Chinese Journal of Chemistry, **2009**, *27*, 1975—1980

Full Paper

Synthesis, Crystal Structure and Complexing Properties of Calix[4]arene Schiff Bases

LI, Liang(李亮) GU, Weiwei(顾薇薇) YAN, Chaoguo*(颜朝国)

College of Chemistry & Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu 225002, China

Four *p-tert*-butylcalix[4]arene derivatives with different Schiff base groups at the lower rim were efficiently prepared in three steps. *p-tert*-Butylcalix[4]arene was firstly *O*-peralkylated with *ω*-haloalkylphthalimide in the system of NaH/DMF to give calixarene tetraalkylphthalimides, which were in turn hydrazinolyzed to give tetraaminoalkylcalixarenes. Then by condensation of the latter with salicylaldehyde and 2-hydroxy-1-naphthaldehyde, a series of calixarene Schiff bases were obtained in satisfying yields. The complexing properties of these Schiff bases for transition metal ions were investigated with UV spectroscopy.

Keywords calixarene, Schiff base, crystal structure, metal complex, UV spectroscopy

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 to the extensive host-guest chemistry and production of chemical entities with the dimensions of nanometers, as in "nanochemistry".[2] Design of highly selective receptors on the basis of calixarenes is an intensively developing branch of supramolecular chemistry.[3,4] The ready availability of calixarenes and versatility of derivations at the upper and/or lower rim(s) make this family of compounds one of the prime building blocks for supramolecular chemistry. The introduction of the high potential Schiff base into calixarene can give rise to interesting and versatile systems with very peculiar coordination and receptor properties. Recently, a number of papers have appeared in the literature concerning the synthesis and characterization of Schiff-base derivatives of calix[4]arenes and their application to either photochromic studies or as ion-selective extractants.[5,6] Schiff bases offer potential as optical switches resulting from their intramolecular hydrogen transfer ability from the hydroxyl oxygen to the imine nitrogen in both solution and solid state. They have been incorporated onto both the upper and the lower rims of calix[4]arenes and their ability to complex transition metals has been assessed.[7-9] In this work we wish to report the introduction of four functional salen groups into the lower rim of calix[4]arene and their complexing properties for transition metal ions.

Results and discussion

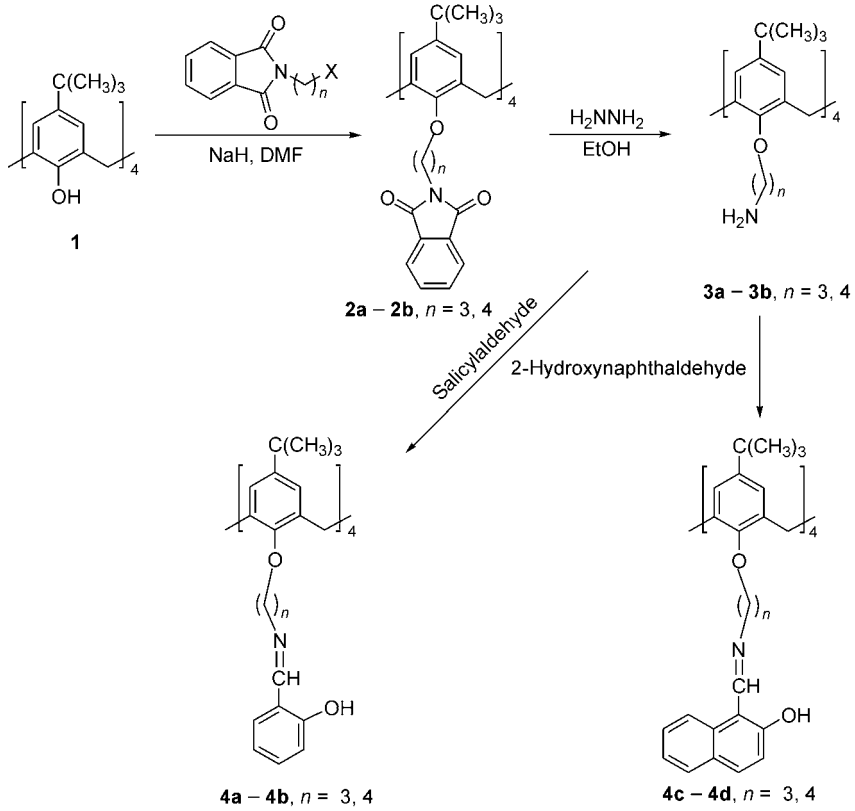
Synthesis and characterization

The tetraamino derivatives at the lower rim of *p-tert*-butylcalixarene were prepared according to procedures reported in the literature with little derivation.[10] At first *p-tert*-butylcalixarene was alkylated with *N*-(3-chloropropyl)phthalimide or *N*-(4-bromobutyl)phthalimide in system of NaH/DMF for 5 d to give tetraphthalimidoalkylcalix[4]arenes **2a**—**2b** (n=3, 4) in moderate yields (55%—60%). The phthalic protecting group could be removed by hydrazinolysis of phthalimido groups of **2a**—**2b** to give the tetraaminoalkyl calixarenes **3a**—**3b** in satisfying yields, which were then reacted smoothly with salicylaldehyde and 2-hydroxy-1-naphthaldehyde in refluxing ethanol to give the desired calixarene Schiff base ligands **4a**—**4d** in 75%—85% yields.

The structures of the prepared products were characterized with ^{1}H NMR, IR spectra and elemental analysis. IR spectra of each compound can be used as a good probe for the structures of the compounds. As for an example the stronger absorption of carbonyl group at 1712 cm^{-1} in **2a**—**2b** indicates that the phthalimido group has been introduced in the calixarene. The disappearance of stronger absorption of carbonyl groups in compounds **3a**—**3b** means that the protecting phthalimido groups have been removed. In the IR spectra of calixarene Schiff base groups **4a**—**4d** the new middle absorption peak at about 1630 cm^{-1} for CH=N group shows formation of functional imine groups. ^{1}H NMR spectra show not only each characteristic peak of each group, but also the steric conformation of each compound. As an example ^{1}H NMR spectra of **2a** show two doublets at about δ 4.35 and 3.10 with a coupling constant larger than 12 Hz, which are characteristic peaks of the axial and equatorial protons of bridging methylene groups in symmetric configuration of calixarene.[11] One singlet for *t*-butyl group at δ 1.03 provides

* E-mail: cgyan@yzu.edu.cn
Received January 1, 2009; revised April 4, 2009; accepted June 4, 2009.
Project supported by the National Natural Science Foundation of China (No. 20672091).

Scheme 1 Synthesis of *p-tert*-butylcalix[4]arene Schiff bases **4a**—**4d**



stronger evidence for calixarene in cone configuration. In the ^{1}H NMR spectra of Schiff base **4a** the bridging methylene groups show two doublets at δ 3.34 and 4.45 and *t*-butyl groups display a singlet at δ 1.06, which also indicates the carlixarene in cone conformation. The proton of CH═N group shows one singlet at δ 8.43 and the proton of phenolic hydroxyl group shows a peak at δ 13.40. The ^{1}H NMR spectrum of naphthyl Schiff base **4d** shows a similar pattern with one singlet for *t*-butyl groups at δ 1.06, two doublets for the bridging methylene groups at δ 3.10 and 4.31, one singlet for imine groups at δ 8.67 and one peak for phenolic hydroxyl groups at δ 14.47. In summary, ^{1}H NMR spectra indicate that the calixarene Schiff bases **4a**—**4d** exist in cone configuration with four imine groups at the lower rim of a clixarene. The single crystal structure of compound **2b** was determined by an X-ray diffraction method. The perspective view is shown in Figure 1. The crystal data and refinement details are given in Table 1. It is clearly seen that calix[4]arene exists in cone conformation. The four phthalimidobutyl groups stretch to the lower rim of calixarene with very little different position.

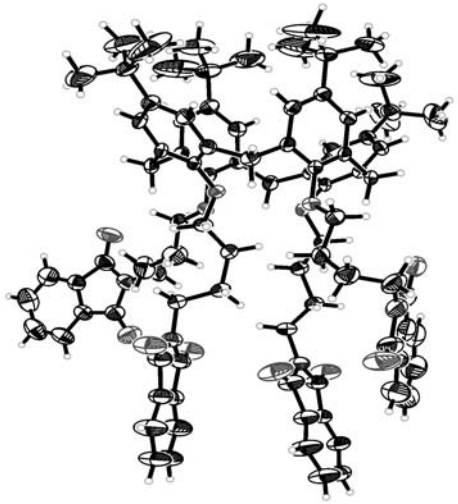


Figure 1 Molecular structure of **2b**, where solvent molecules were omitted for clarity.

Complexing properties

To evaluate the binding ability of new calixarene Schiff bases **4a**—**4d** to transition metal ions, compound **4a** was chosen as an example to coordinate several transition metal ions and their UV-vis spectra were investigated. The maximal absorption of the Schiff base **4a** appears at about 312 nm (Figure 2). Upon the addition of alkali and alkaline earth metal salts, no changes of absorption were observed, indicating that the target compounds have negligible binding ability for these kinds of metal ions. When transition metal salts were introduced the maximal absorption was shifted clearly to longer wavelengths, which means that stronger complexation between them was formed. It is very interest-

Table 1 Crystal data and refinement details of compound **2b**

Molecular formula	$C_{93}H_{101}Cl_3N_4O_{12}$
Formula weight	1573.13
T/K	296(2)
Wavelength/nm	0.71073
Crystal system	Triclinic
Space group	*P*-1
a/nm	1.07886(15)
b/nm	1.27115(18)
c/nm	3.1914(5)
α/(°)	90.448(2)
β/(°)	96.788(2)
γ/(°)	96.240(2)
V/nm^3	4.3194(11)
Z	2
F(000)	1668
D_{calc}/(Mg•m^{-3})	1.210
Absorption coefficient/mm^{-1}	1.68
θ range/(°)	1.61—25.02
Limiting indices	$-12 \leqslant h \leqslant 12$, $-15 \leqslant k \leqslant 15$, $-37 \leqslant l \leqslant 37$
Reflections collected/unique	31820/15122 [R(int)=0.1128]
Completeness to *θ*	99.2%
Data/restraint/parameter	15122/1/1021
Refinement method	Full-matrix least-squares on F^2
Final *R* indices [$I>2\sigma(I)$]	R_1=0.1095, wR_2=0.3296
R indices (all data)	R_1=0.2049, wR_2=0.3808
Goodness-of-fit on F^2	1.019
Largest diff. peak and hole/(e•Å^{-3})	0.587 and −0.462

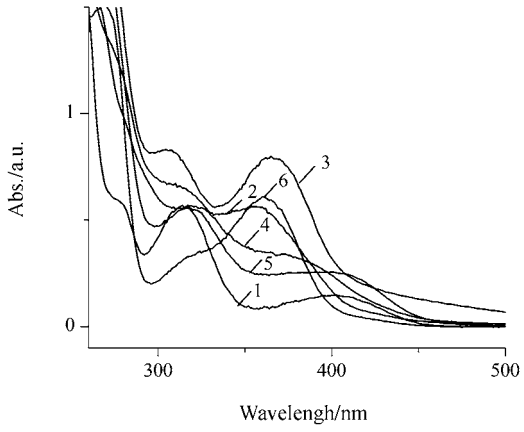


Figure 2 UV-Vis spectroscopy of the ligand **4a** and metal complexes. C_{4a}= $C_{M^{2+}}$ =1.0×10^{-4} mol/L. 1, **4a**; 2, **4a**-Co^{2+}; 3, **4a**-Cu^{2+}; 4, **4a**-Mn^{2+}; 5, **4a**-Ni^{2+}; 6, **4a**-Zn^{2+}.

ing to find the new maximal absorptions of the target compounds with Co^{2+} (356 nm), Cu^{2+} (366 nm), Mn^{2+} (320 nm), Ni^{2+} (320 nm), Zn^{2+} (360 nm). Besides causing very large shift of maximal absorption, the absorptions of **4a** with Cu^{2+}, Zn^{2+} were increased greatly. The UV-Vis spectra of **3a** with Cu^{2+} and Zn^{2+} of different concentrations are shown in Figures 3 and 4. From Figure 3 the isoabsorptive points were clearly observed at 331 and 400 nm with the concentration of Zn^{2+} increasing from 2.0×10^{-5} to 10.0×10^{-5} mol/L. With the saturation method (Figure 5) the molar ratio of complex C_{4a} ∶ $C_{Zn^{2+}}$ was determined as 1∶2. From Figure 4 the isoabsorptive points at 319 and 422 nm were also observed with the concentration of Cu^{2+} increasing from 1.0×10^{-5} to 4.0×10^{-5} mol/L. The molar ratio of complex C_{4a} ∶ $C_{Cu^{2+}}$ was determined as 1∶1 by the saturation method (Figure 6). There are four salen groups on the lower rim of calixarene **4a**, which could coordinate to one or two transition metal ions according to the typical coordination number of metal ions and steric effect. By using the same method the value of stability constants of complexes **4a** with Cu^{2+} and Zn^{2+} were determined as 2.223×10^4 and 1.813×10^4 respectively.

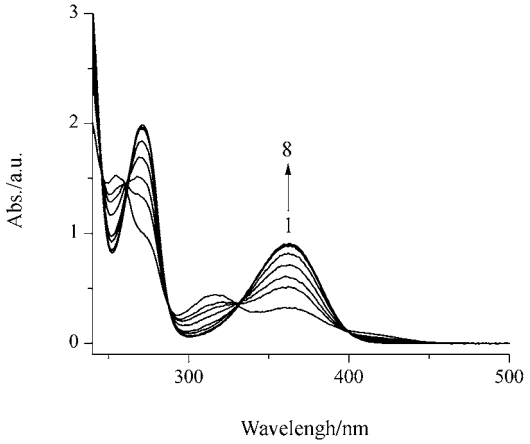


Figure 3 UV-Vis spectra of **4a** (5×10^{-5} mol•L^{-1}) with different concentrations of Zn^{2+}. $C_{Zn^{2+}}$ /(10^{-5} mol•L^{-1}) from 1 to 8: 2.0, 3.2, 4.8, 6.0, 7.2, 8.0, 8.8, 10.0.

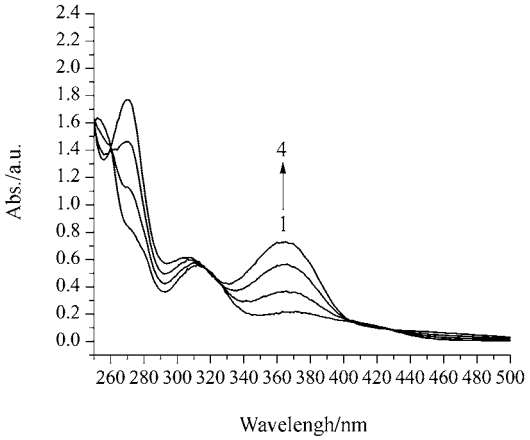


Figure 4 UV-Vis spectra of **4a** (5×10^{-5} mol•L^{-1}) with different concentrations of Cu^{2+}. $C_{Cu^{2+}}$ /(10^{-5} mol•L^{-1}) from 1 to 4: 1.2, 2.0, 3.2, 4.0.

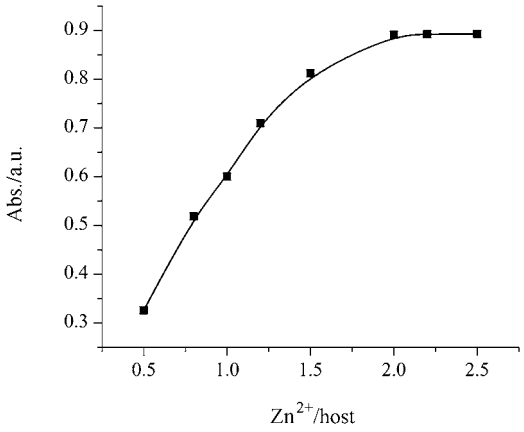


Figure 5 Absorbance plot of **4a** to [Zn^{2+}]/[**4a**].

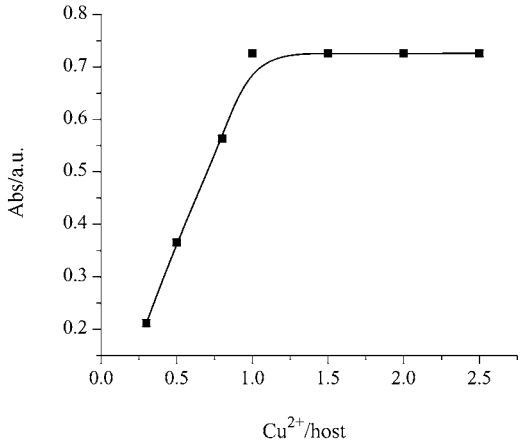


Figure 6 Absorbance plot of **4a** to [Cu^{2+}]/[**4a**].

Experimental

Reagents and instruments

All reagents and solvents were commercial available with analytical grade and used as received. Further purification and drying by standard methods were employed and some were distilled prior to use when necessary. All evaporations of organic solvents were carried out with a rotary evaporator in conjunction with a water aspirator. *p-tert*-Butylcalix[4]arene[12] was prepared according to the published methods.

Melting points were taken on a hot-plate microscope apparatus and uncorrected. ^{1}H NMR spectra were recorded with a Bruker AV-600 spectrophotometer (600 MHz for ^{1}H NMR). IR spectra were obtained on a Bruker Tensor27 spectrometer (KBr disc). UV spectra were recorded on a Shimdazu2501 PC spectrometer. Elemental analysis was determined on a PE 240C instrument. X-ray data were collected on a Bruker Smart APEX-2 diffractometer.

Synthesis of 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetraphthalimidoalkoxycalix[4]arene (2a—2b)

A suspension of *p-tert*-butylcalix[4]arene (**1**) (5.0 mmol, 3.24 g) and sodium hydride (45.0 mmol, 1.80 g) in dry DMF (70 mL) was stirred under nitrogen for 1 h. Then *N*-chloropropylphthalimide or *N*-bromobutylphthalimide (15.0 mmol) was added and the mixture was heated in 60—70 ℃ for 5 d. After adding large portion of water, the residue was extracted with 100 mL of methylene dichloride. The organic layer was washed with water and evaporated to dryness. The resulting precipitates were collected and recrystallized from chloroform/ethanol to give pure solids of **2a**—**2b**[10].

5,11,17,23-Tetra-*t*-butyl-25,26,27,28-tetraphthalimidopropoxycalix[4]arene (**2a**): White solid, yield 55%. m.p. 213—214 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.03 (s, 36H, $C(CH_3)_3$), 2.38 (q, J=6.9 Hz, 8H, CH_2), 3.10 (d, J=12.6 Hz, 4H, $ArCH_2Ar$), 3.86 (t, J=6.9 Hz, 8H, NCH_2), 3.97 (t, J=7.5 Hz, 8H, OCH_2), 4.35 (d, J=12.6 Hz, 4H, $ArCH_2Ar$), 6.71 (s, 8H, ArH), 7.59—7.61 (m, 8H, ArH), 7.69—7.71 (m, 8H, ArH); IR (KBr) v: 3431 (s), 2958 (s), 2867 (m), 1772 (w), 1712 (vs), 1630 (w), 1484 (m), 1382 (m), 1191 (w).

5,11,17,23-Tetra-*t*-butyl-25,26,27,28-tetraphthalimidobutoxycalix[4]arene (**2b**): White solid, yield 60%. m.p. 175 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.06 (s, 36H, $C(CH_3)_3$), 1.70—1.85 (m, 8H, CH_2CH_2), 2.01—2.18 (m, 8H, CH_2CH_2), 3.10 (d, J=13.2 Hz, 4H, $ArCH_2Ar$), 3.77 (t, J=6.6 Hz, 8H, NCH_2), 3.92 (t, J=7.2 Hz, 8H, OCH_2), 4.37 (d, J=13.2 Hz, 4H, $ArCH_2Ar$), 6.75 (s, 8H, ArH), 7.57—7.77 (m, 16 H, ArH); IR (KBr) v: 3430 (s), 2960 (s), 2867 (m), 1772 (w), 1713 (vs), 1630 (w), 1480 (m), 1384 (m), 1190 (w).

Synthesis of 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetraamnioalkoxycalix[4]arene (3a—3b)

To a solution of **2a**—**2b** (2.10 mmol) in 50 mL of ethanol was added hydrated hydrazine (80%, 10 mL) and the mixture was refluxed for 12 h. After cooling to room temperature 300 mL of water was added to the solution. The mixture was extracted with methylene dichloride. The organic layer was dried with $MgSO_4$ and evaporated to give white solid as the products **3a**—**3b**.[10]

5,11,17,23-Tetra-*t*-butyl-25,26,27,28-tetraaminopropoxycalix[4]arene (**3a**): Yield 83%, m.p. 197—201 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.05 (s, 36H, $C(CH_3)_3$), 2.14 (q, J=6.6 Hz, 8H, CH_2), 2.27 (brs, 8H, NH_2), 2.91 (t, J=7.1 Hz, 8H, CH_2), 3.11 (d, J=12.6 Hz, 4H, $ArCH_2Ar$), 3.89 (t, J=7.1 Hz, 8H, OCH_2), 4.33 (d, J=12.6 Hz, 4H, $ArCH_2Ar$), 6.75 (s, 8H, ArH); IR (KBr) v: 3430 (s), 2959 (s), 2867 (m), 1630 (w), 1484 (m), 1382 (m), 1191 (w).

5,11,17,23-Tetra-*t*-butyl-25,26,27,28-tetraaminobutoxycalix[4]arene (**3b**): Yield 90%, m.p. 212—215 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.07 (s, 36H, $C(CH_3)_3$), 1.45—1.69 (m, 8H, CH_2CH_2), 1.93—2.10 (m, 8H, CH_2CH_2), 2.76 (t, J=6.6 Hz, 8H, CH_2), 3.12 (d, J=13.2 Hz, 4H, $ArCH_2Ar$), 3.87 (t, J=7.2 Hz, 8H, OCH_2), 4.38 (d, J=13.2 Hz, 4H, $ArCH_2Ar$), 6.77 (s, 8H, ArH);

IR (KBr) *v*: 3431 (s), 2959 (s), 2867 (m), 1632 (w), 1480 (m), 1384 (m), 1190 (w).

Synthesis of 5,11,17,23-tetra-*p*-butyl-25,26,27,28-tetra(salicylideniminoalkoxy)calix[4]arene (4a—4b)

The mixture of **3a**—**3b** (1.0 mmol) and salicylaldehyde (5.0 mmol, 0.612 g) in 20 mL of ethanol was refluxed for 6 h. The precipitate was filtered and washed with cold ethanol to give the product, which was recrystallized from chloroform and ethanol to give pure products **4a**—**4b**.

5,11,17,23-Tetra-*t*-butyl-25,26,27,28-tetra(salicylideniminopropoxy)calix[4]arene (**4a**): Light yellow solid, yield 80%, m.p. 148—150 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.06 (s, 36H, $C(CH_3)_3$), 2.36 (q, J=6.8 Hz, 4H, CH_2), 2.43 (q, J=6.8 Hz, 4H, CH_2), 3.34 (d, J=12.6 Hz, 4H, $ArCH_2Ar$), 3.94 (t, J=7.1 Hz, 8H, NCH_2), 4.25 (t, J=7.3 Hz, 8H, OCH_2), 4.45 (d, J=12.6 Hz, 4H, $ArCH_2Ar$), 6.84—7.02 (m, 24H, ArH), 8.43 (s, 4H, CH=N), 13.40 (s, 4H, C_6H_4OH); IR (KBr) *v*: 3448 (vs), 2959 (m), 1633 (s), 1463 (m), 1385 (m), 1199 (w), 1122 (w), 756 (m). Anal. calcd for $C_{84}H_{100}N_4O_8$: C 77.98, H 7.79, N 4.33; found C 77.62, H 7.90, N 3.75.

5,11,17,23-Tetra-*t*-butyl-25,26,27,28-tetra(salicylideniminobutoxy)calix[4]arene (**4b**): Light yellow solid, yield 85%, m.p. 144—145 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.07 (s, 36H, $C(CH_3)_3$), 1.72—1.77 (m, 8H, CH_2CH_2), 2.02—2.07 (m, 8H, CH_2CH_2), 3.10 (d, J=13.2 Hz, 4H, $ArCH_2Ar$), 3.55 (t, J=6.9 Hz, 8H, NCH_2), 3.89 (t, J=7.5 Hz, 8H, OCH_2), 4.36 (d, J=13.2 Hz, 4H, $ArCH_2Ar$), 6.76 (s, 8H, ArH), 6.78 (t, J=7.5 Hz, 4H, ArH), 6.90 (d, J=7.8 Hz, 4H, ArH), 7.12 (d, J=6.6 Hz, 4H, ArH), 7.28 (t, J=8.4 Hz, 4H, ArH), 8.24 (s, 4H, CH=N), 13.48 (s, 4H, C_6H_4OH); IR(KBr) *v*: 3448 (vs), 2958 (m), 1634 (s), 1463 (m), 1385 (m), 1199 (w), 1122 (w), 756 (m). Anal. calcd for $C_{88}H_{108}N_4O_8$: C 78.31, H 8.06, N 4.15; found C 78.57, H 8.19, N 4.17.

Synthesis of 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetra-(2-hydroxynaphthylideniminoalkoxy)calix[4]-arene (4c—4d)

The mixture of **3a**—**3b** (1.0 mmol) and 2-hydroxy-1-naphthaldehyde (0.44 mmol, 0.68 g) in 20 mL of ethanol was refluxed for 6 h. The precipitate was filtered and washed with cold ethanol, which was recrystallized from chloform/ethanol to give the products **4c**—**4d**.

5,11,17,23-Tetra-*t*-butyl-25,26,27,28-tetra(2-hydroxynaphthylideniminopropoxy)calix[4]arene (**4c**): Yellow solid, yield 75%, m.p.＞250 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.06 (s, 36H, $C(CH_3)_3$), 2.36 (q, J=6.8 Hz, 4H, CH_2), 2.43 (q, J=6.8 Hz, 4H, CH_2), 3.34 (d, J=12.6 Hz, 4H, $ArCH_2Ar$), 3.94 (t, J=7.1 Hz, 8H, NCH_2), 4.25 (t, J=7.3 Hz, 8H, OCH_2), 4.45 (d, J=12.6 Hz, 4H, $ArCH_2Ar$), 6.75 (s, 8H, ArH), 7.44—8.01 (m, 24H, ArH), 8.67 (s, 4H, CH=N), 14.47 (s, 4H, $C_{10}H_6OH$); IR (KBr) *v*: 3420 (m), 2960 (s), 2869 (m), 1632 (s), 1484 (s), 1386 (w), 1278 (m), 1200 (m), 1125 (m), 874 (w), 781 (m). Anal. calcd for $C_{100}H_{108}N_4O_8$: C 80.39, H 7.29, N 3.75; found C 79.74, H 7.42, N 3.85.

5,11,17,23-Tetra-*t*-butyl-25,26,27,28-tetra(2-hydroxynaphthylideniminobutoxy)calix[4]arene (**4d**): Yellow solid, yield 80%, m.p.＞250 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.06 (s, 36H, $C(CH_3)_3$), 1.81—1.82 (m, 8H, CH_2CH_2), 2.01—2.02 (m, 8H, CH_2CH_2), 3.10 (d, J=13.2 Hz, 4H, $ArCH_2Ar$), 3.51 (t, J=5.7 Hz, 8H, NCH_2), 3.87 (t, J=7.2 Hz, 8H, OCH_2), 4.31 (d, J=13.2 Hz, 4H, $ArCH_2Ar$), 6.75 (s, 8H, ArH), 7.44—8.01 (m, 24H, ArH), 8.67 (s, 4H, CH=N), 14.47 (s, 4H, $C_{10}H_6OH$); IR (KBr) *v*: 3420 (m), 2960 (s), 2866 (m), 1633 (s), 1486 (s), 1386 (w), 1278 (m) ,1203 (m), 1126 (m), 871 (w), 782 (m). Anal. calcd for $C_{104}H_{116}N_4O_8$: C 80.59, H 7.54, N 3.61; found C 80.67, H 7.21, N 3.17.

Supplementary material

Single crystal X-ray diffraction data are deposited with CCDC (Deposition number of **2b**: CCDC715985).

References

1 (a) Bohmer, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713.
(b) Wieser, C.; Dielman, C.; Matt, D. *Coord. Chem. Rev.* **1997**, *165*, 93.

2 (a) Biros, S. M.; Rebek, J. Jr. *Chem. Soc. Rev.* **2007**, *36*, 93.
(b) Pluth, M. D.; Raymond, K. N. *Chem. Soc. Rev.* **2007**, *36*, 161.

3 (a) BaDalgarno, S. J.; Thallapally, P. K.; Barbour, L. J.; Atwood, J. L. *Chem. Soc. Rev.* **2007**, *36*, 236.
(b) Baldini, L.; Casnati, A.; Sansone, F.; Ungaro, R. *Chem. Soc. Rev.* **2007**, *36*, 254.

4 (a) Hadjoudis, E.; Mavrids, I. M. *Chem. Soc. Rev.* **2004**, *33*, 579.
(b) Lalor, R.; Baillie-Johnson, H.; Redshaw, C.; Matthews, S. E.; Mueller, A. *J. Am. Chem. Soc.* **2008**, *130*, 2892.

5 (a) Mahon, M. F.; McGinley, J. A.; Rooney, D.; Walsh, J. *Tetrahedron* **2008**, *64*, 11058.
(b) Creaven, B. S.; Deasy, M.; Flood, P. M.; McGinley, J.; Murray, B. A. *Inorg. Chem. Commun.* **2008**, *11*, 5.

6 (a) Liang, Z.; Liu, Z.; Gao, Y. *Tetrahedron Lett.* **2007**, *48*, 3587.
(b) Singh, N.; Kumar, M.; Hundal, G. *Tetrahedron* **2004**, *60*, 5393.
(c) Liu, Y.; Wang, H.; Wang, L. H.; Li, Z.; Zhang, H. Y.; Zhang, Q. *Tetrahedron* **2003**, *59*, 7967.

7 (a) Rojsajjakul, T.; Veravong, S.; Tumcharene, G.; Seangprasertkij-Magee, R.; Tuntulani, T. *Tetrahedron* **1997**, *53*, 4669.
(b) Hwang, G. T.; Kim, B. H. *Tetrahedron* **2002**, *58*, 9019.
(c) Yilmaz, A.; Memon, S.; Yilmaz, M. *Tetrahedron* **2002**, *58*, 7735.

8 (a) Tamburini, S.; Tomasin, P.; Vigato, P. A.; Casnati, A.; Domiano, L. *Inorg. Chim. Acta* **1997**, *254*, 209.
(b) Amato, M.; Ballistreri, F.; Pappalardo, A.; Tomaselli, G.; Toscano, R.; Williams, D. *Eur. J. Org. Chem.* **2005**, 3562.
(c) Tuntulani, T.; Thavornyutikarn, P.; Poompradub, S.;

Jaiboon, N.; Ruangpornvisuti, V.; Chaichit, N.; Asfari, Z.; Vicens, J. *Tetrahedron* **2002**, *58*, 10277.

9 (a) Liu, Y.; Zhao, B.-T.; Zhang, H.-Y.; Wada, T.; Inoue, Y. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1219.
(b) Pothsree, T.; Seangprasertkij-Magee, R.; Tuntulani, T. *J. Inclusion Phenom. Macrocyclic Chem.* **1997**, *29*, 99.
(c) Seangprasertkij, R.; Asfari, Z.; Arnaud, F.; Vicens, J. *J. Org. Chem.* **1994**, *59*, 1741.

10 (a) Barsobo, S.; Carrera, A. G.; Matthews, S. E.; Arnaud-Neu, F.; Bohmer, V.; Dozol, J.-F.; Rouquette, H.; Schwing-Weill, M.-J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 719.
(b) Casnati, A.; Ca, N. D.; Fontanella, M.; Sansone, F.; Ugozzoli, F.; Ungaro, R.; Liger, K.; Dozol, J. F. *Eur. J. Org. Chem.* **2005**, 2338.
(c) Gac, S. L.; Zeng, X. S.; Reinaud, O.; Jabin, I. *J. Org. Chem.* **2005**, *70*, 1204.

11 Mahon, M. F.; McGinley, J.; Rooney, A. D.; Walsh, J. *Tetrahedron* **2008**, *64*, 11058.

12 Gutsche, C. D.; Dhawan, B.; Leonis, M.; Stewart, H. *Org. Synth.* **1990**, *68*, 238.

(E0901124 Li, L.; Dong, H.)