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

Asmaa Bouyahya
Rouen University: Universite de Rouen
Berthe-Sandra Sembo-Backonly
Rouen University: Universite de Rouen
Audrey Favrelle-Huret
Université des Sciences et Technologies de Lille: Universite de Lille
Sébastien Balieu
Université de Rouen: Universite de Rouen
Frédéric Guillen
Universite de Toulouse 3: Universite Toulouse III Paul Sabatier
Valérie Mesnage
Universite de Rouen
Carole Karakasyan-Dia
Rouen University: Universite de Rouen
Mohammed Lahcini
Université Cadi Ayyad Faculté des Sciences et Techniques Marrakech: Universite Cadi Ayyad Faculte des Sciences et Techniques Gueliz
Didier Le Cerf
Universite de Rouen UFR des Sciences et Techniques
Géraldine Gouhier (geraldine.gouhier@univ-rouen.fr)
Université de Rouen: Universite de Rouen https://orcid.org/0000-0002-3852-1827

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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.

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-D-(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, 1f) 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), Fe_3O_4 (Sinniah et al. 2015, Bahadorikhalili et al. 2019), 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). Finally, magnetic starch based on CD-IL was used as organic catalyst (Bahadorikhalili et al. 2019).

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 polymer attached to Fe_3O_4 nanoparticles achieved the speciation analysis of manganese in water samples (Quin et al. 2016), herbicides in fruits and vegetables (Bakheet et al. 2016a), parabens in cosmetics (Yusoff et al. 2017), rhodamine B in food samples (Bakheet and Zhu 2017b), and PFOA, PFOS and Cr(VI) in wastewater (Badruddoza 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 and 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, 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.

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). Two routes have been developed leading to two different ILs with PF_6^- 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 ($MeSiCl_3$) in 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 KPF_6 in ACN of **4** generated the desired IL **5** with good yield and was confirmed by ^1H, ^{31}P and ^{19}F NMR spectroscopies. Thus, the chemical shift observed for the protons and carbons of the imidazolium group validated this total conversion. As the PF_6^- 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-methylimidazole 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) 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 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 two 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 25–57%. We observed a large increase in water solubility of the CD derivatives in presence of PSS polymer.

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

Theoretical Ratio CD(OMe)-IL 9/SS	M_n (g/mol)	M_w (g/mol)	Rh[a] (nm)	Experimentalratio[b] CD-IL 9/SS	Grafting efficiency[c]
0/1	45,000	68,000	10.4	-	-
1/25	53,000	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 = [Mo(CD-IL)xMn(PSS)]/[[(Mn(CD-IL$^+$PSS–Mn(PSS)]xMo(PSS)] with Mo(CD-IL) = 1579

g/mol and Mo(PSS) = 207 g/mol

[c] x(theoretical)/x (experimental)x100

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 (Đ=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).

Table 2

SEC analysis of CD-IL$^+$PSS$^-$**13** with various ratios

Theoretical Ratio CD-IL 11/SS	M_n g/mol	M_w g/mol	Rh nm	Experimental ratio[a] CD-IL 11/SS	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 = [Mo(CD-IL)xMn(PSS)]/[[(Mn(CD-IL$^+$PSS−Mn(PSS)]xMo(PSS)] with Mo(CD-IL) = 1312.5 g/mol and Mo(PSS) = 207 g/mol

[b] x(theoretical)/x (experimental)x100

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 CDs derivatives and their precursors to evaluate the influence of each modification. Three reference molecules were tested: phenolphtalein (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 (Ks) 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 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 (Ks = 204 M^{-1}) (Tagushi 1986; Gelb and al. 1995) and 2,6-ANS (Ks = 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).

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	90%	0%	22%
10	93%	0%	-
15	94%	0%	25%
20	97%	0%	25%
25	98%	0%	26%
*1/44 CD-IL/SS experimental ratio			

The presence of an ionic liquid linker did not improve the water dissolution of CD(OMe)-IL$^+$PF$_6^-$ **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)-NH$_2$ **8** and CD(OMe)-IL$^+$PF$_6^-$ **9**. As the intermolecular inclusion of counter ion PF$_6^-$ 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 PF$_6^-$ anion of **9** into the cavity. The experiment was carried out on CD(OMe)-IL$^+$PSS$^-$ **12** 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 D$_2$O 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 b-CD moiety fully supports this conclusion (empty scare in Fig. 10). Finally, as the dialysis step eliminated all traces of PF$_6^-$ counter ion, the cavity of CD of **12** is undoubtedly available.

From these preliminary results, we focused our study on CD-LI$^+$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-NH$_2$ **10**, CD-IL$^+$Br$^-$ **11** et 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.

Table 4
Percentage of inclusion of PP in CDs

Equivalent of CD	β-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				

82% And 90% of PP were encapsulated in the CD-IL^+PSS^- **13** and in β-CD in 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-NH_2 **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). Besides, the low concentration used during the immobilization on PSS does not favor the interaction between the IL unit and another CD cavity (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 (Tagushi 1986; Gelb et al. 1995). This experiment was performed with the protonated form of *p*-nitrophenol. A molar extinction coefficient of 18801 $L.mol^{-1}.cm^{-1}$ at 400 nm was confirmed in presence of β-CD. The Job plot experiment also confirmed the 1:1 β-CD/PNP stœchiometry. The study was then carried out with 0 to 1.5 mmol/L of CD-IL^+Br^- **11** (0 to 30 equivalents) and an association constant of Ks = 200 M^{-1} was calculated with a negative standard free enthalpy $\Delta rG°_{exp}$ = -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 (β-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 $\lambda_{F,max}$ at 467 nm in absence of CD at 2 mM

shifted, respectively, of 20, 42, 23, and 20 nm in presence of β-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/Fo obtained depends on the CD derivative concentration provided association constant Ks; a maximal value corresponding to 100% of inclusion (Eq. 1–3, Table 5). Higher values of Ks indicate a higher affinity of ANS for CD because of a more apolar cavity (Favrelle et al. 2015)

$$CD + ANS \leftrightarrow CD{:}\,ANS \quad (1) \qquad Ks = \frac{[CD{:}\,ANS]}{[CD] \times [ANS]} \quad (2) \qquad {}^{F}/_{Fo} = 1 + (F\infty/Fo - 1)\frac{[CD].\,Ks}{(1 + [CD].\,Ks)} \quad (3)$$

F: Integrated area of the fluorescence spectrum; Fo: Total fluorescence intensity in the absence of CD; F∞: Maximum fluorescence enhancement

In 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 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).

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

CD	CD-IL/SS	F_{max}/F_0[a]	Ks (M^{-1})
β-CD	-	8.90	3,360 ± 720
CD-NH_2 **10**	-	11.02	2,210 ± 450
CD-IL^{-}Br^{+} **11**	-	12.41	3,350 ± 430
CD-IL^{+}PSS^{-}**13**	1/25	13.82	9,550 ± 500
CD-IL^{+}PSS^{-}**13**	1/20	14.38	11,070 ± 860
[a]Solvent: methanol:water 30:70 (v:v)			

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 Ks values for CD-IL^{+}PSS^{-} **13** with 1/25 and 1/20 ratio respectively, by comparison with CD-IL^{-}Br^{+} **11**.

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/Fo-1) in function of 1/[CD] is representative of the stœchiometry of the 2,6-ANS/CD complex (Eq. 4) (Favrelle et al. 2015).

1/((F/Fo - 1)) = (1/[CD])

In presence of 1 equivalent of host CD linear plots (R^2 = 0.997) were observed with **13** for both grafting rate (1/25 and 1/20 CD/SS) validating the 1:1 stœchiometry (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 sediments and overestimates the nutrient concentrations by desorbing the ions fixed onto the particles. The second one is based on an *in-situ* approach which uses dialyzer devices that are introduced in the sediment in which the pores are filled after an equilibration time at the sediment water interface. The main strategies of pore-water sampling are dialysis (Hesslein 1976), DET (Diffusive equilibration in thin films, Davison et al. 2000) and DGT (Diffusive gradients in thin films, Zang and Davison 1995).

The support obtained found an application in a dialysis porewater sampler, type Hesslein, to extract and release pollutants from sediment in the long-term (Fig. 13C). This dialyzer is commonly used in geology studies to identify the pollutant concentration in the various layers of estuaries sediment by studying the interstitial water according to a continuous gradient between the sediment and the water column over 30 cm height (Bally et al. 2004, 2005; Mesnage et al. 2007, 2013). The nutrient concentrations gradients led to nutrients fluxes calculation via a numerical diffusion model at the sediment-water interface. The main disadvantage compared to other methods (DGT or DET, Zang and Davison, 1995) is its long equilibration time (20 days related to the sediment type).

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 quencher was introduced into the cavities of the dialyzer and 2,6-ANS was used as a pollutant model (Fig. 13A 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 hours), each cell was extracted and the presence of 2,6-ANS was confirmed by UV-Visible spectroscopy. *In-situ*, in presence of sediment, an equilibration time of 3 weeks is usually needed. 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 presence of PSS$^-$Na$^+$ or CD-LI$^+$Br$^-$ **11** could not be efficient because of the absence of anion interactions with the

polymer or the diffusion of CD-LI$^+$PF$_6^-$ **13** 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. ^{1}H NMR analysis confirmed the decomplexation step (**13** et 2,6-ANS). The 2,6-ANS was recovered quantitatively attesting the future potential of this application.

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. The ionic 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 β-CD. The immobilization of a short ionic linker on β-cyclodextrin inhibited all intramolecular 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 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 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 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).

Declarations

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Authors'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.

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Data availability All data generated or analyzed during this study are included in this published article. Supplementary Materials is represented by the symbol † in the text. The materials, method, synthesis and characterization details of products **2, 3, 4, 7, 9, 11, 12 13** are available online. 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.

Competing interests The authors declare that they have no conflict of interest.

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.

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Figures

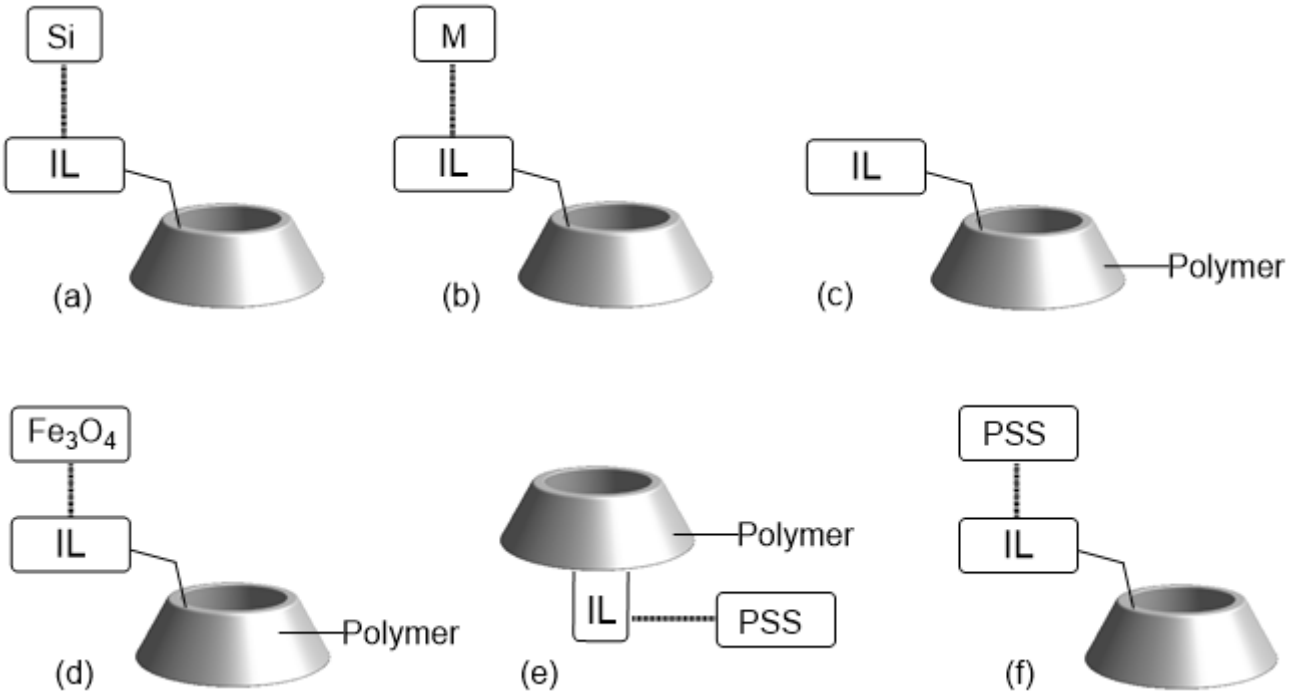

Figure 1

Tripartite associations between cyclodextrin, ionic liquid (IL) and supports: published (a, b, c, d, e), this work (f). M=Metal, Si: silica, PSS: poly(styrene sulfonate)

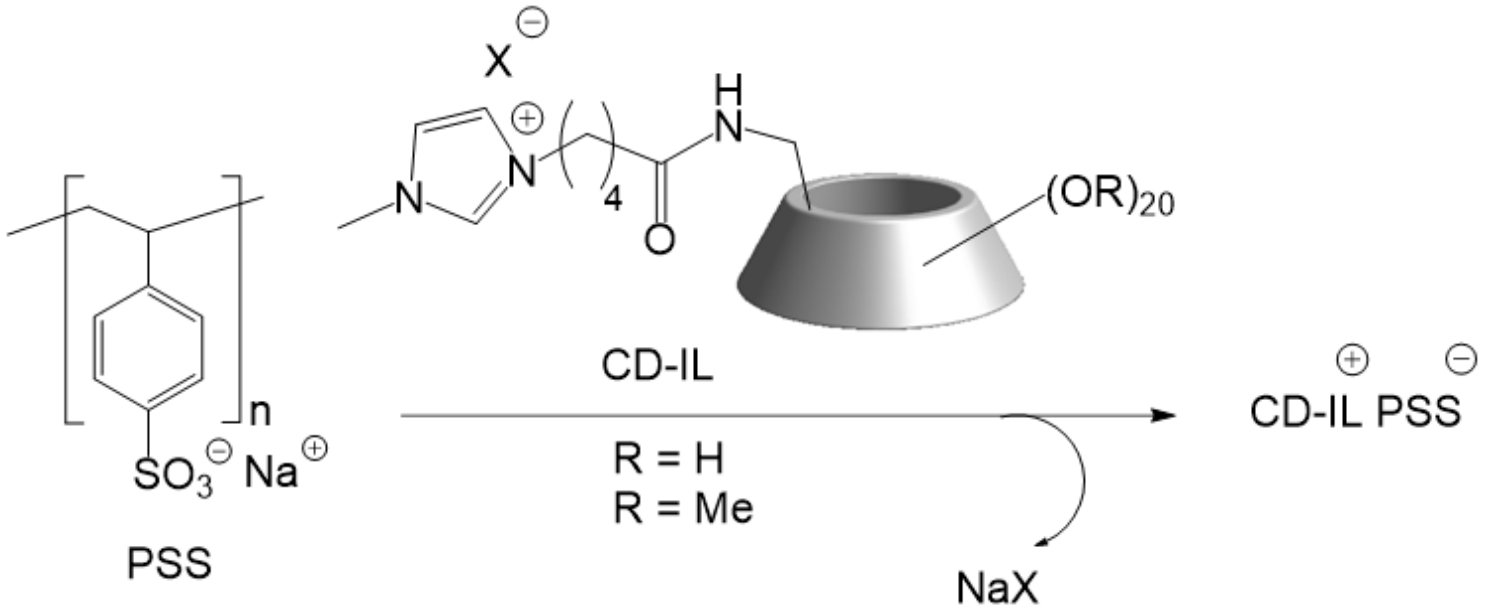

Figure 2

Immobilization of cyclodextrin-ionic liquid (CD-IL) on poly(styrene sulfonate) (PSS)

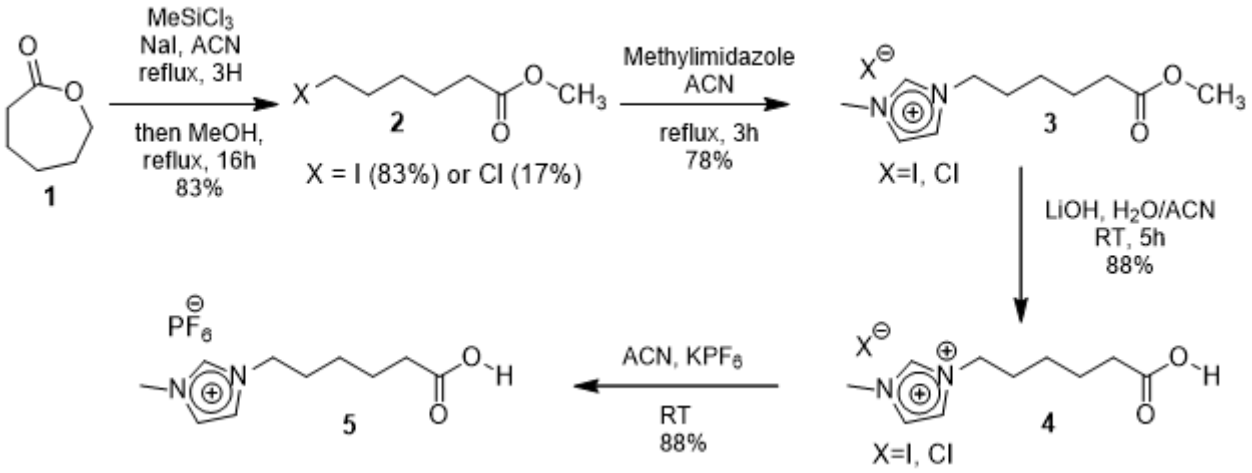

Figure 3

Synthesis of ionic liquid precursor 5

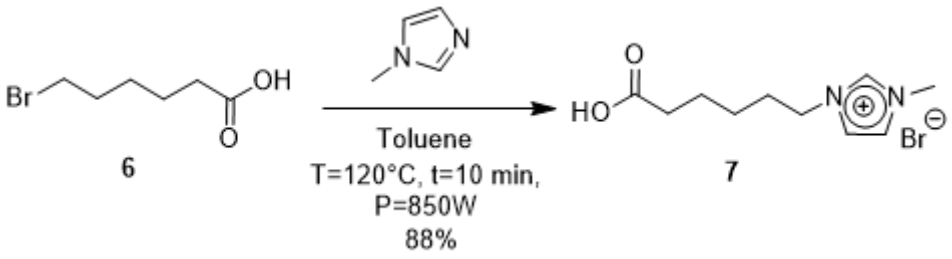

Figure 4

Synthesis of ionic liquid precursor 7

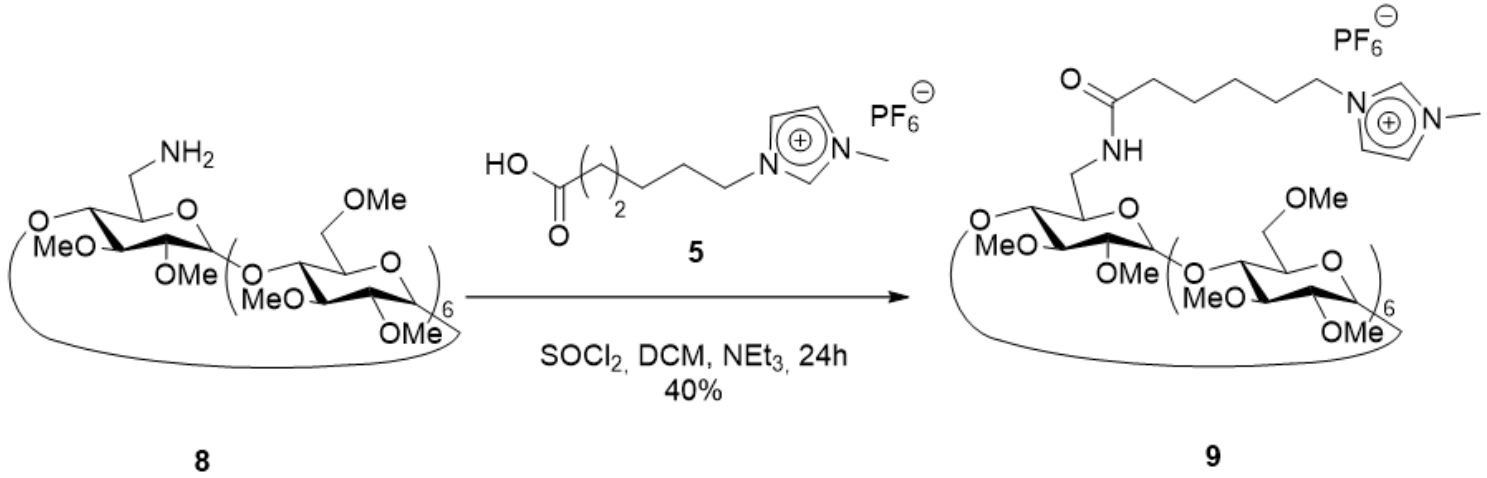

Figure 5

Synthesis of CD(OMe)-IL+PF6- 9

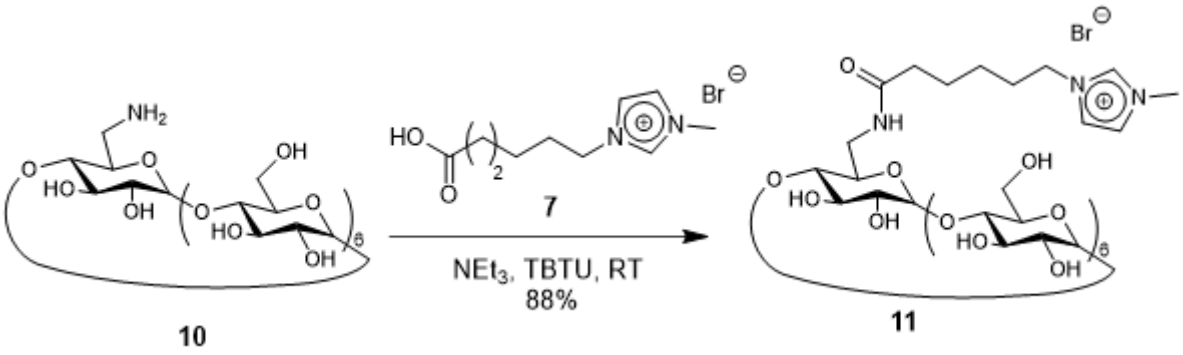

Figure 6

Synthesis of CD-IL+Br- 11

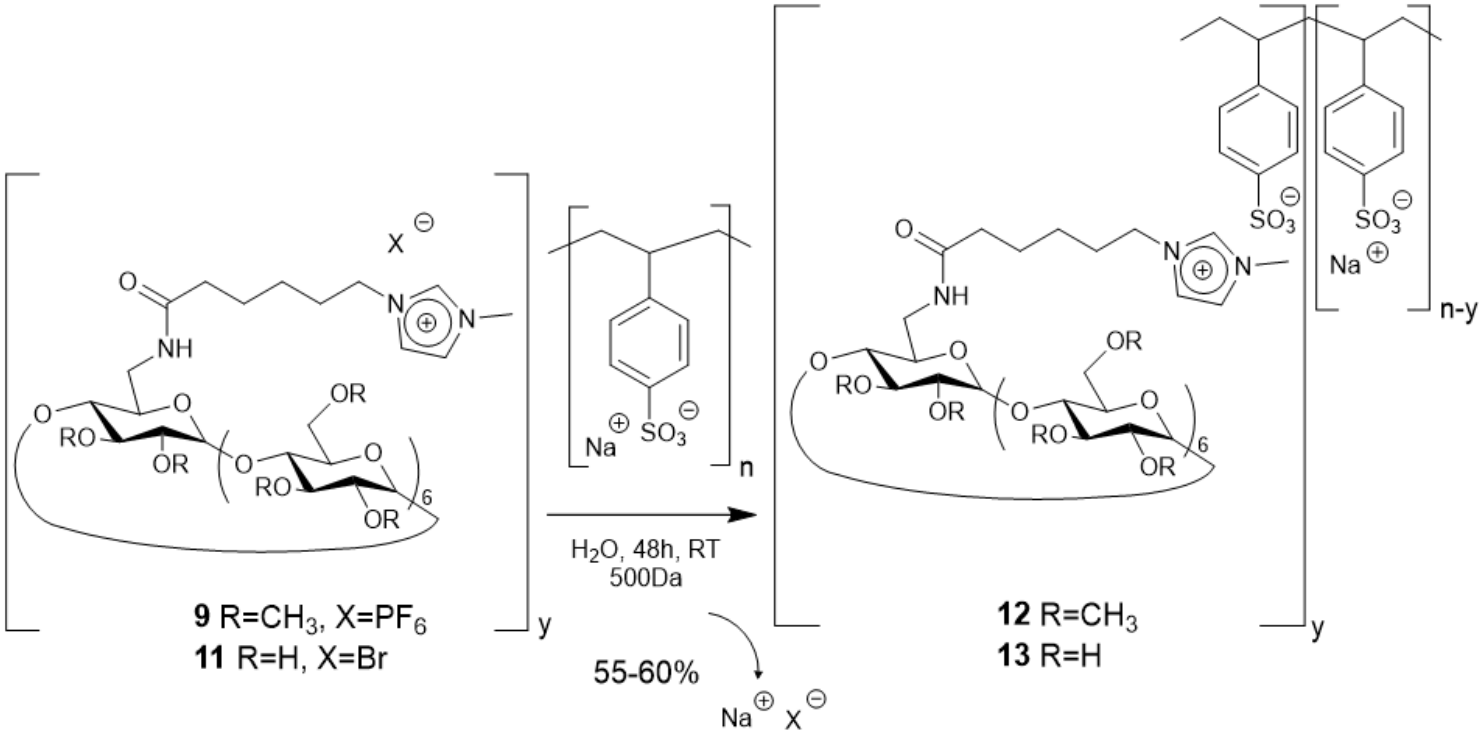

Figure 7

Synthesis of CD(OMe)-IL+PSS- 12 and CD-IL+PSS- 13 by dialysis against deionized water

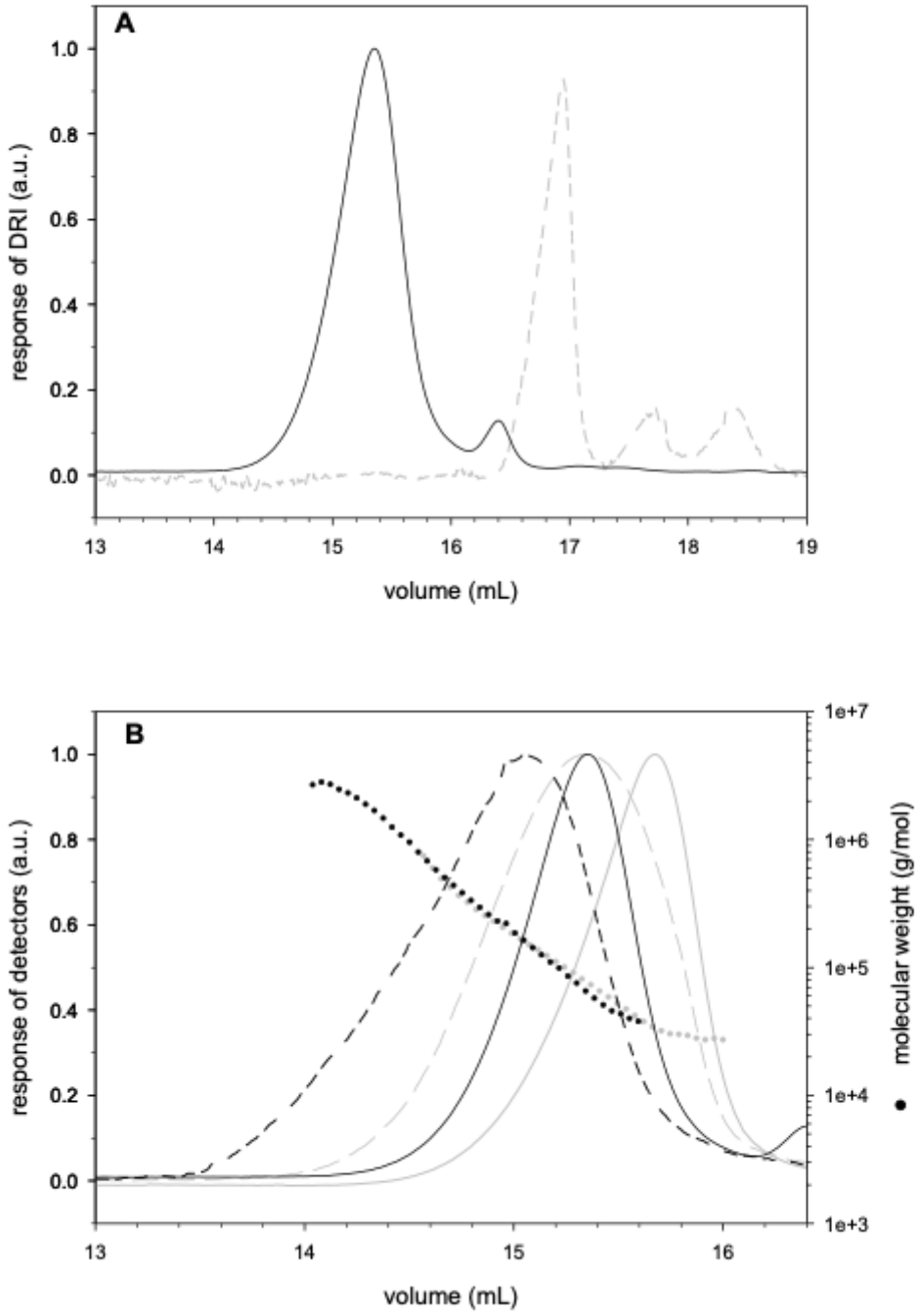

Figure 8

A) Elution profiles obtained by SEC from refractive index of CD(OMe)-IL+Br- 11 (gray dotted line) and CD(OMe)-LI+PSS- 12 with theoretical ratio 1/5 (black full line)) in LiNO3 0.001 mol/L at 25°C; B) Elution profiles obtained by SEC from refractive index (full lines) and Light scattering at 90° (dotted lines) of PSS-Na+ (gray) and CD(OMe)-IL+PSS- 12 with theoretical ratio 1/5 (black) together with molecular weights distribution in LiNO3 0.001 mol/L at 25°C

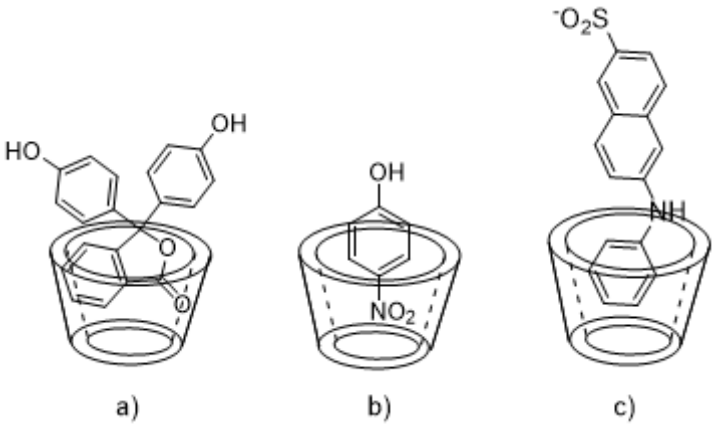

Figure 9

Inclusion complexes studied: a) with phenolphtalein (PP), b) with p-nitrophenol (PNP), c) with anilinonaphthalene-6-sulfonic acid (2,6-ANS)

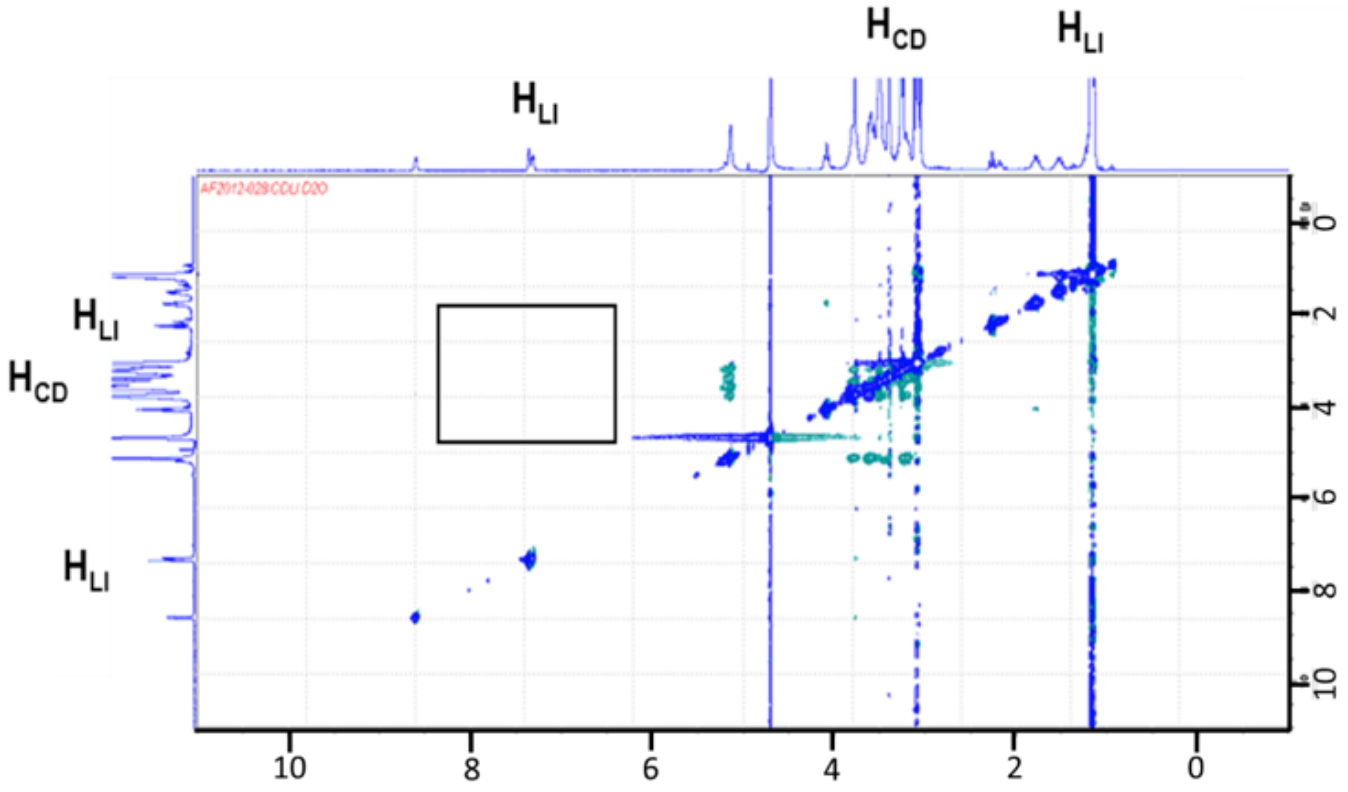

Figure 10

2D ROESY NMR spectrum (D2O, 300 MHz, 400 ms, 16 mM) of CD(OMe)-IL+PF6- 9

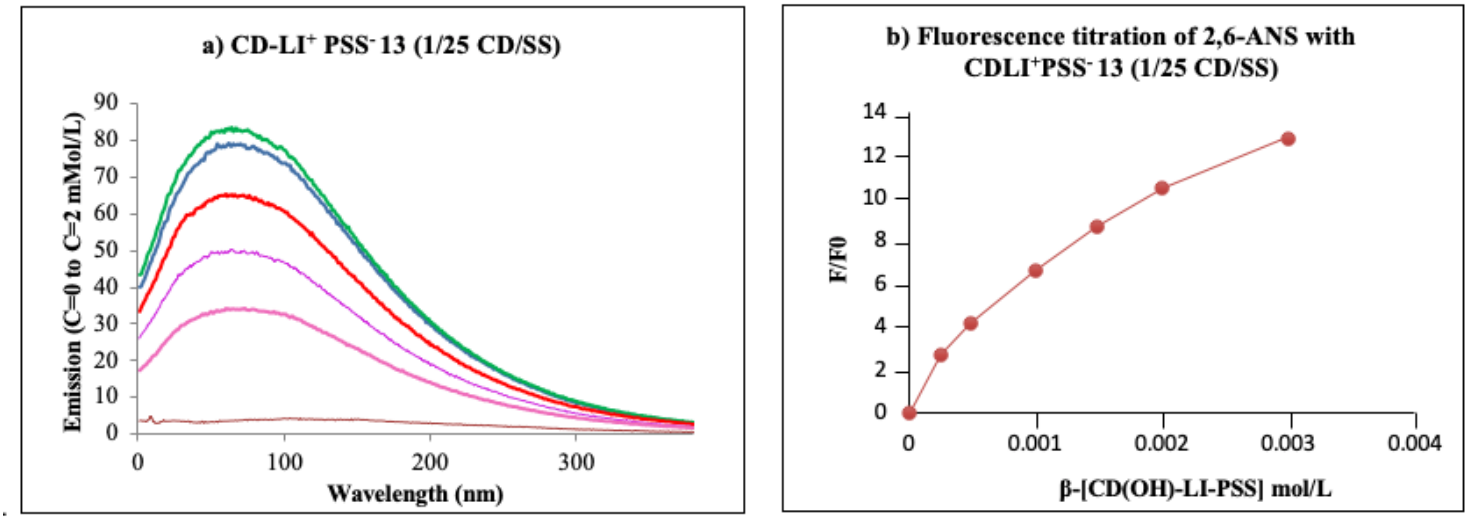

Figure 11

a) Fluorescent spectrum of 2,6-ANS in 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)

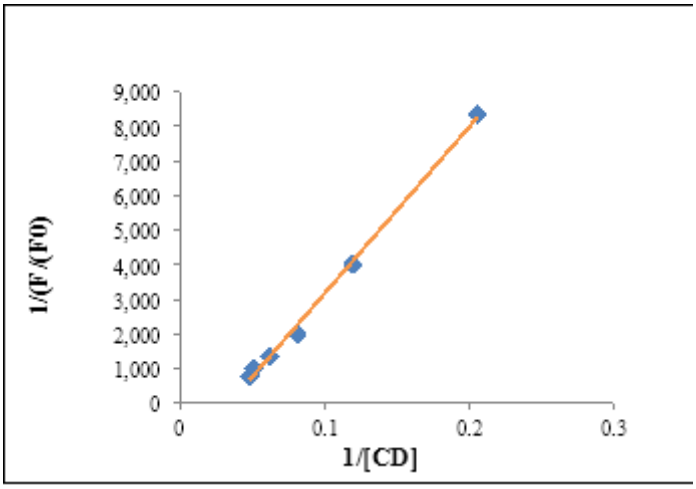

Figure 12

Plot of 1 / (F / F0-1) = f (1 / [CD-LI+PSS-]); the solid line is the linear adjustment.

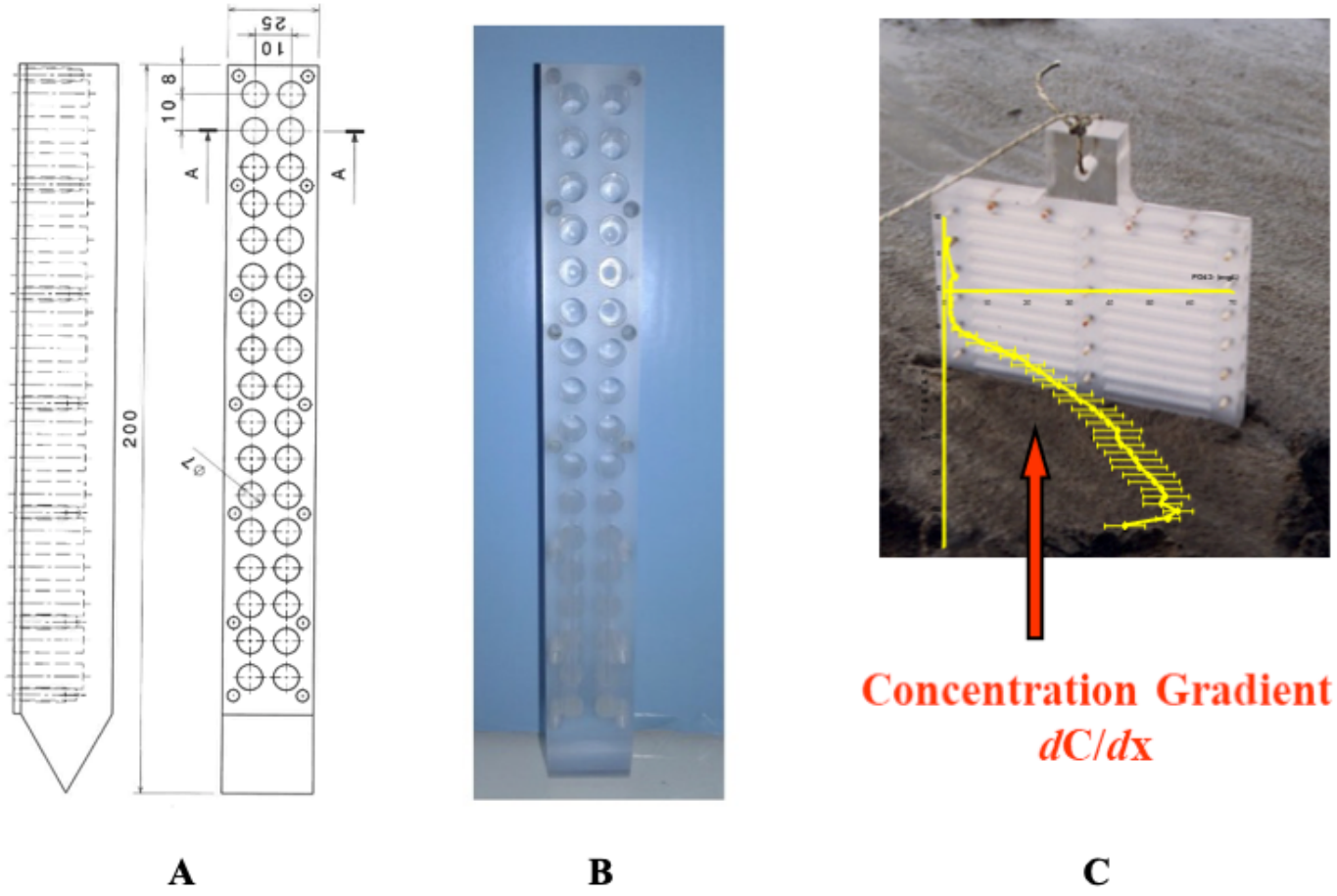

Figure 13

A. Dialyser Design; B. Dialyser used in this study; C. Dialyzer in sediment

Supplementary Files

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