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Aminocalix[4]arene monolayers as magnetoelastic sensor sensing elements for selective detection benzo[a]pyrene

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A wireless magnetoelastic-sensing device for the selective detection of benzo[a]pyrene (BaP) is reported with using aminocalix[4]arene (AC	extsubscript{4}) monolayers as sensor sensing elements and AC	extsubscript{4}-modified Au nanoparticles (AC	extsubscript{4}-Au NPs) as signal-amplifying tags. A sandwich-type detection strategy involves the AC	extsubscript{4} self-assembled on the Au-protected sensor surface and AC	extsubscript{4}-Au NPs, both of which flank the BaP target in sequence. As the AC	extsubscript{4}-Au NPs combined BaP absorbs to the sensor’s surface, there is an increase in the mass load on the sensor, and consequently a decrease in resonance frequency. Under optimal conditions, the sensor shows a linear response to the concentration of BaP in the range of 1.04×10	extsuperscript{-11} M to 1.04×10	extsuperscript{-7} M, with a detection limit of 5.0×10	extsuperscript{-11} M. Other polycyclic aromatic hydrocarbons (PAHs) and environmental pollutants show no interference on the detection.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) belong to the set of persistent organic pollutants (POPs) which are organic compounds of natural or anthropogenic origin that resist photolytic, chemical and biological degradation. PAHs are of hydrocarbons released during the incomplete burning of oil, coal, gas, and other organic materials such as trees during forest fires. Most toxic members of this family known to-date are PAH molecules that have four to seven rings. These pollutants have mutagenic, carcinogenic and endocrine disrupting properties, with a high potential for environmental pollution. Benzo[a]pyrene (BaP) is on the priority list published by the US Environmental Protection Agency (EPA). BaP is the first PAH to be identified as a carcinogen and has therefore been studied most often. Further, it has often been used as a marker for PAH contamination in general. It can be found in different types of water samples, e.g. surface water, tap water, rain water, ground water, and waste water. In the EPA 2009 concerning national recommended water quality criteria, a limit value of 0.0038 μg/L (1.51×10	extsuperscript{-11} M) was set for BaP in surface water. The European Union (EU) has also fixed environmental quality standards in surface water for BaP at a limit value of 0.1 μg/L (3.96×10	extsuperscript{-10} M). The routine quantitation of BaP in surface water at the low levels fixed by the EPA and EU requires the development of analytical methods for detection of BaP. Conventional methods for the detection of BaP/PAHs are based on liquid chromatography, gas chromatography, capillary electrochromatography, supercritical fluid chromatography, fluorescence analysis, high performance liquid chromatography coupled with fluorescence detection and gas chromatography–mass spectrometrical. These methods require relatively expensive equipment, with complex extraction, preconcentration and separation procedures generally required for sensitive detection of BaP/PAHs which prevent on-site analysis. Recently efforts have sought to develop rapid screening methods for environmental monitoring of BaP/PAHs, including immunological analysis, DNA biosensors and QCM.

The development and applications of wireless, passive, remote-query magnetoelastic sensors have been reported over the past several years. The sensor is made of amorphous ferromagnetic alloys composed of iron, nickel, molybdenum and boron. In response to a time-varying magnetic field, the magnetoelastic sensor mechanically vibrates at a characteristic resonance.
frequency, generating magnetic flux that can be remotely detected using a pickup coil. Such a sensor response is depended on the liquid properties (viscosity, density, elasticity, etc.) or mass-loaded on the sensor surface. The inherent passive and wireless nature of the magnetoelastic sensors offers an outstanding opportunity for in situ and in vivo monitoring. Various applications of the magnetoelastic sensor have been reported, including sensors for remote-query monitoring of gastric pH, glucose, organophosphorus pesticides, microorganisms and PAHs. The small sensor size (common sensor lengths are a few mm to a few cm) and low material cost (the material is purchased in ribbon form at a cost of ~$200/km) make it suitable for in site analysis with mass samples where disposable sensors are of the utmost utility.

Calixarenes are synthetic cyclooligomers with a “cup-like” shape, capable of size-selective molecular encapsulation and considered as the third host molecules after crown ethers and cyclodextrins, which have demonstrated outstanding complex ability towards ions, neutral molecules, etc. Because of their adjustable hydrophobic cavities of rich π electron-rich benzene ring, which can form inclusion complexes with a number of neutral organic molecules, such as methanol, benzene, pyridine, chloroform, PAHs, etc, calixarenes and their derivatives as chemosensors become a hot topic gradually, especially for the detection of environmental pollutants. Li and coworkers reported calixarenes-modified CdTe quantum dots as fluorescent probes for PAHs. Han and coworkers synthesized p-sulfonatocalix[6]arene-modified Au NPs as colorimetric probes for pollutant aromatic amines isomers. Guerrini and coworkers synthesized a series of calixarene-modified Ag NPs successful using surface-enhanced Raman for PAHs detection.

In this work a magnetoelastic sensor was developed for the selectively detection of BaP. The selective response was achieved by using aminocalix[4]arene (AC$_4$) as the recognizing element and AC$_4$-modified Au NPs (AC$_4$-Au NPs) as signal-amplifying tags. The AC$_4$-Au NPs-combined BaP adsorbed on the AC$_4$/Au-coated sensor surface by forming a ternary inclusion complex of AC$_4$/BaP/AC$_4$-Au NPs as schematically shown in **Fig. 1**, resulting in a decrease in the sensor resonance frequency due to mass loading. This is the first time to detect BaP in aqueous solution using a wireless AC$_4$-modified magnetoelastic sensor with AC$_4$-Au NPs as signal-amplifying tags.

2. Experimental section

2.1 Materials and reagents

Magnetoelastic sensors of 29 mm length were cut from a 6 mm wide and 28 µm-thick ribbon of Metglas alloy 2826MB (Fe$_{80}$Ni$_{19}$Mo$_{10}$B$_{2}$) purchased from Honeywell Corporation (Morristown, NJ, USA). The resonance frequency of an uncoated-sensor in air is approximately 76.5 kHz.

Glutaraldehyde (50 wt % in water), 2,4,6-trinitrophenol (TNP), 2,4,6-trinitromethylbenzene (TNT) and parachlorophenol (4-CP) were purchased from commercial sources and were used as obtained. Tetraoctylammonium Bromide (TOAB), cysteamine hydrochloride, hydrogen gold tetrachloride trihydrate, glycine, benzo[a]pyrene (BaP), naphthalene (NaP), acenaphthene (Ace), fluorine (Flu), pyrene (Py), fluoranthene (FLU) and pentachlorophenololate (PCP) were purchased from Aldrich-Sigma (Bellefonte, PA, USA). Aminocalix[4]arene (AC$_4$) was provided by Professor De lie An in Hunan university. All chemicals were of analytical grade. Double-distilled water was used for all experiments.

2.2 Preparation of AC$_4$-Au NPs

AC$_4$-Au NPs were synthesized via the slight modification of previously described procedures. To increase the water-soluble of the AC$_4$-Au NPs, a certain amount of glycine was added in the
synthesis of AC₄-Au NPs. First, Au NPs stabilized with TOAB were synthesized in toluene. 4 mL 0.012 M Hydrogen gold tetrachloride trihydrate aqueous solution was added in a single shot to a mixture solution of TOAB (0.16 g, 0.29 mmol) and cysteamine (0.0365 g, 0.47 mmol) dissolved in toluene (10 mL). The resulting biphasic mixture was stirred for 30 min in a 30-ml reagent bottle, and the aqueous phase was discarded. A freshly prepared solution of sodium borohydride (0.032 g, 0.85 mmol) dissolved in distilled water (1 mL) was added in a single shot under vigorous stirring. The initial straw-yellow color of the gold (III) solution became wine red and then blue and turned into colorless finally. After the resulting mixture was vigorously stirred for 3 h, the colorless aqueous phase was discarded. Colorless cysteamine-capped Au NPs in toluene were obtained. Then 25% glutaraldehyde (the molar ratio of glutaraldehyde and cysteamine was 1:1) was added into the colorless cysteamine-capped Au NPs solution activated by glutaraldehyde and vigorously stirred for 1 h. The mixtures were subsequently separatory and the aqueous phase was the AC₄-Au NPs solution.

2.3 Sensor fabrication and measurement

The magnetoelastic sensor was ultrasonically cleaned in Micro-Cleaning solution, followed by acetone and water rinse. Electroplating gold (Au) on magnetoelastic sensors was performed by employing the precise impulse mode of an electrochemical work station (IM6ex, Zahner, Germany) with a platinum wire as the counter electrode. The electrolyte solution was 1 m M HAuCl₄ and then glycine and AC₄ at molar ratio of 1:18, 1:12 and 1:6, respectively, with a certain amount of TOAB in DMSO-water (0.9:1 v/v) were added in cysteamine-capped Au NPs toluene solution. An initial straw-yellow color of the gold (III) solution became wine red and then blue and turned into colorless finally. After the resulting mixture was vigorously stirred for 3 h, the colorless aqueous phase was discarded. Colorless cysteamine-capped Au NPs in toluene were obtained. Then 25% glutaraldehyde (the molar ratio of glutaraldehyde and cysteamine was 1:1) was added into the colorless cysteamine-capped Au NPs for 2 h at room temperature. And then glycine and AC₄ at molar ratio of 1:18, 1:12 and 1:6, respectively, with a certain amount of TOAB in DMSO-water (0.9:1 v/v) were added in cysteamine-capped Au NPs toluene solution activated by glutaraldehyde and vigorously stirred for 1 h. The mixtures were subsequently separatory and the aqueous phase was the AC₄-Au NPs solution.

3. Results and discussion

3.1 Aminocalix[4]arene-Au NPs characterization

Fig. 2 shows Fourier transform infrared (FT-IR) spectroscopy of AC₄, AC₄-Au NPs (KBr discs) and AC₄/Au/sensor (infrared diffuse reflectance). The IR data contains features characteristic of AC₄, as shown in Fig. 2(a): -NH₂ and -OH stretching vibration (3373.7 cm⁻¹), -CH₃ and -CH₂ stretching vibration (2959.0 and 2867.7 cm⁻¹), C-H symmetric deformation vibration in -tBu (1395.4 cm⁻¹ and 1362.2 cm⁻¹), C-O in-plane bending vibration in phenolic hydroxyl group (1204.6 cm⁻¹), C-H bending vibration in -NH₂ (1648.4 cm⁻¹), C-O-C asymmetric and symmetric stretching vibration (1121.7 cm⁻¹ and 1010.5 cm⁻¹), peaks in the benzene ring stretching region (3050.2 cm⁻¹, 1648.4 cm⁻¹, 1598.6 cm⁻¹ and 1557.1 cm⁻¹) and a peak for a tetra-substituted benzene ring (864.5 cm⁻¹). Comparing to the spectra of AC₄, the IR of AC₄-Au NPs not only shows the features characteristic of AC₄, but also shows a small but sharp peak: C=N stretching vibration (1675.8 cm⁻¹), indicating that the reaction of AC₄ with glutaraldehyde to form Schiff base. Evidently, another stronger peak (1764.58 cm⁻¹) was found, assigned to C-O stretching vibration of –COOH on glycine; and the characteristic absorption peak of –NH₂/OH found in pure AC₄ is shifted and turned into a broad peak (3336.3 cm⁻¹). It could confirm the successful binding of AC₄ and glycine to the surface of Au. Fig. 2(c) is the infrared diffuse reflectance characterization of AC₄/Au/sensor. The IR spectra of AC₄/Au/sensor not only shows the characteristic absorption AC₄, but also shows a new sharp peak (C=O, 1660.8 cm⁻¹) which indicates that the reaction of AC₄ with glutaraldehyde to form Schiff base and a strong peak (–CHO, 1735.5 cm⁻¹) which is contributed to the excess of glutaraldehyde on sensor surface. It could confirm the successful binding of AC₄ to the surface of Au/sensor. Table 1 shows the colors of AC₄-Au NPs with different molar ratio of AC₄ and glycine. With the ratio of AC₄ increased, the color of AC₄-Au NPs is changed from yellow-green into a cherry red. Fig. 3 shows the UV-vis spectra of AC₄-Au NPs with the different molar ratio of AC₄ and glycine: (a)1:18, (b)1:12 and (c)1:6. With the ratio of AC₄ increased, no distinct difference but little red shift in the maximum absorbance positions.
3.2 The sensor response

The sensor response to BaP is based on the specific inclusion complexation of AC₄ to BaP through the hydrophobic cave of AC₄ as schematically shown in Fig. 1. The response is amplified by the hydrophobic interaction between BaP and AC₄-Au NPs through forming a stable inclusion complexes of AC₄/BaP/AC₄-Au NPs. Fig. 4A shows the sensor responses to the addition of BaP (a), AC₄-Au NPs (b) and BaP+ AC₄-Au NPs (c). The adsorption of BaP results in a little frequency shift (curve a) due to the relative small molecular mass of BaP, while the direct adsorption of AC₄-Au NPs results in a larger frequency shift (curve b) than BaP. It may be that AC₄-Au NPs can be formed a non-specific adsorption with the hydrophobic cavity of AC₄ due to the complexation of AC₄ to Au NPs. In the presence of both AC₄-Au NPs and BaP, the sensor shows the highest response (curve c), which is higher than the sum of curve (a) and (b), indicating that AC₄-Au NPs can effectively bind with BaP to form a stable inclusion complexes. To further confirm the role of AC₄, BaP and AC₄-Au NPs were introduced into the test solution serially, and the response is shown in Fig. 4B. The addition of 1.04×10⁻⁷ M BaP results in a frequency shift of 170 Hz within 1 h, and following the addition of 4.87×10⁻⁷ M AC₄-Au NPs, the frequency shifts 340 Hz within another 2 h. These results indicate that AC₄ and BaP can be formed a 2:1 stable inclusion complexes by the hydrophobic cavity of AC₄. The sensor response is amplified by the adsorption of AC₄-Au NPs.

Fig. 4 (A) The frequency shifts of the sensor in responses to: (a) BaP, (b) AC₄-Au NPs and (c) BaP + AC₄-Au NPs, respectively. The concentrations of BaP and AC₄-Au NPs are 1.04×10⁻⁷ M and 4.87×10⁻⁷ M, respectively. (B) Frequency change vs time when BaP solution and AC₄-Au NPs were sequentially added to the mannose sensor.

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Table 1 The colors of AC₄-Au NPs with different molar ratio of AC₄ and glycine

<table>
<thead>
<tr>
<th>n AC₄: n glycine</th>
<th>1:6</th>
<th>1:12</th>
<th>1:18</th>
</tr>
</thead>
<tbody>
<tr>
<td>the colors of AC₄-Au NPs</td>
<td>cherry red</td>
<td>cherry red</td>
<td>yellow-green</td>
</tr>
</tbody>
</table>

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Fig. 2 FT-IR spectrum of AC₄ (a), AC₄-Au NPs (b) and AC₄/Au sensor (c).

Fig. 3 UV-vis spectrum of AC₄-Au NPs: The molar ratios of AC₄ and glycine are (a) 1:18, (b) 1:12 and (c) 1:6, respectively.

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Fig. 4A shows the sensor responses to the addition of BaP (a), AC₄-Au NPs (b) and BaP+ AC₄-Au NPs (c). The adsorption of BaP results in a little frequency shift (curve a) due to the relative small molecular mass of BaP, while the direct adsorption of AC₄-Au NPs results in a larger frequency shift (curve b) than BaP. It may be that AC₄-Au NPs can be formed a non-specific adsorption with the hydrophobic cavity of AC₄ due to the complexation of AC₄ to Au NPs. In the presence of both AC₄-Au NPs and BaP, the sensor shows the highest response (curve c), which is higher than the sum of curve (a) and (b), indicating that AC₄-Au NPs can effectively bind with BaP to form a stable inclusion complexes. To further confirm the role of AC₄, BaP and AC₄-Au NPs were introduced into the test solution serially, and the response is shown in Fig. 4B. The addition of 1.04×10⁻⁷ M BaP results in a frequency shift of 170 Hz within 1 h, and following the addition of 4.87×10⁻⁷ M AC₄-Au NPs, the frequency shifts 340 Hz within another 2 h. These results indicate that AC₄ and BaP can be formed a 2:1 stable inclusion complexes by the hydrophobic cavity of AC₄. The sensor response is amplified by the adsorption of AC₄-Au NPs.
3.3 Optimization of detection procedure

In order to increase the water-soluble of the AC₄-Au NPs, a certain amount of glycine was added in the synthesis of AC₄-Au NPs. With glycine molar ratio increased, the water-soluble of the synthesis AC₄-Au NPs increased, but it means that the proportion of AC₄ is decreased, making against the inclusion ability of AC₄-Au NPs to BaP. With the AC₄ molar ratio increased, the water-soluble of the synthesis AC₄-Au NPs decreased. In addition, the steric effect may be existed between AC₄, reducing the stability of AC₄-Au NPs. It also makes against the inclusion ability of AC₄-Au NPs to BaP. So three kinds of AC₄-Au NPs were synthesis, the tested compositions of AC₄-glycine were: 1:18, 1:12 and 1:6 (in molar ratio). Fig. 5 shows the effect of the three AC₄-Au NPs on the sensor response to BaP. The sensor response increases with increasing the AC₄ content. This is reasonable since that more AC₄ is introduced, more hydrophobic cavities are available for BaP combining, and consequently more stable inclusion complexes of AC₄/BaP/AC₄-Au NPs are formed. The AC₄-Au NPs at 1:6 molar ratio of AC₄ and glycine therefore are used in the following tests.

Fig. 5 The frequency shifts of the sensor in responses to AC₄-Au NPs at the different molar ratios of AC₄ and glycine: (a) 1:18, (b) 1:12 and (c) 1:6.

The AC₄-Au NPs play an important role in amplifying the magnetoelastic sensor response, therefore, the concentration of AC₄-Au NPs suitable for optimal BaP detection was investigated. Fig. 6 shows the influence of different concentrations of the AC₄-Au NPs at 1:6 molar ratio of AC₄ and glycine on the sensor to BaP. The sensor response increases with decreasing AC₄-Au NPs concentration low to 4.8×10⁻⁷ M, then tends to balance. As the stability of the 2:1 inclusion complex of AC₄/BaP/AC₄-Au NPs on sensor surface has a great relationship with the number of AC₄-Au NPs in test solution. When much more NPs existed in system, it means more free hydrophobic cavities being able to combine to BaP, then breaks the competition balance between free/stationary AC₄ and BaP, making against the stable inclusion complex AC₄/BaP/AC₄-Au NPs formed. So too many AC₄-Au NPs results in less response. 4.8×10⁻⁷ M AC₄-Au NPs was added in the following experiments.

Fig. 6 The sensor response profiles in different concentrations of AC₄-Au NPs (The molar ratio of AC₄ and glycine is 1:6).

3.4 Detection of PAHs

BaP was detected using the AC₄/Au coated sensor under the optimal conditions obtained above. Fig. 7A shows the time-dependent responses of the sensor as a function of the initial BaP concentrations. The shift in the sensor resonance frequency increases with increasing the BaP concentration. A linear relationship between the frequency shift and BaP concentration was observed in the range of 1.04×10⁻⁷ M to 1.04×10⁻¹¹ M, as illustrated in Fig. 7B, with a limit of detection (LOD) of 5.0×10⁻¹² M (3 times the noise signal). The LOD is below the EU allowable maximum concentration of BaP in surface water, so it is meaningful for the detection of BaP in water samples using the proposed BaP wireless magnetic sensor.

The sensor response of AC₄-Au NPs with various PAHs was conducted to examine the selectivity. Fig. 8 shows the effect of 10⁻⁷ M of relevant PAHs on the sensor response, including NaP, Ace, Flu, FLU, Py and BaP. It shows that BaP results in the largest frequency shift. It was reasonable to believe that AC₄ played an important role in recognition of the PAHs, due to AC₄ containing a π-wall cavity that may complex aromatic compounds easily through π-π...
interation, hydrophobic interactions and host-guest interaction etc. The PAH structure affect the nature of their ternary complexes with AC₄. The orientation of these PAHs in their ternary complexes can be predicted based on the principal of size matching and maximum contact between PAHs and the AC₄ cavity. Estimates of the dimensions of the six PAHs calculated by using the standard bond length of 0.139 and 0.108 nm for the ring C=C and C-H³, respectively, are listed in Table 2. The upper and lower rim diameter of the AC₄ cavity are 1.2 nm and 0.7 nm, respectively. As shown in Table 2, NaP and Ace, with small structure, easy to form 1:1 complexes with AC₄; Flu, Py and FLU, with larger structure, can form 1:1 and 1:2 complexes with AC₄, while BaP can form 1:2 complexes with AC₄, it may be due to it’s larger size in comparison to the other five PAHs, results in largest frequency shift.

![Fig. 7A: The time-dependent frequency shift as a function of the initial concentration of BaP: a 0, b 1.04×10⁻¹¹, c 1.04×10⁻¹⁰, d 1.04×10⁻⁹, e 1.04×10⁻⁸ and f 1.04×10⁻⁷ M. The concentration of AC₄-Au NPs is 4.87×10⁻⁷ M. B: Calibration curve: frequency shift vs BaP concentrations.](image)

![Fig. 8: Effects of 10⁻⁷ M relevant PAHs on the frequency shift without (S1) and with (S2) 4.87×10⁻⁷ M AC₄-Au NPs.](image)

Table 2 Selected properties of PAHs used in this study

<table>
<thead>
<tr>
<th>PAHs</th>
<th>NaP</th>
<th>Ace</th>
<th>Flu</th>
<th>FLU</th>
<th>Py</th>
<th>BaP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width (nm)</td>
<td>0.5</td>
<td>0.71</td>
<td>0.71</td>
<td>0.71</td>
<td>0.71</td>
<td>0.71</td>
</tr>
<tr>
<td>Length (nm)</td>
<td>0.71</td>
<td>0.71</td>
<td>0.92</td>
<td>1.06</td>
<td>0.89</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Table 3 The frequency shifts of the sensor in response to mixed PAHs (Δf)

<table>
<thead>
<tr>
<th>Compounds of PAHs (Δf)</th>
<th>NaP</th>
<th>Ace</th>
<th>Flu</th>
<th>FLU</th>
<th>Py</th>
<th>BaP</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaP 31.4</td>
<td>34.0</td>
<td>15.2</td>
<td>38.7</td>
<td>78.7</td>
<td>14.8</td>
<td>-0.46</td>
</tr>
<tr>
<td>Ace 14.7</td>
<td>15.9</td>
<td>7.1</td>
<td>18.0</td>
<td>36.7</td>
<td>6.91</td>
<td>-0.40</td>
</tr>
<tr>
<td>Flu 0</td>
<td>4340</td>
<td>640</td>
<td>6620</td>
<td>3640</td>
<td>0.015</td>
<td>-0.24</td>
</tr>
<tr>
<td>FLU 0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>14.8</td>
<td>-0.43</td>
</tr>
<tr>
<td>Py 0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6.91</td>
<td>-0.41</td>
</tr>
<tr>
<td>BaP 0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.015</td>
<td>-0.23</td>
</tr>
</tbody>
</table>

As PAHs co-exists in environment, the sensor response to the PAH mixture is investigated, as shown in Table 3. The sensor responses to different combination of PAH mixture are similar with the sensor responses to the same BaP concentrations. Because BaP is easy to form 1:2 complexes with AC₄, which can selectively recognize BaP in PAH mixture solution.

3.5 Investigation in the interferences
3. Analysis of BaP in water samples

The real application of this proposed sensor was investigated by analysis of three kinds of water samples: tap water, spring water and river water (xiang jiang). In the test water samples, 4.87×10^-7 M AC_Au NPs were added. The sensor responses to these samples are -200±10 Hz (tap water), -180±15 Hz (spring water) and -180±15 Hz (river water). The results are shown in Table 4. These responses to the three waters are at the level of blank, indicating the impossible existence of BaP.

<table>
<thead>
<tr>
<th>Water sample</th>
<th>Tap water</th>
<th>Spring</th>
<th>River water (Xiangjiang)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δf / Hz</td>
<td>-200±10</td>
<td>-180±15</td>
<td>-230±10</td>
</tr>
</tbody>
</table>

4. Conclusions

A wireless, low cost, and hence readily disposable remote query magnetoelastic sensor was proposed for the detection of BaP. The sensitivity was significantly enhanced by using AC_Au monolayers as magnetoelastic sensor sensing elements and AC_Au NPs as amplifying tags. The hydrophobic cavities of AC_Au NPs adsorb BaP forming a ternary inclusion complex of AC_Au/BaP/AC_Au NPs on the sensor surface through AC_Au modifying both the Au-coated sensor surface and the Au nanoparticles, amplifying the sensor response to BaP. In view of sensitivity and selectivity, it thus afforded a very sensitivity detection system for BaP. A linear relationship was found between the frequency shift and the logarithm of BaP concentration ranging from 1.04×10^-7 M to 1.04×10^-11 M, with a limit of detection (LOD) of 5.0×10^-11 M. The LOD is below the EPA and EU allowable maximum concentration of BaP in surface water, so it is meaningful for the detection of BaP in water samples using the proposed BaP wireless magnetic sensor.

Acknowledgements

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