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PAPER

Recognition and determination of multi-metal ions based on silver nanoclusters capped by polyethyleneimine with different molecular weights

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Ag nanoclusters templated by hyperbranched polyethyleneimine (PEI) with different molecular weights have been developed as a new fluorescent platform for sensitive and selective recognition of Hg^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+} based on fluorescence quenching of Ag nanoclusters. This sensing system shows good linear ranges and lower detection limits: the linear ranges are 0.1 nM to 10 μM for Hg^{2+}, 0.1 nM to 20 μM for Cu^{2+}, 1 nM to 20 μM for Co^{2+}, and 1 nM to 30 μM for Ni^{2+}, respectively; the limits of detection for Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} are estimated to be 35 pM, 28 pM, 0.33 nM, 0.30 nM, respectively. In addition, the different molecular weights of PEI reveal a little effect on the sensitivity and linear ranges of detection. Most importantly, by adding different masking agents, Hg^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+} could be quantified selectively without interference of other metal ions, for instance thymine for masking Hg^{2+}, potassium pyrophosphate for masking Cu^{2+}, nitrilotriacetic acid for masking Co^{2+} and dimethylglyoxime for masking Ni^{2+}. On this basis, not only the content of single metal ion but also the total amount of metal ions could be readily detected, which would further improve the convenience and practicability of metal ion sensors. Furthermore, this sensing system has been applied successfully to the detection of Hg^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+} in real water samples.

1. Introduction

Heavy metal ions, such as Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}, have become serious, urgent, and ubiquitous pollutants because they could cause a detriment to people and the environment. For example, Hg^{2+} could make several bad influences on human bodies, including the nerve, brain, and heart damage, lung irritation, eyes swelling, skin rashes, fever and headache;[1,2] when Cu^{2+} is presented in excess, it may be harmful to the central nervous system and disorders associated with neurodegenerative diseases (e.g., Wilson's diseases and Alzheimer's disease);[3,4] Co^{2+} may lead to loss of appetite, hair loss, flushing and blood system diseases;[5,6] the accumulation of Ni^{2+} in the body results in lung fibrosis, kidney diseases, allergic dermatitis and eczema.[7-9] Hence, the reasonable design and utilization of efficient sensors to selectively detect these metal ions at environmental and biological levels are necessary. Among them, metal ion sensors based on nano-materials have aroused great attention due to their easy preparation, chemical stability, favorable biocompatibility and unique optical properties.[10-14]

As a novel type of fluorescent nanoprobes, Ag nanoclusters have been used extensively to construct sensors for the detection of metal ions.[11,13,15,16,17] However, due to the different templates and synthetic conditions, the selectivity and sensitivity of these small clusters were far apart. For example, Guo et al. designed sliver nanoclusters capped by denatured bovine serum albumin, as a fluorescent sensing platform, to detect Hg^{2+} on the basis of the $5d^{10}$ (Hg^{2+})-$4d^{10}$(Ag^+) metallophilic interaction, leading to the fluorescence quenching of Ag nanoclusters.[18] This quenching mechanism was direct action between Ag nucleus and Hg^{2+}, which had no necessary connection with the templates and synthetic methods, so almost all of the silver nanoclusters synthesized with various templates could be utilized to determine Hg^{2+}, and in the meanwhile, Cu^{2+} and Cr^{3+} would not interfere with the detection of Hg^{2+} as reported in the literature.[2,11,17,18,19,20,21,22,23,24] However, there were also some Ag nanoclusters that were reported to sense Cu^{2+} and Cr^{3+} with no interference of Hg^{2+}.[25,26] Some studies explained that the differences of selectivity were caused by the templates, and the interaction between templates and metal ions may produce electrons transfer[27] or energy transfer,[15, 28] which could also cause the fluorescence quenching of Ag nanoclusters. Nevertheless, using the same or similar templates, it also showed an obvious difference in the selectivity of metal ions. For instance, the fluorescence of poly (methacrylic acid) (PMAA)-templated Ag nanoclusters was found to be quenched effectively only by Cu^{2+},[29] while another Ag nanoclusters capped by PMAA-Na could be used as a fluorescence probe for the determination of Cr^{3+} with high sensitivity and selectivity.[26] It suggests that a feature of one type of

Ag nanoclusters is sometimes seen to be less effective in other types. However, the above phenomena will result in some confusion of the applications of Ag nanoclusters. It is still a question whether sliver nanoclusters have special selectivity to a certain kind of metal ion. Moreover, there is little literature reporting on the differences of the sensitivity and selectivity of Ag nanoclusters caused by templates in analysis and detection.

On the other hands, several metal ions generally coexist in heavy metal polluted soil and water, thus nano-probes based on selective response to a certain kind of metal ion are not preferred in practice. Hence, it is highly desired to develop and construct sensors in recognition and determination of multi-metal ions.

Herein, utilizing fluorescent Ag nanoclusters templated by polyethyleneimine (PEI) with different molecular weights (abbreviated as Ag NC-PEIs), we constructed a novel metal ion sensing system, which could response to Hg^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+} based on fluorescence quenching of Ag nanoclusters. Most importantly, by adding different masking agents, Hg^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+} could be quantified selectively without interference of other metal ions, for instance thymine for masking Hg^{2+}, potassium pyrophosphate for masking Cu^{2+}, nitrilotriacetic acid for masking Co^{2+} and dimethylglyoxime for masking Ni^{2+}, respectively. Taking advantage of this multi-metal ion sensing system, not only the total amount of metal ions but also the content of single metal ion could be readily detected, which could further improve the convenience and practicability of metal ion sensors. Additionally, Ag nanoclusters capped by PEI with different molecular weights reported in this paper did not show special selectivity on a certain kind of metal ion, and the molecular weights of template exhibit a little effect on the sensitivity of Ag NC-PEIs in response to metal ions. Therefore, we believe that this work would shed some light on the confusion of the applications of Ag nanoclusters and suggest a new strategy for the recognition and determination of multi-metal ions.

2. Experimental section

2.1 Chemicals and reagents

Silver nitrate ($AgNO_3$), hyperbranched polyethyleneimine (PEI, Mw=600, 99%; Mw=1800, 99%; Mw=70000, 50%), Britton-Robison (BR) buffers (pH 1.81-11.98) were prepared by mixing 0.2 M NaOH and a mixture of 0.04 M H_3PO_4, H_3BO_3, and CH_3COOH according to suitable proportion. Potassium pyrophosphate, thymine, nitrilotriacetic acid, dimethylglyoxime, formaldehyde (35wt %) and other metal salts were purchased from Aladdin Reagent Co., Ltd., China. All reagents used are of at least analytical reagent grade. The water used was purified through a Millipore system. All solutions were freshly prepared before use.

2.2 Characterization

Fluorescence measurements were performed on a Hitachi F-7000 fluorescence spectrophotometer. The emission spectra of the as-prepared Ag nanoclusters were recorded upon excitation at 375 nm. The samples were placed in a 10 mm optical path length quartz cuvette for the fluorescence measurements. And the ultraviolet-visible (UV-vis) absorption spectra were obtained on a Cary 300 Bio

UV-vis spectrophotometer. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) of Ag NC-PEIs were carried out on a Tecnai G2 F20 electron microscope.

2.3 Synthesis of silver nanoclusters

Typically, PEI was first dissolved in Milli-Q water by stirring for 2 min, and then with the addition of a certain amount of $AgNO_3$, the solution was stirred for 2 min. Next, formaldehyde solution was added. Subsequently, under vigorous stirring to form a homogeneous solution, the color of the mixture changed from colorless to yellow, indicating the formation of PEI-capped Ag nanoclusters. Then the final solution was stored at room temperature for at least 4 days before its further application. According to this method, it was feasible to synthesize Ag nanoclusters with different molecular weights of PEI. In this study, we abbreviated Ag nanoclusters templated by PEI with different molecular weights as Ag NC-PEIs. For example, Ag NC-PEI 600 was the abbreviation of "Ag nanoclusters templated by PEI with molecular weight 600".

2.4 Fluorescence detection of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}

A typical metal ion detection procedure was conducted as follows. Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} aqueous solutions with different concentrations were freshly prepared before use. The as-prepared Ag NC-PEIs solutions were diluted 10 times before detection. Generally, 5 μL diluted Ag NC-PEIs, 200 μL BR buffer solution (pH 10) and various concentrations of Hg^{2+} (Cu^{2+} / Co^{2+} / Ni^{2+}) were mixed together. The mixtures were equilibrated at room temperature for 30 min before fluorescence measurements.

2.5 Masking assay

Different masking agents were chosen for masking Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}, respectively, such as thymine for masking Hg^{2+}, potassium pyrophosphate for masking Cu^{2+}, nitrilotriacetic acid for masking Co^{2+}, and dimethylglyoxime for masking Ni^{2+}. Taking Hg^{2+} as an example, 100 μM thymine, 8 μM Hg^{2+}, 5 μL diluted Ag NC-PEIs and 200 μL BR buffer solution (pH 10) were blended together and the solution was placed for 30 minutes at room temperature before detection.

2.6 Real sample detection

In this assay, we detected the concentrations of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} in tap water. The Ag NC-PEIs solutions were diluted 10 times and the real samples were adjusted to pH 10 before detection. With addition of certain amounts of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} (with known concentrations as C_0) in the tap water, the fluorescence of Ag-PEIs was quenched obviously, and this fluorescence intensity was recorded as F_0. At first, thymine was added to mask Hg^{2+}, and the fluorescence intensity of Ag NC-PEIs could be restored, and the fluorescence intensity was recorded as F_1, $F_1 - F_0 = \Delta F_1$, and $\Delta F_1 / F_1$ would be represented as the fluorescence-quenched efficiency of Hg^{2+}. This value ($\Delta F_1 / F_1$) was substituted in the linear equation of Hg^{2+}, and then the concentration of Hg^{2+} added could be calculated. Subsequently, adding potassium pyrophosphate to mask Cu^{2+}, the fluorescence intensity of Ag NC-PEIs could be restored to some degree again, which was recorded as F_2, $F_2 - F_1 = \Delta F_2$, and $\Delta F_2 / F_2$ would be represented as the fluorescence-quenched efficiency of

Cu^{2+}. This value ($\Delta F_2 / F_2$) was substituted in the linear equation of Cu^{2+}, and the concentration of Cu^{2+} added could be calculated. Similarly to the procedure as mentioned above, by adding nitrilotriacetic acid for masking Co^{2+} and dimethylglyoxime for masking Ni^{2+}, the corresponding concentration of Co^{2+} and Ni^{2+} could be calculated. At last, these concentrations added together were the total amount of metal ions in the tap water.

3. Results and discussion

3.1 Fluorescence responses of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}

In our previous report, Ag nanoclusters capped by PEI with molecular 10000 have been synthesized and utilized as a fluorescent and colorimetric sensor for halide ions.[30] However, PEI with different molecular weights (Mw 600, 1800, and 70000) could also be used to prepare silver nanoclusters based on PEI-modified silver mirror reaction. TEM and HRTEM images of Ag NC-PEIs were shown in Figure S1. Ag NC-PEIs exhibited an approximately spherical shape and well-dispersed. HRTEM images displayed the diameters of Ag NC-PEIs clearly, such as Ag NC-PEI 600 2.95 nm, Ag NC-PEI 1800 4.4 nm, and Ag NC-PEI 70000 1.95 nm. Besides, these Ag NC-PEIs also displayed similar optical features. For instance, the maximum emission wavelength was 435 nm when Ag NC-PEIs were excited at 375 nm; two absorbance bands were located at 268 and 354 nm, respectively (Figure S1). Additionally, the newly synthesized Ag nanoclusters in our experiment should be placed at room temperature for at least four days to obtain the maximum fluorescence intensity, and then the fluorescence intensity of Ag NC-PEIs could remain stable for at least 1 month at room temperature (Figure S2).

With the addition of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}, all of the Ag NC-PEIs exhibited obvious fluorescence quenching, in which Hg^{2+} and Cu^{2+} were the most effective quenching agents, while Co^{2+} and Ni^{2+} showed the relatively weak quenching abilities (Figure 1).
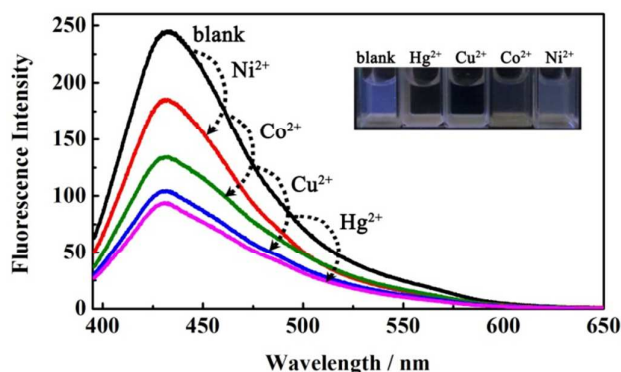

Figure 1. Fluorescence emission spectra of Ag NC-PEI 600 in the absence (blank) and presence of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} (Inset: photographs under UV light at 365 nm). The final concentration of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} were 8 μM, 8 μM, 8 μM, and 15 μM, respectively.
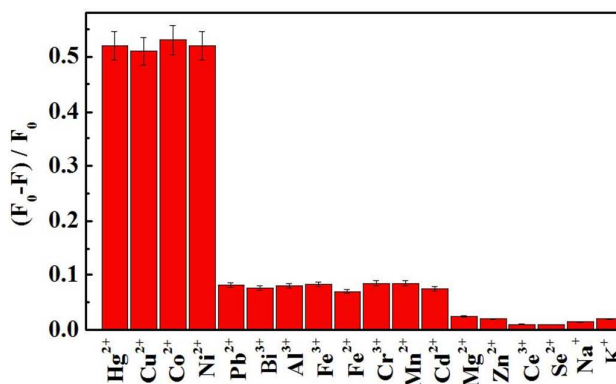

Figure 2. Selectivity of Ag NC-PEI 600 for the detection of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}: the concentrations of Hg^{2+} and Cu^{2+} were 8 μM, Co^{2+} 15 μM, Ni^{2+} 25 μM; the concentrations of other metal ions: Pb^{2+}, Bi^{3+}, Al^{3+}, and Fe^{3+} were 30 μM; Fe^{2+}, Cr^{3+}, Mn^{2+}, and Cd^{2+} are 50 μM; Mg^{2+}, Zn^{2+}, Ce^{3+}, Se^{2+}, Na^+, and K^+ were 100 μM.

The reaction conditions, such as the concentration of probe, reaction time and pH values, were also investigated in this article (Figure S3-S5). The optimal concentration of probe was 5 μL mL^{-1} for Ag NC-PEI 600 and 1800, and for Ag NC-PEI 70000 was 10 μL mL^{-1}. The reactions could complete within 30 min, and the optimal reaction pH was 10 (BR buffer medium). The following experiments were all performed under the optimal conditions.

3.2 Selectivity

To examine the selectivity of sensing system, 14 kinds of metal ions, such as Pb^{2+}, Bi^{3+}, Al^{3+}, Fe^{3+}, Fe^{2+}, Cr^{3+}, Cd^{2+}, Ce^{3+}, Se^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Na^+, and K^+, as control were tested under the same conditions (Figure 2 and Figure S6). The results suggested that this sensing system showed a high tolerance to K^+, Na^+, Mg^{2+}, Zn^{2+}, Ce^{3+}, Se^{2+}, Fe^{2+}, Mn^{2+}, Cr^{3+}, and Cd^{2+}, while Pb^{2+}, Bi^{3+}, Al^{3+}, and Fe^{3+} exhibited slight effects on the fluorescence of Ag NC-PEIs, in which the anti-interference ability of this sensing platform was better for Hg^{2+} and Cu^{2+} than Co^{2+} and Ni^{2+}.

3.3 Sensitivity

On the basis of the optimal conditions, a quantitative analysis of fluorescence intensities was made as a function of the concentrations of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}. In Figure 3, Figure S7 and S8, the fluorescence of Ag NC-PEIs was sensitive and decreased proportionately with increasing concentrations of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} as noted from the relationship between the fluorescence quenching rates and the concentrations of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}. Taking Ag NC-PEI 600 as an example (Figure 3), the good linear correlations were obtained over the concentration ranges from 0.1 nM to 10 μM for Hg^{2+}, 0.1 nM to 20 μM for Cu^{2+}, 1 nM to 20 μM for Co^{2+}, and 1 nM to 30 μM for Ni^{2+}, respectively. The limits of detection (LOD) for Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} were estimated to be 35 pM, 28 pM, 0.33 nM, 0.30 nM, respectively. Therefore, compared to Co^{2+} and Ni^{2+}, Ag NC-PEIs showed higher sensitivity for Hg^{2+} and Cu^{2+}. Moreover, the linear ranges and LOD of this sensing system were also not inferior to other metal ion sensors based nano-materials.[2,10,11,12] In addition, we compared the linear ranges
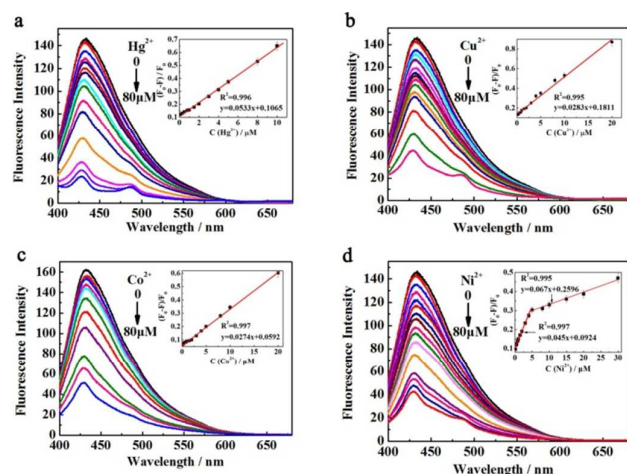
Figure 3. Fluorescence emission spectra of Ag NC-PEI 600 upon addition of different concentrations of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}. The insets of a, b, c, and d display the linear ranges for 0.1 nM to 10 μM Hg^{2+}, 0.1 nM to 20 μM Cu^{2+}, 1 nM to 20 μM Co^{2+}, and 1 nM to 30 μM Ni^{2+}, respectively

Table 1. Detection of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} in tap water.

Ag NC-PEIs	Metal ions	Added (μM)	Found (μM)	Recovery (%)
Ag NC-PEI 600	Hg^{2+}	5	4.38	87.6
	Cu^{2+}	5	4.52	90.4
	Co^{2+}	5	4.78	95.6
	Ni^{2+}	5	4.76	95.2
	total amount of metal ions	20	18.44	92.2
Ag NC-PEI 1800	Hg^{2+}	5	4.35	87.0
	Cu^{2+}	5	4.63	92.6
	Co^{2+}	5	4.82	96.4
	Ni^{2+}	5	4.83	96.6
	total amount of metal ions	20	18.63	93.2
Ag NC-PEI 70000	Hg^{2+}	5	4.45	89.0
	Cu^{2+}	5	4.50	90.0
	Co^{2+}	5	4.68	93.6
	Ni^{2+}	5	4.73	94.6
	total amount of metal ions	20	18.36	91.8

and LOD with Ag NC-PEIs (Table S1). It was clear that these Ag NC-PEIs did not show special selectivity for a certain kind of metal ion; the different molecular weights of PEI revealed a little effect on the sensitivity and linear ranges of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}.

3.4 Reproducibility

To investigate the reproducibility and stability of proposed method, we have calculated and listed the intra-day relative standard deviation (RSD) and the inter-day RSD of the detection of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} in Table S2. The RSD values were in the range of 1.66%-2.8%, indicating a good reproducibility of this multi-metal ion sensing system.
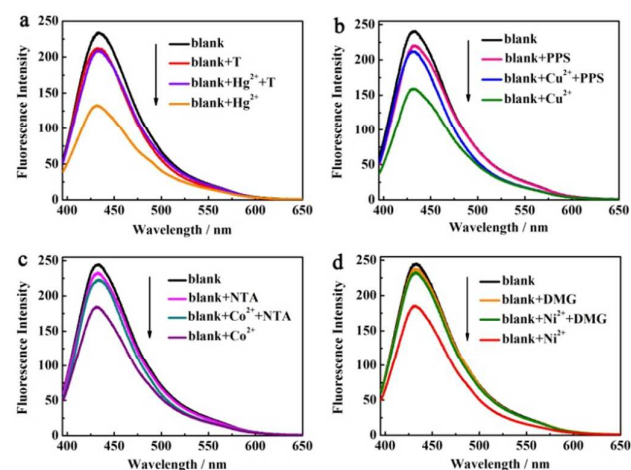

Figure 4. Fluorescence spectra of Ag NC-PEI 600 for detecting Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} in the absence (blank) and presence of masking agents: a, thymine (T) for Hg^{2+} (8 μM); b, potassium pyrophosphate (PPS) for Cu^{2+} (8 μM); c, nitrilotriacetic acid (NTA) for Co^{2+} (8 μM); d, dimethylglyoxime (DMG) for Ni^{2+} (15 μM).

3.5 Masking assay

The fluorescence quenching of Ag NC-PEIs toward Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} was found to be reversible (Figure 4, Figure S9 and S10). With the addition of appropriate masking agents, such as thymine for Hg^{2+}, potassium pyrophosphate for Cu^{2+}, nitrilotriacetic acid for Co^{2+}, and dimethylglyoxime for Ni^{2+}, the fluorescence of Ag NC-PEIs could be restored to 90%, 92%, 96%, and 97% of its original value, respectively (Figure 4). Furthermore, these masking agents would only react with their corresponding metal ions which were masked, and showed no effect on other ions. It was greatly facilitated this sensing system in the application, where both of the content of single metal ion and total amount of metal ions would be readily detected.

3.6 Detection of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} in real samples

To investigate the applicability of this sensing system, we measured the concentrations of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} in tap water. As shown in Table 1, the satisfactory recoveries were obtained in a range of 87%-89% for Hg^{2+}, 90%-93% for Cu^{2+}, 94%-96% for Co^{2+},95%-97% for Ni^{2+}, and 92%-94% for total amount of metal ions. The proposed method provided a good accuracy and precision. Moreover, not only the content of single metal ion but also the total amount of metal ions could be readily quantified.

3.7 Mechanism for the recognition of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}

The UV-vis spectra of Ag NC-PEI 600 and PEI 600 in the presence of Cu^{2+}, Co^{2+}, Hg^{2+}, and Ni^{2+} were displayed in Figure 5. According to the absorption change of PEI, the quenching mechanisms for Cu^{2+}, Co^{2+}, Hg^{2+}, and Ni^{2+} were divided into two types: (1) with the addition of Cu^{2+} and Co^{2+} in PEI (without Ag nanoclusters), a new peak appeared at 275 nm (Figure 5a and 5b), indicating that Cu^{2+} and Co^{2+} could be bound to the PEI protection layer rather than silver nucleus to form a stable cupric amine or cobaltic amine
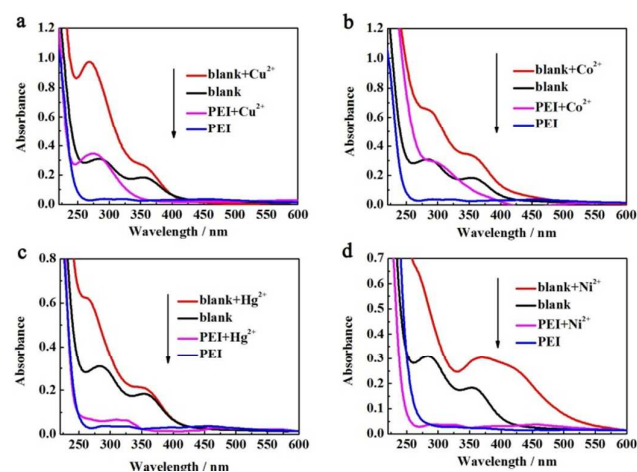
Figure 5. TUV–vis spectra of Ag NC-PEI 600, PEI 600 in the absence (blank) and presence of Cu^{2+} (a), Co^{2+} (b), Hg^{2+} (c), and Ni^{2+} (d).

complexes, and then energy transferred from Ag NC-PEIs to the complexes, giving rise to fluorescence quenching;[31] however, these combinations were revisable, thus in the existence of potassium pyrophosphate or nitrilotriacetic acid, the quenched fluorescence of Ag NC-PEIs was effectively recovered (Figure 4b and 4c). (2) When adding Hg^{2+} and Ni^{2+}, the UV-vis spectra of PEI did not show obvious change (Figure 5c and 5d), suggesting they interacted directly with Ag atoms rather than PEI. Based on the previous literature, Hg^{2+} could efficiently quench the fluorescence of Ag NCs attributed to the $5d^{10}$ (Hg^{2+})-$4d^{10}$ (Ag^+) metallophilic interaction.[18] While thymine was added, the fluorescence intensity of Ag NC-PEIs could be restored (Figure 4a), indicating that Hg^{2+} exhibited a higher binding ability with thymine to form stable thymine–Hg^{2+}–thymine (T–Hg^{2+}–T)[32] pairing than that with Ag atoms in metallophilic interaction. Additionally, in the presence of Ni^{2+}, an obvious absorption arose at about 375 nm in the UV-vis spectrum of Ag nanoclusters, which was consistent with the characteristic peak of Ag-Ni nanoalloys.[33] In the reported literature, Zhang et al. revealed that Ni^{2+} could react with Ag^+ to form Ag_mNi_n nanoalloys under the irradiation of γ-ray beam.[33] However, the reaction conditions of our work were mild, thus we speculated that Ni^{2+}-induced fluorescence quenching of Ag NC-PEIs due to the interaction between Ni^{2+} and Ag nucleus to form silver-nickel mixture. Moreover, this procedure could be interrupted by dimethylglyoxime, producing the fluorescence recovery of Ag NC-PEIs (Figure 4d).

4. Conclusions

In this paper, a simple and cost-effective sensing system of Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} with broad detection ranges and low detection limits was developed by using fluorescent Ag nanoclusters templated by hyperbranched polyethyleneimine with different molecular weights as probes, which did not show a special selectivity to a certain kind of metal ion. The different molecular weights of polyethyleneimine had a little effect on the sensitivity and linear ranges of detection. Besides, with the addition of different masking agents, such as thymine for Hg^{2+}, potassium

pyrophosphate for Cu^{2+}, nitrilotriacetic acid for Co^{2+}, and dimethylglyoxime for Ni^{2+}, the fluorescence of silver nanoclusters could be successfully restored. Therefore, not only the content of single metal ion but also the total amount of metal ions could be detected conveniently. Moreover, this multi-metal ion sensing system revealed good reproducibility, high accuracy, and satisfactory recovery. All of the advantages facilitated the application of the sensing system in the recognition and determination of multi-metal ions.

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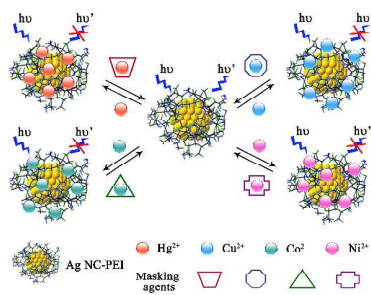
Utilizing suitable masking agents, the quenched fluorescence of Ag nanoclusters by

adding Hg^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} could be restored.