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Biscalix[4]arene-Zn-tetraarylporphyrins

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Abstract: By covalent combination of two calix[4]arene and one Zn-tetraarylporphyrin building blocks novel, large multifunctional receptors for molecular recognition have been prepared.

Design and synthesis of nanosize (1-10^2 nm) receptor molecules is one of the challenges in supramolecular chemistry.[1] We are currently exploring an approach based on the combination of different rigid building blocks (e.g. calix[4]arenes,[2] cavitands,[3] metallosalenes,[4] etc.) for the preparation of host molecules with *large hydrophobic surfaces*. Recently, we have described the preparation of a holand, a molecule consisting of two calix[4]arene and two resorcin[4]arene fragments covalently connected to generate a preorganized surface with a size of 1.5 x 2.0 nm.[3]

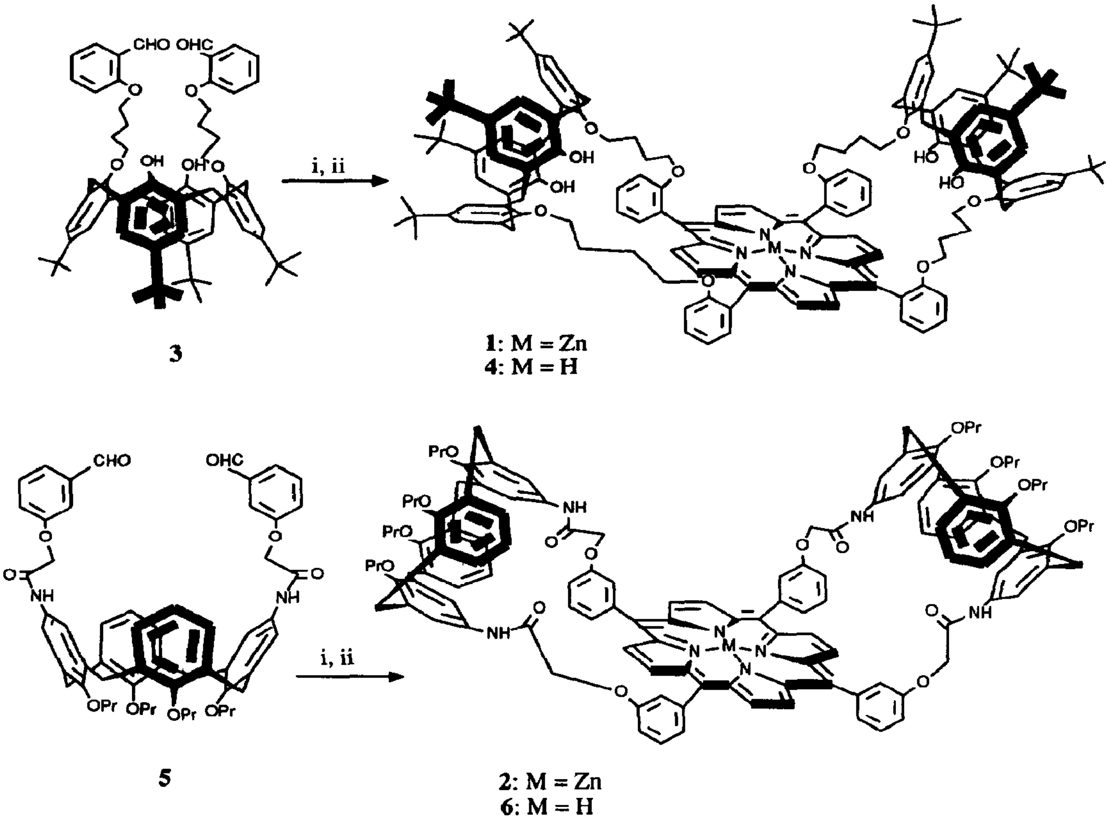
We report here the synthesis of large metalloreceptors **1** and **2** which are formed by combining one Zn-tetraarylporphyrin with two calix[4]arene molecules. Calix[4]arene is a versatile building block in supramolecular chemistry;[5] its rigid and lipophilic platform provides unique possibilities to build up the binding sites for ionic[6] and neutral[7] species. Zn-porphyrins are being used in biomimetic chemistry for recognition of biologically significant structures such as nucleic bases, amino acids, as well as anions.[8] *Covalent* combination of these two structural modules in one *preorganized* molecular shape can lead to receptors with a highly specific multifunctional complexing ability.[9]

The synthesis of **1** and **2** is based on the condensation of pyrrole with calix[4]arene based dialdehydes **3** and **5**, respectively; the aldehyde moieties were immobilized at either the "lower" or the "upper" rim of the calixarene platform (Scheme 1). Dialdehyde **3** was prepared in 74% yield by diametrical alkylation of the "lower" rim of *p-tert*-butylcalix[4]arene[10] with *o*-(4-bromobutoxy)benzaldehyde in refluxing acetonitrile using K_2CO_3 as a base. Reaction of **3** with pyrrole in refluxing propionic acid[11] for 4-5 h afforded biscalix[4]arene-porphyrin **4** in 3-5% yield after purification by column chromatography (silica gel, CH_2Cl_2). Although, due to the hindered rotation of the aromatic rings connected to the porphyrin moiety, three different isomers are theoretically possible,[11-13] only one was isolated.

The positive ion FAB mass spectrum of compound **4** shows a peak at *m/z* 2192.2 with an intensity of 96%, which corresponds to the structure containing one porphyrin and two calix[4]arene moieties. The ^1H NMR spectrum of **4** in $CDCl_3$ shows two characteristic singlets for the porphyrin rings at 8.84 and 8.77 ppm;

the calix[4]arene aromatic region consists of four singlets with equal intensities at 6.93, 6.77, 6.67, and 6.51 ppm. These data clearly prove the adjacent-linked structure[11] of **4**.

Zn-complex **1**[14] was synthesized in 96% yield by refluxing free base porphyrin **4** with $Zn(OAc)_2 \cdot 2H_2O$ in chloroform-methanol, 1:1 (For the ^1H NMR spectrum see Figure 1). In a temperature range of +30 - -95 °C the ^1H NMR spectra (CD_2Cl_2) of the **1**·pyridine complex show only one set of signals for both receptor and guest molecules. No splitting was observed at low temperatures which proves the *adjacent-cis-linked* structure[11] of **1**; the two calix[4]arene fragments are equivalent with respect to the complexed pyridine molecule.



3

1: M = Zn
4: M = H

5

2: M = Zn
6: M = H

Scheme 1. *Reagents and Conditions:* i) pyrrole, propionic acid, reflux 4-5 h; ii) $Zn(OAc)_2 \cdot 2H_2O$, $CHCl_3$-CH_3OH, 1:1, reflux 2 h.

Calixarene **5** which has two aldehyde moieties at the "upper" rim was obtained by reaction of 1,3-bis(chloroacetamido)tetrapropoxycalix[4]arene[4] with *m*-hydroxybenzaldehyde in 64% yield. Compound **6** in which two calix[4]arene cavities are directed towards the porphyrin plane, was prepared analogously to **4** by reaction of **5** and pyrrole in propionic acid [yield after column chromatography (silica gel, CH_2Cl_2-diethyl ether, 5:1) 4%]. Metallation of **6** with $Zn(OAc)_2 \cdot 2H_2O$ gave metalloporphyrin **2**[14] in a quantitative yield.

In compounds **2** and **6** the aromatic rings connected to the porphyrin can freely rotate;[13] the ^1H NMR spectra of **2** and **6** show two singlets for the porphyrin rings at 9.11, 8.89 and 9.03, 8.62, respectively, proving the *adjacent-linked* structures[11] of their cavities.

Biscalix[4]arene-Zn-tetraarylporphyrins **1** and **2** are interesting models for *multifunctional* recognition. Besides the active metallocenter which is able to complex anions and neutral species, compounds **1** and **2** contain two lipophilic calix[4]arene moieties in a large preorganized cavity with a size of 1.0-1.5 nm (according to CPK models). These calixarene fragments possessing OH, C(O)-NH groups may serve as additional receptor sites for hydrogen bonding and dipole-dipole interactions. The complexation properties of receptors **1** and **2** towards organic anions and polar neutral molecules are currently under investigation.

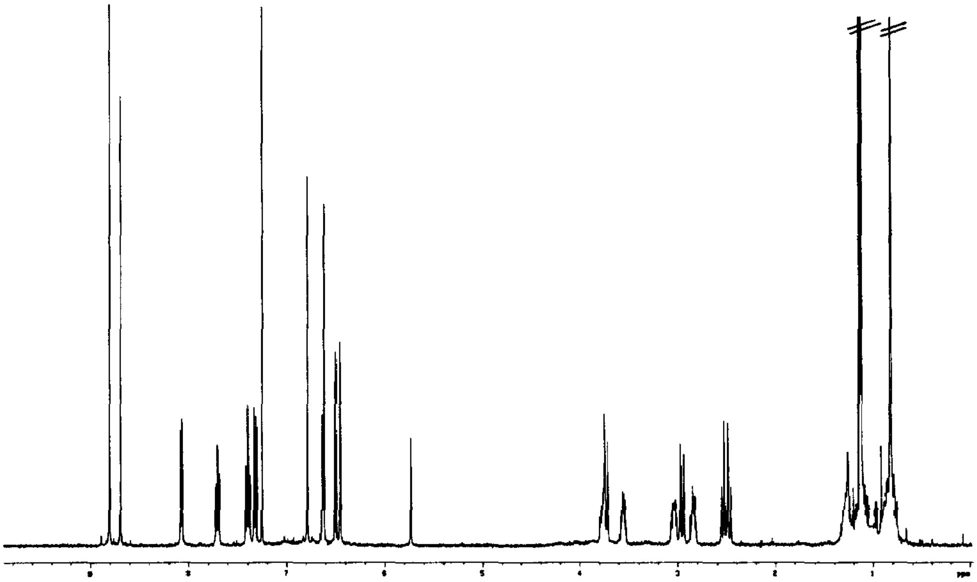


Figure 1. ^1H NMR spectrum of Zn-porphyrin **1** (400 MHz, $CDCl_3$).

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14. Selected data for **1**: m.p. >330 °C; UV-VIS (CH_2Cl_2) λ_{max} 426 nm; ^{1}H NMR ($CDCl_3$) δ 8.82, 8.67 (2 x s, 8H, pyrrole), 8.06 (d, J = 8.0 Hz, 4H, ArH), 7.69, 7.40 (2 x t, J = 8.0 Hz, 8H, ArH), 7.31 (d, J = 8.0 Hz, 4H, ArH), 6.79, 6.59, 6.50, 6.41 (4 x s, 16H, Calix), 6.52, 5.73 (2 x s, 4H, OH), 3.75, 2.94 (2 x d, J = 13.2 Hz, 8H, CH_2-calix), 2.51, 2.48 (ABq, J = 13.2 Hz, 8H, CH_2-calix), 3.8-3.7, 3.6-3.5, 3.1-3.0, 2.9-2.8 (4 x m, 16H, OCH_2), 1.4-1.1 (m, 16H, CH_2), 1.15, 1.11 (2 x s, 36H, *t*-Bu), 0.89 (s, 36H, *t*-Bu); FAB-MS *m/z* 2257.1 (M^+, calc. 2257.0). Selected data for **2**: m.p. >330 °C; UV-VIS (CH_2Cl_2) λ_{max} 424 nm; ^{1}H NMR ($CDCl_3$) δ 9.11, 8.76 (2 x s, 8H, pyrrole), 8.13 (d, J = 8.0 Hz, 4H, ArH), 8.03 (s, 4H, ArH), 7.88 (bs, 4H, NH), 7.88, 7.30 (2 x t, J = 8.0 Hz, 8H, ArH), 7.2-7.0 (m, 10H, Calix), 6.87 (t, J = 7.9 Hz, 2H, Calix), 6.69 (d, J = 7.9 Hz, 4H, Calix), 6.26 (s, 4H, Calix), 4.81 (s, 8H, $CH_2C(O)$), 4.51, 4.39, 3.36, 3.06 (4 x d, J = 13.2 Hz, 16H, CH_2-calix), 4.1-3.8 (m, 16H, OCH_2), 2.2-2.0 (m, 16H, CH_2), 1.10 (t, J = 7.2 Hz, 24H, CH_3); FAB-MS *m/z* 2147.6 ($[M+H]^+$, calc. 2146.9). Satisfactory elemental analyses were obtained for all new compounds synthesized.

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