# Novel cavitands containing electrochemically active 4,4′-bipyridinium subunits

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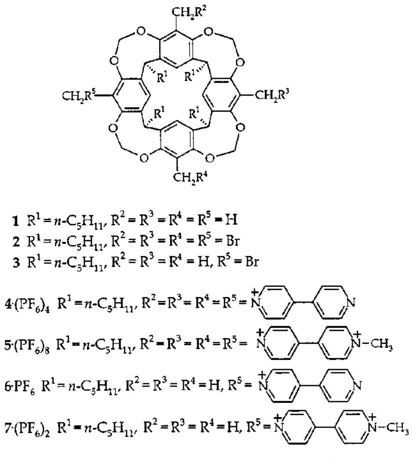
**The synthesis and properties of a series of novel compounds containing one to five cavitand building blocks tethered by 4,4′-bipyridinium subunits is described.**

Cavitands are bowl-shaped compounds that have attracted considerable attention in supramolecular chemistry as building blocks for the construction of carcerands, hemicarcerands, and other hosts.[1,2] Recently, Reinhoudt and co-workers reported the synthesis of tetrabromo cavitand **2** from **1**.[3] Here, we report the synthesis of the monobromo cavitand **3** and the utilization of the brominated cavitands **3** and **2** for the preparation of novel compounds containing several cavitand subunits interconnected by 4,4′-bipyridinium (bipy) tethers.

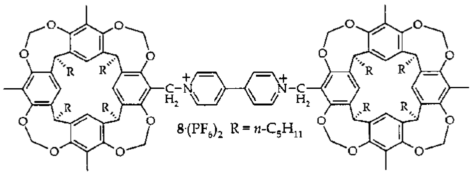
Treatment of **1** with 1 equiv. of NBS under reaction conditions similar to those used by Reinhoudt and co-workers[3] yields monobromo cavitand **3** as the main reaction product.[4] Reaction of **2** and **3** with excess 4,4′-bipyridine at 50 °C gives **4** or **6**, respectively, in high yield ( > 90%).† Alkylation of these cavitands with MeI leads to the fully quaternized 4,4′-bipyridinium derivatives **5** and **7**, which were isolated as their $PF_6^-$ salts after counterion exchange. Molecular modeling results obtained with **4**–**7** and single-crystal X-ray diffraction data for **4** suggest that both the partially and fully quaternized bipy subunits tend to orient themselves on or near the plane defined by the four benzylic carbons through which they are connected to the cavitand bowl. This is clearly evident in the X-ray crystal structure[5] of **4** (Fig. 1).

It is also possible to quaternize the free nitrogens in **4** or **6** by treatment with the monobromo cavitand **3**. Thus, reaction of **6** with 1 equiv. of **3** yields, after counterion exchange, the dimeric cavitand **8**. Similarly, the cruciform pentameric cavitand **9** was obtained by reaction of **4** with 4 equiv. of **3**.

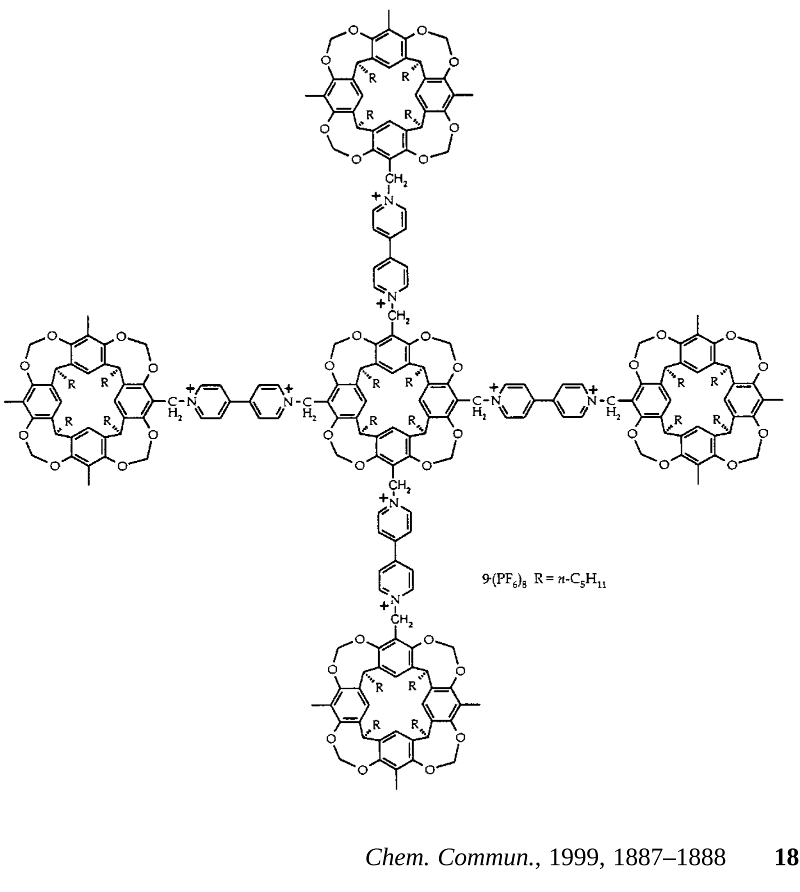
The presence of partially or fully quaternized 4,4′-bipyridinium subunits confers redox properties to these compounds.[6] Their electrochemical behavior in MeCN solution was investigated using cyclic voltammetry. Each monoquaternized bipy residue exhibits a single one-electron reduction ($V^+ \rightarrow V$) and each diquaternized bipy subunit exhibits two consecutive one-electron reductions ($V^{2+} \rightarrow V^+$ and $V^+ \rightarrow V$). The half-wave potentials obtained in these experiments are given in Table 1. The voltammetric behavior of all the compounds having four reducible subunits reveals their non-interacting character, since only one wave is observed for each one of the reduction processes. The multi-electron character of some of these voltammetric waves may be responsible for the departure of the observed peak-to-peak potential differences from the theoretical values expected for Nernstian redox couples. The electrochemical behavior of **4** was strongly affected by precipitation of



**1** $R^1 = n\text{-}C_5H_{11}$, $R^2 = R^3 = R^4 = R^5 = H$
**2** $R^1 = n\text{-}C_5H_{11}$, $R^2 = R^3 = R^4 = R^5 = Br$
**3** $R^1 = n\text{-}C_5H_{11}$, $R^2 = R^3 = R^4 = H$, $R^5 = Br$
**4**·$(PF_6)_4$ $R^1 = n\text{-}C_5H_{11}$, $R^2 = R^3 = R^4 = R^5 =$
**5**·$(PF_6)_8$ $R^1 = n\text{-}C_5H_{11}$, $R^2 = R^3 = R^4 = R^5 =$
**6**·$PF_6$ $R^1 = n\text{-}C_5H_{11}$, $R^2 = R^3 = R^4 = H$, $R^5 =$
**7**·$(PF_6)_2$ $R^1 = n\text{-}C_5H_{11}$, $R^2 = R^3 = R^4 = H$, $R^5 =$



**8**·$(PF_6)_2$ $R = n\text{-}C_5H_{11}$



**9**·$(PF_6)_8$ $R = n\text{-}C_5H_{11}$

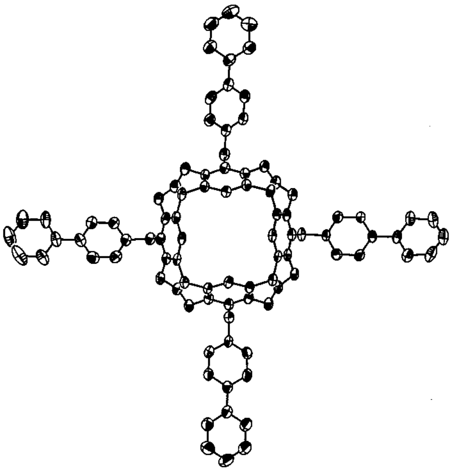


**Fig. 1** X-Ray crystal structure of **4**. The four pentyl chains in the lower rim, hexafluorophosphate counterions and solvent molecules have been removed for clarity.

**Table 1** Electrochemical[a] (half-wave potentials and peak-to-peak potential splittings) and spectroscopic parameters for **4–9**

| | $E$/V *vs.* Ag/AgCl ($\Delta E_p$[b]/mV) | | | |
|---|---|---|---|---|
| Cavitand | $E^1_{1/2}$ | $E^2_{1/2}$ | $\lambda_{max}$/nm | $\varepsilon$/M$^{-1}$ cm$^{-1}$ |
| **4** | [c] | [c] | 266 | 88 400 |
| **5** | −0.28 (87) | −0.81 (74) | 257 | 104 000 |
| **6** | −0.88 (58) | — | 264 | 25 300 |
| **7** | −0.34 (57) | −0.79 (55) | 234 | 34 700 |
| | | | 250 | 31 200 |
| **8** | −0.26 (82) | −0.82 (56) | [d] | [d] |
| **9** | [c] | [c] | 251 | 141 000 |

[a] Electrochemical parameters measured with a glassy carbon working electrode immersed in 0.1 M TBAPF$_6$–MeCN solutions of **4–9**. [b] $\Delta E_p$ values measured at 0.1 V s$^{-1}$. [c] Accurate half-wave potentials could not be obtained (see text). [d] No maxima were observed in the spectrum.

the reduced form on the electrode surface. Compound **9** exhibited complicated voltammetric behavior that is currently under more detailed scrutiny.

Conceptually, these compounds provide an interesting example of covalent self-assembly. Notice that **9**, the largest compound reported here, has a molecular mass of 6138.6 daltons and a branching structure that is similar to that found in dendrimers. We are currently exploring bromination patterns for **1** that may result in different structures after reaction with 4,4′-bipyridine linkers.

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## Notes and references

† All new compounds gave satisfactory elemental analyses. *Selected data* for **3**: $\delta_H$(CDCl$_3$, 400 MHz) 7.14 (s, 1H), 6.97 (s, 3H), 5.95 (d, 2H, $J$ 7.14), 5.87 (d, 2H, $J$ 7.14), 4.81–4.70 (m, 4H), 4.60 (s, 2H), 4.42 (d, 2H, $J$ 7.14), 4.37 (d, 2H, $J$ 7.14), 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); $\delta_C$(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; $m/z$ (FAB, NBA) 953 (MH$^+$); mp 242–244 °C. For **4**: $\delta_H$(CD$_3$CN, 400 MHz) 8.90–8.82 (m, 16H), 8.23 (d, 8H, $J$ 6.35), 7.78 (d, 8H, $J$ 5.55), 7.60 (s, 4H), 6.33 (d, 4H, $J$ 7.14), 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, $J$ 7.14); $\delta_C$(CD$_3$CN, 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; $m/z$ (FAB) 1929 ([M − PF$_6$]$^+$), 892 ([M − 2 PF$_6$]$^{2+}$); mp 255 °C (decomp.). For **6**: $\delta_H$(CD$_3$CN, 400 MHz) 8.92–8.84 (m, 4H), 8.11 (d, 2H, $J$ 6.96), 8.01 (d, 2H, $J$ 6.22), 7.26 (s, 1H), 6.95 (s, 3H), 6.09 (d, 2H, $J$ 7.32), 5.89 (d, 2H, $J$ 7.14), 5.64 (s, 2H), 4.77 (t, 2H, $J$ 8.06), 4.71 (t, 2H, $J$ 8.06), 4.43 (d, 2H, $J$ 7.32), 4.30 (d, 2H, $J$ 7.32), 2.04–2.38 (m, 8H), 2.03 (s, 9H), 1.99 (s, 9H), 1.46–1.22 (m, 24H), 0.95–0.83 (m, 12H); $\delta_C$(CD$_3$CN, 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; $m/z$ (FAB, NOBA) 1029 ([MH − PF$_6$]$^+$); mp 282 °C (decomp.). For **8**: $\delta_H$(CDCl$_3$, 400 MHz) 8.89 (d, 4H, $J$ 6.74), 8.21 (d, 4H, $J$ 6.35), 7.27 (s, 2H), 6.96 (s, 6H), 6.06 (d, 4H, $J$ 7.14), 5.88 (d, 4H, $J$ 7.14), 5.59 (s, 4H), 4.80–4.67 (m, 8H), 4.39 (d, 4H, $J$ 7.14), 4.28 (d, 4H, $J$ 7.14), 2.39–2.02 (m, 16H), 1.98 (s, 18H), 1.47–1.21 (m, 48H), 0.90 (t, 12H, $J$ 6.74), 0.81 (t, 12H, $J$ 6.74); $\delta_C$(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; $m/z$ (MALDI-TOF) 1898 ([M − 2PF$_6$]$^+$); mp 282 °C (decomp.). For **9**: $\delta_H$(CD$_3$CN, 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, $J$ 7.16), 5.83 (d, 8H, $J$ 7.16), 5.57 (br s, 8H), 5.50 (s, 8H), 4.73–4.51 (m, 24H), 4.49 (d, 8H, $J$ 7.16), 4.17 (d, 8H, $J$ 7.16), 2.44–2.15 (m, 40H), 1.43–1.09 (m, 120H), 0.93–0.74 (m, 60H); $\delta_C$(CD$_3$CN, 100 MHz) 154.6, 154.5, 154.2, 154, 151.2, 151.1, 147, 140.8, 139.9, 139.8, 139.2, 138.3, 128.2, 125.9, 125.8, 125.7, 120.98, 120.93, 119.7, 100.6, 100.4, 99.8, 56.3, 56.1, 38.58, 38.47, 32.92, 32.86, 30.6, 30.43, 28.5, 28.39, 29.29, 23.39, 23.34, 23.30, 14.89, 14.46, 10.36, 10.32; mp 280–282 °C (decomp.).

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2 A. Jasat and J. C. Sherman, *Chem. Rev.*, 1999, **99**, 931.

3 H. Boerrigter, W. Verboom and D. N. Reinhoudt, *J. Org. Chem.*, 1997, **62**, 7148.

4 The reaction also produced small amounts of tribromo and dibromo derivatives that we are currently trying to prepare and isolate in larger yields.

5 *Crystal data* for **4**: C$_{104}$H$_{112}$F$_{24}$N$_8$O$_{12}$P$_4$, $M$ = 2245.88, triclinic, space group $P\bar{1}$, $a$ = 17.9704(9), $b$ = 18.3237(9), $c$ = 19.771(1) Å, $\alpha$ = 67.629(1), $\beta$ = 67.447(1), $\gamma$ = 78.767(1)°, $V$ = 5550.9(5) Å$^3$, $T$ = 173(2) K, $Z$ = 2. Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A hemisphere of data (1381 frames) was collected using the $\omega$-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on $I$ was < 1%). Absorption corrections by integration were applied based on measured indexed crystal faces. The structure was solved by the direct methods in SHELXTL5, and refined using full-matrix least-squares. The non-H atoms were treated anisotropically, whereas the methyl hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. Two of the R groups on the cation are disordered. They were refined in two parts each with their site occupation factors dependently refined. All four of the hexafluorophosphates are disordered and were refined with their geometries constrained to form perfect octahedra around the P atoms. The structure consists of the macrocycle cation, four hexafluorophosphates and a variety of solvent molecules most of which are disordered or partially present in the lattice. Some of the solvents identified and included in the refinement include MeCN, acetone, EtOH, MeOH and water. Because of the large lattice volumes occupied by disordered solvents, a precise formula weight could not be used but instead an approximate formula was used to reflect all that was refined. It should be noted that the refinement provided acceptable anisotropic models for the cation and four anions while all of the solvents were treated isotropically. A total of 1688 parameters, with 248 constraints, were refined in the final cycle of refinement using 14505 reflections with $I > 2\sigma(I)$ to yield $R_1$ and $wR_2$ of 8.46 and 20.58%, respectively. Refinement was done using $F^2$. CCDC 182/1372. See http://www.rsc.org/suppdata/cc/1999/1887/ for crystallographic data in .cif format.

See, for instance: A. Mirzoian and A. E. Kaifer, *Eur. J. Chem.*, 1997, **3**, 1052.

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