



## Colorimetric ‘naked eye’ sensing of anions using a thiosemicarbazide receptor: a case study of recognition through hydrogen bonding versus deprotonation

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### ABSTRACT

The thiosemicarbazide receptors **1** and **2**, containing three N–H donors (including a thiourea motif), have been synthesized and studied for their anion binding abilities. The recognition of **1** and **2** with various anions [ $\text{AcO}^-$ ,  $\text{F}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{SO}_4^{2-}$  and  $\text{OH}^-$  for **1**;  $\text{OAc}^-$  and  $\text{F}^-$  for **2**] as their tetrabutylammonium salts was studied spectroscopically in  $\text{CH}_3\text{CN}$  and  $\text{EtOH}$ . Significant changes were observed in the UV–vis absorption spectra of **1** which was red-shifted in both solvents when titrated with these anions. A dramatic colour change from yellow to red was also clearly observed. In contrast, the absorption changes for **2** were smaller with a colour change from colourless to yellow. These changes were determined to be due to deprotonation of the central N–H moiety (belonging to the thiourea) and not due to hydrogen bonding of these anions to the receptors. This was confirmed using single crystal X-ray crystallography, as crystals of **1** grown with TBAc were found to correspond to the deprotonated structure **3**.

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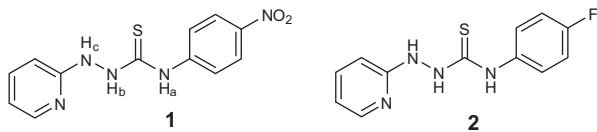
Hydrogen bonding donors such as amines, amides, ureas, thioureas, guanidines and more recently squaramides, have been extensively employed in the recognition of anions.<sup>1–6</sup> In a non-aqueous solution, the  $\text{pK}_a$  of such donors can vary greatly, and the boundaries between recognition through hydrogen bonding versus deprotonation of such moieties often become blurred.<sup>7–10</sup> This is often the case for the recognition of anions such as fluoride, acetate and even phosphate, which in solvents such as DMSO,  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  can also function as effective bases, but less so for other anions such as chloride and bromide. This issue extends further, as the use of the above functional groups in organocatalysis is fast growing, and the issue of hydrogen bonding versus deprotonation should also be considered for such systems. Experimentally, it has often been difficult to elucidate the real mechanism for such anion recognition and sensing, as the changes in the experimental output, which is usually monitored by  $^1\text{H}$  NMR, UV–vis absorption or fluorescence emission spectroscopy can be quite similar for the two events; as for a deprotonation event the initial point of contact has to be in the form of hydrogen bonding which is then followed by full proton transfer from the donor to the acceptor.<sup>11,12</sup> In parallel with researchers such as Gale,<sup>13,14</sup> Fabbrizzi,<sup>15,16</sup> Pfeffer,<sup>17</sup> Jiang<sup>18</sup> and Hay,<sup>19</sup> we have investigated this phenomenon in detail using the aforementioned spectroscopic techniques.<sup>20–23</sup> We have been able to use structures such as naphthalimide-based thioureas or thiosemicarbazides<sup>24,25</sup>

and have shown that in some cases, the UV–vis absorption spectra differ depending on the nature of the anion recognized.<sup>26</sup> We have also shown that deprotonation always occurs, as one would expect, at the most acidic site by using combinations of thiourea and amine based sensors. However, this can be difficult to elucidate accurately in systems where several possible deprotonation sites exist, with similar  $\text{pK}_a$ . Recently, solid state analysis has been employed to demonstrate whether or not anion recognition occurs via hydrogen bonding or deprotonation, but Gale and co-workers have shown crystallographic evidence that pyrroles,<sup>27</sup> sulfonamides<sup>28</sup> and even ureas<sup>29</sup> can be deprotonated in the presence of anions. With the aim of trying to determine if anion recognition occurs through hydrogen bonding or deprotonation, we have developed the simple thiosemicarbazide-based receptors **1** and **2**, **Figure 1**, possessing three possible deprotonation sites. Our objective was to allow for correlation between the results obtained from UV–vis absorption spectroscopy and crystallographic studies. These systems have several deprotonation sites, the deprotonation of which could/should be distinguishable from the absorption spectra. However, crystallography would give the ultimate proof, which would then allow for a correlation to be made between the two techniques. This study should greatly add to our understanding of anion recognition phenomenon in supramolecular chemistry, particularly within systems where a distinction between several possible deprotonation sites is possible.<sup>30</sup>

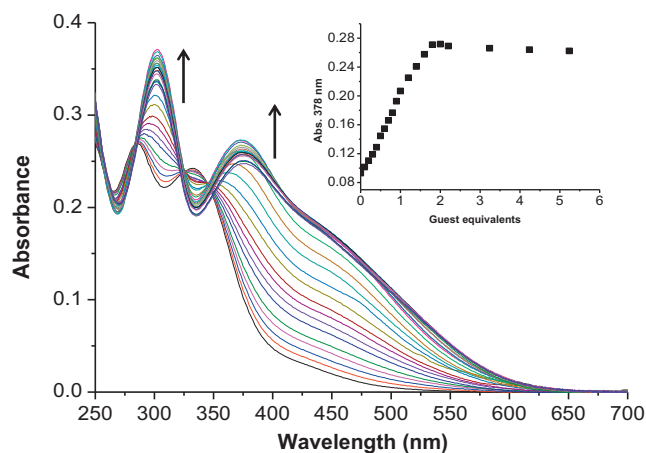
We have recently reported the synthesis and structural analysis of thiosemicarbazide receptors **1** and **2**, as part of an investigation into the development of a novel hydrogen bonding supramolecular

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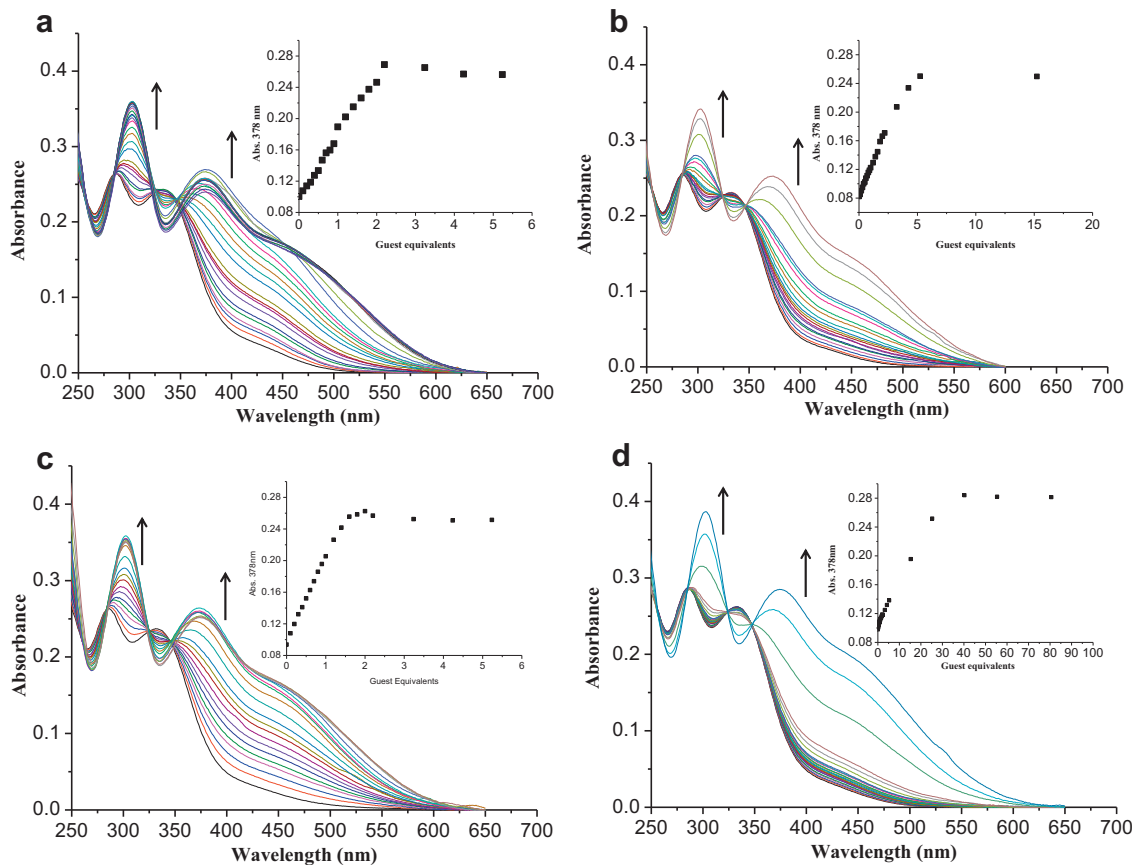


**Figure 1.** Thiosemicarbazide receptors **1** and **2** used in the current study.<sup>30</sup>



**Figure 2.** The changes in the absorption spectra of **1** in  $\text{CH}_3\text{CN}$  [ $1 \times 10^{-5}$  M] upon addition of  $\text{AcO}^-$  (0→20 equiv). Inset, the changes at 378 nm with 0→6 equiv of  $\text{AcO}^-$ .

network, using microwave-assisted synthesis, from commercially available isothiocyanates.<sup>31</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ) analysis of these structures showed the presence of three N–H protons, occurring at 10.31, 10.13 and 8.67 ppm for **1**, and at 9.88, 9.75 and 8.55 ppm for **2**. The spectroscopic studies of receptors **1** and **2** were carried out in acetonitrile ( $1 \times 10^{-5}$  M) using tetrabutylammonium salts of  $\text{AcO}^-$ ,  $\text{F}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{SO}_4^{2-}$  and  $\text{OH}^-$  for the anion binding studies. Receptor **1** exhibited a  $\lambda_{\text{max}}$  at 334 nm and 287 nm with a shoulder appearing at 229 nm as shown in Figure 2, which also shows typical anion titration results. Here, upon sequential addition of  $\text{AcO}^-$ , the development of a new absorption band occurred at a longer wavelength, centered at 378 nm, and a second band at higher energy. These spectral changes were accompanied by several pseudo-isosbestic points appearing at ca. 344 nm, 324 nm and 284 nm and a concomitant colour change from colourless to pink which was clearly visible to the naked eye, even at such a low concentration. No changes were observed in the absorption spectra beyond the addition of 2 equiv of acetate, as can be seen from the titration profile shown as an inset in Figure 2. Furthermore, the most significant changes occur within the addition of 1 equiv of the anion. Such long wavelength changes signify that the HOMO–LUMO gap has become smaller; a consequence of possible enhanced ICT character within the structure due to hydrogen bonding of the anion to the thiourea receptor. Alternatively, this could be due to deprotonation of one of the three N–Hs. Furthermore, no further changes were observed in the absorption spectra beyond the addition of 2 equiv of the anion. Generally, colour changes such as those observed here, are typical of those seen for anions interacting through anions at aryl



**Figure 3.** The changes in the absorption spectra of **1** in  $\text{CH}_3\text{CN}$  [ $1 \times 10^{-5}$  M] upon addition of the anions (0→15 equiv); (a)  $\text{TBAF}^-$  (inset shows the changes at absorbance 378 nm with 0→6 equiv); (b)  $\text{TBAH}_2\text{PO}_4^-$  (inset shows the changes at absorbance 378 nm with 0→20 equiv of anion); (c)  $\text{TBAOH}^-$  in  $\text{CH}_3\text{CN}$  (inset, the changes in the absorbance at 378 nm with 0→6 equiv); (d)  $\text{TBASO}_4^{2-}$  in  $\text{CH}_3\text{CN}$  (inset shows the changes at absorbance 378 nm with 0→80 equiv of anion).

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