Fluorescent carbazolylurea anion receptors

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

Supplementary information

General remarks: All reactions were performed using oven-dried glassware under 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 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), calibrated to the solvent peak set. 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 deuterio-dimethylsulfoxide. Infrared (IR) spectra were recorded on a Matterson Satellite (ATR). FTIR 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 TBA salt) (0.15 M) in a solution of the receptor (0.01M) in DMSO-$d_6$ to a solution of the receptor (0.01M). Fluorescence titrations were performed by adding aliquots of the putative anionic guest (as the TBA salt or TEA salt in the case of bicarbonate) (1×10$^{-3}$ M) in a solution of the receptor (1×10$^{-5}$ M) in DMSO/water 0.5%. All spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. Luminescence quantum yields (were determined using quinine sulfate in a 1 M H$_2$SO$_4$ aqueous solution (Φ = 0.546) as a reference.

1-Aminocarbazole 1-Nitrocarbazole was synthesised via a literature procedure$^1$ with an alteration to the separation of 1 and 3-nitrocarbazole in this case with 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. yield 100%; $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$: 5.14 (s, amine NH, 2H), 6.65 (dd, 1H, ArH), 6.91 (t, 1H, ArH), 7.08-7.13 (m, 1H ArH), 7.31-7.36 (m, 2H ArH), 7.49 (d, 1H, ArH), 7.99 (d, 1H, ArH), 10.77 (s, 1H, indole NH); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$: 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 data.2

1-Isocyanato-9H-carbazole A solution of 1-amino carbazole (0.17 g, 0.94 mM) in DCM (20 ml) was added dropwise over 2 minutes to a stirring solution of triphosgene (0.28 g, 0.94 mM) in a two phase DCM (20 ml) and a saturated aqueous solution of NaHCO3 (40 mL) solution. The solution was stirred vigorously under argon overnight. The organic phase was then washed with water (250 ml), dried with MgSO4 and taken to dryness affording a white solid (the isocyanate) which was used immediately due to its high reactivity.

1,3-di(9H-carbazol-1-yl)urea (1) A solution of 1-isocyanato-9H-carbazole (0.24 g, 1.16 mM) in DCM (20 ml) was added dropwise to a solution of 1-aminocarbazole (0.21 g, 1.16 mM) in chloroform (25 ml). Triethylamine (2 ml) was added and the solution heated at reflux for 2 hrs. The product was isolated as a white precipitate which was removed by filtration. Yield 0.19 g, 41%; mp. 260 °C decomposition; 1H NMR (300 MHz, DMSO-d6): δ: 7.13-7.20 (m, 4H, ArH), 7.38-7.46 (m, 4H, ArH), 7.61 (d, 2H, ArH), 7.92 (d, 2H, ArH), 8.12 (d, 2H, ArH), 8.84 (s, 2H, urea NH), 10.94 (s, 2H, indole NH); 13C NMR (75 MHz, DMSO-d6): δ: 111.4 (ArCH), 116.1 (ArCH), 118.7 (ArCH), 118.8 (ArCH), 119.1 (ArCH), 120.2 (ArCH), 122.7 (ArC), 123.5 (ArC), 123.9 (ArC), 125.6 (ArCH), 133.3 (ArC), 139.6 (ArC), 153.7 (CO); IR (film): ν = 3391 (indole NH stretching), 3240 (urea NH stretching), 1614 (urea CO stretching); LRMS (ES−): m/z: 389 [M−H]−; HRMS (ES+): m/z: act: 391.1554 [M+H]+ cal: 391.1553 [M+H]+

1-(9H-carbazol-1-yl)-3-(1H-indol-7-yl)urea (2) A solution of 1-isocyanato-9H-carbazole in chloroform (15 ml) was added dropwise to a stirring solution of 7-aminoindole3 (0.12 g, 0.94 mM) and TEA (2 ml) in chloroform (25 ml). The solution was heated to reflux under argon overnight. The product was isolated as a white precipitate which was removed by filtration and washed with hexane (20 ml). Yield 0.08 g, 26%; mp. 275 °C decomposition; 1H NMR (300 MHz, DMSO-d6): δ: 6.99 (t, 1H, ArH), 7.11-7.20 (m, 3H, ArH), 7.31-7.46 (m, 4H, ArH), 7.58 (d, 1H, ArH), 7.90 (d, 1H, ArH), 8.11 (d, 1H, ArH), 8.84 (s, 1H, urea NH), 8.88 (s, 1H, urea NH), 10.86 (s, 1H, indole NH), 10.93 (s, 1H, indole NH); 13C NMR (75 MHz, DMSO-d6): δ: 79.7 (ArCH), 101.5 (ArCH), 111.4 (ArCH), 113.4 (ArCH), 115.8 (ArCH), 115.9 (ArCH), 118.7 (ArCH), 118.8 (ArCH), 119.0 (ArCH), 120.2 (ArCH), 122.7 (ArC), 123.6 (ArC), 123.9 (ArC), 124.2 (ArC), 125.1 (ArCH), 125.6 (ArCH), 128.9 (ArC), 129.3 (ArC), 133.3 (ArC), 139.5 (ArC), 153.6 (CO); IR (film): ν = 3390 (indole NH stretching),

1-(9H-carbazol-1-yl)-3-phenylurea (3) A solution of phenylisocyanate (0.10 ml, 0.94 mM) in dichloromethane (10 ml) was added drop wise to a stirring solution of 1-aminocarbazole (0.12 g, 0.94 mM), in dichloromethane (30 ml). The solution was heated at reflux overnight and a white precipitate was removed by filtration and washed with dichloromethane (10 ml) and dried under vacuum. Yield 0.20 g, 69%; mp. 238 °C decomposition; ¹H NMR (300 MHz, DMSO-d₆): δ: 6.98 (t, 1H ArH), 7.10-7.19 (m, 2H, ArH), 7.30 (t, 2H, ArH), 7.36-7.42 (m, 2H, ArH), 7.52-7.59 (m, 3H, ArH), 7.89 (d, 1H, ArH), 8.10 (d, 1H, ArH), 8.53 (s, 1H, urea NH), 8.87 (s, 1H, urea NH), 10.81 (s, 1H, indole NH); ¹³C NMR (75 MHz, DMSO-d₆): δ: 111.4 (ArCH), 116.0 (ArCH), 118.4 (ArCH), 118.8 (ArCH), 119.3 (ArCH), 120.2 (ArCH), 121.8 (ArCH), 122.7 (ArC), 123.2 (ArC), 123.9 (ArC), 125.6 (ArCH), 128.8 (ArCH), 133.5 (ArC), 139.6 (ArC), 140.0 (ArC), 153.2 (CO); IR (film): ν = 3389 (indole NH stretching) , 3257 (urea NH stretching), 1626 (urea CO stretching); LRMS (ES⁺): m/z: 300 [M-H]⁺; HRMS (ES⁺): m/z: act: 302.1285 [M+H]⁺ cal: 302.1288 [M+H]⁺

Figure S1 ¹H NMR spectrum of 1-aminocarbazole in DMSO-d₆.
Figure S2 $^{13}$C NMR spectrum of 1-aminocarbazole in DMSO-$d_6$.

Figure S3 $^1$H NMR spectrum of compound 1 in DMSO-$d_6$. 
Figure S4 $^{13}$C NMR spectrum of compound 1 in DMSO-$d_6$.

Figure S5 $^1$H NMR spectrum of compound 2 in DMSO-$d_6$. 
**Figure S6** $^{13}$C NMR spectrum of compound 2 in DMSO-$d_6$.

**Figure S7** $^1$H NMR spectrum of compound 3 in DMSO-$d_6$. 
Figure S8 $^{13}$C NMR spectrum of compound 3 in DMSO-$d_6$. 
$K_a = <10^4 \text{ M}^{-1}$ Error = NA

**Figure S9** NMR titration of compound 1 vs. TBAAcO in DMSO-$d_6$/H$_2$O 0.5%.

$K_a = 5666 \text{ M}^{-1}$ Error = 10%

**Figure S10** NMR titration of compound 1 vs. TBABzO in DMSO-$d_6$/H$_2$O 0.5%.

$K_a = 102 \text{ M}^{-1}$ Error = 5%

**Figure S11** NMR titration of compound 1 vs. TBACl in DMSO-$d_6$/H$_2$O 0.5%.
Figure S12 NMR titration of compound 1 vs. TBAH$_2$PO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.

K$_a$ > 10$^4$ M$^{-1}$

Figure S13 NMR titration of compound 1 vs. TEAHO$_3$ in DMSO-$d_6$/H$_2$O 0.5%.

K$_a$ > 10$^4$ M$^{-1}$

Figure S14 NMR titration of compound 2 vs. TBAOAc in DMSO-$d_6$/H$_2$O 0.5%.
$K_a = 5880 \text{ M}^{-1}$ Error = 10%

**Figure S15** NMR titration of compound 2 vs. TBAOBz in DMSO-$d_6$/H$_2$O 0.5%.

$K_a = 139 \text{ M}^{-1}$ Error = 6%

**Figure S16** NMR titration of compound 2 vs. TBACl in DMSO-$d_6$/H$_2$O 0.5%.

**Figure S17** NMR titration of compound 2 vs. TBAH$_2$PO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.
$K_a = 154 \text{ M}^{-1}$ Error = 46%

**Figure S18** NMR titration of compound 2 vs. TBAF in DMSO-$d_6$/H$_2$O 0.5%.

$K_a > 10^4 \text{ M}^{-1}$

**Figure S19** NMR titration of compound 2 vs. TEAHO$_3$ in DMSO-$d_6$/H$_2$O 0.5%.

$K_a = > 10^4 \text{ M}^{-1}$

**Figure S20** NMR titration of compound 3 vs. TBAOAc in DMSO-$d_6$/H$_2$O 0.5%.
$K_a = 3420 \text{ M}^{-1} \text{ Error} = 10\%$

**Figure S21** NMR titration of compound 3 vs. TBAOBz in DMSO-$d_6$/H$_2$O 0.5%.

$K_a = 85 \text{ M}^{-1} \text{ Error} = 1\%$

**Figure S22** NMR titration of compound 3 vs. TBACl in DMSO-$d_6$/H$_2$O 0.5%.

$K_a = 6138 \text{ M}^{-1} \text{ Error} = 10\%$

**Figure S23** NMR titration of compound 3 vs. TBAH$_2$PO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.
$K_a = 36 \text{ M}^{-1}$ Error = 19%

**Figure S24** NMR titration of compound 3 vs. TBAF in DMSO-$d_6$/H$_2$O 0.5%.

$K_a > 10^4 \text{ M}^{-1}$

**Figure S25** NMR titration of compound 3 vs. TEA$\text{HCO}_3$ in DMSO-$d_6$/H$_2$O 0.5%.
**Figure S26** Fluorescence quenching of 1 in DMSO upon the addition of tetrabutylammonium acetate.

**Figure S27** Fluorescence quenching of 1 in DMSO upon the addition of tetrabutylammonium chloride.
**Figure S28** Fluorescence quenching of 1 in DMSO upon the addition of tetrabutylammonium fluoride.

**Figure S29** Fluorescence quenching of 1 in DMSO upon the addition of tetrabutylammonium dihydrogen phosphate.
Figure S30 Fluorescence quenching of 1 in DMSO upon the addition of tetraethylammonium bicarbonate.

Figure S31 Fluorescence quenching of 2 in DMSO upon the addition of tetrabutylammonium acetate.
Figure S32 Fluorescence quenching of 2 in DMSO upon the addition of tetrabutylammonium benzoate.

Figure S33 Fluorescence quenching of 2 in DMSO upon the addition of tetrabutylammonium chloride.
**Figure S34** Fluorescence quenching of 2 in DMSO upon the addition of tetrabutylammonium fluoride.

**Figure S35** Fluorescence quenching of 2 in DMSO upon the addition of tetrabutylammonium dihydrogen phosphate.
Figure S36 Fluorescence quenching of 2 in DMSO upon the addition of tetraethylammonium bicarbonate.

Figure S37 Fluorescence quenching of 3 in DMSO upon the addition of tetrabutylammonium acetate.
Figure S38 Fluorescence quenching of 3 in DMSO upon the addition of tetrabutylammonium benzoate.

Figure S39 Fluorescence quenching of 3 in DMSO upon the addition of tetrabutylammonium chloride.
**Figure S40** Fluorescence quenching of 3 in DMSO upon the addition of tetrabutylammonium fluoride.

**Figure S41.** Fluorescence quenching of 3 in DMSO upon the addition of tetrabutylammonium dihydrogen phosphate.
Figure S42. Fluorescence quenching of 3 in DMSO upon the addition of tetraethylammonium bicarbonate.

Figure S43. Effect of increasing anion concentration upon the relative fluorescence emission of receptor 2 in DMSO/0.5% water.
**Figure S44.** Effect of increasing anion concentration upon the relative fluorescence emission of receptor 3 in DMSO/0.5% water.

**Figure S45** Effect of increasing tetraethylammonium bicarbonate concentration on the UV/vis spectrum of compound 1 between 0 and 9 eq anion.
**Figure S46** Effect of increasing tetrabutylammonium fluoride trihydrate concentration on the UV/vis spectrum of compound 1 between 0 and 9 eq anion.

**Figure S47** Effect of increasing tetrabutylammonium benzoate concentration on the UV/vis spectrum of compound 1 between 0 and 9 eq anion.
Figure S48 Effect of increasing tetaethylammonium hydrogen carbonate concentration on the UV/vis spectrum of compound 2 between 0 and 9 eq anion.

Figure S49 Effect of increasing tetrabutylammonium fluoride trihydrate concentration on the UV/vis spectrum of compound 2 between 0 and 9 eq anion.
**Figure S50** Effect of increasing tetrabutylammonium benzoate concentration on the UV/vis spectrum of compound 2 between 0 and 9 eq anion.

**Figure S51** Effect of increasing tetraethylammonium bicarbonate concentration on the UV/vis spectrum of compound 3 between 0 and 9 eq anion.
Figure S52 Effect of increasing tetrabutylammonium fluoride trihydrate concentration on the UV/vis spectrum of compound 3 between 0 and 9 eq anion.

Figure S53 Effect of increasing tetrabutylammonium benzoate concentration on the UV/vis spectrum of compound 3 between 0 and 9 eq anion.
