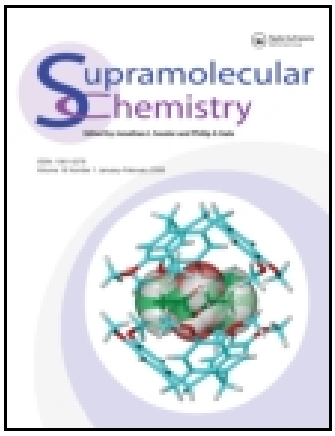

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Jennifer R. Hiscock [a], Philip A. Gale [a], Claudia Caltagirone [b], Michael B. Hursthouse [a] & Mark E. Light [a]

[a] School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK

[b] Dipartimento di Chimica Inorganica ed Analitica, Universita' degli Studi di Cagliari, S.S. 554 Bivio per Sestu, Monserrato (CA), Italy

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Fluorescent carbazolylurea- and carbazolylthiourea-based anion receptors and sensors

Jennifer R. Hiscock[a], Philip A. Gale[a]*, Claudia Caltagirone[b], Michael B. Hursthouse[a] and Mark E. Light[a]

[a]*School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK;* [b]*Dipartimento di Chimica Inorganica ed Analitica, Universita' degli Studi di Cagliari, S.S. 554 Bivio per Sestu, Monserrato (CA), Italy*

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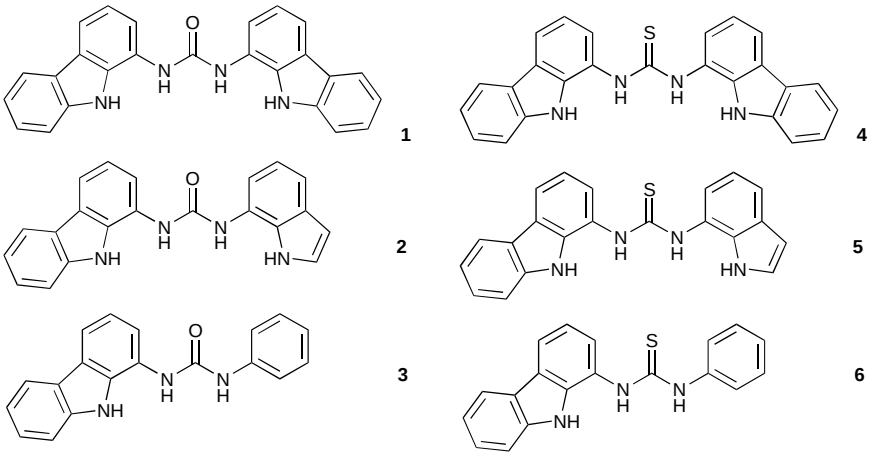
A series of carbazolylurea- and carbazolylthiourea-based receptors have been synthesised and their anion complexation and fluorescence properties were studied. The urea compounds show selectivity for oxo-anion complexation over chloride and the fluorescence of compound **1** is selectively quenched by benzoate anions in DMSO/0.5% water. However, the thiourea compounds show reduced anion affinities compared to the urea analogues.

Keywords: anion binding; indole; hydrogen bonding; crystallography

Introduction

Interest in new hydrogen bond donor receptors for anionic species has led our group and others to begin to explore indole, carbazole, indolocarbazoles and biindoles as components of new anion complexation agents (*1*). We have recently reported that indole-appended isophthalamides and pyridine-2,6-dicarboxamides function as selective fluoride binding agents (*2*). Our interest in urea (*3*) as a receptor for oxo-anions led us to synthesise oxo-anion selective urea-functionalised 2,7-disubstituted indoles (in collaboration with Albrecht and Triyanti) (*4*) and, most recently, both functionalised and unfunctionalised diindolylureas that have particularly high affinities for dihydrogen phosphate anions (*5*). In fact, when dihydrogen phosphate is bound to diindolylureas containing pendant additional hydrogen bond donor groups, the pK_a of the anion is reduced to such an extent that it can be deprotonated by dihydrogen phosphate free in solution (*6*).

We wished to study diindolylurea analogues and synthesised a series of carbazole urea and thiourea compounds and studied their anion complexation and fluorescence properties. Aspects of this work have been communicated previously (*7*).



Experimental

General remarks

All reactions were performed using oven-dried glassware under a slight positive pressure of nitrogen/argon (as specified). ^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra were determined on a Bruker AV300

*Corresponding author. Email: philip.gale@soton.ac.uk

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spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were determined on a Bruker AV400 spectrometer. Chemical shifts for ^{1}H NMR are reported in parts per million (ppm) and calibrated to the solvent peak set, with coupling constants reported in Hz. The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet. Chemical shifts for ^{13}C{^{1}H} NMR are reported in ppm, relative to the central line of a septet at $\delta = 39.52$ ppm for deuteriodimethylsulphoxide. Infrared (IR) spectra were recorded on a Matterson Satellite (ATR). FT-IR are reported in wavenumbers (cm^{-1}). All solvents and starting materials were purchased from chemical sources where available. NMR titrations were performed by adding aliquots of the putative anionic guest (as the tetrabutylammonium (TBA) or tetraethylammonium (TEA)) salt (0.15 M) in a solution of the receptor (0.01 M) in DMSO-d_6 to a solution of the receptor (0.01 M). Fluorescence and UV–vis titrations were performed by adding aliquots of the putative anionic guest (as the TBA or TEA salt in the case of bicarbonate) (1×10^{-3} M) in a solution of the receptor (1×10^{-5} M) in DMSO/0.5% water. All fluorescence and UV–vis spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer and Thermo Nicolet Evolution 300 spectrophotometer, respectively. Luminescence quantum yields were determined using quinine sulphate in a 1 M H_2SO_4 aqueous solution ($\Phi = 0.546$) as a reference.

Compounds **1**–**3** were synthesised by our previously published procedures (*7*).

1-Aminocarbazole

1-Nitrocarbazole was synthesised according to a literature procedure (*8*) modified by separation of 1- and 3-nitrocarbazoles via chloroform flash chromatography (see the Supplementary Information for details, available online). Characterisation data agreed with previously published characterisation data (*9*).

1-Isothiocyanato-9H-carbazole

1-Isothiocyanato-9H-carbazole was prepared by the reaction of 1-aminocarbazole with thiophosgene in a mixture of dichloromethane (DCM) and a saturated aqueous solution of $NaHCO_3$ (see the Supplementary Information for details).

1,3-di(9H-Carbazol-1-yl)thiourea (4)

A solution of isothiocyanate (0.23 g, 1.04 mM) in chloroform (20 ml) was added dropwise to a solution of 1-aminocarbazole (0.19 g, 1.04 mM) in chloroform (25 ml). The solution was heated at reflux overnight with triethylamine (2 ml). The solution was evaporated to dryness and the product was isolated by filtration and recrystallized from ether/methanol by slow evaporation to give a light green solid. Yield 36%, 0.15 g; mp 221°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.13–7.20 (m, 4H), 7.33 (d, $J = 7.7$ Hz, 2H), 7.40–7.45 (m, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 8.03 (d, $J = 7.7$ Hz, 2H), 8.12 (d, $J = 7.7$ Hz, 2H), 9.71 (s, thiourea NH, 2H), 11.27 (s, indole NH, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 111.2 (CH), 118.5 (CH), 118.6 (CH), 118.7 (CH), 120.2 (CH), 122.7 (C), 123.1 (C), 124.0 (C), 124.2 (CH), 125.7 (CH), 136.3 (C), 139.8 (C), 180.8 (CS); IR (film): $\nu = 3389$, 3281, 1148 cm^{-1}. LR-MS (ES^-): *m/z*: 405 $[M - H]^-$; HR-MS (ES^+): *m/z*: act: 407.1332 $[M + H]^+$ cal: 407.1325 $[M + H]^+$.

1-(9H-Carbazol-1-yl)-3-(1H-indol-7-yl)thiourea (5)

A solution of 7-aminoindole (0.31 g, 2.35 mM) and 1-isothiocyanatocarbazole (0.53 g, 2.36 mM) was stirred in dry pyridine (20 ml) at room temperature for 48 h. The solution was washed with hexane and evaporated to dryness and the oil was dissolved in hot methanol (2 ml) and left to cool to room temperature. White crystals were isolated by filtration after 24 h and washed with hexane (25 ml) and dried under vacuum. Yield 48%, 0.41 g; mp 144°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.48 (dd, 1 $J_1 = 1.83$ Hz, $J_2 = 2.55$ Hz, ArH), 6.99 (t, $J = 7.7$ Hz, 1 ArH), 7.06–7.20 (m, 3 ArH), 7.29 (d, $J = 7.7$ Hz, 1 ArH), 7.38–7.47 (m, 3 ArH), 7.57 (d, $J = 8.1$ Hz, 1 ArH), 8.00 (d, $J = 7.7$ Hz, 1 ArH), 8.12 (d, $J = 7.7$ Hz, 1 ArH), 9.59 (s, thiourea NH, 1H), 9.61 (s, NH, 1H), 11.11 (s, NH, 1H), 11.19 (s, NH, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 101.6 (ArCH), 111.2 (ArCH), 118.4 (ArCH), 118.6 (ArCH), 118.6 (ArCH), 118.6 (ArCH), 118.8 (ArCH), 119.3 (ArCH), 120.2 (ArCH), 122.7 (ArC), 123.2 (ArC), 123.6 (ArC), 123.9 (ArC), 124.0 (ArCH), 125.4 (ArCH), 125.7 (ArCH), 129.3 (ArC), 132.0 (ArC), 136.2 (ArC), 139.7 (ArC), 180.7 (CS); IR (film): $\nu = 3380$, 3280, 1210 cm^{-1}; LR-MS (ES^-): *m/z*: 355 $[M - H]^-$; HR-MS (ES^+): *m/z*: act: 357.1168 $[M + H]^+$ cal: 357.1166 $[M + H]^+$.

1-(9H-Carbazol-1-yl)-3-phenylthiourea (6)

A solution of phenylisothiocyanate (0.41 g, 3.00 mM) in chloroform (20 ml) was added dropwise to a stirring solution of 1-aminocarbazole (0.21 g, 1.18 mM) in chloroform (20 ml). The solution was then heated to reflux under argon for 48 h. The solution was then reduced in volume to 2 ml, and DCM (10 ml) and hexane (20 ml) were added. The solution was then sonicated for 5 min and a dark green semi-solid was removed and a white precipitate was collected, washed with hexane (10 ml) and dried under vacuum. Yield 41%, 0.16 g; mp 169°C; ^{1}H NMR

(300 MHz, DMSO-d_6): δ 7.11–7.19 (m, 3 ArH), 7.28–7.41 (m, 4 ArH), 7.53–7.60 (m, 3 ArH), 8.01 (d, $J = 7.7$ Hz, 1 ArH), 8.11 (d, $J = 7.7$ Hz, 1 ArH), 9.65 (s, thiourea NH, 1H), 9.83 (s, thiourea NH, 1H), 11.14 (s, indole NH, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 111.3 (ArCH), 118.3 (ArCH), 118.5 (ArCH), 118.7 (ArCH), 120.2 (ArCH), 122.6 (ArC), 123.2 (ArCH), 123.9 (ArC), 124.5 (ArCH), 125.7 (ArCH), 128.4 (ArCH), 136.0 (ArC), 139.6 (ArC), 139.8 (ArC), 180.4 (CS) (there are overlapping signals in the ^{13}C NMR resulting in fewer than expected carbon resonances); IR (film): $\nu = 3300$, 3320, 1220 cm^{-1}; LR-MS (ES$^-$): *m/z*: 316 $[M - H]^-$; HR-MS (ES$^+$): *m/z*: act: 318.1059 $[M + H]^+$ cal: 318.1031 $[M + H]^+$.

Crystal data for compound **1**, tetrabutylammonium benzoate, $C_{48}H_{59}N_5O_3$, Mr = 754.00, $T = 120(2)$ K, triclinic, space group $P1$, $a = 10.980(5)$, $b = 13.774(5)$, $c = 15.173(5)$ Å, $\alpha = 68.760(5)°$, $\beta = 85.232(5)°$, $\gamma = 81.541(5)°$, $V = 2114.5(14)$ Å^3, $\rho_{calc} = 1.184$ g cm^{-3}, $\mu = 0.074$ mm^{-1}, $Z = 2$, reflections collected: 44,837, independent reflections: 9728 ($R_{int} = 0.1052$), final R indices [$I > 2\sigma I$]: $R_1 = 0.0661$, $wR_2 = 0.1368$, R indices (all data): $R_1 = 0.1190$, $wR_2 = 0.1589$ (*7*).

Results and discussion

The synthesis of compounds **1**–**3** has been communicated previously (*7*). 1-Aminocarbazole was prepared by literature methods (*8*). This was converted to isothiocyanate by the reaction with thiophosgene in CH_2Cl_2/sat. $NaHCO_3$(aq). Compounds **4** and **5** were prepared by the reaction of isothiocyanate with 1-aminocarbazole or 7-aminoindole, respectively. Compound **6** was prepared by the reaction of phenyl isothiocyanate with 1-aminocarbazole in chloroform.

Stability constants for the compounds with a range of anionic guests were determined using ^{1}H NMR titration techniques with stability constants calculated using the EQNMR computer program (Table 1) (*10*). The results show that all the compounds bind acetate and bicarbonate strongly. NMR titrations with $H_2PO_4^-$ show titration profiles usually indicative of strong binding but the titration curves for compounds **1** and **2** show features at 1 and 2 equivalents of anion that cannot be fitted adequately to a binding model (*7*). It is possible that an anion deprotonation process is occurring in these cases (*6*). Titrations with F^- resulted in the broadening of the NH resonances in all cases, thus it was not possible to determine an accurate stability constant. Shifts of the NH resonances suggest weak complex formation (i.e. a continuous downfield shift – see the Supplementary Information for compounds **2** and **3**).

Compounds **4**–**6** displayed reduced affinities for anions as compared to the urea analogues **1**–**3** (Table 2).

Table 1. The stability constants (K_a, M^{-1}) of compounds **1**–**3** with a variety of anionic guests (added as TBA salts except bicarbonate which was added as a TEA salt) at 298 K in DMSO-d_6/0.5% water as determined by the following urea NH resonance adjacent to the carbazole.

Anion	Compound **1**	Compound **2**	Compound **3**
Acetate	$>10^4$	$>10^4$	$>10^4$
Benzoate	5670	5880	3420
Dihydrogen phosphate	[a]	[a]	6140
Chloride	102	139	85
Bicarbonate	$>10^4$	$>10^4$	$>10^4$

Notes: In all cases, a 1:1 receptor:anion stoichiometry was observed. Errors were estimated to be no more than ± 15%.
[a] NMR titration curve could not be fitted to a 1:1 or 1:2 receptor:anion binding stoichiometry but indicates strong binding.

This is unusual as thioureas are more acidic than ureas, and hence would be expected to form stronger hydrogen bonding interactions. Interestingly though, the reduction in affinity in thiourea analogues of urea-based receptors was also observed with diindolylurea-based receptors, which was attributed to either size or conformational interconversion effects (*5*). The work presented here further highlights that thiourea-based receptors do not always possess higher affinities for anions than urea-based systems.

Figure 1 shows a comparison of the ^{1}H NMR titration curves for compounds **1** and **4** with tetrabutylammonium benzoate in DMSO-d_6/0.5% water solution. Upon addition of excess benzoate salt to compound **1** (dicarbazolylurea), the urea NH shifts downfield by 2.3 ppm while the indole NH shifts downfield by approximately 1 ppm. Compound **4** is the thiourea analogue of compound **1**. In this case, while the thiourea NH groups shift downfield by 2.8 ppm, the indole NH shifts downfield by only 0.4 ppm. The lower affinity of the thiourea analogues of our original diindolylurea compounds was attributed to a conformation effect that caused the thiourea receptors to adopt a twisted

Table 2. The stability constants (K_a, M^{-1}) of compounds **4**–**6** with a variety of anionic guests (added as TBA salts except bicarbonate which was added as a TEA salt) at 298 K in DMSO-d_6/0.5% water as determined by the following urea NH resonance adjacent to the carbazole.

Anion	Compound **4**	Compound **5**	Compound **6**
Acetate	2230	1800	1780
Benzoate	658	675	870
Dihydrogen phosphate	687	1340	[a]
Chloride	15	17	23
Bicarbonate	[a]	[a]	[a]

Notes: In all cases, a 1:1 receptor:anion stoichiometry was observed. Errors were estimated to be no more than ± 15%.
[a] Peak broadening prevented a stability constant from being determined in these cases.

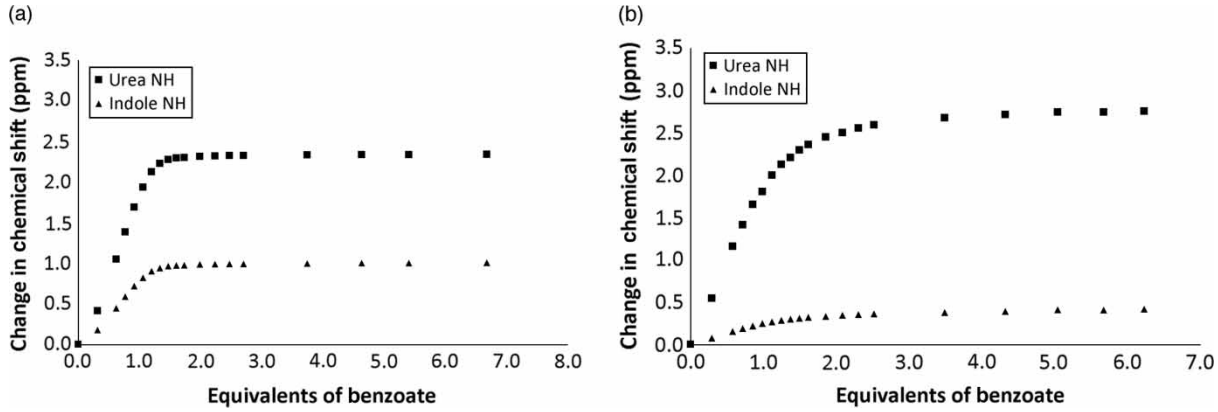

Figure 1. Proton NMR titration curves for compounds (a) **1** and (b) **4** with tetrabutylammonium benzoate in DMSO-d_6/0.5% water showing shifts of indole and urea NH groups.

conformation due to the large size of the sulphur atom present in these compounds (*5*). The NMR evidence presented here is consistent with this theory in that if the compound is adopting a twisted conformation, we would expect a less linear relationship between the carbazole NH hydrogen bond donors and the benzoate oxygen atoms resulting in a weaker interaction.

Crystals of the benzoate complex of compound **1** were grown by slow evaporation of a DMSO solution of the receptor in the presence of excess tetrabutylammonium benzoate. The unit cell contains two crystallographically distinct benzoate complexes which adopt similar conformations. In both benzoate complexes, one of the carbazoles is in the plane of the urea while the other is twisted out of plane by 37.1° or 43.0° (Figure 2). Each benzaote anion is bound by four hydrogen bonds in the range N···O 2.762(5)–2.996(5) Å (*7*).

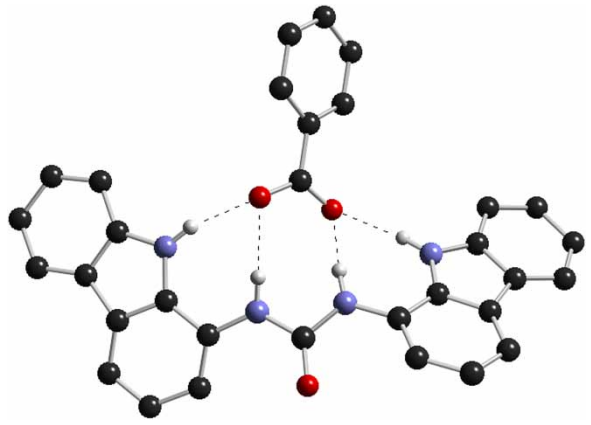

Figure 2. The X-ray crystal structure of one of the two crystallographically distinct benzoate complexes present in the unit cell of the tetrabutylammonium benzoate complex of receptor **1**. TBA counter cations and selected hydrogen atoms have been omitted for clarity.

In order to investigate the ability of compounds **1**–**3** to act as sensors, fluorescence studies were performed in a DMSO/0.5% water solution. Under these conditions, receptor **1** displays an intense fluorescence emission ($\Phi = 0.549$) with maxima at 363 and 376 nm when excited at 270 nm. As shown in Figure 3, upon addition of increasing amounts of tetrabutylammonium benzoate, a selective quenching of the fluorescence emission was observed ($I_{res} = 10\%$).

Addition of the TBA salts of fluoride, chloride, acetate, dihydrogen phosphate and tetraethylammonium bicarbonate resulted in significantly less dramatic fluorescence quenching, as shown in Figure 4. Addition of acetate resulted in only a partial quenching of the emission ($I_{res} = 50\%$) while a stronger quenching of the fluorescence emission was observed upon addition of >3.0 equivalents of fluoride, a finding which may be indicative of receptor deprotonation (*11*). Smaller perturbations of the fluorescent emission of **1** were observed in the presence of $H_2PO_4^-$ ($I_{res} = 68\%$) and

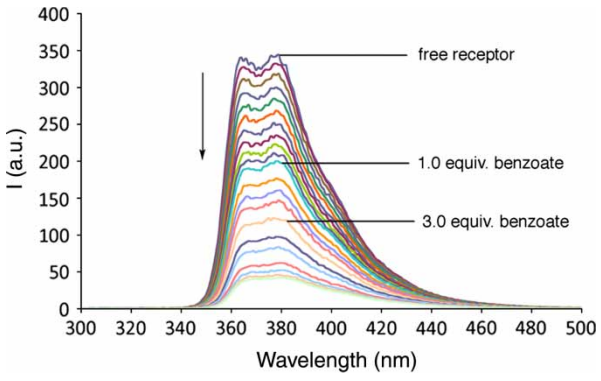

Figure 3. Fluorescence quenching of receptor **1** in DMSO/0.5% water upon addition of increasing amounts of tetrabutylammonium benzoate (for benzoate concentrations for each fluorescence spectrum, see Figure 4).

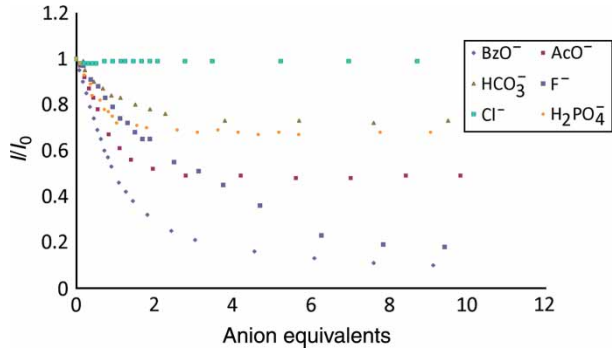

Figure 4. Effect of increasing anion concentration upon the relative fluorescence emission of receptor **1** in DMSO/0.5% water.

HCO_3^- ($I_{res} = 73\%$). Chloride did not affect the emission of the system. The trend in fluorescence quenching is similar to that found for the stability constants by ^{1}H NMR titrations with the exception for benzoate. This may be due to a π−π interaction in the excited state between the aromatic groups of the receptor and the guest.

Compounds **4**–**6** did not reveal any selectivity for the anionic guests considered in this study and had significantly lower quantum yields ($\Phi = 0.01$, 0.0025 and 0.0019 for **4**, **5** and **6**, respectively) than those observed for compounds **1**–**3**. When excited at 332 nm (compounds **4** and **5**) and 344 nm (compound **6**), they showed two maxima in their fluorescence emission, at 379 and 395 nm in DMSO/0.5% water, in the case of **4**, a less structured spectrum with a maximum at 390 nm in the case of compound **5** and a maximum at 385 nm with a shoulder at 404 nm in the case of compound **6**. Only compound **4** in the presence of tetrabutylammonium benzoate showed a partial quenching of the fluorescence ($I_{res} = 54\%$), which is much less pronounced than that observed with the same anion and urea analogue **1** ($I_{res} = 10\%$). With the other anions, only negligible changes in fluorescence were observed upon addition to the three thiourea receptors.

Conclusions

Carbazole ureas are effective hosts for oxo-anions binding acetate selectively in DMSO-d_6/water solutions. Compound **1**, a dicarbazolylurea, functions as a selective fluorescent sensor for benzoate anions. In contrast to these results, however, thiourea-based analogues show reduced affinities and selectivity for anionic guests and show reduced perturbations to their fluorescence properties in the presence of anions. These findings further highlight that thiourea-based anion receptors do not always have higher affinities for guests than urea-based analogues.

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References

(1) For monographs and reviews on anion complexation see:, Sessler, J.L.; Gale, P.A.; Cho, W.-S. *Anion Receptor Chemistry*; Stoddart, J.F., Ed.; RSC: Cambridge, 2006; Schmidtchen, F.P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609–1646; Gale, P.A., *Acc. Chem. Res.* **2006**, *39*, 465–475; Gale, P.A. *Chem. Commun.* **2005**, 3761–3772; Bowman-James, K. *Acc. Chem. Res.* **2005**, *38*, 671–678; Gale, P.A.; Quesada, R. *Coord. Chem. Rev.* **2006**, *250*, 3219–3244; Gale, P.A.; García-Garrido, S.E.; Garric, J. *Chem. Soc. Rev.* **2008**, *37*, 151–190; Caltagirone, C.; Gale, P.A. *Chem. Soc. Rev.* **2009**, *38*, 520–563. For an overview of indole-based receptors, see: Gale, P.A. *Chem. Commun.* **2008**, 4525–4540. For important contributions, see: Chang, K.-J.; Moon, D.; Lah, M.S.; Jeong, K.-S. *Angew. Chem. Int. Ed.* **2005**, *44*, 7926–7929. Chang, K.-J.; Chae, M.-K.; Lee, C.; Lee, J.-Y.; Jeong, K.-S. *Tetrahedron Lett.* **2006**, *47*, 6385–6388; Kwon, T.H.; Jeong, K.-S. *Tetrahedron Lett.* **2006**, *47*, 8539–8541; Chang, K.-J.; Kang, B.-N.; Lee, M.-H.; Jeong, K.-S. *J. Am. Chem. Soc.* **2005**, *127*, 12214–12215; Lee, J.-Y.; Lee, M.-H.; Jeong, K.-S. *Supramol. Chem.* **2007**, *19*, 257–263; Suk, J.-M.; Chae, M.K.; Kim, N.-K.; Kim, U.-l.; Jeong, K.S. *Pure Appl. Chem.* **2008**, *80*, 599–608; Curiel, D.; Cowley, A.; Beer, P.D. *Chem. Commun.* **2005**, 236–238; Sessler, J.L.; Cho, D.-G.; Lynch, V. *J. Am. Chem. Soc.* **2006**, *128*, 16518–16519; Hu, X.; Hu, S.; Liu, K.; Guo, Y.; Xu, J.; Shao, S. *Org. Lett.* **2006**, *8*, 333–336; Pfeffer, F.M.; Lim, K.F.; Sedgwick, K.J. *Org. Biomol. Chem.* **2007**, *5*, 1795–1799; Wang, T.; Bai, Y.; Ma, L.; Yan, X.-P. *Org. Biomol. Chem.* **2008**, doi: 10.1039/b801447 g; Zieliński, T.; Dydio, P.; Jurczak, J. *Tetrahedron* **2008**, *64*, 568–574; Yu, J.O.; Browning, C.S.; Farrar, D.H. *Chem. Commun.* **2008**, 1020–1022; Dydio, P.; Zielinski, T.; Jurczak, J. *Chem. Commun.* **2009**, 4560–4562; Naidu, V.R.; Suk, J.M.; Lee, G.W.; Jeong, K.S. *Bull. Korean Chem. Soc.* **2009**, *30*, 482–485.

(2) Bates, G.W.; Gale, P.A.; Light, M.E. *Chem. Commun.* **2007**, 2121–2123.

(3) Brooks, S.J.; Gale, P.A.; Light, M.E. *Chem. Commun.* **2006**, 4344–4346; Brooks, S.J.; Edwards, P.R.; Gale, P.A.; Light, M.E. *New J. Chem.* **2006**, *30*, 65–70; Brooks, S.J.; Gale, P.A.; Light, M.E. *Chem. Commun.* **2005**, 4696–4698; Brooks, S.J.; Garcia-Garrido, S.E.; Light, M.E.; Cole, P.A.; Gale, P.A. *Chem. Eur. J.* **2007**, *13*, 3320–3329.

(4) Bates, G.W.; Triyanti; Light, M.E.; Albrecht, M.; Gale, P.A. *J. Org. Chem.* **2007**, *72*, 8921–8927, see also: Makuc, D., Lenarčič, M., Bates, G.W., Gale, P.A., Plavec, J. *Org. Biomol. Chem.* **2009**, *7*, 3505–3511; see also Makuc, D.; Triyanti; Albrecht, M.; Plavec, P.; Rissanen, K.; Valkonen, A.; Schalley, C.A. *Eur. J. Org. Chem.* **2009**, 4854–4866.

(5) Caltagirone, C.; Gale, P.A.; Hiscock, J.R.; Brooks, S.J.; Hursthouse, M.B.; Light, M.E. *Chem. Commun.* **2008**, 3007–3009; Caltagirone, C.; Hiscock, J.R.; Hursthouse, M.B.; Light, M.E.; Gale, P.A. *Chem. Eur. J.* **2008**, *14*, 10236–10243; Edwards, P.R.; Hiscock, J.R.; Gale, P.A.

Tetrahedron Lett. **2009**, *50*, 4922–4924; Edwards, P.R.; Hiscock, J.R.; Gale, P.A.; Light, M.E. *Org. Biomol. Chem.*, doi: 10.1039/b917140a.
(6) Gale, P.A.; Hiscock, J.R.; Moore, S.J.; Caltagirone, C.; Hursthouse, M.B.; Light, M.E. *Chem. Asian J.*, doi: 10.1002/asia.200900230.
(7) Hiscock, J.R.; Caltagirone, C.; Light, M.E.; Hursthouse, M.B.; Gale, P.A. *Org. Biomol. Chem.* **2009**, *7*, 1781–1783.
(8) Merisor, E.; Beifuss, U. *Tetrahedron Lett.* **2007**, *48*, 8383–8387.
(9) Cadogan, J.I.G.; Hutchison, S.H.; McNab, H. *J. Chem. Soc. Perkin Trans. 1* **1987**, 1407–1411.
(10) Hynes, M.J. *J. Chem. Soc. Dalton Trans.* **1993**, 311–312.
(11) Lin, C.I.; Selvi, S.; Fang, J.-M.; Chou, P.-T.; Lai, C.-H.; Cheng, Y.-M. *J. Org. Chem.* **2007**, *72*, 3537–3542, for other examples of anion triggered deprotonation, see: Camiolo, S.; Gale, P.A.; Hursthouse, M.B.; Light M.E.; Shi, A.J. *Chem. Commun*. **2002**, 758–759; Gale, P.A.; Navakhun, K.; Camiolo, S.; Light M.E.; Hursthouse, M.B. *J. Am. Chem. Soc.* **2002**, *124*, 11228–11229; Camiolo, S.; Gale, P.A.; Hursthouse, M.B.; Light, M.E. *Org. Biomol. Chem.* **2003**, *1*, 741–744; Evans, L.S.; Gale, P.A.; Light, M.E.; Quesada, R. *Chem. Commun.* **2006**, 965–967; Evans, L.S.; Gale, P.A.; Light, M.E.; Quesada, R. *New J. Chem.* **2006**, *30*, 1019–1025; Caltagirone, C.; Bates, G.W.; Gale, P.A.; Light, M.E. *Chem. Commun.* **2008**, 61–63; Gunnlaugsson, T.; Kruger, P.E.; Jensen, P.; Pfeffer, F.M.; Hussey, G.M. *Tetrahedron Lett.* **2003**, *44*, 8909–8913; Costero, A.M.; Banuls, M.J.; Aurell, M.J.; Ward, M.D.; Argent, S. *Tetrahedron* **2004**, *60*, 9471–9478; Boiocchi, M.; Del Boca, L.; Esteban-Gómez, D.; Fabbrizzi, L.; Licchelli, M.; Monzani, E. *J. Am. Chem. Soc.,* **2004**, *126*, 16507–16514; Esteban-Gómez, D.; Fabbrizzi, L.; Licchelli, M. *J. Org. Chem.* **2005**, *70*, 5717–5720; Boiocchi, M. Del Boca, L. Esteban-Gómez, D.; Fabbrizzi, L.; Licchelli, M.; Monzani, E. *Chem. Eur. J.* **2005**, *11*, 3097–3104.