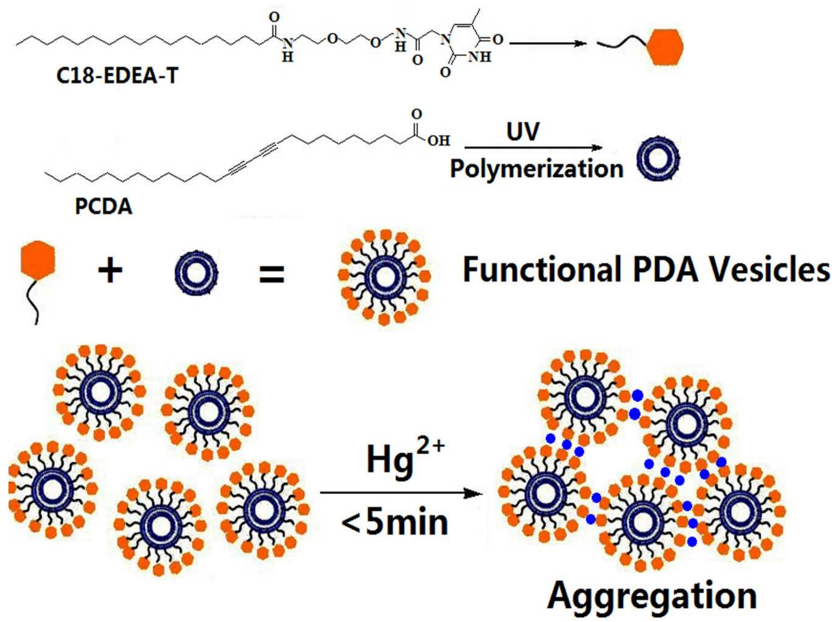
Sensitive Naked-Eye Detection of Hg^{2+} based on the Aggregation and Filtration of Thymine Functionalized Vesicles Caused by Selective Interaction between Thymine and Hg^{2+}

A sensitive and low-cost method is based on rapidly interaction between functionalized PDA vesicles and Hg^{2+} for the naked-eye detection.



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Sensitive Naked-Eye Detection of Hg^{2+} based on the Aggregation and Filtration of Thymine Functionalized Vesicles Caused by Selective Interaction between Thymine and Hg^{2+}

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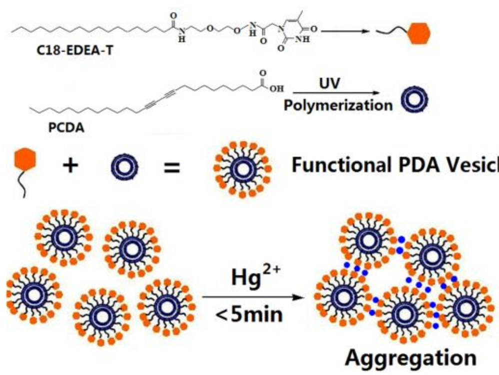
We report a sensitive, selective and low-cost method for the naked-eye detection of Hg^{2+}, The principle is based on rapidly interaction between functionalized PDA vesicles and Hg^{2+}, which lead to obvious aggregation of vesicles. Furthermore, only using a simple filtration process, without using any other color indicator or specialized equipment, a higher detection sensitivity for Hg^{2+}(0.1 μM) than chromophoric colorimetric sensors (approximately 1-100 μM) was obtained.

Mercury ions are highly toxic environmental pollutants and have serious medical effects. Solvated mercuric ion (Hg^{2+}) is one of the most stable inorganic forms of mercury[1] and is considered highly toxic due to its interaction with various biomolecules in living organisms.[2] Therefore, much attention has been paid to the development of methods for the simple and fast detection of Hg^{2+} in aqueous media.[3] Polydiacetylene (PDA) is a unique conjugated polymer that undergoes well-known color change resulting from the conformational change of the conjugated backbone. This color change can be induced by external stimuli, such as heat, pH change, solvent and ligand-receptor interactions.[4] Because of their color change ability, PDA vesicles have been widely used as fast and convenient sensors for the detection of metal ions, such as Hg^{2+}, Pd^{2+}, Al^{3+}, and K^{+}.[5] Recently, it has been reported that a color-changeable PDA sensor is triggered by specific interaction between Hg^{2+} and thymine.[5a,5f]. it is interesting to explore the principle of thymine coordinate with Hg^{2+}(Fig.S2,ESI†). In this sensor, the T-Hg^{2+}-T bonding strains the conjugated backbone of PDA vesicles, which produces conventional color change from blue to red. However, this type of sensor has shown low sensitivity for Hg^{2+} detection as compared with the classical methods, such as the colorimetric method,[6] the fluorometric method[7] and the electrochemical method[8]. Later, some higher sensitivity sensors for Hg^{2+} have been developed based on Thymine-functionalized gold nanoparticles.[9,10] However, the complexity of their preparation and the necessity of special indicators or specialized expensive equipment have limited wide application of these sensors. Many efforts have been reported in enhancing detection sensitivity.[4-10] Compared to recent researches, the detection limit of the PDA microarray for Hg^{2+} which using the fluorescence microscopy images was only 5 μM[5a]. In addition, the limit of visual detection of Hg^{2+} by other method was 0.5 μM[6f]. Herein we report a sensitive, selective and low-cost method for the naked-eye detection of Hg^{2+}, the principle is based on rapidly interaction between functionalized PDA vesicles and Hg^{2+}, which lead to obvious aggregation of vesicles(Scheme 1), a higher detection sensitivity for Hg^{2+} (0.1 μM) was obtained.



Scheme.1 Schematic illustration of the forming and aggregation of functional PDA vesicles.

Different types of thymine-containing probes with aliphatic hydrocarbon chain length (C_n=14 and 18) were synthesized by an improved processing method(Fig.S1,ESI†) and mixed with diacetylene(10,12-pentacosadiynoic acid=PCDA) which were polymerized under ultraviolet irradiation at λ=254nm, the final

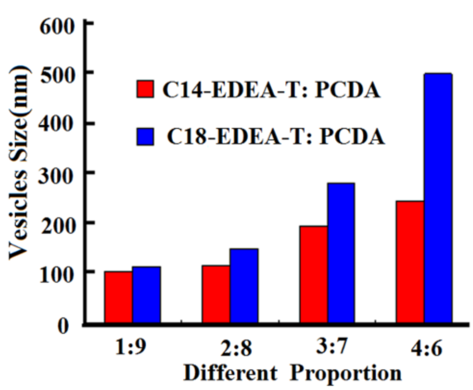


Fig.1 Influence of the length of aliphatic hydrophobic chain and the proportion of T-probes on the size of functional PDA vesicles, measured by DSL equipment.

probes(T-probes) which were tethered to the surface of PDA steps was putting mixture together to form different size of functional PDA vesicles. The Hg^{2+} ions interacted with thymine vesicles, causing aggregation of vesicles which was easily observed by the naked eye.

Concentration(μM)	0	0.1	0.5	1	2	5
Size (nm)	146.2	384.2	425.3	488.3	502.6	794.1

Table.1 the relation between various concentration of Hg^{2+} and the average size of vesicle in given conditions (C18-EDEA-T: PCDA=2:8).

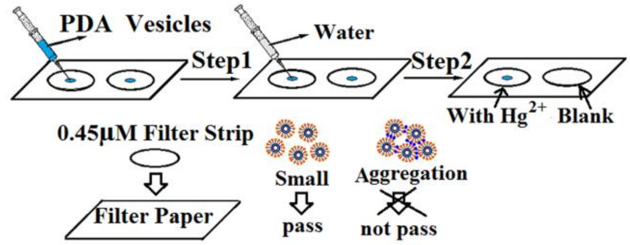
It is easy to find that the length of aliphatic hydrophobic chain have greatly affected the size of vesicles(Figure 1 and Table 1). Figure 1 shows the results of the dynamic light scattering (DLS) measurements, Table 1 displays the relation between various concentration of Hg^{2+} and the average size of vesicle in given conditions. these data indicated that two factors have greatly influence on the aggregation of vesicle. One is the chain length of the probes, other is the T-probe population on the vesicle surface. So the longer the chain length of the T-probe, the larger blue vesicle aggregates will be. The greater concentration of probe the lower detection level of Hg^{2+}. What's more, the large size of PDA vesicles are easier to aggregate, promoting aggregation can reduce reaction energy which will lead to lower detection level of Hg^{2+}.[11]

To further study the vesicle aggregation caused by Hg^{2+}, PDA vesicles of different sizes were compared by using DLS (Table. 1). If vesicles composed of C18-EDEA-T and PCDA with a mixing ratio of 2:8, we have found that when the concentration of Hg^{2+} increases, the aggregate size of the vesicle quickly increases from 146 nm to 1078 nm within 5 min. Interesting, even at a concentration of 0.1 μM Hg^{2+}, the aggregation of the vesicles were observed. Meanwhile, vesicles which were formed by C14-EDEA-T and PCDA at the different ratio also be explored(Table 2). Table 2 shows Hg^{2+} naked-eye limit of detection for different probe proportion in test tube. These interesting phenomenons were giving us a new idea , using simple aggregation caused by selective interaction between the functionalized PDA vesicles and Hg^{2+} to create a novel sensitive, selective and low-cost method for the naked-eye detection of Hg^{2+}.

Cn-EDEA-T : PCDA	1:9	2:8	3:7
C14-EDEA-T : PCDA	100μM	80 μM	50 μM
C18-EDEA-T : PCDA	10 μM	5 μM	vesicles unstable

Table 2. Naked-eye detection limit of Hg^{2+} for different probe proportion in test tube.

Based on the aggregation and sedimentation results for the functionalized PDA vesicles, a novel filtration method similar to ELISA(enzyme linked immunosorbent assay)[12] was explored. As described in Scheme 2, a drop of the vesicle solution was placed onto a piece of cellulose acetate (CA) filter strip and was sucked through placing a larger piece of commercial filter paper on the back side. Then, a drop of water was added to CA filter strip and was sucked by the filter paper on the back side to wash the vesicles on the strip. As a result, the aggregates vesicles larger than the pores of the filter paper remained on the CA filter strips, whereas the unaggregates vesicles smaller than the pores passed



Scheme.2 Schematic illustration of naked-eye detection of Hg^{2+}.

through the CA filter strip. Therefore, a blue spot could be clearly observed on the CA filter strip when the vesicles have aggregated in the presence of Hg^{2+} ions. According to Table.1, the greater concentration of Hg^{2+}, the larger aggregation of vesicles will be. Based on this phenomena and strategy, a CA filter strip with a pore size of 0.45 μM was used, a relatively low concentration of Hg^{2+}(0.1 μM) could be detected by the naked eye without any special equipment or color detector. Scheme 2 shows the procedures and results obtained using this method. In addition, we also naked-eye detected different concentration of Hg^{2+} by 0.45 μM filter strip (Fig. 2).

The selectivity of this method towards other metals ions (Ni^{2+}, Mg^{2+}, Co^{2+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, Ca^{2+})was examined using vesicles composed of C18-EDEA-T and PCDA with a mixture ratio of 2:8. As shown in Figure 3, almost no blue spot was observed upon the addition of other ions at concentrations as high as 10μM. It was further demonstrated that only Hg^{2+} induced the T-Hg^{2+}-T bonding can caused the aggregation. Some reported methods for detecting Hg^{2+} generated an undesired response to Pb^{2+} in the absence of masking reagents.[13] The results obtained here indicated that no such reagents are required in the present method.

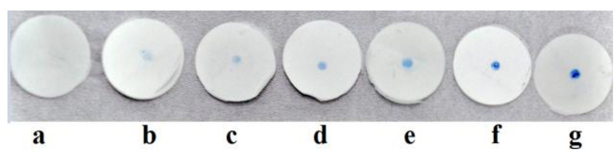


Fig.2 Naked-eye detection of Hg^{2+} by 0.45 μM filter strip. Concentration of Hg^{2+} is (a) 0 μM (b) 0.1 μM (c) 0.5 μM (d) 1 μM (e) 2 μM (f) 5 μM (g) 10 μM, the mixture vesicles(C18-EDEA-T:PCDA=2:8) were used.

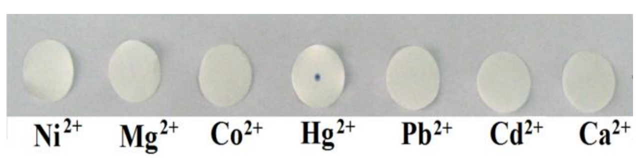


Fig.3 Selectivity of this method, Ni^{2+}, Mg^{2+}, Co^{2+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, Ca^{2+} at the concentration of 10 μM were examined.

Conclusions

In conclusion, we report a sensitive, selective and low-cost PDA sensory system for Hg^{2+} detection by the naked eye, which is based on the selective interaction between thymine and Hg^{2+}. When using 0.45μm filter film, the detection limitation for Hg^{2+} is 0.1 μM. Other metal ions such as Ni^{2+}, Mg^{2+}, Co^{2+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, Ca^{2+} do not interfere with the detection of Hg^{2+}, even when present at a concentration of 10μM. In contrast to previous methods for detecting Hg^{2+} by the naked eye, three remarkable features as follows. (1) this method does not require the use of special color indicators, enzyme treatment, temperature control or special expensive equipment. The blue PDA vesicles used in this method play the roles of color indicator and recognition element. (2) exploring different aliphatic hydrocarbon chain of probes which were tethered to the surface of functional PDA vesicles appears to be unprecedented, we found the length of aliphatic hydrophobic chain have greatly affected on the size of vesicles. (3) naked-eye detection rely on obvious phase change of PDA vesicles can be a unique strategy for recognition application. This strategy described here may serve as guidance for exploring and designing other sensory systems with novel functions and properties. We believe this sensitive, selective and low-cost method should have wide applications in the detection of metallic ions and pollutants in water.

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Notes and references

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