Rationally Designed Calix[4]arene−Pyrrolotetrathiafulvalene Receptors for Electron-Deficient Neutral Guests

Matthias H. Düker,[†] Hannes Schäfer,[†] Matthias Zeller,[‡] and Vladimir A. Azov*,[†]

[†]Department of Chemistry, University of Bremen, Leobener Strasse NW 2C, D-28359 Bremen, Germany

[‡]One University Plaza, Youngstown State University, Youngstown, Ohio 44555-3663, United States

Ⓢ *Supporting Information*

ABSTRACT: Four upper rim bis-monopyrrolotetrathiafulvalene-calix[4]-arene conjugates **2a,b** and **3a,b** have been efficiently synthesized using a modular construction approach. The new compounds feature a molecular tweezer architecture with a quasi-parallel arrangement of redox-active tetrathiafulvalene (TTF) arms, which serve as the guest binding centers. Complexation studies using UV/vis binding titrations revealed a high affinity of the calixarene−TTF receptors for planar electron-deficient guests, leading to formation of deeply colored charge-transfer complexes in solution. The binding efficiency of the receptors depends on the flexibility of the calixarene scaffolds and the electronic nature of the TTF arms: the highest binding efficiency is shown by receptor **2b**, featuring a highly preorganized molecular structure and an electron-rich TTF moiety.
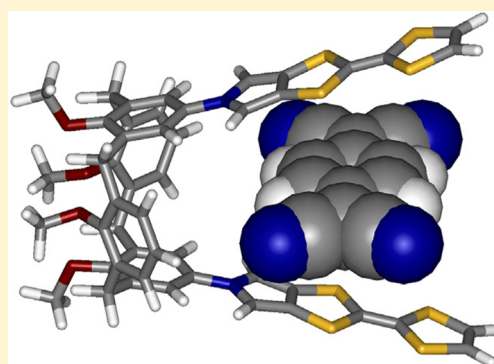
INTRODUCTION

With the advent of efficient and selective preparation methods,[1] calixarenes, a family of macrocyclic compounds, have been extensively used in various areas of supramolecular chemistry.[2] They can be readily modified at the phenolic hydroxyl groups (lower rim) as well as at the positions *para* to the HO-groups (upper rim) and have proven to be superb molecular scaffolds for the assembly of receptors for neutral and charged guests,[3] as well as of molecular capsules.[4] Calix[4]arene, the smallest member of the family, can be locked in any one of four possible, geometrically precisely defined conformations, which can be employed for exact control of the spatial arrangement of the attached functional groups.[5]

Tetrathiafulvalenes[6] (TTFs) are redox active heterocyclic compounds that quickly found use in the field of organic electronics[7] due to their ability to form conductive phases in the solid-state. In later years, they were widely employed as building blocks in diverse supramolecular systems, where they have played the role of switching units[8] in different types of molecular architectures.[9] In numerous interlocked supra-molecular devices,[10] the TTF moiety has been employed as a redox-switchable electron donor: it drastically reduces its electron-donating properties upon oxidation and, thus, can serve as a molecular motor inducing positional displacement of supramolecular components.

Despite the promising prospects of combining these two building blocks in one larger assembly, only relatively few tetrathiafulvalene−calixarene derivatives have so far been reported.[11−14] Of these few, almost all were lower rim calix[4]arene[12] or thiacalix[4]arene[13] conjugates, which were employed for sensing of cations and anions via polar (ion-dipole and H-bonding) interactions centered on the TTF−

calixarene linkers,[12b−g] or for the study of metal-promoted electron-transfer.[12h,i] In the only two recent reports that describe upper rim-modified calix[4]arenes with multiple TTF substitution,[14] the tetrathiafulvalene−calixarene derivatives were employed for anion recognition via hydrogen bonding with amido groups, linking the TTF units to the calixarene scaffolds. Due to cooperative effects of four proximal amido groups very high binding constants (up to 5×10^4 M^{-1}) were achieved,[14a] and the binding process could be followed both spectroscopically (UV/vis) as well as electrochemically.

Recently, we have reported the synthesis of calix[4]arenes **1** with two upper rim TTF bridges (Figure 1), which were also tested as receptors for planar electron-deficient guests but were shown to be only moderately effective.[15] The low binding affinity of receptors **1** (Figure 1), determined by NMR binding titrations, can be attributed to two factors. First and foremost, thioalkyl-substituted tetrathiafulvalenes, although easy to synthesize, are relatively electron-poor TTF derivatives, which do not afford good stabilization of electron-deficient molecules by means of charge-transfer and π−π interactions.[16] On the other hand, weak guest complexation is also due to the rather broad conformational space of the receptors which allows many possible mutual orientations of the TTF arms, most of which are not suitable for guest binding.

To improve binding properties, the following modifications were proposed. As a first measure, monopyrrolotetrathiafulva-lenes (MPTTFs) were chosen as binding elements for the proposed receptors. Pyrrolo-annealed tetrathiafulvalenes[17] are known to display good binding affinity toward electron-
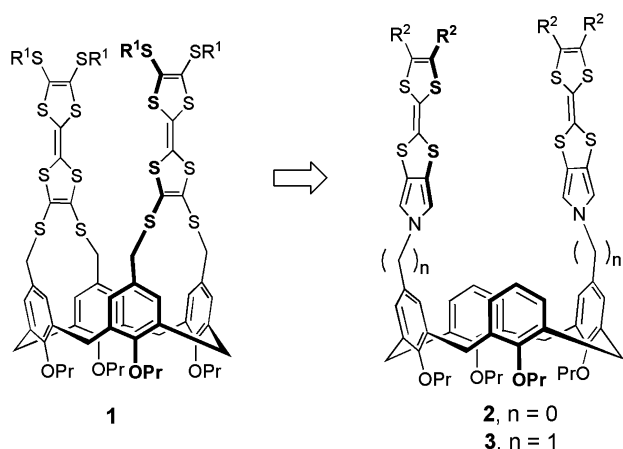
Figure 1. Molecular design of the calyx[4]arene-tetrathiafulvalene receptors of the first, **1**, and second, **2** and **3**, generations. R^1 = alkyl, R^2 = SPr, H.

deficient cyclobis(paraquat-*p*-phenylene) macrocycles,[16,18] much surpassing those of tetrakis-alkylthio TTFs. In addition, monopyrrolo-TTFs have also been successfully employed for the construction of TTF-calix[4]pyrrole receptors,[19] which comprised four TTF units and showed excellent binding of planar electron-poor nitroaromatic guests between their TTF arms, as well as in several other types of supramolecular hosts.[20] As a second structure modification, we also changed the way of TTF attachment to the calixarene backbone (Figure 1): each monopyrrolotetrathiafulvalene unit was symmetrically appended through a single bond connecting the apex N-atom of the pyrrole to the *para*-position of the calixarene phenyl groups. To evaluate the influence of flexibility on the receptors' efficiency, we decided to compare the directly linked "rigid" receptor **2** with the "flexible" receptor **3**, containing an additional methylene group in the TTF-calixarene link.

Molecular modeling[21] using semiempirical methods showed that receptors **2** should have only two low-lying "open" and "closed" *pinched cone* conformations with a low transition barrier between them (Figure 2). In the "closed" conformation,
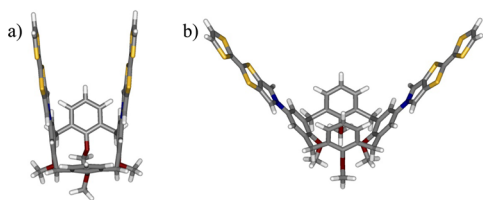

Figure 2. Two possible *pinched-cone* conformations of **2b** with (a) closed and (b) open TTF arms (PM3). Propyl groups on calixarenes are replaced with methyl groups.

the MPTTF arms lie almost parallel to each other at a distance of ca. 6.5−7.5 Å, indicating a distance suitable for π-stacking with an aromatic guest and making **2** another member of the family of molecular tweezer-like receptors.[22,23] In the "open" conformation, the MPTTF arms are almost orthogonal to each other, making an angle of 85°. Importantly, the planes of the MPTTF units and adjacent aromatic rings are expected to be coplanar, which was also observed before in several X-ray structures of similar derivatives.[24]

The conformational space of **3** is defined by interconversion between the two pinched cone conformations of the calix[4]-

arene bowl as well as the almost free rotation around the Ar—CH_2 bond. Because of the latter, both the "closed" and "open" pinched cone conformations can attain parallel arrangement of two TTF units. On one hand, this gives additional flexibility to the receptor and improves its adaptability to accommodate guest molecules. On the other hand, this flexibility also makes the receptor structure less preorganized for binding due to much broader conformational space, which might make it less specific for any particular molecular guest.

■ RESULTS AND DISCUSSION

Synthesis. Rigid receptors **2** were synthesized employing the copper-catalyzed Ullmann-type N-arylation reaction[25] between MPTTF derivatives **4a,b** and Br-substituted calix[4]-arenes (Scheme 1). Bis-alkylthio MPTTF **4a**[26] is quite stable and easy to handle, whereas nonsubstituted MPTTF **4b**[18a] is more sensitive but was expected to render better binding with electron-deficient species. To obtain the reference compounds and to test the coupling reaction, which is relatively new to pyrrolo-TTF chemistry,[27] two mono-TTF derivatives **5a** and **5b** were first prepared in relatively good yields. The same reaction from 5,17-dibromocalix[4]arene **6** afforded receptors **2a,b**.[28] In the case of **2a**, the yield was rather low due to the relative instability of the product on silica gel columns and very similar R_f values for **2a** and its monosubstituted byproduct.

Receptors **3a,b** were efficiently prepared by reaction of a deprotonated MPTTF unit with the previously reported 5,17-dibromomethylcalix[4]arene[29] derivative **7** (Scheme 2).

The new MPTTF derivatives were obtained as bright yellow or pale yellow crystalline powders for derivatives of **4a** and **4b**, respectively. Solubility in nonpolar organic solvents, such as CH_2Cl_2 or toluene, is good (all derivatives of H-MPTTF **4a**) or fairly good (derivatives of PrS-MPTTF **4b**, with the exception of poorly soluble **5b**), giving solutions that are stable at room temperature in air. Of the six newly prepared compounds, only **5a** afforded crystals suitable for X-ray structural analysis.[21] The crystal structure features two crystallographically distinct molecules, both featuring a coplanar arrangement of the TTF and aromatic units, as predicted by modeling and observed in other X-ray structures of related derivatives.[24] In the crystal packing, molecules are interconnected via several nonclassical weak intermolecular hydrogen bonds and S−S interactions.

^{1}H NMR spectra of the calixarene-MPTTF conjugates indicate that the calix[4]arene bowl shows a preference for one of the asymmetric pinched cone conformations, as seen from the presence of two pronounced nonequivalent pairs of OPr chains and differences in chemical shifts of protons attached to pairs of diametrically opposite aromatic rings.[30] Aromatic hydrogens of the *p*-substituted phenyl groups (ArH_{sub}) display a relatively strong high field shift (6.23−6.45 ppm) when compared with those of the nonsubstituted phenyls (ArH_{unsub}, 6.70−6.95 ppm). Pyrrolic protons of the MPTTF moiety are also shifted upfield (6.03−6.09 ppm) in comparison with similar signals of derivatives **5a,b** (6.83−6.84 ppm). This evidence implies that the "closed" *pinched cone* conformation with quasiparallel orientation of the two aromatic rings is preferred. The fact that only one set of signals is observed in the ^{1}H NMR spectra may be explained either by fast interconversion on the NMR time scale between the two possible pinched cone conformations with a strong preference for the "closed" one or by slow interconversion of the same conformers with an overwhelming prevalence for the "closed" isomer. The pattern of the ^{1}H NMR signals in the aromatic

Scheme 1. Synthesis of Pyrrolotetrathiafulvalene Derivatives 2 and 5[a]

4a, R = SPr
4b, R = H

5a, R = SPr, 72%
5b, R = H, 52%

2a, R = SPr, 44%
2b, R = H, 25%

6
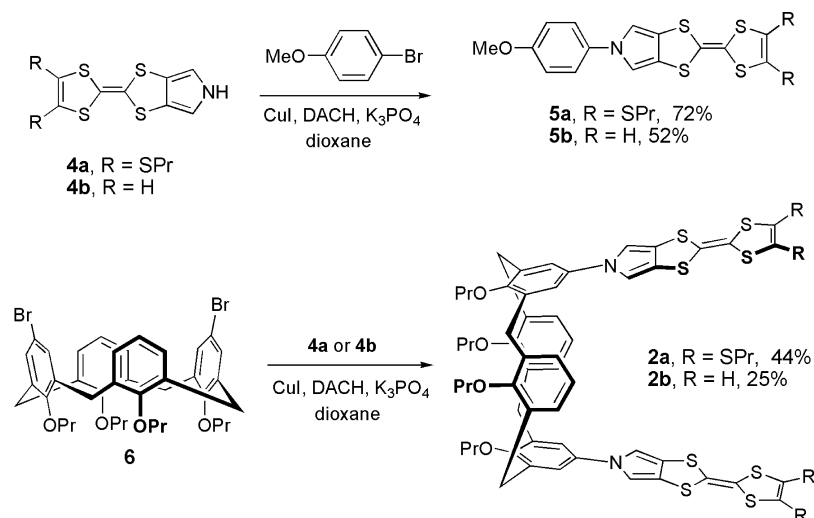
[a]DACH = *trans*-diaminocyclohexane.

Scheme 2. Synthesis of Monopyrrolotetrathiafulvalene-calix[4]arene Derivatives 3

7

3a, R = SPr, 43%
3b, R = H, 37%
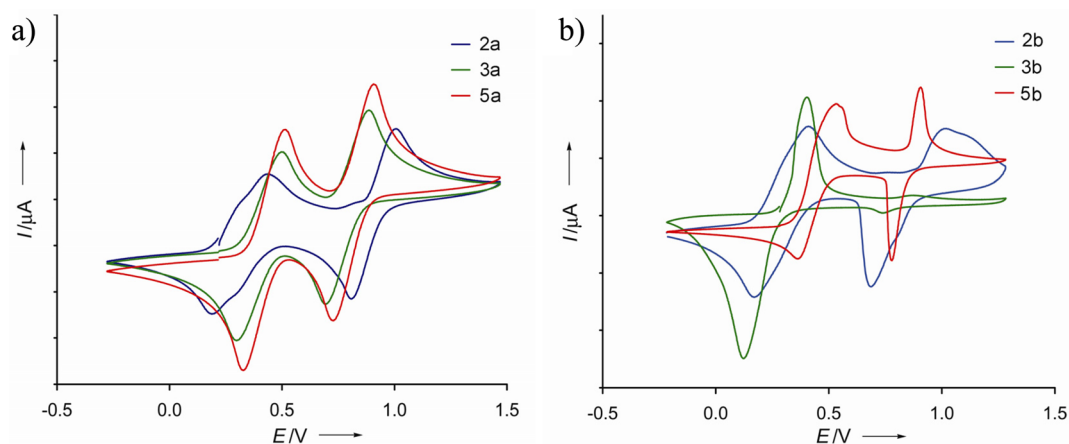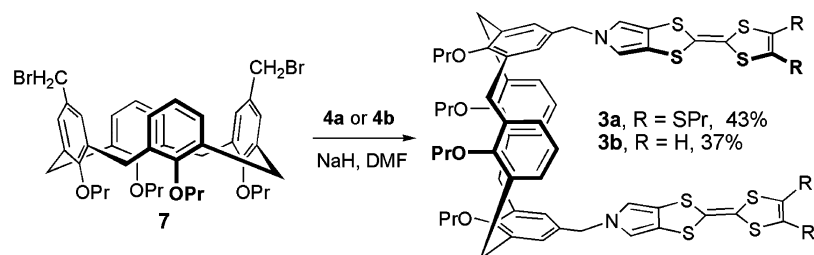
Figure 3. Cyclic voltammograms of pyrrolo-TTF derivatives: (a) with PrS-substituted TTFs **2a**, **3a**, and **5a**; (b) with H-substituted TTFs **2b**, **3b**, and **5b**. CH$_2$Cl$_2$/0.1 M Bu$_4$NClO$_4$, scan rate 100 mV/s, potentials are plotted vs SCE.

region is solvent-dependent: compounds **2a**, **2b**, and **3b** show broadening of their ArH$_{sub}$ signal in CD$_2$Cl$_2$ and CDCl$_3$, whereas the same signal in the spectrum of **2a** becomes sharp upon measurement in C$_6$D$_6$.[21,31] Such behavior implies that "closed"–"open" conformational equilibration is relatively fast on the NMR time scale at rt in chlorinated solvents with only modest line broadening due to exchange processes and significant preference for the closed conformation due to intramolecular TTF–TTF interaction. Upon change to benzene, which affords better TTF solubilization due to its π-

system, conformational interconversion becomes even faster, leading to observation of sharp signals for all aromatic protons.

The UV/vis spectra of compounds **2a**, **3a**, and **5a** (CH$_2$Cl$_2$, 293 K) show the common absorption pattern[32] for thioalkyl-substituted TTF derivatives with maximum absorption at λ$_{max}$ of ca. 310−330 nm, as well as a shoulder at ca. 390 nm and a long tail with low absorption reaching to ca. 500 nm. The UV/vis spectra of **2b**, **3b**, and **5b** display the same absorption maximum and tailing low absorption up to 500 nm but were missing the shoulder at 390 nm, which manifested itself in a much paler yellow color for these derivatives.

Redox Properties. The electrochemical properties of all new MPTTF derivatives were investigated by cyclic voltammetry (CV) in dichloromethane/Bu$_4$NClO$_4$ solutions (Figure 3a,b). Mono-TTF compounds **5a,b** display the classical electrochemical behavior of tetrathiafulvalene derivatives,[7c] showing two quasi-reversible electrochemical processes on the cathodic scan, the first one leading to the TTF radical cation and the second affording the dication. Bis-SPr-substituted **5a** shows a slightly higher first oxidation potential than **5b** (Table 1), as expected due to the electron-withdrawing effect of the

Table 1. Electrochemical Data of New Pyrrolo-TTF Derivatives[a]

compd	$E_{1/2}^{ox1}$ (V)	$E_{1/2}^{ox2}$ (V)
5a	0.42	0.82
2a	0.31	0.91
3a	0.40	0.78
5b	0.40	0.84
2b	0.29	0.85
3b	0.22	(0.73)[b]

[a]Data were obtained using a one-compartment cell in CH$_2$Cl$_2$/0.1 M Bu$_4$NClO$_4$, Pt as the working and counter electrodes, and a nonaqueous Ag/Ag+ reference electrode; scan rate 100 mV/s. Values given at room temperature vs SCE; the Fc/Fc$^+$ couple (0.480 V vs SCE) was used as an internal reference.[39] [b]Very weak oxidation wave.

two thioalkyl groups.[16,33] Rigid receptors **2a,b** display a broadening of the first oxidation waves and their shift to lower oxidation potentials in comparison to their corresponding mono-TTF counterparts **5**. These effects are often observed in CVs of TTF derivatives with two or several spatially proximal tetrathiafulvalene groups[12d,34,35] and are explained by the formation of mixed valence TTF dimers (TTF−TTF$^{•+}$),[36] stabilized by intramolecular charge transfer (CT) interaction. The flexible PrS-substituted receptor **3a** shows usual redox behavior, very similar to that of **5a**, whereas the voltammogramm of its nonsubstituted counterpart **3b** is rather uncommon. The CV of **3b** presents one strong low-lying oxidation potential, presumably leading to two monooxidations of the two MPTTF groups, while only a very small wave is observed at the position of the expected second oxidation potential. Additionally, the peak separation ΔEp is larger than for other monopyrrolotetrathiafulvalene derivatives and grows rapidly with increasing sweep rate,[21,37] indicating the irreversibility of the electron-transfer process. The nature of this irreversibility has not been yet clarified. We speculate that this effect may be due an intramolecular reaction, such as pyrrole electrodimerization,[38] between two spatially proximal MPTTF moieties. The reversibility for both oxidation processes for other bis-MPTTF derivatives can be explained as follows: compounds **2a** and **3a** possess deactivated PrS-substituted MPTTF moieties, while in compound **2a** and **2b** MPTTFs are rigidly attached to the calix[4]arene backbone, making the attainment of a suitable mutual orientation for such a tentative dimerization impossible.

Binding Studies. Receptors **2a,b** adopt quasiparallel orientation of the two MPTTF arms, which make them similar to tetrathiafulvalene−calix[4]pyrrole receptors,[19] which showed good binding affinity toward electron-deficient 2,5,7-trinitro-9-dicyanomethylenefluorene (TNF) and 1,3,5-trinitrobenzene (TNB). Binding was due to CT intermolecular interactions, as well as additional stabilization, provided by H-bonding

between the NH protons of the host and nitro groups of the guests. A structurally similar bis(tetrathiafulvalene)calix[2]-pyrrole[2]thiophene receptor[40] showed affinity to 7,7,8,8-tetracyanoquinodimethane (TCNQ), although the binding was found to be much weaker than for TTF-calix[4]pyrroles, likely due to the lack of additional stabilization through H-bonding interactions.

We have chosen TCNQ and TNF as test compounds for our study, the former being a relatively compact planar molecule, while the latter having an extended π-system and distorted planarity due to out of plane rotation of the nitro groups.[41] Initial qualitative visual experiments, performed by mixing of diluted host and guest solutions in CH$_2$Cl$_2$, immediately provided evidence for host−guest interactions. Different degrees of color change, induced by the build up of CT bands, were observed for different receptors. The deepest coloration of a solution was achieved upon mixing of receptor **2b** with TCNQ (strong green color, Figure 4) or TNF (dark
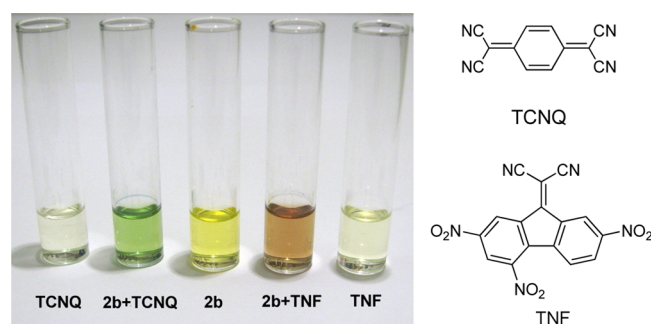

Figure 4. Change of solution color upon formation of charge-transfer complexes between **2b** and 7,7,8,8-tetracyanoquinodimethane (TCNQ) or 2,4,7-trinitro-9-fluorenylidenemalononitrile (TNF) in CH$_2$Cl$_2$. [Guest] ≈ [host] ≈ 0.3 × 10^{-3} M. The structures of TCNQ and TNF are shown.

brown color). Receptor **2a** was second in efficiency, while other MPTTF derivatives showed rather limited (bis-derivatives **3a,b**) or almost no color changes (monoderivatives **5a,b**), even at higher concentrations.

All new TTF derivatives, as well as the guest compounds, do not show any notable absorption above 500 nm. Titration of TCNQ solution with **2a** results in appearance of two strong CT band centered at λ_{max} = 748 and 850 nm, whereas for TNF a very broad absorption band beginning below 500 nm and with a maximum above 1100 nm (beyond the measurement range of our instrument) is observed (Figure 5).

Binding studies[42] were performed by UV/vis binding titrations in CH$_2$Cl$_2$ to determine the binding constants K_a and extinction coefficients ε of the CT complexes. The results (Table 2) gave us insight into the influence of electron-donating properties of differently substituted MPTTFs and of receptors' rigidity/flexibility on their affinity toward the two structurally different guest compounds. First, receptors **2b** and **3b** with nonsubstituted MPTTF arms are stronger binders than their counterparts **2a** and **3a**, containing deactivated PrS-substituted MPTTF units. Second, rigid and highly preorganized receptors **2a,b** display higher binding constants than flexible receptors **3a,b**. More detailed examination of the binding constants shows that the binding efficiency of flexible receptors **3a,b** toward TNF decreases much less than toward TCNQ, when compared with receptors **2a,b**. Thus, receptors **2** are much stronger binders of TCNQ than of TNF, which
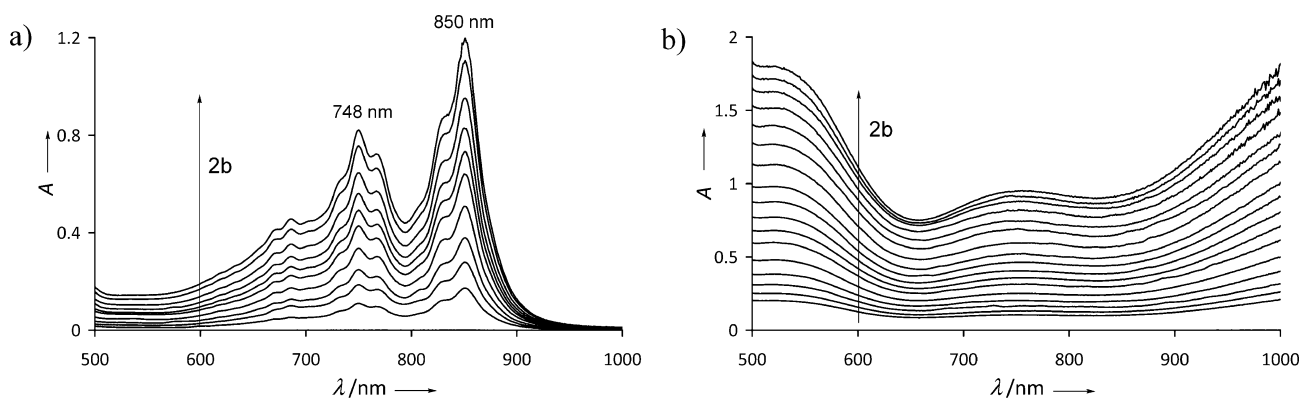
Figure 5. Absorption spectra of (a) TCNQ (constant concentration of 0.5×10^{-3} M, CH$_2$Cl$_2$) recorded upon variation of the concentration of **2b** $(0-1.25 \times 10^{-3}$ M); (b) TNF (constant concentration of 1.0×10^{-3} M, CH$_2$Cl$_2$) recorded upon variation of the concentration of **2b** $(0-3.0 \times 10^{-3}$ M).

Table 2. Binding Properties of the Pyrrolo-TTF Receptor Derivatives[a]

compd	K_a, M^{-1} (ε_{850}, M^{-1}cm^{-1}) with TCNQ[b]	K_a, M^{-1} with TNF
2a	750 (4200)	170
2b	3000 (3200)	670
3a	110 (600)	75
3b	160 (910)	500

[a]Data were obtained in CH$_2$Cl$_2$ solution using UV/vis binding titrations at room temperature. [b]850 nm is the absorption maximum for CT complexes of TCNQ with receptors **2a,b** and **3a,b**.

manifests itself also by much higher extinction coefficients of their CT complexes in comparison with **3**. On the other hand, the binding efficiency of receptors **3** toward TNF is almost the same (**3a**) or even stronger (**3b**) than toward TCNQ. Such an interesting behavior can be rationalized by a slight nonplanarity of the TNF molecules, making them too thick to fit into the relatively narrow gap of **2**. Moreover, molecular modeling provided qualitative evidence for better stacking between the MPTTF arms and TNF guest in case of receptor **3**.[21]

Overall, receptor **2b**, the best binder in the new family of MPTTF−calix[4]arene receptors, shows binding constants similar to those of the MPTTF−calix[4]pyrrole receptors,[19] even though, in the case of receptors **2**, the binding was due only to CT and π−π interactions without any further stabilization via additional host−guest H-bonds. Such a high binding affinity confirms the feasibility of our receptor design and paves the way for a variety of additional modifications, which can be readily implemented due to the versatility of calix[4]arene chemistry. On the upper calixarene rim, the 4-fold MPTTF substitution offers itself as a possibility for additional receptor improvement. Upon proper modifications of the lower rim, it will be possible to render solubility in polar solvents and introduce metal-binding sites or anchor groups for surface immobilization into the receptor structures. In addition, a comprehensive search will be performed to identify other suitable electron-deficient guests.[43] Moreover, the redox nature of the TTF moieties introduces an opportunity to control the guest binding process via their oxidation or reductio, or, vice versa, to sense the binding processes via electrochemical means.

CONCLUSIONS

In conclusion, a family of upper rim calix[4]arene−monopyrrolotetrathiafulvene receptors has been prepared, starting

from two different calixarene backbones and two monopyrrolotetrathiafulvalenes and using a modular assembly approach. The rigid preorganized calixarene-MPTTF molecular receptors **2a,b** show strong binding with TCNQ and TNF in solution, giving deeply colored CT complexes, whereas the flexible receptors **3a,b** are, overall, less efficient. The remarkable color change upon formation of CT complexes makes the observation of the binding process straightforward to follow and the incorporation of the guest is readily sensed. Such MPTTF−calixarene molecular tweezers possess a high modification potential and should serve as a starting point for design and construction of a variety of novel receptor architectures.

EXPERIMENTAL SECTION

General Methods. 5,17-Dibromo-25,26,27,28-tetra(1-propoxy)-calix[4]arene **6**,[28] 5,17-dibromomethyl-25,26,27,28-tetra(1-propoxy)-calix[4]arene **7**,[29] and TTF derivatives **4a**[17c,26] and **4b**[18a] were prepared as reported previously. Reagent-grade chemicals and solvents (including absolute DMF and dioxane) were used without further purification unless stated otherwise. All reactions were carried out under an atmosphere of dry N$_2$. Sodium hydride was used as a 60% slurry in oil and washed with pentane before use. Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS; the residual solvent signals were used as reference: CDCl$_3$ (7.26 ppm for ^{1}H, 77.0 ppm for ^{13}C), CD$_2$Cl$_2$ (5.32 ppm for ^{1}H, 53.8 ppm for ^{13}C), or C$_6$D$_6$ (7.15 ppm for ^{1}H, 128.0 ppm for ^{13}C). ^{1}H NMR coupling constants (J) are reported in hertz (Hz), and multiplicity is indicated as follows: br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sext (sextet), sept (septet), or m (multiplet). High-resolution ESI-MS-spectra (HRMS) were measured with a Thermo Fisher Scientific LTQ Orbitrap spectrometer. UV/vis measurements were performed in a 1 cm path length quartz optical cell. Binding constants were determined by means of UV/vis binding titrations.[21] Cyclic voltammetry (CV) measurements were performed in a three-electrode single-compartment cell.[21]

The X-ray structure of **5a** was solved by direct methods and refined by full-matrix least-squares analysis using SHELXTL[44] and ShelXle.[45] All non-hydrogen atoms were refined with anisotropic ADPs. One of the propyl groups is disordered over two alternative positions with an occupancy ratio of 0.877(2) to 0.123(2). The minor moiety was restrained to have a similar geometry as the major one, and ADPs of equivalent atoms in both moieties were constrained to be identical. Reflection 0 0 1 was obstructed by the beam stop and was omitted from the refinement.

Melting points were determined using a capillary melting point apparatus and are uncorrected. R_f values were determined using 0.2 mm silica gel F-254 TLC cards; the plates were inspected under UV

light. Flash chromatography (FC) was carried out using 230−440 mesh (particle size 36−70 μm) silica gel.

Pyrrolo-TTF−calixarene Coupling: General Procedure. A heavy-walled Schlenk tube equipped with a wide bore Teflon stopcock was charged with **4a** or **4b**, CuI, K_3PO_4, (±)-*trans*-1,2-diaminocyclohexane, aromatic bromide (4-bromoanisole or calix[4]arene **6**), and absolute dioxane. The reaction mixture was degassed by three freeze−pump−thaw cycles, and the vessel was filled with nitrogen, sealed, and stirred at 110 °C for 18−24 h. The progress of the reaction was controlled by TLC, and samples were taken under a counter flow of nitrogen. When the reaction was complete, the mixture was filtered through a plug of Celite, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel to afford pure products **5a,b** and **2a,b**.

2-[4,5-Bis(propylthio)-1,3-dithiol-2-ylidene]-5-(4-methoxyphenyl)-5H-1,3-dithiolo[4,5-c]pyrrole 5a. Prepared from **4a** (0.054 g, 0.138 mmol), CuI (0.012 g, 0.063 mmol), K_3PO_4 (0.082 g, 0.386 mmol), *trans*-diaminocyclohexane (7.5 μL, 0.062 mmol), and 4-bromoanisole (0.038 g, 0.204 mmol) in 2 mL of dioxane. The crude product was washed with pentane to remove unreacted bromoanisole and purified by flash chromatography (CH_2Cl_2/cyclohexane, 1:1) to afford bright yellow crystals. X-ray quality crystals were grown by slow diffusion of hexane into a benzene solution. Yield: 49.6 mg (0.10 mmol, 72%). Mp: 159−163 °C. R_f = 0.73 (CH_2Cl_2). ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.22−7.30 (m, 2H), 6.91−6.99 (m, 2H), 6.84 (s, 2H), 3.82 (s, 3H), 2.81 (t, [3]J = 7.2 Hz, 4H), 1.66 (sext, [3]J = 7.2 Hz, 4H), 1.01 (t, [3]J = 7.2 Hz, 6H). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 158.4, 134.2, 129.9, 127.9, 122.1, 121.4, 119.4, 115.0, 111.8, 55.9, 38.5, 23.5, 13.2. UV/vis (CH_2Cl_2): λ_{max} (ε) 309 nm (24900 L·mol^{-1}·cm^{-1}), 328 (24900), 450 sh (1100). MS (EI): m/z 497 (100) [M]$^+$, 454 (10) [M − Pr]$^{+•}$, 421 (20) [M − SPr]$^+$. HRMS (EI): m/z [M]$^+$ calcd for $C_{21}H_{23}NOS_6^+$ 497.01040, found 497.00895. CV (vs SCE, CH_2Cl_2): $E_{1/2}^{ox1}$ = 0.42 V, $E_{1/2}^{ox2}$ = 0.82 V.

2-(1,3-Dithiol-2-ylidene)-5-(4-methoxyphenyl)-5H-1,3-dithiolo[4,5-c]pyrrole 5b. Prepared from **4b** (0.075 g, 0.308 mmol), CuI (0.021 g, 0.107 mmol), K_3PO_4 (0.194, 0.914 mmol), *trans*-diaminocyclohexane (12.5 μL, 0.104 mmol), and 4-bromoanisole (0.093 g, 0.495 mmol) in 2 mL of dioxane. The crude product was washed with pentane to remove unreacted bromoanisole and purified by flash chromatography (CH_2Cl_2/cyclohexane, 1:1, 1% Et_3N) to afford pale yellow crystals. Yield: 55.7 mg (0.159 mmol, 52%). Mp: 175−181 °C. R_f = 0.42 (CH_2Cl_2/cyclohexane, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.22−7.30 (m, 2H), 6.91−6.99 (m, 2H), 6.83 (s, 2H), 6.37 (s, 2H), 3.81 (s, 3H). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 158.4, 134.3, 122.1, 121.9, 119.0, 115.0, 111.7, 55.9. UV/vis (CH_2Cl_2): λ_{max} (ε) 309 nm (23000 L·mol^{-1}·cm^{-1}), 321 (23500), 425 sh (460). MS (EI): m/z 349 (100) [M]$^{+•}$, 334 (5) [M − Me]$^{+•}$. HRMS (EI): m/z [M]$^+$ calcd for $C_{15}H_{11}NOS_4^+$ 348.97235, found 348.97299. CV (vs SCE, CH_2Cl_2): $E_{1/2}^{ox1}$ = 0.40 V, $E_{1/2}^{ox2}$ = 0.84 V.

5,17-Bis[2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5H-1,3-dithiolo[4,5-c]pyrrol-5-yl]-25,26,27,28-tetra(1-propoxy)calix[4]arene 2a. Prepared from **4a** (0.101 g, 0.258 mmol), CuI (0.017 g, 0.089 mmol), K_3PO_4 (0.166 g, 0.782 mmol), *trans*-diaminocyclohexane (10 μL, 0.083 mmol), and **6** (0.074 g, 0.099 mmol) in 2 mL of dioxane. The crude product was purified by flash chromatography (CH_2Cl_2/cyclohexane, 1:2) to afford bright yellow crystals. Yield: 59.3 mg (0.043 mmol, 44%). Mp: 118−122 °C. R_f = 0.29 (CH_2Cl_2/cyclohexane, 1:3). ^{1}H NMR (360 MHz, C_6D_6): δ 6.75 (s, 6H), 6.43 (s, 4H), 6.04 (s, 4H), 4.49 (d, [2]J = 13.3 Hz, 4H), 3.84 (t, [3]J = 7.6 Hz, 4H), 3.78 (t, [3]J = 7.6 Hz, 4H), 3.09 (d, [2]J = 13.3, 4H), 2.59 (t, [3]J = 7.2 Hz, 8H), 1.90 (sext, [3]J = 7.2 Hz, 4H), 1.88 (sext, [3]J = 7.2 Hz, 4H), 1.48 (sext, [3]J = 7.2 Hz, 8H), 0.94 (t, [3]J = 7.2 Hz, 6H), 0.92 (t, [3]J = 7.2 Hz, 6H), 0.79 (t, [3]J = 7.2 Hz, 12H). ^{13}C NMR (90 MHz, C_6D_6): δ 156.9, 154.8, 136.5, 135.3, 134.9, 128.8, 128.1, 122.9, 122.4, 120.6, 119.8, 110.7, 110.4, 77.2, 77.1, 38.2, 31.4, 23.6, 23.5, 23.3, 13.2, 10.5, 10.4. UV/vis (CH_2Cl_2): λ_{max} (ε) 308 nm (44000 L·mol^{-1}·cm^{-1}), 324 (41000), 450 sh (1100). MS (ESI$^+$): m/z 1370 (100) [M]$^+$. HRMS (ESI$^+$): m/z [M]$^+$ calcd for $C_{68}H_{78}N_2O_4S_{12}^+$ 1370.26046, found 1370.26032. CV (vs SCE, CH_2Cl_2): $E_{1/2}^{ox1}$ = 0.31 V, $E_{1/2}^{ox2}$ = 0.91 V.

5,17-Bis[2-(1,3-dithiol-2-ylidene)-5H-1,3-dithiolo[4,5-c]pyrrol-5-yl]-25,26,27,28-tetra(1-propoxy)calix[4]arene 2b. Prepared from **4b** (0.058 g, 0.24 mmol), CuI (0.016 g, 0.084 mmol), K_3PO_4 (0.153 g, 0.72 mmol), *trans*-diaminocyclohexane (10 μL, 0.083 mmol), and **6** (0.068 g, 0.091 mmol) in 2 mL of dioxane. The crude product was purified by flash chromatography (CH_2Cl_2/cyclohexane, gradient 1:3 → 1:2, 1% Et_3N) to afford pale yellow crystals. Yield: 24 mg (0.0223 mmol, 25%). Mp: 189−193 °C. R_f = 0.22 (CH_2Cl_2/cyclohexane, 1:3). ^{1}H NMR (360 MHz, $CDCl_3$): δ 6.98−6.84 (m, 6H), 6.22 (bs, 8H), 6.06 (s, 4H), 4.47 (d, [2]J = 13.3 Hz, 4H), 3.99 (t, [3]J = 7.9 Hz, 4H), 3.73 (t, [3]J = 7.2 Hz, 4H), 3.16 (d, [2]J = 13.3, 4H), 1.98 (sext, [3]J = 7.9 Hz, 4H), 1.90 (sext, [3]J = 7.2 Hz, 4H), 1.07 (t, [3]J = 7.2 Hz, 6H), 0.94 (t, [3]J = 7.2 Hz, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 157.2, 153.9, 135.8, 135.3, 128.8, 126.6, 122.49, 121.7, 119.5, 118.4, 110.2, 77.2, 31.0, 23.4, 23.0, 10.6, 9.9. UV/vis (CH_2Cl_2): λ_{max} (ε) 312 nm (31000 L·mol^{-1}·cm^{-1}), 422 (900). MS (ESI$^+$): m/z 1074 (100) [M]$^{+•}$, 1097 (10) [M + Na]$^+$. MS (ESI$^-$): m/z 1073 (100) [M − H]$^-$, 1031 (30) [M − Pr]$^-$. HRMS (ESI$^+$): m/z [M]$^+$ calcd for $C_{56}H_{54}N_2O_4S_8^+$ 1074.18438, found 1074.18432. CV (vs SCE, CH_2Cl_2): $E_{1/2}^{ox1}$ = 0.29 V, $E_{1/2}^{ox2}$ = 0.85 V.

5,17-Bis[[2-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene]-5H-1,3-dithiolo[4,5-c]pyrrol-5-yl]methyl]-25,26,27,28-tetra(1-propoxy)calix[4]arene 3a. Pyrrolo-TTF **4a** (250 mg, 0.64 mmol) was dissolved in absolute DMF (40 mL) and degassed by a freeze−pump−thaw cycle. The reaction mixture was then cooled with an ice bath, and NaH (65 mg 1.63 mmol) was added, followed by **7** (226 mg, 0.29 mmol) in 5 mL of absolute THF (dried over Ph_2CO/Na before use). The mixture was allowed to warm to rt and stirred for an additional 3 h. Then the mixture was slowly added to ca. 400 mL of brine and extracted three times with ca. 100 mL of CH_2Cl_2. The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by flash chromatography (CH_2Cl_2/cyclohexane, 2:3) to afford bright yellow crystals. Yield: 174 mg (0.124 mmol, 43%). Mp: 225−227 °C. R_f = 0.53 (CH_2Cl_2/cyclohexane 1:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ 6.69−6.79 (m, 6H), 6.44 (s, 4H), 6.05 (s, 4H), 4.50 (s, 4H), 4.44 (d, [2]J = 13.1 Hz, 4H), 3.92 (t, [3]J = 7.6 Hz, 4H), 3.78 (t, [3]J = 7.4 Hz, 4H), 3.14 (d, [2]J = 13.1 Hz, 4H), 2.81 (t, [3]J = 7.2 Hz, 8H), 1.99 (sext, [3]J = 7.6 Hz, 4H), 1.91 (sext, [3]J = 7.2 Hz, 4H), 1.67 (sext, [3]J = 7.2 Hz, 8H), 1.05 (t, [3]J = 7.4 Hz, 6H), 1.02 (t, [3]J = 7.2 Hz, 12H), 0.97 (t, [3]J = 7.2 Hz, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 156.5, 156.1, 135.2, 134.9, 129.2, 128.4, 127.6, 127.4, 122.4, 120.0, 118.5, 112.5, 110.6, 77.2, 53.8, 38.2, 30.8, 23.3, 23.1, 13.2, 10.4, 10.1. UV/vis (CH_2Cl_2): λ_{max} (ε) 283 nm (37800 L mol^{-1} cm^{-1}), 328 (32000), 403 sh (2600), 452 sh (1100). MS (ESI$^+$): m/z 1398 (100) [M]$^{+•}$, 1421 (40) [M + Na]$^+$. HRMS (ESI$^+$): m/z [M]$^+$ calcd for $C_{70}H_{82}N_2O_4S_{12}^+$ 1398.29176, found 1398.29178. CV (vs SCE, CH_2Cl_2): $E_{1/2}^{ox1}$ = 0.40 V, $E_{1/2}^{ox2}$ = 0.78 V.

5,17-Bis[[2-(1,3-dithiol-2-ylidene)-5H-1,3-dithiolo[4,5-c]pyrrol-5-yl]methyl]-25,26,27,28-tetra(1-propoxy)calix[4]arene 3b. Pyrrolo-TTF **4b** (88 mg, 0.36 mmol) was dissolved in abs DMF (5 mL) and degassed by a freeze−pump−thaw cycle. The reaction mixture was then cooled with an ice bath, and NaH (37 mg, 0.92 mmol) was added followed by **7** (120 mg, 0.15 mmol) in 2 mL of abs THF (dried over Ph_2CO/Na before use). The mixture was allowed to warm to rt and stirred for additional 3 h. Then the mixture was slowly added to 100 mL of brine and extracted three times with 25 mL of CH_2Cl_2. The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by flash chromatography (CH_2Cl_2/cyclohexane, 1:1, 1% Et_3N) to afford pale yellow crystals. Yield: 61 mg (0.055 mmol, 37%). Mp: 219−220 °C. R_f = 0.41 (CH_2Cl_2/cyclohexane 1:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ 6.71−6.82 (m, 6H), 6.43 (s, 4H), 6.32 (bs, 4H), 6.03 (s, 4H), 4.48 (bs, 4H), 4.43 (d, [2]J = 13.3 Hz, 4H), 3.92 (t, [3]J = 7.6 Hz, 4H), 3.77 (t, [3]J = 7.4 Hz, 4H), 3.14 (d, [2]J = 13.3 Hz, 4H), 1.99 (sext, [3]J = 7.6 Hz, 4H), 1.90 (sext, [3]J = 7.4 Hz, 4H), 1.02 (t, [3]J = 7.4 Hz, 6H), 0.96 (t, [3]J = 7.4 Hz, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 156.6, 156.0, 135.3, 134.8, 129.2, 128.5, 127.7, 122.5, 118.8, 118.6, 112.4, 77.2, 53.7, 30.9, 23.3, 23.1, 10.4, 10.1. UV/vis (CH_2Cl_2): λ_{max} (ε) 292 nm (27000 L mol^{-1} cm^{-1}), 321 (25000), 423 sh (1300). MS (ESI$^+$): m/z 1102 (100) [M]$^{+•}$, 1125 (15) [M + Na]$^+$. MS (ESI$^-$): m/z 1101 (100) [M − H]$^-$,

1059 (30) [M − Pr]⁻. HRMS (ESI⁺): m/z [M]⁺ calcd for $C_{58}H_{58}N_2O_4S_8^+$ 1102.21568, found 1102.21687. CV (vs SCE, CH₂Cl₂): $E_{1/2}^{ox1}$ = 0.22 V ($E_{1/2}^{ox2}$ = 0.73 V).

■ ASSOCIATED CONTENT

⑤ Supporting Information

X-ray data, NMR spectra, and signal assignment for the new compounds, CV experimental details, descriptions of binding experiments, and molecular modeling. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vazov@uni-bremen.de.

Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor Fredric M. Menger (Emory University) on the occasion of his 75th birthday.

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