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Bis(tetrathiafulvalene)-Calix[2]pyrrole[2]-thiophene and Its Complexation with TCNQ

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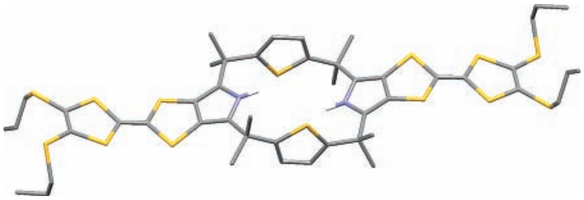
ABSTRACT



The synthesis of a rare example of a calix[2]pyrrole[2]thiophene derivative incorporating two tetrathiafulvalene units is described along with its X-ray crystal structure. Complexation studies between the bis(tetrathiafulvalene)-calix[2]pyrrole[2]thiophene and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) were carried out in solution using absorption and ESR spectroscopies as well as in the solid state using X-ray crystallography and IR spectroscopy.

The discovery[1] of the first metallic charge transfer (CT) complex between tetrathiafulvalene[2] (TTF) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) in 1973 prompted a huge interest in TTF and its derivatives in the search for new and improved superconducting CT complexes and radical cation salts.[3] The emergence of supramolecular chemistry[4] and the fact that TTF is a good electron donor that can exist in three stable redox states (TTF^0, TTF$^{\bullet+}$, and TTF^{2+}) has prompted chemists from a variety of backgrounds to develop elaborate molecular and supramolecular TTF systems, such as shuttles,[5] switches,[6] muscles,[7] springs,[8] charge-separating ligands,[9] and chemical sensors.[10]

Calix[4]pyrroles,[11] first synthesized in 1886 by Baeyer,[12] have been studied extensively in the past decade for possible use as receptors for anionic and neutral substrates.[13] We have

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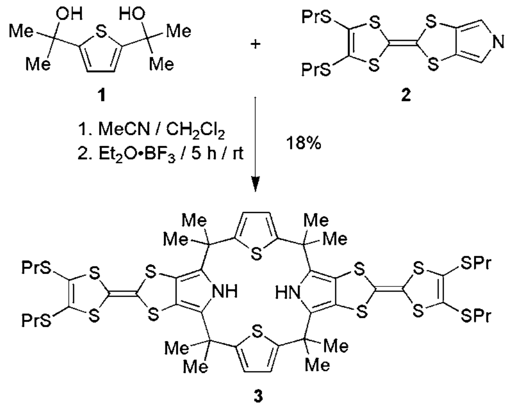
recently described the synthesis of a tetra-TTF-calix[4]pyrrole derivative,[14] which can function as a receptor for both neutral electron-deficient guests, such as 1,3,5-trinitrobenzene[14] (TNB) and C$_{60}$,[15] and different anions.[16] Although a large number of calix[4]pyrroles have been reported,[17] there are very few examples in which one or more of the pyrrole units in the calixpyrrole ring system has been substituted with thiophene moieties.[18]

In this letter, we describe the synthesis of a bis-TTF-calix[2]pyrrole[2]thiophene derivative **3** incorporating two thiophene moieties and two monopyrrolotetrathiafulvalene[19] (MPTTF) units within the calix ring system, together with preliminary complexation studies between the receptor **3** and TCNQ, carried out in solution employing absorption and ESR spectroscopies, as well as in the solid state using X-ray crystallography and IR spectroscopy.

The bis-TTF-calix[2]pyrrole[2]thiophene receptor **3**, containing two TTF electron donor units, was designed to act as a host for electron-deficient guests, such as TCNQ.[20] By attaching two TTF units directly to the flexible calix[2]pyrrole[2]thiophene scaffold,[18b] it was believed that the bis-TTF-calix[2]pyrrole[2]thiophene receptor **3**, in its 1,3-alternating conformation, would be capable of forming a sandwich-like complex with electron-deficient guests. In the 1,3-alternating conformation, the two thiophene moieties act as spacers that serve to keep the two TTF units apart with an approximate interplanar distance of 7 Å, thus optimizing[21] the possibility for CT and $\pi-\pi$ interactions between the two electron-donating TTF units in the receptor **3** and electron-deficient guests.

The bis-TTF-calix[2]pyrrole[2]thiophene **3** was synthesized as illustrated in Scheme 1. A dilute mixture of 2,5-bis(1-hydroxymethylethyl)thiophene[22] (**1**), the MPTTF[23] derivative **2**, and a catalytic amount of Et$_2$O•BF$_3$ in MeCN/CH$_2$Cl$_2$ was stirred for 5 h, affording the receptor **3** as a yellow solid in 18% yield[24] after column chromatography.

Scheme 1. Synthesis of Bis-TTF-Calix[2]pyrrole[2]thiophene **3**



The high-resolution matrix-associated laser desorption ionization mass spectrum (HiRes-MALDI-MS) recorded of **3** showed a peak at $m/z = 1133.0599$ corresponding to the $[M + \mathrm{Na}]^+$ ion (calculated for $C_{48}H_{58}N_2S_{14}Na^+ = 1133.0582$). The ^{1}H NMR spectrum of **3** (see Supporting Information) recorded in CDCl$_3$ at 298 K showed one broad singlet resonating at $\delta = 6.70$ ppm that can be assigned to the two chemically equivalent NH protons. The thiophene β-protons

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appear as a singlet resonating at $\delta = 6.73$ ppm. Also seen in the aliphatic region of the spectrum are the expected signals associated with the *n*-propyl chains and the *meso*-methyl groups. The electrochemical properties of **3** and **2** were studied in solution using cyclic voltammetry (CV). The CV of **3** recorded in CH_2Cl_2 revealed two well-defined reversible bielectronic redox processes at $E_{1/2}^1 = 0.24$ V and $E_{1/2}^2 = 0.65$ V (vs Ag/AgNO$_3$),[25] which can be assigned to the simultaneous first and second reversible oxidations of the two TTF units in **3**. For comparison, the CV recorded of compound **2** under similar conditions showed two well-defined reversible monoelectronic redox processes at $E_{1/2}^1 = 0.20$ V and $E_{1/2}^2 = 0.65$ V (vs Ag/AgNO$_3$).

Diffraction quality single crystals of **3** were obtained as yellow laths by slow diffusion of Me_2CO into a CH_2Cl_2 solution containing **3**. The resulting X-ray structure (Figure 1) revealed that **3** does not adopt a 1,3-alternating conformation in the solid state, but instead a centrosymmetric 1,2-alternating conformation in which the S atoms of the thiophene moieties point in opposite directions with respect to the plane of the central calix ring, and the two TTF units extend in opposite directions along the longer axis of the receptor.

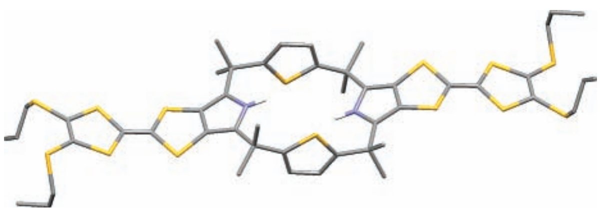

Figure 1. Solid-state conformation of the bis-TTF-calix[2]pyrrole-[2]thiophene **3** obtained by X-ray crystallography. H atoms bound to C atoms are omitted for clarity.

The complexation between receptor **3** and the electron-deficient guest TCNQ was investigated in a solution of CH_2Cl_2 using UV−vis−NIR and ESR spectroscopies. TCNQ does not give (Figure 2) any notable absorption at $\lambda \geq 500$ nm, while receptor **3** does not give any notable absorption at $\lambda \geq 700$ nm. Addition of 1 equiv of TCNQ to a CH_2Cl_2 solution of **3** resulted in the appearance (Figure 2) of two new CT absorption bands centered at $\lambda_{max} = 749$ and 851 nm ($\epsilon = 10$ and 14 M^{-1} cm^{-1}, respectively) in the absorption spectrum. An ESR spectrum recorded in CH_2Cl_2 on a 1:1 mixture of **3** and TCNQ showed a weak radical signal centered around $g = 2.010$, which is in the region characteristic[26] for both a TTF radical cation and a TCNQ radical anion. These results show that in solution some CT takes place between the TTF unit(s) and TCNQ.[27]

Complexation studies in the solid state were carried out using X-ray diffraction analysis and IR spectroscopy. Black single crystals of the complex between **3** and TCNQ were grown by evaporation of a CH_2Cl_2 solution containing **3** and TCNQ in a 1:1 ratio. Synchrotron single-crystal X-ray diffraction revealed an overall stoichiometry of $\mathbf{3}\bullet(TCNQ)_2\bullet CH_2Cl_2$ in the solid state.

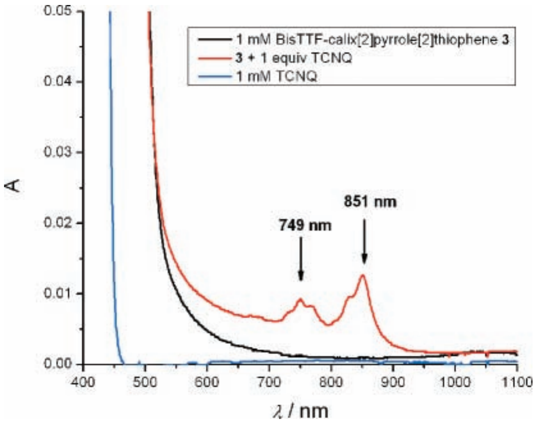

Figure 2. Absorption spectra (CH_2Cl_2, 25 °C) of the receptor **3**, a 1:1 mixture of **3** and TCNQ, and TCNQ.

The receptor **3** adopts (Figure 3) the anticipated 1,3-alternating conformation, with one TCNQ molecule positioned inside the cavity of the receptor, oriented so that its long axis lies orthogonal to the long axes of the two TTF units. A second TCNQ moiety is complexed between two adjacent molecules of **3**, aligned so that its long axis lies parallel to the long axes of the two adjacent TTF units. The structure also contains one CH_2Cl_2 solvent molecule for each

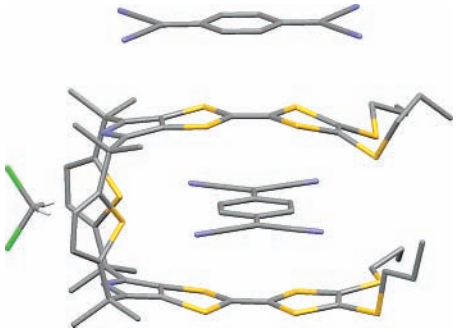

Figure 3. Asymmetric unit of the complex $\mathbf{3}\bullet(TCNQ)_2\bullet CH_2Cl_2$ obtained by X-ray crystallography. H atoms, except those of the CH_2Cl_2 molecule, are omitted for clarity.

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(25) CV was carried out using a 0.5 mM solution of **3** in CH_2Cl_2 with *n*-Bu_4NPF_6 (0.10 M) as the supporting electrolyte and Ag/AgNO$_3$ as the reference electrode at a scan rate of 100 mV s^{-1}.

(26) The ESR signal at $g = 2.010$ is likely to be composed of both a contribution from the TTF radical cation (i.e., $TTF^{\bullet+}$) which normally appears at *g* values around 2.009 (see: Wudl, F.; Smith, G. M.; Hufnagel, E. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1453−1454 and Nielsen, K.; Jeppesen, J. O.; Thorup, N.; Becher J. *Org. Lett.* **2002**, *4*, 1327−1330) and the TCNQ radical anion (i.e., $TCNQ^{\bullet-}$) which normally appears at *g* values around 2.003 (see: Bryce, M. R.; Moore, A. J.; Tanner, B. K.; Whitehead, R.; Clegg, W.; Gerson, F.; Lamprecht, A.; Pfenninger, S. *Chem. Mater*. **1996**, *8*, 1182−1188).

receptor **3** which is involved in C−H$\cdots\pi$ interactions with the two thiophene rings. Complexation of the TCNQ molecules both internal and external to the receptor cavity results in a continuous donor−acceptor stack in the solid state (Figure 4). The interplanar distances between the TCNQ molecules and the TTF units are approximately 3.3 Å for both TCNQ guests, resulting in an approximate interplanar distance of 6.7 Å (measured as the cross-cavity C$\cdots$C distances between the C atoms of the central C−C bond) between the two TTF units in the calix ring system, close to the optimal distance for CT and $\pi-\pi$ interactions to take place between a receptor and guest.[21]

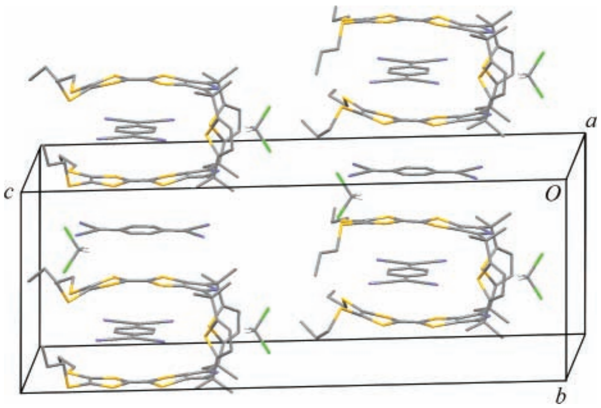

Figure 4. Partial packing diagram of the complex **3**•(TCNQ)$_2$•CH$_2$Cl$_2$ showing continuous donor−acceptor stacks running along the crystallographic *b*-axis. H atoms, except those of the CH$_2$Cl$_2$ molecules, are omitted for clarity.

The IR spectrum recorded on the black **3**•(TCNQ)$_2$•CH$_2$Cl$_2$ crystals showed two nitrile absorptions at 2220 and 2182 cm^{-1}, consistent with the presence of two different TCNQ moieties in **3**•(TCNQ)$_2$•CH$_2$Cl$_2$. Comparison of the absorption bands for **3**•(TCNQ)$_2$•CH$_2$Cl$_2$ with the absorption band for uncomplexed TCNQ (2225 cm^{-1}) indicates that CT is taking place in the solid state between the TTF donors and the TCNQ acceptors.[28] Although it is possible in principle[29] to quantify the negative charge accommodated on the TCNQ molecules using differences in bond lengths between neutral TCNQ[30] and the TCNQ radical anion,[31] limited precision of the synchrotron single-crystal X-ray analysis prohibits any such assessment in this case.

In summary, the synthesis of a bis-TTF-calix[2]pyrrole-[2]thiophene derivative **3** has been achieved, and its ability to function as a receptor for TCNQ was established. The resulting complex was characterized both in solution and in the solid state. Further host−guest studies will be carried out with guests such as TCNE (tetracyanoethylene) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-*p*-quinodimethane to explore fully the ability of receptor **3** to function as a host for polynitrile guests.

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Supporting Information Available: The synthesis of receptor **3** along with its ^{1}H NMR and ^{13}C NMR spectra, and CV traces together with crystallographic data and cif files for **3** and **3**•(TCNQ)$_2$•CH$_2$Cl$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) A Job plot was carried out in CH$_2$Cl$_2$ to determine the stoichiometry between **3** and TCNQ in solution; however, no reliable results were obtained.

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