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Fluorescent Recognition of Functional Secondary Amines in the Fluorous Phase

Le Jiang,[a] Jun Tian,[a] Feng Zhao,[a] Shanshan Yu,*[a] Dan Shi,[a] Xinjing Wang,[a] Xiaoqi Yu,*[a] and Lin Pu*[a,b]

Abstract In a fluorous solvent (perfluorohexane, FC-72), a perfluoroalkyl substituted 2-hydroxy-1-naphthaldehyde (**1**) was found to show greatly enhanced fluorescence when treated with certain functional secondary amines but little fluorescence response was observed with unfunctional amines as well as functional primary and tertiary amines. The study of the reaction of **1** with 2-methylamino ethanol (**8**) reveals a facile cyclocondensation of the aldehyde group of **1** with this 1,2-amino alcohol to form a 5-membered ring oxazolidine product which turns on the fluorescence. The reaction of **1** with the amino alcohol was found to be more favorable in the fluorous solvent than in a common organic solvent. The use of the fluorous phase-based fluorescence measurement in this work provides a potentially more sensitive as well as selective method in amine sensing.

Introduction

Organic amines are ubiquitous in environment, chemical industry and biological systems.[1-6] Detection of amines has become important in monitoring pollution in environment, occupational safety, food freshness and many biological processes, and a number of analytical methods have been developed.[2-7] Because fluorescence spectroscopy analysis has many advantages such as easily available instruments, on line monitoring and high sensitivity, extensive investigations have been conducted on the fluorescence-based amine detection.[8-15] However, it is still quite a challenge to distinguish various types of amines by fluorescence measurement. For example, fluorescent probes that can selectively detect secondary amines over primary and tertiary amines are rare. Recently, we found that in an organic solution, the fluorescence of a 1,1'-binaphthyl molecule can be turned on by functional secondary amines but not by the corresponding primary and tertiary amine analogs.[16] It can be used for the selective detection of certain functional secondary amines.

In recent years, the fluorous phase-based separation technique has been extensively applied in chemical synthesis and catalysis because of the hydrophobic, lipophobic and fluorophilic properties of highly fluorinated materials.[17-19] We are interested in using the unique properties of the fluorinated compounds to develop the fluorous phase-based molecular recognition. When highly fluorinated fluorescent probes are used to conduct the substrate detection in the fluorous phase, since most other chemicals cannot be dissolved in the fluorous phase, their interference on the fluorescence measurement should be minimized. On the basis of our previous use of the 1,1'-binaphthyl-based molecular probe,[16] we have synthesized a fluorinated naphthalene compound to carry out a highly selective fluorescent recognition of functional secondary amines in the fluorous phase. Herein, these results are reported.

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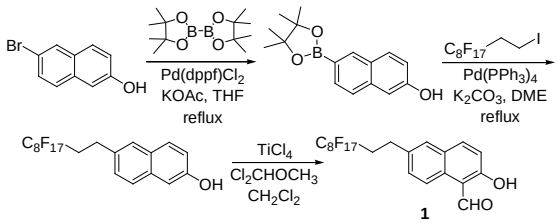
Supporting information for this article, including additional fluorescence spectra, and NMR and mass spectra, is given via a link at the end of the document

Results and Discussion

1. Fluorescent Responses of Compound 1 in the Fluorous Phase Toward Various Amines

Previously, we reported the circular dichroism spectroscopic responses of the fluorinated compound **1** in the presence of chiral amines.[20] In a way similar to the previous synthetic procedure, we have prepared this compound according to Scheme 1. This compound contains an aldehyde group ortho to a hydroxyl group on the naphthalene ring which can be used to interact with various amines.

Scheme 1. Synthesis of the Fluorinated Compound **1**.



Compound **1** is soluble in perfluorohexane (FC-72), a fluorous solvent. In FC-72, it shows weak emission at 354 nm when excited at 285 nm. We studied the fluorescence response of **1** toward the organic amines **2** - **12** listed in Figure 1. Because of a better solubility of compound **1** in FC-72 at 33.5 °C, all the interactions with amines and the fluorescence measurements were conducted at this temperature. It was found that when the FC-12 solution of **1** (5.0×10^{-5} M) was treated with the unfunctionalized primary, secondary and tertiary amines **2** - **4**, little change in fluorescence was observed. Similarly, the primary amine-based amino alcohols **5** - **7** also did not generate significant fluorescence response of **1**. However, when **1** was treated with a secondary amino alcohol **8**, large fluorescence enhancement was observed. As shown in Figure 2, in the

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presence of 10 equiv **8**, the fluorescence intensity of **1** at 365 nm was increased to 40 fold. The other 1,2-secondary amino alcohol **9** and the 1,3-secondary amino alcohol **10** also greatly enhanced the fluorescence of **1**. Further increasing the distance between the methyl amine group and the hydroxyl group as in the 1,4-secondary amino alcohol **11** diminished the fluorescence enhancement effect. The tertiary amine-based 1,2-amino alcohol **12** cannot turn on the fluorescence of **1**.

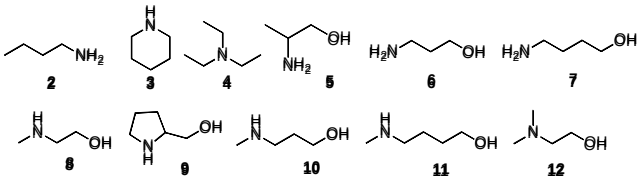


Figure 1. Various amines used to interact with **1**.

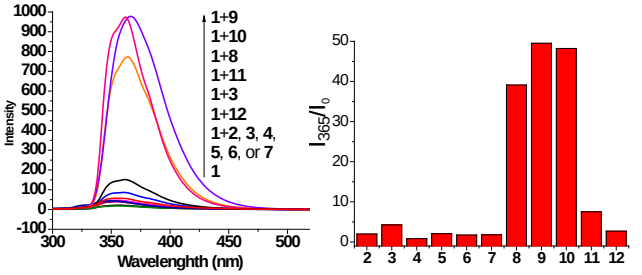
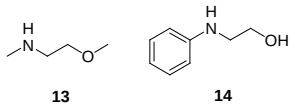


Figure 2. (a) Fluorescence response of **1** (5.0×10^{-5} M) in the presence of amines **2** - **12** (5.0×10^{-4} M) in FC-72/2% CH_2Cl_2 after 3 h. (b) The fluorescence intensity ratio I_{365}/I_0 (Temperature: 33.5 °C. λ_{ex} = 285 nm. Slit widths: E_x/E_m = 5 nm/5 nm).

The above fluorescence experiments demonstrate that in a fluorous solution, compound **1** can selectively recognize the secondary amine-based 1,2- and 1,3-amino alcohols over the unfunctionalized amines as well as the primary and tertiary amine-based amino alcohols. We found that when the hydroxyl group of **8** was methylated, the resulting compound **13** gave only small fluorescence enhancement for **1** in FC-72 (Figure S1 in SI). The aromatic amine-based amino alcohol **14** cannot enhance the fluorescence of **1** (Figure S1 in SI).



We further studied the fluorescence response of **1** with the diamines listed in Figure 3. When the FC-72 solution of **1** (5.0×10^{-5} M) was treated 10 equiv of the 1,2-disecondary amine **15** in FC-72, the fluorescence intensity at 365 nm was increased to 33 fold (Figure 4). When the 1,3-disecondary amine **16** was used, similar large fluorescence enhancement was observed. However, the fluorescence enhancement was greatly reduced when the distance between the two secondary amine groups is increased as in the 1,4-disecondary amine **17**. The 1,2-diamine **18** containing a secondary and a primary amine group cannot enhance the fluorescence of **1**. The primary amine-based diamines **19** – **22** and compound **23** containing a tertiary and a primary amine group also cannot increase the fluorescence of **1**.

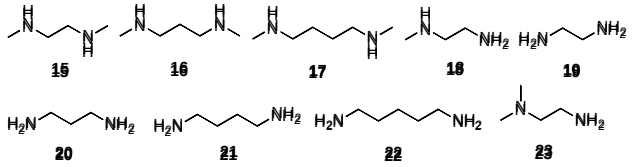


Figure 3. Various diamines used to interact with **1**.

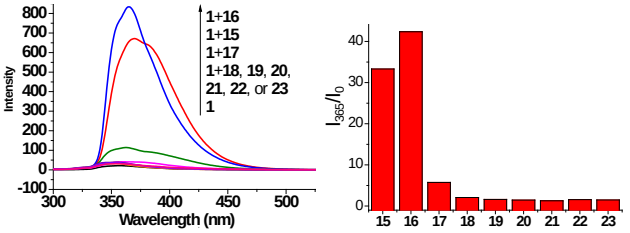


Figure 4. (a) Fluorescence response of **1** (5.0×10^{-5} M) in the presence of various diamines **15** - **23** (5.0×10^{-4} M) in FC-72/2% CH_2Cl_2 after 3 h. (b) The fluorescence intensity ratio I_{365}/I_0 (Temperature: 33.5 °C. λ_{ex} = 285 nm. Slit widths: E_x/E_m = 5 nm/5 nm).

2. Investigation on the Reaction of 1 with the Secondary Amino Alcohol 8

The fluorescence response of **1** toward the secondary amino alcohol **8** in FC-72 at various concentrations was studied. As shown in Figure 5, the fluorescence of **1** at λ = 365 nm increased as the concentration of **8** increased which reached a plateau when the concentration of **8** was greater than 10 equiv. The reaction time (3 h) was chosen as we found that when **1** was reacted with 10 equiv **8**, the fluorescence enhancement reached maximum over 1.5 h and was stable during 1.5 – 3.5 h (Figure S2 in SI). Figure 5 demonstrates that **1** can be used to detect the secondary amino alcohol **8** at concentrations ≤ 5 x 10^{-4} M. We have determined the limit of detection (LOD) as 3 x 10^{-8} M (Figure S3 in SI).

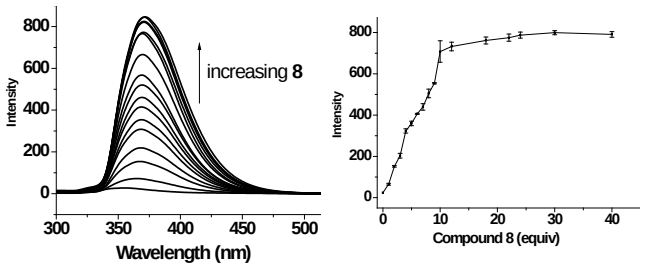


Figure 5. (a) Fluorescence spectra of **1** (5.0×10^{-5} M) in the presence of **8** (0 - 1.5×10^{-3} M) in FC-72/2% CH_2Cl_2 after 3 h. (b) Fluorescence intensity I_{365} versus the concentration of **8** (Temperature: 33.5 °C. λ_{ex} = 285 nm. Slit widths: E_x/E_m = 5 nm/5 nm).

In order to gain a better understanding on the selective fluorescence response of the probe **1** toward **8**, we conducted a ^{1}H NMR spectroscopic study on the reaction of **1** with **8** in FC-72. As shown in Figure 6, when **1** (8.3 mM) was treated with ≥ 2 equiv **8** in FC-72, the aldehyde signal of **1** at δ 9.93 disappeared with the appearance of very broad signals for the reaction mixture. This could be attributed to the reduced solubility of the reaction product in the fluorous solvent. Formation of oily red precipitate was observed. No precipitate was observed in the fluorescence measurement when **1** was treated with **8** in FC-72/2% CH_2Cl_2 which is attributed to the much lower concentration in the fluorescence experiment. We also studied the reaction of **1** with **8** in $CDCl_3$. As shown in Figure 7, when **1** was treated with **8**, the NMR signals remained to be sharp with the

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increase of the concentration of **8**. It was observed that while the aldehyde signal of **1** at δ 9.97 was decreasing, a new signal at δ 5.63 was growing. This new signal can be assigned to H_a of the proposed oxazolidine product **26** shown in Scheme 2. The reaction of **1** with **8** can generate the intermediates **24** and **25** which upon intramolecular nucleophilic cyclization should give **26** (Scheme 2). Comparison of Figure 6 with Figure 7 indicates that the reaction of **1** with **8** is more favourable in the fluorous phase than in $CDCl_3$ since the disappearance of the aldehyde signal of **1** occurred at lower concentration of **8** in FC-72 (≤ 2.0 equiv) than in $CDCl_3$ (> 10 equiv). Thus **1** is more sensitive toward **8** in the fluorous phase. Formation of **26** is also supported by a mass spectroscopic analysis of the reaction mixture of **1** with **8** in FC-72 which gives a base peak at m/z = 676.1147 corresponding to the molecular ion of **26** (calcd for $M+H^+$: 676.1144).

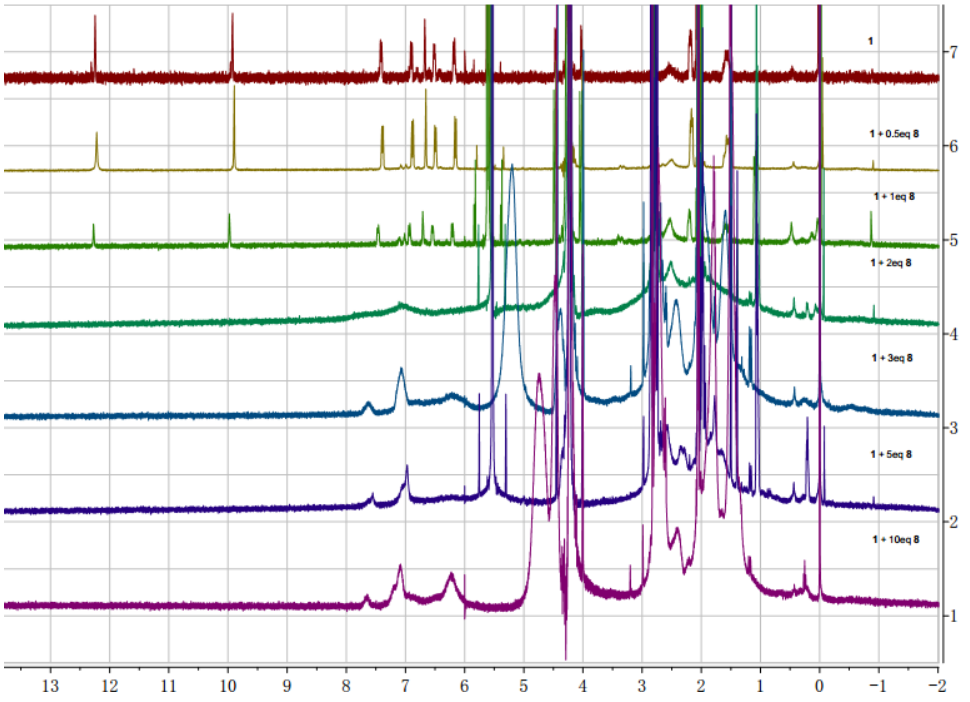

Figure 6. ^1H NMR spectra (FC-72/5% CH_2Cl_2) of **1** (8.3 mM) with 0, 0.5, 1.0, 2.0, 3.0, 5.0, and 10.0 equiv. of compound **8** after 3 h at 33.5 °C.

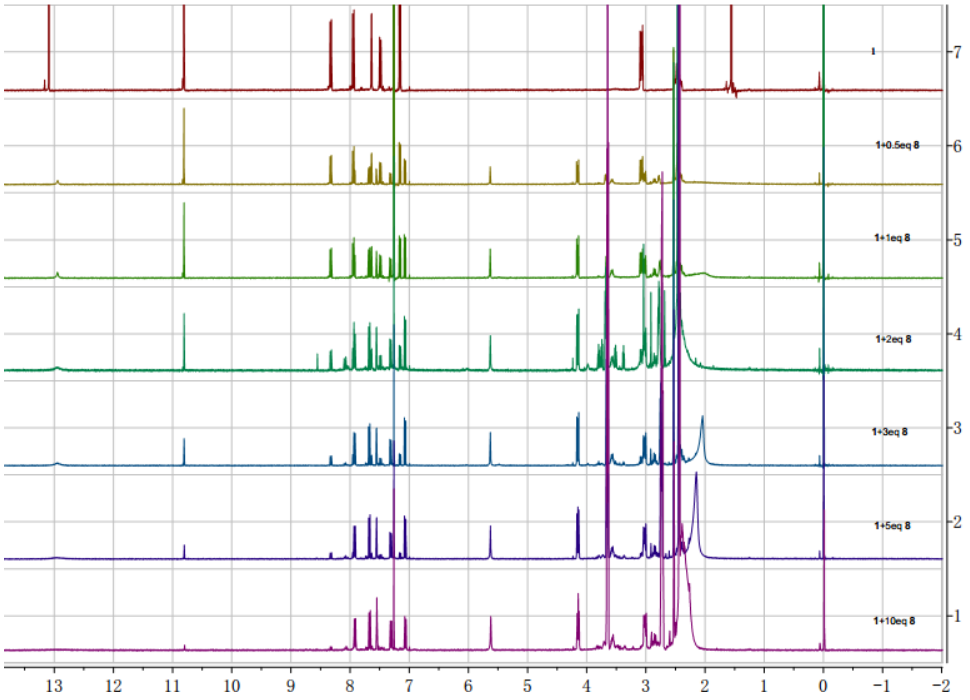

Figure 7. ^1H NMR spectra ($CDCl_3$) of **1** (8.3 mM) with 0, 0.5, 1.0, 2.0, 3.0, 5.0, and 10.0 equiv of compound **8** after 3 h at 33.5 °C.

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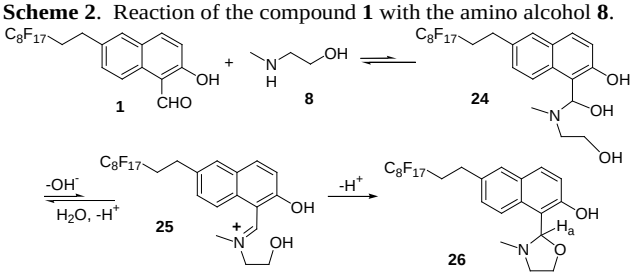
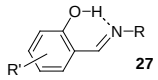
Scheme 2. Reaction of the compound **1** with the amino alcohol **8**.



Formation of **26** from the reaction of **1** with **8** removes the conjugation of the aldehyde group of **1** with the ortho hydroxyl group. This should disrupt the excited state proton transfer process between the hydroxyl and the aldehyde group[21] and turn on the fluorescence. In the conversion of **1** and **8** to **26** shown in Scheme 2, formation of the intermediates **24** and **25** is reversible favouring the starting materials, but the cyclization from **25** to **26** to form the stable 5-membered ring product is irreversible which drives the reaction forward. This explains the observation that the secondary amines **3** and **13** without the hydroxyl group of **8** can only produce small fluorescence enhancement. When compound **10** was used, its reaction with **1** is expected to be similar to **8** to generate a stable 6-membered ring product, giving the observed large fluorescence enhancement. The secondary diamines **15** and **16** can also react with **1** to form the corresponding 5- and 6-membered ring aminal products[16] similar to those formed from **8** and **10** and thus give the observed large fluorescence enhancement. Formation of a 7-membered ring product from the reaction of **11** or **17** with **1** is unfavorable thus gives much lower fluorescence enhancement. It is known that when the salicyl aldehyde derivatives like **1** are treated with primary amines, they normally produce the corresponding aldimine products stabilized by an intramolecular hydrogen bond with the ortho hydroxyl group[22] as represented by **27** which gives very weak fluorescence due to both the excited state proton transfer and the excited state isomerization of the imine C=N bonds.[22,23] Therefore all the compounds containing one or more primary amine groups such as **2**, **5** – **7**, and **18** - **23** cannot enhance the fluorescence of **1**. The reactions of **1** with the tertiary amines **4** and **12** and the aromatic secondary amino alcohol **14** are not favourable which give no fluorescence enhancement.



Conclusion

We have found that the perfluoroalkyl substituted compound **1** shows large fluorescence enhancement in the presence of certain functional secondary amines in the fluorous phase. It can be used to conduct selective detection of these secondary amines. Little fluorescence enhancement is observed when **1** is treated with unfunctional amines and functional primary or tertiary amines. Spectroscopic investigation reveals that compound **1** can react with a 1,2-secondary amino alcohol to form the corresponding 5-membered ring oxazolidine product to turn on the fluorescence. It was also found that the reaction of **1** with the amino alcohol is more favorable in the fluorous solvent than in a common organic solvent. The use of the fluorous phase in this work provides a potentially more sensitive as well as selective method in amine sensing.

Experimental Section

General information. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. THF and CH_2Cl_2 were dried according to the standard methods prior to use. All the solvents for the optical spectroscopic studies were either HPLC- or spectroscopic-grade. NMR spectra were measured on a Bruker AM400 NMR spectrometer. Fluorescence emission spectra were obtained by using FluoroMax-4 Spectro fluorophotometer (HORIBA Jobin Yvon).

Synthesis and characterization of compound 1. Step 1: Under argon, 6-bromo-2-naphthol (5.0 g, 22.5 mmol), bis(pinacolato)-diboron (6.86 g, 27 mmol), 1,1'-bis(diphenylphosphino)ferrocene dichloropalladium (II) (1.65 g, 2.25 mmol) and potassium acetate (8.84 g, 90.1 mmol) were dissolved in anhydrous THF (100 mL). The reaction mixture was stirred at 80 °C for 12 h and then cooled to room temperature. After filtration through a Buchner funnel, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) to afford 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-ol as a white solid in 80 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1 H), 7.76 (t, J = 7.9 Hz, 2 H), 7.63 (d, J = 8.2 Hz, 1 H), 7.12 (m, 2 H), 5.64 (s, 1 H), 1.38 (s, 12 H). Step 2: Under an argon atmosphere, 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-ol (1.0 g, 3.5 mmol) and 1-(perfluorooctyl)- 2-iodoethane (2.92 g, 5.1 mmol) were dissolved in DME (20 mL), which was combined with $Pd(PPh_3)_4$ (0.4 g, 5 mol-%) and K_2CO_3 (20 mL, 2 M). The mixture was heated at 95 °C to reflux for 5 h and then cooled to room temperature. Ethyl acetate (20 mL) and water (10 mL) were added. The organic layer was separated and washed with water and brine, then dried with Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by flash column chromatography on silica gel (ethyl acetate/CH_2Cl_2, 1:20) to afford 6-(1H,1H,2H,2H-perfluorodecyl)naphthalen-2-ol as a yellow solid in 37 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.7 Hz, 1 H), 7.65 (d, J = 8.5 Hz, 1 H), 7.58(s, 1 H), 7.29 (d, J = 8.4 Hz, 1 H), 7.12 (dt, J = 8.8, 4.9 Hz, 2 H), 4.98(s, 1 H), 3.03 (m, 2 H), 2.45 (m, 2 H). Step 3: A solution of $TiCl_4$ (0.71 g, 3.75 mmol) and dichloromethyl methyl ether (0.14 g, 1.25 mmol) in anhydrous CH_2Cl_2 (4.0 mL) was stirred at 0 °C for 15 min. A solution of 6-(1H,1H,2H,2H-perfluorodecyl)naphthalen-2-ol (0.74 g, 1.25 mmol) in anhydrous CH_2Cl_2 (2.0 mL) was added dropwise, and the resulting mixture was warmed up to room temperature. The mixture was stirred for 12 h, and then the reaction was quenched with the addition of 1 N HCl (10.0 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), and the organic layers were combined and dried with Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by flash column chromatography on silica gel (CH_2Cl_2/petroleum ether, 5:1) to afford **1** as an off-yellow solid in 80 % yield (618 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.09 (s, 1 H), 10.79 (s, 1 H), 8.33 (d, J = 8.6 Hz, 1 H), 7.96 (d, J = 9.1 Hz, 1 H), 7.64 (s, 1 H), 7.50 (d, J = 8.5 Hz, 1 H), 7.17 (d, J = 9.1 Hz, 1 H),3.10 (t, J = 8.3 Hz, 2 H), 2.46 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.14, 164.89, 138.60, 135.23, 131.62, 129.70, 128.31, 128.01, 119.62, 119.23, 111.22, 32.76 (t, J = 22.0 Hz), 29.11. ^{19}F NMR (376 MHz, $CDCl_3$) δ –80.73 (t, J = 9.9 Hz, 2 F), –114.45 (t, J = 13.5 Hz, 2 F), –121.77 (d, J = 87.7 Hz, 7 F), –122.68 (s, 2 F), –123.39 (s, 2 F), –125.98(m, 2 F). HRMS: m/z calcd. for $C_{21}H_{11}F_{17}O_2 - H^+$: 617.0409; found: 617.0406.

Preparation of samples for fluorescence measurements. A solution of **1** (5.0 μL, 5.0 x 10^{-3} M) in CH_2Cl_2 was mixed with

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various equiv of amino alcohols and amines (5.0×10^{-2} M in CH_2Cl_2) in a 2 mL test tube. Then FC-72 was added to reach 500 μL with 5 – 35 μL CH_2Cl_2. The resulting solution was maintained at 33.5 °C for 3 h and shaken well before fluorescence measurement.

Preparation of the samples of 1 with 0 – 10 equiv 8 in FC-72 for NMR measurements. To a NMR tube containing **1** (250 mM in CH_2Cl_2, 20.0 μL), various amounts of **8** (0 – 10 equiv) in CH_2Cl_2 and FC-72 were added, and the total volume was made up to 0.6 mL FC-72 with 5% CH_2Cl_2. The final concentration of **1** was 8.3 mM in FC-72. The solutions were mixed at 33.5 °C for 3 h before the ^{1}H NMR spectra were taken. Acetone-d_6 sealed in two capillary tubes was used as the external standard for field locking.

Preparation of the samples 1 with 0 – 10 equiv 8 in $CDCl_3$ for NMR measurements. To a NMR tube containing **1** (16.7 mM in $CDCl_3$, 0.30 mL), various amounts of **8** (0 – 10 equiv) in $CDCl_3$ were added, and the total volume was made up to 0.6 mL with $CDCl_3$. The final concentration of **1** was 8.3 mM in $CDCl_3$. The solutions were mixed at 33.5 °C for 3 h before the ^{1}H NMR spectra were taken.

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Supplementary Materials Available: Detailed experiments and additional spectroscopic data.

Keywords: Fluorescence Sensor Fluorous phase Secondary amines Aldehydes

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TOC Graph

Key topic: Fluorescent sensor

Certain functional secondary amines are found to turn on the fluorescence of a perfluoroalkyl substituted 2-hydroxy-1-naphthaldehyde (**1**) in a fluorous phase but other amines cannot. This compound can be used as a fluorescent probe to selectively detect functional secondary amines.