#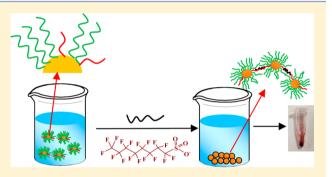 Sensitive Colorimetric Visualization of Perfluorinated Compounds Using Poly(ethylene glycol) and Perfluorinated Thiols Modified Gold Nanoparticles

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ABSTRACT: In this work, we have developed a novel sensing strategy employing mixed poly(ethylene glycol)-terminated (PEG-thiols) and perfluoroalkyl-terminated (F-thiols) alkanethiols modified gold nanoparticles (Au@PEG-F NPs) as a probe to detect perfluorinated compounds (PFCs) from water samples. PEG-thiols with high density and long carbon chains make the Au NPs probe well-dispersed in solution and stable even in high concentration of salt solution; F-thiols provide specific fluorous–fluorous interactions to PFCs, which results in adsorption of PFCs on Au@PEG-F NPs. The adsorbed PFCs cause the aggregation of Au@PEG-F NPs probes and thus induce the insolubility of probes and precipitation directly from reaction solution due to the superhydrophobicity of perfluorocarbon monolayers, leading to color and absorbance response of the assay to PFCs. The preparation of the Au@PEG-F NPs probe is very simple, and the colorimetric assay based on this mechanism for the detection of PFCs is selective and convenient. Combined with UV–vis spectrophotometry, the assay demonstrates good sensitivities to PFCs with wide linear range. In the designed concentration range, the response of the colorimetric assay to long-chain PFCs (perfluoroalkyl chain ≥7) is discerned even as the concentration of these PFCs is as low as 10 μg L^{-1}. This low-cost and sensitive assay shows great potential to measure total PFCs in water samples. To the best of our knowledge, this is the first application of the specific fluorous–fluorous interactions and Au NPs based probes for colorimetric recognition for PFCs.

Perfluorinated compounds (PFCs) are a specialty class of chemicals employed for a variety of applications, including lubricants, paints, cosmetics, and fire-fighting foams. They are highly stable, bioaccumulative, and resistant to degrade in the environments and have been regarded as a new class of emerging organic pollutants. PFCs have been detected in the atmosphere, water, soil, and wildlife all over the world, even in Antarctic and Arctic areas.[1−5] Most PFCs lack chromophores and are nonvolatile; derivatization techniques coupled with spectrofluorometric detector,[6] high-performance liquid chromatography with fluorescence detection (HPLC-FLD),[7] gas chromatography with electron capture detection (GC-ECD), and mass spectrometry with electron impact ionization (GC-EI–MS)[8,9] were employed for the determination of PFCs. However, these methods have limited utility for the detection of PFCs in environmental matrixes due to the complex procedure.[5] Ion chromatography coupled with conductivity detection and an electrophoretic method to measure PFCs are also reported; but the limits of detection are general in the milligram per liter level.[10,11] These days, the routine and robust analytical technique for PFCs is liquid chromatography/tandem mass spectrometry (LC/MS/MS), which still is too expensive for common application in environmental monitoring. Thus, the

development of simple, easy-to-operate, inexpensive, and sensitive assays for PFCs is in high demand.

Over the past decade, gold nanoparticles (Au NPs) based colorimetric assays have become an important research topic and been applied to monitor (bio)chemical substances. The concentration change of targets can be easily transformed into color changes, which is observed by the naked eye alone; hence, no sophisticated instruments are required. The color change of Au NPs colloid is highly sensitive to the size, shape, capping agents, and medium refractive index, as well as the aggregation state of Au NPs.[12] Combined with UV−vis spectrophotometry or fluorescence resonance energy transfer techniques, Au NPs based colorimetric assays for DNA, proteins, ions, and organic molecules (such as cysteine, melamine, cocaine, ATP, pyrophosphate ion, glucose, and dopamine) have been developed.[12−26] However, the establishment of colorimetric assays for PFCs has not been reported yet. Actually, the applications of colorimetric assays based on Au NPs for environmental pollutants are scarce,

and only very few colorimetric assays have been designed for TNT,[27,28] organophosphorus and carbamate pesticides,[29] and phthalates.[30]

Selective isolation of fluorinated targets from convoluted mixtures has become increasingly popular using liquid–liquid separations, solid–liquid separations (such as fluorous solid-phase extraction), and fluorous chromatography.[31–37] Most of these types of separations rely on a fluorous silica solid phase coupled with an organic solvent. On the basis of the highly specific fluoruos–fluorous (F–F) interactions, fluorous molecules are retained by fluorous silica gel while nonfluorous molecules are not.[32,34] Fluorous-tagged analytes such as triphenylphosphine oxide,[33,34] fluoroalkyl-substituted phenyl bromides,[35] oligonucleotides,[36] and peptides[37] have been successfully separated from nonfluorous analytes by using fluorinated adsorbent or fluorinated monolithic columns. However, there is no application of fluorinated Au NPs in adsorption, separation, or detection of fluorous analytes by far.

In the present study, Au NPs based colorimetric assays for PFCs were established. The surfaces of Au NPs were functionalized with mixed self-assembled monolayers of alkanethiolates terminated with poly(ethylene glycol) (PEG-thiols) and alkanethiolates terminated with perfluoroalkyl (F-thiols) (Au@PEG-F NPs). The PEG-thiols increased the dispersibility of Au NPs in water, while the F-thiols were capable of binding PFCs by providing unique F–F interactions to PFCs. The adsorption of PFCs on Au@PEG-F NPs probes surface increased the hydrophobicity of the probes and led to the precipitation of Au@PEG-F NPs out of solution. The color of Au@PEG-F colloids faded clearly as PFCs were added into the solution, and the absorbance decreased linearly with PFCs concentration. The comparison study showed that the nonperfluorinated compounds did not interfere with the detection of PFCs.

■ EXPERIMENTAL SECTION

Materials and Instrumentation. Chloroauric acid tetrahydrate (HAuCl$_4$·4H$_2$O), sodium borohydride (NaBH$_4$), and ethanol were obtained from Sinopharm Chemical Reagent Company, Ltd. (Beijing, China). Alkanethiol terminated with poly(ethylene glycol) HS(CH$_2$)$_{11}$–(OCH$_2$CH$_2$)$_n$–OH (n = 6) and alkanethiol terminated with perfluoroalkyl HS(CH$_2$)$_{11}$–O–(CH$_2$)$_2$–(CF$_2$)$_5$–CF$_3$ were from ProChimia, Poland. Perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), and perfluorooctadecanoic acid (PFODA) were purchased from Alfa Aesar; perfluorooctanesulfonate (PFOS) was obtained from Sigma-Aldrich. All chemicals were used as received without further purification. Ultrapure water was prepared using a Milli-Q SP reagent water system (Millipore, Bedford, MA, U.S.A.).

UV–vis spectra were recorded using a Beckman DU 800 nucleic acid/protein analyzer (Rosemead, CA). X-ray photoelectron spectroscopy (XPS) measurements were conducted by applying a Thermo Scientific ESCA-Lab-200i-XL spectrometer (Waltham, MA) with monochromatic Al Kα radiation (1486.6 eV). The size and morphology of Au@PEG-F NPs was observed with a Hitachi H-7500 transmission electron microscope (TEM, Tokyo, Japan). The amount of Au NPs in colloid after addition of PFCs was determined using inductively coupled plasma mass spectrometry (ICPMS) (7500A, Agilent).

The ζ-potential of Au@PEG-F NPs at different pHs and hydrodynamic radius, Rh (nm), of Au@PEG-F NPs in the presence and absence of PFCs were measured using Zetasizer Nano series, (Malvern, United Kingdom).

Synthesis of PEG- and F-thiols Mixed Capped AuNPs (Au@PEG-F) and Sensing PFCs. The AuNPs were prepared by reducing HAuCl$_4$ with NaBH$_4$ in the presence of PEG thiols as stabilizers. In brief, 1.872 mg of PEG-thiols was added to 40 mL of HAuCl$_4$ ethanol solution (5 × 10^{-4} M); the terminal concentration of PEG-thiols was 0.1 mM. After mixing, 1 mL of freshly prepared 0.1 M of NaBH$_4$ solution was added into the mixture and the color of solution turned to deep red immediately. The reaction solution was stirred for 30 min. Next, 0.275 mg of F-thiols was added into the PEG-capped Au NPs dispersion; the terminal concentration of F-thiols was 0.0125 mM. The mixture stood overnight. After that, the ethanol solvent was evaporated to about 1 mL under N$_2$ stream followed with redispersing the PEG- and F-thiols mixed capped Au NPs with 40 mL of purified water. Finally, the Au@PEG-F NPs suspension was centrifuged at 13 000 rpm to remove the possible precipitated Au@PEG-F NPs. The developed reagent was stored at room temperature until use.

The colorimetric sensing of PFCs using the Au NPs probes was performed by mixing different amounts of PFCs solution with the as-synthesized Au@PEG-F NPs colloids at a volume ratio of 1:1. Since the concentrations of organic pollutants in the environment usually are expressed as mass per liter, the mass concentrations were used for PFCs in this study. After incubation for 0.5 h at room temperature, the precipitated Au@PEG-F NPs were removed from the reaction solution through centrifugation at 13 000 rpm. The supernatants are used for absorbance measurement at a wavelength of 520 nm.

■ RESULTS AND DISCUSSION

Colorimetric Sensor for PFCs. The amount of Au@PEG-F NPs sensors in the suspension was 0.25 mM (representing the concentration of Au^{3+} in the initial reaction solution to synthesize Au NPs). After addition of different concentrations of PFCs, the reaction solution was incubated for 30 min. The color of the Au@PEG-F NPs suspension faded gradually with the increase of PFCs (PFOS) concentration, and a small amount of Au@PEG-F NPs precipitated from reaction solutions (Figure 1A). The adsorption spectrum for each sample is shown in Figure 1B. The results exhibited that only the surface plasmon resonance (SPR) peak at about 520 nm presented in the spectra regardless of the concentration of PFOS, and the absorbance of reaction solution decreased linearly with the increase of PFOS concentration (Figure 1C). The shift in the spectra accompanying the binding of PFOS to Au@PEG-F NPs did not occur regardless of the amount of PFOS present.

To investigate the mechanism of the assay, TEM images of as-prepared Au@PEG-F NPs and those in the presence of PFOS (ranged in 0.1–1000 μg L^{-1}) were taken. After reaction, the Au@PEG-F NPs colloid suspensions were centrifuged at 13 000 rpm and the supernatants were collected for TEM observations. As a result, the as-synthesized Au@PEG-F NPs were well-dispersed and about 2–4 nm in diameter (Figure 2A). With the addition of 0.1 μg L^{-1} of PFOS, only two or three Au NPs were drawn closer to one another, and the number of these "aggregated Au NPs" was low (Figure 2B); as PFOS concentration was enhanced to 0.5 μg L^{-1}, the number of aggregated Au NPs increased clearly and more Au NPs were
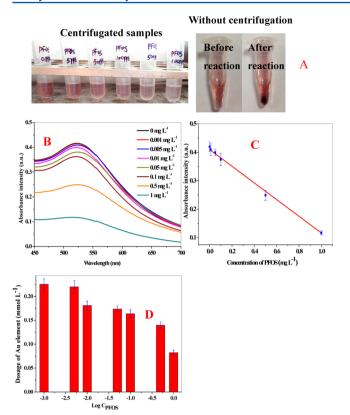
Figure 1. (A) Photographs of centrifuged Au@PEG-F NPs suspension containing different amounts of PFOS; from left to right: 0, 5, 50, 100, 500, and 1000 μg L^{-1}, and Au@PEG-F NPs suspension before and after reaction with PFOS without centrifugation. (B) Absorbance of Au@PEG-F NPs suspension at pH 5.5 in response to different concentrations of PFOS. (C) The plot of absorbance against C_{PFOS} for PFOS analysis. (D) T corresponding amount of Au atom in supernatants after reaction.

drawn close (Figure 2C). However, the association of a small amount of Au NPs would be insufficient to generate the color change and shift of the SPR peak in UV−vis spectra. With the

further increase of PFOS concentration, the degree and number of "aggregated Au NPs" decreased gradually and tiny deposited Au NPs were seen in the bottle of the cuvette after centrifugation (Figure 2D). When the concentration of PFOS was higher than 10 μg L^{-1}, aggregation of nanoparticles disappeared in the supernatant of reaction solution (Figure 2E). The precipitates were also examined using TEM and found to be composed of heavily aggregated Au@PEG-F NPs (Figure 2F). We measured the average hydrodynamic radii (Rhs) of controlled Au@PEG-F NPs and those in the supernatant after reaction with 500 μg L^{-1} of PFOS. Figure 3 exhibits that the
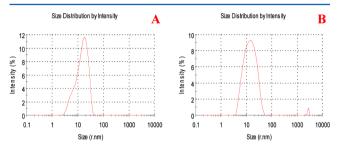

Figure 3. Hydrodynamic radius (Rh) distributions of as-prepared Au@PEG-F NPs (A) and Au@PEG-F NPs after reaction with 500 μg L^{-1} PFOS (B). Both of the solutions are centrifuged, and the supernatants are used to determine Rh of probes.

Rhs of as-prepared Au@PEG-F NPs are 15.8 nm and identical with those of the probers that remained in the supernatant after reaction with PFOS (15.7 nm).

The next experiment was conducted to determine the amount of Au element in the supernatant of the suspension after reaction with PFOS. The results showed that the amounts of Au element decreased with the increase of PFOS concentration (Figure 1D). This phenomenon was rather consistent with the trend of absorbance at 520 nm in UV−vis spectra (Figure 1B), suggesting that the decreased absorbance of the reaction solution was due to the precipitation of Au@PEG-F NPs.
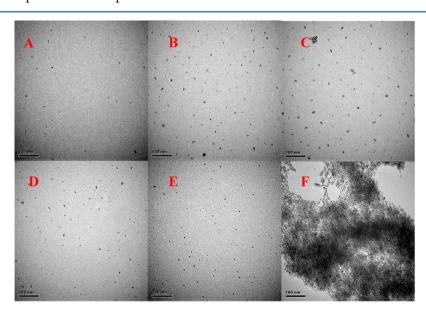

Figure 2. TEM images of as-prepared Au@PEG-F NPs (A) and Au@PEG-F NPs in the supernatants of reaction solution with the addition of 0.1 (B), 0.5 (C), 1.0 (D), and 10 μg L^{-1} (E) of PFOS, and heavily aggregated Au@PEG-F NPs in precipitates (F); the scale bar is 100 nm.

In a preliminary study, we optimized the ratios of PEG-thiols to F-thiols on the surface of Au NPs probes. We found that gold nanoparticles merely modified with PEG-thiols (Au@PEG NPs) were deep red in color and exhibited an SPR peak at about 515 nm. As the ratios of PEG/F were 20:1 and 10:1 (representing the ratio of PEG-thiols and F-thiols added in reaction solution), the Au NPs colloids were deep wine red with the SPR peaks located at about 518 nm. As the PEG/F thiols ratio decreased to 8:1, the nanoparticles were also deep wine red, but the SPR peak shifted to 520 nm; at the same time small amounts of Au@PEG-F (8:1) deposited from water solution. If the PEG/F ratio decreased to 6:1, plenty of Au NPs deposited from polar solvents (methanol, ethanol, water). After removal of the precipitated Au NPs through centrifugation, the Au@PEG-F (6:1) NPs suspension was pale red, while the SPR peak was still located at about 520 nm. We collected Au@PEG-F (8:1) NPs and Au@PEG-F (6:1) NPs well-dispersed in solution by evaporating the reaction solution under N_2 stream, subsequently washing with ethanol and water several times to determine the element contents of Au@PEG-F (8:1) and Au@PEG-F (6:1) using XPS. Consequently, the ratios of PEG/F thiols were about 8.7/1 on the surface of the two Au NPs (Table 1), indicating that the minimum PEG/F thiols ratio on

Table 1. Element Composition and Contents on the Surface of Au NPs Modified with Different Ratios of PEG- and F-thiols

element	Au@PEG NPs (%)	Au@PEG-F (8:1) NPs (%)	Au@PEG-F (6:1) NPs (%)
Au	1.06	1.09	0.98
S	1.74	1.88	2.01
C	74.1	72.6	70.4
O	23.1	20.2	22.5
F		4.23	4.11

Au NPs sensor was 8.7. The fluorocarbon monolayers are superhydrophobic, and the fluorinated alkyl thiolate [such as perfluorodecanethiol (F8) and perfluorooctanethiol (F6)] modified Au NPs are insoluble in common hydrocarbon media and only well-dispersed in fluorinated solvents.[38−40] Therefore, further increase of the perfluorinated groups on Au@PEG-F NPs will enhance the hydrophobicity of Au NPs sensor, which makes the sensor insoluble in polar solvents and finally deposits from reaction solution. That is the reason for the same characteristic SPR peak in the spectra of Au@PEG-F (8:1) and Au@PEG-F (6:1).

All the above-mentioned results indicated that the added PFCs would adsorb on the surface of Au@PEG-F NPs through F-thiols, which might cause the aggregation of Au NPs. With the increase of PFCs in reaction solution, more Au NPs were drawn closer, resulting in the increase of the Au NPs probes' hydrophobicity. Since the perfluorocarbon monolayers are superhydrophobic and readily precipitate from water solution, the aggregated Au NPs would precipitate directly from reaction solution as the concentration of PFCs was high enough, leading to color and absorbance response of the assay to PFCs. The possible mechanism of the assay is shown in Figure 4.

Effects of Solution pH and Electrolytes. The stability of Au@PEG-F NPs in solution at different pHs was investigated using UV−vis spectroscopy. In the pH range of 2.5−6.5, the absorbance reduced gradually and a sharp decrease occurred at pH 7.5, after which the intensities increased with pH values (Figure 5A). The change of extinction coefficient with solution
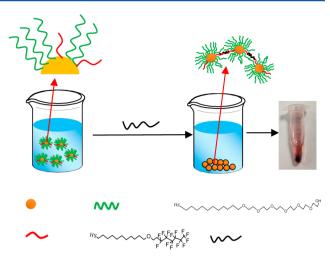

Figure 4. Mechanistic assay for colorimetric detection of PFCs with perfluorinated and PEG thiols modified Au NPs.
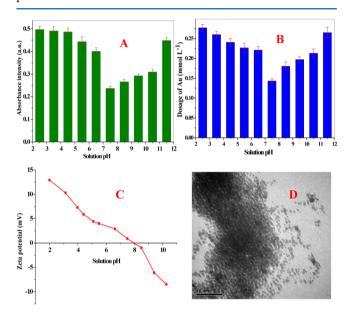

Figure 5. Absorbance (A), concentration of Au element (B), and ζ-potential (C) of Au@PEG-F NPs suspension at different pHs, and TEM image of Au@PEG-F NPs (D) at pH 7.5.

pH was consistent with the variation of the corresponding Au element amount (Figure 5B) at different solution pHs. To interpret the effect of solution pH on Au@PEG-F NPs stability, we measured ζ-potentials of Au@PEG-F NPs in aqueous solutions. The isoelectric point (IEP) of the Au NPs sensor was found at about pH 8.0 (Figure 5C). At pH < pH$_{IEP}$, the oxygen atoms in the PEG chains can adsorb H_3O^+ through hydrogen bonds, leading to the positive surface of Au@PEG-F NPs, while the OH groups of PEG-thiols can ionize to form negatively charged surface at pH > pH$_{IEP}$. Therefore, the PEG chains maintain a brushlike conformation in which the chains extend out into solution both in acid and strong alkaline solution due to repulsive reaction between positively or negatively charged PEG-thiols, imparting the stability of Au@PEG-F NPs colloids. At about pH$_{IEP}$, the electrostatic interaction between PEG chains decreases and cannot counteract the hydrophobic interaction among the hydrophobic regions ($-CH_2-CH_2-$), and the PEG chains display a conformation as a random coil, allowing the F-thiols exposure in solution and inducing the
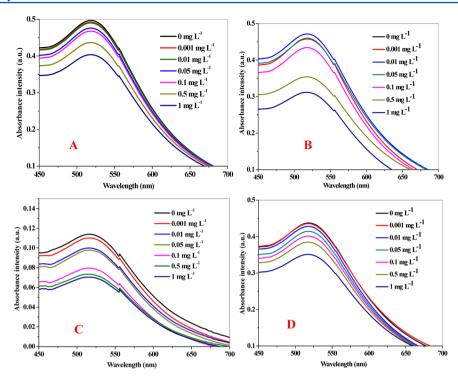
Figure 6. UV−vis spectra of the Au@PEG-F NPs in response to different concentrations of PFOS at pH 2.5 (A), pH 4.5 (B), pH 7.5 (C), and pH 11.5 (D), from lower to upper: 0, 1, 10, 50, 100, 500, and 1000 $\mu g\ L^{-1}$ of PFOS.

interaction among Au NPs. This could be confirmed by their TEM images, in which highly aggregated Au@PEG-F NPs were observed at pH 7.5 (Figure 5D). In literature, PEG-modified Au NPs are stable at wide pH range due to the strong interactions between water and PEG chains. But the molecular weight of these PEGs is usually larger than 1000 Da.[41,42] In this study, the molar mass of PEG units was low (M = 281) and the interactions between water and PEG chains were weak, so the stability of Au@PEG-F NPs was sensitive to solution pH.

The sensitivity of the assay to PFCs at different solution pHs was studied with the concentrations of PFOS ranging in 1−1000 $\mu g\ L^{-1}$. In acid and strong alkaline solution, F-thiols on Au NPs sensors were sheltered by the long-chain PEG-thiols in brushlike conformation, which impeded the interaction between PFCs and F-thiols. Therefore, the sensitivities of the assay to PFCs at pH 2.5 and pH 11.5 were low (Figure 6, parts A and D). In neutral and weak alkaline solution, the F-thiols were exposed to solution and readily contacted with PFCs. The sensitivities of the assay should be high in these pH ranges. However, we found that the assay showed low sensitivity to PFOS at pH 7.5−9.5 perhaps due to the extremely low amount of Au NPs sensors that remained in the reaction solution (Figure 6C). In the pH range of 3.5−6.5, the sensitivities of the assay to PFOS were higher and generally increased with pH value (Figures 1B and 6B). But the highest sensitivity to PFOS was achieved at pH 5.5; thus, solution pH of the assay was set at about pH 5.5 in the following experiment.

Colloidal Au NPs have a tendency to easily aggregate in the presence of high salts, which is the primary obstacle for the application of most colorimetric assays in environmental samples.[12] In this study, we studied the effects of salts (including NaCl, MgCl$_2$, and CaCl$_2$) concentrations on the stability of Au@PEG-F NPs. The concentration of these salts ranged in 0.5−500 mM. We found that the Au@PEG-F NPs colloid remained very stable in the whole salts concentration

range. The absorption intensities of reaction solution at 520 nm were nearly unchanged compared with the controlled solution (Figure 7). In the presence of 500 mM of each salt, 500 $\mu g\ L^{-1}$
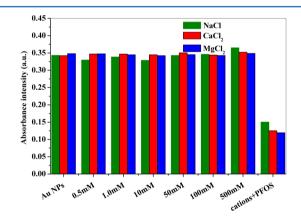

Figure 7. Absorbance of Au@PEG-F NPs suspension in the presence of different concentrations of NaCl, MgCl$_2$, and CaCl$_2$ with and without PFOS (500 $\mu g\ L^{-1}$); the amount of each salt in solution containing PFOS is 500 mM.

of PFOS was added to the reaction solution, and the intensities at 520 nm decreased obviously, indicating that the assay was not affected by the coexisting high amount of salts. The extremely high stability of PEG−SH-modified Au NPs colloid in salt solution was also reported by Gao et al.[43] They suggested that the PEG polymers can provide steric hindrance among Au NPs and result in an increased stability of Au NPs in solution. Although the molecular weight of PEG−SH in this study was far lower than the one at Gao's study (5 kDa), the Au@PEG-F NPs still showed excellent anti-interference ability to high concentration of salts, indicating the application potential of this assay in environmental samples.

Selectivity. The selectivity of the assay was investigated by addition of nonfluorinated alkyl carboxyl acid, alkyl alcohol, alkylamine, and cationic and anionic surfactants bearing long carbon chains to the reaction solution including octanoic acid, decanoic acid, dodecanoic acid, 1,2-dodecandiol, 1-dodecylamine, 1-hexadecylamine, sodium dodecyl sulfate (SDS), sodium hexadecanesulfonate (SHDS), sodium octadecanesulfonate (SODS), sodium dodecyl benzenesulfonate (SDBS), and hexadecyltrimethylammonium bromide (CTAB). In the presence of 500 μg L^{-1} of each nonfluorinated compound, the absorbance of reaction solution did not change, indicating that the assay was insensitive to these nonfluorinated compounds (Figure 8). We further tested the selectivity of
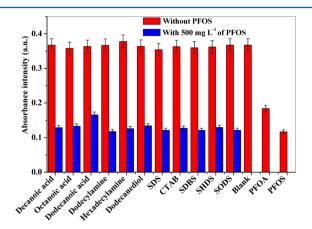

Figure 8. Absorbance of Au@PEG-F NPs suspension in the presence 500 μg L^{-1} of each nonfluorinated compound with and without 500 μg L^{-1} of PFOS.

the assay to PFCs by recording the UV−vis spectrum of Au NPs suspension with the coexistence of PFOS and each of the nonfluorinated compounds (500 μg L^{-1}). With the addition of 500 μg L^{-1} PFOS, the peak intensity at 520 nm decreased remarkably and was comparable to that without nonfluorinated compounds. These results disclosed that the assay had excellent selectivity to PFCs over the nonfluorinated compounds.

Detection Sensitivity to Different PFCs. Different amounts of each perfluorinated compound were added to the reaction solution. The final concentrations for short-chain PFBS (F4), PFHxS (F6), and PFHpA (F6) ranged in 0.1−10 000 μg L^{-1}; those for long-chain PFCs (F7−F17) were in the range of 0.1−1000 μg L^{-1}. The UV−vis spectrum of each reaction solution under the optimal condition was recorded.

The dose-dependent responses of PFCs are shown in Table 2. In a wide concentration range, the UV−vis absorbance decreased linearly with PFCs concentration. The sensitivities of the assay to PFCs increased with the elongation of perfluoroalkyl chain (CF$_2$). For PFBS, obvious dose-dependent response to the assay only could be discerned when the PFBS concentration was higher than 1000 μg L^{-1}. As to PFHxS and PFHpA, the response of the two PFCs to the assay was identified when their concentrations were higher than 100 μg L^{-1}. The hydrophobicity of PFCs increased with the elongation of CF$_2$; therefore, Au NPs probes adsorbed with longer-chain PFCs were more readily precipitated from water solution, which resulted in low sensitivity of this assay to short-chain PFCs. For long-chain PFCs (perfluoroalkyl chain CF$_2$ ≥7), the decrease of absorbance could be observed even when the concentration was as low as 10 μg L^{-1} (11−24 nM). The slopes of the linear equations (representing the sensitivity of the assay to PFCs) for three perfluorinated sulfonates (PFSAs) and seven perfluorinated carboxylic acids (PFCAs) increased generally with the elongation of CF$_2$. This trend was more obvious if we normalized the linear equations with molecular weight. Table 2 also exhibits that the assay demonstrates higher sensitivity to perfluorinated sulfonates than perfluorinated carboxylic acids with the same length of perfluoroalkyl chain, which might be caused by the higher hydrophobicity of PFSAs than those of PFCAs.

In general, the colorimetric assays based on Au@PEG-F NPs showed high sensitivities for long-chain PFCs (CF$_2$ ≥7) with wide linear range. The concentrations of total PFCs in natural water samples are in the range of tenths to hundreds of parts per trillion.[1−11] Only application of LC/MS/MS allows better limits of detection (LODs) to be obtained. However, the drawback of the mass spectrometer is its instrumental price and the running cost. There are also challenges with LC/MS/MS systems that are composed of fluorinated polymers from which PFCs, most notably PFOA, can be leached, causing background problems.[8] The LODs obtained for derivatization techniques coupled with spectrofluorometric detector,[6] HPLC-FLD,[7] GC-ECD,[8,9] and GC-EI−MS/MS[8,9] were in the range of tens of parts per billion to parts per million levels. The LODs for the PFCs with ion chromatography coupled with conductivity detection[10] and the electrophoretic method[11] were around the parts per million level and too high for their application to directly analyze PFCs in environmental samples (excluding cases of heavy contamination). Water samples are required to be pretreated with solid-phase extraction (SPE) or liquid−liquid separation methods in advance. Even with the LC/MS/MS

Table 2. Linear Range, Linear Equation, and Correlation Coefficients of the Colorimetric Assay to Different PFCs

	linear range		linear equation		
PFCs	mg L^{-1}	μmol L^{-1}	mg L^{-1}	μmol L^{-1}	R^2
PFBS	1.0−10	3.3−33	$y = -0.009x + 0.181$	$y = -0.003x + 0.181$	0.982
PFHxS	0.05−5.0	0.125−12.5	$y = -0.055x + 0.387$	$y = -0.022x + 0.387$	0.990
PFOS	0.01−1.0	0.02−2.0	$y = -0.301x + 0.411$	$y = -0.151x + 0.411$	0.995
PFHpA	0.05−5.0	0.137−13.8	$y = -0.030x + 0.248$	$y = -0.011x + 0.248$	0.995
PFOA	0.01−1.0	0.024−2.4	$y = -0.173x + 0.355$	$y = -0.072x + 0.355$	0.994
PFNA	0.01−1.0	0.021−2.1	$y = -0.147x + 0.245$	$y = -0.068x + 0.245$	0.993
PFTrDA	0.01−1.0	0.015−1.5	$y = -0.278x + 0.395$	$y = -0.171x + 0.395$	0.993
PFTeDA	0.01−1.0	0.014−1.4	$y = -0.276x + 0.396$	$y = -0.194x + 0.396$	0.996
PFHxDA	0.01−1.0	0.013−1.2	$y = -0.257x + 0.392$	$y = -0.209x + 0.392$	0.997
PFODA	0.01−1.0	0.011−1.1	$y = -0.12x + 0.398$	$y = -0.11x + 0.398$	0.992

method, PFCs always need to be preconcentrated with the SPE method from water samples. After preconcentration for hundreds of times, the sensitivities of these methods developed for PFCs will increase greatly and the LODs can decrease to sub parts per trillion to parts per billion levels, which meets the requirements of high sensitivity and selectivity for PFCs measurement. In the designed concentration range, the response of the colorimetric assay based on the Au@PEG-F NPs sensor we developed to long-chain PFCs ($CF_2 \geq 7$) was observed even as the concentration of these PFCs was as low as 10 μg L^{-1}. The sensitivity of this assay to PFCs was superior to or comparable with those of HPLC-FLD and GC-ECD techniques, indicating that this colorimetric assay could be employed to measure total PFCs in real water samples after preconcentrating with an SPE method. In addition, the developed assay was lower in cost with use of much simpler and more commonly employed instruments. Both the synthesis of Au@PEG-F NPs probers and implementation of the assay were very simple and convenient because we did not need to derivatize PFCs and add any additives such as organic dyes and enzymes into the reaction solution.

The Au@PEG-F NPs sensor was employed to analyze PFOS in tap water and river water samples. Water samples were filtered through a nylon film (0.45 μm) before extraction. An aliquot of 200 mL of blank water samples and those spiked with 10 ng of PFOS were extracted with an HLB cartridge (6 cc, 150 mg; Waters Corp. Milford, U.S.A.), respectively. After sample loading, the cartridges were washed with 5 mL of purified water and dried with a gentle steam of N$_2$. The adsorbed PFOS was eluted with 5 mL of methanol. The eluate was then concentrated to 0.2 mL and added to 0.8 mL of Au NPs solution. After reaction for 30 min, the Au NPs reaction solution was centrifuged and the supernatant was measured using UV−vis spectrometry at 520 nm. The result showed that no PFOS was detected in all the water samples. The recoveries of PFOS in the river water and tap water samples were 85% ± 10% and 115% ± 12%, respectively.

CONCLUSIONS

In summary, we have demonstrated the feasibility of using Au NPs based colorimetric assay in the detection of PFCs in aqueous solution. The preparation of Au NPs probe modified with mixed perfluoroalkyl and PEG groups can be achieved just by soaking Au NPs in ethanol solvent containing thiols. The strong and specific F−F interaction between PFCs and F-thiols results in the adsorption of PFCs on Au NPs, which increases the hydrophobicity of the Au NPs and leads to the participation of the Au NPs sensors. The color of the reaction solution and UV−vis absorbance changes with PFCs concentration. This developed assay is lower in cost and more convenient to implement and shows excellent selectivity and sensitivities to PFCs. To our knowledge, this is the first application of the specific fluorous−fluorous interactions and Au NPs based probes for colorimetric assays for PFCs or even emerging pollutants. More importantly, this study opens new opportunities for the design of novel sensing strategies for organic environmental pollutants.

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