New chromogenic azocalix[4]arene podands incorporating 2,2′-bipyridyl subunits†

Farhana Oueslati, Isabelle Dumazet-Bonnamour and Roger Lamartine

Laboratoire de Chimie Industrielle, UMR CNRS 5078, 43 Bd. Du 11 novembre 1918, 69622, Villeurbanne Cedex, France. E-mail: i.bonnamour@cdlyon.univ-lyon1.fr; Fax: 04 7244 8438; Tel: 04 7244 8014

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Six new calix[4]arenes **2**, **3** and **4** functionalized with 2,2′-bipyridyl and azophenyl groups at the lower rim and the upper rim respectively have been synthesized and their complexing properties towards Zn^{2+} have been determined by UV-Vis titrations in organic media. The conformational properties of these ligands were obtained by ^1H NMR spectroscopy. The stoichiometries of zinc complexes were determined by both the mole ratio method and Job plots. A stoichiometry of 1:1 was found for the complexes Zn-**2** and Zn-**3** and 1:2 for the complex Zn-**4** as a function of the number of grafted bipyridyl groups. The association constants for 1:1 complexes were determined by using the Benesi–Hildebrand plot and also by linear regression analysis.

Introduction

In recent years, there has been growing interest in developing chemical sensors and systems that can exhibit colour changes due to ionic or molecular interactions. In this field, chromoionophore calixarenes have received considerable attention because of their potential for the synthesis of highly efficient and selective receptors.[1–3] Among these studies azo phenyl groups are one of the most frequently employed functions as a signalling device for the design of chromogenic compound.[4] We have recently reported the synthesis of pre-organised azocalixarene–dithiazolyl podands for the development of a new class of chromoionophore sensors.[5] In order to extend our investigations, we have decided to incorporate other heterocyclic chelating agents such as 2,2′-bipyridyl group at the lower rim of azocalix[4]arene. The synthesis and study of the complexation properties of various podands incorporating 2,2′-bipyridyl chelating groups at the lower rim of the *p-tert*-butylcalix[4]arene platform[6–8] show that these groups are good candidates for the selective binding[9,10] and extraction of metal ions.[11] This led us to present here the synthesis of six new chromogenic ionophore calixarenes **2a**, **2b**, **3a**, **3b**, **4a**, and **4b** (Scheme 1) which incorporate the 2,2′-bipyridyl moiety as a metal binding site and the azophenol moiety as a coloration site. A study of complexation efficiency of these new receptors towards Zn(II) has been investigated in solution by UV-Vis spectrophotometric titration to determine both the stoichiometries and the stability constant values of the complex species.

Results and discussion

Synthesis and characterization

The diazo-coupling reaction of calix[4]arene with substituted diazonium BF_4 salts produced as described in the literature the *p*-tetrakis(phenylazo)- and *p*-tetrakis(nitrophenylazo)-substituted calix[4]arenes[12] **1a** and **1b** respectively in cone conformation. The 6-bromomethyl-6′-methyl-2,2′-bipyridyl[13] subunits were grafted on the lower rim of the azocalixarene platform according to our previous report[5] by *O*-alkylation.[14–17] The bases were chosen *versus* their ability to selectively deprotonate one or more phenolic OH groups.[1,18] The reactions of **1a** and **1b** with 6-bromomethyl-6′-methyl-2,2′-bipyridine in anhydrous CH_3CN, in the presence of $KHCO_3$ and K_2CO_3, afforded respectively ligands **2a** and **2b** (31%, 23% yield). The use of $KHCO_3$ with **1b** gave essentially the starting azocalix[4]arene with a small amount of **2b** that we could not isolate. That is why we have chosen K_2CO_3 as the base, which gave selectively **2b**. ^1H NMR confirmed the cone conformation of these two podands with the presence of two AB systems for the bridging CH_2 groups according to the literature.[14] Reaction of **1a** with BaO, $Ba(OH)_2{\cdot}8H_2O$ and 6-bromomethyl-6′-methyl-2,2′-bipyridine in anhydrous DMF resulted in the formation of ligand **3a** (48% yield). The same reaction with **1b** gave **3b** (38% yield).The structures of **3a** and **3b** were analysed by ^1H and ^{13}C NMR spectroscopy. Their ^1H NMR spectra show a characteristic one single AB system for the bridging methylene groups, a singlet for the OCH_2-bpy moieties. The signals for the bridging methylene groups appear at $\delta = 32.06$ and 32.64 ppm respectively in the ^{13}C NMR spectra. These results show that we have a 1,3-distal substitution of the calix[4]arene and clearly indicate a cone conformation. Moreover, the reactions of **1a** and **1b** with Cs_2CO_3 in dry acetone gave compounds **4a** and **4b** both in a 1,3-alternate conformation in solution at room temperature. The presence of Cs^+ permits the formation of a 1,3-alternate conformation in accordance with the literature.[19] This is proved by the presence of only one singlet for $ArCH_2Ar$ groups, $\delta = 4.09$ ppm for **4a** and 4.66 ppm for **4b**, in the ^1H NMR spectra and one signal for the corresponding carbons, at $\delta = 37.43$ and 37.82 ppm respectively, in the ^{13}C NMR spectra.[20,21] Different bases such as NaH and K_2CO_3 were tested to try and prepare **4** in cone conformation.[22] But in each case we obtained a mixture of mono-, di-, tri- and tetrasubstituted species from which these compounds could not be isolated. Only Cs_2CO_3 gave selectively tetra-substituted compounds in good yield in a 1,3-alternate conformation.

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† Electronic supplementary information (ESI) available: mole ratio plot for mixtures of **4a** and $Zn(CF_3SO_3)_2$; UV-Vis spectra for **4a** (5×10^{-6} mol l^{-1}) when Zn^{2+} (5×10^{-5} mol l^{-1}) is added to the CH_2Cl_2 host solution. See http://www.rsc.org/suppdata/nj/b2/b209528a/

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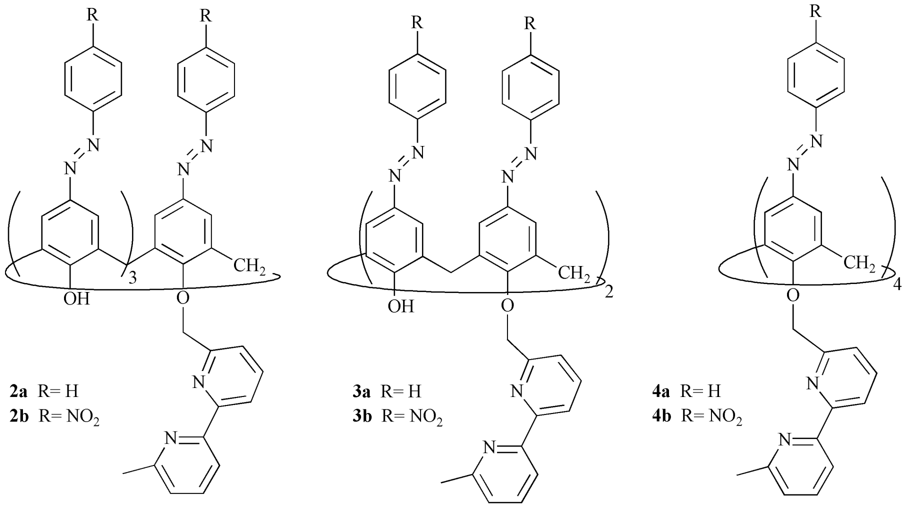
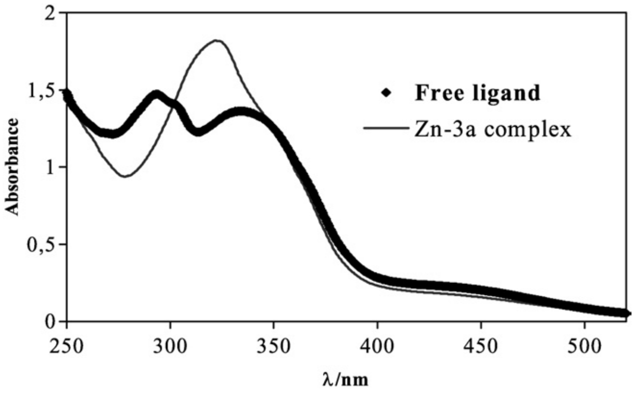


Scheme 1 Azocalix[4]arenes incorporating 2,2′-bipyridyl units.

Spectrophotometric titration

Complexation properties of these podands were tested with various kinds of transition-metal cations. The best preliminary results were obtained with zinc(II). We chose $ZnCl_2$ for the complexation of **2a** and **2b** in order to achieve intramolecular complexation with the formation of a mononuclear complex. Moreover, we know that zinc(II) adopts a tetrahedral geometry with 6,6′-methyl-2,2′-bipyridyl[23] and that $ZnCl_2$ should be coordinated to one bipyridyl unit and two chloride ions.[9] With the aim of preparing a mononuclear zinc(II) complex, we changed the chloride ion to the non-coordinating trifluoromethanesulfonate ion for the ligands **3a**, **3b**, **4a** and **4b**. The UV spectra of these podands show two absorption bands, due to the absorption of bipyridine–calixarene around 290 nm with a shoulder around 305 nm and of phenylazo groups at around 330 nm. The modifications of the absorption spectrum upon gradual addition of $ZnCl_2$ for **2** and $Zn(CF_3SO_3)_2$ for **3** and **4** were used to monitor the metal complexation equilibrium. Upon addition of Zn solutions, the UV-Vis ligand spectrum undergoes clean changes that indicate the formation of at least one metal complex species. The addition of aliquots of Zn^{2+} (from 0.1 to 1 equiv.) to a solution of **3a** leads to the apparition of a new absorption band centred at 322 nm (Scheme 2). The same results were obtained with compounds **2a**, **2b**, **3b**. Moreover in the titrations of **2a**, **2b**, **3a** and **3b** with Zn^{2+}, isosbestic points were observed and indicate the existence of new species. For compounds **4a** and **4b**, we observed the same results: the new centred absorption bands appeared at 322.5 and 322 nm respectively when aliquots of Zn^{2+} are added (from 0.1 to 2 equiv.) confirming the formation of a dinuclear complex.



Scheme 2 UV-Vis spectra for compound **3a** (5×10^{-5} mol l^{-1}) when Zn^{2+} (5×10^{-4} mol l^{-1}) is added to the CH_2Cl_2 host solution.

The stoichiometries of the complexes between the metal salt and the ligand were determined by the Job plot[24] and the mole ratio[25] methods. These two methods were used for ligand **3a** to confirm that they gave the same results. Thus we have found the formation of 1:1 Zn-**2a**, Zn-**2b**, Zn-**3a,** Zn-**3b** complexes. In the case of **3a**, the Job plot was obtained from UV measurements at 322 nm for mixtures of **3a** and Zn^{2+} salt at constant total concentrations (5×10^{-5} M) (Scheme 3). A stoichiometry of 2:1 was found for Zn-**4a** and Zn-**4b** complexes in CH_2Cl_2. The stoichiometry of these complexes indicates that the metal ions are coordinated by the heteroaromatic nitrogen donor groups of bipyridine.[9,23]

The stability constants, log K_{11}, were extracted from the Benesi–Hildebrand plots.[26,27] The data are given in Table 1. Log K values of 4.10, 3.94, 5.24 and 4.38 for **2a**, **2b**, **3a** and **3b** respectively, show that the complexation of Zn^{2+} by these podands is highly favoured, thus indicating the good efficiency of these ligands toward the target ions.[28,29] Moreover the stability of **2b** and **3b** complexes is lower than **2a** and **3a**. These differences are probably due to the presence of the nitrophenol azo groups on the macrocycle which form less stable Zn(II) complexes.

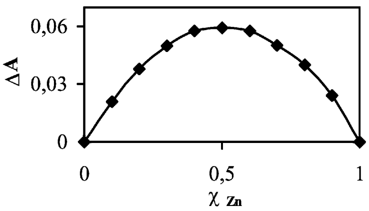
The azocalix[4]arenes incorporating bipyridine undergo naked-eye detectable changes in colour for **3a** and **4a**: from pale yellow to bright yellow in the case of Zn-**4a** complex and light yellow for Zn-**3a** complex in the presence of Zn^{2+} in CH_2Cl_2.

Finally, we have developed a new type of chromogenic sensors towards Zn^{2+}. These preliminary complexation studies will be completed with other metals.

Experimental

General

Solvents were purified and dried by standard methods prior to use. All reactions were carried out under nitrogen. Column



Scheme 3 Job plot for mixtures of **3a** and $Zn(CF_3SO_3)_2$.

Table 1 The UV-Vis properties of the podand upon addition of Zn solutions

Ligands	λ_{max}/nm of the new ligand	λ/nm of the isobestic points	Log K_{11}
2a	321	303	4.10
2b	320	304	3.94
3a	322	302	5.24
3b	319	303	4.38

chromatography was performed with silica gel 60 (0.040–0.063 mm) from Merck. Melting points were recorded on an Electrothermal 9100 capillary apparatus and were uncorrected. UV measurements were recorded on a Shimadzu UV-2401 PC spectrophotometer, λ_{max} in nm. Infrared were performed on a Mattson 5000 FT apparatus (ν in cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 300 (300.13 and 75 MHz), (chemical shifts in ppm, J in Hertz). Mass spectra were obtained by the electrospray technique (positive mode).

5,11,17,23-Tetra(azophenyl)-25-mono[(6-(6′-methyl-2,2′-bipyridyl)yl)methoxy]-26,27,28-trihydroxycalix[4]arene (2a). 1a (0.25 g, 0.297 mmol) and $KHCO_3$ (0.05 g, 0.594 mmol) were stirred in refluxing CH_3CN (25 ml) under nitrogen for 1 hour. A solution of 6-bromomethyl-6′-methyl-2,2′-bipyridine (0.156 g, 0.594 mmol) in CH_3CN (6 ml) was added dropwise and reflux continued for 28 hours. After evaporation to dryness, the residue was dissolved in CH_2Cl_2 (50 ml) and extracted with water (2 × 20 ml). The organic phase was dried over Na_2SO_4 and removed by evaporation. The product was purified by column chromatography on silica gel (CH_2Cl_2/MeOH; 97/3) to give red powder (0.0975 g, 32%). Mp: 239–241 °C. ^1H NMR ($(CD_3)_2CO$): 2.33 (s, 3H, CH_3–bpy); 3.72, 4,22 (‘q’, AB, J_{AB} = 13.5, 4H, Ar–CH_2–Ar); 3.72, 4.54 (‘q’, AB, J_{AB} = 13, 4H, Ar–CH_2–Ar); 5.26 (s, 2H, O–CH_2–bpy), 7.04 (m, 4H, H–Ar); 7.18–7.25 (m, 12H, H–Ar(azo)); 7.35 (m, 2H, H–bpy); 7.45 (t, 2H, H–bpy); 7.51 (s, 2H, H–Ar); 7.65 (m, 8H, H–Ar(azo)); 7.70 (s, 2H, OH); 7.73 (m, 2H, H–bpy); 7.85 (s, 2H, H–Ar); 8.45 (s, 1H, OH). ^{13}C NMR (C_5D_5N): 25.12 (CH_3–bpy); 30.66, 32.21 (Ar–CH_2–Ar); 74.13 (OCH_2–bpy); 117.50, 120.04, 122.95, 123.17, 129.27, 130.0 (C(H)–bpy); 123.34, 124.00, 123.32, 125.12, 125.28, 134.37, 135.35, 136.00, 147.30, 149.69, 150.40, 152.87, 153.46 (C–Ar); 153.52, 154.85, 160.67, 162.77 (C–bpy). ES-MS m/z: 1023.2 $[M+H]^+$ (calcd. 1023.3).UV: 286 (15 000); 346 (10 952). IR: 3338 (OH), 3059 (C–H), 1471.5, 1439.6, 1392.4 (C=C, N=N), 1572 (C=N).

5,11,17,23-Tetra(azonitrophenyl)-25-mono[(6-(6′-methyl-2,2′-bipyridul)yl)methoxy]-26,27,28-trihydroxycalix[4]arene (2b). 1b (0.30 g, 0.293 mmol) and K_2CO_3 (0.081 g, 0.586 mmol) were stirred in refluxing acetone (20 ml) under nitrogen for 1 hour. A solution of 6-bromomethyl-6′-methyl-2,2′-bipyridine (0.154 g, 0.586 mmol) in acetone (10 ml) was added dropwise and reflux continued for 48 hours. After evaporation to dryness, the residue was dissolved in CH_2Cl_2 (50 ml) and extracted with water (2 × 20 ml). The organic phase was dried over Na_2SO_4 and removed by evaporation. The product was purified by column chromatography on silica gel (AcOEt/n-hexane; 60/40) to give red powder (0.069 g, 19.5%). Mp: 235–236 °C. ^1H NMR ($CDCl_3$): 2.51 (s, 3H, CH_3–bpy); 4.04, 4.89 (‘q’, AB, J_{AB} = 13.1, 4H, Ar–CH_2–Ar); 4.94, 5.01 (‘q’, AB, J_{AB} = 13, 4H, Ar–CH_2–Ar); 5.09 (s, 2H, O–CH_2–bpy); 6.45 (d, J = 7.7, 2H, H–bpy); 6.49 (s, 2H, H–Ar); 6.90 (t, J = 7.7, 2H, H–bpy); 7.19–7.25 (m, 16H, H–Ar(azo)); 7.43 (m, 6H, H–Ar); 7.51 (m, 2H, H–bpy). ^{13}C NMR (C_5D_5N): 25.06 (CH_3–bpy); 32.09 (Ar–CH_2–Ar); 73.86 (OCH_2–bpy); 122.67, 122.80, 124.93, 125.00 (C(H)–bpy); 129.24, 129.57, 129.66, 130.22, 130.80, 146.21, 149.80, 150.16 (C–Ar); 153.36, 157.76, 159.72, 168.86 (C–bpy). ES-MS m/z: 1203.3 $[M+H]^+$ (calcd. 1203.2). UV: 284 (16 400); 341 (11 200). IR: 3351.6 (OH), 3100 (C–H), 1472.7, 1445.9, 1409.9 (C=C, N=N), 1591 (C=N)

5,11,17,23-Tetra(azophenyl)-25,27-di[(6-(6′-methyl-2,2′-bipyridyl)yl)methoxy]-26,28-dihydroxycalix[4]arene (3a). 1a (0.350 g, 0.416 mmol), $Ba(OH)_2 \cdot 8H_2O$ (0.391 g, 1.248 mmol) and BaO (0.190 g, 1.248 mmol) were mixed in dry DMF (25 ml) under nitrogen for 5 hours at room temperature. After addition of 6-bromomethyl-6′-methyl-2,2′-bipyridine (0.328 g, 1.248 mmol), the mixture was stirred at room temperature for 48 hours. Then water (40 ml) was added to this solution and the resulting precipitate was filtered off, washed with water (20 ml) and then dissolved in CH_2Cl_2. The residue was extracted with water and dried over Na_2SO_4. The product was recrystallised with CH_2Cl_2/MeOH (98/2) affording an orange powder (0.24 g, 48%). Mp: 243–244 °C. ^1H NMR ($CDCl_3$): 2.50 (s, 6H, CH_3–bpy); 3.67, 4.56 (‘q’, AB, J_{AB} = 13.2, 8H, Ar–CH_2–Ar); 5.21 (s, 4H, OCH_2–bpy); 7.01 (d, J = 7.7, 2H, H–bpy); 7.18 (m, 4H, H–Ar); 7.25 (d, J = 7.8, 2H, H–bpy); 7.34 (t, J = 7.8, 2H, H–bpy), 7.55 (m, 12H, H–Ar(azo)); 7.68 (m, 2H, H–bpy); 7.81 (d, J = 8.6, 8H, H–Ar(azo)); 8.14 (d, J = 7.7, 2H, H–bpy); 8.35 (d, J = 7.6, 2H, H–bpy); 8.64 (s, 4H, H–Ar). ^{13}C NMR ($CDCl_3$): 25.09 (CH_3–bpy); 32.06 (Ar–CH_2–Ar); 79.37 (OCH_2–bpy); 118.73, 121.73, 122.86, 123.11, 137.43, 138.53 (C(H)–bpy); 123.87, 124.86, 128.17, 129.28, 129.44 (C–H, Ar); 133.86, 146.30, 150.42, 152.90, 153.39, 154.67, 155.52 (C–Ar); 155.76, 156.70, 157.12, 158.35 (C–bpy). ES-MS m/z: 1205.3 $[M+H]^+$ (calcd. 1205.4), 1227.3 $[M+Na]^+$ (calcd. 1227.4).UV: 294 (29 450), 335 (27 244). IR: 3361.7 (stretching, OH), 3103.8 (C–H), 1508.1, 1472.4, 1445.9, 1408.8 (C=C, N=N), 1591.7 (C=N).

5,11,17,23-Tetra(azonitrophenyl)-25,27-di[(6-(6′-methyl-2,2′-bipyridyl)yl)methoxy]-26,28-dihydroxycalix[4]arene (3b). As described for **3a**, with **1b** (0.15 g, 0.147 mmol), $Ba(OH)_2 \cdot 8H_2O$ O (0.138 g, 0.441 mmol), BaO (0.067 g, 0.441 mmol) and 6-bromomethyl-6′-methyl-2,2′-bipyridine (0.19 g, 0.73 mmol) in dry DMF (10 ml) under nitrogen for 48 hours at room temperature. Column chromatography (SiO_2; CH_2Cl_2/MeOH 98/2) gave an orange powder (0.078 g, 38%). Mp: 254–255 °C. ^1H NMR (CD_2Cl_2): 2.33 (s, 6H, CH_3–bpy); 3.85, 4.59 (‘q’, AB, J_{AB} = 13.5, 8H, Ar–CH_2–Ar); 5.33 (s, 4H, OCH_2–bpy); 7.16 (s, 4H, H–Ar); 7.65–7.74 (m, 4H, H–bpy); 7.91 (d, J = 9, 8H, H–Ar(azo)); 8.00 (s, 4H, H–Ar); 8.12 (d, J = 9, 8H, H–Ar(azo)); 8.28 (d, J = 7.1, 2H, H–bpy); 8.48 (d, J = 7.1, 2H, H–bpy); 8.52 (m, 4H, H–bpy). ^{13}C NMR (C_5D_5N): 23.10 (CH_3–bpy); 32.64 (Ar–CH_2–Ar); 73.63 (OCH_2–bpy); 116.91, 120.85, 122.74, 122.86, 128.91, 128.97 (C(H)–bpy); 122.97, 123.30, 123.63, 123.95, 124.57, 124.84, 129.10, 130.09, 134.97, 135.63, 149.69, 150.05 (C–Ar); 152.66, 153.11, 157.52, 167.79 (C–bpy). ES-MS m/z: 1385.2 $[M+H]^+$ (calcd. 1385.4). UV: 280 (48 100); 362 (42 080). IR: 3355.7 (stretching, OH), 3050 (C–H), 1508.5, 1472.3, 1409, 1373.4 (N=N), 1591.8 (C=N).

5,11,17,23-Tetra(azophenyl)-25,26,27,28-tetra[(6-(6′-methyl-2,2′-bipyridyl)yl)methoxy]calix[4]arene (4a). 1a (0.110 g, 0.131 mmol) and Cs_2CO_3 (0.426 g, 1.31 mmol) in acetone (30 ml) was stirred under nitrogen at 60 °C. 6′-Bromomethyl-6′-methyl-2,2′-bipyridine (0.20 g, 0.786 mmol) was added after 1 hour. The reaction was cooled to room temperature after 2 days. The solvent was removed and the residue was dissolved in CH_2Cl_2 and the resulting precipitate was filtered off on Celite®. The filtrate was concentrated by evaporation. Then MeOH was added to the residue and the precipitate was filtered off, affording a red powder (0.085 g, 41%). Mp: 256–257 °C. ^1H NMR ($CDCl_3$): 2.41 (s, 12H, CH_3–bpy); 4.09

(s, 8H, Ar–CH_2–Ar); 5.15 (s, 8H, OCH_2–bpy); 6.89 (m, 6H, H–bpy); 7.37–7.53 (m, 12H, H–Ar(azo)); 7.58 (s, 8H, H–Ar); 7.063 (m, 4H, H–bpy); 7.74 (m, 4H, H–bpy); 7.81 (m, 4H, H–bpy), 7.84–7.93 (m, 8H, H–Ar(azo)); 8.15 (t, 2H, H–bpy); 8.22–8.38 (m, 4H, H–bpy). ^{13}C NMR ($CDCl_3$): 22.39 (CH_3–bpy); 37.43 (Ar–CH_2–Ar); 79.78 (OCH_2–bpy); 124.53, 125.31, 128.39, 128.53 (C(H)–bpy); 126.07, 126.65, 126.75, 128.21, 128.26, 129.52, 130.27, 131.93 (C–Ar); 132.56, 132.73, 134.83, 135.19 (C–bpy). ES-MS m/z: 1570.7 $[M+H]^+$ (calcd. 1570.8). UV: 286 (159 200); 302 (shoulder 129 320); 334 (111 080). IR: 3058.2 (C–H), 1469.1, 1440.7 (N=N, C=C). 1583.6 (C=N).

5,11,17,23-Tetra(azonitrophenyl)-25,26,27,28-tetra[(6-(6′-methyl-2,2′-bipyridyl)yl)methoxy]calix[4]arene (4b). 1b (0.120 g, 0.117 mmol), 6-bromomethyl-6′-methyl-2,2′-bipyridine (0.24 g, 0.936 mmol) and Cs_2CO_3 (0.38 g, 1.17 mmol) in refluxing acetone (20 ml), 36 h. Purification: column chromatography (SiO_2, AcOEt/n-hexane, 7/3) affording an orange powder (0.037 g, 17%). Mp: 256–258 °C. ^1H NMR (DMSO): 2.63 (s, 12H, CH_3-bpy); 4.80 (s, 8H, Ar–CH_2–Ar); 5.35 (s, 8H, OCH_2–bpy); 7.22 (d, $J = 7.3$, 4H, H–bpy); 7.30 (d, $J = 7.4$, 4H, H–bpy); 7.61–7.65 (m, 16H, H–Ar(azo)); 7.76 (s, 8H, H–Ar); 7.81–7.86 (m, 8H, H–bpy); 8.24 (d, $J = 7.3$, 4H, H–bpy); 8.36 (d, $J = 7.3$, 4H, H–bpy). ^{13}C NMR (C_5D_5N): 23.05 (CH_3–bpy); 37.82 (Ar–CH_2–Ar); 69.06 (OCH_2–bpy); 98.35, 100.90, 106.75, 116.28 (C(H)–bpy); 119.58, 123.69, 129.15, 130.48, 135.66, 149.09, 150.02, 153.43 (C–Ar); 153.67, 154.50, 159.12, 161.55 (C–bpy). ES-MS m/z: 1750.5 $[M^+ + H]$ (calcd. 1750.6). UV: 285 (165 800); 300 (shoulder, 154 000); 333 (162 000). IR: 3105.4 (C–H); 1514.2, 1448.5 (C=C, N=N); 1581.8 (C=N).

Spectrocopic measurements

The UV-Vis tritrations were carried out at 25 °C in CH_2Cl_2 using a Shimadzu UV-2401 PC spectrophotometer. Titrations were performed in a spectrophotometric cell: typically, to record a spectrum, the reagent was delivered by a precision syringe (Halminton, 50 μl) and the solution allowed to equilibrate for two minutes. Usually a 5×10^{-5} mol l^{-1} solution of metal cation was added to a 5×10^{-6} mol l^{-1} solution (1 ml) of compounds **2** and **4**. In the case of compounds **3**, a 5×10^{-4} mol l^{-1} solution of metal cation was added to a 5×10^{-5} mol l^{-1} solution of host. The spectrophotometric data were collected over the range 220–600 nm for all the podands investigated.

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