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Highly selective fluorescent recognition of phenyl amino alcohol based on ferrocenyl macrocyclic derivatives

Guang-yan Qing [a,b,*], Tao-lei Sun [b], Yong-bing He [a], Feng Wang [a], Zhi-hong Chen [a]

[a] College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, PR China
[b] Physikalisches Institut, Münster University, Münster 48149, Germany

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ABSTRACT

Four ferrocenyl macrocyclic derivatives **3** and **4** containing anthracene fluorophores have been synthesized. The fluorescent properties of these receptors have been studied in three organic solvents, both in the absence and presence of phenyl amino alcohols. All receptors exhibit sensitive fluorescence response to L- or D-phenylglycinol, a strong emission band is produced due to the intermolecular exciplex between host and guest. These special phenomena were not observed when other species were used as the guests; such highly selective fluorescent response indicates that these receptors can easily discriminate phenylglycinol from other similar species. Solvent comparative experiments also indicate that acetonitrile is the most appropriate solvent to detect this fluorescent change. The intramolecular energy transfer between excited anthracene and ferrocene, and π–π stacking interaction between the aromatic rings play critical roles in this special fluorescence enhancement. Model calculations at DFT level further suggest the possible interaction modes, structures and relatively steric position between the host and guest also influence the optical response.

1. Introduction

The design of chemosensors that are able to selectively recognize and sense specific analytes has attracted considerable interest due to their importance in biological and environmental settings.[1] On account of its high sensitivity and potential applications in analytical, biological, and clinical biochemical environments, fluorescence is becoming of increasing importance for the chemical trace detection.[2] Much effort has been devoted to developing fluorescent sensors for cations,[3a,b] anions,[3c,d] and neutral guests,[2b,3e] the classical signaling mechanisms include competitive binding, photo-induced electron transfer (PET), intermolecular charge transfer, metal-to-ligand charge transfer (MLCT), and excimer/exciplex formation.[2]

Ferrocene and ferrocenyl derivatives are also widely used in luminescent/fluorescent systems; they are classical quenchers of excited state, and both energy and electron transfer may be involved.[4] Taking advantage of this quenching effect, many ferrocene sensors have been developed in the fields of molecular recognition and analytical chemistry, the presence of a guest can be sensitively indicated through fluorescence extinction or recovery.[5]

Chiral amino alcohols are useful as intermediates for making a variety of biologically active molecules and as ligands for stereoselective catalysts. There have been numerous publications on developing receptors for amino alcohols,[6] especially the enantioselective recognition of phenylglycinol[7] due to its potential application of (*R*)-phenylglycinol in the synthesis of a key precursor of HIV-1 protease inhibitors.[8] In our previous work, a series of two-armed chiral calix[4]arenes have been synthesized and fluorescence 'Off–On' behavior was reported for phenylglycinol.[9] Although there are many report of the recognition of amino alcohols, most of them focus on the classical supramolecular platform, such as calix[4]arene, binaphthol, crown ethers, and molecular tweezers. To the best of our knowledge, similar chemosensors based on ferrocene platform are still rare. Introducing ferrocenyl derivatives to the fluorescence system may induce a special optical response, which inspired us to design some novel ferrocenyl fluorescent sensors to recognize amino alcohols.

In this work, we report the synthesis of a series of ferrocenyl macrocyclic derivatives and their recognition properties toward amino alcohols have been investigated through fluorescence titration experiments. The results indicate that these receptors have sensitive fluorescent response to phenylglycinol, a strong exciplex emission band could be observed due to π–π stacking interaction between host and guest; while these phenomena were not found when the receptors interacted with other amino alcohols or reference guests. Through the unique enhancement in the fluorescence spectra of these sensors, phenylglycinol could be easily distinguished from other similar species, which has potential for analytical detection.

* Corresponding author.
E-mail address: qing@uni-muenster.de (G. Qing).

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2. Results and discussion

2.1. Synthesis

The synthesis of four ferrocenyl macrocyclic derivatives is outlined in Scheme 1. The starting materials **1a** and **1b** were synthesized according to the literature,[10] then reacted with 1,1′-ferrocenediacetic chloride to obtain two macrocyclic derivatives **2** that differ in the size of macrocycle. The Boc-protecting group of **2a** or **2b** was removed with TFA, then reacted with 9-anthraldehyde, followed by addition of $NaBH_4$ to reduce the Schiff's bases to obtain compound **3**. Compound **4** was prepared from **2** and 9-isothiocyanatomethyl anthracene. Four reference compounds **5a**–**5d** were synthesized according to the literatures;[11,19] their structures are shown in Scheme 2. The structures of these compounds were characterized by IR, ESI-MS, ^{1}H NMR, ^{13}C NMR, and elemental analysis.

2.2. Fluorescence spectra study

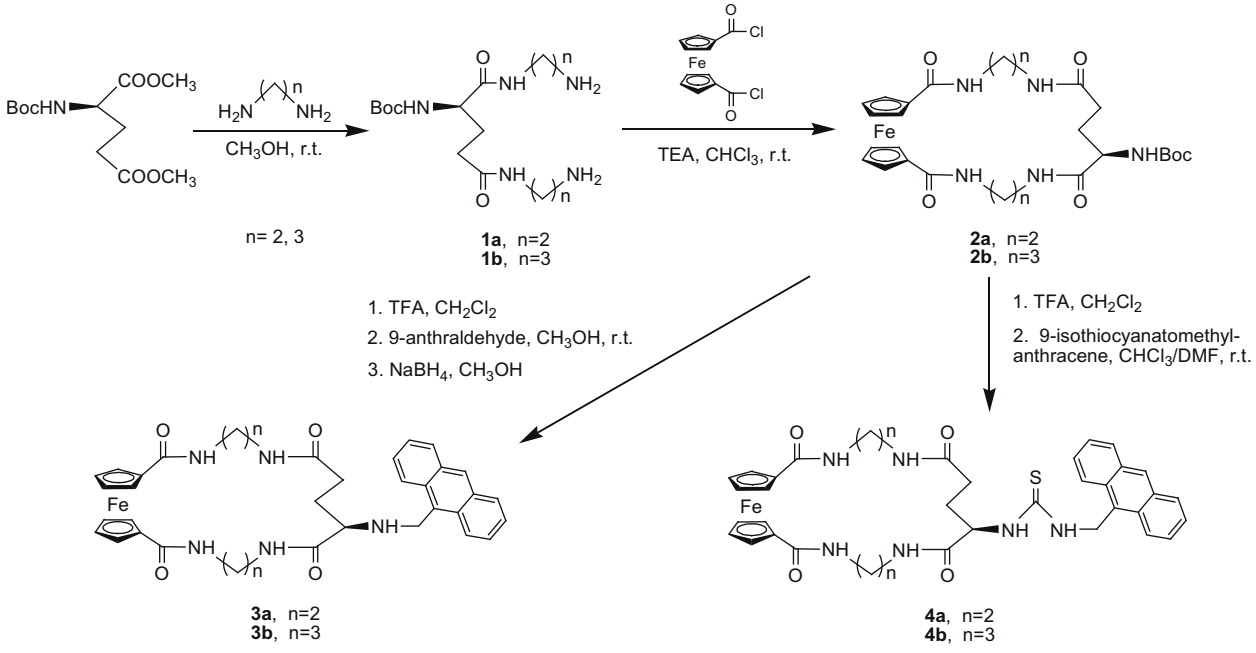
The fluorescence spectra were recorded from solutions of **3a**–**4b** in the absence and presence of two kinds of amino alcohols such as phenylglycinol and phenylalaninol. Considering most amino alcohols are well soluble in the organic solvents, acetonitrile was first chosen as the solvent to investigate the fluorescence response. Figure 1 shows the fluorescence emission of receptor **3a** (5.0×10^{-5} mol L^{-1}) with different concentrations of L-phenylglycinol. In the absence of guest, the spectra of **3a** exhibited the characteristic emission spectrum with a monomeric anthracene maximum at 414 nm when it was excited at 367 nm.[12] Subsequently, the binding behaviors of **3a** with different concentrations of phenylglycinol were investigated by means of titration fluorimetry. The fluorescence emission intensities of **3a** at 394, 414, and 438 nm increased gradually upon addition of L-phenylglycinol, while a strong emission band ranging from 450 nm to 570 nm was produced. When 42.5 equiv amount of guest was added to the solution of **3a**, the intensity at 438 nm increased about 180%, while the intensity at 475 nm increased about 550%. The obvious fluorescence enhancement clearly illustrated that the receptor **3a** could interact with L-phenylglycinol and a host-guest complex may occur.

Different phenomena were observed when L-phenylalaninol was added into the solution of **3a** in CH_3CN, as shown in Figure 2. The characteristic peaks of anthracene increased gradually with increasing concentration of guest, but the strong emission band around 500 nm could not be observed, which is very different from the phenomena observed in Figure 1. When 60 equiv of guest was added, the fluorescence intensity at 414 nm increased about 30%, while the intensity at 438 nm only increased about 38%, such kind of fluorescence enhancement could be found in the classical literature.[12b] Satisfactory nonlinear curve fitting (the correlation efficient is over 0.99) confirmed that **3a** could form 1:1 complex with L-phenylglycinol or L-phenylalaninol (see the inset of Figs 1 and 2). For a complex of 1:1 stoichiometry, the association constant (K_{ass}) can be calculated by using nonlinear fitting equation from the Origin 7.0 software.[12a,13]

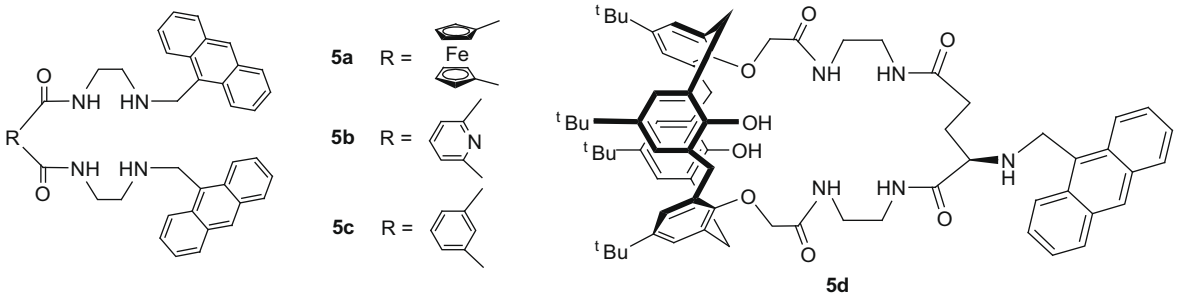
$$I = I_0 + \frac{I_{lim} - I_0}{2C_0}\left\{C_H + C_G + 1/K_{ass} - \left[(C_H + C_G + 1/K_{ass})^2 - 4C_H C_G\right]^{1/2}\right\}$$

Where I represents the fluorescence intensity, and C_H and C_G are the corresponding concentrations of host and guest. The association constant for the interaction of **3a** with L-phenylglycinol is 23.8 M^{-1}, whereas that for association of **3a** with L-phenylalaninol is 44.5 M^{-1}, which illustrates that **3a** has different binding abilities toward these amino alcohols. Through the dramatically different fluorescent responses, **3a** could be used as a fluorescent sensor to discriminate phenylglycinol from phenylalaninol.

The fluorescent responses of receptors **3b**, **4a** and **4b** to amino alcohols were also investigated by means of titration fluorimetry in CH_3CN. All these receptors exhibited obvious fluorescence enhancements when interacted with L-phenylglycinol, while a strong emission band ranging from 450 nm to 570 nm could be observed clearly, the intensities increased gradually with increasing concentration of guest, similar to the phenomena shown in Figure 1. But when they interacted with L-phenylalaninol, only the characteristic peaks of anthracene exhibited weak fluorescence enhancement, the emission band around 500 nm could not be ob-



Scheme 1. Synthetic scheme for compounds **3** and **4**.



Scheme 2. The structures of reference compounds.

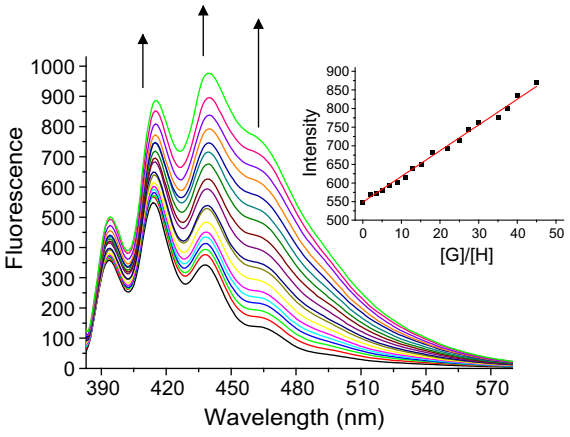


Figure 1. Fluorescence spectra of receptor **3a** (5.0×10^{-5} mol L^{-1}) upon the addition of various amounts of L-phenylglycinol in CH_3CN. Equivalent of guest: 0, 2, 3.5, 5, 7, 9, 11, 13, 15, 18, 22, 25, 27.5, 30, 35, 37.5, 40, and 45. λ_{ex} = 367 nm (EX: 10, EM: 5). Inset: changes in the fluorescence intensity of **3a** at 414 nm upon addition of L-phenylglycinol. The line shown is a line-fitted curve.

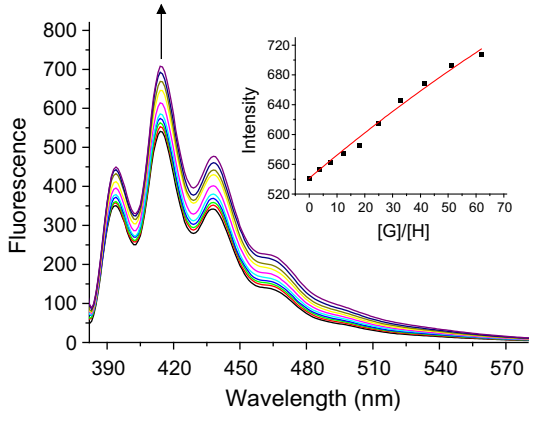


Figure 2. Fluorescence spectra of receptor **3a** (5.0×10^{-5} mol L^{-1}) upon the addition of various amounts of L-phenylalaninol in CH_3CN. Equivalent of guest: 0, 3.5, 7.5, 12, 18, 25, 30, 40, 50, and 60. λ_{ex} = 367 nm (EX: 10, EM: 5). Inset: changes in the fluorescence intensity of **3a** at 414 nm upon addition of L-phenylalaninol. The line shown is a line-fitted curve.

served in any experiment. The association constants (K_{ass}) of receptors with amino alcohols could be calculated from the changes of fluorescent intensity (at 414 nm); the results are listed in Table 1. The K_{ass} of **4a** with L-phenylglycinol is 46.3 M^{-1}, while that with L-phenylalaninol is 212.3 M^{-1}, the large differences in the K_{ass} illustrate that **4a** also has good chemo-selectivity toward these amino alcohols.

Table 1
Association constants (K_{ass}) of receptors **3a**–**4b** with L- or D-phenylglycinol, L- or D-phenylalaninol in CH_3CN, $CHCl_3$, or DMSO at 25 °C.

Guest	K_{ass} (M^{-1})[a]			
	Receptor **3a**	Receptor **3b**	Receptor **4a**	Receptor **4b**
In CH_3CN				
L-Phenylglycinol	23.8 ± 5.8[b]	45.2 ± 15.6[b]	46.3 ± 13.2[b]	6.9 ± 1.2[b]
D-Phenylglycinol	33.2 ± 4.2[b]	13.1 ± 4.8[b]	36.8 ± 12.8[b]	33.1 ± 7.6[b]
L-Phenylalaninol	44.5 ± 6.2[b]	[c]	212.3 ± 40.0[b]	99.1 ± 22.7[b]
D-Phenylalaninol	42.1 ± 2.1[b]	[c]	565.5 ± 66.2[b]	281.2 ± 37.5[b]
In $CHCl_3$				
L-Phenylglycinol	38.0 ± 5.6[b]	61.0 ± 14.5[b]	33.9 ± 2.7[b]	20.2 ± 4.2[b]
D-Phenylglycinol	57.9 ± 8.3[b]	25.7 ± 3.6[b]	20.3 ± 4.1[b]	24.8 ± 4.1[b]
L-Phenylalaninol	75.2 ± 8.9[b]	[c]	[c]	[c]
D-Phenylalaninol	51.0 ± 9.3[b]	[c]	[c]	[c]
In DMSO				
L-Phenylglycinol	13.1 ± 1.2[d]	13.3 ± 2.1[d]	580.3 ± 48.5[d]	16.4 ± 2.8[d]
D-Phenylglycinol	6.4 ± 1.5[d]	6.5 ± 2.2[d]	621.0 ± 55.6[d]	10.0 ± 1.4[d]
L-Phenylalaninol	[c]	[c]	503.5 ± 34.2[d]	[c]
D-Phenylalaninol	[c]	[c]	523.2 ± 38.5[d]	[c]

[a] The values of K_{ass} were calculated from results of fluorescence titrations; all error values were obtained by nonlinear curve fitting.
[b] The values of K_{ass} were calculated from the change of fluorescence intensity at 414 nm.
[c] The association constants of receptors with L-phenylalaninol could not be obtained due to the too small change in the fluorescence spectra.
[d] The values of K_{ass} were calculated from the change of fluorescence intensity at 475 nm; because the changes at 414 nm were too small to be calculated.

Considering the chirality of these ferrocenyl macrocycles, their enantioselective recognition properties toward amino alcohols have also been investigated. Receptor **4a** was found to have good chiral discrimination ability toward phenylalaninol in acetonitrile, the different fluorescent intensity changes toward the L- or D-enantiomers are shown in Figure 3. The $K_{ass(\mathbf{4a}+\text{L-phenylalaninol})}$ is 212.3 M^{-1}, while $K_{ass(\mathbf{4a}+\text{D-phenylalaninol})}$ is 565.5 M^{-1}, corresponding to the D/L selectivity ($K_{(D)}/K_{(L)}$) is 2.66; similar chiral selectivity was also obtained when **4b** interacted with this guest. Through the different fluorescence enhancement, these receptors could also be used as chiral sensors for the enantiomers of phenylalaninol. Interestingly, such chiral recognition effects could not be observed when the $CHCl_3$ or DMSO was chosen as the solvent, which indicate that the polarity of solvent could also influence the complexation between host and guest.

In order to explore the mechanism of fluorescence enhancement, more reference guests were introduced to perform control experiments; the structures of these guests are listed in Scheme 3. The structure of 2-aminopropanol is similar to that of phenylglycinol except for the phenyl group. When 20 equiv of 2-aminopropanol was added to the solution of **3a**, only a weak fluorescent enhancement was observed, the intensity at 438 nm increased about 9%, while the same amount of L-phenylglycinol could induce 82% intensity enhancement, as shown in Figure 4. On the basis of

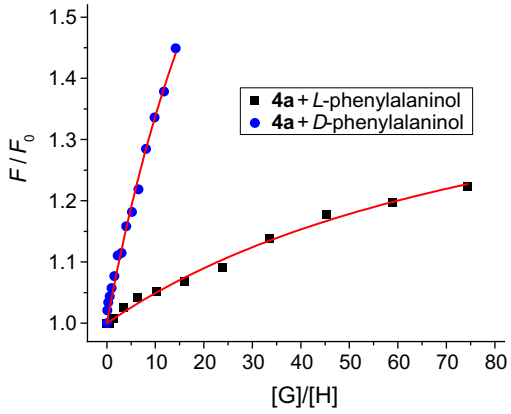


Figure 3. Fluorescence intensity changes (at 414 nm) of receptor **4a** (5.0×10^{-5} mol L^{-1}) upon the addition of various amounts of L- or D-phenylalaninol in CH_3CN. The line shown is a line-fitted curve.

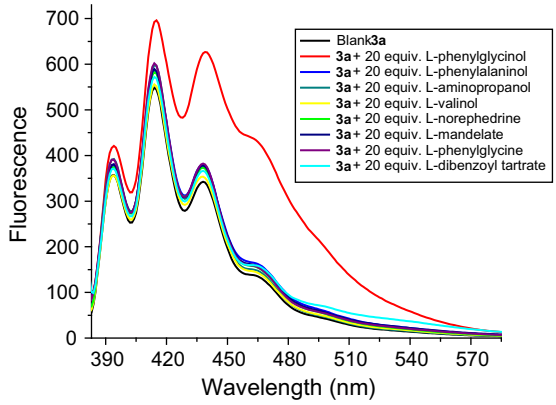


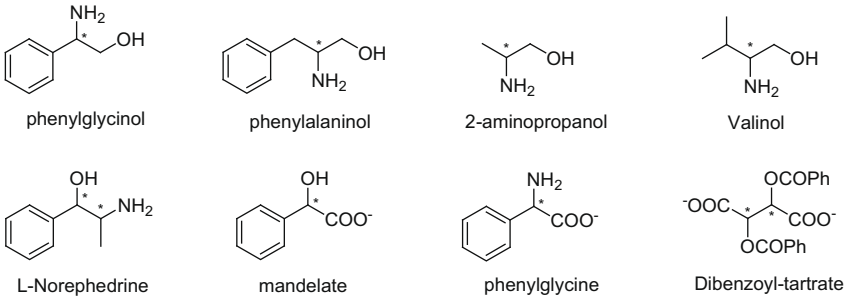
Figure 4. Fluorescence spectra of receptor **3a** (5.0×10^{-5} mol L^{-1}) with various guests (1.0×10^{-3} mol L^{-1}) in CH_3CN. λ_{ex} = 367 nm (EX: 10, EM: 5).

this result, we presume that the π–π stacking interaction between the phenyl of phenylglycinol and the anthracene of the host is the critical factor for obvious fluorescence enhancement.[3e,6h,9,14] But when phenylalaninol was used as the guest, such enhancement could not be observed, which inspired us to use other phenyl-containing molecules such as L-norephedrine, mandelate, phenylglycine, or dibenzoyl tartrate to do the controlled experiments. From the spectra in Figure 4, the addition of these species could not lead to the strong fluorescence emission band at around 500 nm, while the changes in the characteristic peaks were also very small. These phenomena indicate that **3a** could easily discriminate phenylglycinol from other species, which will take great advantage in the fluorescent detection. We presume that the interaction between **3a** and phenylglycinol is largely due to a special energy transfer process; only phenylglycinol promotes the energy transfer from the excited state of anthracene to the ground state of phenyl, which further induces the strong emission band in fluorescence spectra.

Owing to their fairly high stability under visible irradiation, ferrocene and ferrocenyl derivatives are widely used in luminescent systems. They are classical quenchers of excited states.[4] Both energy and electron transfer may be involved, depending on the nature of the excited species. According to the explanation reported in the literature, we assume a possible mechanism for the fluorescence enhancement as shown in Figure 5. When the anthracene is excited, the excitation energy can be transferred according to $A^* + FeCp_2 \rightarrow A + FcCp_2^*$, which may be followed by the thermal relaxation of the excited state, giving $A + FeCp_2$ + thermal energy. Due to this intramolecular energy transfer process, the fluorescence was substantially quenched by ferrocene. Traverso et al. reported a similar example, in which energy transfer was also involved when ferrocene quenched the fluorescence of naphthalene in a chloroform–ethanol solution.[15]

Then the addition of phenylglycinol could cut off this energy transfer process, due to the π–π stacking interaction between the anthracene of the host and the phenyl of the guest. The fluorescence of **3a** was observed to revive gradually with increasing the amount of guest. The occurrence of a strong emission band (ranging from 450 nm to 570 nm) could be attributed to the intermolecular exciplex; the energy was transferred from the excited state of anthracene to the ground state of phenyl, which further promoted the fluorescent enhancement. In order to prove this assumption, reference compounds **5a**–**5d** were synthesized. Acyclic receptor **5a** had similar fluorescence property to other ferrocenyl receptors **3a**–**4b**, except that its fluorescence response was much slower, only a large amount of guest could lead to an obvious change. But when receptors without ferrocene unit **5b** and **5c** were used as the probes, different phenomena were found; both exhibited the same fluorescence enhancement to phenylglycinol and phenylalaninol, only the characteristic peaks increased about 20%, the respective strong emission band (around 500 nm) could not be observed even when excess amounts of guests were added. Calix[4]arene macrocyclic derivative **5d** was also introduced to do the controlled experiment, but the selectivity between these two amino alcohols could not be observed either. These results convincingly prove that the energy transfer process from anthracene to the ferrocene unit plays a critical role in the recognition process, and further induces the high selectivity toward these two amino alcohols.

The fluorescence spectra of **3a** with phenylglycinol were measured in different solvents to examine the effects of the solvent polarity. Acetonitrile, chloroform, and DMSO are the most common



Scheme 3. The structures of guests.

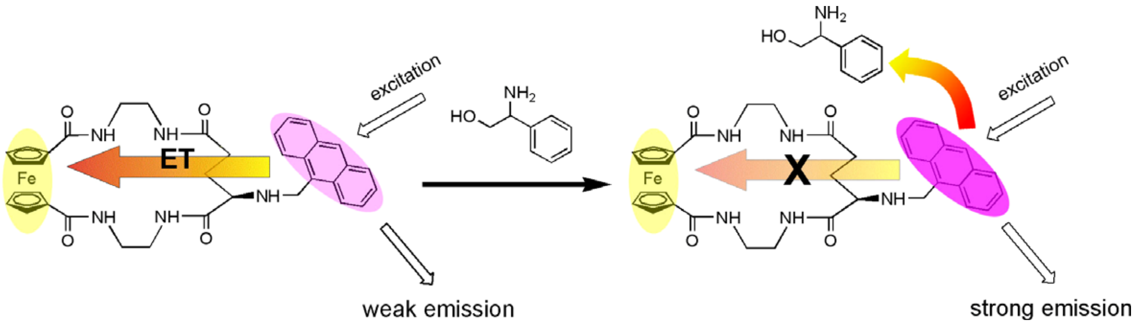


Figure 5. The possible interaction mechanism of **3a** with phenylglycinol.

organic solvents in the fluorescence detection, they are chosen as the solvents for the comparison experiments. When **3a** was excited at the same wavelength (367 nm) in these three solvents, all of them exhibited three characteristic peaks; the strongest emission was produced in DMSO solution, while the weakest one was found in $CHCl_3$ solution, which indicates that increasing the solvent polarity will eliminate the quenching effect by ferrocene. When L-phenylglycinol was added to these solutions, respectively, different fluorescence enhancements in the emission spectra were found. Figure 6 shows the fluorescence intensity changes (at 475 nm) of **3a** upon the addition of L-phenylglycinol in these solvents; for ease of comparison, the normalized fluorescence intensity enhancement (F/F_0) is used as the Y-parameter. **3a** exhibited the most obvious fluorescence enhancement in CH_3CN, 45 equiv of guest could lead the F/F_0 approach 6.5, while this value could approach 4.0 in $CHCl_3$ solution. The weakest response was observed in the DMSO solution, the F/F_0 was only 1.5 when the same amount of guest was added. Sensitivity is an important parameter for the fluorescent detection, through these solvent comparison experiments, acetonitrile was found to be the most proper solvent for the detection of phenylglycinol in this system.

In this work, four cyclic ferrocenyl derivatives have been synthesized; **3a** was found to have excellent fluorescent response to phenylglycinol and could discriminate it from other species through the occurrence of a strong exciplex band. Similar phenomena were also observed when other three ferrocenyl derivatives **3b** and **4a**–**4b** were used as the probes. In comparison with the data obtained from controlled experiments, **3a** was still found to have the best fluorescence response to phenylglycinol, as shown in Figure 7. The structure of **4a** is similar to that of **3a**, but its fluorescence response is inferior to **3a**. Initially we assume that this may be due to the different hydrogen-bonding abilities, because thiourea is usually regarded as a hydrogen bond donor while an amine is regarded as a hydrogen bond acceptor. ^1H NMR spectroscopy is a useful tool to investigate the interaction details, especially for the hydrogen-bonding system. In order to clarify whether the hydrogen bond took part in the complexation, ^1H NMR titrations were adopted to examine the chemical shifts of the amide and thiourea protons of **3a** or **4a** when different equivalents of phenylglycinol were added to the host solutions.[16] However, we could not observe any changes in the amide and thiourea protons of the host in the ^1H NMR spectra although large amounts of guests were added, the chemical shift changes of these protons were all less than 0.02 ppm with the addition of 20 equiv of phenylglycinol, which may be due to hydrogen-bonding interactions being too weak; on the other hand, this result proves that hydrogen bonding does not contribute to the complexation, some classical works also indicate that hydrogen bond factors are not responsible for the fluorescence or absorbance response when the hosts interact with amino alcohols.[7e,f,9,17]

On the basis of the possible mechanism raised before, the ferrocene unit quenched the fluorescence through the intramolecular energy transfer process; we assume that the relatively steric positions between ferrocene and fluorophore may have an effect on the recovery of fluorescence. Thiourea is a much rigid functionality, which results in the anthracene of **4a** being located in a relatively remote position to ferrocene, which further weakens the energy transfer process. Further model calculation results agree well with this assumption.

The macrocyclic structure also plays an important role in the fluorescence response. In comparison with the obvious enhancements of receptors **3a**–**4b** in the emission spectra, the acyclic

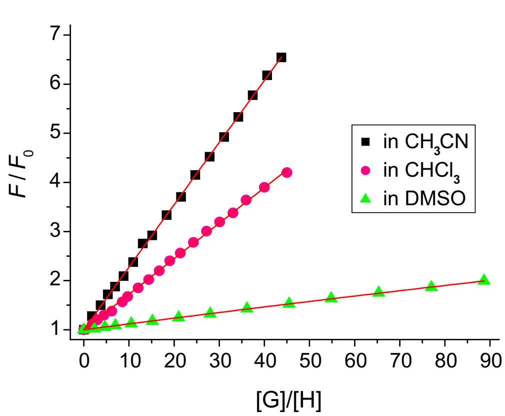


Figure 6. Fluorescence intensity changes (at 475 nm) of receptor **3a** (5.0×10^{-5} mol L^{-1}) upon the addition of various amounts of L-phenylglycinol in CH_3CN, $CHCl_3$, or DMSO. λ_{ex} = 367 nm.

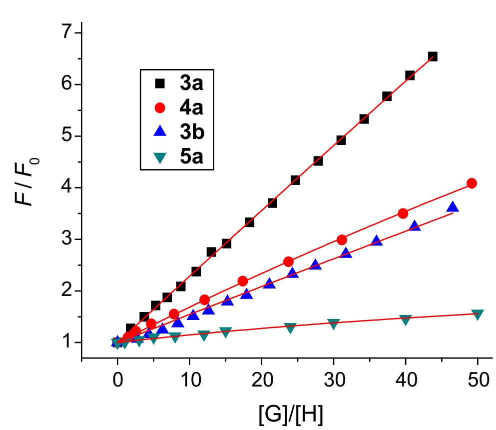


Figure 7. Fluorescence intensity changes (at 475 nm) of receptor **3a**, **4a**, **3b**, or **5a** (5.0×10^{-5} mol L^{-1}) upon the addition of various amounts of L-phenylglycinol in CH_3CN.

derivative **5a** exhibited a rather weak change when 50 equiv of L-phenylglycinol was added to the solution, the intensity at 475 nm only increased about 50%, which is far lower than those of macrocyclic receptors. We assume that the macrocycle provides the appropriate preorganized structure for the interaction, leading to the ferrocene center and anthracene fluorophore being located in favorable positions to promote the intramolecular energy transfer process.

The size of the ferrocenyl macrocycle could also be adjusted upon the introduction of longer propyl chains onto the macrocycle **3b**; if the cavity of the macrocycle becomes larger, the anthracene might be located in a more remote position to ferrocene unit, and maybe this can explain why the fluorescence response of **3b** is inferior to that of **3a**. We tried to synthesize similar ferrocenyl macrocycle with smaller cavities, using hydrazine in place of the ethylic linkages, but the cyclization reaction failed due to the strong rigidity of structure. But we can predict that the fluorescence recovery will become more intense if anthracene is located in a closer position to ferrocene due to the more effective intramolecular energy transfer.

2.3. Theoretical calculations

The structures of ferrocene and other metallocenes have been the subject of numerous theoretical studies. It has been shown that DFT calculations give a good description of geometry and other properties of this system.[18] Therefore quantum chemical calculations at DFT level of theory have been carried out to obtain the possible structures of **3a** and **4a**. The minimum energy structures are shown in Figure 8. From the calculation results, the geometry of the macrocycle is nearly the same for these two compounds, the diameter of the cavity is approximately 8.0 Å. However, the anthracene is located in a different position, for **3a**, the anthracene ring is located in close proximity to the ferrocene unit; the minimum distance from anthracene ring to the ferrocene center is 9.8 Å, while the maximum distance is 12.56 Å, but for **4a**, due to the rigidity of thiourea functionality, the anthracene ring is located in a remote position, the minimum distance from anthracene ring to ferrocene center increases to 12.73 Å, while the maximum distance is up to 15.94 Å. On the basis of these models, we can presume that the anthracene ring of **3a** is more inclined to overlap with ferrocene, which will benefit the intramolecular energy transfer.

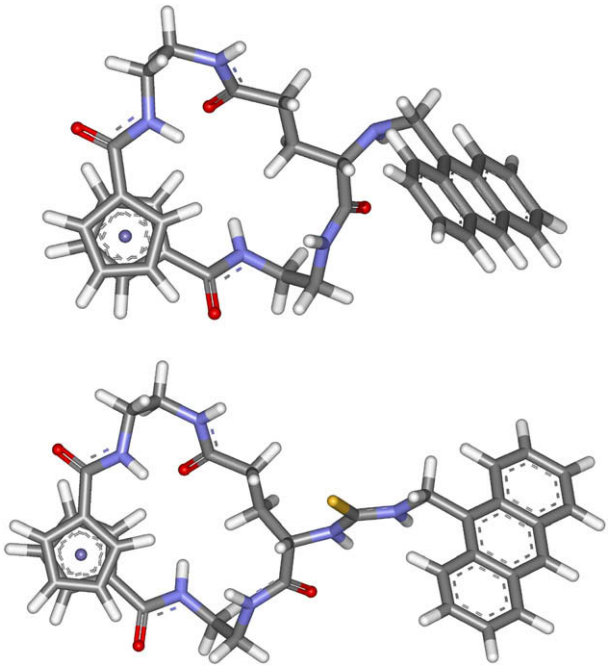


Figure 8. Calculated (B3LY/6-31G*) structures for receptors **3a** (upper) and **4a** (lower).

In order to obtain the interaction modes of receptors **3a**, **4a** with phenylglycinol, we also used model calculations to investigate the interaction between the host and guest. From the results shown in Figure 9 (the upper one), the phenylglycinol locates between the anthracene and the ferrocene unit of **3a**, the distance from the center of phenyl to iron atom is 5.95 Å, while that to the center of anthracene is 7.21 Å. The phenyl ring could partly overlap with anthracene ring; the dihedral angle between two rings is approximately 49°. This mode agrees well with the mechanism raised before, in which the phenylglycinol prohibits the initial intramolecular energy transfer process from excited anthracene to ferrocene, while π–π stacking between two aromatic rings could happen due to the favorable position. In comparison to **3a**, **4a** adopts a rather stretched conformation. The phenyl ring of the guest is located in a remote position from the ferrocene center; the average distance is 10.9 Å, while the average distance between an anthracene ring and a phenyl ring is 9.96 Å, the dihedral angle between two rings is about 75.6°. All these values are larger than those of **3a**, indicating that guest could not influence the energy transfer process of **4a** similar to that of **3a**, while the less efficient π–π stacking effect also leads to the comparatively weak fluorescence response.

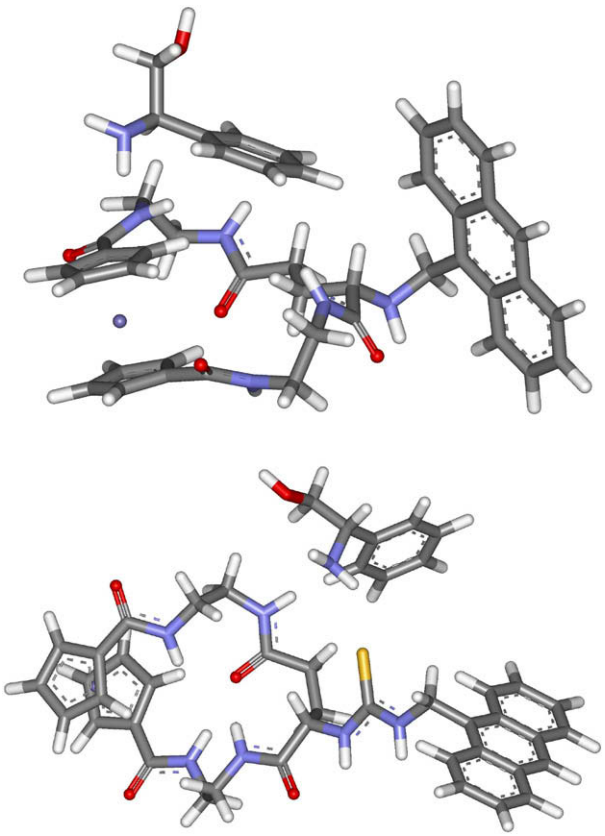


Figure 9. Calculated (B3LY/6-31G*) structures of inclusion complex between receptor **3a** (upper) or **4a** (lower) and phenylglycinol.

3. Conclusion

In summary, four macrocyclic ferrocenyl derivatives containing anthracene fluorophores have been synthesized. Receptor **3a**

exhibited the best fluorescence response to phenylglycinol in acetonitrile, and a strong emission band can be observed due to the intermolecular exciplex between host and guest. These special fluorescence enhancement phenomena were only observed when phenylglycinol was used as the guest, while other species could not induce such obvious changes. Control experiments indicate that the macrocyclic structure and the ferrocene unit play critical roles in the recognition process, the addition of phenylglycinol destroys the initial intramolecular transfer process from excited anthracene to ferrocene, while a strong exciplex was formed to promote the recovery of fluorescence. Model calculations further supplied the possible structures of **3a** and **4a** and their complexes with guests, indicating that the relatively steric position between ferrocene, fluorophore, and phenylglycinol is an important factor for the fluorescence recovery. Although there are many exquisite works carried out on the recognition of amino alcohols, such special fluoro-sensors have not been reported before; in particular the emission change is through the recovery of fluorescence quenched by ferrocene. Through their excellent selectivity toward phenylglycinol, these receptors can be developed as chemosensors for phenylglycinol for analytical detection; initial experiments also indicate that these receptors have chiral recognition abilities toward phenylalaninol, which provide a new promising application for these sensors.

4. Experimental

4.1. General

Ethenediamine and propyldiamine were distilled before being used. $CHCl_3$ was washed with water and dried over $CaCl_2$, Et_3N was dried and distilled from CaH_2 and KOH, respectively. Compounds **1a**, **1b,** and 1,1′-ferrocenediacetyl chloride were synthesized according to the method reported in the literature.[10,19] Reference compounds **5a**–**5c** were synthesized according to the literature.[11b] L- or D-Phenylglycinol and phenylalaninol were purchased from Alfa Corporation (Germany). All other commercially available reagents were used without further purification. Melting point was determined with a Reichert 7905 melting-point apparatus (uncorrected). Optical rotations were taken on a PerkinElmer Model 341 polarimeter. IR spectra were obtained on a Nicolet 670 FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Inova unity-600 MHz spectrometer. ^{13}C NMR spectra were recorded on a Varian Inova unity-600 MHz spectrometer. ESI-Mass spectra were recorded on a Finnigan LCQ advantage mass spectrometer. Elemental analysis was determined with a Carlo-Erba 1106 instrument. The anions were used as their tetrabutylammonium salts.

4.2. Synthesis

4.2.1. Synthesis of ferrocenyl macrocyclic derivatives 2

Under an argon atmosphere and ice-bath, a solution of compound **1a** or **1b** (5 mmol) in dry $CHCl_3$ (200 mL) and 1,1′-ferrocenediacetyl chloride (1.55 g, 5 mmol) in dry $CHCl_3$ (200 mL) were simultaneously added dropwise (about 10 h) into a vigorously stirring solution of $CHCl_3$ (500 mL) and triethylamine (10 mmol). After addition, the mixture was stirred at room temperature for a further 24 h, and then washed with water for three times and the organic layer was dried over anhydrous Na_2SO_4. The crude products were purified by column chromatography on silica gel to give the pure product **2a** or **2b** as a nacarat powder, respectively.

4.2.1.1. Compound 2a. (Eluant: $CHCl_3/CH_3OH$ = 40:1(V/V)). Pure product was obtained as a nacarat powder (1.20 g) in 42%. Mp 112–114 °C; $[\alpha]_D^{20} = +41.4$ (c 0.010, $CHCl_3$); IR (KBr/cm^{-1}) ν: 3309, 2933, 1636, 1547, 1432, 1367, 1305, 1245, 1166, 755; ^{1}H NMR ($CDCl_3$): δ (ppm) 1.39(s, 9H, Bu^t), 1.75–1.78 (m, 2H, CCH_2C), 2.15–2.21 (m, 2H, $COCH_2C$), 2.98–3.03 (m, 1H, NCH_2C), 3.27–3.36 (m, 2H, NCH_2C), 3.46–3.48 (m, 1H, NCH_2C), 3.78–3.87 (m, 4H, NCH_2C), 4.29 (s, 2H, Cp-H), 4.36 (s, 3H, Cp-H), 4.41 (d, J = 6.6 Hz, 2H, Cp-H), 4.47 (s, 1H, Cp-H), 4.65–4.67 (m, 1H, NC*HCO), 5.63 (d, J = 8.1 Hz, 1H, Boc-NH), 6.80 (s, 1H, CONHC), 7.35 (s, 1H, CONHC), 8.33 (s, 1H, CONHC), 8.46 (s, 1H, CONHC); ^{13}C NMR ($CDCl_3$): δ (ppm) 28.4, 32.3, 32.9, 39.7, 40.1, 41.0, 46.3, 52.7, 67.2, 69.5, 80.4, 157.2, 170.6, 171.8, 172.7, 173.6; ESI-MS m/z (%): 568.2(M^+-1, 100); Elemental Anal. Calcd for $C_{26}H_{35}N_5O_6Fe$: C, 54.81; H, 6.20; N, 12.30. Found: C, 54.56; H, 6.35; N, 12.20.

4.2.1.2. Compound 2b. (Eluant: $CHCl_3/CH_3OH$ = 50:1(V/V)). Pure product was obtained as a nacarat powder (0.92 g) in 31%. Mp 116–118 °C; $[\alpha]_D^{20} = +17.3$ (c 0.010, $CHCl_3$); IR (KBr/cm^{-1}) ν: 3421, 2933, 1636, 1549, 1452, 1368, 1304, 1254, 1167; ^{1}H NMR ($CDCl_3$): δ (ppm) 1.45 (s, 9H, Bu^t), 1.80–1.87 (m, 2H, CCH_2C), 2.30–2.32 (m, 2H, $COCH_2C$), 3.03–3.14 (m, 3H, CCH_2C), 3.26–3.28 (m, 2H, NCH_2C, CCH_2C), 3.43–3.57 (m, 7H, NCH_2C), 4.33–4.44 (m, 4H, Cp-H), 4.53–4.56 (m, 4H, Cp-H), 4.64–4.67 (m, 1H, NC*HCO), 5.61 (d, J = 7.2 Hz, 1H, Boc-NH), 6.97–7.04 (m, 2H, CONHC), 7.59 (s, 1H, CONHC), 7.79 (s, 1H, CONHC); ^{13}C NMR ($CDCl_3$): δ (ppm) 28.5, 28.9, 29.6, 31.4, 32.9, 36.3. 36.7, 37.0, 53.9, 67.2, 78.7, 80.3, 156.6, 171.1, 171.4, 171.9, 173.2; ESI-MS m/z (%): 597.2(M^+, 100); Elemental Anal. Calcd for $C_{28}H_{39}N_5O_6Fe$: C, 56.26; H, 6.58; N, 11.72. Found: C, 56.10; H, 6.74; N, 11.51.

4.2.2. Synthesis of ferrocenyl macrocyclic derivatives 3

TFA (5 mL) was added to the solution of compound **2** (0.8 mmol) in dry CH_2Cl_2 (10 mL). The mixture was stirred at ambient temperature for 30 min to remove the Boc-protecting groups. Then the solvent and excess acid was removed in vacuo, giving the TFA salt of ferrocenyl cyclic derivative as a brown solid, which was used directly without further purification. The brown solid and triethylamine (0.1 mL) were dissolved in dry CH_3OH (30 mL), and a solution of 9-anthraldehyde (0.165 g, 0.8 mmol) in CH_3OH (20 mL) was added slowly to the above mixture. After addition, the mixture was stirred for 24 h at room temperature. Then $NaBH_4$ (0.15 g) was poured into the solution. The mixture was stirred for 24 h under Ar protection at ambient temperature. Then the mixture was heated to 50 °C and stirred for 2 h. The solvent was removed under reduced pressure and the residue was washed with water. The crude product was purified by column chromatography on silica gel to obtain the pure product **3a** or **3b**, respectively.

4.2.2.1. Compound 3a. (Eluant: $CHCl_3/CH_3OH$ = 15:1(V/V)). Pure product was obtained as a nacarat powder (0.30 g) in 52%. Mp 198–200 °C; $[\alpha]_D^{20} = +21.15$ (c 0.010, $CHCl_3$); IR (KBr/cm^{-1}) ν: 3305, 2931, 1635, 1541, 1431, 1360, 1303, 1238, 1185, 1115, 733; ^{1}H NMR ($CDCl_3$): δ (ppm) 1.90–1.92 (m, 2H, CCH_2C), 2.05–2.10 (m, 1H, $COCH_2C$), 2.31–2.38 (m, 1H, $COCH_2C$), 2.77–2.80 (m, 2H, NCH_2C), 3.11–3.13 (m, 2H, Anthr-CH_2), 3.23–3.26 (m, 2H, NCH_2C), 3.43–3.47 (m, 2H, NCH_2C), 3.60–3.65 (m, 2H, NCH_2C), 3.77–3.91 (m, 1H, Anthr-CNH), 4.14 (s, 1H, Cp-H), 4.25 (s, 1H, Cp-H), 4.32 (s, 1H, Cp-H), 4.35 (s, 4H, Cp-H), 4.40 (s, 1H, Cp-H), 4.70–4.77 (m, 1H, NC*HCO), 6.44 (s, 1H, CONHC), 6.49 (s, 1H, CONHC), 6.78 (d, J = 5.1 Hz, 1H, CONHC), 7.44–7.49 (m, 2H, Anthr-H), 7.51–7.58 (m, 2H, Anthr-H), 7.92 (s, 1H, CONHC), 7.97 (d, J = 9 Hz, 2H, Anthr-H), 8.28 (d, J = 8.7 Hz, 1H, Anthr-H), 8.36 (d, J = 8.7 Hz, 2H, Anthr-H); ^{13}C NMR ($CDCl_3$): δ (ppm) 18.6, 30.2, 32.7, 39.7, 40.2, 40.5, 40.6, 44.2, 58.3, 61.8, 70.4, 70.8, 71.2, 71.4, 124.1, 125.3, 125.9, 127.3, 129.5, 130.4, 130.8, 131.2, 131.6, 171.0, 171.4, 173.5, 174.9; ESI-MS m/z (%): 660.2([M+1]$^+$, 100); Elemental Anal. Calcd for $C_{36}H_{37}N_5O_4Fe$: C, 65.53; H, 5.66; N, 10.62. Found: C, 65.38; H, 5.82; N, 10.46.

4.2.2.2. Compound 3b. (Eluant: $CHCl_3/CH_3OH$ = 20:1(V/V)). Pure product was obtained as a nacarat powder (0.28 g) in 47%. Mp 206–208 °C; $[\alpha]_D^{20} = +8.8$ (*c* 0.010, $CHCl_3$); IR (KBr/cm^{-1}) *v*: 3290, 2922, 1635, 1541, 1446, 1383, 1301, 1214, 1180, 1027, 732; ^{1}H NMR ($CDCl_3$): δ (ppm) 2.05–2.11 (m, 2H, CCH_2C), 2.22–2.32 (m, 2H, $COCH_2C$), 2.82–2.95 (m, 2H, Anthr-CH_2), 3.15–3.24 (m, 4H, CCH_2C, 1H Anthr-CNH), 3.34–3.42 (m, 4H, NCH_2C), 3.58–3.61 (m, 2H, NCH_2C), 3.71–3.73 (m, 2H, NCH_2C), 4.37 (s, 3H, Cp-H), 4.40 (s, 2H, Cp-H), 4.43 (s, 1H, Cp-H), 4.46 (s, 2H, Cp-H), 4.68–4.80 (m, 1H, NC*HCO), 6.57 (s, 1H, CONHC), 6.66 (s, 1H, CONHC), 7.00 (s, 1H, CONHC), 7.43–7.48 (m, 2H, Anthr-H), 7.53–7.58 (m, 2H, Anthr-H), 7.63 (s, 1H, CONHC), 8.00 (d, *J* = 7.8 Hz, 2H, Anthr-H), 8.33 (d, *J* = 9 Hz, 2H, Anthr-H), 8.43 (s, 1H, Anthr-H); ^{13}C NMR ($CDCl_3$): δ (ppm) 18.6, 28.9, 29.6, 30.1, 32.8, 35.9, 36.1, 36.4, 37.1, 44.5, 58.3, 62.1, 70.6, 70.8, 71.0, 71.1, 78.7, 124.1, 125.3, 126.6, 127.8, 129.5, 130.4, 130.7, 131.7, 171.0, 171.2, 173.0, 174.7; ESI-MS *m*/*z* (%): 686.3(M^+−1, 100); Elemental Anal. Calcd for $C_{38}H_{41}N_5O_4Fe$: C, 66.38; H, 6.01; N, 10.18. Found: C, 66.21; H, 6.20; N, 10.09.

4.2.3. Synthesis of ferrocenyl macrocyclic derivatives 4

Same process was adopted to remove the Boc-protecting group of compound **2**. The brown solid was dissolved in 20 mL $CHCl_3$, and 2 mL of dry DMF was added to increase the solubility of this solid. Then a solution of 9-isothiocyanatomethyl anthracene (0.20 g, 0.8 mmol) in $CHCl_3$ (10 mL) was added dropwise to the above mixture. The reaction mixture was then stirred at room temperature for 24 h. The mixture was washed with water for three times, the organic layer was dried over anhydrous Na_2SO_4 overnight. Evaporation of the solvent and purification by column chromatography on silica gel gave the pure product **4a** or **4b**, respectively.

4.2.3.1. Compound 4a. (Eluant: $CHCl_3/CH_3OH$ = 30:1(V/V)). Pure product was obtained as a croci powder (0.42 g) in 80%. Mp 166–168 °C; $[\alpha]_D^{20} = -33.6$ (*c* 0.010, $CHCl_3$); IR (KBr/cm^{-1}) *v*: 3301, 2931, 1636, 1544, 1431, 1383, 1303, 1241, 1187, 735; ^{1}H NMR ($CDCl_3$): δ (ppm) 1.56–1.59 (m, 2H, CCH_2C), 2.01–2.04 (m, 2H, $COCH_2C$), 2.86–2.94 (m, 4H, NCH_2C), 3.60–3.70 (m, 4H, NCH_2C), 4.13 (s, 1H, Cp-H), 4.32 (s, 1H, Cp-H), 4.38 (s, 2H, Cp-H), 4.41 (s, 2H, Cp-H), 4.45 (s, 1H, Cp-H), 4.55 (s, 1H, Cp-H), 5.08–5.10 (m, 1H, NC*HCO), 5.47 (d, *J* = 14.1 Hz, 1H, Anthr-CH_2), 5.62 (d, *J* = 13.2 Hz, 1H, Anthr-CH_2), 6.73 (s, 1H, CONHC), 7.12 (s, 1H, CONHC), 7.37 (s, 1H, CNHCS), 7.47–7.57 (m, 4H, Anthr-H), 7.63 (s, 1H, CNHCS), 8.07 (d, *J* = 8.1 Hz, 2H, Anthr-H), 8.20 (d, *J* = 8.7 Hz, 2H, Anthr-H), 8.28 (s, 1H, CONHC), 8.50 (s, 1H, CONHC), 8.56 (s, 1H, Anthr-H); ^{13}C NMR (DMSO-d_6): δ (ppm) 35.3, 36.9, 61.2, 71.8, 74.1, 76.1, 77.7, 83.3, 83.9, 84.6, 129.8, 130.7, 132.0, 134.4, 134.7, 135.4, 136.5, 174.3, 175.1, 176.0, 177.6, 186.5; ESI-MS *m*/*z* (%): 741.2([M+Na+1]$^+$, 100); Elemental Anal. Calcd for $C_{37}H_{38}N_6O_4SFe$: C, 61.82; H, 5.33; N, 11.70. Found: C, 61.67; H, 5.46; N, 11.58.

4.2.3.2. Compound 4b. (Eluant: $CHCl_3/CH_3OH$ = 40:1(V/V)). Pure product was obtained as a croci powder (0.42 g) in 76%. Mp 124–128 °C; $[\alpha]_D^{20} = +4.25$ (*c* 0.010, $CHCl_3$); IR (KBr/cm^{-1}) *v*: 3432, 2928, 1637, 1548, 1437, 1384, 1303, 1254, 1122, 735; ^{1}H NMR ($CDCl_3$): δ (ppm) 2.02–2.05 (m, 2H, CCH_2C), 2.18–2.27 (m, 2H, $COCH_2C$), 3.02–3.04 (m, 4H, CCH_2C), 3.18–3.20 (m, 2H, NCH_2C), 3.37–3.40 (m, 2H, NCH_2C), 3.50–3.53 (m, 4H, NCH_2C), 4.35 (s, 3H, Cp-H), 4.39 (s, 3H, Cp-H), 4.51 (s, 1H, Cp-H), 4.58 (s, 1H, Cp-H), 5.07–5.10 (m, 1H, NC*HCO), 5.61–5.65 (m, 2H, Anthr-CH_2), 6.70 (s, 1H, CONHC), 6.80 (s, 1H, CONHC), 6.96 (s, 1H, CNHCS), 7.45–7.51 (m, 4H, Anthr-H), 7.70 (s, 1H, CNHCS), 7.78 (s, 1H, CONHC), 7.91 (s, 1H, CONHC), 7.97 (d, *J* = 8.1 Hz, 2H, Anthr-H), 8.23 (d, *J* = 8.1 Hz, 2H, Anthr-H), 8.42 (s, 1H, Anthr-H); ^{13}C NMR (DMSO-d_6): δ (ppm) 33.8, 34.7, 35.2, 36.9, 40.6, 41.0, 41.4, 42.1, 57.0, 61.7, 75.2, 75.8, 83.3, 84.0, 84.6, 129.8, 131.9, 133.0, 134.4, 135.4, 136.4, 173.2, 174.1, 176.2, 176.9, 181.3; ESI-MS *m*/*z* (%): 745.3(M^+−1, 100); Elemental Anal. Calcd for $C_{39}H_{42}N_6O_4SFe$: C, 62.71; H, 5.67; N, 11.26. Found: C, 62.53; H, 5.80; N, 11.15.

4.2.4. Synthesis of reference compound 5a

Ferrocenyl diethenamine was prepared according to the literature,[11a] then reacted with 9-anthraldehyde in methanol for 12 h at room temperature. After that $NaBH_4$ was added to reduce the Schiff's bases. The mixture was washed with water (3 times) and then the organic layer was dried over anhydrous Na_2SO_4. After filtration the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica (eluant: $CHCl_3/CH_3OH$ = 30:1(V/V)).

4.2.4.1. Compound 5a. Pure product was obtained as a croci powder (0.32 g) in 78%. Mp 88–90 °C; IR (KBr/cm^{-1}) *v*: 3421, 2927, 1631, 1542, 1445, 1384, 1299, 1181, 1118, 1030, 733; ^{1}H NMR ($CDCl_3$): δ (ppm) 2.96 (d, *J* = 5.1 Hz, 4H, NCH_2C), 3.19 (d, *J* = 5.1 Hz, 4H, NCH_2C), 3.70 (s, 2H, CNHC), 4.26 (s, 4H, Cp-H), 4.40 (s, 4H, Cp-H), 4.71 (s, 4H, Anthr-CH_2), 7.20 (s, 2H, CONHC), 7.40–7.48 (m, 8H, Anthr-H), 7.95 (d, *J* = 7.2 Hz, 4H, Anthr-H), 8.25 (d, *J* = 7.8 Hz, 4H, Anthr-H), 8.36 (s, 2H, Anthr-H); ^{13}C NMR (DMSO-d_6): δ (ppm) 44.8, 49.4, 69.5, 71.2, 77.8, 124.8, 125.0, 125.8, 126.5, 128.7, 129.9, 131.0, 132.2, 168.3; ESI-MS *m*/*z* (%): 738.3(M^+, 100); Elemental Anal. Calcd for $C_{46}H_{42}N_4O_2Fe$: C, 74.77; H, 5.73; N, 7.59. Found: C, 74.56; H, 5.90; N, 7.48.

4.2.4.2. Synthesis of reference compound 5d. The calix[4]-arene cyclic derivative material was prepared according to similar methods reported in the literature.[20] The Boc-protecting group was eliminated with TFA, then reacted with 9-anthraldehyde in methanol and reduced by $NaBH_4$. The crude product was purified by column chromatography on silica (eluant: $CHCl_3/CH_3OH$ = 40:1 (V/V)).

4.2.4.3. Compound 5d. Pure product was obtained as a yellow powder (0.29 g) in 31.5%. Mp 188–190 °C; $[\alpha]_D^{20} = +9.5$ (*c* 0.010, $CHCl_3$); IR (KBr/cm^{-1}) *v*: 3421, 2935, 1681, 1566, 1448, 1382, 1299, 1204, 1161, 1118, 1030, 886, 733; ^{1}H NMR ($CDCl_3$): δ (ppm) 1.05 (s, 18H, Bu^t), 1.26 (s, 18H, Bu^t), 1.90–1.93 (m, 2H, CCH_2C), 2.05–2.10 (m, 1H, $COCH_2C$), 2.31–2.38 (m, 1H, $COCH_2C$), 2.78–2.84 (m, 2H, NCH_2C), 3.12–3.14 (m, 2H, Anthr-CH_2), 3.23–3.27 (m, 2H, $COCH_2C$, 2H, NCH_2C), 3.43–3.48 (m, 4H, $ArCH_2Ar$, 2H, NCH_2C), 3.61–3.64 (m, 2H, NCH_2C), 3.82–3.91 (br, 1H, Anthr-CNH), 4.08–4.13 (m, 4H, $ArCH_2Ar$), 4.20 (d, *J* = 13.2 Hz, 2H, OCH_2-CO), 4.71–4.75 (m, 1H, NC*HCO), 4.91 (d, *J* = 13.1 Hz, 2H, OCH_2CO), 6.88 (s, 2H, ArH), 6.91 (s, 2H, ArH), 7.01 (s, 2H, ArH), 7.04 (s, 2H, ArH), 7.45–7.49 (m, 2H, Anthr-H), 7.55–7.58 (m, 2H, Anthr-H), 7.82 (s, 2H, CONHC), 7.95 (d, *J* = 9 Hz, 2H, Anthr-H), 8.28 (d, *J* = 8.1 Hz, 1H, Anthr-H), 8.35 (d, *J* = 8.7 Hz, 2H, Anthr-H), 8.48 (s, 2H, ArOH), 9.62 (s, 2H, CONHC); ^{13}C NMR ($CDCl_3$): δ (ppm) 28.3, 31.1, 31.3, 32.1, 32.9, 39.3, 39.7, 40.0, 40.2, 46.3, 69.5, 74.6, 123.9, 124.1, 125.3, 125.8, 126.8, 127.3, 127.4, 129.4, 130.4, 130.8, 131.2, 131.6, 132.7, 134.2, 142.7, 148.1, 149.7, 150.4, 171.0, 171.4, 173.5, 175.3; ESI-MS *m*/*z* (%): 1149.6 (M^+, 100); Elemental Anal. Calcd for $C_{72}H_{87}N_5O_8$: C, 75.15; H, 7.63; N, 6.09. Found: C, 75.01; H, 7.98; N, 6.00.

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