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# Synthesis and electrochemical properties of cavitands functionalized with 4,4′-bipyridinium units

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**Abstract**—Four new brominated resorcinarene cavitand derivatives (**3**–**6**) and the already known tetrakis(bromomethyl)cavitand **2** have been synthesized, starting from the tetramethylcavitand **1**. These brominated cavitands constitute excellent building blocks for the covalent assembly of new structures containing one (**8**), two (**9** and **10**), three (**11**) and four (**7**) monoquaternized bipyridine units attached to the upper rim of the cavitand bowl. The free terminal nitrogens in these structures can be methylated to yield compounds with one to four 4,4′-bipyridinium (viologen) units attached to the cavitand (**12**–**16**), or treated with monobromocavitand **3** to produce oligomeric structures containing from two to five cavitand units connected by viologen residues (**17**–**21**). Compounds **8**–**16**, **18** and **20** show the electrochemical reactivity anticipated from their reducible units (mono- or diquaternized bipyridines) with no detectable level of electronic communication between them. Surprisingly, compounds **17**, **19** and **21** exhibit more complicated electrochemical behavior, which simplifies and becomes more reversible as the temperature increases. 

## 1. Introduction

To a large extent, the progress of supramolecular chemistry[1] relies on the diversity of building blocks available for the construction or synthesis of novel structures with functional properties. In this regard, *cavitands* are certainly one of the most important classes of host molecules possessing well-defined cavities. The original term was coined by Cram,[2] who defined cavitands as 'synthetic organic compounds with enforced cavities large enough to complex complementary organic compounds or ions'. Although this definition is general enough to include many other types of molecular hosts, Cram's own extensive work has contributed to narrow the definition.[2] For most researchers in the field, cavitands are hosts derived from the acid-catalyzed condensation of aldehydes and resorcinols (see Scheme 1). This reaction produces initially macrocyclic 'resorcinarenes' whose phenolic OH groups can be further 'bridged' with appropriate bifunctional reagents ($CH_2Br_2$ would be the simplest example) to yield the bowl-shaped cavitands (Scheme 1). The majority of the published work with cavitands has dealt with tetrameric macrocycles, that is, cavitands produced by the cyclic condensation of four aldehyde and four resorcinol units. However, in collaboration with Sherman and coworkers, we have recently shown that the synthesis and isolation of [*n*]cavitands (where $n$=4–7) is also possible.[3] A few recent reviews of the extensive research work on cavitands[4] and related hosts[5] are available.

Our group is generally interested in the functionalization of host and guest compounds with redox active subunits. In such cases, it is possible to exert some degree of control on the corresponding binding interactions through the manipulation of the oxidation states.[6,7] Recently, we started a research program to investigate the functionalization of cavitands with electroactive 4,4′-bipyridinium (viologen) residues.[8] Here, we describe a range of compounds containing a central tetrameric cavitand and one, two, three or four covalently attached viologen units, which, at their other ends, may be connected to methyl groups or terminal cavitand residues. This work takes a modular approach to the construction of compounds with relatively large molecular weights. Starting from a few building blocks that contain a simple 'information code' based on highly efficient, reactive centers, it is possible to generate in a predictable way a fairly large number of molecules, some of which approach the molecular weights and branching structures characteristic of dendrimers.[9]

## 2. Results and discussion

### 2.1. Synthesis

The key cavitand building blocks utilized in this work are derivatives of cavitand **1** (see structures in Chart 1). The

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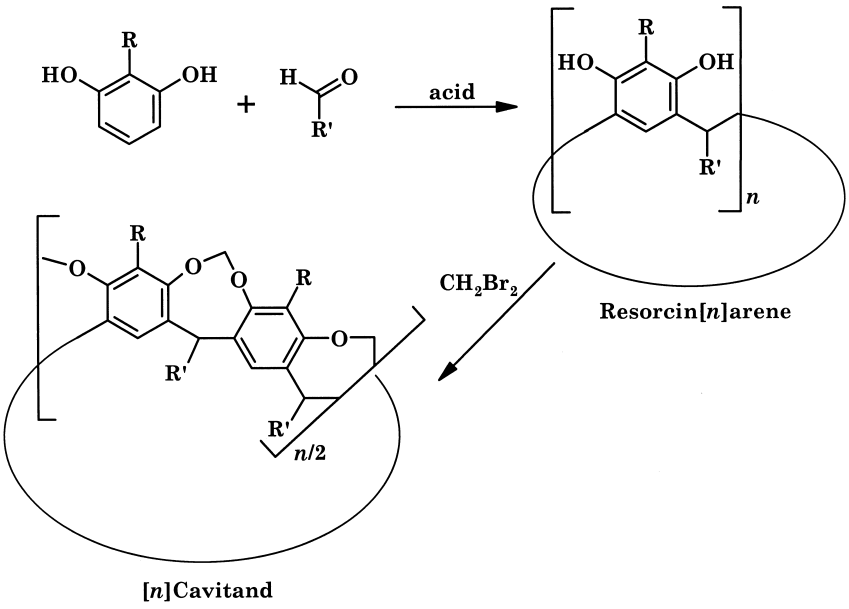
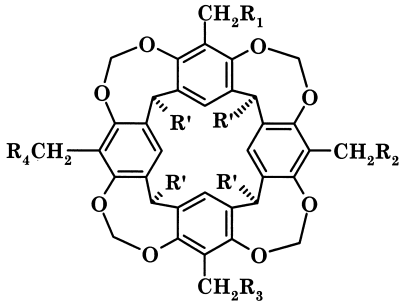



**Scheme 1.** Resorcin[*n*]arenes and [*n*]Cavitands.




**1**, R' = $(CH_2)_4CH_3$, $R_1$=$R_2$=$R_3$=$R_4$=H
**2**, R' = $(CH_2)_4CH_3$, $R_1$=$R_2$=$R_3$=$R_4$=Br
**3**, R' = $(CH_2)_4CH_3$, $R_1$=$R_2$=$R_3$=H, $R_4$=Br
**4**, R' = $(CH_2)_4CH_3$, $R_1$=$R_2$=H, $R_3$=$R_4$=Br
**5**, R' = $(CH_2)_4CH_3$, $R_1$=$R_3$=H, $R_2$=$R_4$=Br
**6**, R'= $(CH_2)_4CH_3$, $R_1$=H, $R_2$=$R_3$=$R_4$=Br

**Chart 1.** Structures of cavitand **1** and its brominated forms.

bromination of **1** with NBS to produce tetrabromocavitand **2** was first reported by Reinhoudt and coworkers.[10] We have modified their method to prepare and isolate monobromocavitand **3**, dibromocavitands **4** and **5**, and tribromocavitand **6** (Chart 1).[11] Not surprisingly, the use of less than 4 equiv. of NBS in the reaction leads to mixtures of **3**, **4**, **5** and **6**. If the [NBS]/[**1**] ratio is close to unity, the reaction produces a mixture of **3**, **4** and **5**. Compound **3** can be separated from this mixture by column chromatography, but the separation of **4** and **5** requires medium pressure liquid chromatography. Under these conditions **3** was isolated in 55% yield. If the [NBS]/[**1**] ratio is close to ~3, the product mixture is richer in compounds **4**, **5**, **6**, as well as in the tetrabromocavitand **2**. The tribromocavitand **6** can again be separated by column chromatography (20% yield), but the presence of **2** interferes with the separation of **4** and **5**. Therefore, even though the combined yield of **4** and **5** increases under the latter conditions, we isolated pure samples of **4** and **5** from reaction mixtures containing ~1 equiv. of NBS, due to the absence of **2** in the resulting product mixtures.

Treatment of each of these bromocavitands with excess 4,4′-bipyridine leads to the corresponding bipyridine-functionalized cavitands (see Chart 2 for structures) in good to high yields. The corresponding hexafluorophosphate forms can be readily obtained from the bromides by counterion exchange. It is interesting to note that each of these compounds has from one to four reactive centers (the terminal nitrogen atoms) located along well defined, approximately co-planar directional axes, with adjacent axes perpendicular to each other. This spatial arrangement results form the geometry around the methylenic carbons that connect the cavitand bowl to the bipyridine units, as steric requirements force the alignment of the bipyridine residues near the plane defined by the four connecting methylenes. This is clearly evident from molecular mechanics calculations (data not shown) and from the solid state structure obtained by X-ray diffraction with a single crystal of the tetra(bipy)-cavitand **7** (see Fig. 1).[8]

The free nitrogens in these compounds can be easily quaternized by treatment with a slight excess of iodomethane to yield the cavitand derivatives **12**, **13** and **16**, as hexafluorophosphate salts after counterion exchange. Each of these compounds contains four, one and three

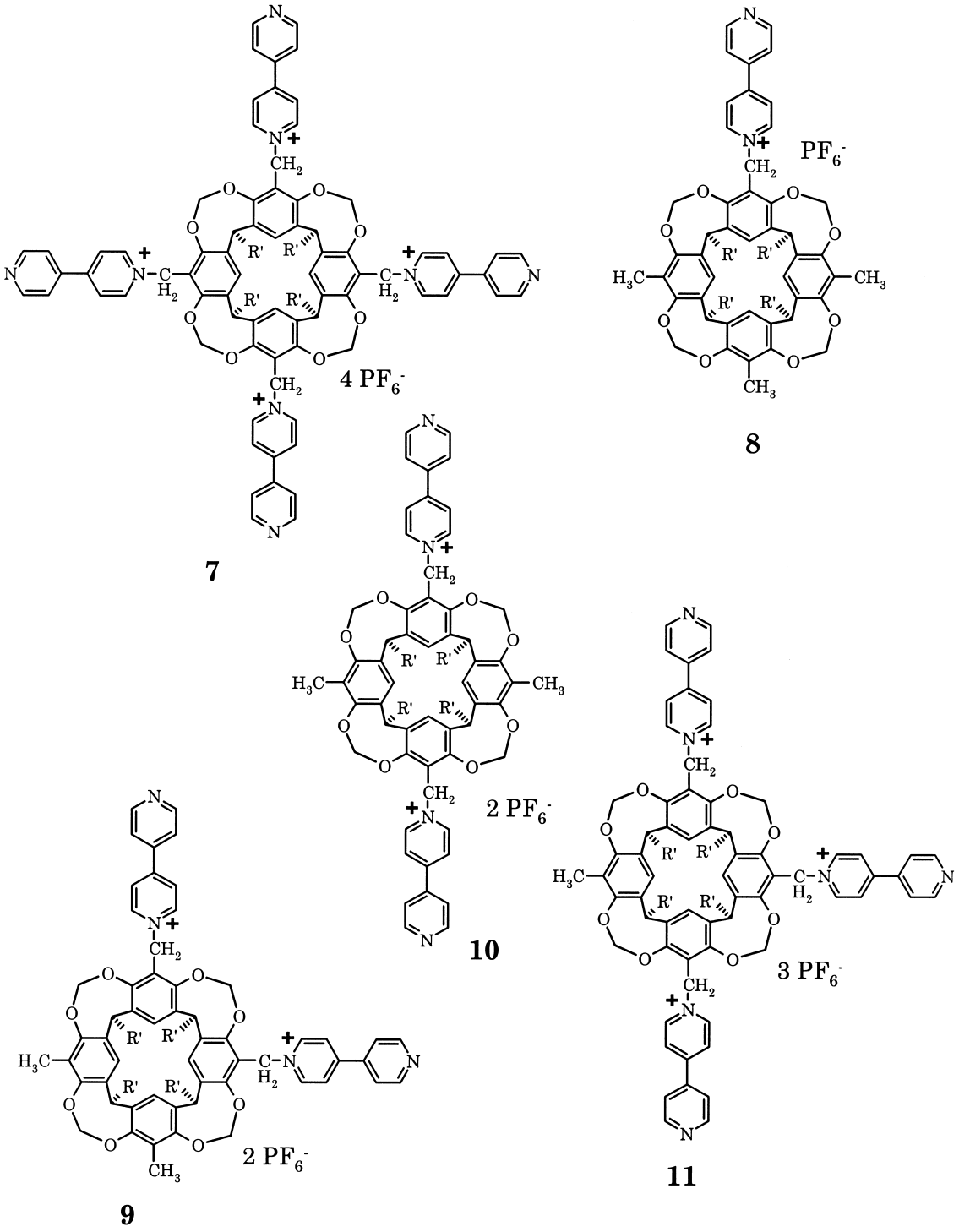



**Chart 2.** Structures of the bipy-cavitands.

4,4′-bipyridinium (viologen) residues, respectively. The bis(viologen)cavitands **14** and **15** were not prepared, but they should be readily accessible by the same procedure. Alternatively, it is also possible to treat any of the compounds in the series **7**–**11** with excess monobromocavitand **3** to yield the much higher molecular weight compounds **17**–**21**, also as hexafluorophosphate salts after counterion exchange. Each of these compounds contains $m$ viologen units ($1<m<4$) and $m+1$ cavitand bowls (one in the center of the molecule and $m$ in the periphery). The molecular structures of compounds **12**–**21** are shown in Schemes 2 and 3, using a pictorial system that simplifies their representation.

The directional reactivity characteristic of the bromocavitands **2**–**6** and the bipy-functionalized cavitands **7**–**11**, may be utilized to prepare other structures, which will be the subject of future reports.

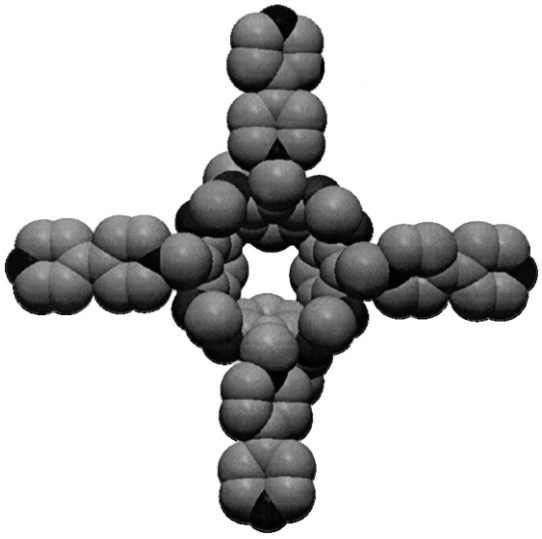
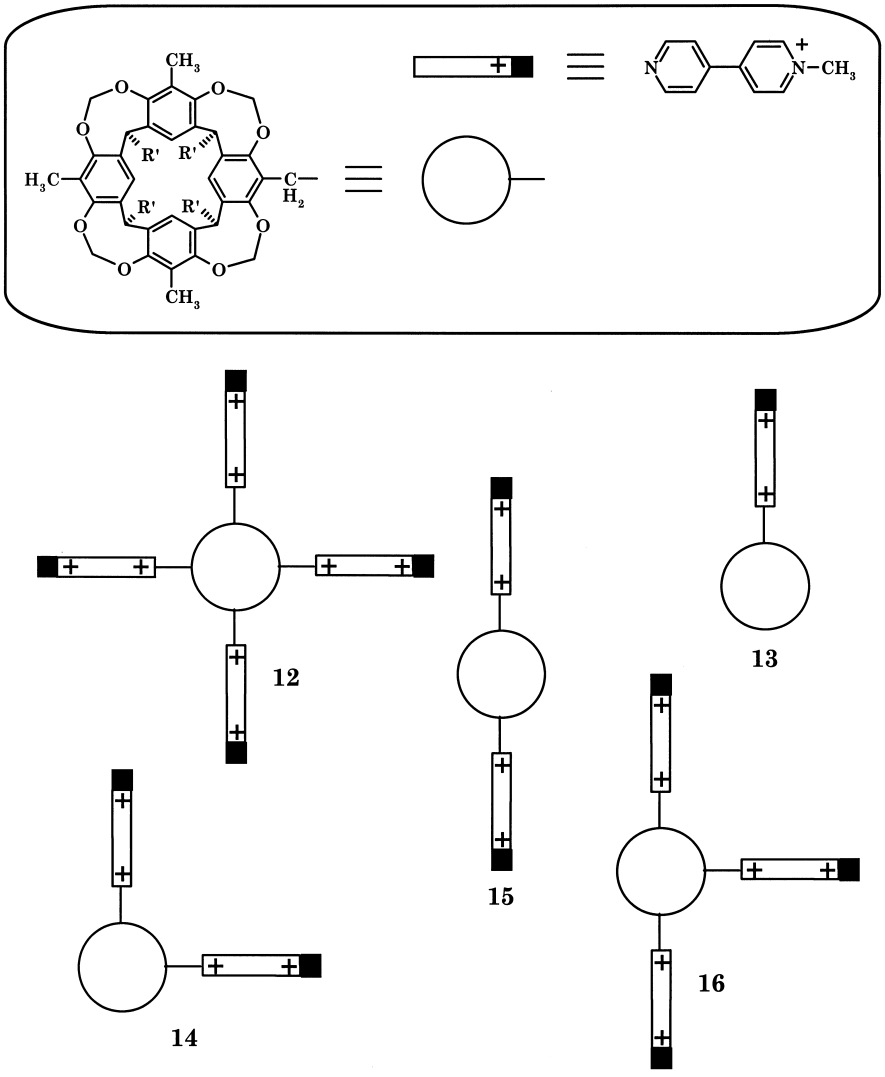


**Figure 1.** Space filling representation of the X-ray crystal structure of **7**. The four pentyl chains in the lower rim, hexafluorophosphate counterions and solvent molecules have been removed for clarity. See Ref. 8 for additional details.

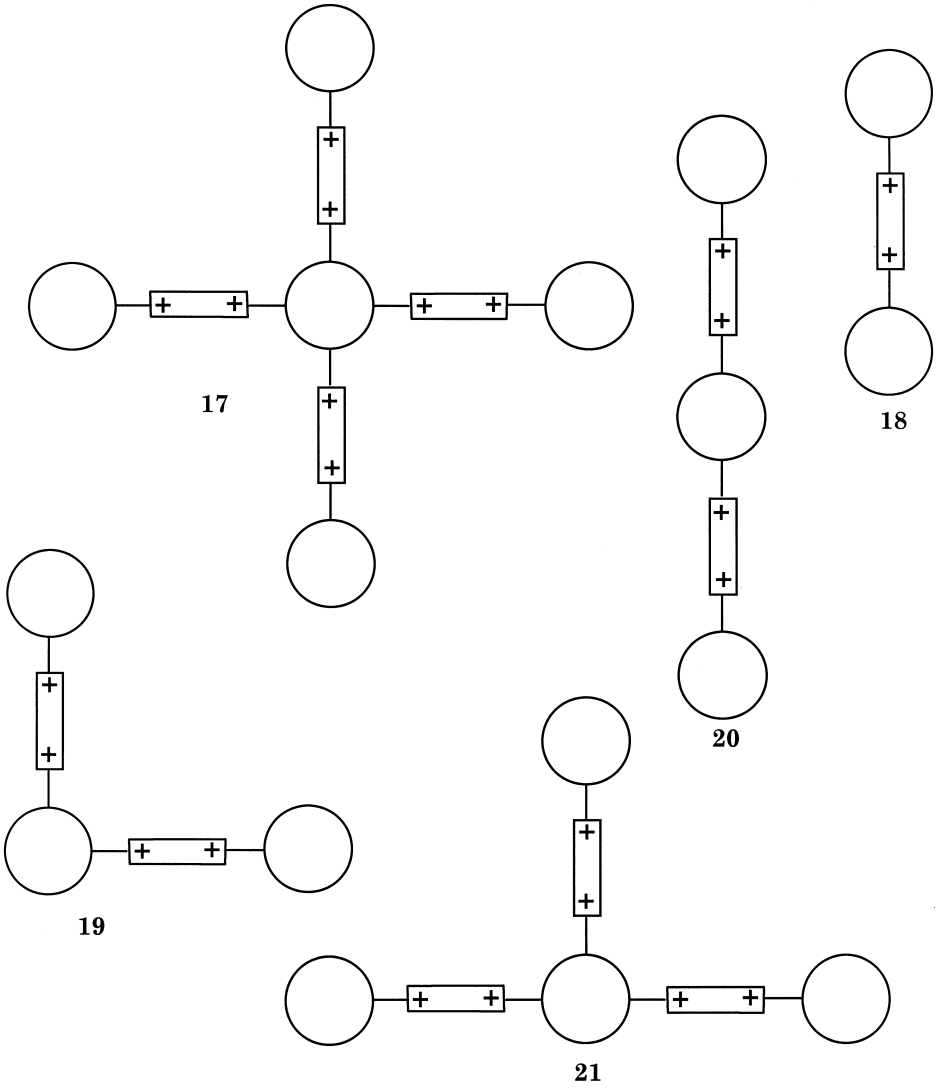
## 2.2. Electrochemistry

The mono- or diquaternized 4,4′-bypiridine moieties in most of the cavitand derivatives reported in this work give them interesting redox properties. The electrochemistry of a monoquaternized 4,4′-bipyridine unit is characterized by a single, one-electron reduction ($V^+ \rightarrow V$), while diquaternized 4,4′-bipyridines (viologens) exhibit two reversible, one-electron reductions ($V^{2+} \rightarrow V^+$ and $V^+ \rightarrow V$).[12,13] Most of the cavitand derivatives surveyed here contain multiple bipyridine units and, therefore, the voltammetric behavior includes information on the extent of electronic communication between equivalent reducible groups.[14]

The cyclic voltammogram of mono(bipy)cavitand **8** in acetonitrile solution shows a reversible reduction process at a half-wave potential ($E_{1/2}$) of −0.88 V vs Ag/AgCl (Fig. 2A). However, the cyclic voltammogram of the tetra(bipy)cavitand **7** (Fig. 2B) exhibits a poorly defined reduction peak and a sharp anodic spike on the reverse scan. This behavior is characteristic of precipitation of the reduced species on the electrode surface and subsequent re-dissolution upon oxidation in the anodic scan.[15] The




**Scheme 2.** Shorthand representation of viologen-functionalized cavitands **12**–**16**. The shorthand key is given inside the upper rectangle.




**Scheme 3.** Shorthand representation of cavitand oligomers **17**–**21**. The shorthand key is the same as in Scheme 2.

tris(bipy)cavitand **11** exhibits voltammetric behavior similar to **7**, but the distortion of the voltammetric waves due to precipitation effects is not so pronounced. Our data reveals that the tendency of the reduced bipy-functionalized cavitands to precipitate increases with the number of bipyridine residues. Since the reduction of all the bipyridine units takes place at essentially the same potential, i.e. they behave as essentially independent groups (without any significant electronic communication), the tetra(bipy)cavitand undergoes a dramatic structural and polarity change as four electrons are injected into the four bipyridine residues over a relatively narrow potential range. The four-electron reduced form of this cavitand is much less polar and has a much more extended aromatic surface than the oxidized form of the molecule, which explains its tendency to precipitate out of acetonitrile solution upon reduction. As the number of bipyridine residues attached to the central cavitand decreases, the relative structural and polarity changes brought about by reduction should also decrease. Therefore, the mono(bipy)cavitand does not show any precipitation associated with the electron transfer reaction and the voltammetric process is reversible.

The cyclic voltammogram of mono(viologen)cavitand **13** is shown in Fig. 3A. Two reversible, one-electron reduction processes are clearly visible, as expected for any compound containing a diquaternized 4,4′-bipyridine moiety. The corresponding half-wave potentials are −0.28 and −0.81 V vs Ag/AgCl. The electrochemistry of the tetra(viologen)cavitand **12** in acetonitrile solution shows two voltammetric waves at −0.34 and −0.79 V vs Ag/AgCl (see Fig. 3B). This means that each of these voltammetric waves represents the uptake of four electrons, one by each of the viologen residues, which behave as essentially independent units, revealing no apparent electronic communication among them.[14] This result is rather general as none of the cavitand derivatives reported in this work showed electrochemical behavior consistent with electronic communication among identical reducible units. Thus, a cavitand derivative having *m* viologen units undergoes two reduction processes. The first one corresponds to the uptake of *m* electrons as each of the units undergoes the $V^{2+}$-to-$V^{+}$ conversion, and the second one to the uptake of another *m* electrons for the corresponding $V^{+}$-to-V conversion.

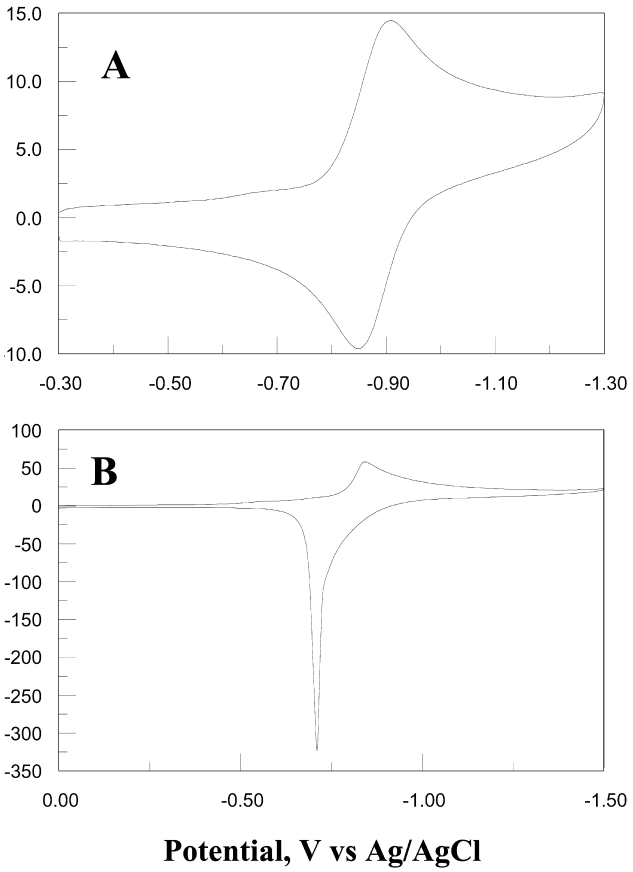



**Figure 2.** Cyclic voltammetric response on a glassy carbon electrode of 0.1 M $TBAPF_6$/acetonitrile solutions also containing: (A) 1.0 mM **8** and (B) 0.2 mM **7**. Scan rate: 0.100 V/s. The current units for the vertical axes are μA.

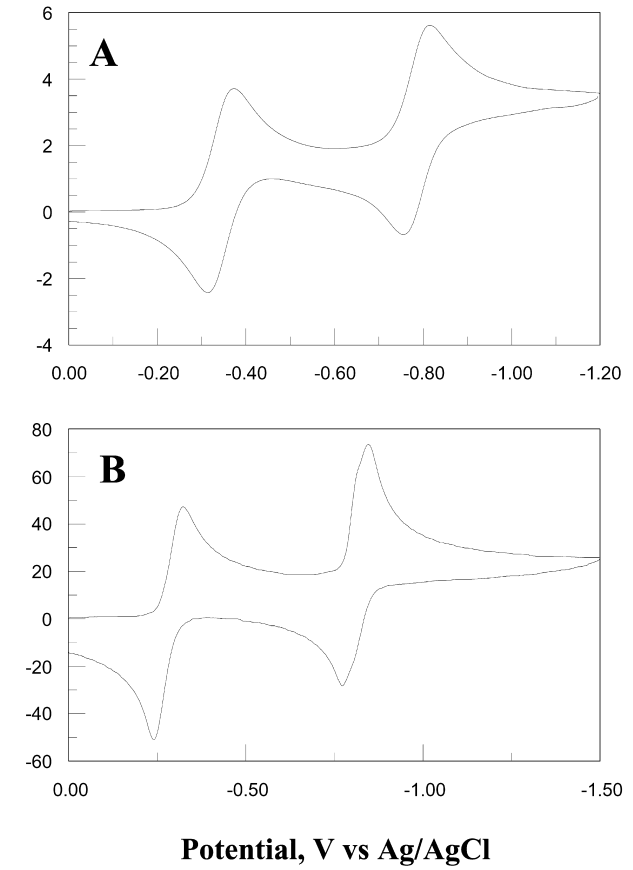



**Figure 3.** Cyclic voltammetric response on a glassy carbon electrode of 0.1 M $TBAPF_6$/acetonitrile solutions also containing: (A) 1.0 mM **13** and (B) 0.2 mM **12**. Scan rate: 0.100 V/s. The current units for the vertical axes are μA.

Partial or full reduction (loss of positive charge) of the viologen-functionalized cavitands introduces considerable changes in these compounds, which may lead to their precipitation from acetonitrile solution. Again, these effects are expected to be more pronounced for those cavitands which contain more viologen units. This is clearly visible in the cyclic voltammograms of Fig. 3 as the voltammetric peaks for compound **12** show more distortions from the reversible shape than those for compound **13**.

The voltammetric behavior of the oligomeric cavitands **17**–**21** turned out to be more complicated. While cavitands **18** and **20** exhibited cyclic voltammograms typical of viologen-containing compounds, compounds **17**, **19** and **21** present electrochemical behavior that is completely unexpected for viologen derivatives. For instance, the cyclic voltammogram obtained for **17** in acetonitrile solution is depicted in Fig. 4. The irreversible cyclic voltammetric response associated with the first reduction process is also obtained when the scan was restricted to potentials around the first wave. This type of response is similar to that observed with compounds **19** and **21** and reflects the presence of three cavitand units, arranged in an L shape and connected by two viologen groups (see Scheme 4). This conclusion emerges very clearly from the comparison between the voltammetric behavior exhibited by the two isomeric compounds **19** and **20**. While compound **20** shows two reversible waves, as anticipated for two equivalent viologen units, compound **19**, also containing two equivalent viologen units, exhibits 'anomalous' behavior, similar to that shown in Fig. 4. It is thus clear that the L shape of **19**, also present in compounds **17** and **21**, must be responsible for the observed voltammetric behavior. However, the presence of two viologen units, connected to

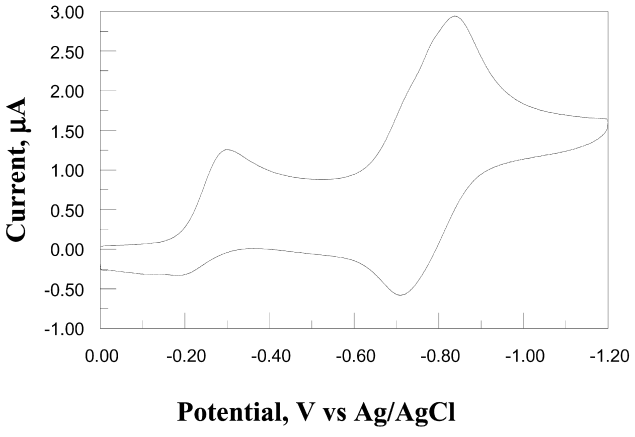
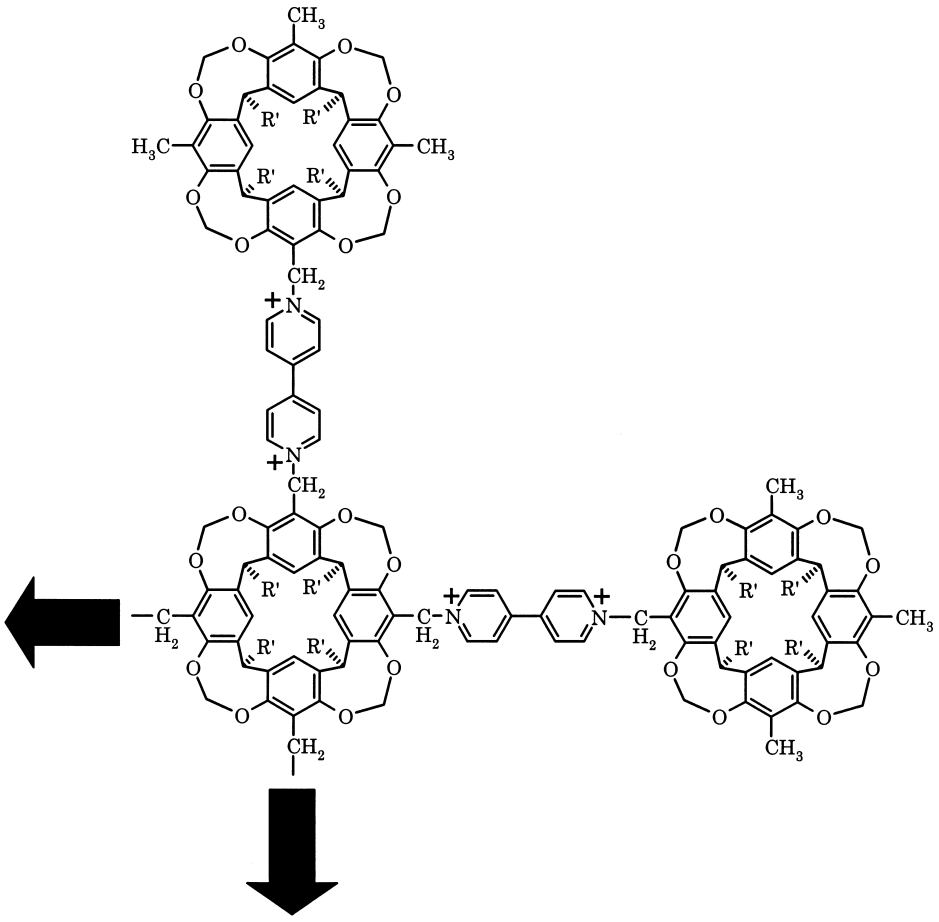



**Figure 4.** Cyclic voltammetric response on a glassy carbon electrode of a 0.1 M $TBAPF_6$/acetonitrile solution also containing 0.2 mM **17**. Scan rate: 0.100 V/s. The current units for the vertical axes are μA.



**Scheme 4.** L-shape cavitand/viologen arrangement that results in 'anomalous' electrochemical behavior.

the central cavitand bowl and oriented at 90° angles, does not give rise by itself to this behavior, as evidenced by the 'normal' voltammetric behavior observed with compounds **12** and **16**.

So far, we have not been able to fully rationalize the voltammetric behavior of compounds **17**, **19** and **21**. Variable temperature voltammetric experiments reveal that the electrochemistry of these compounds becomes closer to that expected for viologen derivatives as the temperature increases. For instance, Fig. 5 shows a comparison of the first voltammetric wave for compounds **19** and **20**. Notice that the first reduction for **20** remains essentially reversible and unchanged throughout the temperature range surveyed, but the same process is very sensitive to temperature for **19**. In fact, the first reduction of **19** clearly approaches voltammetric reversibility as the temperature increases. Similar variable temperature results were obtained with compounds **17** and **21**. At this point, we can only speculate that the departure from electrochemical reversibility at room temperature for compounds **17**, **19** and **21** may be related to slow relative motions of the aromatic rings in the bipyridinium units, caused by their relative orientation and the large cavitand macrocycles attached to them, which may delay their adaptation to the conformational changes necessary to accommodate the electron transfer reactions. We are currently investigating this behavior further and will report our findings in due time.

## 3. Conclusions and outlook

We have shown in this work that the bromination of cavitand **1** to yield derivatives with different functionalization patterns is possible. We have further prepared cavitands functionalized with one, two (both adjacent and opposite), three and four mono- or diquaternized bipyridinium units. Derivatives containing diquaternized bipyridinium (viologen) units can also be made with one central and several peripheral cavitands. The reactivity of the building blocks reported here has been used to produce a series of compounds that have interesting and, sometimes, unexpectedly complex electrochemical properties. Furthermore, compounds **7**–**11** contain terminal nitrogen atoms, whose chemistry can be further exploited using a variety of binding interactions (taking advantage of hydrogen bonding or metal coordination, for instance) to continue building a large array of high molecular weight structures, which may find applications as anion sensors and information storage materials.

## 4. Experimental

### 4.1. Materials

All solvents and chemicals for synthesis were commercially available or reagent grade quality and were used without

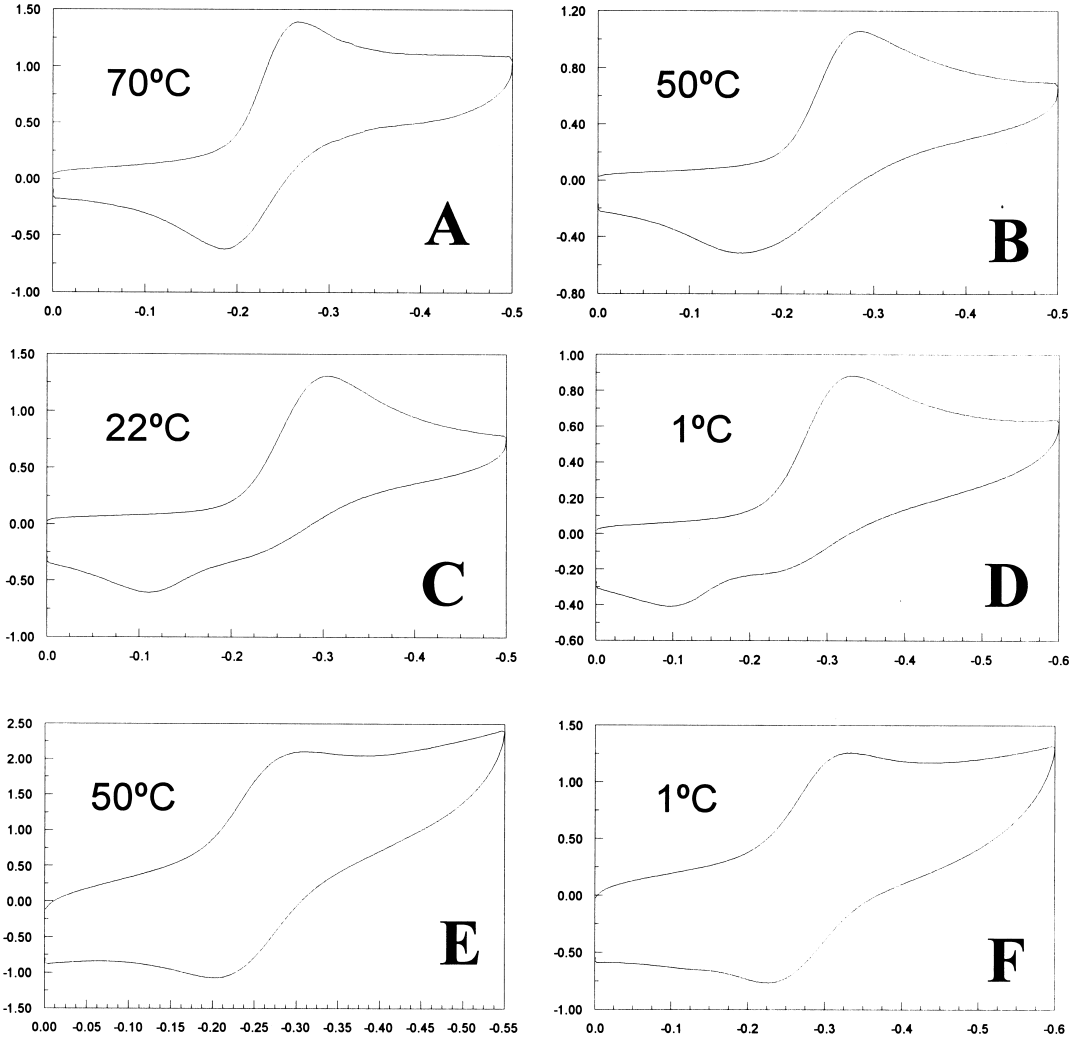



**Figure 5.** Cyclic voltammetric response at several temperatures on a glassy carbon electrode of a 0.1 M $TBAPF_6$/acetonitrile solution also containing (A–D) 0.2 mM **19** and (E,F) 0.2 mM **20**. Scan rate: 0.100 V/s. The current units for the vertical axes are μA.

any further purification. NBS was recrystallized from boiling water. All reactions were carried out under a nitrogen atmosphere. Compounds **1** and **2** were prepared as previously reported.[10] Acetonitrile for the electrochemical experiments was purchased from Sigma–Aldrich (99.9%, HPLC grade) and used without further purification.

**4.1.1. Monobromocavitand 3.** Cavitand **1** (4.40 g, 5.04 mmol) was dissolved in 88 mL of carbon tetrachloride. NBS (0.898 g, 5.04 mmol) and a spatula tip of azo-bis isobutyronitrile (AIBN) was added. The solution was refluxed with vigorous stirring for 24 h. When the reaction flask was sufficiently cold, the content was filtered and washed with some $CCl_4$. The mother liquor was evaporated under vacuum. The resulting solid was chromatographed on a silica column [hexanes and AcOEt (25:1)] to give, after vacuum drying at room temperature, 1.05 g of compound **3** and 2.50 g of starting material **1**. The overall yield was 55.3% (based on starting material recovered). A small portion was recrystallized and submitted to elemental analysis. $^1$H NMR ($CDCl_3$, 400 MHz): 7.14 (s, 1H), 6.97 (s, 3H), 5.95 (d, 2H, $J$=7.1 Hz), 5.87 (d, 2H, $J$=7.1 Hz), 4.81–4.70 (m, 4H), 4.60 (s, 2H), 4.42 (d, 2H, $J$=7.1 Hz), 4.37 (d, 2H, $J$=7.1 Hz), 2.24–2.16 (m, 8H), 2.03 (s, 3H), 1.95 (s, 6H), 1.48–1.22 (m, 24H), 0.96–0.88 (m, 12H). $^{13}$C NMR ($CDCl_3$, 100 MHz): 153.65, 153.58, 153.38, 153.32, 138.41, 138.18, 137.87, 137.06, 123.97, 123.90, 121.87, 117.32, 117.23, 99.11, 98.33, 37.05, 36.98, 32.09, 32.02, 31.59, 30.17, 30.14, 27.67, 27.61, 22.69, 22.67, 14.10, 14.07, 10.53, 10.24. Mp 242–244°C. MS (FAB, NBA $m/z$): 953 ($MH^+$). Anal. Calcd for $C_{56}H_{71}O_8Br$: C, 70.65; H, 7.52. Found: C, 70.81; H, 7.66.

**4.1.2. Dibromocavitands 4 and 5.** A solution of **1** (1.00 g, 1.15 mmol), NBS (0.225 g, 1.27 mmol) and a catalytic amount of AIBN in $CCl_4$ (50 mL) was refluxed for 10 h. After cooling to room temperature, the precipitate was filtered off. After evaporation of the solvent at reduced

pressure, the residue was subjected to flash chromatography ($SiO_2$, hexanes/dichloromethane, 3:2) to yield **1** (370 mg, 68% recovery), **3** (340 mg, 31%), **6** (38 mg, 3%). The fraction containing a mixture of the dibromocavitands **4** and **5** was further purified by MPLC ($SiO_2$, hexanes/AcOEt, 40:1) to afford **4** (94 mg, 8%) and **5** (47 mg, 4%). Cavitand **5** was recrystallized from hexanes/dichloromethane.

**4.1.3. Compound 4.** $^1$H NMR ($CDCl_3$, 200 MHz): 7.15 (s, 2H), 7.00 (s, 2H), 6.05–5.88 (m, 4H), 4.83–4.70 (m, 4H), 4.60–4.48 (m, 8H), 2.28–2.10 (m, 8H), 2.01 (s, 6H), 1.48–1.23 (m, 24H), 0.97–0.85 (m, 12H). $^{13}$C NMR ($CDCl_3$, 50 MHz): 153.77, 153.66, 153.55, 153.35, 138.63, 137.95, 137.61, 137.05, 124.27, 124.02, 121.22, 117.08, 99.34, 98.83, 98.63, 37.06, 36.94, 36.83, 32.09, 32.04, 31.98, 30.35, 30.15, 30.04, 27.67, 27.61, 23.75, 22.70, 14.10, 10.77. Mp 248–249°C. MS (FAB, NBA, *m/z*): 1030 ($M^+$), 950 $(M-Br)^+$, 870 $(M-2Br)^+$. Anal. Calcd for $C_{56}H_{70}Br_2O_8$: C, 65.24; H, 6.84. Found C, 65.22; H, 6.70

**4.1.4. Compound 5.** $^1$H NMR ($CDCl_3$, 200 MHz): 7.14 (s, 2H), 6.98 (s, 2H), 5.96 (d, 4H, *J*=7.3 Hz), 4.77 (t, 4H, *J*=8.3 Hz), 4.52 (d, 4H, *J*=7.3 Hz), 4.59 (s, 4H), 2.30–2.10 (m, 8H), 1.96 (s, 6H), 1.48–1.17 (m, 24H), 0.99–0.81 (m, 12H). $^{13}$C NMR ($CDCl_3$, 50 MHz): 153.72, 153.09, 138.23, 137.30, 124.35, 124.18, 121.59, 116.96, 99.00, 36.94, 32.01, 30.12, 27.58, 23.46, 22.67, 14.10, 10.66). Mp 219–220°C. MS (FAB, 3-NBA *m/z*): 1030 ($M^+$), 950 $(M-Br)^+$, 870 $(M-2Br)^+$. Anal. Calcd for $C_{56}H_{70}Br_2O_8$: C, 65.24; H, 6.84. Found C, 65.24; H, 6.31.

**4.1.5. Tribromocavitand 6.** Cavitand **1** (3.00 g, 3.44 mmol) was dissolved in 60 mL of $CCl_4$. NBS (1.65 g, 9.28 mmol) and a spatula tip of AIBN were added. The reaction mixture was refluxed for 24 h with efficient stirring and subsequently allowed to cool down for 1 h. After reaching room temperature, the reaction mixture was filtered and washed with some $CCl_4$. The mother liquor was evaporated under vacuum to afford a mixture of mainly tribromo and dibromo cavitands that was chromatographed on silica with a mixture of hexanes/$CH_2Cl_2$ (3:1) until the first traces of dibromo cavitands were detected at the end of the column. Then, a mixture of hexanes/$CH_2Cl_2$ (2:1) was passed through the column to collect the remaining compounds. This provided 0.44 g of pure compound **6**. Additionally, column chromatography of some other fractions along with crystallization provided 0.33 g of cavitand **6**. The overall yield was 20.1%. This procedure also afforded a mixture of dibromocavitands **4** and **5** (see text). $^1$H NMR: ($CDCl_3$, 400 MHz) 7.13 (s, 3H), 6.98 (s, 1H), 6.03 (d, 2H, *J*=7.4 Hz), 5.96 (d, 2H, *J*=7.3 Hz), 4.77 (t, 4H, *J*=8.0 Hz), 4.58 (d, 2H, *J*=7.3 Hz), 4.51–4.49 (m, 6H), 4.38 (s, 2H), 2.28–2.18 (m, 8H), 1.97 (s, 3H), 1.45–1.25 (m, 24H), 0.91 (m, 12H). $^{13}$C NMR: ($CDCl_3$, 100 MHz) 153.79, 153.63, 153.51, 153.45, 138.66, 138.13, 137.7, 137.31, 124.35, 124.31, 121.26, 120.94, 116.94, 36.98, 36.88, 32.01, 31.97, 30.18, 30.03, 27.59, 27.54, 23.34, 23.10, 22.67, 14.07, 10.71. MS (FAB, NBA *m/z*): 1109 ($M^+$), 1028 $(M-Br)^+$, 947 $(M-2Br)^+$.

**4.1.6. Tetra(bipy)cavitand 7.** Tetrabromocavitand **2** (0.500 g, 0.420 mmol) was dissolved in 20 mL of DMF and to 4,4′-bipyridine (1.32 g, 8.46 mmol) was added to this solution. The reaction mixture was stirred for 20 h at 45°C. After cooling, $Bu_4N^+Cl^-$ (1.22 g) was added and the solid formed was filtered off and washed with $Et_2O$. This material was dissolved in 10 mL of warm water and $NH_4PF_6$ (satd.) was added to the solution until further precipitate formation was not observed. Filtration gave a white powder that was recrystallized from a mixture of acetone, methanol and water. This compound was dried at 40°C under vacuum to yield 0.60 g of cavitand **14** (68.8% yield). $^1$H NMR ($CD_3CN$, 400 MHz): 8.90–8.82 (m, 16H), 8.23 (d, 8H, *J*=6.3 Hz), 7.78 (d, 8H, *J*=5.5 Hz), 7.60 (s, 4H), 6.33 (d, 4H, *J*=7.1 Hz), 5.58 (s, 8H), 4.74–4.62 (m, 8H), 2.40–2.30 (m, 8H), 1.42–1.20 (m, 24H), 0.86 (t, 12H, *J*=7.1 Hz). $^{13}$C NMR ($CD_3CN$, 100 MHz): 155.52, 154.48, 152.13, 146.29, 142.21, 139.88, 127.02, 125.53, 122.90, 121.17, 100.62, 55.51, 38.63, 32.78, 30.59, 28.25, 23.29, 14.44. MS (FAB, *m/z*) 1929 ($[M-PF_6]^+$), 892 ($[M-2\ PF_6]^{2+}$). Mp 255°C (decomp.). Anal. Calcd for $C_{96}H_{100}O_8N_8P_4F_{24}-2H_2O$: C, 54.65; H, 4.96. Found: C, 54.60; H, 4.95.

### 4.2. Synthesis of the remaining bipy-functionalized cavitands 8–11

The procedures were similar to that used for the synthesis of **7**, but starting from the corresponding bromo-functionalized cavitand.

**4.2.1. Mono(bipy)cavitand 8.** Yield: 90%. $^1$H NMR ($CD_3CN$, 400 MHz): 8.92–8.84 (m, 4H), 8.11 (d, 2H, *J*=6.9 Hz), 8.01 (d, 2H, *J*=6.2 Hz), 7.26 (s, 1H), 6.95 (s, 3H), 6.09 (d, 2H, *J*=7.3 Hz), 5.89 (d, 2H, *J*=7.1 Hz), 5.64 (s, 2H), 4.77 (t, 2H, *J*=8.0 Hz), 4.71 (t, 2H, *J*=8.0 Hz), 4.43 (d, 2H, *J*=7.3 Hz), 4.30 (d, 2H, *J*=7.3 Hz), 2.04–2.38 (m, 8H), 2.03 (s, 6H), 1.99 (s, 3H), 1.46–1.22 (m, 24H), 0.95–0.83 (m, 12H). $^{13}$C NMR ($CD_3CN$, 100 MHz): 155.54, 154.66, 154.28, 154.06, 153.38, 152.19, 142.12, 140.79, 139.93, 139.24, 138.40, 127.01, 125.84, 125.81, 125.79, 122.88, 121.19, 119.75, 119.73, 100.47, 99.83, 55.71, 38.59, 38.51, 32.94, 32.86, 30.64, 30.46, 28.52, 28.39, 23.40, 23.36, 14.50, 14.47, 10.36, 10.33. MS (FAB, NOBA) *m/z*: 1029 ($(MH)^+-PF_{6^-}$). Mp 282°C (decomp.). Anal. Calcd for $C_{66}H_{79}O_8N_2PF_6$: C, 67.56; H, 6.79. Found: C, 67.48; H, 6.79.

**4.2.2. Bis(bipy)cavitand 9.** Yield: 95%. $^1$H NMR: ($CD_3CN$, 200 MHz) 8.87 (m, 8H), 8.30 (d, 4H, *J*=6.8 Hz), 7.80 (d, 4H, *J*=6.3 Hz), 7.60 (s, 2H), 7.33 (s, 2H), 6.35 (d, 1H, *J*=7.8 Hz), 6.16 (d, 2H, *J*=7.8 Hz), 5.95 (d, 1H, *J*=7.3 Hz), 5.57 (s, 4H), 4.82–4.59 (m, 5H), 4.51 (d, 2H, *J*=7.8 Hz), 4.32 (d, 1H, *J*=7.3 Hz), 2.50–2.24 (m, 8H), 2.05 (s, 6H), 1.50–1.20 (m, 24H), 0.99–0.85 (m, 12H). $^{13}$C NMR ($CD_3CN$, 50 MHz): 155.42, 154.54, 154.45, 153.88, 151.98, 146.14, 142.04, 141.22, 139.69, 138.23, 126.90, 125.83, 125.49, 122.75, 121.11, 119.51, 100.84, 100.28, 99.63, 55.35, 38.46, 38.37, 32.77, 32.70, 32.61, 30.51, 30.32, 30.23, 28.32, 28.19, 28.06, 25.75, 23.23, 23.19, 23.13, 14.35, 14.32, 10.20. Mp 200–210°C (decomp.). MS (ES, $CH_3CN$ *m/z*): 1327 ($[M-PF_6]^+$), 591 ($[M-2PF_6]^{2+}$). Anal. Calcd for $C_{76}H_{86}F_{12}N_4O_8P_2$: C, 61.95; H, 5.88; N, 3.80. Found C, 60.48; H, 5.50; N, 3.84.

**4.2.3. Bis(bipy)cavitand 10.** Yield: 94%. $^1$H NMR: ($CD_3CN$, 200 MHz) 8.91–8.83 (m, 8H), 8.29 (d, 4H, *J*=6.8 Hz), 7.79 (d, 4H, *J*=6.3 Hz), 7.57 (s, 2H), 7.35 (s,

2H), 6.17 (d, 4H, *J*=7.3 Hz), 5.53 (s, 4H), 4.72 (t, 4H, *J*=8.0 Hz), 4.49 (d, 4H, *J*=7.8 Hz), 2.55–2.21 (m, 8H), 2.08 (s, 6H), 1.50–1.20 (m, 24H), 0.99–0.85 (m, 12H). $^{13}$C NMR ($CD_3CN$, 50 MHz): 155.29, 154.27, 154.09, 152.01, 146.17, 141.93, 140.56, 138.87, 126.81, 125.89, 125.51, 122.69, 121.22, 119.46, 100.25, 55.48, 38.46, 32.71, 30.33, 28.21, 23.21, 14.32, 10.20. Mp 175–180°C (decomp.). MS (ES, $CH_3CN$ *m/z*): 1327 ($[M-PF_6]^+$), 591 ($[M-2PF_6]^{2+}$). Anal. Calcd for $C_{76}H_{86}F_{12}N_4O_8P_2$: C, 61.95; H, 5.88; N, 3.80. Found C, 61.86; H, 5.42; N, 3.49.

**4.2.4. Tris(bipy)cavitand 11.** Yield: 74%. $^1$H NMR: ($CD_3CN$, 400 MHz) 8.9–8.8 (m, 12H), 8.31–8.25 (m, 6H), 7.8–7.75 (m, 6H), 7.59 (s, 1H), 7.58 (s, 2H), 7.33 (s, 1H), 6.36 (d, 2H, *J*=7.7 Hz), 6.17 (d, 2H, *J*=7.7 Hz), 5.60 (s, 2H), 5.56 (s, 4H), 4.75–4.6 (m, 6H), 4.53 (d, *J*=7.7 Hz), 2.42–2.2 (m, 8H), 2.06 (s, 3H), 1.4–1.2 (m, 24H), 0.9–0.8 (m, 12H). $^{13}$C NMR: ($CD_3CN$, 100 MHz) 155.72, 155.66, 154.73, 154.48, 154.4, 154.06, 152.2, 146.28, 142.13, 141.25, 140.43, 139.74, 138.96, 127.09, 127.05, 126.06, 125.59, 122.88, 121.3, 119.6, 100.95, 100.40, 55.5, 55.38, 38.68, 38.63, 32.83, 32.75, 30.56, 30.45, 28.3, 28.17, 23.33, 23.27, 14.44, 14.42, 10.32. MS (FAB) *m/z*: 1628 ($[M-PF_{6^-}]+$). Anal. Calcd for $C_{86}H_{93}O_8N_6P_3F_{18}$–1/2 $CHCl_3$: C, 56.67; H, 5.14. Found: C, 56.52; H, 5.45.

**4.2.5. Tetra(viologen)cavitand 12.** Compound **7** (0.20 g, 0.096 mmol) and iodomethane (0.68 g, 4.78 mmol) were dissolved in 5 mL of acetonitrile and this mixture was stirred at room temperature for 48 h. The solvent was partially evaporated under reduced pressure and 10 mL of water were added. Then, a saturated solution of ammonium hexafluorophosphate ($NH_4PF_6$) was added dropwise until precipitation was complete. The solid was filtered and dried at room temperature under vacuum to give 0.24 g of compound **12** (92% yield). $^1$H NMR ($CD_3CN$, 400 MHz): 9.02 (d, 8H, *J*=7.3 Hz), 8.86 (d, 8H, *J*=6.6 Hz), 8.44–8.35 (m, 16H), 7.63 (s, 4H), 6.35 (d, 4H, *J*=7.3 Hz), 5.66 (s, 8H), 4.74 (d, 4H, *J*=7.3 Hz), 4.68 (t, 4H, *J*=8.0 Hz), 4.41 (s, 12H), 2.42–2.30 (m, 8H), 1.47–1.20 (m, 24H), 0.87 (t, 12H, *J*=7.32 Hz). $^{13}$C NMR ($CD_3CN$, 100 MHz): 154.50, 151.41, 150.61, 147.49, 146.49, 139.83, 128.22, 127.92, 125.72, 120.86, 100.57, 55.15, 49.62, 38.66, 32.82, 30.63, 28.28, 23.30, 14.46. MS (FAB, *m/z*) 1212 ($[M-2PF_6]^{2+}$]. Mp 245–247°C. Anal. Calcd for $C_{100}H_{112}O_8N_8P_8F_{48}$–$3H_2O$: C, 43.39; H, 4.29. Found: C, 43.30; H, 4.17.

### 4.3. Synthesis of viologen-functionalized cavitands 13 and 16

The procedures were similar to that used for the synthesis of **12**, but starting from the pertinent bipy-functionalized cavitands. The bis(viologen)cavitands **14** and **15** were not prepared, although they should be accessible using similar procedures.

**4.3.1. Mono(viologen)cavitand 13.** Yield: 71%. $^1$H NMR ($CDCl_3$, 400 MHz): 8.88 (d, 2H, *J*=6.6 Hz), 8.65 (d, 2H, *J*=6.6 Hz), 8.25 (d, 2H, *J*=6.6 Hz), 8.20 (d, 2H, *J*=6.6 Hz), 7.26 (s, 1H), 6.96 (br s, 3H), 6.04 (d, 2H, *J*=6.6 Hz), 5.86 (d, 2H, *J*=6.6 Hz), 5.56 (s, 2H), 4.82–4.66 (m, 4H), 4.39 (d, 2H, *J*=6.6 Hz), 4.32–4.20 (m, 5H), 2.35–2.06 (m, 8H), 1.97 (s, 3H), 1.95 (s, 6H), 1.47–1.20 (m, 24H), 0.90 (t, 6H, *J*=7.1 Hz), 0.79 (t, 6H, *J*=7.1 Hz). $^{13}$C NMR ($CDCl_3$, 100 MHz): 153.79, 153.35, 153.14, 153.11, 150.39, 149.10, 146.21, 145.61, 139.82, 138.56, 137.73, 136.47, 126.74, 126.58, 124.10, 123.88, 118.57, 117.14, 99.20, 98.59, 55.25, 48.51, 37.12, 37.01, 32.06, 30.17, 29.84, 27.65, 22.69, 22.62, 14.09, 13.99, 10.37, 10.15. MS (FAB) *m/z*: 1043 ($[M-2PF_{6^-}]+$). Mp 283°C (dec.). Anal. Calcd for $C_{67}H_{82}O_8N_2P_2F_{12}$: C, 60.36; H, 6.20. Found: C, 60.49; H, 6.08.

**4.3.2. Tris(viologen)cavitand 16.** Yield: 82% yield. $^1$H NMR ($CD_3COCD_3$, 400 MHz): 9.3–9.2 (m, 12H), 8.7–8.6 (m, 12H), 7.75 (s, 1H), 7.72 (s, 2H), 7.41 (s, 1H), 6.35 (d, 2H, *J*=7.7 Hz), 6.14 (d, 2H, *J*=7.6 Hz), 5.83 (s, 6H), 4.8–4.62 (m, 6H), 4.61 (s, 9H), 4.46 (d, 2H, *J*=7.7 Hz), 2.60–2.12 (m, 8H), 1.92 (s, 3H), 1.3–1.1 (m, 24H), 0.77–0.72 (m, 12H). $^{13}$C NMR ($CD_3COCD_3$, 100 MHz): 154.80, 154.61, 154.55, 154.16, 151.50, 151.46, 150.63, 150.55, 147.77, 147.00, 140.92, 139.89, 139.32, 138.22, 128.24, 127.81, 125.60, 125.16, 121.11, 121.00, 119.49, 100.63, 100.35, 56.05, 49.40, 38.44, 38.25, 32.69, 28.49, 28.42, 23.36, 23.27, 14.33, 10.21. MS (FAB) *m/z*: 1963 ($[M-2PF_{6^-}]+$), 1818 ($[M-3PF_{6^-}]+$). Anal. Calcd for $2C_{89}H_{102}O_8N_6P_6F_{36}$–$CHCl_3$: C, 46.47; H, 4.47. Found: C, 46.59; H, 4.62.

**4.3.3. Pentameric cavitand 17.** A solution of compound **7** (78.5 mg, 0.0378 mmol) and cavitand **3** (360 mg, 0.378 mmol) in DMF (6 mL) was stirred at 50°C for 36 h. The solvent was evaporated under vacuum and the remaining solid was thoroughly washed with hexane and filtered. The solid was dissolved in 7 mL of acetone and precipitated by adding a saturated solution of potassium hexafluorophosphate in water. Water was then added and the precipitate was filtered, washed with excess water and dried under vacuum overnight. The product was then thoroughly washed with ethyl acetate and dried under vacuum overnight to give 0.127 g of compound **17** (55% yield). $^1$H NMR ($CD_3CN$, 400 MHz): 9.00–8.82 (m, 16H), 8.38–8.16 (m, 16H), 7.53 (s, 4H), 7.46 (s, 4H), 7.21 (s, 12H), 6.28 (br s, 4H), 6.05 (d, 8H, *J*=7.1 Hz), 5.83 (d, 8H, *J*=7.1 Hz), 5.57 (br s, 8H), 5.50 (s, 8H), 4.73–4.51 (m, 24H), 4.49 (d, 8H, *J*=7.1 Hz), 4.17 (d, 8H, *J*=7.1 Hz), 2.44–2.15 (m, 40H), 1.97 (s, 12H), 1.95 (s, 24H), 1.43–1.09 (m, 120H), 0.93–0.74 (m, 60H). $^{13}$C NMR ($CD_3CN$, 100 MHz): 154.60, 154.50,154.20, 154.00, 151.20, 151.10, 147.00, 140.80, 139.90, 139.80, 139.20, 138.30, 128.20, 125.90, 125.80, 125.70, 120.98, 120.93, 119.70, 100.60, 100.40, 99.80, 56.30, 56.10, 38.58, 38.47, 32.92, 32.86, 30.6, 30.43, 28.5, 28.39, 28.29, 23.39, 23.34, 23.30, 14.89, 14.46, 10.36, 10.32. Mp 280–282°C (decomp.). Anal. Calcd for $C_{320}H_{384}O_{40}N_8P_8F_{48}$: C, 62.56; H, 6.30. Found: C, 60.61; H, 6.30.

### 4.4. Synthesis of the remaining oligomeric cavitands 18–21

The procedures were similar to that used for the synthesis of **17**, but starting from the pertinent bipy-functionalized cavitands.

**4.4.1. Dimeric cavitand 18.** Yield: 60.0%. $^1$H NMR ($CDCl_3$, 400 MHz): 8.89 (d, 4H, *J*=6.7 Hz), 8.21 (d, 4H, *J*=6.3 Hz), 7.27 (s, 2H), 6.96 (s, 6H), 6.06 (d, 4H,

$J$=7.1 Hz), 5.88 (d, 4H, $J$=7.1 Hz), 5.59 (s, 4H), 4.80–4.67 (m, 8H), 4.39 (d, 4H, $J$=7.1 Hz), 4.28 (d, 4H, $J$=7.1 Hz), 2.39–2.02 (m, 16H), 1.98 (s, 18H), 1.47–1.21 (m, 48H), 0.90 (t, 12H, $J$=6.7 Hz), 0.81 (t, 12H, $J$=6.7 Hz). $^{13}$C NMR ($CDCl_3$, 100 MHz): 153.83, 153.37, 153.19, 153.11, 145.70, 139,81, 138.56, 137.73, 136.42, 126.77, 124.17, 123.89, 118.59, 117.13, 117.11, 99.27, 98.64, 55.40, 37.09, 37.02, 32.07, 32.00, 30.19, 29.85, 27.66, 27.58, 22.69, 22.63, 14.07, 13.96, 10.35, 10.16. Mp 282°C (dec.). MS (MALDI-TOF) $m/z$: 1898 ($M^+-2PF_{6^-}$). Anal. Calcd for $C_{122}H_{150}O_{16}N_2P_2F_{12}$: C, 66.90; H, 6.90. Found: C, 66.25; H, 6.90.

**4.4.2. Trimeric cavitand 19.** Yield: 92%. $^1$H NMR: ($CD_3CN$, 200 MHz) 9.02 (m, 8H), 8.33 (br s, 8H), 7.60 (s, 2H), 7.56 (s, 2H), 7.35–7.25 (m, 8H), 6.40 (d, 1H, $J$=7.8 Hz), 6.25–6.10 (m, 6H), 6.02–5.87 (m, 5H), 5.73–5.56 (m, 8H), 4.82–4.62 (m, 13H), 4.58–4.44 (m, 6H), 4.38–4.21 (m, 5H), 2.58–2.22 (m, 24H), 2.08–1.99 (m, 24H), 1.50–1.13 (m, 72H), 1.02–0.80 (m, 36H). $^{13}$C NMR ($CD_3CN$, 50 MHz): 154.51, 154.42, 154.04, 153.91, 150.69, 150.57, 146.92, 141.35, 140.79, 140.76, 139.73, 139.11, 138.09, 130.04, 129.41, 127.97, 125.92, 125.76, 120.89, 120.84, 119.51, 100.30, 99.63, 56.20, 38.46, 38.35, 32.83, 30.50, 30.33, 28.45, 28.33, 23.31, 23.27, 23.15, 14.38, 10.27, 10.21. Mp 240–245°C (decomp.). MS (ES, $CH_3CN$ $m/z$): 1024 ($[M-3PF_6]^{3+}$), 732 ($[M-4PF_6]^{4+}$). Anal. Calcd for $C_{188}H_{228}F_{24}N_4O_{24}P_4$: C, 64.37; H; 6.55, N, 1.60. Found C, 63.51; H, 6.22; N, 1.49.

**4.4.3. Trimeric cavitand 20.** Yield: 93%. $^1$H NMR: ($CD_3CN$, 338 K, 200 MHz) 9.24–9.10 (m, 8H), 8.66–8.54 (m, 8H), 7.70 (br s, 4H), 7.52–7.35 (m, 8H), 6.22–6.04 (m, 8H), 5.94 (d, 4H, $J$=7.3 Hz), 5.77–5.62 (m, 8H), 4.78–4.54 (m, 16H), 4.45 (d, 4H, $J$=7.8 Hz), 4.12 (d, 4H, $J$=7.3 Hz), 2.42–2.10 (m, 24H), 2.06–1.88 (m, 24H), 1.50–1.20 (m, 72H), 0.97–0.76 (m, 36H). Mp 215–220°C (decomp.). MS (ES, $CH_3CN$ $m/z$): 1024 ($[M-3PF_6]^{3+}$) 732 ($[M-4PF_6]^{4+}$). Anal. Calcd for $C_{188}H_{228}F_{24}N_4O_{24}P_4$: C, 64.37; H, 6.55; N, 1.60. Found C, 64.85; H, 6.18; N, 1.60.

**4.4.4. Tetrameric cavitand 21.** Yield: 52%. $^1$H NMR ($CD_3CN$, 400 MHz): 9.32–8.22 (m, 12H), 8.66–8.58 (m, 12H), 7.78–7.67 (m, 6H), 7.43–7.33 (m, 10H), 6.34 (d, 2H, $J$=7.3 Hz), 6.14 (d, 2H, $J$=7.3 Hz), 6.11–6.05 (m, 6H), 5.91–5.78 (m, 18H), 4.77–4.62 (m, 18H), 4.50–4.41 (m, 8H), 4.17 (d, 6H, $J$=8.0 Hz), 2.49–1.99 (m, 32H), 1.92–1.86 (m, 30H), 1.34–1.11 (m, 96H), 0.83–0.71 (m, 48H). $^{13}$C NMR ($CD_3COCD_3$, 100 MHz): 154.71, 154.64, 154.59, 154.22, 154.12, 151.52, 151.35, 151.26, 147.01, 146.96, 140.95, 140.64, 140.58, 139.78, 139.66, 139.37, 139.15, 138.20, 137.93, 137.88, 128.34, 128.30, 125.69, 125.61, 125.24, 124.99, 124.96, 124.79, 121.19, 121.11, 121.02, 119.72, 119.65, 119.46, 100.59, 100.33, 100.12, 99.69, 56.23, 56.08, 38.45, 38.27, 38.12, 32.75, 28.56, 28.51, 23.41, 23.35, 23.30, 14.36, 10.22. MS (MALDI-TOF) $m/z$: 1465 ($[M-3PF_{6^-}]^{3+}$), 1062 ($[M-4PF_{6^-}]^{4+}$), 820 ($[M-5PF_{6^-}]^{5+}$). Anal. Calcd for $C_{254}H_{306}O_{32}N_6P_6F_{36}$: C, 63.21; H, 6.40. Found: C, 60.88; H, 6.45.

### 4.5. Electrochemical experiments

Cyclic voltammetric measurements were carried out with a Bioanalytical Systems (BAS) 100 B/W electrochemical analyzer. A single-compartment electrochemical cell was fitted with a glassy carbon working electrode (0.018 $cm^2$), a Pt auxiliary electrode and a Ag/AgCl reference electrode (BAS). Typically, a 0.1–0.2 mM solution of the electroactive compound was prepared in pure acetonitrile also containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. This solution was purged with pure nitrogen before the experiments and kept under nitrogen throughout the measurements. The working electrode was polished with a few drops of an aqueous slurry of 0.05-μm alumina on a felt surface before each set of measurements.

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