Synthesis and Host−Guest Properties of Multi-Crown Dendrimers towards Sodium Pertechnetate and Mercury(II) Chloride

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Dedicated to Prof. Peter Mühl (Dresden) on the occasion of his 70th birthday

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Multi-crown dendrimers of four different generations have been synthesized by grafting 4, 8, 16, and 32 benzo[15]-crown-5 units at the periphery of POPAM dendrimers. The binding of sodium pertechnetate and mercury(II) chloride by the multi-crown dendrimers has been studied by liquid-liquid extraction using the radioactive probes $^{22}Na^+$, $^{99}TcO_4^-$, and $^{203}Hg^{2+}$. The third- and fourth-generation dendrimers **3** and **4**, in particular, are capable of extracting mercury(II) with high efficiency (ca. 12 Hg^{II} ions per dendrimer molecule, even at low generation). It has been shown that the guest molecules investigated are preferentially encapsulated inside the dendrimers.

Introduction

Due to their unique topology, dendrimers show unusual guest-binding behaviour,[1] and there are almost unlimited possibilities for the structural modification of dendritic hosts. In principle, dendrimers can accommodate different kinds of guests, such as anionic species,[2] metal ions,[3] and neutral substrates,[4] either within the porous interior or at the exterior of the multifunctional periphery. Furthermore, there is an almost infinite variability regarding the solubility behaviour. Thus, water-soluble unimolecular micelles have been developed, having a hydrophobic interior and hydrophilic shells, which are capable of encapsulating hydrophobic guests.[5] Recently, oligoethyleneoxy-modified polypropyleneamine dendrimers (POPAM dendrimers) possessing hydrophilic interiors and exteriors were shown to function as water-soluble hosts for hydrophilic xanthene dyes.[6] On the other hand, hydrophilic guests can be transported from water into an organic phase or liquid carbon dioxide by the use of inverted unimolecular micelles based on a POPAM skeleton with grafted aliphatic and fluorinated chains.[7] Such hydrophobic dendrimers have been discussed as a new generation of extractants.[8] This stems mainly from the unique ability of dendrimers to encapsulate a multitude of guests. In this context, dendritic hosts have been propagated as nanoscopic reactors for environmental remediation.[9] Additionally, dendrimers are gaining in importance in the development of novel diagnostic and therapeutic agents with high specific activities.[10] For both applications, dendrimers based on multiple 1,4,7-triazacyclononane derivatives seem to be very promising.[11] These molecules coordinate multiple Cu^{2+} and Ni^{2+} ions, whereby each triazacyclononane unit can be loaded with the metal ions under investigation. Likewise, cascade molecules having up to 21 diaza[18]crown-6 moieties have been reported.[12] These dendrimers were shown to extract alkali metal ions in a generation-independent manner. The experimental results indicated only 1:1 complexes of the crown subunits with Cs^+, without any sandwich species.

Herein, we present the synthesis of multi-crown dendrimers having a different structure. Specifically, benzo[15]-crown-5 units have been grafted onto the periphery of four generations of POPAM dendrimers (Scheme 1). The combination of protonated amine nitrogen atoms in the dendrimer core, which can bind anions, together with cation-active crown ether moieties, represents an approach for the simultaneous binding of cations and anions. The host−guest properties of these dendrimers **1**−**4** have been investigated by liquid-liquid extraction. Sodium pertechnetate, as a typical contaminant of nuclear waste,[13] and mercury(II) chloride, as a pollutant of chloride-containing effluents of incineration processes,[14] were selected as guests for our studies.

Results and Discussion

The new dendritic family consists of four different generations of benzo-crown-modified polypropyleneamine

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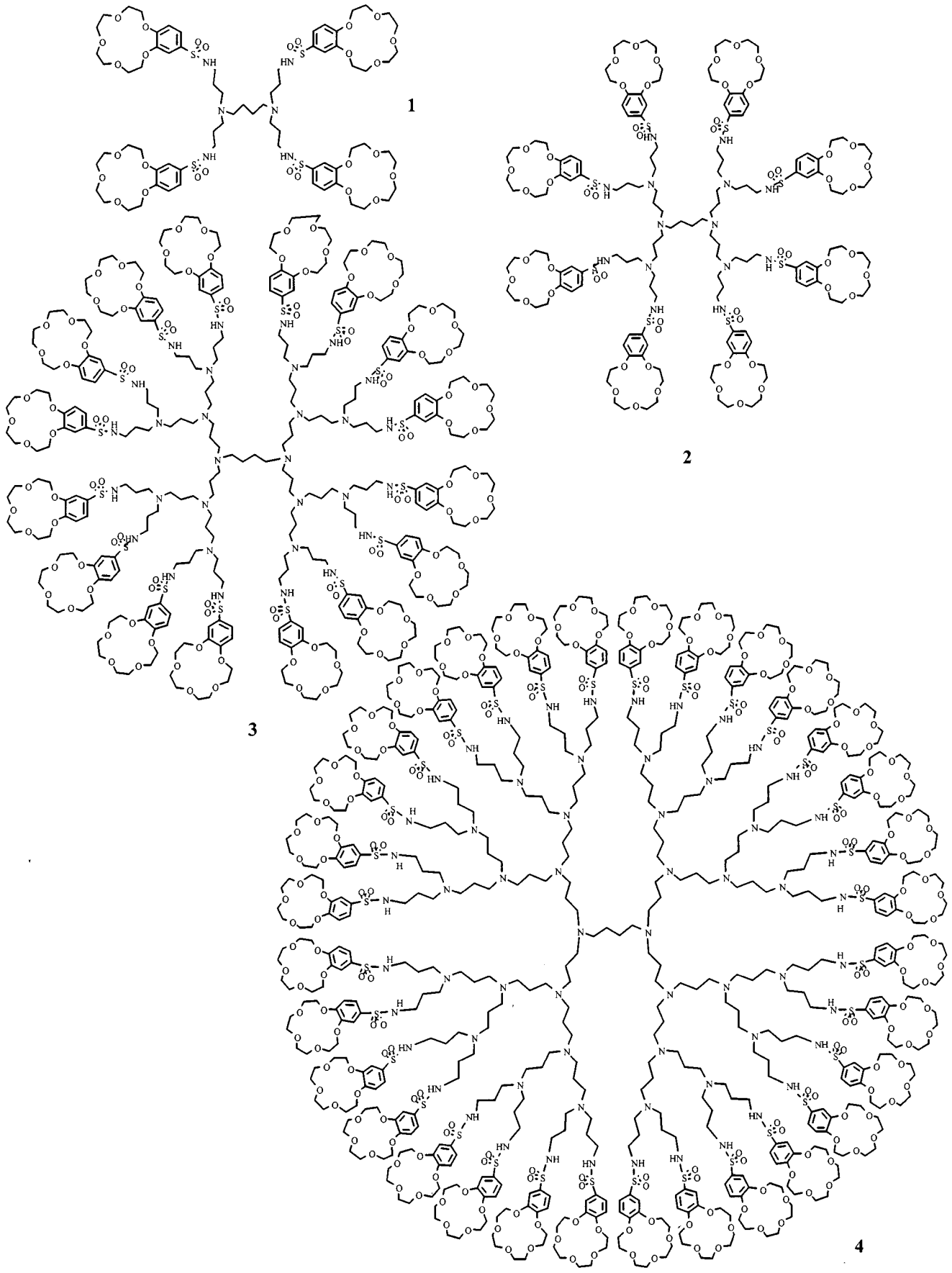
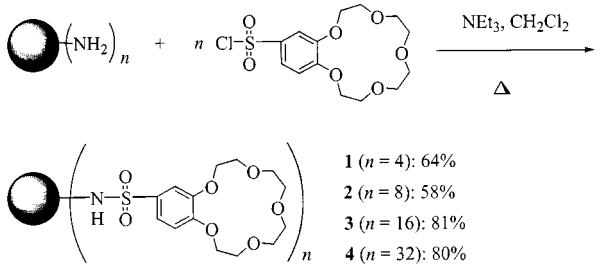


Scheme 1. Constitutions of the investigated multi-crown dendrimers

(POPAM, PPI) dendrimers. They were synthesized by treating amine-functionalized POPAM dendrimers with 1 equiv. (with respect to the primary amino groups of the dendrimer) of benzo[15]crown-5-4′-sulfonyl chloride in the presence of triethylamine (Scheme 2). The monofunctionalized multi-crown dendrimers **1**−**4** were characterized by ^1H and ^{13}C NMR spectroscopy as well as by MALDI-TOF mass spectrometry.[15] Dendrimers **1**−**4** were found to be soluble in common organic solvents but not in water. The melting points of the products ranged from 74 °C (**1**) to 85 °C (**4**).



Scheme 2. Preparation of multi-crown dendrimers

The synthesized multi-crown dendrimers were found to exhibit good solubility in solvents of low polarity, such as dichloromethane and chloroform, making them attractive as extractant and carrier molecules for separation processes. Solvent extraction was thus chosen to characterize the host−guest properties. In all cases, the experimental parameter of interest was the distribution ratio *D*, defined as the quotient of the relative amounts of the species present in the organic and aqueous phases. Aqueous solutions of sodium pertechnetate and mercury(II) chloride were extracted with solutions of the multi-crown dendrimers in chloroform. Excellent coalescence behaviour and the rapid attainment of extraction equilibria (within a few minutes) was observed.

The extraction of pertechnetate by the multi-crown dendrimers was investigated as a function of dendrimer concentration at pH = 7.5 (see Figure 1). As expected, the extraction efficiency increases with increasing dendrimer generation.[16] This finding is consistent with the results of pertechnetate extraction studies using urea- and methyl-orange-functionalized dendrimers,[10c,10d] confirming that the anion is bound by protonated tertiary amine groups in the interior of the dendrimer. Analysis of the organic phase revealed that no sodium ions were co-extracted, indicating that the crown ether moieties at the periphery of the dendrimer were not involved under the experimental conditions used.[17] Further insight into the extraction mechanism was gained by studying the effect of pH on the distribution ratio D_{TcO_4}.

Figure 2 summarizes the extraction of pertechnetate by the third-generation crown-ether dendrimer **3** as a function of pH and dendrimer concentration. The highest efficacy was obtained at pH = 5.4,[18] at which most of the tertiary amine groups should be protonated.[19] Increasing the pH led to a decrease in the efficiency of the pertechnetate extraction, in agreement with the decreasing degree of protonation of the dendrimer. It is worth mentioning that the buffer composition plays only a minor role. Likewise, the presence of a competing anion such as chloride[20] has only a small influence on the extraction of pertechnetate. At pH < 11, sodium ions were not extracted into the organic phase. Thus, we conclude that in this pH range the binding of pertechnetate occurs mainly by electrostatic attraction of the protonated amine groups. The peripheral groups play only a minor role. This was corroborated by the results of control experiments using dendrimers bearing 3,4-dimethoxybenzenesulfonamide peripheral groups.[21] Only at pH > 12 was the co-extraction of sodium ions observed. We found that the extraction efficacy of sodium pertechnetate from sodium hydroxide solution using dendrimer **3** was rather poor (Figure 2). However, it is known that benzo[15]-crown-5 shows only a weak affinity in the binding and extraction of sodium ions.[22] Despite this, the multi-benzo[15]crown-5 dendrimers investigated show considerable sodium uptake when the dendrimer concentration is increased and the hydrophobic picrate counterion is used (see Figure 3). As expected, the sodium uptake increases with increasing dendrimer generation. The introduction of more suitable crown ether units such as cyclohexano[18]-

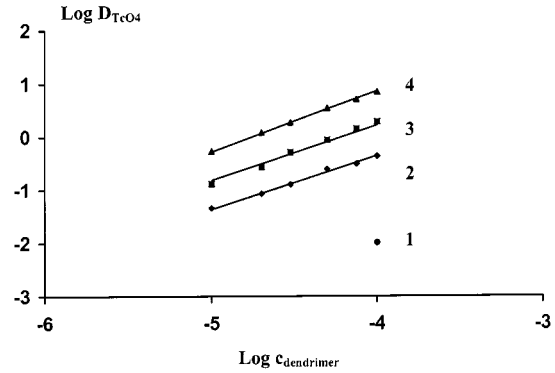


Figure 1. Variation of log D_{TcO_4} with dendrimer concentration for the extraction of pertechnetate with dendrimers **1**−**4**; c_{NaTcO_4} = 1×10^{-5} M, pH = 7.5 (TRIS/HCl buffer), $c_{dendrimer} = 1 \times 10^{-5}$ to 1×10^{-4} M in $CHCl_3$

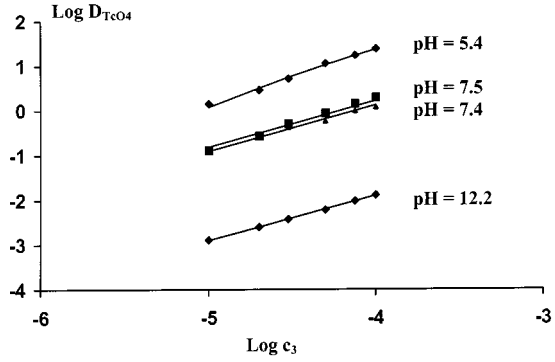


Figure 2. Variation of log D_{TcO_4} with pH for the extraction of pertechnetate with **3**; $c_{NaTcO_4} = 1 \times 10^{-5}$ M, pH = 5.4 (MES/NaOH), 7.4 (HEPES/NaOH), 7.5 (TRIS/HCl), 12.2 (1.5×10^{-2} M NaOH), $c_3 = 1 \times 10^{-5}$ to 1×10^{-4} M in $CHCl_3$

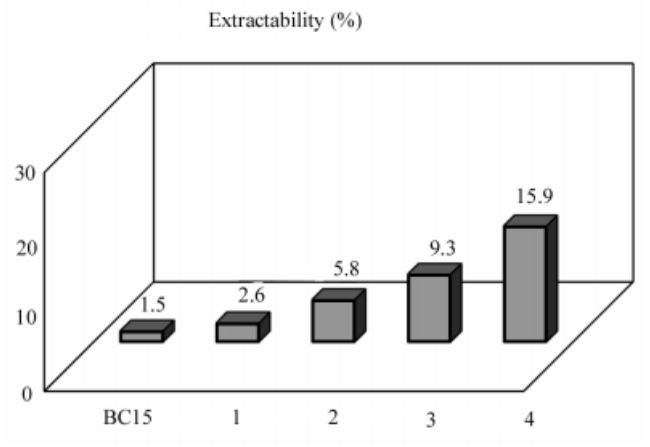


Figure 3. Extractability of sodium ions by benzo-15-crown-5 (BC15) and dendrimers **1**−**4**; $c_{NaOH} = 1.5 \times 10^{-2}$ M, $c_{HPic} = 1.5 \times 10^{-2}$ M, $c_{ligand} = 1 \times 10^{-3}$ M in $CHCl_3$

crown-6[23] at the periphery of the dendrimers can be expected to lead to higher sodium ion extraction efficiency.

Interestingly, in all cases, the slopes of the lines in the log D_{TcO_4}/log $c_{dendrimer}$ plots (Figures 1 and 2) were unity, indicating a clean 1:1 composition (pertechnetate:dendrimer) of the extracted complexes.[24] This finding is mainly attributable to the experimental conditions used. The concentration of the dendrimer was equimolar or in excess with respect to the pertechnetate concentration, which is a prerequisite for obtaining reliable information about the stoichiometries of the extracted complexes.[25] On the other hand, an excess of the dendrimer with respect to the pertechnetate concentration favours the formation of some partially loaded host−guest species. This is clearly evident from Figure 4.

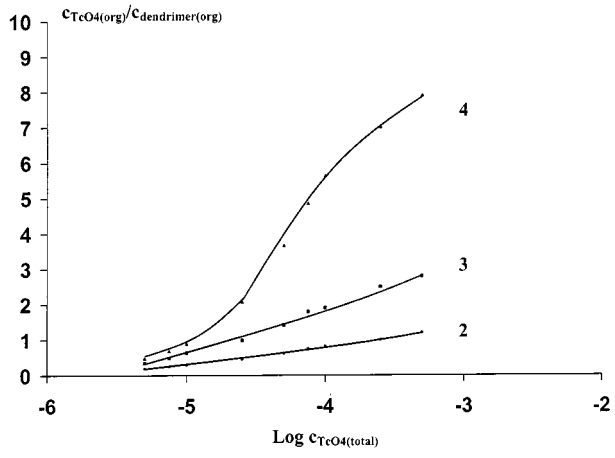


Figure 4. Variation of ratio $c_{TcO_4(org)}/c_{dendrimer(org)}$ with log $c_{TcO_4(total)}$ for the extraction of pertechnetate with dendrimers **2**−**4**; $c_{TcO_4} = 5 \times 10^{-6}$ to 5×10^{-4} M, pH = 5.4 (MES/NaOH), $c_{dendrimer} = 1 \times 10^{-5}$ in $CHCl_3$

Thus, at low pertechnetate concentration, the ratio $c_{TcO_4(org)}/c_{dendrimer(org)}$ is ≤ 1. The higher the generation of the dendrimer and the concentration of pertechnetate, the higher the loading capacity of the dendrimer with pertechnetate. At a total pertechnetate concentration of 5×10^{-4} M, approximately eight pertechnetate anions are extracted into the organic phase per fourth-generation dendrimer **4**.

Multi-crown dendrimers are also capable of extracting mercury(II) ions from chloride-containing solutions. The same trends were observed as in the case of pertechnetate extraction. As shown in Figure 5, the extraction efficiency of mercury(II) ions increases with increasing dendrimer generation. Benzo[15]crown-5 shows only a poor ability to transfer mercury(II) ions into an organic phase.

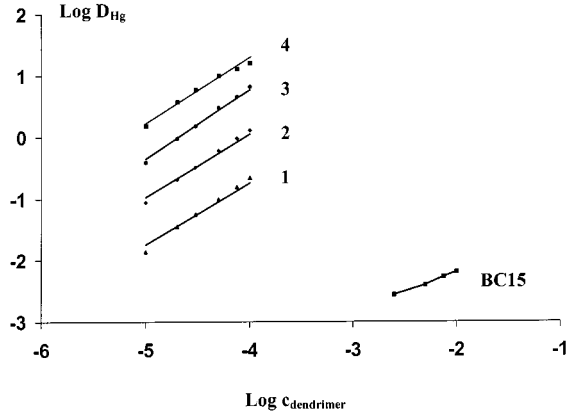


Figure 5. Variation of log D_{Hg}^{II} with dendrimer concentration for the extraction of mercury(II) with dendrimers **1**−**4** and benzo-15-crown-5 (BC15); $c_{HgCl_2} = 1 \times 10^{-5}$ M, pH = 7.5 (TRIS/HCl buffer), $c_{dendrimer} = 1 \times 10^{-5}$ to 1×10^{-4} M in $CHCl_3$, c_{BC15} 1×10^{-3} to 1×10^{-2} M in $CHCl_3$

The different extraction behaviour of multi-crown dendrimers as compared to benzo[15]crown-5 is not caused by a dendritic effect. Apparently, it is determined by the binding mode. Benzo[15]crown-5 is known as a weak extraction agent for $HgCl_2$.[22b] In general, mercury(II) prefers nitrogen and sulfur as donor atoms.[26] Hence, POPAM dendrimers are ideally suited to the binding and extraction of mercury(II) in the presence of chloride. Both neutral undissociated $HgCl_2$ as well as anionic $HgCl_3^-$ and $HgCl_4^{2-}$ may be bound by unprotonated and protonated tertiary amine groups, respectively.[27] The third- and fourth-generation dendrimers **3** and **4** in particular were found to be capable of extracting mercury(II) ions with high efficiency. Furthermore, these dendrimers can be loaded with a multitude of mercury(II) species. Thus, we found that the third-generation dendrimer **3** could accommodate approximately 12 Hg^{II} guests per molecule when mercury(II) was extracted from an aqueous solution ($c_{HgCl_2} = 5 \times 10^{-2}$ M; pH = 7.5; TRIS/HCl buffer) using only a low dendrimer concentration ($c_{\mathbf{3}} = 5 \times 10^{-5}$ M in $CHCl_3$).

Conclusion

It has been demonstrated that novel multi-crown dendrimers are easily accessible by grafting benzo[15]crown-5 units at the periphery of POPAM dendrimers. These multi-

crown dendrimers of four different generations, having 4, 8, 16, and 32 crown moieties at the exterior, are most soluble in organic solvents of low polarity and may serve as a new kind of carrier molecules for transport processes. Extraction studies performed with sodium pertechnetate and mercury(II) chloride have shown that the guest molecules are mainly bound in the interior of the polyamine skeleton. The crown ether units are rather inferior in terms of their complexation behaviour. Replacing the benzo[15]crown-5 units by more suitable [18]crown-6 moieties would seem to be an interesting line of future research, not only with regard to binding metal salts, but also for the complexation of biologically relevant substrates such as amino acids in their zwitterionic forms.

Experimental Section

General Remarks: All synthetic experiments were routinely carried out under dry nitrogen. Starting materials (POPAM dendrimers, generations 1 to 4) were purchased from Aldrich. Benzo[15]crown-5-4′-sulfonyl chloride was prepared according to a published procedure.[28] − NMR-spectroscopic data were obtained at 400 MHz with a Bruker AM 400 spectrometer (for ^{1}H and ^{13}C NMR spectra, the $CDCl_3$ signals were used as an internal reference; shifts are quoted with respect to TMS). − MALDI-TOF mass spectra were obtained with a TofSpec E & SE instrument from Micromass, Manchester.

General Synthetic Procedure for the Multi-Crown Dendrimers 1−4: 1/*n* equiv. of the starting polypropyleneamine dendrimer-$(NH_2)_n$ and 1.1·*n* equiv. of triethylamine were dissolved in dry dichloromethane (150 mL) (where *n* is the number of primary amino groups on the dendrimer). The mixture was heated to reflux, whereupon a solution of *n* equiv. of benzo[15]crown-5-4′-sulfonyl chloride in dichloromethane (50 mL) was added dropwise. The reaction mixture was stirred for 3−5 d under reflux under argon. The solvent was then removed in vacuo, the residue was taken up in dichloromethane, and the resulting solution was thoroughly washed with water, aq. sodium hydrogen carbonate solution, and again water (three times). After drying the organic phase with sodium sulfate and evaporation of the solvent, the multi-crown dendrimers were obtained as bright-yellow solids.

4-Cascade:1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)^1: benzo[15]crown-5-4′-sulfonamide (1): Reaction procedure as described above. Amounts of reagents used to obtain the 4-cascade: 1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)^1:aminopropane (0.20 g, 0.63 mmol), triethylamine (0.28 g, 2.77 mmol), benzo[15]crown-5-4′-sulfonyl chloride (0.93 g, 2.53 mmol). We obtained 0.66 g (0.40 mmol, 64%) of a bright-yellow solid; m.p. 74−76 °C. − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.39−1.65 (br, 12 H, CH_2), 2.25−2.43 (br, 12 H, CH_2N), 2.79−2.92 (br, 8 H, CH_2NHSO_2), 3.61−3.75 (m, 32 H, OCH_2), 3.76−3.91 (m, 16 H, OCH_2), 4.01−4.21 (m, 16 H, OCH_2), 6.82−6.92 (d, 4 H, CH_{ar}), 7.25−7.32 (s, 4 H, CH_{ar}), 7.35−7.45 (d, 4 H, CH_{ar}). − ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 25.1 ($CH_2CH_2NHSO_2$), 25.6 (CH_2CH_2N), 42.9 (CH_2NHSO_2), 53.1, 53.5 (CH_2N), 68.9, 69.0, 69.2, 70.2, 70.3, 71.2, 71.2 (OCH_2), 111.1, 111.9, 121.9, 135.9, 149.1, 154.9 (CH_{ar}). − MALDI-TOF MS (matrix: 2,5-DHB; $CHCl_3$/EtOH, 3:1): *m*/*z* (%) = 1659.2 (100) $[M + Na]^+$, 1636.1 (60) $[M]^+$, 1306.6 (8) [M − crown]$^+$, 846.1 (37) $[M/2 + 2CH_2]^+$. − $C_{72}H_{112}N_6O_{28}S_4$: 1638.0.

8-Cascade:1,4-Diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)^2: benzo[15]crown-5-4′-sulfonamide (2): Reaction procedure as described above. Amounts of reagents used to obtain the 8-cascade: 1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)^2:aminopropane (0.23 g, 0.30 mmol), triethylamine (0.26 g, 2.64 mmol), benzo[15]-crown-5-4′-sulfonyl chloride (0.88 g, 2.40 mmol). We obtained 0.58 g (0.17 mmol, 58%) of a bright-yellow solid; m.p. 79−80 °C. − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.32−1.61 (br, 28 H, CH_2), 2.21−2.41 (br, 36 H, CH_2N), 2.75−2.92 (br, 18 H, CH_2NHSO_2), 3.55−3.75 (br, 64 H, OCH_2), 3.80−3.92 (br, 32 H, OCH_2), 4.00−4.20 (m, 32 H, OCH_2), 6.82−6.93 (d, 8 H, CH_{ar}), 7.25−7.32 (s, 8 H, CH_{ar}), 7.35−7.43 (d, 8 H, CH_{ar}). − ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 24.0 ($CH_2CH_2NHSO_2$), 25.9 (CH_2CH_2N), 42.6 (CH_2NHSO_2), 51.7, 51.9, 52.6 (CH_2N), 68.9, 69.0, 69.19, 70.2, 70.3, 71.16, 71.19 (OCH_2), 111.05, 111.86, 121.91, 135.89, 149.12, 154.89 (CH_{ar}). − MALDI-TOF MS (matrix: 2,5-DHB; $CHCl_3$/EtOH, 3:1): *m*/*z* (%) = 3434.3 (100) $[M + Na]^+$, 3411.7 (47) $[M + H]^+$, 3082.2 (9) [M − crown]$^+$, 1734.7 (32) $[M/2 + 2\ CH_2]^+$. − $C_{152}H_{240}N_{14}O_{56}S_8$: 3413.4.

16-Cascade:1,4-Diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)^3: benzo[15]crown-5-4′-sulfonamide (3): Reaction procedure as described above. Amounts of reagents used to obtain the 16-cascade: 1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)^3:aminopropane (0.23 g, 0.14 mmol), triethylamine (0.25 g, 2.46 mmol), benzo[15]-crown-5-4′-sulfonyl chloride (0.82 g, 2.24 mmol). We obtained 0.77 g (0.11 mmol, 81%) of a bright-yellow solid; m.p. 80−82 °C. − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.45−1.65 (br, 60 H, CH_2), 2.21−2.58 (br, 84 H, CH_2N), 2.78−2.95 (br, 32 H, CH_2NHSO_2), 3.65−3.81 (br, 128 H, OCH_2), 3.82−3.97 (br, 64 H, OCH_2), 4.03−4.21 (br, 64 H, OCH_2), 6.82−6.92 (d, 16 H, CH_{ar}), 7.25−7.32 (s, 16 H, CH_{ar}), 7.35−7.45 (d, 16 H, CH_{ar}). − ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 24.3 ($CH_2CH_2NHSO_2$), 26.1 (CH_2CH_2N), 42.6 (CH_2NHSO_2), 51.8−52.5 (CH_2N), 68.9, 69.0, 69.2, 70.2, 70.3, 71.2, 71.2 (OCH_2), 111.1, 111.9, 121.9, 135.9, 149.1, 154.9 (CH_{ar}). − MALDI-TOF MS (matrix: THAP; $CHCl_3$/EtOH, 3:1): *m*/*z* (%) = 6969.9 (87) $[M]^+$, 6992.6 (69) $[M + Na]^+$, 3512.1 (40) $[M/2 + CH_2]^+$. − $C_{312}H_{496}N_{30}O_{112}S_{16}$: 6973.0.

32-Cascade:1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)^4: benzo[15]crown-5-4′-sulfonamide (4): Reaction procedure as described above. Amounts of reagents used to obtain the 32-cascade: 1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)^4:aminopropane (0.24 g, 0.07 mmol), triethylamine (0.25 g, 2.46 mmol), benzo[15]-crown-5-4′-sulfonyl chloride (0.82 g, 2.24 mmol). We obtained 0.77 g (0.06 mmol, 80%) of a bright-yellow solid; m.p. 84−85 °C. − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.41−1.72 (br, 124 H, CH_2), 2.19−2.67 (br, 180 H, CH_2N), 2.79−2.92 (br, 64 H, CH_2NHSO_2), 3.49−3.75 (br, 256 H, OCH_2), 3.76−3.91 (m, 128 H, OCH_2), 4.01−4.21 (br, 128 H, OCH_2), 6.72−6.92 (br, 32 H, CH_{ar}), 7.23−7.32 (br, 32 H, CH_{ar}), 7.35−7.45 (br, 32 H, CH_{ar}). − ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 26.0 ($CH_2CH_2NHSO_2$), 26.0 (CH_2CH_2N), 42.4 (CH_2NHSO_2), 51.7−52.8 (CH_2N), 68.9, 69.0, 69.2, 70.2, 70.3, 71.2, 71.2 (OCH_2), 111.1, 111.9, 121.9, 135.9, 149.1, 154.9 (CH_{ar}). − $C_{632}H_{1008}N_{62}O_{224}S_{32}$: 14085.

Liquid-Liquid Extraction Procedure: Extraction studies were performed at 25 ± 1 °C in 2-mL microcentrifuge tubes by mechanical shaking.[29] The phase ratio $V_{(org)}/V_{(w)}$ was 1:1 (0.5 mL each); the shaking period was 30 min. The extraction equilibrium was attained within this period. All samples were centrifuged after extraction. The pertechnetate and metal concentrations in both phases

were determined radiometrically using β-emission ($^{99}TcO_4^-$; Beckman LS 6000 LL liquid scintillation counter) and γ-radiation [^{22}Na, ^{203}Hg; Cobra II/Canberra Packard NaI(Tl) scintillation counter]. The pH of the aqueous solution was adjusted using 0.05 M 2-(*N*-morpholino)ethanesulfonic acid (MES)/NaOH (pH = 5.4), *N*-(2-hydroxyethyl)piperazine-*N*′-(2-ethanesulfonic acid) (HEPES)/NaOH (pH = 7.4), and tris(hydroxymethyl)aminomethane (TRIS)/HCl buffer (pH = 7.5).

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[15] MALDI-TOF spectra of multi-crown dendrimers **1**−**3** are available as Supporting Information; see footnote on the first page of this article.

[16] The extractability of pertechnetate using benzo[15]crown-5 ($c = 1 \times 10^{-2}$ M in $CHCl_3$) was lower than 1% under the experimental conditions used.

[17] Co-operative pertechnetate anion−sodium cation binding has been described for a tripodal tris(amidobenzo[15]crown-5) ligand; see: P. D. Beer, P. K. Hopkins, J. D. McKinney, *Chem. Commun.* **1999**, 1253−1254.

[18] At pH < 5, the solubility of lipophilic POPAM dendrimers in the aqueous phase is noticeably increased. This is obviously due to the higher hydrophilicity of the higher protonation state. Thus, dendrimers incorporating amino groups are rather unsuitable as extractants in more acidic media.

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[20] In the case of TRIS/HCl buffer (pH = 7.5), the chloride concentration is 4.2×10^{-2} M, which represents a huge excess over the pertechnetate concentration (ratio Cl^-/TcO_4^- = 4200:1).

[21] Dendrimers bearing 3,4-dimethoxybenzene peripheral groups extract pertechnetate with comparable efficiency as multi-crown dendrimers. Thus, at pH = 7.4, the third-generation 3,4-dimethoxybenzene-functionalized dendrimer ($c_{dendrimer} = 1 \times 10^{-4}$ M) extracts 42.1% of the pertechnetate into the or-

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