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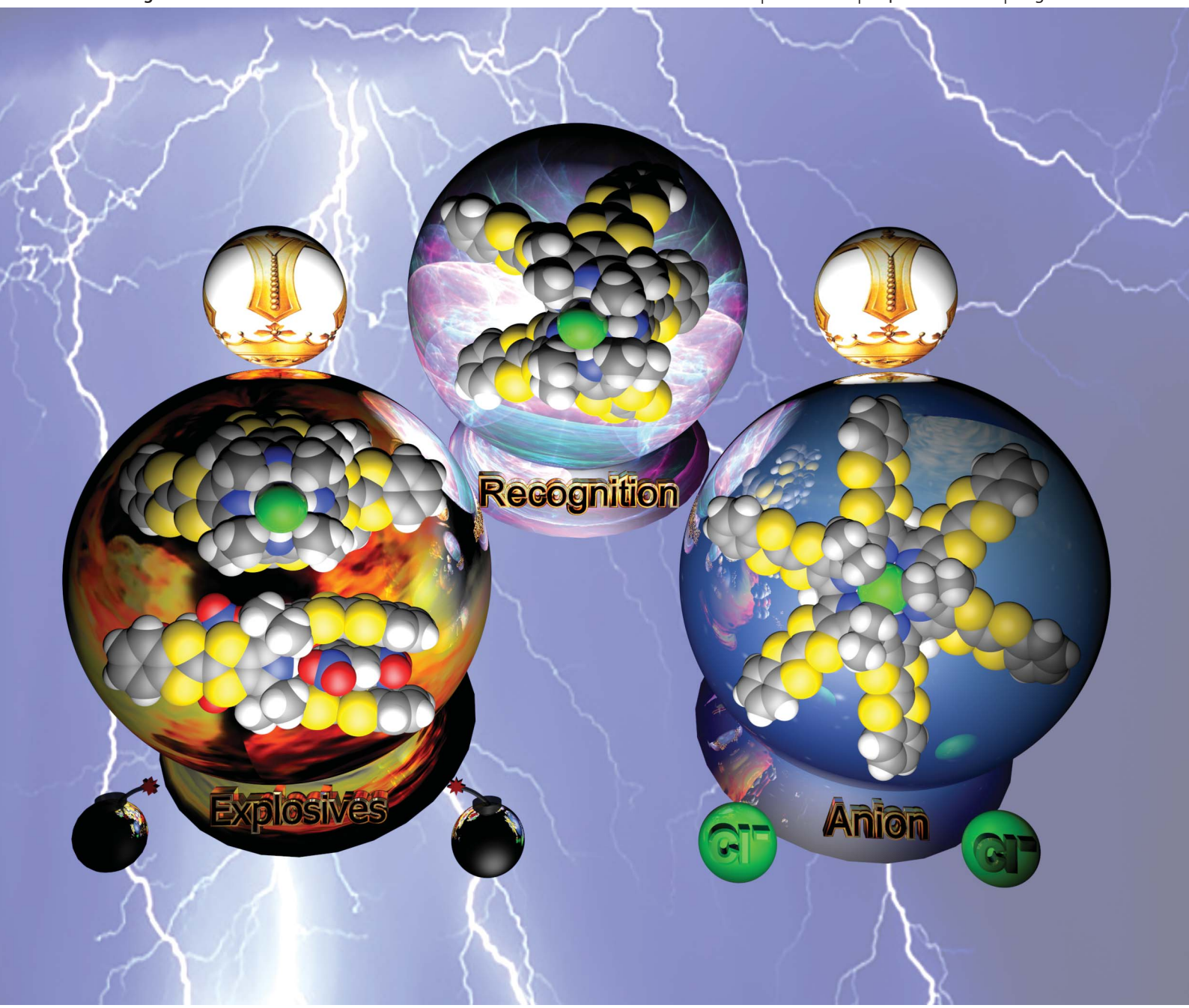

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Synthesis and recognition properties of higher order tetrathiafulvalene (TTF) calix[*n*]pyrroles (*n* = 4–6)†

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Two new benzoTTF-annulated calix[*n*]pyrroles (*n* = 5 and 6) were synthesized *via* a one-step acid catalyzed condensation reaction and fully characterized *via* single crystallographic analyses. As compared to the known tetra-TTF annulated calix[4]pyrrole, which is also produced under the conditions of the condensation reaction, the expanded calix[*n*]pyrroles (*n* = 5 and 6) are characterized by a larger cavity size and a higher number of TTF units (albeit the same empirical formula). Analysis of the binding isotherms obtained from UV-Vis spectroscopic titrations carried out in $CHCl_3$ in the presence of both anionic (Cl^-, Br^-, I^-, CH_3COO^-, $H_2PO_4^-$, and HSO_4^-) and neutral (1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitrotoluene (TNT)) substrates revealed that as a general rule the calix[6]pyrrole derivative proved to be the most efficient molecular receptor for anions, while the calix[4]pyrrole congener proves most effective for the recognition of TNB and TNT. These findings are rationalized in terms of the number of electron rich TTF subunits and NH hydrogen bond donor groups within the series, as well as an ability to adopt conformations suitable for substrate recognition, and are supported by solid state structural analyses.

Recent years have been marked by ongoing efforts to develop artificial synthetic receptors with an ability to recognize specific chemical species and to understand the underlying determinants that promote selectivity.[1] Among the many molecular frameworks that have been extensively studied in this context, calix[4]pyrrole derivatives have received particular scrutiny because of (i) their ability to bind a range of anions and neutral molecules and (ii) their dynamic conformation features.[2] Indeed, a large number of calix[4]pyrrole derivatives have been synthesized and studied with a view to understanding better the features that control their guest binding properties.[3] Although several of the basic frameworks are known, much less attention has been paid to the recognition features of higher order calix[*n*]pyrroles (*n* > 4).[3–9] Such extended-cavity receptors are of interest because it might be expected that they will display altered guest binding affinities on account of variations in cavity size, shape, number of NH hydrogen bond donor units, and conformational properties that differ from those of the calix[4]pyrroles.[4] However, to date systematic studies of calix[*n*]pyrroles where *n* > 4 are limited. In fact, detailed comparisons of the molecular recognition features within a well-defined series of calix[*n*]pyrrole analogues (where, *e.g.*, *n* = 4, 5, and 6) are essentially nonexistent.[3b,c] On the other hand, were such comparison data available, it could provide important insights into the fundamental relationship between the nature of the calix[*n*]pyrrole framework and its guest binding properties. Here, we report a one-step synthesis of two new benzoTTF-calix[*n*]pyrroles (TTF = tetrathiafulvalene; *n* = 5 and 6). These systems, which have been characterized by spectroscopic and electrochemical means, as well as by single crystal X-ray diffraction analysis, were studied for their ability to recognize simple anionic substrates and electron deficient guests, specifically, 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitrotoluene (TNT). As detailed below, the calix[6]pyrrole derivative proved to be the most effective receptor for anions, whereas the parent calix[4]pyrrole, a known compound,[9] was found to interact more strongly with TNB and TNT than its *n* = 5 or *n* = 6 calix[*n*]pyrrole homologues.

To date, it has proved difficult to synthesize and isolate appreciable quantities of higher order symmetrical-calix[*n*]pyrroles (*n* > 4) *via* the one-step acid catalyzed condensation of ketones and pyrroles used to prepare calix[4]pyrroles because of the predominant formation of the corresponding cyclic tetramers.[10]

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† Electronic supplementary information (ESI) available: Spectral and other characterization data (^1H, ^{13}C NMR, and MALDI-TOF mass spectra, combustion analysis) for new compounds; X-ray experimental, binding studies and electrochemical data. CCDC 868898 for **2·TBACl**, CCDC 868897 for **3·THACl**, and CCDC 868896 for **4·TBACl**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2sc20636f

As a consequence, a variety of covalent templates,[5] post-synthetic modification strategies,[6] and multi-step approaches[7] have been employed. Elegant as these approaches are, there is still considerable appeal associated with obtaining higher order calix[*n*]pyrroles ($n > 4$), *via* the direct, acid catalyzed condensation of simple pyrrolic precursors. Unfortunately, to the best of our knowledge, such a direct condensation procedure has proved effective in only two cases. First, using 3,4-difluoro-1*H*-pyrrole as a precursor, it proved possible to isolate in good yield the corresponding calix[5]- and calix[8]pyrrolic products.[8] Second, when bismuth nitrate was employed as a Lewis acid catalyst *meso*-pentaspirocyclohexyl-calix[5]pyrrole could be obtained from the condensation of pyrrole and cyclohexanone.[3b] Neither of these sets of calix[*n*]pyrrole congeners bears ancillary β-pyrrolic functionality, such as TTF, that would be expected to modulate their basic binding properties. In fact, it is important to note that, in spite of what one might intuit, it is not possible to prepare calix[*n*]pyrroles bearing β-pyrrolic substituents *via* either the simple acid-catalyzed condensation methods used to prepare simple calix[4]pyrroles or *via* any of the procedures currently known in the literature. This lack of precedent led us to explore the synthesis of higher order TTF functionalized calix[*n*]pyrrole derivatives (TTF-C*n*Ps; $n > 4$).

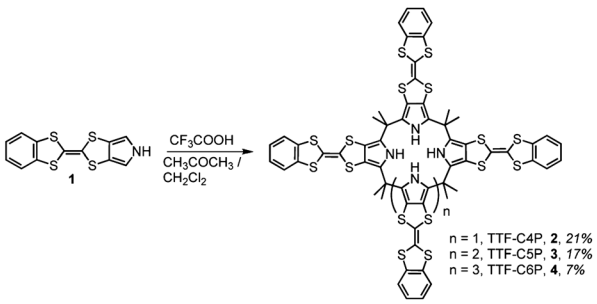
Recently we reported the synthesis of several TTF-C4Ps and their supramolecular interactions with anions,[11] C_{60},[12] flat nitroaromatic explosives,[9,13] and other electron deficient guests.[14] As with simple, unfunctionalized calix[4]pyrroles, chemical switching effects were noted. For instance, the most stable conformation in the absence of a bound anion, the so-called 1,3-alternate conformation of the TTF-C4Ps, was found to bind flat-electron deficient substrates, such as TNT, TNB, or 2,4,6-trinitrophenol (TNP) in a 1 : 2 fashion in a positive cooperative manner.[9,13] However, in the presence of a coordinating anion, such as chloride, the so-called cone conformation is stabilized. This bowl-like form is too large to bind TNT, TNB, or TNP effectively. On the other hand it is effective for C_{60} encapsulation[12] and for the recognition of electron deficient substrates, such as either bis-imidazolium quinone ($BIQ^{2+}2X^-$) or $[Li@C_{60}]^+$, which allows anion-triggered electron transfer processes to be engendered and controlled.[15] Given these interesting features of the TTF-C4Ps, we sought to prepare higher order TTF-C*n*Ps ($n > 4$) species. Towards this end, we focused on the use of the benzannulated TTF-functionalized pyrrole **1**, as the key precursor since enhanced affinities for electron deficient guests had previously been observed for the corresponding TTF-C4P as compared to the original bis-propylthio-TTF derivative.[9,16]

As shown in Scheme 1, a series of benzoTTF-calix[*n*]pyrroles (BzTTF-C*n*Ps) **2**, **3**, and **4** could be prepared easily *via* the one-step, trifluoroacetic acid (TFA) catalyzed condensation of **1** with an excess of Me_2CO at room temperature in CH_2Cl_2. Compared to the standard protocol used to produce octamethylcalix[4]pyrrole, which involves a stoichiometric ratio between pyrrole and Me_2CO, as well as a catalytic amount of TFA, it was found that the preparation of these TTF-annulated analogues required substantially longer reaction times (1–2 days at room temperature), the use of larger amounts of TFA (*i.e.*, 2–3 equiv) and more Me_2CO. However, using these modified conditions, yields of 21%, 17%, and 7% were obtained for **2**, **3**, and **4**, respectively. In the course of the present investigation, we also found that by adopting the procedure used to obtain **2**–**4** to the original bis-propylthio pyrrolo-TTF analogous to **1** (compound **5**), it proved possible to isolate the bis-propylthio calix[5]pyrrole analogue of **3**.[17]

In order to evaluate the effect of the calixpyrrole framework on the anion binding affinities within the present matched set of structures, the interactions between the three benzoTTF-calix[*n*]pyrroles **2**, **3**, and **4** with a series of anions (as their corresponding tetrabutylammonium, TBA^+, salts) were investigated. This was done by means of standard UV-Vis spectrophotometric titrations carried out in $CHCl_3$. The change in the absorption intensity at 370 nm as a function of increasing anion concentration was then used to construct binding isotherms and calculate the association constants, K_a, in accord with standard methods as we have used previously in studies of calixpyrroles.[2] Details of the binding isotherms and the resulting curve fits are included in the ESI†. The results themselves are summarized in Table 1.

Based on the K_a values in Table 1, it can be concluded that within this matched set the calix[6]pyrrole **4** is the best anion binding agent. Of all the anion–receptor permutations analyzed, the highest anion affinity was seen for the combination of chloride and receptor **4** (5 300 000 M^{-1} in $CHCl_3$). However, a strong association with acetate was also observed for both **4** and **2** in this same medium (K_a = 870 000 and 140 000 M^{-1} for these two systems, respectively). Across the board, receptor **4** was found to display the highest anion binding affinity. In general, the affinity sequence **4** > **2** > **3** was followed, although in the case of HSO_4^- the order of relative affinities was found to be **4** > **3** > **2**. On this basis, we conclude that the calix[6]pyrrole system **4** is the best anion binding agent and that the anion affinities are not directly correlated with either the number of NH hydrogen bonding donors or the size of the macrocyclic cavities. This conclusion is consistent with what might be inferred from extraction (as opposed to binding) studies carried out by Kohnke *et al.* using β-free calix[4]- and calix[6]-, but not calix[5]pyrroles.[6b]

A priori, we considered it likely that the higher order calix[*n*]-pyrroles derivatives **3** and **4**, possessing extended cavities and a larger number of NH donor sites, would show enhanced relative affinities for the larger halides, Br^- and I^- with respect to Cl^-. In fact, the relative binding order for these two new receptors proved to be the same as for **2**, namely $Cl^- > Br^- > I^-$, although receptor **4** was found to display somewhat larger binding affinities for Br^- and I^- relative to receptor **2**. We interpret this binding order in terms of the strength of the hydrogen bonding interactions between these halide ions and the pyrrollic NH



Scheme 1 Synthesis of benzoTTF-calix[*n*]pyrroles **2**, **3**, and **4** ($n = 4$, 5, and 6).

Table 1 Effective association constants (K_a, M^{-1}) corresponding to the interaction between the benzoTTF-calix[*n*]pyrroles of this study (compounds **2**, **3**, and **4**) with nitroaromatic (TNB and TNT) guests and the TBA salts of selected anions in $CHCl_3$[a]

Compound	**2**	**3**	**4**
Cl^-	520 000	13 000	5 300 000
Br^-	21 000	8300	34 000
I^-	480	Nd	1800
CH_3COO^-	140 000	22 000	870 000
$H_2PO_4^-$	100 000	14 000	110 000
HSO_4^-	140	2650	7000
TNB	2800, 17 000[b]	870	1200
TNT	570, 2600[b]	220	480

[a] All K_a values were obtained from UV-Vis spectrophotometric titration experiments carried out in $CHCl_3$ at 296 K. The binding stoichiometries (1 : 1 or 1 : 2 receptor–substrate when one or two K_a values are listed, respectively) are on the basis of curve fits or continuous variation (Job) plots; see ESI. The anions were studied in the form of their tetrabutylammonium (TBA^+) salts. The estimated errors are ≤15%. [b] Data from ref. 9.

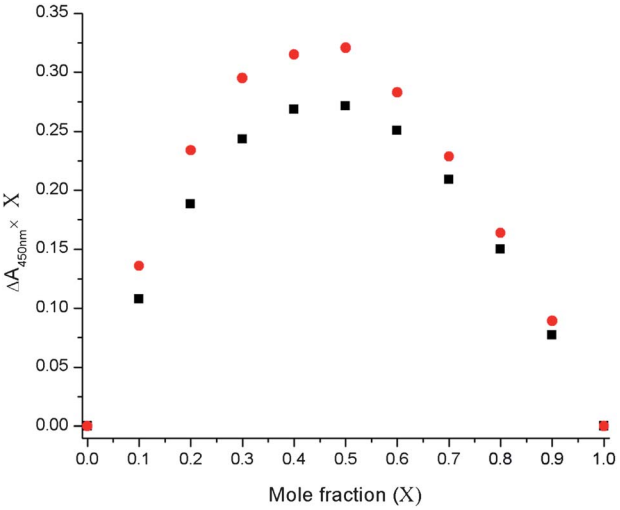


Fig. 2 Continuous variation plots for $CHCl_3$ mixtures of [**3** + TNB] and [**4** + TNB]. These plots were constructed by plotting the product of the change in the absorption at 450 nm and the mole-fractions of the receptor **3** (black squares) or **4** (red circles) *vs.* the corresponding mole fractions of **3** and **4**.

protons, which reflects the charge density of the anion in question ($Cl^- > Br^- > I^-$). It is however worth noting that receptor **4** displays a significantly higher selectivity factor for chloride with respect to bromide than does either **2** or **3** (*i.e.*, $K_{a\ TBACl}/K_{a\ TBABr} \approx 156$ for **4**, 25 for **2**, and 1.6 for **3**). We ascribe the high binding affinities and selectivities displayed by receptor **4** to a macrocyclic inclusion effect that serves to enhance the effects of size discrimination within the cavity, as well as to the presence of two additional N–H···X^- hydrogen bonds. In contrast, for **2** and **3** anion complexation involves a facial arrangement of hydrogen bonding interactions, which is thought to favor the smaller halide anions, such as chloride and bromide.

The above rationalization is supported by X-ray crystallographic analyses of the chloride bound forms of receptors **2**, **3**, and **4**.‡ X-Ray quality single crystals were obtained by allowing pentane to diffuse slowly into equimolar mixtures of **2**, **3**, and **4** and tetrabutylammonium chloride or tetrahexylammonium chloride in chloroform. In this way, yellow, diffraction-quality single crystals were obtained for [**2** + TBACl], [**3** + THACl], and [**4** + TBACl]. The resulting structures are shown in Fig. 1 and served to confirm that all three receptors form 1 : 1 complexes with the chloride anion in the solid state. In the case of receptor **4**, all six pyrrolic protons interact with the bound chloride, as inferred from the structural parameters (Cl···H–N distances = 2.39 ± 0.01 Å). The chloride anion itself is perfectly centered in the cavity and resides within an imaginary plane defined by the hexagonal arrangement of the pyrrolic nitrogen atoms. In contrast, four NH···Cl^- hydrogen bonding interactions are seen in the case of receptors **2** and **3**, as judged from the Cl···HN distances (2.49 ± 0.07 Å for **2** and 2.43 ± 0.01 Å for **3**). On this basis, we conclude that receptor **3** is not optimized for chloride anion binding. In contrast, the existence of two additional NH hydrogen bonds and encapsulation of the chloride anion is fully supportive of the high K_a value and high selectivity seen for the chloride anion complex of **4** in $CHCl_3$ solution (*vide supra*).

Although both **2** and **3** adopt a cone conformation in the presence of chloride, receptor **3** is characterized by a more distorted geometry and less favourable hydrogen bonding modes as compared to those present in the chloride anion complex stabilized by receptor **2**. It is also worth noting that the TBA^+ counter cation is bound inside the "cup" of the bowl-shaped cavity of the

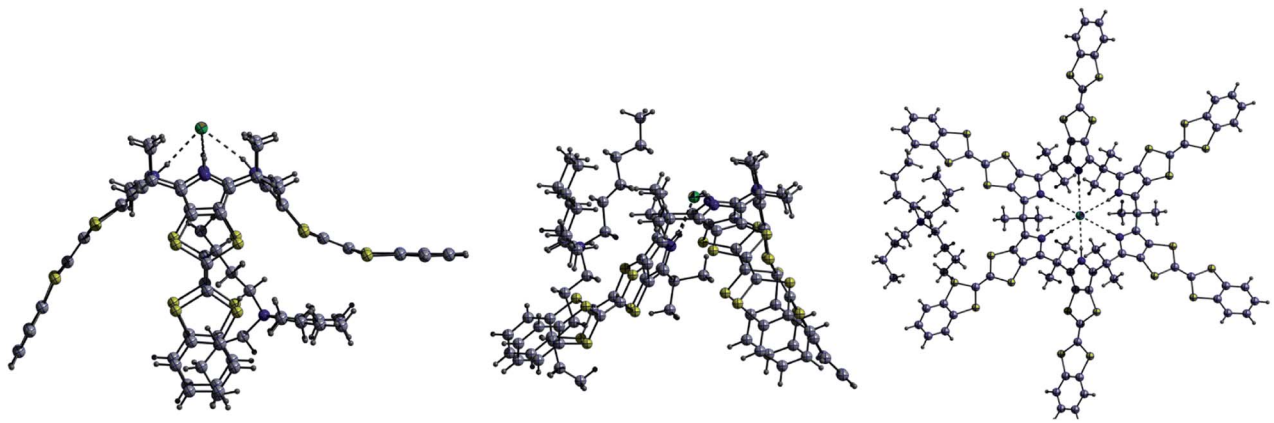


Fig. 1 X-Ray crystallographic analyses of chloride bound benzoTTF-calix[*n*]pyrroles **2**–**4** (*n* = 4, 5, and 6).

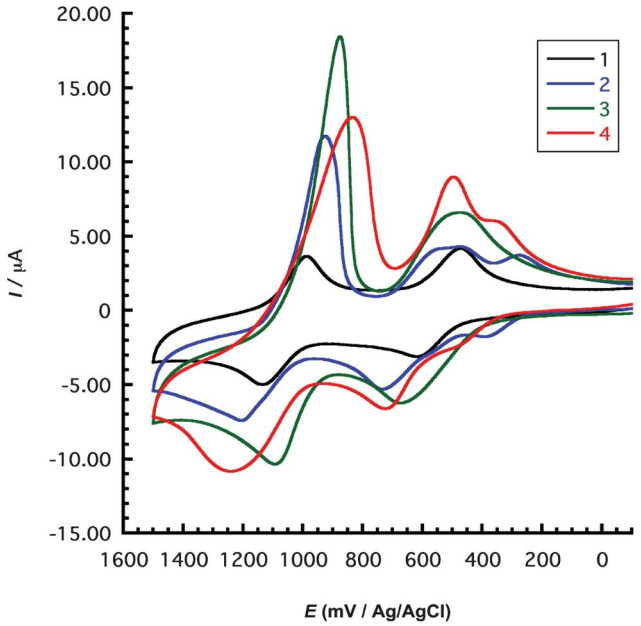


Fig. 3 Overlaid cyclic voltammograms of 0.2 mM solutions of **1–4** in $CHCl_3$ using 0.4 M $TBAPF_6$ as the supporting electrolyte, Ag/AgCl as the reference electrode, platinum wire as the counter electrode, glassy carbon as the working electrode, and a scan rate of 100 mV s^{-1}.

Table 2 Cyclic voltammetric data for **1–4** in $CHCl_3$

Compound	E_1 [a] (mV)	E_1' [a] (mV)	E_2 [a] (mV)
1	+540		+1070
2	+330	+600	+1060
3	+570		+980
4	+430	+610	+1040

[a] Half-wave potentials (*vs* Ag/AgCl) for compounds **1–4** (0.2 mM) at room temperature using a Pt wire, glassy carbon, and Ag/AgCl as the counter, working, and reference electrodes, respectively. $TBAPF_6$ (0.4 M) was used as the supporting electrolyte.

receptor in the case of the chloride anion complex **2**. Such inclusion of small ammonium cations by TTF-C4P frameworks was also seen in prior studies with this and related TTF-C4Ps.[15,16] The resulting recognition of both pairs of ions (Cl^- and TBA^+), and the underlying cooperative binding of the salt, could account for the higher relative affinity seen in the case of **2**, as compared to **3**.

The interactions between the benzoTTF-calix[*n*]pyrroles and the test electron deficient substrates, TNB and TNT, were also probed in $CHCl_3$ solution. Here, continuous variation and binding isotherm analyses were carried out using standard UV-Vis spectrophotometric titrations. Details of these experiments and the resulting binding isotherms are included in the ESI†.

Prior to the present study, we showed that receptor **2** (a calix[4]pyrrole) displays positive homotropic allosterism when interacting with flat, electron deficient polynitro-aromatic substrates, such as TNB, TNP, and TNT.[9] In this prior work (wherein anion affinities were not considered *per se*), it was concluded that 1 : 2 complexes, such as **2**·$(TNP)_2$ and **2**·$(TNB)_2$, are formed, both in solution and in the solid state. This conclusion was reached on the basis of both continuous variation plots showing a maximum at 0.33 and X-ray crystallographic analyses. On the other hand, the new systems **3** and **4** both bind TNB to form a complex of net 1 : 1 stoichiometry, as inferred from the maxima at 0.5 seen in the Job plots (Fig. 2). This difference in complexation stoichiometry between receptor **2** and its expanded calixpyrrole systems **3** and **4** is striking, especially since the latter two receptors incorporate a greater number of electron rich TTF units and might thus be expected to interact with a greater, not lesser, number of electron deficient substrates.

As in the case of **2**, adding either TNB or TNT to a $CHCl_3$ solution of **3** or **4** led to a progressive color change from yellow to green. Based on quantitative analyses of the interaction, as reflected in the K_a values summarized in Table 1, receptor **2** was found to display the strongest binding affinities for both TNB and TNT with the affinity sequence being **2** $\gg$ **4** > **3**. We rationalize the better binding seen in the case of **2** in terms of a combination of favorable geometric and cooperative effects. The latter require the presence of a well-defined 1,3-alternate conformation, which is only possible in the case of the smallest calix[*n*]pyrrole, **2**. In this conformation, receptor **2** is capable of sandwiching TNB and TNT *via* a combination of hydrogen bonding and donor–acceptor interactions,[9,14] whereas receptors **3** and **4** cannot adopt conformations that would stabilize these interactions.

The cyclic voltammetric properties of receptors **2–4** and precursor **1** were studied in $CHCl_3$ solution at room temperature using standard electrochemical methods (*cf.* Fig. 3). The corresponding half-wave potentials, tabulated with respect to a Ag/AgCl reference electrode, are summarized in Table 2. These data highlight structural differences: in spite of the fact that receptors **2**, **3**, and **4** all contain identical benzoTTF redox-active subunits connected *via* analogous sp^3-hybridized bridging *meso*-carbon atoms, their electrochemical features are different. For instance, receptors **2** and **4** display lower first-oxidation potentials than either **1** or **3**, with the sequence **2** < **4** < **1** < **3** being observed. The cyclic voltammograms of both **2** and **4** are also characterized by the presence of three consecutive anodic steps, while those of **1** and **2** possess two consecutive oxidation steps.

The lower first oxidation potential of **2** with respect to **1**, as well as the observed "splitting" of the first redox process, is rationalized in terms of the formation of stable mixed valence dimers $[(TTF)_2]^+$. These dimers are stabilized by through-space interactions supported by the TTF-calix[4]pyyrole framework, which allows access to structures containing parallel pairs of TTF units upon oxidation, as seen in the case of a related TTF-C4P related to **2**.[15a] Based on an analysis of the structure, we do not believe that such intra-macrocycle stabilization of $[(TTF)_2]^+$ subunits is possible in the case of **5**. Nor, is it possible in the case of monomer **1**. An intermediate level of interaction is inferred in the case of **4**.

Conclusions

In summary, we report the synthesis and characterization of two new expanded benzoTTF annulated-calix[*n*]pyrroles. On the basis of anion binding studies, it was concluded that the calix[6]pyrrole framework **4** displays the strongest binding affinities toward anions in general, being particularly selective for the chloride anion among the species tested. This relatively high

affinity and selectivity is ascribed to a combination of stronger hydrogen bonding and macrocyclic inclusion effects. In contrast, particularly low affinities were noted in the case of the calix[5]-pyrrole **3**.

A very different binding trend was seen for flat aromatic guests. Here, the greatest affinities were seen in the case of calix[4] pyrrole **2**. Here, a 2 : 1 receptor : substrate binding stoichiometry is observed with the high affinity ascribed to a combination of size matching, hydrogen bonding, donor–acceptor interactions, and cooperative effects that are either not operative or less prevalent in the case of the higher homologues.

On the basis of the present findings, we conclude that the combined actions of various factors, including the number and strength of participating hydrogen bonds, the complementarity of the underlying receptor–substrate interactions, conformational features, as well as ion-pairing and solvation effects in the case of charged species, can all play a role in mediating the binding events in functionalized calix[*n*]pyrroles. In particular, we have found that in the present set of congeneric receptors "size matters" but that "bigger isn't always better". This finding, which reflects different trends for different classes of substrates (neutral *vs.* anionic), is expected to animate further efforts to design and prepare selective multi-substrate recognition systems.

Acknowledgements

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Notes and references

‡ X-Ray crystallographic data for **2·TBACl** were collected on a Rigaku AFC8 diffractometer equipped with a Saturn CCD area detector and a graphite monochromatized MoK_α source ($\lambda = 0.71070$ Å). The data were collected at 100 K under a cold nitrogen stream. X-Ray crystallographic data for **3·THACl** were collected on Rigaku R-Axis Spider with Image Plate detector using a graphite monochromator with CuK_α radiation ($\lambda = 1.5418$ Å). The data were collected at 100 K using a Rigaku XStream low temperature device. X-Ray crystallographic data for **4·TBACl** were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoK_α radiation ($\lambda = 0.71073$ Å). The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collections, and structure refinements of **2·TBACl**, **3·THACl**, and **4·TBACl** are listed in the ESI†. CCDC 868898 for **2·TBACl**, CCDC 868897 for **3·THACl**, and CCDC 868896 for **4·TBACl**.

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17 The synthesis and characterization together with a preliminary analysis of the substrate binding properties of this new compound (**6**) are included in the ESI†. As expected, calix[5]pyrrole **6** proved capable of recognizing Cl^-, Br^-, $CH_3CO_2^-$, $H_2PO_4^-$, TNT, and TNB, with an efficacy that generally parallels that of **3**. For instance, in $CHCl_3$ K_a TBACl = (18 000 ± 6,000) and (13 000 ± 1000) M^{-1} for **6** and **3**, respectively. Likewise, K_a TNB = (190 ± 50) and (870 ± 130) M^{-1} in $CHCl_3$ for **6** and **3**, respectively. As true for **3**, in both cases the values for **6** proved lower than those noted previously for the calix[4]pyrrole analogue[9,13].