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"Turn-On" Conjugated Polymer Fluorescent Chemosensor for Fluoride Ion

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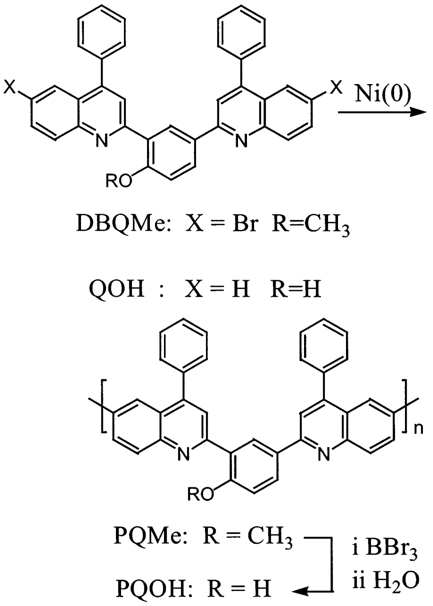
Fluorescent chemosensors have attracted much attention due to their potential applications in chemistry and biology.[1] The research of conjugated polymer-based fluorescent chemosensors is emerging as an area of current interest in these years.[2] Most conjugated polymer fluorescent chemosensors are based on the fluorescence quenching effect of the conjugated polymers.[3] However, there are very few examples of conjugated polymer fluorescent chemosensors exhibiting a dramatically brighter response, although the "turn-on" sensors in which the fluorescent intensity enhances greatly from its initial low level upon the addition of an analyte would be much more desirable.[4] To our best knowledge, most conjugated polymer fluorescent chemosensors have been used to sense positively charged or neutral species.[5] Only a few of them are constructed for the detection of negatively charged species,[6] although many anions (such as fluoride, chloride, and phosphate ions) are important in numerous biological and chemical processes.[7] It is clear there is a need for developing the "turn-on" anion fluorescent chemosensors based on conjugated polymers. Of the conjugated polymers, polyquinolines have been studied as a kind of fluorescent chemosensors according to the prior works of Jenekhe and Bunz et al.[8] Here we report a conjugated polyquinoline with hydroxyl side group (PQOH),[9] which not only is a highly selective chemosensor for F^- ion but also exhibits large fluorescent enhancement upon the addition of F^- ion. Its design is based on the consideration that the hydroxyl group will interact with anion through the hydrogen-bonding interaction or the formation of salt complex in the organic phase,[10] and such interactions may influence both absorption and the fluorescence spectra.

PQOH was synthesized through a two-step process (Scheme 1): (1) the preparation of PQMe by the nickel(0)-catalyzed coupling reaction; (2) the demethylation of PQMe by reacting with BBr_3 followed by water as the method described by Jen et al.,[11] and nearly quantitative conversion could be confirmed by the disappearance of the peaks for methoxy protons in ^1H NMR. PQMe is obtained as yellowish powder and is soluble in common organic solvents such as chloroform and tetrahydrofuran. Its molecular weight (M_n) is determined to be 6000 ($M_w/M_n = 1.15$) by GPC using polystyrene as standard. PQOH is a red powder and is soluble in formic acid, *m*-cresol, DMSO, etc.

The coordination ability of PQOH (5 μM corresponding to the repeat unit) and its model compound QOH (5 μM) in DMSO to F^-, Cl^-, Br^-, and $H_2PO_4^-$ (as their tetrabutylammonium salts) anions was investigated using UV−vis absorption and fluorescence emission methods.

Scheme 1



As shown in Figure 1A, the absorption spectrum of PQOH does not exhibit obvious change upon the addition of Cl^-, Br^-, and $H_2PO_4^-$ ions. However, in the presence of fluoride ion, a new peak at around 500 nm appears, implying the change in electron density within the main chain induced by F^- ion. In fact, the polymer solution undergoes a dramatic colorless to red color change, while no color change can be observed in the presence of even much more excess other anions (>1.5 mM). This color change can be used as "naked- eye" detection of F^- in the presence of Cl^-, Br^-, $H_2PO_4^-$ ions. The effect of anions on the fluorescence spectrum of PQOH is also studied (Figure 1B). Addition of F^- ion leads to the emergence of a long-wavelength emission band at around 620 nm. In contrast, the addition of other anions has no detectable effect on the emission band around 620 nm. The fluorescence spectra for titration of PQOH with F^- ion are shown in Figure 2. Upon the addition of F^-, the fluorescent intensity around 620 nm increases greatly. These results suggest PQOH has high selectivity for F^- over various anions in DMSO and can be used as both colorimetric and fluorescent chemosensor for fluoride ion. The absorption and fluorescence spectra of the model compound QOH after the adding of different anions are displayed in Figure 3. On treatment with F^- ion, QOH also exhibits a significant color change from colorless to yellow corresponding to the appearance of a new broad absorption band centered at around 460 nm, and the long wavelength emission band around 590 nm increases.[12] However, similar emission enhancement can be observed upon the addition of $H_2PO_4^-$ ion, although the magnitude of the enhancement is much smaller than F^- ion, indicating that QOH has a lower selectivity than PQOH. On the basis of the fact that the addition of 100 equiv of F^- ion leads to 147-fold enhancement of the long-wavelength emission for PQOH, while only 17-fold for QOH, PQOH has higher sensitivity than QOH.

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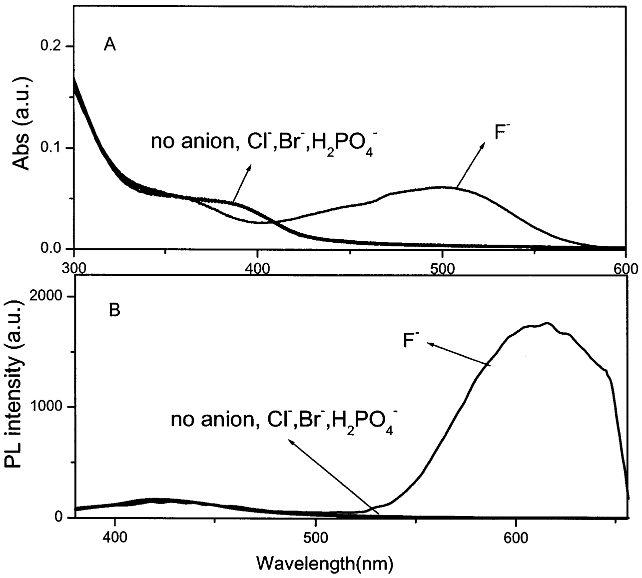

Figure 1. Absorption and fluorescence spectra of PQOH (5 μM) in DMSO after the addition of 100 equiv of representative anions.

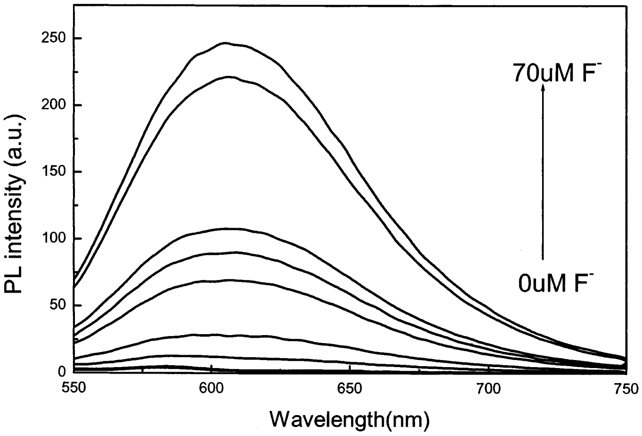

Figure 2. Titration of PQOH in DMSO with F^- ion, excited at 499 nm.

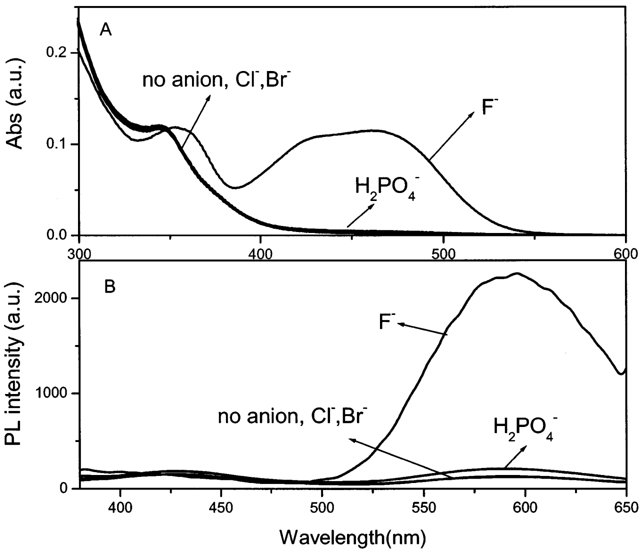

Figure 3. Absorption and fluorescence spectra of QOH (5 μM) in DMSO after the addition of 100 equiv of representative anions.

Regarding the origin of the long-wavelength absorption and emission of PQOH and QOH, two possibilities may be involved. The first is attributed to the formation of the hydrogen-bonded complex between the hydroxyl group and F^- ion.[10a] The second is the result of the phenolate formation induced by fluoride ion as the base.[10b] ^1H NMR titration measurements of QOH provide the evidence for the phenolate formation. Upon the addition of F^- ion, the signal of the proton in hydroxyl group disappeared.[13] In fact, the treatment of QOH with OH^- leads to the similar long-wavelength absorption and emission, implying that the phenolate formation is originated from the acid−base process between the hydroxyl group and F^- ion. Moreover, the quinoline moiety plays the important role in the formation of the phenolate anion and the appearance of the long-wavelength absorption and emission, because the incorporation of the quinoline as a strong electron-withdrawing group leads to the increasing of the phenol's acidity and the occurrence of the intramolecular charge transfer (ICT) effect between quinoline moiety and the phenolate anion, which is responsible for the long-wavelength absorption and emission.[14] And because Cl^- and Br^- ions are not as basic as F^-, the addition of them will not lead to the formation of phenolate anion.

Regarding the origin of the higher selectivity of PQOH than its model compound QOH, the chain conformation of PQOH must be considered. In DMSO, the main chain of PQOH may coil, and it will be much more difficult for larger anions such as $H_2PO_4^-$ ion to access the hydroxyl group than a smaller anion F^- ion. While for QOH, there is not such a problem, and $H_2PO_4^-$ ion can interact with the hydroxyl group easily.

In conclusion, we have presented conjugated polymer PQOH and its model compound QOH as both colorimetric and fluorescent chemosensors for fluoride ion in DMSO. The large fluorescent enhancement is observed upon the addition of fluoride ion. And higher selectivity and sensitivity are achieved for PQOH compared to QOH. We are currently working to prepare more elaborate systems, including conjugated polyquinolines with both anion interaction sites (such as OH or NH) and quaternary ammonium functionalized side groups.

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Supporting Information Available: The synthetic procedure and characterization of PQMe, PQOH, and QOH; the fluorescence excitation spectra of PQOH and QOH upon adding F^- ion. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The red emission of QOH itself is attributed to an excited-state tautomer of QOH formed through the excited-state intramolecular proton transfer (ESIPT) (see Supporting Information).

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