“Turn-Off” Supramolecular Fluorescence Array Sensor for Heavy Metal Ion Identification

Qin Wang, Kai-Ni Wei, Shu-Zhen Huang, Qing Tang, Zhu Tao, and Ying Huang*

Cite This: ACS Omega 2021, 6, 31229−31235

Read Online

ACCESS

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: A “turn-off” supramolecular fluorescence array sensor based on the host−guest complexes between fluorescence dyes and cucurbit[n]urils for sensing metal ions was developed. Three fluorescent probes (RhB@Q[7], H33342@2Q[7], and BRE@Q[7]) were used as the sensing units to construct a supramolecular fluorescence array sensor. The binding ability of the metal ions and cucurbituril-dye probes varied; therefore, the probes and metal ions produced different fluorescence responses. When combined with linear discriminant analysis (LDA), the qualitative and quantitative detection of seven metal ions was achieved. In analytical samples, the supramolecular fluorescence array sensor recognized and distinguished seven metal ions. These results provided new research ideas for the rapid analysis and real-time monitoring of different heavy metal ions.

1. INTRODUCTION

In industrial production activities, heavy metal ions are released into the environment and into rivers, lakes, oceans, and soil. Therefore, heavy metal ions continuously circulate with the water and atmospheric cycles and enter the ecological environment. Due to their high toxicity, persistence, and accumulation, heavy metal ions cause serious harm to human health.1 Therefore, it is imperative to develop reliable, fast, sensitive, and simple methods for the detection of heavy metal residues.

There are many detection technologies for metal ions, including inductively coupled plasma atomic emission spectrometer (ICP-AES),2 atomic absorption spectrometry (AAS),3 and inductively coupled plasma mass spectrometry (ICP-MS).4 Although these methods are sensitive, they are costly and require cumbersome sample pretreatment processes. Inspired by the mammalian olfactory system, array-based sensing technology has emerged as a potentially powerful method for detecting and identifying multiple analytes. In recent years, array-based sensing technology has become a potential method for detecting and identifying a variety of metal ions. Some sensor arrays involving biomolecules, dyes, nanomaterials, and carbon dots have been developed for metal ions.5−9 For example, Deng et al. reported a facile fluorescent sensor array for the rapid discrimination of heavy metal ions (HMI) based on a single gold nanocluster (AuNC) probe.10 A colorimetric-sensor array composed of three recognition receptors (cysteine, 1-glutathione, and melamine) was developed for the fast discrimination of toxic metal ions.11 A protein/lanthanide complex (BSA/Tb3+)−based sensor array in two different pH buffers has been designed for high-throughput recognition and time-resolved fluorescence (TRF) detection of metal ions in biofluids.12 Lin group have developed a colorimetric array test strip for both qualitative and semiquantitative multianalyte analyses of Hg2+, Ag+, and Cu2+.13

In general, macrocyclic molecules, such as crown ethers, cyclodextrins, calixarenes, and cucurbiturils have no optical properties. They can interact with suitable dyes to form optical probes, which can interact with a wide variety of analytes to produce specific responses and achieve the purpose of molecular recognition.14 Cucurbit[n]urils (Q[n]s, n = 5−8, 10, 13−15) are a type of macrocyclic compound formed by n glycouril units through 2n methylene bridges and have a nearly neutral cavity and two negatively charged carbonyl ports.15 They can include guest molecules to form host−guest inclusion complexes16 and can coordinate with metal ions to form complexes.17 Fortunately, the detection and recognition...
of multitarget analytes by the cucurbiturils-based supramolecular sensor array system has gradually attracted attention, and some progress has been made in the detection of amine bioactive molecules. Garcia et al. constructed a colorimetric and fluorescent sensor array system based on the cucurbituril-dye complex and identified and detected 14 organic amines and quaternary ammonium salts.\(^{18}\) Isaacs et al. reported a supramolecular assay based on two fluorescent cucurbit[\(n\)]uril probes for the recognition and quantification of cancer-associated nitrosamines.\(^{19}\) A host–guest complex between fluorescence dyes and cucurbit[\(n\)]urils was exploited as a multiple sensor element to provide arrays for sensing biogenic amines using principal component analysis as described by Kim et al.\(^{20}\) In this article, we used three fluorescent probes (RhB@Q[7], H33342@2Q[7], and BRE@Q[7]) as the sensing units to construct a supramolecular fluorescence array sensor. Combined with linear discriminant analysis (LDA), qualitative and quantitative detection of seven metal ions was achieved (Figure 1). In analytical samples, the supramolecular fluorescence array sensor recognized and distinguished seven metal ions. This provided new research ideas for the rapid analysis and real-time monitoring of different heavy metal ions.

2. RESULTS AND DISCUSSION

2.1. Fluorescence Response of the Probes to the Metal Ions. First, the binding behaviors of Q[7] and the dyes were investigated. Figure S1 shows the fluorescence spectra of the dyes with Q[7] in an aqueous solution. For RhB, a red dye, the fluorescence intensity increased gradually at 584 nm upon the gradual addition of Q[7] to RhB (Figure S1a). The molar ratio curve and Job plots showed the formation of a 1:1 inclusion complex between Q[7] and RhB (Figure S1b). The \(^1\)H NMR titration spectrum indicated that the proton signals for the diethylamino moiety of the RhB@Q[7] complex exhibited an upfield shift, which showed the host–guest interaction between RhB and Q[7] (Figure S1c). The second dye, Hoechst 33342, a well-known DNA-marker dye, after forming a host–guest complex with Q[7], the fluorescence intensity of Hoechst 33342 was also significantly enhanced and formed a 2:1 inclusion complex (H33342@2Q[7]), which was confirmed by \(^1\)H NMR (Figure S2a–c). The third compound was BRE, an isoquinoline alkaloid, also known as berberine. The fluorescence intensity of BRE was also significantly enhanced when it formed a 1:1 host–guest complex with Q[7] (BRE@Q[7]), which was also confirmed by \(^1\)H NMR (Figure S3a–c).

The fluorescence responses of the three fluorescent probes (RhB@Q[7], H33342@2Q[7], and BRE@Q[7]) with seven metal ions (Hg\(^{2+}\), Fe\(^{3+}\), Fe\(^{2+}\), Cr\(^{3+}\), Al\(^{3+}\), Pb\(^{2+}\), Ba\(^{2+}\)) were investigated. The fluorescence titration spectra, concentration range, calibration curve, and detection limit of the fluorescent probes and metal ions are shown in Figures S4–S6 and Tables S1–S3. The RhB@Q[7] probe responded to Hg\(^{2+}\) (0–600 \(\mu\)M), Fe\(^{3+}\) (0–450 \(\mu\)M), Cr\(^{3+}\) (0–700 \(\mu\)M), Pb\(^{2+}\) (0–600 \(\mu\)M), and Ba\(^{2+}\) (0–400 \(\mu\)M). The response sensitivity for Ba\(^{2+}\) was the highest. The H33342@2Q[7] probe produced a response to Hg\(^{2+}\) (0–300 \(\mu\)M), Fe\(^{3+}\) (0–400 \(\mu\)M), Fe\(^{2+}\) (0–700 \(\mu\)M), Cr\(^{3+}\) (0–500 \(\mu\)M), and Al\(^{3+}\) (0–700 \(\mu\)M), with the highest sensitivity to Hg\(^{2+}\). The BRE@Q[7] probe responded to Fe\(^{3+}\) (0–680 \(\mu\)M), Fe\(^{2+}\) (0–680 \(\mu\)M), Pb\(^{2+}\) (0–650 \(\mu\)M), and Ba\(^{2+}\) (0–720 \(\mu\)M). It had the highest response sensitivity.

![Figure 1. Cucurbit[7]urils (a), fluorescence dyes (b–d), and the supramolecular fluorescence array sensor for differential sensing of the metal ions (e).](https://doi.org/10.1021/acsomega.1c04956)
to Ba\(^{2+}\) and the widest response concentration to Ba\(^{2+}\). Therefore, the three fluorescent probes produced differential responses to the seven metal ions.

Next, the fluorescence responses of the three sensors were analyzed against 50 equiv of the metal ions. In most cases, the metal ions elicited a quenching response to varying degrees (Figure 2). For example, seven metal ions (500 μM) were detected by the RhB@Q\([7]\) (10 μM) sensor. Notably, Fe\(^{3+}\) quenched the fluorescence intensity of the sensor (Figure 2a) and the solution lost its fluorescence under the ultraviolet lamp at 365 nm (line 1 of Figure 2g). Ba\(^{2+}\), Pb\(^{2+}\), Hg\(^{2+}\), and Cr\(^{3+}\) reduced the fluorescence intensity of the sensor to a small degree, and the solution became lighter under the ultraviolet lamp at 365 nm. However, only minor changes in the fluorescence spectra and color were observed upon the addition of Al\(^{3+}\) and Fe\(^{2+}\) ions. In contrast, for the H33342@
2Q[7] sensor, the order of fluorescence quenching by the metal ions was \( \text{Hg}^{2+} > \text{Fe}^{3+} > \text{Fe}^{2+} > \text{Cr}^{3+} > \text{Al}^{3+} > \text{Pb}^{2+} > \text{Ba}^{2+} \). For the BRE@Q[7] sensor, the order of fluorescence quenching by the metal ions was \( \text{Fe}^{3+} > \text{Fe}^{2+} > \text{Ba}^{2+} > \text{Pb}^{2+} > \text{Hg}^{2+} > \text{Cr}^{3+} > \text{Al}^{3+} \). The results showed that the three fluorescent sensors had different responses to the seven metal ions. Furthermore, ITC titration showed that the three sensors had different affinities for the metal ions (Figures S7–S9 and Tables S4–S6 in the Supporting Information). Therefore, the decrease in fluorescence amplitude depended on the affinity of the sensors and the metal ions in an aqueous solution.

Because the binding ability of the metal ions and cucurbituril-dye probes was different, the probes and metal ions produced different fluorescence responses. The fluorescence intensity changes before and after the addition of metal ions were obtained by \( (I - I_0)/(I_1 - I_0) \) \((I_1\) is the fluorescence intensity of the dye after adding metal ions, \(I_0\) is the fluorescence intensity of the dye, and \(I_1\) is the fluorescence intensity of the probe without adding metal ions), and the “characteristic fingerprint” of each metal ion was obtained. The results are shown in Figure 3a. These seven metal ions had different degrees of influence on the fluorescence intensity of the three fluorescent probes. The results indicated that the fluorescent probe could be used as the sensing element of the sensor array to identify different metal ions. In addition, Figure 3b shows the CIE chromaticity diagram of the three fluorescent probes RhB@Q[7], H33342@2Q[7], and BER@Q[7] in the presence of seven metal ions. The figure shows that the color of RhB@Q[7] was concentrated in the yellow area, H33342@2Q[7] was concentrated in the cyan area, and BER@Q[7] was concentrated in the green area. The colors of the three fluorescent probes interacting with the metal ions were significantly different. Therefore, the fluorescence array sensor constructed in this paper was feasible.

2.2. Qualitative and Quantitative Analyses. To test the qualitative recognition ability of the supramolecular fluorescence array sensor for metal ions, we repeated the experiment five times for each metal ion sample. LDA was performed on the resulting data (Tables S7–S9), and the eigenvectors corresponding to the first two factors were taken to obtain the three-dimensional LDA diagram of the response of the fluorescent array sensor to the seven metal ions, as shown in Figure 4. The test points of the same metal ion were concentrated in the same area, and different metal ions were distributed in different areas, and there was no overlap between them. Through the leave-one-out crossover method verification (Table S9), this sensor array correctly classified 90.2% of the metal ions. The main errors were Ba^{2+} and Pb^{2+}. Two Pb^{2+} were misidentified as Ba^{2+}, and one Ba^{2+} was misidentified as Pb^{2+}. Therefore, there was a certain mutual interference between Ba^{2+} and Pb^{2+} in the sensor array in aqueous solutions.

Next, we examined the ability of the fluorescence array sensor to distinguish between metal ion mixtures. We distinguished the two metal ions of \( \text{Pb}^{2+}−\text{Hg}^{2+} \) mixtures in different ratios (0:600, 100:500, 300:300, 500:100, and 600:0). After processing the data obtained by the fluorescence array sensor (Tables S10–S12), the LDA result obtained is shown in Figure 5. Five parallel points of different ratios were gathered and could be well separated from the measurement points of the binary metal ion mixtures of other ratios. In addition, we observed that as the proportion of Pb^{2+} increased, its four parallel points got closer and closer to the measurement points of pure Pb^{2+}. These results indicated that the fluorescence array sensor distinguished different ratios of \( \text{Pb}^{2+}−\text{Hg}^{2+} \) binary metal ion mixtures. Therefore, this array sensor had the potential for practical application in the identification of mixed-metal-ion samples.

To test the sensitivity of the fluorescence array sensor to recognize different concentrations of metal ions, taking Pb^{2+} as an example, a fluorescence array sensor was used. The experiment was repeated five times (Tables S13–S15), and the scores of the two most significant factors were used to plot the results (Figure 6). Each point in Figure 6 represents the response of the array sensor to a certain concentration of Pb^{2+}. Figure 6 shows that the test points of the same concentration were gathered in one area and were distributed in different areas from the test points of other concentrations. The regions, namely, the six concentrations of Pb^{2+}, were clearly distinguished. To test the ability of the array to quantitatively analyze the concentration of the metal ions, we classified a 200 \( \mu\text{M} \) Pb^{2+} as an “unknown” sample on the array. The results showed that the array successfully discriminated four data points in the unknown data into the concentration range of 200 \( \mu\text{M} \) and misidentify one data point as 300 \( \mu\text{M} \) (Table

![Figure 4](https://doi.org/10.1021/acsomega.1c04956)

Figure 4. Results of the qualitative LDA of seven metal ions using an array sensor based on the RhB@Q[7], H33342@2Q[7], and RBE@Q[7] sensors.

![Figure 5](https://doi.org/10.1021/acsomega.1c04956)

Figure 5. Canonical score plot for the response patterns as obtained from the LDA for mixed Pb^{2+}/Hg^{2+} in different ratios.
S15). The results further showed that the sensor array quantitatively detected and identified the metal ions.

2.3. Analytical Sample Sensing. To explore the applicability of the supramolecular fluorescence array sensor, we measured the ability of the array sensor to distinguish different metal ions incorporated into analytical samples. We used Huaxi River water and bottled mineral waters (Nongfushan Spring and Wahaha) as the analytical samples. To minimize the interference caused by the particulate impurities in the analytical samples to the sensor, the Huaxi River water was centrifuged and then filtered through a 0.22 μm filter prior to analysis. Subsequently, seven metal ions (500 μM) were added to the sensor array containing Huaxi River water, Nongfushan Spring water, and Wahaha mineral water. In the samples, when different metal ions were present, the sensor array produced different fluorescence response patterns, and the data were processed and LDA performed (Tables S16–S24). The results are shown in Figure 7. The Huaxi River water itself produced a unique array response, and the seven metal ions were clustered in seven nonoverlapping groups. The first two typical factors were 71.9 and 24.4%, accounting for 96.3% of the total variation (Figure 7a), which indicated that the sensor array had the potential to distinguish and identify metal ions in analytical samples. Through the leave-one-out crossover method verification (Table S18), this sensor array correctly classified 100% of the metal ions in the Huaxi River water. For the Nongfushan Spring and Wahaha mineral waters, this sensor array also produced a unique array response, and the seven metal ions were clustered into seven nonoverlapping groups. Through the leave-one-out crossover method verification (Tables S21 and S24), this sensor array correctly classified 100% of the metal ions in the Nongfushan Spring mineral water and 97.5% of metal ions in the Wahaha mineral water.

3. CONCLUSIONS

In this study, we constructed a fluorescent array sensor based on the specific response of three fluorescent probes to different metal ions and achieved the differentiation and identification of seven metal ions. Moreover, the distinction and identification of different concentrations of the same metal ion (Pb^{2+}) and binary metal ion mixtures were achieved. In addition, the constructed array sensor distinguished and identified seven metal ions in analytical samples. Compared to the published fluorescence-based sensing arrays,7,13 recognition of low concentration of metal ions for supramolecular array sensing systems is still a challenge, and further research is needed.

4. MATERIALS AND METHODS

4.1. Materials. Cucurbit[7]uril was prepared according to the literature with little modification.21 Rhodamine B (RhB), Hoechst 33342, berberine hydrochloride (BRE), and perchlorate salts of the metal ions were provided by Aladdin Industrial Corporation (Shanghai, China). Ultrapure water (UPW) was utilized throughout the study.

4.2. Measurement of the Fluorescence Spectra. The fluorescence experiments were performed on a Varian Cary Eclipse fluorescence spectrometer (Varian, Inc., Palo Alto, CA).

Q[7] (1.00 × 10^{-3} mol L^{-1}), H33342 (1.00 × 10^{-3} mol L^{-1}), RhB (1.00 × 10^{-3} mol L^{-1}), and BRE (1.00 × 10^{-3} mol L^{-1}) were prepared in aqueous solution. For the fluorescence spectral studies, Q[7] (0.00–3.00 × 10^{-5} mol L^{-1}) was added to free RhB, H33342, or BER in a concentration of 1.00 × 10^{-5} mol L^{-1}. The fluorescence spectrum was obtained at 550 nm for RhB, at 352 nm for H33342, and at 353 nm for BER. The excitation and emission bandwidths were 5 nm in all cases.

Aqueous solutions of the RhB@Q[7], H33342@2Q[7], and BER@Q[7] complexes (1.00 × 10^{-6} mol L^{-1}) were prepared and known quantities of seven different perchlorate metal ion complexes were added to the sensor array containing Huaxi River water.
solutions (Ba^{2+}, Hg^{2+}, Fe^{3+}, Fe^{2+}, Pb^{2+}, Al^{3+}, Cr^{6+}, 5.00 × 10^{-4} mol L^{-1}) were added to the solutions containing the RhB@Q[7], H33342@2Q[7], and BER@Q[7] inclusion complexes, respectively. Fluorescence spectra were recorded under the single excitation at 550 nm (RhB@Q[7]), 352 nm H33342@2Q[7], and 353 nm BER@Q[7].

4.3. Isothermal Titration Calorimetry (ITC). ITC experiments were carried out with a Nano ITC apparatus (TA, Northampton) at 298.15 K. All solutions were prepared in UPW and degassed prior to titration. The obtained ITC data were fitted by Nano software. All of the data obtained were an average of three repeats.

4.4. Array Experiments. Aqueous solutions of the RhB@Q[7], H33342@2Q[7], and BER@Q[7] complexes (10 μM) and seven different perchlorate metal ion solutions (5.00 × 10^{-2} mol L^{-1}) were prepared. The array experiments were performed on a 96-well microtiter plate. A mixture of 300 μL of RhB@Q[7], H33342@2Q[7], or BER@Q[7] sensor with a concentration of 10 μM and the seven metal ions (500 μM) was added to each well. The maximum emission fluorescence intensity of the samples in the 96-well microtiter plate was read on a microplate detector (SYNERGY-H4, BioTek) at 25 °C. The maximum fluorescence emission intensity was measured at 580 nm for the corresponding samples of RhB@Q[7], at 482 nm for the corresponding samples of H33342@2Q[7], and at 500 nm for the corresponding samples of BER@Q[7]. All measurements were made with the gain set at 50. Five sets of data were acquired for each sample in parallel. This resulted in a training data matrix of three sensors × seven metal ions × five replicates which were subjected to LDA using the IBM SPSS Statistics 22 software.

4.5. Identification of Mixed-Metal Ions and Determination of Their Concentrations. Thirty microliters of three supramolecular fluorescent probes (RhB@Q[7], H33342@2Q[7], and BER@Q[7]), 1.00 × 10^{-3} mol L^{-1}) were pipetted into 3 mL centrifuge tubes; then, the concentration ratio of C_{Pb^{2+}} (2.00 × 10^{-1} mol L^{-1})/C_{Hg^{2+}} (2.00 × 10^{-1} mol L^{-1}) was changed to 0:600, 100:500, 300:300, 500:100, and 600:0. Nine microliters of C_{Pb^{2+}}/C_{Hg^{2+}} mixed ions in different proportions were pipetted into the above three supramolecular fluorescent probes and diluted to 3 mL with UPW (the total concentration of fixed C_{Pb^{2+}} + C_{Hg^{2+}} was always 600 μM, the probe concentration was 10 μM). After mixing well, the reaction was complete; 300 μL of the above samples was transferred to a 96-well microtiter plate. A microplate detector (SYNERGY-H4) was used to detect the fluorescence intensity of the samples. Five replicates were performed for each sample. A data matrix of three sensor elements × seven metal ions × five replicates was obtained, and the data were imported into the IBM SPSS Statistics 22 software for LDA.

4.6. Analytical Sample Detection. The Huaxi River water sample was centrifuged and then filtered through a 0.22 μm filter prior to use as a stock solution. The bottled mineral waters (Wahaha and Nongfushan Spring) were sampled directly. Thirty microliters of the three supramolecular fluorescent probes (RhB@Q[7], H33342@2Q[7], and BER@Q[7]), all 1.00 × 10^{-3} mol L^{-1}) were pipetted into 3 mL centrifuge tubes. Then, 7.5 μL of the seven metal ions (Ba^{2+}, Hg^{2+}, Fe^{3+}, Fe^{2+}, Pb^{2+}, Al^{3+}, Cr^{6+}, 2.00 × 10^{-1} mol L^{-1}) were added to the above 3 mL centrifuge tubes. The Huaxi River water, Wahaha mineral water, and Nongfushan Spring water were used to dilute the volume to 3 mL. After the above three samples were fully mixed and the reaction was complete, 300 μL of the samples was transferred to a 96-well microtiter plate, a microplate detector (SYNERGY-H4) was used to detect the fluorescence intensity of the samples. Five replicates were performed for each sample. A data matrix of three sensor elements × seven metal ions × five replicates was obtained, and the data were imported into the IBM SPSS Statistics 22 software for LDA.

ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04956.

Additional data, 1H NMR, fluorescence spectra, ITC spectra, and table for the array sensor (PDF)

AUTHOR INFORMATION

Corresponding Author

Ying Huang – Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province and The Engineering and Research Center for Southwest Biopharmaceutical Resources of National Education Ministry of China, Guizhou University, Guiyang 550025, China; orcid.org/0000-0002-1823-9197; Email: yinghun128@163.com

Authors

Qin Wang – Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, China
Kai-Ni Wei – Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, China
Shu-Zhen Huang – Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, China
Qing Tang – Department College of Tobacco Science, Guizhou University, Guiyang 550025, China
Zhu Tao – Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, China; orcid.org/0000-0002-8313-1430

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c04956
Author Contributions
Q.W. performed the research, analyzed the data, wrote the original draft. K.-N.W. carried out additional analyses and finalized this paper. S.-Z.H. performed additional analyses and finalized this paper. Q.T. analyzed the data with software. Z.T. conceived the idea of the study. Y.H. gave the ideas, formulated or developed the overarching research goals and aims, reviewed and edited the paper.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was supported by the Natural Science Foundation of the Science and Technology Department of Guizhou Province (Grant No. ZK-2021-024) and the National Natural Science Foundation of China (Grant No. 22061009).

REFERENCES
(1) Vardhan, K. H.; Kumar, P. S.; Panda, R. C. A review on heavy metal pollution, toxicity and remedial measures: Current trends and future perspectives. J. Mol. Liq. 2019, 290, No. 111197.
(2) Sixto, A.; Fiedoruk-Pogrebniak, M.; Rosende; Cocovi-Solberg, M.; Knochen, D. M.; Miro, M. A mesosilicid platform integrating restricted access-like sorptive microextraction as a front end to ICP-AES for the determination of trace level concentrations of lead and cadmium as contaminants in honey. J. Anal. At. Spectrom. 2016, 31, 473–481.
(3) Mollo, A.; Sixto, A.; Falchi, L.; Medina, M.; Knochen, M. Zinc determination in Tannat wine by direct injection onto graphite tube: Electrothermal AAS as an alternative to flame AAS. Microchem. J. 2017, 135, 239–244.
(4) Kupper, H.; Bokhari, S. N. H.; Jaime-Pérez, N.; Lyubenova, L.; Ashraf, N.; Andersen, E. Ultratrace metal speciation analysis by coupling of sector-field ICP-MS to high-resolution size exclusion and reversed-phase liquid chromatography. Anal. Chem. 2019, 91, 10961–10969.
(5) Chen, Z. H.; Fan, Q. X.; Han, X. Y.; Shi, G.; Zhang, M. Design of smart chemical ‘tongue’ sensor arrays for pattern-recognition-based biochemical sensing applications. TrAC, Trends Anal. Chem. 2020, 124, No. 115794.
(6) Sun, J. W.; Lu, Y. X.; He, L. Y.; Pang, J. W.; Yang, F. Y.; Liu, Y. Y. Colorimetric sensor array based on gold nanoparticles: design principles and recent advances. TrAC, Trends Anal. Chem. 2020, 122, No. 115754.
(7) Leng, Y. M.; Qian, S. H.; Wang, Y. H.; Lu, C.; Ji, X. X.; Lu, Z. W.; Lin, H. W. Single-indicator-based multidimensional sensing: detection and identification of heavy metal ions and understanding the foundations from experiment to simulation. Sci. Rep. 2016, 6, No. 25354.
(8) Pan, L. L.; Sun, S.; Zhang, A. D.; Jiang, K.; Zhang, L.; Dong, C. Q.; Huang, Q.; Wu, A. G.; Lin, H. W. Truly Fluorescent excitation-dependent carbon dots and their applications in multicolor cellular imaging and multidimensional sensing. Adv. Mater. 2015, 27, 7782–7787.
(9) Qiao, L. N.; Qian, S. H.; Wang, Y. H.; Yan, S. F.; Lin, H. W. Carbon-dots-based lab-on-a-nanoparticle approach for the detection and differentiation of antibiotics. Chem. - Eur. J. 2018, 24, 4703–4709.
(10) Zhang, X. P.; Huang, K. Y.; He, S. B.; Peng, H. P.; Xia, X. H.; Chen, W.; Deng, H. H. Single gold nanocluster probe-based fluorescent sensor array for heavy metal ion discrimination. J. Hazard. Mater. 2021, 405, No. 124259.
(11) Li, X.; Li, S. Q.; Liu, Q. Y.; Chen, Z. B. Electronic-tongue colorimetric-sensor array for discrimination and quantitation of metal ions based on gold-nanoparticle aggregation. Anal. Chem. 2019, 91, 6315–6320.