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1        **Cationic amine-bridged periodic mesoporous organosilica materials for off-line**  
2        **solid-phase extraction of phenoxy acid herbicides from water samples prior to**  
3        **their simultaneous enantiomeric determination by capillary electrophoresis.**

4

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18

19       **Abstract**

20

21       Two novel materials based on periodic mesoporous organosilica (PMO) with  
22       cationic amine-bridged ligands, (styrylmethyl)bis(triethoxysilylpropyl)ammonium  
23       chloride (PMO-STPA) and bis(3-triethoxysilyl)amine (PMO-TEPA), were synthesized  
24       in this work to obtain materials with reverse-phase/strong anionic exchange mixed-  
25       mode or strong anionic exchange retention mechanism, respectively. The resulting  
26       materials were comprehensively characterized and showed functionalization with

27 cationic amine-bridged ligands, and an acceptable surface area. These materials were  
28 evaluated for the off-line solid-phase extraction (SPE) of a mixture of six phenoxy acid  
29 herbicides (fenoprop, mecoprop, dichlorprop, 2-(4-chlorophenoxy)propionic acid (4-  
30 CPPA), 2-(3-chlorophenoxy)propionic acid (3-CPPA), 2-phenoxypropionic acid (2-  
31 PPA)) from water samples previous to their simultaneous enantiomeric analysis by CE  
32 using a dual chiral selector system (20 mM of heptakis(2,3,6-tri-O-methyl)- $\beta$ -CD (TM-  
33  $\beta$ -CD) and 7 mM of (2-hydroxypropyl)- $\beta$ -CD (HP- $\beta$ -CD) dissolved in 50 mM  
34 phosphate buffer, pH 7.0) which enabled the simultaneous enantiomeric separation of  
35 the six phenoxy acid herbicides in 11 min. SPE parameters were optimized and  
36 recoveries obtained for PMO-STPA and PMO-TEPA sorbents were compared. Under  
37 the optimized conditions, it was demonstrated that using 100 mg of PMO-STPA  
38 sorbent, a preconcentration factor (PF) of 1500 was achieved with 750 mL of solution,  
39 allowing recoveries between 75.5 and 112.2%, with good repeatability (RSD =1.9-  
40 8.7%, n= 6). Analytical characteristics of the method were evaluated in terms of  
41 precision, linearity and accuracy with method quantitation limits (MQL) between 1.5  
42 and 3.3  $\mu$ g/L. The developed method was applied to the analysis of river samples and  
43 effluents from wastewater treatment plants, with recoveries ranging from 78.3 to 107.5  
44 %.

45

46 *Keywords:* Periodic mesoporous organosilica, Cationic amine-bridged ligands, Solid-  
47 phase extraction, Capillary electrophoresis, Chiral phenoxy acid herbicides,  
48 Simultaneous enantioseparation.

49

50

### Highlights

- Two novel PMOs were synthesized for phenoxy acid herbicides solid-phase extraction
- A preconcentration factor of 1500 enabled to detect phenoxy acids at  $\mu\text{g/L}$  levels
- The use of a mixture of two CDs allowed acceptable chiral resolution for herbicides
- The simultaneous enantiomeric separation of six phenoxy acids is obtained in 11 min

## 51 **1. Introduction**

52

53           Nowadays, many commercial agrochemicals are chiral and about 30% of them  
54 are pesticides with active ingredients containing one or more chiral centers, being  
55 herbicides one of the pesticides most used today [1]. The enantiomers of chiral  
56 herbicides possess different enantioselectivity on target weeds and different toxic effects  
57 on non-target organisms because of their enantioselective interactions with enzymes and  
58 biological receptors in organisms. Some chiral herbicides are sold as pure active  
59 stereoisomers, but for economic reasons, many other are still used as racemates, being  
60 commonly only one enantiomer active [1]. In the case of phenoxy acid herbicides, the  
61 *R*-enantiomer is biologically active [1, 2], whereas the other isomer is inactive or less  
62 active enantiomer, which simply contributes to the chemical load that pollutes the  
63 environment. For these reasons, analytical methods are needed to separate the  
64 stereoisomers of these compounds and to evaluate the pollution grade.

65           Phenoxyalkanoic acids and derivatives comprise a broad spectrum of herbicides  
66 extensively used in agriculture. Their behavior in soils (solubility, adsorption-  
67 desorption, chemical resistance and biodegradation) is governed by their chemical  
68 structures whose essential features are the presence of a carboxylic acid group and a  
69 chlorinated aromatic ring. A filtering process may occur through the soils originating  
70 that these herbicides can achieve ground waters, so that rivers, dams, etc., can be  
71 polluted at concentrations in the  $\mu\text{g/L}$  levels [3], so that it is usually necessary to use a  
72 preconcentration process, such as SPE, prior to their analysis, being this technique  
73 widely used to clean samples.

74           In recent years, the application of mesostructured materials as new sorbents has  
75 considerably increased for sample preparation. These materials present high surface

76 area, well-defined pore size distribution, large pore volume and can be chemically  
77 modified with organo-functional groups to obtain functionalized silicas with specific  
78 binding sites on their surface, which is potentially useful in those processes where the  
79 specific and selective retention of different kinds of compounds is required [4, 5].  
80 Moreover, the preparation for the first time in 1999 of the so-called periodic  
81 mesoporous organosilica (PMOs) offered a new family of hybrid mesoporous materials  
82 with very interesting surface and mechanical properties [6]. These materials are organic-  
83 inorganic hybrid materials that combine the properties of the organic functionality and  
84 the chemical stability of the inorganic silica as well as some other desirable  
85 characteristics like great surface area. Generally, PMOs are synthesized by the sol-gel  
86 method, using bridged organosilane precursors of the type  $(R'O)_3Si-R-Si(R'O)_3$ , as Si  
87 source and at the same time as organic moiety in which -R is the organic functional  
88 group, and a directing agent [7]. These materials suppose a great advantage with respect  
89 to other mesoporous materials and have originated a great interest among the  
90 researchers. PMOs incorporate the organic functionalities directly into the silica  
91 framework, as molecular bridging ligands, in contrast to other modified mesoporous  
92 silicas where the organic groups are pending from the walls. This aspect allows higher  
93 degrees of organic functionality and a more homogenous distribution of them through  
94 the whole framework. This improves the chemical and thermal properties of the  
95 materials and reduces the problems of channel blockage or diffusion of analytes, in  
96 comparison with other mesoporous materials functionalized with the post-synthesis  
97 method [8]. On the other hand, PMOs can be modified or tuned with different organic  
98 moieties (such as methylene, ethylene, ethenylene, phenylene) and other more complex  
99 functionalities like thiol, metal complexes, chiral groups, ionic entities or disulfide  
100 groups [9, 10]. These organic functionalizations allow the modification and

101 optimization of their hydrophobic/hydrophilic behavior [11] or the ability to form metal  
102 complexes, among others [10]. All these properties stated above confer to these  
103 materials a wide variety of applications such as catalysis, drug delivery, sensing,  
104 adsorption, preparation of stationary phases for chromatography, separation, etc.

105 Among the different analytical techniques enabling the separation of  
106 stereoisomers, CE has widely been employed with this aim due to its advantages, such  
107 as simplicity, the use of small volume of reagents and samples, high efficiency and  
108 resolution power, rapid analysis and a reasonable operating cost which presents a high  
109 interest from the economic and environmental viewpoints. The most employed  
110 separation mode in chiral CE is Electrokinetic Chromatography (EKC) in which a chiral  
111 selector is added to the buffer to allow the separation of enantiomers. A wide range of  
112 chiral selectors have been tested, such as cyclodextrins (CDs), proteins, surfactants,  
113 antibiotics, polysaccharides, etc, being CDs the most widely used chiral selectors [12,  
114 13].

115 In this article, a simple method of synthesis, with only one step, is described for  
116 the preparation of two new PMOs using styrylmethylbis(triethoxysilylpropyl)  
117 ammonium chloride (STPA) or bis(3-triethoxysilylpropyl)amine (TEPA) and  
118 tetraethylorthosilicate (TEOS) as silica sources. All the materials were thoroughly  
119 characterized and evaluated as SPE sorbents for the extraction of six phenoxy acid  
120 herbicides (fenoprop, mecoprop, dichlorprop, 2-(4-chlorophenoxy)propionic acid (4-  
121 CPPA), 2-(3-chlorophenoxy)propionic acid (3-CPPA), 2-phenoxypropionic acid (2-  
122 PPA)) from water samples, before their simultaneous enantiomeric separation and  
123 determination by CE. The effect of the different interactions between sorbents and  
124 analytes due to a reverse-phase/strong anionic exchange mixed-mode (PMO-STPA) or

125 strong anionic exchange (PMO-TEPA) retention mechanism on the performance of the  
126 extraction was also investigated.

127127

## 128 2. Materials and methods

129129

### 130 2.1. Reagents

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132 Poly(ethylene glycol) (EO20PO70EO20, Pluronic 123), cetyltrimethyl-  
133 ammonium bromide (CTAB) 98%, orthophosphoric acid 85%, sodium hydroxide  
134 (NaOH), ammonium formate, formic acid, boric acid and TEOS 98% were purchased  
135 from Sigma-Aldrich (St. Louis, MO, USA). TEPA 95% and STPA 40% were obtained  
136 from ABCR GmbH (Karlsruhe, Germany). Methanol (MeOH), ethanol (EtOH) 99.5%,  
137 hydrochloric acid solution 37% and ammonia solution (NH<sub>3</sub>) 32% were obtained from  
138 Scharlau Chemie (Barcelona, Spain).

139 The employed water was Milli-Q quality (Millipore, Bedford, MA, USA).  $\alpha$ -  
140 Cyclodextrin ( $\alpha$ -CD), heptakis (2,6-di-O-methyl)- $\beta$ -cyclodextrin (DM- $\beta$ -CD) and TM-  
141  $\beta$ -CD were bought in Sigma Aldrich (St. Louis, MO, USA);  $\beta$ -cyclodextrin ( $\beta$ -CD) and  
142 HP- $\beta$ -CD in Fluka (Buchs, Switzerland); and (2-hydroxypropyl)- $\gamma$ -cyclodextrin (HP- $\gamma$ -  
143 CD) was obtained from Cyclolab (Budapest, Hungary).

144

### 145 2.2. Standard solutions and water samples

146

147 Standard compounds with high purity (> 98%) were purchased: (R,S)-2-(2,4,5-  
148 trichlorophenoxy)propanoic acid (fenoprop) 97%, (R,S)-2-(4-chloro-2-  
149 methylphenoxy)propanoic acid (mecoprop), (R,S)-2-(2,4-dichlorophenoxy)propanoic



150 acid (dichlorprop), 4-CPPA and 3-CPPA from Sigma-Aldrich (St. Louis, MO, USA). 2-  
151 PPA from Chem Service (West Chester, USA). Stock standard solutions were prepared  
152 in MeOH (in a concentration of 1000 mg/L) and then diluted with Milli-Q water until  
153 desired concentration to obtain working solutions, and were stored at 4 °C. All solutions  
154 were filtered through 0.45 µm pore size nylon membrane filters before analysis. For  
155 SPE optimization purposes, an herbicide mixture of fenoprop at a racemic concentration  
156 of 5 mg/L, and 10 mg/L for the rest of phenoxy acid herbicides, was analyzed.

157 Water samples (WS) analyzed in this work were collected through different  
158 locations: WS 1 was obtained from effluent treatment plant (Cádiz, Spain, pH 7.6), WS  
159 2 from an effluent treatment plant (Sevilla, Spain, pH 7.3), and WS 3 from Henares  
160 river (Alcalá de Henares, Spain, pH 7.8). WS were stored in glass bottles at 8 °C and  
161 filtered with 0.45 µm nylon filters before being analyzed.

162162

### 163 2.3. *Synthesis of periodic mesoporous organosilicas*

164

165 For the synthesis of the PMO materials, chemicals were added in a molar ratio as  
166 follows: 1 (ligand): 0.05 Pluronic 123: 0.15 CTAB: 7.14 NH<sub>3</sub>: 56.4 EtOH: 1471.4 H<sub>2</sub>O:  
167 10 TEOS (in the case of TEPA ligand) and :14 TEOS (in the case of STPA ligand). For  
168 the synthesis of the organosilica employing STPA as organic ligand and TEOS as silica  
169 sources (denoted PMO-STPA), 2.7 g of Pluronic 123 and 0.5 g of CTAB were dissolved  
170 in a solution formed by mixing 31 mL of NH<sub>3</sub> 2M, 229 mL H<sub>2</sub>O and 28 mL EtOH. After  
171 1 h of stirring, a mixture of 13.8 mL of STPA and 27 mL TEOS (with molar ratio 1:14)  
172 was added with droplet system. In the case of TEPA as organic ligand and TEOS as  
173 silica sources (denoted PMO-TEPA), 4.6 g of Pluronic 123 and 0.8 g of CTAB were  
174 dissolved in a solution formed by mixing 52 mL of 2 M ammonia solution, 384 mL H<sub>2</sub>O

175 and 48 mL EtOH. After 1 h of stirring, a mixture of 6.4 mL of TEPA and 31.8 mL of  
176 TEOS (with molar ratio 1:10) was added with a droplet system and stirring for 1 h.  
177 After the addition of the ligand, each solution was transferred into a teflon-lined steel  
178 Parr autoclave and heated at 100 °C for 16 h. The precipitate (white colour with TEPA  
179 and orange colour in the case of STPA) was filtered off, washed with Milli-Q water and  
180 EtOH, and dried at 60 °C for 6 h.

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#### 182 2.4. Characterization of periodic mesoporous organosilicas

183183

184 N<sub>2</sub> gas adsorption–desorption isotherms were obtained using a Micromeritics  
185 ASAP 2020 analyzer (Norcross, Atlanta, GA, USA). Adsorption isotherms were  
186 measured at -196 °C over the interval of relative pressures from 10<sup>-4</sup> to 0.993. Prior to  
187 each adsorption analysis the samples were outgassed at 90 °C in vacuum during 10 h in  
188 the port of degasification of the instrument. Such temperature was chosen to avoid any  
189 degradation of the organic ligands and to remove adsorbed species, solvents and water.  
190 The specific surface areas were calculated using the BET model. The pore size  
191 distributions were calculated using the Barrett–Joyner–Halenda (BJH) model on the  
192 desorption branch. Elemental analysis (%C, %N, %H) was performed with a LECO  
193 CHNS-932 analyzer (St. Joseph, MI, USA). Thermogravimetric analysis (TGA) was  
194 carried out using a Setsys 18 A (Setaram, Caluire, France) thermogravimetric analyzer  
195 with a 100 µL platinum crucible, in a synthetic air atmosphere with a temperature  
196 increasing from 25 °C to 800 °C at a speed of 10 °C per min. <sup>13</sup>C CP/MAS NMR was  
197 recorded on a Bruker Avance III/HD Spectrometer (Rheinstetten, Germany) at 100.53  
198 MHz as resonance frequency (2000 transients, spinning speed of 12 KHz, contact time 3  
199 ms, pulse delay 5 s) and <sup>29</sup>Si MAS NMR spectra was recorded on a Bruker Avance

200 III/HD 9.4T Spectrometer (Rheinstetten, Germany) at 79.49 MHz, as resonance  
201 frequency and  $^1\text{H}$  resonance frequency of 400 MHz (1000 transients, spinning speed of  
202 5 KHz, contact time 3 ms, pulse delay 60 s), using high power decoupling pulse  
203 program with unplugging as sequence and a Varian sounding line arranged to a Bruker  
204 7.5 mm T3 HX.

205 Scanning electron microscopy (SEM) was carried out on a XL20 ESEM Philips  
206 (Resto, VA, USA) with an energy-dispersive spectrometry system (EDS). Samples were  
207 treated with a sputtering method with the following parameters: sputter time 100 s,  
208 sputter current 30 mA, and film thickness 20 nm using sputter coater BAL-TEC SCD  
209 005. SEM was used to study the morphology and size of the particles of the materials  
210 prepared in this work. Conventional transmission electron microscopy (TEM) was  
211 carried out on a TECNAI 20 Philips microscope (Hillsboro, OR, USA) operating at 200  
212 KV, with a resolution of 0.27 nm and  $\pm 70^\circ$  of sample inclination, using a beryllium  
213 oxide sample holder. The samples were prepared by dispersing the powder products as  
214 slurry in acetone and subsequently deposited and dried on a honey carbon film on a Cu  
215 grid.

216 Finally, the infrared spectra were recorded on a Perkin Elmer Frontier FTIR  
217 spectrophotometer (Waltham, MA, USA) in the region of  $4000\text{-}400\text{ cm}^{-1}$  by using  
218 spectra quality KBr powder, to determine the presence of functional groups in the  
219 mesoporous structure.

220220

## 221 2.5. CE separation

222

223 Electrophoretic experiments were carried out on a HP  $^3\text{D}$ CE system from Agilent  
224 Technologies (Palo Alto, CA, USA) with a diode array detector (DAD) controlled by a

225 HP <sup>3D</sup>CE ChemStation software. Background electrolytes (BGE) tested in the CE-DAD  
226 experiments consisted of 50 mM formate buffer (pH 5.0), 50 mM phosphate buffer (pH  
227 7.0) containing individual CDs as chiral selectors or a dual system of CDs at different  
228 concentrations. Separations were performed in an uncoated fused-silica capillary of 50  
229  $\mu\text{m}$  I.D. and a total length of 58.5 cm or 63.5 cm (50 or 55 cm effective length,  
230 respectively) acquired in Polymicro Technologies (Phoenix, AZ, USA). Different  
231 separation voltages (15, 20, 25 and 30 kV) and working temperatures (15, 20 and 25  $^{\circ}\text{C}$ )  
232 were tested. Injections were carried out by applying 50 mbar for 5 or 10 s. Detector  
233 parameters were as follows: a response time of 1.0 s and a wavelength of 194 nm (2-  
234 PPA and 4-CPPA), 200 nm (mecoprop, dichlorprop and 3-CPPA) and 210 nm  
235 (fenoprop) (bandwidth 5 nm). At the beginning of each working day the capillary was  
236 flushed with NaOH 0.1 M for 5 min, Milli-Q water for 5 min, buffer solution for 5 min  
237 and BGE for 10 min, and at the end of the day it was flushed with NaOH 0.1M and  
238 Milli-Q water, both of them for 5 min. In order to ensure the repeatability between  
239 injections, the capillary was flushed with Milli-Q water for 2 min, NaOH 0.1 M for 2  
240 min, Milli-Q water for 2 min and BGE for 5 min.

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## 242 2.6. SPE conditions

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244 The extraction procedure was carried out in a 20-position extraction manifold  
245 purchased from Waters (Barcelona, Spain), at a flow rate of 1 mL/min, connected to a  
246 vacuum pump at 16 InHg. SPE 6 mL cartridges (65 mm length, 11 mm diameter) were  
247 packed with 100 or 200 mg of each PMO synthesized (PMO-STPA or PMO-TEPA) and  
248 plugged with polyethylene frits at both ends along with a 0.45  $\mu\text{m}$  pore size nylon filter  
249 membrane inserted at the bottom of the mesoporous silica bed in order to avoid the

250 material lost during the sample loading. The work methodology was carried out as  
251 follows: the conditioning process previous to sample loading was realized with 5 mL  
252 MeOH and 5 mL Milli-Q water. Once the sample was loaded at a flow of 1 mL/min,  
253 cartridges were dried by passing just air for 20 min without any solvent to delete the  
254 interferences. Elution was performed by passing 2 x 4 mL MeOH and picked up in a  
255 vial whose eluate was evaporated to dryness in a Eppendorf Concentrator plus (1400  
256 rpm, 250 RCF, 30°C) coupled with a 6 cone-shaped tube rotor, purchased from  
257 Eppendorf Ibérica S.L.U. (Madrid, Spain), and re-dissolved in 500 µL of MeOH:Milli-  
258 Q water (10:90 v/v) for subsequent analysis by CE.

259         The optimization of the extraction procedure was carried out using three  
260 different solutions spiked with the six phenoxyacid herbicides, two of them prior to  
261 extraction and one of them after extraction process (simulated sample) in the desired  
262 level concentration to obtain a final extract of 500 µL of MeOH:Milli-Q water (10:90  
263 v/v) with a racemic concentration of 5 mg/L for fenoprop and 10 mg/L for the rest of  
264 phenoxy acids for subsequent analysis by CE. Recovery values were calculated by  
265 comparison of the corrected peak areas for the phenoxy acid herbicides studied with  
266 those obtained for the simulated sample.

267         When water samples from river and effluents of treatment plants were analyzed,  
268 method accuracy was evaluated as the recovery values obtained for the phenoxy acid  
269 herbicides studied at low and high concentrations levels when comparing the spiked  
270 amounts added to the water samples and the herbicides concentrations by using the  
271 developed methodology.

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273     2.7. *Data treatment and calculations*

274274

275 Microsoft Excel Professional Plus 2010 was employed for calculations of  
276 recoveries and statistical analysis. OriginPro 8 software was used to create the artwork.  
277 Van der Waals forces and Hückel charges calculations were carried out by means of  
278 Chem3D Pro 12.0 software.

279279

### 280 3. Results and discussion

281281

#### 282 3.1. Synthesis and characterization of the periodic mesoporous organosilica materials

283283

284 PMO-STPA and PMO-TEPA materials have not been synthesized previously.  
285 Compared with common synthesis used for PMO type materials, the main variation  
286 presented in this work was the use of a basic medium instead of acid. In the acid  
287 medium, the synthesis employing STPA or TEPA as cationic amine-bridged ligands  
288 was completely unsuccessful to obtain PMOs. A possible explanation for these results  
289 can be the fact that these ligands (employed in the synthesis of PMOs for the first time  
290 in this work) are positively charged in strong acid media, due to the amino groups that  
291 they have in their structures. Therefore, these positive charged ligands can suffer  
292 electrostatic repulsions with the ions of the CTAB template not allowing the correct  
293 formation of the micelles, necessary to obtain a mesoporous structure.

294 N<sub>2</sub> adsorption-desorption isotherms obtained for PMO-STPA and PMO-TEPA  
295 materials are shown in **Figures 1a** and **1c**, respectively. For PMO-STPA material (**Fig.**  
296 **1a**) the isotherm is a typical type IV isotherm, which corresponds with mesoporous  
297 materials, according to the IUPAC classification. The isotherm has a very prominent  
298 adsorption step at around 0.9 P/P<sub>0</sub>, this steep capillary condensation shows that the  
299 capillary condensation of nitrogen takes place in highly uniform mesopores [14].

300 Although the desorption branch of the material has no a tailing before it reaches the  
301 adsorption branch, the isotherm does not show a plateau at high pressures. This fact  
302 could indicate the presence of some amorphous non-mesostructured domains in the  
303 material, and the pore size distribution of the material could have some non-uniformity  
304 of pore opening sizes. This is also in good agreement with the wide pore size  
305 distribution that the material shows (**Fig. 1b**) with most of the pores centered at 235 Å,  
306 which could be explained as a consequence of the big size of the STPA ligand (see  
307 **Table 1**). The isotherm also has a H1 type hysteresis loop with almost parallel branches  
308 confined to relative pressures between 0.85 and 0.95, this fact indicates the  
309 irreversibility of the adsorption-desorption behavior in primary mesopores [15]. All  
310 these features are characteristic of large channel mesostructures and pores with  
311 cylindrical shape. In the case of the PMO-TEPA material, the N<sub>2</sub> adsorption-desorption  
312 isotherms (**Fig. 1c**) also show a typical type IV isotherm, which corresponds with  
313 mesoporous materials. The isotherm has a very prominent adsorption step at around 0.8  
314 P/P<sub>0</sub>, this steep capillary condensation and the final adsorption plateau show that the  
315 capillary condensation of nitrogen takes place in more uniform mesopores compared  
316 with the PMO-STPA material. This result is also confirmed by the narrower pore size  
317 distribution of the PMO-TEPA material (**Fig. 1d**) which most of the pores centered at  
318 152 Å. In addition, the lower value of the pore size obtained with PMO-TEPA  
319 compared to PMO-STPA is in agreement with the smaller size of the TEPA ligand. The  
320 isotherms also have a H1 type hysteresis loop with almost parallel branches confined to  
321 relative pressures between 0.8 and 0.95, these facts indicating the irreversibility of the  
322 adsorption-desorption behavior in primary mesopores and large channel mesostructures  
323 with pores with cylindrical shape in PMO-STPA material.

324 The SEM micrographs (**Figs. S1 a and c** in supplementary material) show that  
325 the morphology of these materials is not well defined, where small numbers of the  
326 particles are spherical, being most of them amorphous or prism-shaped. This fact can be  
327 explained taking into account the size and the shape of the STPA and TEPA ligands  
328 (**Fig. 2**) and the basic pH employed in the synthesis. Also, the high ratio surfactant/silica  
329 source (w/w) employed in the synthesis, 9.8% and 12.8% for STPA and TEPA,  
330 respectively, can avoid the formation of spherical micelles during the synthesis of the  
331 materials and affect the shape of the particles [16]. The dispersion in particle size in  
332 both materials is quite big, which in the case of PMO-STPA goes from 16 to 30  $\mu\text{m}$ ,  
333 whereas the material PMO-TEPA shows bigger particles that go from 12 to 40  $\mu\text{m}$ . On  
334 the other hand, TEM images (**Figs. S1 b and d** in supplementary material) show that  
335 both materials have a porous structure with a wormhole-like arrangement of channels.  
336 These results are in agreement with previous works that reveal that high ratios of  
337 surfactant lead to a non-hexagonal pore arrangement material [17, 18].

338 The FTIR spectra of the two materials synthesized (**Fig. S2** in supplementary  
339 material) show a similar pattern for both, with most remarkable peaks in the fingerprint  
340 region. Stretching bands between 1645 and 1379  $\text{cm}^{-1}$ , as well as C-H bend bands at  
341 1456  $\text{cm}^{-1}$  confirmed the presence of the aromatic moiety in the solid framework of  
342 PMO-STPA. At the same time, the N-H bend of amine moiety could be overlaid at 1625  
343  $\text{cm}^{-1}$ , which is more intense in the case of PMO-TEPA. In addition, this region bending  
344 and rocking bands of C-H bonds of alkane moiety appear. These FTIR spectra showed  
345 that the organic ligand was correctly introduced in the PMO network. In order to  
346 quantify the amount of organic ligand incorporated into the silica framework, by means  
347 of elemental analysis, the %N was calculated. As shown in **Table 1**, PMO-STPA has a  
348 functionalization degree of 0.93 mmol ligand/g material whereas for PMO-TEPA it was



349 1.14 mmol ligand/g material, which means that ligands were successfully incorporated  
350 in the framework of each material. What is more, the decrease in the amount of the  
351 ligand STPA, incorporated into the silica framework of PMO-STPA compared with  
352 PMO-TEPA is due to the higher steric hindrance of the more voluminous STPA ligand.  
353 To corroborate the presence of the ligand in the framework and the thermal stability of  
354 the materials, TGA was carried out. **Figure S3** (supplementary material) shows the  
355 TGA curves for these materials. It can be observed a loss in mass (8.25% and 16% for  
356 PMO-STPA and PMO-TEPA, respectively) that occurs between 300 °C and 600 °C  
357 (exothermic process) and that is due to cleavage / degradation of the ligand in the frame.  
358 The thermal stability of these samples is also in agreement with previous results given  
359 in the literature for other functionalized organo silicas [10].

360 Additional characterization of PMO-STPA material was also carried out by  
361 solid-state <sup>13</sup>C and <sup>29</sup>Si NMR spectroscopy (**Figs. 3a and 3b**, respectively) that  
362 confirmed the presence of the STPA ligand in the material. The high ratio between the  
363 Q/T sites in the <sup>29</sup>Si MAS NMR spectrum (**Fig. 3b**) shows that the silicate bonds are  
364 mainly present in the framework of the silica, which can be explained because of the  
365 low ligand/TEOS ratio used during the synthesis.

366366

### 367 *3.2. Simultaneous enantiomeric separation of a mixture of phenoxy acid herbicides by* 368 *CE*

369 In order to develop a CE method enabling the simultaneous enantiomeric  
370 separation of six chiral phenoxy acid herbicides (fenoprop, mecoprop, dichlorprop, 4-  
371 CPPA, 3-CPPA and 2-PPA) with an acceptable enantioselectivity and enantioresolution,  
372 and based on previous chiral separations reported in the literature for some of the  
373 herbicides studied [19-28], in which neutral CDs [19-22] or dual system of CDs were

374 usually employed [20, 23], an initial screening of neutral CDs was carried out ( $\alpha$ -CD,  
375  $\beta$ -CD, DM- $\beta$ -CD, TM- $\beta$ -CD, HP- $\beta$ -CD and HP- $\gamma$ -CD). For this purpose, a 15 mM  
376 concentration of each neutral CD in a 50 mM formate buffer at pH 5.0, a separation  
377 voltage of 20 kV and a temperature of 25 °C, were chosen. Among the CDs studied, the  
378 best chiral separation for the group of compounds analyzed was achieved with  $\beta$ -CD  
379 ( $R_s$  between 0.7 and 4.4, no chiral separation of dichlorprop, in 27.5 min), HP- $\beta$ -CD  
380 ( $R_s$  between 1.4 and 2.7, no chiral separation of fenoprop, in 27.4 min) and TM- $\beta$ -CD  
381 ( $R_s$  between 0.8 and 5.2, no chiral separation of 2-PPA, in 36.7 min), whereas no  
382 enantioseparation was obtained with the remaining CDs studied for the herbicides  
383 analyzed.

384 With the aim to increase the  $R_s$  values obtained for the six herbicides, dual CDs  
385 systems were employed using different combinations of the three CDs ( $\beta$ -CD, HP- $\beta$ -CD  
386 and TM- $\beta$ -CD) that originated enantioseparation when employed individually. Each CD  
387 was at a 15 mM concentration in the dual mixture and the same experimental conditions  
388 were employed. Among the three possible combinations, only the HP- $\beta$ -CD/TM- $\beta$ -CD  
389 dual system allowed the simultaneous separation of the enantiomers of the six  
390 herbicides studied although the  $R_s$  obtained for fenoprop was low ( $R_s$  0.4).

391 Once selected the most suitable combination of CDs, the effect of their  
392 concentration was evaluated in the range from 5 to 20 mM (5, 7, 10, 15 and 20 mM). It  
393 could be observed that fenoprop, mecoprop, dichlorprop and 4-CPPA improved their  $R_s$   
394 at low HP- $\beta$ -CD concentrations, whereas 3-CPPA and 2-PPA improved their  $R_s$  at high  
395 TM- $\beta$ -CD concentrations. A 7 mM HP- $\beta$ -CD/20 mM TM- $\beta$ -CD dual system enabled  
396 the simultaneous separation of all compounds with  $R_s$  values between 1.2 (fenoprop)  
397 and 3.0 in an analysis time of 34.9 min.

398 In order to decrease the analysis time, a 50 mM phosphate buffer (pH 7.0) was  
399 employed. Under these conditions an important decrease in the analysis time (11.7 min)  
400 was achieved without significant loss in Rs (Rs between 1.0 and 2.5).

401 Finally, the effect of different instrumental parameters on the separation was  
402 also evaluated. First, to obtain an increase in the Rs, an injection of 50 mbar in 5 s was  
403 tested, but a loss of sensitivity was observed without improving de Rs. Hence, the  
404 previous injection conditions (50 mbar x 10 s) were chosen. The influence of the  
405 temperature on the Rs values was also investigated using values of 15, 20 and 25 °C.  
406 The results obtained showed that a temperature of 15 °C gave rise to a slightly decrease  
407 in the analysis time (11 min) and Rs values slightly increased (Rs between 1.1 and 2.7).  
408 Hence a temperature of 15 °C was chosen. Finally, the influence of the applied voltage  
409 between 15 and 30 kV (15, 20, 25, 30 kV) was also investigated. An increase in the  
410 separation voltage originated a decrease in the analysis time but a slight variation of the  
411 Rs values between 15 and 25 kV, with total loss of resolution for most compounds at 30  
412 kV. Therefore, a separation voltage of 25 kV was considered as the best.

413 Under the optimal separation conditions (50 mM phosphate buffer at pH 7.0, 7  
414 mM HP- $\beta$ -CD - 20 mM TM- $\beta$ -CD, 25 kV, 15 °C, hydrodynamic injection of 50 mbar x  
415 10 s), the simultaneous enantiomeric separation of the six phenoxy acid herbicides  
416 studied was obtained in 11 min with Rs values  $\geq 1.6$  for mecoprop (Rs 2.7), dichlorprop  
417 (Rs 1.9), 4-CPPA (Rs 1.8) and 2-PPA (Rs 1.6) and Rs values of 1.1 and 1.2 for  
418 fenoprop and 3-CPPA, respectively.

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420 *3.3. Evaluation of PMO materials for solid-phase extraction of phenoxy acid herbicides*  
421 *from water samples*

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423 The two PMOs synthesized in this work were evaluated as sorbents in SPE to  
424 study the extraction efficiency of six chiral phenoxy acid herbicides from water samples  
425 and to select the sorbent providing the highest recovery for these analytes. The PMO-  
426 STPA material shows a reverse-phase/strong anionic exchange mixed-mode retention  
427 mechanism due to this material possesses a styrylmethyl moiety that interacts by means  
428 of Van der Waals forces with the aromatic ring of the phenoxy acids at the same time  
429 that ionic interaction occurs between carboxyl and positively charged amine groups,  
430 whereas in the case of PMO-TEPA material only strong anionic exchange retention  
431 mechanism takes place (see **Fig. 2**). Related to textural properties previously discussed  
432 for both materials, it has not been found notable differences between them except for  
433 the greatest surface BET ( $S_{\text{BET}}$ ) and pore volume in PMO-STPA material with respect  
434 to PMO-TEPA material, that could favor the interaction with phenoxy acid herbicides  
435 given the big substituent linked to the amine moiety in PMO-STPA.

436 With the aim to calculate the recovery values for the analytes in the SPE process,  
437 solutions of each racemic herbicide were prepared in Milli-Q water so that applying the  
438 corresponding PF in each optimization step, the final analyzed concentration by CE was  
439 5 mg/L for fenoprop, and 10 mg/L for the rest of the phenoxy acids studied.

440 First of all, different sorbent amounts (100 and 200 mg) and pH values of elution  
441 solvent (2 x 4 mL of MeOH at pH 5.6 or 1.8) were tested by passing 100 mL of Milli-Q  
442 water solution (pH = 6.3) spiked with the compounds (25  $\mu\text{g/L}$  of fenoprop and 50  $\mu\text{g/L}$   
443 for the remaining herbicides) through the cartridge. As can be seen in **Figure 4**, at a pH  
444 of 5.6, using PMO-STPA material as sorbent, recovery values between 90.2 and 103.7%  
445 were obtained with 100 mg (**Fig. 4a**) and recovery values between 89.0 and 109.2%  
446 with 200 mg (**Fig. 4b**). However, with 100 mg of PMO-TEPA material sorbent (**Fig.**  
447 **4a**) eluting with MeOH at pH 5.6, a poor recovery value between 20.3 and 59.7% was

448 obtained, except for fenoprop (recovery 84.3%), whereas using 200 mg of sorbent (**Fig.**  
449 **4 b**), with the same elution process, the recovery values were higher, between 89.2 and  
450 105.3% for mecoprop, dichlorprop and fenoprop, and between 37.8 and 73.9% for 4-  
451 CPPA, 3-CPPA and 2-PPA.

452 To increase the recovery values with PMO-TEPA as sorbent, it was decided to  
453 use MeOH acidified at pH 1.8 as elution solvent, in order to avoid the deprotonation of  
454 the carboxyl moiety in phenoxy acids, whose pKa values are between 2.8 and 4.3, and  
455 to break up the ionic interaction with positive amine moiety (see **Fig. 2**). As it can be  
456 seen in **Figure 4**, with 100 mg of this sorbent, an increase in the recovery from 20.3-  
457 82.0% to 39.9-110.2% took place, whereas using 200 mg of this sorbent the increase in  
458 recovery percentages reached values from 37.8-105.3% to 65.2-178.3%, obtaining  
459 always the lowest recoveries for 4-CPPA, 3-CPPA and 2-PPA. There is hard evidence  
460 that the ionic interaction plays an important role in the recovery process, although  
461 values up to 178.3% showed some questionable interferences in the extraction of the  
462 analytes under these conditions with PMO-TEPA and eluting with MeOH at pH 1.8.

463 The differences observed in the recovery values comparing both sorbents could  
464 be explained as a function of the Van der Waals forces and Hückel charge values shown  
465 in **Table S1** (supporting material). Both cationic amine ligands show a similar value of  
466 Hückel charge but STPA possesses a high value of Van der Waals forces. With regard  
467 to analytes, all of them show similar Van der Waals forces values, whereas a noticeable  
468 difference in the Hückel charge of oxygens in the carboxyl moiety was observed, whose  
469 values are lower for 4-CPPA, 3-CPPA and 2-PPA (**Table S1**). This fact confirms that  
470 the PMO-STPA material involves a mixed-mode mechanism retention by Van der  
471 Waals forces and ionic exchange that favor the retention of 4-CPPA, 3-CPPA and 2-  
472 PPA, whose values of Hückel charge are lower and show higher recovery values

473 compared with PMO-TEPA sorbent that only shows anionic interaction with the  
474 negatively charged analytes. Hence, PMO-STPA was selected in order to achieve the  
475 higher efficiency in the extraction of the six chiral phenoxy acid herbicides in water  
476 samples.

477 Using PMO-STPA, the next step was to study the breakthrough volume,  
478 parameter that determines the maximum volume of sample that can be passed through  
479 the sorbent without losing a significant recovery. This study was carried out with 100  
480 mg of PMO-STPA and the volume of spiked sample was increased sequentially to 100,  
481 200, 500, 750 and 1000 mL. The highest recoveries (see **Fig. 5**) were obtained up to 750  
482 mL, considered the optimum volume, with values between 75.5 and 112.2% and a PF of  
483 1500, since with 1000 mL the enantiomeric recovery value obtained for 2-PPA  
484 decreased from 75.5 - 77.1% to 55.5 - 56.6%, although the remaining compounds kept  
485 their recovery values between 89.6 and 102.4%. These results show that PMO-STPA  
486 possesses a high capacity to concentrate the phenoxy acid herbicides studied in this  
487 work in diluted samples.

488 **Table S2** (supplementary material) groups the recovery values reported  
489 previously in the pre-concentration of some of the phenoxy acids studied in this work in  
490 water samples employing other commercial and non-commercial SPE sorbents [29-44].  
491 Different types of materials have been used, some commercials such as Oasis HLB  
492 [29,30,34,37,42] or C18 [31,32,35,36] and C18 assisted with CTAB [43,44], and other  
493 non-commercial such as polystyrene-divinylbenzene polymer [33], molecularly  
494 imprinted polymers (MIPs) [38, 39], graphene oxide [40] and graphitized carbon black  
495 (GCB) [41]. As it can be seen, most of the extraction procedures carried out with water  
496 samples were focused on fenoprop, mecoprop and dichlorprop, whereas 4-CPPA has

497 only been extracted in one of them [33], and 3-CPPA and 2-PPA have not been  
498 analyzed in none of them.

499 In general terms recovery values obtained in all cases are higher than 80%,  
500 except in two of them that use graphene oxide as sorbent [40] or a commercial Oasis  
501 HLB SPE cartridge [29], in which recovery values between 40 and 75% were obtained.  
502 Basically, all these procedures are based on the Van der Waals, noncovalent or  
503 hydrophobic interactions in order to retain the analytes, although some of them [43,44]  
504 joined the effect of the sorbent with an ion-pairing agent, such as CTAB to achieve an  
505 increase of the recovery thanks to the exchange mixed-mode, such as it has been made  
506 in this work, which could provide an increase of recovery values.

507 Regarding PF obtained in the published papers (see Table S2, supplementary  
508 material) only when commercial sorbents were employed, higher PFs were achieved  
509 between 200 and 5000, whereas with non-commercial sorbents PF obtained were found  
510 in the range from 2 to 100, with the exception of the employ of graphene oxide as  
511 sorbent that provided a PF of 2000 but a very low recovery value (40%).

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### 513 *3.4. Analytical characteristics of the developed SPE-CE method and analysis of water* 514 *samples*

515 Analytical characteristics of the developed SPE-CE method using PMO-STPA  
516 sorbent were evaluated in terms of linearity, precision, accuracy, instrumental limits of  
517 detection (LOD) and quantitation (LOQ), and method limits of detection (MDL) and  
518 quantitation (MQL) (see **Table 2**).

519 Linearity was determined by plotting the corrected peak area as a function of the  
520 enantiomer concentration for each compound with a total of six standard solutions  
521 injected by triplicate, at different concentrations (mg/L) as follows: fenoprop (2-30),

522 mecoprop (3-30), dichlorprop (4-30), 4-CPPA (4-30), 3-CPPA (3-25) and 2-PPA (5-  
523 25). This procedure was repeated during three different days to fix the linear range for  
524 each compound. Linear equations were expressed according to a confidence range  
525 taking into account the mean value of the slope and its statistical error at 95% (**Table 2**).  
526 Satisfactory results were obtained in terms of linearity with  $R^2$  values  $\geq 0.995$  in all  
527 cases. ANOVA confirmed through the p-values (p-value  $> 0.09$  in all cases for a 95%  
528 confidence level) that the experimental data fit properly to linear models.

529 Instrumental LODs and LOQs were calculated considering 3 and 10 times the  
530 S/N ratio, respectively, with values ranging from 0.7 to 1.5 mg/L and from 2.2 to 5.0  
531 mg/L, respectively. MDLs and MQLs were experimentally calculated considering 3 and  
532 10 times the S/N ratio, respectively, estimated from the lowest concentration level of the  
533 calibration curve and taking into account a PF of 1500. Values for MDLs ranged from  
534 0.5 to 1.0  $\mu\text{g/L}$  and for MQLs from 1.5 to 3.3  $\mu\text{g/L}$  (**Table 2**).

535 Precision of the method was evaluated in terms of instrumental repeatability and  
536 intermediate precision. The first one was determined from nine repeated injections of a  
537 standard solution in Milli-Q water at low (5 mg/L for each enantiomer of all  
538 compounds) and high (25 mg/L for each enantiomer of 3-CPPA and 2-PPA and 30  
539 mg/L for each enantiomer of fenoprop, mecoprop, dichlorprop and 4-CPPA)  
540 concentration levels without employing the SPE procedure, that is, by directly injecting  
541 the different standard solutions in the CE system. RSD values (%) were between 4.8  
542 and 12.9% for corrected peak areas ( $A_c$ ) and between 1.2 and 2.8% for migration time  
543 ( $t_m$ ) at both concentrations levels. Intermediate precision was determined also at the  
544 above-mentioned concentration levels for three consecutive days injecting each sample  
545 by triplicate each day, with RSD values in a range from 2.8 to 12.7% for corrected peak  
546 area and 0.6 to 3.6% for migration time.



547 Finally, accuracy was evaluated as recovery values obtained for three spiked WS  
548 from different locations at low and high concentration levels (**Table 3**). Since phenoxy  
549 acid herbicides were not detected in these samples, they were spiked at a concentration  
550 so that after preconcentration process, analytes were detected and quantified just beyond  
551 their LOD and LOQ, respectively. For WS 2 and 3, due to the plugging of the pores of  
552 the packed material produced by the presence of organic matter, only 200 mL of these  
553 spiked water sample (PF = 400) were passed through the cartridge, whereas 750 mL (PF  
554 = 1500) were passed with WS 1. As observed in **Table 3**, accuracy was acceptable  
555 (without significant differences at both concentration levels) with values for WS 1 from  
556 96.3 to 107.5%, for WS 2 from 91.7 to 104.2% and for WS 3 from 78.3 to 105.9%.  
557 **Figure 6** shows the electropherogram obtained for spiked and non-spiked WS 1 using  
558 100 mg of PMO-STPA sorbent, 750 mL of sample volume and elution with 2 x 4 mL  
559 MeOH pH 5.6.

560 Comparing the results obtained in this work with those reported in the literature,  
561 high recovery values were obtained in addition to the simultaneous determination of 6  
562 phenoxy acid herbicides as well as a high PF of 1500 with only 100 mg of a novel  
563 PMO-STPA material as sorbent, amount much lower than that usually employed in the  
564 extraction of these compounds for SPE.

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#### 566 **4. Concluding remarks**

567

568 Two novel materials based on periodic mesoporous organosilica with cationic  
569 amine-bridged ligands, (styrylmethyl)bis(triethoxysilylpropyl)ammonium chloride  
570 (STPA) and bis(3-triethoxysilyl)amine (TEPA), were synthesized in this work using  
571 tetraethyl orthosilicate as additional silica source in basic medium, in order to obtain

572 materials with reverse-phase/strong anionic exchange mixed-mode or strong anionic  
573 exchange retention mechanism, respectively. Although interesting characteristics with  
574 good recovery values for six phenoxy acid herbicides from several water samples were  
575 shown by PMO-TEPA material, PMO-STPA was found to be the best sorbent for the  
576 off-line solid-phase extraction of the compounds studied, which confirmed that a  
577 mixed-mode retention mechanism by Van der Waals forces and ionic exchange, that  
578 favor the retention of 4-CPPA, 3-CPPA and 2-PPA, was necessary for the extraction of  
579 these selected compounds. Optimized conditions for SPE enabled a preconcentration  
580 factor of 1500 using 100 mg sorbent and 750 mL of water sample allowing high  
581 recovery values for the compounds studied and enabling method quantitation limits  
582 from 1.5 to 3.3 µg/L using CE for the simultaneous enantiomeric separation of the six  
583 phenoxy acid herbicides in 11 min. The results presented in this article show the high  
584 potential of the PMO materials synthesized in this work as sorbents for off-line SPE  
585 previous to CE separation in the simultaneous chiral analysis of phenoxy acids in water  
586 samples.

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## 596 5. References

597597

- 598 [1] W. Liu, M. Tang, Enantioselective activity and toxicity of chiral herbicides, in: M.  
599 N. Hasaneen (Ed.), *Herbicides - Mechanisms and Mode of Action*, InTech, Rijeka,  
600 2011, pp. 63-80.
- 601 [2] Z. Ujang, W. Husain, M. Seng, A. Rashid, The kinetic resolution of 2-(4-  
602 chlorophenoxy)propionic acid using *Candida rugosa* lipase, *Process Biochem.* 38  
603 (2003) 1483-1488.
- 604 [3] H. Tabani, A.R. Fakhari, A. Shahsavani, M. Behbahani, M. Salarian, A. Bagheri, S.  
605 Nojavan, Combination of graphene oxide-based solid phase extraction and electro  
606 membrane extraction for the preconcentration of chlorophenoxy acid herbicides in  
607 environmental samples, *J. Chromatogr. A* 1300 (2013) 227-235.
- 608 [4] N. Casado, D. Pérez-Quintanilla, S. Morante-Zarcero, I. Sierra, Current development  
609 and applications of ordered mesoporous silicas and other sol-gel silica-based materials  
610 in food sample preparation for xenobiotics analysis, *TrAC* 88 (2017) 167-184.
- 611 [5] J. Gañán, D. Pérez-Quintanilla, S. Morante-Zarcero, I. Sierra, Comparison of  
612 different mesoporous silicas for off-line solid phase extraction of 17 $\beta$ -estradiol from  
613 waters and its determination by HPLC-DAD, *J Hazard Mater.* 260 (2013) 609-617.
- 614 [6] T. Asefa, M. MacLachlan, N. Coombs, G. Ozin, Periodic mesoporous organosilicas  
615 with organic groups inside the channel walls, *Nature* 402 (1999) 867-871.
- 616 [7] D. Perez-Quintanilla, S. Morante-Zarcero, I. Sierra, Preparation and characterization  
617 of mesoporous silicas modified with chiral selectors as stationary phase for high-  
618 performance liquid chromatography, *J. Colloid Interface Sci.* 414 (2014) 14-23.

619 [8] H. Wu, C. Liao, Y. Pan, C. Yeh, H. Kao, Synthesis and characterization of cubic  
620 thiol-functionalized periodic mesoporous organosilicas as effective mercury ion  
621 adsorbents, *Microporous Mesoporous Mater.* 119 (2009) 109-116.

622 [9] D. Esquivel, E. De Canck, C. Jimenez-Sanchidrian, F.J. Romero-Salguero, P. Van  
623 der Voort, Pyrrole PMOs incorporating new N-heterocyclic compounds on an ethene-  
624 PMO through Diels-Alder reactions, *Mater. Chem. Phys.* 148 (2014) 403-410.

625 [10] M. Imamoglu, D. Perez-Quintanilla, I. Sierra, Bifunctional periodic mesoporous  
626 organosilicas with sulfide bridges as effective sorbents for Hg(II) extraction from  
627 environmental and drinking waters, *Microporous Mesoporous Mater.* 229 (2016) 90-97.

628 [11] C. Sanchez, F. Jeremias, S. Ernst, S.K. Henninger, Synthesis, functionalization and  
629 evaluation of ethylene-bridged PMOs as adsorbents for sorption dehumidification and  
630 cooling systems, *Microporous Mesoporous Mater.* 244 (2017) 151-157.

631 [12] J.M. Saz, M.L. Marina, Recent advances on the use of cyclodextrins in the chiral  
632 analysis of drugs by capillary electrophoresis, *J. Chromatogr. A* 1467 (2016) 79-94.

633 [13] M.L. Marina, A. Ríos, M. Valcárcel, Eds., *Analysis and Detection by Capillary*  
634 *Electrophoresis*, in *Comprehensive Analytical Chemistry*, Vol. XLV, Elsevier,  
635 Amsterdam, 2005.

636 [14] Y. Ji, L. Black, R. Koester, M. Janek, Hydrophobic coagulation and aggregation of  
637 hematite particles with sodium dodecylsulfate, *Colloids Surf. A Physicochem. Eng.*  
638 *Asp.* 298 (2007) 235-244.

639 [15] M. Kruk, M. Jaroniec, A. Sayari, Relations between pore structure parameters and  
640 their implications for characterization of MCM-41 using gas adsorption and X-ray  
641 diffraction, *Chem. Mater.* 11 (1999) 492-500.

642 [16] J.L. Blin, A. Léonard, B.L. Su, Well-ordered spherical mesoporous materials CMI-  
643 1 synthesized via an assembly of decaoxyethylene cetyl ether and TMOS, Chem. Mater.  
644 13 (2001) 3542-3553.

645 [17] S.A. Bagshaw, E. Prouzet, T.J. Pinnavaia, Templating of mesoporous molecular  
646 sieves by non-ionic polyethylene oxide surfactants, Science 269 (1995) 1242-1244.

647 [18] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, Nonionic triblock and star  
648 diblock copolymer and oligomeric surfactant syntheses of highly ordered,  
649 hydrothermally stable, mesoporous silica structures, J. Am. Chem. Soc. 120 (1998)  
650 6024-6036.

651 [19] Y. Martin-Biosca, C. Garcia-Ruiz, M. Marina, Enantiomeric separation of chiral  
652 phenoxy acid herbicides by electrokinetic chromatography. Application to the  
653 determination of analyte-selector apparent binding constants for enantiomers,  
654 Electrophoresis 22 (2001) 3216-3225.

655 [20] M. Miura, Y. Terashita, K. Funazo, M. Tanaka, Separation of phenoxy acid  
656 herbicides and their enantiomers in the presence of selectively methylated cyclodextrin  
657 derivatives by capillary zone electrophoresis, J. Chromatogr. A 846 (1999) 359-367.

658 [21] K. Otsuka, C.J. Smith, J. Grainger, J.R. Barr, D.G. Patterson, N. Tanaka, S. Terabe,  
659 Stereoselective separation and detection of phenoxy acid herbicide enantiomers by  
660 cyclodextrin-modified capillary zone electrophoresis-electrospray ionization mass  
661 spectrometry, J. Chromatogr. A 817 (1998) 75-81.

662 [22] O. Zerbinati, F. Trotta, C. Giovannoli, Optimization of the cyclodextrin-assisted  
663 capillary electrophoresis separation of the enantiomers of phenoxyacid herbicides, J.  
664 Chromatogr. A 875 (2000) 423-430.

665 [23] S. Tsunoi, H. Harino, M. Miura, M. Eguchi, M. Tanaka, Separation of phenoxy  
666 acid herbicides by capillary electrophoresis using a mixture of hexakis(2,3-di-*O*-  
667 methyl)- and sulfopropylether- $\alpha$ -cyclodextrins, *Anal. Sci.* 16 (2000) 991-993.

668 [24] A.K. Malik, J.S. Aulakh, A. Fekete, P. Schmitt-Kopplin, Separation of the phenoxy  
669 acid herbicides and their enantiomers by capillary zone electrophoresis in presence of  
670 highly sulphated cyclodextrins, *J. Chin. Chem. Soc.* 56 (2009) 1163-1167.

671 [25] J.L. Haynes III, S.A. Shamsi, F. O'Keefe, R. Darcey, I.M. Warner, Cationic  $\beta$ -  
672 cyclodextrin derivative for chiral separations, *J. Chromatogr. A* 803 (1998) 261-271.

673 [26] F. O'Keefe, S.A. Shamsi, R. Darcy, P. Schwinte, I.M. Warner, A persubstituted  
674 cationic  $\beta$ -cyclodextrin for chiral separations, *Anal. Chem.* 69 (1997) 4773-4782.

675 [27] Y. Xiao, T.T. Ong, T.T.Y. Tan, S.C. Ng, Synthesis and application of a novel  
676 single-isomer mono-6-deoxy-6-(3R,4R-dihydroxypyrrolidine)- $\beta$ -CD chloride as a chiral  
677 selector in capillary electrophoresis, *J. Chromatogr. A* 1216 (2009) 994-999.

678 [28] C. Desiderio, C.M. Polcaro, P. Padiglioni, S. Fanali, Enantiomeric separation of  
679 acidic herbicides by capillary electrophoresis using vancomycin as chiral selector, *J.*  
680 *Chromatogr. A* 781 (1997) 503-513.

681 [29] E. Terzopoulou, D. Voutsas, G. Kaklamanos, A multi-residue method for  
682 determination of 70 organic micropollutants in surface waters by solid-phase extraction  
683 followed by gas chromatography coupled to tandem mass spectrometry, *Environ. Sci.*  
684 *Pollut. Res.* 22 (2015) 1095-1112.

685 [30] V. Fauvelle, N. Mazzella, S. Morin, S. Moreira, B. Delest, H. Bidzinski,  
686 Hydrophilic interaction liquid chromatography coupled with tandem mass spectrometry  
687 for acidic herbicides and metabolites analysis in fresh water, *Environ. Sci. Pollut. Res.*  
688 22 (2015) 3988-3996.

689 [31] C. Xu, D.W. Armstrong, High-performance liquid chromatography with paired ion  
690 electrospray ionization (PIESI) tandem mass spectrometry for the highly sensitive  
691 determination of acidic pesticides in water, *Anal. Chim. Acta* 792 (2013) 1-9.

692 [32] B. Jin, F. Xiao, B. Chen, P. Chen, L. Xie, Simultaneous determination of 42  
693 organic chemicals in bottled water by combining C18 extraction disk with GC-MS and  
694 LC/MS/MS technique, *J. Water Health* 8 (2010) 116-125.

695 [33] L.Z. Yu, M.J.M. Wells, Establishing the feasibility of coupled solid-phase  
696 extraction-solid-phase derivatization for acidic herbicides, *J. Chromatogr. A* 1143  
697 (2007) 16-25.

698 [34] I. Rodriguez Pereiro, R. González Irimia, E. Rubí Cano, R. Cela Torrijos,  
699 Optimisation of a gas chromatographic-mass spectrometric method for the  
700 determination of phenoxy acid herbicides in water samples as silyl derivatives, *Anal.*  
701 *Chim. Acta* 524 (2004) 249-256.

702 [35] W. Qin, S.F.Y. Li, Determination of chlorophenoxy acid herbicides by capillary  
703 electrophoresis with integrated potential gradient detection, *Electrophoresis* 24 (2003)  
704 2174-2179.

705 [36] Y.S. Fung, J.L.L. Mak, Determination of pesticides in drinking water by micellar  
706 electrokinetic capillary chromatography, *Electrophoresis* 22 (2001) 2260-2269.

707 [37] M. Peruzzi, G. Bartolucci, F. Cioni, Determination of phenoxyalkanoic acids and  
708 other herbicides at the ng/mL level in water by solid-phase extraction with  
709 poly(divinylbenzene-co-*N*-vinylpyrrolidone) sorbent and high-performance liquid  
710 chromatography-diode-array detection, *J. Chromatogr. A* 867 (2000) 169-175.

711 [38] C. Baggiani, C. Giovannoli, L. Anfossi, C. Tozzi, Molecularly imprinted solid-  
712 phase extraction sorbent for the clean-up of chlorinated phenoxyacids from aqueous  
713 samples, *J. Chromatogr. A* 938 (2001) 35-44.

714 [39] C. Baggiani, C. Giovannoli, Molecular imprinted solid-phase extraction for  
715 cleanup of chlorinated phenoxyacids from aqueous samples, in: J.L. Martínez Vidal,  
716 A.G. Frenich (Eds.), Pesticide protocols. Method in biotechnology, Vol 19, Humana  
717 Press, New York, USA, 2006, pp. 421-433.

718 [40] H. Tabani, A.R. Fakhari, A. Shahsavani, M. Behbahani, M. Salarian, A. Bagheri, S.  
719 Nojavan, Combination of graphene oxide-based solid phase extraction and electro  
720 membrane extraction for the preconcentration of chlorophenoxy acid herbicides in  
721 environmental samples, *J. Chromatogr. A* 1300 (2013) 227-235.

722 [41] X.J. Yang, Z. Du, A. Lin, Q. Yuan, P. Wan, C. Wong, Simultaneous determination  
723 of neutral, basic and acidic pesticides in aquatic environmental matrices by solid-phase  
724 extraction and liquid chromatography electrospray ionization mass spectrometry, *Anal.*  
725 *Methods* 5 (2013) 2083-2092.

726 [42] R. Rodil, J.B. Quintana, P. López-Mahía, S. Muniategui-Lorenzo, D. Prada-  
727 Rodríguez, Multi-residue analytical method for the determination of emerging  
728 pollutants in water by solid-phase extraction and liquid chromatography-tandem mass  
729 spectrometry, *J. Chromatogr. A* 1216 (2009) 2958-2969.

730 [43] Y. Xu, W. Qin, Y.H. Lau, S.F.Y. Li, Combination of cationic surfactant-assisted  
731 solid-phase extraction with field-amplified sample stacking for highly sensitive analysis  
732 of chlorinated acid herbicides by capillary zone electrophoresis, *Electrophoresis* 26  
733 (2005) 3507-3517.

734 [44] N. Li, H.K. Lee, Sample preparation based on dynamic ion-exchange solid-phase  
735 extraction for GC/MS analysis of acidic herbicides in environmental water, *Anal.*  
736 *Chem.* 72 (2000) 3077-3084.

737  
738



739 **Figure captions**

740

741 **Figure 1.** N<sub>2</sub> adsorption-desorption isotherms and pore-size distribution of PMO-STPA  
742 (a and b) and PMO-TEPA materials (c and d).

743

744 **Figure 2.** Schematic representation for retention mechanism inside the pore of PMO-  
745 STPA and PMO-TEPA materials.

746

747 **Figure 3.** <sup>13</sup>C CP/MAS NMR spectra (a) and <sup>29</sup>Si MAS NMR spectra (b) of PMO-  
748 STPA material.

749

750 **Figure 4.** Recovery percentages and error bars obtained for each enantiomer of the six  
751 phenoxy acid herbicides using 100 mg (a) and 200 mg (b) of sorbent packing at two pH  
752 values of elution solvent (5.6 and 1.8) and 100 mL of Milli-Q water sample spiked in a  
753 concentration of 25 µg/L for fenoprop, and 50 mg/L for the other five phenoxy acid  
754 compounds. F: fenoprop, M: mecoprop, D: dichlorprop, 4C: 4-CPPA, 3C: 3-CPPA, 2P:  
755 2-PPA. 1: First-migrating enantiomer, 2: Second-migrating enantiomer. Experimental  
756 conditions: BGE, 50 mM phosphate buffer (pH 7.0), 20 mM TM-β-CD and 7 mM HP-  
757 β-CD, capillary (50 µm I.D., total length of 58.5 cm (50 cm effective length)), injection:  
758 50 mbar x 10 s, temperature: 15 °C, separation voltage: 25 kV, UV detection at 194 nm  
759 (2-PPA and 4-CPPA), 200 nm (mecoprop, dichlorprop and 3-CPPA) and 210 nm  
760 (fenoprop) (bandwidth 5 nm).

761761

762 **Figure 5.** Recovery percentages and error bars obtained for each enantiomer of the  
763 phenoxy acid herbicides taking into account the breakthrough volume loaded in the

764 cartridges (n = 6) at 100, 200, 500, 750 and 1000 mL of spiked Milli-Q water solution  
765 with phenoxy acid herbicides at a concentration of 5 mg/L for fenoprop, and 10 mg/L  
766 for the other five phenoxy acid compounds using 100 mg of PMO-STPA as sorbent. F:  
767 fenoprop, M: mecoprop, D: dichlorprop, 4C: 4-CPPA, 3C: 3-CPPA, 2P: 2-PPA. 1:  
768 First-migrating enantiomer, 2: Second-migrating enantiomer. Other experimental  
769 conditions as in **Fig. 4**.

770770

771 **Figure 6.** Electropherograms obtained for the enantiomeric separation of the mixture of  
772 six phenoxy acid herbicides in spiked (top) and non-spiked (down) WS 1 using 100 mg  
773 of PMO-STPA sorbent and 750 mL of sample volume. Spiked concentrations of 3.3  
774  $\mu\text{g/L}$  for the six phenoxy acids. Compounds: F: fenoprop ( $R_s = 1.1$ ), M: mecoprop ( $R_s$   
775  $= 2.7$ ), D: dichlorprop ( $R_s = 1.9$ ), 4C: 4-CPPA ( $R_s = 1.7$ ), 3C: 3-CPPA ( $R_s = 1.2$ ), 2P:  
776 2-PPA ( $R_s = 1.6$ ). 1: First-migrating enantiomer, 2: Second-migrating enantiomer. UV  
777 detection at 200 nm. Other experimental conditions as in **Fig. 4**.

778

779 **Table 1.-** Textural properties of the PMO materials synthesized in this work.

Material	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ ) <sup>a</sup>	Pore volume ( $\text{cm}^3/\text{g}$ ) <sup>b</sup>	Pore size ( $\text{Å}$ ) <sup>c</sup>	Elemental analysis (%)			
				C	N	H	mmol ligand/ $\text{g}^{\text{d}}$
PMO-STPA	316	1.30	235.0	18.4	1.3	2.9	0.93
PMO-TEPA	238	0.85	152.3	11.8	1.6	2.5	1.14

780 a: BET stands for Brunauer, Emmett and Teller.

781 b: Total pore volume were measured at relative  $P/P_0 = 0.97$ .

782 c: Pore diameter estimated by using the BJH (Barrett, Joyner and Halenda) model applied on the  
783 desorption branch of the isotherm.

784 d: mmol of ligand per gram of PMO calculated with the %N obtained in elemental analysis.

785785

786 **Table 2.** Analytical characteristics of the developed CE method for the enantiomeric determination of phenoxy acid herbicides in water samples.

Analyte	Linearity			Precision						
	Linear range (mg/L)	Linear equation bx + a R <sup>2</sup>	Sb Sa	b ± t Sb	Instrumental repeatability		Intermediate precision		LOD (mg/L) / MDL (µg/L)	LOQ (mg/L) / MQL (µg/L)
					Ac // tm (RSD (%)) Low concentration	Ac // tm (RSD (%)) High concentration	Ac // tm (RSD (%)) Low concentration	Ac // tm (RSD (%)) High concentration		
Fenoprop (E1)	0-30	0.48x-0.38 0.9950	0.11 0.46	0.48 ± 0.25	6.6 // 1.8	6.3 // 2.0	10.4 // 2.9	5.5 // 0.6	0.7 / 0.5	2.3 / 1.5
Fenoprop (E2)	0-30	0.42x-0.17 0.9957	0.07 0.38	0.42 ± 0.16	5.2 // 1.8	12.3 // 1.9	10.4 // 3.0	6.6 // 0.6	0.7 / 0.5	2.2 / 1.5
Mecoprop (E1)	2-30	0.62x-0.25 0.9966	0.13 0.33	0.62 ± 0.29	7.0 // 1.2	5.4 // 2.1	7.9 // 3.1	4.3 // 0.6	0.8 / 0.5	2.6 / 1.7
Mecoprop (E2)	2-30	0.68x-0.51 0.9953	0.17 0.47	0.68 ± 0.38	7.3 // 1.2	6.0 // 2.2	6.7 // 3.1	6.1 // 0.6	0.8 / 0.5	2.7 / 1.8
Dichlorprop (E1)	1-30	0.45x-0.23 0.9962	0.06 0.32	0.45 ± 0.14	10.1 // 1.2	9.2 // 2.1	10.6 // 3.1	2.8 // 0.6	1.0 / 0.7	3.3 / 2.2
Dichlorprop (E2)	1-30	0.51x-0.37 0.9961	0.11 0.16	0.51 ± 0.25	11.9 // 1.2	4.8 // 2.2	9.6 // 3.1	4.7 // 0.7	1.0 / 0.7	3.4 / 2.3
4-CPPA (E1)	1-30	0.66x-0.50 0.9965	0.13 0.48	0.66 ± 0.29	5.0 // 1.3	6.1 // 2.2	8.1 // 3.1	5.3 // 0.7	1.2 / 0.8	4.0 / 2.7
4-CPPA (E2)	1-30	0.65x-0.39 0.9962	0.12 0.45	0.65 ± 0.27	7.2 // 1.3	6.9 // 2.3	8.8 // 3.2	4.2 // 0.7	1.2 / 0.8	4.0 / 2.7
3-CPPA (E1)	2-25	0.69x-0.36 0.9987	0.12 0.34	0.69 ± 0.27	7.3 // 1.3	5.8 // 2.3	12.7 // 3.2	5.3 // 1.2	0.9 / 0.6	2.9 / 1.9
3-CPPA (E2)	2-25	0.60x-0.19 0.9977	0.08 0.26	0.60 ± 0.18	5.8 // 1.3	7.0 // 2.3	9.2 // 3.2	4.2 // 1.2	0.8 / 0.5	2.7 / 1.8
2-PPA (E1)	5-25	0.71x-0.75 0.9981	0.16 0.53	0.71 ± 0.36	11.3 // 1.6	7.2 // 2.7	8.7 // 3.6	4.8 // 1.4	1.5 / 1.0	5.0 / 3.3
2-PPA (E2)	5-25	0.68x-0.55 0.9974	0.13 0.51	0.68 ± 0.29	12.9 // 1.6	6.9 // 2.8	9.3 // 3.6	3.2 // 1.4	1.4 / 0.9	4.7 / 3.1

787 a: intercept; b: slope; Sa: intercept standard deviation; Sb: slope standard deviation; Confidence interval at 95% as confidence level (n = 9); E1: first-migrating enantiomer;  
 788 E2: second-migrating enantiomer; Ac: corrected area; tm: migration time; LOD: instrumental limit of detection; LOQ: instrumental limit of quantification; MDL: method  
 789 limit of detection; MQL: method limit of quantification; Low concentration level for each enantiomer: 5 mg/L. High concentration level for each enantiomer: 25 mg/L in the  
 790 case of 3-CPPA and 2-PPA or 30 mg/L in the case of Fenoprop, Mecoprop, Dichlorprop and 4-CPPA.

791

792 **Table 3.** Recovery values (%) and RSD (%) obtained for phenoxy acid herbicides using 100 mg PMO-STPA and 750 mL sample volume for  
 793 WS1 and 200 mL for WS2 and WS3 (n=6).

Analyte	Water sample 1				Water sample 2				Water sample 3			
	Recov ery	RSD	Recover y	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
	Low concentration		High concentration		Low concentration		High concentration		Low concentration		High concentration	
<b>Fenoprop (E1)</b>	100.5	2.9	97.3	1.3	96.5	3.9	99.8	4.3	88.5	6.2	100.5	2.3
<b>Fenoprop (E2)</b>	103.5	4.6	96.3	1.1	96.2	2.3	100.4	4.8	86.0	7.9	100.9	2.0
<b>Mecoprop (E1)</b>	105.0	1.8	100.6	1.8	91.9	2.7	99.7	4.6	98.6	8.5	101.6	0.8
<b>Mecoprop (E2)</b>	101.8	1.5	101.6	4.1	91.7	1.9	100.1	3.4	98.2	7.5	101.4	1.4
<b>Dichlorprop (E1)</b>	99.3	2.2	100.5	3.3	95.2	2.3	104.2	7.4	95.1	11.4	101.7	1.2
<b>Dichlorprop (E2)</b>	98.6	2.5	100.2	1.8	95.6	2.8	99.4	4.5	100.5	10.4	101.9	1.1
<b>4-CPPA (E1)</b>	101.7	3.1	103.3	1.5	102.2	2.5	100.6	5.4	93.3	9.1	103.5	1.5
<b>4-CPPA (E2)</b>	103.8	5.2	98.5	0.6	101.2	4.9	103.4	5.7	93.2	9.4	103.7	1.3
<b>3-CPPA (E1)</b>	102.2	4.0	102.8	1.9	96.9	2.4	101.4	4.0	92.6	9.5	102.4	1.4
<b>3-CPPA (E2)</b>	103.4	3.3	100.9	1.2	98.6	7.1	98.7	5.7	91.3	8.1	104.8	1.6
<b>2-PPA (E1)</b>	104.7	3.5	107.5	1.7	95.4	3.5	97.8	5.3	78.3	9.2	105.9	1.6
<b>2-PPA (E2)</b>	99.9	4.0	103.3	1.7	93.4	5.0	98.0	7.2	83.0	8.1	104.5	1.7

794 **Experimental conditions:** BGE: 50 mM phosphate buffer (pH 7.0) / 20 mM TM- $\beta$ -CD - 7 mM HP- $\beta$ -CD, injection: 50 mbar x 10 s, voltage: 25 kV,  
 795 temperature: 15 °C, capillary: 58.5 cm total length (50 cm effective length) x 50  $\mu$ m I.D. Concentration levels spiked in water samples for each enantiomer  
 796 ( $\mu$ g/L): WS 1 (Low 3.3 and High 16.7 for 3-CPPA and 2-PPA or 20 for Fenoprop, Mecoprop, Dichlorprop and 4-CPPA); WS 2 and WS 3 (Low 12.5 and  
 797 High 62.5 for 3-CPPA and 2-PPA or 75 for Fenoprop, Mecoprop, Dichlorprop and 4-CPPA). Water samples were collected from: WS1 from effluent treatment  
 798 plant in Cádiz (Spain); WS2 from effluent treatment plant in Sevilla (Spain); WS3 from Henares river in Alcalá de Henares (Spain).

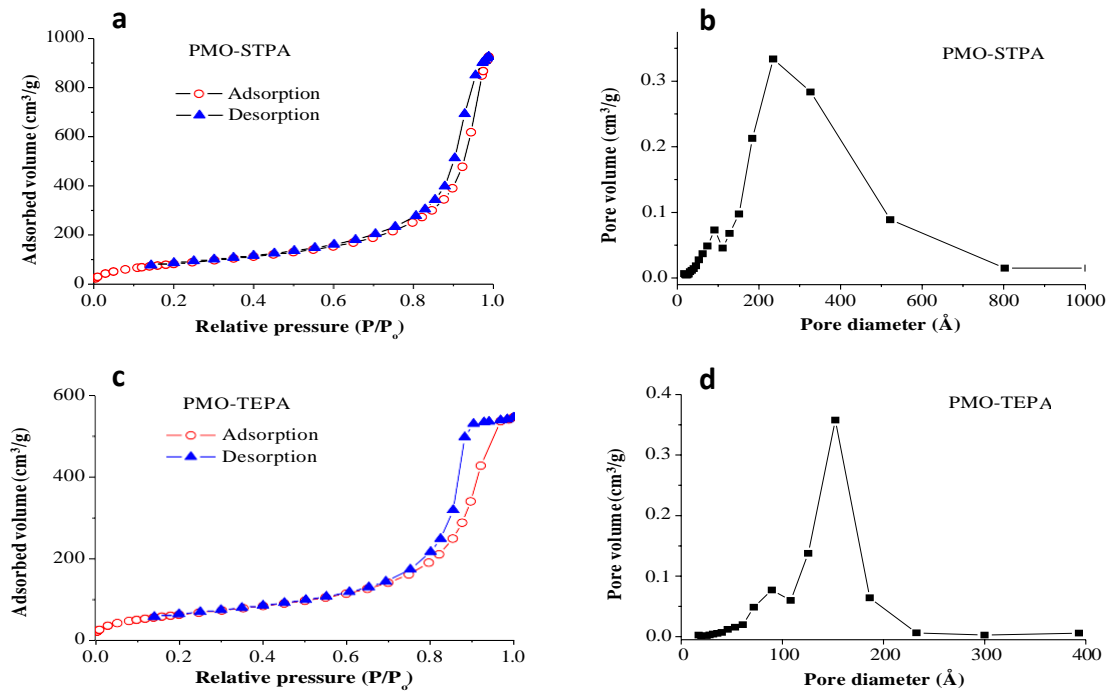


Fig. 1

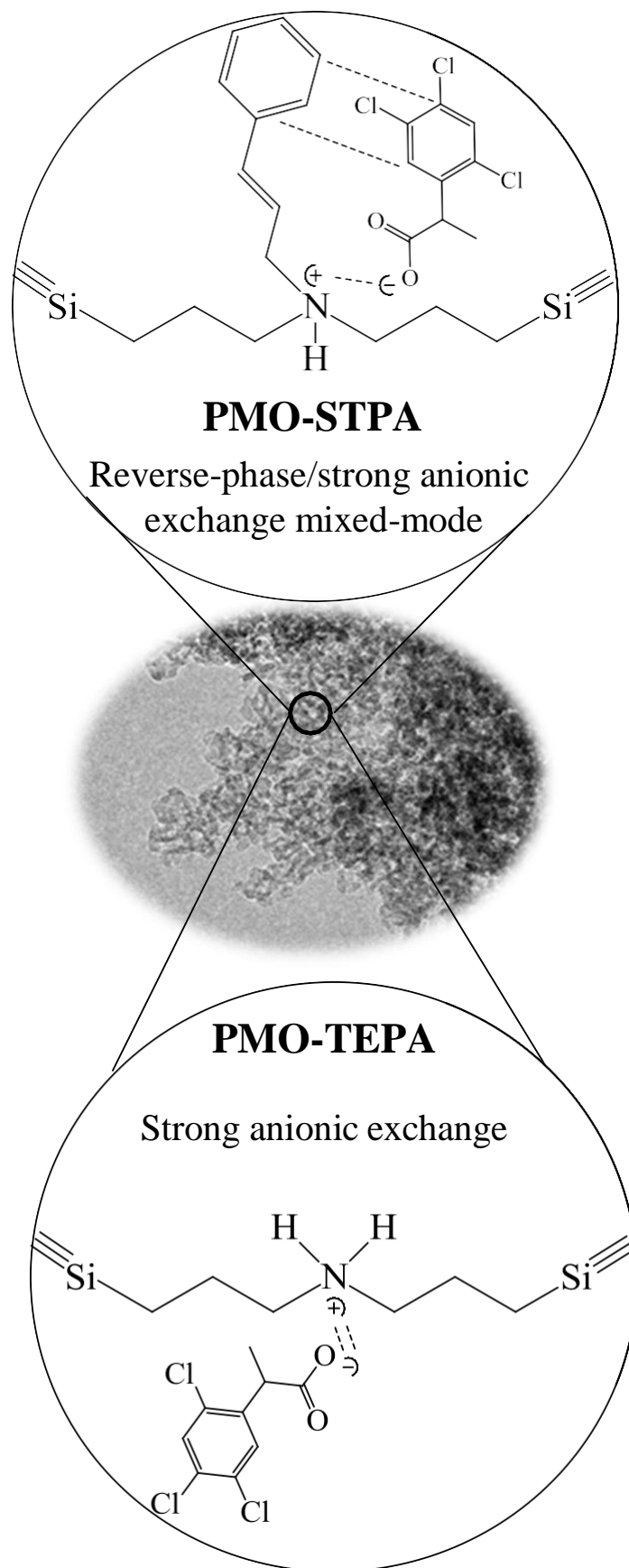


Fig. 2

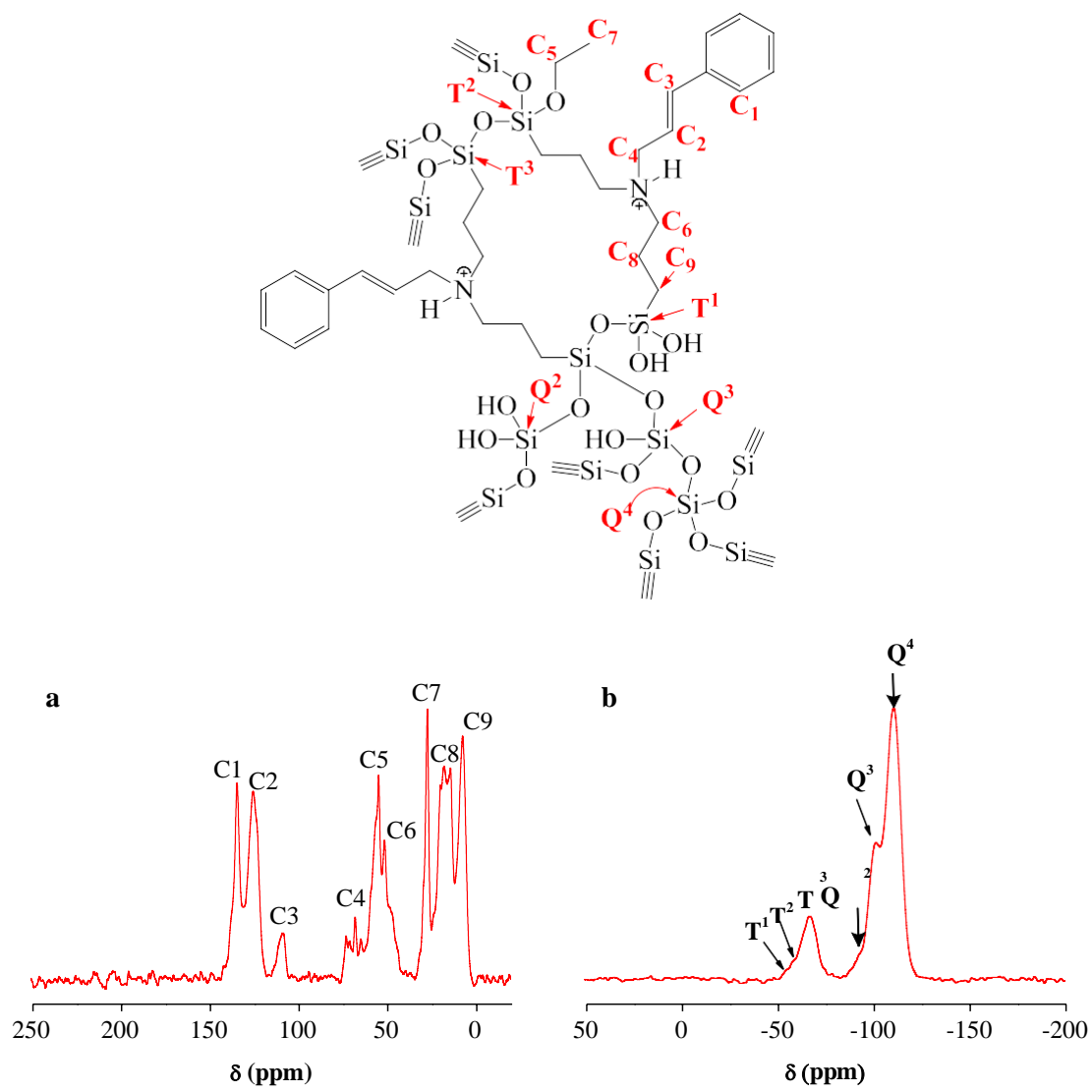


Fig. 3



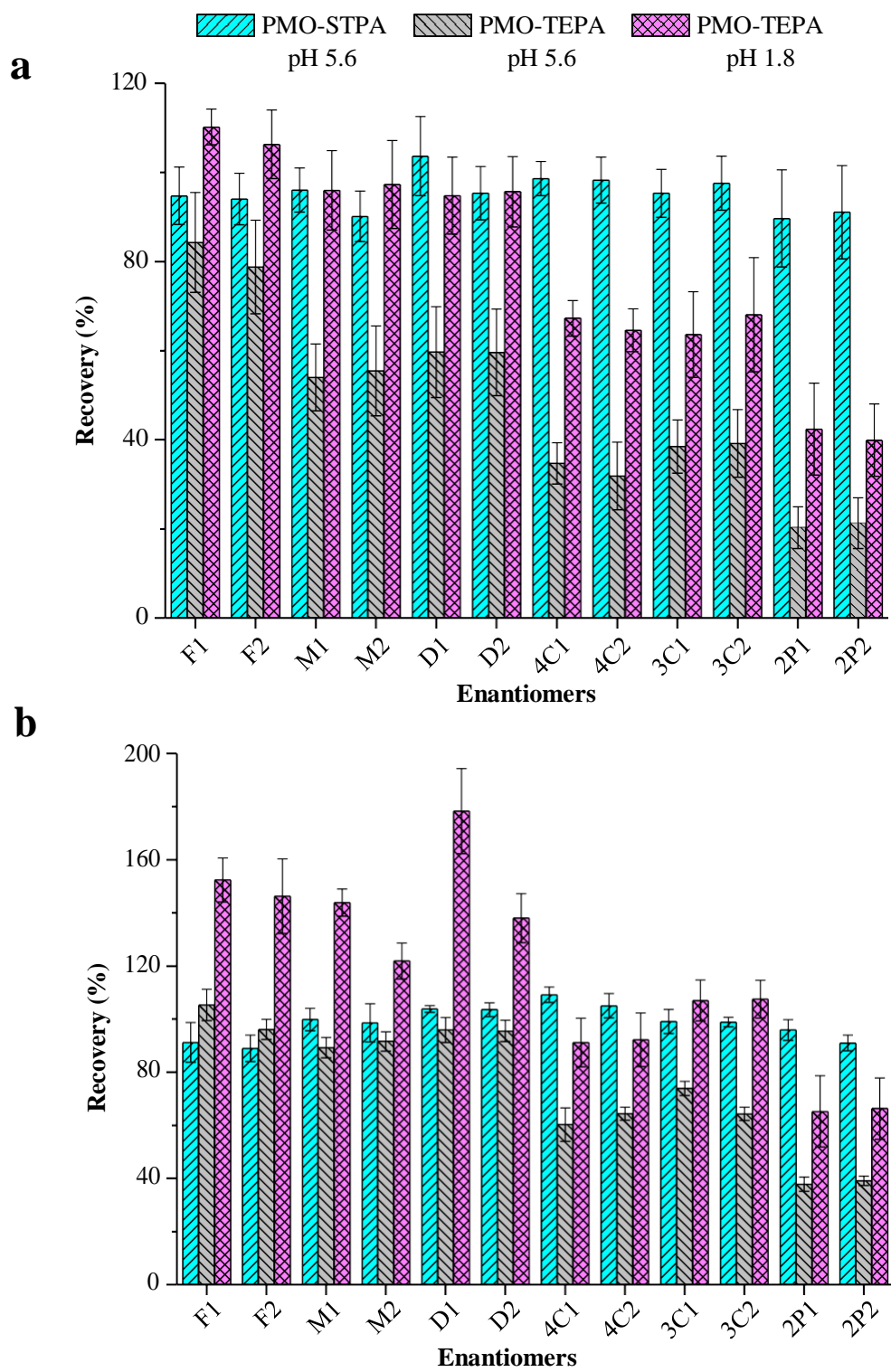


Fig. 4

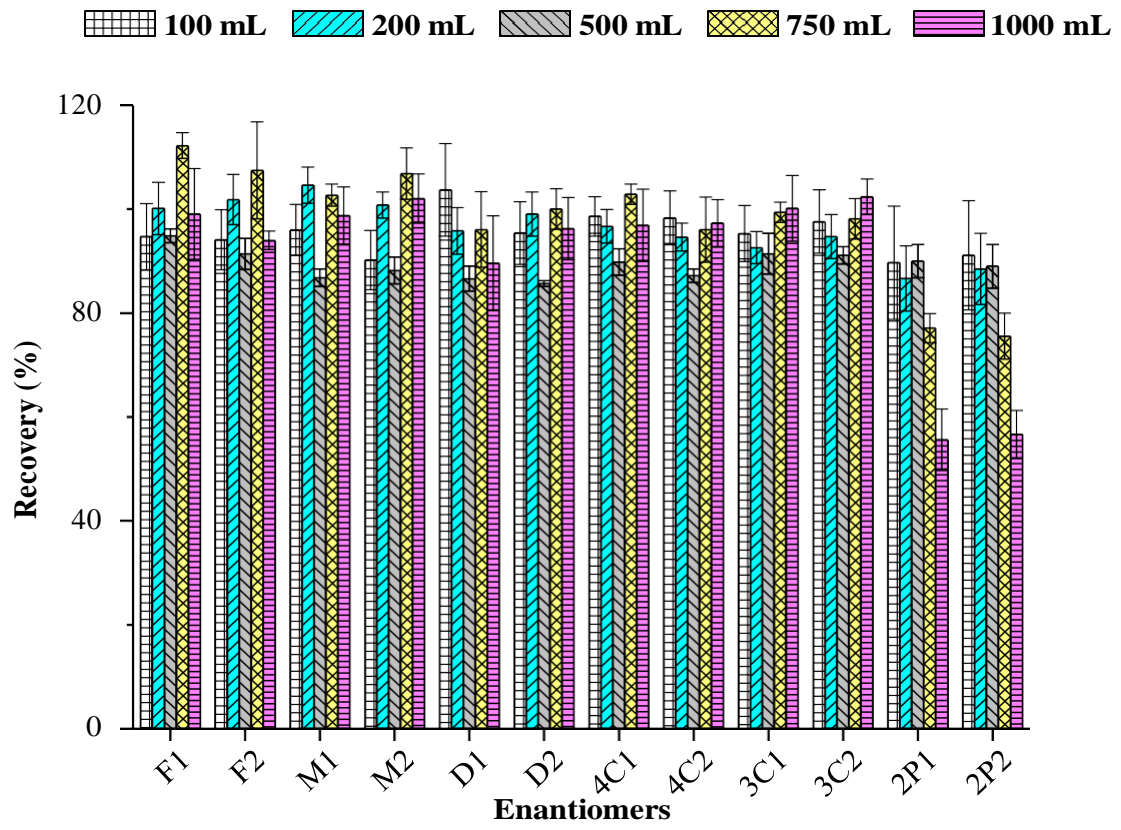


Fig. 5

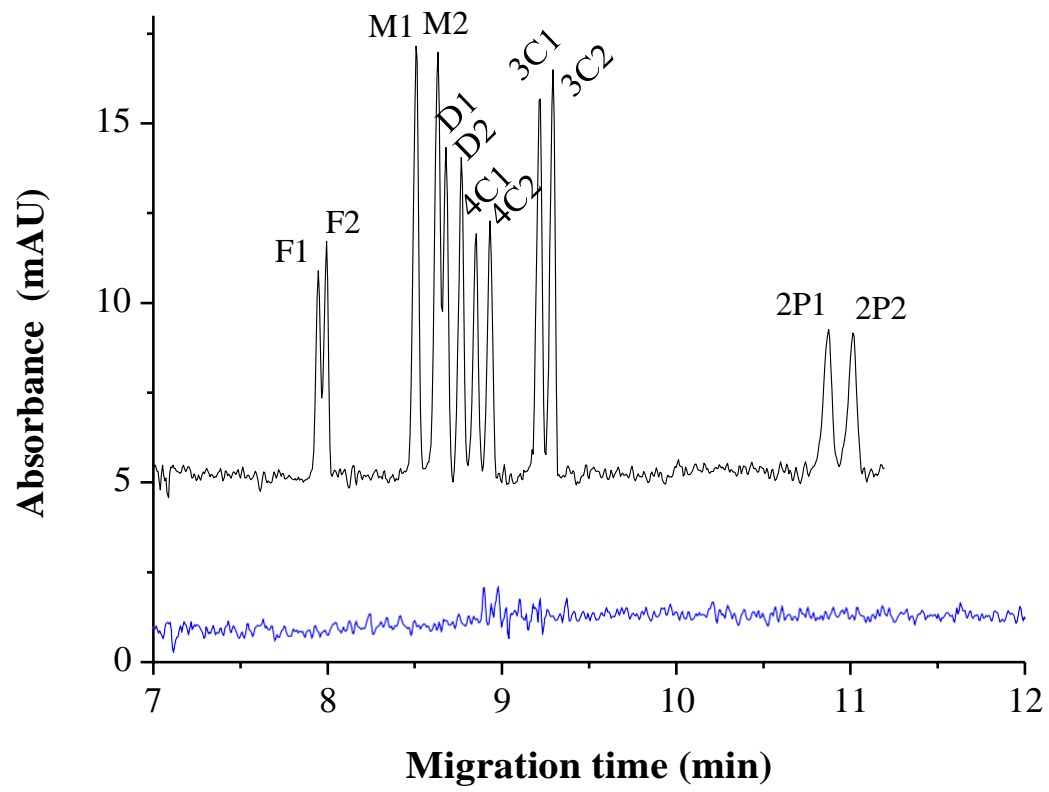
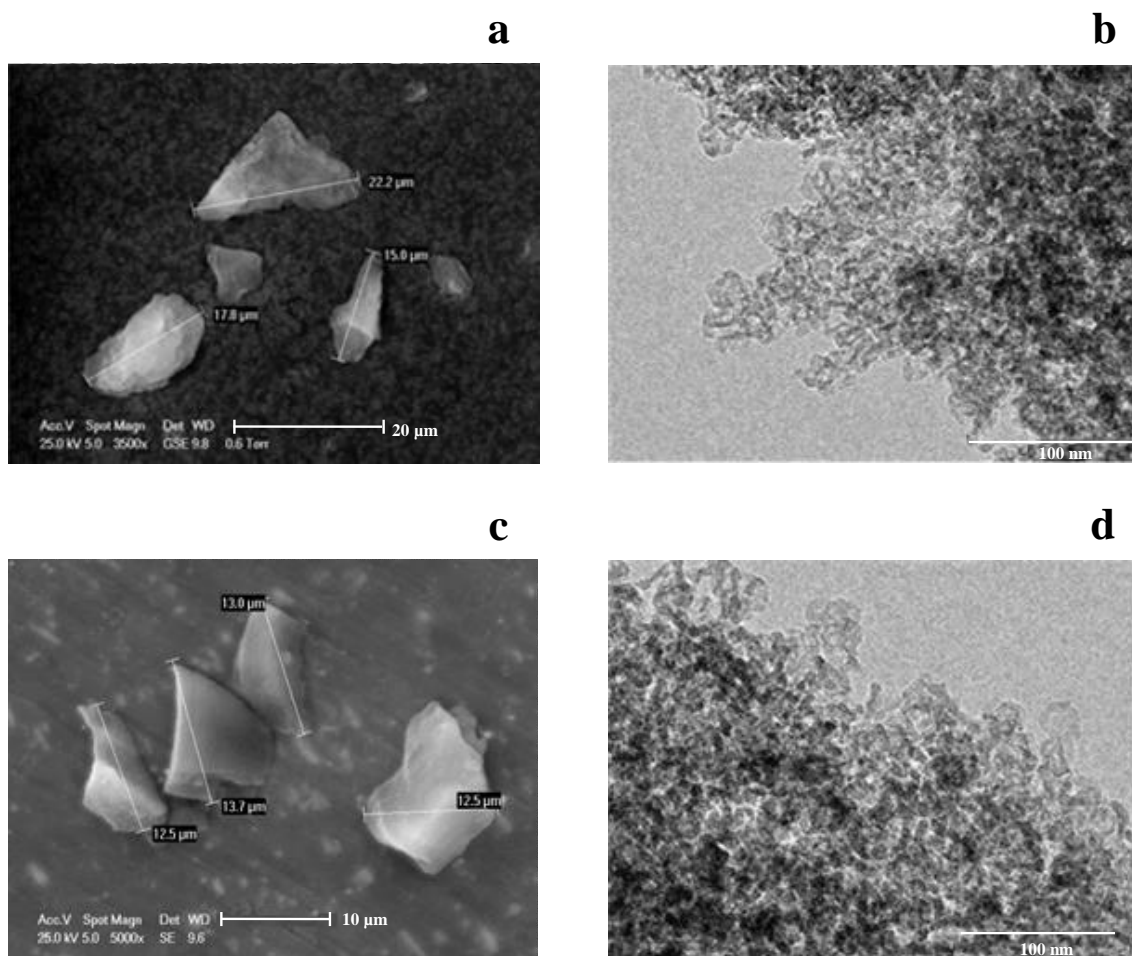
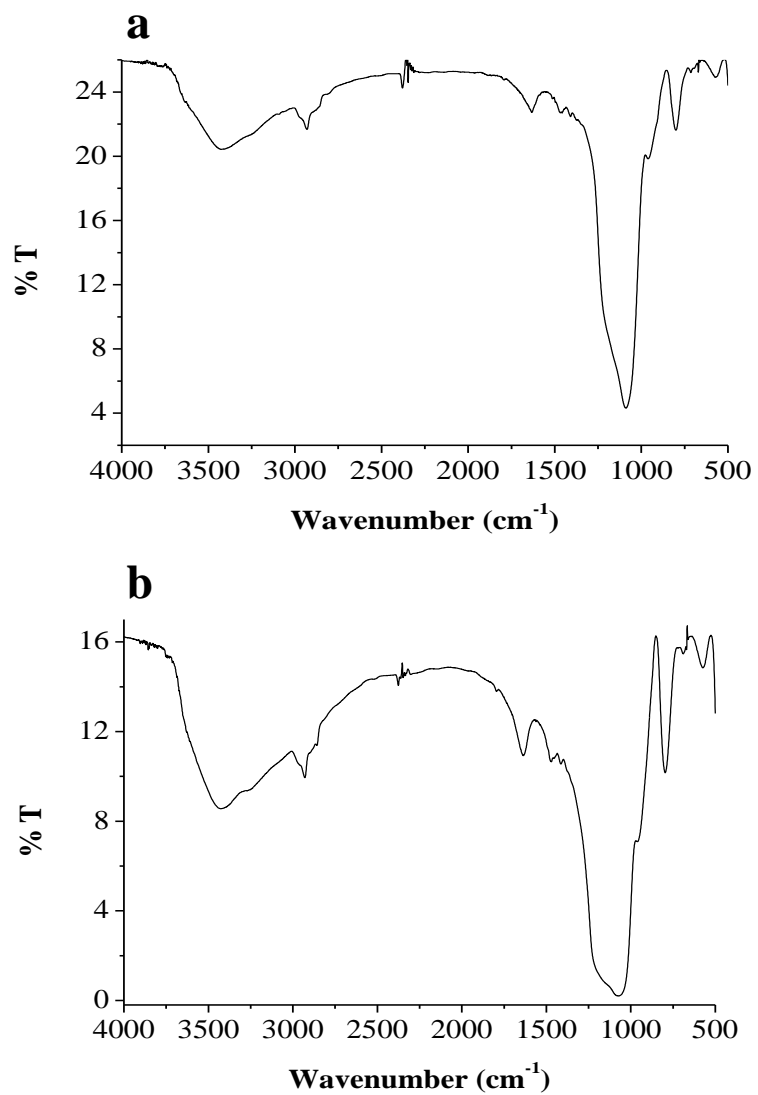


Fig. 6

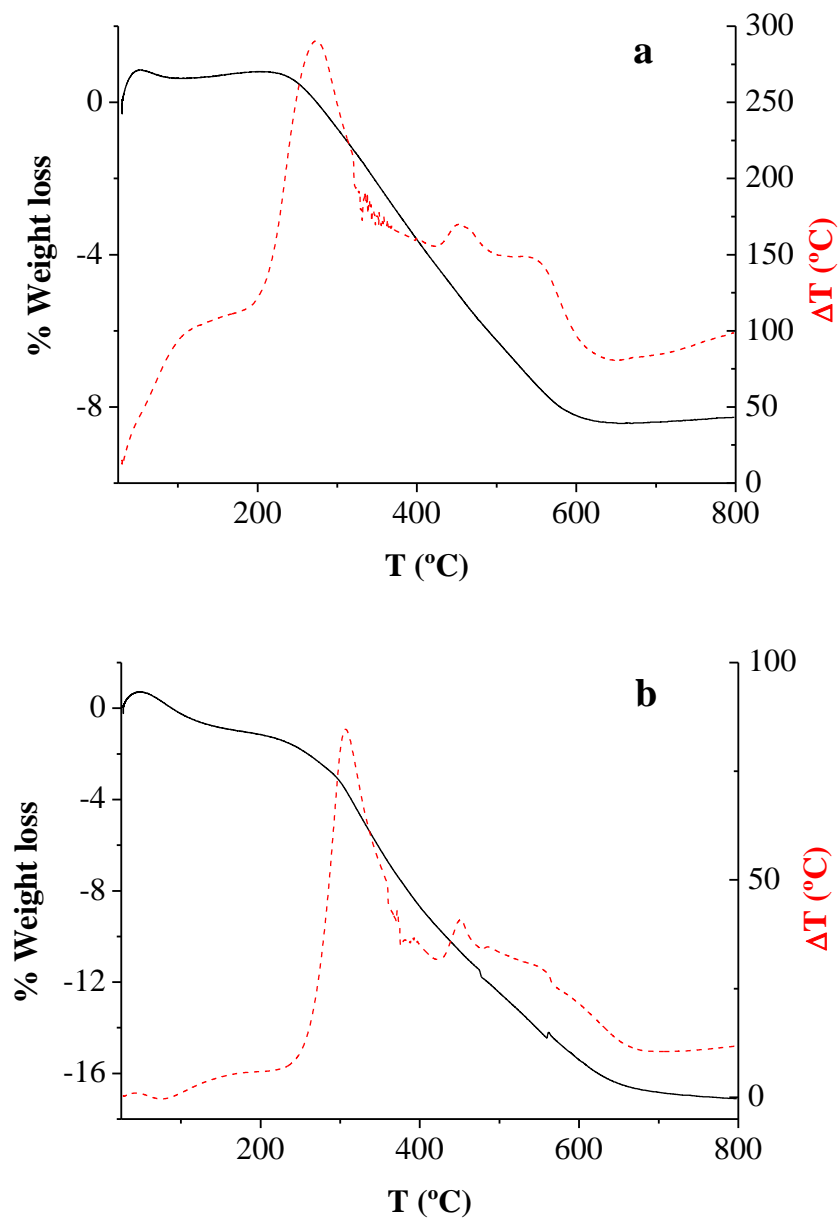
Supplementary Material



**Figure S1.** SEM micrographs (a, c) and TEM pictures (b, d) for PMO-STPA and PMO-TEPA materials, respectively.



**Figure S2.** FTIR spectra of PMO-STPA (a) and PMO-TEPA (b) materials.



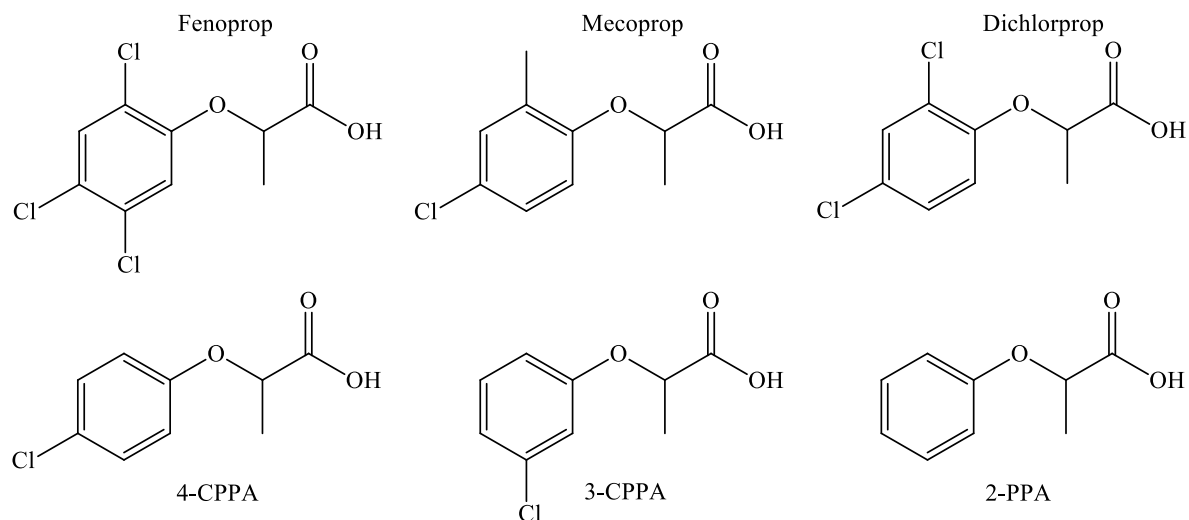
**Figure S3.** Thermogravimetric analysis of PMO-STPA (a) and PMO-TEPA (b) materials.

**Table S1.** Values of Van der Waals forces and Hückel charge of ligands (STPA and TEPA) and phenoxyacid herbicides studied.

	Cationic amine-bridge ligand		Phenoxyacid herbicides					
	STPA	TEPA	Fenoprop	Mecoprop	Dichlorprop	4-CPPA	3-CPPA	2-PPA
<b>Van der Waals forces (Kcal/mol)</b>	29.6	19.2	12.0	10.8	11.4	9.9	10.0	9.5
<b>Hückel charge</b>	+0.7006 <sup>a</sup>	+0.6464 <sup>a</sup>	-0.7694 <sup>b</sup>	-0.6698 <sup>b</sup>	-0.6490 <sup>b</sup>	-0.4599 <sup>b</sup>	-0.4332 <sup>b</sup>	-0.4523 <sup>b</sup>

a: Hückel nitrogen charge for amine moiety.

b: Hückel oxygen charge for carboxyl moiety (Mean value of charge of two oxygens).



**Table S2.** Use of other commercial and non-commercial materials for SPE extraction of the phenoxyacid herbicides studied from water samples.

Analyte	Sorbent (Amount)	Recovery (%)	PF	Sample	Ref.
Mecoprop	Oasis HLB (200 mg)	42-65	2000	Surface waters	[29]
Dichlorprop		55-75			
Fenoprop	Oasis HLB (150 mg)	90	3177	Drinking water	[30]
Mecoprop		100			
Dichlorprop		85			
Fenoprop	C18 (N/A)	93	133	Water	[31]
Mecoprop					
Dichlorprop	C18 (N/A)	84-92	1000	Drinking water	[32]
Mecoprop		83-101			
Fenoprop		81			
Dichlorprop	Polystyrene-divinylbenzene (N/A)	143	100	Water samples	[33]
4-CPPA		85-94			
Mecoprop		79-86			
Fenoprop		79-88			
Fenoprop	Oasis HLB (60 mg)	94-98	1000-2000	River and sewage water	[34]
Mecoprop		82-103			
Dichlorprop	C18 (500 mg)	83-98	4000	Tap water	[35]
Mecoprop		96-103			
Dichlorprop	C18 (500 mg)	93-96	1000	Drinking water	[36]
Mecoprop		89			
Dichlorprop		96			
Fenoprop	Oasis HLB (500 mg)	86	5000	River water	[37]
Mecoprop		86			
Dichlorprop	MIP (500 mg)	84	500	River water	[38]
Fenoprop		81-93			
Mecoprop		89			
Dichlorprop	MIP (200 mg)	89-114	2	Deionized water	[39]
Mecoprop		88			
Dichlorprop	Graphene oxide-based SPE and electro membrane extraction (N/A)	95	1950-2000	River and sea water	[40]
Fenoprop		96			
Dichlorprop	GCB (300 mg)	40	10	River water	[41]
Mecoprop		40			
Dichlorprop		83-103			
Mecoprop	Oasis HLB (200 mg)	80-107	200-500	Tap, Surface and wastewater	[42]
Fenoprop		91-131			
Mecoprop	C18 assisted with CTAB (500 mg)	97-117	100	Pond water	[43]
Dichlorprop		91-120			
Dichlorprop		100			
Fenoprop	C18 and CTAB (500 mg)	97	N/A	Tap water	[44]
Fenoprop		85-105			
Mecoprop	C18 and CTAB (500 mg)	90-102	N/A	Tap water	[44]
Dichlorprop		94-101			

N/A: Not available; PF: Preconcentration factor.

MIP: Molecularly imprinted polymers

GCB: Graphitized carbon black