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Sensors

Fluorescent Recognition of 1,2-Diamines by a 1,1′-Binaphthyl-Based Trifluoromethyl Ketone

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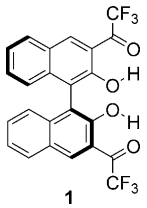
Abstract: The fluorescent responses of a 1,1′-binaphthol (BINOL)-based trifluoromethyl aryl ketone toward a variety of amines have been studied. The aliphatic 1,2-diamines, especially ethylenediamine, can greatly enhance the fluorescence of this compound, but under the same conditions, other mono- and diamines cause much smaller fluorescent responses. This compound can be used as a fluorescent sensor for the detection of ethylenediamine at concentrations over micromolar levels. UV absorption and NMR spectroscopic methods have been used to study the interactions of the sensor with ethylenediamine. These studies have demonstrated that the trifluoromethyl ketone of the sensor reacts with ethylenediamine much more favorably than with other amines. The hydroxyl groups of the sensor and those of the hemiaminal adducts formed in the presence of the amines are important for the highly selective fluorescent response.

Introduction

Aliphatic diamines are widely used building blocks in chemical synthesis with extensive applications in coordination chemistry, biochemistry, agrochemicals, dye manufacturing, and pharmaceutical industry. Among the aliphatic diamines, ethylenediamine (**14**) is a 1,2-diamine compound broadly used in both industrial manufacture and academic laboratories.[1] It is used for the production of ethylenediaminetetraacetic acid (EDTA), organic flocculants, urea resins, and fatty bis-amides. It is also used in making pharmaceutical ingredients and synthetic pesticides, as an accelerator/curing agent in epoxy coatings/resins, and to construct formulations for use in the printed circuit board and metal finishing industries. The world annual production of **14** is over 500 000 tons. It is important to monitor the presence of this compound to minimize both occupational and environmental concerns. Fluorescence, as a simple and effective real-time analytical method, has been actively investigated for the detection of amines, diamines, and polyamines.[2,3] However, fluorescent sensors capable of discriminating 1,2-diamines from other diamines are rare.[4]

The reversible reaction of the highly electrophilic trifluoromethyl ketones has been actively pursued for molecular recognition of amines.[5] Recently, we reported that the 1,1′-binaphthol (BINOL)-based trifluoromethyl ketone **1** can be used for the fluorescent recognition of diamines.[6] We found that this compound showed greatly enhanced fluorescence toward 1,2- and 1,5-diamines, but much weaker response toward other di- and monoamines. Thus, this compound can be used to selectively detect 1,2- and 1,5-diamines. We have conducted a structural modification of **1** and have achieved highly selective fluorescent recognition of 1,2-diamines, particularly **14**, by using the newly developed fluorescent sensor. Herein, these results are reported.



1

Results and Discussion

Design and synthesis of a new 1,1′-binaphthyl-based trifluoromethyl ketone 4

Previously, we reported that when a solution of **1** in CH_2Cl_2 was used to interact with aliphatic amines, diamines, such as 1,2-, 1,3-, 1,4-, and 1,5-diamines, generated much greater fluorescence enhancement than the monomer amines, such as 1-propylamine and 1-butylamine.[6a] It was also found that **14** and 1,5-diaminopentane caused greater fluorescent enhance-

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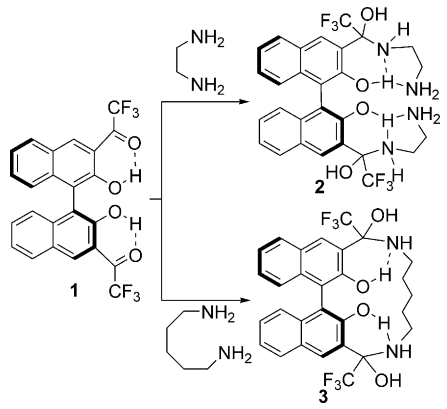


Scheme 1. Proposed reactions of **1** with ethylenediamine (**14**) and 1,5-diaminopentane in CH_2Cl_2.

ment than the other diamines (Scheme 1). It was proposed that fluorescence enhancement by **14** might be due to the formation of the hemiaminal intermediate **2** from the reaction with **1**. Nucleophilic addition to the carbonyl groups of **1** breaks conjugation of the carbonyl groups with the naphthyl ring and disrupts the original intramolecular hydrogen bonds with the carbonyl groups, contributing to fluorescent enhancement. In addition, the hydrogen-bonding interaction provided by the central BINOL hydroxyl groups of **1**, as shown in the structure of **2**, should facilitate the reaction with **14** more favorably than with other amines. For the reaction with 1,5-diaminopentane, the two trifluoroacetyl groups of **1** could cooperate with each other to form the 1:1 adduct **3** as one of the possible products. This indicates that the distance between the two carbonyl groups of **1** could be important for the fluorescent recognition of diamines.

To further develop the selective fluorescent recognition of diamines, we have designed a structurally modified BINOL-based trifluoromethyl ketone **4**. Figure 1 shows an energy-minimized molecular model of **4**. In this compound, one benzene ring is inserted between the central BINOL unit and each of the trifluoroacetyl groups. This structural change should increase the distance between the two trifluoroacetyl groups to make them more independent of each other in the reaction with amines. The *meta* substitution of the trifluoroacetyl groups on the benzene rings in **4** should also break conjugation between the electron-donating hydroxyl groups and the

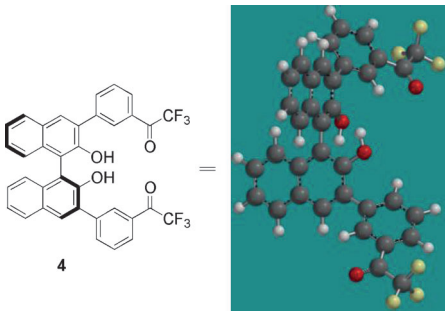
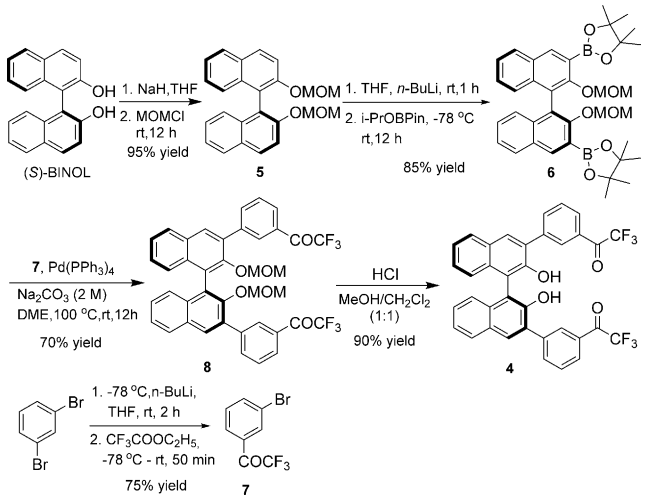


Figure 1. Molecular model of **4**.

electron-withdrawing trifluoroacetyl groups. In addition, the arrangement of the functional groups of **4** should make it impossible to form intramolecular hydrogen bonds between the central hydroxyl groups and the carbonyl groups, as shown in the structure of **1**. It would be interesting to explore how these structural changes influence the fluorescent response of **4** toward amines.

Compound **4** is synthesized according to Scheme 2. Protection of (*S*)-BINOL with MOM groups gave **5** in 95% yield.[7] Treatment of **5** with *n*BuLi followed by the addition of *i*PrOBPin produced **6** as a white solid in 85% yield.[8] Treatment of 1,3-di-



Scheme 2. Synthesis of the BINOL derivative **4**. MOM = methoxymethyl, *i*PrOBPin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, DME = dimethoxyethane.

bromobenzene with *n*BuLi, followed by addition of ethyl trifluoroacetate, produced *m*-bromotrifluoroacetylbenzene **7** as a colorless liquid in 75% yield.[9] The Suzuki coupling of **6** with **7** gave **8** as a white solid in 70% yield.[8] The MOM groups of **8** were removed in the presence of HCl to generate the desired product **4** as a white solid in 90% yield. In the ^{1}H NMR spectrum of **4** in $CDCl_3$, the hydroxyl proton signal is at $\delta =$ 5.40 ppm, which is much more upfield than that of **1** at $\delta =$ 10.51 ppm. This indicates that, unlike **1**, there is no intramolecular hydrogen bond between the hydroxyl groups and carbonyl groups in **4** as we expect.

Interactions of 4 with amines

We studied the interaction of **4** with the structurally diverse amines listed in Figure 2. These included primary and secondary monoamines **9**–**13** and aliphatic diamines **14**–**17**.

Fluorescence and UV spectroscopic studies

Unlike BINOL, compound **4** gives very weak emission. When the solution of **4** (1.0×10^{-5} M in CH_2Cl_2) was treated with monoamines **9**–**13** (1.0×10^{-3} M), very little change in fluorescence was observed (Figure 3). When aliphatic diamines **14**–

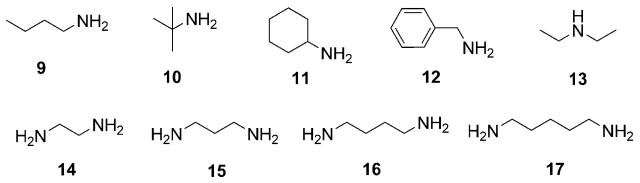


Figure 2. Structures of various amines investigated.

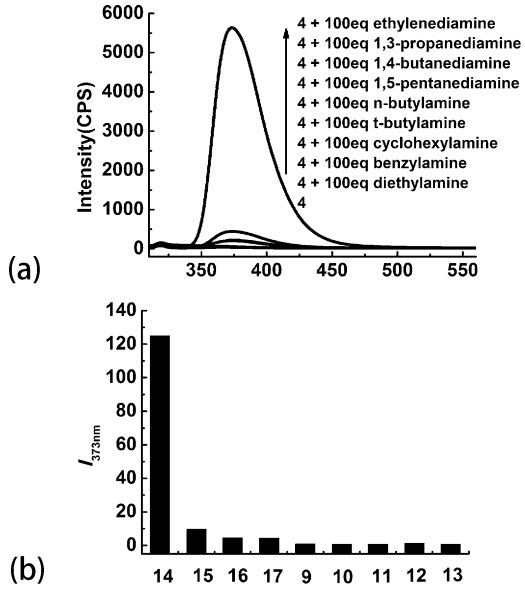


Figure 3. a) Fluorescent spectra of **4** (1.0×10^{-5} M in CH_2Cl_2) in the presence of amines **9**–**17** (1.0×10^{-3} M). b) Plots of fluorescent enhancement, I_{373nm}/I_o, with amines **9**–**17** (1.0×10^{-3} M). ($\lambda_{exc}=290$ nm, slit: 5/5 nm.)

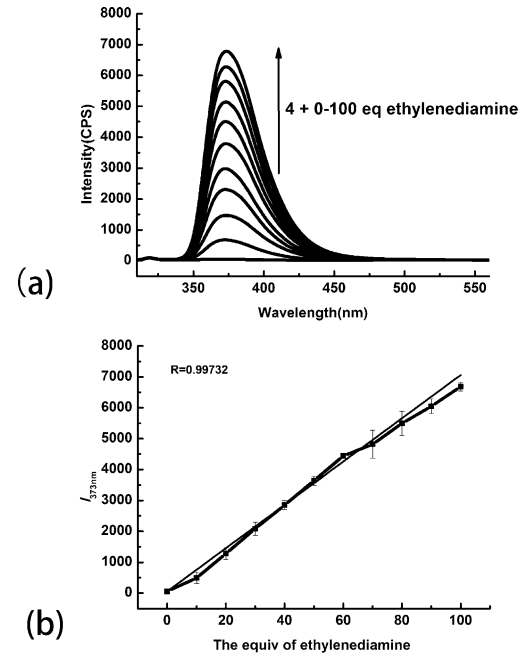


Figure 4. a) Fluorescence spectra of **4** (1.0×10^{-5} M in CH_2Cl_2) in the presence of **14**. b) Plots of I_{373nm} for **4** (1.0×10^{-5} M in CH_2Cl_2) in the presence of varying concentrations of **14**. ($\lambda_{exc}=290$ nm, slit: 5/5 nm. The error bars are obtained with three independent measurements.)

17, including 1,2-, 1,3-, 1,4-, and 1,5-diamines, were used under the same conditions, the diamine **14** caused a large fluorescence enhancement at $\lambda=373$ nm with $I/I_0=125.3$, but the enhancement caused by the other diamines at $\lambda=373$ nm were much smaller with $I/I_0=9.9$ for **15**, 4.7 for **16**, and 4.5 for **17**. These experiments demonstrate that the new BINOL-based trifluoromethyl ketone **4** is a highly selective fluorescent sensor for the 1,2-diamine.

We studied the effect of the concentration of **14** on the fluorescence of **4**. As shown in Figure 4, in the diamine concentration range of $0–1.0\times10^{-3}$ M, the fluorescence intensity of **4** (1.0×10^{-5} M in CH_2Cl_2) at $\lambda=373$ nm is linear with respect to the concentration of **14**. We further measured the fluorescence response of **4** in the presence of **14** in the concentration range of $5.0\times10^{-7}–1.0\times10^{-5}$ M in CH_2Cl_2 (Figure S2 in the Supporting Information). It shows that **4** can be used to detect **14** at concentrations over micromolar levels.

We also explored the effect of the reaction time on the fluorescent response of **4** toward **14**. As shown in Figure S3 in the Supporting Information, the fluorescence measurements taken 30 s after mixing are very close to those taken after 4 h or 2 d. Thus, the reaction of **4** with **14** quickly led to fluorescent enhancement with only small changes over an extended reaction time.

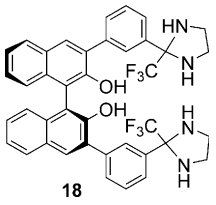
The UV/Vis spectrum of **4** (1.0×10^{-5} M in CH_2Cl_2; Figure S5 in the Supporting Information) shows a strong absorption band at λ_{max} (ε) = 252 nm (1.110×10^5) and a weaker one at $\lambda=$ 227 nm (6140). With the addition of varying concentrations of **14**, a slight decrease at λ_{max} (ε) = 252 nm (1.053×10^5) and a slight increase at $\lambda=227$ nm (7980) were observed.

NMR spectroscopy study

We conducted ^1H and ^{19}F NMR spectroscopic titrations of **4** with 0.5, 1.0, 2.0, and 3.0 equivalents of **14** in $CDCl_3$. The 10.0 mM solutions of **4** (0.5 mL) in $CDCl_3$ were prepared in an NMR tube. The 0.1 M solution of **14** (1 mL) in $CDCl_3$ was prepared in a small vial as a stock solution. The stock solutions of **14** at 25, 50, 100, and 150 μL were added to solutions of **4** in $CDCl_3$ and the NMR spectra of these solutions were recorded. The ^1H NMR spectrum of **4** showed a characteristic singlet at $\delta=8.47$ ppm, which was assigned to the aromatic proton *ortho* to $-COCF_3$. This signal decreased with the addition of **14** as a new singlet signal at $\delta=8.15$ ppm started to appear (Figure S7a in the Supporting Information). In the ^{19}F NMR spectra, compound **4** gave a singlet ^{19}F signal at $\delta=-71.22$ ppm (Figure S7b in the Supporting Information). With the addition of **14**, signals at $\delta=-82.09$ (m) and -71.20 ppm appeared; these increased as the signal at $\delta=-71.22$ decreased. We also recorded the ^{19}F NMR spectra of the above reaction mixtures after 12 d. A new signal at $\delta=-78.84$ ppm started to appear after the extended reaction time (Figure S8 in the Supporting Information).

We conducted the reaction of **4** with **14** in CH_2Cl_2 at elevated temperature in the presence of 4 Å molecular sieves to ac-

celerate the formation of the final product. After the solution of **4** and **14** in CH_2Cl_2 was heated at reflux for 18 h, the diaminal product **18** was obtained and characterized. The ^1H NMR spectrum of **18** in $CDCl_3$ gives proton signals of the two aminal rings at $\delta = 3.21$ (d, $J = 5.3$ Hz, 4H; CH_2), 3.11 (d, $J = 4.8$ Hz, 4H; CH_2), and 2.44 ppm (s, 4H; NH) and that of the BINOL hydroxyl signal at $\delta = 5.49$ ppm (s, 2H). The ^{19}F NMR spectrum of **18** gives a singlet at $\delta = -78.82$ ppm, which is the same as the second signal that appears in Figure S8 in the Supporting Information after the reaction of **4** with **14** for 12 d at room temperature. In other words, at room temperature, compound **18** was only slowly generated from the reaction of **4** with **14** over days.



18

Figure 5 compares the fluorescence spectrum of **18** with those of **4** and **8** at 1.0×10^{-5} M in CH_2Cl_2. It shows that the fluorescence intensity of **18** at $\lambda = 378$ nm is 372.0-fold that of **4** and 41.4-fold of that of **8**. The trifluoromethyl ketone groups of **4** and **8** greatly reduce their fluorescence. The greater fluorescence of **8** than that of **4** also indicates that the acidic protons of **4** can inhibit the fluorescence of the compound probably by excited-state proton transfer.[10]

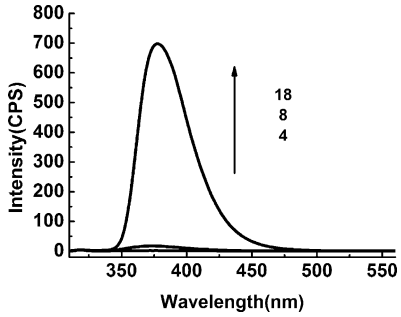
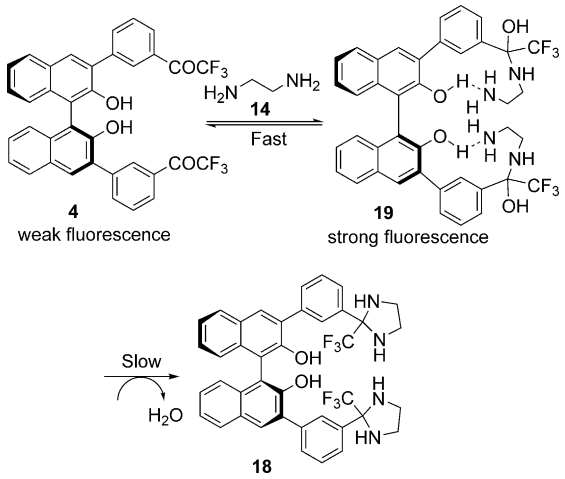


Figure 5. Fluorescence spectra of **4**, **8**, and **18** (1.0×10^{-5} M in CH_2Cl_2; $\lambda_{exc} = 290$ nm, slits: 5/5 nm).

Proposed reaction mechanism of 4 with 14

On the basis of the above experimental results and previous reports on the reaction of trifluoroacetyl groups with amines,[5,6] a two-stage mechanism is proposed for the reaction of **4** with **14**. As shown in Scheme 3, in the first stage, diamine **14** adds to the electron-deficient carbonyl groups of **4** to generate the dihemiaminal **19**. The multiple signals at $\delta = -82.04$ ppm (m) in the ^{19}F NMR spectrum (Figure S7b in the Supporting Information) can be assigned to the CF_3 groups of the diastereomers of **19** due to the formation of new chiral carbon centers. At elevated temperature or over an extended reaction time at room temperature, compound **19** was converted into the diaminal product **18**.

We have compared the ^{19}F NMR spectra of **4** after treated with various diamines (3 equiv) in $CDCl_3$ for 1 h. As the results



Scheme 3. A two-stage reaction of **4** with **14**.

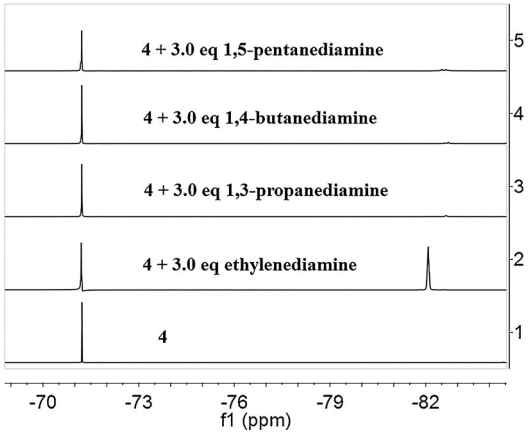


Figure 6. ^{19}F NMR spectra of **4** in $CDCl_3$ after being treated with various diamines (3.0 equiv) for 1 h.

in Figure 6 show, compound **4** reacted with 1,2-diamine **14** to form a significant amount of the corresponding hemiaminal product, but there was little reaction with the 1,3-, 1,4-, and 1,5-diamines. This contributes to the observed much greater fluorescence enhancement of **4** by **14**.

Interaction of 4 with 1,2-cylohexanediamine

We also studied the fluorescent responses of **4** toward the two enantiomers of *trans*-1,2-diaminocyclohexane (*R*,*R*)-/(*S*,*S*)-**20**. Similar to the interaction with **14**, both enantiomers of this 1,2-diamine greatly enhanced the fluorescence at $\lambda = 373$ nm, with I/I_0 of 66.4 and 65.7, respectively (Figure 7). The smaller fluorescence enhancement of **4** toward **20** than **14** could be attributed to the greater steric bulkiness of **20** relative to that of **14**, which makes the reaction of **20** less favorable. Unlike **1**, which shows a highly enantioselective fluorescent response toward this chiral diamine, the essentially non-enantioselective fluorescent response of **4** could be attributed to the greater

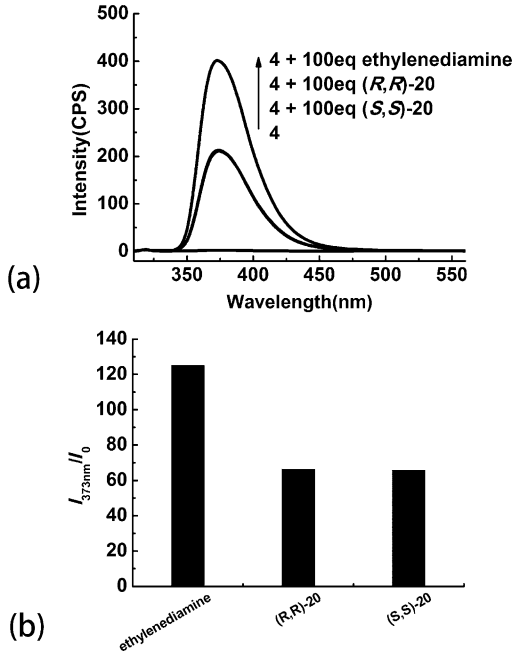
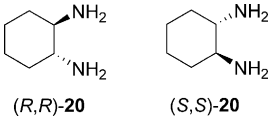


Figure 7. a) Fluorescent spectra of **4** (1.0×10^{-5} M in CH_2Cl_2) in the presence of two enantiomers (*R*,*R*)-/(*S*,*S*)-**20** (1.0×10^{-3} M) and **14** (1.0×10^{-3} M). b) Plots of fluorescent enhancement, I/I_o, for (*R*,*R*)-/(*S*,*S*)-**20** (1.0×10^{-3} M) and **14** (1.0×10^{-3} M). ($\lambda_{exc}=290$ nm, slit: 5/5 nm.)

distance between the trifluoroacetyl groups and the chiral BINOL unit in **4**.



Comparison of 4 with 8 to probe the fluorescent response mechanism

To gain a further understanding of the fluorescent properties of **4**, we have compared this compound with its analogue, **8**. Figure 8 gives the fluorescent spectra of **4** and **8** in CH_2Cl_2. Compound **4** shows very weak emissions at $\lambda=373$ and 520 nm (also see Figure S2 in the Supporting Information). Protection of the BINOL hydroxyl groups of **4** in **8** increases the fluorescence intensity at $\lambda=373$ nm by 9.0-fold. Because compound **8** does not show an emission at $\lambda=520$ nm, this weak, long-wavelength emission of **4** can be attributed to the emission of deprotonated **4** generated by an excited-state proton transfer process.[10] The excited-state proton transfer of **4** greatly reduces the fluorescence of **4** at $\lambda=373$ nm in comparison with that of **8**.

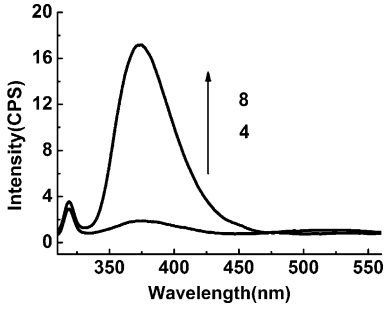


Figure 8. Fluorescence spectra of **4** and **8** (1.0×10^{-5} M in CH_2Cl_2; $\lambda_{exc}=290$ nm, slits: 5 nm/5 nm).

We studied the fluorescent response of **8** in the presence of various amines. As the results in Figure 9 show, monoamines

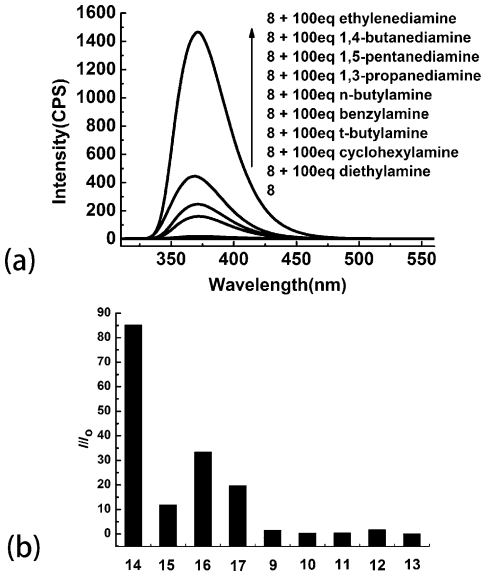
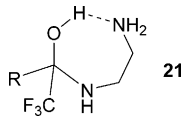


Figure 9. a) Fluorescent spectra of **8** (1.0×10^{-5} M in CH_2Cl_2) in the presence of amines **9**–**17** (1.0×10^{-3} M). b) Plots of fluorescent enhancement, I_{373nm}/I_o, for amines **9**–**17** (1.0×10^{-3} M; $\lambda_{exc}=290$ nm, slit: 5/5 nm).

9–**13** (1.0×10^{-3} M) caused little fluorescent enhancement for **8** (1.0×10^{-5} M in CH_2Cl_2). Diamines **14**–**17** caused various degrees of fluorescent enhancement for **8**, but 1,2-diamine **14** still gave the highest enhancement. It was found that **14** caused a large fluorescence enhancement at $\lambda=373$ nm with $I/I_0=85.2$, but diamines **15**, **16**, and **17** gave lower I/I_0 values of 12.0, 33.5, and 19.9, respectively.

Because the two trifluoroacetyl groups of **8** are far away from each other, they should react with the diamines independently. The selective fluorescent enhancement of **8** toward the 1,2-diamine versus monoamines and other diamines could be attributed to intramolecular hydrogen bonding between the NH_2 groups of an ethylenediamine unit and its adjacent hemiaminal hydroxyl group, as shown by **21**, which can stabilize the nucleophilic addition product and facilitate the reaction.[4a,11] As the distance between the two nitrogen atoms of the diamine units gets longer, it would be more difficult to generate such a hydrogen-bonding interaction.



21

A comparison of the results in Figures 9 and 3 demonstrates that **4** exhibits significantly higher selectivity than that of **8** in the fluorescent recognition of the 1,2-diamine over other diamines. This higher selectivity of **4** indicates that there should be additional factors besides the hydrogen-bonding interaction shown by **21**. It is proposed that hydrogen-bonding interactions between the BINOL hydroxyl groups of **4** with the NH_2 groups of **14** should facilitate nucleophilic addition to the carbonyl groups to form **19** (Scheme 3). Because the distance between the BINOL hydroxyl groups of **4** and the carbonyl groups matches better with the chain length of **14** than with those of the other diamines, highly selective responses toward the 1,2-diamines are observed.

Figure 10 gives the HOMO and LUMO of **4** obtained by conducting a Hartree–Fock (HF) DFT self-consistent field (SCF) calculation (EDF2, 6-31G(D)) with the Spartan program. It shows that the HOMO of **4** is located on the central BINOL unit, but the LUMO is located on the benzene rings containing the trifluoroacetyl groups. This indicates that there should be a photoinduced electron transfer (PET) process for **4** between an electron-rich naphthol unit and an electron-deficient trifluoroacetyl benzene ring.[12,5g] Thus, the weak fluorescence of **4** at $\lambda = 373$ nm can be attributed to both excited-state proton transfer of the hydroxyl groups and the PET process. After **4** reacts with diamine **14** to form the aminal species, such as **19** shown in Scheme 3, the PET process is inhibited and the fluorescence of the BINOL unit is recovered to give the large fluorescence enhancement. Compound **8** should have a similar PET process between the hydroxyl-protected naphthol units and the trifluoroacetyl rings, but without excited-state proton transfer. The PET process of **8** is inhibited upon reaction with **14** to give the observed large fluorescence enhancement.

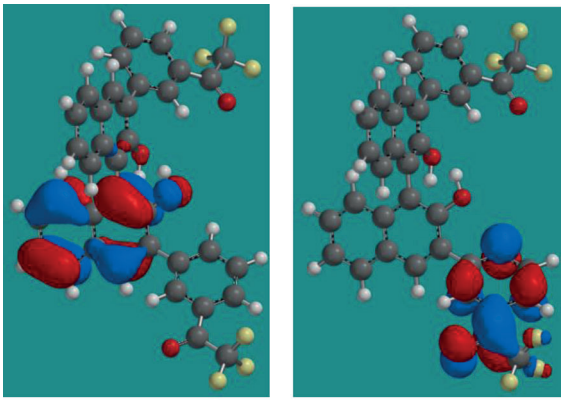


Figure 10. Calculated HOMO and LUMO of **4**.

The UV spectrum of MOM derivative **8** is similar to that of **4** (Figure S4 in the Supporting Information). This is very different from what was observed when the UV spectrum of **1** was compared with that of its MOM derivative, in which the two hydroxyl groups of **1** are protected.[6a] From the MOM derivative to the deprotected compound **1**, all absorption bands undergo a redshift. In particular, the longest wavelength absorption is shifted from λ_{max} (ε) = 357 nm (3.5×10^3) for the MOM derivative to λ_{max} = 432 nm (4.8×10^3) for **1** in CH_2Cl_2. This long-wavelength absorption of **1** is attributed to a hydrogen-bonded donor–acceptor conjugation between the *ortho*-hydroxyl and carbonyl groups. Because there are neither hydrogen-bonding interactions nor conjugation between the donor and acceptor groups in **4**, this compound gives shorter wavelength absorptions than those of **1**, although it contains an extra benzene ring on each naphthalene unit. When **8** is treated with **14**, the UV spectrum (Figure S6 in the Supporting Information) shows changes similar to those observed for the reaction of **4** with the diamine (Figure S5 in the Supporting Information).

Conclusions

We have demonstrated that a new BINOL-based trifluoromethyl ketone **4** can be used for the selective fluorescent recognition of aliphatic 1,2-diamines, especially **14**, over other di- and monoamines. The observed large fluorescent enhancement of **4** by the 1,2-diamines enables this compound to detect **14** at low concentrations. NMR spectroscopic studies showed that the trifluoromethyl ketone of the sensor reacted with **14** much more easily than with other diamines; this contributed to the observed highly selective fluorescent response. Comparative studies of **4** and the hydroxyl-group protected **8** demonstrate that the highly selective fluorescent response of **4** toward the 1,2-diamine can be attributed to two types of hydrogen-bonding interactions provided by the BINOL hydroxyl groups of the sensor and the hemiaminal hydroxyl groups of the amine adduct.

Experimental Section

General

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. All solvents were either HPLC- or spectroscopic-grade in the optical spectroscopic studies.

Synthesis and characterization of 8

Under nitrogen, compound **5** (0.75 mmol, 0.19 g) and $[Pd(PPh_3)_4]$ (0.025 mmol, 0.029 g) were mixed in DME (20 mL) in a round-bottomed flask at room temperature. Compound **7** (0.25 mmol, 0.16 g) and a 2 M aqueous solution of Na_2CO_3 (3 mL) were added, with stirring, to the mixture. The resulting mixture was stirred and heated to reflux for 10 h, cooled to room temperature, and passed through a pad of Celite. After the solvent was evaporated, the residue was dissolved in CH_2Cl_2 (30 mL); washed with a saturated aqueous solution of NH_4Cl (15 mL), water (15 mL), and brine (3× 30 mL); and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography on silica gel eluted with petroleum ether/ethyl acetate (5:1) to afford **8** as a white solid (70%, 0.175 mmol, 0.125 g). $[\alpha]_D = 70.2$ ($c = 0.23$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.45$ (s, 2H), 8.17 (d, $J =$ 7.7 Hz, 2H), 8.10 (d, $J = 7.5$ Hz, 2H), 8.00 (s, 2H), 7.94 (d, $J = 8.1$ Hz, 2H), 7.68 (t, $J = 7.8$ Hz, 2H), 7.47 (t, $J = 7.2$ Hz, 2H), 7.37–7.29 (m, 4H), 4.39 (d, $J = 5.8$ Hz, 2H), 4.35 (d, $J = 5.9$ Hz, 2H), 2.39 ppm (s, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -71.25$ ppm (s, 6F);

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 180.5$ (q, $J = 35.2$ Hz), 151.1, 140.2, 137.0, 133.9, 133.7, 131.0, 130.82, 130.75, 130.2, 129.0, 128.9, 128.1, 127.0, 126.5, 126.3, 125.7, 116.7 (q, $J = 192.6$ Hz), 98.8, 56.0 ppm; HRMS: *m/z* calcd for $C_{40}H_{28}F_6O_6Na$ $[M+Na]^+$: 741.1688; found: 741.1680.

Synthesis and characterization of 4

After compound **8** (0.175 mmol, 0.125 g) was dissolved in CH_2Cl_2/MeOH (20 mL/20 mL), HCl (4 mL, 12 N in water) was added slowly, and the mixture was stirred at room temperature, overnight. A saturated aqueous solution of $NaHCO_3$ was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3×30 mL). The combined organic extracts were washed with brine (3×30 mL) and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography on silica gel eluted with petroleum ether/ethyl acetate (5:1) to afford compound **4** as a white solid (90%, 0.158 mmol, 0.100 g). $[\alpha]_D = -71.2$ ($c = 0.21$, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.47$ (s, 2H), 8.15–8.07 (m, 6H), 7.98 (d, $J = 7.9$ Hz, 2H), 7.67 (t, $J = 7.8$ Hz, 2H), 7.48–7.43 (m, 2H), 7.42–7.36 (m, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 5.37 ppm (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -71.22$ ppm (s, 6F); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 180.5$ (q, $J = 35.2$ Hz), 150.1, 138.7, 136.8, 133.1, 132.1, 131.2, 130.0, 129.4, 129.2, 129.0, 128.8, 128.7, 128.2, 124.9, 124.0, 116.7 (q, $J = 292.6$ Hz), 111.8 ppm; HRMS: *m/z* calcd for $C_{36}H_{20}F_6O_4$ $[M]^-$: 629.1188; found: 629.1182.

Synthesis and characterization of 18

After compound **4** (0.1 mmol, 0.063 g) was dissolved in CH_2Cl_2 (30 mL), dry 4 Å molecular sieves was added. Compound **14** (1 mmol, 0.060 g) was added, with stirring, to the mixture. The resulting mixture was stirred and heated at reflux for 18 h. It was then cooled to room temperature, and passed through a filter paper. After evaporation of the solvent, the residue was purified by column chromatography on silica gel eluted with petroleum ether/ethyl acetate (1:1) to afford compound **18** as a white solid (32%, 0.032 mmol, 0.023 g). $[\alpha]_D = -30.2$ ($c = 0.13$, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.07$ (s, 2H), 8.04 (s, 2H), 7.93 (d, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 7.7$ Hz, 2H), 7.67 (d, $J = 7.8$ Hz, 2H), 7.50 (t, $J = 7.8$ Hz, 2H), 7.43–7.37 (m, 2H), 7.37–7.30 (m, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 5.49 (s, 2H), 3.21 (d, $J = 5.3$ Hz, 4H), 3.11 (d, $J = 4.8$ Hz, 4H), 2.44 ppm (s, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) $\delta = -78.82$ ppm (s, 6F); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 150.2$, 138.6, 137.7, 133.0, 131.7, 130.3, 130.1, 129.5, 128.6, 128.2, 127.7, 127.5, 126.1, 124.6, 124.2, 112.3, 83.3 (q, $J = 28.6$ Hz), 46.9 ppm; HRMS: *m/z* calcd for $C_{40}H_{32}F_6O_4$ $[M]^-$: 713.2351; found: 713.2351.

Preparation of samples for fluorescent measurement for interactions with the diamines and monoamines

Stock solutions of 1.0 mM **4** and **8** in CH_2Cl_2 were freshly prepared for each measurement. For the fluorescent enhancement study, a solution of **4** or **8** (10^{-5} M, 2.5 mL) was mixed with various equivalents of solutions of the di- or monoamine (50 mM in CH_2Cl_2) in a 3.5 mL test tube. The resulting solution was allowed to stand at room temperature for 30 s and the fluorescent spectra were recorded within 1 h.

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Keywords: amines · fluorescence · molecular recognition · sensors · trifluoromethyl ketones

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FULL PAPER

Sensors

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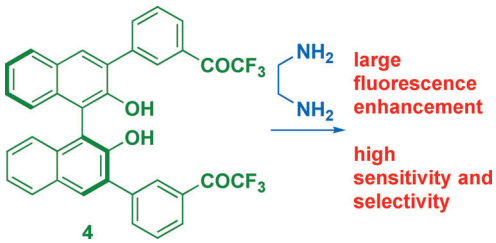
Fluorescent Recognition of 1,2-Diamines by a 1,1′-Binaphthyl-Based Trifluoromethyl Ketone



Detecting amines: A trifluoromethyl ketone molecule is found to exhibit large fluorescent enhancement in the presence of 1,2-diamines, especially ethylenediamine (see scheme). Other amines, including mono- and diamines, have much smaller effects on the fluorescence of this compound.