New ternary water-soluble support from self-assembly of β-cyclodextrin-ionic liquid and an anionic polymer for a dialysis device

Asmaa Bouyahya1,2 · Berthe-Sandra Sembo-Backonly1 · Audrey Favrelle-Huret1,3,4 · Sébastien Balieu1 · Frédéric Guillen1,5 · Valérie Mesnage6 · Carole Karakasian-Dia3 · Mohammed Lahcini2,7 · Didier Le Cerf3 · Géraldine Gouhier1

Received: 14 April 2021 / Accepted: 2 September 2021 / Published online: 14 September 2021
© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2021

Abstract

We developed a new hybrid material resulting from an innovative supramolecular tripartite association between an ionic liquid covalently immobilized on primary β-cyclodextrins rim and an anionic water-soluble polymer. Two hydrophilic ternary complexes based on native and permethylated β-cyclodextrins substituted with an ionic liquid and immobilized on poly(styrene sulfonate) (CD-IL+PSS− and CD(OMe)IL+PSS−) were obtained by simple dialysis with a cyclodextrin maximal grafting rate of 25% and 20% on the polymer, respectively. These polyelectrolytes are based on electrostatic interactions between the opposite charges of the imidazolium cation of the ionic liquid and the poly(styrene sulfonate) anion. The inclusion properties of the free cavities of the cyclodextrins and the synergic effect of the polymeric matrix were studied with three reference guests such as phenolphthalein, p-nitrophenol, and 2-anilinonaphthalene-6-sulfonic acid using UV-visible, fluorescent, and NMR spectroscopies. The support has been applied successfully in dialysis device to extract and concentrated aromatic model molecule. This simple and flexible synthetic strategy opens the way to new hybrid materials useful for fast and low-cost ecofriendly extraction techniques relevant for green analytical chemistry.

Keywords Ionic liquid · β-Cyclodextrin · Host-guest inclusion complex · Poly(styrene sulfonate) · Metathesis · Pollutant · Dialyzer

Introduction

Ionic liquids (ILs) are a broad class of salts with melting points below 100 °C and are generally composed of an organic cation (such as imidazolium, pyridinium, phosphonium, or ammonium cation), and an organic or inorganic anion. Ionic liquids are known to be flexible solvents because most of their properties, such as thermal stability, electrolytic conductivity, viscosity, and miscibility with other solvents, can be easily tuned by modifying either the anionic or the cationic part of the salt. Their low volatility makes them especially relevant in the context of green chemistry by facilitating their confinement and recycling. They have therefore been used in various domains of chemistry including among others: separation chemistry, analytical chemistry to improve the sensitivity, selectivity, and detection limit of analytical applications (Pandey 2006; Koel 2016; Anderson and Clark 2018) and in the development of new materials (Hallett and Welton 2011; Hayes et al. 2015).
β-cyclodextrin (CD) is a macrocyclic oligosaccharide composed of seven α-(1,4)-glucopyranoside moieties (D’Souza 1998). This natural compound is produced from starch by the action of glucanotransferase. Its toroidal shape is lined with C-6 primary hydroxyl groups on the narrow rim and C-2 and C-3 secondary hydroxyl groups on the wider rim. Thus, this cavity can welcome hydrophobic molecules in aqueous media, thanks to van der Waals force, hydrophobic interaction, electrostatic affinity, dipole-dipole interaction, and hydrogen bonding. This host-guest inclusion property has found many industrial applications in the formulations, extraction, and analytical processes, in domains as diverse as pharmaceutical, food, cosmetic, and textile chemistry. The covalent (Fig. 1a–d, f) or non-covalent (Fig. 1e) associations between ionic liquid and cyclodextrin have opened the way to new applications in function of the nature of the selected support.

In the majority of the reported cases, the IL is covalently bound to the CD rim. As an example, ionic liquid grafted by the nitrogen atom of imidazolium on the primary face of β-cyclodextrin was immobilized on modified silica and used as chiral support in high-performance liquid chromatography (Rahim et al. 2016a; Rahim et al. 2016b), in capillary gas chromatography (Zhang et al. 2011), or in capillary electrophoresis (Zhou et al. 2017) (Fig. 1a). The presence of the ionic species improved the enantioseparation of β-blockers and flavonoids, thanks to the formation of intermolecular inclusion complex but also owing to an original π-π interaction between the aromatic guest and the imidazolium cycle (Rahim et al. 2016a; Rahim et al. 2016b). The original electrochemical properties of ionic liquids and the high supramolecular recognition properties of cyclodextrins were also tested on metallic supports such as Pt-Co (Zhao et al. 2010), graphite (Mohamad et al. 2015; Rasdi et al. 2016), and Au-graphene oxide (Li et al. 2016) producing new nanoparticles and hybrid nanomaterials (Fig. 1b). The ionic liquid playing the role of supported stabilizer electrolyte provides higher sensitive carbon paste electrodes leading to environmentally friendly electrochemical sensors for non-enzymatic glucose reaction (Zhao et al. 2010) or to detect 2,4-dichlorophenol (Mohamad et al. 2015; Rasdi et al. 2016). In the same way, magnetite nanoparticles coated with β-CD-IL produced new electrode material able to recognize bisphenol A (Sinniah et al. 2015) and sunset yellow (Li et al. 2016). Green analytical chemistry is also based on low cost and fast eco-friendly extraction techniques possible, thanks to the ionic liquid properties (Kissoudi and Samanidou 2018). Immobilization of IL on polymers of β-CD produced macroporous insoluble material used as solid phase extraction (SPE) tool to extract and analyze traces of organic and metal toxic derivatives in water (Mahlambi et al. 2010, 2011; Raoov et al. 2013, 2014a, 2014b), drug (Zhou and Zhu 2014), blood (Qin and Zhu 2017), and pyrethroids (Gao et al. 2020) (Fig. 1c). Vortex-assisted liquid-liquid microextraction (Yang et al. 2015) or effervescence-assisted dispersive solid-phase extraction (Wu et al. 2016) methods using a magnetic β-CD-IL sorbed on attapulgite clay (Fig. 1b) were also used for the fluorometric determination of aliphatic amines pollutant and fungicide detection in honey and juice, respectively. Other magnetic preconcentration procedure based on ionic liquid-β-cyclodextrin under monomer or polymer forms attached to Fe₃O₄ nanoparticles achieved the speciation analysis of biphenol A (Sinniah et al. 2015), manganese in water samples (Quin et al. 2016), herbicides in fruits and vegetables (Bakheet and Zhu 2017), parabens in cosmetics (Yusoff et al. 2017), rhodamine B in food samples (Bakheet and Zhu 2017), and PFOA, PFOS, and Cr(VI) in wastewater (Badrudoza et al. 2017) (Fig. 1d).

The supramolecular interactions between the cationic or anionic parts of ionic liquid and the hydrophobic cavity of cyclodextrin (IL/CD) are well known and have found applications in polymer chemistry, molecular devices, and nanoscience (Rogalski et al. 2013; Mofaddel et al. 2016). The addition of an anionic polymer to this IL/CD combination led to new supramolecular architectures. In 2004, Amiel et al. described the first water-soluble ternary complexes mixing a
polymer of β-CDs, a cationic surfactant, and anionic polymers. These polyelectrolyte complexes were based on two interactions: electrostatic interactions between the opposite charges of the surfactant and the poly(styrene sulfonate) (PSS) and, inclusion complex interactions between the lipophilic part of the surfactant and the neutral β-cyclodextrin polymer (Fig. 1e) (Galant and Amiel 2004; Amiel et al. 2004; Antoniuk and Amiel 2016). The formation of aggregates was observed when this interpolyelectrolyte complex was formed in stoichiometric conditions reducing the water solubility of the system. As an application, DNA extraction mimicking a self-assembly biological process by forming supramolecular multilayers has been developed (Antoniuk and Amiel 2016). The reversibility of the system has a great potential for the formation of microcapsules and modified surfaces in the gene delivery domain.

Surprisingly, the non-covalent interaction between an ionic liquid covalently bound to a cyclodextrin and an anionic polymer has been unexplored until now (Fig. 1f). We selected the commercially available, water-soluble sodium poly(styrene sulfonate) (PSS Na+) as an anionic polymer exchanger. Sulfonate function is a strong electrolyte whose charge is little affected by a change in pH value. The formation of the complex between anionic PSS and amphiphilic IL has been already studied and has found applications as magnetic nanoparticles for conductive membrane (Jiao et al. 2015; Barhoumi et al. 2016). When long-chain imidazolium is used as a surfactant, electrostatic and hydrophobic interactions drive self-assembly between the PSS backbones and the alkyl tail to form ordered micelles with specific surface tension useful in colloid and interface sciences. Herein, we exploited the ionic strength between PSS and a non-amphiphilic butylimidazolium cation grafted on β-CD (CD-IL+X−) to form a new hydrophilic extractive CD-IL+PSS− tool. The coupling between the two entities will be carried out by simple ion metathesis between the ionic polymer and the IL covalently immobilized on the macrocycle (Fig. 2). By avoiding any intramolecular inclusion of the ionic liquid, this new assembly will keep the cavity of the β-cyclodextrin available and consequently improve the potential of extraction and preconcentration of molecules of interest. Moreover, this aqueous soluble support will extend the field of analytical applications.

The host-guest inclusion properties were studied using three reference guests, namely, phenolphthalein, p-nitrophenol, and 2-anilino-6-naphtalene sulfonate (2,6-ANS), using UV-visible, fluorescence, and NMR spectroscopies. Finally, this innovative support has been tested to extract and concentrate 2,6-ANS as a model in a pore water dialysis sampler.

Materials and instruments

The equipment, materials, methods, synthesis, and characterization details of products 2-4, 7, 9, and 11-13 are available in the experimental section. Graphs of p-nitrophenol inclusion study (absorbance and job plot, stability constants table) and NOESY NMR of inclusion complex of 13 2,6-ANS obtained with the dialyzer were also reported. All data represent the means from at least three different experiments.

Results and discussion

Synthesis of supports

The ionic liquid has been designed with a carboxylic acid function to bind the macrocycle via an amide bonding and with a flexible carbon linker of five carbon atoms (long enough to avoid steric hindrance but short enough to prevent intramolecular inclusion complexation) (Zgani et al. 2016). Two routes have been developed leading to two different ILs with PF6− and Br− counter ions. The first one was obtained in four steps (Fig. 3), when the second one in only one step by microwave activation (Fig. 4).

The ring-opening of ε-caprolactone 1 by methyltrichlorosilane (MeSiCl3) in the presence of NaI in ACN led to methyl 6-halohexanoate 2 (as a 83/17 mixture of the iodo and chloro derivatives). Nucleophilic substitution of the haloester 2 by methylimidazole formed the ionic adduct 3 with 78% yield (Mincheva et al. 2007). After the saponification step, the ion metathesis by addition of KPF6 in ACN of 4 generated the desired IL 5 with good yield and was confirmed by 1H, 31P, and 19F NMR spectroscopies. Thus, the chemical shift observed for the protons and carbons of the imidazolium group validated this total conversion. As the PF6− anion is more hydrophobic than the iodide, we expected that the metathesis with PSS Na+ to give a water-soluble polymer complex would be easier. Moreover, the presence of phosphorus atom would facilitate the follow-up of the reaction by NMR spectroscopy. An alternative strategy was developed to obtain the IL 7 with bromine as a counter ion by using commercial 6-bromohexanoic acid 6 and 1-methylimidazol
under microwave activation with 88% yield in only ten minutes (Fig. 4).

The immobilization of IL 5 on TRIMEB-NH$_2$ 8 (Moutard et al. 2002; Tang and Ng 2008; Nielsen et al. 2010; Jicsinszky et al. 2016; Cyclolab 2021) was obtained after activation of the acid function as an acyl chloride in 40% yield (Fig. 5).

The amidation reaction between CD-NH$_2$ 10 (Moutard et al. 2002; Tang and Ng 2008; Nielsen et al. 2010; Jicsinszky et al. 2016; Cyclolab) and IL 7 was performed in the presence of coupling agent TBTU with 88% after dialysis against water (Fig. 6). Then, a similar protocol was applied with TRIMEB-NH$_2$ 8 leading to CD(OMe)-IL$^+$PF$_6$ 9 in 90% yield.

The metathesis reaction between CD(OMe)-IL$^{-}$PF$_6$ 9 or CD-IL$^{-}$Br 11 and PSS Na$^+$ was performed under mild conditions by dialysis against deionized water using a 500-Da membrane during 2 days, shifting the equilibrium by eliminating NaPF$_6$ and NaBr salts (Fig. 7). After lyophilization, CD(OMe)-IL$^{-}$PSS 12 and CD-IL$^{-}$PSS 13 complexes were obtained with high purities. $^{19}$F and $^{31}$P NMR analysis revealed the presence of NaPF$_6$ salt in the dialysate in the preparation of complex 12.

Various ratios of CD(OMe)-IL$^{-}$PF$_6$ 9/SS Na$^+$ (Styrene Sulfonate SS) varying from 1/25 to 1/1 were tested for the metathesis reaction (Table 1). The size exclusion chromatography analysis (SEC/MALS/VD/DRI) confirmed the good purity of our samples (Fig. 8a) and showed a shift of peaks at lower elution volume with the grafting of CD 9 on PSS in comparison to PSS (Fig. 8b) due to the increase of the molecular weights and the chain length. A calculus-based on the number average molecular weight led to the real ratio of immobilization on polymer evaluated from 1/49 to 1/4 (CD-IL/SS ratio) which correspond to a grafting efficiency ranging from 25 to 57%. We observed a large increase in water solubility of the CD derivatives in the presence of PSS polymer.

Similar immobilization rates were observed when using theoretical ratios of 1/25, 1/20, and 1/15; the overlapping peaks revealed no modification of the conformation of the polymer in solution even when a ratio of 1 CD for 12 styrene sulfonate (SS) moieties was obtained. For the last trial (theoretical ratio 1/1), a higher dispersity ($D = 2.6$) of molecular weight due to a modification of the polymeric organization (aggregation) was detected. Thereafter, the binding of CD-IL$^{-}$Br 11 and PSS Na$^+$ was performed at two theoretical ratios of 1/20 and 1/10, and the experimental ratios of 1/25 and 1/20 were obtained, respectively, with the conservation of the initial conformation of the polymer (Table 2).

As expected, a higher CD-IL/SS ratio generated higher binding efficiency on PSS. Better immobilization rates were obtained with CD-IL 11 (80% for 1/25 ratio) than methylated CD(OMe)-IL 9 (41% for 1/49 ratio) due to higher water solubility.

### Inclusion complex studies

The formation of the host-guest complex depends on the functionalization of the CD. A comparative study has been performed with all non-methylated and methylated CD derivatives and their precursors to evaluate the influence of each modification. Three reference molecules were tested: phenolptalein (PP), p-nitrophenol (PNP), and 2-anilinonaphthalene-6-sulfonic acid (2,6-ANS) (Fig. 9).

PP is known to form an inclusion complex with β-CD with a stability constant ($K_s$) evaluated by UV-visible spectroscopy to 191 M$^{-1}$ (Eftink and Harrison 1981; Wang and Song 2007; Khalafi and Rafiee 2013). At basic pH (10.5), the pink PP color disappears in the presence of CD generating a decrease in absorbance. The accessibility of the cavity of the macrocycles in polymer matrix will also be tested with PNP known as a fungicide derivative ($K_s = 204$ M$^{-1}$) (Taguchi 1986; Gelb et al. 1995) and 2,6-ANS ($K_s = 2220$ M$^{-1}$) (Wagner and Fitzpatrick 2000; Favrelle et al. 2015) a fluorescent probe.
Firstly, the inclusion of PP in native β-CD was tested with various CD/PP ratios ranging from 1 to 25 equivalents. A complete inclusion was observed when 20 equivalents of CD were used (Table 3).

The presence of an ionic liquid linker did not improve the water dissolution of CD(OMe)-IL+PF6− 9. The presence of methoxy groups on permethylated TRIMEB inhibited all inclusion properties of PP whatever the number of equivalents of the host. Similar negative results were obtained with CD(OMe)-NH2 10 and CD(OMe)-IL+PF6− 9. As the intermolecular inclusion of counter ion PF6− was already reported in the literature with a long IL carbon chain, 31 the same experiment was performed using iodide anion, and the same result was obtained, excluding a competitive insertion of PF6− anion into the cavity. The experiment was carried out on CD(OMe)-IL+PSS− 13 with grafting of 1/44 CD-IL/SS and inclusion of PP varying between 16 and 26% was observed, probably due to an increase of water solubility of the complex and better accessibility to CD cavity once immobilized on the polymer backbone. ROESY NMR experiment was performed in D2O to confirm the absence of intramolecular self-inclusion complex of the ionic liquid chain into the cavity of the cyclodextrin 9. The absence of cross-peaks between protons of the ionic liquid chain (1.44 ppm) or imidazolium cycle (8.5 ppm) and β-CD moiety fully supports this conclusion (empty scare in Fig. 10). Finally, as the dialysis step eliminated all traces of PF6− counter ion, the cavity of CD of 12 is undoubtedly available.

From these preliminary results, we focused our study on CD-IL*PSS− 13, and its precursors β-CD, 10, and 11, all water-soluble. The pink PP solution has a maximum of absorption at 553 nm which became colorless in presence of all CD derivatives proving the inclusion phenomena. As expected, the absorbance of PP decreased with the increase of concentration (1, 5, 10, 20 et 25 equivalents) of host molecules β-CD, CD-NH2 10, CD-IL*Br− 11, and CD-IL*PSS− 13 following the Beer-Lambert rule (Table 4) (Eftink and Harrison 1981; Wang and Song 2007; Khalafi and Rafiee 2013). The chemical modifications on the CD rim did not change the inclusion properties. Indeed, similar results were obtained for β-CD, 10, and 11. The weak decrease observed with 13 could be due to steric hindrance induced by the polymeric structure.

A total of 82% and 90% of PP were encapsulated in the CD-IL*PSS− 13 and in β-CD in the presence of 5 equivalents of CD units, respectively. This weak decrease could be due to steric hindrance induced by the polymeric structure. The absence of variation of percentage of inclusion between CD-NH2 10 and CD-IL*Br− 11 (65% and 62%, respectively; Table 4) supports the idea of no competition between the IL linker and the guest.

The monosubstitution on the primary face of the β-CD did not interfere with the formation of the inclusion complexes. The short ionic linker grafted on the CD rim reduces its mobility and limits the inclusion of the IL unit into the cavity (intramolecular inclusion) (Zgani et al. 2016). Besides, the low concentration used during the immobilization on PSS may not favor the interaction between the IL unit and another CD cavity due to lower statistical meeting (intermolecular inclusion). Consequently, the inclusion efficiency corresponds to direct accessibility of the CD site, and a perhydroxylated β-CD is required to form supramolecular complexes.

The influence of the IL immobilized on the rim of β-CD on its complexation ability was studied via the inclusion of p-nitrophenol (PNP pKa 7.04) as a model by UV-visible
spectroscopy (Taguchi 1986; Gelbe et al. 1995). This experiment was performed with the protonated form of \( p \)-nitrophenol. A molar extinction coefficient of 18,801 L mol\(^{-1}\) cm\(^{-1}\) at 400 nm was confirmed in presence of \( \beta \)-CD. The Job plot experiment also confirmed the 1:1 \( \beta \)-CD/PNP stoichiometry. The study was then carried out with 0 to 1.5 mmol/L of CD-IL\(^+\)Br\(^-\) (0 to 30 equivalents) and an association constant of \( K_s = 200 \) M\(^{-1}\) was calculated with a negative standard free enthalpy \( \Delta r G^\circ_{\exp} = -13.2 \) KJ/mol.†

2-Anilino-6-naphtalene sulfonate (2,6-ANS) is a polar sensitive fluorescent probe towards their local environment (Eftink and Harrison 1981; Wang and Song 2007; Khalafi and Rafiee 2013). The fluorescent properties decrease with the increase of polarity such as in water and are applied for host-guest inclusion complexes with cyclodextrins. The fluorescence intensity of 2,6-ANS increased with the addition of the four CD derivatives (\( \beta \)-CD, 10, 11, and 13 with grafting rate of 1/25 CD/SS) attesting of inclusion complex phenomena (for 13, Fig. 11). Indeed, maximal wavelengths \( \lambda_{F_{\text{max}}} \) at 467 nm in absence of CD at 2 mM shifted, respectively, of 20, 42, 23, and 20 nm in the presence of \( \beta \)-CD, 10, 11, and 13 confirming the absence of modification of inclusion properties of the modified CDs.

The fit of the fluorescent titration ratio \( F/F_0 \) obtained depends on the CD derivative concentration provided association constant \( K_s \), a maximal value corresponding to 100% of inclusion (Eqs. 1–3; Table 5). Higher values of \( K_s \) indicate a higher affinity of ANS for CD because of a more apolar cavity (Favrelle et al. 2015)

\[
\text{CD} + \text{ANS} \leftrightarrow \text{CD} : \text{ANS}
\]

\[
K_s = \frac{[\text{CD} : \text{ANS}]}{[\text{CD}] \times [\text{ANS}]}
\]

\[
\frac{F}{F_0} = 1 + \left( \frac{F_{\infty}}{F_0} - 1 \right) \frac{[\text{CD}]K_s}{(1 + [\text{CD}]K_s)}
\]

\( F \) : integrated area of the fluorescence spectrum; \( F_0 \) : total fluorescence intensity in the absence of CD; \( F_{\infty} \) : maximum fluorescence enhancement

In the presence of 2,6-ANS, CD-IL\(^+\)PSS\(^-\) 13 (with grafting ratio 1/20 CD/SS) generated the higher \( F/F_0 \) value, due to the

![Synthesis of CD(OMe)-IL\(^+\)PSS\(^-\) 12 and CD-IL\(^+\)PSS\(^-\) 13 by dialysis against deionized water](image)

### Table 1 SEC results of CD(OMe)-IL\(^+\)PSS\(^-\) 12 with various ratios of CD(OMe)-IL 9 to SS

| Theoretical ratio | \( M_w \) (g/mol) | \( M_m \) (g/mol) | \( R_h \) (nm) | Experimental ratio \( F/F_0 \) | Grafting efficiency\( ^c \) |
|------------------|------------------|------------------|-------------|-----------------------------|-----------------------------|
| CD(OMe)-IL 9/SS  |                  |                  |             |                             |                             |
| 0/1              | 45,000           | 68,000           | 10.4        | -                           | -                           |
| 1/25             | 55,000           | 80,000           | 10.8        | 1/44                        | 57%                         |
| 1/20             | 52,000           | 84,000           | 12.3        | 1/49                        | 41%                         |
| 1/15             | 52,000           | 94,000           | 12.1        | 1/49                        | 31%                         |
| 1/5              | 73,000           | 121,000          | 13.3        | 1/12                        | 42%                         |
| 1/1              | 132,000          | 350,000          | 16.4        | 1/4                         | 25%                         |

\( ^a \) Weight average hydrodynamic radius

\( ^b \) \( x = \frac{[\text{Mo(CD-IL)xMn(PSS)}][((\text{Mn(CD-IL+PSS-Mn(PSS)}))x\text{Mo(PSS)}]}{[\text{Mo(CD-IL)}] = 1579 \text{ g/mol and Mo(PSS)} = 207 \text{ g/mol}} \)

\( ^c \) \( x(\text{theoretical})/x(\text{experimental}) \times 100 \)
higher affinity of the hydrophobic part of guest for CD cavity (Table 5). The influence of grafting rate (1/25 and 1/20 CD/SS) on the inclusion of 2,6-ANS has been studied (Table 5). High association constants were observed in both cases underlying the weak influence of the grafting efficiency in the range studied (1/25 and 1/20; Table 5). Consequently, the ionic PSS has a positive and significant impact on inclusion properties, with a factor of 2.9 and 3.3 on $K_s$ values for CD-IL$^+$PSS$^{-}$ with 1/25 and 1/20 ratio respectively, by comparison with CD-IL$^+$Br$^+$.

![Fig. 8](image)

**Table 2** SEC analysis of CD-IL$^+$PSS$^{-}$ with various ratios

| Theoretical ratio, CD-IL | $M_n$, g/mol | $M_w$, g/mol | Rh, nm | Experimental ratio$^a$, CD-IL | Grafting efficiency$^b$ |
|-------------------------|--------------|--------------|--------|-------------------------------|------------------------|
| 1/20                    | 49,000       | 87,000       | 10.9   | 1/25                          | 80%                    |
| 1/10                    | 60,000       | 98,000       | 11.5   | 1/20                          | 50%                    |

$^a x = [M_n(CD-IL)xM_n(PSS)]/[(M_n(CD-IL)^+PSS^- Mn(PSS))] x Mo(PSS)]$ with $Mo(CD-IL) = 1312.5$ g/mol and $Mo(PSS) = 207$ g/mol

$^b x(\text{theoretical})/x(\text{experimental}) \times 100$
In both cases, the cavities of CDs were accessible in a similar manner confirming the absence of intermolecular interaction between the IL linker and another CD cavity. The reciprocal curve 1/(F/F₀ − 1) in function of 1/[CD] is representative of the stoichiometry of the 2,6-ANS/CD complex (Eq. 4) (Favrelle et al. 2015).

\[
\frac{1}{(F/F₀ - 1)} = \frac{1}{[CD]}
\]

In the presence of 1 equivalent of host CD linear plots (R² = 0.997) were observed with 13 for both grafting rate (1/25 and 1/20 CD/SS) validating the 1:1 stoichiometry (Fig. 12).

Dialysis pore water sampler development

The accurate knowledge of the pollution level in pore-water sediment is a challenge for geologists. The literature on the porewater sampling methods is based on two different approaches. The first one is at a laboratory scale and requires sediment cores that are cut into several centimeter fractions. Then, the porewater is extracted by centrifugation under nitrogen squeeze (Bufflap and Allen 1995; Brinkman et al. 1982). This method requires physical pressures onto sediment cores that are cut into several centimeter fractions. The yellow graph (Fig. 13c) illustrates the concentration gradient of pore-water dissolved nutriments obtained with the dialyzer inserted into the sediments of lake or estuary. The ratio between the concentration of nutriments and the depth into the sediment (dC/dx) gives the flux value at the sediment-water interface via a numerical diffusion model. We tested this tool to extract and analyze pollutants.

Indeed, owing to this ternary water-soluble support, the organic pollutants could be extracted, concentrated, and analyzed under their organic forms. Moreover, the presence of the support should modify the equilibrium time, and consequently reduce the collection time of the estuaries water samples. To test the efficiency of the technique, the water-soluble material was introduced into the cavities of the dialyzer and 2,6-ANS was used as a pollutant model (Fig. 13 a and b). A specific membrane based on polysulfone was used to avoid biodegradation during the dialysis by the bioorganisms present in the sediment. The dialyzer was used in the presence of 2 mM of 2,6-ANS water solution and stoichiometric CD-LI⁺PSS⁻ 13.

After non-optimized equilibration time (8 h), each cell was extracted and the presence of 2,6-ANS was confirmed by UV-visible spectroscopy. The samples were collected and analyzed by NMR spectrometry. A slight shift was detected between 2,6-ANS with and without CD-LI⁺PSS⁻ 13. NOESY experiment showed the interaction between the aromatic group of 2,6-ANS and H3 and H5 of the internal cavity of the cyclodextrin proving the formation of an inclusion complex and the absence of free 2,6-ANS.† Similar experiments in the presence of PSS "Na⁺" or CD-LI⁺X⁻ 9 or 11 are not relevant because of the absence of ionic interactions between the pollutant and the polymer or because of the physical diffusion of CD-LI⁺X⁻ through the dialysis membrane. After validation of the extraction capacity of the support in dialyzer conditions, a liquid/liquid extraction led to the pollutant model and regenerated after lyophilization the free support CD-LI⁺PSS⁻ 13, ready for a new use. Consequently, even if the complexation between CD-LI⁺X⁻ and PSS "Na⁺" are due to weak associations,

![Fig. 9 Inclusion complexes studied: a with phenolphthalein (PP), b with p-nitrophenol (PNP), and c with anilinonaphthalene-6-sulfonic acid (2,6-ANS)](image)

Table 3 Percentage of inclusion of PP in CDs

| Equivalent of CD | β-CD | TRIMEB CD(OMe)-IL⁺PSS⁻ | 12* |
|------------------|------|-----------------------|-----|
| 1                | 70%  | 0%                    | 16% |
| 5                | 99%  | 0%                    | 22% |
| 10               | 93%  | 0%                    | -   |
| 15               | 94%  | 0%                    | 25% |
| 20               | 97%  | 0%                    | 25% |
| 25               | 98%  | 0%                    | 26% |

*1/44 CD-IL/SS experimental ratio
CD-IL\(^{+}\)PSS\(^{-}\) complex is stable under the conditions of purification and use. \(^1\)H NMR analysis confirmed the decomplexation step (\(^1\)H et 2,6-ANS).\(^\dagger\) The 2,6-ANS was recovered quantitatively attesting the future potential of this application. The inclusion and the release of pollutants in sediments and the recycling study of the material are in progress.

**Conclusion**

Two new ternary complexes CD(OMe)-IL\(^{+}\)PSS\(^{-}\) and CD-IL\(^{+}\)PSS\(^{-}\) were obtained by simple dialysis with a maximal CD/SS grafting rate of 25\% (1/4) and 20\% (1/5), respectively. The precursor can be easily synthesized in two steps in 77\% global yield. Theionic binding between an ionic polymer and a cationic ionic liquid was proved by NMR spectroscopies. The immobilization of CD-IL on polymer PSS was measured by SEC/MALS/DRI analysis. The permethylated CD derivatives showed a weak capacity for complexation. The properties of inclusion of the polyelectrolytes and their CDs precursors were studied by UV-visible, fluorescent, and NMR spectroscopies using three reference guests and compared with the properties of the native \(\beta\)-CD. The immobilization of a short ionic linker on \(\beta\)-cyclodextrin inhibited all intramolecular

| Equivalent of CD | \(\beta\)-CD | CD-NH\(_2\) 10 | CD-IL\(^{+}\)Br\(^{-}\) 11 | CD-IL\(^{+}\)PSS\(^{-}\) 13* |
|------------------|-------------|----------------|-----------------|-----------------|
| 1                | 70\%        | 65\%           | 62\%            | 66\%            |
| 5                | 90\%        | 85\%           | 87\%            | 82\%            |
| 10               | 93\%        | 92\%           | 93\%            | 86\%            |
| 15               | 94\%        | -              | 93\%            | 88\%            |
| 20               | 97\%        | 96\%           | 96\%            | 88\%            |
| 25               | 98\%        | 96\%           | 96\%            | 89\%            |

\(*1/25\) CD-IL/SS experimental ratio

---

**Fig. 10** 2D ROESY NMR spectrum (D\(_2\)O, 300 MHz, 400 ms, 16 mM) of CD(OMe)-IL\(^{+}\)PF\(_6\)\(^{-}\)

**Fig. 11** a Fluorescent spectrum of 2,6-ANS in the presence of various concentrations of CD-IL\(^{+}\)PSS\(^{-}\) 13 in aqueous buffer (concentration varying between 0 to 2 mM). b Fluorescent titration of 2,6-ANS with CD-IL\(^{+}\)PSS\(^{-}\) 13 in aqueous buffer (concentration varying between 0 to 0.004 M)
inclusion phenomena and provided certain flexibility to improve the electrostatic interactions with PSS. This strategy left free the hydrophobic cavities of CD for a complexation. The monosubstitution of hydroxylated CD by an ionic liquid supported by an anionic polymer has a positive effect on the ability of host-guest inclusion. The advantage of using the CD-LI⁺PSS⁻ support instead of CD-LI⁺X⁻ is double: enhancement of the captation rate of pollutant and limitation of the possible diffusion of the material during the dialysis step. Indeed, the higher retention of guests is due to the synergy between the polymeric matrix and the cyclodextrin cavity. Finally, a higher grafting generated the higher complexation abilities proving the absence of intermolecular interactions and the absence of steric hindrance of the polymeric matrix. In perspective, this new water-soluble ternary complex CD-IL⁺PSS⁻ could be an interesting tool for water dialysis device.

In the presence of dialysis membrane, this captor is an alternative to adsorption purification techniques (sand filter, activated charcoal, exchange of ions) and could be kinetically more efficient due to the presence of a the homogeneous medium. Polluting molecules could be faster preconcentrated in a fluid environment. This simple and flexible synthetic strategy opens the way to new hybrid materials with great potential. Complementary tests in the presence of solution sediment suspended are in progress in collaboration with a geology laboratory to reach a gradient concentration of organic pollutants in shorter equilibrium time. Then, the optimized device will be applied in temperate zone of the Seine Estuary (France) and in tropical zone of the Somone Estuary (Senegal).

Table 5  Fluorescent titration and association constants of 2,6-ANS inclusion complex in CDs

| CD         | CD-IL/SS | $F_{\text{max}}/F_0$ | $K_s$ (M⁻¹) |
|------------|----------|----------------------|-------------|
| β-CD       | -        | 8.90                 | 3360 ± 720  |
| CD-NH₂ 10  | -        | 11.02                | 2210 ± 450  |
| CD-IL Br⁺ 11 | -      | 12.41                | 3350 ± 430  |
| CD-IL⁺PSS⁻ 13 | 1/25     | 13.82                | 9550 ± 500  |
| CD-IL⁺PSS⁻ 13 | 1/20     | 14.38                | 11,070 ± 860|

*a Solvent: methanol:water 30:70 (v:v)*

![Plot of $1/(F/F_0 - 1) = f(1/[CD-LI⁺PSS⁻])$; the solid line is the linear adjustment.](image)

**Fig. 12** Plot of $1/(F/F_0 - 1) = f(1/[CD-LI⁺PSS⁻])$; the solid line is the linear adjustment.

**Fig. 13**

a) Dialyzer design. b) Dialyzer used in this study. c) Dialyzer in sediment.
Acknowledgements We thank Christophe Rihouey from PBS laboratory for the chromatography analysis. We are also grateful for the company Cyclolab, https://cyclolab.hu/, for its contribution by sending β-CD-NH₂ 10.

Author contribution Conceptualization, G.G. and D.L.; Methodology, G.G., D.L., C.K.-D., F.G., V.M. and M.L.; Validation, G.G., D.L., C.K.-D., F.G., V.M.; Formal Analysis, A.B., S.B., A.F.-H., F.G., B.S.S.B. and C.K.-D.; Investigation, A.B., S.B., A.F.-H., F.G., B.S.S.B. and C.K.-D.; Writing-Original draft preparation G.G.; Writing-review and editing, G.G., D.L., M.L, F.G, V.M. and C.K.-D.; Supervision, G.G., D.L., C.K.-D., F.G. and M.L.; Project administration, Funding acquisition, G.G., M.L. and D.L.

Funding This work was supported by “le Conseil Régional de Haute-Normandie” and “l’Institut Normand de Chimie Moléculaire, Macromoléculaire et Médicinale” INC3M, FR 3038 CNRS (A. F.-H.). We are grateful to Eramus Mundus program Battuta for the fellowship (A. B.), the CNRS/CNRST international program (A. B.), and the MRT for their financial supports (B. S. S. B). This work has been partially supported by University of Rouen Normandy, INSA Rouen Normandy, the Centre National de la Recherche Scientifique (CNRS), European Regional Development Fund (ERDF), Labex SynOrg (ANR-11-LABX-0029), Carnot Institute I2C, the graduate school for research XL-Chem (ANR-18-EURE-0020 XL CHEM), and by Région Normandie. We also received financial support from the European Union for the purchase of equipment.

Data availability All data generated or analyzed during this study are included in this published article. Supplementary materials are represent ed by the dagger symbol in the text. The materials, method, synthesis, and characterization details of products 2, 3, 4, 7, 9, 11, 12, and 13 are available online. Graphs of ρ-nitrophenol inclusion study (absorbance and job plot, stability constants table) and NOESY NMR of inclusion complex of 13:2,6-ANS obtained with the dialyzer were also reported.

Declarations

Ethics approval The authors confirm that the manuscript has been read and approved by all authors and not under consideration for publication elsewhere.

Consent to participate The authors have been personally and actively involved in substantive work leading to the manuscript and will hold themselves jointly and individually responsible for its content.

Consent for publication The authors consent to publish this research.

Competing interests The authors declare no competing interests.

References

Amiel C, Galant C, Avraay L (2004) Ternary complexes involving a β-cyclodextrin polymer, a cationic surfactant and an anionic polymer. Progr Colloid Polym Sci 126:44–46. https://doi.org/10.1007/bf03967

Anderson JL, Clark KD (2018) Ionic liquids as tunable materials in (bio)analytical chemistry. Anal Bioanal Chem 410:4565–4566. https://doi.org/10.1007/s00216-018-1125-4

Antoniuk I, Amiel C (2016) Cyclodextrin-mediated hierarchical self-assembly and its potential in drug delivery applications. J Pharm Sci 1-19. 105:2570–2588. https://doi.org/10.1016/j.xphs.2016.05.010

Badruddoza AZ, Bhattachar B, Suri RPS (2017) Environmentally friendly β-cyclodextrin-ionic liquid polyurethane-modified magnetic sorbent for the removal of PFOA, PFOS, and Cr(VI) from water. ACS Sustain Chem Eng 5:9223–9232. https://doi.org/10.1021/acssuschemeng.7b02186

Bakheet AAA, Liu J, Zhu X (2016) New magnetic solid phase extractor based on ionic liquid modified β-cyclodextrin polymer/Fe₃O₄ nano-composites for selective separation and determination of Linuron. J Anal Sci Techn 7:1–10. https://doi.org/10.1186/s40543-016-0082-9

Bakheet AAA, Zhu XS (2017) Determination of rhodamine B in food samples by Fe₃O₄@ionic liquids-β-cyclodextrin cross linked polymer solid phase extraction coupled with fluorescence spectroscopy. J Fluoresc 27:1087–1094. https://doi.org/10.1007/s10895-017-2042-1

Bally G, Mesnage V, Deloffre J, Clarisse O, Lafite R, Dupont J-P (2004) Chemical characterization of porewaters in an intertidal mudflat of the Seine estuary: relationship with erosion–deposition cycles. Mar Pollut Bull 49:163–173. https://doi.org/10.1016/j.marpulbul.2004.02.005

Bally G, Mesnage V, Verney R, Clarisse O, Dupont J-P, Ouddanne B, Lafite R (2005) Exchange and release processes dialysis porewater sampler: a strategy for time equilibration optimization. In: Seranno, L., Golteman, H.L., (Eds.), Phosphates in Sediments, Proceedings of the 4th International Symposium. Backhuys, The Netherlands, 9–20.

Barhoumi Z, Saini M, Amdouni N, Pal A (2016) Interaction between amphiphilic ionic liquid 1-butyl-3-methylimidazolium octyl sulfate and anionic polymer of sodium polystyrene sulfate in aqueous medium. Chem Phys Lett 661:173–178. https://doi.org/10.1016/j.cplett.2016.08.016

Brinkman A, Van Raasphorst W, Lijklema L (1982) In situ sampling of interstitial water from lake sediments. Hydrobiologia 92:659–663. https://doi.org/10.1007/BF00000065

Bufflap SE, Allen HE (1995) Sediment pore water collection methods for trace metal analysis: a review. Water Res 29:165–177. https://doi.org/10.1016/0043-1354(94)E0105-F

Cyclolab (2021) Compounds 8 and 10 are also commercially available: https://cyclolab.hu/products/cationic_cyclodextrins-c18

D’Souza VT (1998) Cyclodextrins. Chem Rev 98:1741–2076. https://doi.org/10.1021/cr980027p

Eftink MR, Harrison JC (1981) Calorimetric studies of p-nitrophenol binding to α- and β-cyclodextrin. Bioorg Chem 10:388–398. https://doi.org/10.1016/0045-2068(81)90051-1

Favrelle A, Gouhier G, Guillen F, Martin C, Mofaddel N, Mundy K, Pitre S, Wagner B (2015) Structure–binding effects: comparative binding of 2-anilino-6-naphthalenesulfonate by a series of alkyl- and hydroxyalkyl-substituted β-cyclodextrins. J Phys Chem B 119:12921–12930. https://doi.org/10.1021/acs.jpcb.5b07157

Galant C, Amiel C (2004) Tailorable polyelectrolyte complexes using cyclodextrin polymers. J Phys Chem B 108:19218–19227. https://doi.org/10.1021/jp047494x

Gao Q, Liu W, Zhu X (2020) Glycine ionic liquid functionalized β-cyclodextrin polymer high-performance liquid chromatography for the separation/analysis of pyrethroids. J Liquid Chromat Related Tech 43:809–818. https://doi.org/10.1080/10826078.2020.1816550

Gelb RI, Raso S, Alper JS (1995) Complexation reactions of β-cyclodextrin, β-(2,3,6-O-methyl) cycloheptaamylose and γ-cyclodextrin with phenolphthalein, adamantane carboxylate and adamantane ac etate. Supramol Chem 4:279–285. https://doi.org/10.1080/10610279508028937

Hallett JP, Welton T (2011) Room-temperature ionic liquids: solvents for synthesis and catalysis. Chem Rev 111:3508–3576. https://doi.org/10.1021/cr1003248
dispersive liquid–liquid microextraction coupled with high-performance liquid chromatography for the fast determination of four fungicides in water samples. J Chromatogr A 1381:37–47. https://doi.org/10.1016/j.chroma.2015.01.016

Yusoff MM, Raoov M, Yahaya N, Salleh NM (2017) An ionic liquid loaded magnetically confined polymeric mesoporous adsorbent for extraction of parabens from environmental and cosmetic samples. RSC Adv 7:35832–35844. https://doi.org/10.1039/C7RA06682A

Zgani I, Idriss H, Barbot C, Djedaini-Pilard F, Petit S, Hubert-Roux M, Estour F, Gouhier G (2016) Positive variation of the MRI signal via intramolecular inclusion complexation of a C-2 functionalized β-cyclodextrin. Org Biomol Chem 15:564–569. https://doi.org/10.1039/C6OB02583H

Zhao F, Xiao F, Zeng B (2010) Electrodeposition of PtCo alloy nanoparticles on inclusion complex film of functionalized cyclodextrin-ionic liquid and their application in glucose sensing. Electrochem Commun 12:168–171. https://doi.org/10.1016/j.elecom.2009.11.016

Zhou C, Deng J, Shi G, Zhou T (2017) β-cyclodextrin-ionic liquid polymer based dynamically coating for simultaneous determination of tetracyclines by capillary electrophoresis. Electrophoresis 38:1060–1067. https://doi.org/10.1002/elps.201600229

Zhou N, Zhu XS (2014) Ionic liquids functionalized β-cyclodextrin polymer for separation/analysis of magnolol. J Pharm Anal 4:242–249. https://doi.org/10.1016/j.jpha.2013.12.005

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.