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PAPER

Pyrenyl-functionalized Ferrocences for Multisignaling Recognition of Anions

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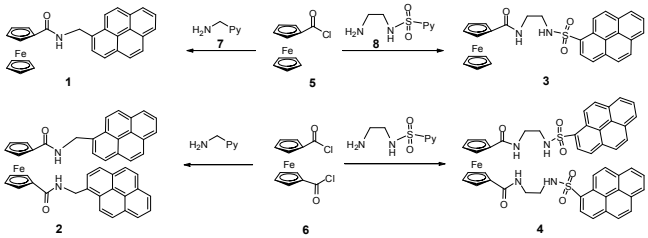
New mono- and di-substituted pyrene-appended ferrocenes bearing amide or amide-sulfonamide binding sites, **1**–**4**, have been synthesized, and their anions recognition abilities been investigated. In CH_3CN solution, all receptors show distinctive electrochemical sensing of F^- and $H_2PO_4^-$ with a large cathodic shift in the ferrocene/ferrocinium redox potential, with **4** showing the strongest anions binding ability. In addition, receptors **3** and **4** bearing amide-sulfonamide binding sites also exhibited fluorescence response to AcO^- and $H_2PO_4^-$ with their emission intensity a large enhancement. The binding mechanisms between **3** and anions are also investigated by ^{1}H NMR titration and DFT calculations.

Introduction

The design of sensors capable of recognizing anions is one of the most challenging topics because anions play ubiquitous roles in chemical and biochemical processes, some of them are also of great environmental and medical concern.[1] Therefore, many man-made receptors incorporating N–H/$(N–H)^+$ (pyrrole, indole, ammonium, guanidinium, urea, thiourea, and amide) or $(C–H)^+$ (imidazolium, triazolium and pyridinium) anions binding sites have been reported.[2,3] In addition, various signaling groups, such as optical (colorimetric and fluorescent) and electrochemical sensing units, have been installed into anion receptors to realize the convenient detection of anions.[4] However, most of them are limited in single signaling changes, multisignaling response sensors for anions recognition are still rare. The multiple signaling systems, which allow anions detection *via* more than one read-out mode, could lower the likelihood of false positives.[5]

Ferrocene is a well known electrochemical active unit for its stable one electron reversible redox potential property and easy functionalization. Ferrocene-base receptors with different anions binding sites have been well documented,[6] in which a negative shift in the redox potential of the receptors upon the addition of target anions, and the complexation ability of the ligand can be switched on and off by varying the applied electrochemical potential. As a typical fluorophore with high quantum yield, pyrene derivatives are often used for fluorescence chemosensors.[7] A change in the intensity of emission or monomer-excimer transformation is observed upon anions interaction. Recently, Molina and coworkers have reported ferrocene-pyrene dyads with the triazole linker,[8] which show electrochemical and fluorescent dual signaling response to phosphate over other anions. However, their binding abilities are relative low for weak C–H anions interaction. Here in, we report four new ferrocene-pyrene dyads **1**–**4** (Scheme 1) with amide or amide/sulfonamide binding sites, and their anions recognition were investigated by the electrochemical (CVs and DPVs), fluorescent and ^{1}H-NMR spectral techniques.

Results and Discussion



Scheme 1. Synthesis route of compounds **1**–**4**

The synthesis route of **1**–**4** is shown in Scheme 1. With commercial available ferrocenecarboxylic acid and 1-pyrenemethylamine as starting materials, we firstly prepared the key precursors chlorocarbonylferrocene (**5**), 1,1′-dichlorocarbonylferrocene (**6**) and *N*-(2-aminoethyl)-1-pyrenesulfonamide (**8**) by the literature methods.[9, 10] The mono-substituted receptors **1** and **3** were obtained by condensation of **5** with **7**/**8**, while 1,1′-difunctionalized receptors **2** and **4** were obtained by condensation of **6** with **7**/**8**, with triethylamine as a base in CH_2Cl_2 solution. The yields of the target compounds were high (75% – 82%). Their molecular structures were confirmed by ^{1}H NMR, ^{13}C NMR and ESI-MS spectra.

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The recognition abilities of **1**–**4** toward various mono-valence anions (F^-, Cl^-, Br^-, I^-, AcO^-, HSO_4^- and $H_2PO_4^-$) in the form of their corresponding tetrabutylammonium (TBA) salts were first investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques with $TBAPF_6$ as a supporting electrolyte. Compounds **1**–**4** exhibited in the CVs a reversible one-electron redox wave, which can be attributed to the ferrocene/ferrocenium redox couple. Upon addition of anions, receptors **1**–**4** show electrochemical response to some selected anions. Owing to the irreversibility of the CV responses when anions were added, we used the DPVs oxidation data to estimate the potential shift upon complexation. DPVs often show well-resolved potential information for removing the effect of electrode capacitive charging.[11]

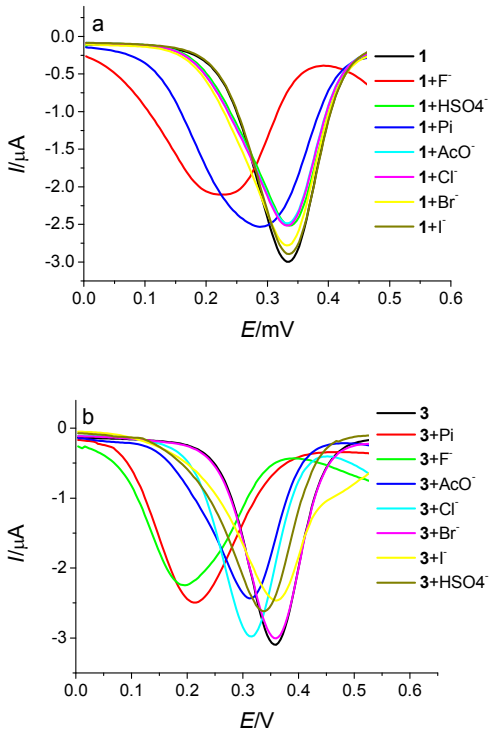

Fig. 1 DPV profile of **1** (a) and **3** (b) upon the addition of equal equiv of (6 equiv) anions in CH_3CN solution (2×10^{-4} M).

The potential changes of **1**–**4** upon addition equal amount of anions are shown in Fig. 1 and S1, and the related data are listed in Table 1. From these data, it can be found that receptors **1** and **2** show electrochemical response of F^- and $H_2PO_4^-$, with F^- > $H_2PO_4^-$. However, receptors **3** and **4** electrochemically respond many of anions with a larege potential cathodic shift. The ΔE_p potential shift of **3** followed the order of F^- (–170 mV) > $H_2PO_4^-$ (–150 mV) > AcO^-(–50 mV)~ Cl^- (–40 mV) > HSO_4^- (–30 mV)> Br^- ~ I^- (less than –10 mV), and the order of **4** was $H_2PO_4^-$ (–200 mV) > F^- (–140 mV) > AcO^- (–120 mV) > Cl^-(–70 mV) > HSO_4^- (–50 mV) > Br^- (–40 mV) > I^- (less than –10 mV), respectively. According to the magnitude of the potential shift, it may be deduced that **4** shows the strongest anions binding ability, followed by **3** > **2** > **1**, which is also proved by the electrochemical titration results (see below). This result is reasonable since **4** has more anions binding sites than others.

Table 1. The potential data of **1**–**4** before and after the addition of various anions [a]

Receptors	E_p (V) [b]	ΔE_p (mV)	Saturated equiv [c]
1	0.34		
1.F^-	0.22	110	9.0
1.Pi	0.29	50	5.0
2	0.64		
2.F^-	0.47	170	7.0
2.Pi	0.59	50	4.0
3	0.36		
3.F^-	0.19	170	7.0
3.Pi	0.21	150	3.0
3.AcO^-	0.31	50	8.0
3.Cl^-	0.32	40	6.0
3.HSO_4^-	0.33	30	5.0
4	0.64		
4.Pi	0.44	200	1.0
4.AcO^-	0.52	120	5.0
4.F^-	0.50	140	3.5
4.Cl^-	0.57	70	4.0
4.HSO_4^-	0.59	50	5.0

[a]Receptors **1**–**3** were determined in CH_3CN solution, and **4** was determined in CH_3CN-DMF (9:1, V/V) solution.
[b]These data were DPV oxidation potential.
[c]Maximumnumber of equivalents needed to saturate the electrochemical response.

To get more information about the anions binding properties, the DPV titrations of **1**–**4** with anions were also investigated. Represent titration profile of **3** with $H_2PO_4^-$ and HSO_4^- are shown in Fig. 2, and others are shown in the supported information (Figs. S1–S8). Upon addition of $H_2PO_4^-$, the redox potential of **3** shows a "two wave behavior" with decreasing the original redox potential at 360 mV, and a concomitantly increasing a new redox potential band at 220 mV, which is attributed to the formation of the **3**·$H_2PO_4^-$ complex in the solution. This displacement of the redox peaks was saturated with addition about 3.0 equiv of $H_2PO_4^-$. The same "two wave behaviour" of **1**–**4** was also observed upon the addition of F^-, $H_2PO_4^-$ and AcO^- (for **3** and **4**). In contrast, the addition of Cl^-, Br^- and HSO_4^- to **3** and **4** shows a "shifting behaviour" potential shift, in which a second redox wave appears with shifting the original potential. The "two wave behaviour" *vs* "shifting behaviour" may also give a clue that **1**–**4** shows stronger binding abilities with F^-, $H_2PO_4^-$ and AcO^- than other anion. The saturated equivalents of potential changes between receptors **1**–**4** and anions are also obtained via the DPV titrations. It was found that **4** needs less amount of anions to saturate its electrochemical response than other receptors. For example, the equivalents

numbers of $H_2PO_4^-$ needed to saturate **1**–**4** electrochemical response are 5, 4, 3 and 1, respectively, which also proved that **4** shows stronger anions binding ability than others.

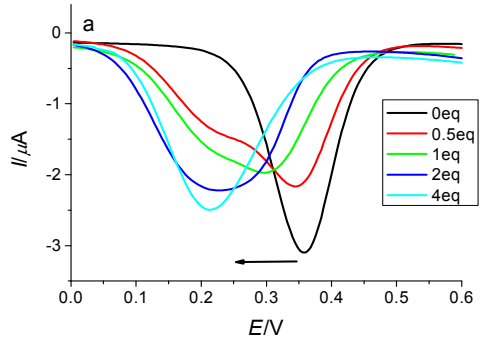

Fig. 2. The DPVs titration of **3** (2×10^{-4} M)upon the addition of various of $H_2PO_4^-$ (a) and HSO_4^- (b) in CH_3CN solution. Reference electrode = $Ag/AgNO_3$; supporting electrolyte = $[n\text{-}Bu_4N]PF_6$ (0.1 M); scan rate = 100 mV S^{-1}.

Considering that receptors **1**–**4** contain fluorescence active pyrene moiety, they may show optical signaling changes upon interaction with anions. Therefore, the anions recognition abilities of **1**–**4** were also investigated by UV-vis and emission spectra techniques. Receptors **1**–**4** show strong pyrene-based absorption bands at about 270 and 350 nm, and a weak ferrocene-based absorption in the region 340–500 nm (Figs. S9-S12). Upon addition of various anions, **1**–**4** show little absorption changes. Therefore their binding properties were then investigated by emission spectra.

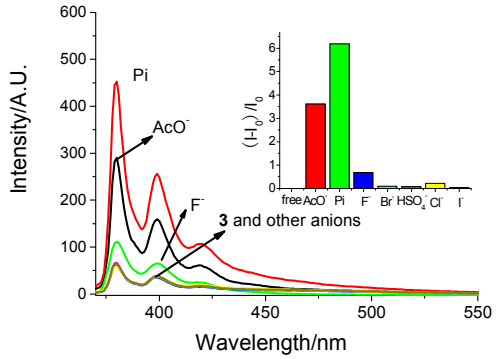

Fig. 3 The emission spectra of **3** (2×10^{-5} M) upon addition various anions (50 equiv) in CH_3CN solution with excitation at 360 nm. Inset: shows the emission intensity at 380 nm upon the addition of various anions.

With excitation at 360 nm in CH_3CN solution, receptors **1**–**4** show weak pyrene-based emission at 380, 399 and 420 nm, respectively, which may be ascribed to the PET (photo-induced electron transfer) quenching effect from the ferrocene moiety to the pyrene flurophore. Ferrocene is a well-known quencher of excited states involving either energy or electron transfer.[12] Upon the addition of anions, **1** and **2** show little emission changes upon interaction. In contrast, **3** and **4** show fluorescence enhancement response of $H_2PO_4^-$ and AcO^-, with $H_2PO_4^-$ larger than AcO^-, and weak or almost no changes with other anions (Fig. 3 and S13). The strong "turn-on" emission response of **3**/**4** induced by the addition of $H_2PO_4^-$ and AcO^- might be ascribed to the inhibition of the PET process from the ferrocene to the pyrene fluorophore, which has been documented in publications.[13]

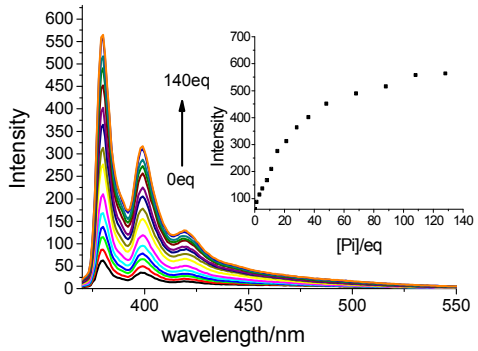

Fig. 4 Emission spectra of **3** (2×10^{-5} M) upon addition various amount of $H_2PO_4^-$ in CH_3CN solution with excitation at 360 nm. Inset: Fluorescence spectra changes of **3** at 380 nm upon the addition of various amount of $H_2PO_4^-$ in CH_3CN solution.

The emission titrations of **3** and **4** toward $H_2PO_4^-$ and AcO^- were then carried out (Fig. 4, S13–S17). Unlike some reported sulfonamide-based receptors, which often show two step processes in their UV-Vis and emission titration for initial forming hydrogen bonding between sulfonamide N-H and anions followed by deprotonation when upon interaction with some basic anions (i.e., F^-, $H_2PO_4^-$ and AcO^-).[14] In our case, only one process was observed between **3**/**4** and $H_2PO_4^-/AcO^-$ complexation, which may be attributed a neat proton transfer occurring from the sulfonamide N-H to $H_2PO_4^-/AcO^-$ (HL + $H_2PO_4^-/AcO^-$ ↔ L^- + H_3PO_4/AcOH) even at low concentration.[15] The ^1H NMR titration can also confirm this assumption (see below). Using the Benesi-Hildebrand method,[16] the emission titration data of **3** with $H_2PO_4^-$ and AcO^- fit a 1:1 complexation, with the **3**•$H_2PO_4^-$ and **3**•AcO^- binding constants K_a $(2.1 \pm 0.3) \times 10^3$ M^{-1} and $(7.8 \pm 0.5) \times 10^2$ M^{-1}, respectively. For receptor **4** bearing two-arm amide-sulfonamide binding sites, the emission titration data of **4** with AcO^- fit a 1:2 complexation, with the binding constant of $(2.6 \pm 0.3) \times 10^8$ M^{-2}. However, **4** with $H_2PO_4^-$ fit a 1:1 complexation, which is also proved by the Job-plot (Fig. S18), with the K_a value of $(3.9 \pm 0.2) \times 10^3$ M^{-1}. These results reveal that the trigonal AcO^- bind each amide-sulfonamide arm of **4**, while the tetrahedral $H_2PO_4^-$ bind both arms of the receptor in the cleft form.[17]

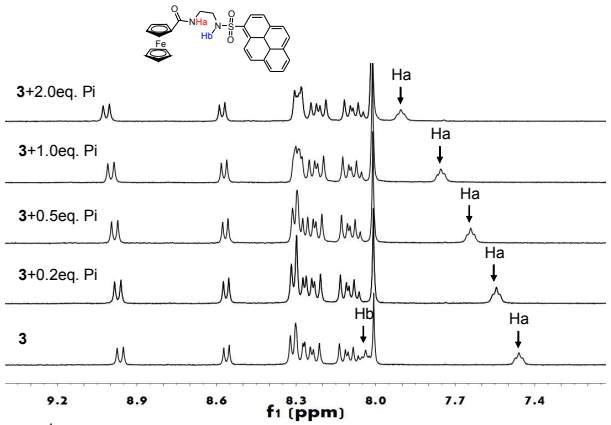

Fig. 5 ^{1}H NMR spectra of **3** upon addition various amount of $H_2PO_4^-$ in DMSO-d_6 solution

To seek detailed information on the binding modes between anions and receptors, ^{1}H NMR titration of **3** with the selected anions ($H_2PO_4^-$, F^- and CH_3COO^-) was carried out in DMSO-d_6 solution (Fig. 5 and S20-S21). The ^{1}H NMR titration of **3** with $H_2PO_4^-$ is shown in Figure 5, which leads to great changes in the amide proton (Ha) and sulfonamide proton (Hb). Upon the addition of $H_2PO_4^-$, the amide proton (Ha) of **3** exhibits a downfield shifted from 7.46 to 7.90 ppm for hydrogen bonding with anions. However, the sulfonamide proton Hb disappeared quickly during the titration, which might attribute to a proton-transfer process from the receptor to $H_2PO_4^-$. Sulfonamide NH is the more acidic donor than amide NH, and may suffer deprotonation on interaction with strongly basic anionic species such as $H_2PO_4^-$, CH_3COO^- and F^-.[15, 18] The ^{1}H NMR titration results reveal that the sulphonamide and amide donors participate in binding with $H_2PO_4^-$. In addition, a little chemical shift changes are also found in the pyrene moiety, which may be attributed to the constrain effect for complexation. The titration of F^- and CH_3COO^- into **3** shows similar chemical shift changes as that of $H_2PO_4^-$, implying that these three anions showing similar binding mode with **3**, even though they have different geometry (tetrahedronal geometry of $H_2PO_4^-$, trigonal of CH_3COO^- and spherical geometry of F^-).

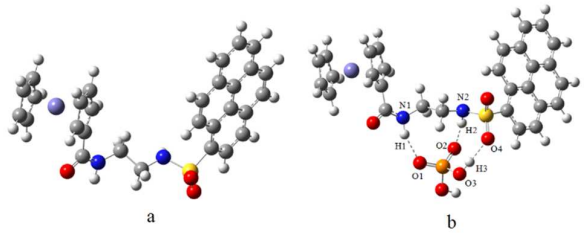

Fig. 6 Calculated structure (B3LYP/6-31G/) of **3** (left) and **3**•$H_2PO_4^-$ (right) complexes. Nitrogen, oxygen, sulfur, carbon and hydrogen atoms are represented as blue, red, yellow, grey and white balls respectively. Selected bond and angles: N1–H1···O1, 2.029 Å, 153.58 °; N2–H2···O2 (1.834 Å, 161.44 °; O3–H3···O4, 1.889 Å, 125.78 °

To further understand the binding behaviour of **3**, density functional theory (DFT) calculations of the anions ($H_2PO_4^-$, CH_3COO^- and F^-) with host molecule have been performed. The optimized conformation of **3** and **3**•$H_2PO_4^-$, in the gas phase, are shown in Fig. 6. The two binding sites (amide N–H and sulfonamide N–H) point almost the same direction with the dihedron angle of 77°, which enables easy coordination of anions. Upon binding with $H_2PO_4^-$, these two donors involved in hydrogen binding, with N2–H2···O2 (1.834 Å, 161.44 °) < N1–H1···O1 (2.029 Å, 153.58 °). According to the bond length, it seems that the sulfonamide N–H make stronger hydrogen binding ability than that of amide N–H. This is reasonable because sulfonamide has high acidity. In addition, the sulfonamide O atom of **3** is also involved in hydrogen binding with $H_2PO_4^-$ (O3–H3···O4, 1.889 Å, 125.78 °). The triple hydrogen binding between **3** and $H_2PO_4^-$ may be attributed to its high binding ability, which makes **3** a large redox potential shift, and fluorescence enhancement.

The DFT calculations of **3**•F^- and **3**•CH_3COO^- (Fig. S23) also investigated, which reveals that only the amide N–H and sulfonamide N–H of are involved in hydrogen binding with anions, with the sulfonamide donor shows stronger anions binding ability than amide NH.

Conclusions

In conclusion, new pyrene-appended ferrocenes bearing amide (**1** and **2**) or amide-sulfonamide (**3** and **4**) binding sites for anions recognition, have been synthesized and characterized. We found that all receptors showed distinctive electrochemical sensing to F^- and $H_2PO_4^-$ with a large cathodic shift in the ferrocene/ferrocinium redox potential. DPVs titrations results reveal that the di-functionalized compound **4** the strongest anions binding ability for bearing multiple anions binding sites. In addition, receptors **3** and **4** bearing amide-sulfonamide binding sites also exhibited fluorescence response to AcO^- and $H_2PO_4^-$ with their emission intensity a large enhancement. The ^{1}H NMR titration and DFT calculations results exhibited that the amide and thiourea N–H protons of **3**/**4** take part in binding with anions.

Experimental section

General instrumentations and reagents

All the starting materials for synthesis were commercially available and used as received. All the solvents used for titration measurements were purified by standard procedures. Chlorocarbonylferrocene (**5**), 1,1′-dichlorocarbonylferrocene (**6**) and N-(2-aminoethyl)-1-pyrenesulfonamide (**8**) were prepared by the literature method.[9,10] UV-vis spectra were recorded on a Hitach UV-3010 spectrophotometer. Emission spectra were recorded on a Hitach F-4500 spectrophotometer. Electrochemical measurements were performed with a CHI 624C instruments. NMR spectra were recorded using Varian instruments (400 MHz). The anions are tetrabutylammonium (TBA) salts.

Preparation of UV-vis, emission and electrochemical titration solutions

Stock solutions of anions (0.01 M) were prepared in CH_3CN solution. The concentration of receptors in the UV-vis and emission titrations was 0.02 mM in CH_3CN solution, which showed the self

emission quenching did not happen at this condition (Figs. S19 and S20). During the titration, anions solution was added into a solution of **1**–**4** (2 mL) using a micro injector and the whole volume of the final system can be considered constant because the volume of anions solution added is negligible compared to that of **1**–**4**.

The electrochemical measurements were carried out in a one-compartment cell under a nitrogen atmosphere at 25 °C, equipped with a Pt disk working electrode, a platinum wire counter electrode, and a $Ag/AgNO_3$ (0.1 M in CH_3CN solution) reference electrode. The working electrode surface was carefully polished with a basic Al_2O_3-water slurry, washed with MeOH and sonicated in a H_2O-MeOH-CH_3CN 1:1:1 mixture at 40 ºC for 15 minutes prior to use. All potentials in this paper were recorded in CH_3CN and are quoted relative to $Ag/AgNO_3$, and were calibrated using decamethylferrocene ($E_{1/2}$ = 0.46 V vs Ag/Ag^+). The supported electrolyte was a 0.10 M CH_3CN solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$). Differential pulse voltammetry (DPV) measurements were also carried out with a 50 ms pulse width. The concentration of **1** for CV/DPV titration is 0.2 mM in CH_3CN solution.

Calculation of the association constants

The binding constants of the inclusion complex were obtained from the fluorescence titration data. According to the Benesi–Hildebrand method,[16] the equation for a 1:n host:guest complex is given below:

$$\frac{1}{I-I_0}=\frac{1}{I'-I_0}+\frac{1}{K(I'-I_0)[M]^n}$$

In the equation, I_0 is the intensity of fluorescence of 1 without M, I is the intensity with a particular concentration of M, I′ is the intensity of the fully complexed form at the highest concentration of M, n is guest : host and K is the binding constant.

Computational details

All structures optimizations were performed using the Gaussian 09 program.[19] The calculations were performed using B3LYP hybrid exchange functional with a CPCM treatment of the solvent and the structures were characterized by computation of vibrational frequencies. The 6-31G (d) basis set was used for C, H and 6-31+G (d, p) was used for N, O, S, and P. For Fe atom, the Lanl2dz basis set was employed

Synthesis

N-(Pyren-1-ylmethyl)ferrocenecarboxamide (**1**).

Under nitrogen, (chlorocarbonyl)ferrocene **5** (0.248 g, 1 mmol), 1-pyrenemethylamine **7** (0.231g, 1 mmol) and triethylamine (0.6 mL) were dissolved in 30mL dry CH_2Cl_2 solvent, and then stirred for 24 h at room temperature. After removal of the solvent, the crude product was purified over silica gel using CH_2Cl_2/MeOH (98:2, v/v) as the eluent to yield **1** as a yellow solid (0.355 g, 80.2% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.38 (d, 1H, J = 9.3 Hz), 8.25-8.15 (m, 4H), 8.10-7.99 (m, 4H), 5.97 (s, 1H), 5.29 (d, 2H, J = 5.3 Hz), 4.64 (s, 2H), 4.30 (s, 2H), 4.11 (s, 5H). ESI-MS (ES^+): m/z = 443.1044

N,*N*′-Bis-pyren-1-ylmethyl-1,1′-ferrocenedicarboxamide (**2**).

Under nitrogen, 1,1′-dichlorocarbonylferrocene **6** (0.301 g, 1 mmol), 1-pyrenemethylamine **7** (0.508 g, 2.2 mmol) and triethylamine (1 mL) were dissolved in 60 mL dry CH_2Cl_2 solvent, and then stirred for 24 h at room temperature. The crude product was purified over silica gel using CH_2Cl_2/MeOH (98:2, v/v) as the eluent to yield **2** as a yellow solid (0.550 g, 78.5% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.34 (d, 2H, J = 9.0 Hz), 8.18-7.88 (m, 16H), 6.96 (s, 2H), 5.21 (d, 4H, J = 5.7 Hz), 4.45 (s, 4H), 4.25 (s, 4H). ESI-MS (ES^+): m/z=723.1587 [M^+ + 23].

2-(Pyrene-1-sulfonylamino)-ethyl-ferrocenecarboxamide (**3**).

Under nitrogen, 0.248 g (1 mmol) **5**, 0.324 g (1 mmol) N-(2-aminoethyl)-1-pyrenesulfonamide **8** and triethylamine (0.6 mL) were dissolved in 30 mL dry CH_2Cl_2 solvent, and then stirred for 24 h at room temperature. After removal of the solvent, the crude product was purified over silica gel using CH_2Cl_2/MeOH (95:5, v/v) as the eluent to yield **3** as an yellow solid (0.423 g, 79.0% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.96 (d, 1H, J = 9.4 Hz), 8.56 (d, 1H, J = 8.2 Hz), 8.35 – 8.19 (m, 5H), 8.11 (dd, 2H, J = 12.5, 8.3 Hz), 8.03 (d, 1H, J = 8.9 Hz), 7.46 (s, 1H), 4.53 (s, 2H), 4.12 (s, 2H), 3.96 (s, 5H), 3.20 (d, 2H, J = 5.9 Hz), 2.93 (d, 2H, J = 6.0 Hz). ^{13}C NMR ($CDCl_3$/DMSO-d_6, 1/1, V/V, 100 MHz): 170.8, 134.6, 131.8, 130.9, 130.1, 129.9, 127.9, 127.1, 127.0, 126.9, 126.8, 125.2, 123.9, 123.4, 75.9, 70.2, 69.6, 43.3, 39.1 ppm. ESI-MS (ES^+): m/z= 536.0881.

N,*N*′-Bis-[2-(pyrene-1-sulfonylamino)-ethyl]-1,1′-ferrocene dicarboxamide (**4**).

Under nitrogen, 1,1'-dichlorocarbonylferrocene **8** (0.301 g, 1 mmol), Pyrene-1-sulfonic acid (2-amino-ethyl)-amide (0.713 g, 2.2 mmol) and triethylamine (1 mL) were dissolved in 60 mL dry CH_2Cl_2 solvent, and then stirred for 24 h at room temperature. The crude product was purified over silica gel using CH_2Cl_2/MeOH (95:5, v/v) as the eluent to yield **4** as an orange solid (0.666 g, 75.2% yield).^{1}H NMR (DMSO-d_6/$CDCl_3$, 1/1, V/V, 400 MHz) δ 8.93 (d, 2H, J = 9.2 Hz), 8.54 (d, 2H, J = 8.2 Hz), 8.26-7.97 (m, 16H), 7.62 (s, 2H), 4.41 (s, 4H), 4.07 (s, 4H),3.21(d, 4H, J = 6.1 Hz), 2.96 (d, 4H, J = 6.1 Hz). ESI-MS (ES^+): m/z = 909.1182 [M^+ + 23]

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References

1. (a) T. Schrader and A. D. Hamilton, *Functional Synthetic Receptors*; Wiley-VCH: Weinheim, Germany, 2005; (b) J. L. Sessler, P. A. Gale and W.-S. Cho, *Anion Receptor Chemistry*; RSC Publishing: Cambridge, U.K., 2006.
2. (a) P. A. Gale, N. Busschaert, C. J. E. Haynes, L. E. Karagiannidis and I. L. Kirby, *Chem. Soc. Rev.*, 2014, **43**, 205; (b) P. Dydio, D. Lichosyt and J. Jurczak, *Chem. Soc. Rev.,* 2011, **40**, 2971; (c) V. Amendola, L.

Fabbrizzi and L. Mosca, *Chem. Soc. Rev.,* 2010, **39**, 3889; (d) V. Amendola, D. E. Gomez, L. Fabbrizzi and M. Licchelli, *Acc. Chem. Res.*, 2006, **39**, 343.

3. (a) Z. Xu, S. K. Kim and J. Yoon, *Chem. Soc. Rev.,* 2010, **39**, 1457; (b) J. Cai and J. L. Sessler, *Chem. Soc. Rev.,* 2014, **43**, 6198; (c) B. Schulze, C. Friebe, M. D. Hager, W. Günther, U. Köhn, B. O. Jahn, H. Görls and U. S. Schubert, *Org. Lett.,* 2010, **12**, 2710; (d) Q.-Y. Cao, Z.-C. Wang, M. Li and J.-H. Liu, *Tetrahedron Lett.*, 2013, **54**, 3933; (e) K. Ghosh, A. R. Sarkar, A. Samadder and A. R. Khuda-Bukhsh, *Org. Lett.*, 2012, **14**, 4314. (f) A. E. Hargrove, S. Nieto, T. Zhang, J. L. Sessler and E. V. Anslyn, *Chem. Rev.*, 2011, **111**, 6603; (g) N. R. Song, J. H. Moon, J. Choi, E. J. Jun, Y. Kim, S.-J. Kim, J. Y. Lee and J. Yoon, *Chem. Sci.*, 2013, **4**, 1765.
4. (a) L. E. Santos-Figueroa, M. E. Moragues, E. Climent, A. Agostini, R. Martínez-Máñez and F. Sancenón, *Chem. Soc. Rev.*, 2013, **42**, 3489; (b) S. Lee, K. K. Y. Yuen, K. A. Jolliffe and J. Yoon, *Chem. Soc. Rev.,* 2015, **44**, 1749; (c) M. H. Lee, Q.-Y. Cao, S. K. Kim, J. L. Sessler and J. S. Kim, *J. Org. Chem.*, 2011, **76**, 870; (d) Q.-Y. Cao, T. Pradhan, S. Kim and J. S. Kim, *Org. Lett.*, 2011, **13**, 4386.
5. C. Bejger, J. S. Park, E. S. Silvera and J. L. Sessler, *Chem. Commun.*, 2010, **46**, 7745.
6. (a) P. D. Beer and S. R. Bayly, *Top. Curr. Chem,* 2005, **255**, 125; (b) P. Molina, A. Tárraga and A. Caballero, *Eur. J. Inorg. Chem.,* 2008, **22**, 3401.
7. (a) J. Huang, Y. Wu, Y. Chen, Z. Zhu, X. Yang, C. J. Yang, K. Wang and W. Tan, *Angew. Chem. Int. Ed.*, 2011, **50**, 401; (b) Q.-Y. Cao, Y.-M. Han, H.-M. Wang and Y. Xie, *Dyes Pigments,* 2013, **99**, 798; (c) L. Gai, H. Chen, B. Zou, H. Lu, G. Lai, Z. Li and Z. Shen, *Chem. Commun.*, 2012, **48**, 10721; (d) S. Karuppannan and J.-C. Chambron, *Chem. Asian. J.*, 2011, **6**, 964; (e) E. Manandhar, K. J. Wallace, *Inorg. Chimi.* Acta., 2012, **381**, 15.
8. (a) T. Romero, A. Caballero, A. Tárraga and P. Molina, *Org. Lett.*, 2009, **11**, 3466; (b) T. Romero, R. Orenes, A. Tárraga and P. Molina, *Organometallics*, 2013, **32**, 5740.
9. (a) P. D. Beer, A. R. Graydon, A. O. M. Johnson and D. K. Smith, *Inorg. Chem.,* 1997, **36**, 2112; (b) Y. G. Zhi, C. E. Dong, J. Han, W. Z. Zhen and L. F. Zhang, *Chem. Res. Appl.*, 2000, **12**, 410.
10. (a) H.-Y. Lu, W. Xu, D.-Q. Zhang, C.-F. Chen and D.-B. Zhu, *Org. Lett.*, 2005, **21**, 4629; (b) Q.-Y. Cao, T.-h. Pradhan, M. H. Lee and J. S. Kim, *Tetrahedron Lett.*, 2012, **53**, 4917.
11. A. Bard, L. Faulkner, 2nd ed.; Wiley: New York, 2001.
12. S. Fery-Forgues and B. Delavaux-Nicot, *J. Photochem. Photobiol. A. Chem.*, 2000, **132**,137.
13. (a) Q.-Y. Cao, Y.-M. Han, P.-S. Yao, W.-F. Fu, Y. Xie and J.-H. Liu, *Tetrahedron Lett.*, 2014, **55**, 248; (b) H. Lu, W. Xu, D. Zhang, C. Chen and D. Zhu, *Org. Lett.*, 2005, **21**, 4629; (c) F. Otón, A. Tárraga, A. Espinosa, M. D. Velasco and P. Molina, *J. Org. Chem.*, 2006, **71**, 4590.
14. (a) V. Amendola, D. E. Gomez, L. Fabbrizzi and M. Licchelli, *Acc. Chem. Res.*, 2006, **39**, 343; (b) M. V. López, M. R. Bermejo, M. E. Vá´zquez, A. Taglietti, G. Zaragoza, R. Pedrido and M. Martíinez-Calvo, *Org. Biomol. Chem.*, 2010, **8**, 357.
15. (a) V. Amendola, L. Fabbrizzi, L. Mosca and F.-P. Schmidtchen, *Chem. Eur. J.*, 2011, **17**, 5972; (b) T.-P. Lin, C.-Y. Chen, Y.-S. Wen and S.-S. Sun, *Inorg. Chem.*, 2007, **46**, 9201.
16. (a) N. J. Turro, Modern Molecular Photochemistry, Benjamin Cummings Publishing Co. Inc., Menlo Park, CA, 1978; (b) J. Szejtli, Cyclodextrine technology, Dodrecht, the Netherlands, Kluwer Academic Publishers, 1988.
17. (a) S. Kubik, *Chem. Soc. Rev.*, 2011, **40**, 3648; (b) R. M. Duke, T. McCabe, W. Schmitt and T. Gunnlaugsson, *J. Org. Chem.*, 2012, **77**, 3115; (c) Q.-Y. Cao, T. Pradhan, S. Kim and J. Seung Kim, *Org. Lett.*, 2011, **13**, 4386.
18. (a) T. Ema, K. Okuda, S. Watanabe, T. Yamasaki, T. Minami, N. A. Esipenko and P. Anzenbacher, Jr., *Org. Lett.*, 2014, **16**, 1302; (b) C. Caltagirone, G. W. Bates, P. A. Gale and M. E. Light, *Chem. Commun.*, 2008, 61.
19. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT*, 2009.

Pyrenyl-functionalized Ferrocences for Multisignaling Recognition of Anions

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New pyrenyl-functionalized ferrocences for fluorescent and electrochemical dual sensing of anions in organic solution is introduced.