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A New "Switch-On" Fluorescence Chemosensor for Anions via Modulation of Intraligand and Metal-to-Ligand Charge-Transfer Emission in a Pd(II)-based Receptor

Li-Rong Lin · Qin-Juan Xu · Xin Wu · Rong-Bin Huang · LanSun Zheng

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Introduction

In recent years there has been great interest in anion recognition and sensing due to the key roles played by anions during chemical, biological and environmental processes [1–13]. Fluorescence chemosensors are used to transduce binding events into a fluorescent signal, and many signaling mechanisms for the sensing of anions have been developed, such as photoinduced electron transfer (PET) [14–17], intramolecular charge transfer (ICT) [18, 19], excited-state proton transfer [20, 21], excimer/exciplex formation [22–24], competitive binding [25–27]and metal-to-ligand charge-transfer (MLCT) [28, 29]. The development of simple and sensitive anion sensors continues to be an important field of research. When a fluorescent ligand is complexed to a metal ion, its fluorescence can be either quenched or enhanced by different metal ions [30]. In general, fluorescence quenching occurs with heavy metal ion complexation due to intramolecular energy transfer from the excited state of the ligand to the localized energy levels of the metal ion, or due to relaxation mechanisms of the heavy metal "paramagnetic effect" for intersystem crossing [31, 32]. Therefore, the fluorescence of intraligand (IL) transitions (between orbitals localized primarily on a coordinated ligand) is quenched by heavy metal ions and fluorescence due to metal-to-ligand charge-transfer (MLCT) transitions is not preferred. Here we describe a new fluorescence-enhanced anion sensor mechanism based on the modulation of IL and MLCT fluorescence emission from a fluorescent metal complex in the presence of certain anions. The syntheses of bis(1-benzylidene-4-phenylthiosemicarbazato)-palladium(II) (**1**) and bis(1-(4-(dimethylamino)benzylidene)-4-phenylthiosemicarbazato)palladium (II) (**2**, Scheme 1) are described, as well as their application as metal-based anion receptors. Complex **2** exhibits intraligand $^1\pi$–π^* (IL) and MLCT dual fluorescence emissions in organic solvents at room temperature that can be modulated in the presence of anions. Complex **2** was found to act as an anion-triggered IL and MLCT emission enhanced chemosensor.

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L.-R. Lin (✉) · Q.-J. Xu · X. Wu · R.-B. Huang · L. Zheng
Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University,
Xiamen 361005, People's Republic of China
e-mail: linlr@xmu.edu.cn

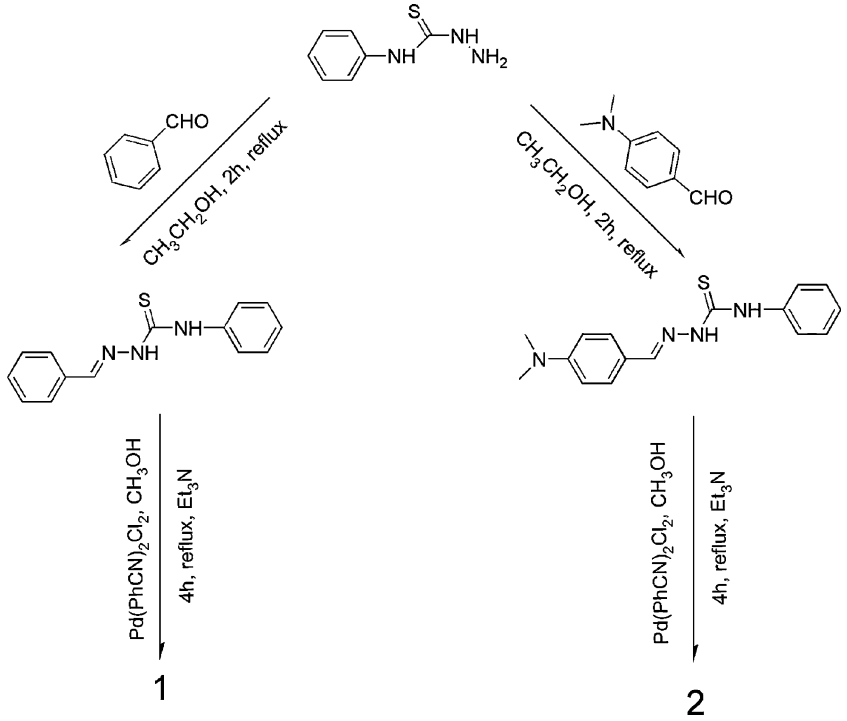
L. Zheng
State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University,
Xiamen 361005, People's Republic of China

Experimental

General

^{1}H NMR data were acquired on a Varian Unity 400 MHz NMR spectrometer using DMSO-d_6 or $CDCl_3$ as a solvent and TMS as an internal standard. ESI-MS data were obtained using a Bruker ESQUIRE-3000 plus LC-MS/MS spectrometer. Elemental analysis of the receptors was performed on a CE Instruments EA 1110. Solid-state infrared spectra of samples were obtained from compressed KBr pellets and recorded on a Nicolet AVATAR FT-IR360 spectrometer. Corrected fluorescence spectra were taken on a Hitachi F-4500 fluorescence spectrophotometer with excitation and emission slits of 5.0 nm, and absorption spectra were scanned on a Shimadzu UV224012PC

Scheme 1 Synthesis of the Pd (II)-based receptors **1** and **2**



absorption spectrophotometer using a 1 cm quartz cell. Spectral titrations were carried out by injection of aliquots of anion solutions into the fluoroionophore solution in a 1 cm quartz cell. Solvents used for spectral investigations were purified by distillation until no fluorescent impurity could be detected. All titration experiments were carried out around 298 K. X-ray diffraction data for crystals were collected on a BRUKER SMART APEX CCD DIFFRACTOMER equipped with a fine-focus sealed tube employing graphite monochromatized Mo kα radiation using ω scan mode. The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares calculations with SHELXL-97 based on F^2 [33]. All non-hydrogen atoms were located at the calculated positions. Detailed structural data were deposited in the Cambridge Crystallographic Data Centre under reference numbers CCDC 787552 and 737248, respectively.

Syntheses of Ligands (L)

1-Benzylidene-4-phenylthiosemicarbazide (L_1) and 1-(4-(dimethylamino)benzylidene)-4-phenylthiosemicarbazide (L_2) were prepared as reported previously [34]. The products were purified by two recrystallizations from ethanol.

L_1, M.P. 209~211 °C, MS (APCI) *m/z* (%): M^+ 278.2, IR (KBr pellet), ν_{max}: 3,443m, 3,299s, 3,158m, 2,990m, 1,594m, 1,539s, 1,513s, 1,440m, 1,275s, 1,203s, 1,064w, 937m, 740m, 695s, 553w. ^{1}H-NMR ($CDCl_3$), δ (ppm): 7.44–7.39 (m,5H,ArH), 7.75–7.65 (m,4H,ArH), 7.96 (s,1H, CH), 9.21(s,1H,NH), 7.29–7.19 (m,1H,ArH), 10.20 (s,1H, NH).

L_2, M.P. 212~213 °C, MS (APCI) *m/z* (%): 299.1, IR (KBr pellet), ν, cm^{-1} : 3,318s, 3,276s, 2,925w, 2,840w, 1,590m, 1,513s, 1,481m, 1,443m, 1,380m, 1,186s, 1,073w. ^{1}H-NMR (400 MHz, DMSO-*d*6), δ (ppm): 2.97 (s, 6H), 6.72 (d, *J*=7.5 Hz, 2H, ArH), 7.17 (d, *J*=7.0 Hz, 2H, ArH), 7.35 (t, *J*=7.0 Hz, 1H, ArH), 7.59 (d, *J*=7.5 Hz, 2H, ArH), 7.68 (d, *J*=7.5 Hz, 2H, ArH), 8.04 (s, 1H, CH), 9.91 (s, 1H, NH), 11.56 (s, 1H, NH).

Syntheses of Palladium Complexes (Receptors **1** and **2**)

$Pd(PhCN)_2Cl_2$ (0.25 mmol in 10 ml methanol) was added to a methanol solution of L (0.50 mmol in 30 ml methanol), and the solution was observed to change to a reddish brown color. Triethylamine (0.50 mmol) was added, and the mixture was refluxed at 60 °C for 4 h. After cooling, the reddish brown precipitate was formed and collected by filtration and washed with hot methanol, then dried. The compound was recrystallized from dimethylformamide (DMF), giving red block crystals.

Receptor **1**, Yield: 61.2%. Anal. cacld. (%) for $C_{28}H_{24}N_6PdS_2$ (M_r=615.9): C, 54.62; H, 3.90; N, 13.66; S, 10.41. Found (%) C, 53.79; H, 3.56; N, 13.61; S, 10.80. IR (KBr pressed), ν_{max}:3,416m, 3,392m, 3,050w, 2,921w, 1,598m, 1,536s, 1,509s, 1,431s, 1,310s, 1,252s, 1,205w. As the solubility of complex 1 in common deuterated reagent is very small, no NMR characterization was tested, but the X-ray powder was tested. The X-ray powder results is

consistent with simulated spectra based on crystal structure (Supplementary data Figure S1).

Receptor **2**, Yield: 65.1%. Anal. cacld. (%) for $C_{32}H_{34}N_8S_2Pd$ (M_r=701.2): C, 54.81; H, 4.89; N, 15.98; S, 9.15 Found (%): C, 53.04; H, 4.95; N, 15.10; S, 9.12. IR (KBr pressed) for $C_{32}H_{34}N_8S_2Pd{\cdot}2\ C_3H_6NO$, ν, cm^{-1} : 3,424s, 3,381s, 2,918w, 2,852w, 1,653s, 1,602s, 1,563s, 1,517s, 1,493m, 1,431m, 1,384s, 1,303m, 1,260m, 1,190m, 1,170m, 1,120w, 1,092w, 1,053w. ^1H NMR (400 MHz, DMSO-*d*6) for $C_{32}H_{34}N_8S_2Pd$, δ (ppm): 3.01 (s, 12H, CH_3), 6.64(d, J=8.7 Hz, 4H, ArH), 6.92 (t, J=7.3 Hz, 2H, ArH), 7.24 (d, J=7.9 Hz, 4H, ArH), 7.59(s, 2H, CH), 7.66 (d, J=8.0 Hz, 8H, ArH), 9.29 (s, 2H, NH).

Results and Discussion

The X-ray quality crystals of receptor **1** were obtained by slow evaporation of a DMF solution and crystallized in the triclinic system, space group Pī with a=9.525 (5), b=10.739(6), c=12.734(6) Å, α=84.590 (7)º, β=174.397(9)º, γ=84.136 (9)º, V=1,245(11) Å^3, Z=2, M_r=615.9, D_c=1.64 g/cm^3, μ=0.944 mm^{-1}, F(000)=624, R=0.0675 and wR=0.1706. X-ray quality crystals of receptor **2** were also obtained by the slow evaporation of a DMF solution with solvent molecules in the unit cell and crystallized in the monoclinic system, space group *C2* with a=18.485(15), b=7.090(5), c=17.595(11) Å, α=90.00º, β=121.21(3)º, γ=90.00º, V=1,972(2) Å^3, Z=2, M_r=847.40, D_c=1.427 g/cm^3, μ=0.624 mm^{-1}, F(000)=880, R=0.0607 and wR=0.1358.

The coordination geometry of the Pd atoms in the two receptors was similar, existing in a distorted square planar geometry with two Pd-N bonds and two Pd-S bonds. The bidentate ligands bound to palladium forming five-membered chelate rings via loss of a proton from their tautomeric thiol form and coordination through the thiol sulfur and the imine nitrogen atom. The ORTEP structures of receptors **1** and **2** are shown in Fig. 1.

Absorption and Fluorescence Properties of Receptors

We focused on anion-triggered IL and/or MLCT emission enhancement in these complexes, because hydrogen bonding between strongly electron donating anions and the receptor, or deprotonation of the receptor, would likely affect the ligand fluorescence of the ligand-metal complex. To explore this, we synthesized two ligands with different electron-donating groups in the 4-position to tune the absorption and emission wavelengths, as shown in Table 1. In MeCN solution, L_1 exhibited an absorption band at 318 nm and L_2 showed two absorption bands at 269 and 365 nm, all with molar absorption coefficients greater than 10^4 L mol^{-1} cm^{-1} characteristic of $^1\pi$–π^* absorption. After complexation of the ligands with palladium(II), the maximum absorption wavelength shifted to lower energy. In the case of **2**, a new band in the absorption spectrum appeared at 475 nm with a slightly weaker molar absorption coefficient of 10^3 L mol^{-1} cm^{-1}, suggesting that this absorption band corresponds to a metal-to-ligand charge-transfer transition (MLCT).

L_2 showed a stronger fluorescence than L_1 due to the electron-donating group at the 4-position of the ligand. The weak fluorescence of L_1 at 433 nm was quenched after complexation with palladium(II) ion to form **1**. Complex **2** also showed weaker fluorescence than its ligand L_2. The weaker fluorescence of the complexes compared with the free ligand is due to the efficient fluorescence quenching characteristics of the transition metal via electron or energy transfer mechanisms.

It is of interest that complex **2** emitted fluorescence at two wavelengths in organic solvents (DMF, MeOH, EtOH, and MeCN) at room temperature (Fig. 2). We propose that

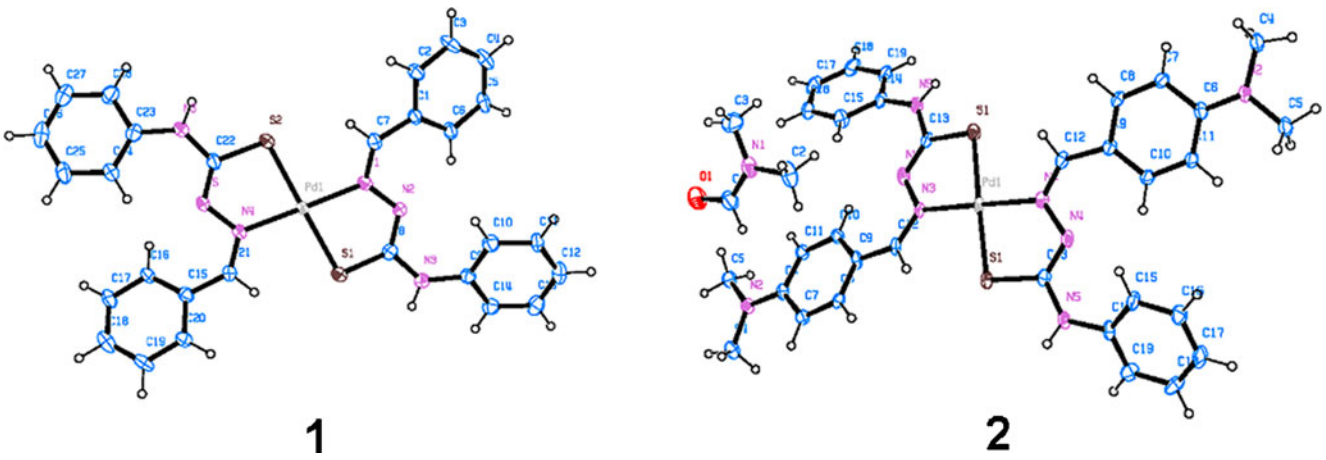


Fig. 1 Receptors **1** and **2** are shown with displacement ellipsoids, drawn at the 30% probability level

Table 1 Photophysical data in MeCN solution

Compound	Abs.($\lambda_{max.}$, nm) (ε, 10^4 mol^{-1} L cm^{-1})	Emission ($\lambda_{max.}$, nm)
L_1	318 (3.53)	433
1	347 (3.95)	No
L_2	269 (3.75), 365 (5.07)	428
2	313 (3.65), 385 (5.63), 475 (0.25)	438, 533

this dual fluorescence originates from two different excited states. The short wavelength emission is assigned to the intraligand $^1\pi$–π* state, because the position and shape of this band is similar to that observed for L_2. The longer wavelength fluorescence likely originates from the MLCT state of receptor **2**, because the long wavelength fluorescence can be excited with MLCT transition at 475 nm and exhibits a stronger fluorescence intensity.

Absorption and Fluorescence Titration Studies

The recognition properties of receptors **1** and **2** towards different anions were studied by absorption and fluorescence titration. The absorption spectra of **1** and **2** were almost unchanged upon introduction of F^-, AcO^-, $H_2PO_4^-$, HSO_4^-, Cl^-, Br^-, NO_3^- and SO_4^{2-} anions, suggesting that these anions are not bound with the receptors. However, because deprotonation of the receptor via Brønsted acid–base interaction would not be expected to affect the receptor's absorption spectrum, a lack of spectral changes does not necessarily mean that anions do not interact with the receptor [34].

Although the absorption spectrum of the receptors did not change with introduction of anions, and no changes in the fluorescence spectrum was observed for **1**, the weak fluorescence spectrum of **2** varied in the presence of strongly basic anions such as F^-, SO_4^{2-}, AcO^- and $H_2PO_4^-$, indicating that these anions interact with **2**. As shown in Fig. 3(a), fluorescence emissions at both 438 and 533 nm (λ_{ex}=340 nm) were enhanced to different extents with the introduction of F^-, SO_4^{2-}, AcO^- and $H_2PO_4^-$. The addition of other anions did not induce enhanced emissions and, therefore, it can be deduced that they do not interact with the receptor. Figure 3(b) shows the dual fluorescence spectra of **2** in the presence of four equivalents of various anions. Receptor **2** therefore acted as a sensor for certain anions as observed by an enhancement in the complex's dual fluorescence emissions, with sensitivity following the order $F^->SO_4^{2-}>AcO^->H_2PO_4^-$. The receptors described herein were designed to use a metal center to organize hydrogen-bond donor functional groups on ligands such that anions could be bound via hydrogen-bond formation. The hydrogen-bond donor functional group in receptor **2** is NH and anions may therefore interact with NH via hydrogen-bonding. However, a Brønsted acid–base interaction by deprotonation of the NH of receptor **2** forming the anion of **2** is an alternative, and more likely, cause for the increase in emission observed. The anionic form of **2** would have a metal center with greater electron density, weakening the metal–ligand interaction and leading to strong intraligand and MLCT fluorescence. We therefore propose that the introduction of strongly basic anions leads to a Brønsted acid–base interaction between the anion and receptor. The extent of anion formation in receptor **2** correlates with the enhancement observed in fluorescence.

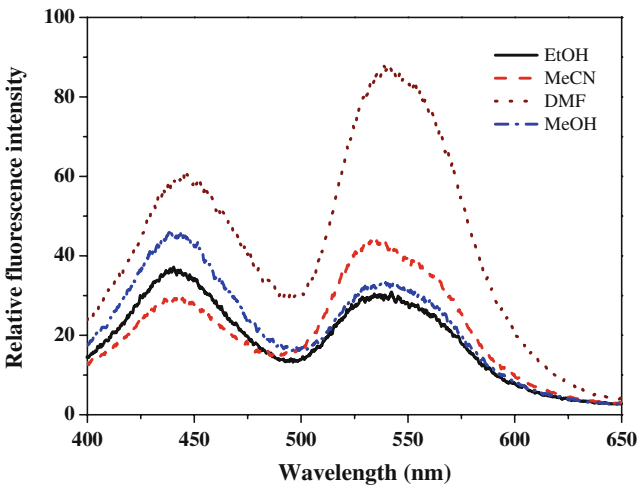


Fig. 2 Fluorescence spectra of **2** (1.0×10^{-5} mol L^{-1}) in different organic solvents

^{1}H NMR Spectral Studies

Analysis of titration ^{1}H NMR spectra can aid the elucidation of the mechanisms of interaction between anions and receptors [7]. Generally, if the chemical shift of an NH proton shifts upfield in the presence of an anion, it indicates that the proton has formed a hydrogen bond with the anion. The loss of the NH proton signal, on the other hand, indicates deprotonation of the receptor by the anion. Thus, ^{1}H NMR spectra of **2** were recorded, using DMSO-d_6 as solvent, in the presence and absence of fluoride ions to elucidate the nature of the interaction between **2** and the anions. From Fig. 4 it can be seen that the NH proton signal of the receptor **2** in the absence of F^- is observed at δ 9.25. When fluoride in the form of tetrabutylammonium salt was titrated into the solution of receptor **2**, the NH proton signal disappeared and the appearance of a new proton signal at δ 16.15 was observed, corresponding to the generation of H_2F^-. The imine and benzene ring protons were observed to shift upfield, indicating an increase in electron density. These combined

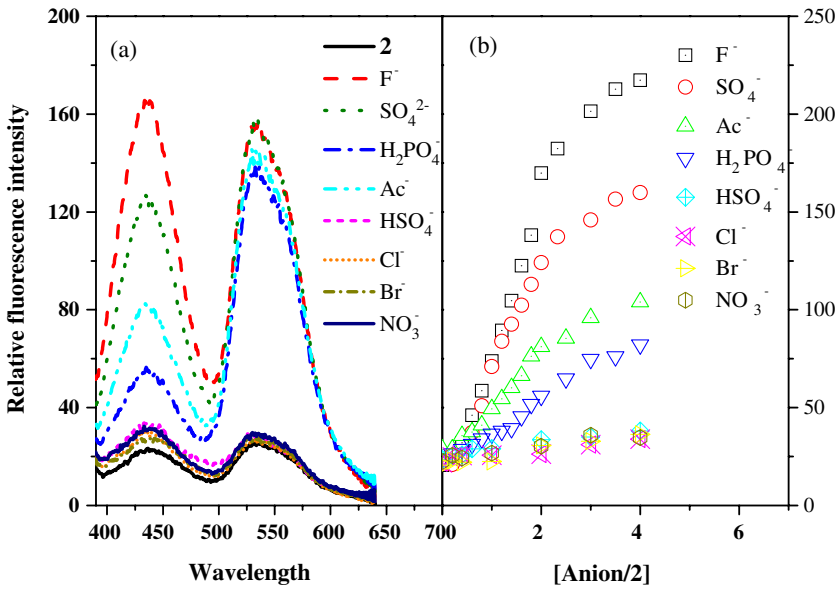


Fig. 3 **a** Fluorescence spectra of **2** (1.0×10^{-5} mol L^{-1}) in acetonitrile after addition of 4.0 equivalents of various anions, **b** a plot of the fluorescence intensity changes observed (λ= 438 nm) when the number of equivalents of different anions added was varied

results indicate that the NH of receptor **2** was deprotonated upon addition of fluoride via a Brønsted acid–base interaction, and it is therefore assumed that the same process occurs with other strongly basic anions.

Conclusion

The weak fluorescence of receptor **2** was significantly enhanced with the introduction of strongly basic anions such as F^-, SO_4^{2-}, AcO^- and $H_2PO_4^-$, as a result of Brønsted acid–base interactions between the anion and receptor **2**. The deprotonation of the NH of receptor **2** by the basic anion increases the electron density of the metal center weakening the interaction of the metal with the ligand and leading to the emission of strong intraligand and MLCT fluorescence. No change in the absorption spectrum of the receptor was observed upon introduction of anions, beacuse the neutral and anionic forms of the receptor have similar absorption properties. In a Brønsted acid–base reaction, the reaction equilibrium constant is inversely proportional to its corresponding conjugate acid–base dissociation constant. Thus, the reaction equilibrium constant of receptor **2** with anions should follow the order $AcO^->F^->H_2PO_4^->SO_4^{2-}$. However, in this system, the receptor **2** acted as an anion sensor via the enhancement of its dual fluorescence following the order $F^->SO_4^{2-}>AcO^->H_2PO_4^-$, which is not in agreement with the basicity order of the anions. This observed recognition order may be attributed to the small size and highly electronegative fluoride ion and the highly charged sulfate.

In conclusion, we have presented a new mechanism for anion sensing by fluorescence spectroscopy based on modulation of intraligand fluorescence (IL) and MLCT emission from a weakly fluorescent metal complex. It will be a kind of fasinating mechanism for anions sensing.

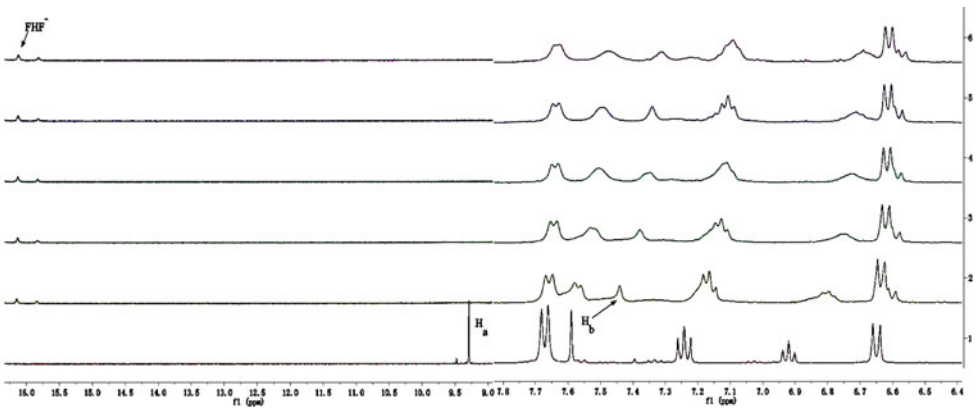


Fig. 4 Partial ^1H NMR spectra of the receptor **2**(1.0×10^{-2} mol L^{-1}) in DMSO-d_6 in the presence of 0, 0.3, 0.6, 0.9, 1.5, and 2.0 equivalents of [nBu$_4$N]F. The NH and imine protons are labeled as H_a and H_b, respectively

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