Research on Dss-I Polymer Probe Based on Schiff Base Dss Probe

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Abstract. 4, 4'-diamino diphenyl sulfone and salicylaldehyde as the main raw material, can be synthesized DSS-I polymer probe based on Schiff base. The DSS-I polymer probe have a similar property with DSS probe, and UV and fluorescence responses to F- and CN- were observed. Although UV color effect weakened, but they have strong fluorescence characteristics, and the fluorescent color is in some changes.

1. Introduction

Schiff base, which is formed by condensation of amine and active carbonyl group, is a kind of compound with important application value. Its structure contains -C=N, and the double-bond group has good coordination performance and spectral activity. In terms of cation recognition, it can with many metal ions to form complexes, and at the same time, in terms of anionic detection, due to the good chemical activity of C = N, Schiff base is still can be used as addition reaction. the reaction of cyanide ion sites at the same time Schiff bases containing active hydrogen can also go through the proton become good anion receptors. In view of its unique structure and properties, Schiff base and its complexes have been widely used in such fields as biological pharmacological activity, anticancer, anti-inflammatory, antibacterial and antitoxic activity, REDOX, photomagnetic materials, catalytic activity and photochromic properties. In addition, Schiff base has good luminescence properties, and - CH = N form about 120° Angle with good coordination effect [1], so as ion probe molecule, it has become a hot spot.

However, it can still be found that probe molecules designed and prepared in many cases are difficult to select multiple ions in multiple channels at the same time through referring to relevant literatures. At the same time, anion probes designed by many studies can only be detected in the presence of high organic solvents [2].

Therefore, the purpose of this study is to make the best use of the mature structure of Schiff base probe DDS to synthesize an anionic probe that can effectively detect F- and CN- under UV-vis and fluorescence channels, and expand the application ability of this probe through macromolecule and functionalization. It is proposed to synthesize a polyschiff base approximation or replace the original anion probe by a new polymerization method. The probe was polymerized into adsorbent
macromolecules with light crosslinking by phenolic resin polymerization. At the same time, relevant performance studies were carried out.

2. Material and methods

2.1. Synthetic materials and instrumentation

**Instruments:** Fourier infrared spectrometer (NEXUS-470), Thermo Nicolet, USA; nuclear magnetic resonance Varian mercury-plus 400, Varian, inc. Uv-visible spectrophotometer (TU-1810), Beijing purdue general instruments co., LTD. Fluorescence spectrophotometer (TU-1810), Hitachi, Japan; High resolution mass spectrometer (Ionspec 4.7), Ionspec, USA.Element analyzer (Vario EI), Elementar, Germany; Constant temperature culture shaker (THZ-103B), Shanghai yiheng instrument co., LTD. Type ii digital ion meter (PXJ-1B), jiangsu jiangfen electric analysis instrument co., LTD.

**Reagent:** 4,4 ’-diaminodiphenyl sulfone, 98%, Aladdin reagent co., LTD.Salicylaldehyde, 99%, Aladdin reagent co., LTD. Methanol,N,N ’-dimethyl formamide, glacial acetic acid, sodium hydroxide, citric acid, sodium citrate, analytically pure, Beijing tongguang fine chemical company; 1,3, 5-trioxane, analytical pure, Aladdin reagent co., LTD.Concentrated sulfuric acid, 95-98%, Beijing tongguang fine chemical company; Formaldehyde solution, 30%, tianjin guangfu fine chemical research institute, Fluorochem Ltd.

2.2. Synthesis

**Synthesis of DSS-I polymer probe:** It is found that DSS monomer itself does not have the potential as a linear polymer monomer. To synthesize compounds containing the same as the DSS structure unit, first of all, take 0.45 g of melamine formaldehyde with 3 mL salicylic aldehyde in 0.3 mL of concentrated sulfuric acid and mixed acid catalyst under the conditions of 9 mL glacial acetic acid (90°C) reaction 2 h - 4 h can be solid yellowish gray, namely salicylic aldehyde dimers; The pure binary aldehydes were obtained by washing with petroleum ether and drying with water. Finally, binary aldehydes and diaminodiphenyl sulfone were uniformly mixed in DMF solution at a ratio of 1:1 to obtain DSS-I functional resin. The synthesis route is shown in figure 1.

![Figure 1 Synthesis of DSS-I resin](image)

By adding ice ethanol, DSS-I resin viscose can be precipitated out of DMF reaction solution, and light yellow solid can be precipitated out after vacuum drying, and DSS-I infrared spectrum can be obtained by KBr tablet pressing method, as shown in **figure 2:** 3500 cm⁻¹ in a broad peak, and is accompanied by two small shoulder peak, can be thought of as - OH on the benzene ring and 4, 4’-diamino diphenyl sulfone in DSS-I base - NH₂ formed in the end, 2900-3000 cm⁻¹ shows for stretching vibration of CH2, 1700 cm⁻¹ for carbon and nitrogen - CH = N stretching vibration peak, while O = S = O characteristic peak at 1150 cm⁻¹, display products and peak on the ownership of the whole.
d6-DMSO was used as the deuterium substitute reagent to test the NMR hydrogen spectrum of DSS-I, as shown in figure 3: the attribution of several active hydrogen contained in the compound was basically normal, and the attribution of active hydrogen of -CH=N could be found from $f=7.9$, $f=10.22$ for hydrogen of -CH$_2$O, $f=10.66$ for hydrogen of Ph-OH. Meanwhile, hydrogen in the benzene ring is located between $f=6.0$-7.8. It can be basically seen from 1H NMR that the condensation polymerization of aldoamine is basically completed.

3. Results and discussion

3.1. DSS-I Polymer probe ion recognition test
Firstly, a solution of $1\times10^{-5}$g/L DSS-I was prepared, and the tetrabutyl ammonium salt of each anion was added at 20 uM. In naked eye detection experiments, the DMF solution DSS-I can and F$^-$ and CN$^-$ shows a different on the color of the blank sample, the color of the DSS monomer itself with the first chapter is relatively similar, but the color effect obviously weakened slightly, while in other ions in solution (Cl$^-$, Br$^-$ and I$^-$, OAc$^-$, PF$_6^-$, HSO$_4^-$, SO$_4^{2-}$ and ClO$_4^-$), no obvious changes, the naked eye pictures as shown in figure 4.
As shown in figure 5, scanning the sample between 220 nm to 800 nm ultraviolet spectrum can be found that DSS - I and the DSS - I solution contained some anions (Cl\(^-\), Br\(^-\), I\(^-\), OAc\(^-\), PF\(_6^-\), HSO\(_4^-\), SO\(_4^{2-}\) and ClO\(_4^-\) ) does not appear new absorption peak, and after joining the F\(^-\), a new absorption peak can be seen at 450 nm. Similarly, after joining CN\(^-\) a new absorption peak can be seen at 580 nm, both can explain that the DSS - I polymer probe has selective recognition effect of recognizing F\(^-\) and CN\(^-\).

![Figure 5](image)

**Figure. 5** Ion selective UV-vis spectrum of DSS-I

By further testing the titration curves of UV-vis (the concentration of F\(^-\) and CN\(^-\) increases from 0 to 40 uM, respectively), the response of DSS to the concentration of F\(^-\) and CN\(^-\) can be effectively observed. The titration curve of F\(^-\) is shown in figure 6(a), and the titration curve of CN\(^-\) is shown in figure 6(b).

![Figure 6](image)

**Figure. 6** UV-vis titration curves of DSS-I

Experimental results show that with the increase of concentration of CN\(^-\), absorbance at 340 nm decay gradually, and had obviously increased in the 565nm (DSS monomer at 525 nm). In F\(^-\) test results, we found that the 450 nm absorbance values increase with the addition of F\(^-\) (DSS monomer at 480 nm). From the comprehensive analysis, it can be found DSS - I has more effect of recognizing F\(^-\) and CN\(^-\) comparing with DSS.

### 3.2. Fluorescence selectivity test of DSS-I polymer probe

After the uv-vis experiment, we naturally thought that dss-i also had the possibility of selective recognition in the fluorescence channel. Similarly, fluorescence photos can distinguish F- and CN- visually, as shown in figure 7.
DSS solution (1×10⁻⁵ g/L) and anionic solution (Cl⁻, Br⁻ and I⁻, OAc⁻, PF₆⁻, HSO₄⁻, SO₄²⁻ and ClO₄⁻) were also prepared. Fluorescence intensity of each sample at 360nm-690nm can be measured by the excitation wavelength of λ=350nm. It can be found that the fluorescence intensity at 390nm, 600nm and 490nm has a more than 400% enhancement effect after the interaction of F⁻ and CN⁻ with DSS. The fluorescence spectra of each ion are shown in figure 8.

Similar to the UV spectrum test, the fluorescence response of DSS-I was tested by the interaction of 0-40 uM ion pattern with DSS-I. FIG. 9 (left) shows the fluorescence titration curve of F⁻, and FIG. 9 (right) shows the fluorescence titration curve of CN⁻. The titration results showed that the fluorescence intensity at 390nm and 600nm increased gradually as the concentration of F⁻ increased, and the fluorescence intensity at 490nm increased gradually as the concentration of CN⁻ increased.
4. Conclusions
A new polyschiff base DSS-I probe was designed and synthesized, which successfully improved the disadvantage of poor solubility of DSS probe. In terms of ion detection, both UV-vis and fluorescence spectra were successfully widened to the peak positions of two kinds of ions, making it easier to distinguish the two kinds of ions in the two kinds of analytical spectra.

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