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Philip Alan Gale

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Fluorescent Anthracene-based Anion Receptors

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Fluorescent anthracene-based anion receptors

Simon J. Brooks,^a Claudia Caltagirone,^a Aimee J. Cossins,^b Philip A. Gale^{*a} and Mark E. Light^a

Supplementary Information.

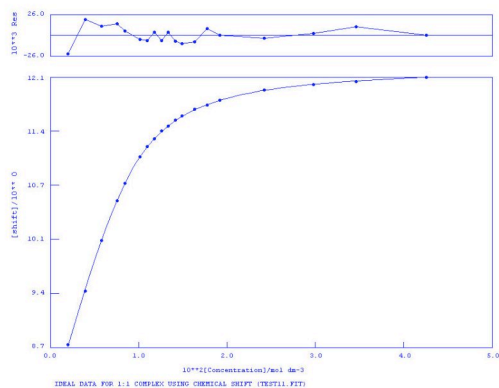
For Peer Review Only

^1H NMR TITRATION CURVES. **N^1,N^2 -dibutylanthracene-1,2-dicarboxamide (1) in $\text{CD}_2\text{Cl}_2-d_2$.**

Benzoate.

 $K_a = 709$

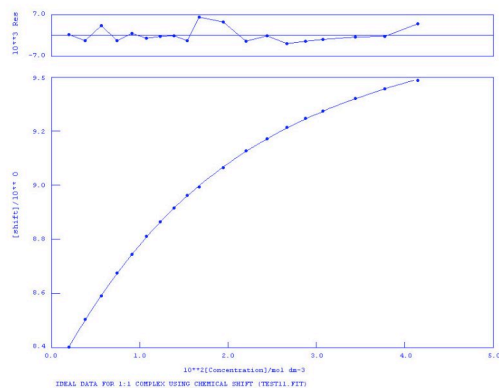
Error = 1.6 %



Bromide.

 $K_a = 67$

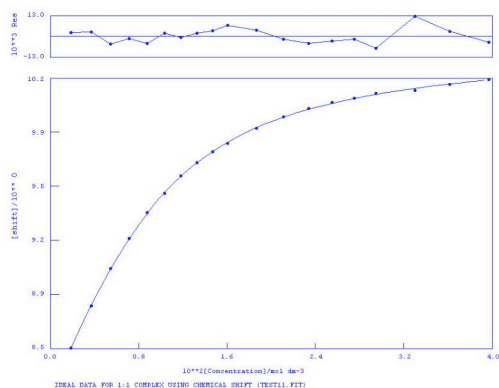
Error = 1.4 %



Chloride.

 $K_a = 238$

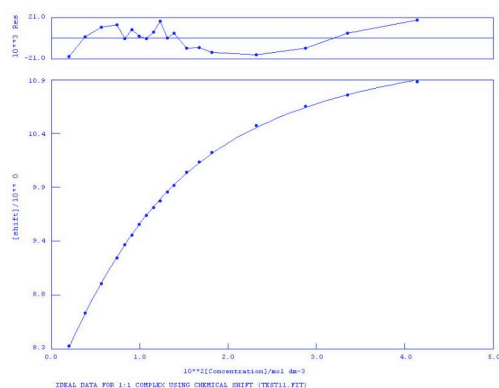
Error = 1.4 %



Dihydrogen Phosphate.

 $K_a = 128$

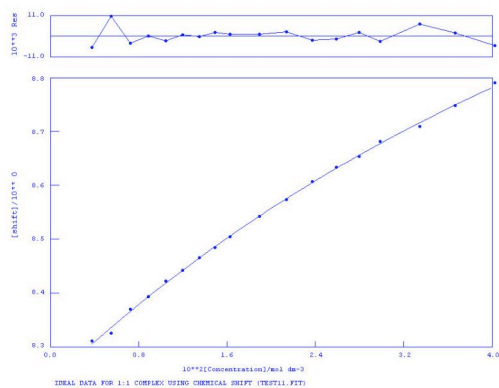
Error = 2.3 %



Hydrogen Sulfate.

 $K_a = 14$

Error = 11.3 %

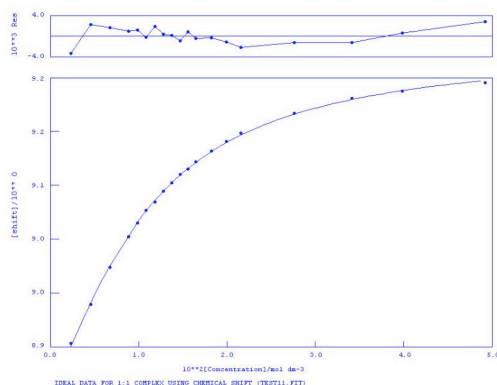


N^1,N^3 -dibutylanthracene-1,3-dicarboxamide (3) in $CD_2Cl_2-d_2$.

Benzoate.

$$K_a = 173$$

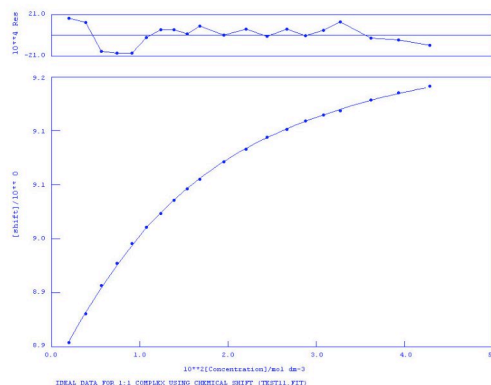
Error = 2.2 %



Bromide.

$$K_a = 92$$

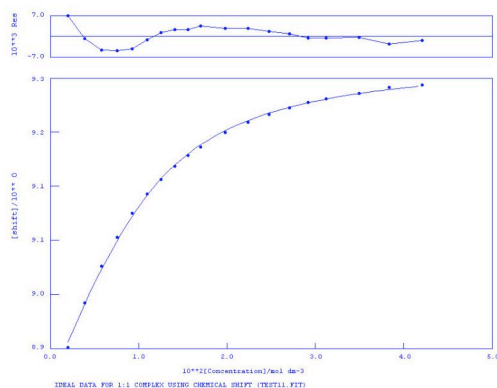
Error = 2.0%



Chloride.

$$K_a = 257$$

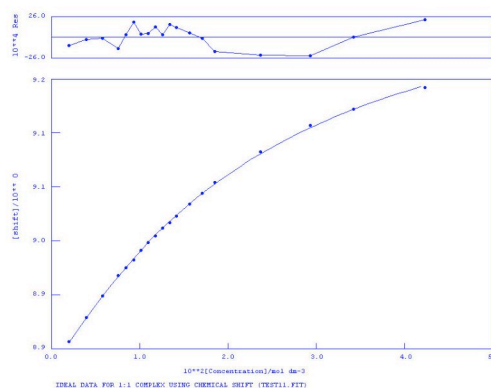
Error = 4.7 %



Dihydrogen Phosphate.

$$K_a = 52$$

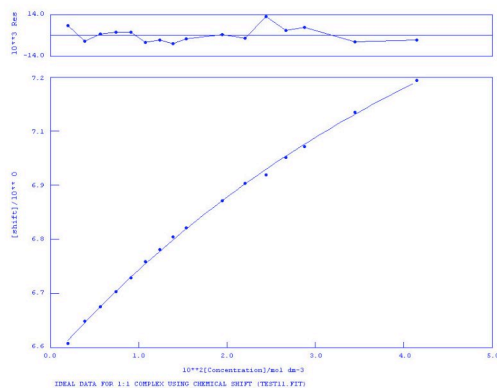
Error = 2.9 %



Hydrogen Sulfate.

$$K_a = 16$$

Error = 10.0 %

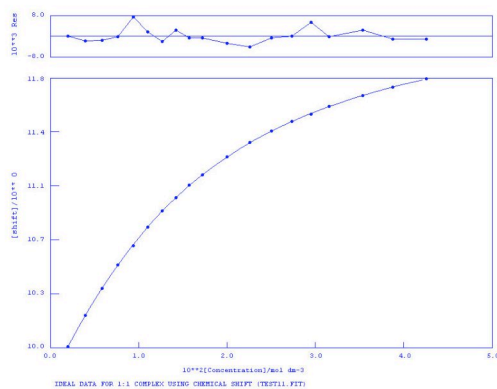


N^1,N^2 -dibutylanthracene-1,2-dicarboxamide (1) in DMSO- d_6 /0.5% water.

Acetate.

 $K_a = 85$

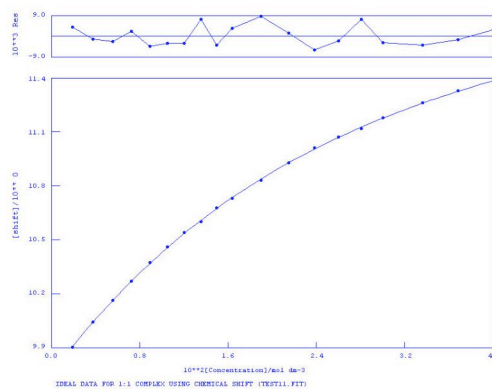
Error = 0.9 %



Benzoate.

 $K_a = 44$

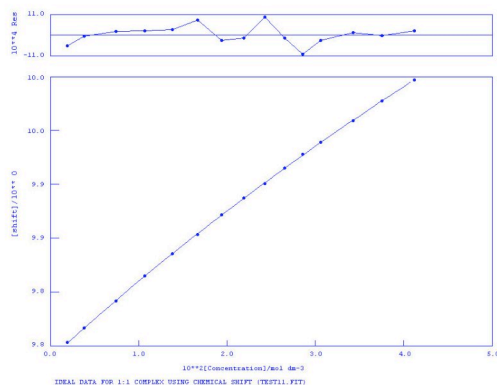
Error = 2.1 %



Chloride.

 $K_a < 10$

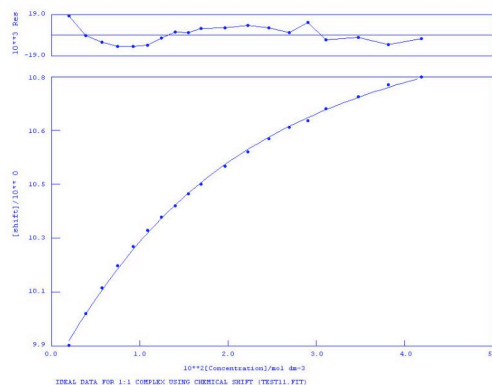
Error = 4.5 %



Dihydrogen Phosphate.

 $K_a = 64$

Error = 5.4 %

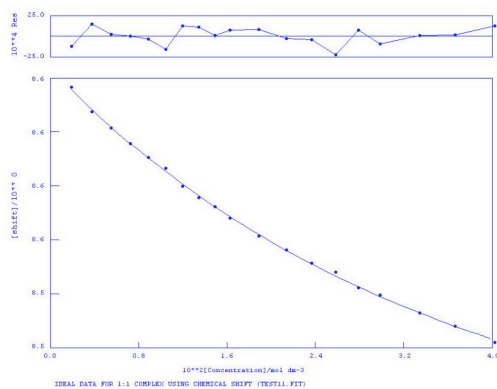


N^1,N^2 -diphenylanthracene-1,2-dicarboxamide (2) in DMSO- d_6 /0.5% H₂O.

Acetate.

$$K_a = 28$$

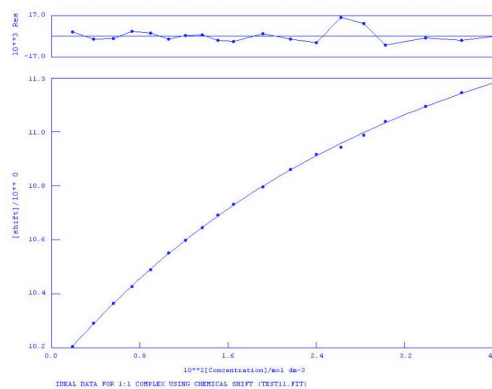
Error = 6.1 %



Benzoate.

$$K_a = 34$$

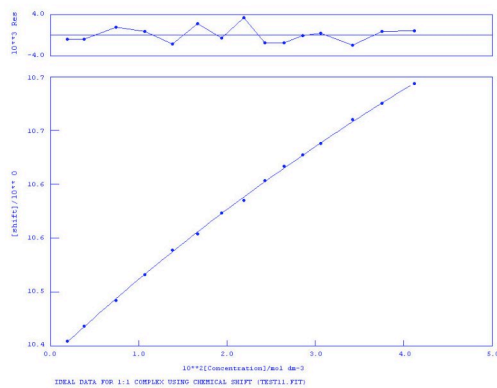
Error = 3.9 %



Chloride.

$$K_a = <10$$

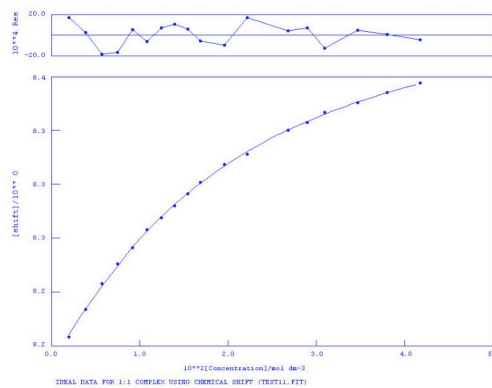
Error = 10.7 %



Dihydrogen Phosphate.

$$K_a = 63$$

Error = 4.1 %

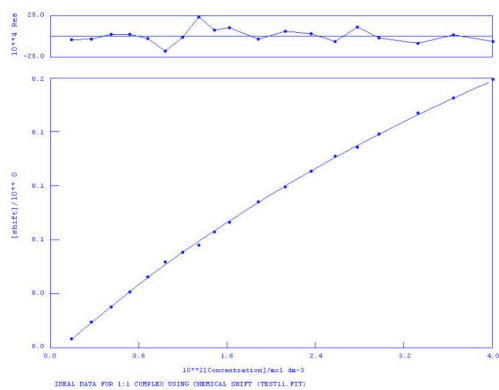


N^1, N^3 -dibutylanthracene-1,3-dicarboxamide (3) in DMSO- d_6 /0.5% water.

Acetate.

 $K_a = 13$

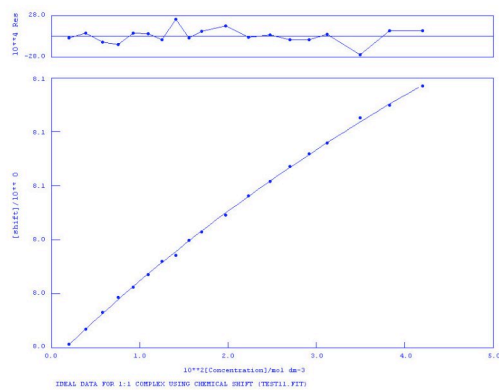
Error = 5.8 %



Benzoate.

 $K_a = <10$

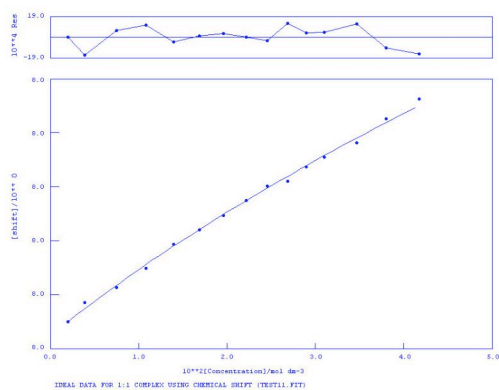
Error = 9.6 %



Chloride.

 $K_a = <10$

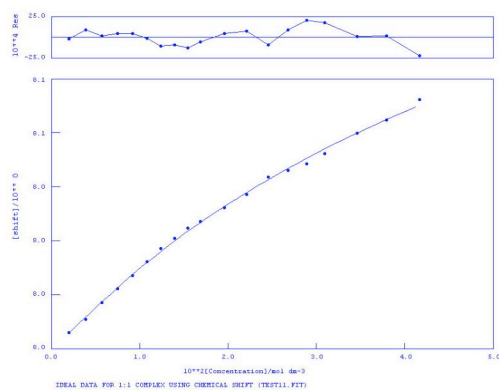
Error = 33.0 %



Dihydrogen Phosphate.

 $K_a = 19$

Error = 10.9 %

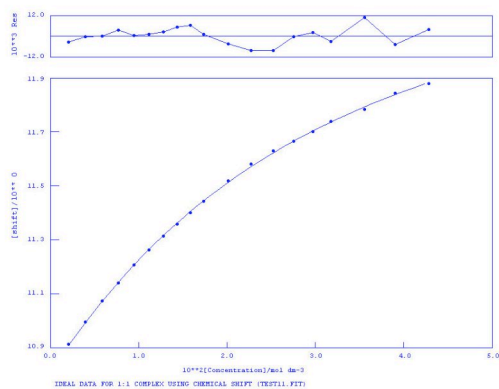


N^1, N^3 -diphenylanthracene-1,3-dicarboxamide (4) in DMSO- d_6 /0.5% water.

Acetate.

$$K_a = 37$$

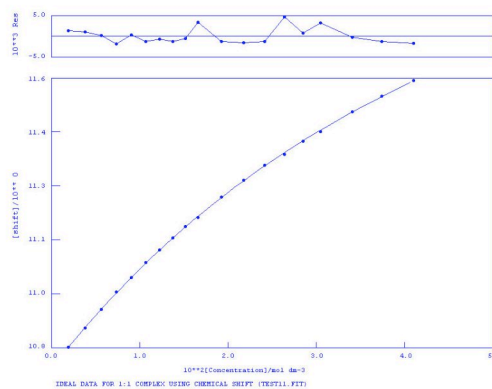
Error = 3.3 %



Benzoate.

$$K_a = 21$$

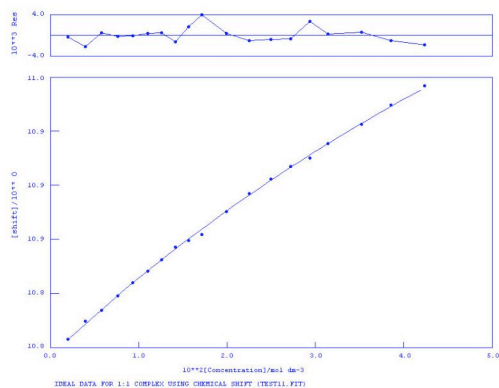
Error = 2.4 %



Chloride.

$$K_a = <10$$

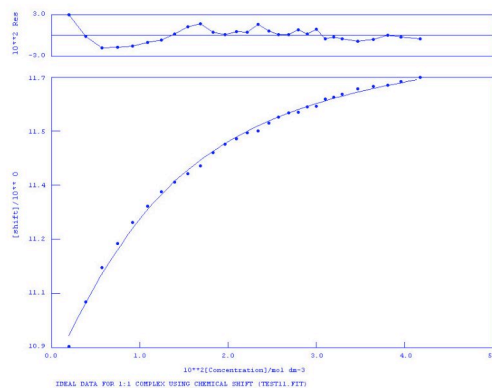
Error = 7.1 %



Dihydrogen Phosphate.

$$K_a = 122$$

Error = 6.6 %

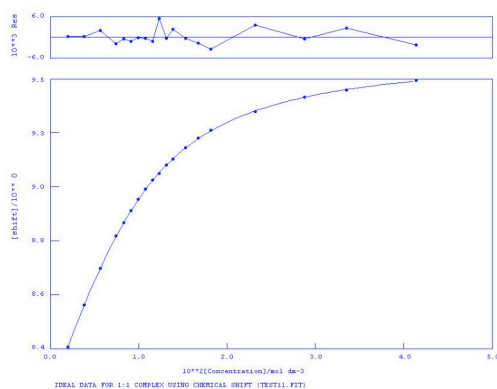


1,2-Anthracene bis-butylurea (5) in DMSO-*d*₆/0.5% water.

Acetate.

$K_a = 277$

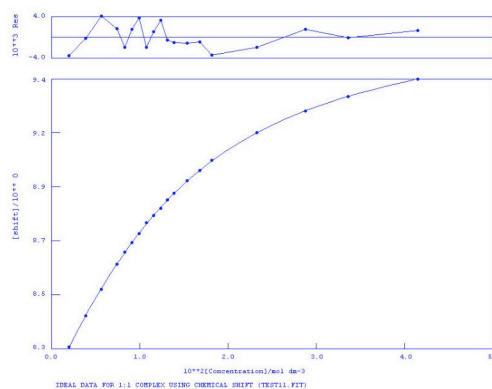
Error = 1.0 %



Benzoate.

$K_a = 107$

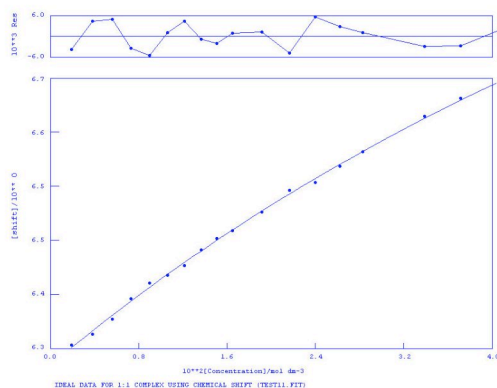
Error = 1.2%



Chloride.

$K_a = 10$

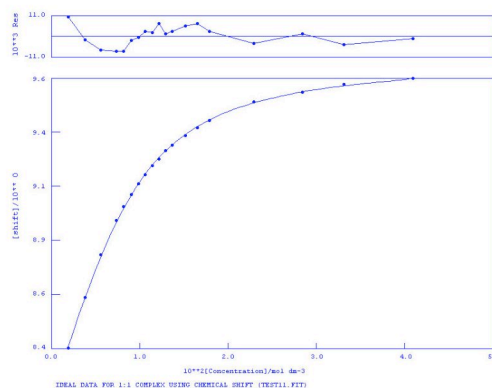
Error = 13.2 %



Dihydrogen Phosphate.

$K_a = 370$

Error = 2.1%

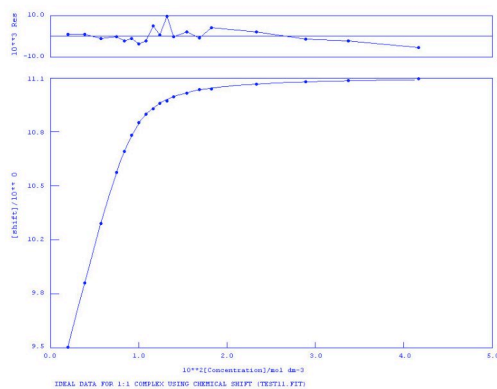


1,2-Anthracene bis-phenylurea (6) in DMSO-*d*₆/0.5% water.

Acetate.

$$K_a = 2539$$

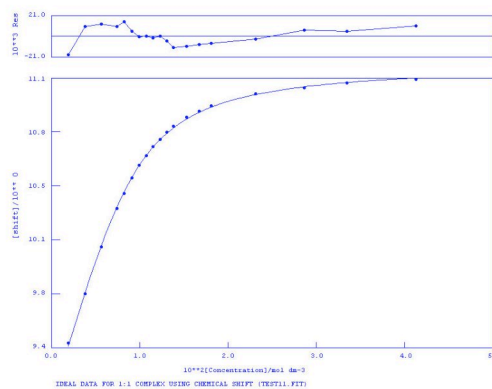
Error = 1.4 %



Benzoate.

$$K_a = 586$$

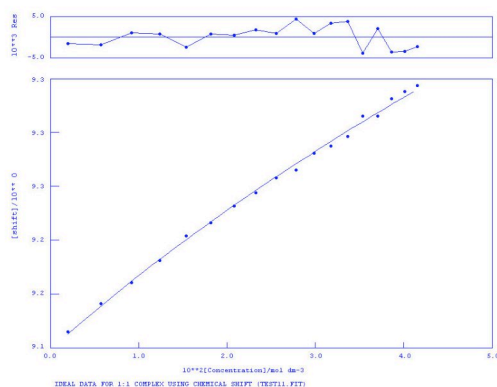
Error = 2.9 %



Bromide.

$$K_a = <10$$

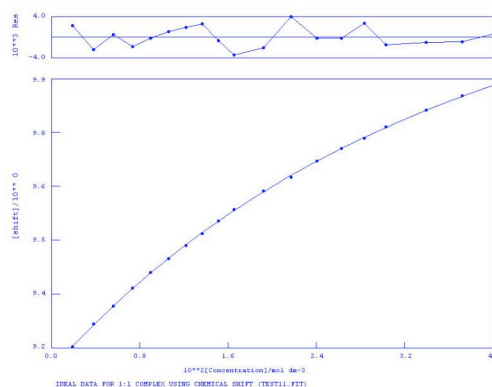
Error = 29.9 %



Chloride.

$$K_a = 27$$

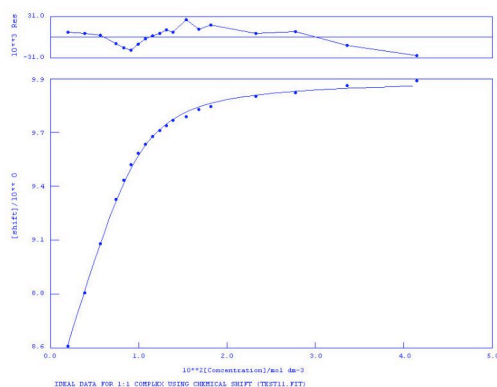
Error = 2.4 %



Dihydrogen Phosphate.

$$K_a = 1166$$

Error = 6.2 %



FLUORESCENCE INTENSITY/MOLAR RATIO PLOTS FOR 5

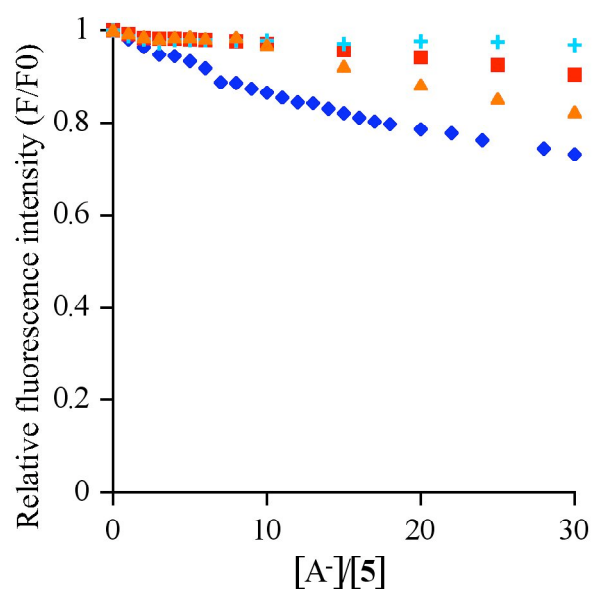


Fig. S1 Fluorescence intensity/molar ratio plots for **5** [1×10^{-6} M, MeCN/DMSO (96.5/3.5 v/v)] in the presence of increasing amounts of AcO⁻ (♦), H₂PO₄²⁻ (▲), BzO⁻ (■) and Cl⁻ (+).

ADDITIONAL CRYSTAL IMAGES

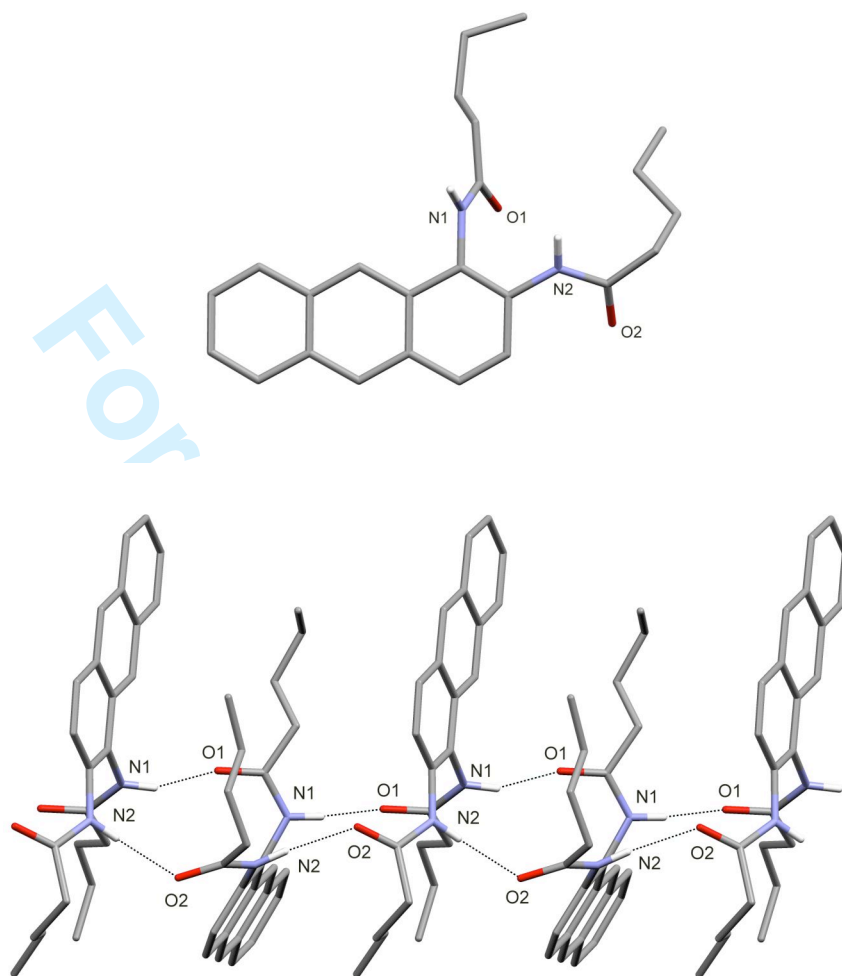


Fig. S2 The solid state structure of **1** obtained from acetonitrile solution, reveals extensive hydrogen bonding interactions in the solid state. Non-acidic protons omitted for clarity.

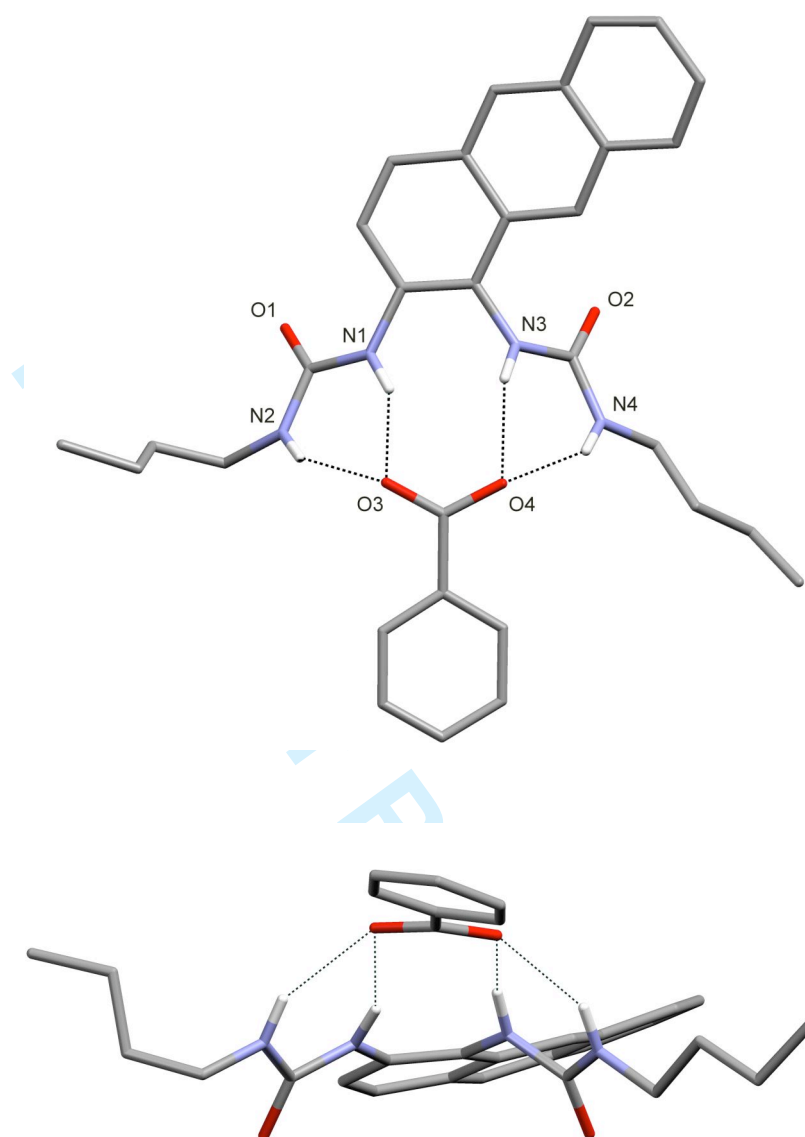


Fig. S3 Benzoate complex of **5** reveals that the anion is bound simultaneously by all four NH donor groups.

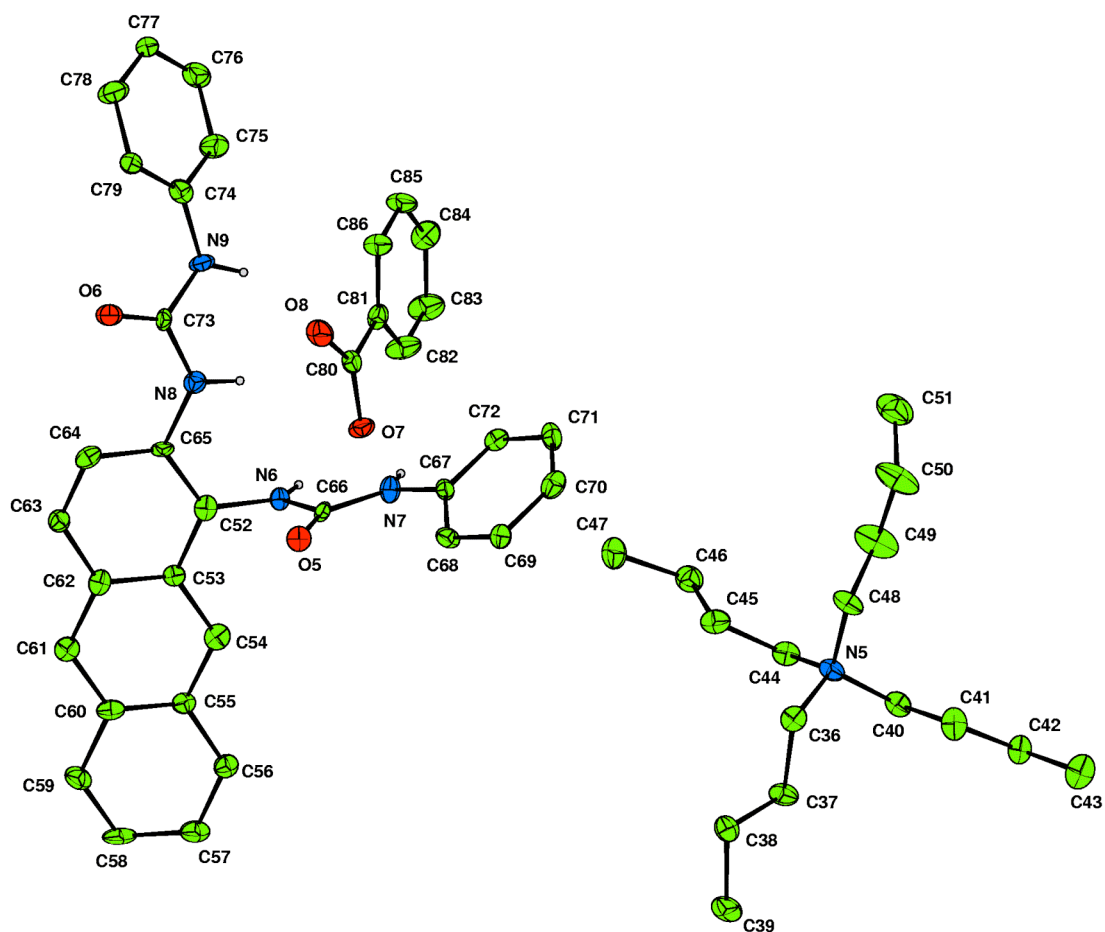


Figure S4 The Tetrabutylammonium benzoate complex of compound 6. Thermal ellipsoids drawn at the 35% probability level. Only half the contents of the asymmetric unit are shown

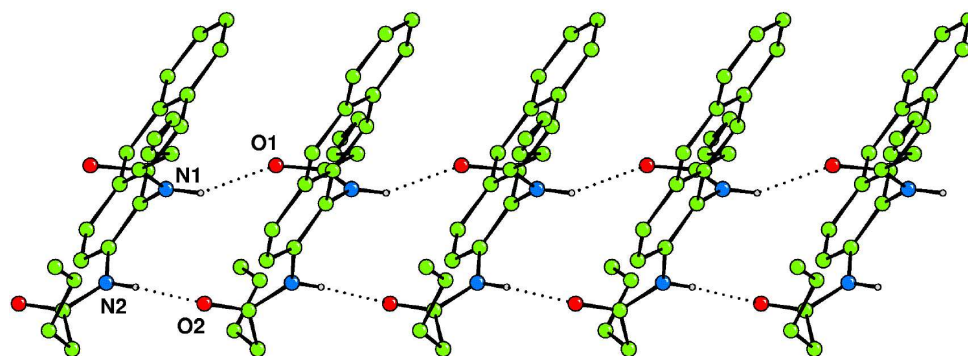


Figure 1. Receptor 1 forms hydrogen-bonded chains in the solid state. Non-acidic hydrogen atoms have been omitted for clarity.
149x54mm (300 x 300 DPI)

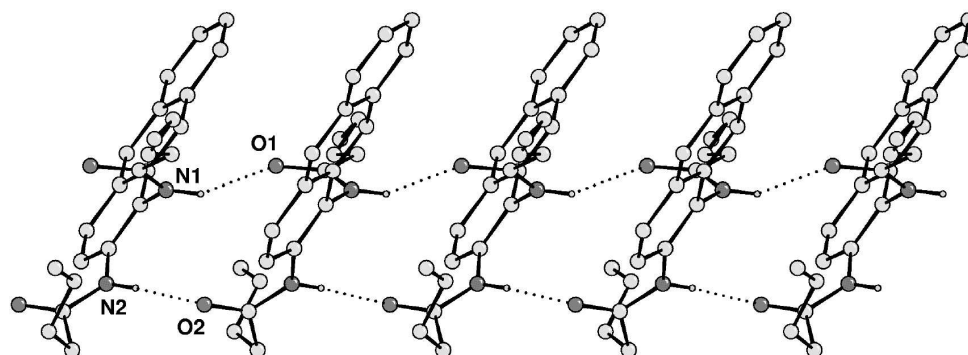


Figure 1. Receptor 1 forms hydrogen-bonded chains in the solid state. Non-acidic hydrogen atoms have been omitted for clarity.
149x54mm (300 x 300 DPI)

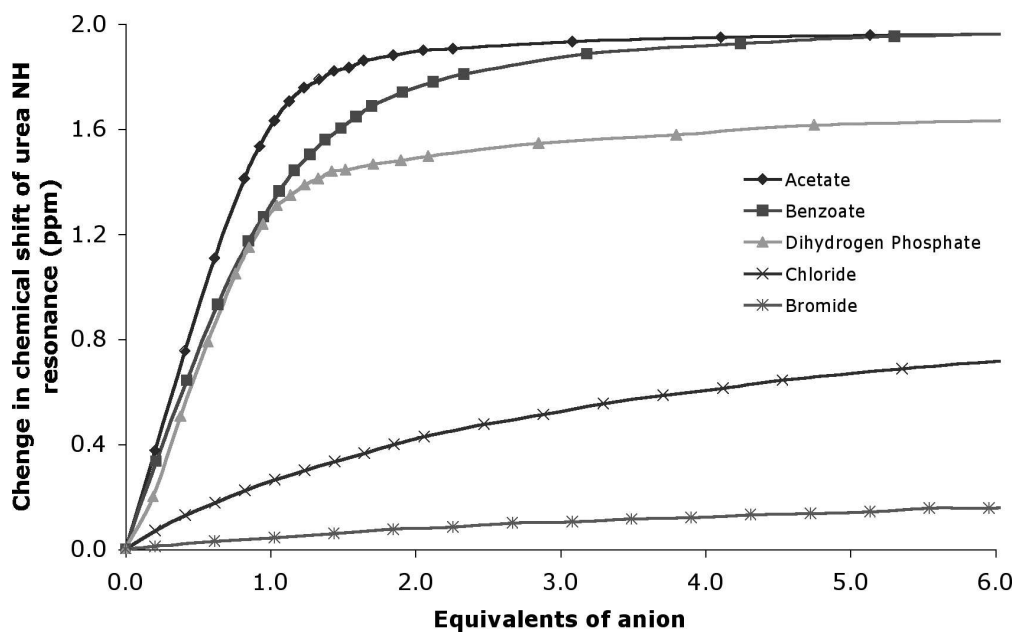


Figure 2. Shifts of the central urea NH groups of compound 6 upon the addition of tetrabutylammonium salts in DMSO-d₆/0.5% water.
143x88mm (300 x 300 DPI)

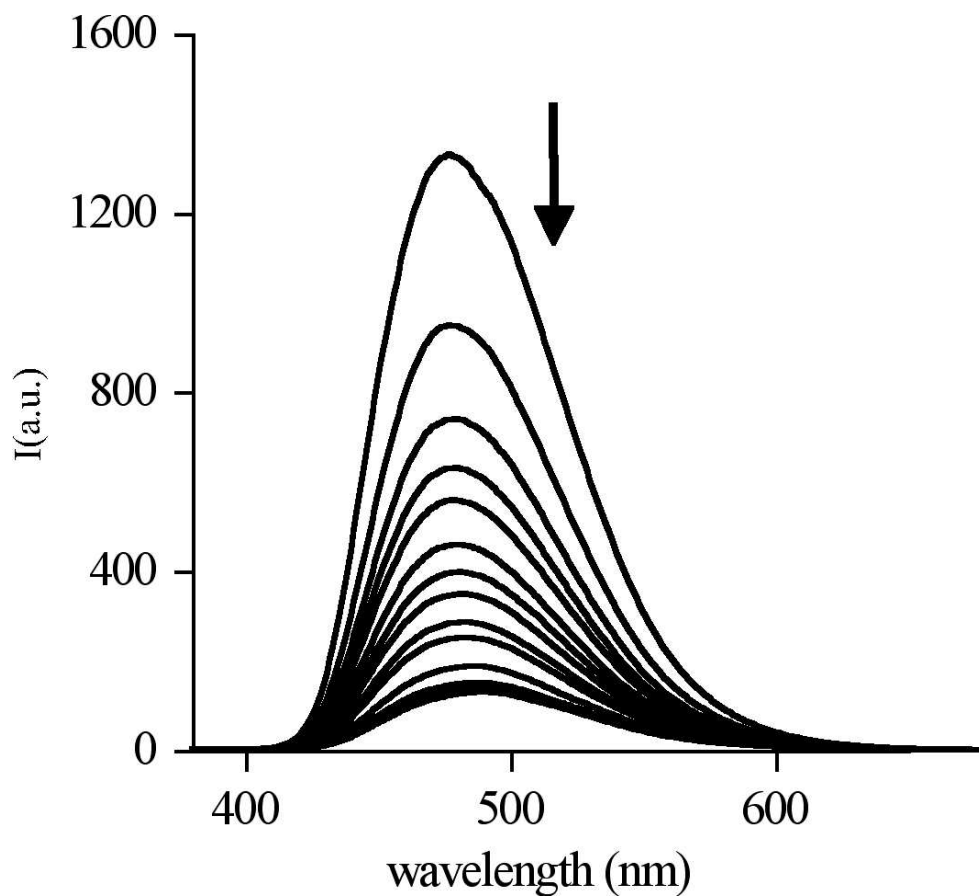
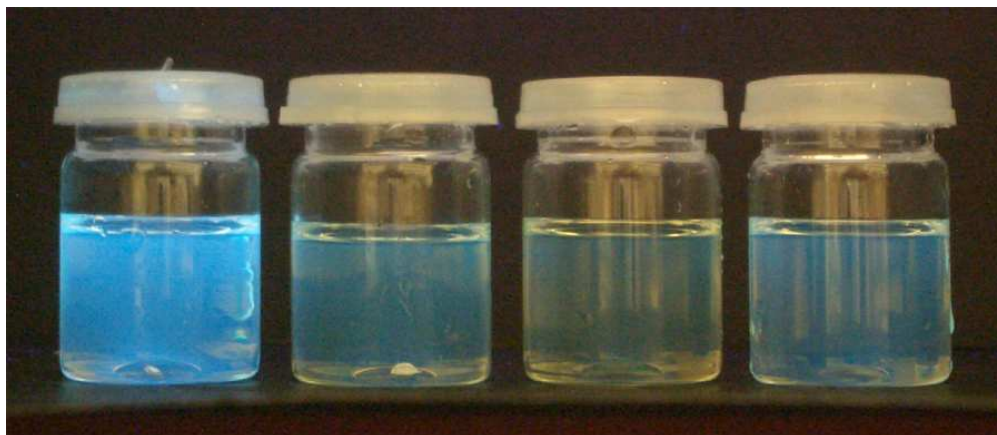


Figure 3. Fluorescence quenching of 6 in DMSO upon the addition of tetrabutylammonium acetate
92x81mm (300 x 300 DPI)

Only



76x32mm (300 x 300 DPI)

er Review Only

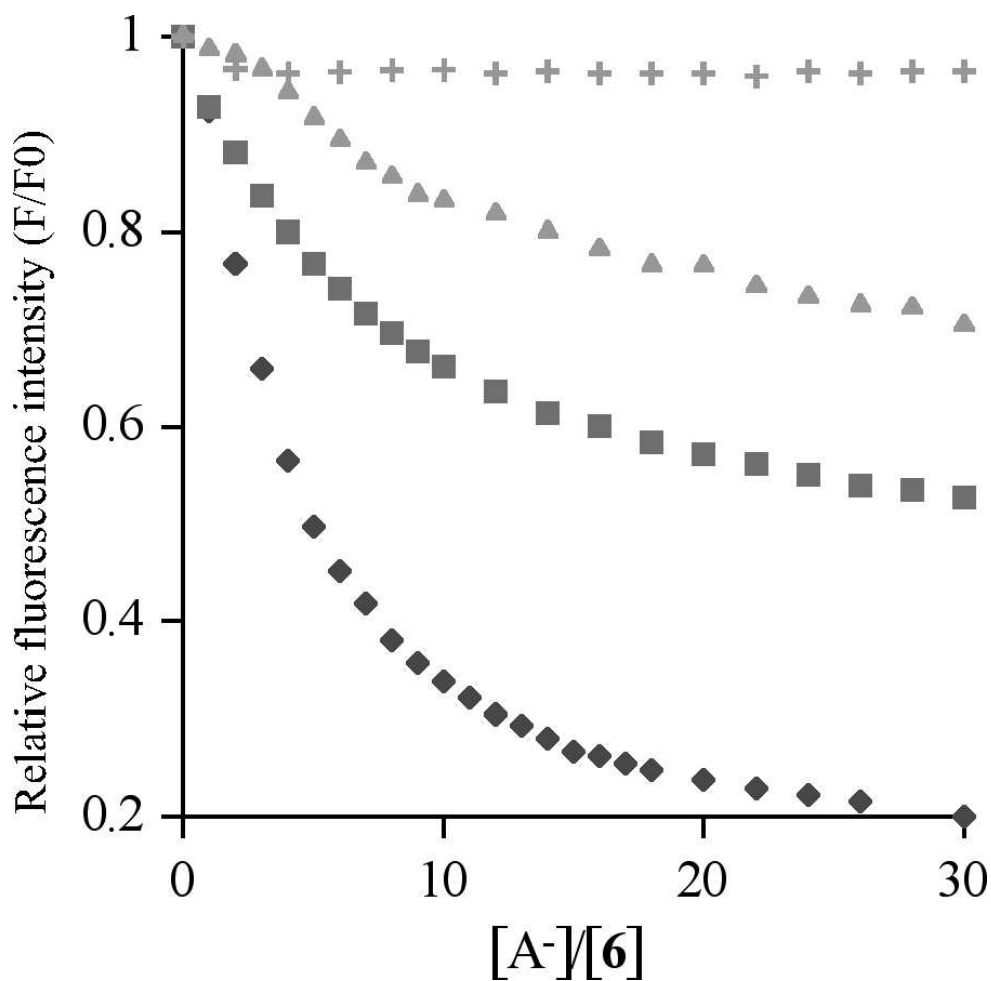


Figure 5. Fluorescence intensity/molar ratio plots for **6** [1×10^{-6} M, MeCN/DMSO (96.5/3.5 v/v)] in the presence of increasing amounts of AcO⁻ (?), H₂PO₄⁻ (?), BzO⁻ (?) and Cl⁻ (+).
78x75mm (300 x 300 DPI)

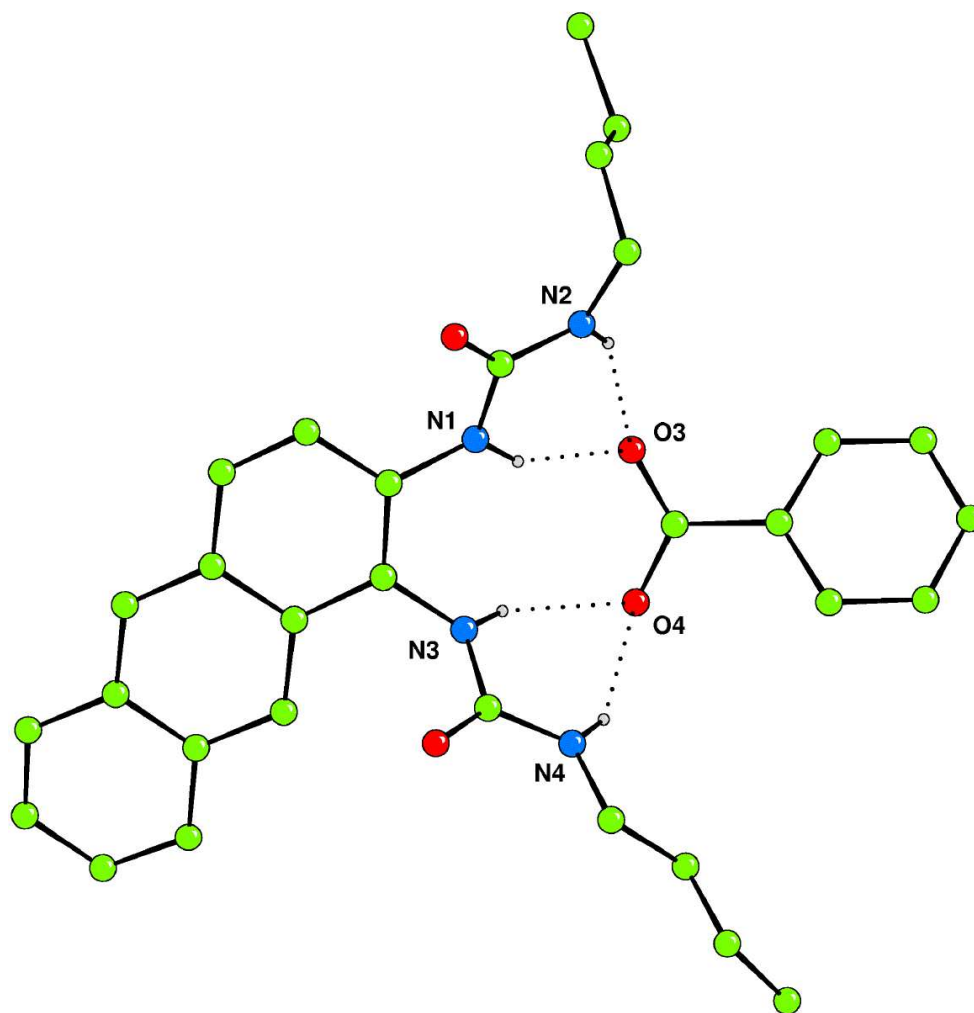


Figure 6 The benzoate complex of 5 showing the formation of four hydrogen bonds between the receptor and the carboxylate anion in the solid state. Tetrabutylammonium counter cations and non-acidic hydrogen atoms omitted for clarity.
100x103mm (300 x 300 DPI)

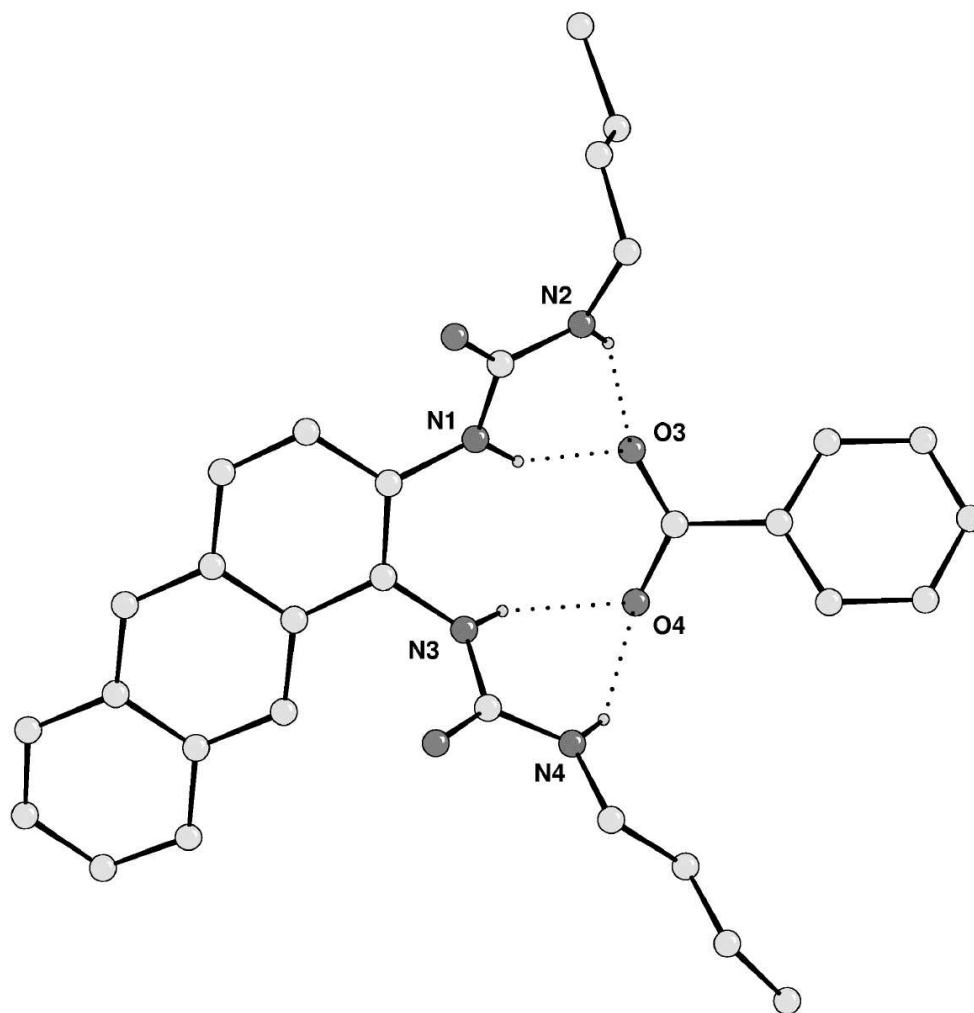


Figure 6 The benzoate complex of 5 showing the formation of four hydrogen bonds between the receptor and the carboxylate anion in the solid state. Tetrabutylammonium counter cations and non-acidic hydrogen atoms omitted for clarity.
100x103mm (300 x 300 DPI)



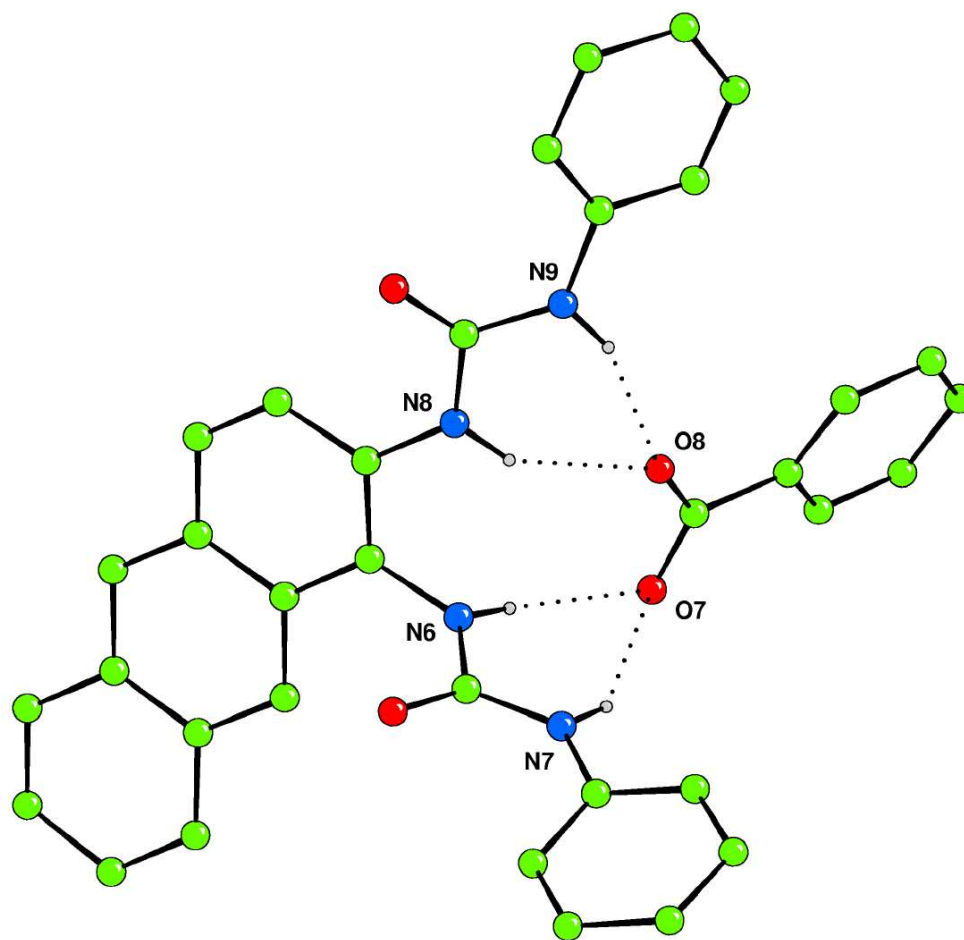


Figure 7 The benzoate complex of 6 showing the formation of four hydrogen bonds between the receptor and the carboxylate anion in the solid state. Tetrabutylammonium counter cations and non-acidic hydrogen atoms omitted for clarity
94x89mm (300 x 300 DPI)

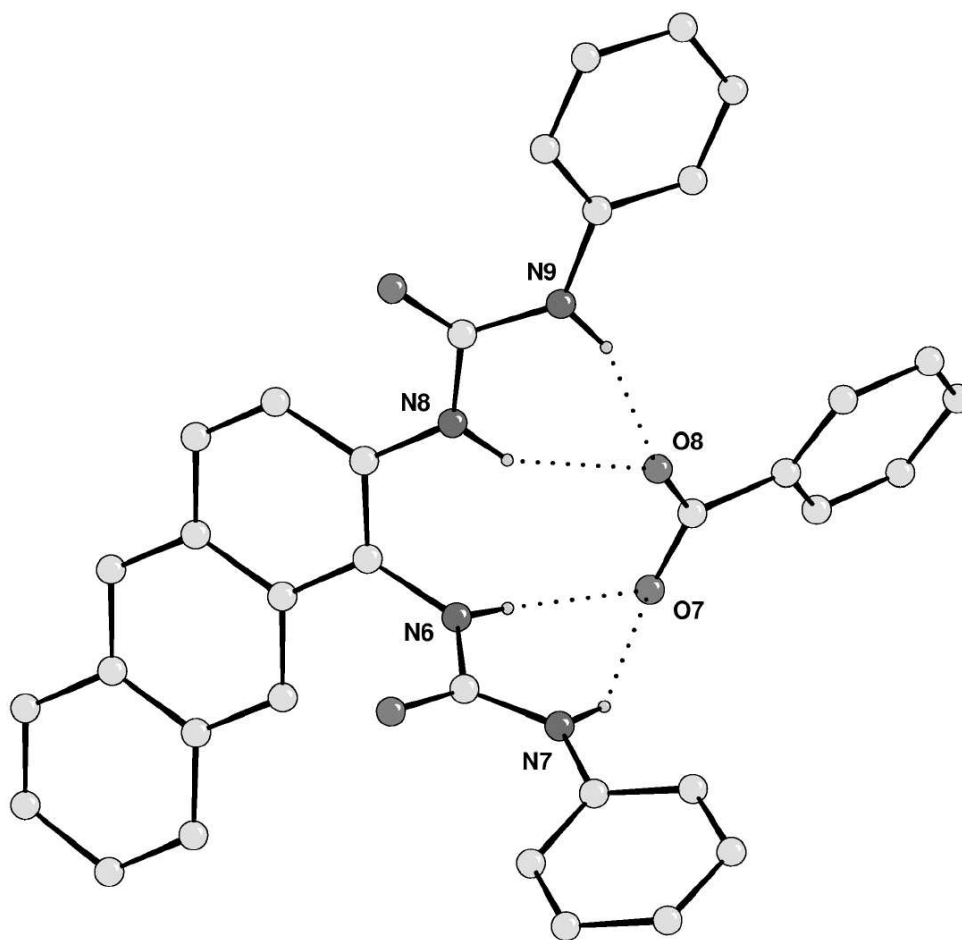


Figure 7 The benzoate complex of 6 showing the formation of four hydrogen bonds between the receptor and the carboxylate anion in the solid state. Tetrabutylammonium counter cations and non-acidic hydrogen atoms omitted for clarity
94x89mm (300 x 300 DPI)

Fluorescent Anthracene-based Anion Receptors

Simon J. Brooks^a, Claudia Caltagirone,^a Aimee J. Cossins^b, Philip A.

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^b*School of Biological Science, University of Southampton, Southampton, SO16 7PX, UK*

Keywords

Anion receptors, fluorescence, urea, crystallography

Abstract

A variety of amide-substituted anthracene derivatives have been synthesised and their anion complexation properties studied using ¹H-NMR titration techniques. Additionally, bis-urea functionalised anthracene derivatives have been shown to serve as excellent receptors for oxo-anions and to function as sensors *via* fluorescence quenching in DMSO-d₆/0.5% water and MeCN/DMSO (96.5:3.5 v/v).

Introduction

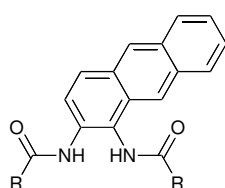
The development of simple hydrogen-bond donor anion receptors and sensors is an area of anion complexation that is yet to be fully explored.¹ In 1997, Crabtree² and Smith³ independently discovered that simple isophthalamides function as effective anion receptors. Since this discovery, this motif has been further exploited in the formation of new anion⁴ and ion-pair receptors⁵ along with anion-templated helices⁶, catenanes⁷ and

1
2
3
4 rotaxanes.⁸ Similarly, ureas⁹ and thioureas¹⁰ have been used for anion complexation due
5
6 to both the relative ease in which they can be synthesized and for their propensity to
7
8 form strong complexes with oxo-anions such as carboxylates and phosphates. Much
9
10 effort has also been devoted to the production of anion sensors that combine both an
11
12 anion binding site and either a chromophore¹¹ or a redox active group¹² that in the
13
14 presence of a coordinating anion show a perturbation in their optical or electrochemical
15
16 properties.
17
18

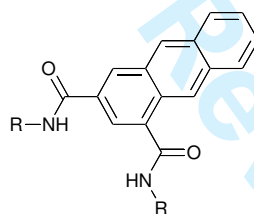
19
20 We have recently reported the synthesis of receptors based upon anthraquinone that
21
22 contain a 'twisted' isophthalamide-like hydrogen-bonding cleft that show an increase in
23
24 oxo-anion selectivity, relative to non distorted isophthalamides¹³, and also receptors
25
26 based upon 1,2-phenylenediamine that contain amide or urea groups that can adopt a
27
28 more planar geometry.¹⁴ We wished to further investigate the relative merits of each
29
30 hydrogen bonding motif in terms of both its strength and selectivity of anion
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32 coordination in potential anion sensor system that would potentially show a change in
33
34 fluorescence properties upon the addition of coordinating anions. Previously, numerous
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36 research groups have produced anthracene based anion sensors¹⁵ including those
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38 reported by Gunnlaugsson and coworkers that demonstrated high affinities for oxo-
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40 anions. Therefore receptors **1-4** based upon 1,2- and 1,3-substituted anthracenes were
41
42 synthesised in an attempt to establish how effective each motif would be at complexing
43
44 anions in both non-polar and competitive solvent mixtures when appended to an
45
46 anthracene backbone by means of ¹H-NMR titrations.
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54 We also wished to investigate the use of bis-urea based anthracene receptors as an
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56 alternative method for complexing anions. Das and coworkers have demonstrated that
57
58 bis-urea and bis-thiourea receptors based upon 1,2-diaminoanthraquinone can form
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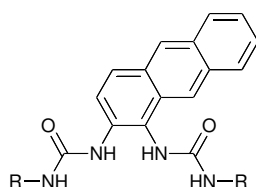
1
2
3
4 strong complexes with a variety of anions in MeCN/DMSO (90/10 v/v) solution.¹⁶
5
6 More recently we have demonstrated that in simpler systems based upon 1,2-
7 phenylenediamine, carboxylate anions can be coordinated to this type of motif in a 1:1
8 anion :receptor stoichiometry through four hydrogen bonds with relatively strong
9 stability constants obtained in DMSO/water solvent mixtures.¹⁷ We hoped similarly
10 strong complexes would be formed with receptors based upon the 1,2-
11 diaminoanthracene subunit. For these reasons we synthesised compounds **5** and **6** and
12 we studied their ability in binding anions by means of ¹H-NMR titrations in DMSO-
13 *d*₆/0.5% water and fluorescent titrations both in DMSO and in MeCN/DMSO (96.5:3.5
14 v/v).
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1 R = Bu
2 R = Ph



3 R = Bu
4 R = Ph



5 R = Bu
6 R = Ph

Experimental

General Methods

Reagents were purchased from the Aldrich Chemical Co. Deuterated solvents were purchased from Apollo Ltd. Chemical shifts reported in ppm and are referenced to the solvent. Proton and ^{13}C -NMR spectra were recorded on a Bruker AV-300 NMR spectrometer. UV/vis absorbance spectra were recorded on a Hitachi U-2001 spectrophotometer with fluorescence emission spectra recorded on a Hitachi F-2000 spectrofluorimeter with a 150W Xenon lamp. The photomultiplier voltage was set to 400V with excitation and emission slits set to 10 mm. Fluorescence titrations were performed by adding to a solution of the receptors (1×10^{-6} M) in DMSO and MeCN/DMSO (96.5/3.5 v/v) solutions of anions (2.5×10^{-3} M) in a solution of the receptor in order to keep constant the concentration of the receptor during the titration.

Luminescence quantum yields were determined using quinine sulphate in 1M H_2SO_4 aqueous solution ($\Phi = 0.546$) as reference.

Elemental analyses were performed by Medac Ltd.

Synthesis

N^1, N^2 -Dibutylanthracene-1,2-dicarboxamide (1).

Anthracene-1,2-diamine (0.50 g, 2.4 mmol), triethylamine (0.74 mL, 5.3 mmol) and DMAP (a few mg, cat.) were stirred together for 15 minutes in dry DCM (15 mL) before the dropwise addition of valeroyl chloride (0.56 mL, 4.8 mmol). The reaction was stirred at ambient temperature under nitrogen for 18 hours. After this time the reaction solvent was washed with water (3×25 mL) before the remaining solvent was removed *in vacuo*. The residue was recrystallized from hot ethyl acetate and purified by

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flash column chromatography (90/10 DCM/MeOH v/v), with the product isolated as a yellow/beige solid. Mass of product = 0.35 g. Yield = 39%. ^1H NMR 300 MHz in DMSO- d_6 δ (ppm): 9.75 (s, 1H, NH), 9.21 (s, 1H, NH), 8.57 (s, 1H, ArH), 8.46 (s, 1H, ArH), 8.04 (m, 3H, ArH), 7.80 (d, 1H, J = 9.1 Hz, ArH), 7.52 (m, 2H, ArH), 2.59 (t, 2H, J = 7.2 Hz, CH₂), 2.39 (t, 2H, J = 7.2 Hz, CH₂), 1.71 (m, 2H, CH₂), 1.62 (m, 2H, CH₂), 1.46 (m, 2H, CH₂), 1.37 (m, 2H, CH₂), 0.97 (t, 3H, J = 7.5 Hz, CH₃), 0.93 (t, 3H, J = 7.5 Hz, CH₃). ^{13}C NMR 75.4 MHz in DMSO- d_6 δ (ppm): 173.6 (CO), 172.83 (CO), 131.78 (C), 131.3 (C), 130.0 (C), 129.3 (C), 128.4 (CH), 128.0 (CH), 127.8 (CH), 127.6 (CH), 126.8 (CH), 126.0 (CH), 125.8 (CH), 123.7 (C), 123.5 (CH), 121.3 (CH), 37.1 (CH₂), 36.6 (CH₂), 28.3 (CH₂), 27.8 (CH₂), 22.6 (CH₂), 22.5 (CH₂), 14.0 (CH₃), 13.9 (CH₃). IR (cm⁻¹): 3241, 2953, 2933, 2868, 1652, 1530, 1425, 1289, 1185, 1093, 880, 736. ES- mass spectrem, m/z , 411.0 [M + Cl]⁻, 489.1 [M + TFA - H]⁻, 787.4 [2M + Cl]⁻, 865.3 [2M + TFA - H]⁻. R_f: 0.56 (90:10 DCM/MeOH). Anal. Found for C₂₄H₂₈N₂O₂ (Calcd) (%) C 76.50 (76.56), H 7.50 (7.50), N 7.42 (7.44)%. m.p. (DCM/MeOH) = 176 °C.

***N*¹,*N*²-Diphenylanthracene-1,2-dicarboxamide (2).**

Anthracene-1,2-diamine (0.77 g, 3.7 mmol), triethylamine (1.12 mL, 8.14 mmol) and DMAP (a few mg, cat.) were stirred together for 15 minutes in dry DCM (75 mL) before the dropwise addition of benzoyl chloride (0.86mL, 7.4 mmol). The reaction was stirred at ambient temperature under nitrogen for 18 hours after which the precipitated product was removed *via* filtration and washed with DCM, water and Et₂O. The product was isolated as a yellow powder. Mass of product = 1.26 g. Yield = 82%. ^1H NMR 300 MHz in DMSO- d_6 δ (ppm): 10.42 (s, 1H, NH), 10.06 (s, 1H, NH), 8.66 (s, 1H, ArH), 8.59 (s, 1H, ArH), 8.14 (m, 5H, ArH), 7.92 (m, 3H, ArH), 7.57 (m, 8H,

ArH). ^{13}C NMR 75.4 MHz in $\text{DMSO}-d_6$ [in the presence of 5 equivalents TBACl] δ (ppm): 165.7 (CO), 165.0 (CO), 133.9 (C), 131.8 (CH), 131.8 (CH), 131.2 (CH), 129.8 (C), 128.7 (C), 128.4 (CH), 128.3 (CH), 128.1 (CH), 127.8 (CH), 127.7 (CH), 126.9 (CH), 16.3 (CH), 125.8 (CH), 125.5 (CH), 124.7 (CH), 122.5 (CH), 57.54 (TBA CH_2), 23.1 (TBA CH_2), 19.2 (TBA CH_2), 13.4 (TBA CH_3). IR (cm^{-1}): 3247, 3037, 1647, 1519, 1459, 1289, 894. LRMS ES- mass spectrum, m/z , 450.9 $[\text{M} + \text{Cl}]^-$, 529.0 $[\text{M} + \text{TFA} - \text{H}]^-$, 945.7 $[2\text{M} + \text{TFA} - \text{H}]^-$. Anal. Found for $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_2 + 0.40 \text{CH}_2\text{Cl}_2$ (Calcd) C 75.98 (75.73), H 4.63 (4.65), N 6.22 (6.22)%. m.p. (Et_2O) = decomp. 251-255 $^\circ\text{C}$.

N^1, N^3 -Dibutylanthracene-1,3-dicarboxamide (3).

n-Butylamine (0.43 mL, 4.4 mmol) was dissolved in dry DCM (25 mL). Trimethylaluminium solution (2M) in hexane (2.2 mL, 4.4 mmol) was added dropwise to the solution and the mixture stirred for 30 minutes. 1,3-Anthracenedimethyl ester (0.64 g, 2.2 mmol) was added and the reaction heated at reflux for 5 days. The reaction mixture was allowed to cool and aqueous HCl solution (1:10 v/v) added until bubbling ceased. A further 50 mL of water was added and the reaction was stirred for a further 30 minutes. The reaction mixture was washed with water (3×50 mL) and the organic phase containing the suspended compound retained. The remaining solvent was removed *in vacuo* and the residue dried under high vacuum. The product was isolated as a pale yellow solid. Mass of product = 0.26 g. Yield = 32%. ^1H NMR 300 MHz in CDCl_3-d_1 δ (ppm): 8.65 (s, 1H, NH), 8.02 (s, 1H, NH), 7.99 (s, 1H, ArH), 7.86 (d, 1H, J = 8.4 Hz, ArH), 7.68 (d, 1H, J = 8.4 Hz, ArH), 7.62 (d, 1H, J = 1.1 Hz, ArH), 7.40 (m, 2H, ArH), 6.79 (m, 2H, ArH), 3.50 (q, 2H, J = 7.0 Hz, CH_2), 3.40 (q, 2H, J = 6.9 Hz, CH_2), 1.64 (m, 4H, overlapping CH_2), 1.43 (m, 4H, overlapping CH_2), 0.97 (m, 6H, overlapping CH_3). ^{13}C NMR 75.4 MHz in CDCl_3-d_1 δ (ppm): 169.3 (CO), 167.4 (CO),

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4 134.9 (C), 133.0 (C), 131.8 (C), 130.3 (C), 130.0 (CH), 129.9 (C), 128.7 (CH), 128.3
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6 (C), 128.2 (CH), 128.0 (CH), 126.6 (CH), 126.3 (CH), 124.6 (CH), 122.2 (CH), 40.2
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8 (CH₂), 40.0 (CH₂), 31.8 (CH₂), 20.4 (CH₂), 13.9 (CH₃). IR (cm⁻¹): 3247, 2954, 1654,
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10 1624, 1553, 1294, 1250, 1157, 875, 733. ES- mass spectrum, *m/z*, 489.0 (M + TFA -
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12 H)⁻, 865.2 (2M + TFA - H)⁻. Anal. Found for C₂₄H₂₈N₂O₂ + 0.17 CH₂Cl₂ (Calcd) C
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14 74.23 (74.30), H 7.41 (7.31), N 7.15 (7.17)%. m.p. (H₂O) = 173 °C.

15 16 17 18 **N¹,N³-Diphenylanthracene-1,3-dicarboxamide (4).**

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20 Aniline (0.54 g, 5.8 mmol) was dissolved in dry DCM (30 mL).
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22 Trimethylaluminium solution (2M) in hexane (2.9 mL, 5.8 mmol) was added dropwise
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24 and the solution stirred for 30 minutes. 1,3-Anthracenedimethyl ester (0.85g, 2.9mmol)
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26 was added and the mixture heated at reflux for 5 days. The reaction mixture was
27
28 allowed to cool and aqueous HCl solution (1:10 v/v) added carefully until bubbling
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30 ceased. A further 75 mL of water was added and the reaction was stirred for 30 minutes
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32 before the reaction mixture was washed with water (3 × 50 mL) and the organic phase
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34 containing the suspended compound retained. The organic phase was reduced *in vacuo*
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36 and the compound dried under high vacuum. Product was isolated as a pale yellow
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38 solid. Mass of product = 0.99 g. Yield = 82%. ¹H NMR 300 MHz in DMSO-*d*₆ δ
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40 (ppm): 10.77 (s, 1H, NH), 10.56 (s, 1H, NH), 8.92 (m, 2H, ArH), 8.89 (m, 1H, ArH),
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42 8.20 (m, 2H, ArH), 7.87 (m, 4H, ArH), 7.61 (m, 2H, ArH), 7.40 (m, 4H, ArH), 7.16 (m,
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44 2H, ArH). ¹³C NMR 75.4 MHz in DMSO-*d*₆ δ (ppm): 166.9 (CO), 164.8 (CO), 139.3
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46 (C), 139.1 (C), 134.8 (C), 132.6 (C), 131.6 (C), 131.2 (CH), 130.3 (C), 130.3 (C), 128.8
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48 (CH), 128.7 (CH), 128.6 (CH), 128.1 (CH), 127.0 (CH), 126.5 (CH), 124.2 (CH), 123.9
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50 (CH), 123.5 (CH), 120.5 (CH), 120.0 (CH). IR (cm⁻¹): 3274, 3126, 1638, 1594, 1526,
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52 1491, 1317, 1247, 893, 865. ES- mass spectrum. *m/z*, 529.0 (M + TFA - H)⁻, 945.1 (2M
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4 + TFA - H⁺, 1362.9 (3M + TFA - H⁺). Anal. Found for C₂₈H₂₀N₂O₂ + 0.20 CH₃CN
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6 (Calcd) C 80.02 (80.32), H 4.81 (4.89), N 6.92 (7.16)%. m.p. (H₂O) = decomp. 243-248
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8 °C.
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10 11 **1,2-Anthracene bis-butylurea (5).**

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13 Anthracene-1,2-diamine (0.20 g, 1.0 mmol) was dissolved in dry DCM (40 mL)
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15 and butylisocyanate (0.22 mL, 2.0 mmol) added dropwise. The reaction was stirred at
16
17 ambient temperature for 18 hours. The solvent was removed *in vacuo* and the residue
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19 redissolved in 90:10 DCM:MeOH and purified by flash column chromatography. The
20
21 product was further purified by recrystallisation from EtOH. The product was obtained
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23 as a brown solid. Mass of product = 0.21 g. Yield = 54%. ¹H NMR 300 MHz in
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25 DMSO-*d*₆ δ (ppm): 8.49 (s, 1H, NH), 8.20 (m, 2H, NH & ArH), 7.92 (m, 4H, ArH),
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27 7.46 (m, 2H, ArH), 7.08 (t, 1H, J = 5.1 Hz, NH), 6.30 (br s, 1H, NH), 3.12 (m, 4H,
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29 CH₂), 1.45 (m, 4H, CH₂), 1.34 (m, 4H, CH₂), 0.90 (m, 6H, CH₃). ¹³C NMR 75.4 MHz
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31 in DMSO-*d*₆ δ (ppm): 15.7.0 (CO), 155.2 (CO), 131.3 (C), 130.1 (C), 129.9 (C), 128.6
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33 (C), 127.9 (CH), 127.7 (CH), 126.4 (CH), 126.2 (CH), 125.7 (CH), 124.8 (CH), 122.3
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35 (CH), 120.0 (CH), 39.22 (CH₂), 38.9 (CH₂), 32.0 (CH₂), 31.8 (CH₂), 19.6 (CH₂), 19.5
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37 (CH₂), 13.7 (CH₃), 13.6 (CH₃). IR (cm⁻¹): 3268, 2953, 2924, 2858, 1637, 1561, 1458,
38
39 1239, 882, 741. ES- mass spectrum, *m/z*, 441.5 [M + Cl]⁻, 519.5 [M + TFA - H]⁻, 848.4
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41 [2M + Cl]⁻, Anal. Found for C₂₄H₃₀N₄O₂ (Calcd) C 70.61 (70.91), H 7.35 (7.44), N
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43 13.58 (13.78)%. m.p. (EtOH) = decomp. 186-188 °C.
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52 **1,2-Anthracene bis-phenylurea (6).**

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54 Anthracene-1,2-diamine (0.35 g, 1.7 mmol) was dissolved in dry DCM (40 mL)
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56 and phenylisocyanate (0.37 mL, 3.4 mmol) added dropwise. The reaction was left
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58 stirring at ambient temperature for 18 hours. The precipitated product was removed by
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5 filtration and the residue washed with DCM (3 × 10 mL) and MeOH (3 × 10 mL).
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7 Product was isolated as a green solid. Mass of product = 0.37 g. Yield = 49%. ¹H NMR
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9 300 MHz in DMSO-*d*₆ δ (ppm): 9.50 (s, 1H, NH), 9.15 (s, 1H, NH), 8.57 (s, 1H, NH),
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11 8.28 (d, 2H, J = 8.8 Hz, ArH), 8.09-8.01 (m, 3H, ArH & NH), 7.52-7.45 (m, 6H, ArH),
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13 7.29 (t, 4H, J = 7.3 Hz), 6.98 (td, 2H, J = 7.3 & 0.7 Hz, ArH). ¹³C NMR 75.4 MHz in
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15 DMSO-*d*₆ δ (ppm): 154.1 (CO), 152.7 (CO), 140.1 (C), 139.7 (C), 133.8 (C), 131.5 (C),
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17 130.2 (C), 129.9 (C), 128.8 (CH), 128.7 (CH), 127.9 (CH), 126.9 (CH), 126.4 (CH),
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19 125.9 (CH), 122.4 (CH), 121.9 (CH), 121.7 (CH), 120.1 (CH), 119.9 (C), 118.3 (CH),
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21 118.2 (CH). IR (cm⁻¹): 3261, 3045, 1598, 1563, 1443, 1313, 1222, 874, 727. ES- mass
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23 spectrum, *m/z*, 559.3 [M + TFA - H]⁻, 927.6 [2M + Cl]⁻, 1005.0 [2M + TFA - H]⁻,
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25 1373.7 [3M + Cl]⁻. Anal. Found for C₂₄H₂₈N₂O₂ + 0.25 CH₂Cl₂ (Calcd) C 72.48
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27 (72.54), H 5.07 (4.85), N 11.70 (11.98)%. m.p. (DCM/MeOH) = decomp. 261-264 °C.
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36 Crystallography

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39 Crystal data for **1** C₂₄H₂₈N₂O₂, Mr = 376.48, T = 120(2) K, monoclinic, space group
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41 *P*2₁/*c*, *a* = 8.8732(3), *b* = 26.9318(10), *c* = 9.3751(3) Å, β = 112.884(2)°, *V* =
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43 2064.05(12) Å³, ρ_{calc} = 1.212 g cm⁻³, μ = 0.077 mm⁻¹, *Z* = 4, reflections collected:
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45 22715, independent reflections: 4700 (*R*_{int} = 0.0742), final *R* indices [*I* > 2σ*I*]: *R*1 =
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47 0.0600, *wR*2 = 0.1355, *R* indices (all data): *R*1 = 0.1322. *wR*2 = 0.1621. CCDC 631103.
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51 Crystal data for the benzoate complex of **5** C₄₇H₇₁N₅O₄, Mr = 770.09.48, T = 120(2) K,
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53 monoclinic, space group *P*2₁/*c*, *a* = 17.0539(11), *b* = 8.8884(4), *c* = 30.0050(17) Å, β =
54
55 96.399(2)°, *V* = 4519.9(4) Å³, ρ_{calc} = 1.132 g cm⁻³, μ = 0.072 mm⁻¹, *Z* = 4, reflections
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57 collected: 40230, independent reflections: 9618 (*R*_{int} = 0.1179), final *R* indices [*I* >
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59 2σ*I*]: *R*1 = 0.1282, *wR*2 = 0.3284, *R* indices (all data): *R*1 = 0.2582. *wR*2 = 0.3922.
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61 CCDC 631102.

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Crystal data for the benzoate complex of **6** C₅₁H₆₃N₅O₄, Mr = 810.06, T = 120(2) K, Monoclinic, space group *P*2₁/*c*, *a* = 37.6085(19), *b* = 23.5672(12), *c* = 10.1095(3) Å, β = 92.486(3)°, *V* = 8951.9(7) Å³, ρ_{calc} = 1.202 g cm⁻³, μ = 0.076 mm⁻¹, *Z* = 8, reflections collected: 37072, independent reflections: 15003 (*R*_{int} = 0.1132), final *R* indices [*I* > 2σ*I*]: *R*1 = 0.1561, *wR*2 = 0.2578, *R* indices (all data): *R*1 = 0.2795. *wR*2 = 0.3252. CCDC 631101.

Results and Discussion

Compounds **1** and **2** were synthesised from an acid chloride condensation reaction between 1,2-diaminoanthracene¹⁸ and valeroyl and benzoyl chloride in the presence of triethylamine and a catalytic quantity of DMAP to afford the products in 39% and 82% respective yields. Receptors **3** and **4** were synthesised by reaction of the 1,3-dimethyl anthracenedicarboxylate¹⁹ and either *n*-butylamine or aniline in the presence of trimethylaluminium solution 2M in dry dichloromethane that afforded the products in 32 and 82% respective yields. Compounds **5** and **6** were synthesized from 1,2-diaminoanthracene and butylisocyanate or phenylisocyanate yielding the two products in 54% and 49% yield respectively.

X-ray quality crystals of **1** were obtained *via* slow evaporation of an acetonitrile solution of the compound. As shown in Figure 1, in the solid-state, the receptor forms an infinite hydrogen bonded chain with bonding interactions between the amide NH groups and the carbonyl groups of an adjacent molecule of **1** [N··O 2.844(2) and 2.910(2) Å]. The structure indicates that both amide NH groups are able to adopt an almost parallel geometry in the solid state and therefore may facilitate the coordination of oxo-anions separate interactions to different oxygen atoms in the anion.

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5 The presence of the butyl groups in **1** and **3** conferred solubility on these
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7 compounds in weakly coordinating dichloromethane (DCM) solution. It was therefore
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9 decided to initially investigate the anion binding properties of **1** and **3** in DCM- d_2 using
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11 ^1H NMR titration techniques (Table 1).
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14 Compound **1** was found to possess a slightly higher oxo-anion affinity than compound
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16 **3** under these solvent conditions however, overall the affinity of the two compounds for
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18 anionic guests was very similar. In order to provide greater insight into the anion
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20 binding behaviour of receptors **1** and **3** and to evaluate the properties of aryl
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22 functionalized receptors **2** and **4**, further ^1H -NMR titration experiments were performed
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24 in the more competitive solvent mixture of DMSO- d_6 /0.5% water (Table 2). As
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26 expected, in, with the exception of dihydrogen phosphate all of the anions are bound
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28 more weakly. Interestingly the halide selectivity displayed by isophthalamide type
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30 receptor **3** in dichloromethane is not observed in DMSO- d_6 /0.5% water, with both
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32 phosphate and carboxylate anions bound more strongly in this solvent mixture.
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34 Compound **4** displays the highest observed stability constant with dihydrogen
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36 phosphate of 122 M^{-1} , consistent with the increase in acidity of the amide NH groups
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38 relative to alkyl derivative **3**.
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45 Anion stability constants with compounds **5** and **6** were also elucidated *via* ^1H -NMR
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47 titration experiments performed in DMSO- d_6 /0.5% water revealing a significant
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49 increase in the values obtained for compounds **1-4** under the same conditions, however
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51 a similar trend of oxo-anion selectivity was observed (Table 3). Of the two compounds
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53 the bis-phenylurea **6** displayed stability constants approaching an order of magnitude
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55 higher than those of **5** (c.f. acetate 277 vs 2540 M^{-1}) presumably arising from the
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57 greater acidity of the outer urea NH protons of receptor **6** due to the presence of the
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4 electron-withdrawing aryl substituents. The titration curves for this compound are
5 shown in Figure 2.
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9 Because receptors **5** and **6** formed complexes with considerably improved stability with
10 respect to those formed by compounds **1-4**, we decided to investigate the photophysical
11 properties of these systems to determine their effectiveness as fluorescent anion
12 sensors. Fluorescence titrations were performed both in DMSO and in the relatively
13 non-competitive MeCN/DMSO (96.5/3.5 v/v) solvent mixture. The UV/vis absorbance
14 spectra of compounds **5** and **6** in DMSO both display similar characteristic shapes, with
15 maximum absorbances centred at 370 ($\epsilon = 4600 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$) and 368 nm (6300
16 $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) respectively. Excitation of the compounds at these wavelengths
17 provided maximum fluorescent emission peaks that were broad in appearance and
18 centred at 493 and 477 nm respectively. The two receptors show very good
19 fluorescence quantum yields ($\Phi = 0.44$ and 0.50 for **5** and **6**, respectively). The effect of
20 increasing concentration of coordinating oxo-anions in the form of their
21 tetrabutylammonium salts upon the fluorescent emission of both receptors **5** and **6** was
22 investigated. Whilst only relatively small changes in the UV/vis absorbance spectra
23 were recorded, a significant reduction in the fluorescence emission was observed
24 (Figures 3 and 4) when a large excess of anion (up to 300 equivalents) was added to the
25 solution of both compounds **5** and **6** in DMSO. We decided to repeat the titrations in a
26 mixture of MeCN/DMSO (96.5/3.5 v/v) and found that the absorption and emission
27 properties of both ligands were similar to those observed in DMSO. We recorded the
28 fluorescence emission exciting both the compounds at 362 nm and found that the
29 maximum emission was at 458 and 465 nm for receptors **5** and **6** respectively. In the
30 case of receptor **6** a partial quenching of the fluorescence emission was evident with
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4 acetate ($I_{res} = 21\%$) and in less extent with benzoate ($I_{res} = 53\%$), dihydrogen phosphate
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6 ($I_{res} = 70\%$) and chloride ($I_{res} = 96\%$) upon addition of 30 equivalents of anions (Figure
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9 5). For receptor **5** we did not observed any significant changes in the fluorescence
10
11 emission upon addition of anions (see Supplementary Informations).
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14 Slow evaporation of an acetonitrile solution of **5** in the presence of excess
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16 tetrabutylammonium benzoate yielded X-ray quality crystals of the complex. The
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18 benzoate anion is bound by the receptor through four hydrogen bonds with both the
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20 inner urea NH groups [$N \cdots O$ 2.851(6) and 2.839(6) Å] and external urea NH groups
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22 [$N \cdots O$ 2.890(6) and 2.830(6) Å] coordinating both of the oxygen atoms of the anion
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24 (Figure 6).
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28 Similarly, slow evaporation of an acetonitrile solution of **6** in the presence of excess
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30 tetrabutylammonium benzoate yielded X-ray quality crystals of the complex. The
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32 benzoate anion is bound by the receptor *via* four hydrogen bonds with both the inner
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34 urea NH groups [$N \cdots O$ 2.828(9) and 2.783(9) Å] and external urea NH groups [$N \cdots O$
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36 2.837(10) and 3.074(9) Å] coordinating both of the oxygen atoms of the anion (Figure
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38 7).
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44 45 Conclusions

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47 The variation of the hydrogen bonding motifs of bis-amide receptors allows the
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49 selectivity to be tuned to a certain extent in weakly coordinating dichloromethane
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51 solution. However in DMSO solution there is little difference between the anion
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53 affinity of the two motifs studied. The bis-urea motif forms stronger complexes with
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55 oxo-anions under more competitive conditions due to the ability of the receptors to
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57 form up to four simultaneous hydrogen bonds to the anion. The incorporation of an
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4 anthracene fluorophore enables the receptor to function as a sensor for carboxylate
5 anions with a good selectivity in a mixture of MeCN/DMSO (96.5/3.5 v/v). We are
6 currently investigating alternative methods of incorporating the bis-urea motif into both
7 optical and electrochemical sensors, the results of which will be published in due
8 course.
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Figure 1. Receptor **1** forms hydrogen-bonded chains in the solid state. Non-acidic hydrogen atoms have been omitted for clarity.

Figure 2. Shifts of the central urea NH groups of compound **6** upon the addition of tetrabutylammonium salts in DMSO-*d*₆/0.5% water.

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4 **Figure 3.** Fluorescence quenching of **6** in DMSO upon the addition of
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7 tetrabutylammonium acetate.
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13 **Figure 4.** Fluorescence solutions of compound **6** in DMSO illuminated at 365 nm
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15 (from left to right) in the absence of an anionic guest, in the presence of an excess of
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17 TBAH₂PO₄, TBAOAc and TBAOBz.
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25 **Figure 5.** Fluorescence intensity/molar ratio plots for **6** [1×10^{-6} M, MeCN/DMSO
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27 (96.5/3.5 v/v)] in the presence of increasing amounts of AcO⁻ (◆), H₂PO₄⁻ (▲), BzO⁻
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29 (■) and Cl⁻ (+).
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37 **Figure 6** The benzoate complex of **5** showing the formation of four hydrogen bonds
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39 between the receptor and the carboxylate anion in the solid state. Tetrabutylammonium
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41 counter cations and non-acidic hydrogen atoms omitted for clarity.
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49 **Figure 7** The benzoate complex of **6** showing the formation of four hydrogen bonds
50
51 between the receptor and the carboxylate anion in the solid state. Tetrabutylammonium
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53 counter cations and non-acidic hydrogen atoms omitted for clarity
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Table 1 Stability constants (M^{-1}) of compounds **1** and **3** with a variety of putative anionic guests (added as tetrabutylammonium salts) at 298 K in DCM- d_2 .^a In all cases a 1:1 receptor : anion stoichiometry was observed. Data fitted using EQNMR.²⁰

Compounds		
Anion	1	3
Cl ⁻	238	257
Br ⁻	67	92
C ₆ H ₅ CO ₂ ⁻	709	251
HSO ₄ ⁻	14	16
H ₂ PO ₄ ⁻	128	68

^a Error estimated to be no more than $\pm 15\%$

Table 2 Stability constants (M^{-1}) of compounds **1-4** with a variety of putative anionic guests (added as tetrabutylammonium salts) at 298 K in DMSO- $d_6/0.5\%$ water.^a In all cases a 1:1 receptor : anion stoichiometry was observed.

Compounds				
Anion	1	2	3	4
Cl ⁻	<10	<10	<10	<10
CH ₃ CO ₂ ⁻	85	28	13	38
C ₆ H ₅ CO ₂ ⁻	44	33	<10	21
H ₂ PO ₄ ⁻	64	63	19	122

^a Error estimated to be no more than $\pm 15\%$

Table 3 Stability constants (M^{-1}) of compounds **5** and **6** with a variety of putative anionic guests (added as tetrabutylammonium salts) at 298 K in DMSO- $d_6/0.5\%$ water.^a In all cases a 1:1 receptor : anion stoichiometry was observed.

Compounds		
Anion	5	6

Cl ⁻	10	27
Br ⁻	-	<10
CH ₃ CO ₂ ⁻	277	2540
C ₆ H ₅ CO ₂ ⁻	107	586
H ₂ PO ₄ ⁻	370	1170

^a Error estimated to be no more than ± 15%

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