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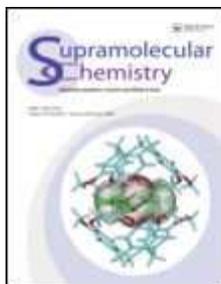
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Fluorescent carbazoylurea and carbazoylthiourea based anion receptors and sensors

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3 Fluorescent carbazoylurea and carbazoylthiourea based anion receptors and sensors
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31 **Abstract**

32
33 A series of carbazoylurea and carbazoylthiourea-based receptors have been
34 synthesized and their anion complexation and fluorescence properties studied. The
35 urea compounds show selectivity for oxoanion complexation over chloride and the
36 fluorescence of compound **1** is selectively quenched by benzoate anions in
37 DMSO/0.5% water. However the thiourea compounds show reduced anion affinities
38 compared to the urea analogues.
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45 **Keywords**

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49 Anion binding, indole, hydrogen bonding, crystallography
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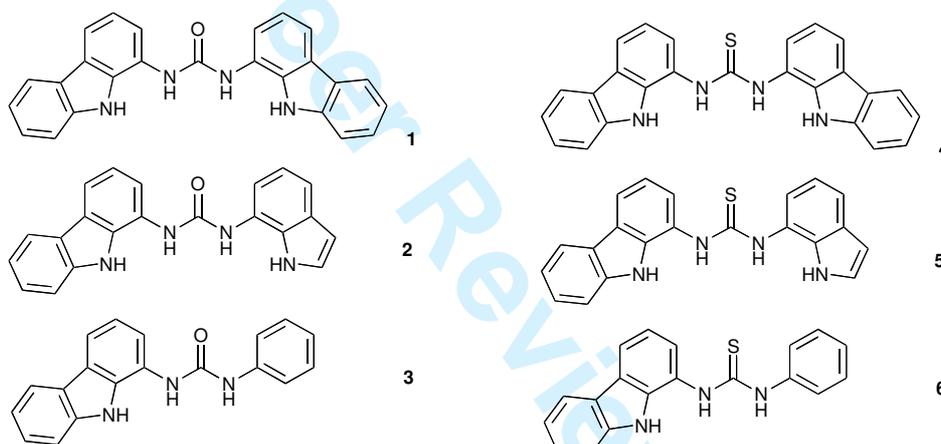
52 **Introduction**

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54 Interest in new hydrogen bond donor receptors for anionic species has led our
55 group and others to begin to explore indole, carbazole, indolocarbazoles and biindoles
56 as components of new anion complexation agents.¹ We have recently reported that
57 indole appended isophthalamides and pyridine-2,6-dicarboxamides function as
58 selective fluoride binding agents,² and our interest in urea³ as a receptor for oxo-
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anions led us to synthesise oxo-anion selective urea functionalized 2,7-disubstituted indoles (in collaboration with Albrecht and Triyanti)⁴ and most recently both functionalized and unfunctionalised diindolylureas 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 pKa 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 analogues of the diindolylurea skeleton 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 slight positive pressure of nitrogen/argon (as specified). ¹H NMR (300 MHz) and ¹³C{¹H} NMR (75 MHz) spectra were determined on a Bruker AV300 spectrometer. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were determined on a Bruker AV400 spectrometer. Chemical shifts for ¹H NMR are reported in parts per million (ppm), calibrated to the solvent peak set, with coupling constants reported in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet. Chemical shifts for ¹³C{¹H} NMR are reported in ppm, relative to the central line of a septet at $\delta = 39.52$ ppm for deuterio-dimethylsulfoxide. Infrared (IR) spectra were recorded on a Matterson Satellite (ATR). FTIR are reported in wavenumbers (cm^{-1}). All solvents and starting materials

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4 were purchased from chemical sources where available. NMR titrations were
5 performed by adding aliquots of the putative anionic guest (as the TBA/TEA) salt
6 (0.15 M) in a solution of the receptor (0.01 M) in DMSO-*d*₆ to a solution of the
7 receptor (0.01 M). Fluorescence and UV-Vis titrations were performed by adding
8 aliquots of the putative anionic guest (as the TBA salt or TEA salt in the case of
9 bicarbonate) (1×10^{-3} M) in a solution of the receptor (1×10^{-5} M) in DMSO/water
10 0.5%. All fluorescence and UV-Vis spectra were recorded on a Varian Cary Eclipse
11 fluorescence spectrophotometer and Thermo Nicolet Evolution 300
12 spectrophotometer, respectively. Luminescence quantum yields were determined
13 using quinine sulfate in a 1 M H₂SO₄ aqueous solution ($\Phi = 0.546$) as a reference.
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22 Compounds **1 – 3** were synthesised by our previously published procedures.⁷
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25 **1-Aminocarbazole** 1-Nitrocarbazole was synthesised according to a literature
26 procedure⁸ modified by separation of the 1- and 3-nitrocarbazoles *via* chloroform
27 flash chromatography (see ESI for details). Characterisation data agreed with
28 previously published characterisation data.⁹
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32 **1-Isothiocyanato-9H-carbazole** was prepared by reaction of 1-aminocarbazole
33 with thiophosgene in a mixture of dichloromethane and a saturated aqueous solution
34 of NaHCO₃ (see ESI for details).
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38 **1,3-di(9H-Carbazol-1-yl)thiourea (4)**

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41 A solution of the isothiocyanate (0.23 g, 1.04 mM) in chloroform (20 ml) was then
42 added dropwise to a solution of 1-aminocarbazole (0.19 g, 1.04 mM) in chloroform
43 (25 ml). The solution was then heated at reflux overnight with triethylamine (2 mL).
44 The solution was then taken to dryness and the product isolated by filtration by
45 recrystallisation from an ether/methanol slow evaporation to give a light green solid.
46 Yield 36%, 0.15g; mp. 221 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ : 7.13-7.20 (m,
47 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 =
48 7.7 Hz, 2H), 8.12 (d, J = 7.7 Hz, 2H), 9.71 (s, thiourea NH, 2H), 11.27 (s, indole NH,
49 2H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ : 111.2 (CH), 118.5 (CH), 118.6 (CH), 118.7
50 (CH), 120.2 (CH), 122.7 (C), 123.1 (C), 124.0 (C), 124.2 (CH), 125.7 (CH), 136.3
51 (C), 139.8 (C), 180.8 (CS); IR (film): ν = 3389, 3281, 1148 cm⁻¹. LRMS (ES⁻): m/z:
52 405 [M-H]⁻; HRMS (ES⁺): m/z: act: 407.1332 [M+H]⁺ cal: 407.1325 [M+H]⁺
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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 hours. The solution was washed with hexane and taken to dryness and the oil was dissolved in hot methanol (2 mL) and left to cool to room temperature. White crystals were removed after 24 hrs and washed with hexane (25 mL) and dried under vacuum. Yield 48 %, 0.41 g; mp. 144 °C; ^1H NMR (300 MHz, $\text{DMSO-}d_6$): 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, $\text{DMSO-}d_6$): 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): $\nu = 3380, 3280, 1210\text{ cm}^{-1}$; LRMS (ES^-): m/z : 355 [M-H] $^-$; HRMS (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 hours. The solution was then reduced in volume to 2ml and DCM (10 ml) and hexane (20 ml) added. The solution was then sonicate for 5 min and a dark green semi-solid removed and a white precipitate collected, washed with hexane (10 ml) and dried under vacuum. Yield 41 %, 0.16 g; mp. 169 °C; ^1H NMR (300 MHz, $\text{DMSO-}d_6$): 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, $\text{DMSO-}d_6$): 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): $\nu = 3300, 3320, 1220\text{ cm}^{-1}$; LRMS (ES^-): m/z : 316 [M-H] $^-$; HRMS (ES^+): m/z : act: 318.1059 [M+H] $^+$ cal: 318.1031 [M+H] $^+$

Crystal data for compound **1**. tetrabutylammonium benzoate: $C_{48}H_{59}N_5O_3$, $M_r = 754.00$, $T = 120(2)$ K, triclinic, space group $P1$ $a = 10.980(5)$, $b = 13.774(5)$, $c = 15.173(5)$ Å, $\alpha = 68.760(5)^\circ$, $\beta = 85.232(5)^\circ$, $\gamma = 81.541(5)^\circ$, $V = 2114.5(14)$ Å³, $\rho_{calc} = 1.184$ g cm⁻³, $\mu = 0.074$ mm⁻¹, $Z = 2$, reflections collected: 44837, independent reflections: 9728 ($R_{int} = 0.1052$), final R indices [$I > 2\sigma I$]: $R1 = 0.0661$, $wR2 = 0.1368$, R indices (all data): $R1 = 0.1190$, $wR2 = 0.1589$.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 the isothiocyanate by reaction with thiophosgene in $CH_2Cl_2/sat.NaHCO_3(aq)$. Compounds **4** and **5** were prepared by reaction of the isothiocyanate with 1-aminocarbazole or 7-aminoindole respectively. Compound **6** was prepared by reaction of phenyl isothiocyanate with 1-aminocarbazole in chloroform.

Stability constants for the compounds with a range of anionic guests were determined using ¹H 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 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 ESI for compounds **2** and **3**).

Table 1 The stability constants (K_a/M^{-1}) of compounds **1**, **2** and **3** with a variety of anionic guests (added as tetrabutylammonium salts except bicarbonate which was added as a tetraethylammonium salt) at 298K in DMSO-*d*₆/0.5% water as determined by following urea NH resonance adjacent to the carbazole. In all cases 1:1 receptor: anion stoichiometry was observed. Errors estimated to be no more than $\pm 15\%$

Anion	Compound	Compound	Compound
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	1	2	3
acetate	$>10^4$	$>10^4$	$>10^4$
benzoate	5670	5880	3420
dihydrogen phosphate	a	a	6140
chloride	102	139	85
bicarbonate	$>10^4$	$>10^4$	$>10^4$

^a NMR titration curve could not be fitted to a 1:1 or 1:2 receptor:anion binding stoichiometry but indicates strong binding.

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

Table 2 The stability constants (K_a/M^{-1}) of compounds **4**, **5** and **6** with a variety of anionic guests (added as tetrabutylammonium salts except bicarbonate which was added as a tetraethylammonium salt) at 298K in DMSO-*d*₆/0.5% water as determined by following urea NH resonance adjacent to the carbazole. In all cases 1:1 receptor:anion stoichiometry was observed. Errors estimated to be no more than $\pm 15\%$

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

^a Peak broadening prevented a stability constant from being determined in these cases.

Figure 1 shows a comparison of the ¹H 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** (the dicarbazolyurea), the urea NH shifts downfield by 2.3 ppm whilst the indole NH shifts downfield by approximately 1 ppm. Compound **4** is the thiourea analogue of compound **1**. In this case whilst 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 the original diindolyurea compounds was attributed to a conformation effect that caused the thiourea receptors to adopt a twisted conformation due to the large size of the sulfur 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.

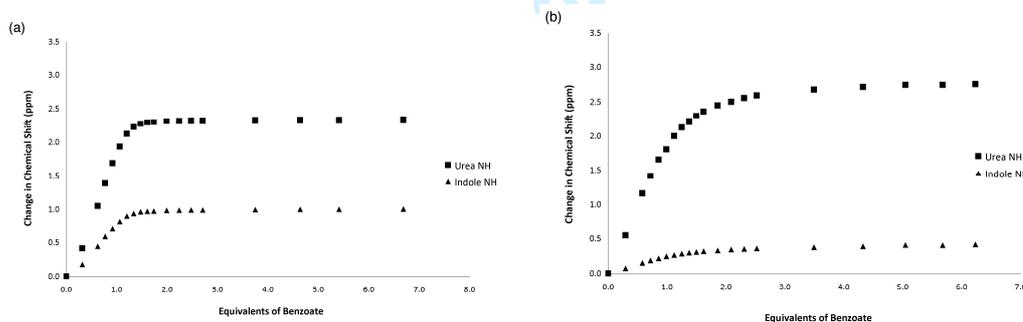
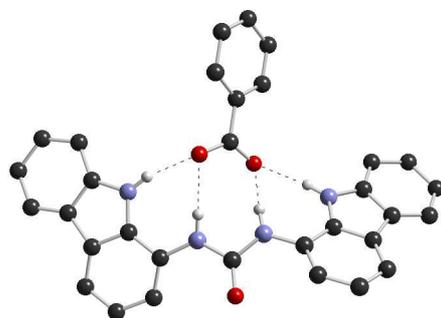


Figure 1 Proton NMR titration curves for compounds **1** and **4** with tetrabutylammonium benzoate in DMSO-*d*₆/0.5% water showing shifts of indole and urea NH groups.

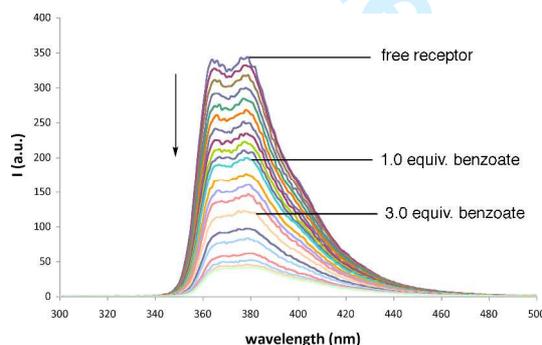
Crystals of the benzoate complex of compound **1** were grown by slow evaporation of a DMSO solution of the receptor in the presence of excess tetrabutylammonium benzoate. The unit cell contains two crystallographically distinct benzoate complexes which adopt similar conformations. In both benzoate complexes one of the carbazoles is in the plane of the urea whilst the other is twisted out of plane by 37.1°

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3 or 43.0° (Figure 2). Each benzoate anion is bound by four hydrogen bonds in the
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5 range N...O 2.762(5) – 2.996(5) Å.⁷
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21 Figure 2 The X-ray crystal structure of one of the two crystallographically distinct
22 benzoate complexes present in the unit cell of the tetrabutylammonium benzoate
23 complex of receptor **1**. Tetrabutylammonium counter cations and selected hydrogen
24 atoms have been omitted for clarity.
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26
27 In order to investigate the ability of compounds **1-3** to act as sensors, fluorescence
28 studies were performed in a DMSO/0.5% water solution. Under these conditions
29 receptor **1** displays an intense fluorescence emission ($\Phi = 0.549$) with maxima at 363
30 nm and 376 nm when excited at 270 nm. As shown in Fig. 3 upon addition of
31 increasing amounts of tetrabutylammonium benzoate, a selective quenching of the
32 fluorescence emission was observed ($I_{\text{res}} = 10\%$).
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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).

Addition of the tetrabutylammonium salts of fluoride chloride, acetate, dihydrogen
phosphate and tetraethylammonium bicarbonate resulted in significantly less dramatic
fluorescence quenching as shown in Fig. 4. Addition of acetate resulted in only a
partial quenching of the emission ($I_{\text{res}} = 50\%$) whilst 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^- ($I_{\text{res}} = 68\%$) and HCO_3^- ($I_{\text{res}} = 73\%$). Chloride did not effect the emission of the system. The trend in fluorescence quenching is similar to that found for the stability constants by ^1H -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 guest.

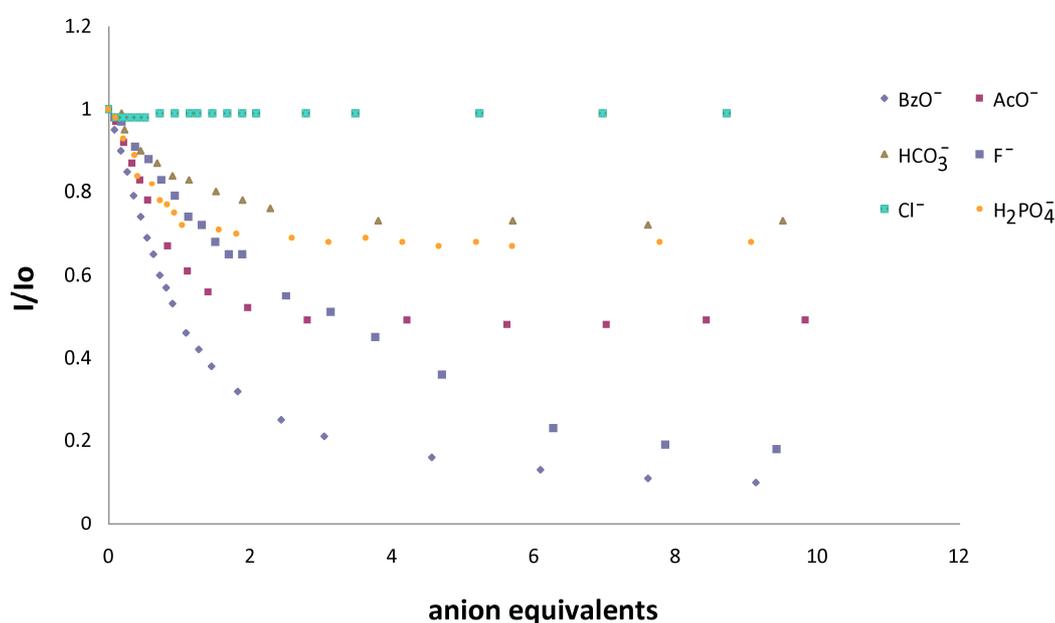


Figure 4. Effect of increasing anion concentration upon the relative fluorescence emission of receptor **1** in DMSO/0.5% water.

Compounds **4-6** did not reveal any selectivity for the anionic guests considered in this study and had significantly lower quantum yields ($\Phi = 0.01$, $\Phi = 0.0025$, $\Phi = 0.0019$ for **4**, **5** and **6** respectively) than those observed for compounds **1-3**. When excited at 332 nm (compounds **4-5**) and 344 nm (compound **6**) they showed two maxima in their fluorescence emission, at 379 and 395 nm in DMSO/water 0.5%, 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 ($I_{\text{res}} = 54\%$) which is much less pronounced than that

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observed with the same anion and urea analogue **1** ($I_{\text{res}} = 10\%$). 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 dicarbazolyurea, 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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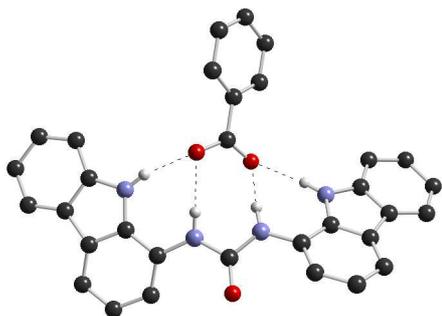
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Graphical abstract



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Fluorescent carbazolylurea and carbazolylthiourea based anion receptors and sensors

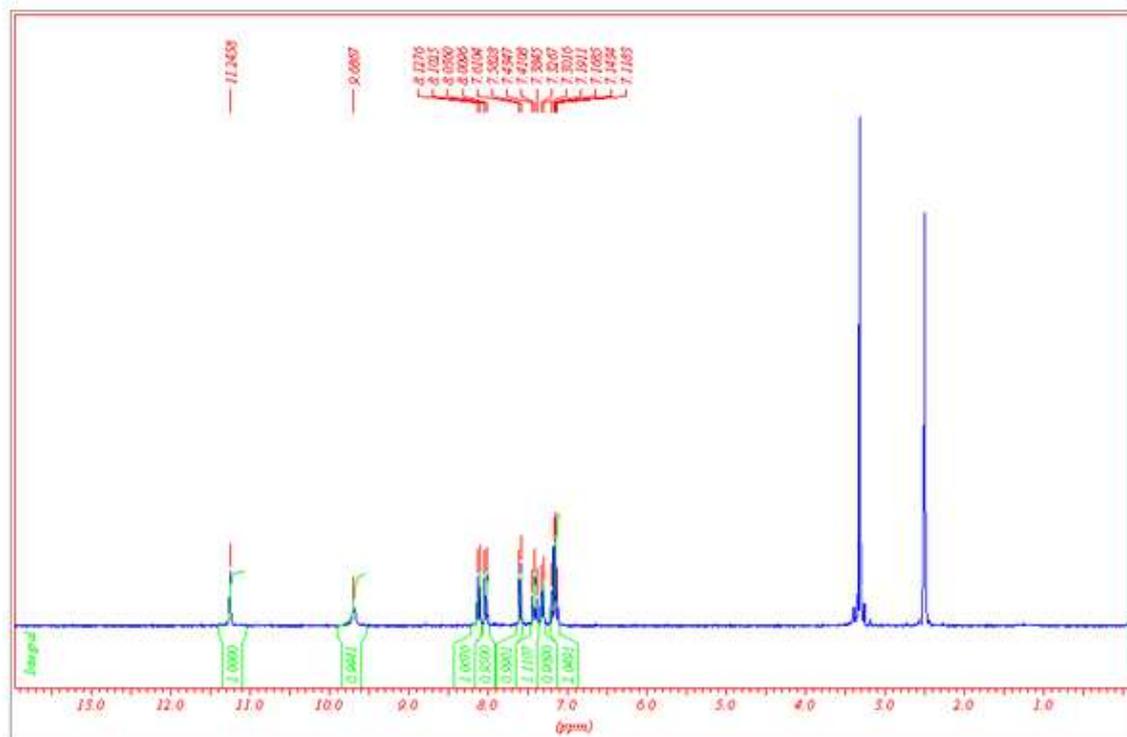
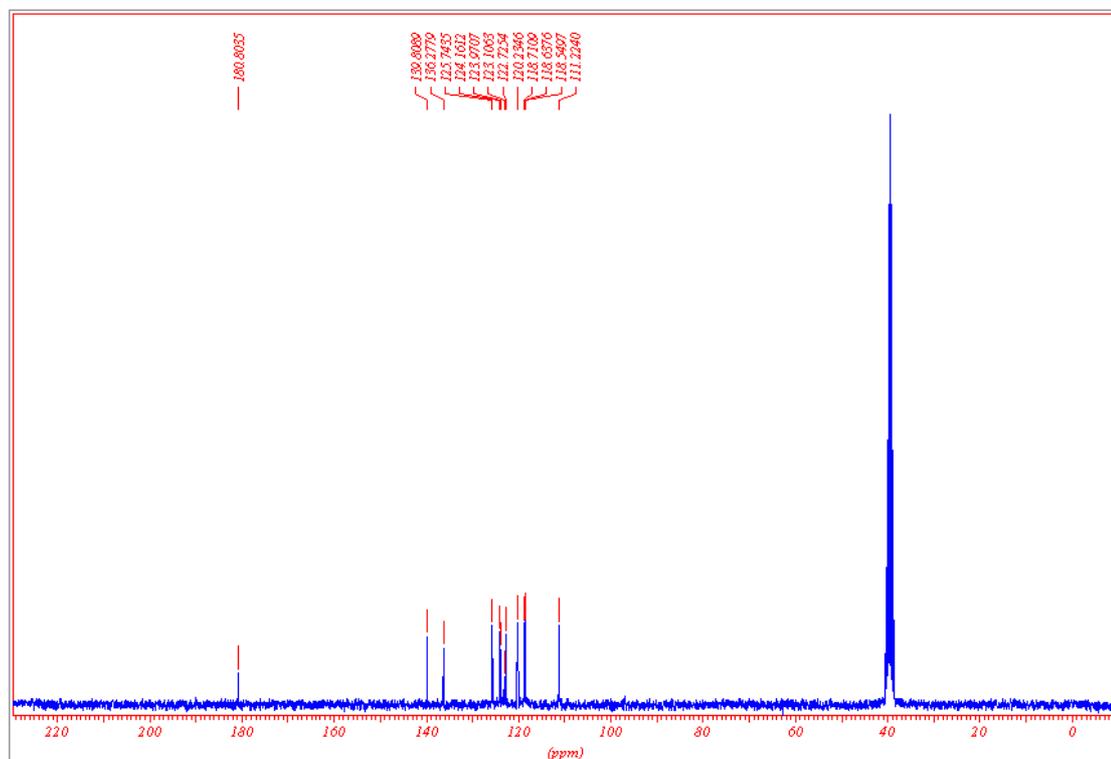
Claudia Caltagirone, Philip A. Gale,* Jennifer R. Hiscock, Michael B. Hursthouse, and Mark E. Light

School of Chemistry, University of Southampton, Southampton, SO17 1BJ UK

Electronic supplementary information

1-Aminocarbazole 1-Nitrocarbazole was synthesised according to a literature procedure⁸ modified by separation of the 1- and 3-nitrocarbazoles *via* chloroform flash chromatography. 1-Nitrocarbazole (0.27 g, 1.28 mM) and a Pd/C 10% catalyst (0.02 g) were suspended in ethanol (25mL). The flask was evacuated and the mixture placed under a hydrogen atmosphere and stirred vigorously for 45 mins. After this time the palladium catalyst was removed by filtration through celite and the filtrate taken to dryness and placed under reduced pressure. This gave a white solid. Assumed yield 100%; ¹H NMR (300 MHz, DMSO-*d*₆): δ: 5.14 (s, amine NH, 2H), 6.65 (dd, J₁ = 7.3 Hz, J₂ = 1.1 Hz, 1 ArH), 6.91 (t, J = 7.7 Hz, 1 ArH), 7.08-7.13 (m, 1 ArH), 7.31-7.36 (m, 2 ArH), 7.49 (d, J = 8.0 Hz, 1 ArH), 7.99 (d, J = 7.7 Hz, 1 ArH), 10.77 (s, indole NH, 1H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ: 108.4 (ArCH), 109.3 (ArCH), 110.9 (ArCH), 118.2 (ArCH), 119.7 (ArCH), 120.2 (ArCH), 122.7 (ArC), 123.2 (ArC), 124.9 (ArCH), 128.7 (ArC), 133.5 (ArC), 139.0 (ArC); LRMS (ES⁺):m/z: 181 [M-H]⁺. These values agree with previously published characterisation data.⁹

1-Isothiocyanato-9H-carbazole 1-Aminocarbazole (0.43 g, 2.36 mM) was dissolved in a mixture of dichloromethane (20 mL) and a saturated aqueous solution of NaHCO₃ (40 mL). Thiophosgene (0.11 mL, 2.36 mM) was added dropwise in dichloromethane (20 mL) and the reaction mixture stirred under nitrogen atmosphere at room temperature overnight. The organic layer was washed with water, dried over MgSO₄, filtered and reduced *in vacuo*. The pure product was obtained by recrystallisation from hot MeOH. The isothiocyanate was isolated as a white solid in quantitative yield.

NMR data**Figure S1** ^1H NMR spectrum of compound **4** in $\text{DMSO-}d_6$.**Figure S2** ^{13}C NMR spectrum of compound **4** in $\text{DMSO-}d_6$.

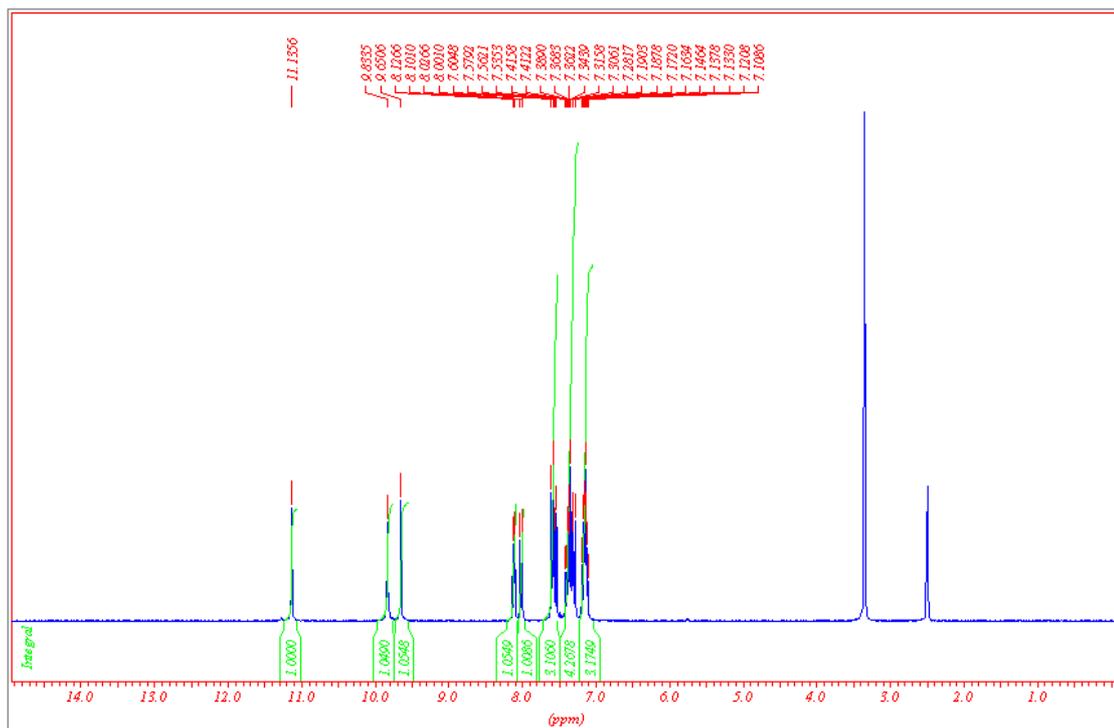


Figure S5 ^1H NMR spectrum of compound **6** in $\text{DMSO-}d_6$.

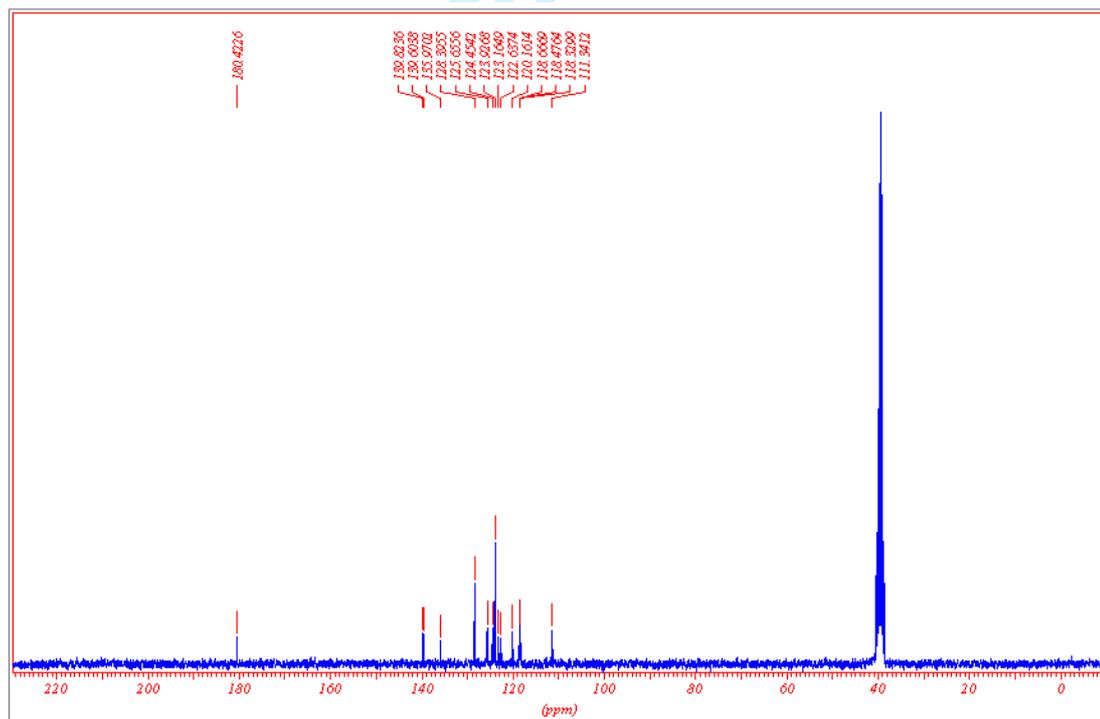
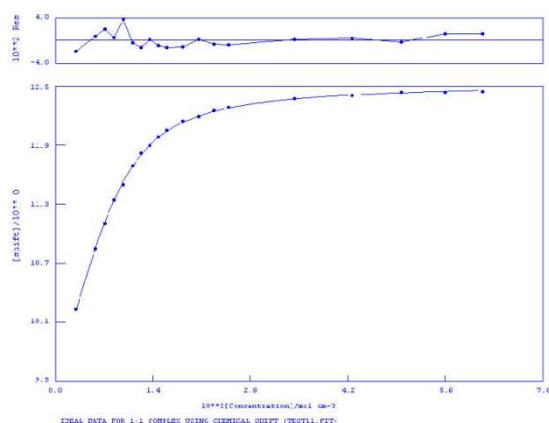


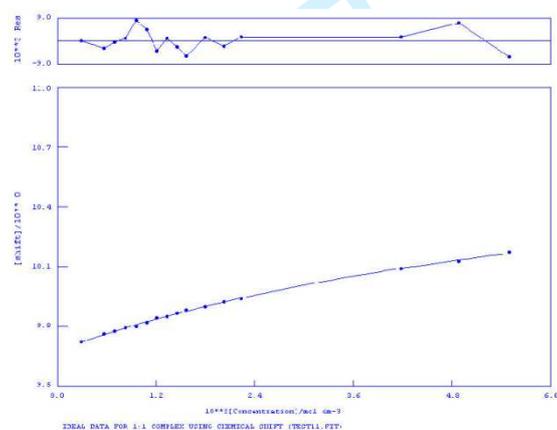
Figure S6 ^{13}C NMR spectrum of compound **6** in $\text{DMSO-}d_6$.

Titration data



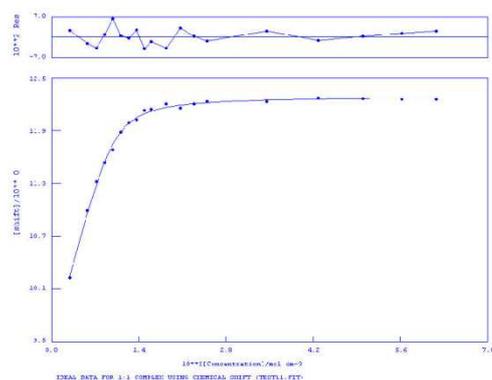
$K_a = 658 \text{ M}^{-1}$ Error = 3 %

Figure S7 NMR titration of compound **4** vs. TBAOBz in DMSO- d_6 /H₂O 0.5%.



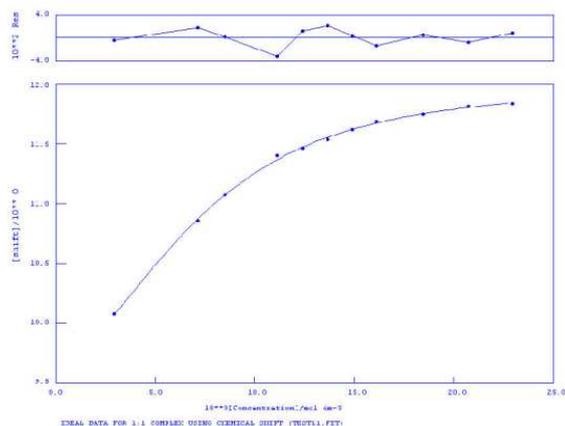
$K_a = 15 \text{ M}^{-1}$ Error = 10 %

Figure S8 NMR titration of compound **4** vs. TBACl in DMSO- d_6 /H₂O 0.5%.



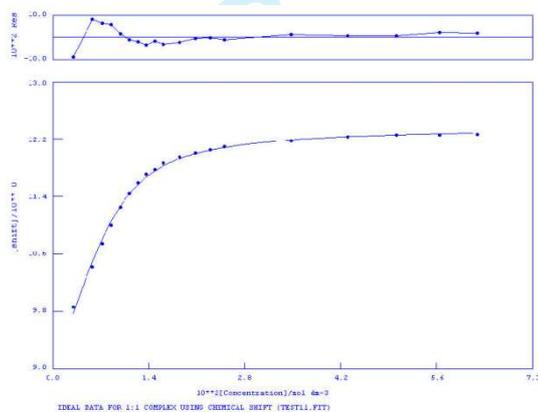
$K_a = 2230 \text{ M}^{-1}$ Error = 9 %

Figure S9 NMR titration of compound **4** vs. TBAOAc in DMSO- d_6 /H₂O 0.5%.



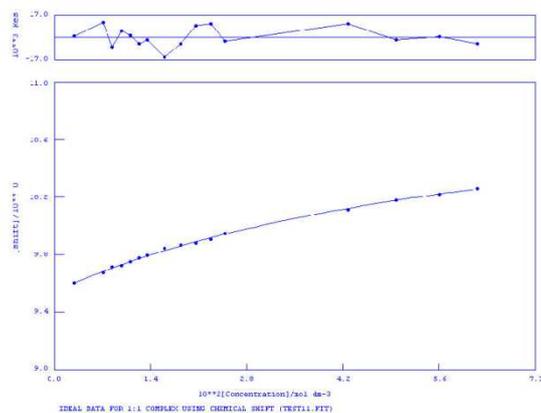
$K_a = 687 \text{ M}^{-1}$ Error = 8 %

Figure S10 NMR titration of compound **4** vs. TBAH_2PO_4 in $\text{DMSO-}d_6/\text{H}_2\text{O}$ 0.5%.



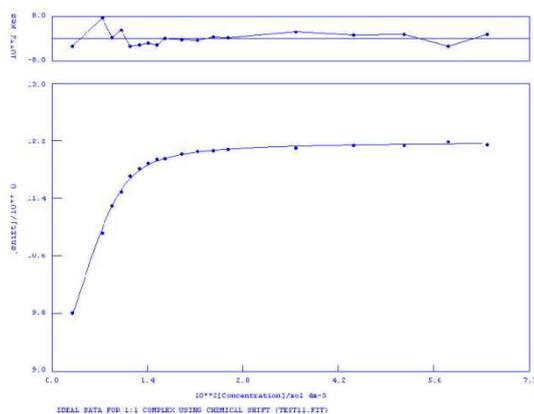
$K_a = 675 \text{ M}^{-1}$ Error = 7 %

Figure S11 NMR titration of compound **5** vs. TBAOBz in $\text{DMSO-}d_6/\text{H}_2\text{O}$ 0.5%.



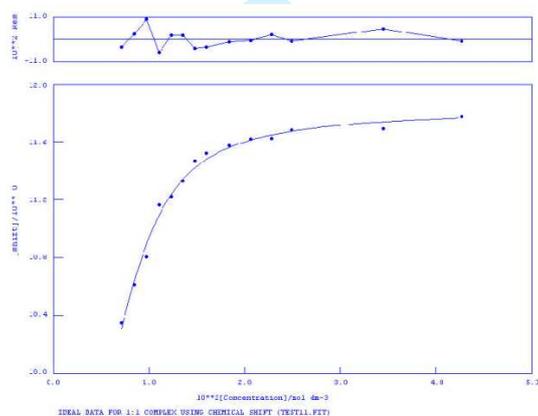
$K_a = 17 \text{ M}^{-1}$ Error = 10 %

Figure S12 NMR titration of compound **5** vs. TBACl in $\text{DMSO-}d_6/\text{H}_2\text{O}$ 0.5%.



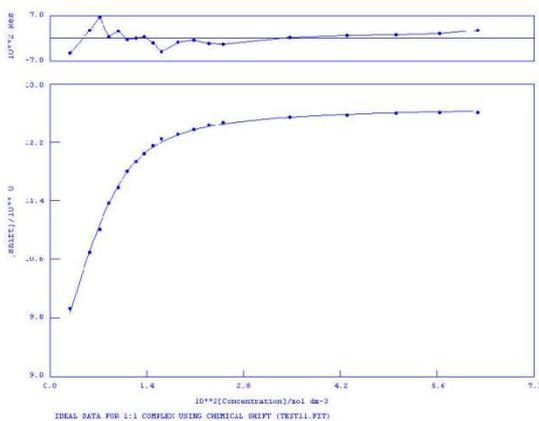
$K_a = 1804 \text{ M}^{-1}$ Error = 7 %

Figure S13 NMR titration of compound **5** vs. TBAOAc in DMSO- d_6 /H₂O 0.5%.



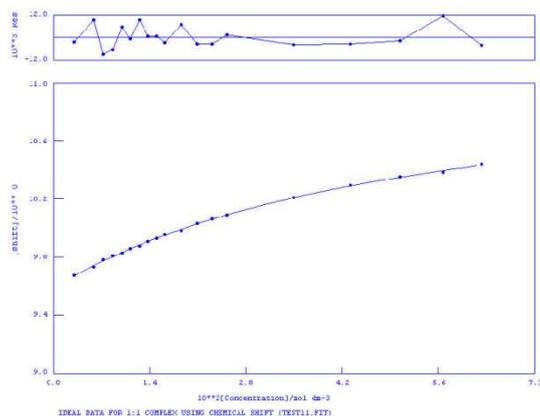
$K_a = 1342 \text{ M}^{-1}$ Error = 12 %

Figure S14 NMR titration of compound **5** vs. TBAH₂PO₄ in DMSO- d_6 /H₂O 0.5%.



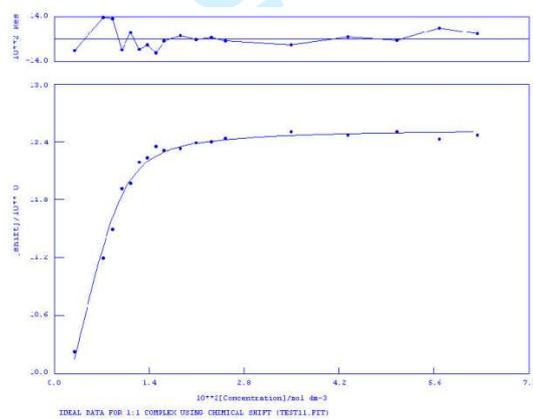
$K_a = 870 \text{ M}^{-1}$ Error = 5 %

Figure S15 NMR titration of compound **6** vs. TBAOBz in DMSO- d_6 /H₂O 0.5%.



$K_a = 23 \text{ M}^{-1}$ Error = 6 %

Figure S16 NMR titration of compound **6** vs. TBACl in DMSO- d_6 /H₂O 0.5%.



$K_a = 1782 \text{ M}^{-1}$ Error = 16 %

Figure S17 NMR titration of compound **6** vs. TBAOAc in DMSO- d_6 /H₂O 0.5%.

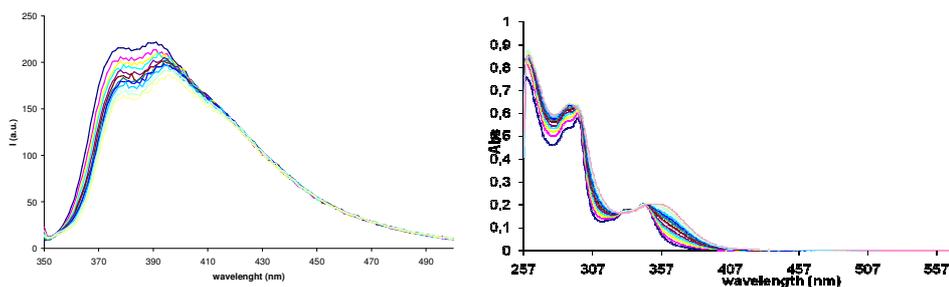
Fluoresce data

Figure S18 Changes in the fluorescence emission and absorption of **4** upon addition of TBAF in dmsol.

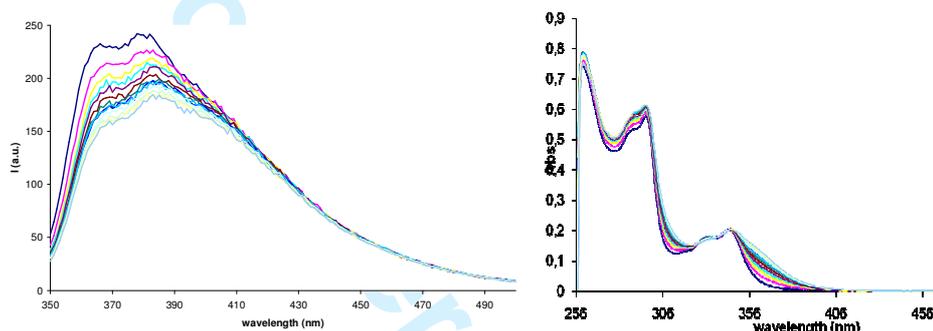


Figure S19 Changes in the fluorescence emission and absorption of **4** upon addition of TBACAc in dmsol.

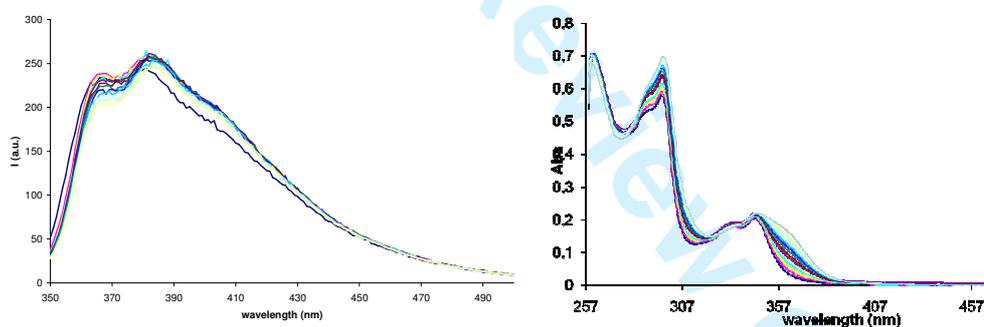


Figure S20 Changes in the fluorescence emission and absorption of **4** upon addition of TBAH₂PO₄ in dmsol.

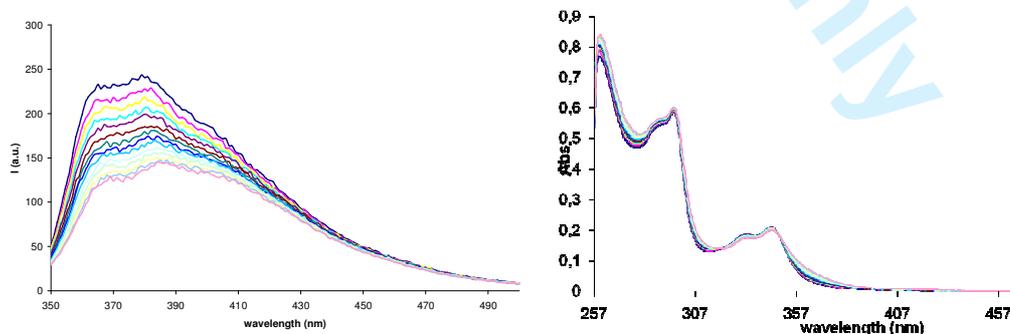


Figure S21 Changes in the fluorescence emission and absorption of **4** upon addition of TBACBz in dmsol.

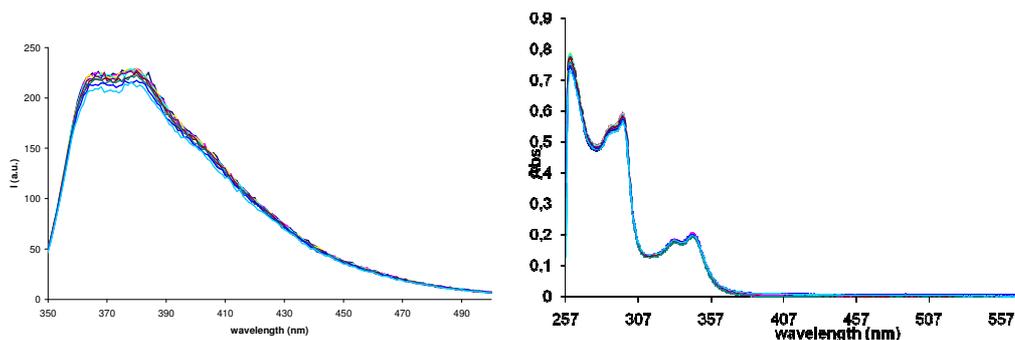


Figure S22 Changes in the fluorescence emission and absorption of **4** upon addition of TBACl in dmsol.

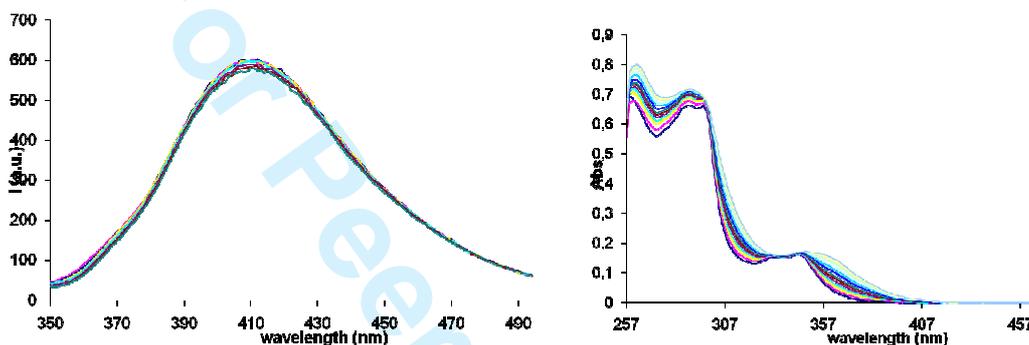


Figure S23 Changes in the fluorescence emission and absorption of **5** upon addition of TBAF in dmsol.

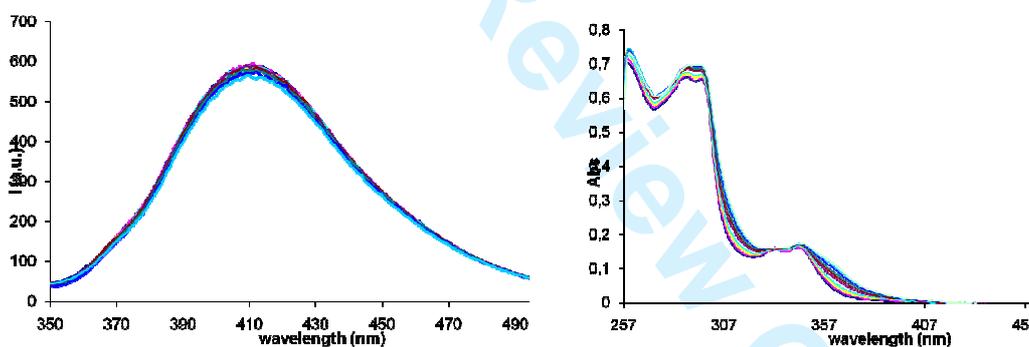


Figure S24 Changes in the fluorescence emission and absorption of **5** upon addition of TBACl in dmsol.

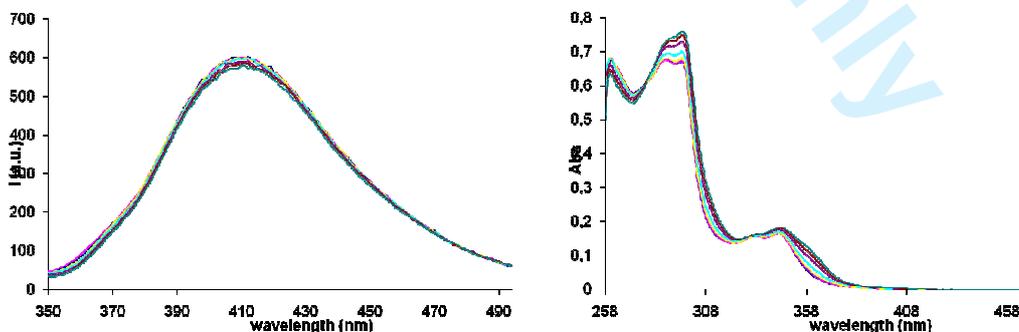


Figure S25 Changes in the fluorescence emission and absorption of **5** upon addition of TBAH₂PO₄ in dmsol.

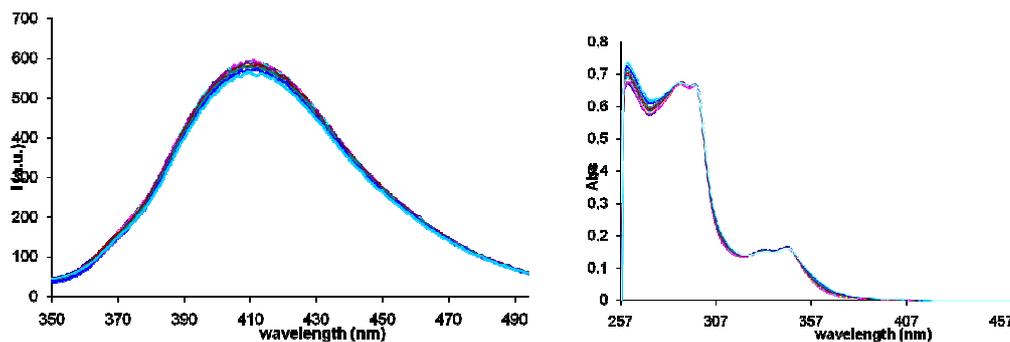


Figure S26 Changes in the fluorescence emission and absorption of **5** upon addition of TBAOBz in dmsol.

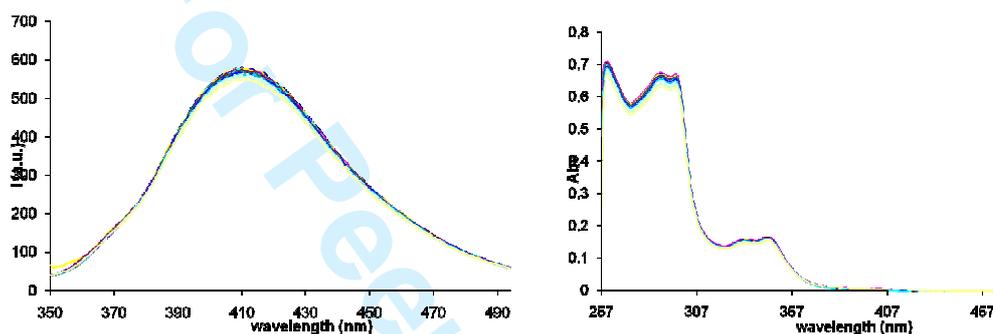


Figure S27 Changes in the fluorescence emission and absorption of **5** upon addition of TBACl in dmsol.

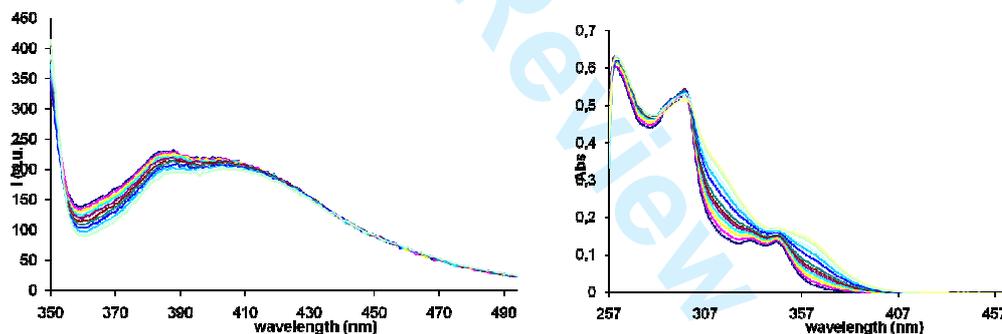


Figure S28 Changes in the fluorescence emission and absorption of **6** upon addition of TBAF in dmsol.

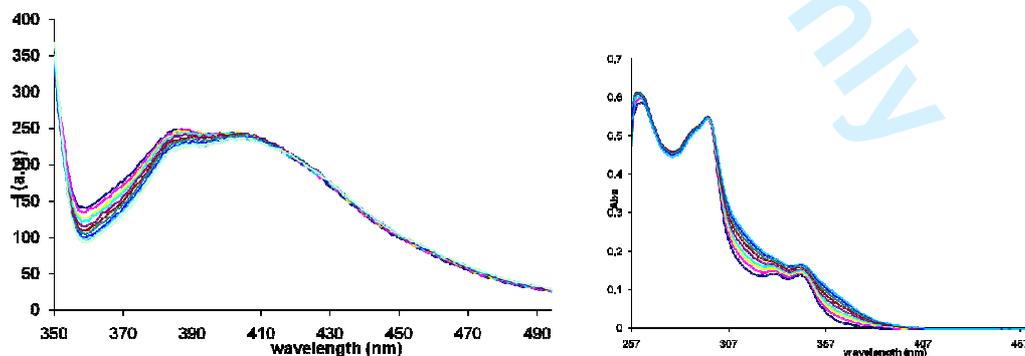


Figure S29 Changes in the fluorescence emission and absorption of **6** upon addition of TBACl in dmsol.

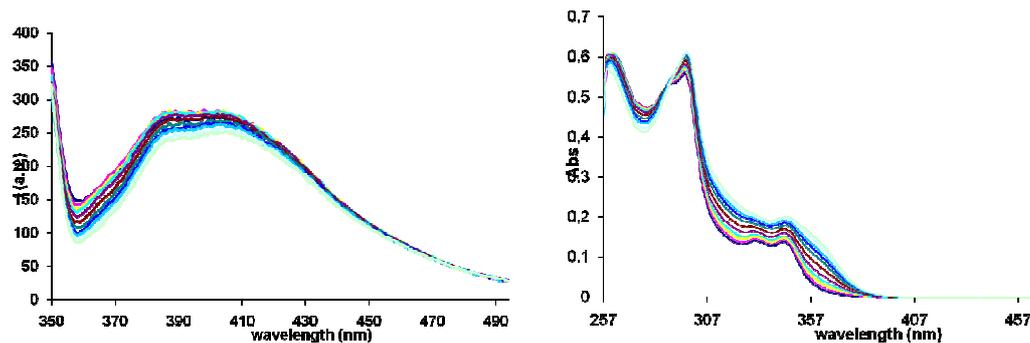


Figure S30 Changes in the fluorescence emission of **6** and absorption upon addition of TBAH₂PO₄ in dmsol.

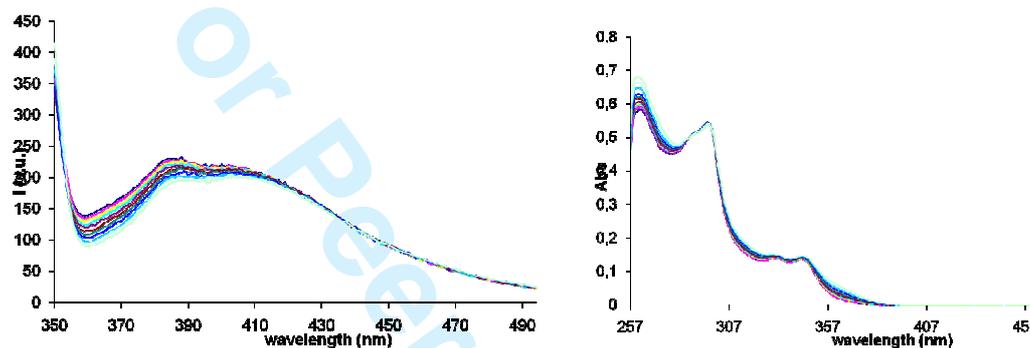


Figure S31 Changes in the fluorescence emission and absorption of **6** upon addition of TBAOBz in dmsol.

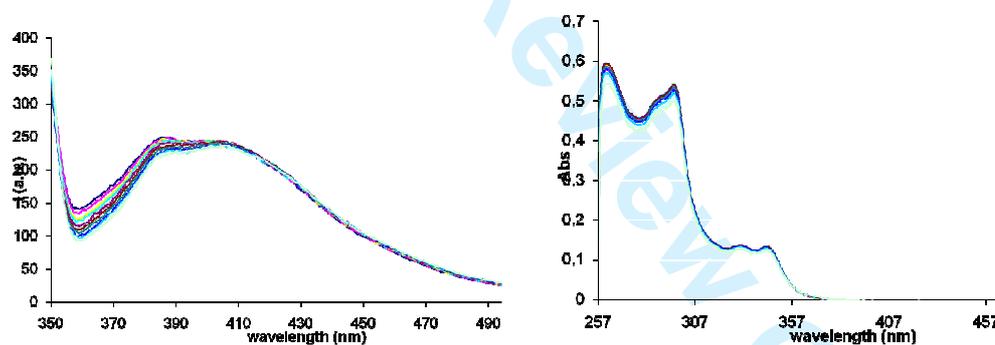
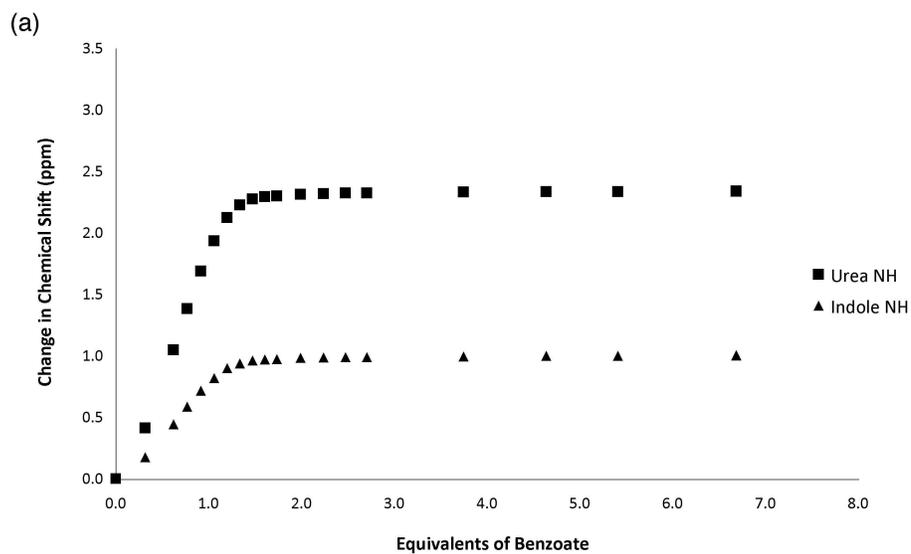
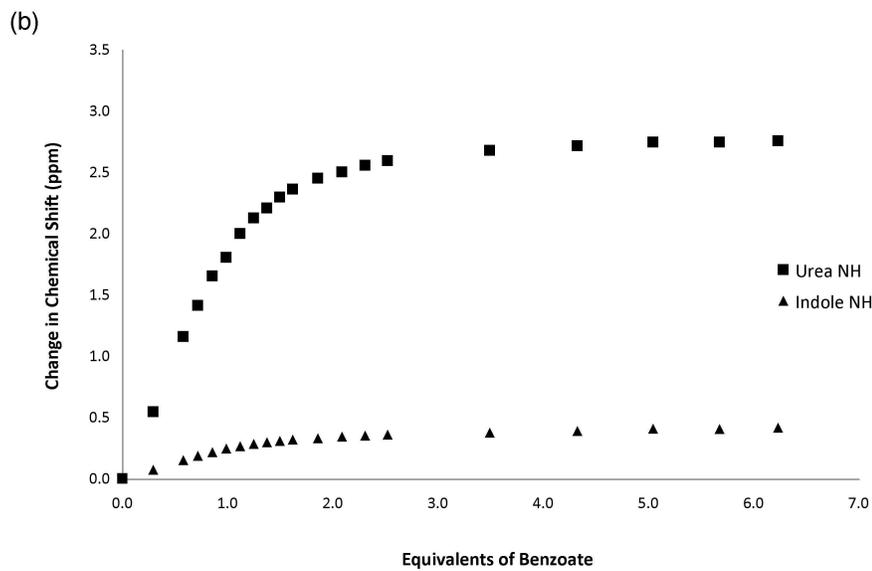


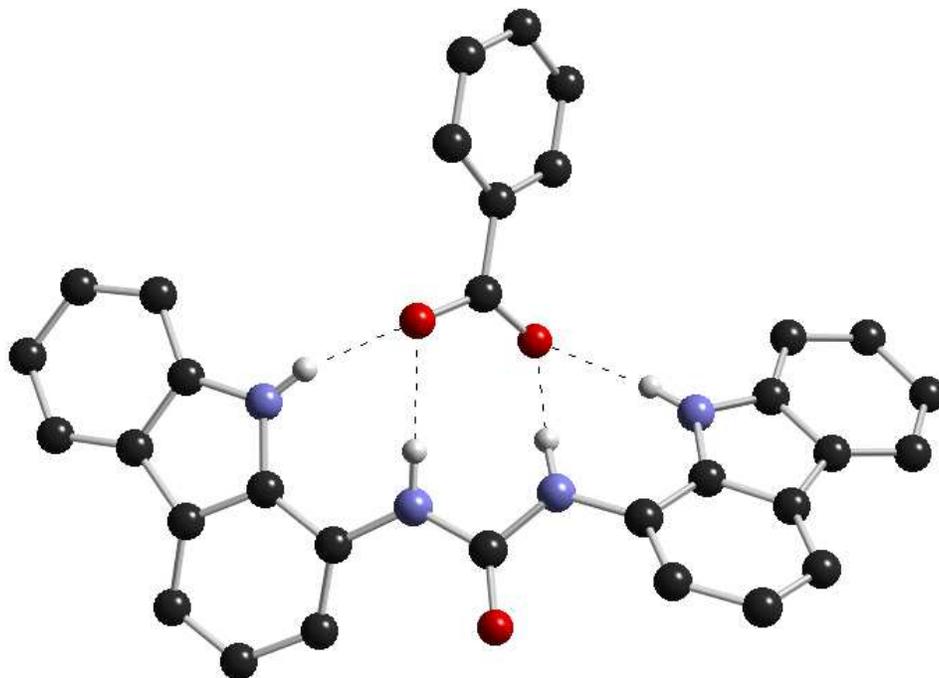
Figure S32 Changes in the fluorescence emission and absorption of **6** upon addition of TBACl in dmsol.



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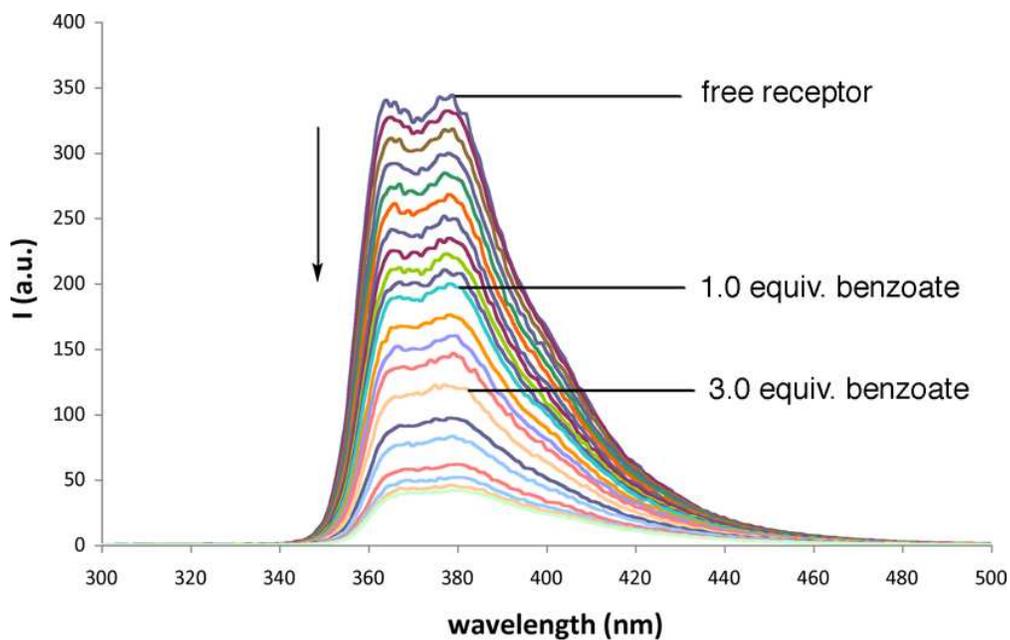


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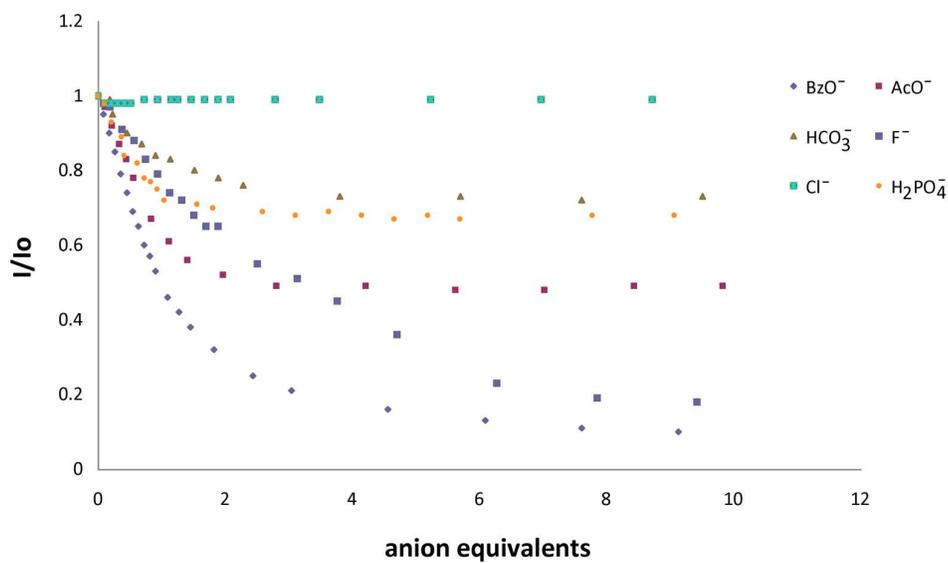
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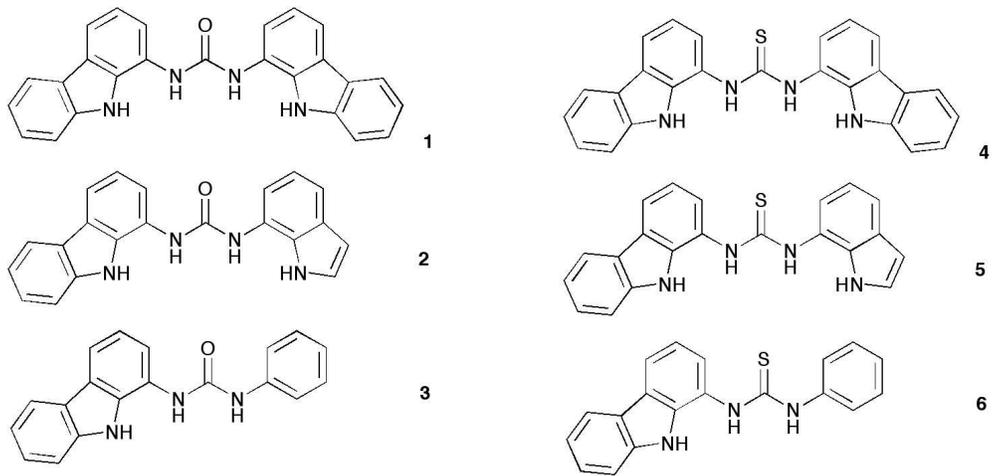


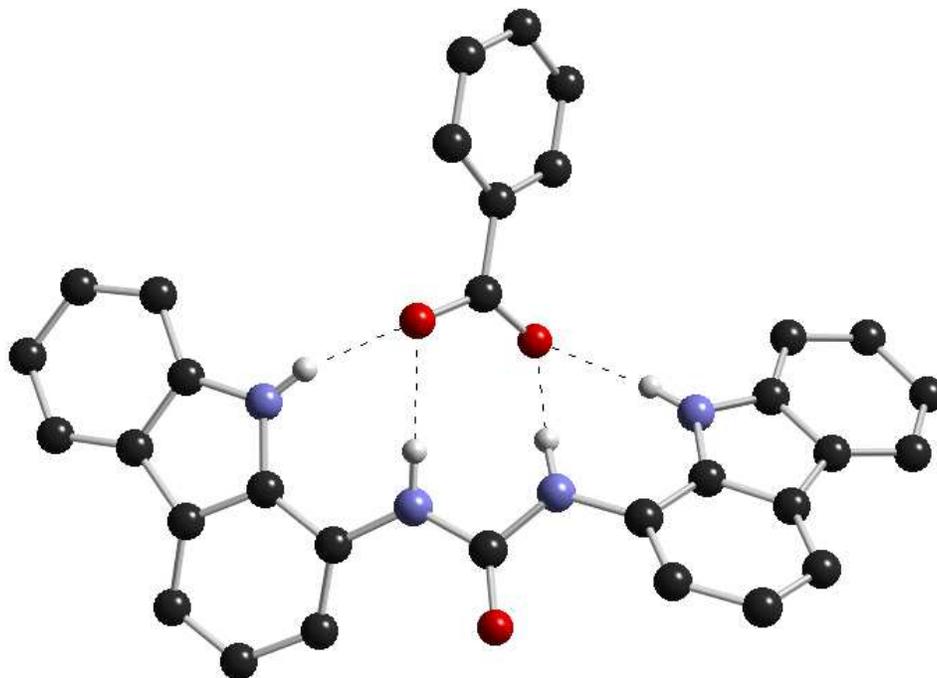
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Review Only



70x42mm (600 x 600 DPI)





60x44mm (300 x 300 DPI)

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