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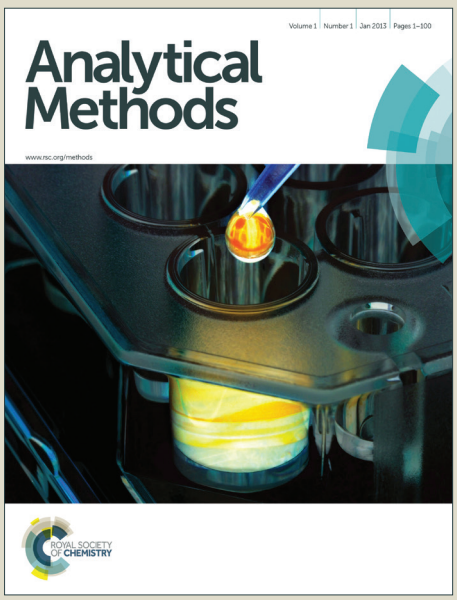

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Response to referees

Manuscript ID AY-ART-04-2014-001011 entitled "A BODIPY based indicator for fluorogenic detection of salicylaldehyde with OFF-ON emission"

Dear Prof. Craig Banks:
Thank you for your hard work and appreciation on our manuscript! All of the authors appreciated the reviewers' hard work and useful comments. The manuscript has been revised according to referees' comments point by point.

Referee: 1

1. For salicylaldehyde, its activity is not as reactive dicarbonyl compounds such as methylglyoxal. The C=N reaction of salicylaldehyde might be gradual. Therefore, the reaction time should be examined in this study.

Authors' response: The reaction time between Probe **1** and salicylaldehyde has been studied, and the Kinetic profiles of the reaction between Probe **1** and salicylaldehyde has been shown in Fig.2.

2. Methods need further be shown in details for repeat.

Authors' response: In fact, the experiments have been repeated several times, and the repeated fluorescent titrations of salicylaldehyde to probe **1** was shown in fig. S3.

3. There are multiple grammatical and spelling errors in the manuscript. It should be rewritten in a concise manner, and checked by a native English language editor.

Authors' response: The manuscript has been checked throughly, and grammatical and spelling errors has been revised accordingly.

4. The abstract section is too simple to summary the keynote of the study.

Authors' response: The abstract has been enlarged.

5. The results and discussion part is disordered, it should be adjusted carefully.

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Authors' response: The results and discussion part has been revised.

6. Figure 4 should be enlarged.

Authors' response: Figure 4 (figure 5 in the revised manuscript) has be enlarged

Referee: 2

1. Probe reacted with salicylaldehyde to form two major products, which should be isolated and well characterized. The percentage of each of them should also be calculated.

Authors' response: The rection of probe **1** with salicylaldehyde has been carried out again, and the two major products have been isolated and characterized by HR-MS and HNMR spectrum. In our experiment, we found the product P1 was not stable and not easy to isolated. Compound P2 was the main product, about 90% was obtained.

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A BODIPY based indicator for fluorogenic detection of salicylaldehyde with OFF-ON emission

Qian Li, Jian Xu,Ying Yue, Yuan Liao and Shijun Shao*

Abstract: A turn-on fluorescent indicator **1** based on BODIPY derivative for the detection of salicylaldehyde in aqueous solution by fluorescence spectroscopy has been developed. The formation of schiff base between probe **1** and salicylaldehyde suppressed the PET process and prohibited the C=N isomerization accounted for the fluorescence response of Probe **1**. Two major reaction products of probe **1** with salicylaldehyde was obtained and characterized by ^{1}H NMR and HR MS spectrum. Weakly fluorescent polymeric films have been obtained by embedding the indicator in the PMMA, which can be used for the fluorescent detection of the salicylaldehyde in polymer matrices.

Introduction

Aldehydes are important industrial chemicals which have been widely utilized in the manufacturing of various materials, ranging from pharmaceuticals to plastic additives. Among various aldehydes, salicylaldehyde is a common organic pollutant that builds up in the environment due to the inefficiency of traditional water purification processes, which finds their way into the water system through pharmaceutical medications, cosmetic products, and agricultural chemicals[1]; On the other hand, salicylaldehyde is neurotoxic and has effect on α-synuclein aggregation[2]. Despite of its vital roles in the environmental events and biological processes, the detection of salicylaldehyde has been less developed [3].

The reliable and economic monitoring of aldehydes is crucial in the field of environmental pollution analysis & control and industrial chemistry. A number of methods have been reported in the literature, which can be classified into electrochemical[4a], chromatographic methods[4b] and spectroscopic techniques[4c]. Among various methods, considerable efforts have been devoted to the optical chemosensors due to their low cost, simplicity, high degree of specificity and low detection limit[5]. Most optical aldehyde detection methods are based on nucleophilic addition of the amine to the aldehyde, forming an imine group (Schiff bases or Hydrazones). The imine formation usually generates a color or emission change, so great effort has gone into the synthesis of sophisticated optical indicators

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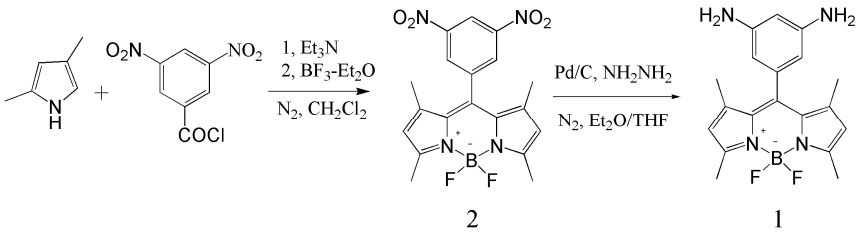
with primary amine groups for aldehydes detection.[6] In previous studies, much attention has been paid to the design of optical indicators for aliphatic aldehydes (Formaldehyde is the most favorable), indicators for aromatic aldehydes have been less developed. So the design of indicators for aromatic aldehydes is important and desirable.

Among various fluorophores, BODIPY dyes have been widely employed to develop optical chemosensors for various species due to the remarkable photophysical properties, such as sharp absorption and fluorescence peaks, high stability, and high fluorescence quantum yield[7]. In spired by previous work on aldehydes detection and our recent work on BODIPY based fluorescent sensors[8], we reported a new BODIPY based indicator **1** with two amino groups for the OFF-ON fluorescent detection of Salicylaldehyde herein. The fluorescence response of **1** to formaldehyde is much smaller compared to that of salicylaldehyde. The Salicylaldehyde induced OFF-ON fluorescence could be attributed to the formation of C=N unit and the geometrically restricted six-membered ring resulted from the intramolecular H-bonding interaction, which suppressed the photo-induced electron transfer (PET) process and prohibited the C=N isomerization.

Results and discussion

The structure and synthesis of Probe **1** were shown in Scheme 1, which was prepared through the condensation reaction of 3,5-dinitrobenzoyl chloride with 2,4-dimethylpyrrole and reduced with Pd/C-N_2H_4 according to a published procedure[9]. The purity and structure of **1** was conformed by the ^{1}H NMR and HRMS spectra (see ESI†, Fig. S1 and Fig. S2), which was consistent with the reported data.



Scheme 1 Synthesis of probe **1**

The sensing properties of probe **1** toward various aldehydes were studied in EtOH-H_2O (v/v=4:1, with AcOH as catalyst) solution. Probe **1** showed quite weak fluorescence with a

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fluorescent emission intensity at 522 nm due to an efficient PET process from the lone pairs of electrons on amino groups, which has inherent electron donating property, to the excited BODIPY fluorophore. Various aldehydes analyte (the formaldehyde, benzaldehyde, p-nitrobenzaldehyde, p-methoxybenzaldehyde, 4-diethylaminobenzaldehyde, salicylaldehyde, 3-hydroxybenzaldehyde, 4-(diethylamino)salicylaldehyde, 4-hydroxybenzaldehyde and 5-nitrosalicylaldehyde) were added to a freshly prepared solution of **1**. The resulting solution was subsequently tempered for 1 h at room temperature and then analyzed by fluorescence spectroscopy. The emission data of Probe **1** for the 10 selected aldehydes are depicted in Fig. 1. Probe **1** exhibited strong OFF-ON fluorescence responses toward salicylaldehyde and the solution gave off visible green fluorescent emission. In the presence of benzaldehyde, the fluorescence was also turned on to some extent, but it was much smaller compared to that of salicylaldehyde. Under the same condition, the fluorescence respenses of **1** toward other aldehydes were slim. So probe **1** could act as an efficient fluorescent indicators for salicylaldehyde.

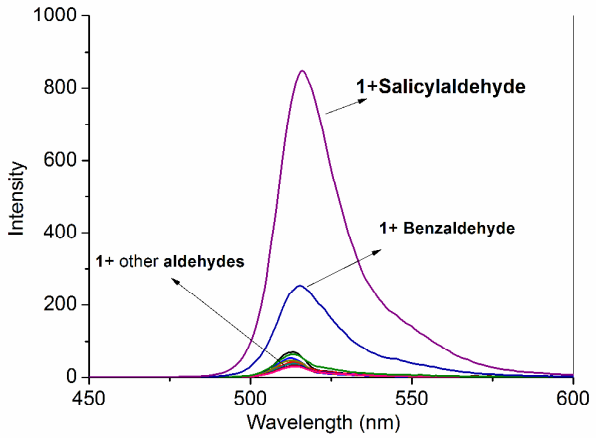

Fig. 1 Changes of the fluorescent emission in EtOH-H_2O solutions containing molecular probe **1** (5 μM) after addition of different aldehydes (5 mM). Prior to the measurement, the solutions were tempered for 1 h at room temperature.

The interaction of probe **1** with salicylaldehyde was further investigated in detail through emission spectroscopic titrations. Time course study revealed that the reaction between Probe **1** and salicylaldehyde was completed at about 50-60 minutes (Fig.2) in EtOH-H_2O solution.

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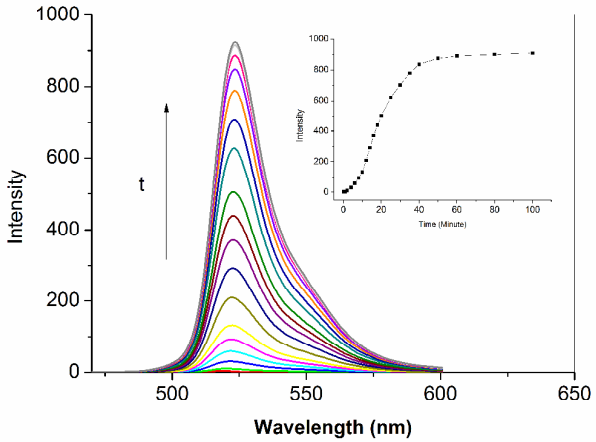

Fig. 2 Kinetic profiles of the reaction between Probe 1 and salicylaldehyde. The reaction process was monitored by fluorescence emission intensity at 522 nm (λex=503 nm) in EtOH-H_2O containing Probe 1 (5 μM) and salicylaldehyde (10 mM).

To access the sensitivity of Probe **1** based assay, various amounts of salicylaldehyde were spiked into the solution of Probe **1**. The solutions were incubated at room temperature for 1 h and then analyzed by fluorometry. Fig. 3 revealed that fluorescence emission centered at 522 nm increased as a function of salicyladehyde concentrations in aqueous soultion with a concentrations between 0.1 and 10 mM were observed, indicating fluorogenic detection of salicyladehyde. Probe 1 showed off-on emission toward salicylaldehyde and this method could be repeated (see ESI†, Fig. S3).

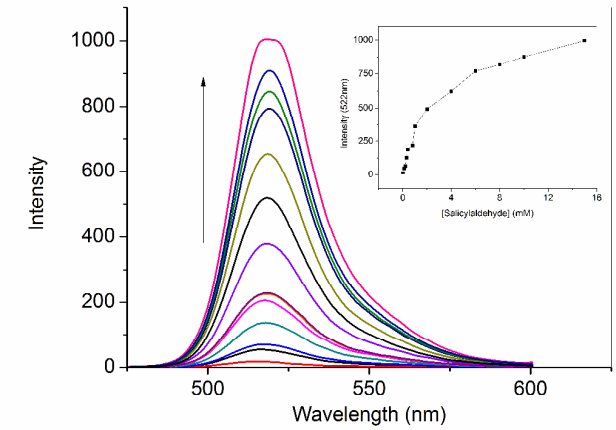

Fig. 3 Fluorescence emission spectra of Probe **1** (5 μM) in EtOH-H_2O solution in the prescence of salicyladehyde (0-15 mM). The inset shows the titration curve of salicyladehyde with Probe **1** by fluorescence emission intensity at 522 nm.

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To access the identity of the possible adduct in the assay conditions, the reaction product of probe **1** with salicylaldehyde was isolated and analyzed by HR-MS and ^{1}HNMR spectrometry. As shown in fig. 4, The major peaks located at 459.2155 and 563.2403 were identified, which were consistent with the theoretical molecular weight of the proposed products P1 ($C_{26}H_{26}BF_2N_4O^+$, M+H: 459.2167) and P2 ($C_{33}H_{29}BF_2N_4O_2^+$; M+H: 563.2430), confirming formation of schiff base in the assay system, as shown in scheme 2. Compound P2 was proposed the main product, and about 90% was obtained.

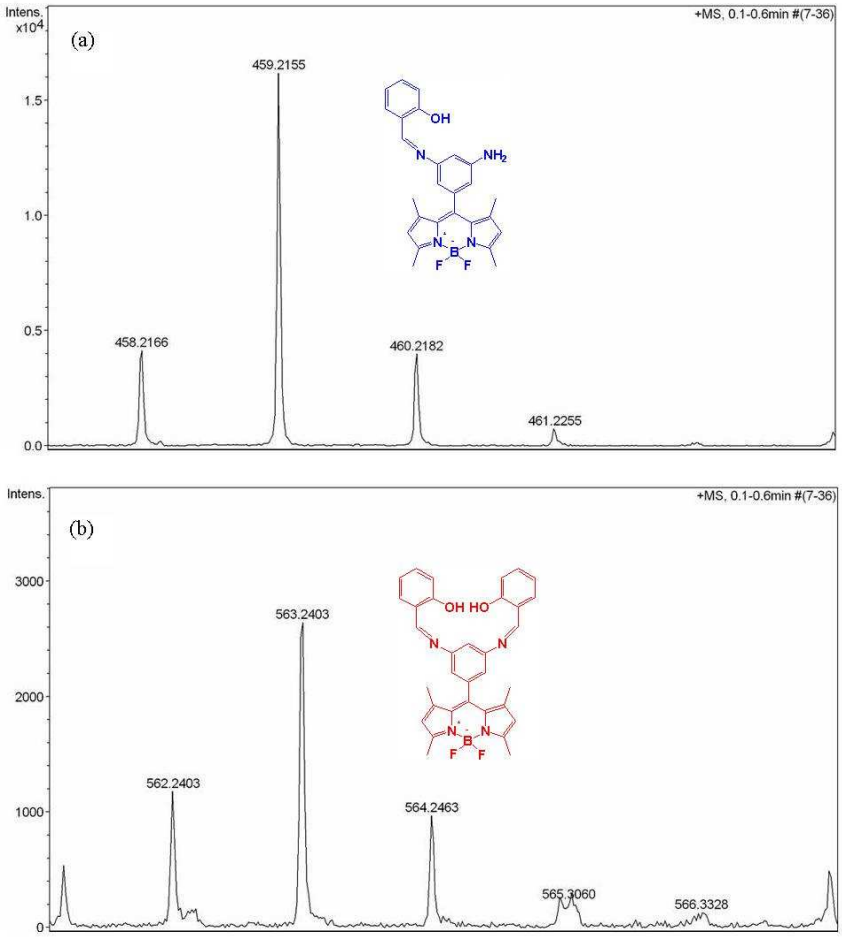

Fig. 4 HR MS spectra of reaction products of probe **1** with salicylaldehyde

From the ^{1}HNMR spectrum(see ESI†, Fig. S4 and S5), the chemical shifts of phenolic proton (OH) of the products P1 and P2 were 12. 86 and 12.85 ppm, respectively, which indicated that OH proton of the adduct formed intramolecular H-bonding with the imine nitrogen[10]. The intramolecular H-bonding resulted in a geometrically restricted six-membered

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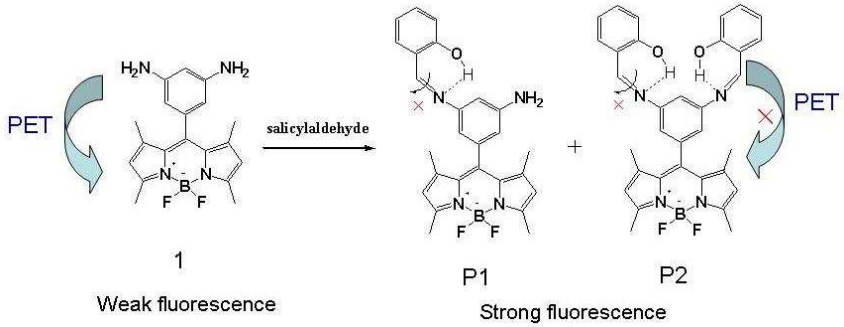
ring and enhanced the reactive activity. The formation of Schiff base suppressed the PET process and the intramolecular H-bonding inhibited the C=N isomerization[11] accounted for the turn on fluorescence response of probe **1** (Scheme 2).



Scheme 2 Proposed mechanism of the turn on fluorescence response of Probe **1** to salicylaldehyde.

Over the passed years, much attention has been focus on the sensors functioning in solution by means of spectroscopic instrumentation, which restricted the practical applications of the sensors. For simplicity, convenient and low cost test kits is highly demanding. We also examined whether Probe **1** could be employed for the sensing of aldehydes in the polymer metrics. For this purpose, a sensor film **F1** with a poly(methyl methacrylate) (PMMA)layer containing 0.5 wt% of Probe **1** were prepared. Sensor film **F1** was intitially nonfluorescent, when in contact with aqueous solutions containing salicylaldehyde, a bight fluorescent emission appeared in two minutes (Fig. 5). Again, probe **1** could function in polymer metric for the efficent detection of salicylaldehyde with off-on fluorescence response, which could be advantageous in application.

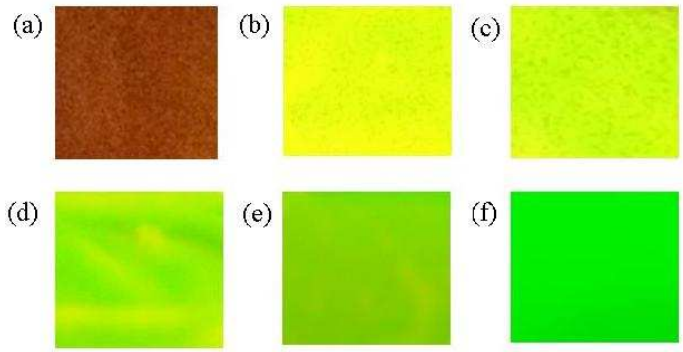


Fig. 5 Changes in fluorescene images (excitation at 365 nm with a UV lamp) of sensor film **F1** containing probe **1** upon contaction with salicylaldehyde solution. ([salicylaldehyde]:b~f, 0.1, 0.2, 0.5, 1, and 5mM)

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Conclusions

In conclusion, using a BODIPY fluorophore, we developed a PET and C=N isomerization-based OFF-ON probe **1** that can selectively detect tracing salicylaldehyde in aqueous solution under mild condition. The probe exhibits a clear salicylaldehyde induced changes in the intensity of emission spectra. When embedded in a polymer film, Probe **1** can also be employed for the fluorescent detection of salicylaldehyde in polymer metrics. The new PET -based probe **1** is expected to be utilized in a variety of chemical applications.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (20972170 and 21275150), the Funds for Distinguished Young Scientists of Gansu (1210RJDA013) & the Natural Science Foundation of Gansu province (1107RJYA069) and the "135" plan of Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.

Notes and references

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† Electronic Supplementary Information (ESI) available:

1. (*a*) N. Matyasovszky, M. Tian and A. C. Chen, *J. Phys. Chem.* A, 2009, **113**, 9348; (*b*) D. Janes and S. Kreft, *Food Chem.*, 2008, **109**, 293; (*c*) N. Radulovic, M. Misic, J. Aleksic, D. Dokovi, R. Palic, G. Stojanovic, *Fitoterapia*, 2007, **78**, 565; (*d*) P. Caboni, N. Aissani, T. Cabras, A. Falqui, R. Marotta, B. Liori, N. Ntalli, G. Sarais, N. Sasanelli and G. Tocco, *J. Agric. Food Chem.*, 2013, **61**, 1794;

2. Y. Ha, H. Liew, H. Y. Park, K. Kim, Y. H. Suh and D. G. Churchill, *Neurosci. Res.*, 2011 **71**, 168.

3. M. L. Liu, J. H. Deng, C. L. Lai, Q. Chen, Q. Q. Zhao, Y. Y. Zhang, H. T. Li and S. Z. Yao, *Talanta*, 2012, **100**, 229.

4. (*a*) D. L. Zhang, J. B. Zhang, M. J. Li, W. L. Li, G. Aimaiti, G. Tuersun, J. N.Ye, Q. C. Chu, *Food Chem.*, 2011,**129**, 206–212; (*b*) J. M.You, T. Yan, H. X. Zhao, Z. W. Sun, L. Xia, Y. R. Suo, Y. L. Li, *Anal. Chim. Acta*, 2009, **636**, 95; (*c*) I. G. Casella, M. Contursi, J. Chromatogr. A , 2005, **1063**,

Analytical Methods Accepted Manuscript

129; (*d*) Y. L. Xing, S. Wang, X. Z. Mao, X. B. Zhao, D. Z. Wei, *J. Fluoresc*., 2011, **21**, 587; (*e*) J. Gerlach, C. Reisinger, B. Pohn, H. Schwab, I. Klimant, Microchim. Acta, 2007, **156**, 209.

5. Important review for optical sensors (a) Y. Yang, Q. Zhao, W. Feng, F. Li, *Chem. Rev.*, 2013, **113**, 192; (b) X. Chen, T. Pradhan, F. Wang, J. Kim, J. Yoon, *Chem. Rev.*, 2012, **112**, 1910; (c) A. Bencini, V. Lippolis, *Coord. Chem. Rev*., 2012, **256**, 149; (*d*) Y. Zhou, J. Yoon, *Chem. Soc. Rev.*, 2012, **41**, 52.

6. methods for optical detection aldenhydes (*a*) H. Song, S. Rajendiran, N. Kim, S. K. Jeong, E. Koo, G. Park, T. D. Thangadurai and S. Yoon, *Tetrahedron Lett.*, 2012, **53**, 4913; (b)Z. Li, Z. W. Xue, Z. S. Wu, J. H. Han and S. F. Han, *Org .Biomol. Chem.*, 2011, **9**, 7652; (*c*) L. Feng, C. J. Musto and K. S. Suslick, *J. Am. Chem. Soc.*, 2010, **132**, 4046; (*d*) N. Jaffrezic-Renault and S.V. Dzyadevych, *Sensors* 2, 2008, **8**, 2569; (*e*) Y. Y. Maruo, J. Nakamura and M. Uchiyama, *Talanta*, 2008, **74**, 1141; (*f*) R. Pal and K. H. Kim, *J. Sep. Sci*., 2007, **30**, 2708; (*g*) L.T. Gibson, W. J. Kerr, A. Nordon, J. Reglinski, C. Robertson, L. Turnbull, C. M. Watt, A. Cheung and W. Johnstone, *Anal. Chim. Acta*, 2008, **623**, 109; (*h*) G. J. Mohr, *Anal. Bioanal. Chem.*, 2006, **386**, 1201; (*i*) K.Toda, K. I. Yoshioka, K. Mori and S. Hirata, *Anal. Chim. Acta*, 2005, **531**, 41; (*j*) K. Kawamura, K. Kerman, M. Fujihara, N. Nagatani, T. Hashiba, E. Tamiya, *Sens. Actuators, B*, 2005, **105**,495; (*k*) R. Yang, K. A. Li, F. Liu, N. Li, F. L. Zhao and Wi. H. Chan, *Anal. Chem.*, 2003, **75**, 3908;

7. BODIPY (a) N. Boens, V. Leen, W. Dehaen, *Chem. Soc. Rev.*, 2012, **41**,1130; (b) G. Ulrich, R. Ziessel, A. Harriman, *Angew. Chem. Int. Ed*., 2008, **47**, 1184; (c) A. Loudet, K. Burgess, *Chem. Rev.*, 2007, **107**, 4891; (d) L. Niu, Y. Guan, Y. Chen, L. Wu, C. Tung and Q. Yang, *J. Am. Chem. Soc.*, **2012**, 134, 18928; (e) A. Palma, L. Alvarez, D. Scholz, D. O. Frimannsson, M. Grossi, S. J. Quinn and D. F. O'Shea, *J. Am. Chem. Soc.*, 2011, **133**, 19618; (*f*)T. I. Kim, J. Park, S. Park,Y. Choi, Y. Kim, *Chem.Commun.*, 2011, **47**, 12640.

8. (*a*) J. Xu, Q. Li, Y. Yue, Y. Guo and S. J. Shao, *Biosens. Bioelectron.*, 2014, 56, 58; (*b*) . Li, Y. Guo and S. J. Shao, *Analyst*, 2012, **137**, 4497; (*c*) Q. Li, Y. Yue, Y. Guo and S. J. Shao, *Sens. Actuators. B Chem.*, 2012, **173**, 797; (*d*) Q. Li, Y. Guo and S. J. Shao, *Sens. Actuators. B C hem.*, 2012, 171-172, 872.

9. R. Ziessel, L. Bonardi, P. Retailleau and G. Ulrich, *J. Org. Chem.*, 2006, **71**, 3093.

10. Intramelcular H-Bonding (a) X. Chen, D. A. Walthall, J. I. Brauman, *J. Am. Chem. Soc.*, 2004, **126**, 12614; (b) X. J. Peng, Y. K.Wu, J. L. Fan, M. Z. Tian, K. L. Han, *J. Org. Chem.*, 2005, **70**,

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10524; (c) H. J. Kim, S. Bhuniya, R. K. Mahajan, R. Puri, H. G. Liu, K. C. Ko, J. Y. Lee and J. S. Kim, *Chem. Commun.*, 2009, 7128.

11. C=N isomerization (*a*) J. Wu,W. Liu, J. Ge, H. Zhang, P. Wang, *Chem. Soc. Rev.*, 2011, **40**, 3483; (b) M. Suresh, A. K. Mandal, S. Saha, E. Suresh, A. Mandoli, R. Di Liddo, P. P. Parnigotto, A. Das, *Org. Lett.*, 2010, **12**, 5406; (*b*) K. K. Upadhyay and A. Kumar, *Org. Biomol. Chem.*, 2010, **8**, 4892.

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Statement of Societal Impact

Salicylaldehyde is a common organic pollutant that builds up in the environment and neurotoxic having effect on α-synuclein aggregation, however the detection of salicylaldehyde has less been developed. In this work, we developed a new PET and C=N isomerization-based OFF-ON fluorescent probe **1** based on BODIPY fluorophore that can selectively detect tracing salicylaldehyde in aqueous solution under mild condition, which is expected to be utilized in a variety of chemical applications.

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A BODIPY based indicator for Fluorogenic detection of Salicylaldehyde with OFF-ON emission

Qian Li, Jian Xu,Ying Yue, Yuan Liao and Shijun Shao*

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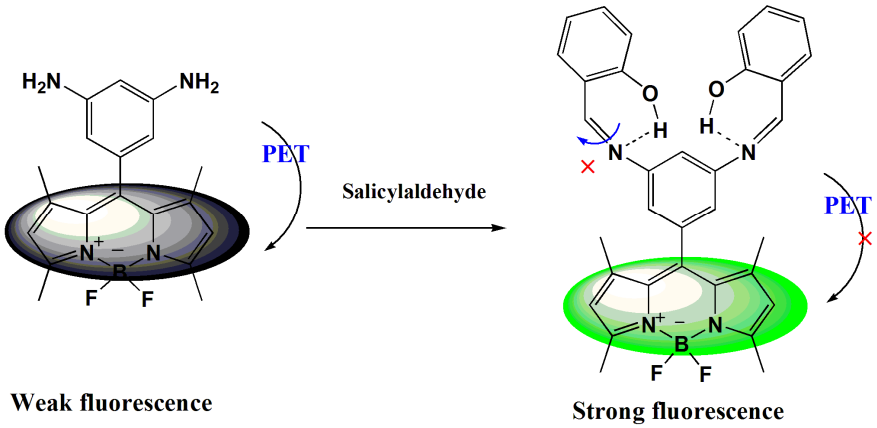
A turn-on fluorescent indicator **1** based on BODIPY derivative for the detection of salicylaldehyde in aqueous solution by fluorescence spectroscopy has been developed. The formation of Schiff base between probe **1** and salicylaldehyde suppressed the PET process and prohibited the C=N isomerization accounted for the fluorescence response of Probe **1**.



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Supporting information

A BODIPY based indicator for Fluorogenic detection of salicylaldehyde with OFF-ON emission

Qian Li, Jian Xu,Ying Yue, Yuan Liao and Shijun Shao*

Key Laboratory of Chemistry of Northwestern Plant Resources and Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China.
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Experimental

Apparatus and materials

^{1}H NMR spectra were recorded in DMSO-d6 solution on the Inova 400 MHz instruments, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. HR MS were carried out on QTof-Micro YA 263 instruments. And fluorescent spectra were recorded on a Perkin Elmer LS55 Fluorescence Spectrophotometer.

Synthesis

Synthesis of compound 2

To a solutionof 2,4-dimethylpyrrole (2 equiv.) in absolute CH_2Cl_2 solution was added the 3,5-dinitrobenzoyl chloride (1 equiv.).The solution was stirred at room temperature for 24 hours, the color changing slowly from pale brown to deep red. Et_3N (6 equiv.) was then added, followed by a subsequent addition of BF_3-Et_2O (8 equiv.). The mixture was stirred for another 6 hours at room temperature. The reaction was stopped by the addition of saturated aqueous $NaHCO_3$ (100ml), and then was washed 3 times with saturated aqueous $NaHCO_3$.The organic layer was then dried over $MgSO_4$, filtered and the solvent removed. Chromatography on silica gel (CH_2Cl_2/cyclohexane, 1:1 as eluent) gave the pure compound 2.

Synthesis of compound 1

Compound 2 (0.7 g, 1.9 mmol) was dissolved in 50 mL of absolute THF and 50 mL of absolute MeOH. After purged with N_2, 5%Pd/C(1.0g) and 2.0 ml hydrazine were added. The

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solution was stirred at reflux under N_2 for 5 hours. When TLC monitoring (silica gel; CH_2Cl_2) showed complete consumption of 2, the reaction mixture was filtered, and evaporated. The compound was purified by silica gel column chromatography (CH_2Cl_2 and CH_2Cl_2/MeOH as eluent) to give a red solid (83%). Recrystallized from CH_2Cl_2/n-hexane to afford orange crystals 1.

^{1}H NMR (DMSO-d6, 400 MHz): 6.13-6.18 (m, 2H), 5.89 (s, 1H), 5.67-5.68 (m, 2H), 4.95 (s, 4H), 2.41-2.48 (m, 6H), 1.68 (s, 6H).

HR-MS $C_{19}H_{21}BF_2N_4$, Anal. Calc. M+Na = 377.1723; Found 377.1734.

Which was consistent with the reported data.

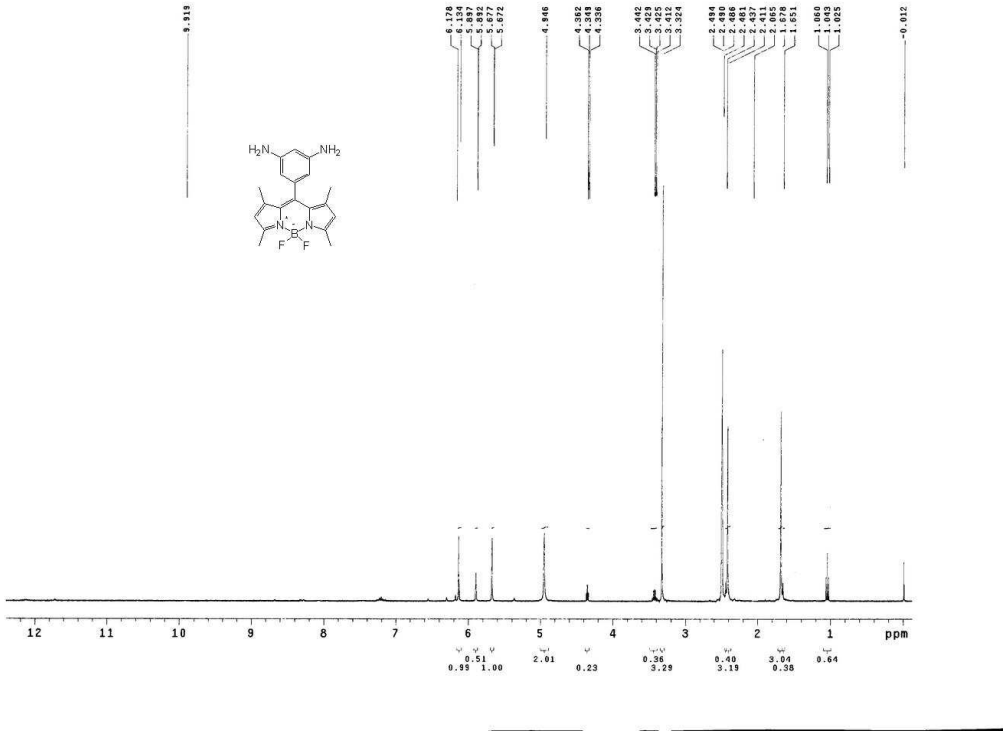

Fig. S1 ^{1}HN MR Spectra of probe 1.

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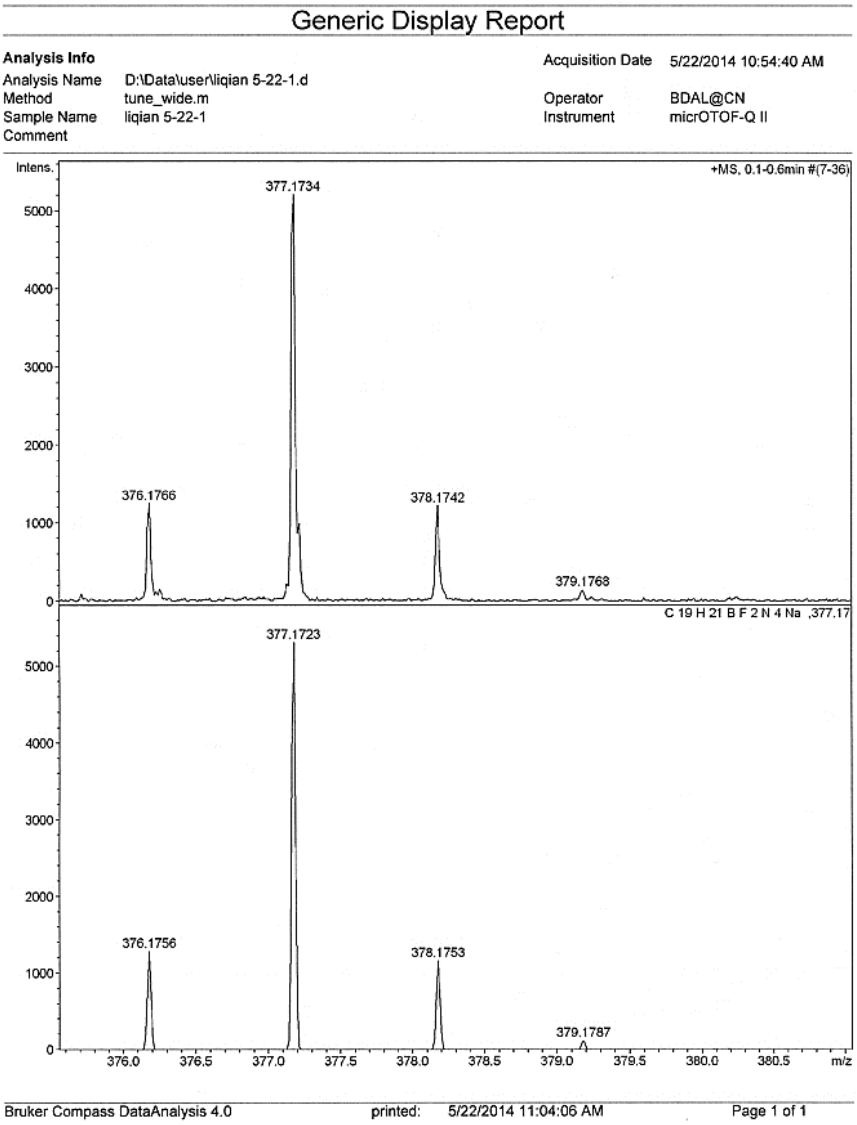

Fig. S2 HR-MS Spectra of probe 1.

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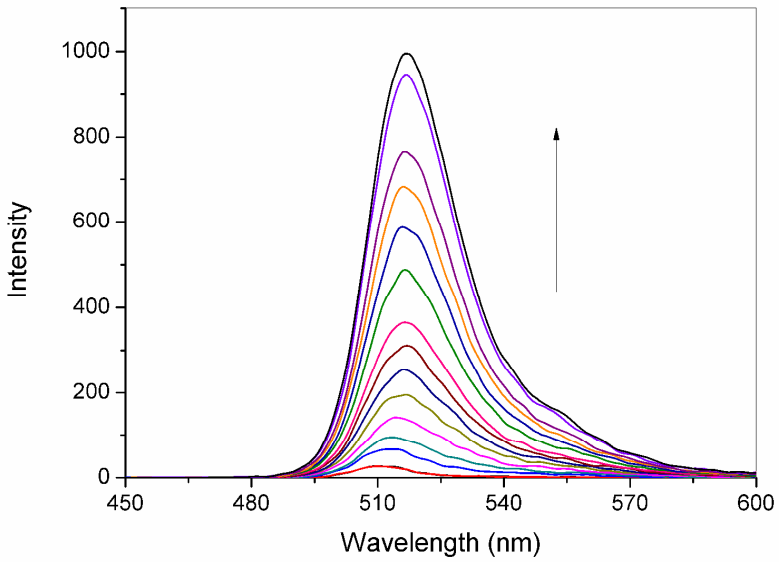

Fig. S3 Fluorescence emission spectra of Probe **1** (5 μM) in EtOH-H_2O solution in the prescence of salicyladehyde (0-15 mM). The inset shows the titration curve of salicyladehyde with Probe **1** by fluorescence emission intensity at 522 nm.

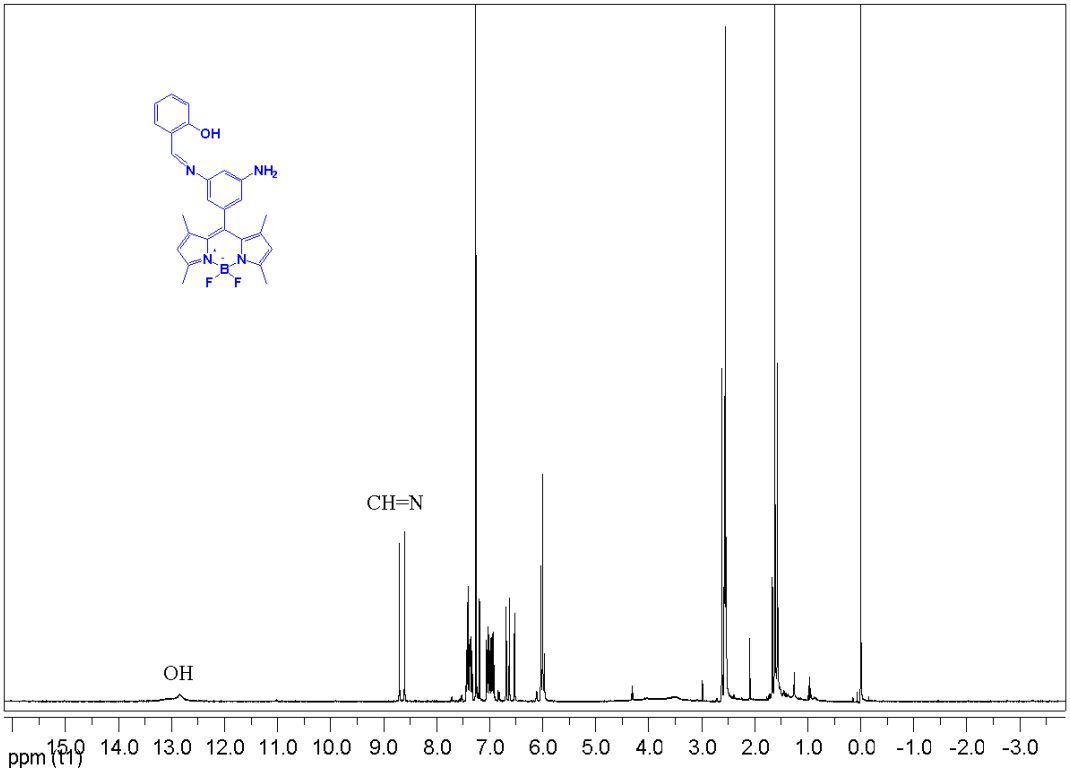

Fig. S4 ^{1}HN MR Spectra of reaction product P1 of probe 1 with salicylaldehyde

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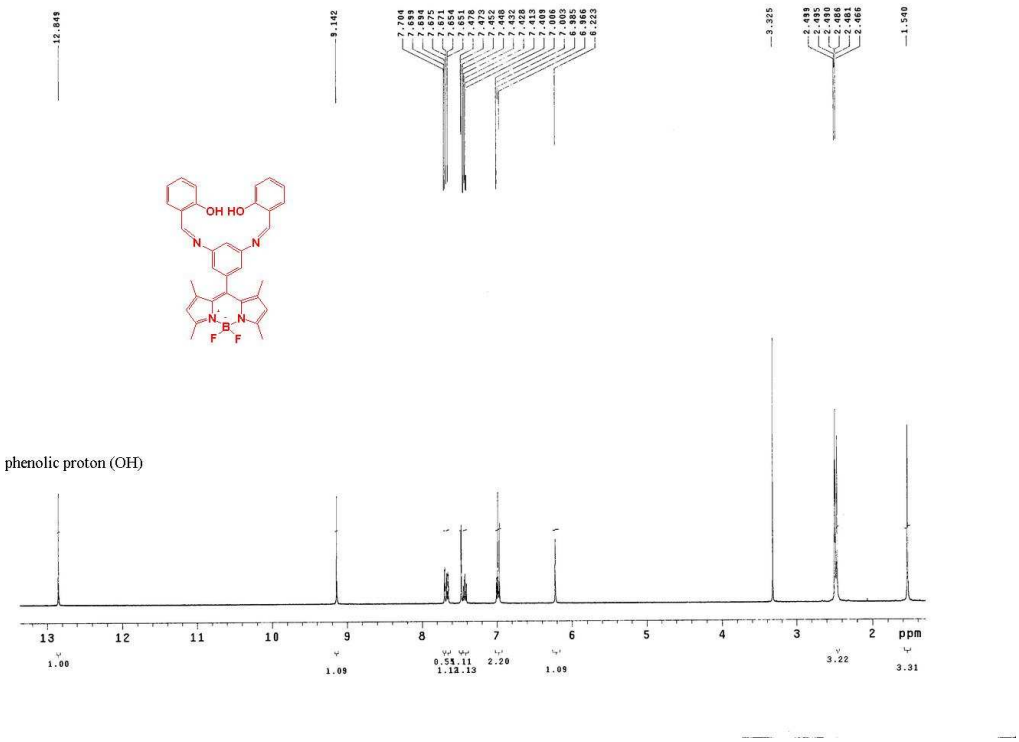

Fig. S5 ^{1}HN MR Spectra of reaction product P2 of probe 1 with salicylaldehyde

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