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A selective fluoride encapsulated neutral tripodal receptor capsule: solvatochromism and solvatomorphism†

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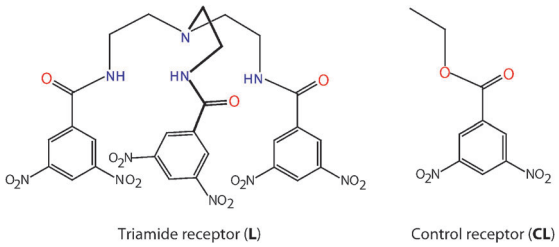
The dinitrophenyl functionalized tris-(amide) receptor behaves as a selective chemosensor for fluoride by encapsulation within the tripodal pseudocavity in polar aprotic solvents exhibiting solvatochromism and solvatomorphism.

Selective anion sensing and recognition has recently developed into an area of immense research interest in supramolecular and biological chemistry.[1] Development of chemosensors for fluoride is important due to their roles in the health, medical, and environmental sciences.[2] Fluoride is one of the most challenging targets for anion recognition because of its high hydration enthalpy. Optical colour changes as a signalling event, employing synthetic receptors, are widely accepted due to the low cost and easy detection of fluoride ions in solution.[3] However, only a few colorimetric anion sensors are able to differentiate selectively between F^- and other anionic substrates of similar basicity and surface charge density. Synthetic anion chemosensors generally involve the covalent linking of an optical signalling chromophoric fragment to a neutral anion receptor containing mostly amide, urea or thiourea units among others (indoles, pyrroles, *etc.*) which can provide multiple H-bonding sites for selective binding and sensing of some anions.[4] Anion receptors in nature often involve amide linkages as H-bond donors; hence, amide based receptors are important for anion binding study.[5]

Tripodal scaffolds offer a flexible and structurally preorganized cavity, which has previously been explored in the area of anion receptor chemistry and anion directed self-assembly formation. In this study we report three solvatomorphs of a fluoride encapsulated neutral molecular capsule of a π-acidic tripodal triamide receptor (**L**) (Scheme 1) which efficiently serves as an optical F^- sensor with characteristic solvent dependent absorptions in the optical spectrum.

Tripodal amide receptor **L** is synthesized in good yield by the reaction of tris(2-aminoethyl)amine with three equivalents of 3,5-dinitrobenzoyl chloride in the presence of triethylamine



Scheme 1 Molecular structures of receptors **L** and **CL**.

in dry chloroform[6] (ESI†).‡ Structural study reveals that the combined effect of intramolecular N–H···O hydrogen bonding and aromatic π···π stacking between the flexible arms of **L** resist the opening of the triamide receptor (ESI†).

The highly ordered hydrogen donating cavity of **L** could give rise to colorimetric changes as the dinitrophenyl moiety being a part of the triamide receptor function can possibly induce a charge-transfer (CT) band in the absorption spectra upon anion recognition. The fluoride recognition chemistry is immediately detected in solution by a dramatic increase in solubility of the receptor in polar aprotic solvents (DMSO, DMF, MeCN, acetone, THF and dioxane) with a concomitant optical signalling from colourless to orange/purple upon addition of TBAF to the suspension of **L**.

Receptor **L**, in the absence of any anionic guest, shows no characteristic absorption in the visible spectrum when recorded in a library of aprotic solvents. The UV/Vis study suggests that **L** can selectively detect fluoride ions colorimetrically even in the presence of other competitive anions like Cl^-, Br^-, I^-, AcO^-, NO_3^-, $H_2PO_4^-$, HSO_4^- and ClO_4^- (Fig. 1a and c). Upon gradual addition of standard F^- solution (10 mM) to a solution of **L** (10 μM) in DMSO, three new absorption bands appear at λ_{max} = 388 (λ_1), 537 (λ_2) and 665 (λ_3) nm and grow with increasing concentration of F^- (Fig. 1b). Intense colorations with emergence of new bands in the optical spectral region can be attributed to the strong anion···π charge-transfer interactions involving a F^- ion and π-acidic dinitrophenyl amide receptor, **L**.[7] The CT absorptions demonstrated a strong solvent dependence which can be visually marked (Fig. 2c) and confirmed by optical spectroscopy (Fig. 2a). However, the CT bands did not exhibit a linear correlation to solvent polarity probably due to the complexity of solute–solvent interactions where the hydrogen bond accepting nature of the solvents plays a critical role. The

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† Electronic supplementary information (ESI) available: Experimental details, crystallographic tables, ^1H, ^{13}C, ^{19}F NMR, ESI-MS and FT-IR Spectra, UV-Vis and ^1H NMR titration experiments. CCDC 795525, 795526, 803581, and 803582. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc05430e

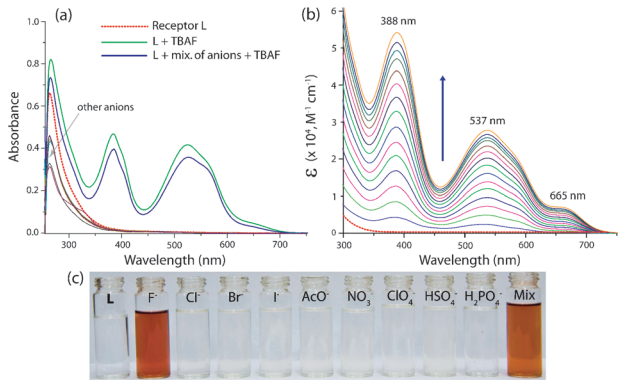

Fig. 1 (a) Changes in the UV/Vis spectrum of **L** in DMSO upon addition of TBA salts of anions (25 equiv.); (b) UV/Vis titration of **L** (10 μM) in DMSO upon addition of F^- solution (10 mM); (c) colour changes observed upon addition of anions (25 equiv.) to DMSO solutions of **L**.

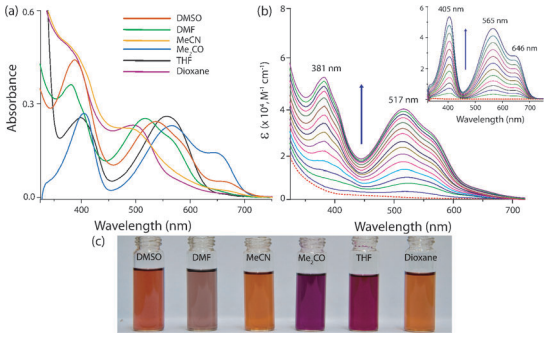

Fig. 2 (a) Changes in the UV/Vis spectrum of **L** in various aprotic solvents upon addition of excess TBAF; (b) UV/Vis titration of **L** (10 μM) in DMF upon addition of standard F^- solution (10 mM) and inset: UV/Vis titration of **L** (10 μM) in acetone with increasing F^- concentration (10 mM); (c) variable colour changes observed with the addition of F^- (25 equiv.) to the solutions of **L** in various polar aprotic solvents.

selectivity and CT character of **L** in response to F^- were confirmed by comparison to a control receptor, **CL** (ethyl ester of carboxy-dinitrobenzene), that cannot differentiate F^- from other basic anions, such as AcO^- and $H_2PO_4^-$, producing an optical signal from colorless to blue irrespective of solvent choice and polarity indicating the worth of a preorganized H-bonding cavity of the tripodal scaffold in **L** towards solvatochromic F^- recognition. UV/Vis titration of **L** with TBAF in acetone exhibited considerable bathochromic shifts of 17 and 28 nm in the λ_1 and λ_2 absorptions (λ_1 = 405 nm and λ_2 = 565 nm), respectively, whereas a hypsochromic shift of 19 nm was observed for λ_3 (λ_3 = 646 nm), indicative of an additional solute–solvent interaction acting as a mechanism to stabilize the complex more in acetone relative to DMSO (Fig. 2b, inset). Similarly in THF, appreciable bathochromic shifts of 12 and 20 nm were observed for the λ_1 and λ_2 absorption maxima (λ_1 = 400 nm and λ_2 = 557 nm). However in DMF, titration curves showed blue shifts of 7 and 20 nm in the absorptions of λ_1 and λ_2 (λ_1 = 381 nm and λ_2 = 517 nm), respectively (Fig. 2b), suggestive of a minor interaction of the [**L**···F^-] complex with the DMF molecules compared to acetone, THF and DMSO. The shortest wavelength for λ_2 absorption was 498 nm recorded in MeCN and dioxane which exhibit identical spectral patterns, and the longest wavelength was 565 nm observed in acetone, indicating that the [**L**···F^-] complex is more stabilized in acetone followed by THF and DMSO among other aprotic solvents. The origin of the multi-CT bands observed can possibly be explained by the existence of weak electron resonance between the lone pair electrons of F^- ions with two closely spaced unoccupied orbitals of the π-acidic receptor.[7]

Efforts were made to examine the binding of F^- with receptor **L** in the solid state, following the selectivity and solvatochromism of **L** towards F^- in the UV/Vis study. Slow evaporation of a solution mixture of **L** with excess TBAF (10 equiv.) in aprotic solvents *viz*. MeCN, DMF and THF resulted in solvatomorphs of fluoride-encapsulated complexes TBA[**L**(F)]·H_2O (**1a**), TBA[**L**(F)]·DMF (**1b**) and TBA[**L**(F)]·3THF (**1c**) respectively. Structural analyses reveal that irrespective of the solvent of crystallization, F^- is encapsulated within the tripodal cavity governed by six strong intramolecular H-bonds involving the amide NH protons and three aryl CH protons (Fig. 3). In solvatomorphs **1a**, **1b** and **1c** the encapsulated F^- is H-bonded to the NH protons with average N···F^- distances of 2.706, 2.679 and 2.705 Å, respectively, whereas the coordinating CH protons interact with average C···F^- distances of 2.998, 2.929 and 2.998 Å, respectively, demonstrating the strong binding of F^- in the solid state (ESI†). Unlike in **1a** and **1c**, the encapsulated F^- in **1b** interacts with the arenes C1g and C3g *via* weak anion···π interactions with distances of 4.007 and 4.054 Å respectively. The FT-IR spectra of the complexes show a considerable shift upto 20 cm^{-1} for the C=O frequency relative to free **L** due to the formation of strong NH···F hydrogen bonds (ESI†). Following the solvatomorphism of the [**L**···F^-] complex, it can be vaguely argued that crystallization of a lattice water in complex **1a** suggests weak interactions of the complex with MeCN and thereby, the shortest λ_{max} values for the complex were observed in MeCN. In contrast, the presence of one DMF and multiple THF molecules in the crystals of **1b** and **1c**, respectively, indicates comparatively better interactions of the complex with the respective solvents demonstrating a gradual bathochromic shift of the CT bands relative to MeCN. With π-acidic arenes, C–H···X^- hydrogen bonds are often in competition with other interaction types and by coordinating to the CH protons they can possibly generate a delocalized anion in solution,

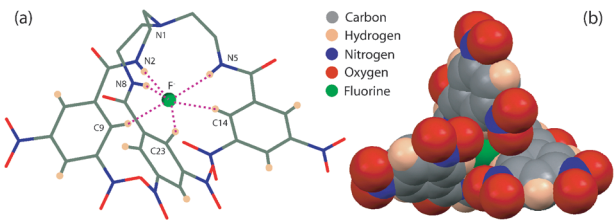

Fig. 3 (a) Crystal structure of **1a** showing encapsulation of F^- inside the tripodal cavity where dotted lines represent (D–H)···F^- interactions; (b) spacefill representation depicting the formation of a F^- encapsulated neutral molecular capsule in **1a**. TBA cations and solvent are omitted for clarity.

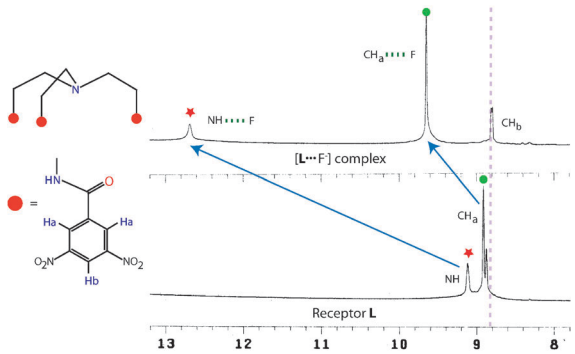

Fig. 4 Partial ^{1}H NMR spectra of **L** (below) in DMSO-d_6 and upon addition of equivalent amount of TBA salt of a fluoride anion (above).

which may also be responsible for the intense coloration of **L** in the presence of F^-.

It is worth mentioning that titration with TBAOH results in similar spectral behaviour of **L** to those observed with F^-. Furthermore, progressive additions of protic solvent (such as methanol or water) result in gradual attenuation of CT bands perhaps due to the capability of protic solvents to compete for F^- with NH functions and π-acidic arenes, disfavoring the formation of anion···π CT complexes[3h,i] (ESI†). Thus, the nature of the chromophoric change can be attributed to F^-···π CT interactions wherein F^- is hydrogen bonded to the NH groups as evident in the crystal structure of solvatomorph **1b**.

The selectivity of **L** towards fluoride was further confirmed by ^{1}H NMR studies. Addition of an equivalent amount of TBAF salt to a solution of **L** in DMSO-d_6 resulted in a significant downfield shift of the amide –NH and aryl –CH_a proton resonances with high $\Delta\delta$ values of 3.55 and 0.72 ppm, respectively, indicative of a structural alteration of **L** that could influence both the –NH as well as –CH protons to encapsulate F^- ions (Fig. 4). However, in cases of other halides and oxoanions (added as TBA salts) no appreciable change in chemical shift values of the –NH and –CH resonances of **L** is observed, suggesting the non-interacting nature or very weak interactions of other anions with **L** (ESI†). The ^{1}H NMR titration curve gives the best fit for a 1 : 1 binding model for host to guest, in agreement with Job's plots indicating a maximum $\Delta\delta$ at 0.5 = [**L**]/([**L**] + [F^-]). The high binding constant value calculated using EQN MR 2 reveals that **L** binds very strongly with F^- having log K > 7.0 M^{-1} (error limit ≤ 15%).[8] In the ^{19}F NMR spectra, addition of one equiv. of **L** to a solution of TBAF in DMSO-d_6 resulted in a significant upfield shift of 1.726 ppm for the free fluoride resonance, indicating the participation of the anion in H-bonding with **L** (ESI†). Whereas, the ^{1}H NMR titration of **CL** shows a gradual upfield shift of the acidic aryl protons with increasing F^- concentration as prevalent in the CT complexes of nitroaromatics with halides (ESI†).[7a]

In conclusion, we have synthesized a tren-based triamide receptor molecule bearing dinitroaryl functions which can selectively sense fluoride ions over other anions by a visible colour change with a remarkable display of solvatochromism and solvatomorphism in various polar aprotic solvents.

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Notes and references

‡ Crystal data for **L**: $C_{29}H_{30}N_{10}O_{16}S$, M = 806.70, triclinic ($P\bar{1}$), a = 11.2942(3), b = 12.4744(4), c = 12.8671(4) Å, α = 84.723(2)°, β = 79.650(3)°, γ = 88.404(2)°, V = 1775.65(9) Å^3, Z = 2, D_c = 1.509 g cm^{-1}, μ = 0.180 mm^{-1}, T = 298(2) K, 13 679 reflections, 8734 independent (R_{int} = 0.0564), $R(F)$ = 0.0508 [$I > 2\sigma(I)$], w$R(F^2)$ = 0.1510 (all data), GOF = 0.911. **1a**: $C_{43}H_{60}FN_{11}O_{16}$, M = 1006.02, monoclinic ($P2_1/c$), a = 16.129(3), b = 15.781(2), c = 25.393(4) Å, β = 127.592(9)°, V = 5121.4(15) Å^3, Z = 4, D_c = 1.305 g cm^{-1}, μ = 0.103 mm^{-1}, T = 298(2) K, 35 440 reflections, 8854 independent (R_{int} = 0.0935), $R(F)$ = 0.0603 [$I > 2\sigma(I)$], w$R(F^2)$ = 0.2034 (all data), GOF = 1.008. **1b**: $C_{46}H_{67}FN_{12}O_{16}$, M = 1063.12, triclinic ($P\bar{1}$), a = 10. 0759(3), b = 16.7929(6), c = 16.8986(5) Å, α = 79.197(2)°, β = 78.461(3)°, γ = 89.753(2)°, V = 2750.23(16) Å^3, Z = 2, D_c = 1.284 g cm^{-1}, μ = 0.100 mm^{-1}, T = 298(2) K, 29 276 reflections, 13 732 independent (R_{int} = 0.0321), $R(F)$ = 0.0693 [$I > 2\sigma(I)$], w$R(F^2)$ = 0.1841 (all data), GOF = 1.011. **1c**: $C_{43}H_{60}FN_{11}O_{15}$, M = 990.02, monoclinic ($P2_1/c$), a = 10.0293(9), b = 33.293(3), c = 19.4982(17) Å, β = 90.382(6)°, V = 6510.4(10) Å^3, Z = 4, D_c = 1.010 g cm^{-1}, μ = 0.079 mm^{-1}, T = 298(2) K, 73 179 reflections, 11 177 independent (R_{int} = 0.0837), $R(F)$ = 0.0814 [$I > 2\sigma(I)$], w$R(F^2)$ = 0.1952 (all data), GOF = 1.018.

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