Communications to the Editor

Highly Selective Fluorescent Chemosensor for Silver(I) Ion Based on Amplified Fluorescence Quenching of Conjugated Polyquinoline

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Fluorescent chemosensors for spying on molecular recognition events are currently of significant importance for both chemistry and biology.[1] Recently, the fluorescent conjugated polymers containing molecular recognition sites have been studied extensively as highly metal-ion-sensitive chemosensors. The amplified fluorescence quenching effect of many conjugated polymers compared to their model compounds has also been reported,[2] because the “molecular wire effect” greatly enhanced the sensitivity of the polymer-based chemosensors.[3] Among most conjugated polymers, PPV-based polymers containing bipyridyl and terpyridyl segments have been found to be highly sensitive to a wide variety of metal ions.[4] These polymers can coordinate with many transition metal ions, and their fluorescence is quenched completely or red/blue-shifted by the addition of metal ions, depending on the kind of metal ion. However, their selectivity to most of the metal ions remains unsatisfactory, because the multipyridyl ligands possess an excellent ability to coordinate a wide variety of metal ions. To our best knowledge, there are few examples on fluorescent chemosensor for detecting metal ions highly selectively using conjugated polymers.[5] For instance, Swager et al. reported a new conjugated poly(*p*-phenylene ethylene) containing crown ether group systems having highly selective for K^+ over Na^+ ions.[6] Of the transition metal ions, silver ion is of great commercial importance in the photographic industry and reliable sensing is needed for low concentrations, and its strongest interferents are the Hg^{2+} ion and other heavy metal ions.[7] Polyquinolines have been extensively studied as one kind of n-type conjugated polymer for applications in many fields.[8] Very recently, Jenekhe et al. demonstrated its sensory properties for pH.[9] In the present work, we describe the amplified fluorescence quenching of two novel polyquinolines (PQH and PQEH) (Figure 1), which exhibit a high selectivity for Ag^+ over most of metal ions such as Hg^{2+}, Pb^{2+}, etc.

The polyquinolines were synthesized by the nickel(0)-catalyzed coupling reaction and were fully characterized by NMR and elemental analysis. Their properties are summarized in Table 1. Both polymers are soluble in common organic solvents such as chloroform and tetrahydrofuran. PQH has strong emission at 415 nm and a shoulder peak at 435 nm in dilute THF solution (5 μM). On protonation of the quinoline nitrogen atoms with formic acid, its emission is red-shifted to 454 nm and the emission in dilute formic acid solution (5 μM) is much lower than that in THF, which is attributed to the enhanced intramolecular charge transfer (ICT) (Figure 2).[11] The corresponding absorption spectra also exhibit a similar trend of red shift as the protonation of the quinoline nitrogen atoms in formic acid solution. Upon increasing the concentration of PQH in THF, it is observed that the emission spectra shape changes and the maximum peak intensity of the emission decreases greatly. Finally, it shows a broad featureless emission peak around 450 nm with no shoulder peak for the concentrated solution (0.5 mmol/L). The spectral behavior demonstrates that there is interpolymer aggregation in concentrated solution, which leads to concentration quenching and red shift. A similar phenomenon can be observed in the formic solution of PQH.

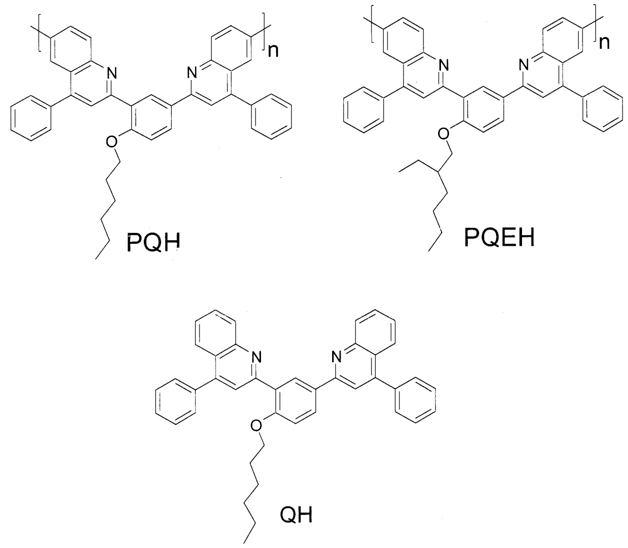

Figure 1. Structures of PQH, its model compound QH, and PQEH.

The effect of a wide variety of monovalence metal ions (K^+, Na^+, Cu^+, Ag^+) and bivalence metal ions (Zn^{2+}, Cu^{2+}, Cd^{2+}, Pd^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, Ca^{2+}) on the fluorescence intensity of PQH and QH at the emission maxima have been studied (λ_{em}, Figure 3). Upon addition of most metal ions, they show almost no change in their emission spectra. In contrast, the addition of Ag^+ ion to the solution of PQH and QH leads to significant fluorescence quenching. Moreover, PQH responds much more strongly to the presence of Ag^+ ion than its model compound (QH). Their fluorescence spectra in THF

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Table 1. Properties of PQH and PQEH

polymer	M_n[a]	M_w	Pd	λ_{max} (nm)[b]	λ_{em} (nm)[b]	quantum yield in THF (%)[c]
PQH	8058	9255	1.15	364	417, 435 (sh)	64
PQEH	8300	10751	1.29	363	415, 434 (sh)	62

[a] Polystyrene was used as the standard and THF as the eluent. [b] [PQH] = [PQEH] = 5 μM in THF. [c] Relative to 10^{-5} M quinine sulfate in 0.1 N H_2SO_4 solution, determined according to the method in the literature.[10]

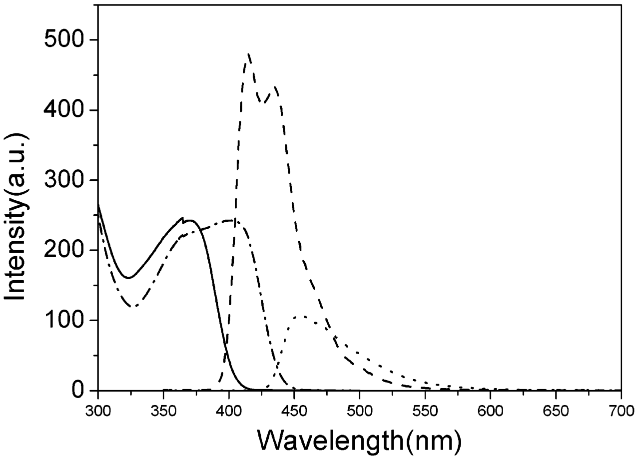

Figure 2. Optical absorption (solid line) and fluorescence spectra (dashed line) of PQH in THF and optical absorption (dash dotted line) and fluorescence spectra (dotted line) of PQH in formic acid.

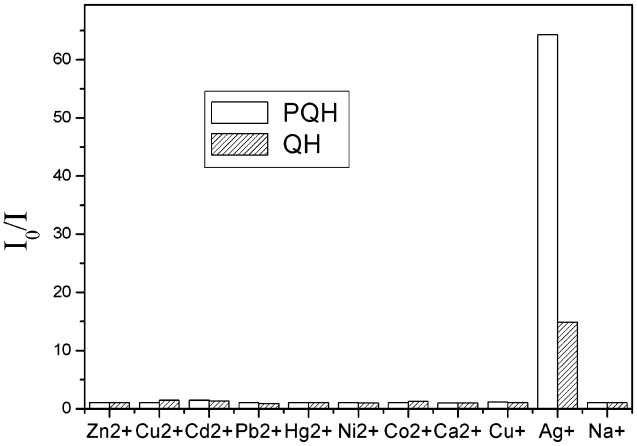

Figure 3. Fluorescence emission response profiles of PQH and QH.

solution are rather stable and exhibit no change for more than 3 days at room temperature. It is worthwhile to note that the Hg^{2+} ion (a much heavier metal ion) has almost no quenching effect on the emission spectrum of PQH; therefore, the "heavy atom" quenching mechanism can be ruled out. Upon increasing [Ag^+], a red shift of the emission maximum and the change of the emission shape are observed, accompanied by a more than 62-fold fluorescence quenching, however, only about 15-fold for QH. Based on the fluorescence titration of PQH and QH in THF with Ag^+ ion, their Stern–Volmer constants (K_{sv}) are determined to be 1.4×10^5 and 9.2×10^3 M^{-1}, respectively. It is obvious that PQH is much more efficient than QH. These results indicate that the polymer chain amplifies the fluorescence quenching. It is also observed that the fluorescent intensity is recovered after the addition of several droplets of ammonia aqueous solution to PQH solution in THF, indicating the reversibility of Ag^+ ion-induced fluorescence quenching. The effect of these metal ions on the absorption of PQH is also examined. The spectra remain unchanged after the treatment with most of metal ions such as Ni^{2+}, Zn^{2+}, Hg^{2+}, etc. In contrast, the absorption peak at 370 nm, which is attributed to the conjugated backbone, is slightly decreased and red-shifted for about 2 nm upon the addition of Ag^+, implying the change in electron density within the main chain induced by the Ag^+ ions.

Regarding the origin of the fluorescence quenching effect, two possibilities must be considered. The first is attributed to electron density variations on the main chains of the polyquinoline, caused by introducing positively charged ions. The second is that the decreased fluorescence is the result of the interpolymer aggregations. Although the addition of Ag^+ ion leads to the same bathochromic effect on the absorption spectrum of PQH as the protonation of the quinoline nitrogen atom in formic acid solution, the red shift in the former is much smaller than that in the latter, indicating that the variation of the electron density of the polymer backbone caused by Ag^+ ion plays a minor role in fluorescent quenching. From the above analysis, it is reasonably deduced that the amplified fluorescence quenching effect of conjugated polyquinoline results mainly from the Ag^+-induced interpolymer aggregation. This judgment is also supported by the fact that PQH exhibits a similar trend of fluorescent spectral behavior[12] as the concentration of PQH or Ag^+ ion increases.

It is well-known that large side groups attached to the polymer backbone will reduce the interpolymer aggregation. To test our deduction, we studied the fluorescent quenching of PQEH in THF solution of the same concentration of the PQH solution upon the addition of Ag^+ ion. Its absorption and photoluminescence spectra, as well as its quantum yield in THF solution, are very similar to PQH (Table 1), which implied the alternation of side groups did not have much effect on the main chain of the polyquinoline. However, Ag^+-induced quenching is much less efficient for PQEH ($K_{sv} = 3.9 \times 10^4$ M^{-1}) than PQH ($K_{sv} = 1.4 \times 10^5$ M^{-1}), which indicates the bulky side groups really stifle interpolymer aggregation and lower the response to silver ion, as expected.[6]

In summary, we have successfully developed a new highly selective fluorescent chemosensor for Ag^+ using conjugated polyquinoline for the first time. Ag^+-induced interpolymer aggregation is believed to play a major role in the amplified fluorescence quenching.

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Supporting Information Available: The synthetic procedure and characterization of PQH, PQEH, and QH and Stern–Volmer quenching plots for their solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The preliminary results of fluorescence lifetime experiments support the existence of polymer aggregation. Both the concentrated solution (500 μM) of PQH and the dilute PQH (5 μM) with Ag^+ ion (1 mM) in THF exhibit longer fluorescence lifetime than the dilute PQH solution (5 μM).

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