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Synthesis and binding studies of multiple calix[4]arenes

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Abstract—As novel host molecules, various double and quadruple calix[4]arenes have been synthesized by using quadruple cycloadditive macrocyclization, Schiff-base formation, and acylation. The interesting features of 'head-to-head' type multiple calix[4]arenes, such as the conformational aspects and cooperative binding, have been studied.

1. Introduction

Calix[4]arenes are macrocyclic molecules in which four phenolic units are linked via methylene bridges at their *ortho* positions.[1] These molecules have great advantage over other members of the family due to many of its salient features, such as easy accessibility, well defined structures with four distinct rings, its ability to form host–guest complexes with various small molecules, and so on. There are many research groups involved in design and synthesis of different kinds of receptor molecules with defined cavities by using calix[4]arenes as a key structural motif. Several double (or multiple) calix[4]arenes[2,3] have been prepared as examples of higher order molecular architectures in the recent past. In these compounds, two or more calix[4]arene units are linked at their upper ('head-to-head' type)[4] or lower rims ('tail-to-tail' type)[5] through one or more spacer molecules. Various structural motifs have been used as spacers, including aliphatic chains, ethers, esters, amides, imines, sulfides, and metallocenes.[2–5] When the upper rims of calix[4]arene molecules are linked together, a hollow and hydrophobic cavity is formed. The interior dimension is large enough to encapsulate small- to medium-sized neutral guest molecules.

Herein, we report efficient syntheses of head-to-head type multiple calix[4]arenes by using quadruple cycloadditive macrocyclizations (QCM), Schiff-base formations, and acylation reactions as key steps.[6] We also describe characterization including X-ray crystal structures and binding properties of multiple calix[4]arenes.

Fig. 1 shows the structures of synthesized double calix[4]-arenes **1**–**8** and quadruple calix[4]arene **9**.

Keywords: calixarenes; cyclophanes; macrocycles; molecular recognition.

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2. Results and discussion

2.1. Double calix[4]arenes by quadruple cycloadditive macrocyclizations and binding studies with cations

Double calix[4]arenes **1** and **2** were prepared from corresponding *para*-related bifunctional dipoles (terephthaldinitrile oxide) and calix[4]arene-based bifunctional dipolarophiles **11** and **12** in reasonable yields by slight modification of the procedure described earlier for similar macrocyclization.[7] Synthetic routes for the preparation of double calix[4]arenes **1** and **2** are shown in Scheme 1. The bifunctional dipoles were generated in situ by the dehydrochlorination of hydroxamic acid chloride **13** under the reaction conditions for macrocycle synthesis. *N*-acryloylation and *N*-propiolation of the diamine **10**[8] afforded the bifunctional dipolarophiles **11** and **12**, respectively. QCM[7] between the dihydroximoyl chloride **13** and compound **11** in the presence of triethylamine in ethanol provided the double calix[4]arene **1** in 27% isolated yield, which corresponds to a 72% yield per cycloaddition. Similarly, the double calix[4]arene **2** was prepared by QCM between compound **12** and **13** in 26% yield. Both the double calix[4]arenes **1** and **2** could be prepared in only two steps from diamine **10** in 21% overall yield. However, when the bifunctional dipolarophile was changed to *meta*-related bifunctional dipoles (isophthaldinitrile oxide), the crude reaction mixture obtained was too complex to separate.

Full characterization data including elemental analysis, mass spectrometry, IR, UV, ^{1}H NMR, and ^{13}C NMR of double calix[4]arenes **1** and **2** suggest that these compounds are quadruple cycloadducts between terephthaldinitrile oxide and the corresponding bifunctional dipolarophiles **11** and **12**, respectively.

The ^{1}H NMR spectra of double calix[4]arenes **1** and **2** were observed to be temperature dependent. Furthermore, double

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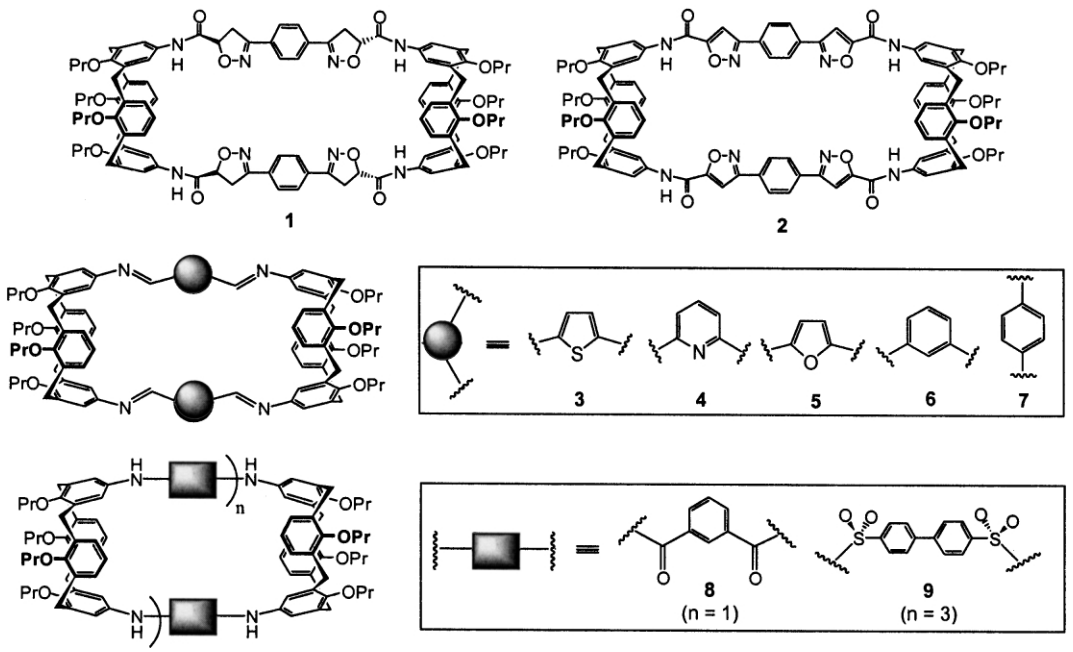
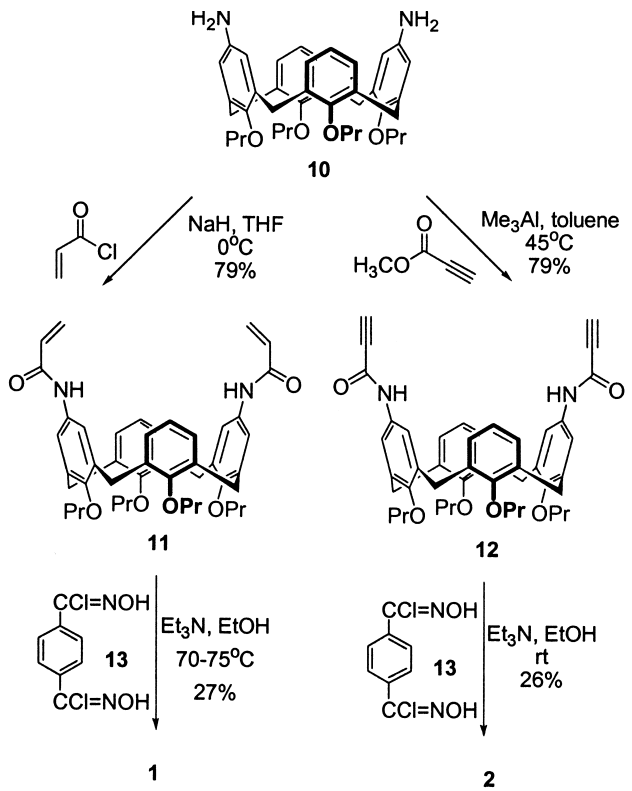


Figure 1. Multiple calix[4]arenes synthesized.

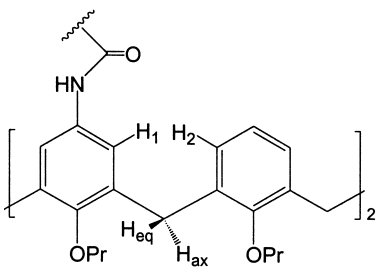
calix[4]arene **1** showed a remarkable solvent dependence of signal patterns for the aromatic protons of the calix[4]arene.[6b] From these phenomena we speculated that double calix[4]arene **1** is conformationally mobile. Furthermore, ^{1}H NMR spectra of double calix[4]arenes **1** and **2** show distinct signals for the aromatic hydrogens of the amido-substituted aromatic rings (H_1, Table 1) at unusually high field (δ=6.44 for **1**, δ=6.38 for **2** in $CDCl_3$). To investigate the conformation of the molecules in solution, we determined the distances between the equatorial proton of the methylene group of the calix[4]arene and the two neighboring aromatic protons by using the initial rate approximation[9] through NOESY. The NOESY spectra of the double calix[4]arenes (**1** and **2**) and bifuntional dipolarophiles (**11** and **12**) were determined at 40, 120, and 200 ms mixing times. The distance of 1.79 Å between the equatorial and axial methylene protons was used as a reference. We found that all calix[4]arenes have pinched cone conformations (Table 1).[10]

To confirm the suggested structure in the solution state and get direct evidence for the pinched cone conformation, we carried out the X-ray crystallographic study. The slow evaporation of the solution containing double calix[4]arene



Scheme 1. Synthesis of double calix[4]arenes **1** and **2**.

Table 1. The distances (Å) between the H_{eq} and the neighboring aromatic protons



Compounds[a]	**11**	**12**	**1**[b]	**2**
H_1	2.61	2.31	2.81–3.53[c] (2.54–2.64)	2.52
H_2	2.32	2.21	2.43 (2.33–2.49)	2.39

[a] The NOESY spectra of the double calix[4]arene **1** was determined in $CDCl_3$/DMSO-d_6 1:1 v/v, rt and those of bifunctional dipolarophiles and double calix[4]arene **2** was determined in $CDCl_3$.
[b] The distances obtained from the X-ray crystal structure are in the parentheses.
[c] Calculated distance range of four distinct H_1 protons.

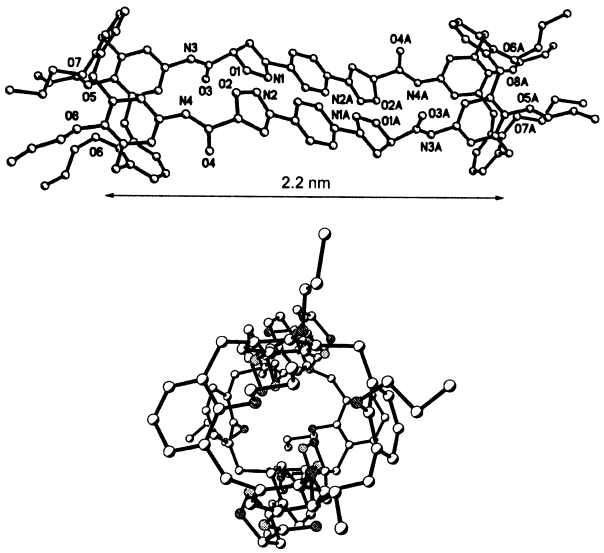


Figure 2. X-ray crystal structure of double calix[4]arene **1** (side view and top view). Two dimethyl sulfoxide solvent molecules and hydrogen atoms are omitted for clarity.

1 (DMSO/$CHCl_3$) gave transparent crystals that were suitable for X-ray analysis. The X-ray crystal structure (Fig. 2, Table 2) clearly shows the chemical structures of **1** including the relative stereochemistry of the four stereogenic centers and reveals the overall topological shape with an inversion center (*i*) of the double calix[4]arene **1**. The distances between the equatorial proton of the methylene group of the calix[4]arene and the two neighboring aromatic protons are 2.54–2.64 and 2.33–2.49 Å, respectively. Furthermore, two aromatic rings containing amide groups are almost parallel to one another (interplanar angle 16.3°), while the other two aromatic rings are almost normal to one another (interplanar angle 89.0°). These results suggest that the double calix[4]arene **1** has a highly distorted pinched cone conformation in the solid state as well as in solution observed from ^{1}H NMR spectra.

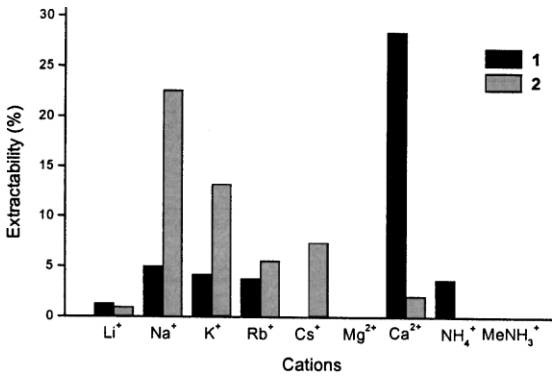


Figure 3. Liquid–liquid extractability spectra of double calix[4]arene **1**.

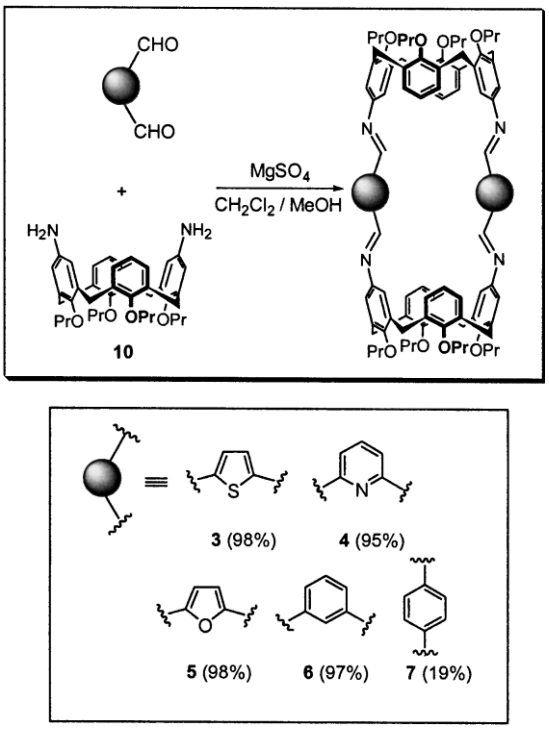
The binding properties of double calix[4]arenes **1** and **2** were studied by two-phase extraction experiments[11] of metal, ammonium, and methylammonium picrates from water into CH_2Cl_2 for the investigation of 'cation–π interactions'[12,13] between double calix[4]arenes and cation picrates. The results, given in Fig. 3, show that double calix[4]arenes **1** and **2** are poor hosts for ammonium and alkylammonium picrates. Double calix[4]arene **1** have a moderate affinity and selectivity for Ca^{2+}, whereas **2** shows a slight preference for Na^+. The rather week cation–π interactions in double calix[4]arenes may be due to the undesirable spatial arrangement of benzene rings in pinched cone conformations for the interactions.

2.2. Double calix[4]arenes by Schiff-base formations and binding studies with viologen-type guests

Schiff-base formation reaction has been recognized and widely used as a highly efficient method for the construction

Table 2. Crystallographic data for compounds **1**, **3**, **4**, and **9**

	1	**3**	**4**	**9**
Formula	$C_{108}H_{116}N_8O_{16}{\cdot}2C_2H_6SO$	$C_{92}H_{100}N_4O_8S_2{\cdot}2CHCl_3$	$C_{94}H_{102}N_6O_8{\cdot}CH_3OH{\cdot}0.5CHCl_3$	$C_{208}H_{224}N_8O_{32}S_8{\cdot}8CH_3OH{\cdot}12H_2O$
Molecular weight	1938.34	1692.62	1535.54	4076.96
Temperature (K)	188 (2)	188 (2)	188 (2)	293 (2)
Mo K_a (λ=0.71073 Å)				
Crystal system	Triclinic	Triclinic	Triclinic	Tetragonal
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$I4_1/a$
Z	1	1	2	4
a (Å)	9.9175 (9)	10.03980 (10)	13.00690 (10)	34.8856 (9)
b (Å)	10.6381 (10)	12.6750 (2)	18.7630 (2)	34.8856 (9)
c (Å)	30.730 (3)	19.0134 (4)	20.87830 (10)	19.8884 (7)
α (°)	87.248 (2)	71.5080 (10)	112.2880 (10)	90
β (°)	81.458 (2)	86.9880 (10)	95.7700 (10)	90
γ (°)	71.205 (2)	73.63 (10)	108.6870 (10)	90
V (Å^3)	3035.2 (5)	2199.75 (6)	4320.41 (6)	24204.3 (12)
ρ (g cm^{-3})	1.060	1.278	1.180	1.119
μ (mm^{-1})	0.105	0.301	0.120	0.145
Crystal size (mm^{-3})	0.3×0.3×0.05	0.35×0.25×0.20	0.6×0.5×0.4	0.70×0.25×0.25
No. of reflections	12412	8962	17302	44362
No. of independent reflections data/restraints/parameters	8866/0/631	6589/58/706	12742/3/1046	9518/3/640
Goodness-of-fit on F^2	2.642	1.174	0.976	2.121
Final R (F)	0.2481	0.0609	0.0801	0.2531
Final R_w (F^2)	0.5357	0.1341	0.2371	0.4890



Scheme 2. Synthesis of double calix[4]arenes **3**–**7**.

of host molecules.[14] We present syntheses of several head-to-head linked double calix[4]arenes which are bridged by π-electron rich or poor aromatic units such as thiophene, benzene, furan, or pyridine. The condensation reactions between dialdehydes and 1.1 equiv. of diaminocalix[4]-arene **10** in refluxing CH_2Cl_2/MeOH (1:1 v/v) in the presence of $MgSO_4$ for 24 h provided the corresponding double calix[4]arenes **3**–**6** in excellent yields (95–98%, Scheme 2). When the reaction was performed with isophthalaldehyde and diaminocalix[4]arene **10**, however, the isolated yield of double calix[4]arene **7** was only 19%. The decreased efficiency of this reaction is ascribed to geometric effect: the efficiency of macrocyclization via imine condensation depends strongly on the geometry of the aldehyde or amine. The structures of double calix[4]arene **3**–**7** were identified by elemental analysis, mass spectrometry, IR, UV, ^{1}H NMR, and ^{13}C NMR. ^{1}H–^{1}H COSY experiments were performed for the ^{1}H NMR spectral assignments. In $CDCl_3$ the ^{1}H NMR spectra of the double calix[4]arenes **3**–**7** show a singlet for the aromatic hydrogens bearing the imine bridges at usually high field (δ=6.03 for **3**, δ=6.20 for **4**, δ=6.12 for **5**, δ=6.11 for **6**, and δ=6.09 for **7**). Also the imine protons of **3**–**7** absorb at high field (δ=7.40 for **3**, δ=7.77 for **4**, δ=7.42 for **5**, δ=7.31 for **6**, and δ=7.38 for **7**). Two opposite aromatic rings substituted with the imine groups fixed in close proximity results in shielding of these aromatic hydrogens. These characteristic shifts correspond to a pinched cone conformation.

The details of X-ray crystal structures of the double calix[4]arenes **3** and **4** are shown in Table 2 and Fig. 4. These double calix[4]arenes are all nanometer-sized macrocycles as shown in **3** (1.7 nm long) and **4** (1.8 nm long), and have good-sized cavities for host–guest com-

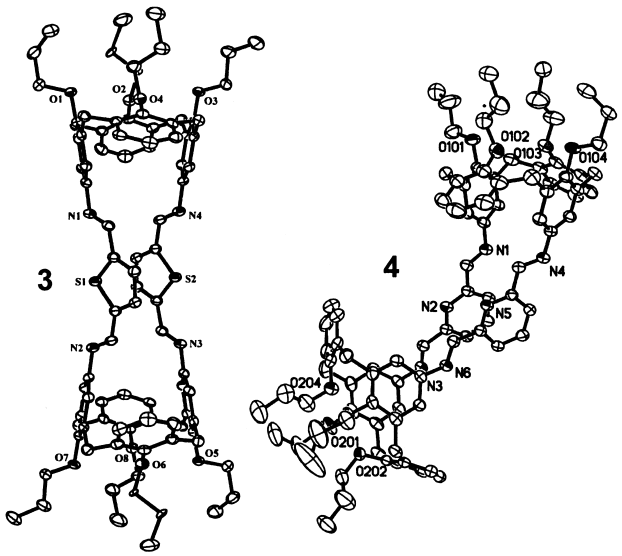


Figure 4. X-ray crystal structure of double calix[4]arene **3** and **4**. Solvent molecules are omitted for clarity.

plexation. The X-ray crystal structures clearly show that these calix[4]arenes also adopt pinched cone conformations in the solid state.

To show the utility of the double calix[4]arene hosts, we have carried out the binding studies between the double calix[4]arenes and viologen-type guest molecules.[15] Viologens[16] are formed by the diquarternizing of 4,4′-bipyridine to form 1,1′-disubstituted-4,4′-bipyridilium salts. They are used in such fields as herbicides, electrochromism, solar energy conversion, molecular electronics, and supramolecular chemistry. The structures and binding constants

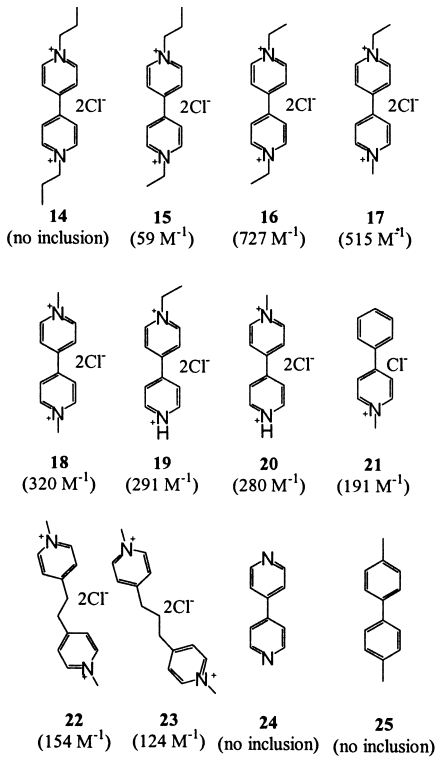


Figure 5. Viologen-type guest molecules and their association constants with double calix[4]arene **3**.

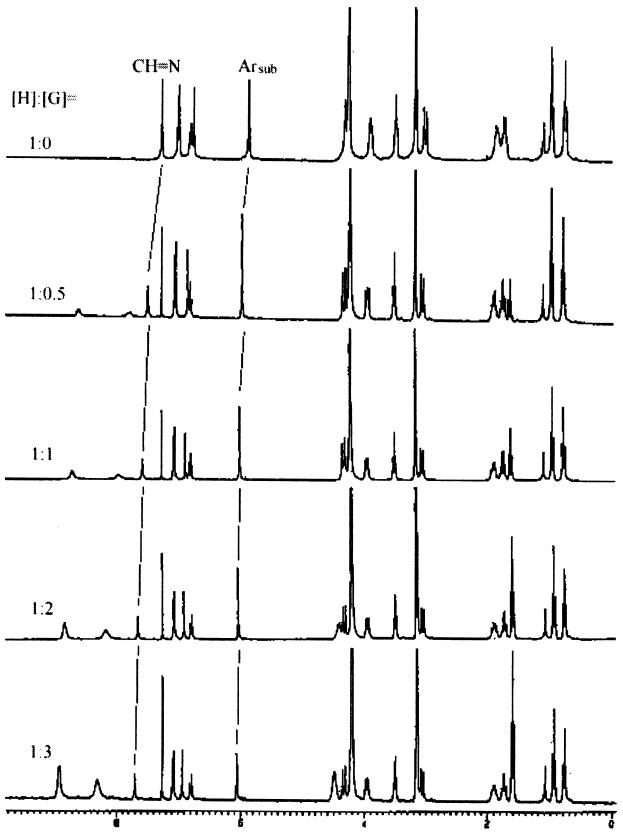


Figure 6. ^{1}H NMR spectra (300 MHz, $CDCl_3/CD_3OD$ 2:1 v/v, 300 K) of double calix[4]arene **3** and spectral changes upon addition of ethyl viologen **16**.

of the various guests chosen for the molecular recognition study with the host **3** are shown in Fig. 5.

The ^{1}H NMR spectrum of host **3** remained unchanged in a wide concentration range (0.25–20 mM in $CDCl_3/CD_3OD$, 2:1 v/v, 300 K), suggesting that no significant structural variation and aggregation occur. The binding property of **3** with viologen-type guest molecules was studied in the above solvent system by ^{1}H NMR titration experiment of double calix[4]arene **3** with ethyl viologen dichloride **16** as shown in Fig. 6. This provides a typical example of fast exchange rate between complexed and uncomplexed species. The signals of imine and aromatic protons in the

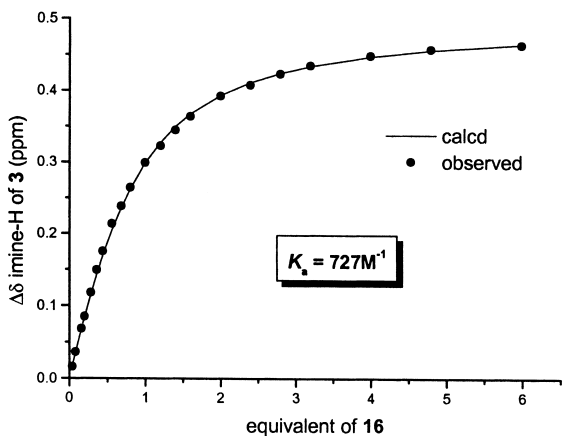


Figure 7. Titration curve of double calix[4]arene **3** with ethyl viologen **16** in $CDCl_3/CD_3OD$ (2:1 v/v, 300 K).

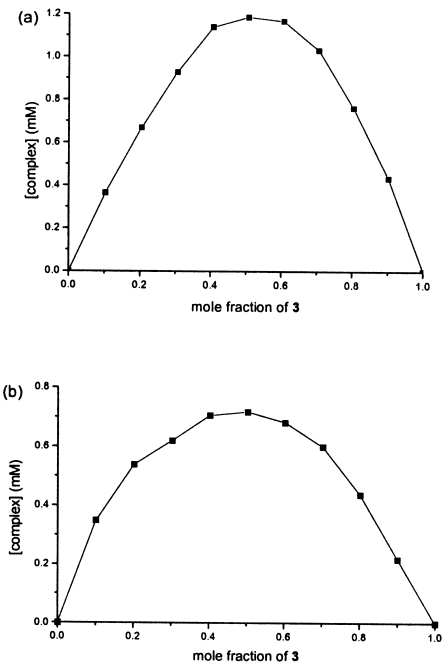


Figure 8. Job plot of double calix[4]arene **3** with (a) viologen **18** and (b) viologen **23** in $CDCl_3/CD_3OD$ (2:1 v/v, 300 K).

double calix[4]arene **3** shifted down-field when the viologens **15**–**23** were added to the host solution, whereas no change in the chemical shift values of **3** are detected when the compounds **14**, **24**, and **25** were added. The different trend in the titration experiments with various viologen-type guest molecules clearly shows that suitable size of *N*-alkyl groups and the presence of the bipyridinium dication in viologens are essential for the inclusion process to occur. Nonlinear least-squares fitting analysis[17] of the complexation with **3** provided the association constant in $CDCl_3/CD_3OD$ (2:1 v/v, 300 K). Fig. 7 shows titration curve of **3** with ethyl viologen **16**. The corresponding association constants are reported in Fig. 5. From these results, the origin of binding mode can be rationalized in terms of aromatic–aromatic interactions between the electron deficient viologen moiety and the electron rich thiophene aromatic linkers. When double calix[4]arene **3** and ethyl viologen dichloride **16** were mixed in $CHCl_3$/MeOH (2:1 v/v), the red color (λ_{max}=489 nm) charge-transfer inclusion complex was formed immediately. The stoichiometry of the above complex was confirmed to be 1:1 by Job plot based on NMR data between double calix[4]arene **3** and the viologens **18** and **23**, respectively (Fig. 8). The postulated binding mode, shown in Fig. 9, can be rationalized in terms of aromatic–aromatic interactions between the electron deficient viologen moiety and the electron rich thiophene aromatic linkers.

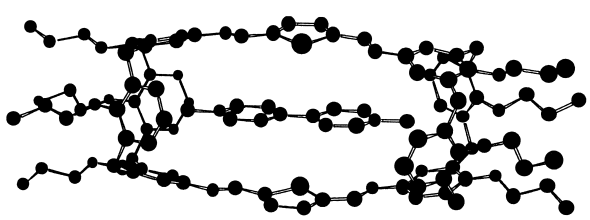
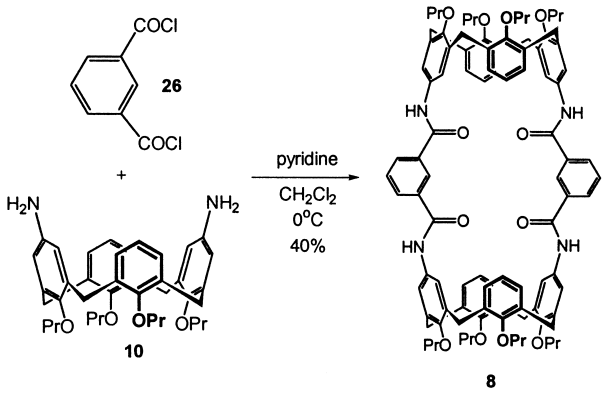


Figure 9. The postulated binding mode between double calix[4]arene **3** and methyl viologen **18**.



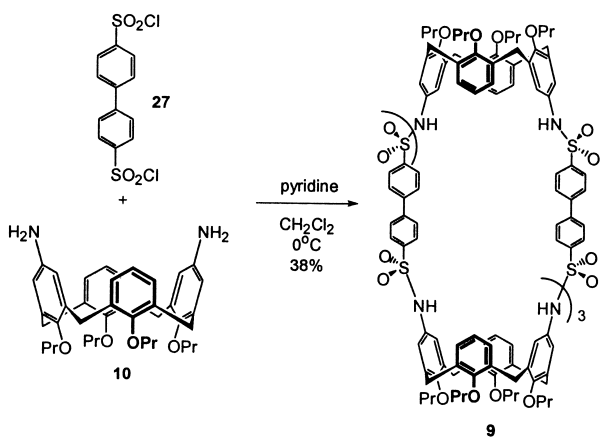
Scheme 3. Synthesis of double calix[4]arene **8**.

The ^{1}H NMR spectra of double calix[4]arenes **4**–**7** remained unaltered upon the addition of any of the viologens **16**, **17**, **22**, and **23**. This indicates that the hosts **4**–**7** have least or no affinity towards viologens. From these results, it can be concluded that overall shape of host molecules and the electron density of aromatic linkers (thiophene, benzene, furan, and pyridine)[18] are the important factors in the binding affinity with the viologen guests.

2.3. Double and quadruple calix[4]arenes by acylations

After having understood the efficiency of the previous synthetic method to arrive at double calix[4]arenes with 2-isoxazoline, 2-isoxazole, and various imine linkages, we also contemplated that modification of the linker unit of two calix[4]arene of the macrocycles with carbonyl will enhance it's binding ability. Keeping this in view we have decided a simple synthetic method involving 2+2 condensation of diaminocalix[4]arene **10** with isophthaloyl dichloride **26** as shown in Scheme 3. When isophthaloyl dichloride **26** was treated with diaminocalix[4]arene **10** in CH_2Cl_2 in the presence of pyridine, double calix[4]arene **8** was isolated in 40% yield. The double calix[4]arene **8** was fully characterized by elemental analysis, mass spectrometry, IR, ^{1}H NMR, and ^{13}C NMR. In contrast, use of terephthaloyl chloride with **10** even under different possible reaction conditions gave no identifiable products.

In yet another modification, the diaminocalix[4]arene **10** was treated with 4,4′-biphenylsulphonyl chloride **27** to



Scheme 4. Synthesis of quadruple calix[4]arene **9**.

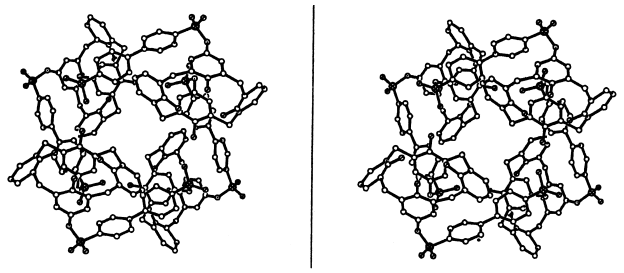


Figure 10. The stereoscopic view of the crystal structure of the quadruple calix[4]arene **9**. Hydrogen atoms, propyl units, and co-crystallized solvent molecules are omitted for clarity.

afford, very interestingly, the quadruple calix[4]arene **9** containing sulfonamide linker units as a major product in 38% yield (Scheme 4). To the best of our knowledge, there is no precedent on synthesis and characterization of quadruple calix[4]arenes of this type. It is astonishing to note that the synthetic yield per sulfonamide bond is 89% and this one step process for the generation of the quadruple calix[4]arene is very efficient mainly due to the preorganization of calix[4]arene moiety. The formation of the quadruple calix[4]arene **9** results from a high degree of molecular assembly between diaminocalix[4]arenes and the biphenyl linkers through eight sulfonamide bonds. This makes it possible to synthesize quadruple calix[4]arenes. In addition, as this quadruple calix[4]arene consists of four isolated cavities with uniform polyhetero-surfaces, it is expected to bind with more than one guest of same or different kind.

Single crystals of quadruple calix[4]arene **9** were grown from chloroform–methanol mixture. The molecular structure of quadruple calix[4]arene **9** is shown in Table 2 and Fig. 10. The crystal structure has an inversion center (*i*) and all four calix[4]arenes point outward. In this compound there are four divergent cavities for binding guests. Of the four aromatic rings in the calix[4]arene ring, the two aromatic rings substituted with the sulfonamido groups are almost parallel to one another (interplanar angle: 12.6°) and the other two are almost perpendicular to one another (interplanar angle: 76.3°). These interplanar angles suggest that the quadruple calix[4]arene **9** has a pinched cone conformation[10] in the solid state. The dihedral angle (24.8°) between two aromatic rings in the biphenyl linkage is directly related to the fact that the quadruple calix[4]arene (4+4 adduct) is formed in preference to a conceivable double calix[4]arene (2+2 adduct). Because of the angle strain, the formation of a double calix[4]arene is quite hindered and we could not isolate any double calix[4]arene products.

We have shown that this new approach to combine diaminocalix[4]arene **10** with 4,4′-biphenylsulphonyl chloride **27** leads to calix[4]arene-based supramolecule with isolated cavities. Current efforts are focused on extension of this approach to arrive at other supramolecular systems.

3. Conclusions

In summary, herein we have demonstrated that head-to-head

multiple calix[4]arenes containing linker units of different length and functionality could be synthesized by suitable choice of reaction pathway. As a first example, double calix[4]arenes **1** and **2** linked by means of heterocycles could be synthesized by QCM, between the bis(amido)-calix[4]arene **11** or **12** and terephthaldicarboximoyl chlorides in 27 and 26% yields, respectively. Similarly, the double calix[4]arenes **3**–**7** with imine linkages (Schiff bases) were obtained by condensation of diaminocalix[4]-arene **10** with of aromatic dialdehydes. Macrocycles containing double calix[4]arenes **8** linked through amido linkages was prepared by treating diaminocalix[4]arene **10** with isophthaloyl dichloride in 40% yield. Whereas the reaction between 4,4′-biphenylsulphonyl chloride and diaminocalix[4]arene affords the sulfonamido linked quadruple calix[4]arene **9** in 38% yield. The structures of all double calix[4]arenes **1**–**7** were characterized by various physical and chemical methods including X-ray crystallography. Also it should be noted that it is for the first time that macrocycle of the type **9** has been well characterized with the aid of X-ray crystallography and the unique conformational and topological aspects of the quadruple calix[4]arene has been well understood. We have also carried studies on the propensities of viologen-type guest molecules to get into the cavities of double calix[4]arenes **3**–**7**, by ^{1}H NMR titration experiments to conclude that thiopheno double calix[4]arene **3** shows better binding affinity than the other macrocycles resulting in the formation of 1:1 complex.

Our synthetic process to the double- and quadruple calix[4]arenes and their molecular recognition study would help us to widen our knowledge about these molecular host systems and accelerate studies on their supramolecular aspects in the future.

4. Experimental

4.1. General

All solvents were carefully dried and distilled prior to use. Melting points (mp) are not corrected. ^{1}H NMR spectra were recorded in $CDCl_3$ at 300 MHz unless otherwise indicated. ^{13}C NMR spectra were recorded at 75 MHz. Tetramethylsilane was used as internal standard for ^{1}H NMR. Chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in ppm (δ). Mass spectra (FAB) were performed by Korea Basic Science Center, Daejeon, Korea. Elemental analyses were performed by Central Laboratory, Kyungbuk National University, Daegu, Korea and Center for Integrated Molecular Systems (CIMS), POSTECH, Pohang, Korea.

All reactions were performed in oven-dried glassware under a positive pressure of argon. Analytical TLC was performed on precoated silica gel plates and visualized with UV light and/or by spraying with *p*-anisaldehyde or phosphomolybdic acid solutions followed by heating with hotplate. Flash column chromatography was performed with silica gel. Diaminocalix[4]arene **10**[8] and terephthaldicarboximoyl chloride (**13**)[7] were synthesized according to literature procedures.

4.1.1. 5,17-Bis(acrylamido)-25,26,27,28-tetrapropoxy-calix[4]arene (11). 5,17-Diaminocalix[4]arene **10** (1.23 g, 1.98 mmol) was dissolved in 20 mL of THF at 0°C with 200 mg (5.00 mmol) of sodium hydride (60% dispersion in mineral oil), followed by a further treatment with acryloyl chloride (4.00 mL, 4.93 mmol). After 10 min, sodium hydride remained was quenched by H_2O. The reaction mixture was then treated with H_2O and organic layer was separated and worked up. Column chromatography (SiO_2, CH_2Cl_2/EtOAc=9:1 v/v) yielded 1.14 g (79%) of **11** as a white power. Mp>195°C dec.; IR ($CHCl_3$) 3276 (NH), 3062, 2962, 2934, 2875, 2740, 1914, 1665 (C=O), 1603 (C=C), 1544, 1465, 1419, 1385, 1332, 1303, 1287, 1217, 1162, 1131, 1106, 1081, 1067, 1038, 1006, 966 cm^{-1}; ^{1}H NMR δ 7.58 (s, 2H; NH), 6.94 (d, 4H, *J*=7.3 Hz; ArH), 6.80 (t, 2H, *J*=7.4 Hz; ArH), 6.39 (s, 4H; ArH), 6.24 (dd, 2H, *J*=14.3, 1.3 Hz; CH=C*H*$_2$), 6.00 (dd, 2H, *J*=16.8, 10.3 Hz; C*H*=CH$_2$), 5.54 (dd, 2H, *J*=11.2, 1.3 Hz; CH=C*H*$_2$), 4.42 (d, 4H, *J*=13.3 Hz; ArC*H*$_2$Ar), 3.95 (t, 4H, *J*=7.9 Hz; OC*H*$_2$), 3.66 (t, 4H, *J*=6.8 Hz; OC*H*$_2$), 3.10 (d, 4H, *J*=13.4 Hz; ArC*H*$_2$Ar), 2.00–1.79 (m, 8H; C*H*$_2$CH$_3$), 1.05 (t, 6H, *J*=14.8 Hz; CH$_3$), 0.90 (t, 6H, *J*=14.9 Hz; CH$_3$); ^{13}C NMR δ 163.9, 157.8, 153.5, 136.5, 134.7, 132.1, 131.7, 129.2, 127.1, 122.5, 121.1, 77.3, 77.0, 31.4, 23.8, 23.4, 11.1, 10.4; HRMS-FAB *m/e*: calcd for M$^+$+1: 731.4060, Found: 731.4072.

4.1.2. 5,17-Bis(ethynylamido)-25,26,27,28-tetrapropoxy-calix[4]arene (12). To a toluene (15 mL) solution of 5,17-diaminocalix[4]arene **10** (1.89 g, 3.03 mmol) at 0°C was added dropwise Me_3Al (7.6 mL, 2.0 M in toluene, 15.2 mmol). The resulting mixture was allowed to warm upto 25°C and further stirred for 1 h. To this aluminum complex was added methyl propiolate (1.4 mL, 15.7 mmol). The resulting mixture was heated to 45°C for 1 h. After cooling to room temperature, 20% aqueous solution of Rochelle salt was added to the reaction mixture, and the mixture was vigorously stirred for several hours until clear phase separation was obtained. The organic layer was extracted with dichloromethane. The organic layer dried over anhydrous $MgSO_4$, and concentrated in vacuo to give the crude product. Purification by column chromatography (SiO_2, hexane/EtOAc=4:1 v/v) gave **12** (1.75 g, 79%). Mp 177–179°C; IR ($CHCl_3$) 3219, 3261 (NH), 3062, 2962, 2933, 2876, 2108 (C≡C), 1660 (C=O), 1646, 1604, 1542, 1464, 1418, 1384, 1287, 1217, 1160, 1131, 1160, 1131, 1079, 1067, 1038, 1006, 966 cm^{-1}; ^{1}H NMR δ 7.64 (s, 2H; NH), 6.97 (d, 4H, *J*=7.3 Hz; ArH), 6.83 (t, 2H, *J*=7.3 Hz; ArH), 6.36 (s, 4H; ArH), 4.42 (d, 4H, *J*=13.2 Hz; ArCH$_2$-Ar), 3.96 (t, 4H, *J*=7.8 Hz; OC*H*$_2$), 3.66 (t, 4H, *J*=6.8 Hz; OC*H*$_2$), 3.21 (d, 4H, *J*=13.3 Hz; ArC*H*$_2$Ar), 2.42 (s, 2H; CCH), 1.98–1.83 (m, 8H; C*H*$_2$CH$_3$), 1.05 (t, 6H, *J*=7.3 Hz; CH$_3$), 0.90 (t, 6H, *J*=7.3 Hz; CH$_3$); ^{13}C NMR δ 157.7, 153.8, 150.3, 136.4, 134.9, 130.8, 129.3, 122.9, 121.3, 78.2, 77.0, 74.9, 31.4, 23.8, 23.4, 11.1, 10.3; MS *m/e* 727.4 (M$^+$+1), 726.4 (M$^+$), 675.4, 19.1; Elemental anal. calcd for $C_{46}H_{50}N_2O_6$: C, 75.75; H, 6.81; N, 3.68. Found: C, 76.01; H, 6.93; N, 3.85.

4.1.3. Double calix[4]arene 1. Terephthaldicarboximoyl chloride (**13**) (80.0 mg, 0.343 mmol) and bis(acrylamido)-calix[4]arene **11** (251 mg, 0.343 mmol) were dissolved in 33 mL of ethanol at 70–75°C. To the reaction mixture was

slowly added Et_3N (110 μL, 0.789 mmol)/EtOH (1.6 mL) using syringe pump for 3 h. The reaction mixture was further stirred for 2 h. After cooling to room temperature, ethanol was concentrated in vacuo to give the crude product. Purification by column chromatography (SiO_2, CH_2Cl_2/EtOAc=4:1 v/v) and then recrystallization from $CHCl_3$/MeOH yielded 86 mg (27%) of white crystals. Mp>238°C dec.; IR ($CHCl_3$) 3396, 3317 (NH), 2962, 2875, 1687 (C=O), 1602 (C=N), 1534, 1465, 1420, 1386, 1353, 1289, 1216, 1133, 1080, 1038, 1007, 996 cm^{-1}; ^1H NMR δ 8.00 (br d, 4H; NH), 7.61–7.54 (m, 8H; ArH), 7.16 (br s, 2H; ArH), 6.71 (br s, 14H; ArH), 6.52 (d, 2H, J=7.1 Hz; ArH), 6.44 (s, 4H; ArH), 5.07–5.01 (m, 4H; CH), 4.43 (d, 8H, J=13.3 Hz; $ArCH_2Ar$), 3.88 (t, 8H, J=7.1 Hz; OCH_2), 3.76 (t, 8H, J=7.3 Hz; OCH_2), 3.62–3.20 (m, 8H; $NCCH_2$), 3.18–3.09 (m, 8H; $ArCH_2Ar$), 1.98–1.84 (m, 16H; CH_2CH_3), 1.02–0.86 (m, 24H; CH_3); ^{13}C NMR δ 168.1, 156.9, 136.0, 135.0, 131.0, 130.7, 130.5, 128.8, 127.6, 122.9, 119.8, 79.5, 77.6, 39.3, 31.4, 23.6, 10.8, 10.7; MS *m/e* 1781.8 (M^++1), 1780.7 (M^+), 1538.7, 648.4, 443.2, 119.1; Elemental anal. calcd for $C_{108}H_{116}N_8O_{16}\cdot 4H_2O$: C, 69.96; H, 6.74; N, 6.04. Found: C, 70.13; H, 6.77; N, 6.02.

4.1.4. Double calix[4]arene 2. Terephthaldicarboximoyl chloride (**13**) (29.7 mg, 0.127 mmol) and bis(ethynylamido)calix[4]arene **12** (92.6 mg, 0.127 mmol) were dissolved in 12 mL of ethanol. To the reaction mixture was slowly added Et_3N (40 μL, 0.287 mmol)/EtOH (570 μL) using syringe pump for 3 h at room temperature. The reaction mixture was further stirred for 2 h. After cooling to room temperature, ethanol was concentrated in vacuo to give the crude product. Purification by column chromatography (SiO_2, CH_2Cl_2/EtOAc=15:1 v/v) and then recrystallization from $CHCl_3$/EtOH yielded 59 mg (26%) of white crystals. Mp>249°C dec.; ^1H NMR δ 7.82 (s, 4H; NH), 7.37 (s, 8H; ArH), 7.13 (d, 8H, J=7.4 Hz; ArH), 6.98 (t, 4H, J=7.4 Hz; ArH), 6.83 (s, 4H; CH), 6.38 (s, 8H; ArH), 4.41 (d, 8H, J=13.4 Hz; $ArCH_2Ar$), 3.99 (t, 8H, J=8.1 Hz; OCH_2), 3.59 (t, 8H, J=6.6 Hz; OCH_2), 3.10 (d, 8H, J=13.4 Hz; $ArCH_2Ar$), 1.97–1.77 (m, 16H; CH_2CH_3), 1.04 (t, 12H, J=7.3 Hz; CH_3), 0.82 (t, 12H, J=7.4 Hz; CH_3); ^{13}C NMR δ 163.7, 162.1, 158.0, 152.9, 152.3, 136.8, 134.3, 130.9, 129.2, 127.0, 122.5, 119.0, 104.7, 77.2, 31.1, 23.5, 22.9, 10.8, 9.8; MS *m/e* 1773.8.8 (M^++1), 1772.7 (M^+), 1603.5, 819.4, 443.2, 154.1; Elemental anal. calcd for $C_{108}H_{108}N_8O_{16}\cdot 2H_2O$: C, 71.66; H, 6.24; N, 6.19. Found: C, 71.60; H, 6.48; N, 6.30.

4.1.5. Double calix[4]arene 3. A solution of diamine **10** (110 mg, 0.177 mmol) and 2,5-thiophenedicarboxaldehyde (22.3 mg, 0.159 mmol) in CH_2Cl_2/MeOH (20 mL/20 mL) was refluxed for 24 h in the presence of $MgSO_4$. The reaction mixture was allowed to cool to room temperature and filtered. Evaporation of the solvent and subsequent purification of the mixture by the column chromatography (SiO_2, hexane/EtOAc=7:1 v/v) gave **3**. Recrystallization of the solid from $CHCl_3$/MeOH afforded pure **3** as light yellow crystals in 98% yield. Mp>330°C dec.; IR ($CHCl_3$) 2961, 2933, 2875, 1611, 1584, 1460, 1385, 1280, 1241, 1213, 1160, 1119, 1077, 1068, 1043, 1005, 963 cm^{-1}; ^1H NMR δ 7.40 (s, 4H; imine H), 7.17 (d, 8H, J=7.3 Hz; ArH), 6.97 (t, 4H, J=7.4 Hz; ArH), 6.91 (s, 4H; $Ar_{th}H$), 6.03 (s, 8H; ArH), 4.44 (d, 8H, J=13.1 Hz; $ArCH_2Ar$), 4.05 (t, 8H, J=8.1 Hz; OCH_2), 3.64 (t, 8H, J=6.6 Hz; OCH_2), 3.16 (d, 8H, J=13.3 Hz; $ArCH_2Ar$), 2.00 (seq, 8H, J=7.4 Hz; CH_2CH_3), 1.89 (seq, 8H, J=7.4 Hz; CH_2CH_3), 1.10 (t, 12H, J=7.4 Hz; CH_3), 0.89 (t, 12H, J=7.4 Hz; CH_3); ^{13}C NMR δ 157.9, 154.0, 150.2 (imine C), 145.9, 145.2, 137.0, 133.8, 130.4, 129.1, 122.1, 120.0, 77.1, 31.1, 23.5, 22.9, 10.8, 9.8; MS *m/e*1453.7 (M^++1), 1452.7 (M^+), 1323.5, 725.3, 343.1; Elemental anal. calcd for $C_{92}H_{100}N_4O_8S_2$: C, 76.00; H, 6.93; N, 3.85. Found: C, 75.88; H, 6.92; N, 3.69.

4.1.6. Double calix[4]arene 4. The compound was synthesized by following the same procedure as described for **3**, refluxing a solution of diamine **10** (129 mg, 0.207 mmol) and 2,6-pyridinedicarboxaldehyde (25.5 mg, 0.189 mmol) in CH_2Cl_2/MeOH (24 mL/24 mL) for 24 h. Column chromatography (SiO_2, hexane/EtOAc=7:1 v/v) gave **4**. Recrystallization of the solid from $CHCl_3$/MeOH afforded **4** as light yellow crystals in 95% yield. Mp>384°C dec.; IR ($CHCl_3$) 2961, 2934, 2875, 1584, 1570, 1461, 1385, 1339, 1295, 1277, 1239, 1213, 1121, 1077, 1068, 1038, 1005, 965 cm^{-1}; ^1H NMR δ 7.77 (s, 4H; imine H), 7.56 (d, 4H, J=7.7 Hz; PyH), 7.20–7.04 (m, 12H; ArH and PyH), 6.90 (t, 2H, J=7.3 Hz; PyH), 6.20 (s, 8H; ArH), 4.44 (d, 8H, J=13.3 Hz; $ArCH_2Ar$), 4.04 (t, 8H, J=8.2 Hz; OCH_2), 3.60 (t, 8H, J=6.6 Hz; OCH_2), 3.37 (d, 8H, J=13.5 Hz; $ArCH_2$-Ar), 1.93–1.76 (m, 16H, J=7.1 Hz; CH_2CH_3), 1.05 (t, 12H, J=7.4 Hz; CH_3), 0.83 (t, 12H, J=6.8 Hz; CH_3); ^{13}C NMR δ 157.9, 157.6, 155.3 (imine C), 155.0, 154.4, 143.4, 136.8, 136.6, 135.9, 134.1, 133.7, 129.3, 129.2, 126.5, 122.8, 122.3, 121.9, 115.4, 77.0, 76.5, 31.4, 31.0, 23.5, 22.9, 22.7, 10.8, 9.7, 9.7; MS *m/e* 1444.7 (M^++2), 1443.7 (M^++1), 1299.6, 812.3, 297.1, 119.1; Elemental anal. calcd for $C_{94}H_{102}N_6O_8\cdot H_2O$: C, 77.23; H, 7.17; N, 5.75. Found: C, 77.54; H, 7.09; N, 5.45.

4.1.7. Double calix[4]arene 5. The compound was synthesized by following the same procedure as described for **3**, refluxing a solution of diamine **10** (123 mg, 0.197 mmol) and 2,5-furandicarboxaldehyde (22.2 mg, 0.179 mmol) in CH_2Cl_2/MeOH (22 mL/22 mL) for 24 h. Column chromatography (SiO_2, hexane/EtOAc=3:1 v/v) gave **5**. Recrystallization of the solid from $CHCl_3$/EtOH afforded **5** as light yellow crystals in 98% yield. Mp>246°C dec.; IR ($CHCl_3$) 2961, 2934, 2875, 1619, 1585, 1508, 1460, 1386, 1345, 1279, 1239, 1214, 1160, 1200, 1077, 1068, 1040, 1004, 965 cm^{-1}; ^1H NMR δ 7.42 (s, 4H; imine H), 7.18 (d, 8H, J=7.2 Hz; ArH), 7.02 (t, 4H, J=7.0 Hz; ArH), 6.56 (s, 4H; $Ar_{furan}H$), 6.12 (s, 8H; ArH), 4.46 (d, 8H, J=13.2 Hz; $ArCH_2Ar$), 4.08 (t, 8H, J=8.2 Hz; OCH_2), 3.66 (t, 8H, J=6.5 Hz; OCH_2), 3.17 (d, 8H, J=13.3 Hz; $ArCH_2$-Ar), 2.05–1.85 (m, 16H, J=7.4 Hz; CH_2CH_3), 1.11 (t, 12H, J=7.3 Hz; CH_3), 0.90 (t, 12H, J=7.4 Hz; CH_3); ^{13}C NMR δ 157.6, 154.3, 153.9, 144.5 (imine C), 144.3, 136.7, 133.9, 129.0, 122.5, 120.2, 114.8, 77.1, 76.4, 31.1, 23.4, 22.8, 10.8, 9.7; MS *m/e* 1422.6 (M^++2), 1421.6 (M^++1), 790.3, 789.3, 220.0, 119.1; Elemental anal. calcd for $C_{92}H_{100}N_4O_{10}\cdot 2.5H_2O$: C, 75.33; H, 7.21; N, 3.82. Found: C, 75.45; H, 7.27; N, 3.62.

4.1.8. Double calix[4]arene 6. The compound was synthesized by following the same procedure as described for **3**, refluxing a solution of diamine **10** (110 mg, 0.177 mmol) and isophthaldehyde (21.6 mg, 0.161 mmol)

in CH_2Cl_2/MeOH (20 mL/20 mL) for 24 h. Column chromatography (SiO_2, hexane/EtOAc=8:1 v/v) gave **6**. Recrystallization of the solid from $CHCl_3$/MeOH afforded **6** as light yellow crystals in 94% yield. Mp>220°C dec.; IR ($CHCl_3$) 2961, 2934, 2875, 1625, 1582, 1461, 1384, 1348, 1290, 1280, 1239, 1214, 1167, 1154, 1119, 1078, 1068, 1041, 1005, 964 cm^{-1}; ^1H NMR δ 7.49 (s, 2H; $Ar_{isophthal}H$), 7.31 (s, 4H; imine H), 7.27 (d, 4H, J=7.7 Hz; $Ar_{isophthal}H$), 7.21 (d, 8H, J=7.2 Hz; ArH), 7.07–6.98 (m, 4H; ArH), 6.86 (t, 2H, J=7.6 Hz; $Ar_{isophthal}H$), 6.11 (s, 8H; ArH), 4.50 (d, 8H, J=13.1 Hz; $ArCH_2Ar$), 4.10 (t, 8H, J=8.1 Hz; OCH_2), 3.68 (t, 8H, J=6.7 Hz; OCH_2), 3.21 (d, 8H, J=13.3 Hz; $ArCH_2Ar$), 2.04 (seq, 8H, J=7.9 Hz; CH_2CH_3), 1.91 (seq, 8H, J=7.1 Hz; CH_2CH_3), 1.13 (t, 12H, J=7.4 Hz; CH_3), 0.92 (t, 12H, J=6.5 Hz; CH_3); ^{13}C NMR δ 157.9, 157.6, 157.2 (imine C), 153.8, 145.3, 137.0, 136.8, 136.1, 134.0, 133.7, 130.4, 129.0, 128.0, 122.7, 121.9, 120.4, 119.4, 77.2, 76.4, 31.2, 23.5, 22.9, 22.9, 10.8, 9.8; MS *m/e* 1441.8 (M^++1), 1440.8 (M^+), 1311.7, 719.4, 402.1, 239.2; Elemental anal. calcd for $C_{96}H_{104}N_4O_8$: C, 79.97; H, 7.27; N, 3.89. Found: C, 80.26; H, 7.33; N, 3.80.

4.1.9. Double calix[4]arene 7. A solution of diamine **10** (102 mg, 0.164 mmol) and terephthaldehyde (20.9 mg, 0.164 mmol) in CH_2Cl_2/MeOH (21 mL/21 mL) was refluxed for 24 h in the presence of $MgSO_4$. The reaction mixture was allowed to cool to room temperature and filtered. Subsequent evaporation of the solvent and column chromatography (SiO_2, hexane/EtOAc=8:1 v/v) gave **7**. Recrystallization of the solid from $CHCl_3$/hexane afforded **7** (22.5 mg) as light yellow crystals in 19% yield. Mp>205°C dec.; IR ($CHCl_3$) 2960, 2933, 2874, 1624, 1586, 1563, 1507, 1461, 1385, 1295, 1280, 1239, 1213, 1160, 121, 1102, 1077, 1045, 1006, 1002, 966 cm^{-1}; ^1H NMR δ 7.38 (s, 4H; imine H), 7.19 and 7.16 (s, 16H, ArH), 6.98 (t, 4H, J=13.1 Hz; ArH), 6.09 (s, 8H; ArH), 4.47 (d, 8H, J=13.1 Hz; $ArCH_2$-Ar), 4.07 (t, 8H, J=8.2 Hz; OCH_2), 3.65 (t, 8H, J=6.6 Hz; OCH_2), 3.18 (d, 8H, J=13.2 Hz; $ArCH_2Ar$), 2.06–1.84 (m, 16H; CH_2CH_3), 1.10 (t, 12H, J=7.4 Hz; CH_3), 0.89 (t, 12H, J=7.4 Hz; CH_3); ^{13}C NMR δ 157.3, 156.7, 153.9, 145.4, 137.7, 136.9, 133.8, 129.1, 128.1, 122.1, 119.9, 77.2, 23.5, 22.9, 10.9, 9.8; MS (FAB, *m/e*) 1441.8 (M^++1), 1440.8 (M^+), 1297.7, 623.4, 622.4, 117.1; Elemental anal. calcd for $C_{96}H_{104}N_4O_8$: C, 79.97; H, 3.89; N, 7.27. Found: C, 80.13; H, 3.59; N, 7.52.

4.1.10. Double calix[4]arene 8. To a suspension of dichloride **26** (20.2 mg, 0.0995 mmol) and diamine **10** (62 mg, 0.0995 mmol) in CH_2Cl_2 (10 mL) was added pyridine (0.02 mL, 0.0247 mmol). After being stirred for 10 h at 0°C, the reaction mixture was extracted with CH_2Cl_2. The organic phase was washed with H_2O and dried over anhydrous $MgSO_4$ and concentrated in vacuo. Column chromatography (SiO_2, hexane/EtOAc=3:1 v/v) gave **8**. Recrystallization of the solid from $CHCl_3$/MeOH afforded **8** (30.1 mg) as white crystals in 40% yield. IR ($CHCl_3$) 3347, 2960, 2933, 2875, 1654, 1606, 1540, 1465, 1414, 1384, 1260, 1216, 1068, 1037, 1007, 966, 770 cm^{-1}; ^1H NMR δ 7.46 and 7.36 (s, 8H; ArH), 7.34 and 7.21 (s, 8H; ArH), 7.08 and 6.91 (t, 4H, J=6.9, 7.7 Hz, respectively; ArH), 6.32 (s, 8H; ArH), 4.43 (d, 8H, J=13.4 Hz; $ArCH_2$-Ar), 4.01 (t, 8H, J=8.1 Hz; OCH_2), 3.58 (t, 8H, J=6.6 Hz; OCH_2), 3.12 (d, 8H, J=13.4 Hz; $ArCH_2Ar$), 1.97–1.75 (m, 16H; CH_2CH_3), 1.05 (t, 12H, J=7.4 Hz; CH_3), 0.82 (t, 12H, J=7.4 Hz; CH_3); ^{13}C NMR δ 163.6, 158.0, 152.6, 136.9, 134.1, 133.9, 131.5, 129.8, 129.3, 128.5, 124.4, 122.5, 119.8, 31.2, 23.5, 22.9, 10.9, 9.7; MS *m/e* 1505.9 (M^++1), 460.4, 307.4; Elemental anal. calcd for $C_{96}H_{104}N_4O_{12}\cdot 5H_2O$: C, 72.24; H, 7.20; N, 3.51. Found: C, 72.12; H, 7.21; N, 3.67.

4.1.11. Quadruple calix[4]arene 9. To a suspension of disulfonyl chloride **27** (18.6 mg) and diaminocalix[4]arene **10** (30 mg) in CH_2Cl_2 (12 mL) was added pyridine (9 μL). After being stirred for 10 h at 0°C, the reaction mixture was extracted with CH_2Cl_2. The organic phase was washed with H_2O and dried over anhydrous $MgSO_4$ and concentrated in vacuo. Column chromatography (SiO_2, hexane/EtOAc=2:1 v/v) gave **9**. Recrystallization of the solid from $CHCl_3$/hexane afforded pure **9** (16.5 mg) as white crystals in 38% yield. Mp>232°C dec.; IR ($CHCl_3$) 3269, 2962, 2934, 2876, 1595, 1464, 1386, 1327, 1217, 1161, 1195, 1037, 1005, 966, 897, 820, 757 cm^{-1}; ^1H NMR δ 7.79 and 7.53 (br s, 16H; biphenyl H), 6.53 (br s, 16H; ArH), 6.24 (br s, 24H; ArH), 4.30 (d, 16H, J=12.7 Hz; $ArCH_2Ar$), 3.76 and 3.67 (br s, 16H; OCH_2), 3.00 (d, 16H, J=12.2 Hz; $ArCH_2Ar$), 1.85–1.77 (m, 32H; CH_2CH_3), 1.01–0.86 (m, 48H; CH_3); ^{13}C NMR δ 162.8, 155.6, 154.1, 143.2, 135.5, 134.9, 130.1, 128.2, 128.1, 127.7, 122.0, 76.8, 30.7, 23.2, 23.0, 10.4, 10.0; Anal. calcd for $C_{208}H_{224}N_8O_{32}S_8\cdot 2H_2O$: C, 68.62; H, 6.31; N, 3.08. Found: C, 68.43; H, 6.37; N, 2.93.

4.2. Cation extraction experiments

Alkali picrates were prepared by adding stepwise a 1.4×10^{-2} M aqueous picric acid solution to metal hydroxide, until neutralization was reached. After water was evaporated, recrystallization of Li^+, Na^+, K^+, Rb^+ and Cs^+ salts from ethyl acetate, H_2O/MeOH (1:1), H_2O/MeOH (1:10), H_2O, and H_2O, respectively, gave yellow crystals. The alkaline-earth metal picrates were obtained from aqueous solutions of picric acid and metal chlorides. The picrates were recrystallized from ethyl acetate/MeOH. Methylammonium picrates were prepared by neutralization of methylamine with picric acid in methanol and purified by recrystallization from methanol. The pure picrates were dried under vacuum for 24 h and protected from moisture and light before use.

5 mL of a 2.5×10^{-4} M aqueous picrate solution and 5 mL of a 2.5×10^{-4} M solution of double calix[4]arene in CH_2Cl_2 were shaken with a Vortex-Genie for 1 min at 25°C and then centrifuged at 1500 rpm for 1 min. After the two phases were allowed to settle for 1 h, the absorbance A of the aqueous phase was measured at 355 nm, i.e. the wavelength of maximum absorption of the picrate ion (λ_{max}=355 nm, ε=14416 mol^{-1} L cm^{-1}). A blank experiment without double calix[4]arene was run under the same conditions, which yielded an absorbance A_0 of the aqueous phase. The percentage cation extracted was calculated as the ratio 100 $(A_0-A)/A_0$.

4.3. Viologens complexation studies

Titration of double calix[4]arene **3** with ethyl viologen dichloride (**16**) is representative. 400 μL of **3** (4.64 mmol)

was transferred into NMR tube and the NMR spectrum was recorded. 10 μL of solution **16** (73.9 mmol) was added and the NMR spectrum was recorded. Addition of an aliquot of 10 μL of solution **16** was continued until total amount added exceeded 100 μL. NMR spectra were recorded after each addition. Aliquot size added increased to 20, 50, 100, finally 200 μL until no significant chemical shift change had taken place.

4.4. General X-ray crystallographic procedure

Crystals of double calix[4]arenes **1**, **3**, **4**, and **9** suitable for X-ray diffraction were grown from chloroform-dimethyl sulfoxide or chloroform–methanol mixture. The data collection was performed at 188 and 293 K on a Siemens SMART diffractometer (Mo K_α, λ=0.71073 Å) equipped with CCD area detector. Their crystallographic data are listed in Table 2. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXTL). All non-hydrogen atoms were refined anisotropically and hydrogens were included with a riding model. Some propyl groups of double calix[4]arenes were found to be disordered; They were refined with suitable disorder models. Crystallographic data for structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 192750 (for compound **1**), CCDC 192751 (for compound **3**), CCDC 192752 (for compound **4**), and CCDC 192753 (for compound **9**).

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