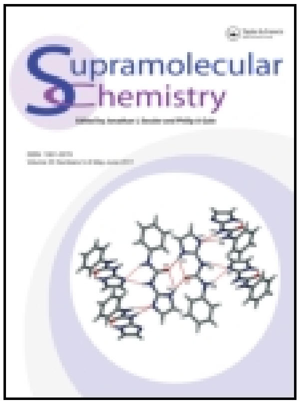

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Synthesis of PAMAM dendrimers with a resorcinarene core and their metal complexation

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Synthesis of PAMAM dendrimers with a resorcinarene core and their metal complexation

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Novel metal-chelating resorcinaren-poly(amidoamine) (PAMAM) dendrimers have been synthesised. The molecular structure of the resorcinaren-PAMAM dendrimers was characterised by ^{1}H NMR, ^{13}C NMR spectroscopy and by elemental analysis. The molecular weight of the dendrimers was confirmed by MALDI-TOF experiments. Gel permeation chromatography indicated that the product contained only one product. The metal-binding properties of the hyperbranched resorcinaren-PAMAM dendrimers were studied by means of the polymer-supported nanofiltration polymer-supported nanofiltration technique. The results show that the second generation resorcinaren-PAMAM dendrimers retained ~80% of Cu(II) and ~35% of Ni(II).

Keywords: resorcinarene; PAMAM; dendrimers; metal complexation

Introduction

In many countries nowadays, industry and other consumers are obliged to reduce their water consumption. That is why a variety of separation processes for heavy metal ions have been developed for industrial needs. These are precipitation, evaporation, liquid–liquid extraction, ion-exchange resins, reverse osmosis and electrodialysis. During recent years, advances in polymer chemistry, especially in the field of dendrimer synthesis, have been providing new opportunities to develop more efficient and cost-effective functional materials for the nanofiltration process (*1–3*). We should say that dendrimers are highly branched polymers with controlled composition and architecture. Complexing functional groups can be incorporated in the interior part of these macromolecules or attached to the surface (*4–7*). Numerous recent studies have focused on the preparation, characterisation and functionalisation of poly(amidoamine) (PAMAM) dendrimers. PAMAM is a class of commercially available dendrimers that have an ethylenediamine core, from which PAMAM repeat monomers extend in all directions (*8*, *9*). A number of studies have focused on the functionalisation of these hydrophilic PAMAM dendrimers for a variety of uses. In practical applications, such as drug delivery scaffolds or chelating agents, ionic dendrimers are designed to operate at different aqueous environments with biological and environmental relevant pH value as guest transport vehicles. As the next stage of dendrimer chemistry, it is proposed to create a macromolecule capable of having inner space (*10–13*). On the other hand, encapsulation of metal ions by PAMAM dendrimers typically involves internal tertiary amine groups. In the case of low-generation PAMAM dendrimers, reactive sites are also localised at the periphery (*14*). According to the recent study by A. Jawor, focused on elucidating the relative abilities of four nanoscale materials, it is possible to bind cadmium ions, and subsequently, to remove them from water with the help of PAMAM dendrimers (*15*). Malgorzata et al. investigated the electron capture dissociation and collision-induced dissociation of complexes of the PAMAMG2OH dendrimer with different metal ions (Ag^{+}, Cu^{2+}, Zn^{2+}, Fe^{2+} and Fe^{3+}). For the Cu^{2+} and the Fe^{3+} complexes, electron capture by the metal resulted in pronounced *a/x* cleavage, suggesting that amide nitrogen atoms and/or oxygen atoms were involved in metal coordination (*16*).

Herein, we describe the synthesis and complexing properties of resorcinaren-PAMAM dendrimer for the selective removal and enrichment of toxically relevant heavy metal ions.

Results and discussion

Synthesis and chemical characterisation of dendrimers

The synthesis of the two series of PAMAM dendrimers with two different centres was carried out applying the divergent approach that consisted of three steps. The first one was the synthesis of resorcinarenes with eight hydroxyl groups, which was followed by the selective formation of generation 0.5 of dendrimers and finally,

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by the introduction of amine group to obtain the first generation PAMAM dendrimers.

Resorcinarene was synthesised for the condensation reaction of resorcinol with two different aldehydes: hydrocinnamaldehyde and dodecyl aldehyde, according to Ref. (*11*).

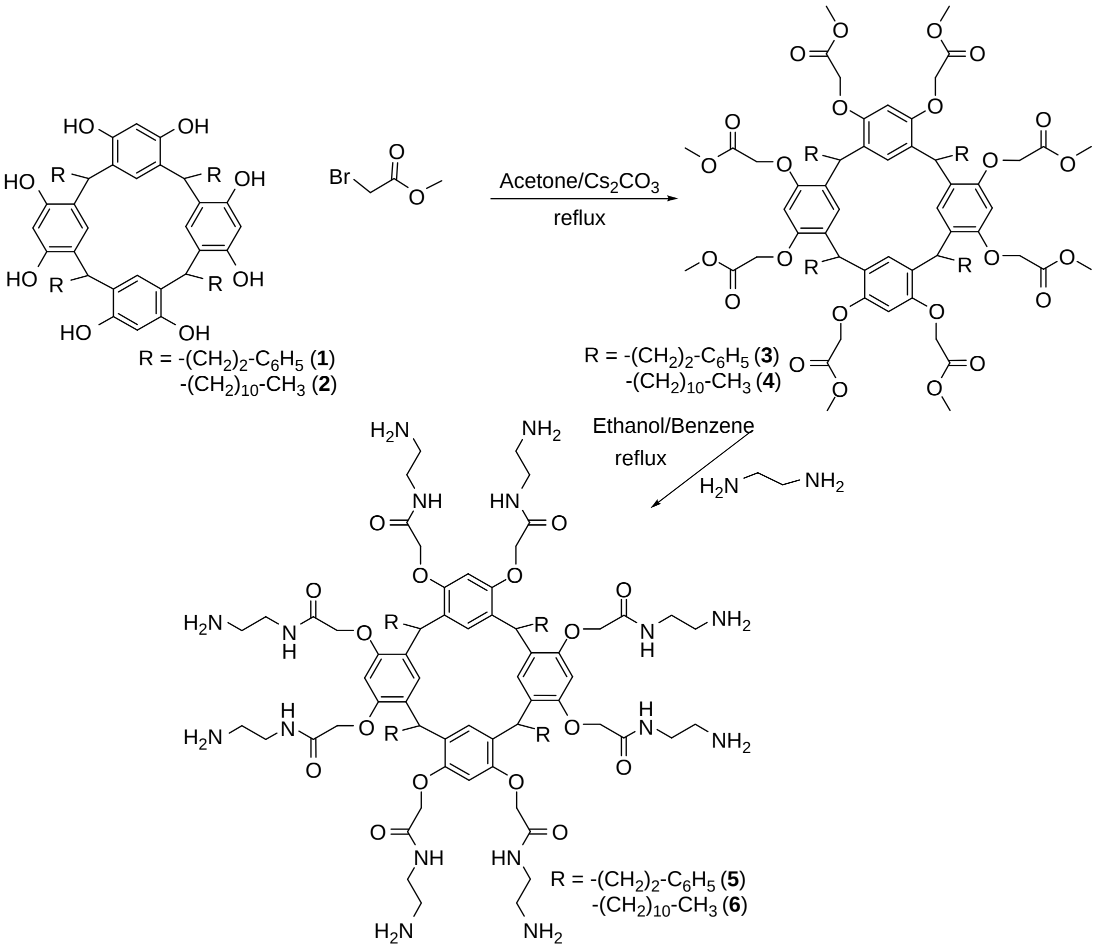
The next step was *O*-alkylation reaction between methyl bromoacetate and resorcinarenes **1** and **2**. The reaction was carried out in acetone and with Cs_2CO_3 as a catalyst, at reflux for 4 days; the dendrimers generation 0.5 (**3** and **4**) were obtained in good yield (82.2 and 78%, respectively). Treatment of **3** and **4** with 1,2-diaminoethane in a mixture of benzene/ethanol 1:1 at 90°C for 1 day resulted in 83.3% yield of compound **5** and 86.7% yield of compound **6** (Scheme 1).

In the ^1H NMR spectrum of dendrimer **3**, the following signals were observed: two signals at 2.02 and 2.60 due to the protons at the CH_2–ethylene group down of the resorcinaren ring, at 3.75 one singlet assigned to the CH_3–O group, at δ_H 4.28, one singlet due to the proton at the CH_2–O at the ether group and the characteristic triplet at δ_H 4.82 due to the CH group with coupling constant $J = 6.0$ Hz. The presence of this triplet in the NMR ^1H spectra confirms that the resorcinaren–dendrimer has a crown conformation (rccc). Two singlets observed at δ_H 6.62 were defined as the aromatic protons at resorcinol ring. Finally, one multiplet at δ_H 7.02–7.15 was defined as the aromatic proton in the bottom of the macrocycle ring.

The structure of the dendrimers was confirmed by fast atom bombardment (FAB) mass and electrospray spectrometry *m/z* of 1480 for **3** and *m/z* of 1704 for **5** (Figure 1(a), (b)).

The second generation of the dendrimers **9** and **10** was obtained with methylacrylate in methanol at room temperature for 2 days and resulted in yield for compound **7** as 81.6% and for compound **8** as 83.1%. Finally, the 1.5 generation dendrimers (**7** and **8**) were treated with 1,2-diaminoethane, which gave the second generation of dendrimers with 74 and 76.9% yield, respectively (Scheme 2).

In the ^{13}C NMR spectra of dendrimer **10** (Figure 2), the following signals were observed at δ_c 14.1 assigned to the CH_3 and at δ_c 22.7, 28.5, 29.3, 29.6 and 29.7 to the CH_2 groups of the aliphatic chain. The signals assigned to CH_2—N, CH_2—NH_2 were observed at δ_c 37.4, 37.8, 49.1



Scheme 1. Synthesis of dendrimers **5** and **6**.

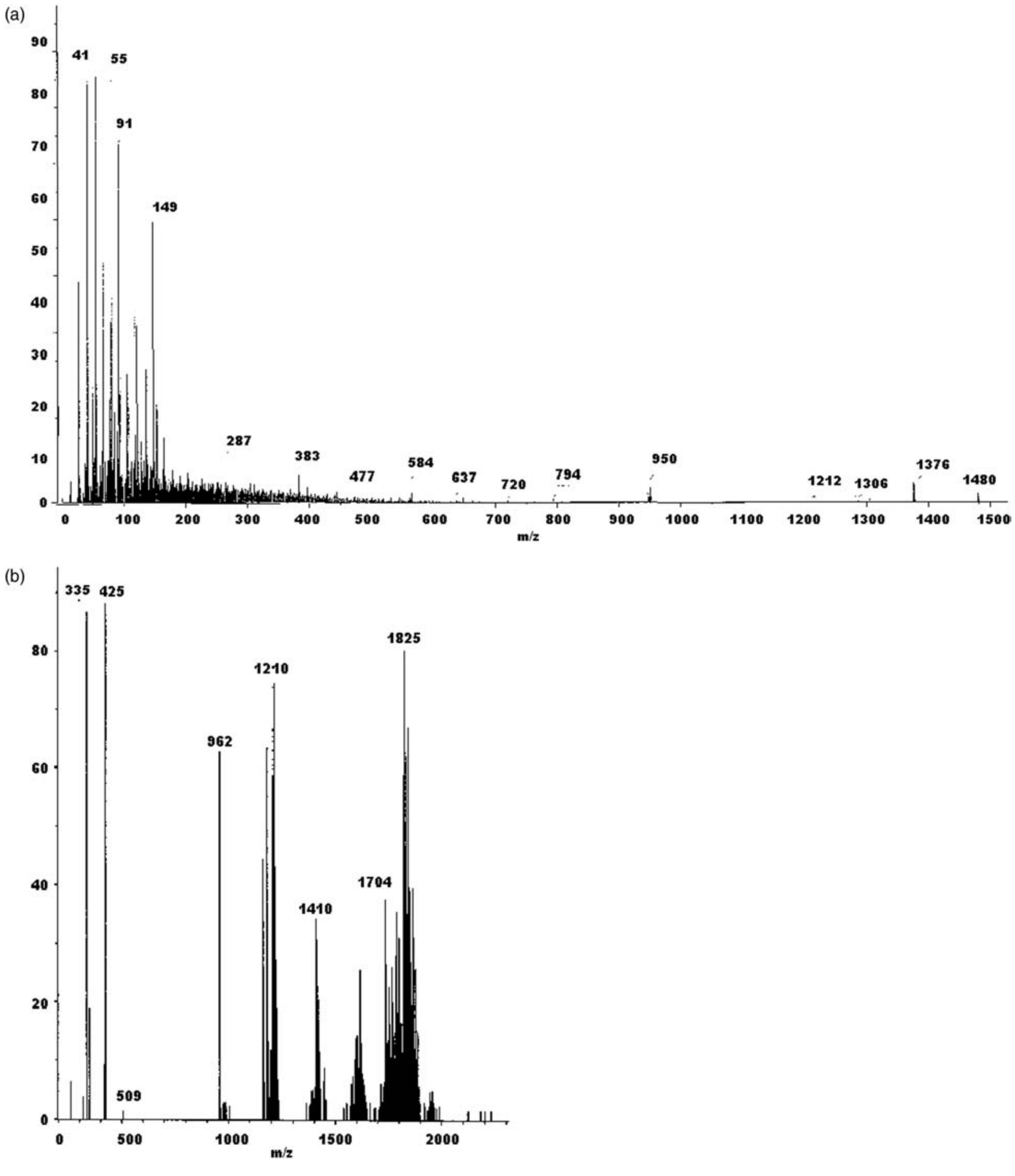
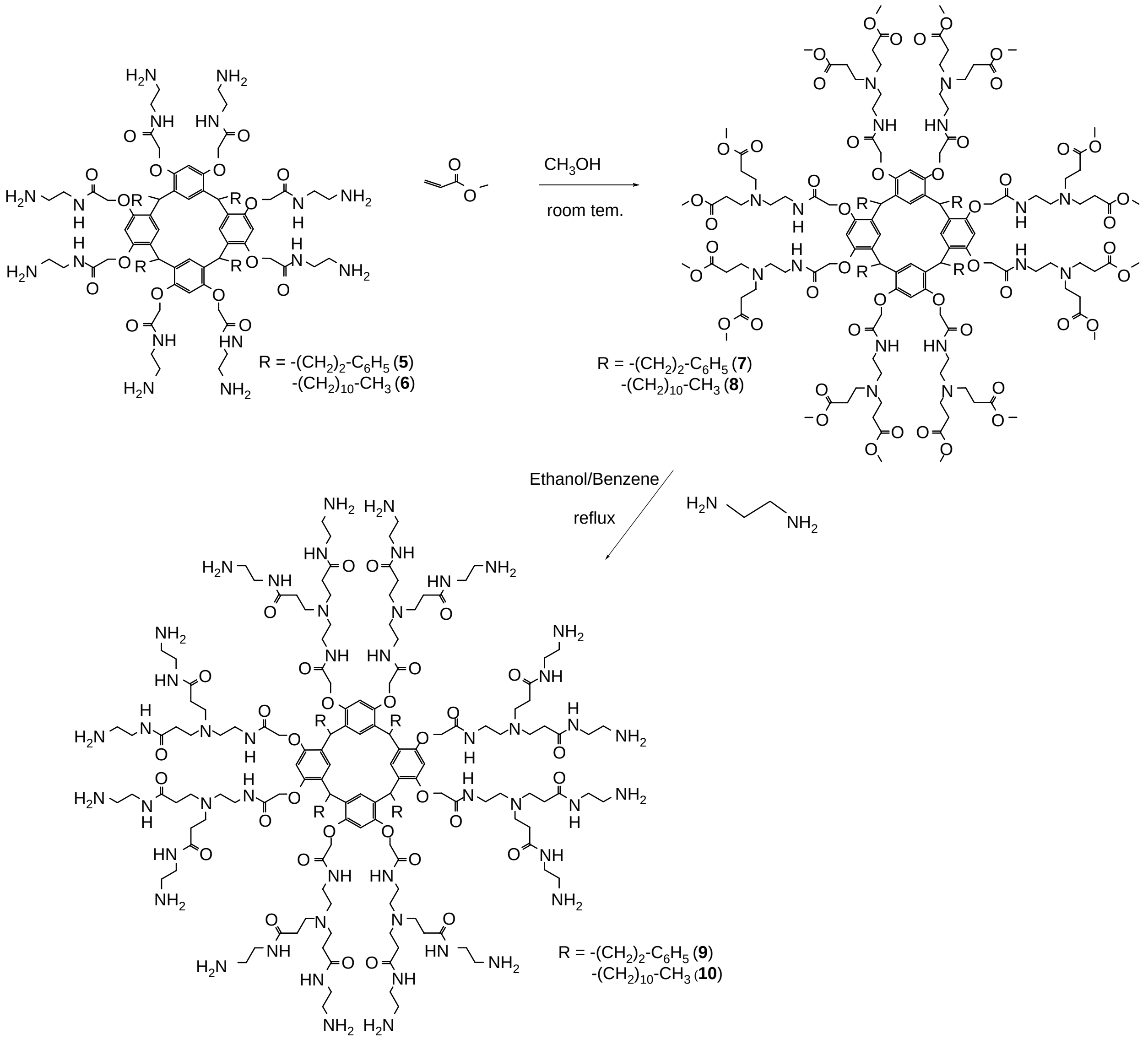


Figure 1. (a) FAB mass spectrum of compound **3**. (b) Electrospray spectrum of compound **5**.

and 51.5. The most important signals for C═O groups were observed at δ_c 168.4 and 172.8.

Preparation of coated membranes

0.003 mmol of dendrimers **5**, **6** or **9**, **10** were dissolved in a solution of 1:1 acetone and 10 ml of ethanol. This solution was added to a ®nylon membrane (pore size of 0.45 μ), after which it was degassed in an oven at approximately 90°C for 1 h (until no air bubbles could be seen). For the complexation studies, 20 ml of an aqueous solution of a metal sulphate salt (metal concentration of 5 ppm/l) was taken. The resulting solution was placed into a reactor system and the nanofiltration process was started. The



Scheme 2. Synthesis of dendrimers **9** and **10**.

membrane morphology was characterised using a scanning electron microscope (SEM; Electron-ESEM) operating at 25 kV (Philips, Neatherland).

To determine the metal complexation and the microphase-separated morphology, SEM was performed. Figure 3 represents a typical micrograph negative, in which ® nylon membrane domains appear as dark regions (a). Both dendrimers (light) (b) and ® nylon membrane domains were observed to form continuous networks, as needed for this application. The dendrimer-rich nanochannels appear to be around 1 nm long.

The SEM cross-sectional images (Figure 3(a)) suggest that the nylon membranes have a compact structure with no crystals embedded in the bulk of the membrane. The resulting dendrimer membrane has a smooth surface (Figure 3(b)), while samples of the dendrimer membranes after metal complexation (Figure 3(c)) have crystals on the surface.

Figure 4 shows the microanalysis of the samples, where no metals are observed in the nylon membrane (a), but in the case of the first (b) and second (c) generation dendrimer membrane after nanofiltration from aqueous CU solution, Cu was observed on the surface.

Selectivity of complex formation

The complexing properties of the dendrimer membrane of two divalent heavy metal ions were studied. It was shown that the effectiveness of the complexing process can be

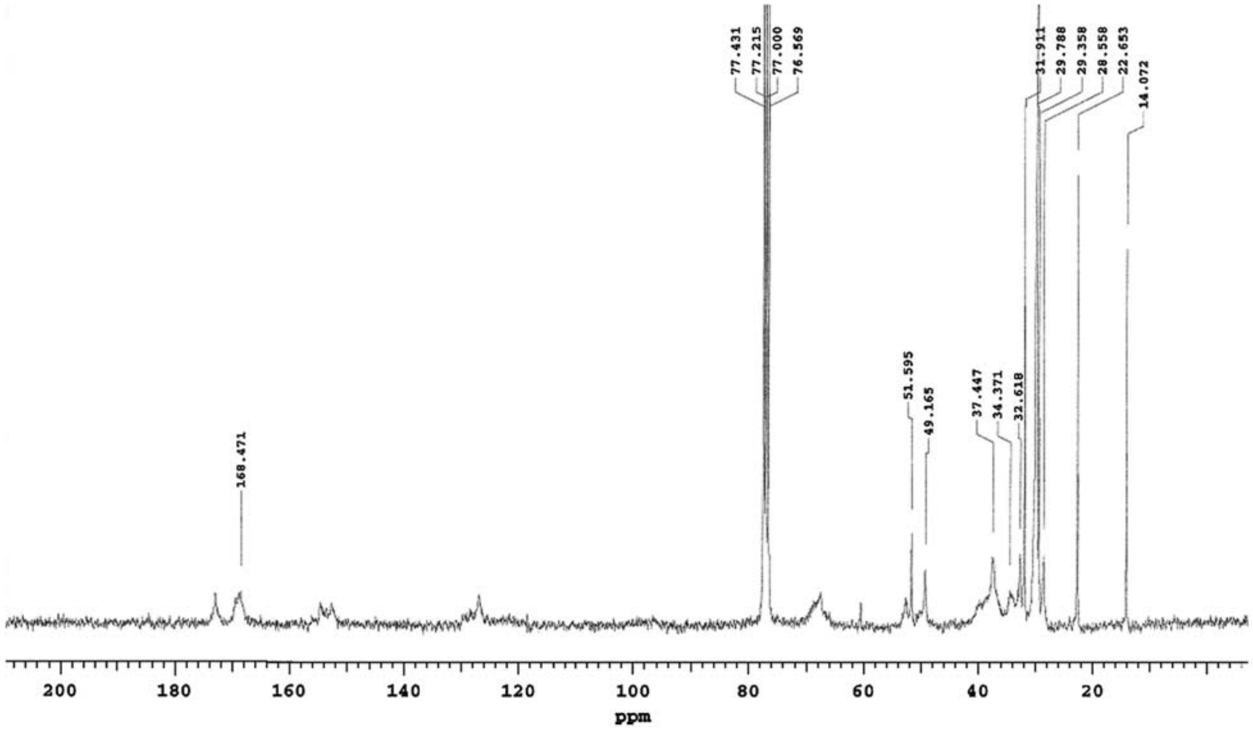


Figure 2. ^{13}C NMR spectrum for compound 10.

expressed by the retention of the metal ions. For a metal ion *i* its retention r_i is defined as:

$$r_i = \left(1 - \frac{C_{p,i}}{C_{r,i}}\right) \times 100(\%),$$

where $C_{p,i}$ and $C_{r,i}$ are the concentrations of the metal ion *i* in the permeate and in the retentate, respectively (*17*). Typical retention profiles are obtained by plotting the retention values of the aqueous solutions. The retention value shown in Tables 1 and 2 reflects the selectivity of the first and second dendrimer against Cu(II) and Ni(II). Cu is strongly bound to the first and second generation dendrimers (**6** and **10**) and it can be retained quantitatively even in high dilute solutions, whereas the complexation of Ni(II) metal ion depends on the concentration of the solution. The retention data depicted in Tables 1 and 2 also indicate that the first generation of dendrimer (**6**) showed good selectivity for copper, forming a complex. Cu(II) can be almost completely retained from high diluted solutions. On the contrary, the first and second generation of dendrímers (**5** and **9**) showed good selectivity for Ni(II).

Conclusions

After a variety of experiments have been carried out, the following conclusions were drawn: novel metal-chelating resorcinaren-PAMAM dendrimers have been synthesised. The resorcinaren-PAMAM dendrimers were characterised by ^{1}H NMR, ^{13}C NMR spectroscopy and elementary analysis. The molecular weight of the dendrimers was confirmed by MALDI-TOF experiments. Gel permeation chromatography indicated that the product contained only one product. The metal-binding properties of the hyperbranched resorcinaren-PAMAM dendrimer were studied by means of the polymer-supported nonofiltration technique. The results show that the modified nylon membrane with resorcinaren-PAMAM dendrimers retained ~80% of Cu(II) and ~40% of Ni(II).

Materials and equipment

Solvents and reagents were purchased as reagent grade and used without further purification. Acetone was distilled over calcium chloride. ^{1}H and ^{13}C NMR were recorded on a Varian-Unity-300 MHz with tetramethylsilane as an internal reference. Infrared (IR) spectra were recorded on a spectrophotometer Nicolet FT-SSX. Elemental analysis was carried out by Galbraith Laboratories, INC Knoxville. FAB + mass spectra were recorded on a JEOL JMS AX505 HA instrument. Electrospray mass spectra were recorded on a Bruker Daltonic, Esquire 6000. MALDI-TOF mass spectra were recorded on a Bruker Omni FLEX. The surface morphologies of the compounds were observed by SEM (Philips, USA) at 25 kV accelerating voltage and energy dispersive X-ray (EDX) detector. For

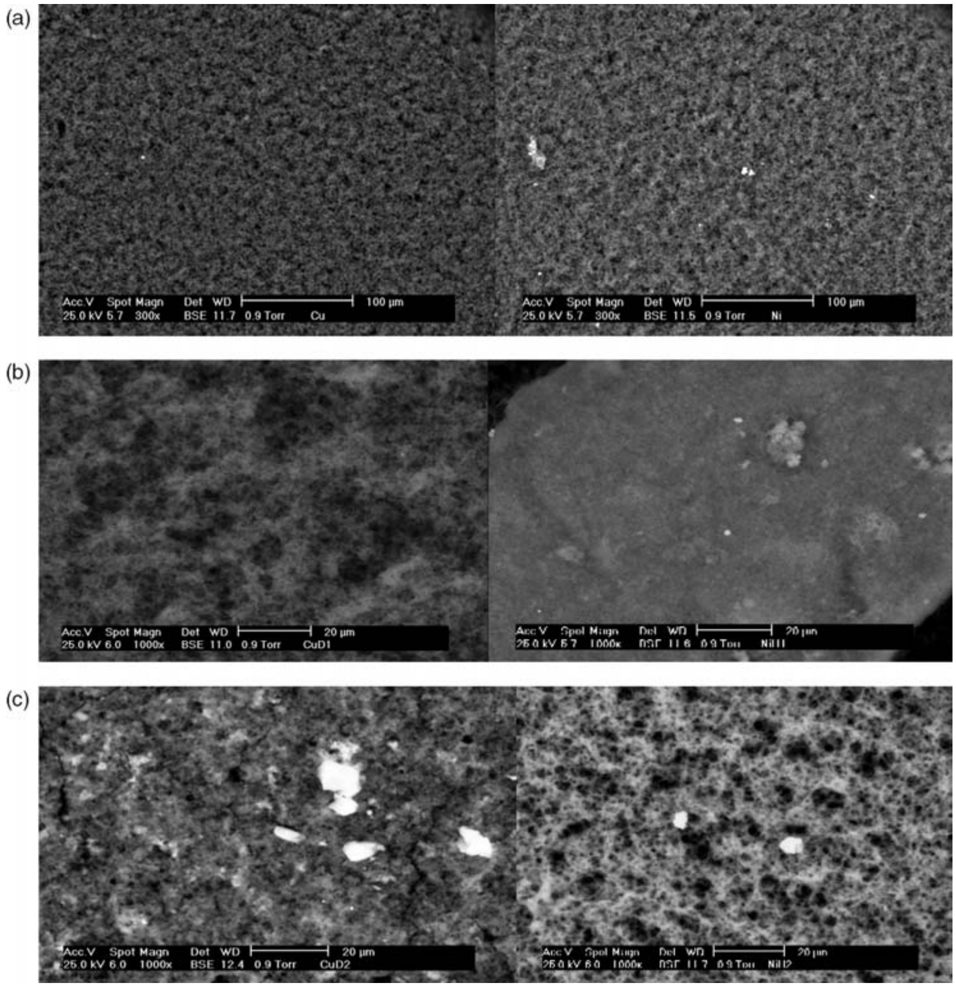


Figure 3. (a) SEM surface images of the nylon membranes, after nanofiltration with Cu and Ni the samples were free of dendrimers. (b) SEM surface images of the first generation dendrimer membrane (compounds **5** and **6**) after nanofiltration with Cu and Ni. (c) SEM surface images of the second generation dendrimer membrane (compounds **9** and **10**) after nanofiltration with Cu and Ni interconnected nanodomains of metal (light) and dendrimer (dark) are shown.

the EDX analysis, three fields of view (100.7 mm^2 each one) were analysed for 60 s at a 25 kV accelerating voltage and at a count rate of 1000–3000 cps. Atomic absorption was recorded on Perkin Elmer, Model A Analyst 100.

General procedure

Synthesis of 0.5 generation dendrimers

To a solution of resorcinarene **1** or **2** (5 mmol) in 50 ml of dry acetone, methyl bromoacetate (40 mmol) and cesium carbonate (5 mmol) were added. The reaction mixture was heated to reflux and stirred vigorously in nitrogen atmosphere for 4 days. After that the mixture was filtered to remove catalyst. The filtrate was evaporated to dryness under vacuum. The residue was dissolved in diethyl ether and washed with an aqueous solution of 5% Na_2CO_3 (three times). The organic layer was evaporated to dryness, and the mixture was purified using the following procedure: the mixture was dissolved in dichloromethane, and then methanol was added to obtain a precipitate. The procedure was repeated three times, obtaining compounds **3** and **4**.

Compound **3**: 6.085 g, 82.2% yield, white powder, m.p. > 300°C, UV–Vis CH_2Cl_2 (nm): 284, 232. IR (KBr, cm^{-1}): 3648, 3501, 3025, 2952, 2857, 1762, 1608, 1586, 1499, 1438, 1214, 1081, 753, 701. ^1H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 2.02 (s, 8H, CH_2), 2.60 (br, 8H, CH_2), 3.76 (m, 24H, O—CH_3), 4.22 (br, 16H, CH_2—O), 4.82 (t, 4H, CH, $J = 6.0$ Hz), 6.26 (s, 4H, Ar), 6.62 (s, 4H, Ar), 7.02–7.12 (m, 20H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 34.4 (CH_2), 35.3 (CH_2), 36.7 (CH), 51.8 (O—CH_3), 66.8 (CH_2—O), 100.7 (Ar), 127.8 (Ar), 127.9 (Ar), 128.0 (Ar), 128.1 (Ar), 128.2 (Ar), 142.2 (Ar_{ipso}), 153.8 (Ar—O), 169.4 (C=O). FAB^+ (*m/z*): 1480 *m/z*. Calcd for $C_{84}H_{88}O_{24}$: C: 68.10, H; 5.99%. Found. C; 68.07, H: 5.98%.

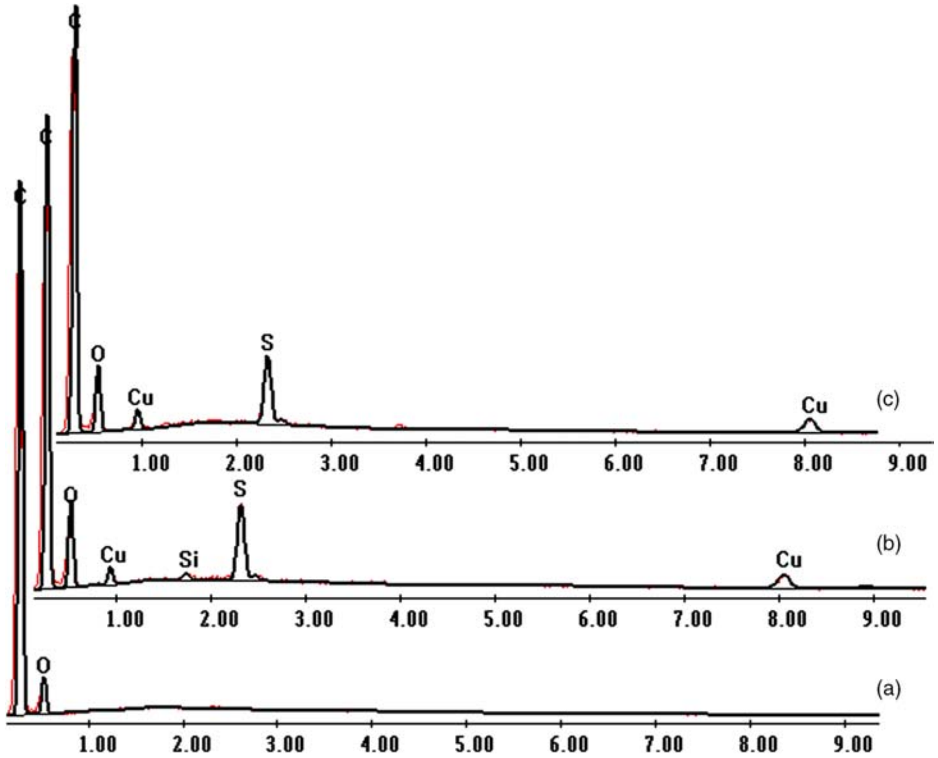


Figure 4. Surface microanalysis of (a) membrane, (b) first generation dendrimer membrane and (c) second generation dendrimer membrane after nanofiltration.

Compound **4**: 6.560 g, 78.0% yield, white powder, m.p. >300°C, UV–Vis CH_2Cl_2 (nm): 283, 235. IR (KBr, cm^{-1}): 3499, 2924, 2853, 1764, 1741, 1611, 1587, 1501, 1439, 1376, 1283, 1211, 1124, 905, 851, 830. ^1H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 0.86 (t, 12H, CH_3, $J = 9.0$ Hz), 1.23 (br, 72H, CH_2), 1.84 (m, 8H, CH_2), 3.75 (s, 24H, O—CH_3), 4.28 (br, 16H, CH_2—O), 4.58 (t, 4H, CH, $J = 8$ Hz), 6.21 (s, 4H, Ar), 6.60 (s, 4H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 14.0 (CH_3), 22.6 (CH_2), 28.0 (CH_2), 29.3 (CH_2), 29.7 (CH_2), 29.9 (CH_2), 31.9 (CH), 34.4(CH_2), 51.8 (CH_3—O), 67.0 (CH_2—O), 100.7 (Ar), 126.4 (Ar), 128.4 (Ar_{ipso}), 154.3 (Ar—O), 169.7 (C═O). FAB^+ (*m/z*): 1681 *m/z*. Calcd for $C_{96}H_{144}O_{24}$: C 68.54, H 8.63%. Found. C: 68.58, H: 8.59%.

Table 1. Retention values of Cu(II) ion for the dendrímers.

Compound	Cu^{2+} (mg/l)	± (mg/l)	Retention (%)
Nylon membrane	4.927	± 0.046	1.46
5	4.143	± 0.132	17.14
9	3.219	± 0.157	35.62
6	1.030	± 0.025	79.40
10	1.445	± 0.024	71.10

Table 2. Retention values of Ni(II) ion for the dendrímers.

Compound	Ni^{2+} (mg/l)	± (mg/l)	Retaining yield (%)
Nylon membrane	4.936	± 0.053	1.28
5	3.247	± 0.055	35.06
9	3.153	± 0.084	36.94
6	4.158	± 0.077	16.84
10	3.247	± 0.045	35.06

General procedure

Synthesis of 1.0 and 2.0 generations of dendrimers

To a solution of compounds **3, 4, 7** and **8** (3 mmol) in 50 ml of a 1:1 mixture of benzene/ethanol, 1,2 ethylenediamine (24 mmoles) was added. The reaction was carried out at 90°C and the mixture was stirred for 24 h. After that the solvents were evaporated under vacuum, the solid obtained was dissolved in dichloromethane and precipitated with hexane and then washed with 750 ml of hexane, obtaining compounds **5**, **6**, **9** and **10**.

Compound **5**. 4.262 g, 83.3% yield, white powder, m.p. >300°C, UV–Vis CH_2Cl_2 (nm): 284, 213. IR (KBr, cm^{-1}): 3402, 3300, 3060, 3026, 2933, 2863, 1675, 1581, 1499, 1444, 1288, 1189, 1052, 909, 700. ^1H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 2.06 (s, 16H, NH_2), 2.68 (br, 16H, CH_2), 3.39 (br, 16H, CH_2—NH_2), 4.31 (br, 16H, CH_2—O), 4.50 (br, 16H, CH_2—NH), 4.61 (br, 4H, CH), 6.49 (br, 4H, Ar), 6.68 (br, 4H, Ar), 7.05–7.11 (m, 20H, Ar), 7.47 (br, 8H, NH) ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 33.7 (CH_2), 35.9 (CH_2), 37.0 (CH_2), 40.4 (CH), 48.7 (N—CH_2), 49.2 (N—CH_2), 66.8 (CH_2—O), 127.8 (Ar), 141.0 (Ar), 141.1 (Ar), 141.2 (Ar), 141.3 (Ar), 141.4 (Ar), 152.3 (Ar_{ipso}), 153.8 (Ar—O), 168.9 (C=O). FAB$^+$ (*m/z*): 1704 *m/z*. Calcd for $C_{92}H_{120}N_{16}O_{16}$: C: 64.77, H: 7.09, N: 13.14%. Found. C: 64.79, H: 7.09, N: 13.11%.

Compound **6**. 4.954 g, 86.7% yield, white powder, m.p. > 300°C, UV–Vis CH_2Cl_2 (nm): 282, 210. IR (KBr, cm^{-1}): 3396, 3310, 3188, 3076, 2925, 2854, 1675, 1539, 1433, 1288, 1192, 1103, 823, 509. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 0.86 (s, 12H, CH_3), 1.22 (br, 88H, CH_2, NH_2), 1.90 (an, 8H, CH_2), 2.94 (br, 16H, CH_2—NH_2), 3.53 (br, 16H, CH_2—NH), 4.51 (br, 4H, CH), 4.74 (s, 16H, CH_2—O), 6.53 (s, 4H, Ar), 6.63 (s, 4H, Ar), 7.61 (s, 8H, NH) ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 14.3 (CH_3), 22.9 (CH_2), 28.7 (CH_2), 29.6 (CH_2), 30.0 (CH_2), 30.4 (CH_2), 30.5 (CH_2), 32.1(CH), 37.5 (CH_2—N), 37.9 (CH_2—NH), 67.9 (CH_2—O), 96.3 (Ar), 122.6 (Ar), 127.2 (Ar_{ipso}), 154.7 (Ar—O), 168.8 (C=O). FAB$^+$ (*m/z*): 1905 *m/z*. Calcd for $C_{104}H_{176}N_{16}O_{16}$: C: 65.51, H: 9.30, N; 11.75%. Found. C: 65.50, H: 9.32, N: 11.74%.

Compound **9**. 1.698 g, 74.0% yield, white powder, m.p. > 300°C, UV–Vis CH_2Cl_2 (nm): 283, 213. IR (KBr, cm^{-1}): 3399, 3290, 3082, 2938, 2861, 1735, 1659, 1546, 1499, 1440, 1288, 1194, 1110, 1054, 700, 589 ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 1.14 (s, 32H, NH_2), 2.14 (s, 16H, CH_2), 2.34 (br, 32H, CH_2—C=O), 2.61 (s, 16H, CH_2—NH), 2.73 (br, 32H, CH_2—NH_2), 2.84 (br, 16H, CH_2—N), 3.28 (br, 32H, CH_2—NH), 3.30 (br, 32H, CH_2—N), 4.44 (br, 4H, CH), 4.87 (br, 16H, CH_2—O), 6.66 (br, 4H, Ar), 6.82 (br, 4H, Ar), 7.08 (br, 20H, Ar), 7.46 (br, 24H, NH) ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 27.6 (CH_2), 32.1 (CH_2), 32.4 (CH_2), 33.1 (CH_2), 36.6 (CH), 37.0 (CH_2), 49.0 (CH_3—O), 51.5 (N—CH_2), 68.3 (CH_2—O), 125.7 (Ar), 128.3 (Ar), 141.8 (Ar), 152.6(Ar), 154.1 (Ar—O), 168.0 (C=O), 172.9 (C=O). MALDI-TOF (*m/z*): 3529 *m/z*. Calcd for $C_{172}H_{280}N_{48}O_{32}$: C: 58.48, H: 7.99, N: 19.03%. Found. C: 58.51, H: 7.97, N: 19.01%.

Compound **10**. 1.865 g, 76.9% yield, white powder, m.p. > 300°C, UV–Vis CH_2Cl_2 (nm): 283, 233. IR (KBr, cm^{-1}): 3400, 3078, 2925, 2853, 1738, 1683, 1612, 1535, 1286, 1197, 1104, 836, 575. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 0.86 (t, 12H, CH_3, $J = 8$ Hz), 1.22 (br, 104H, CH_2—NH_2), 1.88 (br, 8H, CH_2), 2.43 (br, 32H, CH_2-—C=O), 2.63 (br, 16H, CH_2—N), 2.77 (br, 32H, CH_2—N), 2.98 (br, 16H, CH_2—NH) 3.51 (br, 32H, CH_2—NH_2), 3.62 (br, 32H, CH_2—NH), 4.50 (br, 4H, CH), 4.72 (br, 16H, CH_2—O), 6.49 (br, 4H, Ar), 6.91 (br, 4H, Ar), 7.61 (br, 24H, NH). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 14.1 (CH_3), 22.7 (CH_2), 28.5 (CH_2), 29.3 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 31.9 (CH), 32.6 (CH_2—C=O), 37.4 (CH_2—N), 37.8 (CH_2—NH_2), 49.1 (CH_2—NH), 51.5 (CH_2—NH_2), 67.4 (CH_2—O), 117.1 (Ar), 126.8 (Ar), 136.5 (Ar_{ipso}), 152.5 (Ar—O), 168.4 (C=O), 172.8 (C=O). MALDI-TOF (*m/z*): 3730 *m/z*. Calcd for $C_{184}H_{336}N_{48}O_{32}$: C: 59.20, H: 9.07, N: 18.01%. Found. C: 59.23, H: 9.09, N: 17.99%.

Synthesis of 1.5 generation dendrimers

To a solution of compound **5** or **6** (1.2 mmol) in 30 ml of methanol, methylacrylate (19.2 mmol) was added. The reaction mixture was kept at room temperature and stirred for 48 h. After that water was added, and the formed product was filtered. Then it was dried under vacuum, obtaining compounds **7** and **8**.

Compound **7**. 3.016 g, 81.6% yield, white powder, m.p. > 300°C, UV–Vis CH_2Cl_2 (nm): 283, 237. IR (KBr, cm^{-1}): 3409, 3063, 3026, 2946, 2833, 1735, 1692, 1533, 1440, 1288, 1195, 1108, 1050, 910, 700. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 2.40 (br, 32H, CH_2-—C=O), 2.56 (br, 16H, CH_2), 2.74 (br, 16H, CH_2—N), 3.57 (br, 32H, CH_2—N), 3.66 (br, 48H, CH_3—O), 4.31 (br, 16H, CH_2—O), 4.50 (br, 16H, CH_2—NH), 4.61 (t, 4H, CH, $J = 7.0$ Hz), 6.40 (br, 4H, Ar), 6.67 (br, 4H, Ar), 7.06–7.14 (m, 20H, Ar), 7.46 (br, 8H, NH) ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 32.1 (CH_2), 32.4 (CH_2), 33.1 (CH_2), 36.6 (CH), 37.0 (CH_2), 49.0 (CH_3—O), 51.5 (N—CH_2), 68.3 (CH_2—O), 125.7 (Ar), 128.3 (Ar), 141.8 (Ar), 152.6(Ar), 154.1 (Ar—O), 168.0 (C=O), 172.9 (C=O). MALDI-TOF (*m/z*): 3081 *m/z*. Calcd for $C_{156}H_{216}N_{16}O_{48}$: C: 60.77, H; 7.06, N: 7.27%. Found. C: 60.74, H: 7.03, N: 7.28%.

Compound **8**. 3.273 g, 83.1% yield, white powder, m.p. > 300°C, UV–Vis CH_2Cl_2 (nm): 283, 233. IR (KBr, cm^{-1}): 3400, 3078, 2925, 2853, 1738, 1683, 1612, 1535, 1286, 1197, 1104, 836, 575. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 0.86 (t, 12H, CH_3, $J = 8$ Hz), 1.20 (br, 72H, CH_2), 1.86 (br, 8H, CH_2), 2.41 (br, 32H, CH_2—C=O), 2.59 (br, 16H, CH_2—N), 2.75 (br, 32H, CH_2—N), 3.50 (br, 16H, CH_2—NH), 3.62 (br, 48H, CH_3—O), 4.51 (br, 4H, CH), 4.69 (br, 16H, CH_2—O), 6.50 (br, 4H, Ar), 6.98 (br, 4H, Ar), 7.42 (br, 8H, NH). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 14.3 (CH_3), 22.8 (CH_2), 28.7 (CH_2), 30.0 (CH_2), 30.1 (CH_2), 30.2 (CH_2), 30.4 (CH_2), 32.1(CH), 37.4 (CH_2—N), 32.8 (CH_2—C=O), 39.6 (CH_2—NH), 51.9 (CH_3—O), 52.5 (CH_2—N), 53.7 (CH_2—NH_2), 67.3 (CH_2—O), 117.1 (Ar), 122.6 (Ar), 130.1 (Ar_{ipso}), 155.9 (Ar—O), 168.6 (C=O), 173.1 (C=O). MALDI-TOF (*m/z*): 3282 *m/z*. Calcd for $C_{168}H_{272}N_{16}O_{48}$: C: 61.44, H: 8.35, N 6.82%. Found. C: 61.48, H: 8.32, N: 6.83%.

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