Pergamon

Tetrahedron Letters 40 (1999) 5949–5952

TETRAHEDRON
LETTERS

Synthesis of Novel Porphyrin-Based Biscalix[4]arenes

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Received 6 May 1999; accepted 15 June 1999

Abstract: A novel method for the preparation of porphyrin-based biscalix[4]arenes has been developed, starting from appropriate aryldipyrrolylmethane and calix[4]arene monoaldehyde. The condensation reaction in the presence of $BF_3 \cdot Et_2O$ leads to the title compounds in good yields (30-54%). Novel derivatives represent the first example of porphyrin-based calix[4]arenes with directly connected aromatic subsystems of both moieties. The photophysical properties of biscalix[4]arenes are presented.

Keywords: Calix[4]arenes; Porphyrins; Fluorescence, Absorption spectra

Calix[n]arenes, a well known family of macrocyclic oligophenols,[1,2] play an important role in modern supramolecular chemistry.[3] Because of their unique three-dimensional shape and good complexation ability they have found many applications in the design of synthetic receptors and sophisticated molecular assemblies. Likewise, the porphyrins are known to be one of the "*support pillars*" of supramolecular chemistry,[4] having suitable photoactive and electroactive properties for building artificial molecular devices. Therefore, porphyrins with directly linked calixarenes could afford attractive receptors possessing multipoint recognition ability towards noncovalently bound guest molecules.

The tethering of calix[4]arene and porphyrin moieties has been achieved *via* a spacer molecule.[5] Our aim was to synthesize a bis-calix[4]arene with a direct linkage between the upper rim and the porphyrin. We believe that the advantage of the titled receptor is strengthening of the porphyrin-guest interaction by the cation-π and π-π attractive contributions[6] from both calix[4]arene subunits (Figure 1).

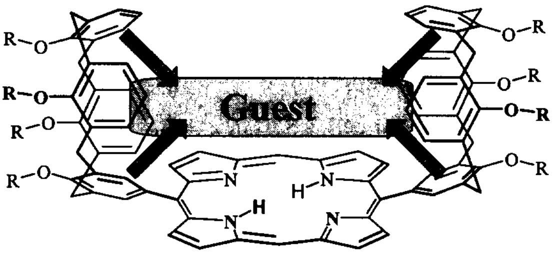

Figure 1: The design of the receptor.

It is well recognised that an aromatic unit can be introduced into the *meso*-position of a porphyrin *via* the aldehyde functionalization route.[7] Hence, monoaldehyde **I** (prepared from 5,11,17,23-tetrapropoxycalix[4]arene by monobromination, lithiation and reaction with DMF in 63% overall yield) was chosen as the starting compound for the synthesis of novel calix[4]arene-porphyrins (Scheme 1). This compound was treated with pyrrole in the presence of boron trifluoride diethyletherate to give the dipyrrolyl derivative[8] **II** (73 %), a key intermediate for the construction of the porphyrin. Unfortunately, several attempts

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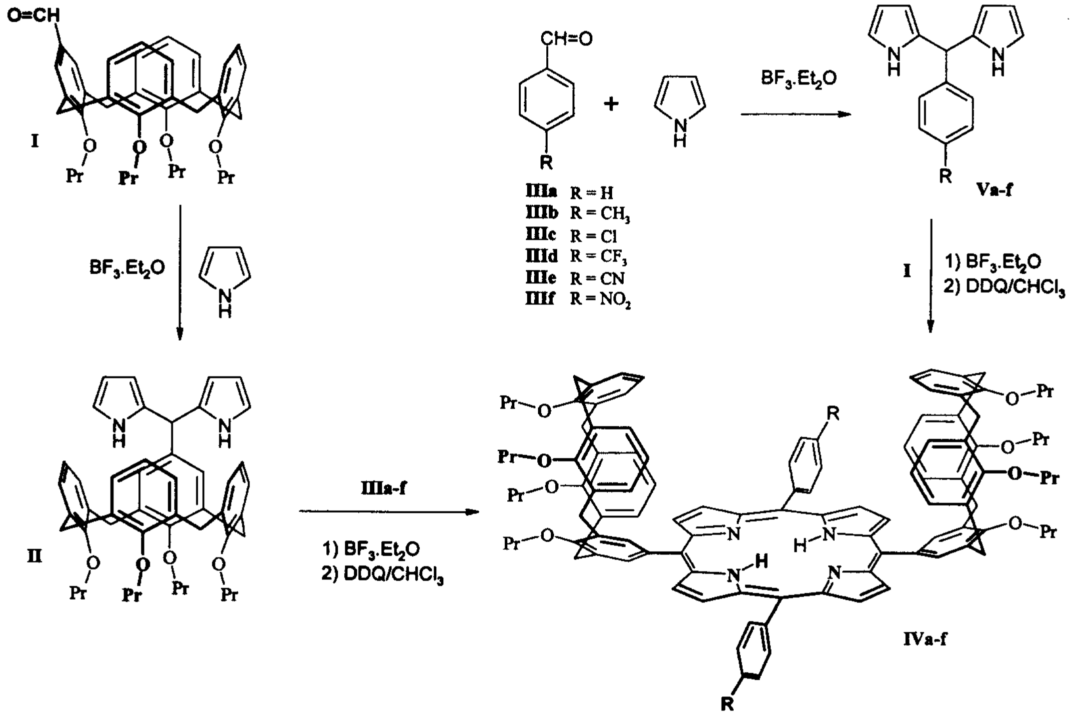
PII: S0040-4039(99)01181-8



Scheme 1: Synthesis of biscalix[4]arenes **IVa-f**.

to condense **II** with benzaldehyde **IIIa** led to a complex reaction mixture, giving biscalixarene **IVa** as only a minor product (< 10 %). Another approach to biscalix[4]arene **IV** was therefore investigated. Aryldipyrrolylmethanes **Va-f** were prepared in high yields (64-85 %) by condensation of the *p*-substituted benzaldehydes **IIIa-f** with pyrrole.[8] Overnight stirring of the precursors **Va-f** and monoaldehyde **I** with catalytic amounts of $BF_3 \cdot Et_2O$ in dry $CHCl_3$ and subsequent treatment with 2 equivalents of DDQ afforded the titled compounds **IVa-f** (29-54%).[9]

The structures of **IV** have been proved using FAB MS spectroscopy where the molecular peaks $[M]^+$ or $[M+1]^+$ are the most intense ones (**IVa** 1645.2, **IVb** 1672.5, **IVc** 1714.9, **IVd** 1780.7, **IVe** 1694.7, **IVf** 1734.7). The ^1H NMR spectra ($CDCl_3$) are characterized by two sets of two doublets (J~13,3 Hz) for the axial and the equatorial hydrogens ($Ar-CH_2-Ar$) of calixarene, i.e., the expected pattern for a monosubstituted calix[4]arene. The porphyrins give typical singlets for the -NH- protons with chemical shifts about -2.8 ppm and corresponding signals in the aromatic region. The formation of the porphyrin moiety was also unambiguously proven by the absorption spectra consisting of the characteristic Soret and Q bands (Table 1).

The spectroscopic properties of the biscalix[4]arenes **IVa-f** and 5,10,15,20-tetraphenylporphyrin (TPP) are listed in Table 1. The Soret and visible (Q bands) absorption bands of **IVa** exhibit a bathochromic shift and the ratio of the absorption coefficients of the Q_1 and Q_2 bands is inverted when compared to TPP. The differences between TPP and **IVa** can be attributed to the electron-donating character[10] of the two -OPr groups of the calix[4]arene phenyl units attached in the porphyrin *meso* position. The presence of the para substituents on **IVb-f** can affect the absorption spectra according to their electron-donating properties.[10]

The most profound substituent effect is observed for **IVf** bearing two nitrophenyl groups. The Soret band is red shifted to 428 nm concomitant with the red shift of the fluorescence emission bands. The changes in the absorption spectra are accompanied by a strong decrease of the fluorescence intensity (Table 1, Figure 2c,d).

Table 1: Summary of absorption and fluorescence results[11] of **TPP** and **IVa-f** in air-saturated CH_2Cl_2. Relative fluorescence quantum yields Φ_f^r (Φ_f^r in parentheses measured in MeOH).

Porphyrin	Absorption spectrum λ_{max}/nm (ε/mM^{-1} cm^{-1})[a] Q_1	Q_2	Q_3	Q_4	Soret	Fluorescence λ_{max}/nm	Φ_f^r [a]
TPP[b]	645 (6.2)	590 (6.4)	551 (8.1)	515 (17.3)	418 (411)	656, 720	1.00[c] (0.96)
IVa	651 (6.7)	594 (4.8)	554 (9.8)	519 (13.9)	422 (349)	659, 724	1.25 (1.19)
IVb	650	594	555	519	423	661, 724	1.15
IVc	649 (5.4)	594 (6.1)	554 (11.3)	518 (19.3)	422 (456)	660, 724	0.87
IVd	650 (5.4)	594 (6.1)	554 (10.4)	518 (19.5)	423 (453)	659, 722	1.07
IVe	652 (4.8)	594 (4.8)	558 (10.3)	521 (14.8)	426 (363)	663, 727	1.11
IVf	652 (5.9)	596 (5.6)	560 (12.4)	523 (16.1)	428 (300)	666, 727	0.67 (0.07)

[a] estimated error: 10 %; [b] absorption spectrum[12] in $CHCl_3$; [c] absolute value in degassed methylcyclohexane[13]: Φ_f = 0.13.

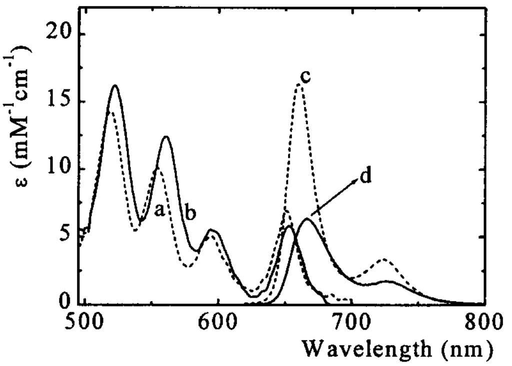


Figure 2: Absorption and fluorescence emission spectra of **IVa** (a, c) and **IVf** (b, d) in air-saturated CH_2Cl_2. Fluorescence intensity in arbitrary units:. λ_{exc} = 518 nm, A_{518} (1 cm cell) = 0.076 ± 0.001.

This quenching may be due to intramolecular electron transfer from the photoexcited porphyrin moiety to the nitrophenyl moiety located at the *meso* position. This process is thermodynamically feasible and its efficiency increases in polar solvents due to the solvation stabilization of the charge-separated ion pair.[14] In accordance with this, the fluorescence emission of **IVf** is almost completely quenched in MeOH (Table 1), more polar solvent than CH_2Cl_2, confirming that electron transfer occurs within the molecule.

In conclusion, using the simple monoaldehyde **I**, novel artificial receptors are easily available. Our synthetic procedure offers direct way to the construction of highly organized molecules well suited for study of molecular recognition behaviour. The complexation abilities of these new compounds are currently under study.

This work was supported by the Grant Agency of the Czech Republic (No. 203/99/1163).

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8. *General procedure for* **II** or **V**: Aldehyde **I** or **IIIa-f** (1 mmol) was dissolved in 40 ml of pyrrole and the solution was then stirred 0.25 h at room temperature under an Ar atmosphere. A catalytic amount of $BF_3{\cdot}Et_2O$ was then added and reaction mixture stirred for 0.5 h. The reaction mixture was extracted with $CHCl_3$, the organic layer washed with 0.1 M aqueous NaOH, water and dried over $MgSO_4$. The evaporation to dryness yielded the crude product, that was purified on silica gel column using CH_2Cl_2/petroleum ether as solvent. Yields: **II** (73 %), **Va** (85 %), **Vb** (81%), **Vc** (73 %), **Vd** (85 %), **Ve** (64 %) a **Vf** (74 %).
9. *Typical procedure (preparation of* **IVd**): A catalytic amount of $BF_3{\cdot}Et_2O$ was added to the solution of **I** (1 mmol) and **Vd** (1 mmol) in 200 ml of dry $CHCl_3$ and the mixture was then stirred 15 h at room temperature under an argon atmosphere. DDQ (2 mmol) was then added and the reaction mixture was stirred for an additional 2 h. The mixture was extracted with $CHCl_3$, the organic layer was washed with aq. $NaHCO_3$ and dried over $MgSO_4$. The crude product was purified on preparative TLC (silica gel) using $CHCl_3$/petroleum ether (1:15) as eluent to give **IVd** in 54 % yield. (m.p.: 263-266 °C, $CHCl_3$-MeOH). ^1H NMR ($CDCl_3$, 300 MHz) δ: -2.85 (s, 2H, NH), 1.14 (m, 18H, $-CH_3$), 1.22 (t, 6H, J=7.7 Hz, $-CH_3$), 2.04-2.24 (m, 16H, $-\underline{CH_2}-CH_3$), 3.28 and 3.45 (2d, 2x4H, J = 13.2 Hz, CH_2-eq.), 3.95 (t, 4H, J = 7.3 Hz, $O-\underline{CH_2}-CH_2-$), 4.07 (t, 8H, J = 7.0 Hz, $O-\underline{CH_2}-CH_2-$), 4.20 (t, 4H, $O-\underline{CH_2}-CH_2-$), 4.62 and 4.81 (2d, 2x4H, J = 13.2 Hz, CH_2-ax.), 6.48 (t, 2H, J=7.7 Hz, H-arom), 6.67-6.90 (m, 16H, H-arom), 7.61 (brs, 4H, H-arom); 8.10 (m, 6H, H-arom), 8,68 (br d, 4H, H-arom), 8,66-8.89 (m, 6H, H-arom). MS FAB calcd. 1780.18, found 1780.7 (M^+). Anal. calcd. for $C_{114}H_{112}N_4O_8F_6$: C, 76.92; H, 6.34; N, 3.15; F, 6.40. Found: C, 76.86; H, 6.72; N, 3.36, F, 6.10. Yields of other derivatives: **IVa** (48 %), **IVb** (49%), **IVc** (29 %), **IVe** (31 %) a **IVf** (29 %).
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11. Fluorescence emission spectra were measured in the region 550 - 900 nm using λ_{exc} = 518 nm and 553 nm. The integrated emission area across the band was corrected for absorbance differences at the excitation wavelength (A_{518} = 0.079 ± 0.003 and A_{553} < 0.054, 10 mm cell) and compared to **TPP** in CH_2Cl_2 yielding relative fluorescence quantum yields Φ_f^r. The fluorescence intensities were corrected by the factor n^2, i.e. the refractive index of the solvent.
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