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PAPER

Fluorogenic sensing of $CH_3CO_2^-$ and $H_2PO_4^-$ by ditopic receptor through conformational change†

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Cyclo-bis-(urea-3,6-dichlorocarbazole) (**1**) forms a 1 : 2 complex with $CH_3CO_2^-$ and $H_2PO_4^-$ through hydrogen bonding with the two urea moieties, resulting in fluorescence enhancement *via* a combined photoinduced electron transfer (PET) and energy transfer mechanism. The binding mechanism involves a conformational change of the two urea receptors to a *trans* orientation after binding of the first anion, which facilitates the second interaction.

Introduction

The prevalent interest in anion sensors, motivated by the importance of ions such as halides, carboxylates and phosphates in biological and environmental processes,[1] has produced inventive methods of detection over the years. Excellent reviews on the progress of this line of research have been recently published.[2] A common mechanism of anion binding is through the formation of hydrogen bonds with neutral receptors such as amides, urea and thiourea, pyrroles, *etc.*[3–6] or charged $(C–H)^+$ binding sites as in imidazolium.[7] An ideal receptor for tetrahedral and Y-shaped anions such as $H_2PO_4^-$ and $CH_3CO_2^-$ is (thio)urea, which can form multitopic H-bonds with anions.[8–14]

The initial binding of the guest brings about either a conformational change or a modification of the electronic structure of the host that facilitates subsequent host–guest interactions.[15–19] A higher selectivity and affinity is thus achieved compared to the usual 1 : 1 binding mode.[20] In the presence of two binding sites, the 1 : 2 (host : guest) complex must have the value of association constant, K_2, more than K_1.[15,21] Such binding is difficult to achieve for a single type of guest (homotropic) as it would involve different types of interaction for the same molecule, which implies the need for dynamic binding sites.[15] This is usually achieved with a π-conjugated polymer as receptor.[22] In the present study, we have utilized a cyclic sensor, which changes its conformation at the binding site. Moreover, the rigid frame would limit anion interaction to the binding site and avoid complicating secondary interactions.[3]

Fluorescence-based sensors are particularly preferable due to simplicity and high detection limit[23] although they do have their drawbacks, which include low signaling output,[4] the need for polar and unstable organic solvents,[24] and interference from other anions.[25] Anion detection is commonly based on fluorescence quenching although the method suffers from possible interference from non-analyte species through static and collisional quenching.[26] Fluorescence enhancement is a rather challenging task but there have been a few reports on effective "turn-on" fluorescence sensors.[27,28] Carbazole is chosen as the fluorophore as it has already been demonstrated to produce a good response not only to fluorescence measurements, but to absorbance and ^{1}H-NMR as well.[8–10] Moreover, substitution in the aromatic ring with electron-withdrawing Cl enhances the acidity of the urea –NH.[29] Our group has already synthesized a number of carbazole–urea-based receptors that have characteristic chromogenic and fluorogenic response to anionic guests.[8,30]

Herein, we report *cyclo*-bis-(urea-3,6-dichlorocarbazole) (**1**) (Scheme 1) as a new fluorogenic sensor which exhibits excellent selectivity toward $H_2PO_4^-$ and $CH_3CO_2^-$ over other anions. UV–vis, fluorescence and ^{1}H-NMR measurements in the presence of tetrabutylammonium (TBA) salts of $CH_3CO_2^-$, $H_2PO_4^-$, HSO_4^-, F^-, Cl^- and I^- have been carried out to assess the anion binding ability of **1** and to distinguish the binding of the oxoanions $H_2PO_4^-$ and $CH_3CO_2^-$. Solid state structures of the $CH_3CO_2^-$ and Cl^- complex have been obtained to determine the binding mode of the anions. We have previously reported on the detection of the strong basic anions, F^- and $HP_2O_7^{3-}$, wherein colorimetric/chromogenic and fluorogenic changes arise from deprotonation of the carbazole –NH of **1**.[30] It is briefly discussed in the paper that we can draw mechanistic differences between the $H_2PO_4^-$ and $CH_3CO_2^-$ binding and the consequent changes in the absorbance, fluorescence and NMR spectra.

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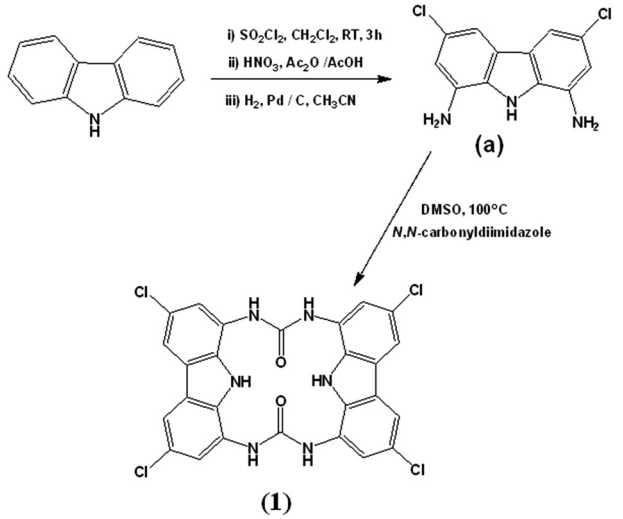

Scheme 1 Synthesis of compound **1**.

Results and discussion

Experiments are performed in dry DMSO. We have previously conducted anion binding studies for **1** in DMSO–0.5% H_2O.[30] Generally, absorbance changes are short-lived in competitive hydrogen-bonding solvents such as ethanol or water.[27] However, the similarity of the absorbance spectra to that in dry DMSO demonstrates that a polar solvent would have no effect on anion detection. It was also observed in a previous study employing a thiourea receptor that the absorption spectra is insensitive to addition of as much as 5% water, citing as a rationale the strong anion–thiourea and DMSO–H_2O hydrogen bonding.[31] While association constants have been known to decrease with addition of water, it does simplify the equilibria in solution.[11]

X-ray data on crystals of **1**·2[$(n\text{-Bu})_4N^+\cdot(CH_3CO_2)^-$]·2DMSO and **1**·2[$(n\text{-Bu})_4N^+\cdot Cl^-$] (Fig. 1) reveal that the anion forms H bonds with the urea –NH located on either side of the carbazole–urea cage to form a 1 : 2 complex. H bond lengths are 1.879–1.890 Å for (NH···O) in **1**·2[$(n\text{-Bu})_4N^+\cdot(CH_3CO_2)^-$]·2DMSO and 3.010–3.127 Å for (NH···Cl) in **1**·2[$(n\text{-Bu})_4N^+\cdot Cl^-$]. The strong H bond interaction between the $CH_3CO_2^-$ oxygen and the urea –NH is confirmed by the large downfield shift ($\Delta\delta$ = 3.56 ppm) in the ^{1}H-NMR spectra in DMSO-d_6 (Fig. 2), whereas the weak interaction between Cl^- and urea –NH is manifested in the broadening and quenching of the urea –NH signal resonance ($\Delta\delta$ = 0.20 ppm). In the case of **1**·2[$(n\text{-Bu})_4N^+\cdot(CH_3CO_2)^-$]·2DMSO, the two urea C═O bonds point away from the plane of the molecule in opposite directions and interact with carbazole –NH at a distance of 2.056 Å. H bonding is confirmed from the comparison of the ^{1}H-NMR spectra of **1** and **1**·2[$(n\text{-Bu})_4N^+\cdot(CH_3CO_2)^-$]·2DMSO, which shows a downfield shift of the carbazole –NH signal resonance from δ = 10.29 to 10.80 ppm. In contrast, the two urea C═O bonds in **1**·2[$(n\text{-Bu})_4N^+\cdot Cl^-$] point toward the same direction above the plane of the molecule. Moreover, the distance for the interaction with carbazole –NH is longer (2.182–2.216 Å), consistent with the unchanged carbazole –NH signal in the ^{1}H-NMR spectra.

Based on theoretical calculations, the lowest energy conformation of the free sensor is characterized by *cis* orientation of the two urea C═O bonds, similar to the Cl^- complex (Table 1, Fig. S8†). The corresponding *trans* conformer of the $H_2PO_4^-$ complex was obtained from calculations and shown in Fig. 1c.

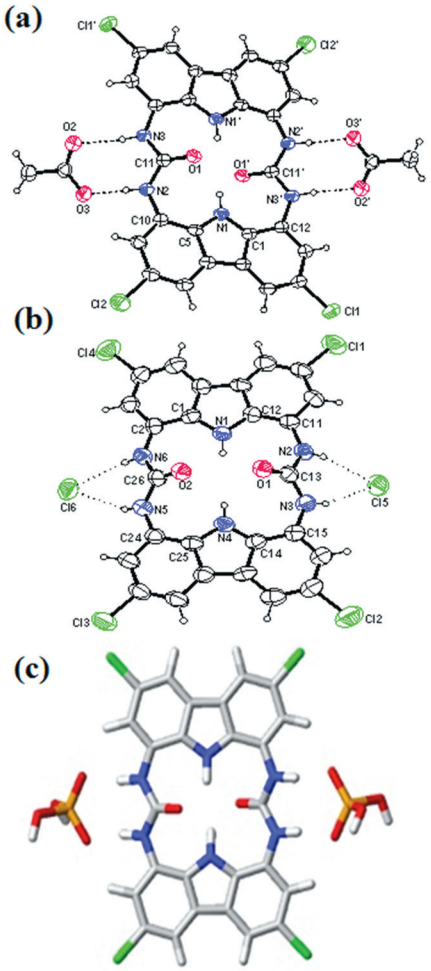

Fig. 1 Crystal structures of (a) **1**·2[$(n\text{-Bu})_4N^+\cdot(CH_3CO_2)^-$] and (b) **1**·2[$(n\text{-Bu})_4N^+\cdot Cl^-$] in DMSO–$CH_3CN$ solution with tetrabutylammonium omitted for clarity. The displacement ellipsoids are given with 30% probability. (c) Calculated structure of **1**·2$H_2PO_4^-$ determined at the B97-D/TZV2P level.

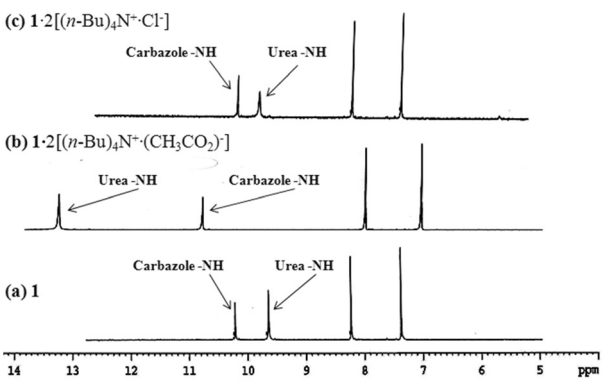

Fig. 2 ^{1}H-NMR spectra of (a) compound **1**, (b) **1**·2[$(n\text{-Bu})_4N^+\cdot(CH_3CO_2)^-$], and (c) **1**·2[$(n\text{-Bu})_4N^+\cdot Cl^-$] in DMSO-$d_6$ solution at 25 °C.

Table 1 Interaction energies and ^{1}H-NMR and UV–vis parameters for the optimized anion complexes of **1** (shown in Fig. S8†) determined at the B97-D/TZV2P level. Computational methods are described in ESI†

	ΔE^a (kcal mol^{-1})		^{1}H-NMR shift^b (ppm)		UV–vis absorption^c	
	Gas phase	DMSO	Urea N–H	Carbazole N–H	λ_{max} (nm)	f
cis-**1**	0.00	0.00	9.87	11.92	357.57	0.3066
trans-**1**	2.57	2.87	9.80	11.32	368.52	0.3067
cis-**1**–2·$CH_3CO_2^-$	72.76	40.14	15.31	12.21	378.88	0.3975
trans-**1**–2·$CH_3CO_2^-$	70.58	37.43	15.31	11.98	387.48	0.3861
trans-**1**–2·$H_2PO_4^-$	55.02	29.24	13.22	11.78	382.18	0.3604

^{a} Reported as relative energies for *cis* and *trans* **1**, with the former as reference. ^{b} TMS HF/6-31G(d) is used as reference for the NMR shielding. ^{c} λ_{max} corresponds to the HOMO–LUMO transition (Fig. S10†) with oscillator strength f.

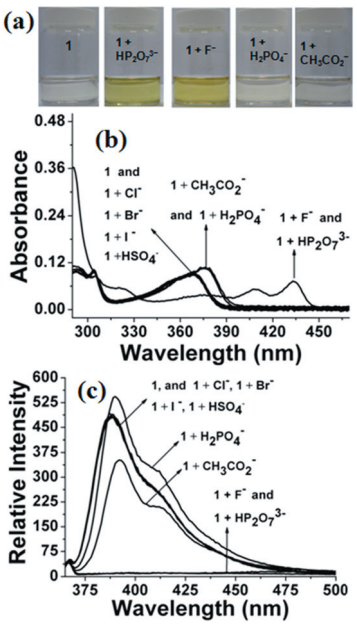

Fig. 3 (a) Visual features of $HP_2O_7^{3-}$, F^-, $H_2PO_4^-$ and $CH_3CO_2^-$ complexes of **1**. (b) Absorption spectra of **1** (10 μM) upon addition of TBA salts of F^-, Cl^-, Br^-, I^-, HSO_4^-, $CH_3CO_2^-$, $H_2PO_4^-$and $HP_2O_7^{3-}$ in a 1 : 100 equiv ratio in DMSO. (c) Fluorescence spectra (slit width = 3 nm; excitation = 365 nm) of **1** (10 μM) upon addition of TBA salts of the same anions in a 1 : 100 equiv ratio in DMSO.

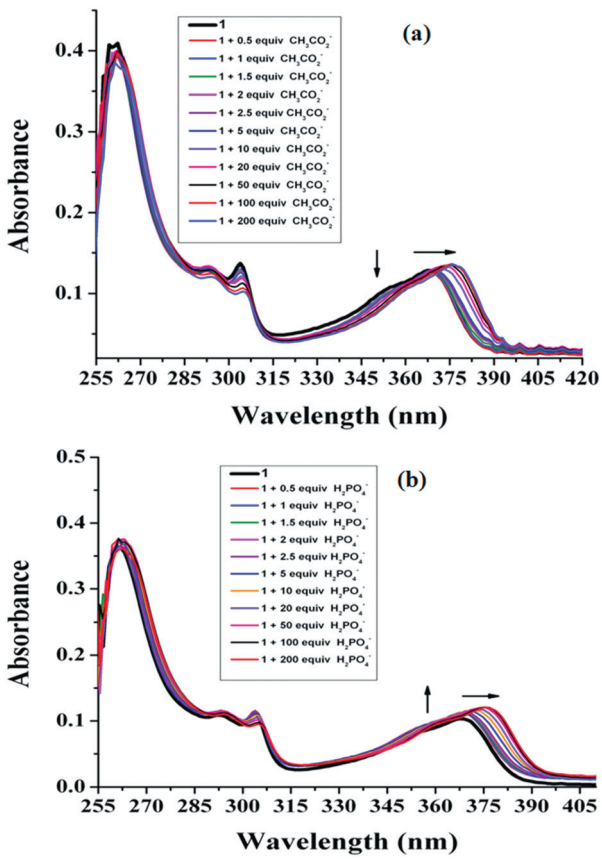

Fig. 4 Absorption spectra of **1** (10 μM) upon titration with 0–200 equiv of TBA salts of (a) $H_2PO_4^-$ and (b) $CH_3CO_2^-$ in DMSO.

The binding energy of the *cis* conformer of **1**–2·$CH_3CO_2^-$ is higher by 2.2 and 2.7 kcal mol^{-1} in the gas phase and DMSO solution, respectively. However, the energy difference from the *trans* conformer is quite small, so it is possible that the order of stability may be different when intermolecular interactions (explicit solvation, countercations, crystal packing effect, *etc.*) and entropy effects are taken into account. On the other hand, the calculated binding energy of the *trans* conformer of **1**–2·$H_2PO_4^-$ is lower at 55.0 and 29.2 kcal mol^{-1} in the gas phase and DMSO solution, respectively the.

The anions considered in the present study have diverse effects on the absorption spectrum of **1**, which has λ_{max} = 372 nm (Fig. 3b). Compound **1** is insensitive to the addition of HSO_4^-, Cl^-, Br^- and I^- due to their weak basicity.[32] The weak binding can be also thought of as a geometric mismatch between the broad binding site and the spherical halides.[5] On the other extreme, binding with strong bases F^- and $HP_2O_7^{3-}$ resulted in the appearance of peaks at 407 and 432 nm, which is visually observed as a color change of the solution from colorless to yellow (Fig. 3a). It was established in the previous paper that this is a consequence of the deprotonation of the more acidic carbazole –NH.[30] Bathochromic shifts of 5 and 6 nm were observed upon addition of $CH_3CO_2^-$ and $H_2PO_4^-$, respectively, with no clear isosbestic points, indicating a complex binding process.

Fig. 4 shows that the bathochromic shift increases with $CH_3CO_2^-$ and $H_2PO_4^-$ concentration. The calculated spectra (Table 1, Fig. S9†) of the optimized *trans* conformer of **1**–2·$CH_3CO_2^-$ puts the λ_{max} at 388 nm whereas that for the

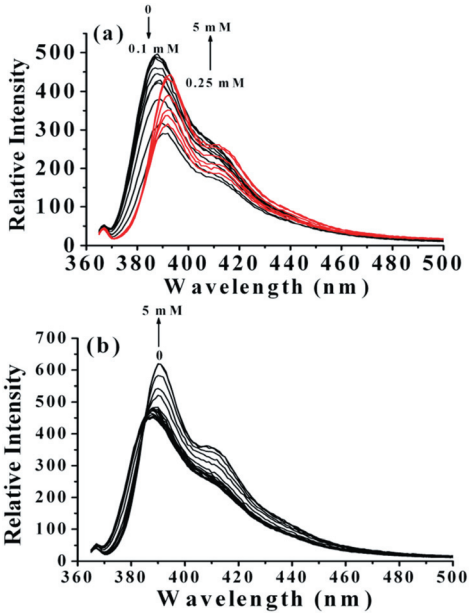

Fig. 5 Emission spectra (slit width = 3 nm; excitation = 365 nm) of **1** (10 μM) in DMSO upon titration with 0–5 mM of (a) $H_2PO_4^-$ and (b) $CH_3CO_2^-$.

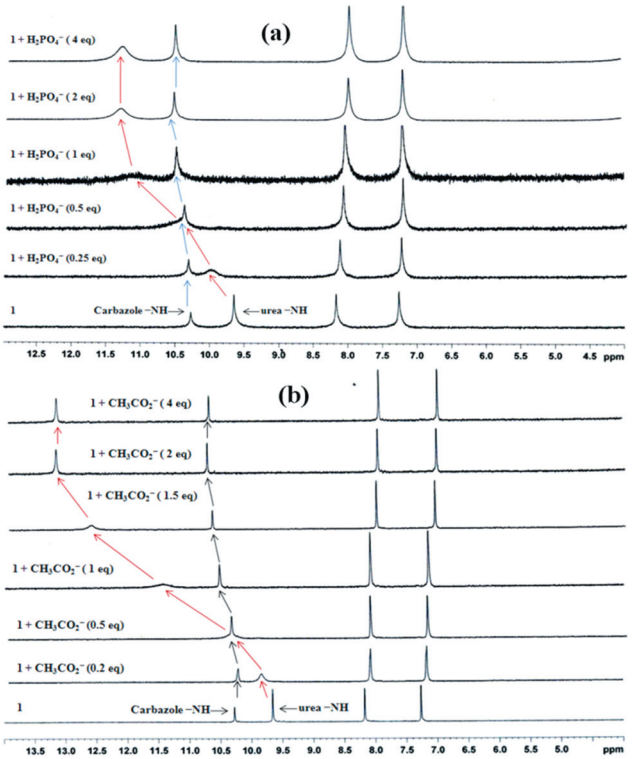

Fig. 6 Changes in the ^{1}H-NMR spectra of **1** in DMSO-d_6 solution upon addition of 0–4 equiv of (a) $H_2PO_4^-$ and (b) $CH_3CO_2^-$.

corresponding *cis* conformer is at 379 nm (Table 1), thus discounting conformational change as the origin of the bathochromic shift. The change in the absorption spectra is a consequence of the direct attachment of the urea and carbazole subunits, thereby allowing energy transfer to occur between receptor and fluorophore.[33] As shown in the HOMO and LUMO orbitals of free and bound **1** (Fig. S10†), electron density is distributed on both receptor and fluorophore. Thus, fluorescence sensing by **1** involves both a PET and energy transfer mechanism.

Consistent with absorbance measurements, the binding of HSO_4^-, Cl^-, Br^- and I^- has no effect on the fluorescence emission spectra of **1** (Fig. 3c), which consists of a single band at 387 nm at excitation wavelength of 365 nm. Deprotonation of the receptor by F^- or $HP_2O_7^{3-}$ is manifested as fluorescence quenching *via* a PET mechanism.[30] In contrast, the binding of $H_2PO_4^-$ resulted in enhanced fluorescence emission that increases with concentration (0–5 mM), accompanied by a 23 nm redshift (Fig. 5a). On the other hand, $CH_3CO_2^-$ binding presents a peculiar case. At low concentrations (0–0.1 mM), fluorescence is quenched as in $F^-/HP_2O_7^{3-}$ binding (Fig. 5b). However, fluorescence is recovered at higher concentrations (0.25–5 mM), similar to that observed for $H_2PO_4^-$ binding, with a redshift of 9 nm. A few papers have reported on similar, albeit acyclic, sensors, which bind the anion to both carbazole and urea –NH, resulting in moderate fluorescence quenching.[8–12] It is possible that the fluorescence enhancement observed in the present study is a consequence of the more rigid structure of the cyclic analogue, compound **1**, in the *trans* conformation, which has weak intramolecular O···H bonds, as has been apparently the case for reported "turn-on" fluorescence sensors.[27] However, in the case of $CH_3CO_2^-$, the change to the *trans* conformer occurred after the addition of the first few equivalents as evidenced by the ^{1}H-NMR spectra, which is concurrent with fluorescence quenching. An alternative explanation for the fluorescence enhancement is that anion binding inhibits the energy transfer between urea and carbazole that normally causes quenching although the mechanism is not clear. The bathochromic shift accompanying the intensity modulation may also be an indication that the fluorescence is not caused by the PET mechanism. Unfortunately, organic fluorescent anion sensors employing an energy transfer mechanism are quite few;[34] hence, anion binding effects on the energy transfer process are not well understood. The initial quenching of the 387 nm band suggests the predominance of the PET mechanism that was observed for $F^-/HP_2O_7^{3-}$ binding. The very short O–H bond (1.64 Å) and concomitant long N–H bond (1.07 Å) in the calculated 1 : 1 complex (Fig. S8†) seems to support the assumption that urea –NH is partially deprotonated in the early stages of binding. Quenching is not observed for $H_2PO_4^-$ binding presumably due to the lower basicity of the anion. However, after addition of excess $CH_3CO_2^-$, fluorescence is restored and both the calculated 1 : 2 complex and experimental data show normal H bonding interaction between anion and receptor.

The binding process is further elucidated with ^{1}H-NMR measurements at different concentrations (Fig. 6). The urea –NH peak centered at 9.65 ppm progressively shifts downfield with increasing $CH_3CO_2^-/H_2PO_4^-$ concentration due to formation of H bonds. The peak is broadened and quenched after addition of the first equivalent. This is accompanied by a slight downfield shift for carbazole –NH (0.53 ppm for $CH_3CO_2^-$ and 0.26 ppm for $H_2PO_4^-$), which indicates a shift to the *trans* conformation where there is weak H bonding with urea C═O. The similarity to the peak broadening and quenching of the carbazole –NH peak in $F^-/HP_2O_7^{3-}$ binding suggests that there is at least partial

Table 2 ^{1}H-NMR data and binding constants K_1 and K_2 obtained from fluorescence titrations of **1** by $CH_3CO_2^-$ and $H_2PO_4^-$

	^{1}H-NMR shift, ppm		Binding constants (Mol^{-1})	
	Urea N–H	Carbazole N–H	K_1	K_2
1	9.65	10.29		
1–2·$CH_3CO_2^-$	13.24	10.82	1.5×10^3	1.5×10^5
1–2·$H_2PO_4^-$	11.33	10.55	1.4×10^3	1.8×10^5

deprotonation of urea –NH as discussed earlier. The peak increases again as H bonds are formed with the added anions. A plateau is reached at 13.24 and 11.33 ppm after the addition of 2 equiv of $CH_3CO_2^-$ and $H_2PO_4^-$, respectively, consistent with the Job plot analysis (Fig. S7†). In the case of $CH_3CO_2^-$, the peaks are sharper and the downfield shift larger, reflecting stronger H bonding.

The proposed stepwise association mechanism, (**1** + A^- ↔ [**1**·A]$^-$) and ([**1**·A]$^-$ + A^- ↔ [**1**·A_2]$^{2-}$), is inferred from the binding isotherms obtained from fluorometric titrations fitted to a two-site model (Fig. S5 and S6†).The association constants K_1 and K_2 for $CH_3CO_2^-$ and $H_2PO_4^-$ (Table 2) provide further evidence by more positive value of K_2 as compared to K_1.[21] A familiar example similar to the present study is the H bond interaction among amide groups in proteins, wherein enhancement in binding arises from the enhanced N–H and C═O bond dipoles upon formation of H bonds.[19] However, in this case, the increased electron density on the other urea group upon binding of the first anion would make the formation of the second bond rather unfavorable (Fig. S11†). It is thus more likely that the enhanced binding observed in the present study is due to the increased rigidity of the sensor from the intramolecular H bonding between urea C═O and carbazole –NH in the *trans* conformation. In other words, the stepwise binding of the oxoanions is entropy-driven.[16,19]

Conclusions

We have developed a new fluorogenic sensor that selectively detects the oxoanions $CH_3CO_2^-$ and $H_2PO_4^-$ through the formation of multitopic H bonds with urea –NH. $CH_3CO_2^-$ has a singular response to fluorescence detection, specifically an initial quenching, which we ascribe to partial deprotonation of urea –NH that enhances the PET mechanism based on the similarity to the corresponding spectra of F^-/$HP_2O_7^{3-}$ binding. The subsequent red-shifted fluorescence enhancement at high concentrations, which was also observed for $H_2PO_4^-$, is attributed to an energy transfer mechanism, supported by the bathochromic shift in the absorbance spectra upon anion binding. Job plot and solid state structure analysis confirms the formation of a 1 : 2 complex. X-ray data shows that the two urea C═O groups have a *trans* orientation with H bond interactions with carbazole –NH in the bound sensor, which was verified by the downfield shift of the carbazole –NH peak in the ^{1}H-NMR spectra. Fluorescence and ^{1}H-NMR data suggests a stepwise mechanism for anion binding at the two urea receptors. The larger binding constant for the addition of the second anion (K_2), provides evidence of enhanced binding. Enhancement in the binding of the oxoanions is entropy-driven, as the shift to the *trans* conformer after binding of the first anion increases the rigidity of the sensor through intramolecular C═O···H–N bonds. Thus, a highly efficient sensor capable of anion detection through fluorescence enhancement can be achieved with cyclic sensors having multiple binding sites.

Experimental section

General procedure

The synthesis of compound **1** is described in a previous paper.[30] UV–vis spectra was recorded with a Shanghi 756 MC UV–vis spectrometer. ^{1}H-NMR measurements were made using a Bruker Advance DPX500 (500 MHz) spectrometer at 298 K. Fluorescence titrations were performed on a Shimadzu RF-5301 PC spectrofluorophotometer at 298 K.

X-ray crystallography

Single crystals of **1**·2[(n-Bu)$_4$N$^+$·(CH_3CO_2)$^-$]·2DMSO and **1**·2[(n-Bu)$_4$N$^+$·Cl$^-$] were isolated by slow evaporation from acetonitrile–DMSO solution at 35 °C and kept under a layer of hydrocarbon oil. A suitable crystal was selected and mounted on a glass fiber, and data was collected at 298(2) K using a Bruker–Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low-temperature device. A full sphere of data, recorded with ω and 2θ scans of 0.3° per frame for 15 s, was retrieved using the SMART Version 5.625[35] software. Data refinement, reduction and correction for Lp and decay were performed using SAINT Plus Version 6.22[36] while absorption corrections were applied using SADABS Version 2.01.[37] The structure was solved by direct methods and refined by full-matrix least-squares method on $F2$ using the SHELXTL Version 6.10 package.[38] All atoms were refined anisotropically and hydrogen atoms were placed in calculated positions.

Crystal Data **1**·2[(n-Bu)$_4$N$^+$·(CH_3CO_2)$^-$]·2DMSO: $C_{62}H_{90}Cl_4N_8O_6$, M = 1185.22, Monoclinic, a = 8.8875(11), b = 13.7511(17), c = 15.0665(19) Å, β = 77.356(3)°, U = 1592.6(3) Å^3, T = 293(2) K, space group $P21/n$, Z = 1, μ(Mo Kα) = 0.241 mm^{-1}, 8908 reflections collected, 5938 unique (R_{int} = 0.0212), R1 = 0.0641, $wR2[I > 2\sigma(I)]$ = 0.1584, CCDC deposition number 820422.†

Crystal Data **1**·2[(n-Bu)$_4$N$^+$·Cl$^-$]: $C_{58}H_{86}Cl_6N_8O_6$, M = 1140.05, Monoclinic, a = 13.644(3), b = 15.163(3), c = 16.546 (4) Å, β = 78.777(4)°, U = 3201.2(12) Å^3, T = 293(2) K, space group $P21/n$, Z = 2, μ(Mo Kα) = 0.313 mm^{-1}, 16 799 reflections collected, 11 123 unique (R_{int} = 0.0401), R1 = 0.0773, $wR2[I > 2\sigma(I)]$ = 0.1903, CCDC deposition number 820423.†

Fluorometric titrations

A stock solution of compound **1** (1 mM) was prepared in DMSO–0.5% water solution and used in the preparation of titration solutions by appropriate dilution of up to 10 μM. Aliquots of $CH_3CO_2^-$ and $H_2PO_4^-$ (as the corresponding TBA salt) in

DMSO were then injected into the sample solution through a rubber septum in the cap. To account for dilution effects, the stock anion solutions also contained the sensor at its initial concentration. The sample solution was magnetically stirred for 1 min after each addition then scanned. The process was repeated until the change in fluorescence intensity became insignificant. Binding constants (K_i) for anions were derived from plots of F/F_0 *vs.* [anion]/M[39] assuming a two-site binding model using OriginLab 7.5.[40] Results reported in the text are the average of at least two independent titrations.

Acknowledgements

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