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Synthesis of Functional *meso*-Aryl Porphomonomethenes and Porphodimethenes: Application to the Preparation of a Chiral Calix[4]phyrin Dimer

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Abstract: Reaction of 5,5-dimethyldipyrromethane (**1**) with electron-deficient aryl aldehydes in the presence of BF_3-Et_2O and NH_4Cl in propionitrile constitutes efficient, easy access to unprecedented, functional porphomonomethenes together with the expected porphodimethenes (calix[4]-phyrins). Alternatively, when the reaction was carried out in CH_2Cl_2 in the presence of an acid and Florisil, the expected bis-arylcalix[4]phyrin was isolated in 41% yield, while no scrambled macrocycle was detected. After reduction of the nitro function, porphomonomethene **9** was efficiently condensed with the binaphthyl diacyl chloride (**10**) leading to the first chiral calix[4]phyrin dimer (**11**) that exhibits a moderate enantiorecognition toward the enantiomers of malic acid.

During the past decade, the chemistry of porphyrinogens received a renewed interest as, among other nonconjugated oligopyrrolic macrocycles, calix[4]pyrroles, namely, *meso*-tetrahydrooctaalkylporphyrin, appeared to offer promising perspectives in the field of anion and neutral substrate recognition.[1] More recently, thanks to their structure that lies between porphyrins and calixpyrroles, calix[*n*]phyrins underwent tremendous strides as their binding properties may exceed those of their parent analogues.[2] Indeed, they are expected to offer interesting porphyrin-like coordinating properties for cations and calix[*n*]pyrrole-like affinity for anions. For the same reasons, any partly oxidized porphyrinogen should possess remarkable binding affinities.

At present, access to porphomono-, di-, and trimethenes still remains challenging. Indeed, it requires either stepwise selective reduction of the corresponding porphyrin[3] or metal-assisted dealkylation of the corresponding octaalkylporphyrinogen.[4] While the harsh conditions required for macrocycle transformations are generally incompatible with the presence of sensitive groups, Sessler et al. overcame this problem by developing a flexible, general stepwise approach that allows the preparation of highly functionalized molecules.[5]

In this note, we wish to report the unexpected reactivity of electron-deficient aryl aldehydes with 5,5-dimethyldipyrromethane (**1**) under acid catalysis in propionitrile that conveniently affords functionalized porphomonomethenes along with the expected parent calix[4]phyrin in good yield. Isolation of the unprecedented *m*-nitrophenylporphomonomethene **7** from the condensation of **1** with *m*-nitrobenzaldehyde (**3**) provides evidence for this particular type of reactivity and the X-ray crystal structure indicates a V-shaped conformation that could have a dramatic effect in molecular recognition processes. Preliminary binding constant measurements (vide supra) toward selected anions revealed good affinities and selectivities for oxo anions such as acetates or salicylates. Further reduction of the nitro groups to the corresponding amino functions followed by reaction with a binaphthyl diacyl chloride (**10**) afforded the first chiral porphomonomethene dimer (**11**) in good yield.

As part of our efforts on the development of easy-to-prepare oligopyrrolic macrocycles, we planned to design a new series of tunable calixphyrin-type systems. Recently, the Sessler group described that the condensation of aryl dipyrromethanes with acetone readily affords calix[*n*]phyrins in good yield.[5] In particular, it was reported that calix[4]phyrin is the only macrocycle isolated when pure dichloromethane is used as solvent and trifluoroacetic acid as catalyst. A similar strategy involving condensation of alkyltripyrromethanes with aldehydes was proposed for the preparation of expanded calixphyrins.[6]

On the basis of these preliminary results, we sought to investigate the reactivity of 5,5-dimethyldipyrromethane (**1**)[7] with pentafluorobenzaldehyde (**2**) using a different set of conditions. Unexpectedly, in dichloromethane and in the presence of TFA, condensation of **1** with **2** afforded the expected bispentafluorophenylcalix[4]phyrin **4** in a poor 15% yield. Considering the low yield of the reaction and our recent results in corrole chemistry,[8] we then considered using Lee's conditions.[9] Surprisingly, condensa-

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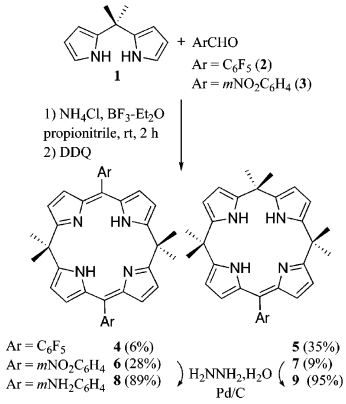
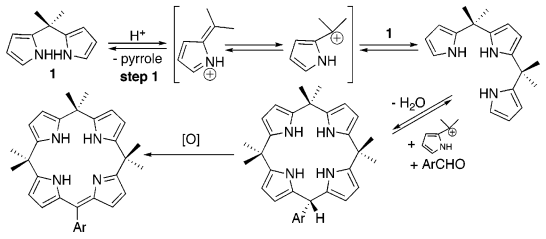
SCHEME 1. Access to Porpho[*n*]methenes



SCHEME 2. Proposed Mechanism for Formation of the Unexpected Monoarylcalix[4]phyrins



tion of **1** with **2** in propionitrile, in the presence of NH_4Cl and BF_3-Et_2O, did not afford the expected "contracted" calixphyrin but mainly the "scrambled" monoarylcalix[4]phyrin (**5**) in 35% yield. As a byproduct, we were also able to isolate calix[4]phyrin **4** in 6% yield (Scheme 1).

Similar particular reactions involving **2** and (oligo)pyrroles were already reported in the literature. For example, Osuka or Gross respectively described the unexpected preparation of hexaphyrins and corroles at the expense of the parent porphyrin in moderate yields.[10,11] In our case, we suspect that the high reactivity of pentafluorobenzaldehyde favors the acidolysis of **1** and further reaction according to Scheme 2.

Condensation of **1** and **2** in the presence of TFA and a basic magnesium silicate solid support, namely Florisil, provided further clues regarding the mechanism. Using these conditions, it was expected that step 1 (Scheme 2) involving addition of H^+ on dipyrromethane **1** would be disfavored (buffer effect) with respect to the classical nucleophilic attack of dipyrromethane **1** on the aldehyde. The hypothesis was confirmed as the expected calix[4]phyrin (**4**) was the only nonoligomeric compound isolated, in 41% yield (Scheme 3). Thus, these optimized conditions not only account for the mechanism proposed above but also constitute a versatile route to **4** in good yield.

To investigate further the general aspect of our approach, we sought to react **1** with the functionalized *m*-nitrobenzaldehyde **3** in the presence of NH_4Cl and BF_3-Et_2O in propionitrile. As expected, calix[4]phyrins **6** and **7** were isolated in 28% and 9% yield, respectively,

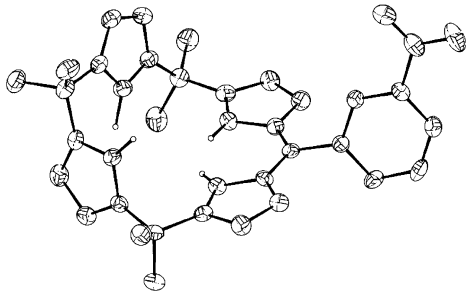
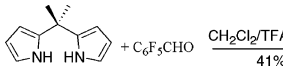


FIGURE 1. ORTEP of **7** with the atom labeling scheme.

SCHEME 3. Optimized Conditions for the Preparation of Calix[4]phyrin 4



after 2 h. When the reaction time was shortened to 1 h, formation of **6** at the expense of **7** was observed whereas the relative proportions of **6** and **7** remained constant when the reaction time was extended up to 24 h.

Further conformational information concerning the structure of porphomonomethene **7** was obtained by single-crystal X-ray diffraction analysis. Single crystals were obtained by slow diffusion of MeOH into a CH_2Cl_2 solution of **7**. The crystal structure reveals a V-shaped conformation more pronounced than that already observed for porphodimethenes (Figure 1).[5] This observation is in agreement with the presence of three sp^3 *meso*-carbon atoms linking the pyrrole units within the macrocycle. The dipyrromethene subunit is almost planar, with the dihedral angle between the two conjugated pyrrole units ca. 8°. The two other pyrrole subunits display rotation angles of 80° and 81°, respectively, out of the mean macrocyclic plane. Additionally, to accommodate the deformation and the steric hindrance due to the sp^3 *meso*-carbon atoms, the two out-of-plane pyrrole subunits adopt an alternating conformation. Finally, despite the presence of the highly polarizing nitro group, no intermolecular H-bond was evidenced in the lattice.

Subsequently, we investigated the reduction of the nitro functions of compounds **6** and **7**. Whereas the commonly used $SnCl_2$/HCl method led only to decomposed products, we found that conditions involving hydrazine and palladium on charcoal[12] efficiently led to the expected bis- and monoamino derivatives **8** and **9** in 89% and 95% yield, respectively.

Having amino-functionalized calix[4]phyrins in hand offered the possibility of constructing elaborated, potentially chiral ditopic receptors. To this end, we considered the use of a rigid, chiral binaphthyl moiety that was already proved to be appropriately designed for the preparation of chiral, clamshell-like sapphyrin dimers used for the chiral recognition of dicarboxylate anions.[13] Despite the conformational flexibility inherent to the system, the chiral sapphyrin dimer appeared to adopt a "pseudo-stacked" conformation in polar media favorable for the coordination of dianionic species. By using a

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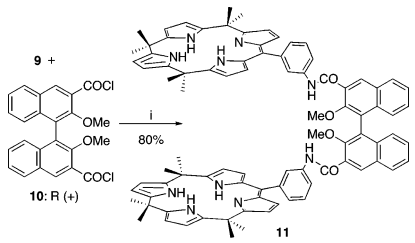
SCHEME 4[a]



[a] Reagents and Conditions: (i) NEt_3, THF, rt.

TABLE 1. Potentiometric Selectivity Coefficients for Salicylate (log $K^{Pot.}_{sal,j}$)[a] of PVC Membranes Based on Receptors 4, 5, and 7[b] toward Selected Anions

	anions			
1	nitrite	−1.04	−1.46	−2.24
2	nitrate	−0.23	−1.20	−0.72
3	acetate	−2.95	−2.25	−3.75
4	lactate	−2.56	−2.24	−3.89
5	benzoate	−2.45	0.07	−0.04

[a] The potentiometric selectivity coefficients were evaluated for solutions at pH 9.0 and were calculated by using the separate solution method with a concentration of primary and interfering anions of 10^{-2} M. [b] The PVC membrane consisted of 3 wt % of receptor, 50 mol % relative to receptor of cationic lipophilic additive TDDMACl (tridodecylmethylammonium chloride), poly(vinyl chloride), and plasticizer *o*-NPOE (*o*-nitrophenyl octyl ether) in the ratio 1:2 wt %.

similar strategy, the chiral dimer **11** was synthesized by reacting **9** with a stoichiometric amount of the binaphthyl diacyl chloride (**10**)[14] in the presence of dry triethylamine (Scheme 4). These conditions afforded the chiral bis-receptor **11** in 80% yield after column chromatography.

Binding properties of selected calix[4]phyrins were studied. As we were interested in the development of sensors which are able to discriminate anions in polar media, we studied calixphyrins **4**, **5**, **7**, and **11** using the potentiometric method in standard liquid membrane ion-selective electrodes (ISEs). This method allows the determination of not only the sensitivity of the membrane toward anions but also the selectivity of the membrane when two or more competitive anions are present. Using this method, we determined that while halides are generally poorly bound to the calix[4]phyrins at pH 9, the receptors show a relatively high affinity toward oxo anions such as benzoate, salicylate, and nitrate over a wide concentration range (Table S1, see the Supporting Information).[15] In addition, we also determined the potentiometric selectivity coefficient (log $K^{Pot.}_{sal,j}$) of the different membranes for salicylates in the presence of an interfering anion. These measurements show that the monoarylcalix[4]phyrins are slightly more selective for salicylates than for nitrates (more negative log *K* values means less interference), in comparison with the parent porphodimethenes (Table 1, entry 2). However, they bind salicylates and benzoates with similar affinities (Table 1, entry 5).

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(15) Complementary studies (UV−vis and electrochemical titrations) revealed a 1:1 binding ratio.

Along with the study of the monomeric calixphyrins, we also studied the chiral calix[4]phyrin dimer **11**. As calix[4]phyrins **4**, **5**, and **7** showed promise for the coordination of oxo anions, we tested the binding affinities of **11** toward the poly-oxygenated D and L enantiomers of malic acid. In this case, the potentiometric method evidenced an encouraging, albeit yet moderate, discrimination between the two enantiomers (log $K^{Pot.}_{L/D}$ = −0.63) in a reasonable working range (Table S2, see the Supporting Information).

In conclusion, we report a new, convenient route to functionalized porphomono- and porphodimethenes in up to 41% yield. In particular, we have shown that tuning of the experimental conditions dramatically influences the distribution of the products. An X-ray crystal structure of the unprecedented monoarylcalix[4]phyrin **7** reveals a V-shaped conformation consistent with the presence of three sp^3 hybridized *meso*-carbon atoms in the macrocycle. Reduction of the nitro group was carried out efficiently with use of hydrazine hydrate and palladium on charcoal. The resulting monoaminocalix[4]-phyrin **9** was dimerized by using a chiral binaphthyl diacyl chloride affording in good yield the first chiral calixphyrin-based ditopic receptor **11**. Electrochemical studies involving the functionalized calixphyrins are presented, providing evidence of good affinities and selectivities toward oxygenated species such as benzoates and salicylates. Modified electrodes involving the chiral binap dimer **11** revealed a promising enantiorecognition of the two enantiomers of malic acid over a reasonable working range. Work is currently in progress in our laboratories to establish whether similar behavior can be observed with modified, chiral calix[4]phyrins.

Experimental Section

5,5-Dimethyldipyrromethane (**1**) was prepared as described previously.[8] Purifications on column were performed with 40−60 μm mesh silica gel.

Procedure A: Synthesis in Propionitrile in the Presence of NH_4Cl. (a) Bis(*m*-nitrophenyl)calix[4]phyrin (6) and *m*-Nitrophenylcalix[4]phyrin (7). Under Ar, a 250-mL round-bottom flask equipped with a stir bar was charged with **1** (1.08 g, 6.2 mmol), *m*-nitrobenzaldehyde (0.83 g, 3.1 mmol), and 60 mL of freshly distilled propionitrile. NH_4Cl (3 g, 56 mmol) was then added to the reaction mixture along with 0.57 mmol (0.07 mL) of BF_3-Et_2O. The reaction was allowed to proceed for 2 h at room temperature and 1.4 g (6.2 mmol) of DDQ was added. The oxidation was completed overnight at room temperature. After filtration on a fritted funnel, the solvent was removed under vacuum, and the residue was directly purified by silica gel column chromatography with a mixture of CH_2Cl_2/cyclohexane (4/6 up to 7/3) as eluent. After evaporation, 270 mg (Y = 28%) of the expected bis-*m*-nitrophenylcalix[4]phyrin (**6**) was first isolated as an orange solid, followed by 140 mg (Y = 9%) of the mono-*m*-nitrophenylcalix[4]phyrin (**7**).

6: ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 14.02 (s, 2H, H_{NH}), 8.22 (m, 4H, H_{Ar}), 7.68 (m, 2H, H_{Ar}), 6.21 (d, 4H, J = 4,1 Hz, H_β), 6.14 (d, 4H, J = 4.1 Hz, H_β), 7.51 (m, 2H, H_{Ar}), 2.09 (s, 12H, H_{Me}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 166.6, 148.1, 140.5, 139.1, 137.2, 136.8, 129.1, 128.3, 125.8, 124.0, 115.6, 38.7, 29.2; IR (ATR) 3081, 1967, 1918, 1733 1718, 1582, 1509, 1447, 727, and 702 (Ar), 2974, 2925, 2882, 2895, 1475, and 1384 (Me group), 1349 (NO_2 group) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 419 nm; HRMS (Maldi−TOF) *m/z* calcd for $[C_{36}H_{30}N_6O_4 + H]^+$ 611.2409, found 611.2401. Anal. Calcd for $C_{36}H_{30}N_6O_4$: C, 70.81; H, 4.95; N, 13.76. Found: C, 70.38; H, 5.02; N, 13.26.

7: ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.33 (m, 1H, H_{Ar}), 8.28 (m, 1H, H_{Ar}), 7.96 (large s, 2H, H_{NH}), 7.72 (m, 1H, H_{Ar}), 7.61 (m,

1H, H_{Ar}), 6.38 (d, 2H, J = 4.2 Hz, H_β), 6.28 (d, 2H, J = 4.2 Hz, H_β), 6.10 (m, 2H, H_β), 6.05 (m, 2H, H_β), 1.69 (s, 6H, H_{Me}), 1.66 (s, 12H, H_{Me}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 166.1, 147.7, 139.6, 139.1, 136.5, 136.1, 135.9, 132.9, 129.0, 128.6, 125.5, 123.4, 115.3, 104.5, 103.6, 37.2, 35.8, 29.1, 28.9; IR (ATR) 3077, 1973, 1919, 1733, 1717, 1581, 1505, 1456, 773, and 787 (Ar), 2969, 2926, 2869, 2852, 1462, and 1374 (Me group), 1348 (NO_2 group) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 450 nm; HRMS (Maldi−TOF) m/z calcd for $[C_{32}H_{33}N_5O_2 + Na]^+$ 542.2532, found 542.2526. Anal. Calcd for $C_{32}H_{33}N_5O_2 \cdot 0.5CH_2Cl_2$: C, 69.44; H, 6.10; N, 12.46. Found C, 69.80; H, 6.65; N, 11.15.

(b) Bis(pentafluorophenyl)calix[4]phyrin (4) and Mono-(pentafluoro)phenylcalix[4]phyrin (5). **4** and **5** were synthesized according to the experimental procedure described above for the preparation of **6** and **7**. Purification by silica gel column chromatography (eluent CH_2Cl_2/cyclohexane: 3/7 then 1/1) afforded bis(pentafluoro)phenylcalix[4]phyrin (**4**) in 6% yield and mono(pentafluoro)phenylcalix[4]phyrin (**5**) in 35% yield.

4: ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 13.8 (s, 2H, H_{NH}), 6.32 (m, 8H, H_β), 1.95 (s, 12H, H_{Me}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 166.7, 146.2, 143.7, 140.1, 138.7, 136.1, 126.5, 122.3, 115.8, 111.7, 53.4, 38.4, 29.1; ^{19}F NMR ($CDCl_3$, 400 MHz) δ (ppm) −161.6 (m, 2F), −153.1 (m, 1F), −138.4 (m, 2F); IR (ATR) 1985, 1926, 1733−1730, 1579, 1494, 1446, 730, and 700 (Ar), 2979, 2970, 2925, 2912, 2882, 2875, 2858, 2851, 1456, and 1384 (Me group) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (nm) 419 nm; LRMS (FAB) m/z calcd for $[C_{36}H_{22}F_{10}N_4 + H]^+$ 700.6, found 701. Anal. Calcd for $C_{36}H_{22}F_{10}N_4$: C, 61.72; H, 3.17; N, 8.00. Found C, 61.82; H, 3.22; N, 7.01.

5: ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 8.63 (s, 2H, H_{NH}), 7.95 (s, 2H, H_{NH}), 6.38 (m, 2H, H_β), 6.31 (m, 2H, H_β), 6.11 (m, 2H, H_β), 6.04 (m, 2H, H_β), 1.70 (s, 6 H, H_{Me}), 1.65 (s, 12 H, H_{Me}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 166.7, 146.6, 142.8, 139.0, 138.9, 135.6, 135.3, 127.4, 121.1, 116.0, 104.4, 103.4, 53.3, 37.1, 35.6, 28.8, 28.6; ^{19}F NMR ($CDCl_3$, 200 MHz) δ (ppm) −162.2 (m, 2F), −153.9 (m, 1F), −139.6 (m, 2F); IR (ATR) 2973, 2930, 2869, 1464, and 1377 (Me group), 2006, 1590, 1495, 1441, 723, and 698 (Ar) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (nm) 450 nm; MS (Maldi−TOF) m/z calcd for $[C_{32}H_{29}F_5N_4 + H]^+$ 565.23, found 565.09. Anal. Calcd for $C_{32}H_{29}F_5N_4 \cdot 0.5CH_2Cl_2$: C, 64.23; H, 4.98; N, 9.22. Found C, 63.28; H, 4.13; N, 7.58.

Procedure B: Synthesis in the Presence of a Solid Support. Bis(pentafluorophenyl)calix[4]phyrin (**4**) and bis(*m*-nitrophenyl)calix[4]phyrin (**6**) were respectively prepared in the absence of the corresponding mono(aryl)calix[4]phyrins when Florisil was used as a solid support.

In a typical experiment, under Ar, 3.08 mmol of the aldehyde were reacted with 3.06 mmol of 5,5′-dimethyldipyrromethane and 20 g of Florisil in 100 mL of dry CH_2Cl_2 in the presence of 0.1 mL of TFA. After 22 h, a Soxhlet extraction followed by an oxidation with DDQ afforded the expected bis(aryl)calix[4]phyrin in 41% yield after column chromatography (SiO_2 15−40 μm, eluent: CH_2Cl_2/cyclohexane).

General Procedure for the Reduction of the Nitrophenylcalix[4]phyrins. In a typical experiment, **6** or **7** was taken in absolute ethanol, and 1.5 equiv of hydrazine hydrate along with a catalytic amount of palladium on charcoal were added. The reaction mixture was brought to reflux overnight. After the reaction was completed, the reaction mixture was filtered through a pad of silica gel and evaporated to dryness. The residue was purified by silica gel column chromatography with CH_2Cl_2 as eluent, affording the pure amino calixphyrins **8** and **9** in 89% and 95% yield, respectively.

8: ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 14.07 (s, 2H, H_{NH}), 7.07 (dd, 2H, J_1 = 7.64 Hz, J_2 = 3.82 Hz, H_{Ar}), 6.76 (m, 2H, H_{Ar}), 6.67 (m, 4H, H_{Ar}), 6.33 (d, 4H, J = 4.32 Hz, H_β), 6.15 (d, 4H, J = 4.08 Hz, H_β), 3.61 (s, 4H, H_{NH_2}), 1.86 (s, 12H, H_{Me}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 145.9, 140.9, 140.7, 138.6, 128.7, 128.7, 121.8, 117.9, 115.6, 114.4, 53.8, 38.6; IR (ATR) 3460, 3371, 3218, and 1615 (NH_2 group), 3058, 1963, 1922, 1729, 1716, 1602, 1505, 1446, 735, and 696 (Ar), 2971, 2923, 2881, 2858, 1464, and 1382 (Me group) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 419 nm; HRMS (Maldi−TOF) m/z calcd for $[C_{36}H_{30}N_6O_4 + H]^+$ 551.2925, found 551.2856. Anal. Calcd for $C_{36}H_{30}N_6O_4 \cdot CH_2Cl_2$: C, 69.91; H, 5.71; N ,13.22. Found: C, 69.78; H, 5.82; N, 11.48.

9: ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 11.56 (s, 1H, H_{NH}), 8.01 (s, 2H, H_{NH}), 7.04 (m, 1H, H_{Ar}), 6.68 (d, 1H, J = 7.4 Hz, H_{Ar}), 6.59 (m, 1H, H_{Ar}), 6.54 (s, 1H, H_{Ar}), 6.37 (d, 2H, J = 4.3 Hz, H_β), 6.22 (d, 2H, J = 4.1 Hz, H_β), 5.98 (m, 2H, H_β), 5.93 (m, 2H, H_β), 3.50 (large s, 2H, H_{NH_2}), 1.58 (s, 6H, H_{Me}), 1.55 (s, 12H, H_{Me}); ^{13}C NMR ($CDCl_3$, 400 MHz) δ (ppm) 165.2, 145.7, 140.3, 140.0, 139.3, 139.2, 136.7, 130.0, 128.5, 122.0, 118.10, 115.6, 114.6, 104.5, 103.8, 37.5, 36.1, 29.3; IR (ATR) 3436, 3366, 3213, and 1615 (NH_2 group), 3057, 1985, 1922, 1716, 1603, 1505, 1456, 772, and 661 (Ar), 2968, 2925, 2869, 2854, 1462, and 1374 (Me group) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 452 nm; HRMS (Maldi−TOF) m/z calcd for $C_{32}H_{35}N_5$ 490.2972, found 490.3022. Anal. Calcd for $C_{32}H_{35}N_5$: C, 78.49; H, 7.20; N, 14.30; Found: C, 78.82; H, 7.34; N, 14.80.

Binap Calix[4]phyrin Dimer (11). Under Ar, a two-neck, round-bottom flask was charged with **9** (0.294 mmol, 144 mg), distilled NEt_3 (0.56 mmol, 78 μL), and dry THF (40 mL). The reaction mixture was cooled to 0 °C in an ice bath, and a THF solution (15 mL) of freshly prepared binap diacyl chloride (**10**) was added dropwise with a syringe. The solution darkened immediately. The reaction mixture was allowed to reach rt, then was stirred overnight. The solvents were evaporated under vacuum, and the resulting solid was taken in the minimum of CH_2Cl_2. The solution was poured on a silica gel column chromatograph prepared with CH_2Cl_2. The expected compound was collected as the main orange band with a 99/1 mixture CH_2Cl_2/MeOH. After evaporation of the solvents, **11** (0.11 mmol, 150 mg) was isolated as an orange solid (Y = 80%).

11: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 2H, H_{NHCO}), 9.02 (s, 2H, H_{binap}), 8.95 (large s, 2H, H_{NH}), 8.10 (d, J = 8.1 Hz, 2H, H_{binap}), 8.00 (br m, 6H, H_{NH} + $H_{Ar-calix}$), 7.67 (s, 2H, $H_{Ar-calix}$), 7.53 (t, 2H, J = 6.7 Hz, $H_{Ar-calix}$), 7.46 (t, 2H, J = 7.8 Hz, H_{binap}), 7.41 (t, 2H, J = 7.8 Hz, H_{binap}), 7.21 (d, 2H, J = 7.8 Hz, H_{binap}), 7.15 (d, 2H, J = 8.5 Hz, $H_{Ar-calix}$), 6.50 (d, 4H, J = 4.0 Hz, H_β), 6.36 (d, 4H, J = 4.0 Hz, H_β), 6.08 (m, 4H, H_β), 6.03 (m, 4H, H_β), 3.46 (s, 6H, OMe), 1.67 (s, 12H, Me), 1.65 (s, 24H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 162.7, 152.6, 139.3, 138.4, 138.3, 138.2, 136.9, 135.7, 135.1, 134.2, 129.9, 129.4, 128.9, 128.5, 127.7, 126.6, 125.7, 125.2, 124.9, 124.7, 122.1, 120.0, 114.1, 103.8, 103.0, 61.6, 52.0, 36.6, 35.0, 28.5; UV−vis (CH_2Cl_2) λ_{max} 465 nm); HRMS (Maldi−TOF) $(C_{88}H_{84}N_{10}O_4 + H)^+$ m/z calcd.1345.6750, found 1345.6281. Anal. Calcd for $C_{88}H_{84}N_{10}O_4$: C, 78.54; H, 6.29; N, 10.41. Found: C, 74.78; H, 6.06; N, 9.80.

Crystal structure determination for 7: $C_{32}H_{33}N_5O_2$, M = 519.60; triclinic, a = 10.318(3) Å, b = 11.071(2) Å, c = 13.310(3) Å, α = 93.10(2)°, β = 100.37(2)°, γ = 113.81(2)°, U = 1354.7(6) Å^3, T = 295 K, space group $P\bar{1}$ (no. 2), Z = 2, μ(Mo Kα) = 0.076 mm^{-1}. A total of 5044 reflections were measured (range 1−25°), 4754 unique (R_{int} = 0.04), on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The structure was solved by using direct methods and refined by full matrix least squares on F to R = 0.0716, R_w = 0.0665 (2206 reflections with $I > 1.5\ \sigma(I)$, and a goodness of fit of 1.19 for 353 refined parameters.

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Supporting Information Available: The instrumentation used for the determination of the potentiometric responses as well as the preparations of the electrodes are reported; Table S1 presenting the potentiometric properties of PVC membranes containing calixphyrins **4**, **5**, and **7** in the presence of nitrite, nitrate, acetate, lactate, benzoate, and salicylate and Table S2 disclosing the potentiometric properties of PVC membranes containing calixphyrins **11**, in the presence of D- and L-malic acid. This material is available free of charge via the Internet at http://pubs.acs.org.

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