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Bis-amidopyrrolyl receptors based on anthracene and carbazole

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A new set of diamide receptors containing anthracene and carbazole bridging subunits and either pyrrole or phenyl substituents were synthesised. The four systems produced in this way were shown to bind representative anions in DMSO-d_6 solution and in the solid state. A higher relative affinity for two test oxoanions, namely dihydrogen phosphate and benzoate, over chloride anion was seen in solution, with the anions in question being studied in the form of their respective tetrabutylammonium salts. However, the specifics of the anion recognition process were seen to depend on structure, with the pyrrole-containing systems displaying higher relative affinities than their corresponding phenyl-containing congeners, and the carbazole receptors proving more effective than the anthracene analogues. Such observations provide support for the notion that both the carbazole NH and the pyrrolic NH protons play an important role in stabilising the receptor-bound anions in solution. Structural analyses of several anion complexes of the diamidopyrrole carbazole receptor reveal that this is not necessarily the case in the solid state; specifically, the pyrrole NH protons are seen to interact with the amide oxygen of another molecule. The net result is an extended one-dimensional coordination polymer.

Keywords: supramolecular chemistry; anion recognition; carbazole; pyrrole; amides

Considerable effort has been devoted to the synthesis and studies of new open-chain anion receptors in recent years (*1–3*). Many of these receptors, including several of our own (*4*), have taken advantage of the basic pyridine biscarboxamide strategy first pioneered by Crabtree (*5*, *6*), and then exploited so effectively by a number of research groups (*7–14*). Noteworthy in this context are the contributions of Gale and co-workers who have extensively studied 2,5-diamidopyrrole-based receptors (*15*). Separate from this carbazole and indole, 'pyrrole-like' binding motifs have emerged recently as a new scaffold (*16*) for the construction of various anion receptors (*17–34*). Jurczak and co-workers (*18*) introduced diaminocarbazoles, such as 1,8-diamino-3,6-dichlorocarbazole, as promising building blocks for preparing various diamide anion receptors, which in separate work were further elaborated to incorporate a diazo chromophore (*20*). In this report, we detail the combination of pyrrole amides with carbazole to produce the bisamidopyrrole carbazole derivative **1**, and show that it acts as a new anion receptor. Also included in this study is a description of the synthesis and anion recognition behaviour of the bisamidobenzene derivative **2**, as well as the bisamidopyrrole anthracene receptor **3** and its phenyl derivative **4** (Scheme 1). This series provides a congruent set of analogues that contain binding pockets of similar geometry and size but which provide a varying number of NH-bond donors. All systems of this study were found to display good selectivity for test carboxylate and phosphate anions relative to chloride anion; however, the absolute and relative binding affinities were found to vary with the specific structure.

Amidocarbazole receptors **1** and **2** were synthesised via condensation of the key precursor 1,8-diamino-3,6-dibutylcarbazole **5** with excess pyrrolyl chloride and benzoyl chloride, respectively (Scheme 2). Diamine **5** was synthesised in four steps from carbazole. First, acylation using butyryl chloride in 1,2-dichloroethane afforded 3,6-dibutyrylcarbazole **6** in an unoptimised yield of 42%. Subsequent reduction afforded dibutylcarbazole **7** in 50% yield. Nitration in acetic acid and acetic anhydride provided the dinitro compound **8** along with minor amounts of the mononitro derivative, which could be separated by tedious column chromatography. Finally, palladium-catalysed hydrogenation of **8** led to diamine **5**. It was subsequently found that the mixture of mono- and dinitro products could be subjected to hydrogenation conditions to yield **5** containing minor quantities of monoamine **9**. Since this latter mixture could be readily separated using column chromatography, we currently favour this alternative sequence. The resulting diamine was then reacted with the appropriate acid chloride to yield receptors 1,8-di(pyrrolylamido)-3,6-dibutylcarbazole **1** and 1,8-di(benzoylamido)-3,6-dibutylcarbazole **2**. Receptors **1** and **2** were characterised by single-crystal X-ray diffraction and the resulting structures are shown in Figure 1.

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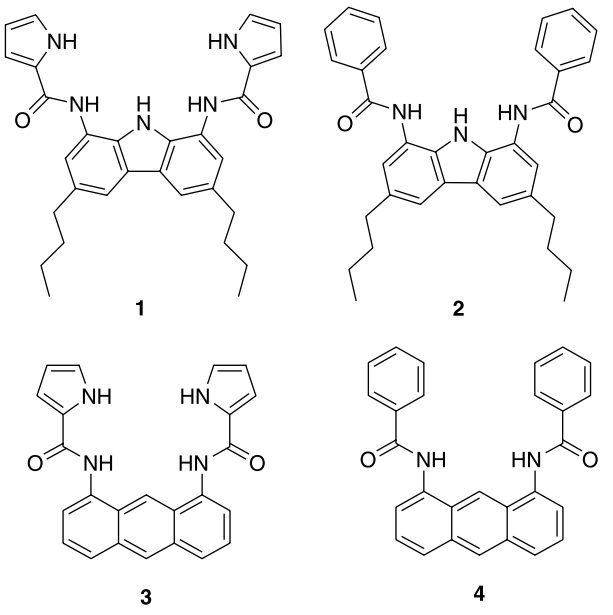


Scheme 1. Compounds considered in this study.

Additionally, the isolated monoamine product **9** was reacted with pyrrole-2-carboxylic acid chloride to yield 1-pyrrolylamido-3,6-dibutylcarbazole **10**. Receptors **3** and **4** were synthesised by the reaction of 1,9-diaminoanthracene (*35*) with excess pyrrole-2-carboxylic acid chloride and benzoyl chloride, respectively.

NMR spectroscopic analyses were used to quantify the interaction of receptors **1**–**4** and anions. For these studies, DMSO-d_6 was chosen as the solvent due to the poor solubility of the anthracene derivatives in other aprotic media. The anions were used in the form of their respective tetrabutylammonium salts.

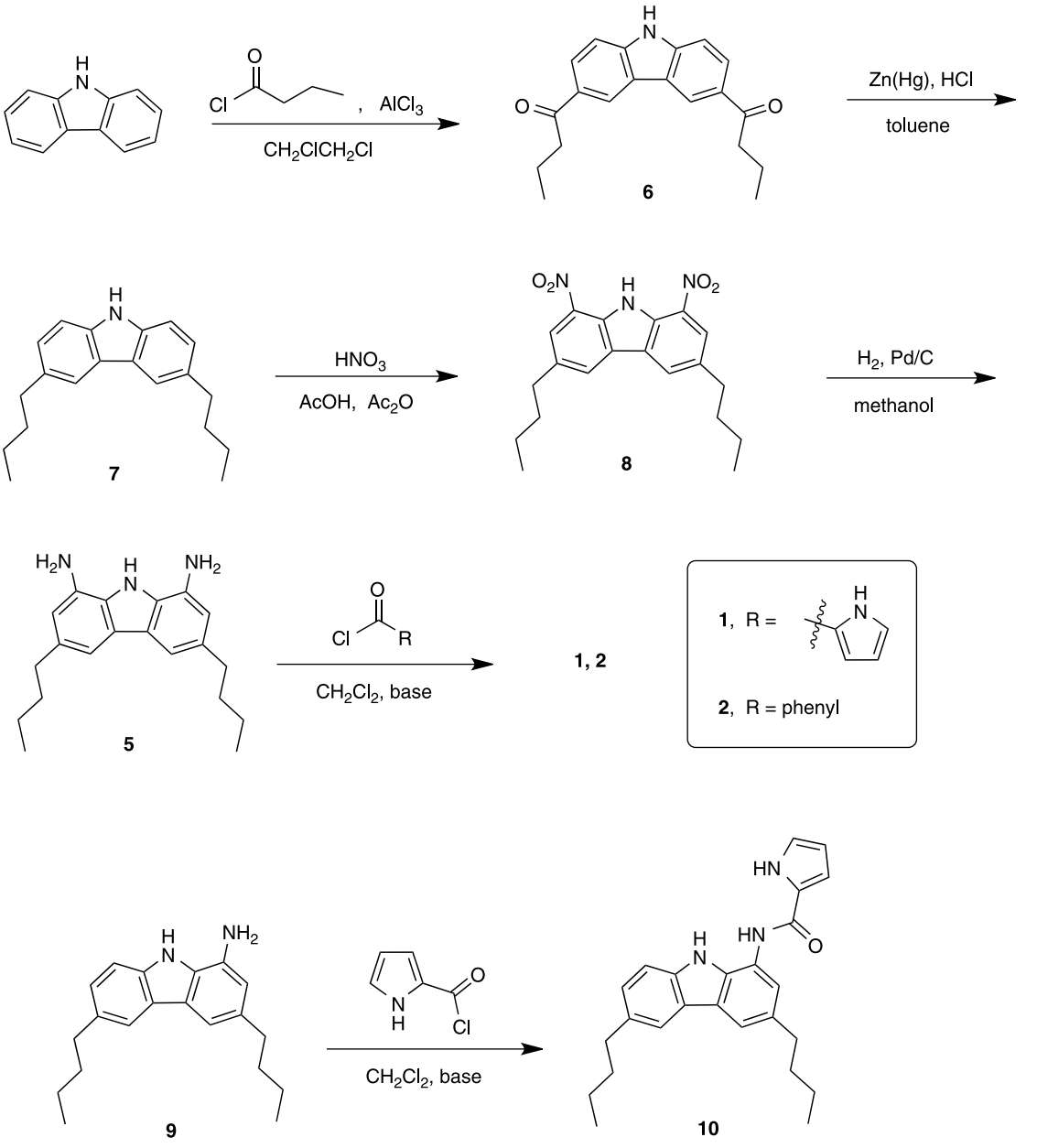
Receptor **3** was found to bind chloride anion weakly, but bind the two test oxoanions of this study, namely benzoate and dihydrogen phosphate, with greater affinity (see Table 1). In the case of dihydrogen phosphate, the measured K_a proved to be $2600\,M^{-1}$, a value that was almost 10 times larger than that of benzoate. This phosphate-over-benzoate (and chloride) selectivity was reduced when the pyrroles were replaced by phenyl groups, i.e. in the case of **4**; here, lower affinities were seen across the board, with dihydrogen phosphate displaying a K_a that was approximately twice that of chloride, whereas the latter was bound with essentially the same affinity as that of benzoate within error. On this basis, we conclude that replacing the more acidic pyrrolic NH proton by a CH proton serves to reduce not just the affinity (the K_a of dihydrogen phosphate was reduced from 2600 to $160\,M^{-1}$) but the anion selectivity as well. This leads us to propose that the presence of the pyrrolic NH is important in stabilising the bound form of the two test oxoanions (benzoate and dihydrogen phosphate), at least in DMSO-d_6 solution.

The carbazole-containing receptors **1** and **2** displayed binding trends similar to those seen for anthracene receptors; however, the binding affinities were generally greater in the case of the oxoanions and reduced in the case of chloride. In the case of **1** vs. **2**, the effect of switching from pyrrole to phenyl substitution on the K_a values was not as great as for **3** and **4**. For instance, when the pyrrole groups were replaced with benzene (i.e. passing from **1** to **2**), the affinity for benzoate was reduced by a factor of *c*.2 ($K_a = 1600$ vs. $790\,M^{-1}$), whereas the corresponding reduction in the K_a for phosphate was even less ($K_a = 2000$ vs. $1400\,M^{-1}$). In addition, receptor **1** displayed a reduced selectivity for dihydrogen phosphate over benzoate than did receptor **3**. Nevertheless, it is important to underscore that for both **1** and **2**, dihydrogen phosphate proved to be the most strongly bound of the three test anions considered in this study.

The trends seen in the case of the diamide receptors **1**–**4** are not reproduced completely in the case of the monoamidopyrrolyl-functionalised receptor **10**. This control system showed an increased affinity for chloride compared to receptor **1**, as well as a decreased affinity for the two test oxoanions. This relative increase in chloride affinity may reflect the more open binding pocket present in receptor **10** relative to the more constrained system **1**, which is expected to be characterised by a less flexible anion binding cavity.

X-ray quality crystals of **1**·acetate (Figure 2) and **1**·chloride (Figure 3) were obtained by the slow evaporation of ethyl acetate solutions containing **1** with excess tetrabutylammonium fluoride (a species that may have promoted the hydrolysis of ethyl acetate and production of the acetate anion) and chloride, respectively. As evidenced by the crystal structure, the receptor binds these two anions in a 1:1 stoichiometry. However, interestingly, the pyrrolic NH protons do not participate in anion binding in the solid state. Instead, these protons are involved in the formation of a hydrogen-bonded network with the amide oxygen of another molecule of **1** (see Figures 2 and 3). This results in a one-dimensional coordination polymer, a geometric motif that was noted rather early in the study of pyrrole amide compounds (*36*). However, in contrast with at least some of the antecedent pyrrole amide systems recorded in the literature, we do not believe that the X-ray structures of **1**·acetate and **1**·chloride are representative of the binding mode operative in DMSO-d_6 solution for these or other typical anions. This conclusion is based on the fact that demonstrable downfield shifts in the pyrrolic NH proton resonance are seen for benzoate and dihydrogen phosphate (0.34 and 1.67 ppm, respectively).

In conclusion, a set of new amidopyrrole and amidophenyl receptors based on anthracene and carbazole



Scheme 2. Synthesis of receptors **1**, **2** and **10**

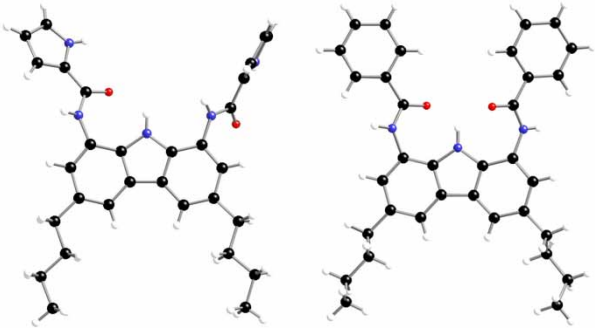


Figure 1. Ball and stick representation of single-crystal X-ray diffraction structures for **1** (left) and **2** (right).

were synthesised and shown to bind anions in DMSO-d_6 solution and in the solid state. These receptors demonstrate a higher relative affinity for oxoanions over chloride anion in solution. An analysis of the specific K_a values, which are

Table 1. Association constants (K_a's) for receptors **1**–**4** and **10** with selected anions in DMSO-d_6.[a]

	1	**2**	**3**	**4**	**10**
Chloride	<50	<50	80	83	280
Benzoate	1600	790	310	65	190
Dihydrogen phosphate	2000	1400	2600	160	880

[a] K_a's in units of M^{-1}; anions used in the form of their tetrabutylammonium salts; host concentration, 4–5 mM.

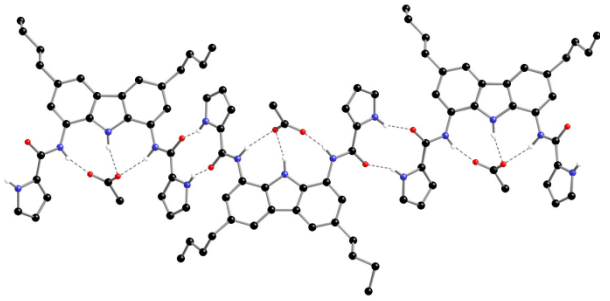


Figure 2. Single-crystal X-ray diffraction structure of **1**·OAc; most hydrogen atoms and the tetrabutylammonium cation have been removed for clarity.

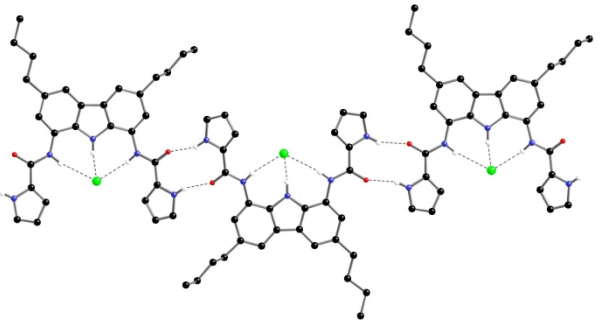


Figure 3. Single-crystal X-ray diffraction structure of **1**·Cl; most hydrogen atoms and the tetrabutylammonium cation have been removed for clarity.

seen to vary with structure, provides support for the notion that the carbazole NH and pyrrolic NH protons play an important role in stabilising the receptor-bound anions in the solution. However, in the case of the carbazole-based receptor, the 'loss' of the pyrrolic NH protons (i.e. moving from **1** to **2**) does not affect the affinity for dihydrogen phosphate all that significantly, a result that serves to make receptor **2**, where phenyl subunits replace the pyrroles, more selective than its pyrrole-containing congener, **1**. Nevertheless, as would be expected for a system containing a greater number of available NH donor groups, this latter system (i.e. **1**) actually displays a higher for-anion affinity than **2**. Similar overall anion affinity effects were also seen in the case of **3** vs. **4**. In contrast, the monoamide control, **10**, displays a different selectivity pattern than is seen for any of the bisamides **1**–**4**.

Experimental

^{1}H NMR spectroscopic titrations

A Varian Mercury 400 MHz NMR spectrometer was used to measure the ^{1}H NMR shifts of the NH proton of the amides. Solutions of **1**–**4** and **10** were titrated with tetrabutylammonium salts of chloride, dihydrogen phosphate and benzoate salt at 25°C in DMSO-d_6. The titration data were plotted as Δ ppm vs. concentration of the guest and fit to a 1:1 binding equation developed by Wilcox (*37*), using the nonlinear curve-fitting procedure available in the Origin software package.

X-ray crystallographic data

Crystal data for **1** CCDC 736624 $C_{30}H_{33}N_5O_2$, $M_r = 495.61$, $T = 153(2)$ K, monoclinic, space group = $P2_1/c$, $a = 21.3540(4)$, $b = 12.9300(5)$, $c = 9.1350(9)$ Å, $\beta = 95.084(2)°$, $V = 2512.3(3)$ Å^3, $\rho_{calc} = 1.310$ Mg/m^3, $\mu = 0.084$ mm^{-1}, $Z = 4$, reflections collected: 7850, independent reflections: 7852, final R indices [$I > 2\sigma I$]: $R1 = 0.1205$, $wR2 = 0.2284$, R indices (all data): $R1 = 0.2027$, $wR2 = 0.2655$.

Crystal data for **2** CCDC 736625 $C_{34}H_{35}N_3O_2$, $M_r = 517.65$, $T = 153(2)$ K, triclinic, space group = P-1, $a = 9.5944(8)$, $b = 9.9023(10)$, $c = 14.8310(15)$ Å, $\beta = 99.086(4)°$, $V = 1385.6(2)$ Å^3, $\rho_{calc} = 1.241$ Mg/m^3, $\mu = 0.077$ mm^{-1}, $Z = 2$, reflections collected: 9412, independent reflections: 6133 ($R_{int} = 0.0448$), final R indices [$I > 2\sigma I$]: $R1 = 0.0687$, $wR2 = 0.1134$, R indices (all data): $R1 = 0.1576$, $wR2 = 0.1433$.

Crystal data for **1**·OAc CCDC 736626 $C_{48}H_{72}N_6O_4$, $M_r = 797.12$, $T = 153(2)$ K, triclinic, space group = P-1, $a = 8.8867(6)$, $b = 15.0233(10)$, $c = 17.1840(12)$ Å, $\beta = 87.019(3)°$, $V = 2236.5(3)$ Å^3, $\rho_{calc} = 1.184$ Mg/m^3, $\mu = 0.076$ mm^{-1}, $Z = 2$, reflections collected: 15,930, independent reflections: 9967 ($R_{int} = 0.0527$), final R indices [$I > 2\sigma I$]: $R1 = 0.0830$, $wR2 = 0.1450$, R indices (all data): $R1 = 0.1952$, $wR2 = 0.1815$.

Crystal data for **1**·Cl CCDC 736627 $C_{46}H_{69}ClN_6O_2$, $M_r = 773.52$, $T = 153(2)$ K, triclinic, space group = P-1, $a = 12.6727(3)$, $b = 14.9621(6)$, $c = 25.2379(12)$ Å, $\beta = 75.550(2)°$, $V = 4493.5(3)$ Å^3, $\rho_{calc} = 1.143$ Mg/m^3, $\mu = 0.128$ mm^{-1}, $Z = 4$, reflections collected: 30,522, independent reflections: 20,063 ($R_{int} = 0.0383$), final R indices [$I > 2\sigma I$]: $R1 = 0.0717$, $wR2 = 0.1340$, R indices (all data): $R1 = 0.1645$, $wR2 = 0.1742$. Portions of two *n*-butyl groups were disordered. One group was on a host molecule and the other was on a cation. The disorder was modelled separately but in the same manner for both groups. The site occupancy factor for one component of the disordered group was assigned the variable x, while the site occupancy factor for the other component was assigned $(1 - x)$. A common isotropic displacement parameter was refined for the methylene atoms and a second isotropic displacement parameter was refined for the methyl carbon atoms. The geometry of the two groups was restrained to be equivalent throughout the refinement. In this way, the site occupancy for the major component of the disorder on the host molecule refined to 55(2)%. The site occupancy factor

for the major component of the cation refined to 65(2)%. The atoms of the disordered groups were refined anisotropically with their displacement parameters restrained to be approximately isotropic.

3,6-Dibutyrylcarbazole (6)

To a mixture of carbazole (30 g, 0.179 mol) and aluminium chloride (53 g) in 1,2-dichloroethane (500 ml), butyryl chloride (43 ml) was added slowly. The reaction was then stirred at 65°C for 5 h and then quenched with water and aqueous HCl solution. The organic solvents were removed under reduced pressure, and the residue was dissolved in warm chloroform and subsequently crystallised upon cooling. This afforded **4** in the form of colourless crystals in 42% yield. ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.79 (d, $J = 1.6$ Hz, 2H), 8.68 (bs, 1H), 8.15 (dd, $J = 1.6$ Hz, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 3.11 (t, $J = 7.4$ Hz, 4H), 1.86 (m, $J = 7.4$ Hz, 4H), 1.07 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (400 MHz; $CDCl_3$) δ 199.9 (C═O), 142.7 (CH), 130.1 (CH), 127.0 (CH), 123.3 (CH), 121.6 (CH), 110.8 (CH), 40.5 (CH_2), 18.2 (CH_2), 14.0 (CH_3). HRMS (ESI) calcd for $C_{20}H_{20}NO_2$ $[M-H]^-$: 306.1493, found: 306.1500.

3,6-Dibutylcarbazole (7)

Zinc (200 g) and mercuric chloride (20 g) were added to 400 ml water containing concentrated hydrochloric acid (26 ml). After stirring for 20 min, additional concentrated hydrochloric acid was added slowly (400 ml), followed by 3,6-dibutyrylcarbazole (16 g, 52 mmol). Toluene (200 ml) was added to the reaction mixture, which was then heated at reflux for 96 h. The toluene layer was separated off and all volatiles were removed under reduced pressure. The resulting light brown solid was purified by column chromatography over silica gel using 2:1 hexanes/DCM as the eluent; this produced **5** in a yield of 50%. ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.89 (s, 2H), 7.77 (bs, 1H), 7.28 (dd, $J = 8$ Hz and 0.4 Hz, 2H), 7.24 (dd, $J = 8$ Hz and 1.2 Hz), 2.81 (t, $J = 7.8$ Hz, 4H), 1.74 (m, $J = 7.6$ Hz, 4H), 1.44 (m, $J = 7.5$ Hz, 4H), 1.00 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (400 MHz; $CDCl_3$) δ 138.2 (CH), 133.7 (CH), 126.4 (CH), 123.3 (CH), 119.5 (CH), 110.2 (CH), 35.7 (CH_2), 34.5 (CH_2), 22.4 (CH_2), 14.0 (CH_3). HRMS (ESI) calcd for $C_{20}H_{24}N$ $[M-H]^-$: 278.1912, found: 278.1914.

3,6-Dibutyl-1,8-dinitrocarbazole (8)

3,6-Dibutylcarbazole (204 mg, 0.7 mmol) was dissolved in acetic anhydride (25 ml) and acetic acid (10 ml). Nitric acid (0.19 ml, 4.5 mmol) was added dropwise. The resulting solution was then heated at 65°C for 2 h, 75°C for 1 h and 100°C for 1 h. After cooling, the solvent was evaporated off under reduced pressure, and the product was purified via column chromatography over silica gel using CH_2Cl_2 as the eluent; this yielded 3,6-dibutyl-1,8-dinitrocarbazole **7** in 55% yield. ^{1}H NMR (400 MHz; $CDCl_3$) δ 11.20 (bs, 1H), 8.24 (s, 2H), 8.22 (s, 2H), 2.88 (t, $J = 7.6$ Hz, 4H), 1.74 (m, $J = 7.6$ Hz, 4H), 1.43 (m, $J = 7.5$ Hz, 4H), 0.98 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 135.9 (CH), 132.5 (CH), 132.3 (CH), 127.5 (CH), 125.9 (CH), 123.3 (CH), 35.2 (CH_2), 33.9 (CH_2), 22.2 (CH_2), 13.9 (CH_3). HRMS (ESI) calcd for $C_{20}H_{22}N_3O_4$ $[M-H]^-$: 368.1609, found: 368.1616.

1,8-Diamino-3,6-dibutylcarbazole (5)

To a solution of 3,6-dibutyl-1,8-dinitrocarbazole (200 mg, 0.54 mmol) in acetonitrile (200 ml), 10% palladium on carbon was added. The air in the flask was evacuated, and the reaction was exposed to H_2. The reaction was allowed to proceed overnight and the yellow solution turned black. The resulting solution was filtered through celite and the solvent was evaporated off under reduced pressure. The crude product obtained in this way was purified via column chromatography over silica gel using 1–2% MeOH in CH_2Cl_2 as the eluent. This gave **8** in 79% yield (132 mg). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.87 (bs, 1H), 7.33 (s, 2H), 6.13 (d, $J = 1.2$ Hz, 2H), 3.13 (bs, 4H), 2.69 (t, $J = 7.6$ Hz, 4H), 1.66 (m, $J = 7.6$ Hz, 4H), 1.38 (m, $J = 7.5$ Hz, 4H), 0.94 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 134.7 (CH), 130.1 (CH), 129.2 (CH), 124.7 (CH), 113.3 (CH), 111.67 (CH), 35.7 (CH_2), 34.4 (CH_2), 22.4 (CH_2), 14.0 (CH_3). HRMS (ESI) calcd for $C_{20}H_{28}N_3$ $[M+H]^+$: 310.2284, found: 310.2277.

1-Amino-3,6-dibutylcarbazole (9)

1-Nitro-3,6-dibutylcarbazole (side product from nitration of **5**) was dissolved in acetonitrile and 10% palladium on carbon was added. The air in the flask was evacuated, and the reaction was exposed to H_2. The reaction was allowed to proceed overnight and the yellow solution turned black. The solution was filtered through celite and the solvent was evaporated off under reduced pressure. ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.8 (s, 1H), 7.71 (bs, 1H), 7.39 (s, 1H), 7.30 (d, $J = 8.4$ Hz, 1H), 7.19 (dd, $J = 8.0$ Hz, $J = 1.4$ Hz, 1H), 6.63 (s, 1H), 3.16 (bs 2H), 2.76 (t, $J = 7.6$ Hz 2H), 7.69 (t, $J = 7.6$ Hz 2H), 1.68 (m, 4H), 1.40 (m, 4H), 0.95 (m, 6H). ^{13}C NMR (90 MHz; $CDCl_3$) δ 138.5 (CH), 135.0 (CH), 134.0 (CH), 129.9 (CH), 129.0 (CH), 126.3 (CH), 124.5 (CH), 124.3 (CH), 119.7 (CH), 113.6 (CH), 111.5 (CH), 110.7 (CH), 35.8 (CH_2), 35.7 (CH_2), 34.5 (CH_2), 34.4 (CH_2), 22.4 (CH_2), 22.4 (CH_2), 14.1 (CH_3), 14.1 (CH_3). HRMS (ESI) calcd for $C_{20}H_{27}N_2$ $[M+H]^+$: 295.2171, found: 295.2169.

1,8-Diamidopyrrolyl-3,6-dibutylcarbazole (1)

A solution of 1,8-diamino-3,6-dibutylcarbazole (500 mg, 1.62 mmol) and pyrrolyl chloride (800 mg) in CH_2Cl_2 was stirred overnight. The solvent was evaporated and the product was purified via column chromatography with 1% MeOH in CH_2Cl_2. The product was precipitated from CH_2Cl_2 in 78% yield. ^{1}H NMR (400 MHz; DMSO-d_6) δ 11.73 (bs, 2H), 10.20 (bs, 1H), 9.92 (bs, 2H), 7.77 (s, 2H), 7.44 (s, 2H), 7.15 (s, 2H), 7.00 (s, 2H), 6.22 (d, $J = 3.2$ Hz, 2H), 2.76 (t, $J = 7.4$ Hz, 4H), 1.68 (m, $J = 7.2$ Hz, 4H), 1.39 (m, $J = 7.5$ Hz, 4H), 0.95 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (100 MHz; DMSO-d_6) δ 158.3 (C═O), 132.8 (CH), 131.7 (CH), 126.0 (CH), 124.3 (CH), 122.46 (CH), 122.43 (CH), 120.7 (CH), 115.9 (CH), 111.7 (CH), 108.9 (CH), 34.9 (CH_2), 33.8 (CH_2), 21.8 (CH_2), 13.9 (CH_3). HRMS (ESI) calcd for $C_{30}H_{33}N_5O_2Na$ $[M+Na]^+$: 518.2538, found: 518.2527.

1-Amidopyrrolyl-3,6-dibutylcarbazole (10)

A solution of 1-amino-3,6-dibutylcarbazole (90 mg) and pyrrolyl chloride in CH_2Cl_2 was stirred overnight. The solvent was evaporated off and the product was purified via column chromatography over silica gel, using CH_2Cl_2 as the eluent (yield 85%). ^{1}H NMR (400 MHz; $CDCl_3$) δ 9.70 (bs, 1H), 9.24 (bs, 1H), 7.90 (s, 1H), 7.84 (s, 1H), 7.75 (s, 1H), 7.25 (d, $J = 8.0$ Hz, 1H), 7.22 (dd, $J = 8.0$ Hz, $J = 1.6$ Hz, 1H), 6.98 (m, 1H), 6.92 (d, $J = 1.2$ Hz, 1H), 6.80 (bs, 1H), 6.26 (m, 1H), 2.77 (q, $J = 8.0$ Hz, 4H), 1.69 (m, 4H), 1.41 (m, 4H), 0.96 (m, 6H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 158.9 (CH), 138.9 (CH), 133.9 (CH), 133.8 (CH), 131.5 (CH), 126.9 (CH), 126.3 (CH), 125.4 (CH), 123.5 (CH), 122.7 (CH), 120.9 (CH), 119.5 (CH), 118.6 (CH), 117.2 (CH), 111.1 (CH), 110.5 (CH), 110.3 (CH), 35.7 (CH_2), 35.4 (CH_2), 34.5 (CH_2), 34.3 (CH_2), 22.4 (CH_2), 22.4 (CH_2), 14.0 (CH_3). HRMS (ESI) calcd for $C_{25}H_{28}N_3O$ $[M-H]^-$: 386.2234, found: 386.2238.

1,8-Diphenylamido-3,6-dibutylcarbazole (2)

A solution of 1,8-diamino-3,6-dibutylcarbazole (90 mg, 0.3 mmol) and benzoyl chloride in CH_2Cl_2 was stirred overnight. The solvent was evaporated off under reduced pressure to give the product. ^{1}H NMR (400 MHz; DMSO-d_6) δ 10.32 (bs, 3H), 8.02 (d, $J = 7.2$ Hz, 4H), 7.79 (s, 2H), 7.61–7.51 (m, 8H), 2.74 (t, $J = 7.4$ Hz, 4H), 1.67 (m, $J = 7.2$ Hz, 4H), 1.37 (m, $J = 7.5$ Hz, 4H), 0.93 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (100 MHz; DMSO-d_6) δ 165.7 (CH), 134.8 (CH), 132.9 (CH), 132.0 (CH), 131.7 (CH), 128.4 (CH), 128.0 (CH), 124.4 (CH), 122.6 (CH), 121.2 (CH), 116.4 (CH), 35.0 (CH_2), 33.9 (CH_2), 21.9 (CH_2), 13.9 (CH_3). HRMS (ESI) calcd for $C_{34}H_{35}N_3O_2Na$ $[M+Na]^+$: 540.2634, found: 540.2622.

1,9-Diamidopyrrolylanthracene (3)

1,9-Diaminoanthracene (*35*) (710 mg, 3.4 mmol) and pyrrole-2-carboxylic acid chloride (1.4 g) were dissolved in CH_2Cl_2 (40 ml). The resulting mixture was stirred for 15 h and then quenched with methanol (40 ml). All volatile solvents were removed under vacuum, yielding a green solid. The solid was washed with consecutive aliquots of methanol and water to yield a light green solid, which was dried under vacuum to afford product **3** in 71% yield. ^{1}H NMR (500 MHz; DMSO-d_6) δ 11.70 (bs, 2H), 10.04 (s, 2H), 9.00 (s, 1H), 8.64 (s, 1H), 7.96 (d, $J = 6.8$ Hz, 2H), 7.81 (d, $J = 5.6$ Hz, 2H), 7.56 (dd, $J = 6.8$ Hz and $J = 1.2$ Hz, 2H), 7.21 (m, 2H), 6.99 (m, 2H), 6.19 (m, 2H). ^{13}C NMR (125 MHz; DMSO-d_6) δ 159.8 (C═O), 133.5 (CH), 131.8 (CH), 126.6 (CH), 126.4 (CH), 126.1 (CH), 125.5 (CH), 125.0 (CH), 122.4 (CH), 121.2 (CH), 117.1 (CH), 111.8 (CH), 108.9 (CH). HRMS (ESI) calcd for $C_{24}H_{19}N_4O_2$ $[M+H]^+$: 395.1509, found: 395.1503; calcd for $C_{24}H_{18}N_4O_2Na$ $[M+Na]^+$: 417.1327, found: 417.1322.

1,9-Diphenylamidoanthracene (4)

1,9-Diaminoanthracene (35) (110 mg, 0.53 mmol), benzoyl chloride (350 μl) and pyridine (200 μl) were dissolved in CH_2Cl_2 (25 ml). The resulting mixture was stirred for 15 h and then quenched with water (50 ml) causing a white precipitate. The precipitate was collected by filtration and washed successively with water and methanol. The resulting white solid was dried under vacuum to afford **4** in 93% yield. ^{1}H NMR (500 MHz; DMSO-d_6) δ 10.60 (bs, 2H), 8.92 (s, 1H), 8.70 (s, 1H), 8.06–8.01 (m, 6H), 7.70 (d, $J = 6.8$ Hz, 2H), 7.61–7.57 (m, 4H), 7.41 (t, $J = 7.8$ Hz, 4H). ^{13}C NMR (125 MHz; DMSO-d_6) δ 166.3 (C═O), 134.8 (CH), 133.9 (CH), 131.8 (CH), 131.4 (CH), 128.3 (CH), 127.8 (CH), 127.3 (CH), 126.8 (CH), 126.2 (CH), 125.4 (CH), 122.9 (CH), 117.97 (CH). HRMS (ESI) calcd for $C_{28}H_{19}N_2O_2$ $[M-H]^-$: 415.1445, found: 415.1452.

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References

(1) Gale, P.A. *Acc. Chem. Res.* **2006**, *39*, 465–475.
(2) Gale, P.A.; Garcia-Garrido, S.E.; Garric, J. *Chem. Soc. Rev.* **2008**, *37*, 151–190.
(3) Bondy, C.R.; Loeb, S.J. *Coord. Chem. Rev.* **2003**, *240*, 77–99.
(4) Sessler, J.L.; Barkey, N.M.; Pantos, G.D.; Lynch, V.M. *New J. Chem.* **2007**, *31*, 646–654.

(5) Kavallieratos, K.; Bertao, C.M.; Crabtree, R.H. *J. Org. Chem.* **1999**, *64*, 1675–1683.
(6) Kavallieratos, K.; de Gala, S.R.; Austin, D.J.; Crabtree, R.H. *J. Am. Chem. Soc.* **1997**, *119*, 2325–2326.
(7) Kang, S.O.; Llinares, J.M.; Powell, D.; VanderVelde, D.; Bowman-James, K. *J. Am. Chem. Soc.* **2003**, *125*, 10152–10153.
(8) Bowman-James, K. *Acc. Chem. Res.* **2005**, *38*, 671–678.
(9) Zhang, Y.; Yin, Z.; He, J.; Cheng, J.-P. *Tetrahedron Lett.* **2007**, *48*, 6039–6043.
(10) Zhang, Y.; Yin, Z.; Li, Z.; He, J.; Cheng, J.-P. *Tetrahedron* **2007**, *63*, 7560–7564.
(11) Chen, C.-L.; Lin, T.-P.; Chen, Y.-S.; Sun, S.-S. *Eur. J. Org. Chem.* **2007**, *2007*, 3999–4010.
(12) Zielinski, T.; Jurczak, J. *Tetrahedron* **2005**, *61*, 4081–4089.
(13) Schmuck, C.; Schwegmann, M. *J. Am. Chem. Soc.* **2005**, *127*, 3373–3379.
(14) Zyryanov, G.V.; Palacios, M.A.; Anzenbacher, P. *Angew. Chem. Int. Ed.* **2007**, *46*, 7849–7852.
(15) Gale, P.A. *Chem. Commun.* **2005**, 3761–3772.
(16) Gale, P.A. *Chem. Commun.* **2008**, 4525–4540.
(17) Piatek, P.; Lynch, V.M.; Sessler, J.L. *J. Am. Chem. Soc.* **2004**, *126*, 16073–16076.
(18) Chmielewski, M.J.; Charon, M.; Jurczak, J. *Org. Lett.* **2004**, *6*, 3501–3504.
(19) Wang, T.; Bai, Y.; Ma, L.; Yan, X.-P. *Org. Biomol. Chem.* **2008**, *6*, 1751–1755.
(20) Thangadurai, T.D.; Singh, N.J.; Hwang, I.-C.; Lee, J.W.; Chandran, R.P.; Kim, K.S. *J. Org. Chem.* **2007**, *72*, 5461–5464.
(21) Curiel, D.; Cowley, A.; Beer, P.D. *Chem. Commun.* **2005**, 236–238.
(22) Suk, J.-M.; Jeong, K.-S. *J. Am. Chem. Soc.* **2008**, *129*, ASAP.
(23) Sessler, J.L.; Cho, D.-G.; Lynch, V. *J. Am. Chem. Soc.* **2006**, *128*, 16518–16519.
(24) Chae, M.K.; Lee, J.-I.; Kim, N.-K.; Jeong, K.-S. *Tetrahedron Lett.* **2007**, *48*, 6624–6627.
(25) Chang, K.-J.; Chae, M.K.; Lee, C.; Lee, J.-Y.; Jeong, K.-S. *Tetrahedron Lett.* **2006**, *47*, 6385–6388.
(26) Chang, K.-J.; Kang, B.-N.; Lee, M.-H.; Jeong, K.-S. *J. Am. Chem. Soc.* **2005**, *127*, 12214–12215.
(27) Chang, K.-J.; Moon, D.; Lah, M.S.; Jeong, K.-S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7926–7929.
(28) He, X.; Hu, S.; Liu, K.; Guo, Y.; Xu, J.; Shao, S. *Org. Lett.* **2006**, *8*, 333–336.
(29) Bates, G.W.; Gale, P.A.; Light, M.E. *Chem. Commun.* **2007**, 2121–2123.
(30) Bates, G.W.; Triyanti; Light, M.E.; Albrecht, M.; Gale, P.A. *J. Org. Chem.* **2007**, *72*, 8921–8927.
(31) Hiscock, J.R.; Caltagirone, C.; Light, M.E.; Hursthouse, M.B.; Gale, P.A. *Org. Biomol. Chem.* **2009**, *7*, 1781–1783.
(32) Caltagirone, C.; Hiscock, J.R.; Hursthouse, M.B.; Light, M.E.; Gale, P.A. *Chem. Eur. J.* **2008**, *14*, 10236–10243.
(33) Caltagirone, C.; Gale, P.A.; Hiscock, J.R.; Brooks, S.J.; Hursthouse, M.B.; Light, M.E. *Chem. Commun.* **2008**, 3007–3009.
(34) Pfeffer, F.M.; Lim, K.F.; Sedgwick, K.J. *Org. Biomol. Chem.* **2007**, *5*, 1795–1799.
(35) Sessler, J.L.; Mody, T.D.; Ford, D.A.; Lynch, V. *Angew. Chem., Int. Ed.* **1992**, *31*, 452–455.
(36) Sessler, J.L.; Berthon-Gelloz, G.; Gale, P.A.; Camiolo, S.; Anslyn, E.V.; Anzenbacher, P., Jr.; Furuta, H.; Kirkovits, G.; Lynch, V.; Maeda, H.; Morosini, P.; Scherer, M.; Shriver, J.; Zimmerman, R.S. *Polyhedron* **2003**, *22*, 2963–2983.
(37) Wilcox, C.S. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J., Dürr, H., Eds.; VCH: Weinheim, 1991; pp 123–143.