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Aqueous Nanodispersion of Acetylene Tethered, Quinoxaline-Containing Conjugated Polymer as Fluorescence Probe for Ag^+

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Abstract: A type of carbazole-based, quinoxaline-containing conjugated polymer with tethered acetylene groups, **P-2**, was successfully synthesized through the desilylation of triisopropylsilyl (TIPS) protected precursor polymer**.** Nanodispersion of **P-2** in water was prepared by reprecipitation treatment and displays acceptable quantum efficiency (QE, 0.20). Optical properties of **P-2** in THF solution and nanodispersion state were characterized by UV-*vis* and photoluminescence (PL) analyses. Specific binding with Ag^+ of **P-2** was validated by UV–*vis* and PL analyses against other metal ions. Corresponding results suggest that **P-2** possesses selectivity and sensitivity toward Ag^+. Around 82% of PL intensity of **P-2** was quenched when the concentration of Ag^+ in probing mixture reached $\sim 5.1\times10^{-4}$ M. The detection limit for Ag^+ was evaluated as ~ 64 nM (*S/N*=3). Synergic effect of the tethered acetylenes and *N*-atoms in the quinoxaline segments to interrelate with Ag^+ is the possible reason for the specific response of **P-2** for Ag^+.

Keywords: Conjugated polymer; Acetylene; Optical response; Nanoparticle; Ag^+ ion

Introduction

Ag^+ has been widely used in electronics, photography, imaging industry and pharmacy in nowadays society. The disservice of Ag^+ received considerable attention because of its bioaccumulation and toxicity to organisms. [1-2] Thus, it is highly desirable to develop sensitive and selective methods for the detection of Ag^+ contaminant for environmental protection and human health. Researchers have reported some efficient methods to realize Ag^+ detection, such as atomic absorption, plasma emission spectroscopy, anodic stripping voltammetry and potentiometry, etc.[3-5] However, most of these methods are cost and time-consuming, and there is still a great challenge to find protocols to support technically simple Ag^+ detection. Therefore, as complement to aforementioned sophisticated methods, simpler detection approaches, such as fluorogenic or chromogenic probes are in demand for the detection of Ag^+ in various situations.[6] There are considerable advantages of fluorescence methods in terms of sensitivity, detection speed, simplicity in operation and non-destructive to the sample.[7-8] Thus, a handful of literatures have reported on fluorescent sensors for Ag^+. However, most of these reported probes are only applicable in organic or aqueous-organic mixed medium. [9-17] Efficient detection in aqueous phase is more favorable due to the avoiding of polluting organic solvents and with the significance in the further potential application in bio-relating probing processes.

Conjugated polymers (CPs) are known to provide the advantage of collective optical response. [18] Sensitivity of CPs in probing application is thus superior to that of small molecular derivatives due to their signal-amplification effect. [19-20] Inspired by this knowledge, some attempts have been made to use CPs to realize Ag^+ detection. Wang *et al.* [21] reported a series of *N*-atom-containing, quinoline-based CPs for Ag^+ ion sensing in organic medium (THF). The detection was based on the Ag^+-induced intermolecular aggregation. How to realize Ag^+'s optical probing by CPs in aqueous medium is still a challenging issue and need further exploration. Synthesis of Ag^+-detectable, and water-soluble CPs has been proven to be a protocol to resolve aforementioned issue. Wang *et al.* took advantage of a water-soluble organometallic conjugated polyelectrolyte and realized the direct colorimetric detection of silver ion in aqueous media. [22] Using CPs-based aqueous nanodispersion to perform the probing is another choice to realize the detection in water. The advantage of this strategy is that the process for the obtainment of aqueous nanodispersion is easy to implement (by practical-simple miniemulsion or reprecipitation protocols) and needs no introduction of extra hydrophilic groups into CPs matrix. [23-25] Along with this line, aqueous nanodispersion of benzothiadiazole-containing CP was prepared and displayed good performance as fluorescence turn-off probe for Ag^+.[26] This is the first report about the application of CP-based aqueous nanodispersion as Ag^+ probe by far.

Acetylene (≡H) is an important group of unsaturated component and possesses binding capability with some metals, such as Ag^+,[27] Hg^{2+} [28] and Cu^+, [29] etc. This endows acetylene-substituted materials with potential probing properties toward these metals. In light of this knowledge, we have synthesized a type of acetylene pendant-substituted, carbazole-based CP and prepared the corresponding aqueous nanodispersion. Such nanodispersion hold the potential to be applied as fluorescence turn-off optical probe toward Hg^{2+}.[30] In the investigation of metal ion's response of this nanodispersion, we found that Ag^{+} also caused a certain extent of fluorescence quenching, which might be due to the association between acetylene and Ag^{+}. We speculate that such fluorescence quenching effect might be strengthened if other types of Ag^{+}-interactive groups are simultaneously introduced into acetylene-bared CPs. It's known that the *N*-atoms in electron-withdrawn, aromatic quinoline and quinoxaline rings can coordinate with Ag^{+}.[31] Along with this line, we want to integrate quinoxaline and acetylene groups into one CP to collaborate their respective efficacy and modify Ag^{+} probing capability of resulted polymer.

In this effort, aqueous nanodispersion of acetylene and quinoxaline-containing CP (**P-2**) was prepared by reprecipitation protocol. Optical response of this dispersion to various metal ions was investigated here. Synergic effect of the tethered acetylene and *N*-atom to interrelate with Ag^{+} in **P-2** suggest that **P-2** can be act as a potential probe for Ag^{+} ion.

Experimental section

Materials

All reagents, unless otherwise specified, were purchased from J&K Scientific Ltd., and used without further purification. Diisopropylamine, toluene and tetrahydrofuran (THF) were distilled from sodium at the presence of benzophenone and degassed before use. The synthesis of polymer **P-2** was followed by reported procedure in our recent work.[32]

Solutions of Ag^{+}, Al^{3+}, Ba^{2+}, Cd^{2+}, Cu^{2+}, Mg^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} were prepared from their nitrate salts; solution of Hg^{2+} was prepared from its acetate salt. Concentrations of metal solutions were controlled at 10^{-1} M in deionized water and were diluted to different concentration stocks for next use.

Measurements and Characterization

UV-visible absorption spectra were recorded on a SHIMADZU UV-2450 UV-*vis* spectrophotometer. PL spectra were recorded on SHIMADZU RF-5301pc spectrophotometer. Transmission electron microscope (TEM) and dynamic light scattering (DLS) were conducted on JEM-2100 (JEOL) and Zetasizer Nano S90, respectively.

Preparation of P-2 nanodispersion in aqueous phase

Polymer nanodispersion in aqueous phase was prepared by following the procedures in previous literatures.[23,25, 30] Briefly, 4 mg of **P-2** was added to a flask containing 100 mL of THF under stirring. The stirring was continued at room temperature overnight. A portion of solution (10 mL) was took out, filtered *via* 0.45 μL filter and added to 40 mL of deionized water in ultrasonic processing. The mixture was disposed by ultrasonication for 20 min. After that, residual THF was removed by heating at 50 ^{o}C to transfer nanoparticles from the organic to the aqueous phase.

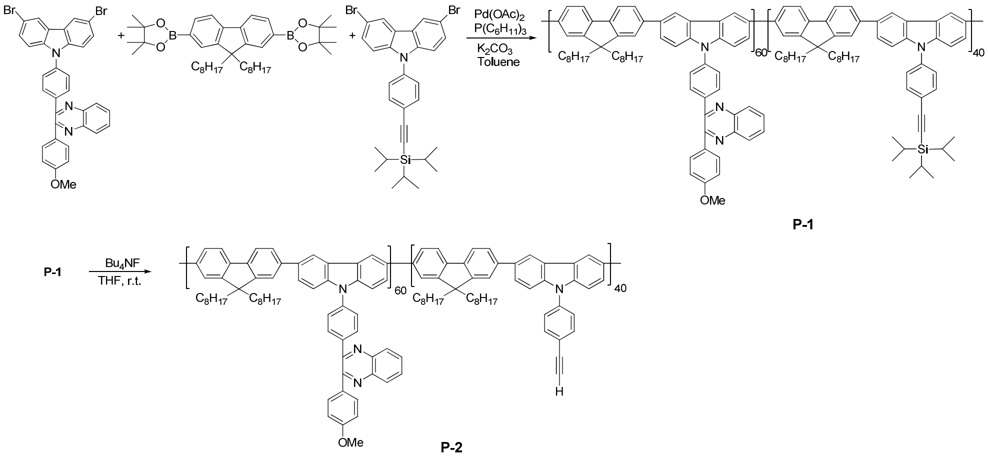
Fluorescence titration of P-2 with metal ions

The aqueous nanodispersion of **P-2** (~ 1×10^{-5} M) was prepared as stated before. Solutions of metal ions were prepared in deionized water with different concentrations. A stock solution of **P-2** (3.0 mL) was placed in a quartz cell (10.0 mm width). Each metal ion solution was introduced by micropipette with aimed volume, and fluorescence intensity changes (excited by 350 nm) and UV-*vis* absorption were recorded 3 min later after the addition of ions each time.

Results and discussion

Preparation of aqueous nanodispersion of P-2

The synthetic route of target polymer is outlined in **Scheme 1**. Detailed information about the synthesis and chemical structure characterization of **P-2** can be traced in our recent work about the preparation of fluorescent-magnetic dualfunctional polymer composite *via* Cu^{+}-catalysed acetylene-azido click reaction.[32] The number average molecular weight (M_n) of **P-2** was estimated by gel permeation chromatography (GPC) against the polystyrene standard with THF as solvent, to be 8016 g/mol and with polydispersity index of 2.2.



Scheme 1. Synthetic route of **P-2**.

Nanodispersion of **P-2** in water was obtained conveniently by reprecipitation treatment as reported by previous literatures.[23,25, 30] As can be seen from **Fig. 1**, the corresponding aqueous nanodispersion is uniform and with good transparency under natural light (**Fig. 1a**). It emits bright sky-blue light when excited by UV light (365 nm, provided by portable ultraviolet lamp, **Fig.**

1b). Its detailed optical properties will be discussed in following section. Dynamic light scattering (DLS) analysis supports the formation of nanoparticles, and the average size was evaluated as ~ 130 (± 20 nm) (**Fig. 1c**). Morphology of the resulted dispersion was characterized by TEM analysis (**Fig. 1d**). One can find that the nanoparticles are approximate to spherical and with tendency to form aggregate.

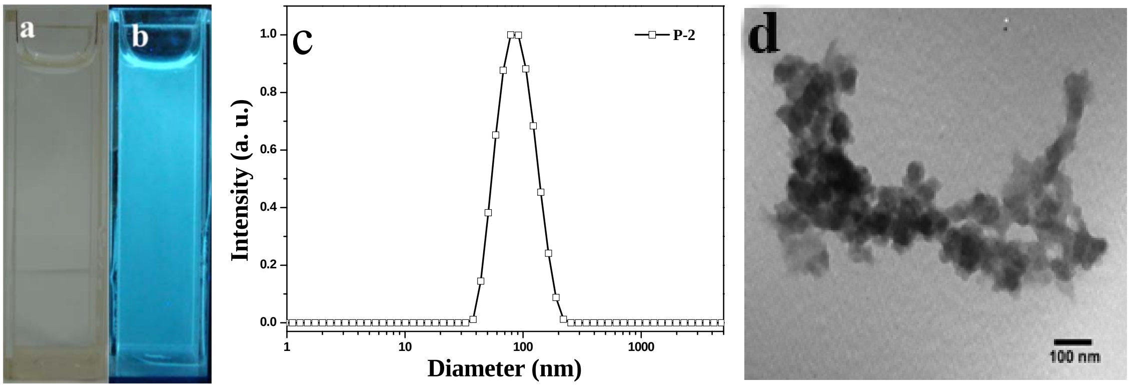


Fig. 1 Visual photograph under natural light (a), ultraviolet light (b), DLS analysis (c) and TEM image (d) of **P-2** aqueous dispersion.

Optical properties

UV-*vis* absorption properties of **P-2** in THF and aqueous dispersion are displayed in **Fig. 2a**. Absorption maxima of **P-2** locate at ~ 350 nm for both states. One can find that there is apparent broaden of absorption profile in aqueous phase as compared to the corresponding one in THF. This indicates that aggregation of polymer chains occurred in aqueous nanodispersion. **Fig. 2b** illustrates photoluminescence (PL) properties of **P-2** in THF and aqueous dispersion. Surprisingly, the emission maximum of **P-2** in nano-state (~ 475 nm) displays blueshift relative to that in THF solution (~ 502), which is disagree with the trend in its absorption case. The similar phenomenon was reported by Schenning *et al*. about the aqueous dispersion of benzothiadiazole-containing small molecular fluorescent compound,[33] which might be stem from the alteration of solvent-induced intramolecular charge transfer (between carbazole and quinoxaline) degree. Fluorescence quantum efficiency (QE) of **P-2** in aqueous phase was evaluated by using 9, 10-diphenylanthracene (QE = 0.90 in cyclohexane) as standard, to be ~ 0.20. This QE is acceptable in terms of CPs-based aqueous nanopaticles according to our previous report.[30] The simultaneous introduction of electron-rich carbazole and electron-deficient quinoxaline moieties into fluorescent compounds is a potential protocol to improve their quantum efficiency according to previous reports.[34,35]

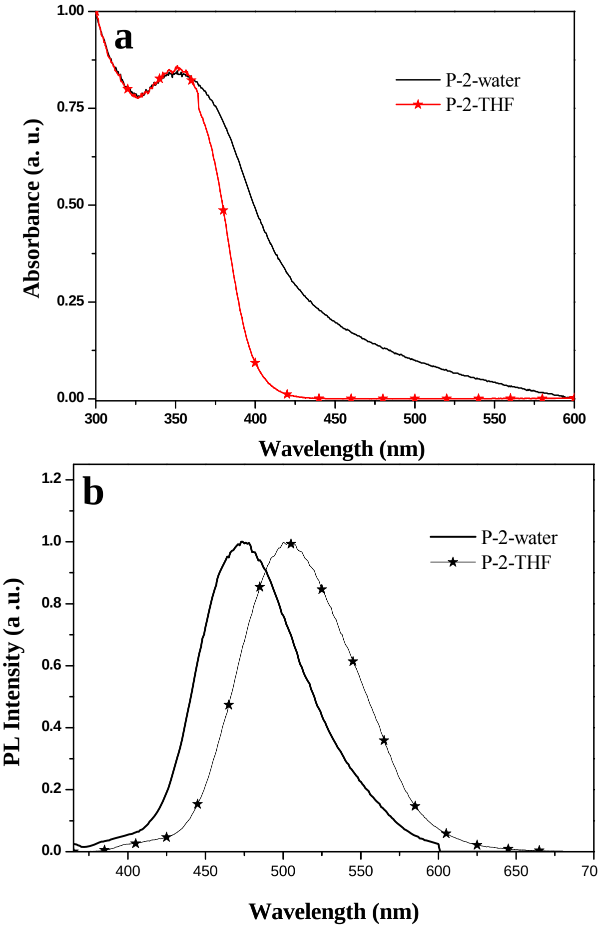


Fig. 2. Normalized UV–*vis* (a) and PL spectra (b) of **P-2** in THF (~ 4×10^{-4} M) and aqueous phase (~ 1×10^{-5} M).

Optical response to metal ions by P-2 aqueous nanodispersion

Optical response of **P-2** to different metal ions (Ag^+, Al^{3+}, Ba^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+}) was detected in aqueous phase. **Fig. 3** illustrates alterations of **P-2**'s PL intensity with the presence of various metal ions (concentrations of **P-2** and metal ions were controlled at ~ 1×10^{-5} and ~ 3.3×10^{-4} M, respectively, PL spectra were recorded 3 min later after the addition of each ion). One can note that compared to other metal ions, Ag^+ caused much more pronounced fluorescent quenching, suggests that **P-2** can act as selective turn-off fluorescence probe for Ag^+.

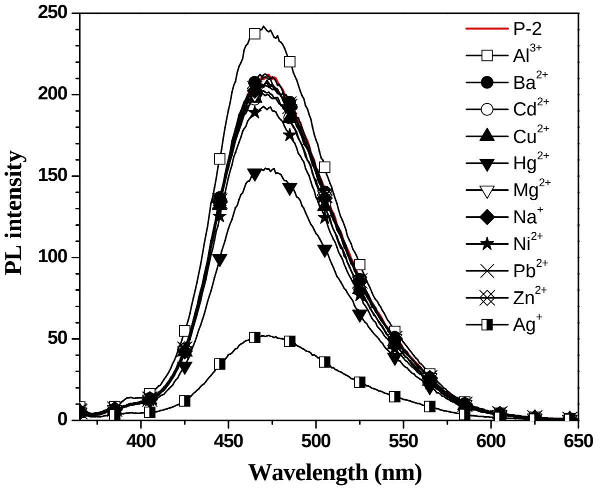


Fig. 3. Fluorescence intensity changes of **P-2** nanodispersion in aqueous phase (with the concentration of ~ 1×10^{-5} M) in the presence of various metal ions (with concentration of ~ 3.3×10^{-4} M). (excitation wavelength is 350 nm and the slit width was identical in all cases).

Optical alterations of **P-2** upon the titration of Ag^+ were investigated subsequently, and corresponding spectra are displayed in **Fig. 4**. One can note from **Fig. 4a** that upon the presence of incremental amount of Ag^+, just tiny alteration of absorption was detected (profiles and intensity of absorption curves of **P-2** were scarcely changed). This means that the conjugation identity of **P-2** was not influenced by the presence of Ag^+. **Fig. 4b** illustrates detailed fluorescence changes of **P-2** upon gradual titration of Ag^+. Around 82% of PL intensity of **P-2** was quenched when the concentration of Ag^+ reached ~ 5.1×10^{-4} M. The quenching efficiency can be reflected by K_{sv} constant, which can be obtained by the calculation of the slope of the linear region of quenching plot (**Fig. 4c**) at low concentration region (with Ag^+ concentration below 1.0×10^{-6} M), to be ~ 3.26×10^5 M^{-1} and with the detection limit (DL) in the range of ~ 6.4×10^{-8} M according to 3σ criteria [37] (the standard deviation (0.007) was obtained by 10 measurements of blank **P-2**'s dispersion, slope was evaluated by the linear response region in **Fig. 4c**).

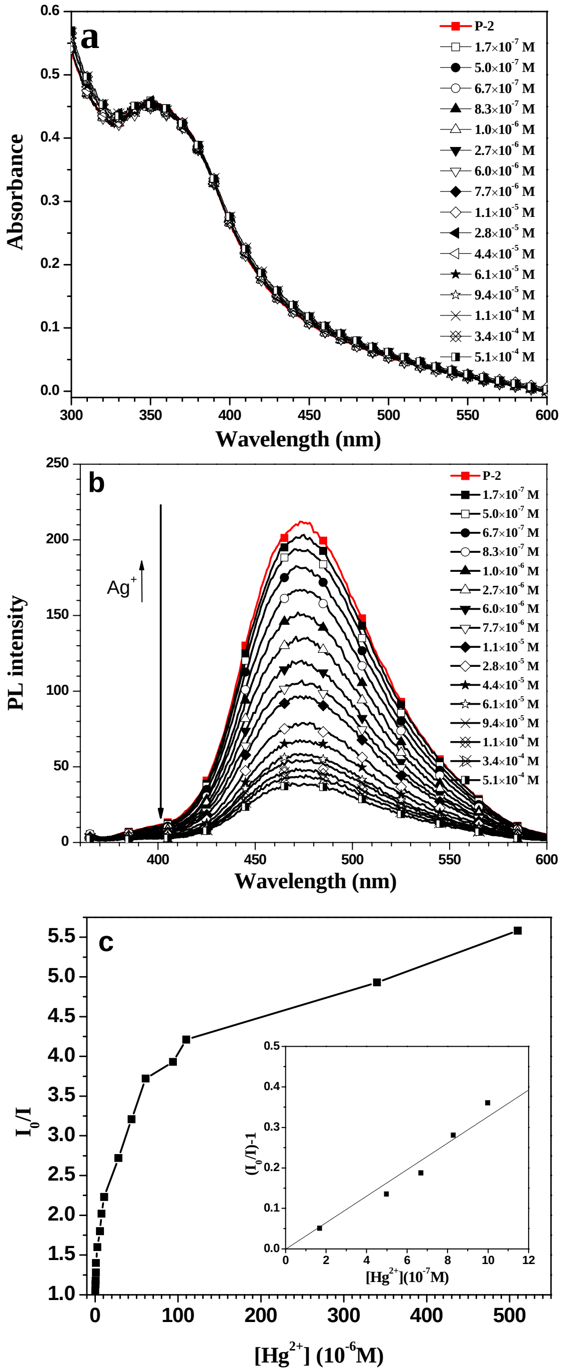


Fig. 4. UV–*vis* (**a**) and fluorescence (**b**) spectra of **P-2** nanodispersion (~ 1×10^{-5} M) upon incremental addition of Ag^+ (0 to 5.1×10^{-4} M) in deionized water, and the corresponding I_0/I values versus Ag^+ concentration (**c**) (inset shows the linear region of **P-2's** PL intensity versus Ag^+ (concentration in the range of 1.7-10 $\times10^{-7}$ M)). Excitation was controlled at 350 nm, and each spectrum was recorded 3 min after adding Ag^+.

An issue lay before us is that what's the constituent in **P-2** is responsible for the quenching toward Ag^+. As was reported in previous literature, [27] complexes can be formed between acetylene derivatives and Ag^+. In the current case, such interaction might also taking place between **P-2** and Ag^+. To find some traces for such speculation, **P-1** aqueous nanodispersion was also prepared (under the same condition as adopted for **P-2)** and subjected to the presence of Ag^+. The corresponding spectra are displayed in **Fig. 5**. With the addition of Ag^+, fluorescence of **P-1** was also quenched. The dropping trend slows down when the concentration of Ag^+ came up to ~ 8.3×10^{-6} M, and the fluorescence almost reaches a plateau when the concentration of Ag^+ exceeds ~ 1.7×10^{-5} M. By the comparison between **Fig. 4b** and **Fig. 5**, against from the dramatic fluorescence quenching for **P-2** (~ 80%), only ~ 40% of PL intensity of **P-1** was quenched when the concentration of Ag^+ reached ~ 1.2×10^{-4} M. Given the same backbone and other alkyl attachments on **P-1** and **P-2**, different response between these two polymers is presumably brought by the difference in their acetylene-pendent. The association with Ag^+ will be helpful to quench **P-2**'s fluorescence while for **P-1** such effect was blocked under the same circumstance due to the presence of TIPS protecting groups. This investigation indicates that the acetylene groups on **P-2** play an important role for the detection of Ag^+.

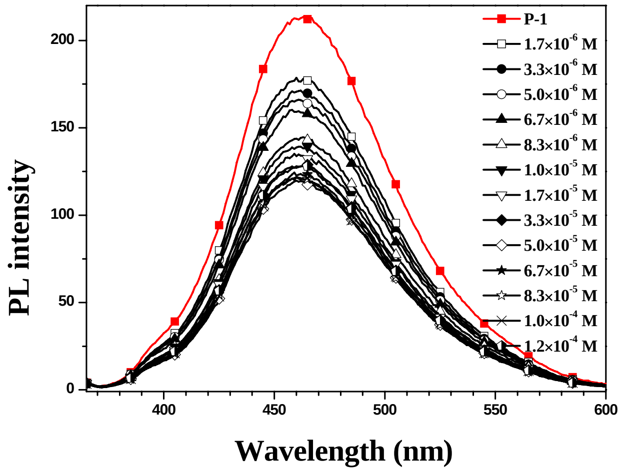


Fig. 5. PL spectra of **P-1** nanodispersion (~ 1×10^{-5} M) upon incremental addition of Ag^+ (0 to ~ 1.2×10^{-4} M) in deionized water. (Excitation was controlled at 350 nm; spectra were recorded 3 min after adding Ag^+).

Another issue, which is interesting to be explored is that, besides acetylene, are there other binding sites between **P-2** and Ag^+? This issue originates from the fact that the fluorescence of **P-1**was also quenched by Ag^+ (**Fig. 5**). Considering the shielding of acetylenes by TIPS groups, one can deduce that the fluorescence of **P-1** should keep unchanged due to the nonexistence of bare acetylenes in its structure. This indicates that there might be other Ag^+'s interactive sites in **P-1**. As was traced by our recent work about fluorene-co-carbazole-based CP's (without quinoxaline groups in its chemical structure) aqueous nanodispersion, the addition of Ag^+ didn't cause such remarkable PL quenching, suggests that neither fluorene nor carbazole segment is responsible for the Ag^+-induced PL quenching of **P-1**. On the other hand, as was mentioned in introduction section, *N*-atoms in quinoxaline hold the potential to coordinate with Ag^+.[31] In this current work, quinoxaline groups exist in both **P-1** and **P-2**, and both polymers displayed fluorescence quenching toward Ag^+ **(Fig. 4b** & **Fig. 5)**. According to this finding, we speculate that quinoxaline groups are the presumable binding points for Ag^+ in this current effort. This speculation can support the interpretation for the fact that as compared to **P-1**, **P-2** displayed more complete quenching. This stems from the synergic effect of the tethered acetylenes and quinoxaline groups to interrelate with Ag^+. That is to say that the Ag^+ detection capability of such *N*-atom containing polymers was modified by the introduction of acetylene.

Interference of other metal ions for **P-2** against Ag^+ was also investigated. **Fig. 6** shows PL intensity alterations of **P-2** before/after the addition of Ag^+ with the presence of various background metal ions. In all cases the addition of Ag^+ caused stronger quenching as compared to those only with background metals. Considering that these spectra were recorded 3 min later with the addition of each ion and Ag^+, **P-2** might be act as a potential immediacy optical probe for Ag^+.

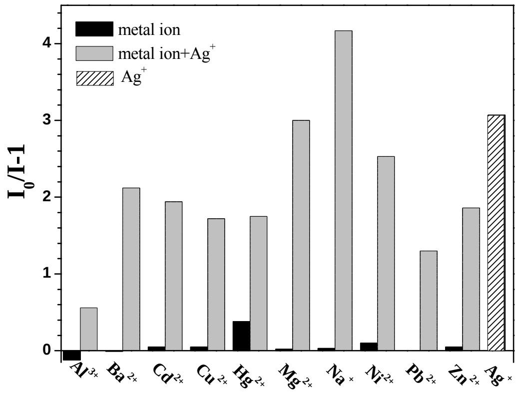


Fig. 6. Fluorescence quenching of **P-2** nanoparticle in aqueous phase (with concentration of ~ 1.0×10^{-5} M) in the presence of various background metal ions (with concentration of ~ 3.3×10^{-4} M) and with sequential addition of Ag^+ (~ 3.3×10^{-4} M). The excitation wavelength is 350 nm.

Conclusions

In summary, a type of quinoxaline-containing, conjugated and fluorescent poly (carbazole-co-fluorene) polymer with tethered acetylenes, **P-2**, was successfully prepared *via* protection-deprotection two-step protocols. Corresponding polymer nanoparticle in aqueous phase with reasonable quantum efficiency was fabricated and displays the potential to be used as Ag^+ fluorescence probe in water. Experimental results demonstrates that **P-2** possess good selectivity and sensitivity toward Ag^+, which presumably stems from the cooperative effect brought by the combined interrelation between acetylene/quinoxaline groups and Ag^+. The work to further modify the probing performance for such conjugated polymer-based aqueous nanodispersion is ongoing now.

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Notes and references

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