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ORIGINAL ARTICLE

Multi-calixarenes with multidentate coordination sites

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Abstract Hyperbranched molecules, **4–8**, based on calixarenes attached to newly synthesised cores **2** and **3** have been prepared. Preliminary complexation studies of the complexation of $Zn(Pic)_2$ by **8** showed that the ligand prefers to bind the picrate anions.

Keywords Multi-calixarenes · Multidentate cores · Picrate anion complexation

Introduction

Calixarenes have been widely exploited in all areas of supramolecular chemistry over the past three decades [1] and many recent developments have concerned their applications in the production of chemical entities with the dimensions of nanometers, as in "nanochemistry" [2]. A special family of new molecular nano-objects based on the chemistry of calixarenes associated to the one of dendrimers are the 'calix-dendrimers' or multi-calixarenes [3]. Recently Matthews and co-workers have prepared amino-functionalised multi-calixarenes which low cellular toxicity, effective DNA binding and, when featuring aliphatic amines, are efficient gene transfection agents [4].

Our investigations on the design of multi-calixarenes as calix-dendrimers started few years ago. In previous publications [5, 6], we described the synthesis of a Y shaped di-calixdendron prepared from monocarboxylethylcalix[4]arene (**1**) and $N(CH_2CH_2NH_2)_3$ ('tren'), which was used for the preparation of hyperbranched molecules and a second generation of a tren-calix dendrimer by further amidation reactions with chosen methyl ester compounds. In order to include a donor site with a higher denticity in the multi-calixarenes, we replaced the 'tren' by tripodal amino-ligands known for their coordination behavior.

Reactions between tripodal $CH_3C(CH_2NH_2)_3$ = 'tame', $CH_3C(CH_2NHCH_2CH_2NH_2)_3$ = 'sen' and $HOCH_2C(CH_2SCH_2CH_2NH_2)_3$ = 'hyten' and the monocarboxylethylcalix[4]arene (**1**) led to the ready isolation of tame-dicalix [7], tame-tricalix [7], sen-tricalix [7], hyten-dicalix [8] and hyten-tricalix [8]. Investigations were conducted with various calix dendrimers of the formation of complex with Zn(II) and Co(III). The cations were observed to be localized in the multidentate coordinating region, clearly demonstrating that the metal may offer a means of controlling the orientation of pendant groups from a coordinating core in the present molecules [5–8]. This property was used to create fluorescent probes from tren-tricalix working with pyrene-excimer emission for detecting Al(III) [9] and tren-dicalix working with pyrene excimer for detecting Al(III) and with FRET (from pyrene excimer to rhodamine B) triggered by Hg(II) [10]. The present note reports the synthesis of new hyperbranched molecules **4–8** constructed by the reaction of dipodal

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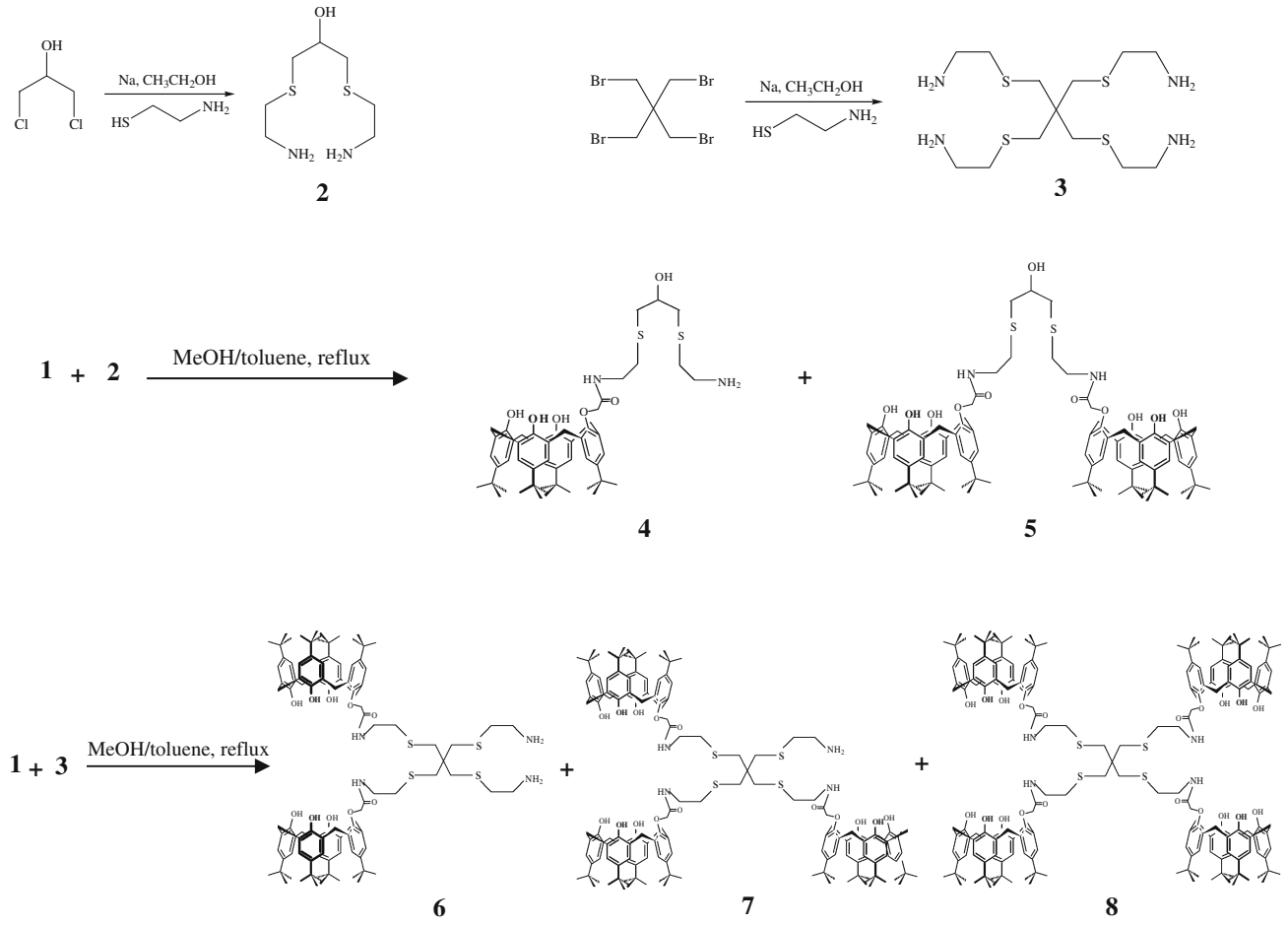
2 = $HOCH(CH_2SCH_2CH_2NH_2)_2$ and tetrapodal **3** = $C(CH_2SCH_2CH_2NH_2)_4$ with monocarboxylethylcalix[4] arene (**1**). These novel multi-calixarenes contains three potential chelating sites at the level of the N,S atoms, OH functionalities and primary amido groups.

Results and discussion

According to Scheme 1, the synthesis of dipodal **2** and tetrapodal **3** was achieved through direct routes in which 1,3-dichloropropan-2-ol (**A**) or pentaerythritol tetrabromide (**B**) were reacted with the sodium salt of 2-aminoethanethiol in EtOH at reflux. The crude reaction mixtures were purified by formation and chromatographic separation of the Cu(II) complexes on SP-Sephadex (Na^+ form) followed by adsorption on Dowex 50Wx2 ion-exchange resin (H^+ form). **2** and **3** were obtained as pure di- and tetraamino compounds ready for further amido reaction $C(CH_2SCH_2CH_2NH_2)_4$ and monocarboxylethylcalix[4]arene (**1**).

The respective reactions of **2** and **3** with **1**, in the cone conformation [11], in 1:1 methanol–toluene refluxing solution (4 days for **2** and 3 days for **3**) proceeded in a stepwise fashion, with the rates for consecutive steps differing sufficiently to allow the ready isolation of mono **4**- and diamido **5**, and, di- **6**, tri- **7** and tetraamido **8**. **4–8** were purified by chromatography on SiO_2 column (eluent ranging from 95:5 CH_2Cl_2: acetone to acetone). The products with the higher weights were eluted first probably due to an increased retention on silica along with the increasing number of NH_2 groups on the molecules. The respective yields for **4–8** were 16%, 36%, 10%, 22%, and 34%. **4–8** were fully characterized by ^{1}H-NMR spectroscopy, mass spectrometry and elemental analysis. The cone conformation was confirmed in all the cases by the presence in the ^{1}H-NMR spectra of two AB systems for the ArCH_2Ar of the calixarene ring closely matching those of the two AB systems at 4.47 and 3.49 ppm of the mono ester **1** [12].

Preliminary investigations were conducted of the extraction of solid zinc picrate hydrate into $CDCl_3$ solution (10^{-3} M) of **8** until the ^{1}H-NMR spectra of the resulting solutions remains unchanged (see Fig. 1). The stoichiometry of the complex was deduced from the integration ratio



Scheme 1 Synthesis of **2–8**

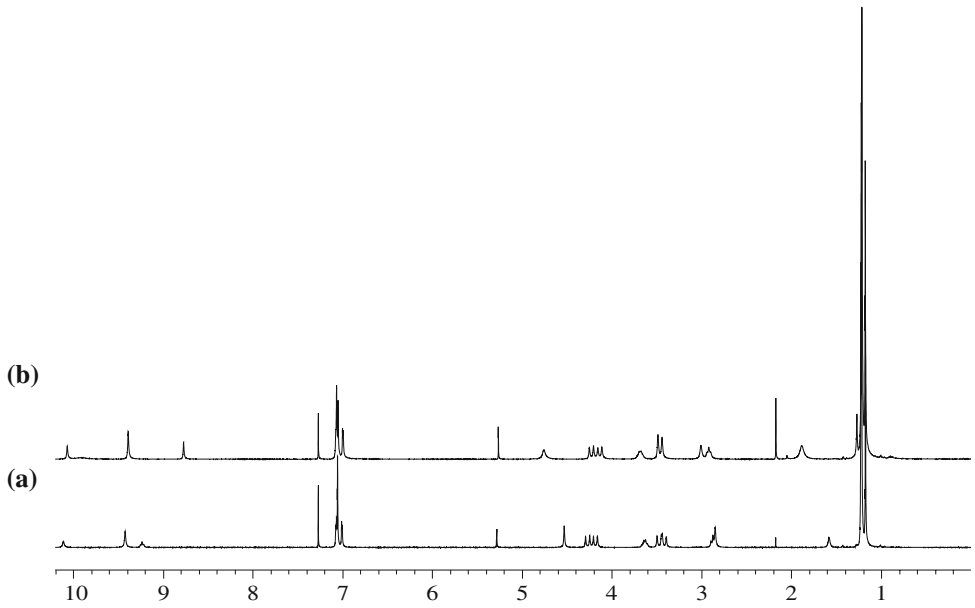


Fig. 1 ^{1}H-NMR ($CDCl_3$) of (**a**) free ligand **8** and (**b**) with $Zn(Pic)_2$

between the singlet of the picrate at 8.77 ppm and the aromatics protons of the ligand.

The complex stoichiometry was found to be 1:1, the most shifted protons being the amido CONH. The symmetrical patterns of both free ligand **8** and **8** · **Zn(Pic)$_2$** complex were very similar. This lead us to assume that the ^{1}H-NMR spectrum of the complex is more representative of a complexation of the two picrate anions, probably through H-bonding with the amido functions, in a symmetrical manner rather than that of complexation of one Zn(II) cation that would have given an asymmetry to the system.

To conclude, we have demonstrated the ready synthesis of five new hyperbranched molecules, **4–8**, based on calixarenes attached to new cores **2** and **3** that are potentially multidentate-N,S ligands. Interestingly, in the case of **8**, we have demonstrated that the multicalixarene ligand prefers to bind more strongly to the picrate anions than the zinc cation. This will be useful for steering of the arms of the hyperbranched molecule. Future work will be directed towards gaining more insight into this complexation process and its possible use. In addition, the synthesis (by 1,3-selective 'esterification' followed by amidation) [5, 6] of wire-like structures made of alignments of same molecular motives **8** presented in this paper.

Experimental part

Preparation of **3**

A solution of Na-metal (4.52 g, 196 mmol) in absolute EtOH (300 mL) was stirred for 2 h. Commercial 2-aminoethanethiol hydrochloride (10.45 g, 130 mmol) was added and the mixture was refluxed for 12 h. After cooling to room temperature, 1,3-dibromo-2,2-bis(bromomethyl) propane (12.63 g, 32.5 mmol) was gradually added. The reaction mixture was refluxed for 48 h. The yellow-brown solution was evaporated to dryness under reduced pressure and the residue was dissolved in MeOH (200 mL). $CuCl_2 \cdot 2H_2O$ (11.6 g, 68 mmol in 200 mL methanol) was added and filtered through Celite after 1 h-stirring. The blue green solution was evaporated to dryness under reduced pressure. The residue was dissolved in H_2O (200 mL) and applied to a column of SP-Sephadex (Na^+ form). Elution with 0.5 mol L^{-1} NaCl revealed two components. The first is the excess aqua-Cu(II). The second eluate was taken and 2 mol L^{-1} HCl (50 mL) was added before adsorption on Dowex 50Wx2 ion-exchange resin (H^+ form). The column was washed with H_2O (500 mL) and 0.5 mol L^{-1} HCl, then eluted with 3 mol L^{-1} HCl. The eluate was evaporated to dryness under reduced pressure. Weight: 6.01 g. The hydrochloride salt was converted into a free ligand by passage of its aqueous solution through a column of hydroxide form Dowex 1 anion exchange resin, to provide $C(CH_2SCH_2CH_2NH_2)_4$ as a yellow oil after evaporation under vacuum. ^{1}H-NMR ($CDCl_3$): 2.79 (t, 8H, $J = 6.0$ Hz, CH_2CH_2), 2.63 (s, 8H, $C(CH_2)_4$), 2.57 (t, 8H, $J = 6.0$ Hz, CH_2CH_2), 1.25 (s, 8H, NH_2). Yield: 3.64 g.

Preparation of **2**

Similar procedure as for **3**: Na-metal (4.08 g, 348 mmol), 2-aminoethanethiol hydrochloride (12.34 g, 156 mmol), commercial 1,3-dichloropropan-2-ol (10.0 g, 77.5 mmol) and $CuCl_2 \cdot 2H_2O$ (13.5 g, 79.2 mmol). Yellow oil. 4.02 (septuplet, 1H, $J = 4.5$ Hz, CH), 2.92 (d, 2H, $J = 4.5$ Hz, $CHCH_2S$), 2.77 (t, 4H, $J = 6.0$ Hz, CH_2CH_2), 2.56 (t, 4H, $J = 6.0$ Hz, CH_2CH_2), 1.24 (s, 4H, NH_2). Yield: 10.4 g.

Preparation of **4** and **5**

$HOCH(CH_2SCH_2CH_2NH_2)_2$ or **2** (120 mg, 0.57 mmol), mono methyle ester calix[4]arene (**1**) (1.03 g, 1.47 mmol), 1:1 methanol:toluene (5 ml) were refluxed for 4 d. After evaporation under reduced pressure, the residue was chromatographed on a SiO_2 column (95:05 CH_2Cl_2/acetone) gave pure **5**. White solid. Mp 217–219 °C. ^{1}H-NMR ($CDCl_3$): 10.07 (s, 2H, ArO*H*), 9.45 (t, 2H, $J = 5.4$ Hz, N*H* amide), 9.42 (s, 4H, ArO*H*), 7.16–7.04 (m, 16H, Ar*H*), 4.63 (s, 4H, OCH_2CO), 4.29 (d, 4H, $J = 13.5$ Hz, AB system, $ArCH_2Ar$), 4.25 (d, 4H, $J = 12.9$ Hz, A′B′ system, $ArCH_2Ar$), 4.00 (septuplet, 1H, $J = 4.5$ Hz, C*H*), 3.7 (q, 4H, $J = 6.0$ Hz, CH_2NH), 3.52 (d, 8H, $J = 13.2$ Hz, AB system, A′B′ system, $ArCH_2Ar$), 2.97 (t, 4H, $J = 6.3$ Hz, SCH_2CH_2), 2.95 (d, 2H, $J = 3.0$ Hz, $CHCH_2S$), 2.92 (d, 2H, $J = 4.5$ Hz, $CHCH_2S$), 2.84 (d, 2H, $J = 7.2$ Hz, SCH_2CH_2), 2.79 (d, 2H, $J = 7.5$ Hz, SCH_2CH_2), 1.27 (s, 54H, *tert*-butyl), 1.22 (s, 18H, *tert*-butyl). ^{13}C NMR ($CDCl_3$): 168.179; 149.162; 148.784; 148.013; 146.888; 144.185; 143.837; 132.779; 128.204; 127.305; 127.109; 126.898; 126.119; 125.865; 75.434; 69.666; 38.647; 38.386; 34.296; 34.087; 33.945; 32.957; 32.508; 32.162; 31.488; 31.422; 31.104. MW = 1588.24 calculated for $C_{99}H_{130}N_2S_2O_{11}$, (MALDI-TOF) $m/z = 1588.75$. Microanalysis: calculated: C, 74.87; H, 8.25; found: C, 74.31; H, 8.18. Yield 36%. Further elution with (80:20 CH_2Cl_2:acetone) gave pure **4**. White solid. Mp 202–204 °C. ^{1}H-NMR ($CDCl_3$): 9.47 (t, 1H, $J = 5.7$ Hz, N*H* amide), 7.09 (d, 2H, $J = 2.4$ Hz, Ar*H*), 7.08 (s, 4H, Ar*H*), 7.02 (d, 2H, $J = 2.4$ Hz, Ar*H*), 4.60 (s, 2H, OCH_2CO), 4.25 (d, 2H, $J = 13.5$ Hz, AB system, $ArCH_2Ar$), 4.20 (d, 2H, $J = 12.0$ Hz, A′B′ system, $ArCH_2Ar$), 3.92 (septuplet, 1H, $J = 4.2$ Hz, C*H*), 3.76 (q, 2H, $J = 6.3$ Hz, CH_2NH_2), 3.49 (d, 4H, $J = 14.1$ Hz, AB system, A′B′ system, $ArCH_2Ar$), 2.95 (t, 2H, $J = 6.6$ Hz, SCH_2CH_2), 2.99–2.84 (m, 2H, SCH_2CH_2), 2.83–2.74 (m, 2H, SCH_2CH_2), 2.71 (d, 2H, $J = 6.6$ Hz, $CHCH_2S$), 2.67 (d, 2H, $J = 2.1$ Hz, $CHCH_2S$), 2.64 (t, 2H, $J = 3.6$ Hz, SCH_2CH_2), 1.26 (s, 9H, *tert*-butyl), 1.23 (s, 9H, *tert*-butyl), 1.22 (s, 9H, *tert*-butyl), 1.18 (s, 9H, *tert*-butyl). ^{13}C NMR ($CDCl_3$): 168.153; 148.367; 148.214; 148.002; 147.651; 144.382; 144.134; 132.899; 128.384; 127.365; 127.324; 127.014; 126.412; 126.107; 75.321; 69.578; 38.555; 38.489; 38.296; 34.057; 33.974; 33.047; 33.008; 32.985; 32.657; 32.308; 32.122; 31.488; 31.422; 31.104. MW = 899.30 calculated for $C_{53}H_{74}N_2S_2O_6$, (MALDI-TOF) $m/z = 899.93$. Microanalysis: calculated: C, 70.79; H, 8.29; found: C, 70.53; H, 8.12. Yield 16%.

Preparation of **6–8**

$C(CH_2SCH_2CH_2NH_2)_4$ or **2** (92 mg, 0.25 mmol), mono methyl ester calix[4]arene (**1**) (800 mg, 1.11 mmol), 1:1 methanol:toluene (5 ml) were refluxed for 3 d. After evaporation of the solvents under reduced pressure, the residue was chromatographed on a SiO_2 column (60:40 CH_2Cl_2:acetone) to give pure **8** as a white solid. Mp 192–194 °C. ^{1}H-NMR ($CDCl_3$): $\delta = 10.09$ (s, 4H, ArO*H*), 9.42 (s, 8H, ArO*H*), 9.24 (t, 4H, $J = 6.0$ Hz, N*H* amide), 7.07 (d, 8H, $J = 5.4$ Hz, Ar*H*), 7.06 (s, 16H, Ar*H*), 7.02 (d, 8H, $J = 2.4$ Hz, Ar*H*), 4.54 (s, 8H, OCH_2CO), 4.28 (d, 8H, $J = 13.0$ Hz, AB system, $ArCH_2Ar$), 4.19 (d, 8H, $J = 13.0$ Hz, A′B′ system, $ArCH_2Ar$), 3.65 (q, 8H, $J = 5.7$ Hz, CH_2NH), 3.48 (d, 8H, $J = 13.0$ Hz, AB system, $ArCH_2Ar$), 3.43 (d, 8H, $J = 13.0$ Hz, A′B′ system, $ArCH_2Ar$), 2.89 (t, 8H, $J = 6.0$ Hz, CH_2CH_2), 2.86 (s, 8H, C $(CH_2)_4$), 1.24 (s, 36H, *tert*-butyl), 1.23 (s, 72H, *tert*-butyl), 1.18 (s, 36H, *tert*-butyl). ^{13}C NMR ($CDCl_3$): 168.135; 149.043; 148.854; 148.116; 147.099; 143.916; 143.600; 132.887; 128.209; 127.436; 127.172; 126.795; 126.037; 125.830; 75.279; 39.190; 34.260; 34.058; 33.921; 33.258; 32.967; 32.168; 31.508; 31.448; 31.127. MW = 3128.45 calculated for $C_{197}H_{256}N_4S_4O_{20}$, (MALDI-TOF) $m/z = 3128.75$. Microanalysis: calculated: C, 75.63; H, 8.25; found: C, 75.45; H, 8.09. Yield 34%. Further elution with (60:40 CH_2Cl_2:acetone) gave pure **7**. White solid. Mp 184–186 °C. ^{1}H-NMR ($CDCl_3$): 9.31 (t, 2H, $J = 6.0$ Hz, N*H* amide), 9.30 (t, 1H, $J = 6.0$ Hz, N*H* amide), 7.08 (d, 6H, $J = 2.1$ Hz, Ar*H*), 7.06 (s, 12H, Ar*H*), 7.02 (d, 6H, $J = 2.4$ Hz, Ar*H*), 4.56 (s, 6H, OCH_2CO), 4.27 (d, 6H, $J = 12.0$ Hz, AB system, $ArCH_2Ar$), 4.21 (d, 6H, $J = 12.0$ Hz, A′B′ system, $ArCH_2Ar$), 3.71 (q, 6H, $J = 7.2$ Hz, CH_2NH), 3.67 (m, 2H, CH_2NH_2), 3.46 (m, 12H, AB system, A′B′ system, $ArCH_2Ar$), 2.92 (t, 6H, $J = 6.0$ Hz, CH_2CH_2), 2.88 (s, 6H, $C(CH_2)_3$), 2.75 (t, 2H, $J = 6.0$ Hz, CH_2CH_2), 2.64 (s, 2H, CCH_2), 2.54 (t, 2H, $J = 6.0$ Hz, NH_2), 1.23 (s, 72H, *tert*-butyl), 1.18 (s, 36H, *tert*-butyl). ^{13}C NMR ($CDCl_3$): 168.316; 148.982; 148.103; 147.069; 144.048; 143.739; 132.854; 128.217; 127.487; 127.186; 126.847; 126.054; 125.881; 75.342; 53.286; 44.301; 40.261; 39.084; 38.359; 34.293; 34.087; 33.955; 33.259; 32.995; 32.198; 31.943; 31.528; 31.463; 31.142; 29.713; 29.373; 22.707; 14.127. MW = 2439.5 calculated for $C_{151}H_{200}N_4S_4O_{14}$, (MALDI-TOF) $m/z = 2439.17$. Microanalysis: calculated: C, 74.84; H, 8.32; found: C, 74.46; H, 8.12. Yield 22%. Further elution with acetone gave pure **6**. Yellow solid. Mp 206–208 °C. ^{1}H-NMR ($CDCl_3$): 9.40 (t large, 2H, N*H* amide), 7.09 (s, 8H, Ar*H*), 7.04 (s, 4H, Ar*H*), 6.94 (s, 4H, Ar*H*), 4.58 (s, 4H, OCH_2CO), 4.37–4.06 (m, 8H, $ArCH_2Ar$), 3.68 (s large, 4H, CH_2NH_2), 3.57–3.38 (m, 8H, $ArCH_2Ar$), 3.28–3.18 (m, 4H, CH_2NH), 2.92 (t large, 12H, CH_2CH_2, C $(CH_2)_2$), 2.54 (s, 4H, C $(CH_2)_2$), 1.24 (s, 36H, *tert*-butyl), 1.20 (s, 36H, *tert*-butyl). ^{13}C NMR ($CDCl_3$): 168.212; 149.080; 148.210; 147.019; 144.102; 143.809; 132.944; 128.212; 127.437; 127.106; 126.888; 126.184; 125.971; 75.642; 53.485; 44.521; 41.001;

39.144; 38.689; 34.147; 34.007; 33.854; 33.212; 32.975; 32.298; 31.743; 31.428; 31.373; 31.212; 29.853; 29.572; 22.807; 14.307. MW = 1750.55 calculated for $C_{105}H_{144}N_4S_4O_{10}$, (MALDI-TOF) $m/z = 1749.72$. Microanalysis: calculated: C, 72.04; H, 8.29; found: C, 71.83; H, 8.04. Yield 10%.

^{1}H-NMR spectrum of **8** · **Zn(Pic)$_2$**: 10.06 (s, 4H, O*H*), 9.91 (broad s, 4H, N*H*), 9.38 (s, 8H, O*H*), 8.77 (s, 4H, picrate), 7.06 (s, 16H, Ar*H*), 7.05 (s, 8H, Ar*H*), 6.99 (d, 8H, $J = 2.4$ Hz, Ar*H*), 4.75 (s, 8H, O–CH_2–C=O), 4.23 (d, 8H, $J = 13.8$ Hz, AB system, ArCH_2Ar), 4.13 (d, 8H, $J = 13.5$ Hz, A′B′ system, ArCH_2Ar), 3.68 (q, 8H, $J = 3.8$ Hz, CH_2NH), 3.46 (d, 16H, $J = 13.5$ Hz, AB and A′B′, ArCH_2Ar), 3.00 (s, 8H, C $(CH_2)_4$), 2.92 (t, 8H, $J = 6$ Hz, CH_2–CH_2), 1.22 (s, 36H, *tert*-butyl), 1.21 (s, 72H, *tert*-butyl), 1.17 (s, 36H, *tert*-butyl).

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