



HAL
open science

Solid–liquid extraction of iodide and bromide from aqueous media by a new water-insoluble phenoxycalix[4]pyrrole-epichlorohydrin polymer

Nancy Alhaddad, Ahmad Rifai, Amaury Kasprowiak, Francine Cazier-Dennin, Pierre-Edouard Danjou

► To cite this version:

Nancy Alhaddad, Ahmad Rifai, Amaury Kasprowiak, Francine Cazier-Dennin, Pierre-Edouard Danjou. Solid–liquid extraction of iodide and bromide from aqueous media by a new water-insoluble phenoxycalix[4]pyrrole-epichlorohydrin polymer. *Organic & Biomolecular Chemistry*, 2019, 17 (31), pp.7330-7336. 10.1039/C9OB01306G . hal-02865848

HAL Id: hal-02865848

<https://hal.science/hal-02865848v1>

Submitted on 22 Jul 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

ARTICLE

Solid-liquid extraction of iodide and bromide from aqueous media by a new water-insoluble phenoxy-calix[4]pyrrole-epichlorohydrin polymer

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Nancy AlHaddad^{a,b}, Ahmad Rifai^b, Amaury Kasprowiak^c, Francine Cazier-Dennin^a and Pierre-Edouard Danjou^{*a}

The present study describes the synthesis of the first phenoxy-calix[4]pyrrole-epichlorohydrin based polymer. The advantage of this latter resides in its fast-single step synthesis protocol, low cost, water insolubility and its unexpected anion extraction capacity. The study of this polymer through various solid/liquid extractions with halides in aqueous solutions and quantitative ion chromatography analysis, showed that unlike other calix[4]pyrrole-based entities, this polymer extracts iodide rather than bromide and fluoride owing to the presence of large extraction pockets. Evidence of an anion exchange process involving preferably chloride and bromide was also highlighted.

Introduction

Growing interest for anion binding chemistry through the use of organic-artificial host molecules emerged in the late 1960s and is considered nowadays one of the main areas of interest in the field of supramolecular chemistry.¹⁻⁴ Due to its potential biological applications, several supramolecules were designed and synthesized specifically to this end.^{5,6} Among these latter's, calix[4]pyrroles (**CP**) first synthesized by Baeyer in 1886⁷ appears to be exceptionally attractive in regard to their ease of synthesis and functionalization, and for their ability to be strong anion binders in non-aqueous media.⁸ Moreover, anion recognition by neutral supramolecular hosts as CP is mostly governed by hydrogen-bonding interactions. These non-covalent bonds are considered weak and make anion binding a hard goal to achieve. However, CPs consisting of an oligo-pyrrolic core offer a four hydrogen-bond platform ready to host anions, especially halides.⁹⁻¹³ Anion binding properties of many CPs have been studied predominantly in organic solvents and it was shown to form complexes mainly with fluorine,^{9,14-19} to a lesser extent with chloride and bromide^{10-13,20} and almost never with iodide due to its increased atomic size that do not fit into the pyrrolic cavity of **CP**. The present work reports the cross-linking and polymerization of phenoxy-calix[4]pyrrole (**PCP**), a supramolecule capable of

complexing mainly fluoride and, with a lesser affinity, chloride.¹⁴ These polymers were prepared by cross-linking the phenolic functional groups of **PCP** with epichlorohydrin (ECH). It is a non-expensive cross-linker widely used in bio-based materials design,²¹ in polysaccharide chemistry and especially for β -cyclodextrins polymerization.²² It bears two reactive functional groups: an epoxide ring and a chloroalkyl moiety which can form bridges with **PCP** (cross-linking) and/or with itself (polymerization). The epichlorohydrin-phenoxy-calix[4]pyrrole synthesized polymer (**PCP-EP**) showed superiority for its anionic recognition capacities over the parent supramolecule (**PCP**) and some other modified non-polymerized derivatives. For the first time, a **PCP**-based entity shows a capacity of extracting iodide and bromide from an aqueous media and a low affinity for fluoride. Removal of iodine and bromine from water appears to be essential as they can lead to toxic brominated and iodinated compounds threatening drinking water resources.²³

Experimental

Instruments and reagents

Nuclear Magnetic Resonance (NMR) spectra were recorded at 25°C using a Bruker Avance III spectrometer operating at 400 MHz and 100 MHz for ¹H and ¹³C, respectively. The peak of residual dimethylsulfoxide (DMSO) was used as an internal standard.

Fourier-transform infrared (FT-IR) spectra were recorded with an ATR module on a PerkinElmer Spectrum BXII spectrometer over 4000-500 cm⁻¹ range with a resolution of 1 cm⁻¹.

Thermal Gravimetric Analyses (TGA) of **PCP** and **PCP-EP** were performed under air flow (100 mL/min) from room

^aUnité de Chimie Environnementale et Interactions sur le Vivant, EA 4492, Université du Littoral Côte d'Opale, 145 Avenue Maurice Schumann, MREI 1, Dunkerque, France

^bLebanese Atomic Energy Commission – Lebanese National Council for Scientific Research – B. P. 11-8281, Riad El Solh, 1107 2260, Beirut, Lebanon

^cDépartement de Chimie, Université du Littoral Côte d'Opale, 220 avenue de l'Université, Dunkerque, France

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

temperature to 800 °C with a heating rate of 5 °C per min using an SDT Q600 apparatus from TA instruments.

Ion chromatography titrations were performed on a Thermofischer DIONEX ICS900 apparatus equipped with DIONEX IonPac AG14 (Guard 4x50mm) pre-column, DIONEX IonPac AS14A (Analytical 4x250mm) column, Electrolytically Regenerated Suppressor (DIONEX AERS 500 4mm) and a DS5 conductivity detector. Sodium carbonate (8 mM) and sodium bicarbonate (1 mM) in ultrapure water were used as an eluant at a rate of 1.2 mL/min. Aqueous solutions containing the tetrabutylammonium salts of the four halides (TBAF, TBACl, TBABr and TBAI) were used for external calibration between 1 and 20 ppm (5 points, $R^2 > 0.999$).

Pyrrole [99%], methane sulfonic acid [99%], epichlorohydrin [99%], tetrabutylammonium fluoride trihydrate (TBAF) [99%], tetrabutylammonium bromide (TBABr) [99%] and tetrabutylammonium iodide (TBAI) [98%] were purchased from Acros organics. 4-hydroxyacetophenone [99%] were purchased from Alfa Aesar and tetrabutylammonium chloride (TBACl) [$>97\%$] as well as sodium hydroxide [$>98\%$] from Sigma Aldrich. All compounds were used as received without further purification. **PCP** was synthesized according to the previously reported procedure.²⁴

General procedure for polymer synthesis

Synthesis of PCP-EP

1.00 g of **PCP** was suspended in water (20 ml) in the presence of NaOH (16 equiv.) at 80°C. The total dissolution of **PCP** was observed after 30 minutes. ECH (32 equiv.) was then added and the reaction was left stirring for four hours. After cooling, the precipitated polymer was washed with ultrapure water (3x50 ml) and filtered to afford a light brown solid (1.51 g) which was then characterized through both NMR and Infra-red spectroscopies. ¹H NMR (400 MHz, DMSO) δ 9.40 (s, NH), 6.92 – 6.78 (phenolic H, 4H), 5.94 (s, pyrrolic H), 5.73–3.34 (H of the cross-linking chain) 1.75 (s, CH₃).

ECH/PCP ratio determination by ¹H NMR

Deuterated trifluoroacetic acid was added to a solution of polymer in d₆-DMSO in order to downfield the signal of residual water over 8 ppm. Then, the integration of pyrrolic protons was set to 8 and the integration of the cross-linking chain was recorded. The ECH/PCP ratio was calculated,

dividing the integration of the cross-linking chain by 5 which is the number of protons in an ECH moiety. The ECH/PCP ratio displays the number of ECH equivalent per PCP unit.

Solid-liquid extraction of anions

For these experiments, solutions of TBAF, TBACl, TBABr and TBAI at ca. 10 ppm were prepared into ultra-pure water. During extraction tests, a volume of 15 mL was taken from each solution. For each batch experiment, time, temperature, agitation and the quantity of **PCP** and **PCP-EP** were fixed to one hour, 30°C, 650 rpm and 95 mg, respectively. After 1 hour of contact time, mixtures were filtered over 0.45 μ m filters prior to quantification of the un-complexed anions via ion chromatography analysis.

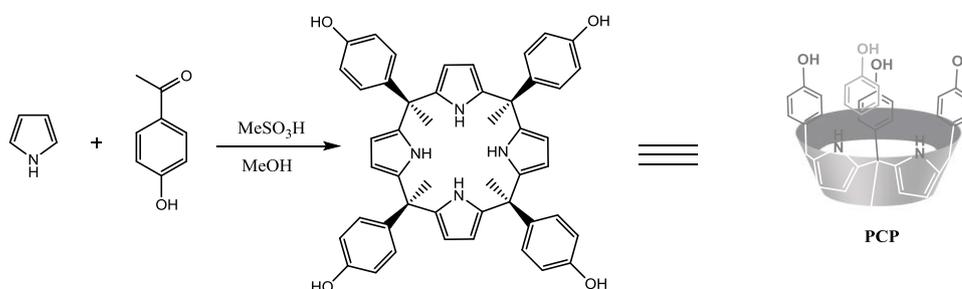
Results and discussion

Synthesis and characterization of PCP-EP

The synthesis of phenoxy-calix[4]pyrrole (**PCP**) or meso-tetra-methyltetraKis(hydroxyphenyl)calix[4]pyrrole was achieved following the Bonomo et al.²⁴ protocol which relies on the condensation of pyrrole with p-hydroxyacetophenone in acidic media (Figure 1). **PCP** was isolated as its $\alpha\alpha\alpha\alpha$ isomer which is characterized by a pre-organized structure where all the phenol groups are set in the same direction so as to form a π -electron rich cavity shielding its pyrrolic cavity. This supramolecule is well-known to complex selectively fluoride over other anions through H-bonds with pyrrolic N-H and anion- π interactions in DMSO and it was described in 2002 by Gale et al. as a “fluoride only” molecule.¹⁵ **PCP** was used as the starting material in the synthesis of **PCP-EP** polymers through a cross-linking with ECH to produce anions extractant.

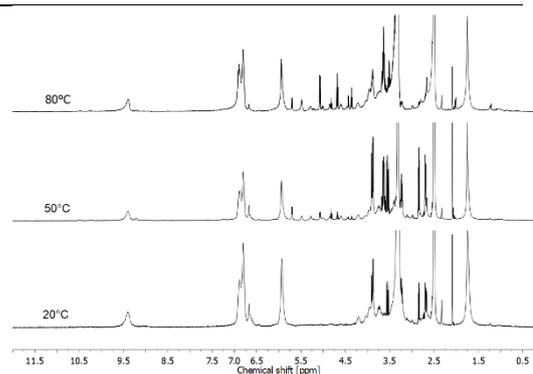
This synthesis took advantage of the four phenolic groups of **PCP** to initiate the cross-linking with highly reactive ECH. Briefly, sodium hydroxide was used to ionize and solubilize **PCP** in water²⁵ and to allow its reaction with ECH. Upon the addition of ECH, immediate cross-linking was observed and when the whole polymerization was achieved, the precipitated polymer was recovered by filtration. Experimental conditions that may influence the polymeric structure such as: temperature, time of reaction and the molar ratio of **PCP**/NaOH/ECH (Table 1) were studied and optimized. In a first approach, the molar ratio of **PCP**/NaOH/ECH was fixed to 1/16/32 and the influence of temperature (20, 50 and 80°C) was evaluated for a fixed 4 hours reaction time (Table 1, entry 1-3).

ARTICLE

Figure 1. Synthesis protocol for **PCP**.Table 1. Variations of **PCP-EP** synthesis conditions carried out on 1 g of **PCP**.

Entry	NaOH (equiv.)	ECH (equiv.)	Time (hrs.)	T (°C)	Appearance	ECH/PCP Ratio	Weight (g)
1	16	32	4	20	Fine powder- White/beige	4.03	1.07
2	16	32	4	50	Porous hard light brown solid	5.01	1.31
3	16	32	4	80	Hard brown solid	7.52	1.51
4	16	32	2	80	Hard brown solid	7.30	1.28
5	16	32	8	80	Hard brown solid	7.43	1.50
6	32	64	4	80	Liquescent brown solid	11.84	1.73
7	64	128	4	80	Brown oil	25.45	2.08

The highest amount of recovered material was obtained for 80 °C which is consistent with ^1H NMR spectra recorded for each sample (Figure 2). Indeed, for those spectra, one can observe that proton signals for the cross-linked chains between 3 and 5 ppm are better developed at 80 °C than at lower temperatures which can explain the difference in the recovered mass of the polymer. This observation can be measured through the ECH/PCP ratio that increased from 4 to 7.5 with increasing synthesis temperature (Table 1).

Figure 2. Influence of synthesis temperature on ^1H NMR spectra of **PCP-EP** in $\text{d}_6\text{-DMSO}$.

Further experiments were then conducted at 80 °C with the same starting materials molar ratio by varying the time of reaction (Table 1, entry 3-5). After 2 hours of reaction, 1.28 g

of polymer was obtained while a 4 hours reaction time provides 25% more material. Longer reaction time (8 hrs.) didn't provide any better yield, indicating that 4 hrs. was the optimal time for this synthesis. At last, molar ratios of ECH and sodium hydroxide were increased (Table 1, entry 6-7) to obtain more complex polymers but failed to provide the desired polymer consistency while our aim was to use these polymeric supports into solid/liquid extractions. High ECH/PCP ratio, superior to 10 ECH equivalent per PCP unit, were found for those polymers, revealing a highly flexible polymeric network (Figure 3, path 2) responsible of their consistency. In fact, the cross-linking consists of the creation of heterogeneous covalent chemical bonds in all directions throughout the polymerization that engenders a greater macromolecular

network. Figure 3 describes the main probable reaction between **PCP** and ECH. In fact, the obtained polymers result from a combination of the three following paths²⁶:

Path (1): Cross-linking of **PCPs** by ECH: this step relies on creating larger three-dimensional networks of **PCP** via glycidyl ether bridges. Owing to their three-dimensional structure, these materials have superiority over the parent material: chemically and thermally.

Path (2): Hydrolysis of the epoxide ring leading to the formation of vicinal hydroxyl groups.

Path (3): Polymerization of ECH in excess: due to its high reactivity enhancing its polymerization in a basic medium and leading to the lowering of the melting point.

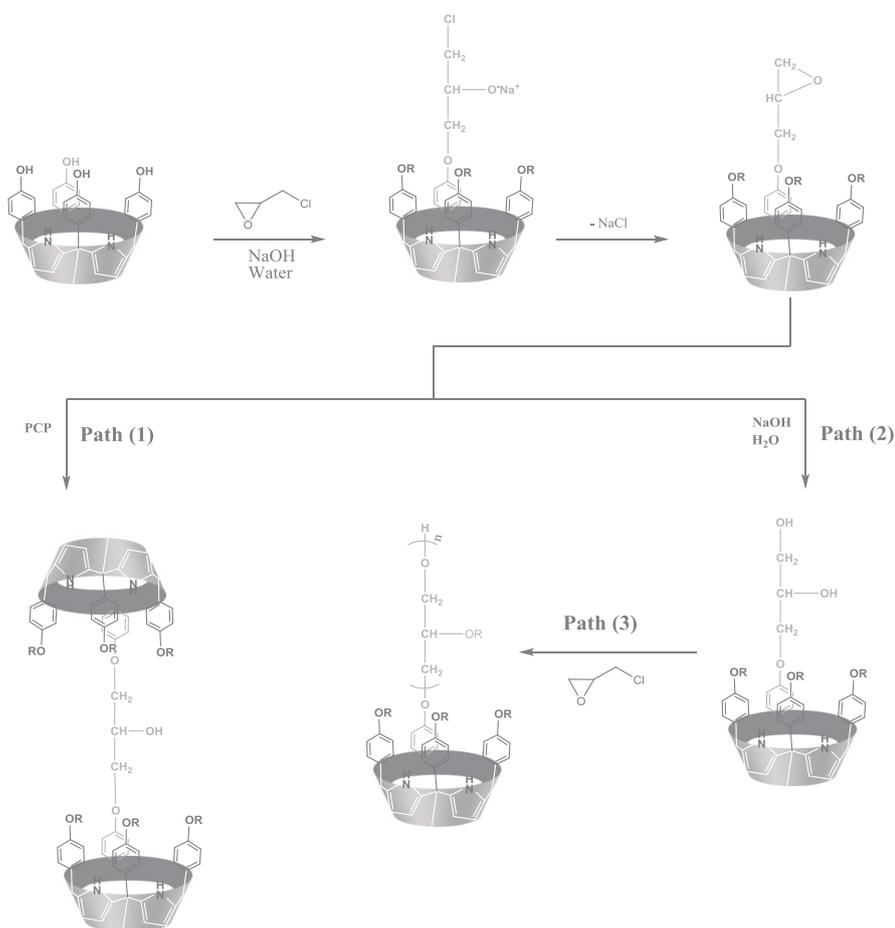


Figure 3. Synthesis protocol for **PCP-EP** representing the three possible paths of polymerization (adapted from reference 26).

ARTICLE

The efficiency of **PCP-EP** synthesis was established by ^1H NMR and FT-IR spectroscopies (Figure 4). **PCP-EP** ^1H NMR spectrum confirms the presence of **PCP** in the polymer network due to the presence of its characteristic proton resonance peaks at 1.75 ppm (methyl), 5.94 ppm (pyrrole methylene) 6.80 ppm (aromatics) and 9.40 ppm (NH). Interestingly enough, no phenol residual peaks were observed indicating the effectiveness of the reaction process. Moreover, the presence of unresolved signals above 3 ppm is clearly consistent with the formation of randomly cross-linked chains from ECH. FT-IR confirms as well the polymerization process

by the appearance of some characteristic wavenumbers: the strong band at 1030 cm^{-1} was attributed to ether functional groups, another medium band at 768 cm^{-1} was assigned to unreacted epoxide ring vibration and a third one at 701 cm^{-1} corresponds to C-Cl stretching vibrations. A drastic diminution of the characteristic bands of the phenols between $1310\text{--}1410\text{ cm}^{-1}$ was attributed to the crosslinking reaction. All of these changes confirm the modifications made to the initial **PCP** molecule and the formation of a new cross-linking chain characteristic of an ECH-based polymerization process.

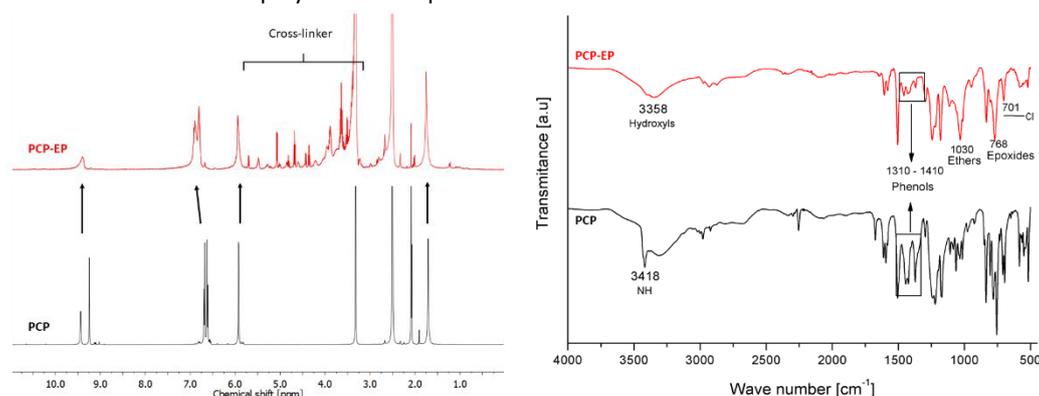
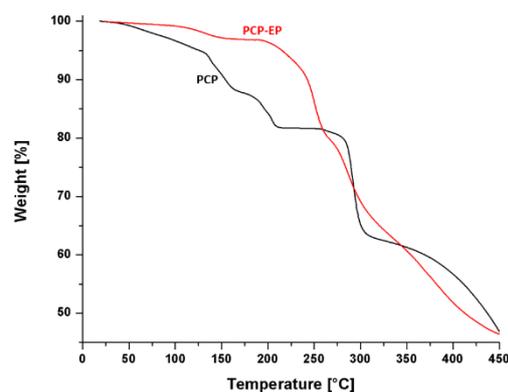


Figure 4. ^1H NMR spectra recorded in $\text{d}_6\text{-DMSO}$ (left) and FT-IR (ATR) spectra (right) of **PCP** (down) and **PCP-EP** (up).

The thermal stability of **PCP** and the synthesized **PCP-EP** polymer was investigated by thermogravimetric analysis (TGA). In both cases, the mass loss from 0 to 100°C was assigned to the adsorbed solvents molecules. As for the stability of these two compounds, **PCP-EP** is more stable and resists temperatures up to 200°C while degradation of **PCP** starts before 150°C (Figure 5). The similar shape for mass loss of the two compounds was due to the degradation of the pyrrolic rings as well as the phenolic aromatic arms, with a delayed degradation for the polymer due to the presence of ECH-based cross-linking chains, forming a more stable and rigid core macromolecular system.²⁷



Solid-liquid extraction of halides

Anion extraction properties of **PCP** and **PCP-EP** were investigated through solid/liquid extractions (Table 2). Quantification of anionic solutions was done through ion chromatography analysis, before and after the interaction with the extracting compounds. Despite our efforts to obtain a clean polymer (through washing with ultrapure water) it appears that chloride release was observed in each

experiment involving **PCP-EP**, mainly due to the affinity of the polymer for the residual traces of sodium chloride resulting from the polymerization process.

Extraction capacities of non-polymerized **PCP** were firstly tested against aqueous solutions containing only one anion as a TBA salt (Table 2, entry 1-4). Surprisingly, no significant

differences were observed for **PCP** extraction abilities towards fluoride, chloride, bromide and iodide.

Figure 5. Thermogravigrams of **PCP** and **PCP-EP**.

Table 2. Results of ion chromatography analysis upon solid/liquid extractions of fluoride, chloride, bromide, iodide (as tetrabutylammonium salt) with **PCP** and **PCP-EP** in water.

Entry	Extractant	Anions	Concentration of initial solution (ppm)	Concentration of solution after treatment (ppm)	Concentration of released Chloride (ppm)	% of extraction
1	PCP	F ⁻	9.52	7.83	-	17.75 ± 0.12
2	PCP	Cl ⁻	9.89	9.75	-	1.42 ± 0.10
3	PCP	Br ⁻	9.98	9.54	-	4.4 ± 1.75
4	PCP	I ⁻	10.09	9.28	-	8.02 ± 0.86
5	PCP-EP	-	-	-	1.28	-
6	PCP-EP	F ⁻	9.75	9.14	2.07	6.3 ± 1.32
7	PCP-EP	Cl ⁻	9.80	10.94	1.14	-
8	PCP-EP	Br ⁻	9.96	1.95	7.79	80.4 ± 2.08
9	PCP-EP	I ⁻	10.37	1.2	3.67	88.4 ± 1.32

Conversely, in the same conditions, **PCP-EP** showed an excellent capacity of extraction towards iodide and bromide (88.4 and 80.4 % respectively) coupled with a disconcerting extraction capacity for fluoride (only 6.3 %). This could be attributed to distortions of the $\alpha\alpha\alpha$ -phenoxy-calix[4]pyrrole core upon polymerization leading to a disorganized structure unable to complex fluoride. Remarkably, the chloride release appears to be strongly dependent on the anions present in solution and could be seen as a marker for anion pocket sizes present in the polymer. It can be seen that the extraction of bromide was accompanied by the strongest release of chloride (Table 2, entry 8) suggesting that chloride and bromide share the same size of pockets. This anion exchange process can be described as “coming-in and kicking out”^{28,29} process. It is interesting to note that during those experiments, sodium release was very weak (about 0.13 ppm) in comparison with the amount of chloride released, indicating that sodium stays trapped in the polymer network potentially playing a role in anion recognition.

Concerning the smaller chloride release observed with iodine extraction (Table 2, entry 9), it could lead to the conclusion that there are some larger pockets able to only host large anions like iodide. To experience this hypothesis, and to evaluate **PCP-EP** extraction capacities, a competition experiment was carried out with a solution containing ca. 10 ppm of each halide. The results are presented in Table 3. Interestingly, the extraction capacities of **PCP-EP** towards iodide were quite unaffected by the presence of other competing anions while extraction of bromide decreased drastically. Furthermore, the released amount of chloride remains unchanged between this experiment and the experiment presented above (Table 2, entry 8) indicating that all the previously chloride-occupied pockets were now occupied by bromide or iodide. Those observations corroborate the previous statement concerning the presence of different pocket sizes and demonstrate a greater affinity of **PCP-EP** for the large iodide anion.

Table 3. Results of ion chromatography analysis upon solid/liquid extraction competition experiment with **PCP-EP** in water.

Anions	Concentration of initial solution (ppm)	Concentration of solution after treatment (ppm)	Concentration of released Chloride (ppm)	% of extraction
F ⁻	11.95	8.41		29.6 ± 1.7
Cl ⁻	9.88	17.59	7.71	-
Br ⁻	9.96	5.04		49.4 ± 4.20
I ⁻	9.83	1.9		80.7 ± 3.51

Conclusions

This study is the first to introduce phenoxy-calix[4]pyrrole-epichlorohydrin (PCP-EP) based polymers. The synthesis of PCP-EP was conducted in water and operating conditions were optimized (temperature, time and ratios of reactants). The polymer with the desired consistency for solid/liquid extraction was characterized through ¹H NMR and FT-IR spectroscopies as well as TGA. Its anion extraction capacity in aqueous solutions towards fluoride, chloride, bromide and iodide was tested through solid/liquid extractions in controlled conditions. It was demonstrated that this polymer possesses a great affinity towards iodide owing to the presence of large pockets able to extract iodide over bromide and smaller anions. The experiments also conclude that an anion exchange process occurs with bromide (and to a lesser extent iodide) as it was able to occupy the same extraction pockets, occupied previously by chloride as evidenced by chloride release. This high affinity mainly for large anions like iodide and bromide was rarely mentioned in the literature for other polymerized and non-polymerized calix[4]pyrrole derivatives and makes this polymer particularly unique. Further studies will be carried out to investigate and optimize the extraction capacities of this polymer, that could be a potential tool for water decontamination.

Conflicts of interest

"There are no conflicts to declare".

Acknowledgements

The authors would like to thank the Lebanese Atomic Energy for Scientific Research (LAEC – CNRS/L) and the Université du Littoral Côte d'Opale (ULCO) for supporting this work and for a research fellowship. AUF (Agence Nationale de Francophonie) and the Lebanese National Council for Scientific Research (CNRS/L) were as well acknowledged for their financial support through SCORE project.

Notes and references

- (1) Scheerder, J.; Engbersen, J. F. J.; Reinhoudt, D. N. Synthetic Receptors for Anion Complexation. *Recueil des Travaux Chimiques des Pays-Bas* **1996**, *115* (6), 307–320. <https://doi.org/10.1002/recl.19961150602>.
- (2) Schmidtchen, F. P.; Berger, M. Artificial Organic Host Molecules for Anions. *Chemical Reviews* **1997**, *97* (5), 1609–1646. <https://doi.org/10.1021/cr9603845>.
- (3) Kubik, S. Anion Recognition in Water. *Chem. Soc. Rev.* **2010**, *39* (10), 3648–3663. <https://doi.org/10.1039/B926166B>.
- (4) Langton, M. J.; Serpell, C. J.; Beer, P. D. Anion Recognition in Water: Recent Advances from a Supramolecular and Macromolecular Perspective. *Angewandte Chemie International Edition* **2016**, *55* (6), 1974–1987. <https://doi.org/10.1002/anie.201506589>.
- (5) Choi, K.; Hamilton, A. D. Macrocyclic Anion Receptors Based on Directed Hydrogen Bonding Interactions. *Coordination Chemistry Reviews* **2003**, *240* (1), 101–110. [https://doi.org/10.1016/S0010-8545\(02\)00305-3](https://doi.org/10.1016/S0010-8545(02)00305-3).
- (6) Hua, Y.; Flood, A. Click Chemistry Generates Privileged CH Hydrogen -Bonding Triazoles: The Latest Addition to Anion Supramolecular Chemistry. *Chemical Society Reviews* **2010**, *39* (4), 1262–1271. <https://doi.org/10.1039/B818033B>.
- (7) Baeyer, A. Ueber Ein Condensationsproduct von Pyrrol Mit Aceton. *Berichte der deutschen chemischen Gesellschaft* **1886**, *19* (2), 2184–2185. <https://doi.org/10.1002/cber.188601902121>.
- (8) Saha, I.; Lee, J. T.; Lee, C.-H. Recent Advancements in Calix[4]Pyrrole-Based Anion-Receptor Chemistry. *European Journal of Organic Chemistry* **2015**, *2015* (18), 3859–3885. <https://doi.org/10.1002/ejoc.201403701>.
- (9) Danil de Namor, A. F.; Shehab, M. Selective Recognition of Halide Anions by Calix[4]Pyrrole: A Detailed Thermodynamic Study. *J. Phys. Chem. B* **2003**, *107* (26), 6462–6468. <https://doi.org/10.1021/jp0226174>.
- (10) Nishiyabu, R.; Palacios, M. A.; Dehaen, W.; Anzenbacher, P. Synthesis, Structure, Anion Binding, and Sensing by Calix[4]Pyrrole

- Isomers. *J. Am. Chem. Soc.* **2006**, *128* (35), 11496–11504. <https://doi.org/10.1021/ja0622150>.
- (11) Yoo, J.; Kim, M.-S.; Hong, S.-J.; Sessler, J. L.; Lee, C.-H. Selective Sensing of Anions with Calix[4]Pyrroles Strapped with Chromogenic Dipyrrolylquinoxalines. *J. Org. Chem.* **2009**, *74* (3), 1065–1069. <https://doi.org/10.1021/jo802059c>.
- (12) Fisher, M. G.; Gale, P. A.; Hiscock, J. R.; Hursthouse, M. B.; Light, M. E.; Schmidtchen, F. P.; Tong, C. C. 1,2,3-Triazole-Strapped Calix[4]Pyrrole: A New Membrane Transporter for Chloride. *Chem. Commun.* **2009**, *0* (21), 3017–3019. <https://doi.org/10.1039/B904089G>.
- (13) Yano, M.; Tong, C. C.; Light, M. E.; Schmidtchen, F. P.; Gale, P. A. Calix[4]Pyrrole-Based Anion Transporters with Tuneable Transport Properties. *Org. Biomol. Chem.* **2010**, *8* (19), 4356–4363. <https://doi.org/10.1039/C0OB00128G>.
- (14) Camiolo, S.; Gale, P. A. Fluoride Recognition in ‘Super-Extended Cavity’ Calix[4]Pyrroles. *Chem. Commun.* **2000**, *0* (13), 1129–1130. <https://doi.org/10.1039/B003229H>.
- (15) Woods, C. J.; Camiolo, S.; Light, M. E.; Coles, S. J.; Hursthouse, M. B.; King, M. A.; Gale, P. A.; Essex, J. W. Fluoride-Selective Binding in a New Deep Cavity Calix[4]Pyrrole: Experiment and Theory. *J. Am. Chem. Soc.* **2002**, *124* (29), 8644–8652. <https://doi.org/10.1021/ja025572t>.
- (16) Danil de Namor, A. F.; Shehab, M. Double-Cavity Calix[4]Pyrrole Derivative with Enhanced Capacity for the Fluoride Anion. *J. Phys. Chem. B* **2005**, *109* (37), 17440–17444. <https://doi.org/10.1021/jp0530707>.
- (17) Danil de Namor, A. F.; Abbas, I.; Hammud, H. H. A New Calix[4]Pyrrole Derivative and Its Anion (Fluoride)/Cation (Mercury and Silver) Recognition. *J. Phys. Chem. B* **2007**, *111* (12), 3098–3105. <https://doi.org/10.1021/jp067798e>.
- (18) Danil de Namor, A. F.; Khalife, R. Calix[4]Pyrrole Derivative: Recognition of Fluoride and Mercury Ions and Extracting Properties of the Receptor-Based New Material. *J. Phys. Chem. B* **2008**, *112* (49), 15766–15774. <https://doi.org/10.1021/jp8045356>.
- (19) Chi, X.; Peters, G. M.; Hammel, F.; Brockman, C.; Sessler, J. L. Molecular Recognition Under Interfacial Conditions: Calix[4]Pyrrole-Based Cross-Linkable Micelles for Ion Pair Extraction. *J. Am. Chem. Soc.* **2017**, *139* (27), 9124–9127. <https://doi.org/10.1021/jacs.7b04529>.
- (20) Anzenbacher, Pavel; Jursíková, K.; Lynch, V. M.; Gale, P. A.; Sessler, J. L. Calix[4]Pyrroles Containing Deep Cavities and Fixed Walls. Synthesis, Structural Studies, and Anion Binding Properties of the Isomeric Products Derived from the Condensation of p-Hydroxyacetophenone and Pyrrole. *J. Am. Chem. Soc.* **1999**, *121* (47), 11020–11021. <https://doi.org/10.1021/ja993195n>.
- (21) Musa, C.; Danjou, P.-E.; Pauwels, A.; Cazier-Dennin, F.; Delattre, F. Ultrasound-Assisted Heterogeneous Synthesis of Bio-Based Oligo-Isosorbide Glycidyl Ethers: Towards Greener Epoxy Precursors. *Molecules* **2019**, *24* (9), 1643. <https://doi.org/10.3390/molecules24091643>.
- (22) Morin-Crini, N.; Crini, G. Environmental Applications of Water-Insoluble β -Cyclodextrin–Epichlorohydrin Polymers. *Progress in Polymer Science* **2013**, *38* (2), 344–368. <https://doi.org/10.1016/j.progpolymsci.2012.06.005>.
- (23) Watson, K.; Farré, M. J.; Knight, N. Strategies for the Removal of Halides from Drinking Water Sources, and Their Applicability in Disinfection by-Product Minimisation: A Critical Review. *Journal of Environmental Management* **2012**, *110*, 276–298. <https://doi.org/10.1016/j.jenvman.2012.05.023>.
- (24) Bonomo, L.; Solari, E.; Toraman, G.; Scopelliti, R.; Floriani, C.; Latronico, M. A Cylindrical Cavity with Two Different Hydrogen-Binding Boundaries: The Calix[4]Arene Skeleton Screwed onto the Meso-Positions of the Calix[4]Pyrrole⁺. *Chem. Commun.* **1999**, *0* (23), 2413–2414. <https://doi.org/10.1039/A907563A>.
- (25) Verdejo, B.; Rodríguez-Llansola, F.; Escuder, B.; Miravet, J. F.; Ballester, P. Sodium and PH Responsive Hydrogel Formation by the Supramolecular System Calix[4]Pyrrole Derivative/Tetramethylammonium Cation. *Chem. Commun.* **2011**, *47* (7), 2017–2019. <https://doi.org/10.1039/C0CC04051G>.
- (26) Morin-Crini, N.; Winterton, P.; Fourmentin, S.; Wilson, L. D.; Fenyvesi, É.; Crini, G. Water-Insoluble β -Cyclodextrin–Epichlorohydrin Polymers for Removal of Pollutants from Aqueous Solutions by Sorption Processes Using Batch Studies: A Review of Inclusion Mechanisms. *Progress in Polymer Science* **2018**, *78*, 1–23. <https://doi.org/10.1016/j.progpolymsci.2017.07.004>.
- (27) Pellicer, J. A.; Rodríguez-López, M. I.; Fortea, M. I.; Lucas-Abellán, C.; Mercader-Ros, M. T.; López-Miranda, S.; Gómez-López, V. M.; Semeraro, P.; Cosma, P.; Fini, P.; et al. Adsorption Properties of β - and Hydroxypropyl- β -Cyclodextrins Cross-Linked with Epichlorohydrin in Aqueous Solution. A Sustainable Recycling Strategy in Textile Dyeing Process. *Polymers* **2019**, *11* (2), 252. <https://doi.org/10.3390/polym11020252>.
- (28) Kim, J. S.; Shon, O. J.; Rim, J. A.; Kim, S. K.; Yoon, J. Pyrene-Armed Calix[4]Azacrowns as New Fluorescent Ionophores: “Molecular Taekowndo” Process via Fluorescence Change. *J. Org. Chem.* **2002**, *67* (7), 2348–2351. <https://doi.org/10.1021/jo010877w>.
- (29) Kim, J. S.; Noh, K. H.; Lee, S. H.; Kim, S. K.; Kim, S. K.; Yoon, J. Molecular Taekwondo. 2. A New Calix[4]Azacrown Bearing Two Different Binding Sites as a New Fluorescent Ionophore. *J. Org. Chem.* **2003**, *68* (2), 597–600. <https://doi.org/10.1021/jo020538i>.