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A new click reaction generated AIE-active polymer sensor for Hg^{2+} detection in aqueous solution

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ABSTRACT

We described herein a new AIE-active polymer sensor incorporating triazole moiety for Hg^{2+} detection in aqueous solution. The polymer sensor **P1** was synthesized from tetraphenylethene and diazidobenzene *via* click reaction. It shows typical AIE feature, and emits cyan fluorescence in the mixture of tetrahydrofuran and water, reaching the strongest fluorescence when the fraction of water (f_w) is 90%. In aqueous solution ($f_w = 90\%$), the polymer sensor can exhibit fluorescence quenching response towards Hg^{2+} over other competing metal ions, with the fluorescence color changed from cyan to almost no emission, which can be clearly observed by the naked eyes under 365 nm UV lamp.

Introduction

As a typical example of most toxic heavy metal ions, mercury ion and its derivatives are significant environmental pollutants which are globally distributed in natural and anthropogenic sources, leading to severe environmental damages.[1] They can also cause serious harm to human health by accumulation in the body through the food chain, due to their high affinity to the thiol groups of enzymes and proteins,[2] resulting in various kinds of major diseases like the infamous Minamata disease.[3] The form of methyl mercury, which can be converted by bacteria from mercury ion, is known to be particularly damaging to the central nervous system[4] because it is lipophilic and can be easily absorbed by living beings.[2a] Therefore, it is highly desirable for the development of selective and sensitive chemosensors for mercury detection.

Until now, lots of fluorescent sensors have been reported and applied in fields like ions detection and pH response.[5] Most of them are based on small organic molecules, which have a large probability in suffering from the aggregation-caused quenching (ACQ) effect when dispersed in aqueous phase, and thus drop sharply in the detecting sensitivity.[6] Tang's group firstly proposed the idea of aggregation-induced emission (AIE), illustrating that the luminogenic molecules had almost no luminescence in solution while stronger emission in aggregate or solid state.[7] Since then, many AIE-active molecules have been designed and applied in various fields, such as fluorescent sensors and optoelectronic devices.[8] Meanwhile, Swager reported that "The conjugated polymers (CPs) can amplify the sensitivity compared with the corresponding repeating small molecule units".[9] Based on the above all, we are devoted to develop the AIE-active fluorescent polymer sensors for mercury ion detection in aqueous solution.

Click reaction, represented by the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC), is a versatile coupling strategy to generate various functional materials due to its dependability, selectivity, and high-yield.[10] Cheng's group made use of click polymerization reactions to synthesize fluorescent polymer sensors and applied them in mercury ion detection.[11] However, all of the detecting processes were carried out in organic solvent instead of aqueous solution, which limit the practical application. Herein, we developed an AIE-active fluorescent polymer sensor **P1** generated by click reaction for Hg^{2+} detection in aqueous solution. The polymer sensor **P1** emits very weak cyan fluorescence in pure THF solution, upon the addition of poor solvent water, the fluorescence intensity gradually increases and reaches the maximum value when the fraction of water (f_w) is 90%. In the aqueous solution ($f_w = 90\%$), **P1** exhibits "turn-off" fluorescence response only towards Hg^{2+} over other competing metal ions, with the fluorescence color changes from cyan to almost no emission, which can be clearly observed by the naked eyes under 365 nm UV lamp.

Results and discussion

The synthetic procedures of the polymer sensor **P1** is outlined in Scheme 1. Two *n*-octyl substituents were modified on monomer **M-1** to improve the solubility of **P1**, monomer **M-2** were

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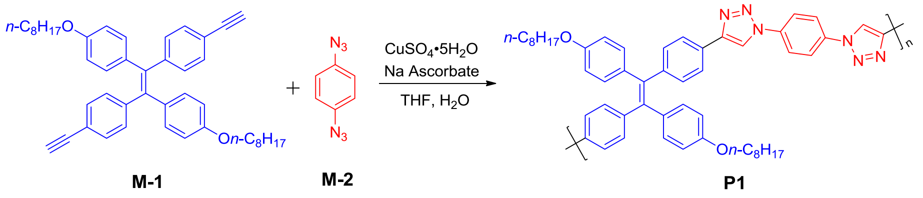

Scheme 1. Synthesis of the polymer sensor **P1**.

synthesized according to the reported literatures[10]. The polymer sensor **P1** could be synthesized by the copper(I)-catalyzed polymerization click reaction of **M-1** and **M-2** in about 76% yield and obtained as yellow solid by precipitating from methanol. The thermogravimetric analysis (TGA) shows that **P1** loses 5% weight before 400 °C, indicating high thermal stability. In addition, **P1** has moderate molecular weights ($M_n = 14350$, $M_w = 10500$, PDI = 1.36) evaluated by gel permeation chromatography (GPC).

The optical measurements of **P1** were conducted in a mixed solvent of tetrahydrofuran (THF, good solvent) and water (poor solvent) at a fixed concentration (1×10^{-5} mol·L^{-1} corresponding to triazole moiety). As shown in Fig. 1a, the polymer sensor **P1** has almost no fluorescence in pure THF solution. Upon the addition of water, the AIE-active polymer sensor **P1** can emit gradual fluorescence enhancement and reaches the strongest emission intensity at $f_w = 90\%$, with the relative emission intensity (I/I_0) up to 13.13-fold at 500 nm (Fig. 1b). In addition, the AIE feature of **P1** could be directly observed by the fluorescence color changes taken under 365 nm UV lamp (Fig. 1b, inset). The fluorescence quantum yields of **P1** in THF and THF/water ($f_w = 90\%$) were determined as 1.24% and 16.7%, respectively, using quinine sulfate (dissolved in water) as standard.

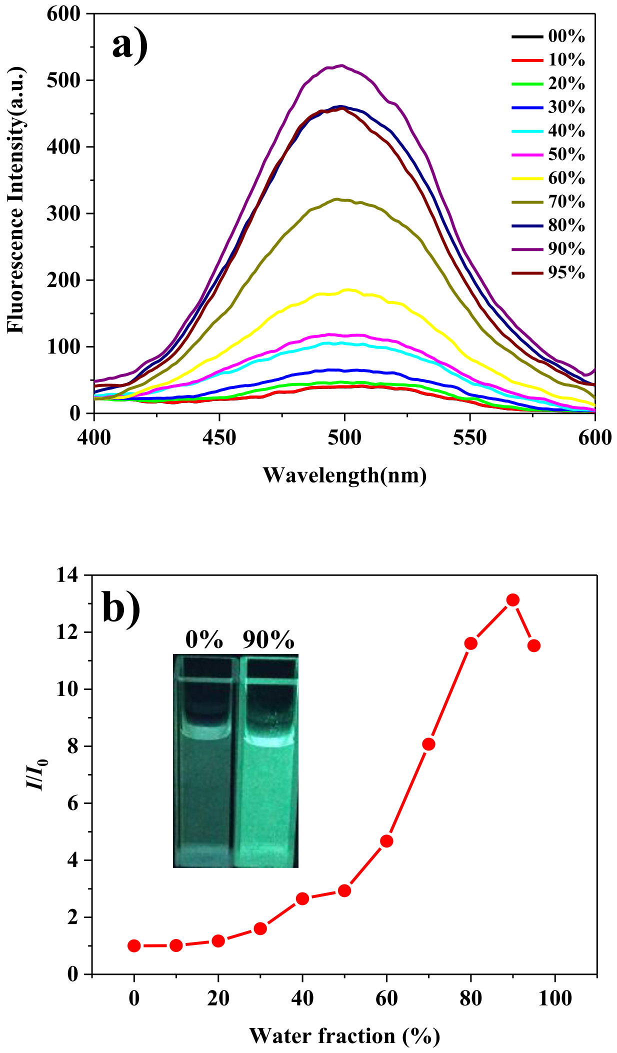

Fig. 1. (a) Fluorescence spectra of **P1** in THF/water mixtures with different water fraction. Solution concentration: 1.0×10^{-5} mol·L^{-1} ($\lambda_{ex} = 320$ nm); (b) Plot of relative emission intensity (I/I_0) values at 500 nm versus the compositions of the aqueous mixtures. I_0 = fluorescence intensity in pure THF solution. Inset: photographs of **P1** in THF/water mixtures (left: $f_w = 0\%$; right: $f_w = 90\%$) taken under 365 nm UV lamp.

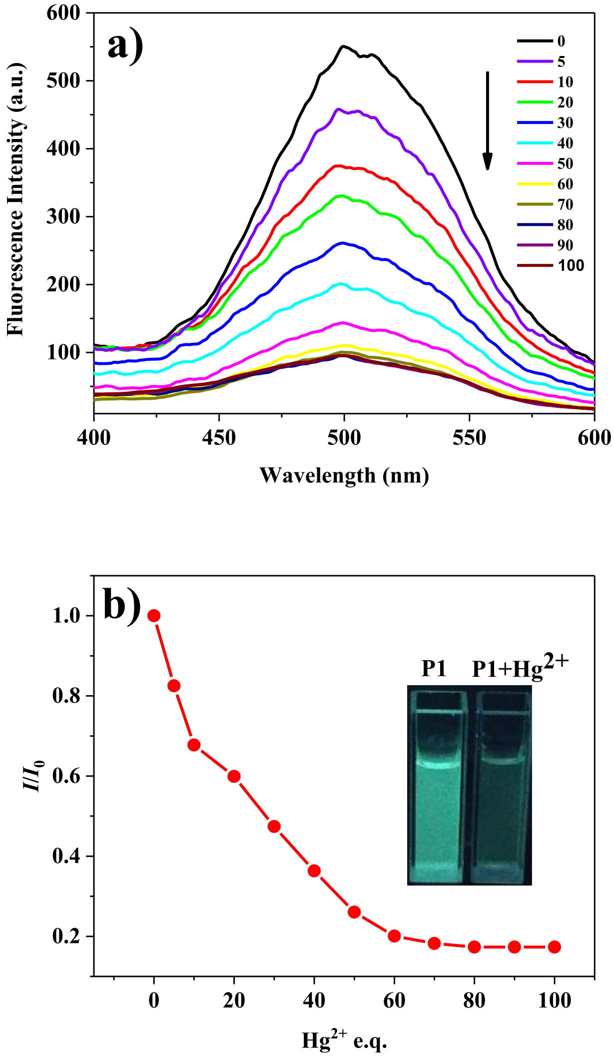

Fig. 2. (a) Fluorescence spectral changes of **P1** (1.0×10^{-5} mol·L^{-1} in THF and water mixtures, $f_w = 90\%$, $\lambda_{ex} = 320$ nm) upon the addition of increasing amounts of Hg^{2+}. (b) Plot of PL quenching efficiencies (I/I_0) versus the concentration of Hg^{2+} at 500 nm. I_0 = fluorescence intensity in the absence of Hg^{2+}. Inset: visible fluorescence of the polymer solution before (left) and after (right) the addition of 100 equivalents of Hg^{2+} under 365 nm UV lamp.