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Synthesis, Recognition of Metal Ions of Salicylideneimine Functionalized *p*-tert-Butylcalix[*n*]arene-core Dendrimers

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A series of salicylideneimine functionalized *p*-tert-butylcalix[*n*]arene-core dendrimers 7a–b were synthesized in higher yields by divergent method from the corresponding ethyl *p*-butylcalix[*n*]arylacetas 2a–b (*n* = 6, 8). 2a–b were first treated with excess of 1,6-diaminohexane to give amide derivatives with free amine terminal groups 3a–b, which in turn reacted with salicylaldehyde in alcohol to yield the first generation of Schiff bases 4a–b. 3a–b reacted with ethyl acrylate, ammonolized with 1,6-diaminohexane and condensed with salicylaldehyde successfully to give the second generation of Schiff bases 7a–b. The extraction and binding properties of the dendritic Schiff bases 4a–b and 7a–b for several kinds of metal ions were studied with UV–Vis spectroscopy and atomic absorption spectroscopy. In which they showed a great affinity for soft Cu²⁺ ions and formed 1:1 or 1:2 stoichiometric complexes.

Keywords: Calixarene; Dendrimer; Extraction; Schiff base; Complexation; Ion recognition

INTRODUCTION

Over the past two decades dendrimers have attracted considerable attention because of their inherently novel structural features and their potential applications to various scientific and industrial fields such as catalysis, carriers of drugs, models of supramolecular biological and colloidal structures, or new material [1]. On the synthetic viewpoint the divergent and convergent methods are two main synthetic ways to build dendrimers. The preparation of such hyperbranched molecules demands the use of particular building blocks with the appropriate stereochemistry and multiple, equivalent reaction centers. The use of highly functionalized core molecules for quickly generating

high molecular weight dendrimers is still an important aspect of dendritic study [2]. For this purpose calixarene seems to be one of the ideal candidates as a polyfunctional core because of their ease of synthesis, high functionality, persistent shape and size as well as easy chemical modification, from which a high molecular weight of dendrimers can be prepared in fewer steps and with greater ease than the conventional divergent approach [3]. Indeed *p*-tert-butylcalix[4]arenes or calix[4]resorcinarenes have been used as core molecules for synthesis of some dendritic molecules with the first work published in 1995 [4]. From then several calixarene-core dendrimers with variable branches such as azobenzene [5], sugar [6], peptide [7], carbamoylmethylphosphine oxide [8], triaminoethylamine [9], crown ether [10] and even calixarene itself [11–13] as well as thiacalix[4]arene [14] have been synthesized in recent years. A timely review focused on the synthesis of dendrimers from calix[4]arenes and thiacalix[4]arenes has appeared this year [15]. On the other hand the dendritic molecules based on calix[4]resorcinarenes have also been developed [16–19]. But to the author's knowledge there are no reports of using larger calix[*n*]arenes (*n* = 6, 8) as the starting core for the synthesis of dendrimer in the literature. The author's recent interests have been focused on the structural modification of calixarenes for the design of new supramolecular systems and synthesis of calixarene-core dendrimers [20–22]. The present article reports a simple and efficient synthesis of polyamidoamine-type dendrimers based on *p*-butylcalix[*n*]arenes (*n* = 6, 8) with terminal salicylideneimine groups and their binding ability for some metal ions.

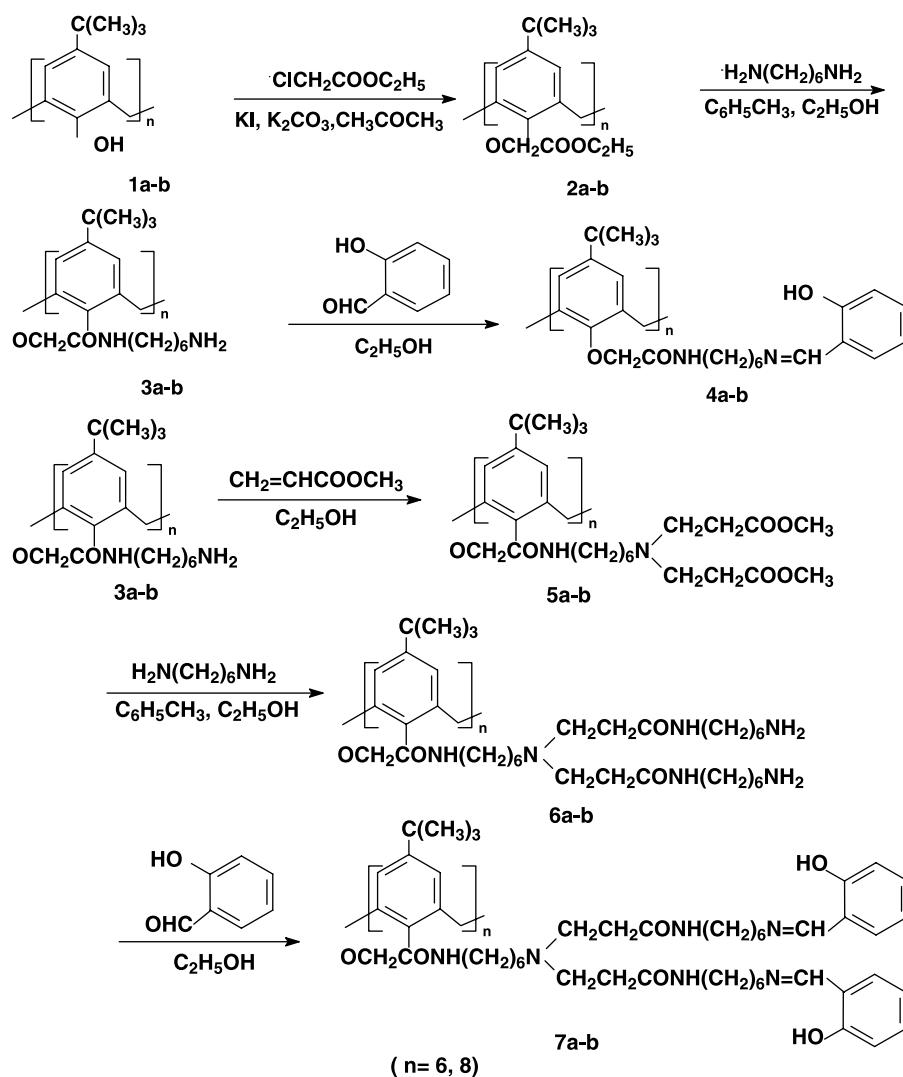
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RESULTS AND DISCUSSION

Synthesis of Calixarene Schiff Bases

Schiff bases or imines are employed widely in the formation of metal complexes and in the study of inclusion phenomena, owing to their relatively easy preparation, remarkable stability and high versatility. In designing new supramolecular receptors imino groups have been incorporated in to the calix[4]arene platform to achieve selective binding or complexation ability [23–26] and as catalyst [27,28]. It is also interesting to find the synthesis of calixarene-like salen or ‘calixsalen’ by using imino groups as ring components of calixarene [29,30]. The synthetic strategy is to provide an efficient and simple procedure to modify the larger cavity calix[*n*]arene at lower rim with salicylideneimine groups. The reaction procedure leading to the first and second generations of target Schiff bases **4a–b** and **7a–b** are shown in Scheme 1. As shown in

Scheme 1, *p*-tert-butylcalix[*n*]arenes **1a–b** (*n* = 6, 8) [31] were fully alkylated with ethyl α -bromoacetate according to the published procedure [32] with a little deviation to give six or eight ethoxycarbonylmethoxy substituted derivatives **2a–b** (**2a**, 86.5%; **2b**, 87.2%). This kind of activated ester group provides an excellent chance for further chemical modification on the lower rim of calixarenes. The esters **2a–b** were refluxed with a large excess of 1,6-diaminohexane $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ in a mixture of ethanol and toluene (v/v, 1:1) for about 24 hours to afford corresponding amides **3a–b** in high yields (69–78%). Excess diamine in the reaction would confirm monoammonolysis of each diamine and give the amide product with free terminal amino groups, which greatly prevented formation of other kinds of diamidation or cyclization products [33]. Besides being highly hydrogynic in air the amides **3a–b** have very poor solubility in common organic solvent such as ether, chloroform, toluene and acetonitrile, only partial dissolving in hot ethanol, which makes it difficult to get satisfactory



SCHEME 1 Synthesis of calixarene Schiff bases **4a–b** and **7a–b**.

characterization data for them. In order to remove the excess unreacted diamine the amide product must be crystallized two times and washed thoroughly with alcohol. All amides **3a–b** have very similar IR spectra. The absorption of C=O in amide shows a very strong band at 1650–1670 cm^{-1} , while the absorption band of C=O in the ester derivatives **2a–b** appears at 1760 cm^{-1} . This means all ester groups in **2a–b** have transferred to amides. The middle stronger bands at 3300–3500 cm^{-1} belong to the absorption of NH_2 or NH groups.

Even if the amides **3a–b** do not have good solubility in ethanol, they can react smoothly with salicylaldehyde in hot ethanol. The suspension of amides and salicylaldehyde in ethanol was stirred under reflux overnight. The white solid disappeared at first and then the expected yellow precipitates of Schiff base were formed. After workup the salicylideneimine derivatives **4a–b** were prepared in moderate yields (40–71%). All the products **4a–b** have six or eight functional salicylideneimine groups with aliphatic amide spacers and have good solubility in common organic solvents. In their UV–Vis spectrum, the new C=N groups has a maximum absorption in CHCl_3 at about 315 ~ 317 nm. In IR spectrum the C=O group of amide shows a very strong absorption at 1654 cm^{-1} , while the C=N group of imines shows a strong peak at 1625 cm^{-1} . On the other hand the reaction of amides **4a–b** with salicylaldehyde can also confirm the existence of free amino group in amide derivatives **3a–b**. In ^1H NMR spectra they all show one peak of phenolic hydroxyl group at about 13.50 ppm and one single broad peak of $\text{ArCH}=\text{N}$ (sometimes with a little splitting) at 8.30 ppm. Protons of t-butyl groups in **4a–b** show two signs at about 1.24 ppm and 0.91 ppm. The signs of cyclic methylene ArCH_2Ar and OCH_2CO groups overlap heavily and show a mixed peak at about 4.00–4.50 ppm. Thus it is difficulty to determine the conformational isomers of these amide derivatives according to the ^1H NMR data.

According to Tomalia's synthetic procedure for PAMAM dendrimer [34,35], the second generation of dendritic compounds were constructed by treating amide **3a–b** with methyl acrylate in alcohol at 45–50°C for at least 5 d to confirm a complete addition reaction. In this step amino groups in **3a–b** were smoothly added to methyl acrylate to yield the corresponding branched methyl aminodipropionate **5a–b** (79 ~ 84%). In IR spectra, the new ester groups show very strong C=O absorption at 1731 cm^{-1} with the peak of CONH group at 1654 cm^{-1} . Consequently **5a–b** were treated with 1,6-diaminohexane again as mentioned above to transform into the second generation amide derivatives with free terminal amino groups **6a–b**. Similarly, the absorption of C=O at 1675 cm^{-1} and those of NH_2 or NH at about 3400 cm^{-1} can be observed in their IR spectrum.

The second generation amide dendrimers **6a–b** reacted smoothly with salicylaldehyde in hot ethanol to give the expected Schiff base derivatives **7a–b** in moderate yields (51 ~ 79%). All the products **7a–b** are yellow solids with a sharp melting point range and are very soluble in common organic solvents. In their UV–Vis spectrum, the new C=N group has a maximum absorption in CHCl_3 at about 317 ~ 320 nm. In IR spectra the C=O group of amide shows a very strong absorption at 1654 cm^{-1} , while the C=N group of imines shows a strong peak at 1625 cm^{-1} . In their ^1H NMR the expected ratios of hydrogen atoms for each characteristic unit were observed by comparison of the integral intensity of their signals, which means the completeness of conversion, and the appropriate formation of dendrimers with less statistical defects. **7a–b** have 12 or 16 terminal salicylideneimine functional groups with soft aliphatic amide chain spacers and the molecular weight of them reached to 4188 for **7a** and 5920 for **7b** respectively. It is a pity that trying to get the suitable single crystals for X-ray analysis was failed until now.

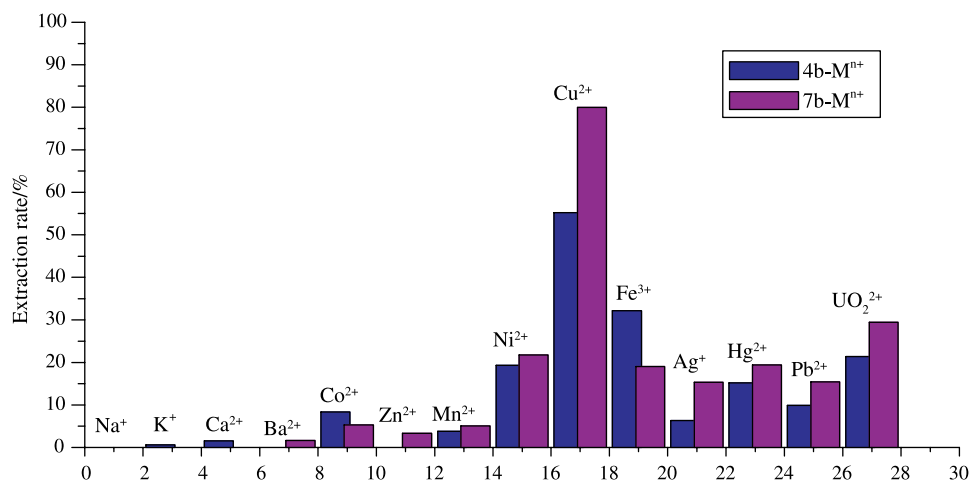
In conclusion a series of salicylideneimine functionalized *p*-tert-butylcalix[n]arene-core dendrimers **7a–b** were easily synthesized in good yields by the divergent method. Their structures are very similar to the famous Polyamidoamine (PAMAM) [35] dendrimer, which makes them ideal building blocks for synthesizing high generation dendrimers. On the other hand they can be looked at as potentially polydentate ligands for coordinating metal ions and organometallic compounds.

Extraction Properties

To evaluate the binding ability of these new calixarene Schiff bases for metal ions, liquid–liquid extractions of different kinds of metal ions were carried out. The extraction percentages are calculated and listed in Table I. The first generation Schiff bases **4a–b** and second generation Schiff bases **7a–b** have very little affinity towards alkali and alkaline earth metal ions (Na^+ , K^+ , Ca^{2+} , Ba^{2+}) and have moderate affinity (6–31%) towards some heavy metal ions such as Hg^{2+} , Fe^{3+} , Pb^{2+} , Ni^{2+} , UO_2^{2+} . They all show stronger extraction efficiencies for Cu^{2+} (50 ~ 80%). It is also interesting to find that the extraction efficiencies of **7a–b** are better than that of **4a–b**, which is clearly due to **7a–b** having 12 or 16 functional salicylideneimine groups and **4a–b** only having 6 or 8 salicylideneimine groups. The extraction percentages of **4b** and **7b** for some metal ions are also listed in Fig. 1. According to the above experimental results, the extraction abilities of these calixarene Schiff bases **4a–b** and **7a–b** are mainly due to the functional salicylideneimine groups and calixarene only acts as a platform to construct the active salicylideneimine groups.

TABLE I Extraction rates of calix[n]arenes **4a–b** and **7a–b** for metal ions

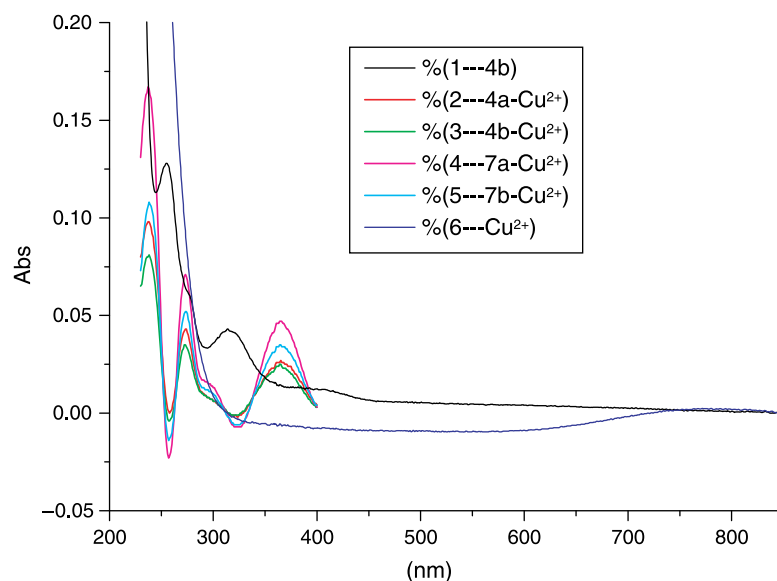
Metal cations	Extraction rate (%)				Metal cations	Extraction rate (%)			
	4a	4b	7a	7b		4a	4b	7a	7b
Na ⁺	–	–	–	–	Ni ²⁺	8.64	19.30	15.42	21.76
K ⁺	–	0.62	–	–	Cu ²⁺	50.50	55.23	75.21	79.96
Ca ²⁺	0.25	1.53	–	–	Fe ³⁺	6.31	32.15	28.20	19.02
Ba ²⁺	–	–	1.08	1.65	Ag ⁺	1.56	6.33	7.96	15.32
Co ²⁺	–	8.31	12.98	5.29	Hg ²⁺	13.15	15.21	21.99	19.39
Zn ²⁺	–	–	10.95	3.33	Pb ²⁺	12.06	9.87	15.88	15.45
Mn ²⁺	–	3.81	7.55	5.06	UO ₂ ²⁺	19.55	21.40	31.20	29.44

FIGURE 1 Extraction rates of calix[n]arenes **4b** and **7b** for metal ions.

UV–Visible Titrations

The binding properties of the target compounds **4a–b** and **7a–b** to metal ions were also studied by UV–Vis spectroscopy. The maximum absorption of the Schiff bases **4a–b** and **7a–b** appear at about 320 nm. Upon the addition of alkali and alkaline

earth metal salts, no changes of absorption were observed. This indicated the target compounds have negligible binding ability for these kinds of metal ions. When transition metal salts were introduced the maximum absorption shifts a little to longer wavelengths ($\Delta\lambda < 10$ nm), which means weak complexation between them. It is very

FIGURE 2 UV–Vis spectroscopy of the ligands and Cu complexes ($C_{\text{ligand}} = C_{\text{Cu}}^{2+} = 2.5 \times 10^{-5}$ mol/L).

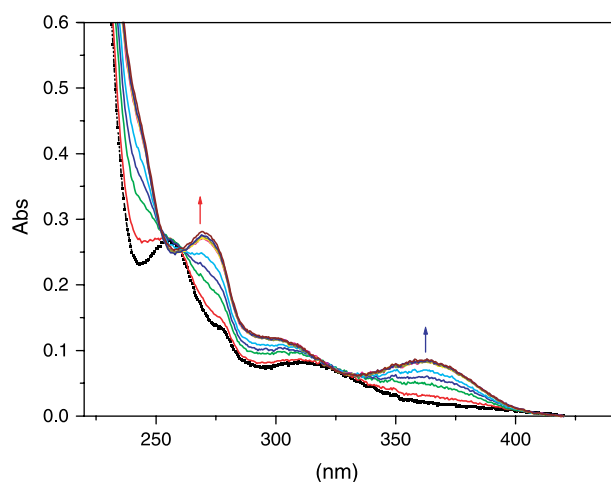


FIGURE 3 UV-Vis spectra of **7b** ($5 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) with different concentration of Cu^{2+} . $[\text{Cu}^{2+}]/[\text{7b}] = 0, 0.2, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0$.

interesting to find that Cu^{2+} ions cause a very large shift of the maximum absorption of the target compounds ($\Delta\lambda > 40 \text{ nm}$). Figure 2 shows the UV-Vis spectra of the Schiff bases **4a-b** and **7a-b** in the presence of Cu^{2+} ions with the spectra of **4a** as a reference for Schiff bases **4a-b** and **7a-b** have very similar absorption bands. From Fig. 2 it can be seen that the maximum absorption band at about 320 nm of the ligands was shifted to 360 nm after adding Cu^{2+} ions.

As an example the UV-Vis spectra of **7b** with different concentration of Cu^{2+} are shown in Fig. 3. From Fig. 3, an isoabsorptive point at 325 nm could be obviously observed. It showed again that **Cu-7b** formed a complex. With the saturation method (Fig. 4) and Job plot method (Fig. 5) the molar ratio of $\text{C}_{7b}:\text{C}_{\text{Cu}^{2+}}$ was determined as 1:2. The value of stability constants and complex ratios of Cu^{2+} complexes of **4a-b** and **7a-b** which were determined by the same methods are shown in Table II. From Table II and Fig. 3, the Cu^{2+} complexes of

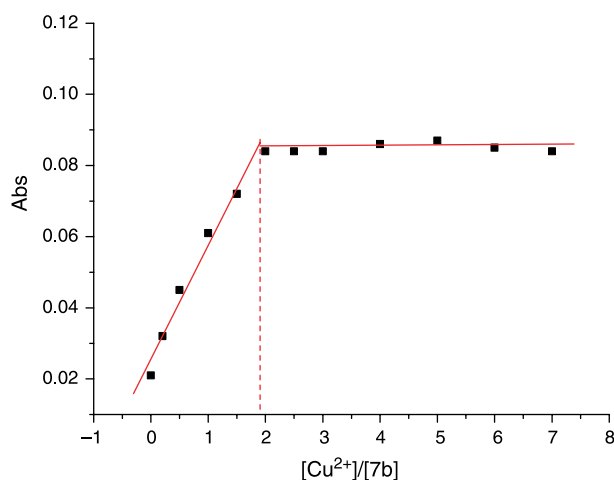


FIGURE 4 Plot of **7b** with Cu^{2+} absorbance (A) to $([\text{Cu}^{2+}]/[\text{7b}])$, $[\text{Cu}^{2+}]/[\text{7b}] = 0, 0.2, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0$.

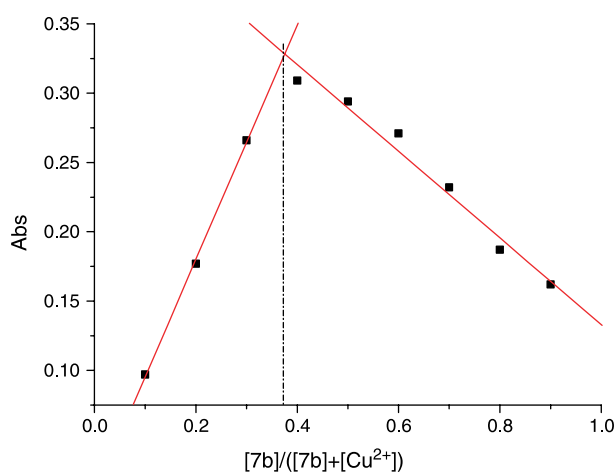


FIGURE 5 Job plot of **7b** with Cu^{2+} absorbance (A) to $([\text{7b}]/([\text{Cu}^{2+}] + [\text{7b}]))$. The total concentration is $0.5 \text{ mmol}\cdot\text{L}^{-1}$.

4a-b and **7a-b** all have an absorption peak near 360 nm. These results showed that calixarene Schiff bases represented the similar outcome for the same action, and along with the more Schiff base groups from **4a-b** to **7a-b**, the complex ratio was gradually changed from 1:1 to 1:2 (L/M^{n+}).

EXPERIMENTAL

Materials and Apparatus

Melting points were taken on a hot-plate microscope apparatus. IR spectra were obtained on a Nicolet FT-IR 740 spectrometer (KBr disc). ^1H NMR spectra were recorded with a Bruker AV-600 spectrometer with CDCl_3 as solvent and TMS as internal standard. UV-Vis spectra were recorded on Shimadzu UV-2501 PC spectrophotometer and atomic absorption spectra were recorded on Australia GBC 932A spectrophotometer. 1,6-Diaminohexane, ethyl acrylate, salicylaldehyde are commercial reagents and used as received. Solvents (acetone, alcohol and dichloromethane, etc) were purified by standard techniques. The reaction process was monitored by TLC. *p*-tert-Butylcalix[*n*]arenes [31] **1a-b** ($n = 6, 8$) and ethyl *p*-tert-butylcalix[*n*]arylacrylates [32] **2a-b** were prepared according to the published methods.

Extraction Studies

The extractions of metal ions by dendritic calixarenes were investigated using metal acetate salts. The organic solutions were prepared by dissolving a weighed amount of the ligand in chloroform. Liquid-liquid extraction experiments were carried out in a flask by shaking the mixture of organic phase and water phase for 12 min. After standing for 12 h the organic phase and water phase were separated. The water phases before and after extraction were analyzed by atomic absorption spectroscopy.

TABLE II Value of stability constants of Cu²⁺ complexes of 4a–b and 7a–b

	4a	4b	7a	7b
Molar ratio (L/M ⁿ⁺)	1:1	1:1	1:2	1:2
K _{ass}	2.067 × 10 ⁵	4.55 × 10 ⁵	3.65 × 10 ⁹	3.94 × 10 ⁹
λ _{max} /nm	360.50	360.50	359.0	360.0

UV–Vis Measurements

UV–Vis titrations were carried at 25°C in ethanol/water (v/v = 9:1) using a Shimadzu UV-2501 PC spectrophotometer. Usually 1.0 mL of ligand solution (5 × 10⁻⁵ mol·L⁻¹) was added to the metal ion solution (5 × 10⁻⁵ mol·L⁻¹) in a 10 mL flask and the solution allowed to equilibrate for 5 min. The spectrometric data were collected over the range 220–600 nm.

General Procedure for the Synthesis of First Generation Amide Derivatives 3a–d

A mixture of ethyl *p*-tert-butylcalix[6]arylacacetate **2a** (1.0 mmol, 1.488 g) and 1,6-diaminohexane (10 mL) in ethanol (25 mL) and toluene (25 mL) was refluxed for 24 h. The organic solvent and excess of diamine was removed in vacuum. The residue was washed thoroughly with alcohol to give the white solid as amide derivatives **3a**, 1.379 g (72.3%); m.p. > 250°C. IR (KBr disc) ν : 3281(w), 3074(w), 2957(s), 2860(m), 1660(vs), 1543(s), 1473(s), 1191(m), 1115(m), 1039(m), 873(w), 729(w) cm⁻¹.

3b was prepared in the same way as **3a** using ethyl *p*-tert-butylcalix[8]arylacacetate **2b** (1.0 mmol, 1.984 g). 1.954 g (76.5%), m.p. > 250°C; IR (KBr disc) ν : 3295(m), 3074(w), 2957(vs), 2867(s), 1660(vs), 1543(s), 1473(s), 1356(m), 1287(m), 1184(m), 1115(m), 873(w), 715(w) cm⁻¹.

General Procedure for the Synthesis of First Generation Schiff Base (4a–b)

To a suspension of amides **3a** (0.954 g, 0.5 mmol) in 30 mL of ethanol was added salicylaldehyde (1.1 mole for each NH₂ group) in 10 mL of ethanol at room temperature. This reaction mixture was stirred at room temperature for 6 h, and then heated to reflux about 12 h under a nitrogen atmosphere. A brown–yellow precipitate was observed. After removal of alcohol the residue was recrystallized from alcohol–chloroform to give Schiff base product **4a**. Yellow solid, 0.991 g (78.3%), m.p. 164–166°C. IR (KBr disc) ν : 3295(w), 3055(w), 2950(s), 2886(m), 2851(m), 1661(vs), 1625(vs), 1541(s), 1470(s), 1450(m), 1273(s), 1175(m), 1111(m), 1034(m) cm⁻¹. UV–Vis λ_{max} (C₂H₅OH): 316.70, 288.80, 255.80 nm. ¹H NMR (CDCl₃) δ : 13.56 (br, 6H, OH), 8.26 (m, 6H, CH=N), 7.31–6.81 (m, 42H, NH, ArH), 4.42–4.10 (m, 24H,

ArCH₂Ar, OCH₂); 3.90–3.20 (m, 24H, NCH₂, CH₂N), 1.61–1.35 (m, 48H, (CH₂)₄), 1.35, 0.88 (s, s, 54H, C(CH₃)₃) ppm.

4b was prepared in the same way as **4a** using **3b** (1.272 g, 0.5 mmol). Yellow solid, 1.017 g (66.4%). m.p. 182°C. IR (KBr disc) ν : 3288(w), 3048(w), 2950(s), 2886(m), 2858(m), 1668(vs), 1625(vs), 1534(s), 1470(s), 1273(s), 1182(m), 1111(m), 1034(m) cm⁻¹. UV–Vis λ_{max} (C₂H₅OH): 315.40, 289.30, 255.70 nm. ¹H NMR (CDCl₃) δ : 13.60 (br, 8H, OH), 8.27 (m, 8H, CH=N), 7.27–6.68 (m, 56H, NH, ArH), 4.37–4.10 (m, 32H, ArCH₂Ar, OCH₂); 3.63–3.19 (m, 32H, NCH₂, CH₂N), 2.30–1.60 (m, 64H, (CH₂)₄), 1.29, 0.83 (s, s, 72H, C(CH₃)₃) ppm.

General Procedure for the Synthesis of Second Generation Amide (6a–b)

A mixture of amides **3a** (0.5 mmol) and ethyl acrylate (15 mL) in ethanol (15 mL) were stirred under an atmosphere of nitrogen at 45–50°C for 5 days. Ethanol and excess of ethyl acrylate was removed *in vacuo*. The residue was crystallized from alcohol/ether to give the ester products (**5a–b**). Then a mixture of **5a** (0.5 mmol) and 1,6-diaminohexane (15 mL) in ethanol (25 mL) and toluene (25 mL) was refluxed for 24 h under an atmosphere of nitrogen. The organic solvent and excess of 1,6-diaminohexane was removed in vacuum. The residue was well washed with alcohol several times to give the amide products **6a**. White solid, 0.969 g (48.9%), m.p. = 163–165°C. IR (KBr disc) ν : 3419(w), 3288(m), 2943(vs), 2860(m), 1653(vs), 1549(s), 1481(m), 1363(m), 1294(m), 1191(m), 1115(m), 1039(m), 873(w), 715(w) cm⁻¹. ¹H NMR (DMSO-*d*₆) δ : 7.80–8.10 (br, NH); 6.70–6.90 (m, ArH), 4.00–4.30 (m, OCH₂CO), 3.60–3.30 (m, ArCH₂Ar, NCH₂, NH₂), 2.30–2.64 (br, CH₂CO), 0.80–1.60 (m, (CH₂)₄, C(CH₃)₃).

6b was prepared in the same way as **6a** using **3b** (1.272 g, 0.5 mmol). White solid, 1.477 g (56.1%), m.p. = 147 ~ 149°C. IR (KBr disc) ν : 3419(w), 3288(m), 2943(vs), 2860(m), 1653(vs), 1549(s), 1481(m), 1363(w), 1294(m), 1191(m), 1115(m), 1039(m), 873(w), 715(w)/cm⁻¹. ¹H NMR (DMSO-*d*₆) δ : 7.70–8.10 (br, NH), 6.70–6.90 (m, ArH), 3.80–4.30 (m, OCH₂CO), 3.60–3.30 (m, ArCH₂Ar, NCH₂, NH₂), 2.30–2.64 (br, CH₂CO), 0.80–1.60 (m, (CH₂)₄, C(CH₃)₃).

General Procedure for the Synthesis of Second Generation Schiff Bases (7a–b)

To a suspension of amides **6a** (0.791 g, 0.2 mmol) in 20 mL of ethanol was added salicylaldehyde (1.1 mole for each NH₂ group) in 10 mL of ethanol at room temperature. This reaction mixture was stirred at room temperature for 6 h, and then heated to reflux about 12 h under a nitrogen atmosphere. A brown–yellow precipitate was observed. After removal of alcohol the residue was recrystallized from alcohol to give Schiff bases **7a**. Yellow solid, 0.627 g (60.3%), m.p. 103–105°C. IR (KBr disk) ν : 3281(m), 3069(m), 2921(s), 2851(m), 1654(vs), 1625(vs), 1456(m), 1273(m), 1189(m), 1111(m), 1034(m) cm⁻¹; ¹H NMR(CDCl₃) δ : 13.64 (br, 12H, OH), 8.30 (br, 12H, N=CH), 7.27–6.82 (m, 78H, NH, ArH), 4.30–2.35 (m, 144H, ArCH₂Ar, OCH₂, NHCH₂, CH₂N, CH₂N(CH₂CH₂)₂), 1.93–0.84 (m, 144H, (CH₂)₄), 1.57–0.84 (m, 54H, C(CH₃)₃) ppm.

7b was prepared in the same way as **7a** using **6b** (1.054 g, 0.2 mmol). 0.658 g (47.4%), m.p. 106–108°C, IR (KBr disk) ν : 3281(m), 3092(m), 2929(s), 2851(m), 1654(vs), 1625(vs), 1534(s), 1470(s), 1273(m), 1189(s), 1111(m), 1034(m) cm⁻¹; ¹H NMR(CDCl₃) δ : 13.60 (br, 16H, OH), 8.32 (br, 16H, N=CH), 7.27–6.85 (m, 104H, NH, ArH), 4.45–2.32 (m, 112H, ArCH₂Ar, OCH₂, NHCH₂, CH₂N), 1.85–0.84 (m, 192H, (CH₂)₄), 1.46–0.84 (m, 72H, C(CH₃)₃) ppm.

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