to trap them from environmental waters through monitoring strategies. Target analytes have been selected trying to have a representative group of contaminants (persistent and emergent) with different structures and properties, thus showing the ability of the MOF to extract them by D-µSPE-UHPLC.

To evaluate the performance of CIM-80 as adequate extraction sorbent for these water contaminants, aqueous standards of the target analytes (at low concentration values to mimic environmental levels) are subjected to the entire D-µSPE-UHPLC method. Thus, the extraction efficiency (ER, in %) is estimated by comparison of the obtained chromatographic signal with the expected signal if the analytes are efficiently extracted and eluted by the MOF in D-µSPE. Another efficient tool to evaluate the performance of the D-µSPE method is the enrichment factor (EF), that is, the preconcentration achieved by the procedure if comparing the isolated UHPLC determination method with the D-µSPE-UHPLC method. Tables S3 and S4 of the ESM include the calibrations obtained with only UHPLC-UV (for the 7 emerging pollutants monitored) and UHPLC-FD (for the 15 PAHs monitored), without the D-µSPE approach, together with a number of analytical features.

Clearly, a number of parameters need optimization in the D-µSPE procedure. To simplify such optimization, several parameters are fixed to common values in the initial stage. This way, the water sample (or aqueous standard) volume is fixed to 10 mL (to simplify the further centrifugation steps while being easy to sample in environmental fields); the vortex time is limited to 3 min (to ensure a quick method); and the elution solvent volume is 500 µL (to ensure a preconcentration procedure, and to minimize environmental wastes). Figure 3 shows a scheme of the entire D-µSPE procedure. Under these conditions, the main variables optimized were the amount of MOF required and the type of elution solvent. It has been pointed that these two variables are the key points to ensure proper efficiency in D-µSPE [13].

Values between 5 and 50 mg of CIM-80 were tested with the fixed conditions abovementioned to select the best amount to work with, while ensuring a microextraction procedure. The elution solvent in these experiments was MeOH. Experiments were carried out in triplicate with the group of emerging pollutants, for being those more difficult to extract in conventional methods if compared to more hydrophobic analytes such as PAHs [19]. From Fig. S10 of the ESM, it can be observed that 20 mg is the best amount to utilize. Lower amounts appear to be insufficient whereas higher amounts probably make the elution step more difficult, thus provoking decreases in the efficiency. The exception was estrone, for which the best amount was the lowest value tested: 5 mg. In order to have the best amount for the majority of compounds, 20 mg of CIM-80 was fixed for further experiments, and the method was further optimized by evaluating the influence of the elution solvent.

Figure 3. Scheme of the dispersive µ-SPE procedure.

Three different solvents were tested in the elution step: ACN, MeOH and isopropanol, for being miscible with the UHPLC mobile phases (and thus avoiding solvent evaporation and solvent exchange steps). Figure 4 shows the extraction efficiencies (ER in %) obtained, specifically for PAHs using UHPLC-FD (Fig. 4a) and for the emerging contaminants using UHPLC-UV (Fig. 4b), while using the fixed conditions above mentioned (and 20 mg of CIM-80).

ACN is, in general, the elution solvent that generates the higher efficiencies. This is particularly clear for PAHs. On the other hand, isopropanol, given its polarity, was unable to elute the PAHs trapped by the MOF. For the emerging contaminants, MeOH behaves nicely, with ACN showing lower performance. Isopropanol would be a better choice for estrone and triclosan. In any case, differences in efficiencies when using ACN, MeOH or isopropanol, with few exceptions, are lower than 10% for emerging contaminants. Therefore, with the purpose of setting up a generic procedure for different contaminants, ACN is the elution solvent selected for PAHs whereas MeOH is the one selected for the emerging contaminants.

The higher efficiencies observed for lighter PAHs can be explained for a better adsorption of the analytes by the MOF material and a better elution when ACN is used. However, for bulkier PAHs the efficiencies are systematically lower, and even negligible when MeOH is the eluent, maybe pointing that the extraction of these bulkier analytes is not very good. In the case of the emerging contaminants, the selection of the eluent is not a key point, since the differences are small. Therefore, dissimilarities in the efficiencies should come from the extraction process. The methyl groups of the mesaconate ligand pointing toward the channels would favour the interaction with the more hydrophobic analytes, and this is supported with the good efficiencies obtained for lighter PAHs. This may be the cause for better extraction in the case of carbamazepine, benzophenone or triclosan; however other factors should play an important role in the case of, for example, methylparaben, for a better extraction is expected regarding its similarities with the other ones (aromatic rings, hydrogen bond donor and acceptor groups, smaller size).

Figure 4. Efficiencies…

Regarding efficiencies, they range from ~50 to ~100% for lighter PAHs, which can be highlighted if considering that efficiencies in microextraction methods are hardly 100% [29,30]. For heavy PAHs, average efficiencies are ~20%. For the majority of emerging contaminants, average efficiencies are ~15%, being ~70% for carbamazepine and triclosan. Independently on the efficiency, precision values (as relative standard deviation, RSD, in %) are always lower than 10.9%, thus supporting the adequate reproducibility of the microextraction strategy. It must be considered that efficiencies are acceptable in a microextraction method as long as the precision values are adequate (RSD <20%) and the enrichment factor attained by the method fulfills environmental policies of sensitivity.

Under the optimum conditions described, the quality analytical parameters obtained for the D-µSPE-UHPLC monitoring method are shown in Table 1. Maximum EF values were obtained for light PAHs such as acenaphthene, phenanthrene, anthracene and fluoranthene, and for emerging pollutants such as carbamazepine (a drug) and triclosan (a disinfectant); which is totally in agreement with the efficiencies obtained for these compounds with the entire method.

One of the main important features of environmental monitoring methods is the sensitivity achieved, in order to reach the levels imposed by regulations. Thus, the estimated limits of quantification obtained with the proposed microextraction method using CIM-80 range from 2.5 to 31 ng·L-1 for PAHs, and from 0.35 to 71 µg·L-1 for emerging contaminants. The United States Environmental Protection Agency (US-EPA) has established that the benz(a)pyrene content in drinking waters should not be higher than 0.2 µ·L-1 [31]. The European Union (EU) legislation terms as priority PAHs: benz(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene, while establishing a maximum value for benzo(a)pyrene of 0.1 µg·L-1 in superficial and drinking waters [32]. The sum of the content of the rest of priority PAHs in superficial waters must not exceed 0.1 µg·L-1. The EU also sets maximum concentration values for anthracene and fluorene: 0.4 µg·L-1 and 1 µg·L-1, respectively. Clearly, the sensitivity achieved using CIM-80 in the D-µSPE-UHPLC-FD method fits perfectly within the imposed limits. With regards to emerging contaminants, there is still a lack of regulations despite growing concerns of their presence in environmental reservoirs. It is also important mentioning that the use of MS detection over UV or DAD clearly improves the sensitivity. If the current D-µSPE method with CIM-80 is used in combination with LC-MS rather than with UHPLC-UV, much lower limits of detection will be obtained.

Table 1. Several features of the analytical performance of the D-µSPE-UHPLC method using CIM-80.

Analyte	EFa	RSDb (%)	LODc (ng·L-1)	LOQd (ng·L-1)
Carbamazepine	15	1.5	1.1 × 102	3.5 × 102
Atrazine	3.1	1.8	1.1 × 103	3.6 × 103
Methylparaben	1.4	17	8.3 × 103	2.8 × 104
Estrone	4.2	6.6	3.5 × 103	1.2 × 104
Progesterone	0.6	5.3	2.1 × 104	7.1 × 104
Benzophenone	6.1	19	3.7 × 102	1.2 × 103
Triclosan	13	6.2	3.3 × 102	1.1 × 103
Naphthalene	10	5.0	3.6	12
Acenaphthene	18	3.5	4.2	14
Fluorene	8.6	1.8	0.93	3.1
Phenanthrene	19	1.9	1.6	5.3
Anthracene	21	0.59	0.75	2.5

Fluoranthene	19	1.3	0.81	2.7
Pyrene	11	1.1	0.78	2.6
Benz(a)anthracene	2.6	1.9	7.8	26
Chrysene	2.4	9.5	1.8	6.0
Benzo(b)fluoranthene	12	7.0	1.7	5.6
Benz(a)pyrene	1.3	11	2.6	8.5
Dibenz(a,h)anthracene	2.9	10	2.9	9.8
Benzo(ghi)perilene	2.2	12	4.5	15
Benzo(k)fluoranthene	7.8	0.85	2.7	8.9
Indeno(1,2,3-cd)pyrene	3.4	15	9.3	31

[a] enrichment factor, being EFmax = 20

[b] relative standard deviation (n = 3)

[c] estimated limit of detection for the entire D-µSPE-UHPLC method

[d] estimated limit of quantification for the entire D-µSPE-UHPLC method

If comparing the performance of CIM-80 for the group of analytes studied with other materials in SPE methods from literature (Table S5 of the ESM), it is important to mention that the sensitivity obtained is comparable to those reports [10,19].

Regarding emerging pollutants, a previous study of our group on the use of the MOF MIL-53(Al) and HPLC-DAD [19] presents comparable sensitivity for carbamazepine, atrazine, and estrone. Thus, the novel material CIM-80 is able to operate as sorbent material in a monitoring method with comparable (and even better) performance of other materials, including the similar MOF MIL-53(Al), but clearly compiling with green chemistry requirements, because its synthesis can be considered as environmental-friendly.

Regarding the water monitoring of PAHs (Table S5 of the ESM), previous studies of our group using a magnetic composite based on MOF and UHPLC-FD [27] shows quite similar sensitivity, and even better when using CIM-80. In this case, lower amount of material and simpler (and greener) preparation routes are also involved.

Conclusions

We have synthesized through a green procedure a new promising material for the determination of pollutants in water through an optimized environmentally friendly methodology that minimizes wastes and maximizes efficiency. The CIM-80 material obtained is stable in water at different pH values, it has a working temperature range from RT to 350 °C, and it also presents low cytotoxicity, with a LC50 value higher than 2 mg·L-1. The efficiencies shown in our analysis of water for 22 pollutants are similar or even better than those reported for MIL-53(Al) and other materials. Ongoing work is aimed to incorporate this material in other miniaturized extraction techniques, particularly considering its analytical performance and partial selectivity with triclosan and carbamazepine, and to give more insights into the extraction mechanism of emerging contaminants through crystallography of inclusion compounds.

Conflicts of interest

There are no conflicts to declare.

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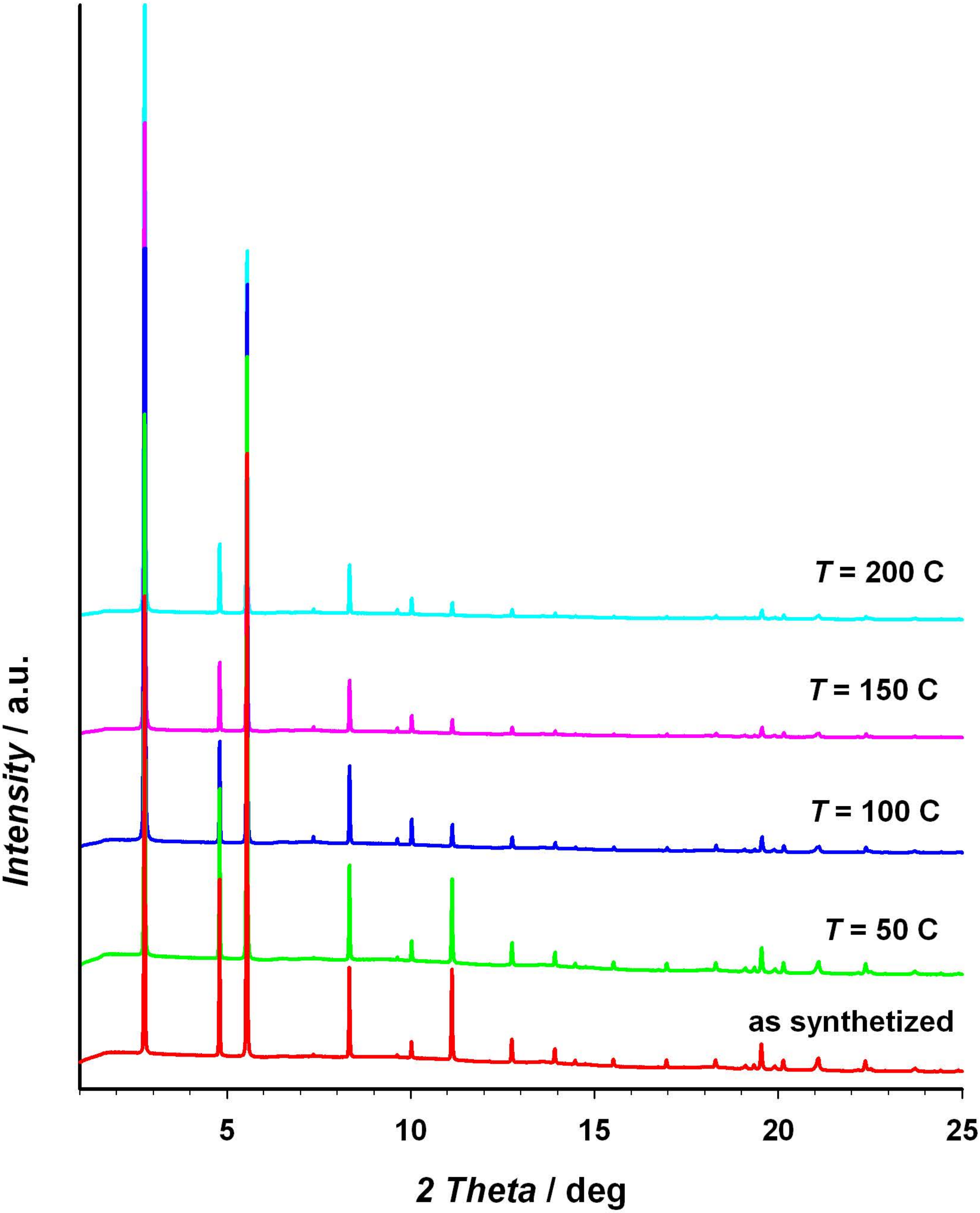
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T = 150 C
T = 100 C
T = 50 C
as synthetized
Intensity / a.u.
2 Theta / deg
5
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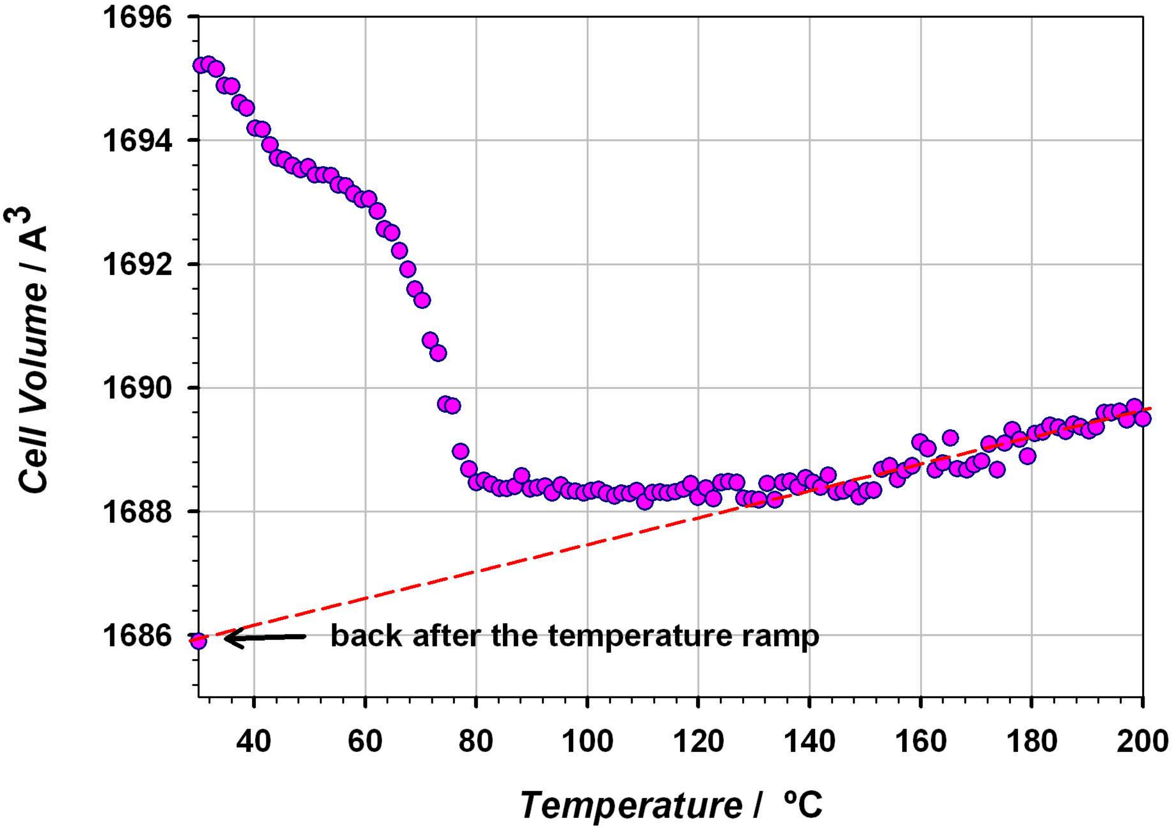
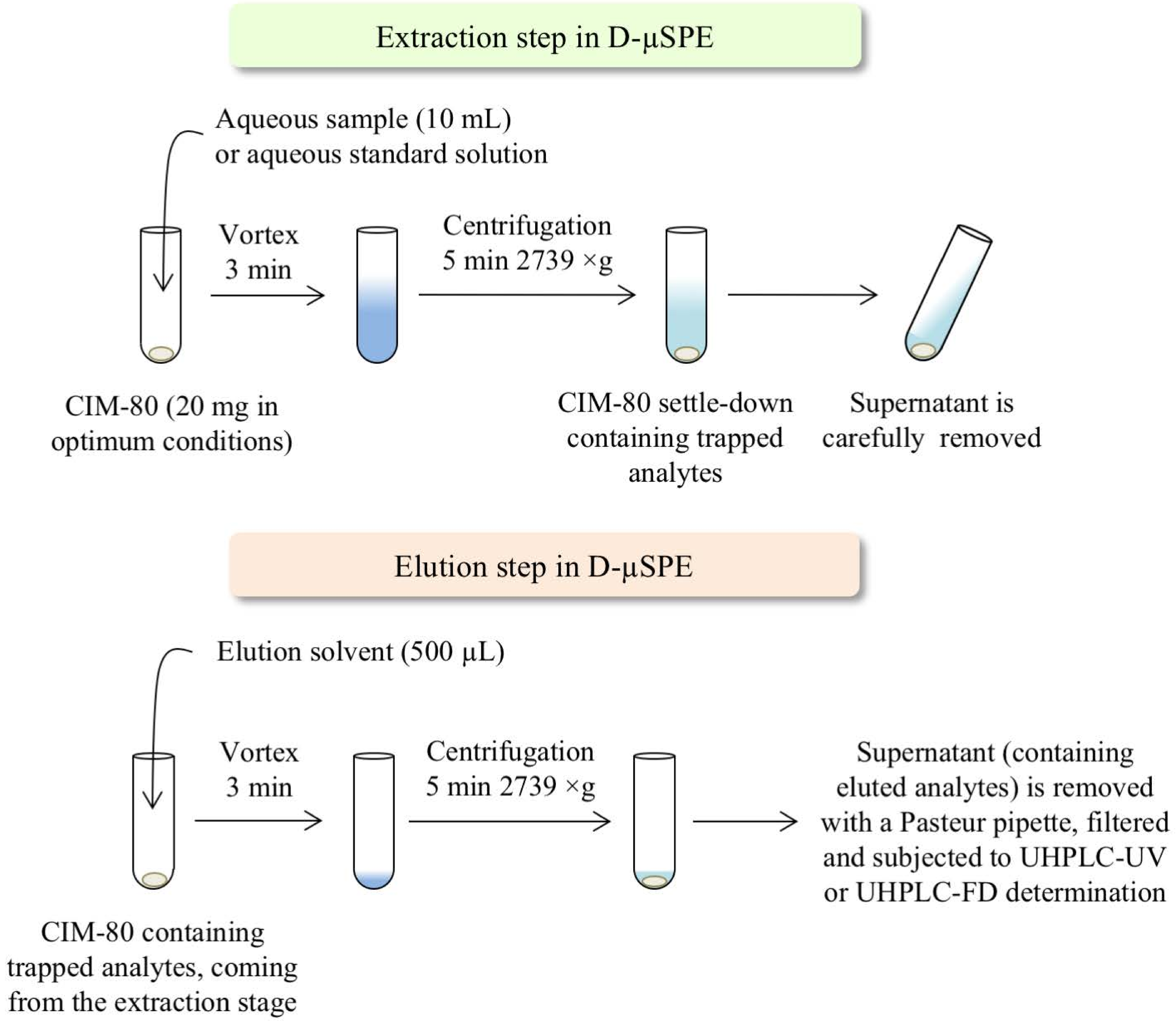
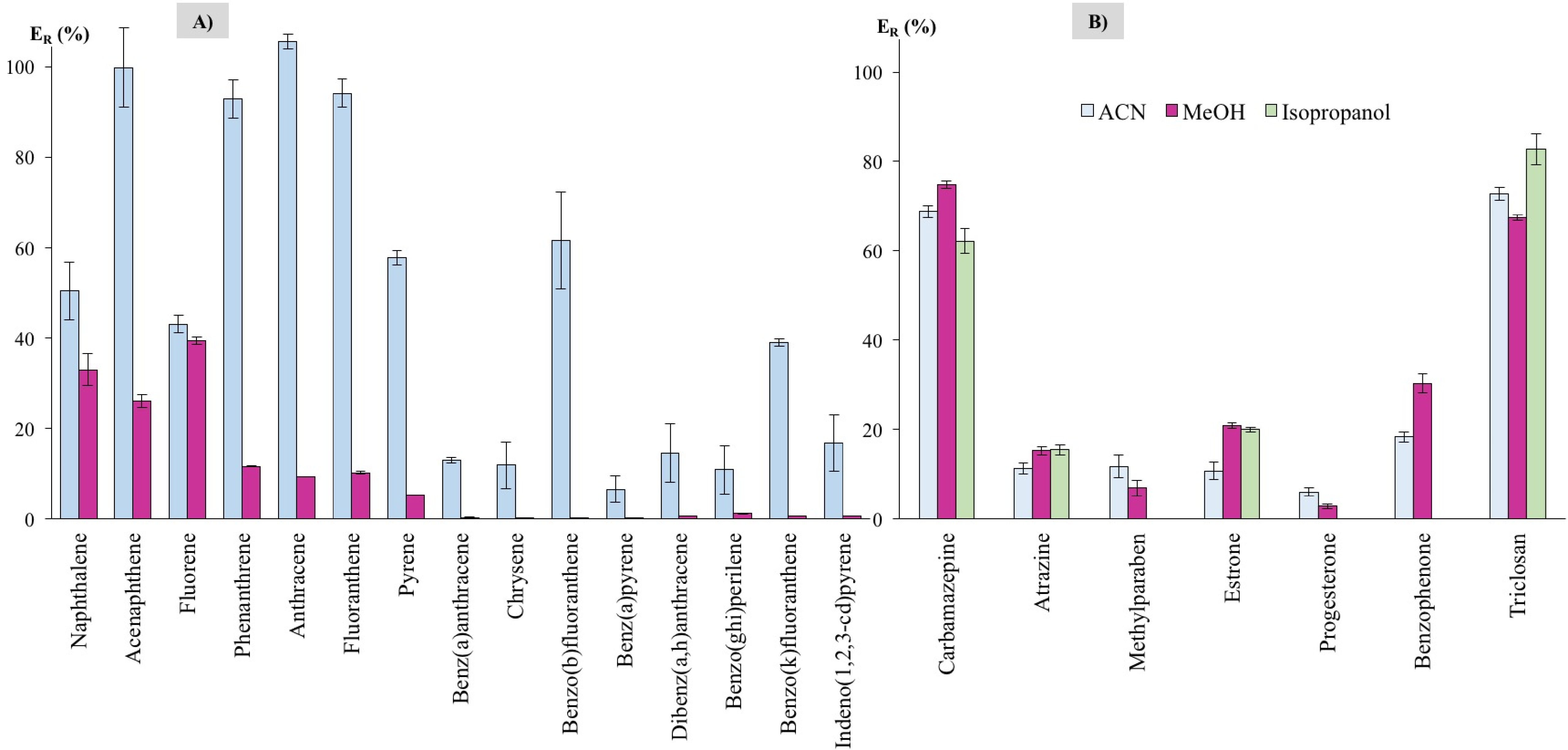

1696
1694
1692
1690
1688
1686
Cell Volume / A^3
40
60
80
100
120
140
160
180
200
Temperature / ºC
back after the temperature ramp


Extraction step in D-μSPE
Aqueous sample (10 mL)
or aqueous standard solution
Vortex
3 min
Centrifugation
5 min 2739 ×g
CIM-80 (20 mg in
optimum conditions)
CIM-80 settle-down
containing trapped
analytes
Supernatant is
carefully removed
Elution step in D-μSPE
Elution solvent (500 μL)
Vortex
3 min
Centrifugation
5 min 2739 ×g
Supernatant (containing
eluted analytes) is removed
with a Pasteur pipette, filtered
and subjected to UHPLC-UV
or UHPLC-FD determination
CIM-80 containing
trapped analytes, coming
from the extraction stage


A)
E_R (%)
0
20
40
60
80
100
Naphthalene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benz(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benz(a)pyrene
Dibenz(a,h)anthracene
Benzo(ghi)perilene
Benzo(k)fluoranthene
Indeno(1,2,3-cd)pyrene
B)
E_R (%)
0
20
40
60
80
100
ACN
MeOH
Isopropanol
Carbamazepine
Atrazine
Methylparaben
Estrone
Progesterone
Benzophenone
Triclosan

Supplementary Material

A green metal-organic framework to monitor water contaminants

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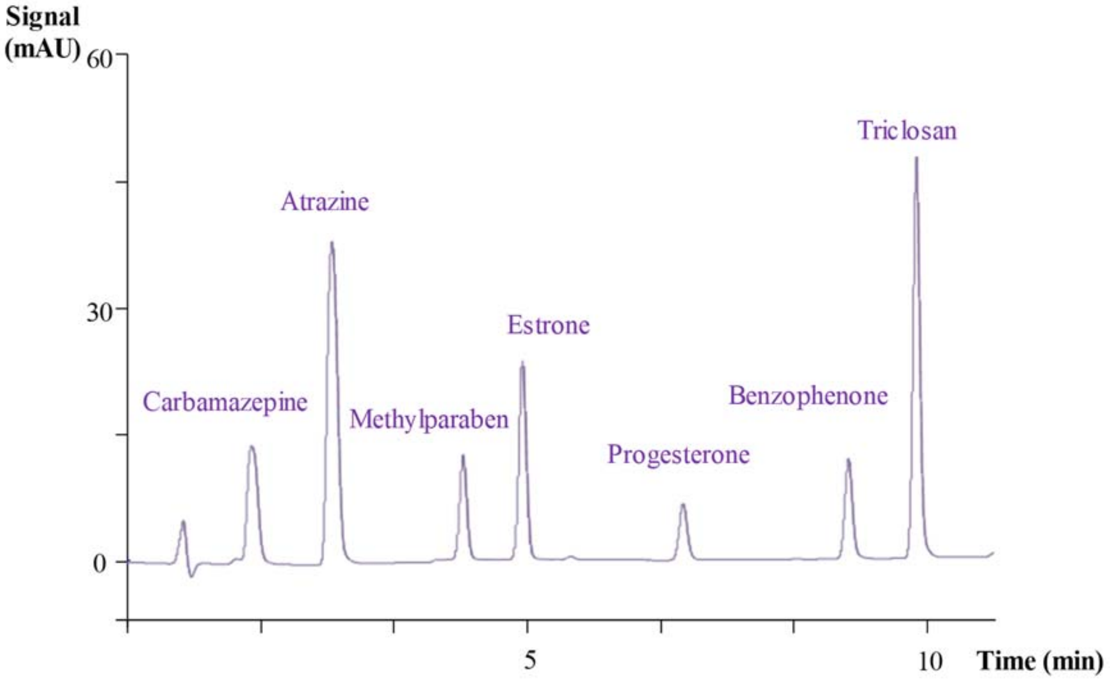


Figure S1. Representative chromatogram of the separation of seven target emerging pollutants. The concentration level of the standard is 100 µg·L^{-1} (in ACN). The UV-Vis detector was set at 220 nm. The UHPLC-UV-Vis separation required a binary mobile phase ACN:water at 0.4 mL·min^{-1} flow rate with the following gradient: initially 40% of ACN, increasing linearly this percentage up to 85% in 20 min. Remaining conditions as described in the experimental section.

s

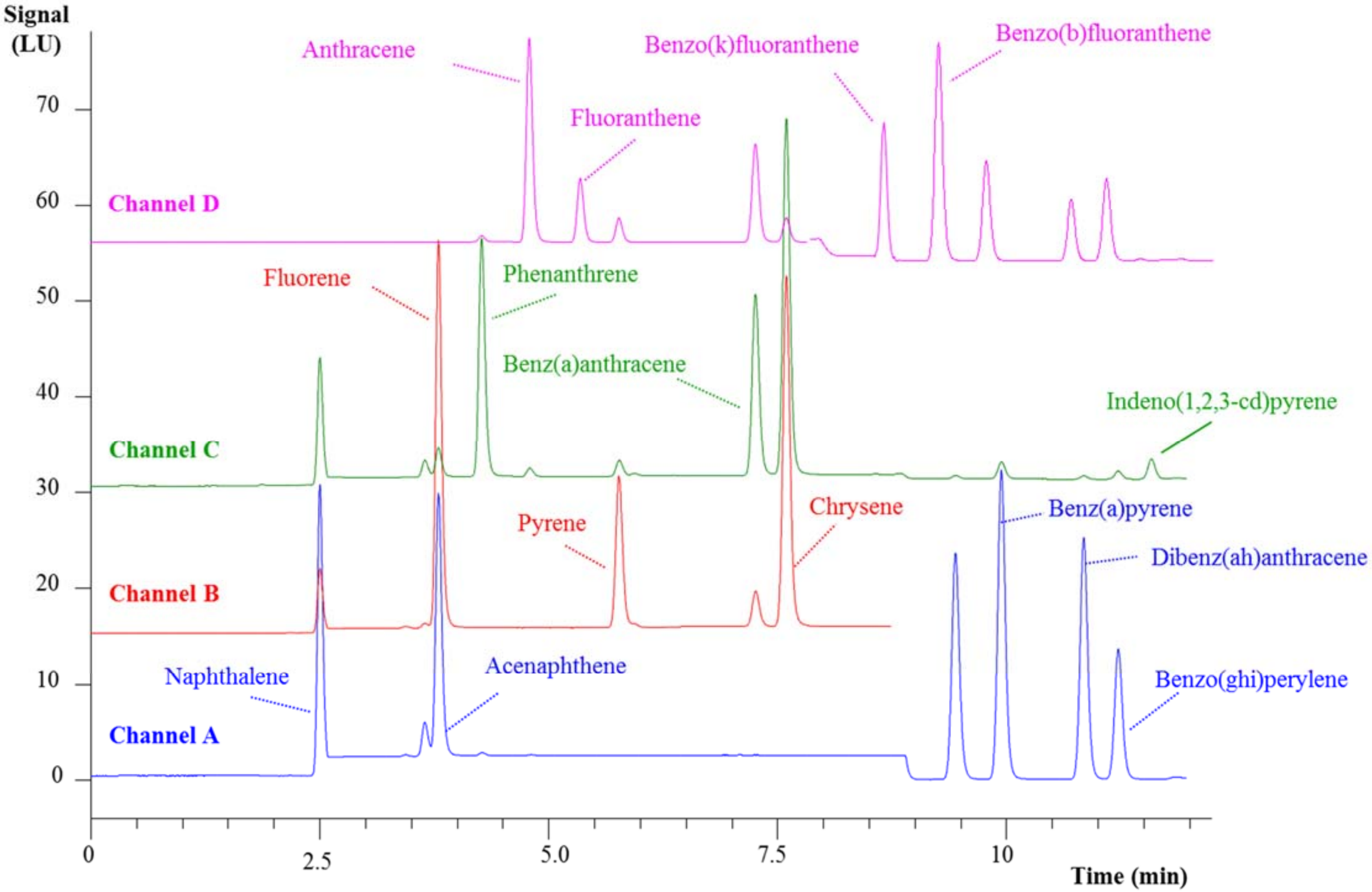


Figure S2. Representative chromatogram of the separation of PAHs by UHPLC-FD, with the wavelength program included in Table S2. The concentration level of the standard is 20 µg·L^{-1} (in ACN). The UHPLC-FD separation required a binary mobile phase ACN:water at 1 mL·min^{-1} flow rate: initially 50% of ACN, and increasing up to 100% of ACN in 11 min, keeping these conditions for 5 min.

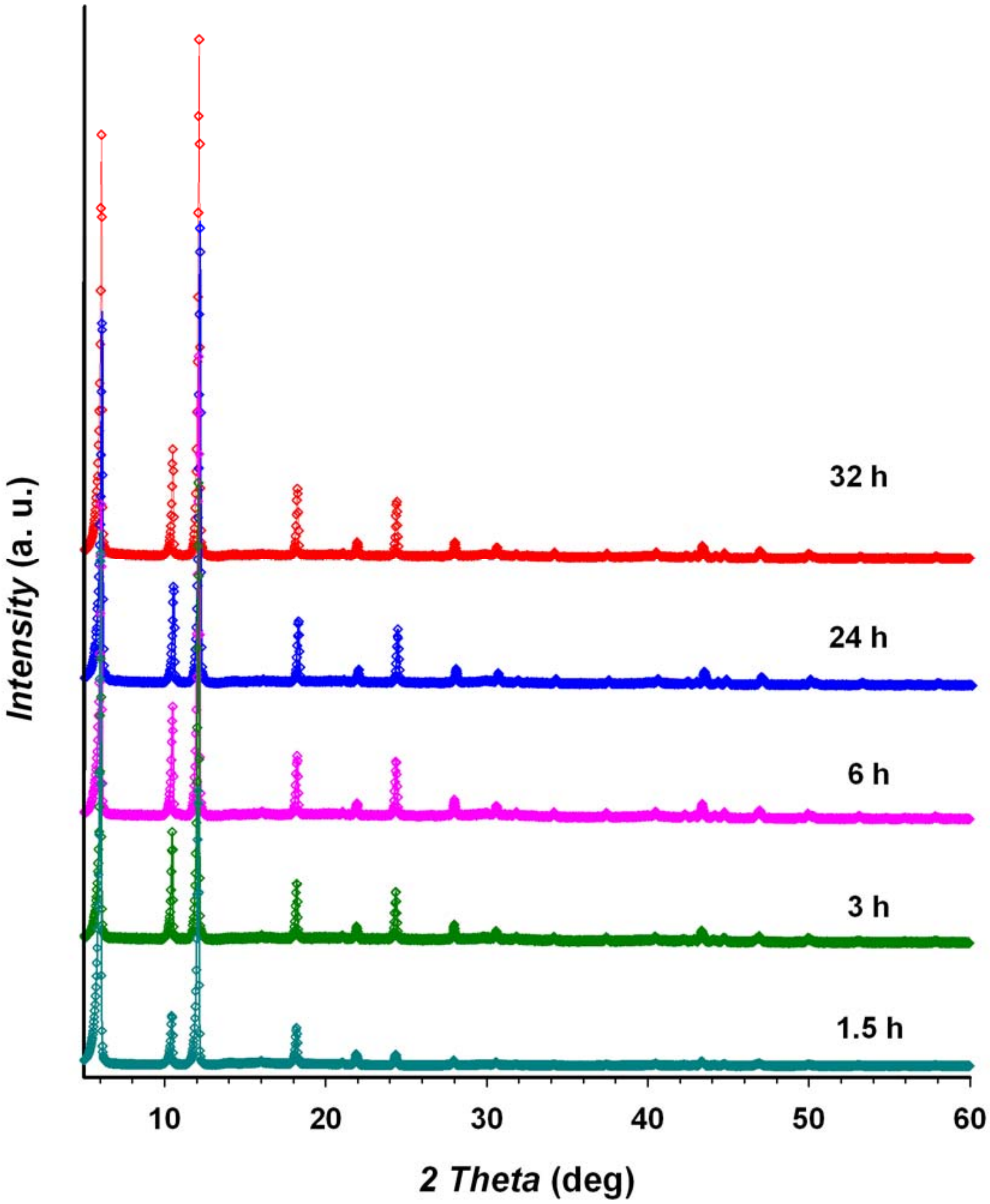


Figure S3. Powder X-ray diffraction patterns collected at the lab diffractometer (λ = 1.5418 Å) in the 5-80° angular range of the as synthetized products at different reaction times, following the procedure described in the Experimental Section.

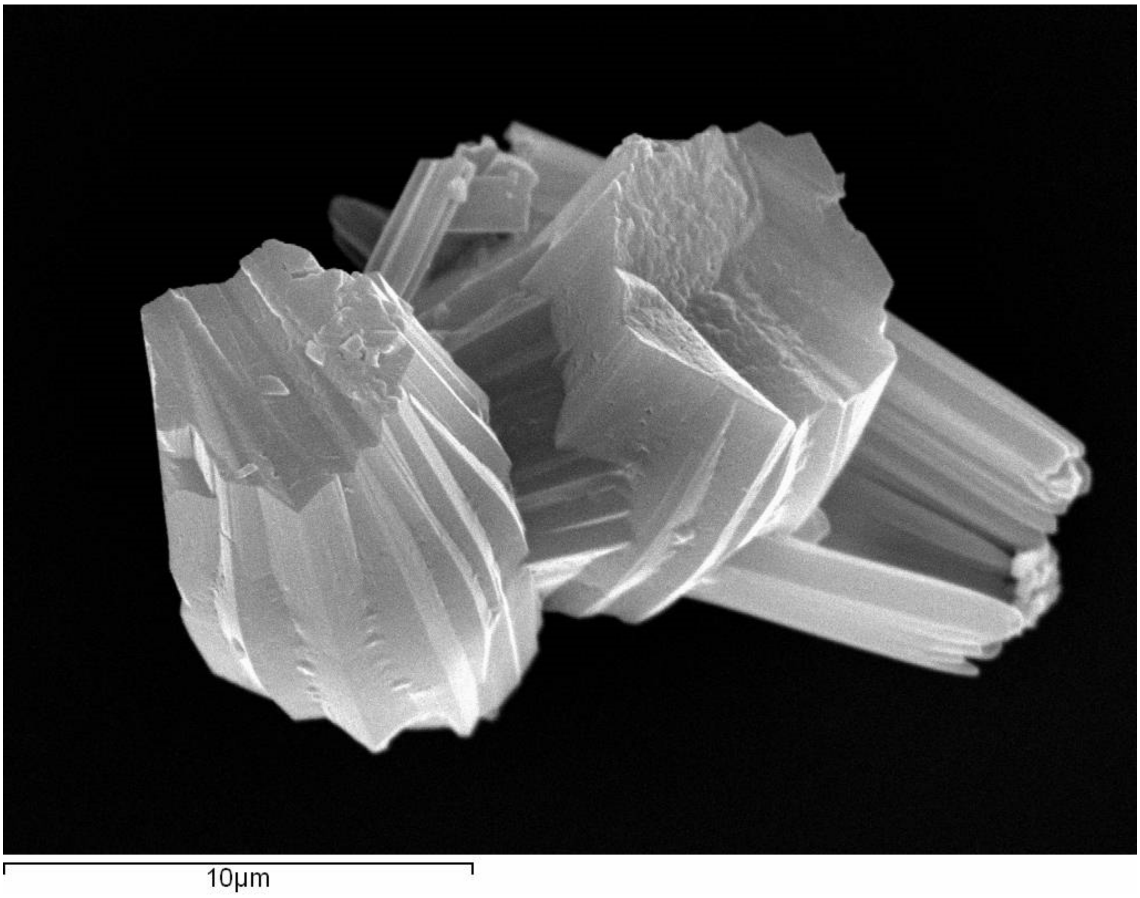


Figure S4. Scanning Electron Microscopy image of the CIM-80 crystallites.

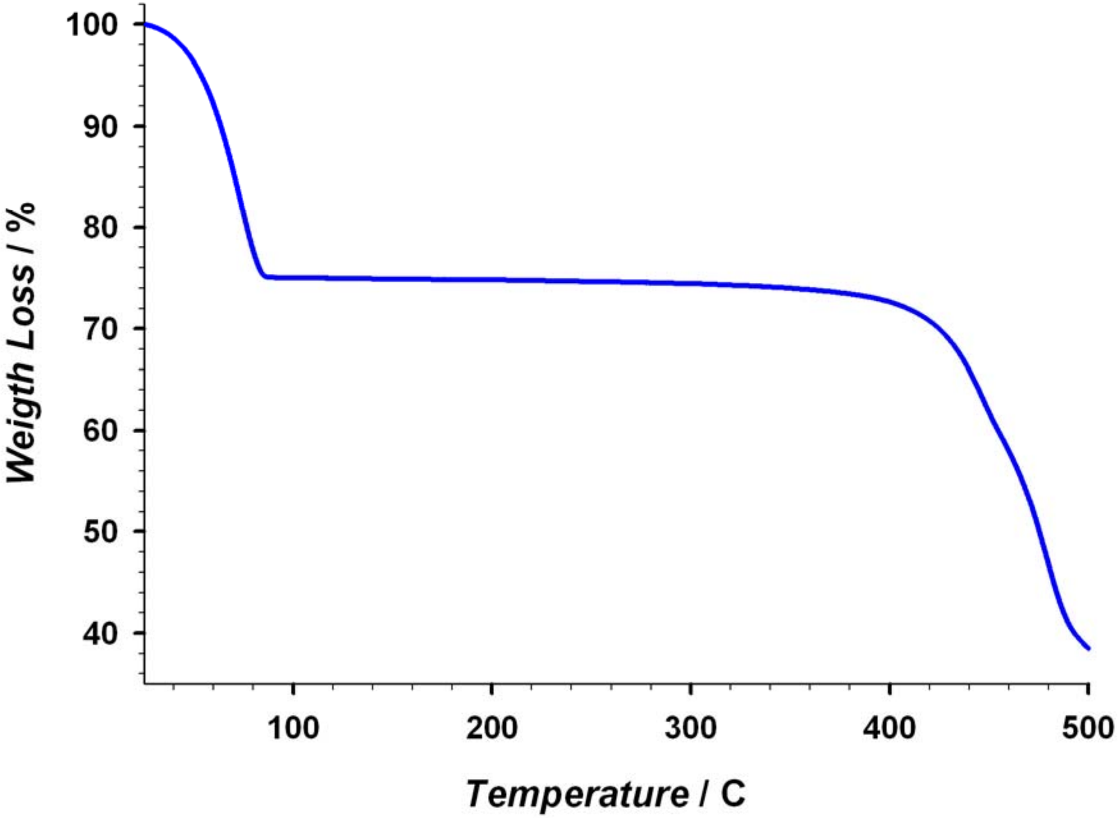


Figure S5. TG/DTA analysis of CIM-80.

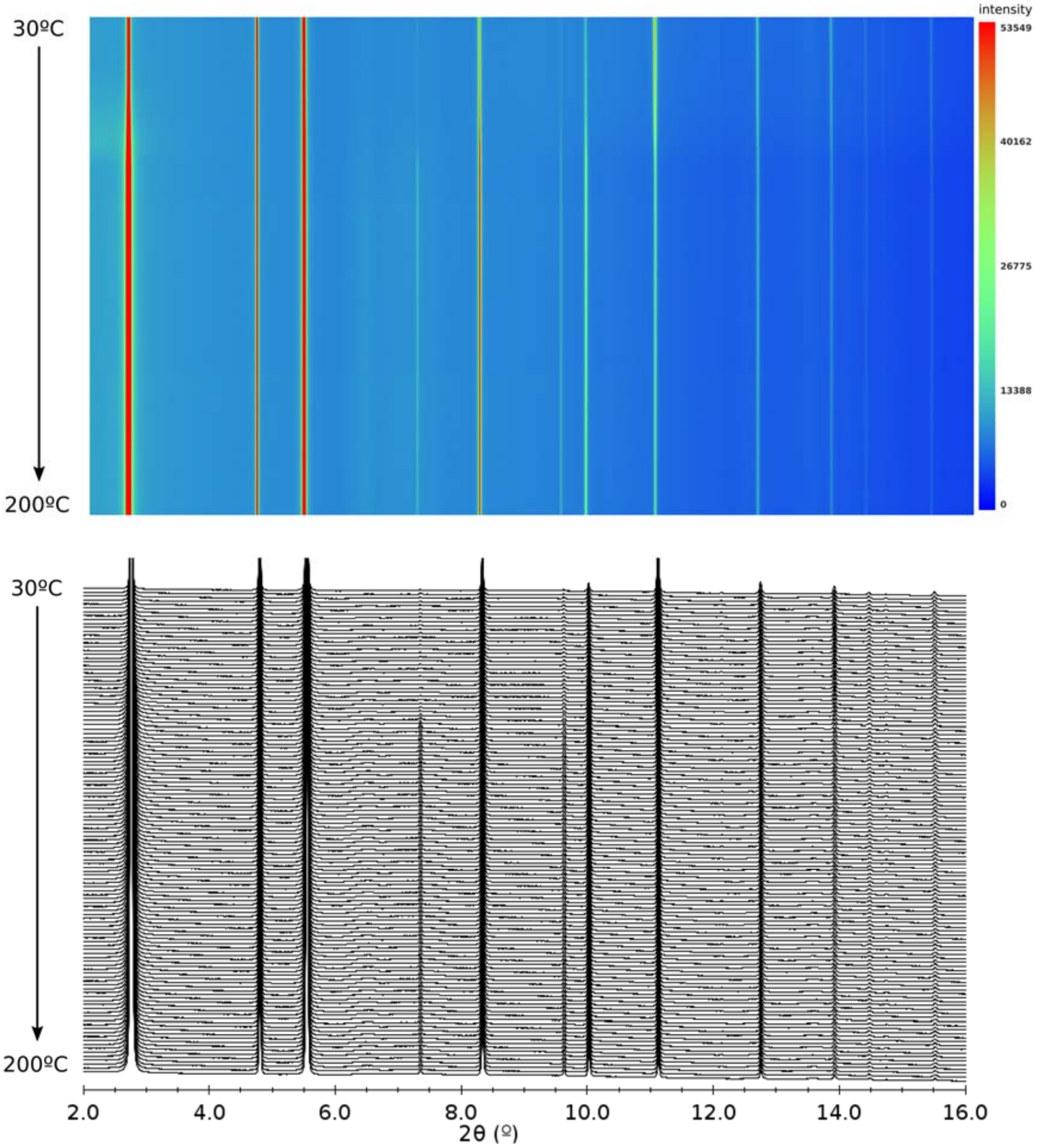


Figure S6. Thermodiffractogram of CIM-80 from 30 to 200 °C performed at BL04-MSPD beamline at ALBA synchrotron with λ = 0.70815.

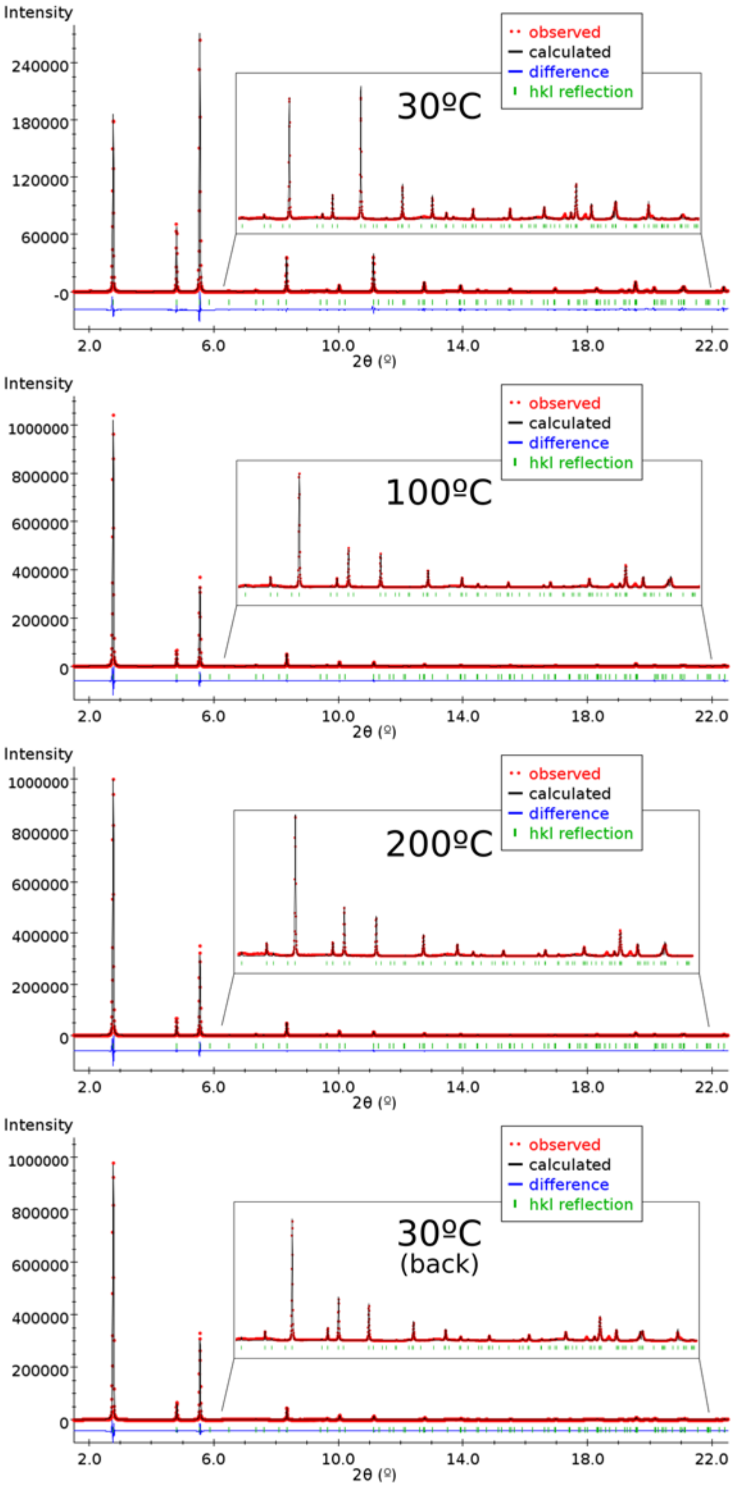


Figure S7. Profile matching of the powder diffraction patterns at selected temperatures.

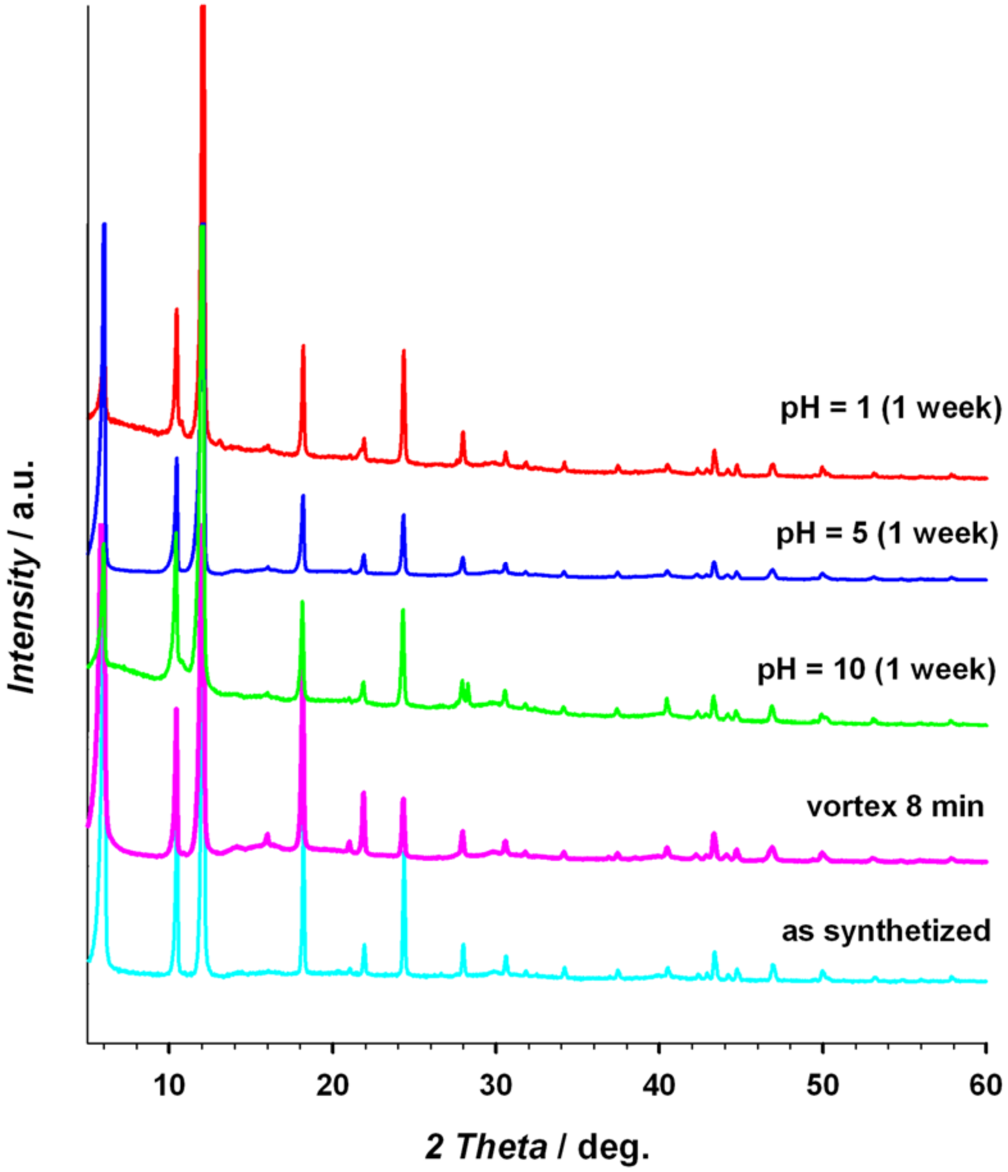


Figure S8. Diffraction patterns of CIM-80 after different stability tests, immersion in water at various pH values and application of vortex.

Figure S9. Images of the incubated cells in contact with the different tested concentrations of the MOF and the Alamar Blue reagent. Blue color indicates the lysis of the cells (none in this case), while pink color indicates the cells have not suffered any damage when they are put in contact with the MOF.

The cytotoxicity of the CIM-80 was evaluated using the Alamar Blue® cell viability assay as it was previously described [PLoS One. 2017;12:e0183795]. Briefly, the cell lines were put in contact with the MOF at different concentrations, ranging from 0.03 to 2 $mg \cdot mL^{-1}$, and incubated in 96-well plates for 24 h. Subsequently, the plates were analyzed by the microplate reader using a test wavelength of 570 nm and a reference wavelength of 630 nm. Dose response curves were plotted, and the 50% cytotoxic concentration (CC50) concentrations were calculated by linear regression analysis with 95% confidence limits. All experiments were performed two times each one, and the mean values were also calculated.

The Alamar Blue Assay Reagent® was provided by Biosource (Europe, Nivelles, Belgium) and the J774.1 murine macrophage cell line by ATCCTIB-67 (American Type Culture Collection LG Promochem, Spain).

A Tali® image cytometer (Thermo Fisher Scientific, Waltham, Massachusetts, USA) and an EnSpire® Multimode Plate Reader (Perkin Elmer, Madrid, Spain) were used.

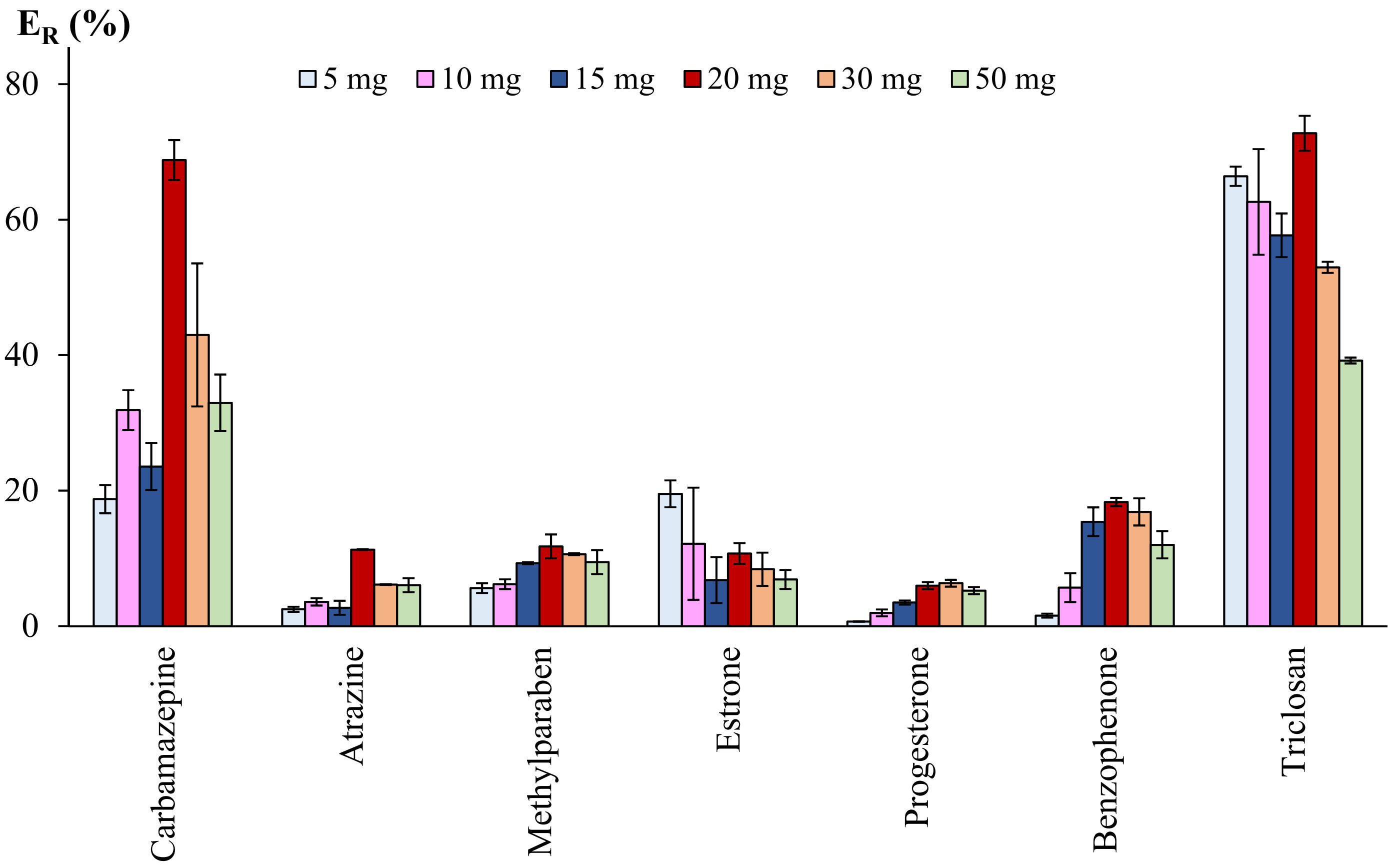
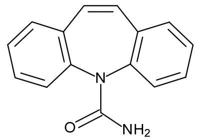
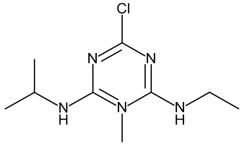
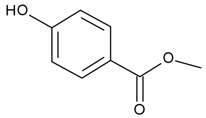
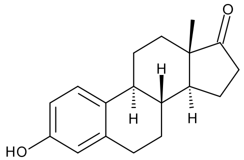
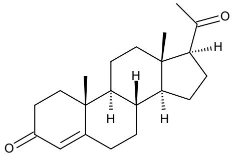
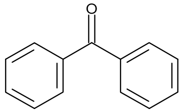
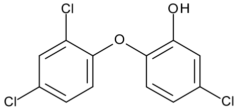
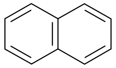
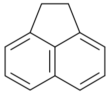
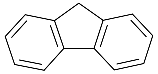
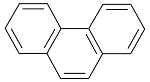
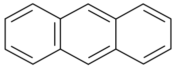
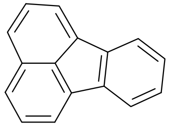
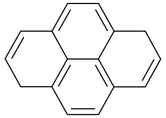
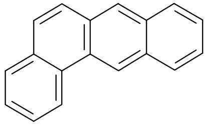
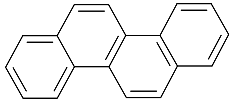
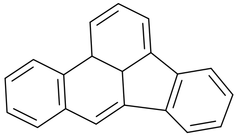
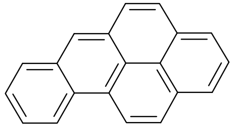
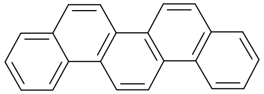
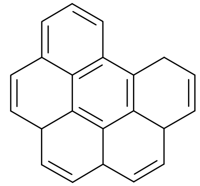
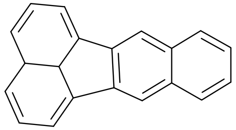
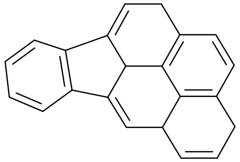


Figure S10. Influence of the amount of MOF CIM-80 in the entire extraction efficiency of the method for the group of emerging contaminants. Experiments were carried out by triplicate: 10 mL of water are mixed with 20 mg of CIM-80, then subjected to vortex stirring during 3 min. The supernatant aqueous phase is removed by centrifugation and decantation. Afterwards, 500 µL of ACN are added to the MOF remaining in the tube (and containing the trapped contaminants). Vortex is then applied for 3 min, followed again by centrifugation.

Table S1. Several characteristics of the group of analytes studied.

Analyte	Structure	Molecular weight (g·mol^{-1})	Volume[a] (Å^{3})	Water solub.[a] (mg·L^{-1}) at 25 ºC	LogK$_{OW}$[a]	pK$_{a}$[a]	Vapor press.[a] at 25 ºC (atm)
Carbamazepine		236.27	210.32	18	2.45	13.9	7.6×10^{-10}
Atrazine		215.68	190.90	35 (26 °C)	2.61	2.27	1.7×10^{-8}
Methylparaben		152.10	208.90	2.5×10^{-3}	1.96	8.50	3.15×10^{-7}
Estrone		270.37	263.17	30	3.13	10.3	2.0×10^{-11}
Progesterone		314.46	321.10	8.8	3.87	-	4.5×10^{-11}
Benzophenone		182.20	278.10	137	3.18	11.3	2.5×10^{-6}

Triclosan		289.54	212.05	10 (20 °C)	4.76	7.80	4.3×10^{-8}
Naphthalene		128.17	205.10	31	3.30	-	$1.0\cdot10^{-4}$
Acenaphthene		152.20	212.90	3.9	4.07	-	$1.2\cdot10^{-6}$
Fluorene		166.22	243.30	1.7	4.18	-	$7.9\cdot10^{-7}$
Phenanthrene		178.23	261.90	1.1	4.46	-	$1.6\cdot10^{-7}$
Anthracene		178.23	261.90	0.040	4.45	-	$1.0\cdot10^{-4}$
Fluoranthene		202.26	269.00	0.23	5.16	-	$1.2\cdot10^{-8}$
Pyrene		202.26	269.00	0.14	4.88	-	$5.\cdot10^{-10}$
Benz(a)anthracene		228.29	318.50	9.1×10^{-3}	5.79	-	$2.78\cdot10^{-7}$

Chrysene		228.29	318.50	2.0×10^{-3}	5.73	-	$8.2\cdot10^{-12}$
Benzo(b)fluoranthene		252.32	325.60	1.5×10^{-3}	6.60	-	$6.6\cdot10^{-10}$
Benz(a)pyrene		252.32	325.60	1.6×10^{-3}	6.13	-	$7.2\cdot10^{-12}$
Dibenz(a,h)anthracene		278.35	375.10	2.5×10^{-3}	6.50	-	$1.35\cdot10^{-12}$
Benzo(ghi)perilene		276.34	332.70	2.6×10^{-4}	6.63	-	$1.\cdot10^{-13}$
Benzo(k)fluoranthene		252.32	-	8.0×10^{-4}	6.11	-	$1.23\cdot10^{-12}$
Indeno(1,2,3-cd)pyrene		276.34	-	1.9×10^{-4}	6.70	-	$1.6\cdot10^{-13}$

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[a]Obtained from SciFinder® 2018 database

Table S2. Wavelength program used in the FD for the UHPLC-FD determination of PAHs, indicating the four emission channels: A, B, C and D.

PAH	**$\lambda_{ex\ max}$[a] (nm)**	**$\lambda_{em\ max}$[a] (nm)**	**time[b] (min)**	**λ_{ex} (nm)**	**λ_{em} (nm) in A**	**λ_{em} (nm) in B**	**λ_{em} (nm) in C**	**λ_{em} (nm) in D**
			0	254	330	312	360	443
			2.0	214	330	312	360	443
Naphthalene	219	321	*2.5*[c]	214	330	312	360	443
			2.6	254	330	312	360	443
Acenaphthene	225	335	*3.6*[c]	254	330	312	360	443
Fluorene	262	311	*3.8*[c]	254	330	312	360	443
Phenanthrene	250	363	*4.3*[c]	254	330	312	360	443
Anthracene	250	424	*4.8*[c]	254	330	312	360	443
			5.2	280	330	312	360	443
			5.3	280	330	375	360	443
Fluoranthene	286	455	*5.4*[c]	280	330	375	360	443
Pyrene	273	371	*5.8*[c]	280	330	375	360	443
			6.9	280	330	375	385	443
			7.0	270	330	375	385	443
Benz(a)anthracene	286	386	*7.4*[c]	270	330	375	385	443
Chrysene	266	385	*7.7*[c]	270	330	375	385	443
			8.6	275	330	375	385	443
			8.7	275	406	375	385	443
			8.8	275	406	375	385	451
Benzo(b)fluoranthene	244	442	*9.0*[c]	275	406	375	385	451
Benzo(k)fluoranthene	290	410	*9.6*[c]	275	406	375	385	451
Benz(a)pyrene	284	405	*10.1*[c]	275	406	375	385	451
			10.5	275	406	375	496	451
			10.6	288	406	375	496	451
Dibenz(a,h)anthracene	295	404	*11*[c]	288	406	375	496	451
Benzo(ghi)perilene	272	470	*11.4*[c]	288	406	375	496	451
Indeno(1,2,3-cd)pyrene	276	307	*11.7*[c]	288	406	375	496	451

[a] maximum excitation and emission wavelength [Appl. Spectroscopy 51 (1998) 380] [b] only one wavelength can be modified at each time [c] average retention time

Table S3. Several quality analytical parameters of the UHPLC-UV method for 7 pollutants subjected study.

Analyte	Retention time ± SD[a]	Range ($\mu g \cdot L^{-1}$)	R	$S_{x/y}$[b]	Slope ± SD[c]	LOD[d] ($\mu g \cdot L^{-1}$)	LOQ[e] ($\mu g \cdot L^{-1}$)	RSD[f] (%)	
								Level 1[g]	Level 2[h]
Carbamazepine	1.6 ± 0.3	25 – 1000	0.9994	9331.4	910 ± 14	1.58	5.25	5.7	0.80
Atrazine	2.6 ± 0.1	25 – 1000	0.9998	10885	1491 ± 12	3.27	10.9	3.0	2.0
Methylparaben	4.1 ± 0.1	50 – 1000	0.9993	3194.1	797 ± 2	11.0	38.0	4.2	5.6
Estrone	4.8 ± 0.6	75 – 1500	0.9997	4035.2	272 ± 3	14.6	48.7	5.4	2.9
Progesterone	7.1 ± 0.5	50 – 1500	0.9998	9210.0	767 ± 6	11.9	39.7	3.6	2.1
Benzophenone	8.4 ± 0.5	25 – 1000	0.9999	2844.0	807 ± 5	2.21	7.40	6.8	4.9
Triclosan	9.9 ± 0.6	25 – 1250	0.9999	2683.8	569 ± 2	4.46	14.9	6.2	3.4

[a] standard deviation (n = 30, inter-day)

[b] standard deviation of the regression (or error of the estimate)

[c] confidence interval for the slope, associated to n = 6 calibration levels

[d] limit of detection

[e] limit of quantification

[f] relative standard deviation, as inter-day precision (n = 6, in 3 non-consecutive days)

[g] concentration level: 50 $\mu g \cdot L^{-1}$

[h] concentration level: 800 $\mu g \cdot L^{-1}$

Table S4. Several quality analytical parameters of the UHPLC-FD method for the PAHs studied.

Analyte	**Retention time ± SD**[a]	**Range ($\mu g\cdot L^{-1}$)**	**R**	**$S_{x/y}$**[b]	**Slope ± SD**[c]	**LOD**[d] **($\mu g\cdot L^{-1}$)**	**LOQ**[e] **($\mu g\cdot L^{-1}$)**	**RSD**[f] **(%)**	
								Level 1[g]	**Level 2**[h]
Naphthalene	2.5 ± 0.7	0.5 – 6	0.996	0.11	0.61 ± 0.03	0.03	0.1	4.1	3.6
Acenaphthene	3.6 ± 0.2	0.5 – 7	0.997	0.03	0.15 ± 0.01	0.06	0.2	4.5	2.5
Fluorene	3.8 ± 0.1	0.05 – 5	0.998	0.15	1.24 ± 0.03	0.006	0.02	4.9	1.4
Phenanthrene	4.32 ± 0.01	0.1 – 5	0.999	0.02	0.64 ± 0.01	0.03	0.09	3.1	2.0
Anthracene	4.8 ± 0.1	0.2 – 5	0.998	0.07	0.47 ± 0.02	0.015	0.05	8.0	4.0
Fluoranthene	5.40 ± 0.01	0.2 – 5	0.999	0.02	0.15 ± 0.01	0.015	0.05	3.4	1.8
Pyrene	5.86 ± 0.01	0.1 – 7	0.999	0.04	0.40 ± 0.01	0.009	0.03	5.6	4.8
Benz(a)anthracene	7.39 ± 0.01	0.1 – 5	0.994	0.11	0.46 ± 0.03	0.015	0.05	1.6	1.7
Chrysene	7.7 ± 0.2	0.05 – 4	0.999	0.06	0.85 ± 0.02	0.003	0.01	5.4	5.0
Benzo(b)fluoranthene	9.0 ± 0.1	0.1 – 5	0.997	0.05	0.30 ± 0.01	0.009	0.03	4.4	6.5
Benz(a)pyrene	9.6 ± 0.1	0.05 – 5	0.997	0.08	0.54 ± 0.02	0.003	0.01	6.2	5.9
Dibenz(a,h)anthracene	10.12 ± 0.01	0.05 – 5	0.995	0.21	0.63 ± 0.05	0.003	0.01	4.8	3.3
Benzo(ghi)perilene	11.0 ± 0.1	0.05 – 5	0.994	0.40	7.25 ± 0.51	0.006	0.02	6.2	10.9
Benzo(k)fluoranthene	11.4 ± 0.1	0.10 – 5.5	0.998	0.04	0.27 ± 0.01	0.006	0.02	6.5	5.4
Indeno(1,2,3-cd)pyrene	11.7 ± 0.1	0.5 – 8	0.999	0.01	0.08 ± 0.01	0.09	0.3	2.5	5.1

[a] standard deviation (n = 30, inter-day)

[b] standard deviation of the regression (or error of the estimate)

[c] confidence interval for the slope, associated to n = 7 calibration levels

[d] limit of detection

[e] limit of quantification

[f] relative standard deviation, as inter-day precision (n = 6, in 3 non-consecutive days)

[g] concentration level: 0.8 $\mu g\cdot L^{-1}$

[h] concentration level: 2 $\mu g\cdot L^{-1}$

Table S5. Analytical performance of methods reported in the scientific literature for the determination of similar water contaminants using SPE.

Contaminant	Sorbent (amount)	Sample prep.	LOD ($ng·L^{-1}$)	Chromatographic method	Reference
Carbamazepine, estrone & triclosan	NVP[a] (2.5 mg)	BAμE[b]	5, 100 & 10	HPLC-DAD	Int. J. Environ. Anal. Chem. 97 (2017) 484
Atrazine	MWCNTs[d] (100 mg)	μSPE[c] cartidges	20	GC-MS	Sci. Total Environ. 396 (2008) 79
Estrone and derivatives	Oasis® HLB (-)	μSPE[c] disks	1.37	GC-MS	Sci. Total Environ. 590 (2017) 832
Progesterone	Poly(THF)[e] (-)	FPSE[f]	60	HPLC-MS/MS	J. Chromatogr. A 1437 (2016) 116
Carbamazepine, atrazine, progesterone, estrone & triclosan	MIL-53(Al) (5 mg)	D-μSPE[h]	13 – 21	HPLC-DAD	Talanta 179 (2018) 775 [19]
8 PAHs	Fe_3O_4/HKUST-1 (25 mg)	M-D-μSPE[i]	2.7 – 15	UHPLC-FD	J. Chromatogr. A 1436 (2016) 42 [10]
16 PAHs	CIM-80 20 mg)	D-μSPE[h]	0.75 – 9.3	UHPLC-FD	Present work
Carbamazepine, atrazine, progesterone, methylparaben, benzophenone, estrone & triclosan	CIM-80 (20 mg)	D-μSPE[h]	0.090 – 21 $μg·L^{-1}$	UHPLC-UV	Present work

[a] *N*-vinylpyrrolidone polymer
[b] bar-adsorptive microextraction
[c] miniaturized solid-phase extraction
[d] multiwalled carbon nanotubes
[e] sol–gel poly(tetrahydrofuran)
[f] fabric-phase sorptive extraction
[g] Quick, Easy, Cheap, Effective, Rugged, and Safe dispersive extraction method
[h] dispersive miniaturized solid-phase extraction
[i] magnetic-based dispersive miniaturized solid-phase extraction