162. Synthesis and Complexation Properties of a New Class of Receptors Based on a Cone-Configurated Tetra-*p*-(*tert*-Butyl)calix[4]arene and Bipyridyl Subunits

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The bipyridyl-armed tetra-*p*-(*tert*-butyl)calix[4]arenes **1–5** were synthesized from tetra-*p*-(*tert*-butyl)-calix[4]arene **A** and 6-(bromomethyl)-6′-methyl-2,2′-bipyridine (**B**) by direct base-strength-driven regioselective *O*-alkylation or by stepwise procedures. Preliminary complexation studies of the ligands **1–3** with Cu^{I} affording the complexes **6–8** are described.

Introduction. – Calixarenes are extensively studied as molecular receptors for neutral or ionic species [1] [2]. Easily synthesized from *p*-alkylphenols and formaldehyde, they combine complexation abilities and a high thermal stability with a good functionalization flexibility. For the latter, the formation of derivatives can be brought about at the *para*-positions or upper rim, or at the OH groups or lower rim, thus calixarenes are excellent platforms/building blocks in supramolecular chemistry [3]. At the lower rim, pendant groups such as esters, amides, carboxylic acids, crown ethers, *etc.* were grafted in view of preparing specific ionophores for metal cations. Among all these studies, we surprisingly found that little attention has been brought to the complexation of transition-metal cations by means of N-donor groups, *e.g.* heterocyclic pendant arms organized as an extension of the symmetric phenolic crown.

The syntheses of *p*-unsubstituted or *p*-(*tert*-butyl)-substituted calix[4]arenes[1]) bearing one or more pendant picolyl or quinolyl groups were described and these compounds subjected to an intensive and didactic ligand-conformation study [4]. At the same time, the lutidyl group was used as a bridging subunit between a calix[4]arene and a diaza-crown ether, leading to a new kind of unsymmetric cryptands [5]. Finally, grafting of the 2,2′-bipyridyl chelating agent was performed either at its 6- [5] or its 5-position [6], designing ligands able to complex Cu^{I} [5] or Ru^{II} [6], the complex with the latter presenting pH-sensitive luminescence properties. In these cases, only one or two bipyridyl subunits were attached. The ligands obtained preserved the cone conformation in the presence or absence of the *p*-(*tert*-butyl) substituents.

In the field of our investigations, we are interested in the formation of a library of lipophilic ligands having a good affinity for transition-metal cations, lanthanides, and actinides, to gain access to new kinds of liposoluble catalysts, luminescent probes, and

[1]) Calix[4]arene (= pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene; for numbering, see **A**).

selective extracting agents. Here we report the synthesis of a complete family of *O*-bipyridyl-grafted tetra-*p*-(*tert*-butyl)calix[4]arenes, containing the mono-(**1**), 1,3-bis-(distal; **2**), 1,2-bis- (proximal; **3**), 1,2,3-tris- (**4**), and 1,2,3,4-tetrakis[(6-methyl-2,2′-bipyridyl-6-yl)methoxy] analogue **5** (locants 1–4 refer to the *ipso*-positions of the 4 aromatic rings), and for which retention of the cone conformation is confirmed. The preliminary complexation studies of **1–3** with copper(I) are also described.

Ligand Synthesis. – The syntheses of ligands **1–5** were performed using the base-strength-driven regioselective *O*-alkylation of calixarenes developed during the last years for non-heterocyclic or heterocyclic substituents [4a–c] [5] [7]. As alkylating agent, 6-(bromomethyl)-6′-methyl-2,2′-bipyridine (**B**) was selected and synthesized as described in [8]. The base was chosen among various carbonates ($NaHCO_3$, Na_2CO_3, K_2CO_3, Cs_2CO_3) and hydrides (NaH), according to their ability to selectively deprotonate one or more phenolic OH groups, keeping in mind targetting of the cone conformation [4]. The solvents were essentially anhydrous MeCN or DMF; attempts to control the stoichiometry of the coupling reaction in dry acetone [9] failed in most cases.

Generally, yields varied from low to moderate, in part due to the fact that we used the corresponding stoichiometric amount of alkylating agent as often as possible. TLC Monitoring indicated the total consumption of the latter which determined the end of the reaction. The crude product mixture contained generally the desired calixarene with some by-products such as other alkylation products (as traces) or some bipyridine-methanol, and starting calixarene. The latter was easily recovered from the crude mixture by precipitation with MeOH. We found that the yields were better and particularly the workup cleaner, when the commercially available calix platform was recrystallized in toluene (see 1:1 complex **A**) [10] prior to the alkylation.

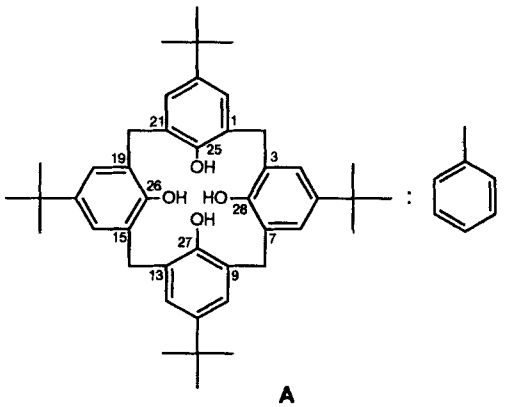
The purification process involved chromatographic steps on alumina and silica gel; the generally recommended conditions (SiO_2, AcOEt/cyclohexane) were ineffective giving overlapping streaking elution fractions. We preferred eluants such as CH_2Cl_2/MeOH, CH_2Cl_2/EtOH, or CH_2Cl_2/hexane.

The molecular weights of the pure compounds **1–5** were determined by electrospray (ES) or by fast-atom-bombardment (FAB; positive mode) mass spectroscopy and their structures established by spectroscopic means.

The structures were analysed by ^{1}H- and ^{13}C-NMR spectroscopy; comparison with the literature [4] [5] showed that, as desired, **1–5** were in the cone conformation (characteristic *AB* pattern for the bridging CH_2 groups). Replacement of picolyl groups [4] by bipyridyl subunits did not change the ^{1}H-NMR chemical-shift values (in $CDCl_3$) of the bridging CH_2 groups. The cone conformation of **1–5** was confirmed, according to the rules found by *de Mendoza et al.* [11], by the ^{13}C-NMR chemical shifts of Ar–CH_2–Ar and OCH_2–bpy, appearing at 30.90–32.97 and 77.10–79.50 ppm, respectively. The aromatic regions in the ^{1}H- and ^{13}C-NMR spectra were characterized by the additivity of the specific patterns of both calixarene and bipyridine subunits. In the cases of **3** and **4**, ^{1}H-NMR assignments were particulary difficult due to a strong overlapping of pyridyl and aryl signals.

The IR spectroscopy (FT-IR, KBr pellets) was consistent with the superposition of the typical data of a calix[4]arene and a bipyridine subunit (sharp medium bands around 3000 cm^{-1} (C–H stretch of aryl and pyridyl)). The low-energy calixarene OH-stretching vibrations (*ca.* 3150–3300 cm^{-1}) decreased in relative intensity from **1** to **4**, in agreement with the successive *O*-alkylations, and the pyridyl C=N stretching band underwent a slight shift from 1615 cm^{-1} (classical value) to 1575 cm^{-1} and increased going from **1** to **5**, as expected.

The UV spectra ($CHCl_3$) of **1–5** displayed a broad absorption pattern between 260 and 320 nm, with a maximum at *ca.* 290 nm and a shoulder at *ca.* 305 nm. Despite the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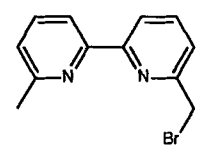
A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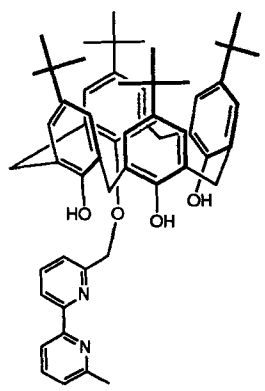
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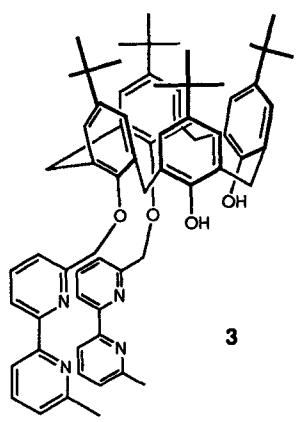
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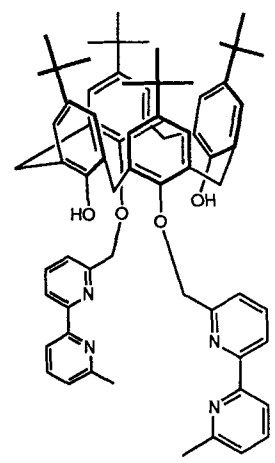
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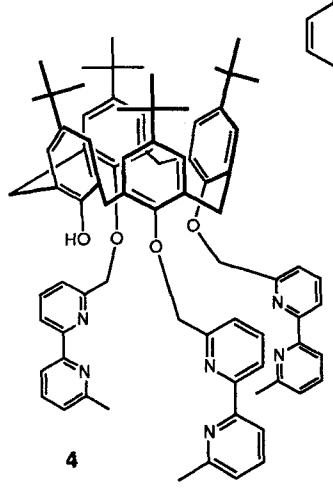
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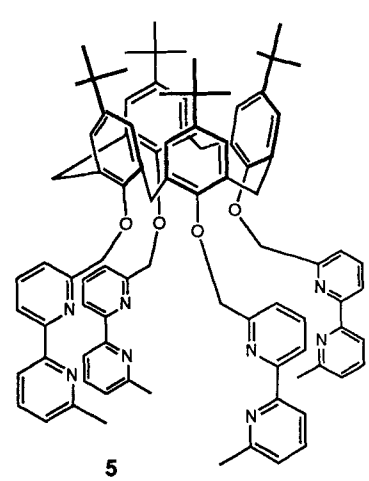
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strong overlap of the absorption bands of the phenolic macrocycle and the pendant arms, the high molar extinction coefficient values measured at *ca.* 290 nm (ε ($mol^{-1}lcm^{-1}$): 21900 (**1**), 38675 (**2**), 39700 (**3**), 50300 (**4**), and 64000 (**5**)) allow us to predict for this new family of ligands good photo-physical properties, *e.g.*, useful photocatalytic and fluorescence energy transfer properties.

Complexation Studies. – Preliminary complexation studies were carried out with Cu^I ions and ligands **1–3**. The Cu^I cation is known to be stabilized by tetrahedral coordination, giving strongly coloured complexes of the general formula $[ML_2]^+$ with α,α'-diimine-type ligands such as 2,2′-bipyridine and related compounds, and is used as a ligand-self-assembly promotor in supramolecular chemistry [12].

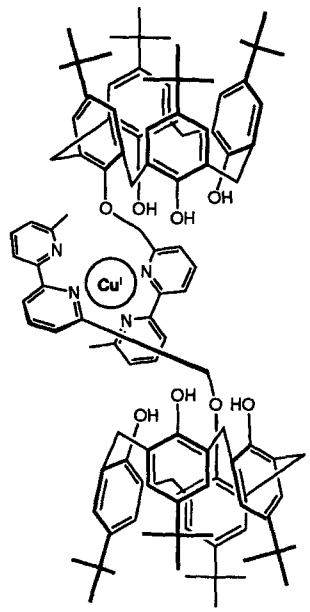
Ligands **1–3** were chosen because of the simplicity of their structural features: **1** was aimed at establishing metal-assisted association of a pair of calixarenes to give a complex of type **6** in which the *O*-substituted phenol moiety is diametrically opposite to the OH possessing the lowest pK_a (*ca.* 4.5) [6] [13]. This may allow pH-sensitive intramolecular metal-centered redox phenomena. *Beer et al.* [5] suggested that the de(*tert*-butyl) analog of **2** gives a mixture of a monomeric and a dimeric species with Cu^I, based on mass-measurement analysis. With **2**, we wanted to verify if, in this sterically highly hindered ligand, the presence of the 4 *t*-Bu groups at the upper rim would give rise to a configuration of the 2 distal bipyridyl units perfectly predisposed for tetrahedral complexation. In this case, intramolecular complexation will be favoured and the formation of dimeric intermolecular complexes disfavoured, blocking formation of a mixture. This is not the case for the ligand **3**, in which the proximal location of the two chelating heterocycles may favour the intermolecular complexation.

The complexes **6–8** were obtained by reacting stoichiometric amounts of the corresponding ligands **1–3** with tetrakis(acetonitrile)copper(I) hexafluorophosphate [14] in MeCN, followed by precipitation with an appropriate solvent (*e.g.* Et_2O, hexane) and, if necessary, by chromatographic purification over alumina or silica gel. The three orange-red solids thus obtained were perfectly stable in air, even at high temperature (dec. at *ca.* 200°), during air drying, or chromatographic purification, presuming an excellent behaviour in various media. The structures of **6–8** were supported by their spectroscopic data.

To obtain a correct view of the effect of the complexation on the NMR patterns of ligands **1–3**, spectra were recorded in CD_3CN. Due to the very low solubility of **2** in this medium, complex **7** was also studied in $CDCl_3$. Whatever the solvent nature, *e.g.* $CDCl_3$ or CD_3CN, **7** displays strongly broadened resonance patterns in the aromatic, CH_2 and Me regions. The 2 *t*-Bu *s* of **2** (0.95 and 1.30 ppm in $CDCl_3$) coalesce for **7** in CD_3CN into 2 br. *s* (0.94 and 1.19 ppm), and the CH_2 resonances undergo a general upfield shift. This seems to indicate, in addition to proving the complexation of Cu^I, the possible presence of more than one species in solution.

Comparison of the *AB* region in the ^{1}H-NMR spectra (CD_3CN) of **1** and **6** show simultaneously an upfield shift from 4.47–3.39 to 4.10–3.03 ppm, a contraction of the whole Ar–CH_2–Ar *AB* system, and a broadening of each of the components. The *Me*–bpy and OCH_2–bpy signals undergo a downfield shift from 2.60 and 5.31 ppm (**1**) to 2.34 and 4.88 ppm (**6**), respectively. It is interesting to notice that the complexation does not create any dissymmetry or chirality which would be characterized by the splitting of the OCH_2–bpy *s* to an *AB* system [12a, b]. The influence of the complexation on the aromatic region is also important: one bipyridine moiety passes from a classical *d*/*t*/*d* resonance pattern (**1**) to a fine *m* (**6**). It seems to indicate that this subunit undergoes the influence of a strong field effect, *e.g.*, the influence of the 3 residual OH groups of the phenolic macrocycle. This is supported by the upfield shift undergone by the OH groups, from 8.89 to 8.60 ppm.

Complexation of Cu^I by **3** induces a drastic change in the ^{1}H-NMR pattern: the 3 well defined *AB* systems featuring the 4 Ar–CH_2–Ar groups of ligand **3** are switched in two families of resonance signals for complex **8**. The



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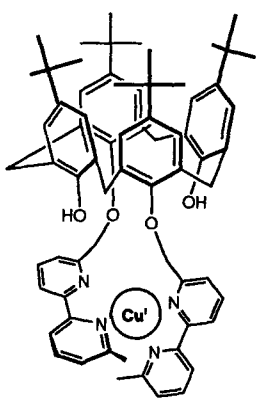

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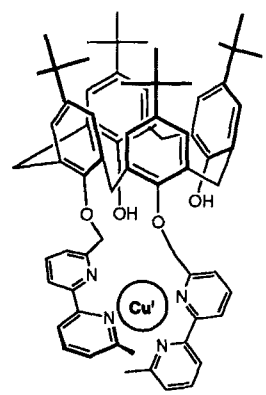

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2 CH_2 groups adjacent to the substituted phenols undergo a broadening of their resonance signals, accompanied by a contraction from 3.33–4.31 ppm (J = 12.8 Hz) to 3.52–4.34 ppm (J = 20 Hz), indicating a strong influence of the complexation on the macrocycle conformation. The two other *AB* systems corresponding to the residual opposite CH_2 groups undergo an upfield shift and a contraction, without strong modification of the J value (13.1 Hz *vs.* 13.0 and 12.00 Hz *vs.* 12.3 Hz, respectively). The complexation influences also the aromatic region, broadening specifically the pyridyl resonances.

Mass measurement of **6** was performed using FAB (pos. mode) and ES techniques, giving in both cases molecular peaks at 1725.1 (ES) and 1725 (FAB), the latter with the correct isotopic pattern. Base peaks were found at 894.3 (ES; $[\mathbf{1} - Cu^I]^+$) and 893.3 (FAB; $[\mathbf{1} - Cu^I]^+$). The complexes **7** and **8** were analyzed by the ES technique which displayed base peaks at 1076.6 mass units for both compounds, corresponding to the species $[\mathbf{2} - Cu^I]^+$ and $[\mathbf{3} - Cu^I]^+$, respectively. We did not find for **7** any traces of dimer, as described by *Beer* for his de(*tert*-butyl) analog [5].

UV Spectroscopy was performed using $CHCl_3$ as solvent; however the low solubility of **7** and **8** in $CHCl_3$ necessitated the addition of a drop of MeCN to the stock solution. Complexation of Cu^I by **1** (→**6**) did not change significantly the main band feature; shoulders can be seen in the case of complex **6** but do not predict the beginning of a band dissociation. A broad absorption appears at *ca.* 445 nm (ε 2990 $mol^{-1}lcm^{-1}$) corresponding to a metal-to-ligand charge-transfer (MLCT) transition. The same MLCT transition appears in the complexes **7** and **8** with a higher value of ε (4800 and 5600 $mol^{-1}lcm^{-1}$, resp.). Upon complexation, the 2 main bands of **2** and **3** undergo a slight bathochromic shift from 290 to 302 nm, revealing an absorption band at 270 nm, attributed to the calixarene moiety.

Conclusion. – Calixarenes are known to be interesting platforms for complexation studies, either for neutral or ionic species. They have been widely functionalized for this purpose, but surprisingly with little attention paid to transition-metal cations. With this work, we completed some preliminary results of other groups [5] [6], covering the five possibilities that tetra-*p*-(*tert*-butyl)calix[4]arene offers at its lower rim, for the grafting of 2,2′-bipyridyl pendant arms. The synthetic tools developed for simpler heterocycles [4] have been, even slightly modified, confirmed. Our results open a wide-scope investigation field in multipurpose complexation studies by crossing different kinds of chelating or simply interacting pendant arms with other known or unknown calixarenes.

Our actual studies are devoted to the complexation properties of the described ligands and parent families towards other transition-metal species as well as those of the organic moiety of the corresponding complexes. At the same time, more detailed structural investigations are *en route* for **6–8**.

Experimental Part

General. All commercially available products were used without further purification, unless specified otherwise. TLC: Plates from *Macherey-Nagel* (SiO_2, *Polygram SIL G/UV254*, ref. 805021). Column chromatography: silica gel (*Merck 7734*, 70–230 mesh).

M.p. *Electrothermal-9100* capillary apparatus; uncorrected. UV Spectra: *Perkin-Elmer-Lambda-2* UV/VIS apparatus; λ_{max} in nm, ε in $mol^{-1}lcm^{-1}$. IR Spectra: *Mattson-5000-FT* apparatus; region 4000–200 cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker-AM-300* (300 MHz) and *Bruker-AC-200* (50.3 MHz) spectrometer; $SiMe_4$ as internal standard, chemical shifts in ppm, *J* in Hz. Mass spectra (MS): electrospray (ES) or fast-atom-bombardment (FAB; positive mode) MS were recorded at the Service Central d'Analyse du CNRS, Solaize. Elemental analyses were performed at the Service Central de Microanalyse, Ecole Supérieure de Chimie, Montpellier.

*5,11,17,23-Tetra(*tert*-butyl)-28-[(6-methyl-2,2′-bipyridyl-6′-yl)methoxy]calix[4]arene-25,26,27-triol*[1] (**1**). Calixarene **A** (0.5 g, 0.675 mmol) and $NaHCO_3$ (0.06 g, 0.675 mmol) were mixed in refluxing MeCN (50 ml) under N_2 during 0.5 h. A soln. of monobromide **B** (0.177 g, 0.675 mmol) in MeCN (20 ml) was added dropwise and reflux continued for 24 h (TLC monitoring (Al_2O_3, $CHCl_2$/hexane 4:1)). After evaporation, the residue was dissolved in CH_2Cl_2 (100 ml), the resulting suspension washed with H_2O (20 ml; removal of residual minerals), the org. phase dried (Na_2SO_4) and evaporated, and the residue chromatographed (SiO_2, MeOH/CH_2Cl_2 1:99→2:98): mixture of **1** and **2** (as traces). Pure **1** was obtained by prep. TLC (SiO_2, CH_2Cl_2/MeOH 99:1): 0.25 g (45%). M.p. 159–160°. UV ($CHCl_3$): 288 (21900), 305 (sh, 8700). ^1H-NMR ($CDCl_3$): 1.20 (*s*, 2 *t*-Bu); 1.21 (*s*, 2 *t*-Bu); 2.63 (*s*, *Me*-bpy); 3.40, 4.21 (‘*q*’, *AB*, J_{AB} = 13.8, 2 Ar–CH_2–Ar); 3.425, 4.48 (‘*q*’, *AB*, J_{AB} = 13, 2 Ar–CH_2–Ar); 5.35 (*s*, OCH_2-bpy); 6.96 (*d*, *J* = 2.3, 2 H, Ar); 7.03 (*s*, 2 H, Ar); 7.06 (*d*, *J* = 2.3, 2 H, Ar); 7.12 (*s*, 2 H, Ar); 7.16 (*s*, 1 H, bpy); 7.65 (*t*, *J* = 7.8, 1 H, bpy); 7.88 (*dd*, *J* = 6.6, 0.5, 1 H, bpy); 7.99 (*t*, *J* = 7.7, 1 H, bpy); 8.30 (*d*, *J* = 7.7, 1 H, bpy); 8.48 (*dd*, *J* = 7.0, 0.7, 1 H, bpy); 9.40 (*s*, 2 OH); 10.08 (*s*, OH). ^1H-NMR (CD_3CN): 1.16 (*s*, *t*-Bu); 1.18 (*s*, 2 *t*-Bu); 1.20 (*s*, *t*-Bu); 2.59 (*s*, *Me*–bpy); 3.39, 4.01 (‘*q*’, *AB*, J_{AB} = 13.4, 2 Ar–CH_2–Ar); 3.50, 4.47 (‘*q*’, *AB*, J_{AB} = 12.8, 2 Ar–CH_2–Ar); 5.31 (*s*, OCH_2–bpy); 7.12–7.28 (*m*, 8 H of Ar, 1 H of bpy); 7.34 (*s*, OH); 7.70–7.79 (*d* + *t*, 2 H, bpy);

8.06 (*t*, *J* = 7.8, 1 H, bpy); 8.44 (*d*, *J* = 7.8, 1 H, bpy); 8.51 (*d*, *J* = 7.6, 1 H, bpy); 8.89 (br. *s*, 2 OH). ^{13}C-NMR ($CDCl_3$): 24.6 (*Me*–bpy); 31.2 (*Me*$_3$C); 31.25 (*Me*$_3$C); 31.5 (*Me*$_3$C); 32.30 (Ar–*C*H$_2$–Ar); 32.97 (Ar–*C*H$_2$–Ar); 33.88 (Me$_3$*C*); 33.97 (Me$_3$*C*); 34.24 (Me$_3$*C*); 79.5 (O*C*H$_2$–bpy); 118.5, 120.8, 122.6, 123.3 (CH, bpy); 125.60, 125.66, 126.5 (CH, Ar); 137.0, 138.0 (CH, bpy); 127.4, 128.0, 128.28, 133.54 (C$_o$, C$_p$, Ar); 142.9, 143.5, 147.7, 148.2, 148.5, 149.6 (C$_o$, C$_p$, Ar); 155.0, 155.3, 156.4, 157.8 (C(2), C(2′), C(6), C(6′) of bpy). ES-MS: 831.8 (*M*$^+$). Anal. calc. for $C_{56}H_{66}N_2O_4$ (831.16): C 80.83, H 8.00, N 3.37; found: C 80.97, H 8.40, N 3.69.

*5,11,17,23-Tetra(*tert*-butyl)-26,28-bis[(6-methyl-2,2′-bipyridyl-6′-yl)methoxy]calix[4]arene-25,27-diol*[1]) (**2**). As described for **1**, with **A** (0.50 g, 0.675 mmol), K_2CO_3 (0.186 g, 1.35 mmol), MeCN (50 ml), and **B** (0.355 g, 1.35 mmol). Column chromatography (Al_2O_3, CH_2Cl_2/hexane 1:1) gave **2** (0.41 g, 60%). White powder. M.p. 220–221°. UV ($CHCl_3$): 291 (38675), 305 (sh, 20280). ^{1}H-NMR ($CDCl_3$): 0.955 (*s*, 2 *t*-Bu); 1.30 (*s*, 2 *t*-Bu); 2.65 (*s*, 2 *Me*–bpy); 3.35, 4.38 (‘*q*’, *AB*, J_{AB} = 13.2, 4 Ar–C*H*$_2$–Ar); 5.26 (*s*, 2 OC*H*$_2$–bpy); 6.82 (*s*, 4 H, Ar); 7.08 (*s*, 4 H, Ar); 7.15 (*d*, *J* = 7.5, 2 H, bpy); 7.37 (*s*, 2 OH); 7.61–7.74 (*d* + *t*, 4 H, bpy); 8.17–8.24 (*d* + *t*, 4 H, bpy); 8.35 (*d*, *J* = 7.7, 2 H, bpy). ^{13}C-NMR ($CDCl_3$): 24.63 (*Me*–bpy); 30.97 (*Me*$_3$C); 31.61 (Ar–*C*H$_2$–Ar); 31.7 (*Me*$_3$C); 33.8, 33.9 (Me$_3$*C*); 78.4 (O*C*H$_2$-bpy); 118.2, 119.9, 121.0, 123.2 (CH, bpy); 125.0, 125.6 (CH, Ar); 136.9, 138.0 (CH, bpy); 127.7, 132.4 (C$_o$, C$_p$, Ar); 141.5, 147.1, 149.6, 150.7 (C$_o$, C$_p$, Ar); 155.5, 155.7, 155.8, 157.8 (C(2), C(2′), C(6), C(6′) of bpy). ES-MS: 1035.9 ([*M* + Na]$^+$), 1013.9 (*M*$^+$). Anal. calc. for $C_{68}H_{76}N_4O_4 \cdot 0.5\ H_2O$ (1022.39): C 79.85, H 7.59, N 5.56; found: C 79.85, H 7.59, N 5.48.

*5,11,17,23-Tetra(*tert*-butyl)-27,28-bis[(6-methyl-2,2′-bipyridyl-6′-yl)methoxy]calix[4]arene-25,26-diol*[1]) (**3**). Calixarene **A** (0.25 g, 0.34 mmol) and NaH (0.04 g, 1.66 mmol) were mixed in dry DMF (7 ml) under N_2. The mixture was stirred at r.t. during 2.5 h and solid **B** (0.2 g, 0.75 mmol) added before heating at 60°. After 1 h, the mixture was cooled and excess of NaH carefully hydrolyzed by addition of MeOH (0.5 ml) followed by H_2O (20 ml). The resulting precipitate was filtered off, rinsed with H_2O (20 ml), then dissolved in CH_2Cl_2 (50 ml). The soln. was washed with H_2O until pH 7.0 was reached. After concentration, MeOH was added and the precipitated **A** filtered off. Evaporation of the filtrate gave a raw material which was submitted to prep. TLC (SiO_2, CH_2Cl_2/MeOH 99:1 to 97:3): **3** (0.125 g, 36%). White powder. M.p. 135–136°. UV ($CHCl_3$): 290 (39700), 305 (sh, 14300). ^{1}H-NMR ($CDCl_3$): 1.15 (*s*, 2 *t*-Bu); 1.20 (*s*, 2 *t*-Bu); 2.61 (*s*, 2 *Me*–bpy); 3.27, 4.32 (‘*q*’, *AB*, J_{AB} = 13.4, 2 Ar–C*H*$_2$–Ar); 3.35–3.41 (two 1/2 *AB*, 4 H, Ar–C*H*$_2$–Ar); 4.23 (1/2 *AB*, J_{AB} = 13.6, 2 H, Ar–C*H*$_2$–Ar); 4.59 (1/2 *AB*, J_{AB} = 12.5, 2 H, Ar–C*H*$_2$–Ar); 4.98, 5.30 (‘*q*’, *AB*, J_{AB} = 12.4, 2 OC*H*$_2$–bpy); 6.95–7.14 (*m*, 10 H, Ar, bpy); 7.50–7.77 (*m*, 6 H, Ar, bpy); 8.15 (*d*, *J* = 7.8, 2 H, bpy); 8.29 (*d*, *J* = 7.3, 2 H, bpy); 9.16 (*s*, 2 OH). ^{1}H-NMR (CD_3CN): 1.19 (*s*, 2 *t*-Bu); 1.21 (*s*, 2 *t*-Bu); 2.55 (*s*, 2 *Me*–bpy); 3.33, 4.31 (‘*q*’, *AB*, J_{AB} = 12.7, 2 Ar–C*H*$_2$–Ar); 3.49, 4.58 (‘*q*’, *AB*, J_{AB} = 12.3, Ar–C*H*$_2$–Ar); 3.32, 4.18 (‘*q*’, *AB*, J_{AB} = 13, Ar–C*H*$_2$–Ar), 4.92, 5.21 (‘*q*’, *AB*, J_{AB} = 12, 2 OC*H*$_2$–bpy); 6.23–7.39 (*m*, 8 H of Ar, 2 H of bpy); 7.57 (*d*, *J* = 7.4, 2 H, bpy); 7.63–7.71 (4*t*, 4 H, bpy); 8.21 (*d*, *J* = 8, 2 H, bpy); 8.27 (*d*, *J* = 7.8, 2 H, bpy); 8.68 (*s*, 2 OH). ^{13}C-NMR ($CDCl_3$): 24.6 (*Me*–bpy); 31.3, 31.5 (*Me*$_3$C); 32.6 (Ar–*C*H$_2$–Ar); 33.8, 34.0 (Me$_3$*C*); 78.6 (O*C*H$_2$–bpy); 118.3, 120.2, 122.5, 123.2 (CH, bpy); 125.3, 126.0 (CH, Ar); 137.0, 137.7 (CH, bpy); 127.6, 128.6, 133.0, 133.9 (C$_o$, C$_p$, Ar); 142.2, 146.7, 149.2, 151.5 (C$_o$, C$_p$, Ar); 155.5, 155.8, 156.3, 157.8 (C(2), C(2′), C(6), C(6′) of bpy). FAB-MS: 1014.2 ([*M* + H]$^+$). Anal. calc. for $C_{68}H_{76}N_4O_4 \cdot 0.5\ H_2O$ (1013.39): C 80.59, H 7.56, N 5.53; found: C 80.16, H 7.69, N 5.40.

*5,11,17,23-Tetra(*tert*-butyl)-26,27,28-tris[(6-methyl-2,2′-bipyridyl-6′-yl)methoxy]calix[4]aren-25-ol*[1]) (**4**). A mixture of **3** (0.15 g, 0.15 mmol), **B** (0.04 g, 0.15 mmol), and Cs_2CO_3 (0.05 g, 0.15 mmol) in DMF (4 ml) was stirred at r.t. under N_2 during 10 min. The temp. was brought to 60°, and after 4 h, a little amount of **B** (0.01 g, 0.038 mmol) was added. The reaction was stopped 2 h later, and DMF was distilled off under reduced pressure to dryness. The residue was mixed with MeOH (3 ml) and added to H_2O (40 ml). The resulting precipitate was filtered off, dried *in vacuo*, and then submitted to prep. TLC (SiO_2, CH_2Cl_2/MeOH 95:5): **4** (0.1 g, 56%). White powder. M.p. 129–130°. UV ($CHCl_3$): 291 (50303), 305 (sh, 27270). ^{1}H-NMR ($CDCl_3$): 0.87 (*s*, 2 *t*-Bu); 1.33 (*s*, *t*-Bu); 1.36 (*s*, *t*-Bu); 2.57 (*s*, 2 *Me*-bpy); 2.60 (*s*, *Me*-bpy); 3.11, 4.35 (‘*q*’, *AB*, J_{AB} = 12.7, 2 Ar–C*H*$_2$–Ar); 3.23, 4.42 (‘*q*’, *AB*, J_{AB} = 13.4, 2 Ar–C*H*$_2$–Ar); 4.78, 4.87 (‘*q*’, *AB*, J_{AB} = 12, 2 OC*H*$_2$–bpy); 5.08 (*s*, OC*H*$_2$–bpy); 6.63 (*dd*, *J* = 13.8, 2, 4 H, Ar); 6.74 (*s*, OH); 7.07–7.11 (*m*, 2 H of Ar, 4 H of bpy); 7.18 (*s*, 2 H, Ar); 7.38 (2*d*, 2 H of bpy, H of bpy); 7.51–7.60 (3*t*, 6 H, bpy); 7.86 (*d*, *J* = 7.8, 1 H, bpy); 7.99–8.08 (2*d*, *J* = 7.6, 3 H, bpy); 8.15 (*d*, *J* = 8, 1 H, bpy); 8.21 (*d*, *J* = 7.7, 2 H, bpy). ^{13}C-NMR ($CDCl_3$): 24.60, 24.67 (*Me*–bpy); 30.9 (Ar–*C*H$_2$–Ar); 31.5 (*Me*$_3$C); 31.53 (Ar–*C*H$_2$–Ar); 31.73, 31.78 (*Me*$_3$C); 33.74, 33.85, 33.97 (Me$_3$*C*); 77.1, 78.5 (O*C*H$_2$–bpy); 117.8, 118.3, 119.2, 119.9, 122.5, 122.7, 123.0, 123.3, 123.8 (CH, bpy); 125.0, 125.6 (CH, Ar); 136.7, 136.9, 137.3 (CH, bpy); 128.4, 132.0, 132.6, 135.6, 141.2, 145.6, 145.8, 150.9, 151.0 (C$_o$, C$_p$, Ar); 155.3, 156.2, 157.5, 157.6 (C(2), C(2′), C(6), C(6′) of bpy). ES-MS: 1218 ([*M* + Na]$^+$), 1195.6 ([*M*]$^+$). Anal. calc. for $C_{80}H_{86}N_6O_4 \cdot H_2O$ (1213.63): C 79.17, H 7.31, N 6.92; found: C 79.29, H 7.53, N 6.77.

*5,11,17,23-Tetra(*tert*-butyl)-25,26,27,28-tetrakis[(6-methyl-2,2′-bipyridyl-6′-yl)methoxy]calix[4]arene*[1]) (**5**). A mixture of **A** (0.25 g, 0.38 mmol), NaH (0.1 g, 4 mmol), and dry DMF was stirred under N_2 at 70° during 0.5 h.

To the white cream thus obtained, **B** (0.4 g, 1.55 mmol) was added and heating continued for 18 h. After cooling, MeOH (2 ml) was added carefully and the resulting mixture poured in H_2O (100 ml). The clear brown precipitate was filtered off, washed with H_2O (10 ml), and then dried *in vacuo*. Dissolution in CH_2Cl_2 and addition of MeOH resulted in the precipitation of **A** which was filtered off. The filtrate was evaporated and the residue chromatographed (Al_2O_3, CH_2Cl_2) to give **5** contaminated with some 6'-methyl-2,2'-bipyridine-6-methanol. The latter was eliminated by precipitation in AcOEt. Evaporation of the AcOEt afforded **5** (0.23 g, 44%). White powder. M.p. > 350° (dec.). UV ($CHCl_3$): 291 (64000), 305 (sh, 34480). ^{1}H-NMR ($CDCl_3$): 1.09 (*s*, 4 *t*-Bu); 2.57 (*s*, 4 *Me*–bpy); 3.00, 4.39 ('*q*', *AB*, J_{AB} = 12.6, 4 Ar–CH_2–Ar); 5.11 (*s*, 4 OCH_2–bpy); 6.81 (*s*, 8 H, Ar); 7.06 (*d*, *J* = 6.9, 2 H, bpy); 7.39 (*t*, *J* = 7.8, 2 H, bpy); 7.50 (*t*, *J* = 7.8, 2 H, bpy); 7.59 (*d*, *J* = 7.2, 2 H, bpy); 7.95 (*d*, *J* = 7.8, 2 H, bpy); 8.16 (*d*, *J* = 7.5, 2 H, bpy). ^{13}C-NMR ($CDCl_3$): 24.6 (*Me*–bpy); 31.25 (Ar–*C*H_2–Ar); 31.46 (*Me*$_3$*C*); 33.9 (Me$_3$*C*); 77.9 (O*C*H_2–bpy); 118.24, 119.6, 113.0, 123.2 (CH, bpy); 125.2 (CH, Ar); 136.9, 137.1 (CH, bpy); 133.8 (C_o, C_p, Ar); 144.7 (C_o, C_p, Ar); 152.9, 155.2, 155.6, 157.5 (C(2), C(2'), C(6), C(6') of bpy). ES-MS: 1378.5 ([*M* + Na]$^+$). Anal. calc. for $C_{92}H_{96}N_8O_4$ (1377.84): C 80.20, H 7.02, N 8.13; found: C 80.25, H 7.05, N 7.95.

Copper(I) Complex **6** *of Ligand* **1**. A soln. of [Cu^I(MeCN)$_4$]PF$_6$ (0.022 g, 0.058 mmol) in MeCN (1 ml) was added under stirring to a mixture of **1** (0.1 g, 0.117 mmol) and MeCN (4 ml). The red-orange soln. was stirred under air during 5 min. After filtration through compressed cotton, the solvent was evaporated, the deep orange residue dissolved in Et_2O (5 ml), and hexane added. The resulting orange precipitate was then collected and dried *in vacuo*: **6** (0.092 g, 85%). M.p. 210° (dec.). UV ($CHCl_3$): 445 (3000), 316 (sh, 22450), 306 (sh, 29900), 290 (35700), 277 (sh, 3100), 272 (25400). ^{1}H-NMR (CD_3CN): 1.14 (*s*, 2 *t*-Bu); 1.16 (*s*, 6 *t*-Bu); 2.34 (*s*, 2 *Me*-bpy); 3.03 (br. '*d*', 1/2 *AB*, J_{AB} = 11.8, 4 H, Ar–CH_2–Ar); 3.38 (br. '*d*', *AB*, J_{AB} = 13.7, 4 H, Ar–CH_2–Ar); 3.60–4.10 (br. *m*, two 1/2 *AB*, 8 H, Ar–CH_2–Ar); 4.88 (*s*, 2 OCH_2–bpy); 7.12 (*m*, 16 H of Ar, 2 OH); 7.49 (*d*, *J* = 7.7, 2 H, bpy); 7.99 (*t*, *J* = 7.7, 2 H, bpy); 8.21 (*d*, *J* = 7.8, 2 H, bpy); 8.40 (*m*, 6 H, bpy); 8.60 (br. *s*, 4 OH). FAB-MS: 1725.0 ([**1** – Cu^I – **1**]$^+$), 893.3 ([**1** – Cu^I]$^+$). ES-MS: 1725.1 ([**1** – Cu^I – **1**]$^+$), 894.3 ([**1** – Cu^I]$^+$), 832.0 ([**1** + H]$^+$). Anal. calc. for $C_{112}H_{132}CuF_6N_4O_8P$ (1870.85): C 71.90, H 7.11, N 2.99; found: C 71.75, H 7.27, N 3.25.

Copper(I) Complex **7** *of Ligand* **2**. As described for **6**, with [Cu^I(Me$_3$CN)$_4$]PF$_6$ (0.022 g, 0.058 mmol), MeCN (1 ml), **2** (0.06 g, 0.059 mmol), and MeCN (3 ml; 10 min). The orange solid, dried *in vacuo*, was dissolved in MeCN (5 ml) and the soln. added to an excess of Et_2O (20 ml). The resulting precipitate was collected, air-dried, then triturated in Et_2O, filtered again, and dried *in vacuo*: **7** (0.062 g, 97%). M.p. 257° (dec.). UV ($CHCl_3$): 449 (4800), 302.4 (32200), 270 (22900). ^{1}H-NMR (CD_3CN): 0.94 (br. *s*, 2 *t*-Bu); 1.19 (br. *s*, 2 *t*-Bu); 2.22 (br. *s*, 2 *Me*–bpy); 2.50–4.00 (br. *m*, 4 Ar–CH_2–Ar); 4.81 (br. *m*, 2 OCH_2–bpy); 6.40–9.00 (br. *m*, 8 H of Ar, 12 H of bpy, 2 H of OH). ES-MS: 1076.6 ([**2** – Cu^I]$^+$). Anal. calc. for $C_{68}H_{74}CuF_6N_4O_4P$ (1221.90): C 66.84, H 6.27, N 4.58; found: C 66.59, H 6.39, N 4.68.

Copper(I) Complex **8** *of Ligand* **3**. As described for **7** (same quantities). The resulting precipitate was subjected to column chromatography (Al_2O_3, CH_2Cl_2/MeCN 95:5): **8** (0.045 g, 62%). Orange powder. M.p. 240° (dec.). UV ($CHCl_3$): 452 (5600), 302 (33300), 270 (22900). ^{1}H-NMR (CD_3CN): 1.13 (*s*, *t*-Bu); 1.17 (*s*, 3 *t*-Bu); 2.05 (br. *s*, MeCN, *Me*–bpy); 2.24 (1/2 *AB*, J_{AB} = 12, 1 H, Ar–CH_2–Ar); 3.27 (1/2 *AB*, J_{AB} = 13.1, 1 H, Ar–CH_2–Ar); 3.52 (br. 1/2 *AB*, J_{AB} = 24, 2 H, Ar–CH_2–Ar); 3.80 (1/2 *AB*, J_{AB} = 12, 1 H, Ar–CH_2–Ar); 3.97 (1/2 *AB*, 1 H, Ar–CH_2–Ar); 4.34 (br. 1/2 *AB*, J_{AB} = 20, 2 H, Ar–CH_2–Ar); 4.90, 5.40 (br. *AB*, J_{AB} = 40, 2 OCH_2–bpy); 7.08 (br. *s*, 3 H, Ar); 7.21 (*d*, 5 H, Ar); 7.49 (*d*, *J* = 7.5, 3 H, bpy); 7.91 (br. *m*, 2 H, bpy); 8.07 (br. *t*, 3 H, bpy); 8.20–8.50 (br. *m*, 4 H of bpy, 2 OH). ES-MS: 1076.6 ([**3** – Cu^I]$^+$). Anal. calc. for $C_{68}H_{74}CuF_6N_4O_4P \cdot H_2O$ (1239.91): C 65.87, H 6.34, N 4.51; found: C 65.81, H 6.34, N 4.57.

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