Selective detection of metal ions based on nanocrystalline ionochromic polydiacetylene

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ABSTRACT

Metal ion detection using commercially available ionochromic polydiacetylenes has not been selective. In this work, we report selective detection of metal ions in small organic compound (SOC)-stabilized poly(10,12-pentacosadiynoic acid) (PDA) nanocrystals suspended in an aqueous solution. These PDA nanocrystals were topochemically polymerized using a 254-nm UV light from the corresponding SOC-stabilized DA nanocrystals prepared by a solvent/nonsolvent micellization method. In this detection, the stabilizing SOC could selectively regulate the intercalation of specific metal ions into the galleries of PDA nanocrystals. Whenever the specific metal ions were intercalated, a fast (<1 min) ionochromic transition was observed. In addition, different metal ion selectivity could be achieved by utilization of different SOCs. For example, selective detections of Pb2+ and Ag+ with different detection sensitivities were achieved for a PDA/glycine (Gly) nanocrystal suspension and selective detection of Zn2+ was found for a PDA/boric acid nanocrystal suspension. X-ray diffraction and Fourier transform infrared studies revealed that Pb2+ and Ag+ intercalated into the galleries of PDA nanocrystals and deprotonated most —COOH groups in the side chains of PDA, forming a strong ionic interaction. This strong ionic interaction effectively reduced the conjugation length in the PDA main chain, and therefore selectively induced a blue-to-red ionochromic transition.

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1. Introduction

Detection of metal ions, especially heavy metal ions, is of great importance, because they play an important role in the survival and development of organisms and the environment. Among numerous analytical methods available for the detection of metal ions, fluorescence detection attracted the most attention because of its high sensitivity and local observation by fluorescence imaging spectroscopy [1–4]. However, precise fluorophore design and complicated organic synthesis largely restrict the development of cheap fluorescence chemosensors for metal ions. Compared with fluorescence sensors, metal ion sensors based on polydiacetylenes have demonstrated some merits: 1) Polydiacetylenes demonstrate obvious changes in color and “turn-on” fluorescence in response to the complexation with metal ions; 2) Precise design of the photo-physics involved in traditional fluorescence sensors is unnecessary for sensors based on polydiacetylenes, since their chromatic change in the main chain is resulted from the perturbation of side chains [5–9].

Successful attempts to fabricate metal ion sensors based on polydiacetylenes can be divided into three categories: 1) Chemical modification of polydiacetylenes to introduce a receptor unit for metal ions [10,11], 2) synthesis of receptor modified amphiphilic diacetylene monomers, followed by self-assembly and subsequent photo-topochemical polymerization [12–16], and 3) embedding of ionophores in the self-assembled polydiacetylene lipids [17]. Nonetheless, in the first and third strategies, there is a risk of inducing chromatic transition by chemical modification of polydiacetylenes and by embedding ionophores in the self-assembled lipids of polydiacetylenes. In the second strategy, the difficulty lies in the self-assembly of chemically modified diacetylenes into properly packed crystals to meet the strict requirements for topochemical polymerization. Therefore, it is highly desirable to develop polydiacetylene-based metal ion sensors without any introduction of receptor units for metal ions by chemical modifications.

To tackle this challenge, for the first time we report a novel strategy towards selective and sensitive detection of metal ions using commercially available 10,12-pentacosadiynoic acid (DA) and
regulating small organic compounds (SOCs), without any chemical modification of the DA or PDA molecules. First, a water-soluble SOC will be used to stabilize DA/SOC nanocrystals by the solvent/non-solvent method for preparing noncovalently connected micelles (denoted as the NCCM method) \cite{18}. Second, UV-induced topochemical polymerization will convert the DA/SOC nanocrystals to PDA/SOC nanocrystals. Third, the SOC will interact with (or “capture”) non-targeted metal ions in solution and only allow targeted metal ions to intercalate into PDA in order to induce ionochromic transition. Therefore, a small PDA crystal size is critical for the fast intercalation of ions into PDA galleries, and the specific regulating ability of the SOC is critical for the detection selectivity.

2. Experimental

2.1. Materials

10,12-pentacosadiynoic acid (DA), CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{11}−C≡C−C≡C−(CH\textsubscript{2})\textsubscript{9}−COOH, was purchased from GFS chemicals, Inc. (Powell, OH). Glycine (Gly), boric acid (BA), and anhydrous ethanol were purchased from Sinopham Chemical Reagent Co., Ltd, China, and were used without further purification.

2.2. Preparation of PDA/SOC nanoaggregate suspension

DA was dissolved in anhydrous ethanol at a concentration of 1.25 mg/mL followed by filtration through a 0.45 μm PTFE filter to remove any pre-polymerized DA impurity prior to use. DA/Gly nanoaggregate suspension was prepared by dropwise addition of 0.4 mL DA ethanol solution into 5.0 mL Gly aqueous solution (5.0 mg/mL) under mechanical stirring at 25 °C. Then, the DA/Gly nanoaggregate suspension in a sealed vial was annealed in a gravity oven at 50 °C for 4 h in the dark. After cooling to room temperature, the DA/Gly nanoaggregate solution in water were polymerized by a 254-nm UV irradiation (ZF-1 UV lamp, Shanghai Baoshan Gucu Electro-optic Instrument Factory, Shanghai, China) for 10 min at room temperature. Similarly, DA/BA nanoaggregate suspension was prepared by dropwise addition of 0.4 mL DA solution into 5.0 mL BA aqueous solution (0.5 mg/mL) under stirring at 25 °C. Then, the DA/BA nanoaggregate suspension was stored in a refrigerator (4 °C) overnight. Finally, PDA/BA nanoaggregates were prepared by a 254-nm UV irradiation for 30 min at room temperature.

2.3. Characterization and instrumentation

Dynamic light scattering (DLS) measurements were conducted at a fixed scattering angle of 90 °C at 25 °C using an ALV-5000 laser light scattering spectrometer equipped with a multi-τ digital time correlation (ALV5000) and a He–Ne laser (λ\textsubscript{0} = 632.8 nm) light source. The \( \langle R_\text{h} > \) and polydispersity index (PDI) were obtained by the CONTIN program. A Shimadzu UV-2550 apparatus was used for UV–Vis measurements. Colorimetric response (CR) describes the relative change in “percent blue” (PB). The initial percent blue, PB\textsubscript{0}, is defined as: \( \text{PB}_0 = \frac{A_{\text{blue}}}{A_{\text{red}}} \times 100\% \), where \( A_{\text{blue}} \) and \( A_{\text{red}} \) are the absorbance at the “blue” (648 nm) and “red” (552 nm) for PDA/Gly and 548 nm for PDA/BA nanocrystals) wavelengths in a UV–Vis spectrum. The CR characterizes the percent conversions in the red phase: \( C = \frac{\text{PB}_0 − \text{PB}_1}{\text{PB}_0} \times 100\% \), where \( \text{PB}_1 \) is the final percent blue after addition of metal ions. All Fourier transform infrared (FTIR) spectra were recorded with 64 scans in the range 4000–400 cm\(^{-1}\) on a Nicolet Nexus 470 spectrometer with a resolution of 4 cm\(^{-1}\). The fluorescence spectra were measured by using an Edinburgh Photonics FLS 920 luminescence spectrometer at 20 °C. PDA/Gly nanocrystal aggregation was excited by 483 nm as determined by the excitation spectrum. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was conducted on a Hitachi P-4010 spectrometer. In detail, metal ions were added to the PDA/Gly nanocrystal suspension. The mixture was stored at ambient temperature for several hours and then measured by ICP-AES. The PDA/Gly nanocrystals were collected by centrifugation at 12,000 rpm for 1.5 h and purified by washing with deionized water for three times. The content of metal ions in the PDA/Gly nanocrystals and supernatant (including the washing solution) was tested, respectively. TEM observation was carried out on a Philips CM120 electron microscope at an accelerating voltage of 80 kV. The sample was drop-cast onto a 400-mesh carbon-coated copper grid. Extra solution was blotted away using a filter paper and the remainder solution was allowed to dry at room temperature.

3. Results and discussion

3.1. Selective detection of Pb\textsuperscript{2+} and Ag\textsuperscript{+} based on PDA/Gly nanocrystal suspension

PDA is known to have an ionochromic property due to the metal ion-carboxylic acid (in the side chains) interaction, which disturbs the main chain conjugation length \cite{13}. However, this ionochromatic detection is not selective at all. To improve the detection selectivity and avoid complicated chemical modification, here we propose a novel strategy. Because PDA has no selectivity to metal ions, we will use a regulating SOC or polymer for two purposes. First, the SOC or polymer will interact with DA via non-covalent bonding and stabilize DA nanocrystals (or prevent DA crystals from growing into large ones). The nanosized PDA crystals can facilitate fast intercalation of metal ions into PDA galleries. Second, the stabilizing SOC or polymer will interact with metal ions and regulate their intercalation into PDA galleries for selective detection.

On the basis of our recent reports \cite{19,20}, water soluble poly(-vinyl pyrrolidone) (PVPy) and poly(vinyl alcohol) (PVA) could stabilize nanosized (a few tens to a hundred nanometers) DA crystals in aqueous solutions, and intercalate into their galleries via intermolecular hydrogen bonding. After UV-initiated topochemical polymerization, reversible thermochromic transitions were observed. However, no ionochromatic transition was studied for these polymer/PDA nanocrystals.

In this work, we focus on water soluble SOCs that could regulate the interaction with metal ions in the aqueous solution. Hydrophilic amino acids were known to have specific interactions with metal ions. Among a number of water soluble amino acids, glycine (Gly) was identified to be able to stabilize DA nanocrystals in an aqueous solution without destroying the capability of topochemical polymerization. In a typical NCCM method, 0.4 mL of DA solution in ethanol was dropwise added into 5.0 mL of an aqueous Gly solution (5.0 mg/mL) under stirring. Due to the insolubility in the mixed solvent (water/ethanol = 12.5/1 vol/vol), DA aggregated into nanosized particles (see Fig. 1A and B). However, further aggregation of these nanoparticles was stopped by the stabilization effect from the DA-Gly interaction.

The DLS result in Fig. 1A shows that the Z-average hydrodynamic radius \( \langle R_\text{h} > \) of DA/Gly NCMC particles is ca. 60 nm. TEM observation in Fig. 1B reveals spherical DA/Gly NCMC particles with the particle size ranging from 25 to 72 nm, nearly consistent with the DLS result. Direct UV irradiation of the DA/Gly NCMC suspension at 254 nm for 10 min only resulted in a very faint blue color. This faint blue color did not deepen even after a prolonging UV irradiation time. We consider that this was probably resulted from the less proper packing of DA molecules in the nanocrystals. Therefore, the DA/Gly NCMC suspension was thermally annealed at 50 °C (below the melting temperature of DA crystals at 62 °C) for...
4 h in a sealed vial. From the TEM image in Fig. 1C, rectangular-shaped nanocrystals were obtained after thermal annealing. Surprisingly, these lamellar DA nanocrystals could be topochemically polymerized with a deep blue color observed after UV irradiation at 254 nm for 10 min. UV–Vis spectrum showed an absorption peak at 655 nm (data not shown), which could be ascribed to the blue-form of PDA crystals.

These polymerized PDA nanocrystals could be stabilized in aqueous Gly solution for at least 2 weeks. Decreasing the Gly concentration or completely removing Gly from the solution by dialysis eventually led to significant precipitation of the PDA nanocrystals. Therefore, Gly must be physically adsorbed on the surface of PDA crystals to stabilize them. Both FTIR and zeta potential studies were employed to investigate this physical interaction. FTIR results of pure DA, Gly, and centrifuged PDA/Gly nanocrystals are shown in Fig. 2. In the FTIR spectrum of the pure DA crystal, the peak at 1693 cm\(^{-1}\) was assigned to the hydrogen-bonded carbonyl stretching band \([\nu(C=O)]\) in the dimer-Lewis acid groups. However, in the spectrum of the PDA/Gly nanocrystals, a new peak appeared at 1665 cm\(^{-1}\) in addition to the strong absorption band at 1693 cm\(^{-1}\). The new peak at 1665 cm\(^{-1}\) could be assigned to partially deprotonated carboxylic acid groups in PDA. In the spectrum of pure Gly crystal, the broad peaks for \([\nu(s)(NH_3^+)]\), \([\nu(p)(NH_3^+)]\), and \([\nu_s(C-N)]\) appeared at 3171, 3054, and 1033 cm\(^{-1}\), respectively, consistent with the fact that the zwitter-ionic form was favored for Gly in both solution and solid state. These absorption bands slightly shifted to higher frequencies (3180, 3065, and 1040 cm\(^{-1}\), respectively) in PDA/Gly nanocrystals. In addition, the measured zeta potential was –33 mV, indicating a moderate electrostatic stabilization of the PDA nanocrystals. Both FTIR and zeta potential results suggested that the physical interaction between PDA and Gly should be electrostatic or ionic. In this interaction, the COOH groups on the PDA crystal surfaces became deprotonized and interacted with the NH3\(^+\) groups in Gly molecules to form electrostatic stabilization of PDA nanocrystals. Judging from the relatively large content of Gly in the centrifuged PDA/Gly nanocrystals (see Fig. 2), the Gly molecules must form multilayer protection on the surface of PDA crystals.

XRD result showed that the crystalline lamellar spacing was 4.7 nm (see Fig. 8) and DSC result showed a sharp melting peak at 62 °C (data not shown). Both results showed that the inside of the PDA/Gly nanocrystals were pure PDA[21,22] and no intercalation of Gly was observed. This was different from the intercalation of water-soluble PVPy and PVA reported before[19,20].

To test the detection selectivity, different kinds of metal ions, i.e., Li\(^{+}\), Na\(^{+}\), K\(^{+}\), Mg\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Zn\(^{2+}\), Al\(^{3+}\), Ca\(^{2+}\), Ba\(^{2+}\), Mn\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Cr\(^{3+}\), Ag\(^{+}\), and Pb\(^{2+}\), were added into the PDA/Gly nanocrystal suspension, respectively. The colorimetric behavior of the PDA/Gly nanocrystal suspension after addition of 65 μM metal ions was studied by UV–Vis spectroscopy. As shown in Fig. 3, only Pb\(^{2+}\) could lead to a significant spectral change: The absorption intensity at 648 nm decreased and a new absorption band at 552 nm, which was ascribed to the red from of PDA, emerged. This indicated that the color of the PDA/Gly nanocrystal suspension changed from blue to red after addition of Pb\(^{2+}\) (see the inset in Fig. 3A). The chromatic change was further quantified by calculating the CR values (Fig. 3B). Again, Pb\(^{2+}\) resulted in the highest CR value. The CR values of the PDA/Gly nanocrystal suspension in the presence of K\(^{+}\), Ba\(^{2+}\), or Ag\(^{+}\) also increase slightly. However, no chromatic change was observed, since the peak at 552 nm for the red form of PDA did not appear (see the inset of Fig. 3B). This result indicated that PDA/Gly nanocrystal suspension had a good selectivity for Pb\(^{2+}\) at a concentration of 65 μM.

The colorimetric behavior of PDA/Gly nanocrystal suspension in the presence of high concentration metal ions was further studied. As shown in Fig. 4, even when the concentration of Li\(^{+}\), Na\(^{+}\), K\(^{+}\), Mg\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Zn\(^{2+}\), Al\(^{3+}\), Ca\(^{2+}\), Ba\(^{2+}\), Mn\(^{2+}\), Ni\(^{2+}\), and Cu\(^{2+}\) was over 1.304 mM, no chromatic change of the PDA/Gly nanocrystal suspension was observed. When the concentration of Cr\(^{3+}\) was over 450 μM, precipitation of PDA/Gly nanocrystals (still in blue color) would take place. Therefore, no result is shown for Cr\(^{3+}\) in Fig. 4. Nonetheless, increasing the Ag\(^{+}\) concentration would lead to a chromatic change of PDA/Gly nanocrystal suspension from blue to red, as shown in Fig. 5. From this figure, the detection limit for Ag\(^{+}\) was between 113 and 131 μM.

To determine the detection limit and speed, fluorescence spectroscopy was used because PDA could also exhibit fluorescence in addition to the UV–Vis absorption. Intriguingly, a “turn-on” fluorescent change was observed for the PDA/Gly nanocrystal...
suspension when the Pb$^{2+}$ concentration increased to 9.9 μM (see Fig. 6A). Afterwards, the fluorescent intensity of the PDA/Gly nanocrystal suspension increased with increasing the Pb$^{2+}$ concentration. After the Pb$^{2+}$ concentration reached 79.8 μM, the increase in fluorescence intensity gradually slowed down. Fig. 6B shows the fluorescence intensity change when the Pb$^{2+}$ concentration suddenly increased from 44.6 μM to 56.6 μM. Beyond 1 min, the fluorescence intensity only increased slightly, indicating that the ionochromic response time was <1 min.

Although we have demonstrated the detection selectivity for Pb$^{2+}$ and Ag$^{+}$ using PDA/Gly nanocrystals, the reason for these detections is still not clear because pure PDA nanocrystals (after complete removal of Gly molecules by dialysis) are entirely nonselective to metal ions. To understand what has happened, we use ICP-AES, FTIR, and XRD to study the structural changes in PDA/Gly nanocrystals. ICP-AES analysis results for different metal ions in PDA/Gly nanocrystals and in solution are shown in Table 1. After centrifuging and washing with deionized water, most metal ions (Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Zn$^{2+}$, Al$^{3+}$, Ca$^{2+}$, Ba$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, and Cr$^{3+}$) were found in the Gly solution. However, most Pb$^{2+}$ and Ag$^{+}$ were found in the PDA/Gly nanocrystals and only a small portion was present in the Gly solution. These results clearly indicated that Pb$^{2+}$ and Ag$^{+}$ were effectively captured by the PDA/Gly nanocrystals. However, it is still not clear whether Pb$^{2+}$ and Ag$^{+}$ were absorbed onto the surface of PDA nanocrystals or intercalated into their galleries.

To answer this question, we performed FTIR study of PDA/Gly nanocrystals in the presence of different metal ions at a concentration of 65 μM, as shown in Fig. 7. Comparing with the spectrum of pure PDA/Gly nanocrystals, no significant changes were observed except for Pb$^{2+}$ and Ag$^{+}$ ions. Namely, both the strong absorption band at 1693 cm$^{-1}$ and the weak band at 1665 cm$^{-1}$ were present, representing the hydrogen-bonded COOH and COO$^-$ groups in the core and at the surface of PDA nanocrystals, respectively. After addition of Pb$^{2+}$ or Ag$^{+}$, the intensity of the absorption band at 1693 cm$^{-1}$ decreased while the band at 1665 cm$^{-1}$ somewhat increased. This result suggested that the COOH groups inside the core of PDA/Gly nanocrystals were deprotonated, presumably complexed with Pb$^{2+}$ and Ag$^{+}$. In other words, Pb$^{2+}$ and Ag$^{+}$ should intercalate into the cores of PDA/Gly nanocrystals, rather than complex with Gly at the PDA nanocrystal surfaces.

To directly prove the intercalation of Pb$^{2+}$ and Ag$^{+}$ into the galleries of PDA/Gly nanocrystals, XRD experiments were carried out.
out for all the ions we studied and results are shown in Fig. 8. For PDA/Gly nanocrystals treated with Li\(^{+}\), Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\), Mg\(^{2+}\), Ba\(^{2+}\), Al\(^{3+}\), Cr\(^{3+}\), Mn\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\), the overall lamellar spacing at \(q = 1.33\) nm\(^{-1}\) was nearly the same as that of pure PDA, i.e., 4.7 nm. However, after interaction with Pb\(^{2+}\) and Ag\(^{+}\), the lamellar spacing increased to 6.1 nm (\(q = 1.0\) nm\(^{-1}\)). From these results, we concluded that Pb\(^{2+}\) and Ag\(^{+}\) should intercalate into the PDA crystal galleries by ionic interaction with the COOH groups in the PDA side chains. This interaction in the side chains effectively changed the conjugation length in the PDA main chain, resulting in an obvious change in the UV–Vis absorption property. However, other metal ions could not be intercalated into the PDA crystal galleries and no ionochromic change was observed. Note that many orders (up to 12) of reflection peaks were seen for Pb\(^{2+}\) and Ag\(^{+}\)-intercalated PDA/Gly nanocrystals. This could be explained by the enhanced electron density contrast after heavy metal ion intercalation into the galleries (similar to the case of silver behenate).

On the basis of the above experimental results, we consider that Gly in the solution or at the outer layer stabilizing the PDA nanocrystals must have played an important role in regulating the intercalation of metal ions into the PDA crystal galleries. It is speculated that most metal ions, such as Li\(^{+}\), Na\(^{+}\), K\(^{+}\), Mg\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Zn\(^{2+}\), Al\(^{3+}\), Ca\(^{2+}\), Ba\(^{2+}\), Mn\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), and Cr\(^{3+}\), could interact with Gly in solution or at the outer stabilizing layer, thus preventing the ion intercalation. However, Pb\(^{2+}\) or Ag\(^{+}\) might not strongly interact with Gly in solution or at the outer layer. Therefore, they could intercalate into the galleries of PDA nanocrystals, leading to chromatic change of PDA/Gly nanocrystal suspension. Currently, this hypothesis is still under investigation and will be reported in the future.

3.2. Selective detection of Zn\(^{2+}\) based on PDA/BA nanocrystal suspension

If the above hypothesis is correct, different metal ion selectivity of PDA/SOC nanocrystal suspension could be achieved by utilizing a different SOC in this strategy. In a first trial, boric acid (BA) was chosen and DA/BA nanoadgregate suspension was prepared by using the NCCM method. DLS and TEM results showed that the DA/
BA nanoaggregates were spherical with an average size of 77 nm (data not shown). However, effective topochemical polymerization could only be achieved by annealing the DA/BA nanoaggregate suspension around 4 °C for 10–12 h, although the exact reason was not well-understood. TEM result showed that nanosized DA/BA crystals were obtained after annealing the nanoaggregates at 4 °C for 10–12 h.

After 254 nm UV irradiation, a transparent blue suspension of PDA/BA nanocrystals was obtained. The colorimetric behavior of the PDA/BA nanocrystal suspension in the presence of different metal ions (Li⁺, Na⁺, K⁺, Mg²⁺, Fe³⁺, Co²⁺, Zn²⁺, Al³⁺, Ca²⁺, Ba²⁺, Mn²⁺, Ni²⁺, Cu²⁺, Cr³⁺, Ag⁺, or Pb²⁺) at 99 μM was studied using UV–Vis spectroscopy, as shown in Fig. 9. The most significant chromatic change was found for Zn²⁺, since the absorption at 638 nm decreased and a new absorption band appeared at 548 nm, which could be attributed to the red-form of PDA. The chromatic change from blue to red was also quantified by the CR value. In accordance with the change in UV spectrum after the addition of metal ions (Fig. 9A), Zn²⁺ also increased the CR value significantly (Fig. 9C).

In addition to Zn²⁺, Pb²⁺ and Cr³⁺ could also slightly induce an increase in the CR value (Fig. 9C). However, the best selectivity was determined for Zn²⁺. As shown in Fig. 10A, when the Zn²⁺ concentration was as low as 6.6 μM, an obvious spectroscopy change of the PDA/BA nanocrystal suspension was observed. With increasing the Zn²⁺ concentration, the intensity of the absorption peak at 548 nm (ascribed to the red-form of PDA) increased. When the Zn²⁺ concentration increased to 76.9 μM, the color of PDA/BA nanocrystal suspension changed to red visually. On the contrary, even when the Pb²⁺ or Cr³⁺ concentration was over 172 μM, the chromatic change of PDA/BA nanocrystal suspension was still weak, as evidenced by the weak absorption peak at 548 nm (Fig. 10B and C).

As discussed above, different detection selectivities for metal ions could be achieved by using different PDA/SOC nanocrystal suspensions: the PDA/Gly nanocrystal suspension displayed the best selectivity for Pb²⁺, while the PDA/BA nanocrystal suspension demonstrated the best selectivity of Zn²⁺. These results indirectly suggested that the SOC in solution or at the outer stabilizing layer of PDA nanocrystals could effectively regulate the intercalation of metal ions into the galleries of PDA lamellar crystals. In the following experiment, we found that the selectivity for Zn²⁺ could be lost once free Gly was added into the PDA/BA nanocrystal suspension. In the presence of free Gly at 13 mM (Fig. 11), the absorption peak at 548 nm, which was ascribed to the red-form of PDA, did not appear even when the Zn²⁺ concentration was as high as 1.131 mM. This result clearly indicated that Gly had a stronger interaction with Zn²⁺ than BA. As a result, the selectivity for Zn²⁺ was weakened.

Table 1

<table>
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<tr>
<th>Metal ion</th>
<th>Weight in PDA/Gly nanocrystals (μg)</th>
<th>Weight in the solution (μg)</th>
<th>Total weight in the feed at 65 μM (μg)</th>
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<tr>
<td>Mg²⁺</td>
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<td>5.10</td>
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<td>4.97</td>
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<td>3.1</td>
<td>135</td>
<td>144.20</td>
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<tr>
<td>Cr³⁺</td>
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<td>10.92</td>
</tr>
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<td>11.54</td>
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Fig. 9. (A and B) UV–Vis spectra of PDA/BA nanocrystal suspension at the metal ions concentration of 99 μM. Nitrate salts: Na⁺, K⁺, Mg²⁺, Fe³⁺, Co²⁺, Zn²⁺, Al³⁺, Ca²⁺, Ba²⁺, Mn²⁺, Ni²⁺, Cu²⁺, Cr³⁺, Ag⁺, or Pb²⁺ and chloride salt: Li⁻. (C) Comparison of CR values of PDA/BA nanocrystal suspensions in the presence of different metal ions.

Fig. 10. UV–Vis spectra of PDA/BA nanocrystal suspensions in the presence of (A) Zn²⁺, (B) Pb²⁺, and (C) Cr³⁺ with increasing the concentration of metal ions.
was completely lost for the PDA/BA nanocrystal suspension in the presence of Gly.

4. Conclusions

In this work, we have developed a novel and simple strategy to enhance the detection selectivity for metal ions by using a PDA/SOC nanocrystal suspension. In this strategy, the SOC was able to selectively regulate the intercalation of metal ions into the galleries of PDA nanocrystals, inducing an ionochromic transition. For example, the PDA/Gly nanocrystal suspension had a good selectivity for Pb$^{2+}$ and Ag$^{+}$ with different detection sensitivities, whereas the PDA/BA nanocrystal suspension had the best selectivity for Zn$^{2+}$. The detection limit of Pb$^{2+}$ and Zn$^{2+}$ was 9.9 and 6.6 $\mu$M for the two systems, respectively. FTIR and XRD results clearly showed that Pb$^{2+}$ and Ag$^{+}$ intercalated into the galleries of PDA nanocrystals and deprotonated most COOH groups in the side chains of PDA to form a strong ionic interaction. This strong ionic interaction effectively reduced the conjugation length in the PDA main chains and induced an ionochromic transition. Comparing with the chemical modification strategy for polydiacetylenes, this method is cheap, versatile, and effective because commercial PDA and SOCs are readily available for the design and fabrication of various metal ion sensors.

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