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Author(s):	Alexei A. Yakushev, Alexei D. Averin, Maria V. Sakovich, Ivan M. Vatsouro,
	Vladimir V. Kovalev, Sergei A. Syrbu, Oskar I. Koifman, Irina P. Beletskaya
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# Synthesis of the porphyrin-calix[4]arene conjugates via Pdcatalyzed amination and their evaluation as fluorescent chemosensors

# Alexei A. Yakushev<sup>a</sup>, Alexei D. Averin<sup>a</sup>, Maria V. Sakovich<sup>a</sup>, Ivan M. Vatsouro<sup>a</sup>, Vladimir V. Kovalev<sup>a</sup>, Sergei A. Syrbu<sup>b</sup>, Oskar I. Koifman<sup>c</sup> and Irina P. Beletskaya<sup>\*</sup>

<sup>a</sup>Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory, 1-3, Moscow 119991, Russia; e-mail: <u>alexaveron@yandex.ru</u>

<sup>b</sup>G.A. Krestov Institute of Solution Chemistry RAS, 1, Akademicheskaya ul., Ivanovo, 153045, Russia.; e-mail: ssa@isc-ras.ru

<sup>c</sup>Ivanovo State University of Chemical Technology, 7, Sheremetevskii prosp., Ivanovo, 153000, Russia.; e-mail:

oik@isuct.ru

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**ABSTRACT:** The synthesis of the porphyrin-calix[4]arene conjugates was carried out using the Pd(0)catalyzed amination of Zn(II) *meso*-(3-bromophenyl)porphyrinate with bis(3-aminopropoxy)substituted calix[4]arenes (in cone and 1,3-alternate conformations). One of the conjugates was demetalated to give free porphyrin base derivative. The investigation of the fluorescence of the conjugates was studied in the presence of 18 metal perchlorates. The zinc porphyrinate derivatives were found to quench fluorescence in the presence of Cu(II), Al(III) and Cr(III) cations as well as on protonation. Metal-free conjugate was shown to act as a molecular probe for Zn(II), Cu(II) and Cd(II) cations due to strong and different changes of the emission caused by these metals.

KEYWORDS: porphyrin, calix[4]arene, Pd catalysis, amination, fluorescence, detection.

\*Correspondence to: Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory, 1-3, Moscow 119991, Russia, phone/fax +7(495)9393618, e-mail : beletska@org.chem.msu.ru.

# **INTRODUCTION**

The importance of the design and synthesis of novel fluorescent chemosensors for detecting metal cations, especially of environmentally relevant, heavy and toxic metals, cannot be overestimated. Calixarenes and their sulfur-containing analogs were found to be quite appropriate for this goal. This is due to wide possibilities of modifying these macrocycles with various signaling groups, additional coordination sites, fine adjustment of the macrocyclic cavity to host certain metal cations. E.g., enough simple derivatives of calix[4]arenes were found to be efficient chemosensors for Pb(II) [1], Cd(II) [2], Hg(II) [3], Ni(II) [4] and Ag(I) [5] cations. Thiacalix[4]arenes proved to be useful to create fluorescent sensors for Ag(I) and Fe(III) cations [6, 7], and more sophisticated macrobicyclic derivatives of these compounds showed their advantages in the detection of Cu(II) [8], Hg(II) [9], Ag(I) [10] and Fe(III) [11]. On the other hand, though porphyrins are well-known chromophores and fluorophores with outstanding properties, their application in the design of chemosensors is to be further developed [12, 13]. The quinoline-containing derivative of porphyrin was described to act as a Hg(II) detector [14]. tetrakis(4-methoxyphenyl)porphyrin was used to detect Ag(I) cations [15]. Interestingly, the formation of chemosensors by introducing the porphyrin moiety in more sophisticated structures is more common than the application of simple porphyrin derivatives [16]. Conjugates of porphyrins with calixarenes constitute one type of such structures. Such molecules present a powerful receptor unit (calixarenes) and an excellent signaling unit (porphyrin or its metal complex) what make them attractive as possible chemosensors. Indeed, the combinations of one calix[4] arene with one porphyrin (taken as a free base or its Zn(II) complex) were described as tweezers for quinone or benzoquinone [17-19]. The conjugates of a calix[4]arene or thiacalix[4]arene with two porphyrin moieties were studied for detecting simple cations like Li(I), Na(I), K(I) and anions (Cl, Br, I, NO<sub>3</sub>). It was found out that the addition of the alkali metals did not change the absorption of the conjugate with thiacalix[4]arene [20], while in the case of calix[4]arene-porphyrin conjugate the response was obtained both for Na(I) cation (enhancement of the intensity of the Soret band) and for anions tested (decrease in the absorption) [21]. Another conjugate of thiacalix[4]arene with two porphyrins was capable of distinguishing between C<sub>60</sub> and C<sub>70</sub> fullerenes: in the latter case the intensity of the Soret band diminished with the bathochromic shift of its maximum [22]. An overview of the synthetic approaches to the porphyrin-calixarene conjugates of various architectures and the formation of supramolecular structures with these compounds is given in [23]. The assembly of the porphyrin and calixarene moieties can be enough diverse: via a direct bond between porphyrin's meso-position and benzene ring of the calixarene [24] or via the acetylene bridge [25]; quite often is the use of the amide bridge [26, 27]. Triazolyl linker for this purpose was reported in [28] while the reaction of aminosubstituted porphyrin with tetraformyl-containing calix[4]arene allowed the synthesis of tetrakis(porphyrin) derivative [29]. It is to be noted that this work is also a rare example of the use of the calix[4] arene in the 1.3-alternate conformation for the purposes of chemical sensing.

Our own interest in the application of porphyrins for the needs of fluorescent detection has recently brought forward first encouraging results. Enough simple conjugate resulting from the modification of the octaalkyl *meso*-phenylporphyrin (taken as its complex with Zn(II)) with the azacrown ether linked by triethylenediamine [30, 31] as well as other polymacrocyclic conjugates of Zn(II) *meso*-phenyl and di-*meso*-phenylporphyrinates with the diazacrown ethers based on biphenyl and naphthalene, or with diazacrown ether macrobicyclic derivatives [32, 33], proved to be interesting in the fluorescent detection. Fine tuning of the structure of these complex molecules led to substantial changes in binding and, therefore, sensing properties. The universal character of the Pd(0)-catalyzed amination reaction [34] which can easily utilize the reactivity of available Zn(II) *meso*-(bromophenyl)porphyrinates directed us to the choice of diamino-substituted

calix[4]arenes as prospective platforms for the creation of the porphyrin-calixarene conjugates. Also we decided to employ calix[4]arenes both in the cone and 1,3-alternate conformations to modulate their binding abilities. It is essential that Zn(II) porphyrinates should be introduced in such reactions as free-base porphyrins were shown by us to be less reactive in the amination processes [30, 31]. No data can be found in literature on the detection properties of the porphyrin-calixarene conjugates towards heavy and toxic metals, thus our second goal was to carry out investigations showing the possibilities of such compounds in the spectrophotometric and fluorometric detection of metal cations.

# **RESULTS AND DISCUSSION**

#### Synthesis of conjugates

As the synthesis of the cone-shaped bis(3-aminopropyl)calix[4]arene **1** has been documented [35] while its 1,3-alternate conformer **2** has not been described, we followed the reported procedure [36] starting from *p-tert*-butylphenol which was stepwise converted into *p-tert*-butylcalix[4]arene (**3**), then into dipropyl derivative 4 which was used for the preparation of bis(phthalimido) derivatives **5** (cone conformation) and **6** (1,3-alternate) (Scheme 1). It is well known from the chemistry of calixarenes that the use of the sodium bases promotes the formation of the calix[4]arene mainly in the cone conformation due to the template effect whereas the application of the casium bases with a larger and softer cation leads to a mixture of the partial cone and 1,3-alternate conformers due to the cation –  $\pi$  interactions [37, 38]. Unlike many previously reported syntheses, in our case the 1,3-alternate **6** was predominant in the presence of a larges excess Cs<sub>2</sub>CO<sub>3</sub> and it was isolated in 53% yield after chromatographic separation from the partial cone conformer which formation is also inevitable.

## Scheme 1

It is interesting that the decrease in the amount of  $Cs_2CO_3$  (from 11 to 3 equiv.) and the use of MeCN instead of DMF as a solvent allowed the synthesis of a less available conformer, i.e. partial cone 7, in reasonable 37% yield after chromatographic separation from the 1,3-alternate conformer. One may assume that under these modified conditions the rate of alkylation decreased allowing better yield of the thermodynamically more stable partial cone conformer. At the last step compounds 5 and 6 were transformed into corresponding diamino derivatives 1 and 2 by a standard reaction with hydrazine hydrate in boiling ethanol (Scheme 2).

# Scheme 2

The reaction of the Zn(II) octaalkyl 5-(3-bromophenyl)porphyrin 8 (2 equiv.) was carried out with diaminosubstituted calix[4]arene 1 in the presence of the standard catalytic system  $Pd(dba)_2/BINAP$  in boiling dioxane using sodium *tert*-butoxide as a base (Scheme 3). To assure the completion of the process, the reaction time was prolonged for 24 h. The amination in this case ran enough smoothly to produce the target symmetrical product 9 possessing two porphyrin and one calix[4]arene structural fragments which was isolated in 56% yield by the column chromatography on silica gel. When the isomeric calix[4]arene 2 was employed under the same conditions, the reaction proceeded with much more difficulties and resulted in a mixture of di- and monosubstituted products 10 and 11. Chromatographic separation of these two compounds turned to be a meticulous procedure thus the yields of individual compounds were enough low: 8% for 10 and 20% for 11 (Scheme 3). We suppose that such pronounced difference in the reactivity of the two isomeric calix[4]arenes was due to a difference in the sterical hindrances of the amino groups. In the case of 3 they are close to spacious *tert*-butyl groups oriented in the same direction while in compound 2 they neighbor flexible and less bulky propyl substituents. The analysis of the reaction mixture by <sup>1</sup>H NMR spectroscopy disclosed the formation of numerous by-products which could not be

isolated in individual state. Presumably, they was due to various reactions other than desirable N,N'-diarylation of diaminocalix[4]arene **2** which was hampered to certain extent.

#### Scheme 3

Bisporphyrinate conjugate **9** was chosen for demetalation in order to compare the sensing abilities of both free base porphyrin and its Zn(II) complex towards metal cations. For this purpose a standard work-up with the excess of glacial acetic acid was inefficient, thus the use of a stronger trifluoroacetic acid was inevitable. Its application led to complete demetalation, however, this process was accompanied with the cleavage of the C-O bond in one propoxyl substituent leading to the formation of the phenol fragment in the calixarene core (Scheme 4). It is notable that the second propyl group was not altered and resulting conjugate **12** was isolated in almost quantitative yield by a simple evaporation of the solvent after neutralization of the solution with sodium carbonate. The molecule is dissymmetric and though two porphyrin moieties are located presumably far from the propoxyl and hydroxyl substituents, they are distinctly inequivalent in the NMR spectra, however, unambiguous assignment of the signals to a certain porphyrin structural fragment is impossible.

# Scheme 4

#### Spectroscopic investigations

All UV-vis and fluorometric investigations with conjugates **9**, **10** and **12** were carried in MeCN (UHPLC grade). These compounds possess the Soret absorption band at 409, 409 and 399 nm, respectively (lgc 5.63, 5.06, 5.26). Q-bands are observed at 540 and 576 nm (for **9**), 538 and 576 nm (for **10**), 503, 534 and 572 nm (for **12**). The excitation at the wavelength of the Soret band results in two emission bands for Zn(II) porphyrinates, the band with a shorter wavelength being *ca* 2 times more intensive (588, 640 nm for **9**, 578, 627 nm for **10**), and the free base conjugate **12** shows the most intensive emission band at 634 nm accompanied by less intensive bands at 667 and 700 nm with a shoulder at *ca* 688 nm. The UV-vis and fluorescence spectra initially were measured in the presence of 5 equiv. of the following metals taken as perchlorate salts: Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), Ag(I), Hg(II). Perchlorates were used to ensure minimal coordination with the anion. The conjugates were worked up with an excess HCl (taken as vapor) to rule out the effect of the protons which may be present in the solutions of some metal perchlorates resulting from the partial hydrolysis of the salts used as hydrates.

The addition of various metals to compound 9 did not notably change the absorption spectrum except for Al(III), Cr(III) and Cu(II) ions (Fig. 1). The first two metals caused slight diminishing of the intensity of the Soret band, while copper (II) led to a dramatic decrease in the intensity of this absorption band simultaneously promoting its broadening, and the titration demonstrated that with 5 equiv. a new broad absorption band at 340 nm emerged (Fig. S1). As for the Q-bands, those belonging to initial conjugate 9 disappeared and two new emerged: one with the maximum at 556 nm and the second one, very broad, with the maximum in the region of 590 nm. The addition of the majority of salts did not seriously alter the fluorescence spectra as well (Fig. 2), except for Cu(II) and Al(III). The titrations with these metals (Figs S2 and S3) showed full quenching of emission in the presence of 10 equiv. of Cu(II) and 5 equiv. of Al(III). Interestingly, the addition of 1 equiv. of each of these salts changed the fluorescence intensity insignificantly. The addition of 10 equiv. of Cr(III) perchlorate caused emission quenching by *ca* 60% (Fig. S4). It is important that no shifts of the maxima of the absorption and emission bands were noted for compound 9 in the presence of any metal. The dramatic changes in the UV-vis and fluorescence spectra of the conjugate in the presence of Cu(II) perchlorate is likely to be due to the oxidation and formation of mono- and dication forms of the Zn(II) porphyrinate leading to the loss of planarity of the macrocyclic system. The process of the oxidation of Zn(II) porphyrinates with Cu(II) cations was described in [39]. Also it is important to take into

consideration the possibility of an easy hydrolysis of  $Al(ClO_4)_{3*}9H_2O$  under the conditions of the spectroscopic experiments. For this purpose the addition of excess HCl into the solution of the conjugate **9** was tried which caused bathochromic shift of the Soret band by 20 nm and the changes in the field of Q bands (one absorption band with the maximum at 560 nm emerged instead of two absorption bands in the initial porphyrinate). Also the formation of the second absorption band at 364 nm is characteristic for the protonated form (Fig. 1). Protonation also almost totally quenched the fluorescence, only the residual weak emission at 618 nm could be observed (Fig. 2). Though the latter to some extent resembles the result of the emission quenching on Al(III) perchlorate addition, the changes in the UV are obviously different. Judging from these facts, one may assume that these observations support the complex formation with Al(III) cations.

The response of the conjugate 10 to the presence of stated metals was quite similar (Fig. 3). In the UV-vis spectrum the addition of Cu(II) led to a similar decrease in the intensity of the Soret band and its broadening with 5 equiv. added (Fig. S5) though no change of the absorption maximum during titration was observed. This fact is explained by the oxidation of the prophyrinate 10 essentially like in the case of compound 9. The addition of Al(III) perchlorate caused another transformations of the UV-vis spectrum (Fig. S6). In the presence of 1 equiv. of this cation no visible changes were observed, the second equiv. diminished intensity of the Soret band by ca 20%, and beginning with 5 equiv. an increase in the intensity with a bathochromic shift from 409 to 415 nm was noted. The addition of 50 equiv. of Al(III) increased the intensity 4 times, and 100 equiv. did not bring further notable enhancement. As this behavior of the absorption was quite remarkable, special experiment was carried on with the protonation of the conjugate. For this purpose a great excess of HCl was added and it led to quite similar result: the intensity of the Soret band increased more than 2 times with simultaneous bathochromic shift of the maximum to 418 nm (Fig. 3). Q-bands also changed identically in both cases - instead of two bands with the maximu at 538 and 576 nm one new, more intensive band with the maximum at 562 nm emerged. These facts support the idea of a partial hydrolysis of  $Al(ClO_4)_3*9H_2O$  under the conditions of spectroscopic experiments and spectral changes can be associated with the protonation and not with Al(III) binding. The spectrum of fluorescence of the conjugate 10 did not alter substantially in the presence of all metal cations except for Cu(II) and Al(III) (Fig. 4). Gradual addition of Cu(II) perchlorate led to full emission quenching with 5 equiv. (Fig. S7) and the addition of 10 equiv. of Al(III) perchlorate caused full quenching of the initial fluorescence at 578 and 627 nm and a new, much weaker emission band emerged at 616 nm (Fig. S8). The result was essentially the same as with the addition of excess HCl (Fig. 4). This independent experiment supports an idea of the hydrolysis of Al(ClO<sub>4</sub>)<sub>3</sub>\*9H<sub>2</sub>O causing the protonation of the conjugate.

The results obtained with the conjugate **12** possessing porphyrin as a free base were quite different. The addition of the majority of metal perchlorates did not change the UV-vis spectrum (Fig. 5). It is noteworthy that Al(III) (5 equiv.) did not alter the absorption spectrum, though excess HCl caused a substantial bathochromic shift of the maximum (from 399 to 429 nm) and a small increase in the intensity. Supposedly, this is due to the fact that only great excess of Al(III) perchlorate can provide comparable changes in the UV spectrum, as it was shown with the compound **10**. In the presence of Cu(II) the sharpening of the Soret band was observed, while three initial Q-bands of the free-base compound **12** (503, 534 and 572 nm) transformed into two bands of the complex with the maxima at 534 and 562 nm (Fig. S9). This fact can be associated with the metalation of the two porphyrin moieties. This supposition is well supported by the data obtained for the Cu(II) porphyrinates of very similar structure which possess Soret band with a maximum at 404 nm and two Q-bands (529 and 565 nm) [40] The addition of Cd(II) led to a bathochromic shift of the maximum (from 399 to 414 nm) without significant changes in the absorption intensity, and the change in Q-bands absorption resulted in a new single band which absorbs at

552 nm in this region (Fig. S10). The most important changes were recorded for Zn(II): in the presence of 3 or more equiv. of this cation the absorption band maximum shifted to 409 nm, the sharpening of the band being observed (Fig. S11). In the region of the Q-bands the addition of Zn(II) showed the formation of two new absorption maxima at 542 and 576 nm These spectral properties are essentially the same as in the conjugate **9** what means the full metalation of both porphyrin rings in the presence of 5 equiv. of Zn(II) perchlorate. The following data considering the spectra of fluorescence will provide additional evidence.

The changes in the emission spectrum of the compound **12** were associated with several metal perchlorates (Fig. 6). It was observed that Al(III), Pb(II), Mn(II), Co(II), Cu(II) and Cd(II) diminished the intensity of the principal band at 634 nm to different extent causing also the changes of the shape and position of the other emission bands. The most important transformation of the spectrum occurred undoubtedly in the presence of  $Zn(ClO_4)_{2*}6H_2O$  (Fig. S12). Upon the addition of this cation emission bands of the initial conjugate gradually disappeared giving rise to two new ones with maxima at 590 and 542 nm what is essentially the same as measured for dizinc(II) bis(porphyrinate) conjugate **9**. The formation of it was almost complete with 10 equiv. of Zn(II) perchlorate. The influence of other cations was as follows. The addition of 5 equiv. of Al(III) diminished the emission by *ca* 15% only while the excess of HCl did not cause any notable change (Fig. 6). In the presence of 5 equiv. of Co(II) salt the fluorescence diminished by 60% without shifting the emission band at 634 nm while the emission in the region 650-700 nm quenched totally (Fig. S13). The comparison of the data on UV-vis and fluorescence spectra of the porphyrinates **9** and **10**, on one hand, and of the metal-free conjugate **12** in the presence of Cu(II) cations, on the other, strongly supports the idea of the formation of dicopper (II) porphyrinate in the case of **12**.

Upon the addition of 10 equiv. of Cd(II) the emission at 634 nm fully guenched and only the band with the maximum at 664 nm was retained, however its intensity was 10 times lower than that of the corresponding band in a free conjugate 12 (Fig. S14). Unlike the results observed in the presence of Zn(II) and Cu(II) which can be reliably explained by the metalation of the free porphyrin moieties, in the case of Cd(II) the process is not as clear. There are data in literature on the Cd(II)sensitive detectors derived from tetraphenylporphyrin which contain chelating triaza-substituents (one with terpyridine [41], another with the aminomethyl derivative of pyridine [42]). In both cases the coordination of Cd(II) is assumed to take place involving these substituents, not interfering with the porphyrin rings, causing either simple emission enhancement or bathochromic/hypsochromic shifts of the Soret band and emission maximum. While the described changes in the UV-vis spectra are similar to our case, the changes in fluorescence are quite different. On the other hand, the data published on Cd(II) tetraphenylporphyrinate demonstrate the absorption at 416 nm (Soret band) and 647 nm (Q-band) with fluorescence maximum at 654 nm [43]. Taking all these facts into consideration, it seems not unlikely that Cd(II) is incorporated into the porphyrin rings, while taken in excess, it may also form the complex with additional Cd(II) cations employing N and O coordination sites of the calix[4]arene. Indeed, the changes in the spectra of 12 are quite notable involving shifts of the absorption/emission maxima to assume the formation of the Cd(II) porphyrinate. Thus one may conclude that the conjugate 12 may serve as a dual-channel molecular probe for Zn(II), Cu(II) and Cd(II) due to differences in the changes caused by these three cations both in UV-vis and fluorescent spectra of 12.

# Conclusions

To sum up, we elaborated a convenient approach to a novel type of the porphyrin-calix[4]arene conjugates *via* Pd(0)-catalyzed amination of Zn(II) *meso*-(bromophenyl)porphyrinates with diaminosubstituted calix[4]arenes, showed the possibility of the use of the calix[4]arenes in cone and 1,3-alternate conformations and carried out the demetalation of the

dizinc (II) conjugate. Also the synthesis of two novel diaminocalix[4]arenes was developed. Bisporphyrin-calix[4]arene conjugates were employed in the spectroscopic investigations with 18 metal perchlorates, conjugates with two Zn(II) porphyrinate units **9** and **10** were demonstrated to change their spectral properties drastically un the presence of Cu(II) due to the oxidation into cationic form. Addition of Al(III) perchlorate also led to full emission quenching. The conjugate **12** bearing two free-base porphyrins behaves in a quite different way and can be regarded as a dual-channel molecular probe for Zn(II), Cu(II) and Cd(II) as these cations pronouncedly affect UV-vis and fluorescence spectra each in its own mode.

# **EXPERIMENTAL**

#### General

All starting materials were purchased from Sigma-Aldrich and Fluka chemical companies and used without further purification. <sup>1</sup>N and <sup>13</sup>C NMR spectra were registered with Bruker Avance 400 spectrometer (400 and 100.6 MHz, respectively) in CDCl<sub>3</sub> at 298K using residual peaks of the solvent as standards (7.26 and 77.0 ppm, respectively). UV-vis spectra were recorded in MeCN (UHPLC grade) with Agilent Cary 60 spectrophotometer. Spectra of fluorescence were obtained with Horiba Jobin Yvon Fluoromax 2 spectrofluorometer also in MeCN (UHPLC grade). MALDI-TOF mass spectra were registered with Bruker Autoflex II mass spectrometer in positive mode using dithranol as matrix and poly(ethylene)glycols as internal standards. Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), Ag(I), Hg(II) perchlorates were used as hydrates as purchased. Calix[4]arene **1** was synthesized according to a procedure reported in [35], calix[4]arene **4** was obtained according to a method described in [36], Zn(II) porphyrinate **8** was synthesized by the method reported in [44], Pd(dba)<sub>2</sub> was obtained *via* a procedure to be found in [45]. Investigations of the dependence of UV-vis and fluorescence spectra on the amount of metal perchlorate added were carried out in a spectrofluorometric cuvette (I = 1 cm) with a tight stopper using 3 ml of the solution of the corresponding conjugate with the following concentrations:  $3.6 \times 10^{-7}$  M (**9**),  $1.19 \times 10^{-6}$  M (**10**),  $7.1 \times 10^{-7}$  M (**12**). 1 mM solutions of metal perchlorates were taken and added at one portion (5 equiv.) directly to the cuvette to observe the spectral response. In the case of titrations metal salts were added stepwise to the cuvette and spectra were registered after each addition.

# Synthesis of calix[4]arenes

**5,11,17,23-Tetra-***tert***-butyl-25,27-dipropoxy-26,28-di(3-phthalimidopropoxy)calix[4]arene** (6). Calix[4]arene **4** (2.50 g, 2.73 mmol) was suspended in dry DMF (60 ml) and stirred for 30 min at room temperature, dry Cs<sub>2</sub>CO<sub>3</sub> (9.98 g, 30.25 mmol) was added, after the addition the mixture was stirred for additional 30 min, *N*-(3-bromopropyl)phthalimide (4.42 g, 16.5 mmol) was added, and the reaction was stirred at 50°C for 24 h. After cooling down the mixture, the solvent was decanted, evaporated at reduced pressure, suspended in CH<sub>2</sub>Cl<sub>2</sub> (50 ml) and washed successively with 1M HCl (50 ml) and water (2x50 ml). Organic layer was filtered, solvent was evaporated *in vacuo*, and the residue was crystallized from CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH. Yield of compound **6** 53% (1.63 g), white crystalline powder, m.p. 245–250 C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 0.66 (t, *J* = 7.5 Hz, 6H), 1.23 (s, 18H), 1.25 (s, 18H), 1.57 (m, 4H), 3.31 (t, *J* = 7.9 Hz, 4H), 3.43 (t, *J* = 7.7 Hz, 4H), 3.61 (t, *J* = 6.8 Hz, 4H), 3.76 (d, *J* = 16.1 Hz, 4H), 3.82 (d, *J* = 16.1 Hz, 4H), 6.95 (s, 4H), 7.01 (s, 4H), 7.71 (m, 4H), 7.82 (m, 4H). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$ , ppm 10.0, 22.3, 29.2, 31.5, 31.6, 33.8, 33.9, 35.4, 39.1, 68.3, 72.0, 123.2, 125.9, 126.0, 132.2, 133.0, 133.2, 133. 8, 143.5, 143.8, 154.6, 154.7, 167.2. HRMS (MALDI-TOF): *m/z* 1107.6527 [M+H]<sup>+</sup> (calcd. for Cr<sub>2</sub>H<sub>87</sub>N<sub>2</sub>O<sub>8</sub> [M+H]<sup>+</sup> 1107.6462).

**5,11,17,23-Tetra-***tert***-butyl-25,27-dipropoxy-26-(3-phthalimidopropoxy)-28-hydroxycalix[4]arene (partial cone)** (7). A mixture of the calix[4]arene **4** (0.37 g, 0.5 mmol), dry Cs<sub>2</sub>CO<sub>3</sub> (0.49 g, 1.5 mmol), *N*-(3-bromopropyl)phthalimide (0.80 g, 3.0 mmol) and dry MeCN (20 ml) were stirred in a close vessel at 70°C for 36 h. After cooling down the mixture was filtered, the residue was washed with CH<sub>2</sub>Cl<sub>2</sub>, combined organic fractions were evaporated *in vacuo*, the residue was again washed in CH<sub>2</sub>Cl<sub>2</sub>, washed with 2M HCl and water, filtered and evaporated *in vacuo*. The residue was washed with methanol and chromatographed on silica gel (eluent CHCl<sub>3</sub>-hexanes). Yield of compound **7** 37% (0.17 g), m.p. 220-225°C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 0.99 (t, *J* = 7.4 Hz, 6H), 1.07 (s, 18H), 1.31 (s, 9H), 1.41 (s, 9H), 1.68 (m, 4H) 1.88 (m, 4H), 3.20 (d, *J* = 12.9 Hz, 2H), 3.34 (t, *J* = 7.7 Hz, 2H), 3.57 (m, 4H), 3.78 (d, *J* = 15.2 Hz, 2H), 3.82 (d, *J* = 15.2 Hz, 2H), 3.90 (m, 2H), 4.12 (d, *J* = 12.9 Hz, 2H), 6.70 (s, 1H), 6.84 (d, *J* = 2.22 Hz, 2H), 6.94 (d, *J* = 2.22 Hz, 2H), 7.04 (s, 2H), 7.21 (s, 2H), 7.71 (m, 4H), 7.84 (m, 4H). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$ , ppm 10.5, 23.3, 29.6, 31.4, 31.5, 31.8, 31.9, 33.93, 33.94, 34.2, 35.2, 38.6, 69.2, 75.6, 123.2, 123.3, 124.7, 126.02, 126.03, 127.6, 128.6, 132.2, 132.6, 133.2, 133.3, 134.0, 141.3, 143.5, 143.9, 145.9, 150.3, 152.6, 154.5, 168.2. HRMS (MALDI-TOF): *m/z* 922.5934 [M+H]<sup>+</sup> (calcd. for C<sub>61</sub>H<sub>80</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 922.5986).

**5,11,17,23-Tetra**-*tert*-**butyl-25,27-dipropoxy-26,28-di**(**3**-aminopropoxy)calix[**4**]arene (**1,3**-alternate) (**2**). The compound was synthesized from calix[4]arene **5** (0.50 g, 0.45 mmol) by the treatment of hydrazine hydrate (1.0 ml, 12.4 mmol) in boiling ethanol (33 ml) in accordance with the procedure described in [32]. Yield of compound **2** 92% (0.35 g), m.p. 290-292°C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{H}$ , ppm 0.63 (t, *J* = 7.8 Hz, 6H), 0.95 (m, 4H), 1.26 (s, 18H), 1.31 (s, 18H), 1.33 (m, 4H), 2.48 (t, *J* = 6.8 Hz, 4H), 3.28 (t, *J* = 7.9 Hz, 4H), 3.47 (t, *J* = 6.4 Hz, 4H), 3.82 (br.s, 4H), 6.96 (s, 4H), 7.00 (s, 4H). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta_{C}$ , ppm 9.9, 22.0, 31.6, 31.7, 33.7, 33.9, 34.0, 39.2, 39.7, 68.8, 71.7, 125.7, 125.8, 132.8, 133.2, 143.6, 154.8, 155.0. HRMS (MALDI-TOF): *m/z* 847.6410 [M+H]<sup>+</sup> (calcd. for C<sub>56</sub>H<sub>83</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 847.6353).

### Synthesis of the porphyrin-calix[4]arene conjugates

Conjugate 9. A two-necked flask equipped with a magnetic stirrer and reflux condenser, flushed with dry argon, was charged with the Zn(II) porphyrinate 8 (0.3 mmol, 226 mg), calix[4]arene 1 (0.15 mmol, 127 mg), Pd(dba)<sub>2</sub> (16 mol%, 14 mg), BINAP (18 mol%, 17 g), absolute dioxane (2 ml). The reaction mixture was stirred for several minutes and then sodium tert-butoxide (0.45 mmol, 43 mg) was added. The reaction mixture was stirred at reflux for 24 h, cooled down to ambient temperature, the solution was filtered, the residue washed with CH<sub>2</sub>Cl<sub>2</sub> (5 ml), combined organic fractions were evaporated in vacuo, and the residue was chromatographed on silica gel (eluent CH<sub>2</sub>Cl<sub>2</sub> - MeOH 20:1). Yield of compound **9** 56% (184 mg). Dark-red crystalline powder, m.p. 240-245°C. UV-vis (MeCN):  $\lambda_{max} = 409$  nm (lgs 5.63), 540, 576 nm. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 1.00 (t, J = 7.2 Hz, 6H), 1.08 (t, J = 7.1 Hz, 12H), 1.25 (s, 18H), 1.26 (s, 18H), 1.57 (sextet, J = 7.0 Hz, 8H), 1.67 (quintet, J = 7.1 Hz, 8H), 1.96 (quintet, J = 7.0 Hz, 8H), 2.16 (quintet, J = 7.3 Hz, 4H), 2.60 (br.s, 4H), 2.64 (s, 12H), 3.22 (br.s, 16H), 3.35 (d, J = 12.3 Hz, 4H), 3.48 (s, 12H), 3.64 (br.s, 4H), 3.99 (t, J = 7.0 Hz, 8H), 4.27 (br.s, 4H), 4.62 (d, J = 12.3 Hz, 4H), 6.95 (s, 4H), 7.00 (s, 4H), 7.19 (d, J = 7.6 Hz, 2H), 7.23 (s, 2H), 7.40 (br.s, 2H), 7.60 (br.t,  $J_{obs} = 7.1$  Hz, 2H), 8.48 (s, 2H), 9.53 (s, 4H), NH protons were not assigned. <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta_{C}$ , ppm 10.3, 11.1, 12.0, 14.2, 15.1, 22.7, 23.5, 25.7, 31.2, 31.5, 32.3, 32.7, 33.9, 41.7, 72.9, 77.1, 95.0, 96.4, 112.1, 119.0, 119.9, 123.5, 125.0, 125.1, 128.0, 133.6, 133.9, 134.7, 137.5, 137.8, 140.1, 144.4, 144.6, 144.8, 146.4, 146.5, 146.8, 147.6, 153.5, some quaternary carbon atoms were not unambiguously identified due to overlapping. MS (MALDI-TOF): m/z2187.20  $[M]^+$  (calcd. for  $C_{140}H_{174}N_{10}O_4Zn_2 [M]^+$  2187.23).

**Conjugate 10.** A two-necked flask equipped with a magnetic stirrer and reflux condenser, flushed with dry argon, was charged with the Zn(II) porphyrinate **8** (0.2 mmol, 151 mg), calix[4]arene **2** (0.1 mmol, 85 mg), Pd(dba)<sub>2</sub> (16 mol%, 9 mg), BINAP (18 mol%, 11 g), absolute dioxane (1 ml). The reaction mixture was stirred for several minutes and then sodium *tert*-butoxide (0.3 mmol, 29 mg) was added. The reaction mixture was stirred at reflux for 24 h, cooled down to ambient temperature, the solution was filtered, the residue washed with CH<sub>2</sub>Cl<sub>2</sub> (3 ml), combined organic fractions were evaporated *in vacuo*, and the residue was chromatographed on silica gel (eluent CH<sub>2</sub>Cl<sub>2</sub> – hexanes 1:1). Yield of compound **10** 8% (18 mg). Dark-red crystalline powder, m.p. 228-230°C. UV-vis (MeCN):  $\lambda_{max} = 409$  nm (lgc 5.06), 538, 576 nm. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 0.61 (t, J = 7.4 Hz, 6H), 0.96 (t, J = 7.1 Hz, 12H), 1.25 (s, 18H), 1.30 (s, 18H), 1.52 (m, 12H), 1.65 (m, 12H), 2.04 (quintet, J = 7.5 Hz, 8H), 2.33 (s, 12H), 3.04 (t, J = 7.3 Hz, 4H), 3.29 (t, J = 7.8 Hz, 4H), 3.31 (s, 12H), 3.32 (s, 12H), 3.54 (m, 12H), 3.86 (s, 8H), 6.82 (d, J = 7.2 Hz, 2H), 6.86 (s, 2H), 6.87 (d, J = 6.8 Hz, 2H), 6.97 (s, 4H), 7.04 (s, 4H), 7.25 (t, J = 7.6 Hz, 2H), 9.04 (s, 2H), 9.56 (s, 4H), NH protons were not assigned. <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$ , ppm 9.9, 11.4, 11.9, 14.2, 15.0, 22.0, 22.7, 26.2, 30.1, 31.5, 31.8, 32.4, 32.9, 33.9, 34.0, 39.3, 41.3, 68.0, 71.7, 95.6, 96.5, 111.7, 118.8, 119.9, 123.1, 125.5, 125.8, 127.8, 132.9, 133.3, 135.2, 137.4, 137.9, 140.5, 143.8, 144.0, 144.2, 146.3, 146.4, 147.1, 147.2, 147.4, 154.6, 155.0, two quaternary carbon atoms were not unambiguously identified due to overlapping. MS (MALDI-TOF): m/z 2187.21 [M]<sup>+</sup> (calcd. for C<sub>140</sub>H<sub>174</sub>N<sub>10</sub>O<sub>4</sub>Zn<sub>2</sub> [M]<sup>+</sup> 2187.23).

**Conjugate 11**. Obtained as the second product in the synthesis of the conjugate **10**. Eluent  $CH_2Cl_2$  – hexanes 1:1). Yield of compound **11** 20% (30 mg). Dark-red crystalline powder, m.p. 183-185°C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{H}$ , ppm 0.84-0.99 (m, 12H), 1.13 (s, 18H), 1.29 (s, 9H), 1.36 (s, 9H), 1.47-1.90 (m, 14H), 2.05 (quintet, J = 7.7 Hz, 2H), 2.15 (quintet, J = 7.8 Hz, 4H), 2.41 (t, J = 7.2 Hz, 2H), 2.61 (s, 6H), 2.78 (t, J = 6.8 Hz, 2H), 3.26 (d, J = 12.9 Hz, 2H), 3.47 (s, 6H), 3.52 (s, 6H), 3.53-3.60 (m, 4H), 3.77 (t, J = 7.5 Hz, 4H), 3.81-3.93 (m, 8H), 4.22 (d, J = 12.9 Hz, 2H), 6.93 (s, 2H), 7.02 (s, 2H), 7.07 (s, 2H), 7.08 (br.s, 1H), 7.12 (s, 1H), 7.16 (s, 2H), 7.39 (d, J = 7.2 Hz, 1H), 7.48 (t, J = 7.9 Hz, 1H), 9.51 (s, 1H), 9.93 (s, 2H), NH and NH<sub>2</sub> protons were not assigned. <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta_{C}$ , ppm 10.4, 11.5, 12.2, 14.2, 15.2, 22.8, 23.0, 26.4, 29.4, 31.4, 31.5, 31.7, 32.4, 32.9, 33.9, 34.0, 39.0, 40.6, 68.9, 75.4, 96.1, 97.0, 111.9, 118.4, 122.9, 124.4, 125.6, 125.9, 127.0, 128.1, 129.2, 132.8, 133.2, 133.9, 135.8, 137.9, 138.6, 141.0, 141.8, 144.2, 144.5, 145.6, 147.0, 147.1, 147.4, 147.7, 147.9, 149.8, 152.8, 154.1, some quaternary carbon atoms were not unambiguously identified due to overlapping. MS (MALDI-TOF): m/z 1516.91 [M]<sup>+</sup> (calcd. for C<sub>98</sub>H<sub>128</sub>N<sub>6</sub>O<sub>4</sub>Zn [M]<sup>+</sup> 1516.93).

**Conjugate 12.** Obtained by the treatment of the conjugate **9** (176 mg, 0.08 mmol) with trifluoroacetic acid (1 ml) in CH<sub>2</sub>Cl<sub>2</sub> (1 ml) at room temperature for 12 h followed by washing with excess sodium carbonate solution, extraction with CH<sub>2</sub>Cl<sub>2</sub>, drying over molecular sieves 4Å and evaporation of the solvent *in vacuo*. Yield 99% (160 mg), dark-red solid. UV-vis (MeCN):  $\lambda_{max} = 399$  nm (lg $\epsilon$  5.26), 503, 534, 572 nm. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{H}$ , ppm -3.30 (br.s, 2H), -3.15 (br.s, 2H), 0.65 (s, 9H), 0.86 (t, J = 6.8 Hz, 3H), 0.99 (t, J = 7.1 Hz, 12H), 1.26 (s, 27H), 1.34 (sextet, J = 7.0 Hz, 8H), 1.42 (quintet, J = 6.2 Hz, 8H). 1.63 (quintet, J = 7.2 Hz, 8H), 2.00 (quintet, J = 8.0 Hz, 4H), 2.06 (s, 6H), 2.21 (quintet, J = 7.1 Hz, 2H), 2.45 (s, 6H), 2.71 (d, J = 13.1 Hz, 2H), 2.86 (d, J = 12.1 Hz, 2H), 3.21 (s, 6H), 3.43-3.56 (m, 6H), 3.47 (s, 6H), 3.49 (s, 6H), 3.65 (d, J = 12.1 Hz, 2H), 3.54 (s, 6H), 3.73 (t, J = 8.2 Hz, 4H), 3.88 (t, J = 6.7 Hz, 4H), 3.90 (t, J = 6.3 Hz, 4H), 4.01 (d, J = 13.1 Hz, 2H), 6.22 (d, J = 7.7 Hz, 2H), 6.27 (s, 2H), 6.30 (s, 2H), 6.56 (s, 2H), 6.91 (s, 2H), 6.94 (d, J = 7.2 Hz, 2H), 7.11-7.16 (m, 4H), 9.74 (s, 2H), 10.08 (s, 2H), 10.14 (s, 2H), NH and OH protons were not assigned. <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta_{C}$ , ppm 9.5, 11.3, 11.6, 12.2, 12.3, 14.1, 14.2, 14.6, 22.6, 22.7, 26.0, 26.4, 28.1, 29.4, 29.4, 30.9, 31.6, 32.0, 32.1, 32.2, 32.6, 32.8, 33.5, 34.0, 34.1, 41.0, 74.6, 76.4, 95.4, 96.4, 109.5, 119.6, 120.3, 121.7, 124.4, 124.8, 124.9, 125.4, 127.8, 129.8, 131.4, 131.8, 135.6, 136.0, 137.2, 137.7, 137.8, 139.9, 140.4, 141.6, 142.3, 142.8, 143.4, 143.6, 144.4, 145.4, 145.8, 144.4, 145.8, 145.8, 144.4, 145.8, 144.4, 145.

144.9, 145.0, 145.2, 145.4, 146.2, 147.1, 150.4, 153, some quaternary carbon atoms were not unambiguously identified due to overlapping. MS (MALDI-TOF): m/z 2021.38 [M]<sup>+</sup> (calcd. for  $C_{137}H_{172}N_{10}O_4$  [M]<sup>+</sup> 2021.36).

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Scheme 4.



**Fig. 1**. Evolution of the UV-vis spectrum of the conjugate **9**  $(3.6 \times 10^{-7} \text{ M} \text{ in MeCN})$  in the presence of 5 equiv. of Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Cd(II), Pb(II), Ag(I), Hg(II) perchlorates.



**Fig. 2**. Evolution of the spectrum of fluorescence of the conjugate 9  $(3.6 \times 10^{-7} \text{ M in MeCN})$  in the presence of 5 equiv. of Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Cd(II), Pb(II), Ag(I), Hg(II) perchlorates.

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**Fig. 3**. Evolution of the UV-vis spectrum of the conjugate **10**  $(1.19 \times 10^{-6} \text{ M} \text{ in MeCN})$  in the presence of 5 equiv. of Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Cd(II), Pb(II), Ag(I), Hg(II) perchlorates.



**Fig. 4**. Evolution of the spectrum of fluorescence of the conjugate **10** ( $1.19 \times 10^{-6}$  M in MeCN) in the presence of 5 equiv. of Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Cn(II), Pb(II), Ag(I), Hg(II) perchlorates.



**Fig. 5**. Evolution of the UV-vis spectrum of the conjugate **12** ( $7.1 \times 10^{-7}$  M in MeCN) in the presence of 5 equiv. of Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Cn(II), Pb(II), Ag(I), Hg(II) perchlorates.



**Fig. 6**. Evolution of the spectrum of fluorescence of the conjugate **12**  $(7.1 \times 10^{-7} \text{ M in MeCN})$  in the presence of 5 equiv. of Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Cd(II), Pb(II), Ag(I), Hg(II) perchlorates.