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A highly sensitive and selective aptamer-based colorimetric sensor for the rapid detection of PCB 77

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HIGHLIGHTS

- A colorimetric aptasensor was fabricated for PCB 77 detection for the first time.
- Truncating the nucleotides sequences was used to optimize the detection of PCB 77.
- High affinity between selected DNA sequences and PCB 77 enhanced the selectivity.
- The colorimetric detection limit reached 0.05 nM.
- PCB 77 determination in real water samples showed high accuracy and stability.

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ABSTRACT

A highly sensitive, specific and simple colorimetric sensor based on aptamer was established for the detection of polychlorinated biphenyls (PCB 77). The use of unmodified gold nanoparticles as a colorimetric probe for aptamer sensors enabled the highly sensitive and selective detection of polychlorinated biphenyls (PCB 77). A linear range of 0.5 nM to 900 nM was obtained for the colorimetric assay with a minimum detection limit of 0.05 nM. In addition, by the methods of circular dichroism, UV and naked eyes, we found that the 35 base fragments retained after cutting 5 bases from the 5 'end of aptamer plays the most significant role in the PCB 77 specific recognition process. We found a novel way to truncated nucleotides to optimize the detection of PCB 77, and the selected nucleotides also could achieve high affinity with PCB 77. At the same time, the efficient detection of the PCB 77 by our colorimetric sensor in the complex environmental water samples was realized, which shows a good application prospect.

1. Introduction

Polychlorinated biphenyls (PCBs) are a sort of typical organic pollutants with high toxicity and persistence in the environment. Since the 20th century, polychlorinated biphenyls (PCBs) pollution has caused irretrievable impacts on the health of human beings and animals as well as the environment [1]. Due to the high toxicity and low lethal dose, PCBs should be given priority for its detection as well as removal. PCBs have been detected from many sewage treatment plants and riversides [2]. They remain in water and soil, then get taken in the human bodies and animal bodies through the food chain, and disrupt multiple body systems irreparably [3]. PCBs are persistent organic pollutants with 209 homologues. Typical PCB 77, PCB 126 and PCB 169 are all coplanar [4], and the coplanar PCBs are much more toxic than non-planar PCBs. They are considered to be one of the most toxic dioxin-like PCBs (DL-PCBs) [5]. The PCBs with high toxicity have low concentrations in the actual water. Therefore, it is of great significance to establish a rapid, simple and sensitive method for the detection of contaminants with highly toxic and low concentrations.

Gas chromatography–mass spectrometry (GC–MS), as the most common standard detection method, which could achieve quantitative detection of PCB [6,7]. However, it requires complex pre-treatment process, specialized personnel operation. In recent years, new experimental methods have also been developed to detect PCB 77, such as photoelectrochemical methods, fluorescence [3] and surface-enhanced Raman [8–11]. Ag dendritic nanostructures were constructed for the SERS matrix to achieve low-concentration PCB 77 rapid detection [12]. Nano-bowl-shaped plasma crystal Ag metal was used to build a new Raman sensor for the detection of PCB 77 [13]. The modification of single-dimension carbon nanotubes and pyrene cyclodextrins were reported to be

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use on GC electrodes to identify PCB 77 [14]. A new type of anodic aluminum oxide capacitive sensor was designed for the detection of PCBs [15]. As a result, looking for a more simple and sensitive method for fast and convenient PCB 77 determination is meaningful and has application prospect for practical environmental monitoring.

As known, colorimetry method has been used for routine analysis for not requiring any special equipment and directly being observed by the naked eyes [16–18]. However, because of the lack of selectivity in complex environmental systems, it is envisaged that aptamers would be used as specific recognition elements in conjunction with colorimetric methods [19,20]. Aptamer was a nucleic acid chain, which could bond with the target that was similar to the antigen and antibody-specific binding, which was also known as "chemical antibodies" [21]. It had the characteristics of structural and chemical stability [22], and it could recognize one or a sort of targets [3,11,23]. This method has been used to detect some endocrine disruptors such as MC-LR [24,25], acetamiprid [26], bisphenol A [27], dopamine [28,29], 17β-estradiol [30–32], etc. To the best of our knowledge, there were some reports on the use of an aptamer probe for the rapid, simple detection of PCB [11,33–35]. However, the research about the colorimetric detection of PCB based on aptamer have not been mentioned.

Hence, in the present work, a representative PCB 77 was chosen as the research target. We gave the first demonstration of the colorimetric detection of PCB 77 using PCB 77-binding aptamer as recognition element and unmodified gold nanoparticles as probes. The random coil aptamer could be easily immobilized onto the surface of AuNPs via Au—S bond [20] and protected the AuNPs from aggregation. However, in the presence of PCB 77, they would change the conformation from a loose random coil into an advanced structure, resulting in the aggregation of AuNPs. The PCB 77 was conveniently quantified through different aggregating extent of Au NPs. The detection could be realized by monitoring the color change of the Au NPs even with naked eyes. The detection conditions were optimized by the volume of NaCl, aptamer and the incubation time in order to achieve the best sensitivity and specificity in the complex water environment. Furthermore, the binding mechanism of PCB 77 with full-length aptamer as well as the binding ability of PCB 77 with different nucleotides sequences truncated was investigated in detail by monitoring the UV absorption and circular dichroism changes of different sequences upon binding of the same target PCB 77. It was found that the nucleotides 9–40 which was shortened from the 5′-end of the aptamer had better binding ability with the PCB 77. And we used this new truncated 35 mer ssDNA aptamer as recognition element for further detection. Finally, a rapid, simple, sensitive and selective colorimetric detection of PCB 77 was developed with the detection limit of 0.05 nM and a linear range from 0.5 nM to 900 nM. Finally, this method has been successfully applied to the detection of water samples in Huangpu River, which shows a good prospect.

2. Experimental

2.1. Chemicals and apparatus

Polychlorinated biphenyls(PCB 72, PCB 77, PCB 101, PCB 126)standard analysis were obtained by American Accustandard Reagent Co.Ltd. Nucleotides1-40 against PCB 77 was developed by Xu et al. [11]. All the nucleotides sequences were synthesized by Shanghai Sangon Biotechnology Co. Ltd. (Shanghai, China) and purified by the method of HPLC.

Nucleotides 1–40: 5′-GGCGGGGCTACGAAGTAGTGATTTTTTCCGATGGCCCGTG-3′

Nucleotides 6–40: 5′-GGCTACGAAGTAGTGATTTTTTCCGATGGCCCGTG-3′

Nucleotides 6–35: 5′-GGCTACGAAGTAGTGATTTTTTCCGATGG-3′

Nucleotides 19–40: 5′-TGATTTTTTCCGATGGCCCGTG-3′

Nucleotides 19–35: 5′-TGATTTTTTCCGATGG-3′.

The different nucleotides sequences were annealed by heating to 95 °C and then cooled to RT over a period of 8 h before recording the CD spectrum [37]. All the solutions were prepared by double distilled water. The apparatus are listed in Supporting information.

2.2. Synthesis of Au NPs

Gold nanoparticles with a diameter of 13 nm were fabricated based on the literature [36] and further adopted as optic probe given its highly sensitive SPR as well as its color alteration when the aggregation happens. Particle sizes were measured as 13 ± 2 nm. The molar extinction coefficient of Au NPs at 520 nm was $2.7 \times 10^8\ M^{-1}\ cm^{-1}$ by UV–vis absorption [38].

2.3. Colorimetric detection of PCB 77

200 μL of the Au NP solution and 55 μL, 2 μM aptamer were added to the system and incubated for 10 min. 15 μL PCB 77 were then added to the system for incubation for 10 min. Finally, 20 μL, 500 mM NaCl was added and mixed thoroughly. The UV–vis spectra and photographs were obtained after 10 min of incubation in RT.

2.4. Determination of the association constant and coordination number

The UV absorption spectra of the aptamers with different concentrations of PCB 77 were determined by UV–vis spectrophotometer (See in SI).

$$n\text{PCB 77} + \text{Aptamer} \rightarrow \text{PCB 77} \cdot \text{Aptamer}$$

$$K_a = \frac{[\text{PCB 77} \cdot \text{Aptamer}]}{[\text{PCB 77}]^n \times [\text{Aptamer}]}$$

$$lg\frac{[\text{PCB 77} \cdot \text{Aptamer}]}{[\text{Aptamer}]} = n lg\,[\text{PCB 77}] + lgK_a$$

$$\lg = \frac{[A_0 - A_x]}{[A_x - A_1]} = n\lg\,[\text{PCB 77}] + \lg K_a$$

2.5. Detection of real water sample

To investigate the effectiveness of this fabricated aptasenor in real water samples, samples were collected from the pond water in Sanhaowu, Suzhou River near Hangyuan Bridge in Tongji University and Huangpu River near Waibaidu Bridge in Shanghai. Firstly, The water samples were filtered several times with a 0.22 μm filter membrane to remove the particles and suspended matters in our experiment. Secondly, the aptasensor system was neutral, all the experiment were operated under the neutral environment and all the solutions we used were duilted by ultra pure water. Thirdly, aptamer was selected as the specific recognization element in our colorimetric system. It has strong binding affinity with the target PCB 77 which means this aptamer has great selectivity in the complex water environment. Last but not least, to purify the water samples, the water samples were filtered several times with a 0.22 μm filter membrane to remove the particles and suspended matters. In order to avoid the effect of the inorganic salt in the actual water sample on the color system, the water samples were diluted