

# Anion-triggered electrodeposition in ferrocene-functionalised *ortho*-phenylenediamine-based receptors†‡

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Ferrocene-functionalised anion receptors based on an *ortho*-phenylenediamine scaffold have been shown to undergo anion-triggered electrochemical deposition. This process may offer a new way of detecting anionic species in solution.

## Introduction

The selective recognition and sensing of anions by artificial host molecules continues to attract the interest of the supramolecular chemistry community.<sup>1</sup> Sensing is achieved by coupling two components: (a) selective binding site and (b) signalling subunits that are perturbed by the presence of the guest and thus exhibit redox shifts, colour changes, or fluorescence quenching or enhancement.<sup>2</sup> As part of the continued interest in the development of novel molecular switches and sensors, redox-active receptors for inorganic cations and anions have been studied in great detail.<sup>3</sup> Ferrocene derivatives that bind and allow the electrochemical sensing of cations<sup>4</sup> and anions<sup>5</sup> are a significant sub-group of this type of sensor. The various interactions that allow these charged species to be electrochemically recognized have been reviewed in detail.<sup>3c</sup>

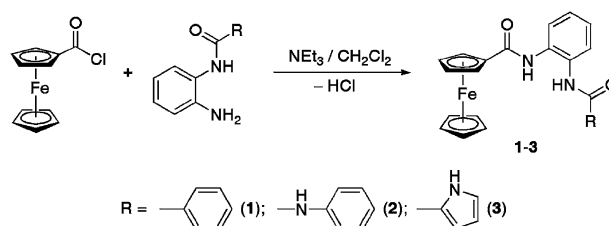
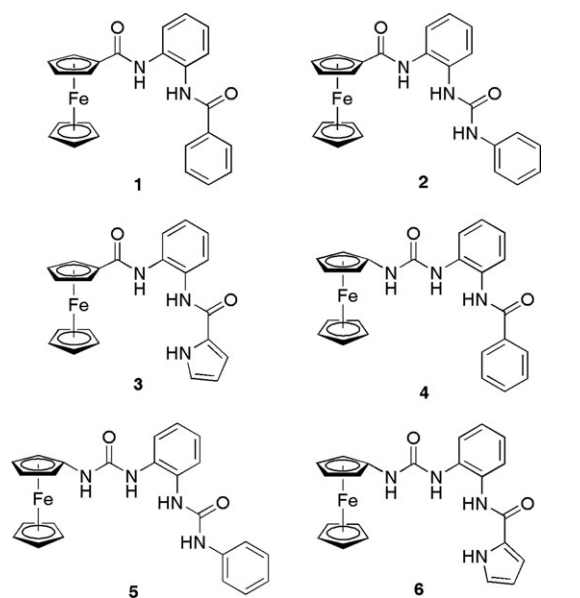
Compounds that contain neutral hydrogen bond donor groups, such as amides<sup>6</sup> or ureas,<sup>7</sup> have been shown to be particularly effective anion receptors in organic solution.<sup>6,7</sup> Hybrid receptors containing both amides and ureas have also been synthesised, and in some cases shown to possess a remarkably high anion affinity and selectivity.<sup>8</sup>

With these precedents in mind, we decided to study a series of receptors formed by combining the redox activity of the ferrocene moiety with the hydrogen bonding ability of amide and urea groups. Here we report the synthesis, characterization, anion coordination properties and electrochemistry of new ferrocene-based anion receptors based on *ortho*-phenylenediamine-functionalised hydrogen bonding arrays. These

compounds were found to undergo an unusual anion-triggered electrochemical deposition process.

## Results and discussion

Treatment of ferrocenecarbonyl chloride<sup>9</sup> with 1 equiv. of *N*-(2-aminophenyl)benzamide,<sup>10</sup> 1-(2-aminophenyl)-3-phenylurea<sup>11</sup> or *N*-(2-aminophenyl)-1*H*-pyrrole-2-carboxamide<sup>12</sup> in dichloromethane, and in the presence of 2.5 equiv. of NEt<sub>3</sub>, generates compounds **1–3** as a yellow-orange solids in 55–77% yield (Scheme 1).

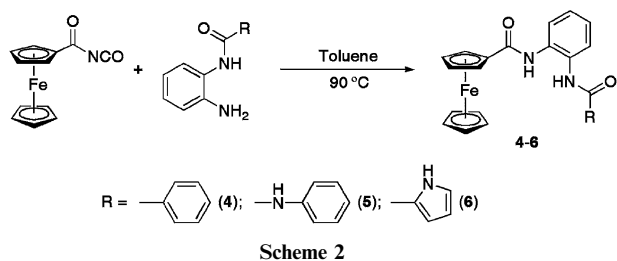


Scheme 1

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‡ Crystal data for **4**. C<sub>24</sub>H<sub>21</sub>FeN<sub>3</sub>O<sub>2</sub>, *M*<sub>r</sub> = 439.29, *T* = 120(2) K, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 15.3994(6), *b* = 9.3582(4), *c* = 14.7688(6) Å, β = 110.351(2)°, *V* = 1995.49(14) Å<sup>3</sup>, ρ<sub>calc</sub> = 1.462 g cm<sup>−3</sup>, μ = 0.782 mm<sup>−1</sup>, *Z* = 4, reflections collected = 25 530, independent reflections = 33 521 (*R*<sub>int</sub> = 0.0927), final *R* indices [*I* > 2σ(*I*)] *R*<sub>1</sub> = 0.0719, *wR*<sub>2</sub> = 0.1321, *R* indices (all data): *R*<sub>1</sub> = 0.0965, *wR*<sub>2</sub> = 0.1431. CCDC 676118. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715125j

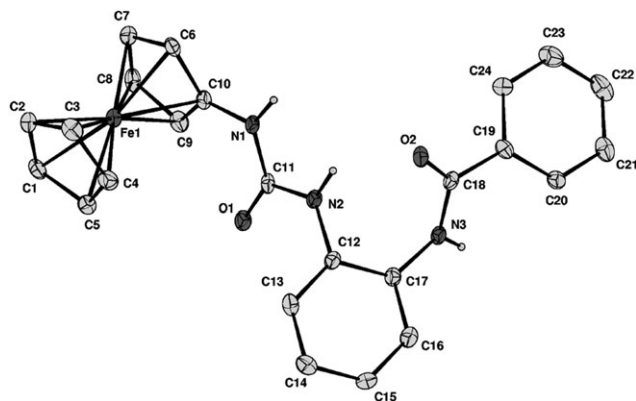


In a similar way, compounds **4–6** were synthesised as brown solids in 55–87% yield by reaction of ferrocenoyl isocyanate, prepared *in situ* from ferrocenoyl azide,<sup>9</sup> with the appropriate primary amine in freshly distilled toluene at 90 °C (Scheme 2).

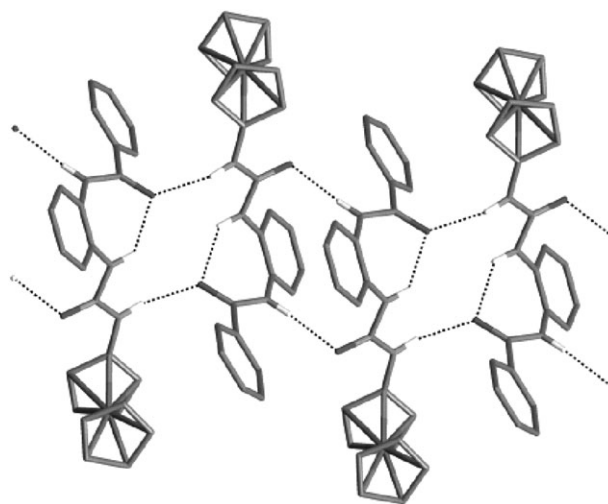
Spectroscopic data (IR and <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR) and elemental analyses for compounds **1–6** are in agreement with the proposed formulations (details are given in the Experimental section). Moreover, the structure of complex **4** has been unequivocally confirmed by a single-crystal X-ray diffraction study. Crystals of **4** were grown by the slow evaporation of a DMSO-*d*<sub>6</sub>-0.5% water solution of the receptor (Fig. 1).<sup>†</sup> The structure shows an intramolecular hydrogen bonding interaction between the oxygen of the amide moiety and the urea-NH group close to the central benzene ring, with a bond distance N2–H2A...O2 of 2.729(5) Å and a bond angle of 134(1)°, in such a way that the amide NH group is orientated in the opposite direction to the two urea NH groups (see Fig. 1). Moreover, in the solid-state, compound **4** forms hydrogen-bonded chains through urea–amide interactions (Fig. 2). These involve intermolecular hydrogen bonds between the NH groups of the amide units and the oxygen of the ureas, as well as between the urea NH groups close to the ferrocene moiety and the oxygen of the amides (see Fig. 2). Representative bond distances for both interactions are: N1–H1A...O2<sup>i</sup> 2.923(5) Å and N3–H3A...O1<sup>ii</sup> 2.865(5) Å, with N–H...O angles being 164 and 155°, respectively (symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + 1, -y, -z + 1$ ).

### Complexation studies

Initial complexation studies on complexes **1–6** were conducted using <sup>1</sup>H NMR titration techniques. Aliquots of the tetra-



**Fig. 1** X-Ray crystal structure of compound **4**. Thermal ellipsoids are drawn at the 35% probability level. Non-acidic hydrogen atoms have been removed for clarity.



**Fig. 2** Hydrogen-bonded chains in the solid-state structure of compound **4**.

butylammonium salts of the putative anionic guest (0.1 mol dm<sup>-3</sup>) were added to a solution of compounds **1–6** (0.01 mol dm<sup>-3</sup>) in DMSO-*d*<sub>6</sub>-0.5% water. The resulting stability constants are summarized in Table 1.

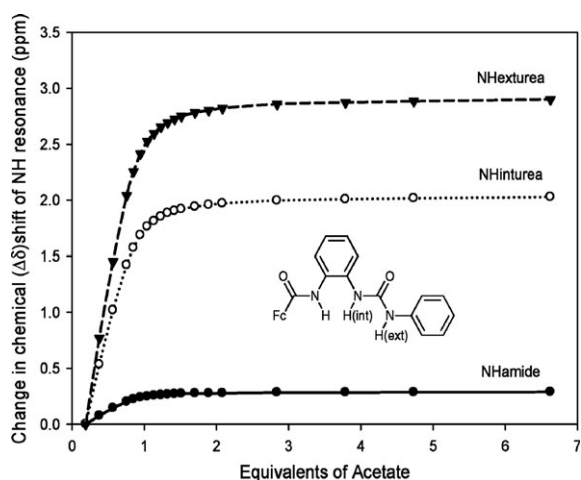
The addition of bromide and hydrogen sulfate did not cause any significant spectral change, even when a high excess of anion was employed. Thus, these anions form no (or very weak) complexes with compounds **1–6** ( $K_a < 10$  M<sup>-1</sup>; see Table 1). On the other hand, analysis of the remaining titration data using the EQNMR<sup>13</sup> computer program revealed that these compounds form 1 : 1 receptor : anion complexes with chloride, acetate, benzoate and dihydrogen phosphate anions, showing a moderate to high affinity of receptors **1–6** for these anions in this competitive solvent medium (CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> > C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub><sup>-</sup> ≈ H<sub>2</sub>PO<sub>4</sub><sup>-</sup> > Cl<sup>-</sup>; Table 1). Significant downfield shifts of the NH protons were observed upon addition of these anions, consistent with the formation of complex–anion hydrogen bonds.

As shown in Table 1, compounds containing urea moieties (**2** and **4–6**) have a considerably higher affinity than compounds with only amide or pyrrole units (**1** and **3**). As an example, the <sup>1</sup>H NMR spectral changes upon addition of tetrabutylammonium acetate to the DMSO-*d*<sub>6</sub>-0.5% water

**Table 1** Stability constants  $K_a$  (M<sup>-1</sup>) of compounds **1–6** with a variety of putative anionic guests (added as tetrabutylammonium salts) at 298 K in DMSO-*d*<sub>6</sub>-0.5% water,<sup>a</sup> as determined by <sup>1</sup>H NMR titration techniques. In all cases, 1 : 1 receptor : anion stoichiometry was observed

Anion	Compounds					
	1	2	3	4	5	6
Cl <sup>-</sup>	12	20	13	11	49	10
Br <sup>-</sup>	<10	<10	<10	<10	<10	<10
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	53	6030	123	1260	709 <sup>b</sup>	1762
C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> <sup>-</sup>	25	514	65	394	430 <sup>b</sup>	690
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	51	877	151	458	270 <sup>b</sup>	490
HSO <sub>4</sub> <sup>-</sup>	<10	<10	<10	<10	<10	<10

<sup>a</sup> Errors estimated to be no more than ±10%. <sup>b</sup> DMSO-*d*<sub>6</sub>-5.0% water.



**Fig. 3** Shifts of the NH protons in compound **2** (from 0.2 to excess equivalents of anion) upon addition of tetrabutylammonium acetate salt in DMSO- $d_6$ -0.5% water.

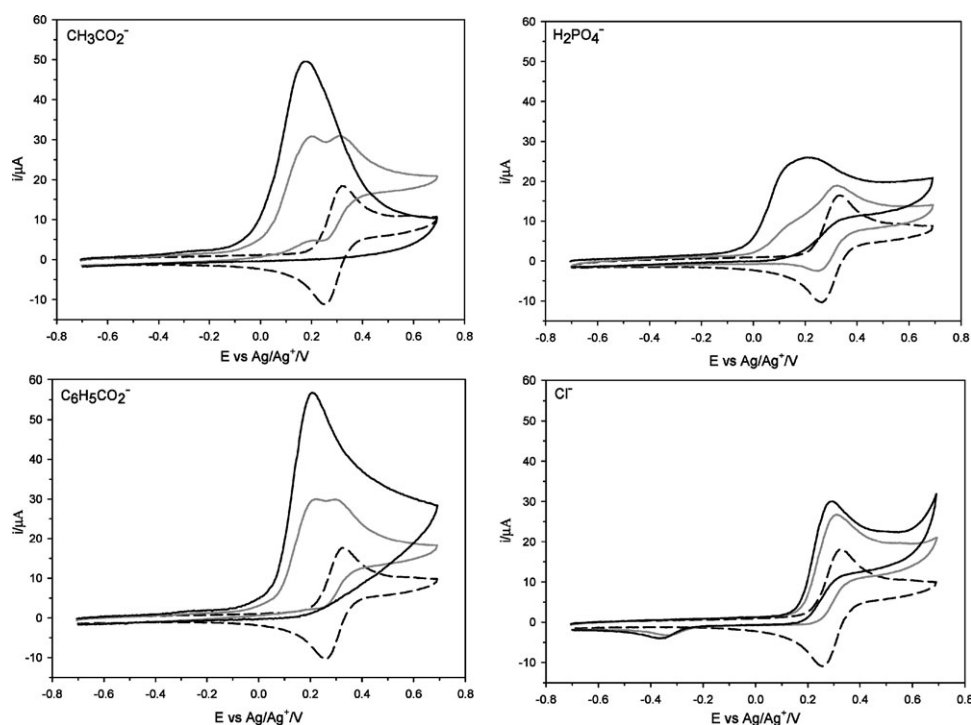
solution of compound **2** is shown in Fig. 3. The spectra show that the urea NH groups shift downfield significantly upon addition of acetate ( $\Delta\delta > 2$  ppm in both cases), but that the amide group is hardly influenced by the presence of the oxo anion ( $\Delta\delta < 0.3$  ppm).

In the case of compound **5**, the stability constants observed after addition of acetate, benzoate and dihydrogen phosphate tetrabutylammonium salts in DMSO- $d_6$ -0.5% water as solvent are greater than  $10^4 \text{ M}^{-1}$ , so are at the upper limits that can be determined by this technique. Owing to this, complexa-

tion studies of **5** were conducted using a more competitive solvent medium (DMSO- $d_6$ -5.0% water), and a moderate-to-high affinity for those anions were still obtained (*i.e.*  $K_a = 709 \text{ M}^{-1}$  for acetate; see Table 1). Thus, except in the cases of compounds **1** and **3**, these compounds show a moderate selectivity towards acetate over chloride, benzoate and phosphate (see Table 1).

Titration studies of complexes **1–6** with tetrabutylammonium fluoride have been also performed. Unfortunately, the  $^1\text{H}$  NMR spectra obtained show a significant broadening of all the NH and CH signals upon addition of the anion salt, making a determination of the stability constant with this anion not possible by this method.

Electrochemical investigations of the compounds have also been undertaken. These take the form of cyclic voltammetry of the ferrocene derivatives in the absence and presence of a variety of anions. Fig. 4 shows a collection of results obtained with compound **1** and a variety of different anions. In each case, the voltammetry is shown at 0, 2 and 5 equivalents of the anion with respect to the receptor. In the absence of an appropriate anion, classic electrochemistry of the ferrocene derivative can be seen (— —). The electrochemistry of this derivative (compound **1**) shows both anodic and cathodic processes, which, if assumed to be a one-electron transfer, can be considered to be close to reversible in nature (peak-to-peak potential  $\sim 69 \text{ mV}$  and ratio of the anodic to cathodic peak 0.98). However, after the addition of an anion, the electrochemical behaviour of this compound shows a distinct change. This was found to be dependent on the particular anion employed (see Fig. 4). In the case of the acetate anion



**Fig. 4** Cyclic voltammetric data gathered for compound (**1**) at a 3 mm diameter glassy carbon disk as a function of the anion to ferrocene receptor concentration ratio (0 : 1 —, 2 : 1 — and 5 : 1 —, respectively). The electrolyte consisted of  $0.1 \text{ mol dm}^{-3}$  TBAPF<sub>6</sub> in (95% CH<sub>3</sub>CN/5% DMSO). The initial ferrocene derivative concentration was 1 mM. All voltammetry was recorded at  $20 \text{ mV s}^{-1}$  under anaerobic conditions at 20–24 °C.

( $\text{CH}_3\text{CO}_2^-$ ), the voltammetry transforms from a redox species exhibiting a one-electron transfer process to a system where only a large anodic signal can be seen. In addition, the voltammetric data shows a shift in the redox potential of the system, with the additional presence of two distinct redox processes at intermediate ratios of anion to receptor (see Fig. 4, —). This experimental data demonstrates that the presence of the binding anion changes the electrochemistry significantly. For example, if the voltammetry of the ferrocene derivative is taken as a one-electron transfer reference peak, then the addition of the anion (at a 5 : 1 anion to receptor ratio) suggests that, on average,  $\sim 2.7$  electrons are transferred to the compound when binding to the anion has occurred (assuming no major changes in the diffusion coefficient of the species involved). In addition, the anodic peak has shifted to +0.176 V compared to the anodic wave of the ferrocene derivative at +0.322 V. In addition to the voltammetric data, it was found by experimental observation that the electrode became passivated after the initial anodic response in the presence of the anion. This passivation could be removed by polishing the electrode surface. If we consider that the ferrocene is only able to accommodate one electron, then the additional electrochemical oxidation must be associated with the *ortho*-phenylenediamine section of the molecule. The passivation of the electrode surface supports this hypothesis as oxidation of *ortho*-phenylenediamine (*o*PD) can lead to electrodeposits, indeed many examples involving the electro-oxidation of *o*PD to form polymer-modified electrodes can be found in the literature.<sup>14</sup> Note also that the mechanistic details for the deposition process are unclear at this stage. However, the experimental evidence supports the hypothesis of additional electrooxidation of the ferrocene derivatives as a result of anion binding. Whether this is as a result of activation of the *o*PD backbone, oligomer formation or polymer formation is unknown at this time. Nevertheless, the binding of the anions clearly dramatically changes the electroactivity of these novel derivatives.

Clearly, this process is dependant on the nature of the anion trigger. Fig. 4 shows that the anions with the strongest polymeric triggering effect are  $\text{CH}_3\text{CO}_2^-$  and  $\text{C}_6\text{H}_5\text{CO}_2^-$ , while the  $\text{H}_2\text{PO}_4^-$  and  $\text{Cl}^-$  ions perturb the electrochemistry of the ferrocene derivative to a lesser extent.

In addition to the electrochemistry of compound **1** and the effects of the anion binding on this compound, the electrochemistry of compounds **3–6** were investigated in a similar manner. In all cases, in the absence of a binding anion, the electrochemistry of the ferrocene moiety was apparently similar (taking minor changes in diffusion coefficient and redox potential into account) with additional redox chemistry apparently depending on the molecule in question. However, anion binding caused large changes to the electrochemistry with multiple redox waves and electrode passivation observed (see ESI†). This suggests that the anion-triggered multi-electron transfer is not a special pathway for compound **1** but a general property of these ferrocene derivatives. The more complex electrochemistry observed with compounds **3–6** vs. compound **1** may be due to the more complex molecular architecture of the anion receptor sections of the derivatives (compounds **3–6**). The derivatives **3–6** may also have a higher

anion affinity, leading to more complex electrochemical processes in the presence of anions, in addition to the electrochemical activity of the starting ferrocene derivative being compound-dependant.

It would thus appear that anion binding by these molecules has the added consequence of changing the electrode potential, over which electrooxidation of the receptors can be driven, and thus provides an interesting new method that may potentially be applied to the detection of anionic species.

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## Experimental

### General procedures

All reactions were performed in oven-dried glassware under a slight positive pressure of nitrogen.  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz) spectra were determined on a Bruker AV300. Chemical shifts for  $^1\text{H}$  NMR are reported in parts per million, calibrated to the residual solvent peak set, with coupling constants reported in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet and br = broad. Chemical shifts for  $^{13}\text{C}\{^1\text{H}\}$  NMR are reported in ppm, relative to the central line of a septet at 39.52 ppm for DMSO- $d_6$ . Deuterated solvents were purchased from Apollo Ltd. ES MS were measured on a Micromass Mattro II instrument. Infrared (IR) spectra were recorded on a Mattson Satellite (ATR) FTIR and are reported in wavenumbers ( $\text{cm}^{-1}$ ). Melting points were measured on a Gallenkamp melting point apparatus. Elemental analyses were performed by Medac Ltd.

### *N*-(2-(Ferrocenecarboxamido)phenyl)benzamide (**1**)

Ferrocenecarbonyl chloride (0.248 g, 1 mmol) was placed in a dry round-bottomed flask under an  $\text{N}_2$  atmosphere and 20  $\text{cm}^3$  of dichloromethane was added. To this was then added *N*-(2-aminophenyl)benzamide (0.212 g, 1 mmol) and  $\text{NEt}_3$  (0.35  $\text{cm}^3$ , 2.5 mmol), and the mixture was left stirring at ambient temperature for 5 h. The solvent was evaporated *in vacuo* and the resulting residue recrystallized from dichloromethane/hexane to obtain an orange solid, which was further purified from acetonitrile to give **1** as an orange powder (0.327 g, 77% yield); mp = 225–228 °C;  $^1\text{H}$  NMR (300 MHz, DMSO,  $\delta$ ): 10.26 (s, 1H, NH), 9.46 (s, 1H, NH), 8.04 (dd,  $J$  = 7.9 and 1.7 Hz, 2H, Ar-H), 7.60 (m, 5H, Ar-H), 7.29 (m, 2H, Ar-H), 4.89 (t,  $J$  = 1.9 Hz, 2H, Cp), 4.46 (t,  $J$  = 1.9 Hz, 2H, Cp), 4.02 (s, 5H, Cp);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz, DMSO,  $\delta$ ): 168.8 (C), 165.2 (C), 133.8 (C), 132.1 (CH), 131.4 (C), 130.8 (C), 128.7 (CH), 127.5 (CH), 125.8 (CH), 125.7 (CH), 125.4 (CH), 125.2 (CH), 75.5 (CH), 70.8 (CH), 69.4 (CH), 68.4 (CH); LRMS ( $\text{ES}^+$ ): 424  $[\text{M}]^+$ , 447  $[\text{M} + \text{Na}]^+$ , 872  $[2\text{M} + \text{Na}]^+$ ; IR (film,  $\text{cm}^{-1}$ ): 3272, 3108, 1652, 1597, 1519, 1496, 1265, 1279, 1264, 1108, 1020, 821, 755, 711, 651, 500, 484, 473. Elemental analysis calc. for  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2\text{Fe}$ : C, 67.94; H, 4.75; N, 6.60. Found: C, 67.96; H, 4.65; N, 6.36%.



### 1-(2-(Ferrocenecarboxamido)phenyl)-3-phenylurea (2)

Ferrocenecarbonyl chloride (0.248 g, 1 mmol) was placed in a dry round-bottomed flask under an N<sub>2</sub> atmosphere and 20 cm<sup>3</sup> of dichloromethane was added. To this was then added 1-(2-aminophenyl)-3-phenylurea (0.227 g, 1 mmol) and NEt<sub>3</sub> (0.35 cm<sup>3</sup>, 2.5 mmol), and the mixture was left stirring at ambient temperature for 3 h. The resulting orange precipitate was removed *via* filtration, and washed with water (3 × 20 cm<sup>3</sup>) and methanol (3 × 20 cm<sup>3</sup>) to afford the product as a pale orange powder (0.290 g, 66%); mp = 201–204 °C; <sup>1</sup>H NMR (300 MHz, DMSO, δ): 9.45 (s, 1H, amide-NH), 9.30 (s, 1H, urea-NH), 8.07 (s, 1H, urea-NH), 7.69 (dd, *J* = 7.9 and 1.1 Hz, 1H, Ar-H), 7.47 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.39 (dd, *J* = 7.5 and 1.5 Hz, 1H, Ar-H), 7.23 (m, 3H, Ar-H), 7.14 (td, *J* = 7.5 and 1.5 Hz, 1H, Ar-H), 6.95 (t, *J* = 7.1 Hz, 1H, Ar-H), 4.95 (t, *J* = 1.9 Hz, 2H, Cp), 4.47 (t, *J* = 1.9 Hz, 2H, Cp), 4.23 (s, 5H, Cp); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO, δ): 168.8 (C), 153.1 (C), 139.8 (C), 133.5 (C), 129.5 (C), 128.8 (CH), 128.7 (CH), 126.5 (CH), 125.7 (CH), 123.5 (CH), 121.8 (CH), 118.2 (CH), 75.8 (C), 70.6 (CH), 69.5 (CH), 68.7 (CH); LRMS (ES<sup>+</sup>): 439 [M]<sup>+</sup>, 462 [M + Na]<sup>+</sup>, 902 [2M + Na]<sup>+</sup>; IR (film, cm<sup>-1</sup>): 3316, 3262, 3203, 3145, 3102, 3054, 1684, 1622, 1598, 1561, 1514, 1500, 1478, 1441, 1323, 1310, 1255, 1203, 1030, 821, 771, 749, 730, 498. Elemental analysis calc. for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>Fe: C, 65.62; H, 4.82; N, 9.56. Found: C, 65.60; H, 4.81; N, 9.40%.

### N-(2-(Ferrocenecarboxamido)phenyl)-1H-pyrrole-2-carboxamide (3)

Ferrocenecarbonyl chloride (0.248 g, 1 mmol) was placed in a dry round-bottomed flask under an N<sub>2</sub> atmosphere and 20 cm<sup>3</sup> of dichloromethane was added. To this was then added *N*-(2-aminophenyl)-1H-pyrrole-2-carboxamide (0.201 g, 1 mmol) and NEt<sub>3</sub> (0.35 cm<sup>3</sup>, 2.5 mmol), and the reaction was then heated to reflux and left stirring for 2 h. The crude product was purified by column chromatography using ethyl acetate : hexane 3 : 7 as the eluent, which yielded compound **3** as a yellow powder (0.227 g, 55%); mp = 138–141 °C; <sup>1</sup>H NMR (300 MHz, DMSO, δ): 11.86 (s, 1H, pyrrol-NH), 9.90 (s, 1H, amide-NH), 9.48 (s, 1H, amide-NH), 7.57 (m, 2H, Ar-H), 7.25 (m, 2H, Ar-H), 7.01 (br s, 2H, Ar-H), 6.21 (t, *J* = 2.6 Hz, 1H, Ar-H), 4.89 (t, *J* = 1.5 Hz, 2H, Cp), 4.46 (t, *J* = 1.5 Hz, 2H, Cp), 4.07 (s, 5H, Cp); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO, δ): 168.4 (C), 159.3 (C), 131.1 (C), 130.6 (C), 125.3 (CH), 125.2 (CH), 125.1 (C), 125.0 (CH), 124.9 (CH), 122.9 (CH), 111.3 (CH), 109.1 (CH), 75.4 (C), 70.6 (CH), 69.3 (CH), 68.2 (CH); LRMS (ES<sup>+</sup>): 413 [M]<sup>+</sup>, 436 [M + Na]<sup>+</sup>, 850 [2M + Na]<sup>+</sup>; IR (film, cm<sup>-1</sup>): 3401, 3245, 3115, 1633, 1595, 1549, 1510, 1481, 1434, 1404, 1377, 1312, 1274, 1127, 1106, 1042, 1027, 822, 744, 607, 526, 484. Elemental analysis calc. for C<sub>22</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>Fe: C, 63.94; H, 4.63; N, 10.16. Found: C, 63.95; H, 4.77; N, 10.10%.

### 1-(2-(Benzamido)phenyl)-3-ferrocenylurea (4)

Ferrocenoyl azide (0.259 g, 1 mmol) and *N*-(2-aminophenyl)-benzamide (0.212 g, 1 mmol) were placed in a dry round-bottomed flask under an N<sub>2</sub> atmosphere and 20 cm<sup>3</sup> of freshly distilled toluene was added. The solution was heated at 90 °C

for 18 h, after which the resulting brown precipitated product was removed by filtration and washed with dichloromethane (3 × 20 cm<sup>3</sup>), with **2** isolated as a brown solid (0.382 g, 87%); mp = 187–190 °C; <sup>1</sup>H NMR (300 MHz, DMSO, δ): 10.06 (s, 1H, amide-NH), 8.37 (s, 1H, urea-NH), 8.06 (d, *J* = 7.0 Hz, 2H, Ar-H), 7.91 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.86 (s, 1H, urea-NH), 7.58 (m, 3H, Ar-H), 7.36 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.23 (t, *J* = 7.0 Hz, 1H, Ar-H), 7.07 (t, *J* = 7.0 Hz, 1H, Ar-H), 4.48 (t, *J* = 1.7 Hz, 2H, Cp), 4.11 (s, 5H, Cp), 3.93 (t, *J* = 1.7 Hz, 2H, Cp); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO, δ): 165.6 (C), 153.2 (C), 134.7 (C), 134.1 (C), 131.7 (CH), 128.4 (CH), 127.9 (C), 127.7 (CH), 127.2 (CH), 126.3 (CH), 122.5 (CH), 121.6 (CH), 96.6 (C), 68.6 (CH), 63.6 (CH), 60.4 (CH); LRMS (ES<sup>+</sup>): 439 [M]<sup>+</sup>, 462 [M + Na]<sup>+</sup>, 902 [2M + Na]<sup>+</sup>; IR (film, cm<sup>-1</sup>): 3315, 3262, 3202, 3144, 3101, 3052, 1684, 1625, 1598, 1561, 1513, 1500, 1477, 1440, 1310, 1255, 1203, 1106, 1030, 821, 749, 691, 529, 498, 484. Elemental analysis calc. for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>Fe: C, 65.62; H, 4.82; N, 9.56. Found: C, 65.52; H, 4.76; N, 9.52%.

### 1-(2-(Phenylureido)phenyl)-3-ferrocenylurea (5)

Ferrocenoyl azide (0.259 g, 1 mmol) and 1-(2-aminophenyl)-3-phenylurea (0.227 g, 1 mmol) were placed in a dry round-bottomed flask under an N<sub>2</sub> atmosphere, 20 cm<sup>3</sup> of freshly distilled toluene was added and the solution was heated at 90 °C for 24 h. The precipitated product was removed *via* filtration before suspending the product in dichloromethane (50 cm<sup>3</sup>) and washing with aqueous HCl solution (3 × 20 cm<sup>3</sup>, pH = 1). The organic phase was retained and the solvent removed *in vacuo*. The residue was recrystallized from hot acetone and dried under high vacuum. The product was isolated as a brown solid (0.313 g, 69%); mp = 164–167 °C; <sup>1</sup>H NMR (300 MHz, DMSO, δ): 9.14 (s, 1H, urea-NH), 8.27 (s, 1H, urea-NH), 8.14 (s, 1H, urea-NH), 8.00 (s, 1H, urea-NH), 7.70 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.52 (m, 2H, Ar-H), 7.27 (t, *J* = 7.5 Hz, 2H, Ar-H), 7.06 (m, 2H, Ar-H), 6.95 (t, *J* = 7.5 Hz, 2H, Ar-H), 4.49 (br s, 2H, Cp), 4.14 (s, 5H, Cp), 3.93 (br s, 2H, Cp); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO, δ): 153.5 (C), 153.3 (C), 139.9 (C), 132.3 (C), 130.0 (C), 128.7 (CH), 124.5 (CH), 124.2 (CH), 123.1 (CH), 122.7 (CH), 121.7 (CH), 118.1 (CH), 96.6 (C), 68.7 (CH), 63.6 (CH), 60.7 (CH); LRMS (ES<sup>+</sup>): 454 [M]<sup>+</sup>, 477 [M + Na]<sup>+</sup>, 931 [2M + Na]<sup>+</sup>; IR (film, cm<sup>-1</sup>): 3293, 3091, 1734, 1635, 1598, 1560, 1498, 1477, 1442, 1294, 1249, 1201, 1104, 1020, 1001, 803, 750, 692, 486. Elemental analysis calc. for C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub>Fe: C, 63.45; H, 4.88; N, 12.33. Found: C, 63.58; H, 4.80; N, 12.42%.

### 1-(2-(1H-Pyrrole-2-carboxamido)phenyl)-3-ferrocenylurea (6)

Ferrocenoyl azide (0.259 g, 1 mmol) and *N*-(2-aminophenyl)-1H-pyrrole-2-carboxamide (0.201 g, 1 mmol) were placed in a dry round-bottomed flask under an N<sub>2</sub> atmosphere and 20 cm<sup>3</sup> of freshly distilled toluene was added. The solution was heated at 90 °C for 8 h, after which the resulting brown precipitated product was removed by filtration and washed with dichloromethane (3 × 20 cm<sup>3</sup>), with **6** isolated as a brown solid (0.253 g, 59%); mp = 162–165 °C; <sup>1</sup>H NMR (300 MHz, DMSO, δ): 11.63 (s, 1H, pyrrol-NH), 9.61 (s, 1H, amide-NH), 8.41 (s, 1H, urea-NH), 8.00 (s, 1H, urea-NH), 7.86 (d, *J* =

6.8 Hz, 1H, Ar-H), 7.36 (d,  $J = 6.8$  Hz, 1H, Ar-H), 7.17 (br s, 1H, Ar-H), 6.99 (m, 3H, Ar-H), 6.18 (br s, 1H, Ar-H), 4.48 (br s, 2H, Cp), 4.11 (s, 5H, Cp), 3.93 (br s, 2H, Cp);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz, DMSO,  $\delta$ ): 159.5 (C), 153.1 (C), 134.1 (C), 127.6 (C), 126.6 (CH), 125.8 (CH), 125.5 (C), 122.2 (CH), 122.1 (CH), 121.1 (CH), 111.0 (CH), 108.7 (CH), 96.4 (C), 68.4 (CH), 63.4 (CH), 60.2 (CH); LRMS ( $\text{ES}^+$ ): 428  $[\text{M}]^+$ , 451  $[\text{M} + \text{Na}]^+$ , 880  $[2\text{M} + \text{Na}]^+$ ; IR (film,  $\text{cm}^{-1}$ ): 3232, 3107, 3034, 1650, 1632, 1589, 1531, 1514, 1494, 1470, 1455, 1436, 1342, 1295, 1275, 1103, 812, 752, 737, 486, 471. Elemental analysis calc. for  $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_2\text{Fe}$ : C, 61.70; H, 4.71; N, 13.08. Found: C, 61.55; H, 4.56; N, 12.92.

## Crystallography

Data for **4** were collected on a Bruker Nonius KappaCCD diffractometer mounted at the window of a Mo rotating anode. $\ddagger$

## Electrochemistry

Electrochemical data was recorded on an in-house-constructed electrochemical workstation and supporting software. Voltammetry was recorded at a 3 mm diameter glassy working carbon electrode in a three electrode arrangement, including a Pt counter and a  $\text{Ag}/\text{Ag}^+$  reference electrode. The working electrode was polished on 0.3  $\mu\text{m}$  diameter alumina on a Microcloth, followed by washing in dry DMSO prior to recording each voltammogram. Data were gathered at room temperature ( $22 \pm 2$   $^\circ\text{C}$ ) under aerobic conditions. The sweep rate, unless stated otherwise, was 20  $\text{mV s}^{-1}$ .

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