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Design and synthesis ethynyl ferrocene-based multifunctional chemosensors for fluoride anion

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Abstract

To exploit novel ferrocene-based small molecules with long conjugated structures as visible and electrochemical multichannel chemosensors, four conjugated ferrocene ethynyl semicarbazide derivatives (Fc-X-An) were synthesized via the Sonogashira coupling reaction. The synthesized Fc-X-Ans are 2-(4-(ferrocenylethynyl) benzylidene) hydrazine-1-carboxamide (Fc-Ph-An), 2-((5-(ferrocenylethynyl) thiophen-2-yl)methylene)hydrazine-1-carboxamide (Fc-Thie-An), 2-((9-ethyl-6-(ferrocenylethynyl)-9H-carbazol-3-yl) methylene)hydrazine-1-carboxamide (Fc-Cz-An) and 2-((10-ethyl-7-(ferrocenylethynyl)-10H-phenothiazin-3-yl) methylene) hydrazine-1-carboxamide (Fc-PTZ-An). The recognition abilities of the semicarbazide derivative Fc-X-Ans for several anions were evaluated from visible absorption spectra, ^{1}H NMR, and electrochemical technique.

Keywords Synthesis · Semicarbazide · Ethynyl ferrocene · Conjugated structure · Chemosensor

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Introduction

Ferrocene (Fc) derivatives have been widely utilized as the multifunctional detectors for ions. They can be applied as an electrochemical signal unit in anion recognition systems owing to its stable and sensitive redox characteristics before and after binding with the anions [1–7]. Fc is also applied as a chromogenic unit in chemosensor molecules, for example Pedro et al. have reported a series of ferrocene-based small receptors for anion and cation recognition in which the ferrocene unit was linked by unsaturated aza bridges to a chromogenic or fluorescent signalling unit [8–11].

Anion sensing has especially attracted attention in the past decades, due to its close relationship with the people's health and the environmental protection [12–16]. Exploiting novel molecular receptors, which could selectively bind and sense the anion by a macroscopic physical response, is an area of intense activity [17]. Anion receptors can be roughly divided into the guest binding and signaling sites according to their role in the recognition processes. The guest binding sites, such as amide [18–21], urea [22–25], imidazole [26, 27], phyrin [28], and rotaxane [29, 30], can bind with the target anions through supramolecular interactions, hydrogen interactions or electrostatics interactions [31–35], while the signaling sites, for example a chromogenic unit, a fluorescent unit [36, 37] or an electrochemical group, can transport the binding information to the physical recordable signal [3, 38, 39].

Except for the demand of sensitivity, receptors consisting of more than one signal unit, are more attractive due to their abilities of multichannel recognition. Thus exploiting novel and efficient multifunctional acceptors for anions deserve more endeavor [40–44]. In this work, we designed and synthesized four conjugated ferrocene ethynyl semicarbazide derivatives Fc-Ph-An, Fc-Thie-An, Fc-Cz-An and Fc-PTZ-An to act as multifunctional chemosensors. With an aim to realize the so-called "naked eye" detection of ions, all receptors in our Fc-X-Ans adopt the highly conjugated molecular skeleton with conjugated Fc and semicarbazide acting as the multichannel signaling and exclusive, sensitive anion binding segments, respectively. The anion binding properties of target acceptors were investigated carefully by electrochemical, ^{1}H NMR, spectral and optical techniques.

Experimental section

General instrumentations and reagents

All chemicals were commercially available and used without further purification. The 2-Bromo-5-formylthiophene [45], 3-bromo-9-ethylcarbazole-6-carboxaldehyde [46], 7-bromo-10-ethyl-10H-phenothiazine-3-carboxaldehyde [47] and ethynylferrocene [48] were synthesized and compared with that of the reported.

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV400 unity spectrometer operated at 400 MHz using acetone-d_6 as deuterated solvent.

Mass spectra were recorded on a Thermo ISQ mass spectrometer using a direct exposure probe. UV–Vis absorption spectra were recorded on a Hitachi U2500 UV–Vis spectrophotometer. Fluorescence spectra were measured on a Hitachi F-7500 fluorescence spectrophotometer. Cyclic voltammetric measurements were performed on a PC-controlled LK98BII electrochemical analyzer, using 1.0 mM dye solution in DMSO at a scan rate of 100 mV/s using 0.1 M tetrabutyl ammonium hexafluorophosphate as supporting electrolyte. The glassy carbon, standard calomel electrode (SCE) and platinum were used as working, reference and auxiliary electrodes, respectively. Deoxygenation of the solutions was achieved by bubbling nitrogen for at least 10 min.

Experimental procedures

(2-(4-Formylphenyl)ethynyl)ferrocene (Fc-Ph-A)

A mixture of 4-bromobenzaldehyde (0.18 g, 1.00 mmol), ethynylferrocene (0.32 g, 1.50 mmol), $Pd(PPh_3)_2Cl_2$ (21.0 mg, 0.03 mmol), CuI (10.0 mg, 0.05 mmol), 1 mL TEA and 10 mL DMF was added to a 100 mL round-bottom flask. Nitrogen was bubbled through the reaction mixture to remove dissolved air. Then the mixture was heated at 90 °C for 8 h. The reaction mixture was then poured in water, and the precipitate was collected by filtration and purified over silica gel with petroleum ether/ethyl acetate (4:1, v/v) as eluent to afford 0.25 g (80%) of a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (*s*, 1H), 7.86 (*d*, $J = 8.1$ Hz, 2H), 7.64 (*d*, $J = 8.1$ Hz, 2H), 4.78–3.84 (*m*, 9H). MS (EI) *m*/*z*: $[M]^+$: calcd for 315.05; found 315.10.

(2-(5-Formyl-2-thienyl)ethynyl)ferrocene (Fc-Thie-A)

The synthesis was performed according to the synthetic procedure described for Fc-Ph-A using 2-bromo-5-formylthiophene instead of 4-bromobenzaldehyde. This gave, after purification by column chromatography over silica gel with petroleum ether/ethyl acetate (4:1, v/v) as eluent, to afford 0.27 g (85%) of a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (*s*, 1H), 7.67 (*d*, $J = 3.9$ Hz, 1H), 7.26 (*d*, $J = 3.9$ Hz, 1H), 4.59–4.53 (*m*, 2H), 4.39–4.32 (*m*, 2H), 4.29 (*s*, 5H). MS (EI) *m*/*z*: $[M]^+$: calcd for 321.00; found 321.13.

(3-(6-Formyl-9-ethyl-9H-carbazolyl)ethynyl)ferrocene (Fc-Cz-A)

The synthesis was performed according to the synthetic procedure described for Fc-Ph-A using 3-bromo-9-ethylcarbazole-6-carboxaldehyde instead of 4-bromobenzaldehyde. This gave, after purification by column chromatography over silica gel with petroleum ether/ethyl acetate (5:1, v/v), as eluent to afford 0.39 g (90%) of a earthy yellow solid. ^{1}H NMR (400 MHz, DMSO): δ 10.08 (*s*, 1H), 8.87 (*s*, 1H), 8.51 (*s*, 1H), 8.04 (*dd*, $J = 8.6$, 1.4 Hz, 1H), 7.83 (*d*, $J = 8.6$ Hz, 1H), 7.73 (*d*, $J = 8.5$ Hz, 1H), 7.65 (*dd*, $J = 8.5$, 1.4 Hz, 1H), 4.63–4.59 (*m*, 2H), 4.54 (*q*, $J = 7.2$ Hz, 2H), 4.36–4.34 (*m*, 2H), 4.31 (*s*, 4H), 1.36 (*t*, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz,

DMSO): 191.75, 129.78, 127.00, 124.63, 124.05, 122.57, 121.92, 110.27, 109.92, 70.96, 69.75, 68.79, 65.07, 37.54, 13.73. MS (EI) *m/z*: $[M]^+$: calcd for 432.11; found 432.21.

(3-(7-Formyl-10-ethyl-10H-phenothiazinyl)ethynyl)ferrocene (Fc-PTZ-A)

The synthesis was performed according to the synthetic procedure described for Fc-Ph-A using 7-bromo-10-ethyl-10H-Phenothiazine-3-carboxaldehyde instead of 4-bromobenzaldehyde. This gave, after purification by column chromatography over silica gel with petroleum ether/ethyl acetate (3:1, v/v), as eluent to afford 0.41 g (90%) of a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (*s*, 1H), 7.65 (*dd*, $J=8.4$, 1.5 Hz, 1H), 7.58 (*s*, 1H), 7.33–7.26 (*m*, 1H), 7.23 (*s*, 1H), 6.92 (*d*, $J=8.4$ Hz, 1H), 6.83 (*d*, $J=8.5$ Hz, 1H), 4.51 (*m*, 2H), 4.26 (*s*, 7H), 3.99 (*q*, $J=6.8$ Hz, 2H), 1.47 (*t*, $J=6.9$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 189.92, 149.64, 142.35, 131.20, 130.73, 130.24, 129.94, 128.23, 123.90, 123.18, 119.18, 115.20, 114.46, 88.84, 84.55, 71.36, 69.99, 68.86, 65.19, 42.63, 12.78. MS (EI) *m/z*: $[M]^+$: calcd for 464.08; found 464.20.

2-(4-(Ferrocenylethynyl)benzylidene)hydrazine-1-carboxamide (Fc-Ph-An)

A mixture of 0.11 g (1.00 mmol) aminourea hydrochloride, 0.25 g (3.00 mmol) sodium acetate, and 30 mL deionized water was added to a 250 mL round-bottom flask. Then the mixture was heated at 95 °C before the adding of 0.31 g (1.00 mmol) Fc-Ph-A in 60 mL isopropanol. The reaction mixture was then poured in water after the reaction was over, and the precipitate was collected by filtration and purified over silica gel with dichloromethane/methanol (10:1, v/v) as eluent to afford Fc-Ph-An 0.26 g (70%) of a brown yellow solid. ^{1}H NMR (400 MHz, DMSO): δ 10.33 (*s*, 1H), 7.85 (*s*, 1H), 7.74 (*d*, $J=7.9$ Hz, 2H), 7.48 (*d*, $J=7.9$ Hz, 2H), 6.54 (*s*, 2H), 4.59 (*s*, 2H), 4.36 (*s*, 2H), 4.29 (*s*, 5H). ^{13}C NMR (101 MHz, DMSO) δ 156.62, 138.40, 134.35, 131.21, 126.69, 123.32, 90.17, 85.54, 71.12, 69.79, 69.08, 64.25. MS (EI) *m/z*: $[M]^+$: calcd for 372.08; found 372.17.

2-((5-(Ferrocenylethynyl)thiophen-2-yl)methylene)hydrazine-1-carboxamide (Fc-Thie-An)

The synthesis was performed according to the synthetic procedure described for Fc-Ph-An using Fc-Thie-A instead of Fc-Ph-A. This gave, after purification by column chromatography over silica gel with dichloromethane/methanol (10:1, v/v), as eluent to afford 0.28 g (75%) of a brown red solid. ^{1}H NMR (400 MHz, DMSO): δ 10.38 (*s*, 1H), 7.99 (*s*, 1H), 7.26 (*m*, 2H), 6.35 (*s*, 2H), 4.61 (*s*, 2H), 4.39 (*s*, 2H), 4.28 (*s*, 5H). ^{13}C NMR (101 MHz, DMSO) δ 156.19, 140.42, 134.02, 132.11, 128.85, 123.23, 94.52, 78.73, 71.18, 69.86, 69.37, 63.46. MS (EI) *m/z*: $[M]^+$: calcd for 378.04; found 378.15.

2-((9-Ethyl-6-(ferrocenylethynyl)-9H-carbazol-3-yl)methylene) hydrazine-1-carboxamide (Fc-Cz-An)

The synthesis was performed according to the synthetic procedure described for Fc-Ph-An using Fc-Cz-A instead of Fc-Ph-A. This gave, after purification by column chromatography over silica gel with dichloromethane/methanol (10:1, v/v), as eluent to afford 0.34 g (70%) of a brown yellow solid. ^{1}H NMR (400 MHz, DMSO): δ 10.20 (*s*, 1H), 8.65 (*s*, 1H), 8.41 (*s*, 1H), 8.02 (*s*, 1H), 7.87 (*d*, $J = 8.6$ Hz, 1H), 7.64–7.62 (*m*, 2H), 7.57 (*d*, $J = 8.4$ Hz, 1H), 6.55 (*s*, 2H), 4.59 (*s*, 2H), 4.46 (*t*, $J = 6.7$ Hz, 2H), 4.34 (*s*, 2H), 4.30 (*s*, 5H), 1.34 (*t*, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 156.94, 140.47, 140.02, 139.36, 129.08, 126.48, 125.13, 123.71, 122.45, 122.01, 119.37, 113.45, 109.72, 109.42, 86.66, 86.24, 70.88, 69.72, 68.72, 65.28, 59.72, 37.26, 13.75. MS (EI) *m*/*z*: $[M]^+$: calcd for 489.14; found 489.24.

2-((10-Ethyl-7-(ferrocenylethynyl)-10H-phenothiazin-3-yl)methylene) hydrazine-1-carboxamide (Fc-PTZ-An)

The synthesis was performed according to the synthetic procedure described for Fc-Ph-An using Fc-PTZ-A instead of Fc-Ph-A. This gave, after purification by column chromatography over silica gel with dichloromethane/methanol (10:1, v/v), as eluent to afford 0.38 g (73%) of a brown yellow solid. ^{1}H NMR (400 MHz, DMSO): δ 10.16 (*s*, 1H), 7.73 (*s*, 1H), 7.63 (*s*, 1H), 7.43 (*d*, $J = 6.6$ Hz, 1H), 7.30 (*d*, $J = 6.9$ Hz, 1H), 7.23 (*s*, 1H), 7.00–6.99 (*m*, 2H), 6.50 (*s*, 2H), 4.55 (*s*, 2H), 4.33 (*s*, 2H), 4.27 (*s*, 5H), 3.95 (*s*, 2H), 1.32 (*s*, 3H). ^{13}C NMR (101 MHz, DMSO) δ 156.75, 143.89, 143.27, 137.96, 130.74, 129.55, 129.00, 126.85, 124.14, 122.45, 116.95, 115.40, 115.16, 88.39, 84.67, 70.96, 69.74, 68.87, 64.62, 59.72, 41.45, 12.37. MS (EI) *m*/*z*: $[M]^+$: calcd for 521.11; found 521.22.

UV–Vis analysis

UV–Vis absorption spectra of Fc-X-An (1×10^{-5} mol/L) in DMSO before and after adding 30 equiv salts named TBAY (where the anion Y is F^-, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, HSO_4^-, Ac^-, PF_6^-, $H_2PO_4^-$) were recorded in the range of 250–700 nm at the room temperature. The stock solution concentrations of Fc-X-An and TBAY are 1.0×10^{-4} mol/L and 5×10^{-4}, 5×10^{-5} mol/L, respectively. Then stock solution (0.50 mL) of Fc-X-An was placed into a 10 mL volumetric flask, and different amounts of the TBAY solutions were added with a micro syringe, finally diluted to 10 mL with the DMSO. After each addition, the absorption spectra were recorded. Statistical analysis of the data was carried out using Origin 8.0. All reaction experiments were carried out at room temperature.

Cyclic voltammetry experiment

A three-electrode system was adopted to test the cyclic voltammetry (CV) with a scanning rate of 0.1 V/s under the nitrogen condition. Sample concentration of target Fc-X-An acceptors is 10^{-3} mol/L in DMSO solution and the oxidation–reduction peak of Fc is utilized as the signaling site. Then the TBAF in DMSO solution is gradually added thereto by a micro-injector. The oxidation–reduction peak of the Fc group was measured again, and observed changes of oxidation–reduction peak when TBAF was gradually add in.

^{1}H Nuclear magnetic resonance titration experiment

Fc-X-An dissolved in DMSO-d_6 with a concentration of 1.0×10^{-2} mol/L was prepared and tested firstly. Then 0–1.25 equiv of TBAF stock solution in DMSO-d_6 was added to the abovementioned samples gradually and the corresponding ^{1}H NMR spectra were recorded again. The chemical shifts of the NH and CH protons were followed and drafted against the equivalents of TBAF.

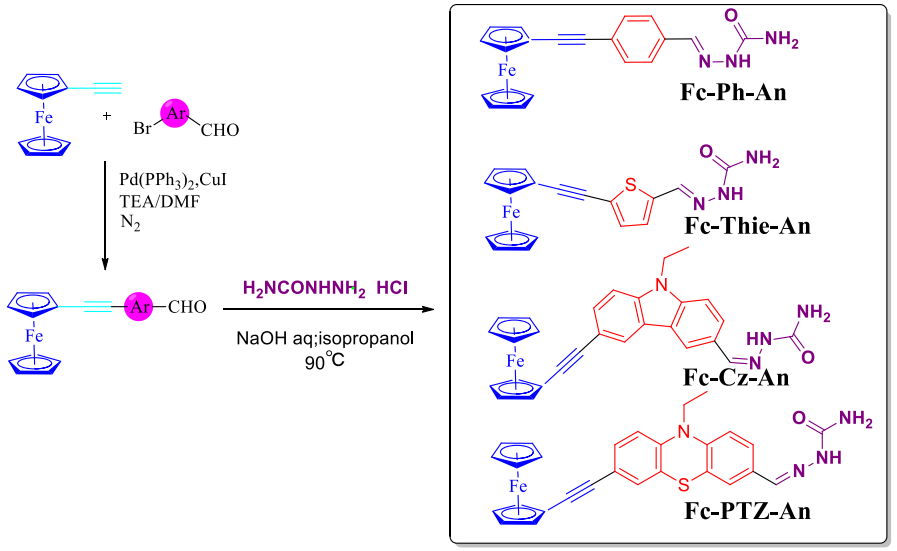
Method for Job's plot

A stock solution of Fc-X-An and the TBAF were prepared with a concentration of 1×10^{-4} mol/L in DMSO, respectively. In the Job's plot experiments, keeping the fixed overall concentration at 1×10^{-5} mol/L, and the molar fraction of TBAF was changed from 0 to 1.0. In the course of preparation of sample solutions, the different amounts of Fc-X-An and TBAF solutions were placed into a 10 mL volumetric flask by using a microsyringe, and then diluted to 10 mL. After mixing the samples in a uniform state, the absorption spectra were recorded in the range of 250–700 nm at the room temperature. Statistical analysis of the data was carried out using Origin 8.0.

Results and discussion

Synthesis

The synthesis route of Fc-X-An is shown in Scheme 1. Ethynyl ferrocene underwent the Sonogashira coupling reaction with bridging ligands to yield the intermediate Fc-X-A with a high yield rate. Following, final acceptors Fc-X-An were obtained after the reaction of Fc-X-A and semicarbazide hydrochloride under the catalysis of sodium acetate. Fc-X-An and Fc-X-A have been characterized and confirmed by ESI–MS, ^{1}H NMR, ^{13}C NMR spectroscopy. Figures S1–S8 list the ^{1}H NMR and ^{13}C NMR of Fc-X-An.



Scheme 1 Synthesis route of Fc-X-An

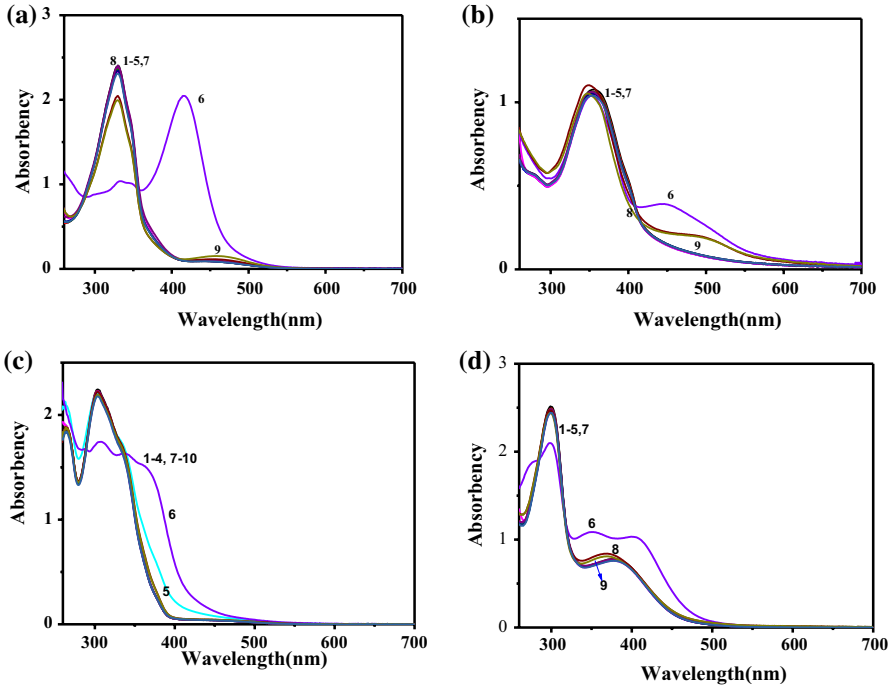


Fig. 1 UV–Vis titration absorption spectra of **a** Fc-Ph-An, **b** Fc-Thie-An, **c** Fc-Cz-An and **d** Fc-PTZ-An (5×10^{-5} mol/L) in DMSO upon addition of 30 equiv of respective anions (1: Cl^-, 2: Br^-, 3: I^-, 4: NO_3^-, 5: AcO^-, 6: F^-, 7: ClO_4^-, 8: HSO_4^-, 9: PF_6^-, 10: $H_2PO_4^-$) as *n*-Bu_4N^+ salt

Table 1 Complexation constant K, correlation coefficient R and LOD between Fc-X-An and F^-

Substances	K (M^{-1})	R	LOD (mol/L)
Fc-Ph-An	123	0.99	2.31×10^{-4}
Fc-Thie-An	448	0.99	1.07×10^{-4}
Fc-Cz-An	593	0.99	2.98×10^{-5}
Fc-PTZ-An	439	0.99	5.93×10^{-5}

UV–Vis titration analysis

The anion-binding properties of Fc-X-An were first studied by UV–Vis spectroscopy in DMSO solution. The UV–Vis titration analysis of Fc-X-An with various anions was exhibited in Fig. 1 and the key parameters are summarized in Table 1. As shown in Fig. 1, no obvious change could be observed upon addition of 30 equiv of Cl^-, Br^-, I^-, NO_3^-, AcO^-, ClO_4^-, HSO_4^-, PF_6^-, $H_2PO_4^-$. Significant variations were found after the adding of F^- to the solution of acceptor.

Moreover, colorimetric receptors were especially attractive as it could be easily monitored by ion-complexation induced changes in UV–Vis absorption spectra, which would allow the so-called "naked eye" detection of ions. As shown in Fig. 2, the solution colors of four receptors changed from light yellow to yellow upon addition of F^-. Compared with other receptors, Fc-Thie-An shown more sensitive to F^- which could be used as an ideal 'Naked-eye' probe for selective F^- sensing. The visual colorimetric responses after and before adding Cl^-, Br^-, I^- in DMSO are listed in Figs. S9–S11.

When comparing with the other, Fc-Ph-An showed a more significant variation during the UV–Vis absorption titration test as seen in Fig. 2a. Then the UV–Vis absorption titration with F^- was studied in detail and the result is shown in Figure S12. Upon the gradual addition of F^-, a decrease at 330 nm as well as an increase with a peak at 417 nm were observed simultaneously and the spectral change almost stopped upon addition of 60 equiv of F^-. Such unique phenomenon suggested

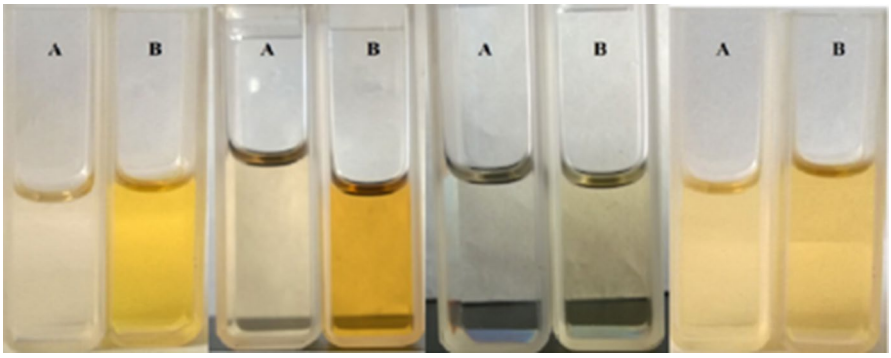


Fig. 2 Visual colorimetric response before (**a**) and after (**b**) addition of F^- in DMSO (the receptor is Fc-Ph-An, Fc-Thie-An, Fc-Cz-An and Fc-PTZ-An from left to right The anions is F^-, Cl^-, Br^-, I^- as n-Bu_4N^+ salt from up to down)

that Fc-Ph-An was suitable to act as a highly exclusive and sensitive chemosensor for fluoride by UV–Vis titration. Moreover, the clear isosbestic points at 295 and 357 nm indicated that a single component was produced in response to the interaction between Fc-Ph-An and F^- [49]. Results of other acceptors are shown in Figures S13, S14 and S15.

With an aim to verify our assumption that target Fc-X-An acceptors associate with F^- in a 1:1 stoichiometry, Benesi–Hildebrand analysis is utilized [50]. When assuming a 1:1 association between Fc-X-An and F^-, the Benesi–Hildebrand equation is given as follows:

$$\frac{1}{A - A_0} = \frac{1}{A_\infty - A_0}\left[\frac{1}{K[F^-]} + 1\right]. \tag{1}$$

A_0 and A_∞ are the absorbency of Fc-X-An before and after adding an excess amount of F^- while the A is the measured absorbency of Fc-X-An after adding F^-; K is the association constant (mol^{-1}), and $[F^-]$ is the concentration of F^- added (mol). As shown in Fig. 3, a plot of $1/(A - A_0)$ against $1/[F^-]$ shows a linear relationship, indicating that Fc-X-An actually associated with F^- in a 1:1 stoichiometry. Besides, such stoichiometry was further confirmed by Job's plot. As exhibited in Fig. 4, the Job's plots suggested a 1:1 binding model between Fc-X-An and F^-. Corresponding

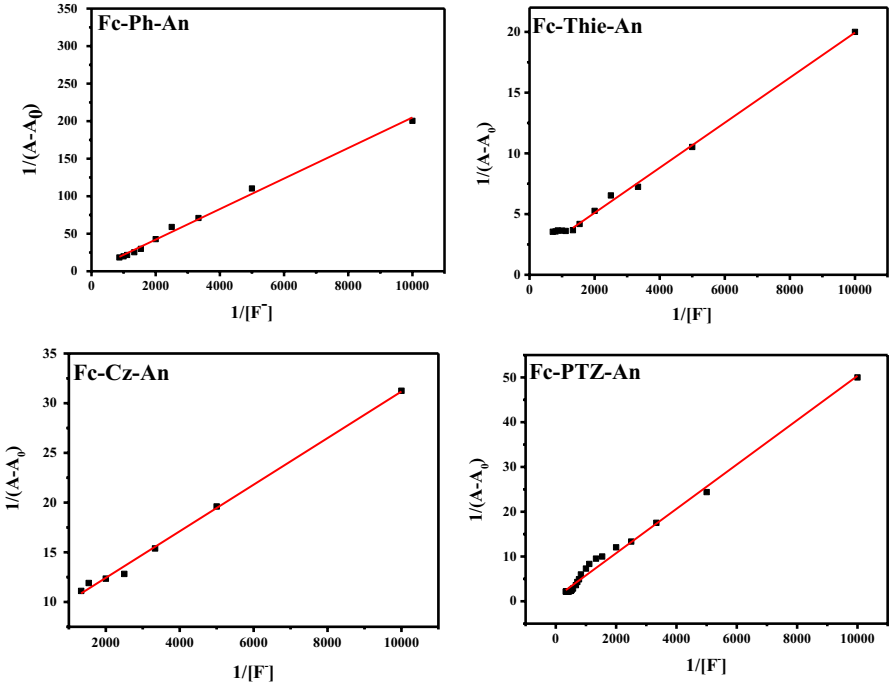


Fig. 3 Benesi–Hildebrand analysis of UV–Vis absorption titration of Fc-X-An with F^- (analysis wavelength of Fc-Ph-An, Fc-Thie-An, Fc-Cz-An and Fc-Cz-An at 413 nm, 444 nm, 376 nm and 376 nm, respectively)

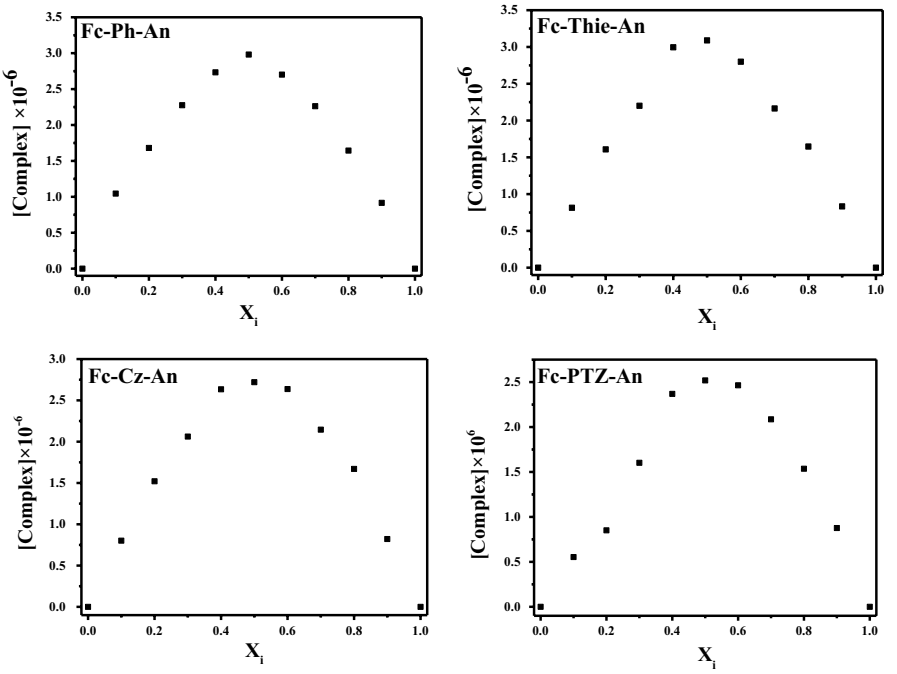


Fig. 4 Job's plot exhibited the inflection point at 0.5 (formation of a 1:1 complex): the total concentration [Fc-X-An] + [F^-] is 10^{-5} mol/L

association constant (*K*) as well as the limit of detection (LOD) are listed in Table 1. From the analysis, we could conclude that Fc-Cz-An is the most sensitive chemosensor for F^- due to its lowest LOD and highest *K*.

Electrochemistry titration

Owing to a stable redox property, the ferrocene (Fc) moiety was widely used as an electrochemical signal transmission group [51]. Electrochemical ferrocene-based receptors for anions are expected to show cathodic shift in their redox-process when complexed to an anion as they are easier to oxidize than the free redox-active receptor [52].

The recognition abilities of Fc-X-An toward F^- in the form of their corresponding tetrabutyl ammonium salts (TBAF) were initially investigated by CV in DMSO solution containing 0.1 mol/L [(n-Bu)$_4$NPF$_6$] as the supporting electrolyte. As shown in Fig. 5, upon gradual addition of TBAF from zero to a 1.4 equiv, the redox potential of Fc-X-An showed a cathodic shifts at 0.90 V, which is attributed to the ferrocene unit. The cathodic shifts of Fc-Ph-An, Fc-Thie-An and Fc-Cz-An were around 10 mV, while Fc-PTZ-An gave a 120 mV cathodic shift which was larger than other receptors. These data suggested that the receptor Fc-PTZ-An was suitable to act as an electrochemical probe for selective F^- sensing.

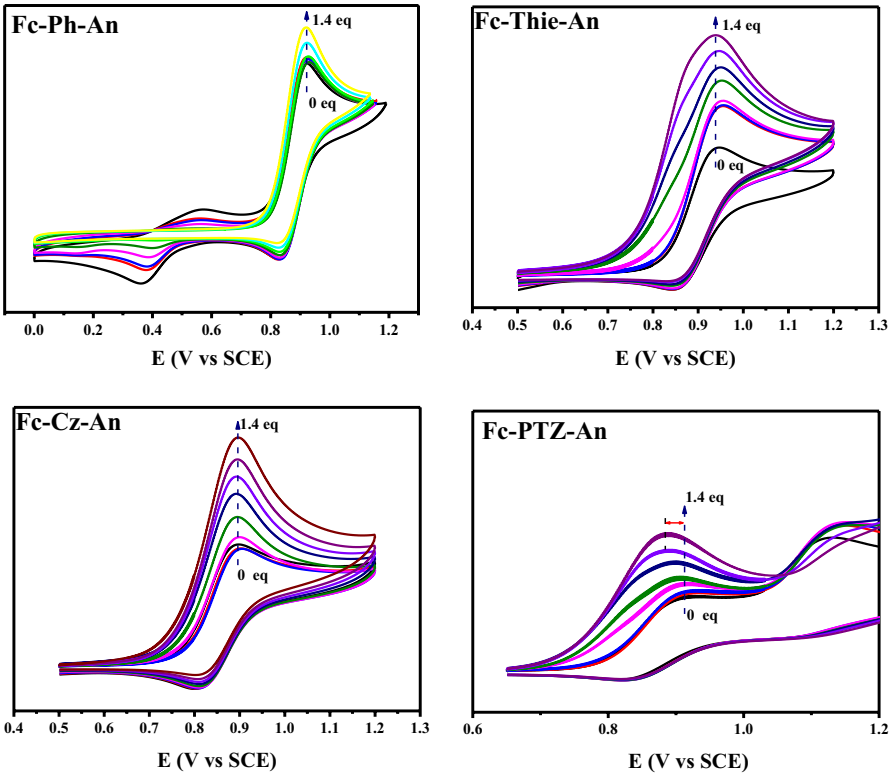


Fig. 5 CV titration of Fc-X-An by adding F^- from 0 to 1.4 equivalents in DMSO

^{1}H NMR titration

To support the results obtained by electrochemical and spectroscopic experiments as well as to obtain additional information about the coordination mode, ^{1}H NMR titrations have been analyzed in DMSO-d_6. Figure 6 shows the corresponding ^{1}H NMR titration results of Fc-Ph-An, Fc-Cz-An with TBAF. ^{1}H NMR titrations of Fc-Thie-An and Fc-PTZ-An are shown in Figures S16 and S17.

As shown in Fig. 6, the NH proton of Fc-Ph-An (H_d, $\delta = 10.32$ ppm) disappeared completely upon gradual addition of TBAF in DMSO-d_6, indicating that F^- indeed interacted with a NH proton [49]. Other protons of Fc-Ph-An shifted upfield, suggesting that this interaction affected π-electrons of Fc-Ph-An and, hence, could lead to the change in absorption and fluorescence spectra. A similar tendency could also be observed in Fc-PTZ-An, the NH proton (H_h, $\delta = 10.19$ ppm) disappeared completely upon F^- addition and other protons shifted upfield except for H_g ($\delta = 8.01$ ppm) which was shifted downfield. The downfield chemical shift of H_g could be aroused by hydrogen bonding of a carbonyl group [22, 53].

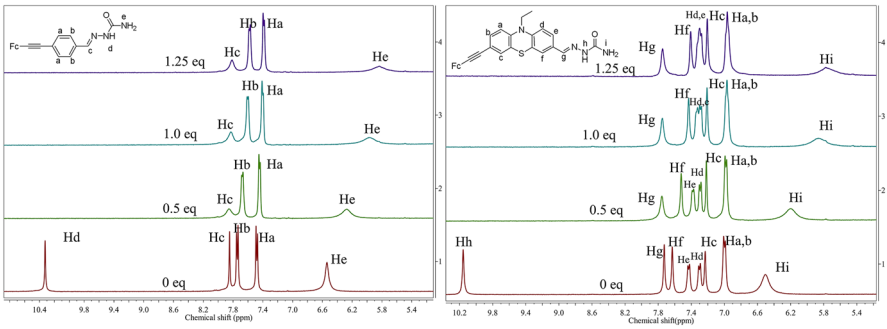


Fig. 6 ^{1}H NMR titration of Fc-Ph-An and Fc-PTZ-An by adding F^- from 0 to 1.25 equivalents in DMSO-d_6

Conclusion

In this work, we have prepared a series of conjugated ferrocene ethynyl semicarbazide derivatives (Fc-X-An), in which the ferrocene unit was linked by an ethyne bridge to a chromogenic or fluorescent signalling unit, and examined its binding properties towards various guest anions using electrochemical, ^{1}H NMR, spectral and optical techniques. The semicarbazide derivative receptors Fc-X-An exhibited high binding affinity and sensitivity for the fluoride anion in DMSO through multichannel methods. Fc-Thie-An is shown to be more sensitive to F^- which could be used as a 'Naked-eye' probe for selective F^- sensing, while Fc-Cz-An was more suitable to act as UV–Vis and fluorescent sensors for F^- because it processed the lowest LOD and highest K. Comparing with others, the receptor Fc-PTZ-An was suitable to act as a eletrochemical probe for selective F^- sensing. Potentially, all these results reveal that malfunction chemosensors of F^- anion were realized by constructing conjugated ferrocene ethynyl semicarbazide derivatives.

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