

Thallium(I) Salts: New Partners for Calix[4]pyrroles

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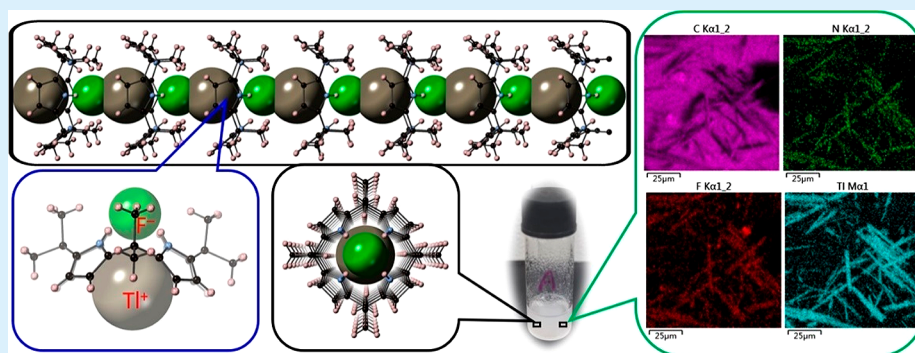
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ABSTRACT: Calix[4]pyrrole **1** can form host–guest complexes with certain thallium salts, for example, TlF, not only in the gas phase but also in solution and in the solid state. The complexation of TlF by calix[4]pyrrole **1** was found to promote self-assembly and the formation of well-defined and highly ordered fibrous supramolecular morphologies, as revealed by polarizing microscopy and scanning electron microscopy. The findings reported here serve to broaden the scope of cationic substrates that may be complexed as ion pairs by calix[4]pyrrole receptors while setting the stage for the development of new hosts for thallium(I) salts.

Thallium is a highly toxic, naturally occurring element that is widely distributed at very low concentrations in the earth's crust. Despite the recognized hazards it poses, thallium continues to see use in the optics and electronic industries.¹ Tl(I) represents the dominant Tl species because under most conditions monovalent thallium is thermodynamically more stable than Tl(III).² Because of the high solubility and mobility of Tl(I) in water, thallium can be readily transported into aqueous environments, resulting in the contamination of drinking water or food chains.^{3–7} Tl(I) salts thus pose a recognized threat to humans and various ecosystems.^{8,9} Over the past decades, effort has been dedicated to the development of new methods for the sensing, extraction, and removal of thallium(I) from soil and groundwater.^{10–14} In this regard, macrocyclic receptors are appealing due in large measure to their ability to recognize various species with high affinity and selectivity.^{15–17} To date, crown-ethers, calix[*n*]arenes (*n* = 4–6), and so-called cryptophane derivatives have shown promise for removing traces of Tl(I).^{10,18–20} For example, Chamsaz et al. reported a single-drop liquid-phase microextraction (SDME) technique that relies on dicyclohexano-18-crown-6 to promote the preconcentration of Tl(I) in an aqueous source phase, allowing for efficient Tl(I) extraction even at very low initial Tl(I) levels (e.g., 0.02 ppm).²¹ Recently, Brotin and coworkers developed a series of cryptophane derivatives bearing either phenolic or carboxylic acid groups on the aromatic rings and showed they were effective for the selective

capture of Tl(I) under either basic or neutral conditions.^{22–25} Nevertheless, the high toxicity of thallium(I) and its continued industrial use provide an incentive to further explore its fundamental complexation chemistry. Here we report that *meso*-octamethylcalix[4]pyrrole **1** can stabilize the ion pair thallium(I) fluoride (TlF) both in organic solution (e.g., 9:1 CDCl₃/CD₃OD v/v) and in the solid state. To the best of our knowledge, this is the first study wherein a calix[4]pyrrole (**1**) is used to stabilize a structurally characterized ion-pair complex of a non-alkaline-metal main-group element.

meso-Octamethylcalix[4]pyrrole **1** and its derivatives are macrocyclic receptors capable of recognizing various neutral and charged species, including ion pairs.^{26–29} To date, cations found to be effective in stabilizing ion-pair complexes of **1** have been limited to quaternary ammonium, phosphonium, imidazolium, and cesium ions (Figure 1).^{28,30,31} In 2012, Křiz and coworkers suggested that calix[4]pyrrole (**1**) might serve as an effective macrocyclic receptor for the univalent thallium cation (i.e., Tl(I)) based on nuclear magnetic

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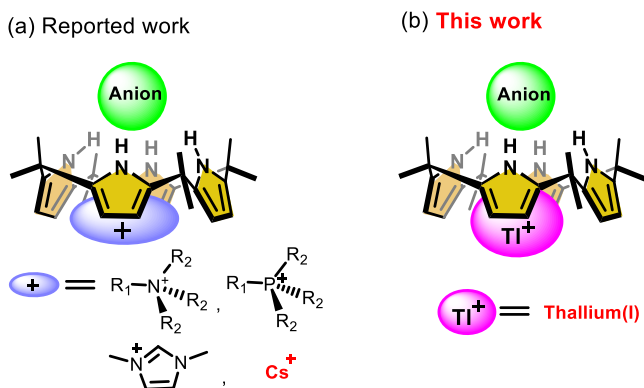


Figure 1. Presentative binding modes seen for ion-pair complexes of meso-octamethylcalix[4]pyrrole (1). (a) Reported quaternary ammonium, phosphonium, imidazolium, or cesium ions known to stabilize ion-pair complexes. (b) Schematic view of thallium(I) ion-pair recognition by 1.

resonance (NMR) spectral studies carried out in nitrobenzene-*d*₅ as well as gas-phase quantum-chemical density functional theory (DFT) calculations.³² In 2018, support for this suggestion came from Vaňura et al., who carried out electrospray ionization mass spectrometric and gas-phase theoretical studies.³³ However, the structure of the putative species 1·Tl⁺, its stability, and its ability to concurrently bind Tl⁺ and anions were not determined.

Mass spectrometry is a recognized technique for studying host–guest interactions in the gas phase.^{34,35} We thus began our own studies by using electrospray ionization high-resolution mass spectrometry (ESI-HRMS) to confirm the reported interaction between 1 and Tl⁺ in gas phase. Commercially available TlNO₃ was employed as the thallium(I) source, which was added to host 1 in CHCl₃/CH₃OH (1:1 v/v). (Caution! TlNO₃, like other thallium salts, is highly toxic, and appropriate care must be taken to avoid inadvertent exposure.) The positive-ion-mode ESI-HRMS for a mixture of TlNO₃ and receptor 1 recorded over the 300–700 *m/z* range (see Figures S1 and S2) revealed a dominant peak in the spectrum at *m/z* 633.2676, with ion cluster peaks between *m/z* 632.6 and 636.8 also being observed. Such findings are in a good agreement with those calculated theoretically (*m/z* 633.2680) for C₂₈H₃₆N₄Tl (i.e., [1·Tl]⁺) (inset). Many other metal ions, such as Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Ca²⁺, and Ag⁺, were also found to interact with 1, as inferred from HRMS and DFT calculations (Table S1 and Figures S3–S11); however, given the prior report from Vaňura and coworkers,³³ we elected to focus on Tl⁺ salts in the present study.

To support the notion that calix[4]pyrrole 1 is capable of capturing thallium(I) salts not only in the gas phase but also in the solid state, efforts were made to obtain single crystals of 1 grown in the presence of various thallium(I) salts. Here TlNO₃ was again used as the thallium(I) source. A series of thallium salts, that is, TlF, TlCl, TlBr, TlOH, and Tl₂SO₄, were then generated *in situ* by adding F[−], Cl[−], Br[−], OH[−], and SO₄^{2−}, all as their tetrabutylammonium (TBA) salts, to solutions of TlNO₃ and 1 in a mixture of CH₂Cl₂/CH₃OH (1:1 v/v). To our delight, X-ray-quality crystals of the thallium(I) fluoride complex of 1 (1·TlF) were obtained by allowing a solution of tetra-*n*-butylammonium fluoride (TBAF) in CH₂Cl₂/CH₃OH (1:1 v/v) to diffuse slowly into a solution of 1 and TlNO₃ in CH₂Cl₂/CH₃OH (1:1 v/v). The resulting crystal structure

revealed that the Tl⁺ cation is symmetrically included in the bowl-like cavity of the calix[4]pyrrole unit (Figure 2a,b), a

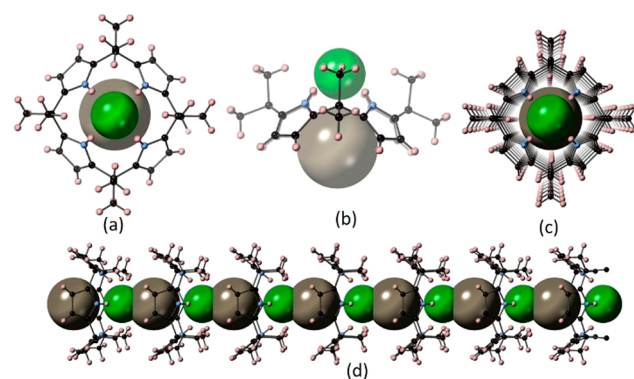


Figure 2. X-ray crystal structure of 1·TlF: (a) Top view. (b) Front view showing the inclusion of the Tl⁺ in the bowl-like cavity of the calix[4]pyrrole and binding of F[−] above the calix[4]pyrrole cone in a host-separated ion-pair mode. (c) Top view and (d) side view of the coordination 1D network induced by the complexation of TlF. Color codes: Tl⁺, gray; F[−], green; C, black; N, light blue; H, pastel red.

finding reminiscent of what is seen in the case of the Cs⁺ cation.³⁰ The distance between the Tl⁺ ion and the centroids of the pyrrole rings of 1 was found to be 3.36 Å. This value is shorter than the 3.39 Å observed in the case of the corresponding cesium fluoride complex, 1·CsF.³⁰ This finding is thus taken as evidence that the bound Tl⁺ cation is stabilized via cation– π interactions. Meanwhile, the F[−] ion is symmetrically bound to the four NH protons of the calix[4]pyrrole via presumed hydrogen bonds. The N...F distance, 2.88 Å, proved similar to the 2.79 Å distance observed previously in the case of the corresponding cesium fluoride complex, 1·CsF.³⁰ The F[−] and Tl⁺ ions within 1·TlF are separated by a distance of 3.77 Å, forming a classical host-separated ion-pair complex.²⁶ Additionally, each F[−] ion is coordinated to a Tl⁺ ion in an adjacent complex with a shorter Tl...F contact of 2.45 Å. This allows for the formation of a 1D coordination polymer (Figure 2c,d). The interactions of 1 and TlF were further analyzed by DFT calculations (Figures S12–S14 and Table S2).

We next sought to explore the host–guest interactions between 1 and thallium(I) salts in solution. In a variety of previous studies involving calix[4]pyrroles, ¹H NMR spectroscopy proved useful in characterizing ion-pair binding.^{27,31} With such an appreciation in mind, ¹H NMR spectroscopic analyses of calix[4]pyrrole 1 and TlF were carried out in a mixture of CDCl₃/CD₃OD (9:1 v/v) at 298 K (Figure 3). It was found that when 5 equiv of TlNO₃ was added to a solution of host 1 (5.1 mM) in CDCl₃/CD₃OD (9:1 v/v), negligible changes in the β -pyrrole proton resonances (in green in Figure 3) at 5.91 ppm and the methyl proton resonances (in pink) at 1.51 ppm were observed; likewise, the signals for the pyrrolic NH protons at 7.58 ppm shifted only slightly to 7.60 ppm. On this basis, we conclude that neither TlNO₃ as an ion pair nor NO₃[−] as an anion is bound appreciably by 1. In contrast, upon adding 5 equiv of TBAF to a 5.1 mM solution of receptor 1 in CDCl₃/CD₃OD (9:1 v/v), the signals for the pyrrolic NH protons (in purple) at 7.58 ppm were seen to shift downfield to 7.71 ppm, whereas the peaks corresponding to the pyrrolic CH protons (in green) at 5.91 ppm and the methyl protons (in pink) at 1.51 ppm shifted only slightly (to 5.90 and 1.52 ppm, respectively). These changes are consistent with formation of a

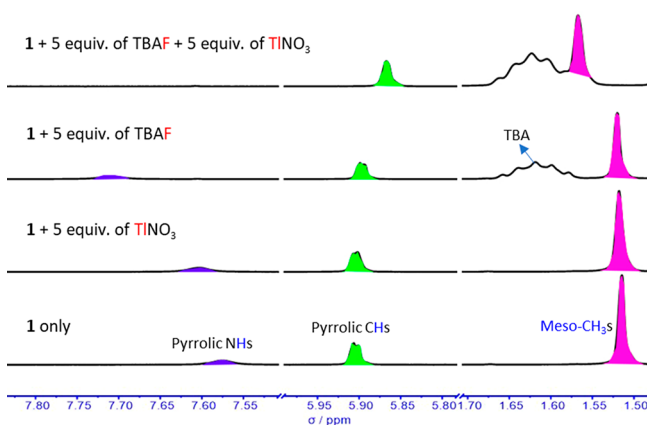


Figure 3. Partial ^1H NMR spectra ($\text{CDCl}_3/\text{CD}_3\text{OD}$ (9:1 v/v), 298 K) of a sample of **1** (5.1 mM) recorded in the absence or presence of 5 equiv of TlNO_3 , 5 equiv of TBAF, or 5 equiv of TBAF + 5 equiv of TlNO_3 , respectively.

fluoride anion complex.³⁶ The subsequent addition of 5 equiv of TlNO_3 into the aforementioned TBAF-containing $\text{CDCl}_3/\text{CD}_3\text{OD}$ (9:1, v/v) solution led to formation of a precipitate that was subsequently identified as being **1**·TlF. The sample as obtained (i.e., without separating off the precipitate) was subject to ^1H NMR spectroscopic analysis. No discernible signals ascribable to the pyrrole NH protons were seen. In contrast, the pyrrolic NH protons signals appear at 8.68 ppm when CD_3OD was replaced with CD_3OH (Figure S15). Meanwhile, the signals for the pyrrolic CH protons and the methyl protons were found to shift upfield to 5.87 ppm and downfield to 1.57 ppm, respectively. These findings are consistent with the binding of Tl^+ by calix[4]pyrrole **1** being affected by fluoride binding and *vice versa*.

We next sought to explore whether conditions other than those used to grow single crystals of **1**·TlF would support self-assembly. We thus prepared a saturated solution of TlNO_3 in a mixture of CHCl_3 and CH_3OH (1:1 v/v), which was used to dissolve calix[4]pyrrole **1** to a final concentration of 50 mM. The addition of 5 equiv of TBAF resulted in the formation of a white precipitate essentially immediately (Figure S16). This precipitate was found to consist of tiny needle-shaped crystals when viewed under a polarizing microscope (Figure 4a and Figures S17 and S18) or a scanning electron microscope (Figure 4b and Figure S19). As a control experiment, 5 equiv of TBAF was added to a saturated solution of TlNO_3 in $\text{CHCl}_3/\text{CH}_3\text{OH}$ (1:1 v/v) in the absence of **1**. Under these conditions, no precipitation was observed. To gain insight into the nature of the needle-like microcrystalline material, SEM-EDS (scanning electron microscopy–energy-dispersive spectrometry) experiments were carried out. EDS elemental mapping associated with an SEM image (Figure 4b–f) revealed all of the elements (i.e., C, N, Tl, and F) expected for microcrystals consisting of **1**·TlF. Fourier transform infrared spectroscopic (FTIR) analyses (Figure S20) confirmed that the spectrum of the microcrystalline material presumed to be **1**·TlF differs from that of calix[4]pyrrole **1** alone. In brief, the IR spectrum of **1** exhibits signature pyrrole NH features at 3441 cm^{-1} (stretching vibration mode), pyrrole CH units at 3106 cm^{-1} (stretching vibration mode), and pyrrole ring moieties at 1576 cm^{-1} (ring-stretching mode). These characteristic peaks ascribable to **1** are also visible in the FTIR spectrum of **1**·TlF (3251 , 3115 , and 1585 cm^{-1} ,

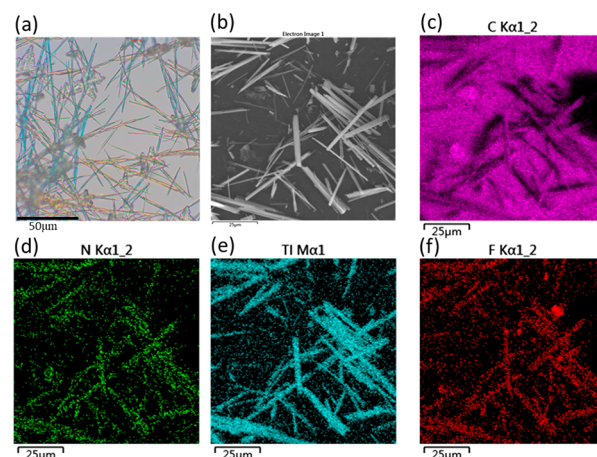


Figure 4. (a) Polarizing microscope picture (crossed polarizers, $\times 60$) of the self-assembled entities formed from calix[4]pyrrole **1** and TlF. (b) SEM image and SEM/EDS mapping for (c) C, (d) N, (e) Tl, and (f) F.

respectively). Furthermore, the addition of 5 equiv of TBAF into a saturated solution of CsNO_3 in $\text{CHCl}_3/\text{CH}_3\text{OH}$ (1:1 v/v) in the presence of **1** gave a clean and transparent solution free of any apparent precipitate. The further addition of 5 equiv of TlNO_3 as a solid to the aforementioned mixture resulted in the near-instantaneous formation of a white precipitate that was found to be chemically identical to the **1**·TlF complex previously discussed (Figure S21). This finding leads us to conclude that **1**·TlF is more prone to undergo self-assembly than **1**·CsF under essentially identical conditions. This could be rationalized in terms of (1) the binding of TlF to **1** being stronger than that of CsF and (2) the Tl^+ being “harder” than Cs^+ , which makes the bridging intracomplex ion-pairing interactions seen in the solid state more favored in the case of TlF than CsF.

In summary, we have shown that calix[4]pyrrole **1** is able to serve as an ion-pair receptor for TlF in the solid state and in organic media, as inferred from a combination of single-crystal X-ray diffraction analyses and ^1H NMR spectroscopic studies carried out in a mixture of $\text{CDCl}_3/\text{CD}_3\text{OD}$ (9:1 v/v). Of particular note is the propensity of **1**·TlF to undergo self-assembly promoted by ion-pair (TlF) complexation, as supported by polarizing microscopic, infrared spectroscopic, and scanning electron microscopic measurements. Given the importance of thallium chemistry, we envision that the finding that calix[4]pyrrole **1** can act as an ion-pair receptor for thallium(I) salts will spur new application opportunities in the near future. More broadly, the present work serves to expand the periodic table of salts that may be targeted by calix[4]pyrrole-type ion-pair receptors.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.1c00555>.

HRMS, NMR studies, X-ray crystallography, DFT calculations of the inclusion complexes, and the morphological analyses and characterization (PDF)

Accession Codes

CCDC 2046393 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge

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Author Contributions

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Notes

The authors declare no competing financial interest.

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