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Synthesis and dihydrogen phosphate binding properties of pyrrole containing *ansa*-ferrocenes

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Abstract

Pyrrole-substituted α,ω-diamines varying in length and number of heteroatoms between the amine functionalities were reacted with 1,1′-ferrocenedimethanol to form *ansa*-ferrocenes. ^{1}H-NMR binding studies in a 2% dimethylsulfoxide-d_6 solution of dichloromethane-d_2 establish a correlation between the affinity for tetrabutylammonium dihydrogen phosphate and the number of heteroatoms in the diamine. Further support for this conclusion came from electrochemical analyses.

Keywords: Ferrocene; Phosphate binding; Amide coupling; Binding constants; Pyrrole; Electrochemical sensor

1. Introduction

Ferrocenes have been incorporated into a number of anion sensors [1,2]. Their well-known redox properties, coupled with the induced electrostatic effects expected upon oxidation, make them attractive components in anion sensing systems. Recent developments in this area include water soluble systems exhibiting binding selectivity [3,4] and the use of dipeptide esters to sense $H_2PO_4^-$, Cl^-, and Br^- [5]. Takenaka and coworkers designed a naphthalene diimide substituted ferrocene that acts as a DNA intercalator and can electrochemically sense DNA when bonded to a gold surface [6]. In spite of this progress, there remains a need for ferrocene-based systems that display greater substrate selectivity, offer improved signal-to-noise ratios, and allow specific anions to be targeted more readily for binding. One way to do this could be to implement pyrroles as key anion binding subunits.

Many systems incorporating multiple pyrrole units into their framework are well known for their ability to bind anions [7–9]. Depending on the design of the system, the binding can be tailored for strength and selectivity. Initial attempts at combining the anion binding affinity of pyrrole systems with the electrochemical sensing ability of ferrocenes resulted in ferrocene–calix[4]pyrrole conjugates wherein the ferrocene moieties were tethered to the calix[4]pyrrole anion recognition unit at either *meso*-like or β-pyrrolic sites via amide linkages [10]. Unfortunately, electrochemical analyses of these systems revealed unpredictable and contradictory responses upon the addition of anions, perhaps as a result of fundamental differences in conformational behavior of these two classes of receptor (i.e. *meso* or β-pyrrole linked). While a full test of this hypothesis awaits experimental verification it was subsequently found that an *ansa*-ferrocene, containing a ferrocene subunit covalently bound within a pyrrole-based macrocyclic framework (compound **1**; Scheme 1), displayed a high intrinsic affinity for Lewis basic anions while acting, concurrently, as an effective electrochemical sensor for F^- and $H_2PO_4^-$ [11]. We now report the synthesis of three new pyrrole-rich *ansa*-ferrocene systems wherein the length and nature of the bridging arm has been varied as detailed below. Both factors play a role in regulating the dihydrogen phosphate anion

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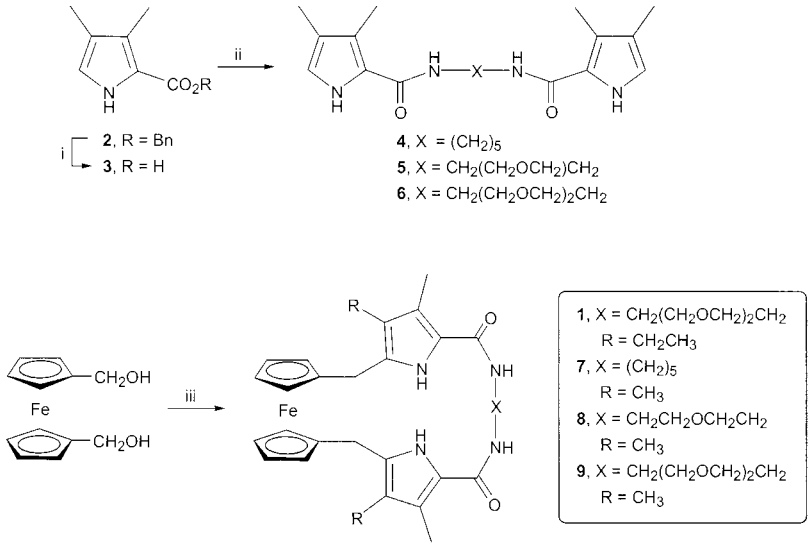

Scheme 1. Synthesis of receptor systems **7**–**9**. Reagents: (i) Pd/C–H_2, Et_3N, THF; (ii) $NH_2(CH_2)_5NH_2$, or $NH_2CH_2(CH_2OCH_2)_2CH_2NH_2$, DCC, DMF, and HOBT (in the case of **4** and **6**) or $NH_2CH_2CH_2OCH_2CH_2NH_2{\cdot}2HCl$, Et_3N, DCC, and CH_2Cl_2 (in the case of **5**); and (iii) **4**–**6**, TFA, CH_2Cl_2.

affinities as well as modulating the nature of the ferrocene/ferrocenium-based electrochemical response.

2. Results and discussion

In the initial bridged pyrrolic *ansa*-ferrocene **1**, a single crystal X-ray diffraction study revealed the presence of a water molecule inside the cavity, as well as a second water molecule not constrained in the cavity but hydrogen bonded to the encapsulated water molecule (Fig. 1). The water molecule bound in the cavity was stabilized by NH···O hydrogen bonds from an amide NH and a pyrrole NH, acting as hydrogen bond donors, as well as an OH···O hydrogen bond from the water to an ether oxygen of the linker, acting as a hydrogen bond acceptor [11].

It was the presence of this latter linker-derived hydrogen bonding interaction, along with evidence of strong dihydrogen phosphate binding in solution, that inspired the present study. Dihydrogen phosphate, an all-important biological anion, has two OH hydrogen bond donor sites that could interact with an ether oxygen atom. To the extent dihydrogen phospate is indeed binding to **1** via these kinds of interactions, a simple test of binding affinity versus number of oxygen atoms present in the linker (0, 1 or 2) should reveal differences. On this basis we decided to prepare receptors **7**–**9** (the latter being analogous to **1**) so as to carry out such a detailed test of anion affinity as a function of *ansa*-ferrocene structure.

The initial system **1** was synthesized previously through a multistep procedure beginning with the pyrrole–cyclopentadiene conjugate, then forming the ferrocene, and ending with an amide coupling of the linker [11]. Briefly, the synthesis involves oxidative coupling of acetoxy-benzyl ester pyrrole to cyclopentadiene with $Pb(OAc)_4$ followed by formation of the cyclopentadienyl anion with TlOEt and creation of the ferrocene with $FeCl_2$. Hydrogenation of the benzyl esters followed by an amide coupling with 2,2′-(ethylenedioxy)bis(ethylamine) using BOP results in the macrocycle **1**. This procedure worked very well initially; however, as the length and heteroatom character of the diamine used in the coupling was varied, both the yields and reactivity were found to suffer.

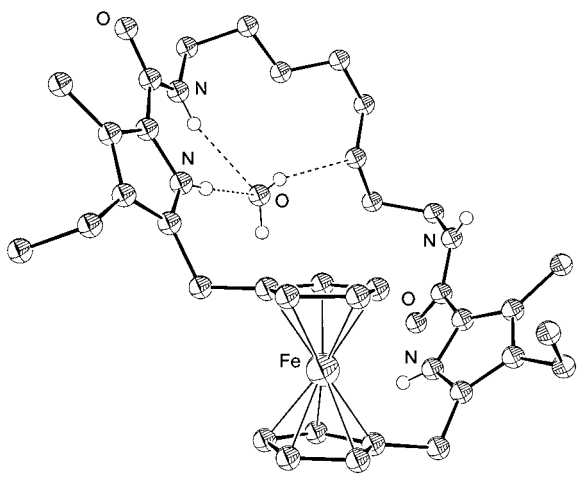

Fig. 1. Solid state structure of $\mathbf{1}{\cdot}2H_2O$ (the second water molecule, not contained in the cavity, has been omitted for clarity), previously published in Ref. [11].

Table 1
Relevant stability constants and electrochemical data for $H_2PO_4^-$ complexes formed with receptors **7**–**9**

Receptor	Oxygens in linker	K_a [a] (M^{-1})	$E_{1/2}$ [b] (mV)	ΔE_c [c] (mV)
7	0	4050 ± 300	432 ± 5	128
8	1	$13\,200 \pm 1500$	428 ± 4	140
9	2	$81\,400 \pm 9700$	432 ± 4	140

[a] Association constants for anion binding recorded in 2% dimethylsulfoxide-d_6–dichloromethane-d_2; determined from ppm NH (amide) [14].

[b] Determined in dichloromethane containing 0.1 M n-Bu_4NPF_6 as the supporting electrolyte. Solutions of **7**–**9** were 0.001 M and the potentials were determined with reference to Ag AgCl over an average of values from 15, 25, 50, 75, and 100 Hz.

[c] Cathodic shift observed after the addition of five molar equivalents of n-$Bu_4NH_2PO_4$.

A simple change in the order of reactivity allowed us to synthesize our targets **7**–**9**. The synthesis of *ansa*-ferrocenes **7**–**9** is summarized in Scheme 1. α-Benzyl ester pyrrole **2** was prepared as previously reported [12]. Deesterification under reductive conditions gave the corresponding acid (**3**), which when treated with the appropriate diamine under standard amide-forming conditions gave the key precursors, **4**–**6**. The macrocyclic receptors were subsequently prepared under *pseudo* high dilution conditions. 1,1′-Ferrocenedimethanol and the appropriate bispyrrole, each dissolved in an equal volume of CH_2Cl_2, were added simultaneously to a vigorously stirred solution of TFA in CH_2Cl_2 to generate the corresponding target molecules **7**–**9**. By placing the key amide coupling step earlier on in the synthetic sequence, we were able to circumvent the relatively low yields seen in the case of the original synthesis. We ascribe this salutary finding to the reduction in incipient steric strain that comes from carrying out the coupling at a stage that involves less hindered precursors.

Compounds **4** and **6** were obtained in 63 and 70% yield, respectively, by coupling of the pyrrole carboxylic acid **3** with the corresponding diamines 1,5-diaminopentane and 2,2′-(ethylenedioxy)bis(ethylamine) using DCC with HOBT in DMF. Compound **5** could not be obtained in this manner, however. The diamine precursor to **5**, 2,2′-oxybis(ethylamine), is commercially available only in the form of its dihydrochloride salt. Initial amide couplings in DMF with excess equivalents of various bases such as triethylamine, TMEDA, and DBU proved unsuccessful. It was then liquid–liquid extracted to obtain the neutral diamine. The resulting free-base was then subjected to the same coupling conditions, however, to no avail. Due to solubility problems this route was abandoned and efforts were made to use the dihydrochloride salt. Coupling this salt with **3** in dichloromethane with DCC in the presence of excess triethylamine was then found to afford **5** in 18% yield. With these precursors (i.e. **4**–**6**) in hand, compounds **7**–**9** were obtained in 33, 20 and 35% yields, respectively, by reacting them with 1,1′-ferrocenedimethanol in the presence of TFA in dichloromethane.

The original *ansa*-ferrocene **1** was shown to have a binding affinity for the tetrabutylammonium salt of dihydrogen phosphate of $11\,305\ M^{-1}$ in CD_3CN. Unfortunately, solubility problems precluded similar studies of **7** and **8** in this solvent. Instead, dichloromethane-d_2 containing 2% dimethylsulfoxide-d_6 was used, with this specific solvent ratio being chosen in an effort to balance solubility needs against a desire to keep the affinity constant values within reasonable detection limits. Mole ratio plots confirmed the proposed 1:1 binding stoichiometry and subsequent standard analyses revealed the affinity constants given in Table 1 [13].

Square wave electrochemical analyses of receptors **7**–**9** were carried out. The results are summarized in Table 1. Unfortunately, reaction coupling efficiencies [2] could not be determined for the binding because it proved necessary to use different solvents to measure the affinity constants and study the electrochemical properties of receptors **7**–**9**. Nonetheless, these results show that the affinity of the receptor for dihydrogen phosphate increases along the series of **7**–**9**, indicating that the oxygen atoms in the linkers are participating in the binding event, while the ferrocene/ferrocenium potentials are seen to shift cathodically upon addition of dihydrogen phosphate anion in a way that is less obvious (i.e. by 128 mV for receptor **7** and 140 mV for receptors **8** and **9**).

Based on the above observations, we conclude that the presence of oxygen atoms in the linker increases the electrochemical response of an *ansa*-ferrocene observed upon the addition of dihydrogen phosphate. The fact that we do not see an increased response going from one to two oxygen atoms in the linker (i.e. upon going from **8** to **9**) means that the additional electrostatic influence in the binding upon oxidation from Fe^{2+} to Fe^{3+} is equal in both molecules. This leads us to propose that the proximity of the bound dihydrogen phosphate anion to the ferrocene-bound iron center is similar in the case of both **8** and **9**. To the extent this is true, it would lead to identical through space interactions and similar electrochemical responses, as indeed is seen by experiment. The fact that the electrostatic interaction relative to the iron center is identical in the case of **8** and **9** highlights the importance, at least as far as an electrochemical 'read-out' response is concerned, of the nature of linker type over cavity size. Compound **9** has a larger cavity than either **7** or **8**; if size were the dominating factor in terms of electrochemical response, a large voltage change in the anion binding would be

seen upon going from **8** and **9**, something that is not observed. On the other hand, if size alone were the major determinant as far as the degree of anion-induced cathodic shift were concerned, the same electrochemical response would be seen for both **7** and **8**, again something that is not observed. Still, it is important to appreciate that the factors regulating anion binding per se are perhaps slightly different. Here, the number of possible OH···O hydrogen bonding interactions is clearly important, as evidenced by the fact that in their neutral ferrocene forms, receptor **8** binds dihydrogen phosphate significantly less well than receptor **9**.

In conclusion, three *ansa*-ferrocenes were synthesized by a new method allowing for higher yields and fewer steps than the procedure originally employed. The binding affinity for dihydrogen phosphate increases stepwise as the number of oxygen atoms in the linking bridge increases from 0 to 2. This is consistent with the ether-type oxygen atoms present in the bridge being involved directly in the anion binding process. Electrochemical studies further support the proposal that these oxygen atoms are involved in dihydrogen phosphate binding. On the other hand, the degree of anion-induced cathodic shift in the ferrocene/ferrocenium potentials does not correlate fully with the number of oxygen atoms present in the bridge. This is consistent with these latter effects reflecting more complex, or at least different, processes than those associated with binding to the reduced, ferrocene form of the receptors. On a more general level, the present results highlight the importance of specific design in generating new pyrrole-based receptors while underscoring in particular the importance of hydrogen bond acceptor sites in regulating both affinities and electrochemical response. As such, they help set the stage for the construction of yet-improved anion recognition and sensing systems.

3. Experimental

3.1. General information

^{1}H- and ^{13}C-NMR spectra were obtained on a Bruker AC250 spectrometer or Varian 300 MHz spectrometer. Square wave voltammetry was carried out at room temperature (25 ± 2 °C) under dry Ar using a Bioanalytic Systems Inc. (BAS) CV-50W Version 2 MF 9093 Voltammetric Analyzer. A platinum disk was the working electrode (1.6 mm diameter), and a platinum wire the auxiliary electrode. An Ag | AgCl couple, separated from the bulk solution by means of a porous Vycor plug, was used as the reference electrode.

3.2. Materials

All reactions were conducted under dry Ar unless otherwise stated. All solvents were of reagent grade quality and purchased commercially. Tetrahydrofuran (THF) was degassed and dried over two columns of activated neutral alumina. *N*,*N*-Dimethylformamide was degassed and dried over two columns of molecular sieves. Dichloromethane and triethylamine (Et_3N) were both dried over CaH_2. All starting materials were purchased from Aldrich Chemical Co. and used without further purification unless otherwise stated. Tetrabutylammonium salts were purchased from Fluka and dried under vacuum at 40 °C for 2 h prior to use. All NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. Thin layer chromatography (TLC) analyses were performed on silica gel 60 F-254 (0.2 mm thickness) using 5% MeOH in CH_2Cl_2 as eluent. Preparative chromatography columns were packed with silica gel (Merck Type 60, 230–400 mesh).

3.3. ^{1}H-NMR titrations

The receptors **7**–**9** were prepared as ca. 9.0×10^{-4} M solutions in CH_2Cl_2-d_2 (2% v/v Me_2SO-d_6) solutions. A stock solution of the tetrabutylammonium salt of dihydrogen phosphate was dissolved in a solution of the receptor at its initial concentration to account for dilution effects. The anion was then added in increasing concentration to the initial receptor solution, in increments from 0.1 equivalent to approximately ten equivalents. The shift of the amide N(H) proton was followed and the data was fit to a 1:1 binding profile according to the Wilcox equation [14], with errors 12%.

3.4. 3,4-Dimethyl-pyrrole-2-carboxylic acid benzyl ester (*2*)

3,4-Dimethyl-pyrrole-2-carboxylic acid benzyl ester (**2**) was prepared as previously reported [12].

3.5. 3,4-Dimethyl-pyrrole-2-carboxylic acid (*3*)

3,4-Dimethyl-pyrrole-2-carboxylic acid benzyl ester (**2**) (500 mg, 2.18 mmol) and 10% Pd/C (250 mg) were suspended in THF (55 ml). Triethylamine (4 drops) was added to the reaction mixture, which was then placed under a hydrogen atmosphere and left to stir at 25 °C for 24 h. The mixture was filtered through a pad of celite and the filtrate was concentrated in vacuo to give **3** as a pale pink solid (303 mg, 100%). The physical properties of this material agree with those previously reported [15].

3.6. 1,5-Bis-(3,4-dimethyl-pyrrole-2-carbonylamino)-pentane (4)

1,5-Diaminopentane (85 mg, 0.83 mmol), 3,4-dimethyl-pyrrole-2-carboxylic acid (**3**) (232 mg, 1.67 mmol) and 1-hydoxybenzotrizole hydrate (225 mg, 1.67 mmol) were dissolved in dry DMF (21 ml). The solution was stirred for 10 min, then *N*,*N*-dicyclohexylcarbodiimide (413 mg, 2.00 mmol) was added, and the reaction mixture was left to stir at 25 °C for 24 h. The reaction mixture was filtered, the filtrate was concentrated in vacuo and the remaining residue was dissolved in $CHCl_3$ (30 ml). The organic phase was washed with 0.5 M HCl (3 × 30 ml), saturated aqueous $NaHCO_3$ (3 × 30 ml), and a saturated NaCl solution (2 × 30 ml). The organic phase was then dried over $MgSO_4$ and the filtrate was concentrated in vacuo to give a light pink solid. Purification by column chromatography (silica, 3% MeOH–CH_2Cl_2) gave **4** as a white solid (179 mg, 63%). ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.46$ (quin., 2H, $NHCH_2CH_2CH_2CH_2CH_2NH$), 1.64 (quin., 4H, $NHCH_2CH_2CH_2CH_2CH_2NH$), 2.02 (s, 6H, pyr–CH_3), 2.24 (s, 6H, pyr–CH_3), 3.42 (br t, 4H, $CONHCH_2CH_2$), 5.95 (br s, 2H, $CONHCH_2$), 6.62 (d, 2H, pyr–*H*), 9.16 (br s, 2H, N*H*). ^{13}C-NMR (62 MHz, $CDCl_3$): $\delta = 10.1$, 10.8, 24.0, 29.5, 39.1, 118.7, 119.6, 120.1, 122.7, 162.5. CIMS [M + H] 345. CIHRMS [M + H] 345.2294 (calc. for $C_{19}H_{29}N_4O_2$, 345.2291).

3.7. 1,5-Bis-(3,4-dimethyl-pyrrole-2-carbonylamino)-3-oxapentane (5)

3,4-Dimethyl-pyrrole-2-carboxylic acid (**3**) (470 mg, 3.38 mmol), 2,2′-oxybis(ethylamine) (176 mg, 1.69 mmol) and *N*,*N*-dicyclohexylcarbodiimide (836 mg, 4.05 mmol) were suspended in dry CH_2Cl_2 (100 ml). Dry Et_3N (0.94 ml, 6.76 mmol) was added causing a momentary clearing of the solution before it became cloudy again. The reaction mixture was left to stir at 25 °C for 24 h. The reaction mixture was filtered and the organic phase was washed with 0.5 M HCl (3 × 50 ml), saturated aqueous $NaHCO_3$ (3 × 50 ml), and a saturated NaCl solution (2 × 50 ml). The organic phase was then dried over Na_2SO_4 and the filtrate was concentrated in vacuo to give a light pink solid. Purification by column chromatography (silica, 3.5% MeOH–CH_2Cl_2) gave **5** as a pale yellow solid (103 mg, 18%). ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.98$ (s, 6H, pyr–CH_3), 2.17 (s, 6H, pyr–CH_3), 3.59–3.64 (m, 8H, $CONHCH_2CH_2O$), 6.20 (br s, 2H, $CONHCH_2$), 6.60 (d, 2H, pyr–*H*), 9.17 (br s, 2H, N*H*). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 10.0$, 10.5, 39.1, 70.0, 118.6, 119.7, 120.0, 122.5, 162.3. CIMS [M + H] 347. CIHRMS [M + H] 347.2082 (calc. for $C_{19}H_{29}N_4O_2$, 347.2083).

3.8. 1,8-Bis-(3,4-dimethyl-pyrrole-2-carbonylamino)-3,6-dioxaoctane (6)

This compound was prepared by the procedure used to prepare **4** but starting from 2,2′-(ethylenedioxy)bis(ethylamine) (162 mg, 1.09 mmol), 3,4-dimethyl-pyrrole-2-carboxylic acid (**3**) (303 mg, 2.18 mmol), 1-hydoxybenzotrizole hydrate (295 mg, 2.18 mmol) and *N*,*N*-dicyclohexylcarbodiimide (540 mg, 2.62 mmol) in DMF (26 ml). Purification by column chromatography (silica, 3.5% MeOH–CH_2Cl_2) gave **6** as a flaky white solid (295 mg, 70%). ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 2.00$ (s, 6H, pyrr–CH_3), 2.23 (s, 6H, pyr–CH_3), 3.56–3.69 (m, 12H, $NHCH_2(CH_2OCH_2)_2$-CH_2NH), 6.40 (br s, 2H, $CONHCH_2$), 6.62 (d, 2H, pyr–*H*), 9.51 (br s, 2H, N*H*). ^{13}C-NMR (62 MHz, $CDCl_3$): $\delta = 10.1$, 10.6, 39.1, 70.1, 70.4, 118.7, 119.9, 120.0, 122.6, 162.3. CIMS [M + H] 391. CIHRMS [M + H] 391.2350 (calc. for $C_{20}H_{31}N_4O_4$, 391.2345).

3.9. 1,1′-[1,5-Bis-(3,4-dimethyl-pyrrole-2-carbonyl-amino-5-diyldimethyl)-pentane]-ferrocene (7)

1,5 - Bis - (3,4 - dimethyl - pyrrole - 2 - carbonylamino)-pentane (**4**) (174 mg, 0.50 mmol) in CH_2Cl_2 (50 ml) and 1,1′-ferrocenedimethanol (124 mg, 0.50 mmol) in CH_2Cl_2 (50 ml) were simultaneously added dropwise over 90 min to a stirred solution of trifluoroacetic acid (115 mg, 1.0 mmol) in CH_2Cl_2 (100 ml) held at 40 °C. After the addition, the mixture was heated at reflux for a further 24 h. The mixture was allowed to cool and was then concentrated to ca. 50 ml. The solution was washed with 1 M NaOH (3 × 50 ml), dried over $MgSO_4$ and concentrated in vacuo to yield a flaky yellow–brown solid. Purification by column chromatography (silica, 2% MeOH–CH_2Cl_2) gave **7** as a yellow solid (90 mg, 33%). ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.57$ (quin., 2H, $NHCH_2CH_2CH_2CH_2CH_2NH$), 1.76 (quin., 4H, $NHCH_2CH_2CH_2CH_2CH_2NH$), 1.91 (s, 6H, pyr–CH_3), 2.29 (s, 6H, pyr–CH_3), 3.41–3.59 (m, 8H, $FcCH_2$, $CONHCH_2CH_2$), 4.07 (br s, 4H, Fc–*H*), 4.14 (br s, 4H, Fc–*H*), 6.57 (br t, 2H, $CONHCH_2$), 9.89 (br s, 2H, N*H*). ^{13}C-NMR (62 MHz, $CDCl_3$): $\delta = 8.9$, 11.0, 23.3, 25.4, 28.6, 38.5, 67.8, 68.9, 77.3, 116.5, 120.0, 122.9, 130.4, 163.1. CIMS [M + H] 555. CIHRMS [M + H] 555.2419 (calc. for $C_{31}H_{39}N_4O_2Fe$, 555.2422). UV–vis: λ_{max} (nm) (ε, $M^{-1}\,cm^{-1}$) (CH_2Cl_2): 426 (196).

3.10. 1,1′-[1,5-Bis-(3,4-dimethyl-pyrrole-2-carbonyl-amino-5-diyldimethly)-3-oxapentane]-ferrocene (8)

This compound was prepared by the procedure used to prepare **7** but starting from 1,5-bis-(3,4-dimethyl-pyrrole-2-carbonylamino)-3-oxaoctane (103 mg, 0.30 mmol), 1,1′-ferrocenedimethanol (73 mg, 0.30 mmol), and trifluoroacetic acid (74 mg, 0.60 mmol) in CH_2Cl_2

(60 ml). Purification by column chromatography (silica, 2% MeOH–CH_2Cl_2) gave **8** as an orange solid (33mg, 20%). ^{1}H-NMR (300 MHz, Me_2SO-d_6): $\delta =$ 1.78 (s, 6H, pyr–CH_3), 2.14 (s, 6H, pyr–CH_3), 3.20–3.78 (m, 12H, NHCH_2CH_2OCH_2CH_2NH, FcCH2,), 3.96 (br s, 8H, Fc–H), 7.68 (br s, 2H, CONHCH_2), 10.80 (br s, 2H, NH). ^{13}C-NMR (125 MHz, Me_2SO-d_6): $\delta = 8.8$, 10.4, 25.4, 38.9, 67.1, 68.7, 69.8, 87.7, 114.5, 119.3, 122.8, 130.2, 161.7. CIMS [M + H] 557. CIHRMS [M + H] 557.2203 (calc. for $C_{32}H_{41}N_4O_4Fe$, 557.2215). UV–vis: λ_{max} (nm) (ε, $M^{-1}\,cm^{-1}$) (CH_2Cl_2): 404 (219).

*3.11. 1,1′-[1,8-Bis-(3,4-dimethyl-pyrrole-2-carbonyl-amino-5-diyldimethyl)-3,6-dioxaoctane]-ferrocene (**9**)*

This compound was prepared by the procedure used to prepare **7** but starting from 1,8-bis-(3,4-dimethyl-pyrrole-2-carbonylamino)-3,6-dioxaoctane (**6**) (271 mg, 0.69 mmol), 1,1′-ferrocenedimethanol (171 mg, 0.69 mmol), and trifluoroacetic acid (158 mg, 1.39 mmol) in CH_2Cl_2 (180 ml). Purification by column chromatography (silica, 2.5% MeOH–CH_2Cl_2) gave **9** as an orange solid (145 mg, 35%). ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.93$ (s, 6H, pyr–CH_3), 2.26 (s, 6H, pyr–CH_3), 3.31 (br s, 4H, FcCH_2), 3.52–3.74 (m, 12H, NHCH_2(CH_2OCH_2)$_2$CH_2NH), 3.88–4.42 (br, 8H, Fc–H), 6.48 (br s, 2H, CONHCH_2), 9.54 (br s, 2H, NH). ^{13}C-NMR (62 MHz, $CDCl_3$): $\delta = 9.0$, 11.1, 25.6, 39.8, 68.0, 69.4, 70.8, 71.3, 77.3, 116.5, 119.8, 122.5, 131.0, 161.9. CIMS [M + H] 601. CIHRMS [M + H] 601.2474 (calc. for $C_{32}H_{41}N_4O_4Fe$, 601.2477). UV–vis: λ_{max} (nm) (ε, $M^{-1}\,cm^{-1}$) (CH_2Cl_2): 413 (166).

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References

[1] P.D. Beer, J. Cadman, Coord. Chem. Rev. 205 (2000) 131.
[2] P.D. Beer, P.A. Gale, G.Z. Chen, Coord. Chem. Rev. 185–186 (1999) 3.
[3] P.D. Beer, J. Cadman, J.M. Lloris, R. Martínez-Máñez, J. Soto, T. Pardo, M.D. Marcos, J. Chem. Soc. Dalton Trans. (2000) 1805.
[4] J.M. Lloris, R. Martínez-Máñez, M.E. Padilla-Tosta, T. Pardo, J. Soto, Helv. Chim. Acta 82 (1999) 1445.
[5] J.F. Gallagher, P.T.M. Kenny, M.J. Sheehy, Inorg. Chem. Commun. 2 (1999) 327.
[6] S. Takenaka, K. Yamashita, M. Takagi, Y. Uto, H. Kondo, Anal. Chem. 72 (2000) 1334.
[7] P. Anzenbacher Jr., K. Jursíková, J.L. Sessler, J. Am. Chem. Soc. 122 (2000) 9350.
[8] P. Anzenbacher Jr., A.C. Try, H. Miyaji, K. Jursíková, V.M. Lynch, M. Marquez, J.L. Sessler, J. Am. Chem. Soc. 122 (2000) 10268.
[9] J.L. Sessler, S.J. Weghorn, Expanded, Contracted and Isomeric Porphyrins, Elsevier, New York, 1997.
[10] J.L. Sessler, A. Gebauer, P.A. Gale, Gazz. Chim. Ital. 127 (1997) 723.
[11] M. Scherer, J.L. Sessler, A. Gebauer, V. Lynch, Chem. Commun. (1998) 85.
[12] J. Zindel, D.A. Lightner, J. Heterocycl. Chem. 32 (1995) 1219.
[13] A.K. Connors, Binding Constants: the Measurement of Molecular Complex Stability, Wiley, New York, 1987.
[14] C.S. Wilcox, in: H.-J. Schneider, H. Durr (Eds.), Frontiers in Supramolecular Organic Chemistry and Photochemistry, VCH, Weinheim, 1991.
[15] Y.-S. Byun, D.A. Lightner, J. Org. Chem. 56 (1991) 6027.