Article

A highly selective fluorescent chemosensor for Al^{3+} based on 2,2':6',2''-terpyridine with a salicylal Schiff base

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Received: date; Accepted: date; Published: date

Abstract: Two 2,2':6',2''-terpyridine-based Schiff bases (**TPySSB** and **TPySB**) have been synthesized. The **TPySSB** shows remarkable selective 'off-on' fluorescence for Al^{3+} by photoinduced electron transfer (PET) mechanism of sensing. Chemosensor **TPySSB** binds Al^{3+} in a 1:2 ratio with an association constant 6.8×10^5 ($R^2=0.98$) and this 1:2 stoichiometric model is established on Job's plot and ^1H NMR. Compared **TPySSB** and **TPySB**, it is of great importance of the existence of salicylidene unit due to its strong binding abilities of both phenol and C=N structure to the Al^{3+}.

Keywords: 2,2':6',2''-terpyridine; Salicylidene Schiff bases; Fluorescence sensor; Al^{3+}

1. Introduction

Al^{3+} ions exists in natural waters and most plants, which can enter the human body through food and water[1]. Since Al^{3+} is closely related to human health, much attention have been paid to developing new fluorescent chemosensors with high selectivity and sensitivity to detect Al^{3+} [2-7]. At present, fluorescent chemosensors have been widely used to detect different metal ions because of their high sensitivity, selectivity and fast response time[8-12]. Typically, metal ion chemosensors are composed of a metal binding unit and signaling unit, which enable the fluorescent chemosensors to coordinate with metal ions. Later on, fluorescent sensors based on a large group of structurally different metal binding units, including pyrazoline[13], peptide[14], salicylimine[15], tetrazole[16], triazole[17], 4,5-diazafluorene[7,8] and 2,2':6',2''-terpyridine (TPy)[18-20] have been developed. Among these receptors, 2,2':6',2''-terpyridine moiety is an ideal model for the construction of fluorescence sensors because of its excellent coordination ability with various metal ions[21]. Indeed, it has become one of the most important chemical sensors in supramolecular chemistry. There are reports about the detection of anion and cation by 2,2':6',2''-terpyridine based fluorescent chemosensor [22-25]. However, there is still no report about fluorescent sensing of Al^{3+} by 2,2':6',2''-terpyridine derivatives. Therefore, the design and preparation of 2,2':6',2''-terpyridine based fluorescent chemosensors are necessary for the construction and development of sensors for detecting Al^{3+} with high selectivity and sensitivity.

Salicylidene Schiff bases (SSB) has attracted increasing attention because they enable simple and inexpensive determinations of various metal ions. Over the past decades, it has been demonstrated that the presence of phenolic OH and the nitrogen atom of azomethine C=N double bond in Schiff base exhibits a strong affinity for transition metal ions[26,27]. Due to the formation of the chelatogenic cycle (metal-oxygen-nitrogen chain), the intramolecular charge transfer (ICT) was highly improved between the π-conjugated rings. Mostly, these kinds of molecules display unique emission enhancement due to strong binding abilities of both phenol and C=N structure to the metal ions. Therefore, combination of 2,2':6',2''-terpyridine and salicylidene Schiff base into a unique entity can give rise to an interesting system with very peculiar coordination properties. Herein, we report

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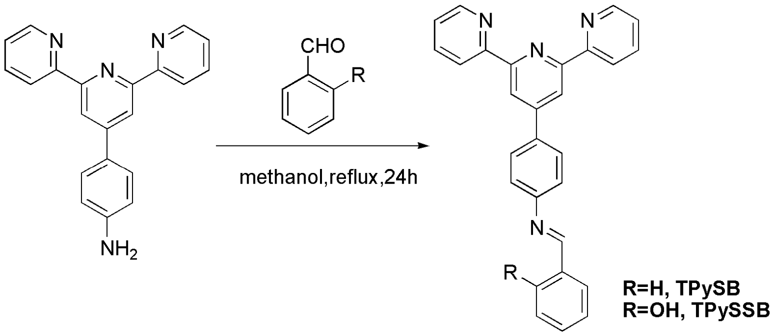
the design and synthesis of two new 2,2':6',2''-terpyridine Schiff base **TPySSB** and **TPySB**. Their binding properties toward metal ions have been investigated. The salicylidene Schiff base **TPySSB** could be used as efficient fluorescence probes for Al^{3+} with high selectivity. As being fluorescence chemosensor, **TPySSB** with phenolic OH groups shows better Al^{3+} sensing properties than TPySB due to the formation of terpyridine-Al^{3+} complex and chelatogenic cycle.

2. Results

2.1. Synthesis and Characterization



Scheme 1. Synthesis of **TPySSB** and **TPySB**

Synthesis of the Schiff base derivatives **TPySSB** and **TPySB** is shown in Scheme 1. Compound **TPySSB** (or **TPySB**) was synthesized by a condensation reaction between 4'-amine-2,2':6',2''-terpyridines and salicylaldehyde (or benzaldehyde) in refluxing methanol. The products were obtained in high yield and characterized by FT-IR and ^1H NMR, respectively. The FT-IR spectra (Figure S1) of compounds **TPySSB** and **TPySB** present the characteristic absorption of (C=N) vibration at 1622 and 1620 cm^{-1}, respectively. An O-H stretching band for **TPySSB** appears as a broad band centered at 3428 cm^{-1}. The ^1H NMR spectra of **TPySSB** and **TPySB** in acetone-d_6 exhibit the signals corresponding to the molecule as expected. The spectrum of **TPySB**, the chemical shift of -CH=N proton shifted downfield about 8.62 ppm (Figure S2). In the spectrum of **TPySSB** displays a singlet at 13.18 ppm corresponding to -OH. And the chemical shift of -CH=N proton shifted downfield about 8.96 ppm comparing with that of **TPySSB** (Figure S3)[28], which confirms the formation of an intermolecular hydrogen bonding of the phenol OH.

2.2. Recognition Experiment of Schiff base (**TPySSB** and **TPySB**) in the Presence of Various Metal Ions

To compare the fluorescence response behavior of Schiff base (**TPySSB** and **TPySB**) in the presence of various metal ions, the recognition experiment of Schiff base (**TPySSB** and **TPySB**) was investigated in ethanol at room temperature. As shown in Figure 1a, **TPySSB** alone and other cations all displayed a weak single fluorescence emission band at 528 nm when it was excited at 265 nm except for Al^{3+} and Pb^{2+}. Upon addition of Al^{3+}, **TPySSB** shows a large fluorescence enhancement at 516 nm due to the formation of **TPySSB**-Al^{3+} complex which inhibits photo-induced electron transfer (**PET**) process[29]. The selectivity of **TPySSB** for Al^{3+} has been plotted as a bar graph in Figure 1b. The fluorescence enhancement efficiency observed was 51-fold at 516 nm, which indicated the Schiff base **TPySSB** is a highly selective fluorescent sensor for Al^{3+}. **TPySB** alone displayed a weak single fluorescence emission band at 329 nm and 410 nm when it was excited at 258 nm. However, upon addition of various metal ions, almost all metal ions exhibited obviously fluorescence significant changes at 329 nm (Ag^+, Cu^{2+}, Fe^{3+}, Fe^{2+}, Cr^{2+} and Al^{3+}) or 410 nm (Co^{2+}, Mn^{2+}, Mg^{2+}, Pb^{2+}, Sr^{2+} and Zn^{2+}) except for alkali metals such as Na^+, K^+ and Li^+(Figure 1c), indicating the formation of metal-ligand complexes. These results prove that terpyridine ligand have strong ability to coordinate with metal ions. By analyzing the structure of **TPySSB** and **TPySB**, we can draw the following conclusions. it is of importance of the present of salicylidene unit due to strong binding abilities of both phenol and C=N structure to the Al^{3+}[30]. Besides, it is the chelation of nitrogen atom of 2,2':6',2''-terpyridine with Al^{3+}, which induced the efficient inhibition for the PET process, that improve the performance of the **TPySSB.** Surprisingly, a highly selective fluorescent sensor for Al^{3+} is designed by combining 2,2':6',2''-terpyridine unit and salicylidene unit.

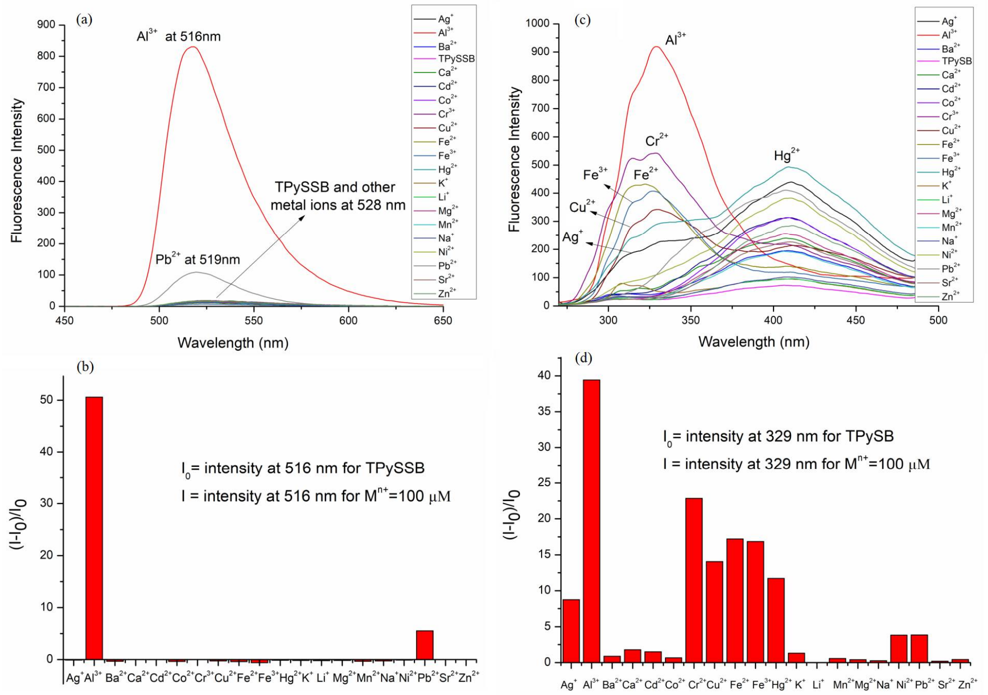


Figure 1. (a) The fluorescence spectra of the **TPySSB** (1×10^{-5} mol/L) in the presence of 10 equiv. of various metal ions in ethanol. Excitation wavelength (nm): 265; (b) The fluorescence spectra of the **TPySB** (1×10^{-5} mol/L) in the presence of 10 equiv. of various metal ions in ethanol. Excitation wavelength (nm): 258; (c) The fluorescence emission response profiles for **TPySSB** (1×10^{-5} mol/L) by adding various metal ions (1×10^{-4} mol/L) at 516 nm in ethanol; (d) The fluorescence emission response profiles for **TPySB** (1×10^{-5} mol/L) by adding various metal ions (1×10^{-4} mol/L) at 329 nm in ethanol.

*2.3. Selectivity Study of Schiff base (**TPySSB** and **TPySB**) for Al^{3+} over Competitive Metal Ions*

The selectivity of chemosensor for Al^{3+} in comparison to other competing metal ions is a very important parameter for evaluating their sensing performance. To further confirm the high selectivity of chemosensor **TPySSB** as selective fluorescent sensors for Al^{3+}, competitive selectivity experiments of chemosensor **TPySSB** toward various metal ions were examined in ethanol. In a single metal system (black bars), all the metal ions (Ag^{+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^{+}, Li^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Sr^{2+}, Pb^{2+} and Zn^{2+}) concentrations were kept as 100 μM towards **TPySSB**. However, for the dual-metal (red bars) studies, two equal amounts of aqueous solutions of Al^{3+} and other metal ions (100 μM+100 μM) were combined. Relatively low interferences were observed for the detection of Al^{3+} in the presence of other metal ions, except for Fe^{3+} (Figure 2). While compared of competitive selectivity experiments of chemosensor **TPySSB**, the results of chemosensor **TPySB** showed high interferences in the presence of other metal ions, except for alkali metals such as Na^{+}, K^{+} and Li^{+}(Figure S4). The unique selectivity of **TPySSB** towards Al^{3+} could be interpreted as the strong ability to coordinate with Al^{3+} of 2,2':6',2''-terpyridine unit and salicylidene unit.

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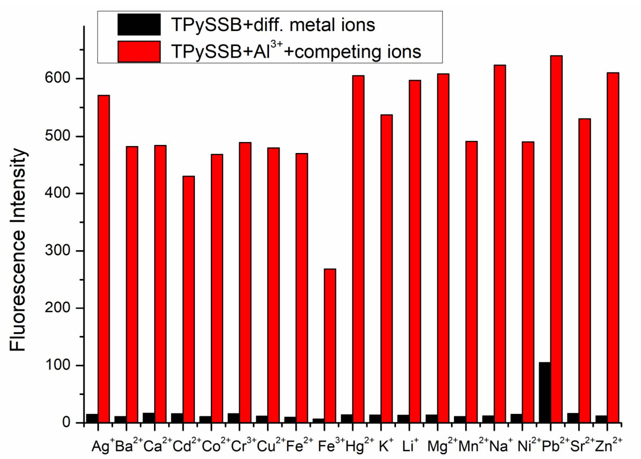

Figure 2. Fluorescence response of receptor **TPySSB** (1×10^{-5} mol/L). The black bar represents emission intensity after adding 10 equvi. selected metal ions in ethanol solution and red bar represent emission intensity after adding 10 equvi. of Al^{3+} ions in each of the above samples. Excitation wavelength (nm): 265

2.4. *Fluorescence Titration of Schiff base (**TPySSB**) in the Presence of Increasing Concentration of Al^{3+}*

Fluorescence titration experiments were carried out to gain insight into the binding interaction between **TPySSB** with Al^{3+}. With an increasing concentration of Al^{3+} resulted in a very small (8 nm) blue-shift of the emission maxima with a 14-fold enhancement of the fluorescence intensity (Figure 3a). The calibration curve is linear with a correlation coefficient (R^2=0.990) between the emission intensity at 516 nm and the Al^{3+} concentration from 30 to 90 μM (Figure 3b).

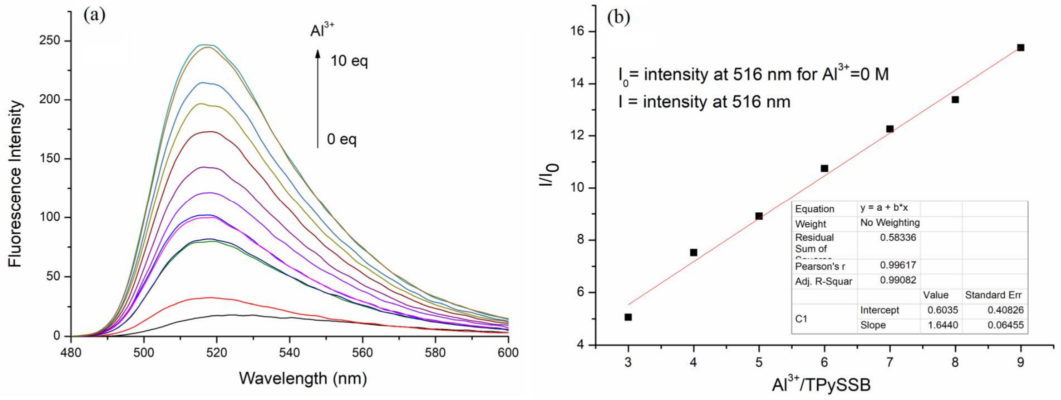

Figure 3. (a) Fluorescence emission spectra of receptor **TPySSB** (1×10^{-5} mol/L) in ethanol solution upon addition of increasing concentration of Al^{3+} (3-9 equvi.). Excitation wavelength (nm): 265; (b) fluorescence intensity at 516 nm versus the number of equivalents of Al^{3+} added

2.5. *UV-vis Titration of Schiff base (**TPySSB**) in the Presence of Increasing Concentration of Al^{3+}*

The chemosensor **TPySSB** toward various metal cations, Ag^+, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+} and Zn^{2+} are investigated by UV-vis spectroscopy in ethanol. The absorption spectrum of chemosensor **TPySSB** exhibited three absorbance peaks. The intense absorption band in high energy region at 210 nm and 275 nm was attributed to the π–π^* transitions of the terpyridine unit[31], and a broad band at 300 to 400 nm could be assigned to $\pi\rightarrow\pi^*$ transition of the C=N group from salicylidene moiety[32]. With the increasing concentration of Al^{3+}, the UV-vis spectrum appeared 14 nm red-shifted in the 210 nm band which was attributed to the form of 2,2':6',2''-terpyridine-Al^{3+} complex, and the absorption maximum at 350 nm decreased which was attributed to the form of salicylidene-Al^{3+} complex (Figure 4b). What' more, no significant absorption spectral change was observed for other cations under similar experimental conditions (Figure 4a).

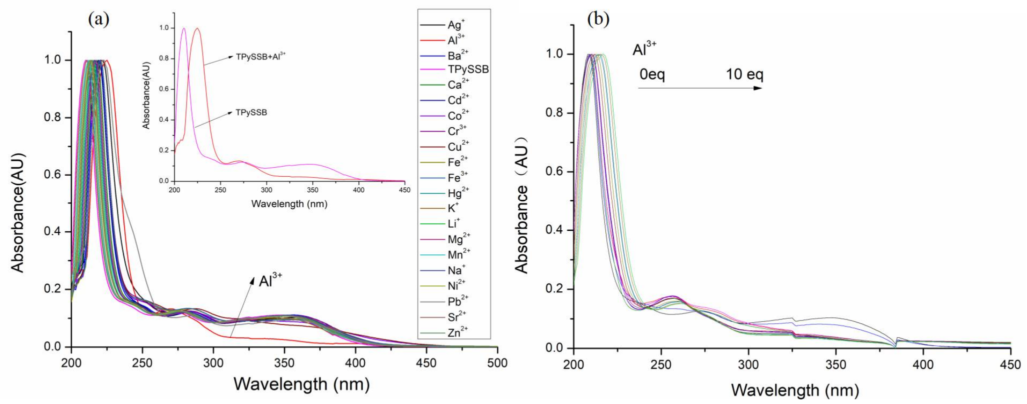

Figure 4. (a) The UV-vis spectra of the **TPySSB** (1×10^{-5} mol/L) in the presence of 10 equiv. of various metal ions in ethanol. (b) Change in absorption spectra of **TPySSB** (1×10^{-5} mol/L) upon addition of increasing concentration of Al^{3+} (0-10 equvi.) in ethanol

2.6. Job's plot measurements

To further explore the binding mechanism, the binding stoichiometry of **TPySSB** with Al^{3+} was investigated via a Job's plot of the fluorescence titrations of Al^{3+}, and the total concentration of Al^{3+} and **TPySSB** was kept as 20 μM as shown in Figure 5. A maximum absorption was observed when the molar fraction reached 0.7, which is indicative of a 1:2 stoichiometric complexation between **TPySSB** and Al^{3+} for the newly formed complex. The binding stoichiometry of **TPySB** with Al^{3+} was also investigated and the results indicated a 1:1 stoichiometric complexation between **TPySB** and Al^{3+} (Figure S5). Therefore, the introduction of the phenolic OH into the 2,2':6',2''-terpyridine-based Schiff base has led to new chemosensor with highly selective detection of Al^{3+}.

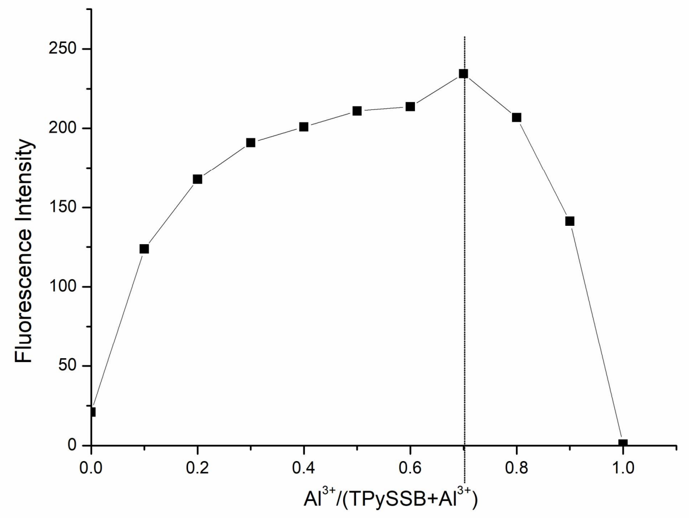

Figure 5. Job's plot for the complexation of **TPySSB** with Al^{3+} in ethanol.

2.7. Determination of Association Constant and Detection Limit

Based on the fluorescence titration of **TPySSB** with Al^{3+}, the association constant has been calculated to be 6.8×10^5 M^{-1} (Figure 6) by a Benesi-Hildebrand equation. The binding constants of the inclusion complex were obtained from the fluorescence titration data. According to the Benesi–Hildebrand method, the equation for a 1:2 host:guest complex is given below:

$$\log\frac{I-I_{\min}}{I_{\max}-I}=\log\left[M\right]^2-\log K_d \qquad (1)$$

In this equation K_d is the dissociation constant and different fluorescence emission intensity I_{min}, I and I_{max} are the find out at λ_{max}=516 nm, for the complex at initial, interval and the final state of complex. Concentrations of metal represent by M and association constant K_a was evaluated graphically by the plot of log [(I-I$_{min}$)/(I$_{max}$-I)] versus log[(Al^{3+})^2]. Figure 3b also further confirms the good linearity between enhancing efficiency (I/I$_0$) at 516 nm and concentrations of Al^{3+} in the range from 30 to 90 μM, indicating that sensor **TPySSB** can detect quantitatively relevant concentrations of Al^{3+}.

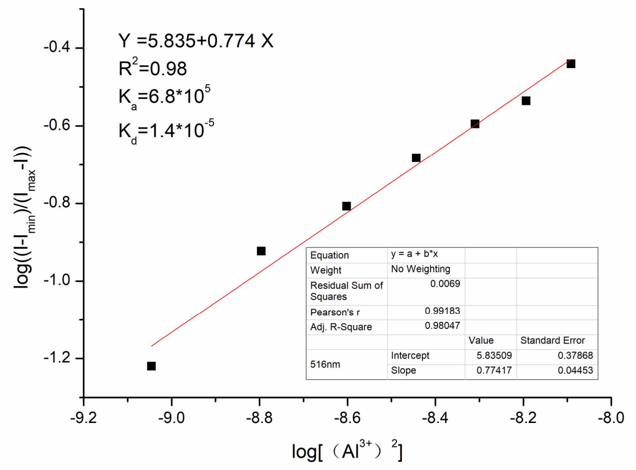

Figure 6. Hill plot of fluorescent probe (**TPySSB**+ Al^{3+}) at λ_{em}=516 nm

The detection limits (DLs) were calculated using the following equation:

$$DL = \frac{3\sigma}{S} \qquad (2)$$

where σ is the standard deviation of the blank measurement, which is 0.4 (n=11) here, and S is the slope between the emission intensity vs the concentration of aluminum ion. The detection limit of Al^{3+} is 3.32×10^{-7} mol/L

*2.8. Effects of solvent on the Sensing Properties of Schiff base **TPySSB** towards Al^{3+}*

Optical sensing nature of chemosensors was found to be depended on the solvent nature, so the response of **TPySSB** towards Al^{3+} was also examined in different solvents such as ethanol, DMF, methanol, THF, 1,4-dioxane at maxima of emission intensity. As shown in Figure 7, the optimum fluorescence enhancement occurred in ethanol. Other solvents such as the THF, 1,4-dioxane, DMF, methanol have no significant effect on the intensity of fluorescent. So ethanol was chosen as solvent.

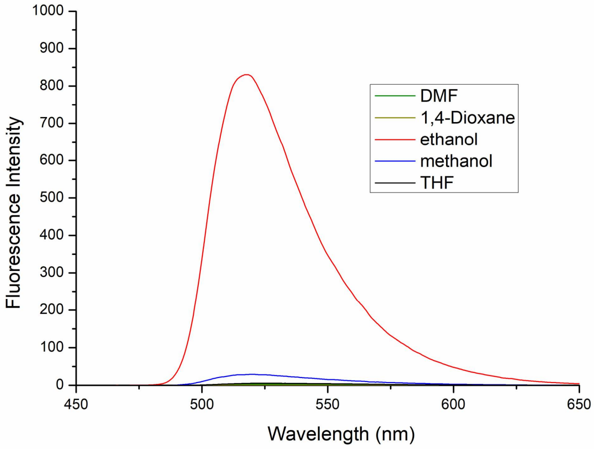

Figure 7. The fluorescence spectra of the ***TPySSB*** (10 μM) in the presence of 10 equiv. of Al^{3+} in different solvents. Excitation wavelength (nm): 265.

2.9. Proposed Binding Mechanism

To gain a clearer understanding of the structure of **TPySSB**-Al^{3+} complex, we used IR spectroscopy to obtain structural information about Al^{3+} binding in **TPySSB**. For the free compound TPySSB, the C=N group of azomethine in Schiff base showed a characteristic IR peak at 1573 cm^{-1}, and the C-O group of salicylidene in Schiff base showed a characteristic IR peak at 1188 cm^{-1}. Upon addition of Al^{3+}, the characteristic IR peak at 1573 and 1188 cm^{-1} disappeared, and new characteristic IR peak at 1703, 1523 and 1385 cm^{-1} appeared (Figure 8). This suggested that the phenolic OH, the nitrogen atom of azomethine and the pyridine participates in the coordination with Al^{3+}.

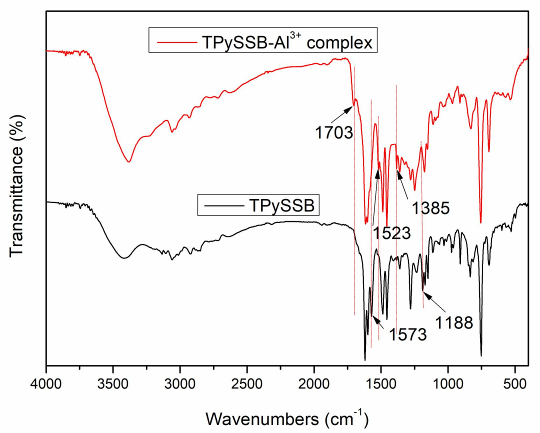

Figure 8. FTIR spectra of chemosensor **TPySSB** and **TPySSB**-Al^{3+} complex.

The complexation of **TPySSB** and Al^{3+} was also supported by Al^{3+} induced chemical shift of **TPySSB** changes in the ^1H NMR spectra. In the presence of 2.1 equivalents of Al^{3+} ions, chemical shift of proton NMR signals corresponding to the proton of the phenolic OH and azomethine-H got disappeared (Figure 9). Based on above IR spectroscopy, NMR spectroscopy studies and Job's plot, the proposed binding model of **TPySSB** with Al^{3+} was shown in Figure 10. The chemosensor **TPySSB** is the most likely to chelate Al^{3+} via its oxygen on phenolic group and nitrogen on the azomethine and pyridine. The capture of Al^{3+} resulted in the photoinduced electron transfer (PET) electron from **TPySSB** to Al^{3+}; thus, TPySSB showed a significant fluorescence enhancement for Al^{3+} and provided a high selectivity for Al^{3+} over the other tested metal ions.

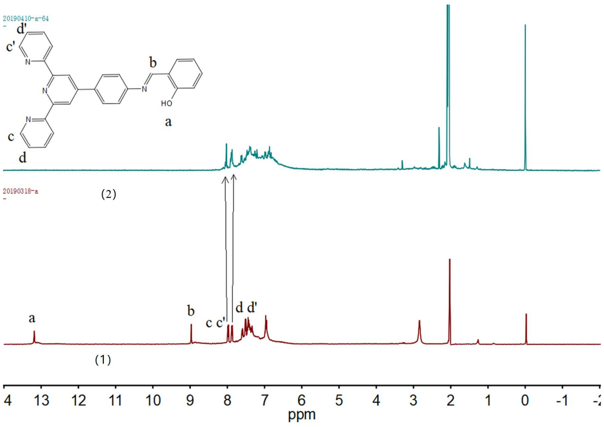

Figure 9. ^1H NMR spectra of **TPySSB** with $Al(NO_3)_3·9H_2O$ in acetone-d_6 (1) **TPySSB**; (2) **TPySSB** with 2.2 equiv. of Al^{3+} complex.

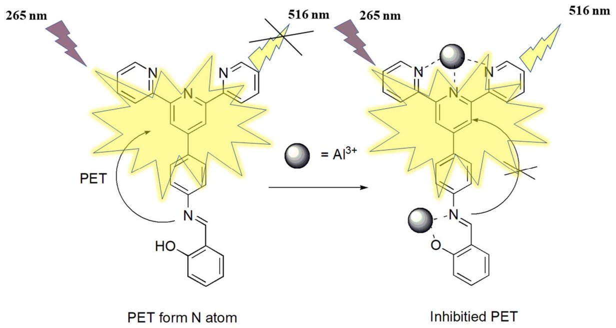

Figure 10. Proposed mechanism for the fluorescent sensing of **TPySSB** to Al^{3+}.

3. Materials and Methods

3.1. Materials and Instruments

4'-amine-2,2':6',2''-terpyridines was synthesized by a method previously described in the literature[33]. Salicylaldehyde and benzaldehyde were purchased from Innochem and used without further purification. All organic solvents were of analytical reagent grade. The metal ions were NaCl, KCl, $CaCl_2$, $MgCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $ZnCl_2$, $BaCl_2{\cdot}2H_2O$, $HgCl_2$, $CoCl_2{\cdot}6H_2O$, $MnCl_2{\cdot}4H_2O$, $FeCl_2{\cdot}4H_2O$, $FeCl_3{\cdot}6H_2O$, $CrCl_3{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Pd(NO_3)_2$, $Al(NO_3)_3{\cdot}9H_2O$, $AgNO_3$. All the metal ion solutions for the study were prepared in distilled water. The ^1H NMR and ^{13}C NMR spectra were measured on a JEOL EX-400 spectrometer using acetone-d_6 as solvent and tetramethylsilane as the internal reference. UV-vis spectra were examined on a Lambda 35 spectrophotometer and fluorescent recorded on a LS-55 spectrofluorophotometer.

3.2. Synthesis

3.2.1. Synthesis of the salicylidene Schiff base (**TPySSB**)

4'-amine-2,2':6',2''-terpyridines (0.324 g, 1 mmol) was placed into a 100 ml round-bottom flask with condenser, thermometer and magnetic stirrer. Methanol (40 ml) was added into the flask and reaction mixture was heated up to 80 °C. A solution of salicylaldehyde (0.122 g, 1 mol) in 10 ml methanol was added into the flask. Reactions were maintained for 24 h under reflux. The resulting solution was cooled to room temperature to give yellow powder, which was filtered, washed with methanol and dried under vacuum to obatin yellow powder product. (0.35 g, yield: 82.4%). FT-IR (KBr, cm^{-1}, Figure S1): 3410 cm^{-1} (O–H), 3054 cm^{-1} (C–N), 1622 cm^{-1} (C=N), 1573 cm^{-1} (C=C), 1493 and 1454 cm^{-1} (C=N), 1279 cm^{-1} (C–O); ^1H NMR (Acetone-d_6, δ, ppm, TMS, Figure S2): 13.18 (*s*, -OH), 8.96 (*s*, -N=CH), 7.96 (*d*, *J*=8 Hz, 2H), 7.86 (*d*, *J*=8 Hz, 2H), 7.58 (*d*, *J*=8 Hz, 2H), 7.49 (*d*, *J*=8 Hz, 2H), 7.31-7.46 (*m*, 8H), 6.94 (*d*, *J*=8 Hz, 2H).

3.2.2. Synthesis of the Schiff base (**TPySB**)

The Schiff base (**TPySB**) was also synthesized by the same method. (0.37 g, yield: 89.8%). FT-IR (KBr, cm^{-1}, Figure S1): 3059 and 3026 cm^{-1} (C–N), 1620 cm^{-1} (C=N), 1517 cm^{-1} (C=C), 1446 cm^{-1} (C=N); ^1H NMR (Acetone-d_6, δ, ppm, TMS, Figure S3): 8.56 (s, -N=CH), 8.02-6.73 (m, 19H).

5. Conclusions

In summary, we have developed two new 2,2':6',2''-terpyridines-derived Schiff base chemosensors (**TPySSB** and **TPySB**) for the highly selective determination of Al^{3+} in ethanol. The sensing property of **TPySSB** and **TPySB** was studied by UV-vis, fluorescence FT-IR and ^1H NMR experiments. Upon addition of metal ions, the **TPySSB** shows remarkable ‘off-on’ fluorescence for Al^{3+}. Moreover, it displayed excellent selectivity to Al^{3+} with a 1:2 binding mode which was proposed based on a Job’s plot and confirmed by ^{1}H NMR analysis. Based on these results, we believe that combining 2,2':6',2''-terpyridine unit and salicylidene unit will offer an important guidance to the development of a highly selective chemosensor base on 2,2':6',2''-terpyridine unit.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure S1: FT-IR spectrum of **TPySB** and **TPySSB**, Figure S2: ^{1}H NMR spectrum of TPySSB, Figure S3. ^{1}H NMR spectrum of TpySB, Figure S4. Fluorescence response of receptor TPySB (1×10^{-5} mol/L). The black bar represents emission intensity after adding 10 equvi. selected metal ions in ethanol solution and red bar represent emission intensity after adding 10 equvi. of Al^{3+} ions in each of the above samples. Excitation wavelength (nm): 258, Figure S5. Job's plot for the complexation of TPySB with Al^{3+} in ethanol.

Author Contributions: conceptualization, Hui Li and Jianzhi Wang; resources, Feng Wang; data curation, Yuling He; writing—original draft preparation, Hui Li; writing—review and editing, Qingyao Fu.

Funding: This research was funded by the National Natural Science Foundation of China, grant number 51808414, China Postdoctoral Science Foundation, grant number 2017M612520, National Science Foundation of Hubei Province of China, grant number 2016CFB264 and 2018CFB108 and the Program of Hubei Provincial Department of Education, China, grant number Q20171507.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Supplementary data.

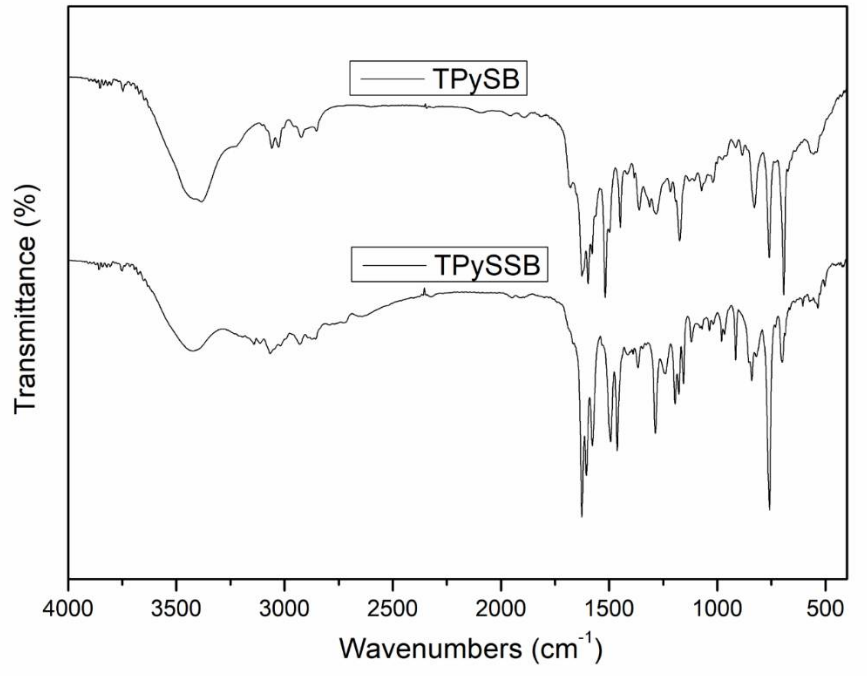

Figure S1. FT-IR spectrum of **TPySB** and **TPySSB**

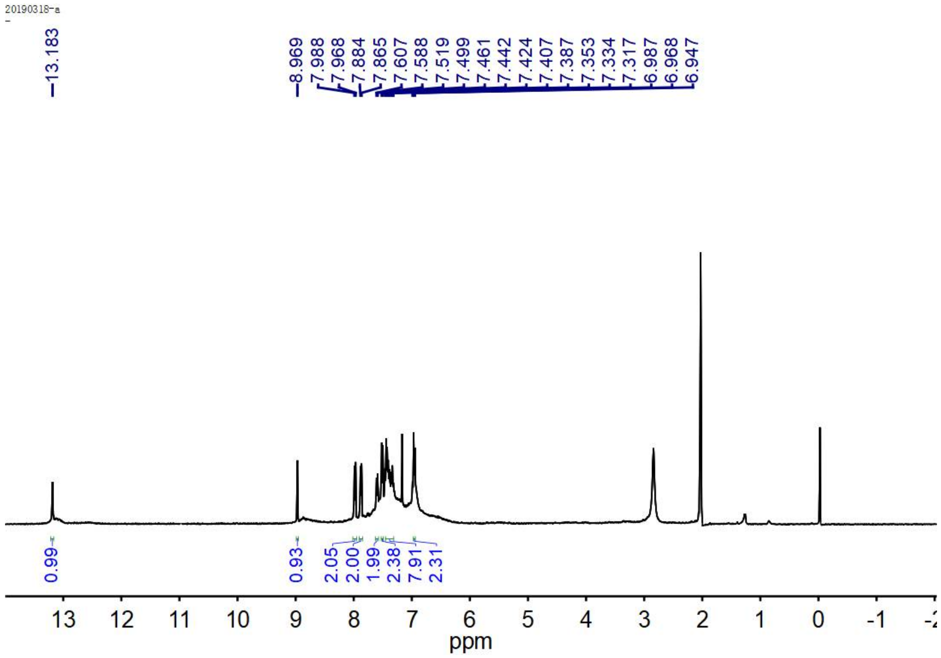

Figure S2. ^{1}H NMR spectrum of TPySSB

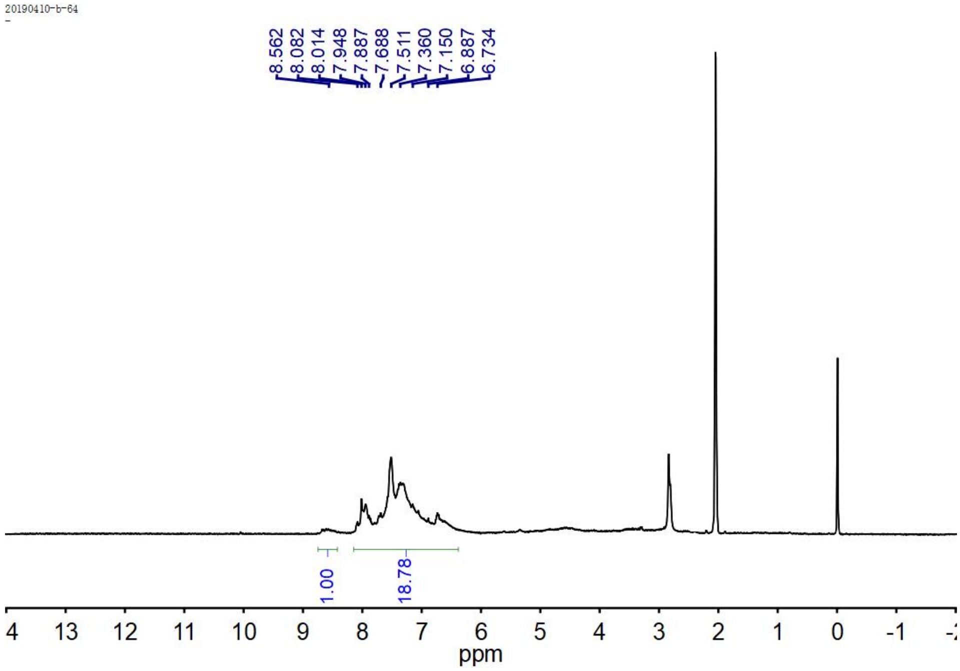

Figure S3. ^{1}H NMR spectrum of **TpySB**

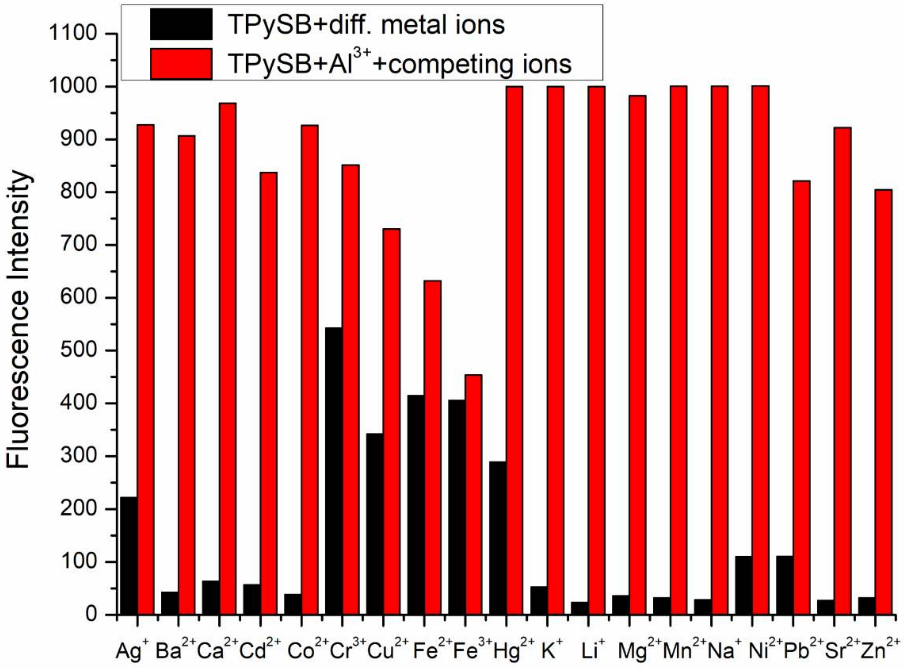

Figure S4. Fluorescence response of receptor **TPySB** (1×10^{-5} mol/L). The black bar represents emission intensity after adding 10 equvi. selected metal ions in ethanol solution and red bar represent emission intensity after adding 10 equvi. of Al^{3+} ions in each of the above samples. Excitation wavelength (nm): 258

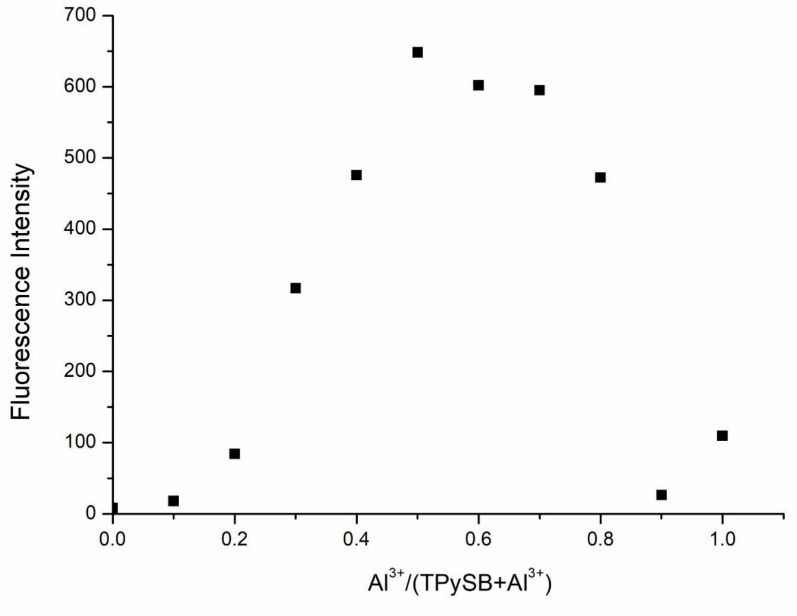

Figure S5. Job's plot for the complexation of **TPySB** with Al^{3+} in ethanol.

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