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Selective Environmental Remediation of Strontium and Cesium Using Sulfonated Hypercrosslinked Polymers (SHCPs)

Alex M. James,[a] Samuel Harding,[a] Thomas Robshaw[ab] Neil Bramall,[a], Mark D. Ogden[b] and Robert Dawson[a]*

[a]Department of Chemistry, Dainton Building, University of Sheffield, UK, S3 7HF

[b]Department of Chemical and Biological Engineering, Sir Robert Hadfield Building, University of Sheffield, UK, S1 3JD

ABSTRACT: Sulfonated hypercrosslinked polymers based on 4,4'-bis(chloromethyl)-1,1'-biphenyl (BCMBP) were synthesized via metal-free (SHCP-1) and conventional Lewis acid-catalyzed (SHCP-2) Friedel-Crafts alkylation routes. The sulfonated polymers possessed BET surface areas in excess of 500 $m^2 \cdot g^{-1}$. SHCP-1 was investigated for its ability to extract Sr and Cs ions from aqueous solutions via the ion-exchange reaction of the sulfonic acid moiety. Equilibrium uptake data could be accurately modelled by the Dubinin-Radushkevich isotherm, with maximum calculated loading values of 95.6 ± 2.8 $mg \cdot g^{-1}$ (Sr) and 273 ± 37 $mg \cdot g^{-1}$ (Cs). Uptake of both target ions was rapid, with pseudo 2nd-order rate constants calculated as 7.71 ± 1.1 (x 10^{-2}) for Sr and 0.113 ± 0.014 for Cs. Furthermore, the polymer was found to be highly selective towards the target ions over large excesses of naturally occurring competing metal ions Na, K, Mg and Ca. We conclude that hypercrosslinked polymers may offer intrinsic advantages over other adsorbents for the remediation of aqueous Sr and Cs contamination.

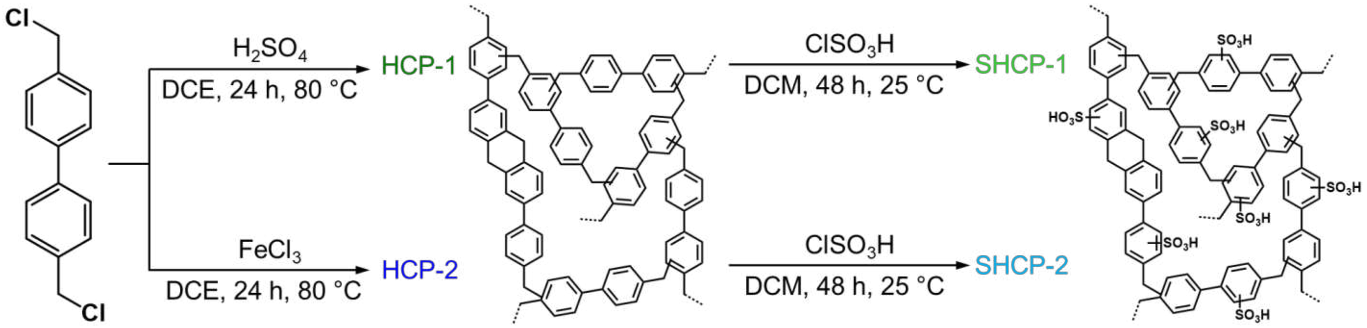
Keywords: porous materials, microporous polymers, metal-free synthesis, ion-exchange, separations,

Introduction

Prior to 1986, the release of fission products to the environment was predominantly as a result of nuclear weapons testing and direct discharges from nuclear reprocessing facilities.[1] Since then, the world has seen two category 7 nuclear accidents at Chernobyl in the Ukraine (1986) and Fukushima Daiichi (2011) in Japan which resulted in the uncontrolled release of fission products into the environment. Fission products ^{137}Cs and ^{90}Sr are of a particular concern due to both their radiotoxicity and their ability to bioaccumulate.[2] ^{137}Cs ($t_{1/2}$ = 30.17 years) is a strong beta–gamma emitter and ^{90}Sr ($t_{1/2}$ = 28.8 years) is a beta emitter and a large source of radiation, having a specific activity of 5.21 $TBq \cdot g^{-1}$.[3] Cesium metabolically and chemically behaves similarly to potassium and sodium in terrestrial ecosystems, whereas strontium behaves analogously to calcium.[4] It is estimated that 1.5 x 10^{16} Bq of ^{137}Cs was released from the Fukushima Daiichi accident and 3.8 x 10^{16} Bq from Chernobyl.[2] ^{90}Sr releases were estimated much lower with activities of 4 x 10^{15} [5] and 3.5 x 10^{13} Bq[6] for the Chernobyl and Fukushima Daiichi accidents respectively.

A variety of techniques have been applied to the removal of these problematic radionuclides from ground water and aqueous solutions. Previous tests, using conventional water treatment technologies of coagulation, flocculation and settling proved only effective enough to remove 56% of ^{137}Cs[7] and 5.9-12% of ^{90}Sr[8] depending on the coagulant. Solvent extraction systems have also been widely studied. These generally use a crown ether functionality, with selectivity related to cavity size. Such materials have demonstrated good recoveries, but require carefully-chosen, poorly-hydrated counteranions to maximize efficiency[9-11] and their potential for use in direct environmental remediation is obviously limited.

In terms of solid-phase extractants, adsorbents based on ion-exchange have demonstrated good efficacy in the removal of these radionuclides from a variety of aqueous solutions. Examples of these are polymeric resins,[4,12] natural and synthetic zeolites,[13,14] titanates,[15] silica,[16] and titanosilicates.[17] Inorganic ion-exchangers are more mechanically and thermally stable than their polymer counterparts, offer good resistance to radiolysis and have high capacity in many cases (>3 $meq \cdot g^{-1}$).[18] However, the exchange processes are often reversible and Na and K ions at high concentrations can be significant interferences,[14,19] which is especially problematic for remediation of brine. Polymeric ion-exchangers are generally more chemically stable[20] and a wide variety of functionalities can be imparted on to the solid matrix for targeted and non-reversible ion removal.[21,22] There is therefore potential for the development of a novel, solid-phase adsorbent for capture of Sr and Cs ions, combining both selectivity and applied practicality. Key parameters for an effective ion-exchanger are the maximum loading capacity, which correlates directly to the number of exchanging moieties on the surface, and the rate of extraction. Porosity of the absorbent can be increased to effectively improve the sur face area but the diffusion of analytes into the porous network can slow the kinetics of the extraction.[20]



Scheme 1. Synthesis and sulfonation of hypercrosslinked polymer networks.

Hypercrosslinked polymers (HCPs) are a sub class of microporous organic polymers (MOPs) with high surface areas (typically 500-2000 $m^2 \cdot g^{-1}$).[23-25] They are both chemically and thermally stable, can be synthesized using cheap and facile methods from readily available precursors and can be easily functionalised.[26] Rigid aromatic monomers possessing "internal crosslinkers", such as chloromethyl groups, can be reacted *via* a Friedel-Crafts alkylation route in the presence of a Lewis-acid such as $FeCl_3$, $AlCl_3$ and $SnCl_4$.[27-29] Rigid aromatic monomers not possessing such internal crosslinkers can also be reacted *via* an "external crosslinker" such as formaldehyde dimethyl acetal. This strategy, referred to as the "knitting" method, was developed in 2011 by Tan and co-workers[30] and is a convenient way to introduce functionalization into the final material.[31,32] Although the metal catalysts used are effective and yield materials with high surface areas, they require stoichiometric quantities, produce large amounts of acidic waste, and have to be rigorously washed out of the network post-synthesis, yet in most cases cannot be completely removed from the final product. This is particularly relevant for water-treatment applications, as iron-fouling can be a significant issue in industrial ion exchange columns. Recently Schute *et al.* used H_2SO_4 as the Lewis-acid catalyst for the hypercrosslinking of a range of monomers *via* both internal and external crosslinking routes.[33] This method took less time to reach full conversion, did not require inert reaction conditions and was more economic and environmentally-friendly than metal-catalyzed synthesis. Although the materials produced had slightly lower surface areas (921 $m^2 \cdot g^{-1}$ vs 1182 $m^2 \cdot g^{-1}$ with α,α'-*p*-dichloroxylene monomer), the technique was a convenient and facile route towards microporous networks.

HCPs have previously been explored for various applications including gas separation,[34] catalysis[23] and wastewater treatment.[35, 36] The ability to tailor the final microstructure[37] and functionality[38] of the polymer towards the application is a key property which makes HCPs inherently suitable materials to treat wastewater streams and remove pollutants. They have not yet however, been investigated for Cs and Sr removal.

The sulfonic acid group is a well-known functionality in the field of ion-exchange and is commonly used with macroporous or gel-type polymer matrices to create the well-known strong acid cation (SAC) ion-exchange resin. There is a well-known order of selectivity of cations for this functionality, influenced by both charge and ionic radius.[39] With this in mind, it can be hypothesized that both Sr and Cs ions will be selectively extracted from aqueous solution by adsorbents incorporating sulfonic acid groups, even with high concentrations of naturally occurring ions such as Na and K, which are markedly lower in the selectivity series.

Therefore, we report the synthesis of BCMBP hypercrosslinked networks synthesized using both H_2SO_4 (HCP-1) and $FeCl_3$ (HCP-2) as the acid catalyst, followed by sulfonation using chlorosulfonic acid as the sulfonating agent (Scheme 1). This is the first report of a functionalized Friedel-Crafts HCP synthesized without metal catalysts and the first ever characterized sulfonic acid-bearing hypercrosslinked polymer networks made by monomer knitting. The polymers are thoroughly assessed for use as selective adsorbents for Cs and Sr and are shown to possess excellent selectivity in solutions of high ionic strength, with high Na and K concentrations, pointing towards potential for environmental remediation of brackish water.

Materials and Methods

Chemical reagents

4,4'-Bis(chloromethyl)-1,1'-biphenyl, (BCMBP, 95%), iron (III) chloride ($FeCl_3$, 97%), anhydrous 1,2-dichloroethane (DCE, 99%), chlorosulfonic acid (99%), strontium chloride ($SrCl_2$, anhydrous powder, >99%) and cesium nitrate (>99.99%) were purchased from Sigma-Aldrich. Sulfuric acid (95%) was purchased from Fischer scientific. Sodium chloride (NaCl, 99.9%) was purchased from VWR chemicals and potassium nitrate (KNO_3, >99%) was purchased from Acros organics. All chemicals were used as received unless otherwise stated.

Synthesis of HCP-1 using H_2SO_4 as the Lewis-acid catalyst

BCMBP (3.00 g, 13.44 mmol, 1 eq.), was dissolved in DCE (30 cm^3) and heated to 80 °C. H_2SO_4 (7.2 cm^3, 13.44 mmol, 1 eq.) was added and the temperature was held for 1 h. The reaction was cooled to 25 °C and the solution was left to stir for 72 h. The resulting black solid was collected *via* vacuum filtration and washed with water and methanol until the solution was neutral. The solid was dried overnight in vacuo at 60 °C to yield the final black product (2.23 g, 73%), Elemental analysis calculated for $C_{14}H_{10}$, Expected: C 94.38%, H 5.62%. Found, C 81.17%, H 5.35%.

Synthesis of HCP-2 using $FeCl_3$ as the Lewis-acid catalyst

BCMBP (2.04 g, 8 mmol, 1 eq.) was added to a round bottom flask under nitrogen before DCE (30 cm^3) was added to dissolve the monomer. To the solution iron chloride (2.80 g, 16 mmol, 2 eq.) was added as a slurry in DCE (20 cm^3) and the mixture was heated to 80 °C for 16 h. The mixture was cooled to room temperature and vacuum filtration afforded a black solid. The solid was extracted with methanol using soxhlet apparatus for 12 h before being dried *in vacuo* at 60 °C to yield the final black product (1.54 g, 108%). Elemental analysis calculated for $C_{14}H_{10}$, Expected: C 94.38%, H 5.62%. Found, C 87.76%, H 5.45%.

Sulfonation of hypercrosslinked polymers (SHCP-1 and SHCP-2 synthesis)

Hypercrosslinked BCMBP (1.50 g) was added to DCE (50 cm^3) and left for 1 h to stir to allow the polymer network to swell in the solvent. Chlorosulfonic acid (10 cm^3) was added to the solution and left to stir at 25 °C for 72 h. The product was collected *via* vacuum filtration and washed with water and methanol ensuring the run off was a neutral pH. The resulting solid was dried under vacuum at 60 °C overnight to yield the final black product. Yields, 1.96 and 1.70 g. Elemental analysis calculated for $C_{14}H_{10}SO_3$, Expected: C 65.12%, H 3.88% S 12.40%. Found, C 60.14%, H 4.20%, S 10.81%; SHCP-2, C 57.75%, H 5.55%, S 7.15%

Characterization

Fourier transform infrared (FTIR) spectroscopy was performed using a Perkin-Elmer Spectrum 100. Samples were mixed with KBr and pressed into a disk before being measured in transmission mode. Solid-State NMR samples were packed into 4 mm zirconia rotors and transferred to a Bruker Avance III HD spectrometer. 1D ^{1}H-^{13}C cross-polarization magic angle spinning (CP/MAS) NMR experiments were measured at 125.76 MHz (500.13 MHz ^{1}H) at a MAS rate of 10.0 kHz. The ^{1}H $\pi/2$ pulse was 3.4 µs, and two-pulse phase modulation (TPPM) decoupling was used during the acquisition. The Hartmann-Hahn condition was set using hexamethylbenzene. The spectra were measured using a contact time of 2.0 ms. The relaxation delay D_1 for each sample was individually determined from the proton T_1 measurement (D_1 = 5 x T_1). Samples were collected until sufficient signal to noise was observed, typically greater than 256 scans. The values of the chemical shifts are referred to that of TMS.

Elemental analysis was performed through burning an amount of sample in a stream of pure oxygen. The sample was placed in a tin capsule and introduced into the combustion tube of the Elementar Vario MICRO Cube CHN/S analyzer via a stream of helium. Combustion products were analyzed through first passing the sample through a copper tube to remove excess oxygen and reduce any NO_x to N_2. Gases were separated using a Thermal Programmed Desorption column and detected using a Thermal Conductivity Detector.

Scanning electron microscopy (SEM) images were recorded using a Jeol JSM-6010LA instrument. Samples were mounted on carbon tape on aluminum stubs, without any coating treatment.

Gas sorption measurements were performed using a micromeritics ASAP 2020Plus analyzer employing high purity gases. Nitrogen gas sorption measurements were analyzed at 77 K using ~100 mg of sample. BET surface areas were calculated over a relative pressure range of 0.01-0.15 P/P_0. Differential pore sizes were calculated using the NL-DFT method using the model for Carbon Slit Pores by NLDFT. All samples were degassed at 120 °C under dynamic vacuum immediately prior to analysis.

TGA analyses were obtained using a Perkin Elmer thermogravimetric analyzer under a nitrogen atmosphere. 4.5 mg of each sample was heated from 25 to 800 °C at a rate of 10 °C per minute.

Metal uptake studies

Solutions of various Sr, Cs, Na, K, Mg and Ca concentrations were made up in accordance with the information presented in Table S1 by dissolving the relevant metal salts in 100 cm^3 of deionized water. Because the intended end use of the polymers was treatment of environmental water, all experiments were conducted at the natural pH of the metal ions solution, this being ~7. 20 mg of SHCP-1 was added to a sample vial along with 5 cm^3 of the chosen solution. Samples were left to stir for a defined time period, before the solid was filtered out using a 0.25 µm filter. Samples for equilibrium studies were left for 24 h. Samples for kinetic studies were left for 1 - 60 min. The resulting solutions were analyzed by inductively coupled plasma mass spectrometry (ICP-MS), using an Agilent 7500CE Mass Spectrometer, to determine accurate metal concentrations of solutions. The metal solution concentrations were also determined prior to contact with the polymers. The equilibrium pH of solutions, both before and after polymer-contact, was also determined, using a standard combination electrode.

Results and Discussion

Synthesis and sulfonation of hypercrosslinked polymers SHCP-1 and SHCP-2

Hypercrosslinked BCMBP was synthesized *via* a hypercrosslinking reaction using either H_2SO_4 (HCP-1) or $FeCl_3$ (HCP-2) as the catalyst, resulting in black solids collected in good yields of 73% and 96% respectively. Post-synthetic sulfonation of HCP-1 and HCP-2 was carried out *via* a similar procedure to that reported by Lu *et al.* to sulfonate a porous polymer network (PPN-6),[40] using chlorosulfonic acid as the sulfonating agent, to yield SHCP-1 and SHCP-2. Although PPN-6-SO_3H is superficially similar to our own networks, the high cost of the homocoupling monomer (> £200 g^{-1}) would limit the use of this material as an environmental remediation tool. There are many previous reports of functionalized HCPs,[31, 32, 41] but they have all used metal catalysts such as $FeCl_3$ to synthesize the porous network. Hence to date, there have been no reports of functionalized HCPs synthesized *via* metal-free routes, which is more environmentally benign and avoids the possibility of contamination from residual catalyst still present in the network. As expected, an increase in mass upon the addition of the sulfonic acid group was observed after the reaction with chlorosulfonic acid. A mass increase of 30% was observed upon sulfonation of HCP-1 while for HCP-2 the mass increase was 13%, suggesting a lesser degree of sulfonation.

Table 1. Elemental analysis data for polymer networks. All values refer to mass %

	HCP Expected[a]	HCP-1	HCP-2	SHCP Expected[b]	SHCP-1	SHCP-2
C	94.38	81.17	87.76	65.12	60.14	57.75
H	5.62	5.35	5.45	3.88	4.20	5.55
S	0.00	1.95	0.00	12.40	10.81	7.15

[a]Assuming no sulfonation. [b]Assuming 1 site is sulfonated per monomer.

Solid-state analysis of materials

A combination of SEM, TGA, FTIR spectroscopy, solid-state NMR, elemental analysis and gas sorption studies were employed to characterize the products. Scanning electron micrographs of HCP-1 and SHCP-1 (Figure S1) demonstrated a very inconsistent morphology, with occasional microspheres of different diameters being visible within the overall fused network. The sulfonation functionalization did not change the visible morphology, as would be expected from previous literature.[42]

The FTIR spectra (Figure S2) of HCP-1 and SHCP-1 both contain similar stretches at 1600, 1500 and 1200 cm^{-1} relating to the C=C stretches from the aromatic rings in the final network.[43] Signals at 600 and 1050 cm^{-1}, present in the spectrum of the sulfonated SHCP-1, are assigned to the C-S stretch and the S=O symmetric stretch respectively. The presence of these additional signals demonstrates the successful incorporation of the sulfonate groups into the polymer network. However, these signals, along with a broad stretch at 3500 cm^{-1} indicating the presence of an –OH group, are also present in the HCP-1 spectrum, albeit much less intense than those in the sulfonated product. This suggests that the hypercrosslinking reaction, which uses H_2SO_4 as the acid catalyst, was also able to partially sulfonate the material.[33]

Elemental analysis further evidences the successful incorporation of the sulfonate groups (Table 1). 1.95% S was observed for HCP-1, again suggesting that some sulfonation of the network had taken place during hypercrosslinking. After the reaction with chlorosulfonic acid, this increased to 10.81% for SHCP-1. An expected calculation based on one sulfonation per monomer would yield 12.4 % S content. From the elemental analysis we can therefore assume a substitution of slightly less than one sulfonic acid group per monomer within the network. As expected, the hypercrosslinking reaction using $FeCl_3$ (HCP-2) shows S content of 0.00%.

Thermogravimetric analysis of samples SHCP-1 and SHCP-2 (Figure S4) shows a mass loss of 10-15% at around 100 °C which we attribute to the loss of water vapor adsorbed into the samples. SHCP-2 is stable up to around 200 °C while SHCP-2 is slightly more stable with the onset of decomposition at around 250 °C.

The solid-state NMR spectrum of sample HCP-1 (Figure S3) shows resonances at ~138 ppm, attributed to quaternary aromatic carbon environments; ~130 ppm, attributed to aromatic carbons adjacent to hydrogen and ~37 ppm, attributed to the -CH_2- bridges. After sulfonation, there is a change in the intensity of the aromatic resonances, with a reduction in the intensity of the Ar-H signal compared to that of the quaternary carbons, due to sulfonation. Nitrogen adsorption/desorption isotherms were carried out at 77 K in order to determine both the surface area and pore size of all materials synthesized in this work (Figure 1). All isotherms exhibit a steep uptake at low relative pressure ($P/P_0 < 0.1$), indicative of the presence of micropores within the sample. The BET surface areas of all networks were calculated over a pressure range of 0.01-0.15 P/P_0 (Table 2). Initially HCP-1 and -2 exhibit high surface areas of 1239 and 1918 $m^2 \cdot g^{-1}$ respectively, similar to the reported surface areas for these two materials.[33, 44] The $FeCl_3$-catalysed route results in a material with some larger mesopores as evidenced by the hysteresis loop around 0.8 P/P_0. This is confirmed by NLDFT pore size distributions (Figures S4 – S6) which shows the main pore sizes of HCP-2 to be centered around 0.5 and 1.5 nm with some further mesoporosity. Upon sulfonation there is a notable drop in surface area of both HCPs, as would be expected from the addition of mass from the sulfonic acid group. The $FeCl_3$-catalysed HCP-2 shows a significant drop in surface area to 580 $m^2 \cdot g^{-1}$ while the metal-free HCP-1 shows a less prominent decrease in surface area to 850 $m^2 \cdot g^{-1}$. The large decrease in surface area from HCP-2 to SHCP-2 is most likely due the loss of the larger mesopores (Fig. S5) with the pore size distribution shifting towards the smaller 0.5 nm pore. The pore volume of HCP-2, calculated at 0.1 P/P_0 ($V_{0.1}$), remains unchanged after sulfonation whilst the total pore volume (V_{tot}, $P/P_0 = 0.99$) significantly drops from 2.4 to 0.35 cm^3/g with $V_{0.1/tot}$ increasing from 0.03 to 0.22. For the metal free route (HCP-1), $V_{0.1}$ also remains unchanged after sulfonation, while the total pore volumes drop from 0.86 to 0.51 $cm^3 \cdot g^{-1}$ and $V_{0.1/tot}$ increases from 0.20 to 0.33. It is therefore likely that the sulfonation occurs mainly in the mesopores of the HCPs rather than the micropores. This is further demonstrated by the fraction of pore volumes at 0.1 P/P_0 *via* both routes increasing after sulfonation. Mesopores have previously been postulated to play an important role in the mass transfer of ions to active sites in porous adsorbents.[36]

Uptake of Sr and Cs ions from aqueous solution

Metal-organic frameworks (MOFs) such as the sulfonate-functionalized MIL-101-SO_3H have been previously shown to selectively uptake both Sr and Cs ions (Table S7 provides a summary of Cs and Sr uptakes in other porous materials). Our metal-free catalyzed SHCP-1 however, is synthesized from readily-available and economic starting materials and contains no metal ions which may leach into solution. In general, porous polymers also have increased thermal and chemical stability compared to MOFs and are therefore ideal candidates for metal uptake in harsh environments.[25,36,38] To date there have been no reports of the uptake of Sr and Cs ions by microporous polymers, therefore we investigated the use of SHCP-1 for the selective capture of these ions from solution. A simple immersion of HCP-1 and SCHP-1 in deionized water (Figure S7) demonstrated the greatly improved wettability of the polymer upon addition of the hydrophilic sulfonic acid groups, as has previously been observed,[42] and suggested rapid uptake might be possible due to the enhanced hydrophilicity of the material.

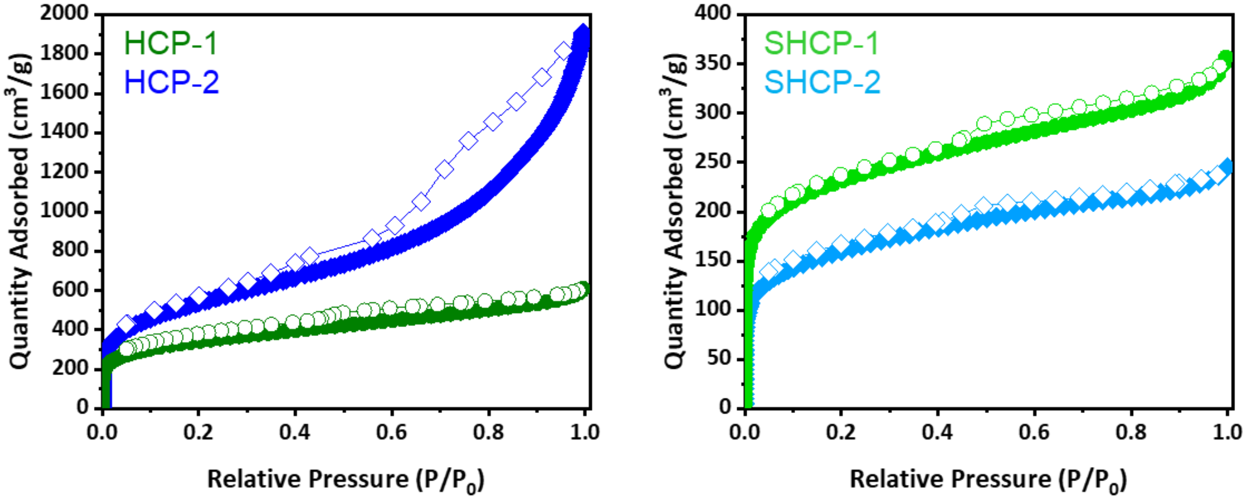


Figure 1. Gas sorption isotherms of HCP-1 and HCP-2 (left) and the sulfonated SHCP-1 and SHCP-2 (right). H_2SO_4 synthetic route (circles) and $FeCl_3$ route (diamonds). Filled symbols show adsorption and empty symbols desorption.

Table 2. Gas sorption properties of the synthesized polymers, determined by N_2 adsorption.

Catalyst	**Sample**	**Surface area (m^2 g^{-1})[a]**	**V_{tot} (cm^3/g)[b]**	**$V_{0.1}$ (cm^3/g)[c]**	**$V_{0.1/tot}$**
H_2SO_4	HCP-1	1239	0.86	0.17	0.20
	SHCP-1	850	0.51	0.17	0.33
$FeCl_3$	HCP-2	1918	2.4	0.08	0.03
	SHCP-2	580	0.35	0.08	0.22

[a] Apparent BET surface area calculated over the relative pressure range 0.01-0.15. P/P_0 [b] Total pore volume calculated at 0.99 P/P_0. [c] Micropore volume calculated at 0.1 P/P_0.

Isotherm studies

Single metal-loading isotherm data were fitted to the Langmuir and Dubinin-Radushkevich (D-R) adsorption models (Equations 1 and 2) *via* non-linear least-squares regression, using the Microsoft Excel SOLVER program. Errors were calculated using Billo's Solver Statistics add-in. The Langmuir model has been frequently used to describe the uptake of Sr and Cs ions by various adsorbents and for uptake behavior of the sulfonic acid functionality,[45,46] whereas the D-R model is less commonly applied.[47]

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (1)$$

$$q_e = (q_{max})\, exp\left(-B_D \left[RTln\left(1 + \frac{1}{C_e}\right)\right]^2\right) \qquad (2)$$

For these isotherm models, q_e is the equilibrium uptake capacity of the polymer ($mg \cdot g^{-1}$), q_{max} is the theoretical saturation uptake capacity ($mg \cdot g^{-1}$), K_L is a Langmuir equilibrium constant ($L \cdot mg^{-1}$), C_e is the concentration of metal ion at equilibrium ($mg \cdot L^{-1}$), B_D is a D-R constant (J^2 mol^2), R is the gas constant (8.314 $J \cdot K^{-1} \cdot mol^{-1}$) and T is the experimental temperature (K). The D-R model can be used to estimate the desorption energy of the system, according to Equation 3:

$$E_{des} = {}^{1}\!/\!\sqrt{2B_D} \qquad (3)$$

where E_{des} is the mean desorption energy ($kJ \cdot mol^{-1}$). The isotherms produced for Sr and Cs uptake are shown in Figure 2, while the extracted parameters for both models are shown in Table 3.

The uptake of both metals was more closely described by the D-R model than Langmuir, which suggests that the energies of binding follow a Gaussian distribution, rather than being strictly degenerate.[48] There was also a clear relationship observed, in both cases, between the number of metal ions adsorbed and the number of protons liberated into solution (Figure S8). Overall, it can be inferred that the extraction of Sr and Cs was due to the expected sulfonic acid group ion-exchange mechanism. It is unusual, though not unheard of, for the D-R model to demonstrate superior description to the Langmuir model for metal uptake by ion-exchange on to a functionalized polymer.[20,22,49] It is possible in this instance that the hydrophobic pore interiors of varying volumes create a number of different microenvironments where binding could occur. The E_{des} values returned, being >8 $kJ \cdot mol^{-1}$, strongly suggested a chemisorption mechanism was prevalent, rather than physisorption.[48] The binding energies for Sr are unusually high for an ion-exchange process, which typically results in values in the range of 8-16 $kJ \cdot mol^{-1}$.[22,49,50] This suggests the Sr ions in particular are strongly held and would be unlikely to leach back into the environment. Although Cs uptake appears to be a weaker interaction, the q_{max} values from both models were higher. A comparison of q_{max} values from the D-R model

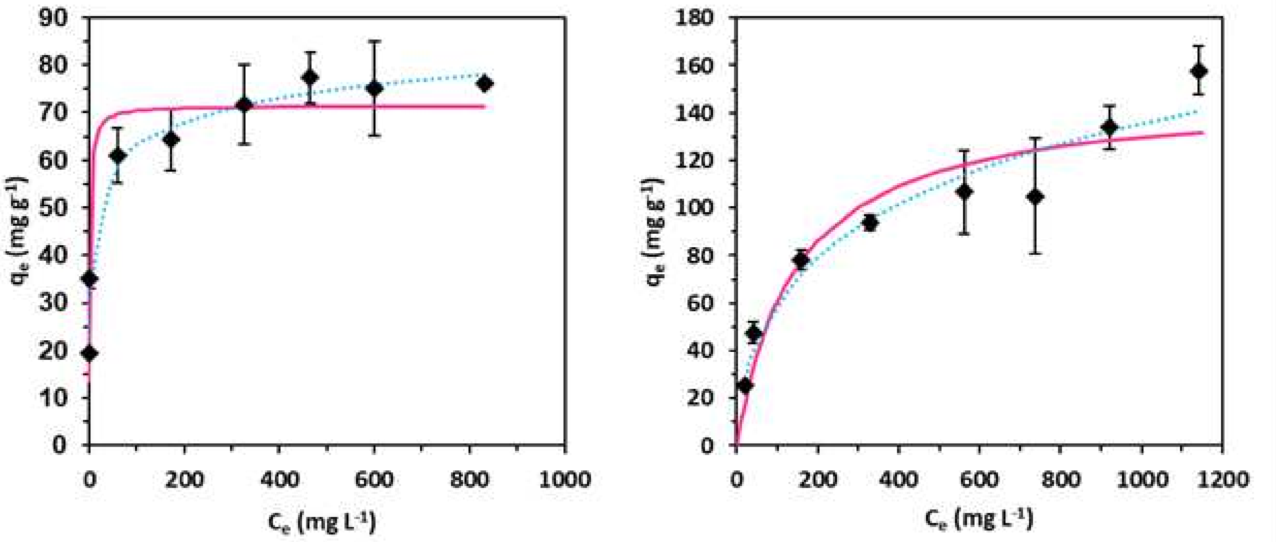


Figure 2. Metal adsorption isotherms for uptake of Sr (left) and Cs (right) by SHCP-1. Polymer mass = 20 mg. Solution volume = 5 mL. Initial metal concentration = 1-15 mM. Contact time = 24 h. T = 20°C. Solid line = Langmuir isotherm model. Dashed line = D-R isotherm model.

with the found S mass % of SHCP-1 results in a theoretical maximum loading efficiency of ~61% for Cs and ~32% for Sr.This indicates that some sulfonation took place within the micropores, creating sites unavailable to the metal ions. It also suggests that some Sr cations may bridge across 2 sulfonic acid groups, which would explain the high mean E_{des} value observed. This can be seen in Figure S8, which shows that the number of protons released into the aqueous phase is greater for Sr solutions, even though the molar uptake of metal is lesser.

The calculated q_{max} values from the D-R model compare favorably to those attained by adsorption of Sr *via* crown ether-functionalized ion-exchange resins (7.7 mg Sr·g^{-1})[51] and adsorption of Cs and Sr on mineral-based extractants (91.7 mg Cs·g^{-1}; 44.7 mg Sr·g^{-1}).[52] Indeed, the polymer exhibits a capacity of the same order of magnitude as a commercial ion-exchange resin with a far larger and more elaborate phosphonic acid-based functional group (315 mg Cs·g^{-1}).[53] Further comparison with literature values is seen in Table S7.

Table 3. Extracted parameters for uptake of Sr and Cs by SHCP-1 by fitting to Langmuir and Dubinin-Radushkevich isotherm models.

Model	Parameter	Sr	Cs
Langmuir	K_L (L·mg^{-1})	0.65 ± 0.20	7.0 ± 3.1 (x 10^{-3})
	q_{max} (mg·g^{-1})	71.5 ± 2.6	148 ± 16
	R^2	0.993	0.981
Dubinin-Radushkevich	B_D (J^2·mol^2)	1.50 ± 0.11 (x 10^{-9})	4.77 ± 0.38 (x 10^{-9})
	q_{max} (mmol·g^{-1})	1.09 ± 0.03	2.06 ± 0.28
	q_{max} (mg·g^{-1})	95.6 ± 2.8	273 ± 37
	E_{des} (kJ·mol^{-1})	18.2 ± 1.3	10.2 ± 0.8
	R^2	0.998	0.990

Kinetic studies

Results from the single metal-loading kinetic study demonstrated a rapid uptake of Sr and Cs by SHCP-1 (Tables S1 and S2) with >80% of the apparent equilibrium uptake capacity achieved within 60 seconds. In order to confirm the uptake mechanism of metal adsorption, data were fitted to the well-known pseudo 1st-order (PFO) and pseudo 2nd-order (PSO) kinetic models (Equations 4 and 5), using linear regression.

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (4)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \qquad (5)$$

For these kinetic models, q_t is the uptake of metals at time t (mg g^{-1}), k_1 is the pseudo 1st-order rate constant (min^{-1}) and k_2 is the pseudo 2nd-order rate constant (g mg^{-1} min^{-1}). Additional parameters, derived from PFO and PSO equations, were calculated using Equations 6 and 7:

$$t_{1/2} = \frac{1}{k_n q_e} \qquad (6)$$

$$h_0 = k_2 q_e^2 \qquad (7)$$

where n = 1 or 2, corresponding to PFO or PSO equations, $t_{1/2}$ is the sorption half-time (min) and h_0 is the initial sorption rate (mg g^{-1} min^{-1}) Agreement with film diffusion and intra-particle diffusion models was also checked (Supporting Information, pages S6-8). The PSO model was found to give an accurate description of the uptake behavior, as seen in the associated plots of t/q_t vs t (Figure 3). Calculated parameters for kinetic data are presented in Table 4.

Table 4. Extracted parameters from data-fitting to kinetic models.

Kinetic model	Parameter	Sr	Cs

Pseudo 1st-order	q_e (mg g^{-1})	60.3 ± 6.9	99.9 ± 0.2
	k_1 (min^{-1})	1.27 ± 0.48	2.73 ± 7.23
	R^2	0.724	0.244
Pseudo 2nd-order	q_e (mg g^{-1})	62.1 ± 0.1	101 ± 1
	k_2 g (mg^{-1} min^{-1})	7.71 ± 1.1 (x 10^{-2})	0.113 ± 0.018
	$t_{1/2}$ (min^{-1})	0.209 ± 0.031	8.80 ± 1.4 (x 10^{-2})
	h_0 (mg g^{-1} min^{-1})	297 ± 44	1150 ± 180
	R^2	0.999	0.998
Film layer diffusion	R^2	0.175	0.095
Intra-particle diffusion	R^2	0.609	0.042

The uptake of both metals was well-described by the PSO model, which has often been observed to give an accurate description of chemisorption-dominated systems.[54,55] This appears to confirm that the ion-exchange process of the functional groups was responsible for the uptake of metals. The fit of the data to the PFO model and to both diffusion-based models (Figures S8-S11) was poor and the parameters returned were not considered valid. The data overall suggest that the rate-limiting kinetic processes for the removal of metals from solution were the diffusion of ions across the hydration layer of the adsorbent particles and/or the ion-exchange reaction at the polymer surface, rather than diffusion through the pores.[56,57] This is common for adsorbents with a high accessible surface area.[55, 58] The calculated k_2, $t_{1/2}$ and h_0 values all indicated that Cs uptake was more rapid than Sr. Assuming the divalent Sr ions do indeed bridge across two sulfonic acid groups, the Sr uptake can be considered a pseudo-chelating interaction, which is generally a slower process than monovalent ion-exchange.[59] Nonetheless, the derived k_2 values for both metals are relatively high in comparison to the literature,[51,60,61] which again can be attributed to the microporous nature of the adsorbent.

Competition with other cations

In order to be considered viable for removing problematic metal ions for environmental remediation, a material must not only possess a high loading capacity but also demonstrate selectivity against competing ions in solution. Radioactive Cs and Sr contamination is of particular importance in estuarine environments. For example, following the Fukushima Daiichi disaster, the highest ^{137}Cs activity recorded outside the actual plant boundaries was in brackish ground water >10 Km from the site.[62] We therefore studied removal of the target ions with a large excess of Na (as NaCl). Other potentially competing cations present in saline water at significant levels are K, Mg and Ca.

Table 5 shows the results of the selectivity studies. Experiment 1 involved Sr and Cs only. Experiment 2 involved Sr and Cs in the presence of 10 molar equivalents of Na. Experiment 3 involved Sr and Cs with 10 molar equivalents of all the coexisting cations. In all cases, the distribution coefficient (K_d) for each metal ion was calculated (Supporting Information, p S10).

It was found that SHCP-1 possessed very high selectivity towards Sr and Cs ions. In every experiment, the polymer was able to selectively extract Sr and Cs, showing little to no affinity towards any of the other ions, despite their much higher concentrations. Separation factors (S.F.) for Sr and Cs vs competing ions were calculated as measures of the selectivity of SHCP-1 for target ions, relative to co-contaminants (Supporting Information, p S10) and are presented in Table 6. It is clear from Tables 5 and 6 that the selectivity of SHCP-1 follows the order: Sr > Cs >> Ca > K ≈ Mg >> Na, with Sr uptake showing the largest K_d values and S.F.s across all experiments. SAC selectivity is strongly influenced by valance, with divalent ions being preferred over monovalent, a phenomenon termed as "electroselectivity" by Helfferich.[39] However, a further factor is free energy of solvation, which decreases with ionic radius for the species studied, with Na and K hence preferring to remain in the aqueous phase over Cs, and Mg and Ca doing likewise over Sr.[63] The selectivity of SHCP-1 agrees exactly with the established cation-exchange affinities for SAC resins.[63]

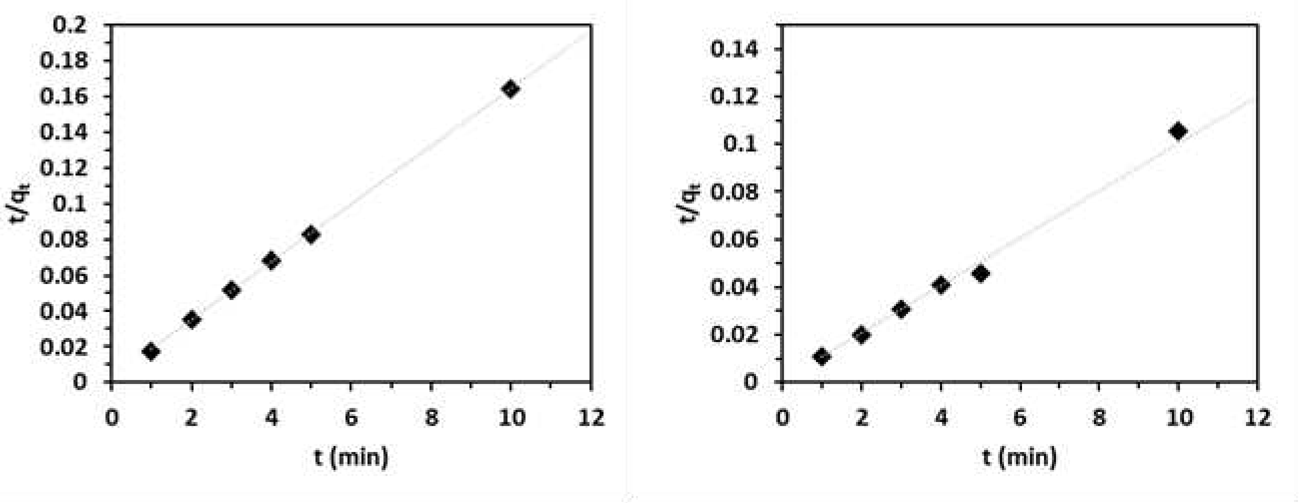


Figure 3. Linear fitting of uptake of Sr (left) and Cs (right) by SHCP-1 over time to PSO kinetic model. Polymer mass = 20 mg. Solution volume = 5 mL. Initial metal concentration = 10 mM. Initial pH ≈ 6.0. T = 20°C.

Table 5. Sr and Cs uptake performance of SHCP-1 in solutions of competing ions. Polymer mass = 20 mg. Solution volume = 5 mL. Contact time = 24 h. T = 20°C.

Experiment	Ionic strength (mmol·L^{-1})	Metal	C_o (mg·L^{-1})	q_e (mg·g^{-1})	K_d
1	46.5	Sr	817	63.3	112
		Cs	1230	42.0	39.6
2	249	Sr	840	51.3	80.7
		Cs	1250	51.3	49.1
		Na	2320	10.0	4.39
3	153	Sr	121	30.2	2.16 (x 10^5)
		Cs	185	46.1	9.23 (x 10^4)
		Na	378	<0.1	<0.1
		K	611	5.25	8.90
		Mg	360	2.50	7.14
		Ca	500	15.0	34.1

However, the preference of the polymer for Sr over Cs becomes less pronounced in solutions of higher ionic strength. It is known that high ionic strength can modify SAC selectivity, due to the decrease in water activity in the aqueous phase, thus changing the degree of solvation required for the different ions.[67] Chelating uptake processes can also be strongly suppressed by the ionic strength of the solution, specifically for alkali earth metal uptake,[64,65] which further evidences the proposed Sr bridging interaction.

From a selectivity point of view, upon comparison to other materials used to remove Sr and/or Cs from solution, SHCP-1 compares favorably (Table S7). The MOF MIL-101-SO_3H was previously investigated for Sr and Cs removal and possesses the same chemical moieties to SHCP-1.[66] The S.F. values for MIL-101-SO_3H were found to be several orders of magnitude lower than those of SHCP-1 for the same ions, despite the identical sulfonic acid functionalities. Porous uranyl networks recently reported by Sun *et al.*[67] and Wang *et al.*[68] also showed lesser selectivity than SHCP-1. It is known from classical ion-exchange literature that increasing the degree of cross-linking (and therefore the hydrophobicity) of the resin matrix imparts better selectivity to SAC resins.[63,69] It is thus suggested that HCPs are a more appropriate scaffold for the performance of the sulfonic acid functionality than MOFs. Indeed, SAC selectivity is proportional to matrix swelling pressure, which in turn is dictated by the degree of resin crosslinking. Therefore, HCPs may even offer advantages over conventional ion-exchange resins in this regard.

Table 6. Separation factors for both Sr and Cs in the presence of Na and K. Experimental parameters are as per Table 4.

Experiment	Ion (x)	S.F.					
		x/Cs	x/Sr	x/Na	x/K	x/Mg	x/Ca
1	Sr	2.83					
	Cs		0.353				
2	Sr	1.64		18.4			
	Cs		0.609	11.2			
3	Sr	2.34		>2 (x 10^6)	2.43 (x 10^4)	3.02 (x 10^4)	6.33 (x 10^3)
	Cs		0.427	>9 (x 10^5)	1.04 (x 10^4)	1.29 (x 10^4)	2.71 (x 10^3)

SHCP-2 was also investigated for its metal uptake capabilities, it was found that after 24 h, 134 mg of Cs was removed from solution, much less than the 466 mg removed by SHCP-1 (Table S4). Considering the S mass % for each polymer (Table 1), it seems this is not the only relevant parameter for the uptake of aqueous metal ions and that accessible surface area of the materials is also important. The loss of a large fraction of mesopores in HCP-2 upon sulfonation (Figure S4) may result in some of the sulfonic acid groups being inaccessible for the target ions. HCP-1 loses much less surface area upon sulfonation

(Table 2), hence contributing to the superior uptake observed. Correlations between BET surface area and capacity for contaminants have previously been observed for microporous materials.[42,70] Additionally, it was found that residual Fe, present from the $FeCl_3$ catalytic route, leached into solution during polymer contact (Table S5). This had survived Soxhlet extraction with methanol, post-synthetic modification with chlorosulfonic acid and further washing with water, thus highlighting the issue of obtaining a pure product from hypercrosslinking reactions when using metal catalysts. Residual Fe associated with the polymer is a particular worry when applying these materials to adsorption of metal ions given that uptake performance may suffer, essentially due to competition from leached Fe^{3+} ions. These would be more strongly bound to the sulfonate moiety, owing to higher valance.[39] The H_2SO_4 catalyzed synthesis therefore seems to provide the optimum route towards a material which has a high surface area, contains no residual impurities, is readily post-synthetically modified and capable of extracting both Sr and Cs ions in a selective and efficient manner.

Conclusions

4,4’-bis(chloromethyl)-1,1’-biphenyl (BCMBP) was hypercrosslinked, using H_2SO_4 as the catalyst, and post-synthetically sulfonated by reacting with chlorosulfonic acid. The resulting polymers possessed high BET surface areas, with the as-synthesized polymer (HCP-1) measuring 1239 $m^2 \cdot g^{-1}$ and the sulfonated version (SHCP-1) measuring 850 $m^2 \cdot g^{-1}$. SHCP-1 was successfully applied to remove both Cs and Sr from solution with q_e values of 273 and 95.6 $mg \cdot g^{-1}$ respectively, calculated via fitting to the Dubinin-Radushkevich isotherm model. Furthermore, SHCP-1 was found to be extremely selective towards these ions, even in the presence of competing ions (Na and K). Separation factors of 18.4 (Sr/Na) and 11.2 (Cs/Na) are superior to many other published adsorbents used for uptake of these ions, which we attribute to the hydrophobic, densely crosslinked nature of the material positively influencing the order of cation selectivity. Moving towards industrial implementation, the ability to desorb the hazardous ions from the polymers and regenerate their exchange capacity is a parameter that will require investigation. The working pH range is also a factor for the versatility of an adsorbent, which is to be further probed. It is hoped that this work will stimulate further studies into the use of hypercrosslinked polymers for environmental remediation, a purpose for which they are intrinsically suitable.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:
SEM images, FTIR spectra, gas sorption analysis, metal uptake and selectivity studies.

AUTHOR INFORMATION

Corresponding Author

* Dr Robert Dawson r.dawson@sheffield.ac.uk

Author Contributions

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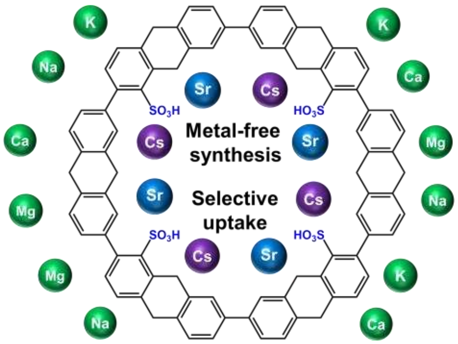
K
Na
Ca
Mg
Sr
Cs
SO_3H
HO_3S
Metal-free synthesis
Selective uptake