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Hydrogen and Halogen bonding in a concert act of anion recognition: F^- induced atmospheric CO_2 uptake by an iodophenyl functionalized simple urea receptor

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Two simple urea based para-halo substituted [Iodo ($\mathbf{L_1}$) and Bromo ($\mathbf{L_2}$)] acyclic receptors have been extensively studied as a receptor for various anions. The receptors $\mathbf{L_1}$ efficiently uptake atmospheric CO_2 and stabilize as air-stable crystals of HCO_3^- dimer (Complex **1a**) in presence of n-tetrabutylammonium (*n*-TBA) fluoride through simultaneous formation of hydrogen and halogen bonding resulting a tetrahedrally surrounded non-covalent coordinated complex. However, the receptor $\mathbf{L_2}$ in presence of *n*-TBA salt of F^- has been found to form complex with octahedral SiF_6^{2-} anion where the coordination environment of the anion is merely governed by multiple N−H···F (anion) interactions. The fluoride induce uptake of areal CO_2 only for $\mathbf{L_1}$ is due to the unique ability of $\mathbf{L_1}$ to form both H-bond bond and halogen bond with anionic guest simultaneously. The most decisive evidence supporting the ability of $\mathbf{L_1}$ to form halogen bond is obtained via crystallizing the acetate complex of both the receptors. The receptor $\mathbf{L_1}$ stabilizes acetate anion via both H-bonding and halogen bonding interactions. While the receptor $\mathbf{L_2}$ only form H-bonding interactions with acetate anion. The solution-state anion binding properties of $\mathbf{L_1}$ and $\mathbf{L_2}$ has been investigated by qualitative and quantitative ^1H NMR titration experiments with halides and oxyanions in DMSO-d_6. Both the receptors showed strong solution-state binding with F^-, HCO_3^- and CH_3COO^- as observed in the solid-state, whereas both has been found to be less interactive with other anions such as Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, and $H_2PO_4^-$.

INTRODUCTION

Halogen bonding (XB), the parallel non-covalent world to Hydrogen bonding (HB) is the charge-transfer interaction between Lewis bases and polarizable halogen atoms.[1] Halogen-bonding is continuing to expand its horizon[2] in a rapid way because of its widespread applicability in assembly of functional materials (such as liquid crystals and molecular-imprinted polymers),[3] conducting and magnetic molecular materials,[4] to tune second-order nonlinear optical responses,[5] supramolecular polymers and crystalline assemblies,[6] even in medicinal chemistry.[7] In last few years halogen bonding has also been established as a potential tool for the rational design and construction of molecular materials with DNA and other biological macromolecules.[8] Ho and co-workers have studied the Holliday junctions (four-stranded DNA junctions, the key structural intermediates during homologous recombination of DNA) and estimated that a halogen bond which can direct the conformation of a biological molecule is stronger than the analogous hydrogen bond in the same environment.[8c]

The first case of intermolecular donor-acceptor complexes was reported by Benesi and Hildebrand which were formed from iodine and aromatic hydrocarbons.[9] But it was O. Hassel who introduced this promising non-covalent interaction, halogen bonding to the people as 'interatomic charge transfer bonding' in 1970[10] and the first use of the term "halogen bond" was by Dumas et al. in 1978.[11] After a dormant period for decades in 90's by Legon[12] with the gas-phase study and specially in 21st century halogen bonding is being grown up well by a few people like Resnati, Metrangolo et al.,[2] Mark S. Taylor and his co-workers.[13] Though it is still a challenge to study XB in solution-phase,[14] numerous theoretical studies of XB have been reported till date.[15]

While HB is a full-blown tool in molecular recognition as well as anion recognition,[16] XB is still adolescent from this point of view, though XB has been sensibly approached in recently developed anion recognition.[13,17] Recently, a series of urea-based anion receptors bearing one or two halogen bond donors has been designed to probe the potential for anion recognition through combinations of hydrogen and halogen bonding by

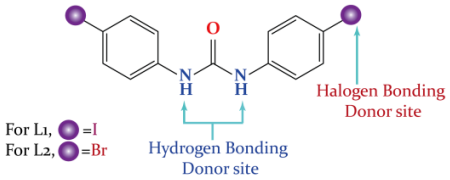
Taylor et al.[13e] NMR studies revealed that two distinct noncovalent interactions act in concert to achieve selective binding of halides over oxyanions, a conclusion being further supported by computational studies. Supramolecular anion host systems utilizing both with defined functions are a challenging prospect.

Direct F^- recognition as well as sensing is an area of immense research interest in supramolecular and biological chemistry.[18,23(e,h)] Interestingly, indirect results obtained by employing F^- anion also has developed into an emerging field of research. A major environmental issue of major concern is the significant rise in the CO_2 concentration in the atmosphere which eventually demands the efficient fixation and activation of atmospheric CO_2 into green chemicals.[19] Microporous aluminosilicates, activated carbons, and metal-organic frameworks (MOFs) have widely been employed to capture and store CO_2 by converting it into green chemicals for the synthesis of specific chemical intermediates.[20] However, in light of supramolecular chemistry, efficient fixation of aerial CO_2 as carbonate/bicarbonate can be achieved with artificial H-bonding receptors in the presence of hydroxide and fluoride ions.[21,23b] Gale *et al.* have also demonstrated CO_2 capture as carbamates (alkylammonium/alkylcarbamate) by a series of urea-based receptors in the presence of aliphatic amines (CO_2 scrubbers) bubbled with CO_2 in dimethyl sulfoxide (DMSO).[22]

Continuing our research in the field of anion recognition,[23] here we report F^- ion induced uptake of atmospheric CO_2 and stabilize as HCO_3^- anion (air-stable crystals) by a structurally simple acyclic 1,3-bis(4-iodophenyl)urea (**L_1**) receptor. The *in situ* formed HCO_3^- complex (**1a**) is stabilized by a concert act of hydrogen and halogen bonding donated by the receptors. To the best of our knowledge, 1,3-bis(4-iodophenyl)urea is the simplest of anion receptors that shows CO_2 uptake and stabilize the *in situ* formed HCO_3^- by a combination of hydrogen and halogen bonding. Further evidence of halogen bonding with the 1,3-bis(4-iodophenyl)urea receptor has been observed in the CH_3COO^- complex (**1b**), validating the interplay of both hydrogen and halogen bonding in the stabilization of bicarbonate in a receptor−fluoride solution. Following the trend in strength of halogen bond formation *viz.*, −I > −Br > −Cl,[2b, 24] we have examined the structural aspects of anion binding with the 1,3-bis(4-bromophenyl)urea (**L_2**) as a control receptor, where the halogen bond donating iodine substituent is replaced by bromine. Interestingly, halogen bonding was found to be completely lacking in both the structurally elucidated anion complexes **2a** and **2b** (SiF_6^{2-} and CH_3COO^- complexes, respectively) of **L_2**.

RESULTS AND DISCUSSION

In 2004, Fabbrizzi *et al.* has shown the anion recognition properties of 1,3-bis(4-nitrophenyl)urea, which due to the presence of electron withdrawing nitro chromophore resulted in a fluoride ion induced –NH deprotonation with subsequent absorption of atmospheric CO_2 in moist THF.[25] Encouraged by such exciting results, we envisioned that the simple 1,3-bis(4-halophenyl)urea receptors could turn out to be excellent candidates for anion complexation *via* a combined act of hydrogen and halogen bonding (Scheme 1).



Scheme 1: Molecular Structure of the Receptors.

Structural elucidation of Fabbrizzi's HCO_3^- complex showed dimeric association of urea bound HCO_3^- anions, while a crystallized water molecule is hydrogen bonded to a HCO_3^- oxygen atom. However, in the present case, the urea bound HCO_3^- dimer is additionally stabilized by a pair of halogen boding interactions donated from the iodophenyl ring of an adjacent receptor to the –OH oxygen atom of each HCO_3^- anion. Further, a distinct directional coordinative environment has been observed in the CO_2 absorbed HCO_3^- complex of **L_1**. From the perspective of anion receptor chemistry, crystallization has traditionally been a route to understand the structural insights of the anion complexes formed, primarily by single-crystal XRD analysis, which are then related to the observed selectivity in solution. Thus, efforts were made to explore the solid-state binding properties of **L_1** and **L_2** with different anions, by charging excess quaternary ammonium [*n*-TBA (tetrabutylammonium)/TEA (tetraethylammonium)] salt of anions to the individual receptor solutions in aprotic solvents such as MeCN or DMSO and allowed to crystallize at room temperature. Addition of F^-, HCO_3^- and CH_3COO^- solubilize the otherwise insoluble receptors **L_1** and **L_2** in MeCN, indicating a strong receptor-anion interaction. It is interesting to note that, single crystals of HCO_3^- complex *n*-TBA[**L_1**·HCO_3] (**1a**) was obtained upon slow evaporation of the F^- containing acetonitrile solution of receptor **L_1**. The source of HCO_3^- is from the atmosphere where hydroxide ion generated in situ from the basic receptor-F^- solution dissolves aerial CO_2 into HCO_3^-.

$$2F^- + H_2O \longrightarrow OH^- + HF_2^-$$

$$OH^- + CO_2 \longrightarrow HCO_3^-$$

The anion binding topology of the in situ generated HCO_3^- complex (**1a**) revealed the involvement of both hydrogen and halogen bonding in a concert act of anion recognition. The potentiality of **L_1** as a halogen bond donor is unanimous as confirmed by single crystal analysis of the *n*-TBA[**L_1**·CH_3COO] complex (**1b**), where each –NH group share one of the acetate oxygen atoms, which in turn is halogen bonded to the iodophenyl ring of an adjacent receptor. However, anion complexes of **L_2** (SiF_6^{2-} and CH_3COO^- complexes) did not showcase the formation of any halogen bonds with the hydrogen bonded anions. Attempts to obtain

complexes with other anions (NO_3^-, HSO_4^-, $H_2PO_4^-$, Cl^-, Br^-, I^-) of $\mathbf{L_1}$ and $\mathbf{L_2}$ resulted in crystallization of the free receptor.

Accounts of Crystal Structures

Receptors $\mathbf{L_1}$ and $\mathbf{L_2}$. Single crystals of $\mathbf{L_1}$ and $\mathbf{L_2}$ suitable for XRD analysis were obtained from DMSO and both crystallize monoclinic system with centrosymmetric space group C2/*c*. Structural analysis showed weak π-stacking interactions between the receptor molecules that are N−H···O hydrogen bonded with one another. The π-stacked urea tapes are interlinked with one another by halogen-halogen (I···I) interactions in $\mathbf{L_1}$, whereas $\mathbf{L_2}$ in spite of having similar π-stacked tape motif lacks halogen-halogen (Br···Br) interaction. Thus, from the structural features it can be presumed that $\mathbf{L_1}$ has the possibility for special noncovalent feature.

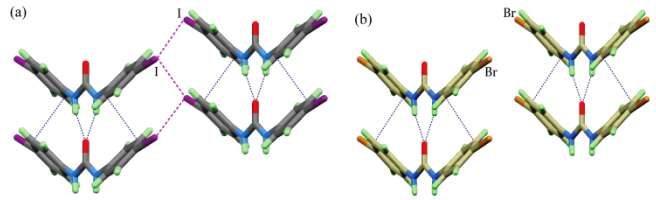


Fig. 1 (a) X-ray structure of $\mathbf{L_1}$ shows the urea tape hydrogen bond motif along with π-stacking and I•••I interactions, and (b) X-ray structure of $\mathbf{L_2}$ showing the urea tape hydrogen bond motif along with π-stacking interactions.

Bicarbonate-Complex, *n*-TBA[$\mathbf{L_1}$·HCO_3], (1a). The *in situ* generated bicarbonate complex crystallized in the monoclinic system with C_2 space group, from an acetonitrile solution of $\mathbf{L_1}$ containing excess fluoride ions. The source of HCO_3^- is from the atmosphere where hydroxide ions generated *in situ* from the basic receptor-fluoride solution dissolves aerial CO_2 into HCO_3^- at the air/solvent interface and thereby, resulting in the formation of air-stable crystals of dimeric HCO_3^- complex stabilized by a combined act of hydrogen and halogen bonds. Structural elucidation revealed a 1:1 complex stoichiometry and dimeric association between two receptor coordinated HCO_3^- anions. Each urea bound HCO_3^- anion donates and accepts an O−H···O hydrogen bond (1.796 Å) to/from another urea bound HCO_3^- ion, giving rise to a dimeric anion complex. The $-COO^-$ fragment of a HCO_3^- anion is hydrogen bonded to the urea–NH groups with a donor-acceptor (N−H···O) distance of 1.921(5) and 2.104(4) Å for O_2 and O_3, respectively. Additionally, HCO_3^- oxygen O_2 and O_3 is hydrogen bonded to an aryl –CH proton (*ortho* w.r.t. to urea function) with a donor-acceptor (C−H···O) distance of 2.571(4) and 2.644(4) Å, respectively.
Most importantly, the –OH group of HCO_3^- anion accepts one strong C−I···O halogen bond from the iodophenyl ring of an adjacent anion bound receptor molecule. Thus, each HCO_3^- anion is coordinated to a receptor by four hydrogen bonds and to another by a halogen bond, which implies that a HCO_3^- dimer is coordinated to four receptor molecules via two distinct types of noncovalent interactions (Fig. 2a). The HCO_3^- dimer is located below the hydrogen bond donor and above the halogen bond donor platform. The spatial position of the HCO_3^- dimer looks as if the dimer is hanging by holding the hydrogen bonding threads which is supported by two halogen bonding pillars from the bottom (Fig. 2b). In other words, it is the halogen bonds that pulled the HCO_3^- dimer out of the more common hydrogen bonded planar structure, as observed in the case of HCO_3^- complex of 1,3-bis(4-nitrophenyl)urea reported by Fabbrizzi et al. Furthermore, the exposed area at the top and bottom created due to the tetrahedral like environment around the bicarbonate dimer are capped by the *n*-TBA cations *via* contact ion-pairing (C−H···Anion interactions) and C−H···π interactions with the phenyl rings to form a compact enclosed system surrounding the in situ generated anion

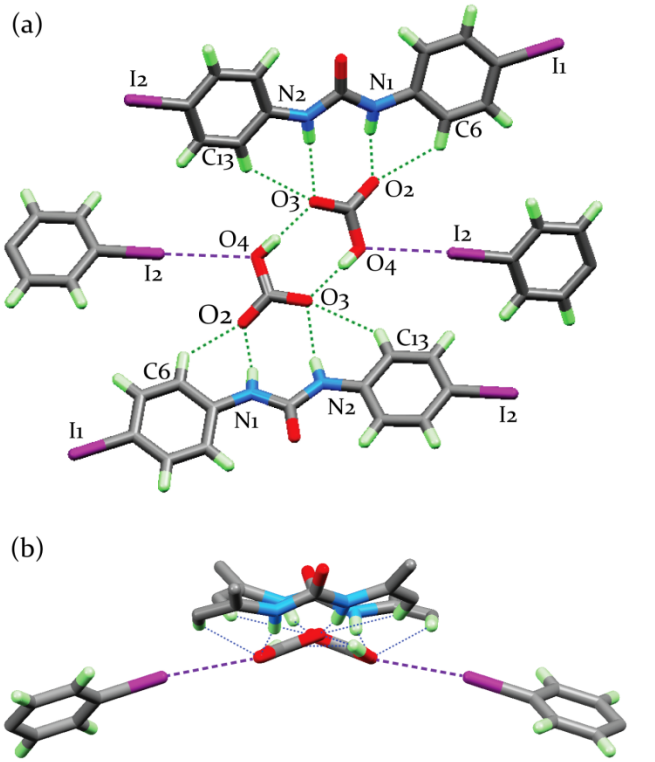


Fig. 2 (a) Ball-and-stick representation depicting the hydrogen and halogen bonding contacts on HCO_3^- dimer in complex **1a** as viewed down the crystallographic *b*-axis, and (b) Ball-and-stick representation showing the tetrahedral spatial orientation of the bicarbonate dimer in complex **1a** as viewed down the crystallographic *c*-axis (*n*-TBA cations are omitted for clarity of the presentation).

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The halogen bonding contact (I2···O4) in complex **1a** has a distance of 3.183(4) Å (Fig. 3a), which corresponds to 9% shortening of the sum of their van der Waals radii (3.50Å) (The van der Waals radii of O and I are 1.52 and 1.98 Å).[26] Parthasarthy *et al.* has reported the crystallographic evidence of directional preferences of intermolecular forces around halogen atoms[27] where they have shown that nucleophiles in general tend to approach the C−X bond in a "head-on" fashion with Γ≈165(8)° for C−I bond. Similar results were obtained by Allen *et al.*[26a] and Glaser *et al.*[28b] In complex **1a** the iodophenyl unit is "head-on" with the HCO_3^- oxygen at an angle ∠(C−I2···O4)

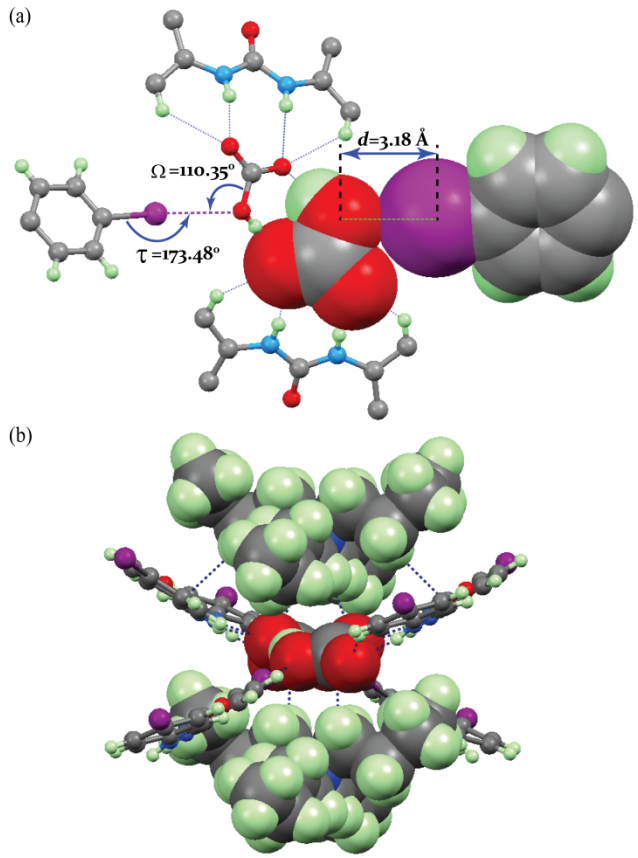

Fig. 3 (a) A magnified view of the coordination environment in complex **1a** highlighting halogen bonding distances and angles, (b) Ball-and-stick (host) and spacefill (guest) representation depicting the aliphatic C–H···O and C–H···π interactions from the *n*-TBA cations to the dimeric anion and receptors respectively.

of Γ=173.6°(2) close to 180° [∠(C−O4···I2) angle Ω=110.0(3)°, Fig. 3a]. The ^{1}H NMR spectrum of complex **1a** (DMSO-d_6) showed appreciable downfield shift and concomitant broadening of the urea −NH resonance with Δδ = 1.84 ppm, indicating strong solution-state binding of HCO_3^- with the urea function. The strong interaction of HCO_3^- has also been confirmed by monitoring the differences in the chemical shifts of ^{13}C NMR signals of TEA salt of HCO_3^- and complex **1a**. TEA(HCO_3) in DMSO-d_6 showed a sharp ^{13}C NMR resonance at 158.91 ppm, whereas in complex **1a** the HCO_3^- resonance originated at 182.12 ppm showing a large downfield shift of 23.27 ppm (Figure S11, ESI).

Acetate-Complex, *n*-TBA[L_1·CH_3COO], (1b). Complex **1b** crystallized in the monoclinic system with P_21/c space group, where each acetate oxygen atom is hydrogen bonded to a receptor molecule by a pair of N−H···O and aryl C−H···O bonds. A correlation of the N−H···O angle versus the N−H···O distance shows that both the N−H···O hydrogen bonds are in very strong hydrogen-bonding interaction regions of *d*(H···O) < 2.5 Å and d(D···O) < 3.2 Å (Table S2, ESI). Furthermore, each acetate oxygen atom interacts with a neighbouring receptor molecule by accepting a halogen bond each from two different iodophenyl rings. The halogen bonding contacts (I···O) in this complex were determined to be, *d*(I1···O2)=3.144 Å and *d*(I2···O3)=3.482 Å (Fig. 4b), which corresponds to 11% and 1% shortening of the sum of their van der Waals radii (3.5Å). The ∠(C−I···O) angles were measured to be Γ=156.6(8)° and Γ=144.77(8)° for I1···O2 and I2···O3 halogen bonds, respectively. The details of the halogen bonding contacts and angles in complexes **1a** and **1b** are listed in Table 1. In complex **1b**, the acetate anion resides in the plane of the XB donating iodophenyl rings, rather than the HB donating urea function (Fig. 4d), showcasing the effect of XB on H-bonded urea-acetate complex, unlike the most common urea-acetate cases.[29] Recently, Ho and coworkers have reported that the halogen bonds can adopt an orthogonal (perpendicular) geometry, and energetically independent of hydrogen bonds that share a common acceptor atom.[8c] Based on their calculations on biomolecules they found that, in most of the cases the X···O···H angle lies in the range of ±(85-89)°. Our attempt to analyse the orthogonality of the halogen bonds in acetate complex (**1b**), we find that the –NH related I···O···H angles are in the range of 110-115° and –CH related I···O···H angles are in the range of 63-66°. Thus, it may be assumed that the halogen bonds are maintaining an orthogonal relationship to the –NH and –CH hydrogen bonds with an average angle of ±89° (Fig. 4d).

Table 1 Detail of Halogen Bonding Contacts in the Complexes **1a** and **1b**.

complex	**1a**	**1b**	**1b**
C−I···O	C11−I2···O4	C1−I1···O2	C11−I2···O3
d(I···O)/Å	3.187(4)	3.144(4)	3.482(5)
d(C−I···O)/Å	5.272(6)	5.143(4)	5.339(5)
I···O [%][a]	90.8%	89.8%	99%
∠C−I···O/deg (Γ)	173.6(2)	156.60(8)	144.77(8)
∠C−O(A⁻)···I/deg (Ω)	110.0(3)	132.8(4)	133.4(4)

[a][%] Of VdW radii

^{1}H NMR spectrum of the crystalline complex **1b** (DMSO-d_6) showed a large downfield shift of the –NH resonance with Δδ = 2.83 ppm indicating a strong host-guest relationship.

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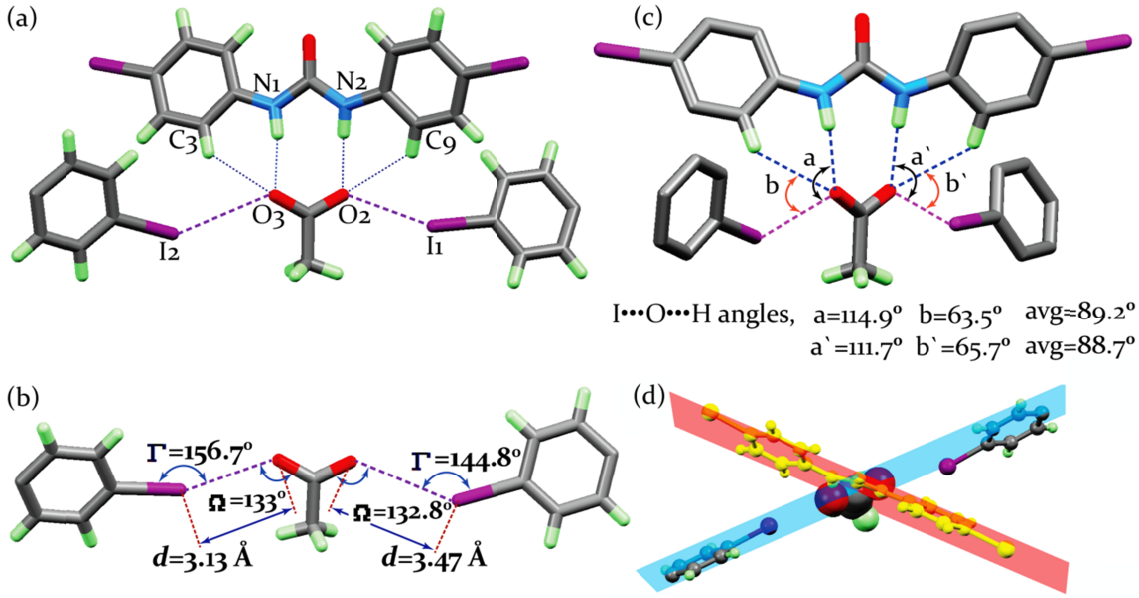

Fig. 4 Ball-and-stick representation of complex **1b** depicting (a) the hydrogen and halogen bonding contacts on CH_3COO^- anion along the crystallographic *a*-axis, (b) halogen bonding distances and angles, (c) orthogonal relationship between hydrogen and halogen bonds, (d) A magnified view depicting the planarity of acetate anion with the halogen bond donating iodophenyl rings (light blue collared plane) and not with the hydrogen bonded urea function (light pink collared plane) (*n*-TBA cations are omitted for clarity of the presentation).

Acetate-Complex, *n*-TBA[L_2·CH_3COO], (2b). Identical to **1b**, complex **2b** crystallized in the monoclinic system with P_21/c space group, with a 1:1 complex stoichiometry. However, there are significant differences in the acetate coordination on switching from the 1,3-bis(4-iodophenyl)urea to 1,3-bis(4-brmophenyl)urea. In complex **2b**, each acetate oxygen atom behaves as a bifurcated hydrogen bond acceptor, where oxygen

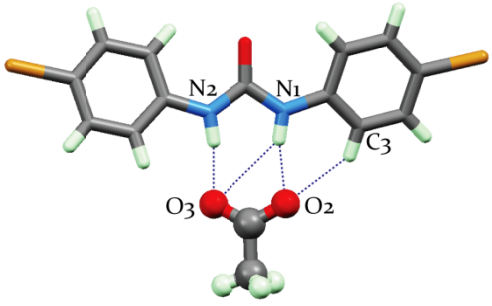

Fig. 5 Ball-and-stick representation depicting the H-bonding contacts of complex **2b** on AcO^- (n-TBA cations are omitted for clarity of the presentation).

O2 is hydrogen bonded to a –NH proton and an aryl –CH proton, and oxygen O3 is hydrogen bonded to both the urea –NH protons (Fig. 5b). Whereas, in complex **1b** a pair of halogen bonds (I···O) provide added stabilization to the hydrogen bonded acetate anion. Such a feature showcasing halogen bond formation with the anion was found to be absent in complex **2b**. However, the urea bound acetate complex is sandwiched between two *n*-TBA cations by forming several C–H···O interactions and thereby, gained some added solid-state stabilization. Further, lack of halogen bonding in **2b** contributes to the planarity of the complex.

^{1}H NMR spectrum of complex **2b** (DMSO-d_6) also showed a large downfield shift of the –NH resonance with $\Delta\delta$ = 2.515 ppm, similar to complex **1b** indicating a strong host-guest binding.

Solution-State Anion-Binding Study

The solution-state anion binding properties of $\mathbf{L_1}$ and $\mathbf{L_2}$ were investigated by qualitative as well as quantitative ^{1}H NMR experiments in DMSO-d_6 using quaternary ammonium (*n*-TBA/TEA) salt of monovalent anions such as, F^-, Cl^-, Br^-, I^-, HCO_3^-, CH_3COO^-, NO_3^-, $H_2PO_4^-$ and HSO_4^-. Figure 6a and 6b shows the chemical shift changes observed upon one equivalent addition of different anions to the individual solutions of $\mathbf{L_1}$ and $\mathbf{L_2}$ respectively, in DMSO- d_6. The most significant change has been observed for the urea –NH proton in presence of F^-,

HCO_3^- and CH_3COO^-, indicating that the −NH function act as the primary site for anion recognition.

^{1}H NMR titration of **L_1** with a standard HCO_3^- solution, **a** large downfield shift of urea −NH resonance with Δδ = 2.13 ppm, and a notable upfield shift of *ortho*-aryl proton with Δδ= 0.06 ppm (*ortho w.r.t.* urea group) were observed. Tracking the shift of the −NH resonance, the binding constant (log K_a) for HCO_3^- was (WinEQNMR2) calculated to be 5.16 with a 1:1 host/guest stoichiometry, in agreement with Job's plot analysis (Figures S28 and S29, ESI). However the best fitted curve obtained from WinEQNMR2 was for a mixture of 1:1 and 1:2 host/guest stoichiometry. Similarly, titration data for F^- has given a log K_a value of 4.95 (Figure S34, ESI) for 1:1 stoichiometry. The highest downfield shift of −NH resonance has been observed with acetate anion with Δδ = 2.73 ppm. The binding constant (log K_a) for CH_3COO^- was calculated to be 3.69 with a 1:1 host/guest stoichiometry (Figure S31 and S32, ESI).

Table 2 Association constants in log $K_a(M^{-1})$ of **L_1** and **L_2** with different anions in DMSO-d_6 at 298 K, calculated using WinEQNMR2

Receptor	Anions (TBA/TEA salts)	log K_a	
		LogK_{11} (1:1=host:guest complex)	Log K_{12} (1:2=host:guest complex)
L_1	F^-	4.95	8.37
L_1	AcO^-	3.69	6.34
L_1	HCO_3^-	5.16	9.06
L_2	F^-	4.40	8.24
L_2	AcO^-	3.66	6.53
L_2	HCO_3^-	3.32	6.79

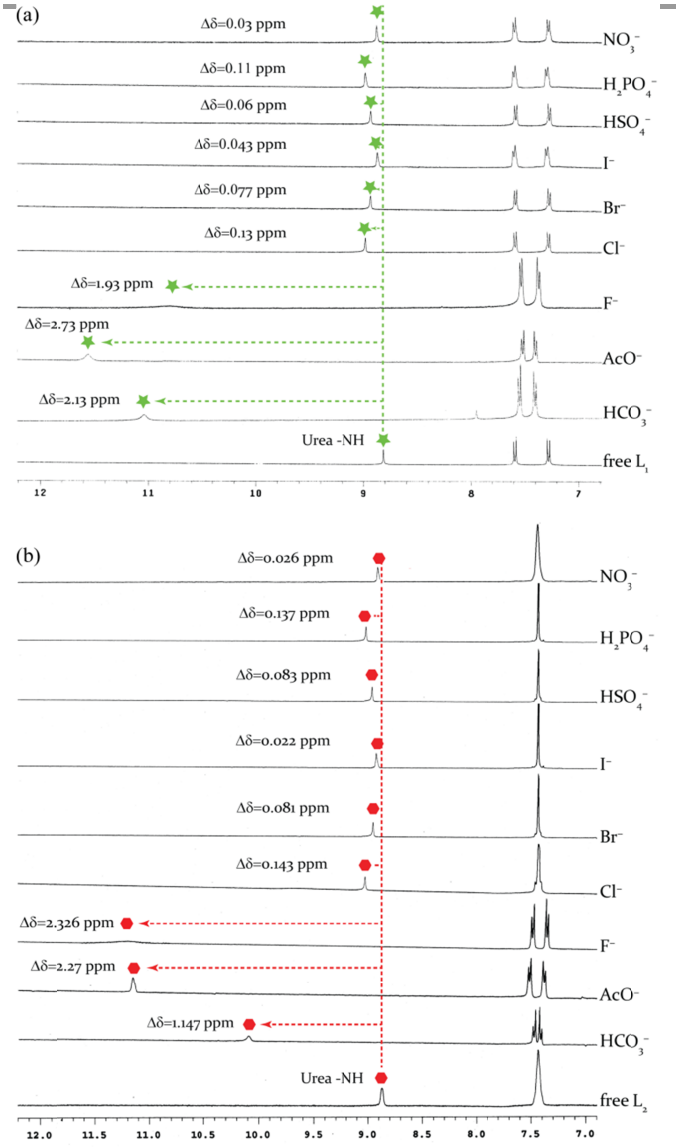

Fig. 6 Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6) of (a) **L_1** and (b) **L_2** with maximum observable shifts of urea −NH resonance upon the addition of 1 equivalent of HCO_3^-, CH_3COO^-, F^-, Cl^-, Br^-, I^-, HSO_4^-, $H_2PO_4^-$ and NO_3^- as their TEA/*n*-TBA salts.

Titration of **L_2** with F^- and CH_3COO^- showed a huge downfield shift of the –NH resonance with Δδ = 2.32 ppm and 2.27 ppm for F^- and CH_3COO^- **r**espectively. However, titration with HCO_3^- resulted in a comparatively lesser shift of Δδ = 1.14 ppm for **L_2** −NH resonance, which is ~1.00 ppm less than that of **L_1**. In all three cases, the host/guest stoichiometry was found to be 1:1 in agreement with the Job's plot analyses (Figures S44, S47 and S50, ESI**)** and the binding constants (log *K*) were calculated to be 4.40, 3.66 and 3.32 for F^-, CH_3COO^- and HCO_3^- respectively (Table 2). However in all the cases WinEQNMR2 has given the best fit curve for the equilibrium mixture of 1:1 and 1:2 host/guest stoichiometry Other halides (Cl^-, Br^-, I^-) and oxyanions (NO_3^-, $H_2PO_4^-$, HSO_4^-) hardly had any effect on the urea −NH resonance indicating very weak interactions with **L_1** and **L_2**.

We have also checked the UV/Vis absorption properties of both the receptors in presence of all the common anions in excess. Except F^-, AcO^- and $HCO3^-$ ions both the receptors show no response towards the other anions in dilute MeCN solution. With F^-, AcO^- and $HCO3^-$ both the receptors get red shifted supporting the solid-state evidences. We have checked both the receptors with excess of each of the anions, where $\mathbf{L_1}$ gets red shifted by 10 nm with F^- as well as AcO^- and 8 nm with $HCO3^-$ (Figue S51). Similarly $\mathbf{L_2}$ gets red shift by 10 nm with F^- and 5 nm with $HCO3^-$ as well as AcO^- (Figure S52).

CONCLUSION

In the 1,3-bis(4-nitrophenyl)urea compound, electron withdrawing nitro groups render the urea protons sufficiently acidic to get deprotonated in the presence of fluoride ions and eventually can capture CO_2 as HCO_3^- hydrogen bonded to the urea receptor.[25] As anticipated, utilization of 1,3-bis(4-iodophenyl)urea (**L_1**) decreases the possibility of fluoride ion induced urea deprotonation due to the less electronegative character of iodine. However, **L_1** showcase the exciting property of fluoride ion induced CO_2 capture as HCO_3^- complex (**1a**) stabilized by a combined act of hydrogen and halogen bonding. Whereas in a control experiment, 1,3-bis(4-bromophenyl)urea (**L_2**) crystallized as hydrogen bonded SiF_6^{2-} complex in presence of excess fluoride ions, suggesting its impotency to act as a CO_2 scrubber. The proficiency of **L_1** as a halogen bond donor has also been authenticated in the crystal structures of the free receptor and the acetate complex, **1b**. The inability of **L_2** to form halogen bonds with anions have also been confirmed by the structural elucidation of its hydrogen bonded acetate complex **2b**, suggesting that it is the combined act of hydrogen and halogen bonding which prompted the CO_2 uptake from a fluoride containing solution of 1,3-bis(4-iodophenyl)urea. Overall, we have shown that a subtle variation in the electronic properties of 1,3-bis(4-halophenyl)urea receptors resulted in a drastic change in their anion recognition properties in solution as well as solid-state.

EXPERIMENTAL SECTION

Materials, Instruments and Methods

All reagents and solvents were obtained from commercial sources and used as received without further purification. Phenyl-isothiocyanate, 4-iodo and 4-bromophenylisothiocyanate, tetraalkylammonium salts and 4-iodo and 4-bromoaniline were purchased from Sigma-Aldrich and used as received. Solvents for synthesis and crystallization experiments were purchased from Merck India, and used as received.

The FT-IR spectra of air dried samples were recorded on a Perkin-Elmer-Spectrum One FT-IR spectrometer with KBr disks in the range 4000–400 cm^{-1}.^{1}H NMR spectra were recorded on a Varian FT-400 MHz and Bruker 600 MHz instrument and chemical shifts were recorded in parts per million (ppm) on the scale using tetramethylsilane (TMS) or residual solvent peak as a reference and ^{13}C NMR spectra were obtained at 100 MHz and 150 MHz.

Association constants were obtained by ^{1}H NMR (Varian-400 MHz) titrations of the ligands with tetraethyl ammonium (TEA)/n-tetrabutylammonium (*n*-TBA) salts of respective anions in DMSO-d_6 at 298 K. The initial concentration of corresponding receptor solution was 10 mM. Aliquots of anions were added from 50 mM stock solutions of anions (up to 1:5 host/guest stoichiometry) and each titration was performed with 15-20 measurements at room temperature. WinEQNMR2 software was used to calculate the Binding constants (K) values.[30]

X-ray crystallography

In each case, a crystal of suitable size was selected from the mother liquor and immersed in silicone oil, and it was mounted on the tip of a glass fibre and cemented using epoxy resin. The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo-Kα radiation (λ = 0.71073 Å) at 298(3) K, with increasing ω (width of 0.3o per frame) at a scan speed of 5 s/ frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP[31] software. Multi-scan empirical absorption corrections were applied to the data using the program SADABS.[32] Structures were solved by direct methods using SHELXS-97[33] and refined with full-matrix least-squares on F^2 using SHELXL-97.[34] All non-hydrogen atoms were refined anisotropically and hydrogen atoms attached to all carbon atoms were geometrically fixed and the positional and temperature factors are refined isotropically. Hydrogen atoms attached with the urea nitrogen atoms were located from electron Fourier map and refined isotropically. Usually, temperature factors of H-atoms attached to carbon atoms are refined by restraints -1.2 or -1.5 Uiso (C), although the isotropic free refinement is also acceptable. Structural illustrations have been drawn with MERCURY-2.3[35] for Windows. Parameters for data collection and crystallographic refinement details of isolated anion complexes **1a-b** and **2b** are summarized in Supporting Information, Table S1. However we were not able to make publishable data of the complex **2a** due to poor quality of the obtained crystal.

Synthesis and characterizations

L_1 and **L_2**: The symmetric receptors **L_1** and **L_2** has been synthesised in quantitative yield by the equimolar reaction of the aromatic amine (4-iodoaniline and 4-bromoaniline) with the corresponding phenylisocyanate in tetrahydrofuran (THF) and the colourless product obtained in both the cases were characterized by NMR, FT-IR, and single-crystal XRD analyses.

L_1: ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) at 298 K, 7.28 (d, 4H, ArH), 7.59 (d, 4H, ArH), 8.832 (s, 2H, −NH). ^{13}C NMR

(150 MHz, DMSO-d_6): δ (ppm) 84.98 (2C, ArH), 120.67 (4C, ArH), 137.43 (4C, ArH), 139.49 (2C, ArH), 152.30 (1C, C=O). ESI-Mass: m/z = 463.07 $[M]^+$. FT-IR (ν, cm^{-1}): 1005 (C-I), 1236 (C-N), 1549 (C=C), 1637 (-C=O), 3301 (N-H).

L_2: ^{1}H NMR (DMSO-d_6, 600 MHz): δ (ppm) at 298 K, 7.417 (d, 4H, ArH), 7.435 (d, 4H, ArH), 8.829 (s, 2H, −NH).^{13}C NMR (150 MHz, DMSO-d_6): δ (ppm) 113.609 (2C, ArH), 120.457 (4C, ArH), 131.675 (4C, ArH), 139.027 (2C, ArH), 152.434 (1C, C=O). ESI-Mass: m/z = 369.06 $[M]^+$. FT-IR (ν, cm^{-1}): 1070 (C-Br), 1236 (C-N), 1555 (C=C), 1641 (-C=O), 3299 (N-H).

Complex 1a, *n*-TBA[L_1.HCO_3^-]: Colorless block-shaped crystals bicarbonate complex, 1a suitable for single-crystal X-ray diffraction analysis were obtained by charging an excess (10 equiv.) of n-tetrabutylammonium fluoride (*n*-TBAF) into a 5 mL MeCN solution of **L_1** (46.4 mg, 0.1 mmol). After the addition of *n*-TBAF, the initially insoluble **L_1** gets dissolved in MeCN and the solution was stirred for about 30 minute at room temperature and filtered in a test tube for slow evaporation. After 4−5 days the isolated yield of **1a** was 92%. Mp: 140 °C. ^{1}H NMR, DMSO-d_6, (Bruker-600 MHz) at 298 K, δ (ppm)1.011 (t, 12H, n−TBA-CH_3), 1.28 (q, 8H, n−TBA-CH_2), 1.533 (q, 8H, n−TBA-CH_2), 3.125 (t, 8H, n−TBA-N^+CH_2), 7.57 (d, 4H, ArH), 7.520 (d, 4H, ArH), 10.67 (s, 2H, −NH).^{13}C NMR, DMSO-d_6 (Bruker-150 MHz) at 298 K, δ (ppm) 13.59 (4C, n−TBA-CH_3), 19.29 (4C, n−TBA-CH_2), 23.15 (4C, n−TBA-CH_2), 57.64 (4C, n−TBA-N^+CH_2), 84.12 (2C, ArH), 120.15 (4C, ArH), 137.21 (4C, ArH), 140.46 (2C, ArH), 153.05 (1C, C=O), and 182.12 (1C, HCO_3^- anion), FT-IR (ν, cm^{-1}): 822 (HCO_3^-1), 1231 (C-N), 1537 (C=C), 1577(C-O), 1697 (-C=O), 2960 (C-H), 3420 (N-H), 3511(O-H).

Complex 1b, *n*-TBA[L_1.CH_3COO^-]: Acetate-complex **1b** was obtained by adding excess of n-tetrabutylammonium acetate into a 5 mL MeCN solution of **L_1** (46.4 mg, 0.1 mmol). In the same fashion after the addition of acetate salt the initially insoluble **L_1** gets dissolved in MeCN and the solution was stirred for about 30 minute at room temperature and filtered in a test tube. Slow evaporation of the filtrate at room temperature yielded colorless crystals suitable for single crystal X-ray crystallographic analysis within 8−10 days. The isolated yield of **1b** was 70%. Mp: 178 °C. ^{1}H NMR, $CDCl_3$, (Varian-400 MHz) at 298 K, δ (ppm), 0.93 (t, 12H, n−TBA-CH_3), 1.294 (q, 8H, n−TBA-CH_2), 1.43 (t, 8H, n−TBA-CH_2), 2.029 (s, Acetate−CH_3), 2.987 (t, 8H, n−TBA-N^+CH_2), 7.485 (d, 4H, ArH), 7.53 (d, 4H, ArH), 11.67 (s, 2H, −NH). ^{13}C NMR, DMSO-d_6 (Bruker-150 MHz) at 298 K, δ (ppm) 13.57 (4C, n−TBA-CH_3), 19.27 (4C, n−TBA-CH_2), 23.12 (4C, n−TBA-CH_2), 24.73 (1C, Acetate−CH_3), 57.61 (4C, n−TBA-N^+CH_2), 84.17 (2C, ArH), 120.59 (4C, ArH), 137.21 (4C, ArH), 140.43 (2C, ArH), 152.97 (1C, C=O) and 176.53 (Acetate−COO^-). FT-IR (ν, cm^{-1}): 642(-COO deformation), 823 (-COO), 1003(C-I), 1235 (C-N), 1553 (C=C), 1634 (-C=O), 2961 (C-H), 3301 (N-H).

Complex 2a, 2*n*-TBA[L_2.SiF_6^{2-}]: The SiF_6^{2-} complex **2a** of **L_2**was obtained during the similar attempt as in the case of complex **1a**, but with a complete different result. After the addition an excess of n-tetrabutylammonium fluoride (*n*-TBAF) into a 5 mL MeCN solution of **L_2** (37 mg, 0.1 mmol) contained in a glass vowel, the solution was stirred for about 30 minute at room temperature and filtered in a test tube. Slow evaporation of the filtrate at room temperature yielded colorless crystals suitable for single crystal X-ray crystallographic analysis within 7−8 days. Isolated yield of **2a** was 65%.Mp: 133 °C. ^{1}H NMR, DMSO-d_6, (Bruker-600 MHz) at 298 K, δ (ppm) 0.922 (t, 12H, n−TBA-CH_3), 1.30 (s, 8H, n−TBA-CH_2), 1.55 (p, 8H, n−TBA-CH_2), 3.143 (s, 8H, n−TBA-N^+CH_2), 7.374 (d, 4H, ArH), 7.52 (d, 4H, ArH), 11.043 (s, 2H, −NH).^{13}C NMR, DMSO-d_6 (Bruker-150 MHz) at 298 K, δ (ppm) 13.54 (4C, n−TBA-CH_3), 19.27 (4C, n−TBA-CH_2), 23.14 (4C, n−TBA-CH_2), 57.64 (4C, n−TBA-N^+CH_2), 112.69 (2C, ArH), 120.14 (4C, ArH), 131.31 (4C, ArH), 140.44 (2C, ArH) and 153.41 (1C, C=O). FT-IR (ν, cm^{-1}): 740(SiF_6^{2-}), 1008(C-Br), 1227 (C-N), 1648 (-C=O), 2962 (C-H), 3422 (N-H).

Complex 2b *n*-TBA[L_2.CH_3COO^-]: Acetate-complex **2b** was obtained in the same way as complex **1b**. Mp: 118 °C. ^{1}H NMR, DMSO-d_6 (Bruker-600 MHz) at 298 K, δ (ppm), 0.91 (t, 12H, n−TBA-CH_3), 1.293 (q, 8H, n−TBA-CH_2), 1.541 (s, 8H, n−TBA-CH2), 1.799 (s, Acetate−CH_3), 3.132 (s, 8H, n−TBA-N^+CH_2), 7.384 (d, 4H, ArH), 7.547 (d, 4H, ArH), 11.39 (s, 2H, −NH). ^{13}C NMR, DMSO-d_6 (Bruker-150 MHz) at 298 K. δ (ppm) 13.57 (4C, n−TBA-CH_3), 19.29 (4C, n−TBA-CH_2), 23.15 (4C, n−TBA-CH_2), 24.74 (1C, Acetate−CH_3), 57.65 (4C, n−TBA-N^+CH_2), 112.49 (2C, ArH), 120.15 (4C, ArH), 131.31 (4C, ArH), 140.46 (2C, ArH), 153.44 (1C, C=O) and 176.53 (Acetate−COO^-). FT-IR (ν, cm^{-1}): 642(-COO deformation), 829 (-COO), 1070(C-Br), 1236 (C-N), 1564 (C=C), 1634 (-C=O), 2962 (C-H), 3305 (N-H).

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Notes and references

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† Electronic Supplementary Information (ESI) available: X-ray crystallographic file of the structures in CIF format, characterization data including ^{1}H NMR and FT-IRSpectra, ^{1}H titration spectra and additional crystallographic data. See DOI: 10.1039/b000000x/

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