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DOI: 10.1002/slct.201803577

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Organic & Supramolecular Chemistry

Anion Selective Disruption of Strong Intramolecular –NH···O=C Hydrogen Bonds in a Nonchromogenic Tripodal Benzoylthiourea Receptor to Display Colorimetric Response

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Tris(2-aminoethyl)amine based tripodal benzoylthiourea receptor (**L**) showed colorimetric response for fluoride and acetate in aprotic solvents within a range of competitive anions studied. The strong intramolecular –NH···O=C hydrogen bonding in the C_3 symmetric receptor was not disrupted upon addition of any other anions except for fluoride and acetate as confirmed by ^{1}H-NMR experiments in DMSO-d_6. The cavity of the tripodal receptor is locked due to the inward orientation of the intramolecular hydrogen bonded donor-acceptor groups as confirmed by single crystal X-ray crystallography. Fluoride and acetate could selectively disrupt the intramolecular –NH···O=C hydrogen bonds to establish intermolecular hydrogen bonds with both the –NH protons from each receptor side arm and showed visual colour change from colourless to yellow. However, hydrogen bonding observed in the solution state does not provide sufficient stabilization to the receptor fluoride/acetate complexes to be crystallized in the solid state and the receptor crystallised as solvates both from DMSO and THF in the presence of excess fluoride/acetate. From UV-vis and ^{1}H-NMR experiments, it was confirmed that the colorimetric sensing by the nonchromogenic benzoylthiourea receptor is due to strong hydrogen bonding between thiourea –NH groups and fluoride/acetate.

Introduction

Anion recognition and sensing by synthetic receptors has developed into an established field of research in the past two decades due to their biological significance and harmful effects of different anions on environment and human health.[1] Anion selective chemosensors generally involve the covalent linking of an optical signalling chromophore/fluorophore fragment to a hydrogen bonding receptor containing a cleft or cavity ideal for the recognition of a specific anion.[2] In other words, the receptor anion complementarity plays a crucial role in selective anion sensing. Interestingly, fluoride sensing by far has been more frequently studied among other anions, possibly due to its duplicitous nature.[3] However, most of the chromogenic or fluorogenic anion receptors studied in polar aprotic solvents have been observed not to differentiate fluoride with other basic anions such as acetate and phosphate.[2–3] Nonetheless, there are several neutral receptors reported to selectively sense fluoride in organic solvents or semi-aqueous solvent media.[4] However, it is often difficult to structurally correlate between the anion selective receptors considering the different sensing mechanism involved with receptors having different signalling unit (chromophore/fluorophore) and recognition sites. Another approach that has been frequently employed for selective fluoride sensing is chemodosimeter (reactive sensors), where a anion specific reactive site is cleverly incorporated in the sensor molecule to obtain optical signalling from the insitu product formed.[5] One aspect of anion receptor chemistry that has not been paid much attention in the past is the effect of intramolecular hydrogen bonding on anion sensing phenomena,[6] especially with reference to the tripodal receptors which have been widely explored in the area of anion recognition chemistry and anion directed self-assembly formation.[7]

We have previously observed that tris(2-aminoethyl)amine (Tren) based tripodal amide and urea/thiourea receptors are engaged in intramolecular –NH···X=C (X=O/S) hydrogen bonding between two receptor side arms which eventually perish in the presence of an anion (F^-, Cl^-, AcO^-, $H_2PO_4^-$ and HSO_4^- as tetrabutylammonium salts) to establish intermolecular –NH···Anion interactions via anion encapsulation.[8] In order to explore the effect of intramolecular hydrogen bonding on the anion sensing properties of a designed receptor, we have synthesized a Tren based benzoylthiourea receptor **L** (Scheme 1) and studied its anion recognition properties by UV-vis spectroscopy, ^{1}H-NMR spectroscopy and crystallization experiments. Here, we report solution state conformational alteration of **L** selectively in the presence of fluoride and acetate via disruption of strong intramolecular hydrogen bonds and could sense these anions in aprotic solvents by strong –NH hydrogen bonding with anion. Anion induced conformational

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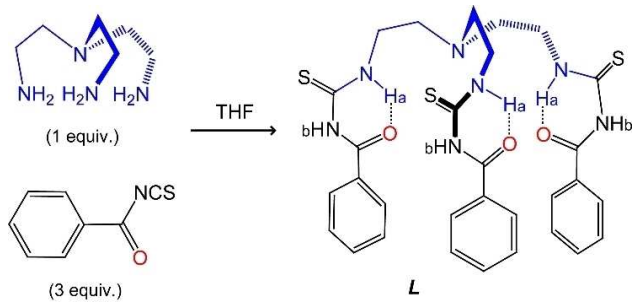
Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.201803577



Scheme 1. Synthesis of tripodal benzoylthiourea receptor **L** having intramolecular –NH···O=C hydrogen bonds.

alteration with concomitant optical signalling of a nonchromogenic tripodal receptor is not well explored in the realm of anion receptor chemistry, to the best of our knowledge.

Results and Discussion

Tripodal benzoylthiourea receptor **L** was synthesized by the reaction of tris(2-aminoethyl)amine with three equivalents of benzoyl isothiocyanate in THF and the reaction mixture was allowed to evaporate at room temperature to obtain colorless crystals of **L** in quantitative yield (see supporting information). ^{1}H-NMR spectrum of **L** showed origin of the two different –NH_a and –NH_b protons at 11.01 and 11.21 ppm, respectively (see supporting information). This implies that the –NH_b proton is slightly more acidic than the –NH_a since the –NH_b nitrogen is bonded to a carbonyl and a thiocarbonyl groups, which was also confirmed by theoretical charge density analysis (discussed later). From single crystal X-ray diffraction (XRD) analysis, it has been observed that **L** crystallized in the highly symmetric rhombohedral space group R_3c with two molecules in the asymmetric unit (each having a C_{3v} axis of symmetry) and a disordered THF molecule. Each receptor side arm is involved in strong intramolecular –NH···O=C hydrogen bonding (N–O distance 2.65 Å) between the –NH_a and benzoyl C=O group (Scheme 1 and Figure 1). Due to the inward orientation of the intramolecular hydrogen bonded groups, the benzoyl amide –NH_b proton is projected away from the tripodal cavity. Each tripodal unit interact with three surrounding neighboring molecules *via* NH_b···S=C (N–S distance 3.71 Å) and aryl CH···S (C–S distance 3.61 Å) hydrogen bonds. It is evident that the intermolecular NH_b···S=C hydrogen bond is much weaker than the intramolecular –NH···O=C hydrogen bonding. Further, S atom from each tripodal arm is also involved in weak CH···S hydrogen bond with lattice THF molecule. Overall non-covalent interactions resulted in the formation of 3D hydrogen bonded network when viewed along crystallographic *c*-axis.

Intramolecular –NH···O=C hydrogen bonding observed in fluoro-benzoylthiourea and N-benzamido benzoylthiourea compounds have been reported to perish in the presence of anions such as fluoride and acetate due to the formation of hydrogen bond between the two –NH protons of the receptor and anion, which they confirmed by ^{1}H-NMR spectroscopy.[6]

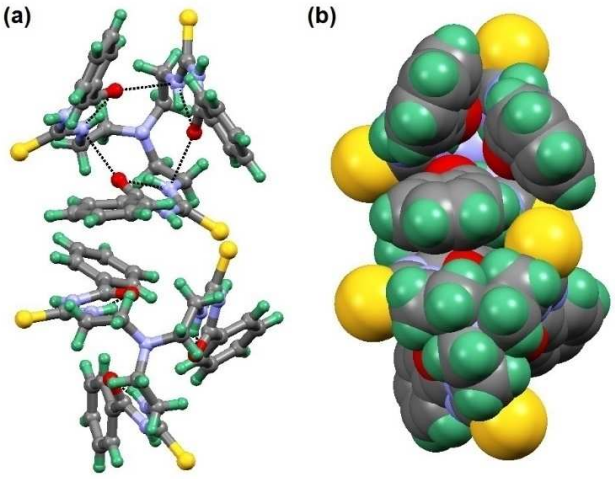


Figure 1. Single crystal X-ray structure of receptor **L·THF** (lattice THF molecule has been omitted for clarity) (a) showing intramolecular –NH···O=C hydrogen bonding within each receptor sidearm, and (b) spacefill representation showing congested tripodal cavity.

Similarly, our experimental results for **L** revealed the persistent nature of the intramolecular hydrogen bonds in the presence of different anions, except for fluoride and acetate. In order to understand the anion recognition chemistry of tripodal benzoylthiourea receptor, we have carried out detailed ^{1}H-NMR, UV-vis, and crystallization experiments with **L** in the presence of different anions.

Whereas, reported fluoro-benzoylthiourea and N-benzamido benzoylthiourea based receptors bearing only one hydrogen bonding thiourea groups are expected to show only 1:1 receptor-anion binding, tripodal benzoylthiourea receptor **L** could either encapsulate an anion within the cavity to form 1:1 complex or 1:2 and 1:3 complexes where anion(s) could form hydrogen bonds with the thiourea functions of two or three receptor side arms respectively.

To compute the acidic nature of two –NH protons (–NH_a and –NH_b), we have carried out theoretical calculations based on density functional theory (DFT)[9] to obtain charge distribution on the energy optimized structure of **L**. We have performed CHELPG charge density analysis,[10] where atomic charges are fitted to reproduce net molecular electrostatic potential. The electrostatic negative potential on thiourea nitrogen (average charge on NH_b −0.371 a.u.) bonded to the carbonyl and thiocarbonyl group is higher than the other thiourea nitrogen atom (average charge on NH_a −0.202 a.u.) bonded to the ethylamine fragment (see supporting information, Table S1 and Figure S15-S16). This indicates that –NH_b nitrogen is more electronegative (or electron withdrawing) than –NH_a nitrogen which results in higher acidity for benzamido –NH_b proton as compared to thioureido –NH_a proton. Thus, –NH_b proton is expected to appear at higher chemical shift than –NH_a in the ^{1}H-NMR spectrum of **L**. However, the fact that –NH_a signal (11.01 ppm) occurs very close to the –NH_b signal (11.21 ppm) is due the intramolecular hydrogen bonding present between –NH_a and C=O groups.

Energy optimization of the crystal structure based on density functional theory (DFT) was carried out to investigate if the pseudo-cavity is maintained in the lowest energy conformation of **L**. As anticipated, the optimized structure also showed a pseudo-cavity where the $-NH_a$ and C=O groups are oriented towards the cavity as observed in the crystal structure (see supporting information, Figure S14). Overlay of the optimized structure with the crystal structure showed close structural similarity except the terminal benzene ring which is twisted away with respect to the crystal structure.

^{1}H-NMR spectroscopy experiments have been carried out by adding excess of different anions (F^-, Cl^-, AcO^-, $H_2PO_4^-$ and HSO_4^- as tetrabutylammonium salts) to the DMSO-d_6 solutions of **L**. Anions such as Br^-, I^-, NO_3^- and ClO_4^- have not been studied here, because urea/thiourea based receptors have not been observed to interact well with these anions in published literature reports.[7] No change in chemical shift of the hydrogen bonded $-NH_a$ proton has been observed in the presence of different anion other than fluoride and acetate confirming the persistent nature of the intramolecular –NH···O=C hydrogen bond in **L** in the presence of less basic anions (Figure 2).

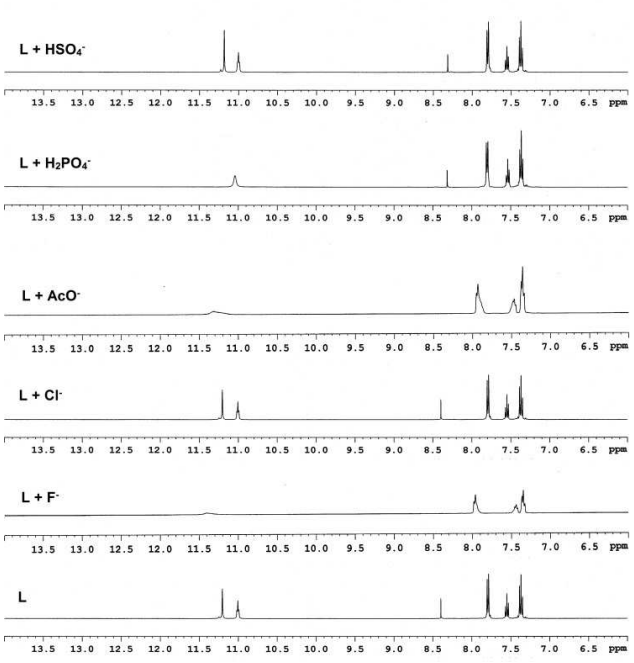


Figure 2. Changes in the ^{1}H-NMR spectrum of **L** (aromatic region) on addition of TBA salts of fluoride, chloride, acetate, hydrogenphosphate and sulfate.

Addition of fluoride (3 equivalents) resulted in disappearance of the $-NH_b$ proton and significant broadening of the $-NH_a$ proton signals. The disappearance of the –NH proton signals can be attributed to the hydrogen bond induced broadening of ^{1}H-NMR signals. This suggests that the intramolecular –NH···O=C hydrogen bond perishes in the presence of excess fluoride to establish intermolecular hydrogen bonds with F^- using both $-NH_a$ and $-NH_b$ protons from each receptor sidearm of **L**. Broadening of the aromatic –CH proton signals were accompanied by a distinct downfield shift of the ortho –CH protons and slight upfield shift of the meta– and para –CH proton signals were also observed (Figure 2). Similar broadening of –NH and –CH peaks were also observed in the case of acetate (Figure 2). On the other hand, only the benzoyl amide $-NH_b$ proton has been observed to disappear in the presence of $H_2PO_4^-$ (3 equivalents) indicating hydrogen bonding interactions between $-NH_b$ of **L** and tetrahedral phosphate (Figure 2). Based on the single crystal X-ray structure of **L** and ^{1}H-NMR experiments, it can be rationalized that the receptor anion interaction occurs outside the cavity for phosphate because the benzoyl $-NH_b$ is projected away from the receptor cavity and the intramolecular hydrogen bonding is not affected.

In the ^{1}H-NMR titration, addition of just 0.15 equivalents of TBAF resulted in disappearance of the benzoyl $-NH_b$ proton (see supporting information, Figure S4-S9), and further addition of TBAF up to 1.5 equivalents showed gradual downfield shift of the $-NH_a$ and ortho –CH proton by 0.2 ppm and 0.1 ppm respectively. The fact that $-NH_b$ proton disappeared upon first addition of fluoride (0.15 equiv.) while the $-NH_a$ proton remains unaffected, suggests that $-NH_b$ proton is more acidic than $-NH_a$ and could easily form hydrogen bond with fluoride due to its outward orientation away from the receptor pseudocavity and not being involved in any intramolecular hydrogen bonds. Addition of more than 2 equivalents of TBAF resulted in significant broadening of the $-NH_a$ proton suggesting formation of intermolecular –NH···F^- hydrogen bonds by disruption of intramolecular –NH···O hydrogen bonds. The ortho –CH proton experienced further downfield shift at higher fluoride concentration with concomitant broadening. The distinct downfield shift of the ortho –CH proton signal upon gradual addition of fluoride is a possible indication towards weak –CH···F^- interaction and the upfield shift of the meta- and para –CH proton signals are possibly due to the electronic effects resulted from strong –NH···F^- and weak –CH···F^- hydrogen bonds. Similar downfield shift of –NH and ortho –CH protons upon addition of anions have previously been reported for tren based amide and urea/thiourea compounds, which were also supported by single crystal X-ray structure of anion complexes.[4a,7] Since, a gradual shift of the –NH protons could not be observed during the course of titration due to disappearance and significant broadening of $-NH_b$ and $-NH_a$ protons respectively, the receptor fluoride binding stoichiometry in DMSO-d_6 could not be estimated from ^{1}H-NMR experiments. Thus, we have then carried out UV-vis experiments in dimethylsulfoxide (DMSO) and tetrahydrofuran (THF) to further understand the anion binding capability of **L**.

In a typical qualitative experiment, 10 equivalents of an anion (using 0.1 M solution) was added to a solution of **L** (2×10^{-5} M) in DMSO. **L** in the absence of any anionic guest, showed a characteristic absorption band at around 280 nm in DMSO medium. This absorption in the UV spectral region can be assigned to intramolecular charge transfer (ICT) from the oxygen or sulfur atom to the weakly electron deficient benzoyl group.[11] From DFT based charge density analysis, it has been confirmed that strong electrostatic negative potential is

localized on the oxygen (average charge −0.467 a.u.) and sulfur (average charge −0.414 a.u.) atoms, and weak negative potential is localized on the benzoyl ring (see supporting information, Table S1 and Figure S15-S16). Thus, it is very likely that an internal charge transfer from the oxygen or sulfur atom to the weakly electron deficient benzoyl ring is responsible for the occurrence of the absorption band at 280 nm in UV-vis spectroscopy.

In DMSO medium, addition of fluoride showed the development of a new peak at 315 nm that tails towards higher wavelength near 400 nm in the visible region of the spectrum (Figure 3a). However, the peak at 315 nm was not observed upon addition of acetate and showed only tailing of the ICT band close to 400 nm. Other anions did not show any observable spectral change in DMSO. Since, absorption in the spectral range of around 400 nm is accompanied by transmission of the complementary yellow colour (560-580 nm), a colorless DMSO solution of **L** upon addition of excess fluoride or acetate turned yellow (Figure 3c). In UV-vis titration, upon gradual addition of standard fluoride solution (1×10^{-3} M) to a DMSO solution of **L** (2×10^{-5} M), we observed a gradual attenuation of the ICT band and development of the new peak at 315 nm which grows with increasing anion concentration up to three equivalents, beyond which no significant spectral changes were observed (Figure 3b). A clear isosbestic point has also been observed during the titration process suggesting the possible formation of one type of hydrogen bonded complex. To determine the receptor-fluoride stoichiometry we have generated the Jobs plot from UV-vis titration data and also plotted the absorbance vs. fluoride concentration at 315 nm (see supporting information, Figure S19 and S20). The plot of absorbance vs. fluoride concentration showed a sigmoidal curve with changes in absorbance at 315 nm up to 3 equivalents of fluoride suggesting the possible formation of LF_3 complex by stepwise complexation. However, the maxima on the Jobs plot is located at 0.29 exactly between the critical values of 0.33 (1:2 stoichiometry) and 0.25 (1:3 stoichiometry) suggesting the formation of both 1:2 (LF_2) and 1:3 (LF_3) receptor-fluoride complexes, which implies that the formation of LF_3 complex is not completed during the course of titration. It has been pointed out by Jurczak et al. and Thordarson et al. that if both 1:1 and 1:2 host-guest complexes are formed in solution, then the maximum on the Job plot will lie somewhere between 0.5 (1:1 stoichiometry) and 0.33 (1:2 stoichiometry).[12] Along the same line, it can be reasoned that when both 1:2 and 1:3 host-guest complexes are formed in solution, then the maximum on the Job plot would lie somewhere between 0.25 (1:3 stoichiometry) and 0.33 (1:2 stoichiometry). Stepwise binding constants for 1:2 receptor-fluoride complex was calculated from the UV-vis titration data using BINDFIT calculator (see supporting information, Figure S21).[13] The calculator performs a non-linear regression analysis using the exact binding equation on the data that includes host and guest concentrations at each titration points, and UV-vis absorbance at a given wavelength. The binding constant were calculated to be $K_{1:1}=(3.28\pm0.3)\times10^3\ M^{-1}$ and $K_{1:2}=(4.07\pm0.4)\times10^4\ M^{-1}$. The fact that $K_{1:2}$ is ten times higher than that of

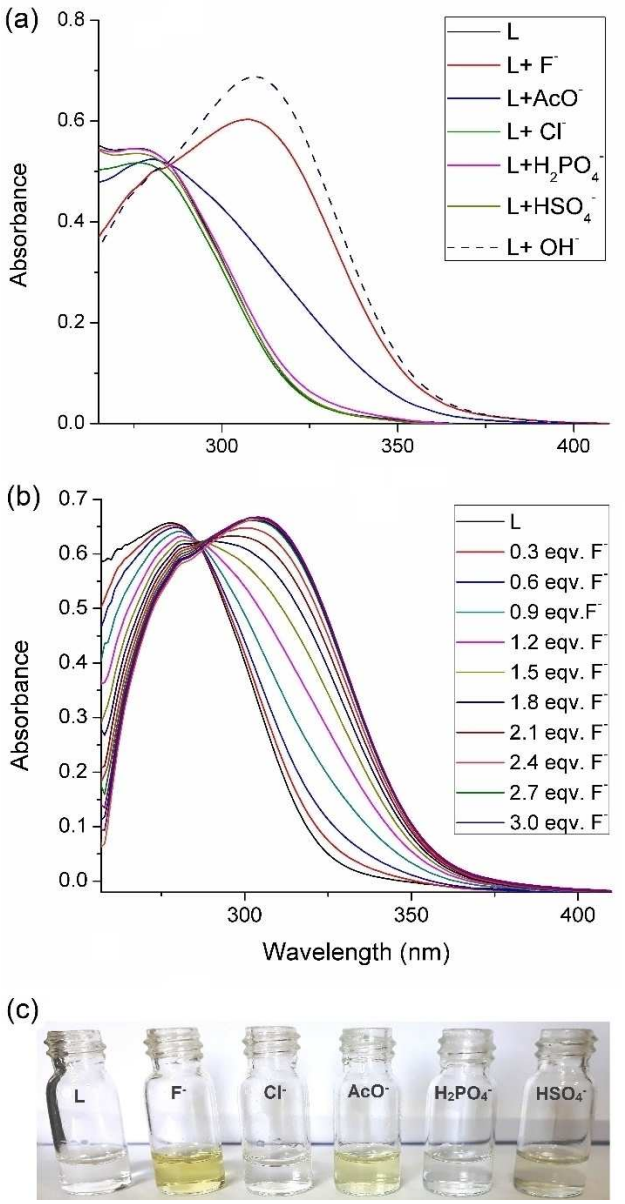
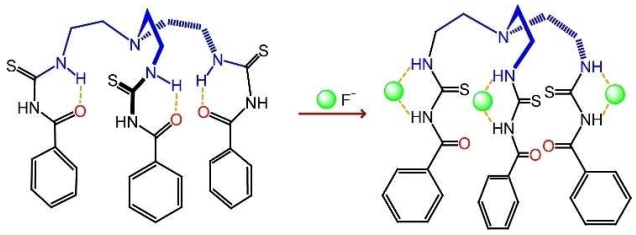


Figure 3. (a) Changes in the UV-Vis spectrum of **L** in DMSO upon addition of TBA salts of different anions (10 equiv.), (b) UV-Vis titration of **L** (2×10^{-5} M) in DMSO upon addition of standard fluoride solution (1×10^{-3} M). (c) colour changes observed upon addition of TBA salts of anions (F^- 3 equiv., Cl^- 100 equiv., AcO^- 10 equiv., $H_2PO_4^-$ 100 equiv., HSO_4^- 100 equiv.,) to 1 ml DMSO solutions of **L** (10^{-2} M).

$K_{1:1}$ is an indication of positive cooperative effect. Positive cooperativity implies binding of a fluoride ion to one of the tripodal thiourea arms increases the binding affinity of the other thiourea arms for fluoride giving LF_2 and LF_3 complexes successively. UV-vis titration data of **L** with standard TBA(AcO) solution could not produce a conventional Jobs plot which could fit any host-guest stoichiometry following the changes in absorbance at 280 nm (see supporting information, Figure S17 and S22). It is to be noted that, the Jobs plot for fluoride binding was obtained by following the changes in absorbance

at 315 nm which was not observed in the case of acetate titration.

Thus, from the ^{1}H-NMR and UV-vis experimental results, it can be concluded that both the –NH protons from each receptor side arm forms hydrogen bonds with a fluoride ion to give 1:3 complex in DMSO solution (Scheme 2) in a stepwise



Scheme 2. Formation of 1:3 receptor-fluoride hydrogen bonded complex in DMSO by disruption of intramolecular hydrogen bonds in **L**.

manner. Encapsulation of fluoride within the receptor cavity is ruled out because in such cases 1:1 complex was observed to form with N-bridged tripodal urea/thiourea receptors.[7]

Anion induced spectral changes of **L** have also been monitored in THF by UV-vis spectroscopy (see supporting information, Figure S18). Similar to the changes observed in DMSO, addition of excess (10 equivalents) fluoride resulted in the development of a new peak at 315 nm in THF, and showing colorimetric response from colourless to yellow due to the tailing of the absorption band near 400 nm.

Colorimetric response could be observed upon addition of fluoride and acetate to 10^{-2} M solution of **L** (Figure 3c). Since, it is the tail of the absorption spectrum extending near 400 nm is responsible for the optical colour change of **L** in the presence of fluoride and acetate, an excess of acetate (10 equivalents of TBA acetate) is required to bring the optical colour change due to the lower absorbance values observed as compared to fluoride which can turn on the optical signal with just 3 equivalents of TBAF.

Hydroxide has been tested in each case in order to confirm that the basicity of anions has a prominent effect in determining the colorimetric response. Addition of hydroxide (0-5 equivalents) showed identical spectral changes in different solvent media by developing a new peak at 315 nm tailing beyond 400 nm (see supporting information, Figure S23). UV-vis spectrum of **L** in the presence sodium tert-butoxide has also been recorded to prove that hydrogen bond formation is insensitive to steric effects (see supporting information, Figure S24). Identical spectral changes have been observed upon addition of same amount (0-5 equivalents) of hydroxide and tert-butoxide, suggesting that hydrogen bond formation in **L** with basic anions is insensitive to steric effects. Since, no new peak has been observed to appear upon increasing addition of hydroxide (or tert-butoxide) to **L**, -NH deprotonation in **L** can be ruled out which was further supported by crystallization experiments (discussed later). Consequently, colourless solution of **L** (10^{-2} M) has been observed to turn yellow in the presence of both hydroxide and tert-butoxide similar to that observed for fluoride.

We have then attempted to crystalize the hydrogen bonded fluoride complex by slow evaporation of THF and DMSO solutions of **L** mixed with excess of TBAF (10-15 equivalents). Interestingly, in each case we have obtained crystals of **L** as confirmed by ^{1}H-NMR spectroscopy. Powder X-ray diffraction (PXRD) pattern of the isolated crystals from THF match with the simulated PXRD pattern generated from the single crystal structure (see supporting information, Figure S25). Single crystal XRD analysis of crystals obtained from DMSO was not fruitful. However, TGA analysis of the isolated crystals revealed the presence of a DMSO molecule in the crystal lattice (see supporting information, Figure S26). Crystallization experiments revealed that hydrogen bonding observed in the solution state does not provide sufficient stabilization to the 1:3 receptor fluoride complex to be crystallized in the solid state and the receptor crystallised as solvates both from THF and DMSO. Similarly, attempted crystallization of AcO^- complex from a DMSO solution of **L** and TBA acetate yielded exclusively crystals of **L**, confirmed by ^{1}H-NMR analysis.

Thus, from the results discussed above, it is evident that the carbonyl (C=O) group linking the hydrogen bond donor thiourea function with the phenyl ring plays key role in determining the 1:3 receptor-anion binding stoichiometry and also colorimetric response for selective anions by acting as intramolecular hydrogen bond acceptor. In contrast, analogous tren based tripodal receptors where the urea/thiourea function is directly linked with a phenyl ring (substituted) could form 1:1 complex with halides (F^-, Cl^-, Br^-) and 1:1 or 2:1 receptor-anion complexes with oxyanions ($H_2PO_4^-$ and HSO_4^-).[7]

Conclusions

We have experimentally demonstrated solid and solution state evidences of strong intramolecular hydrogen bonding in a tripodal benzoylthiourea receptor. Due to these intramolecular hydrogen bonds organized inward in a highly symmetric tripodal structure, the thiourea $–NH_a$ protons do not interact with any other anions except for fluoride and acetate. The receptor has been observed to interact with hydrogenphosphate only through benzoyl $–NH_b$ protons without disrupting the intramolecular hydrogen bond. However, due to the higher basicity of fluoride and acetate compared to other anions, F^- and AcO^- can disrupt the intramolecular hydrogen bonds to establish intermolecular hydrogen bonds with **L** resulting in colorimetric change from colorless to yellow in aprotic solvents. Thus, we have been able to validate the importance of intramolecular hydrogen bonds in selective sensing of anions using a nonchromogenic benzoylthiourea based tripodal receptor. Notably, incorporation of C=O group linking the thiourea and the phenyl ring in **L** significantly limits the encapsulation of anion in the solid and solution states, which is not commonly observed in urea/thiourea based tripodal receptors.[7]

Supporting Information Summary

Experimental details including synthesis and characterization of tris-benzoylthiourea receptor (**L**), ^{1}H-NMR and UV-vis experiments for anion binding studies, and details of theoretical DFT calculations can be found in the Supporting information.

Acknowledgements

SKD acknowledges the Department of Science and Technology (DST) India, for providing financial support through Inspire Faculty award (DST/INSPIRE/04/2016/001867). We thank Prof. S. G. Tilve from Department of Chemistry, Goa University for providing access to NMR facility. We also thank Luann D'Souza for recording the FT-IR spectrum and TGA of the compound. BGH acknowledges the SEGAI-ULL facility of La Laguna University.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Anion · hydrogen bond · sensor · tripodal · thiourea

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Submitted: November 17, 2018
Accepted: March 25, 2019