Talanta 108 (2013) 103–108

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A fluorometric paper-based sensor array for the discrimination of heavy-metal ions

Liang Feng [a,*], Hui Li [a], Li-Ya Niu [b], Ying-Shi Guan [b], Chun-Feng Duan [a], Ya-Feng Guan [a], Chen-Ho Tung [b], Qing-Zheng Yang [b,*]

[a] Laboratory of Instrumentation and Analytical Chemistry, Key Lab of Separation Science for Analytical Chemistry of CAS, Dalian Institute of Chemical Physics, CAS, Dalian, Liaoning 116023, PR China
[b] Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, CAS, 29 Zhongguancun East Road, Beijing 100190, PR China

ARTICLE INFO

Article history:
Received 16 January 2013
Received in revised form
20 February 2013
Accepted 27 February 2013
Available online 7 March 2013

Keywords:
BODIPY
Fluorometric
Sensor array
Heavy-metal ion

ABSTRACT

A fluorometric paper-based sensor array has been developed for the sensitive and convenient determination of seven heavy-metal ions at their wastewater discharge standard concentrations. Combining with nine cross-reactive BODIPY fluorescent indicators and array technologies-based pattern-recognition, we have obtained the discrimination capability of seven different heavy-metal ions at their wastewater discharge standard concentrations. After the immobilization of indicators and the enrichment of analytes, identification of the heavy-metal ions was readily acquired using a standard chemometric approach. Clear differentiation among heavy-metal ions as a function of concentration was also achieved, even down to 10^{-7} M. A semi-quantitative estimation of the heavy-metal ion concentration was obtained by comparing color changes with a set of known concentrations. The sensor array was tentatively investigated in spiked tap water and sea water, and showed possible feasibility for real sample testing.

1. Introduction

With almost the world's largest population and a huge industrial system, China is undergoing an unprecedented process of rapid industrialization. As this industrialization goes on, various forms of pollution have increased, which has caused widespread environmental and health problems. Among all these pollutions, China's water pollution, seriously contaminated by industrial discharges, has been increasing most notably with its industrialization [1].

Heavy metals, by definition, are metals with a density >5 g/cm^3. The increasing concern for the impact of heavy metals has stimulated active investigations. These heavy metals arise mainly from industrial wastewater and exist in cationic forms. While low concentrations of heavy-metal ions may not pose immediate danger, they tend to accumulate in organisms [2]. Once these heavy-metal ions enter the human food chain, they cannot be degraded and represent a serious health hazard. Some can cause serious damages, and others affect the central nervous system, the kidney, liver, bones, or teeth. Some heavy-metal ions (*e.g.*, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, *etc*) are, on the one side, essential for life, but on the other side, toxic to organism if they are in excess [3,4].

Past analytical approaches include relatively expensive instrumentation (*e.g.*, AAS, ICP-AES, ICP-MS, anodic stripping voltammetry, X-ray fluorescence spectrometry, graphite furnace atomic absorption spectrometry (GFAAS), atomic fluorescence spectrometry (AFS), *etc*) [5–9]. These prior methods are generally cumbersome and multi-step. Some heavy-metal ions may change their forms after sampling, *e.g.*, from inorganic to organic (mercuric salts to methylmercury), or may be oxidized or reduced to different value state. As a result, there is an urgent need for low-cost, highly sensitive and selective methods of discrimination of heavy-metal ions, especially at their wastewater discharge standard concentrations (some of them are as low as 10^{-7} M).

Instead of trivial analytical instrument methods, a number of inexpensive colorimetric sensors for the detection of heavy-metal ions have been proposed (*e.g.*, modified or functionalized nanoparticles, DNAzyme, nanosized dye based test strips, *etc*) [10–12]. Combining with sensor array technology and pattern recognition method, optical sensor arrays have been extensively applied for the determination of toxic industrial gases [13,14], nucleic acid and biomolecules [15], diols [16], and even for diagnostic [17], *etc*. General colorimetric arrays offer a good discrimination capability, but do, however, suffer from the poor sensitivity of indicators.

As an alternative, fluorometric approach shows unique potential due to its high sensitivity. Commercially available fluorescence

---

* Corresponding authors. Tel.: +86 411 84379660/+86 10 82543450.
E-mail addresses: fengl@dicp.ac.cn (L. Feng), qzyang@mail.ipc.ac.cn (Q.-Z. Yang).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.02.073

indicators were combined to build up fluorometric sensor arrays for the determination of heavy-metal ions [18,19]. Though these fluorescence indicators showed remarkable enhancement of sensitivity, the limit of detection was not satisfactory. Anzenbacher group recently prepared a series of derivatives of 8-hydroxyquinoline as fluorescent indicators for metal ions array and obtained impressive selectivity due to its high cross reactivity. The interaction of 8-hydroxyquinoline moieties in the sensor molecules with metal ions is, however, relatively weak in aqueous solution, which makes the discrimination of low concentration metal ions difficult [20,21]. Therefore, extending this performance to the environmentally relevant μM concentrations remains a challenge because of the lack of suitable fluorescent indicators.

In recent years, paper-based sensor devices have been widely investigated due to the low-cost, easy of use, portability, and disposability [22]. Paper-based microfluidic devices use the inherent flow properties (capillary force) of channels within paper, and so they require no external equipment or power sources. Here we demonstrate a highly sensitive fluorometric paper-based sensor for the determination of heavy-metal ions at their wastewater discharge standard concentrations based on a series of new BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene)-based fluorescent indicators. Combined with array technologies-based pattern-recognition, we obtained the discrimination capability of seven different heavy-metal ions at their wastewater discharge standard concentrations.

2. Experimental

2.1. Chemicals and materials

All the reagents and solvents are of commercial quality and without further purification. Deionized water was used throughout this work. 2,2′-dipicolylamine, bis(triphenyl-phosphine) palladium(II) chloride were purchased from TCI Co., Diethyl malonate, sodium methoxide, methyl mercaptoacetate were purchased from Alfa Aeser Co., 4-methoxyphenylacetylene were purchased from Sigma-Aldrich Co.. The heavy-metal ions stock solutions were Hg^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Co^{2+} in the form of their chloride salts (Ag^{+} was in its nitrate salt) in deionized water (2.5×10^{-4} M). All the heavy-metal salts used were analytical-reagent grade, obtained from Alfa Aesar Co., and used without further purification unless otherwise specified. pH was adjusted to 6.5 in aqueous solutions and metal ions stock solutions by addition of NaOH (0.01 M) or HCl (0.01 M) utilizing a Titrator T50 (Mettler Toledo Co.) and all the solutions were used immediately after preparation.

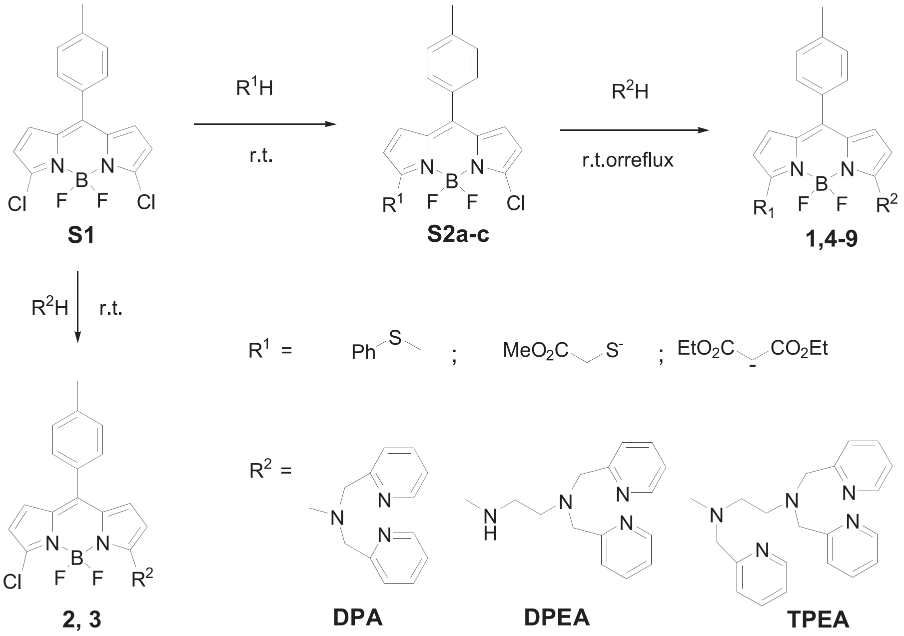
^{1}H NMR spectra were recorded on an Advance Bruker 400 M spectrometer and referenced to solvent signals. Mass spectra were obtained on Bruker Apex IV fourier transform mass spectrometer. Fluorescence spectra were determined on a Hitachi 4500 spectrophotometer. Absorption spectra were determined on a Shimadzu UV-1601PC UV–visible spectrophotometer.

2.2. The synthesis of BODIPY-based di-2-picolyamine (DPA) derivatives

The BODIPY-based DPA derivatives **1**–**9** were synthesized according to previous reports. As shown in Scheme 1, **S2a–c** were synthesized by reacting S1 with corresponding substrate under different conditions. 50 mg compound **S2a–c** (compound **S1** for the synthesis of **2** and **3**) was dissolved in 20 mL acetonitrile and 50 μL triethylamine was added. To this solution 2 equiv of di-2-picolyamine (DPA), N,N-di(pyridin-2-ylmethyl)-ethane-1,2-diamine (DPEA) or N,N,N′-tri(pyridin-2-ylmethyl)- ethane-1,2-diamine (TPEA) in 10 mL acetonitrile was added dropwise with stirring. The reaction was kept at different temperature until the disappearance of the starting materials detected by TLC. The reaction mixture was evaporated to dryness and purified through column chromatography over silica gel to give **1**–**9** (see the Supporting Information, Fig. S1).

2.3. The fabrication of sensor array paper.

The wax-based paper was prepared according to previous report [23,24]. A Xerox Phaser 8560DN (Fuji, Japan) wax printer was utilized to print wax-based pattern on Whatman grade no. 41 quantitative filter paper (GE healthcare, UK). The printer head dispensed melted wax as liquid droplets of approximately 50–60 μm in diameter on the surface of the paper, and solidify



Scheme 1. Synthesis of BODIPY-based DPA derivatives.

instantaneously without further spreading. The printed paper was then baked in the oven at 120 °C for 30 min, and the wax re-melted and penetrated through the thickness of the paper, forming the hydrophobic barriers.

The BODIPY-based DPA derivatives were separately dissolved in absolute alcohol at 5×10^{-4} M and then 7–40 μm silica particles (380 m^2/g) were introduced to at its final concentration 80 mg/mL. After the physical absorption, the silica particles were washed with distilled water for three times. The obtained silica particles were then uniformly dispersed in a 5% starch solution by sonication. 2 μL dispersions of these silica particles immobilized with different BODIPY-based DPA derivatives were individually printed on the hydrophilic spots of wax-based paper. The sensor array papers were then stored in N_2 bag at 33% relatively humidity for at least three days before any experiments.

2.4. *The detection procedure.*

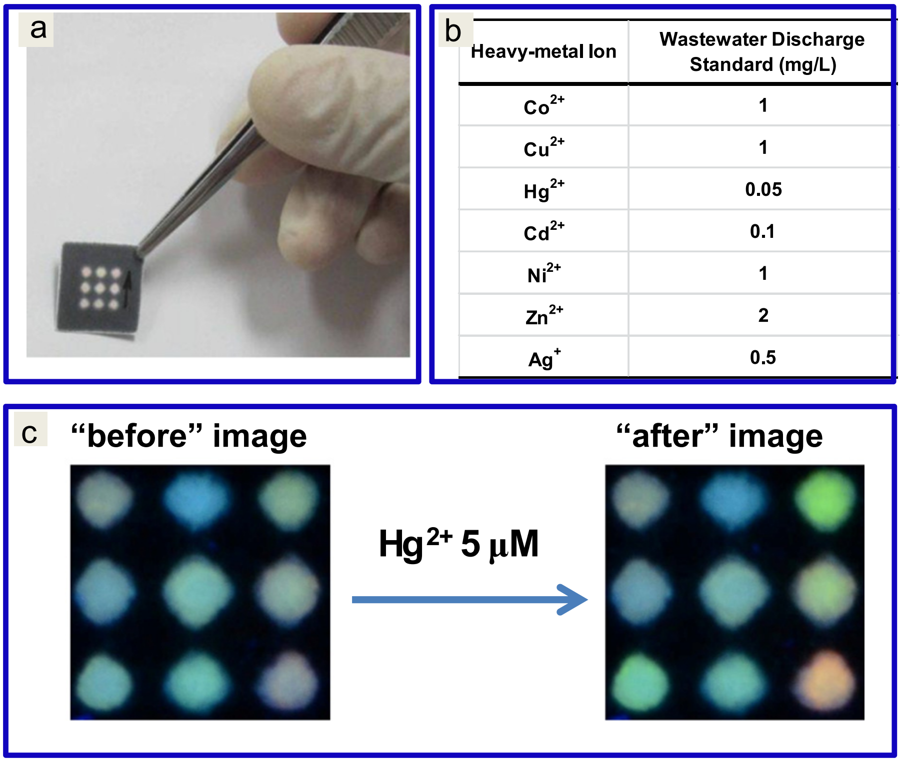
600 μL of the heavy-metal ion solutions with the desirable concentrations were introduced to the sensor array paper. The water-absorbent materials (qualitative filter paper in this case) were placed under the array paper, so the analyte solution could only pass through the hydrophilic spots of the sensor array paper continuously. The heavy-metal ions were then enriched and efficiently reacted with BODIPY-based DPA derivatives immobilized in the array paper. The fluorescent imaging was performed using the home-made imaging system.

A UV LED array equipped with a 365 nm narrow band filter (Band width = 12 nm) was used as excitation light source (see the Supporting Information, Fig. S2). After filtering the UV source light using a 400 nm short wavelength pass filter (400–700 nm), the excited fluorescence array images in a light-tight cylinder “before” and “after” exposure of heavy-metal ions were acquired from the bottom of the vials using a Nikon D7000 digital camera with a AF-S 60 mm f/2.8 G macro lens. Difference maps were obtained by subtracting the digital red, green, and blue values of “after-exposure” and “before-exposure” images of the fluorescence array consisting of 9 indicators. Adobe Photoshop™ was used to digitize this color difference. Chemometric analyses were carried out on the color difference vectors using the multi-variate statistical package. Ward’s minimum variance criterion was used to minimize the total within-cluster variance. At each step the pair of clusters with minimum cluster distance is merged. A hierarchical cluster result was easily achieved.

3. Results and discussion

A practical fluorometric indicator for heavy-metal ions should meet at least four criteria: (1) large fluorescence change in the presence of heavy-metal ions, (2) a receptor with a high affinity to the analytes to achieve high sensitivity, (3) similar photophysical properties of all fluorophores in the sensor to enable the use of a single monochromatic light source to excite all fluorescent indicators, (4) low-cost and highly efficient synthesis of the indicators.

Following these criteria, we designed fluorometric indicators for heavy-metal ions determination based on BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) as fluorophore and di-2-picolyamine (DPA) derivatives as receptors. The variety of synthetic pathways to BODIPY-based fluorophores allows efficient preparation. The fluorescence properties of BODIPY were tunable by simple substitution at various positions of the difluoroboron dipyrromethene core [25–27]. DPA and its derivatives DPEA and TPEA, are well-known receptors for heavy-metal ions [28–30]. The DPA derivatives combine high affinities for a variety of heavy-metal ions with the capacity to perturb the fluorescence



Heavy-metal Ion	Wastewater Discharge Standard (mg/L)
Co^{2+}	1
Cu^{2+}	1
Hg^{2+}	0.05
Cd^{2+}	0.1
Ni^{2+}	1
Zn^{2+}	2
Ag^{+}	0.5

Fig. 1. (a) The wax-based nine BODIPY DPA derivatives array paper. (b) The wastewater discharge standard concentrations of seven heavy-metal ions. (c) Raw fluorescence images of the array before and after exposure to 5 μM Hg^{2+} ion.

properties of BODIPY, making them the most promising candidates for the design of fluorometric sensor arrays for heavy-metal ions.

We constructed BODIPY-based indicators from readily available building blocks of 3,5-dichloroBODIPY and multi-pyridyl receptors following the elegant method of Dehaen [31,32]. A single chlorine of 3,5-dichloroBODIPY could be replaced with different substituents by carefully tuning the reaction conditions, as shown in Scheme 1. The other chlorine could then be replaced with a multi-pyridyl receptor such as DPA, DPEA and TPEA with extended reaction times or at elevated temperatures (see the Supporting Information, Table S1).

Based upon above mechanisms, we created a sensor array comprised of 9 fluorescent indicators by combining methoxy, mercapto, chloride, alkyl, aniline or alkynyl-subsituted BODIPY fluorophore with DPA, DPEA, and TPEA chelators. Combining the paper-based sensing technique, we developed BODIPY-based fluorometric sensor array for the determination of heavy-metal ions.

The array was used to efficiently discriminate among seven heavy-metal ions (Hg^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, and Ag^{+}) at their wastewater discharge standard concentrations. Since some of the concentrations were as low as 10^{-7} M, the enrichment was utilized. As shown in Fig. 1a, due to the hydrophobicity of wax pattern, the analyte solution can only penetrate through the indicator-immobilized hydrophilic silica particles. The heavy-metal ions could be efficiently enriched and react with BODIPY-based DPA derivatives. Thus, the sensitivity is obviously improved, and the sensor array paper will be capable of discriminate heavy-metal ions at their wastewater discharge standard concentrations (Fig. 1b).

Though most BODIPY-based fluorescent indicators show the largest absorption and emission at around 500 nm and 550 nm, respectively, in order to develop a handheld unit in a relatively simple way, we used a UV LED array equipped with a 365 nm narrow band filter as an excitation light source (see the Supporting Information, Fig. S2). After the UV source light was filtered through a 400 nm short wavelength filter (400–700 nm), the excited fluorescence array images "before" and "after" exposure of heavy-metal ions were acquired using a digital camera, as shown in Fig. 1c. The difference maps were obtained by subtracting the digital red, green, and blue values of "after" and "before" images of the fluorescence array allowed clear differentiation of the ions.

After exposure to seven heavy-metal ions at their wastewater discharge standard concentrations, the difference maps provided a fingerprint that effectively identified the heavy-metal ions to which the sensor array has been exposed. The 27-dimensional (9 indicators × 3 channels of red, green and blue) fluorometric response pattern of our array to the seven heavy-metal ions (Hg^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, and Ag^{+}) was statistically explored using the standard chemometric techniques, the hierarchical cluster analysis (HCA) [33]. HCA is a classification scheme based on the Euclidean distance (total length of 27-dimensional color-difference vector, that is, the total array response) among data points in their full dimensionality. The dendrograms generated by HCA are shown in Fig. 2. All seven heavy-metal ions and a control were accurately classified with no misclassification out of 40 cases.

The ability of BODIPY-based array to discriminate seven heavy-metal ions is impressive and largely the result of the high dimensionality of the array data. The multidimensional response pattern was also investigated by principal component analysis (PCA), which is a statistical treatment used to reduce multidimensional data for easier interpretation. Based on the 40 trials of eight heavy-metal ions and a control, using 45 trials with centered, standardized color difference vectors, the PCA of our array requires 11 dimensions to describe 99% of the discriminatory range (see the Supporting Information, Fig. S3). In contrast, most prior arrays are dominated by only two independent dimensions, and have typically 90% of discrimination in the first principal component. This limited dispersion indicates that very little of the total diversity of chemical properties is being probed in traditional liquid sensing.

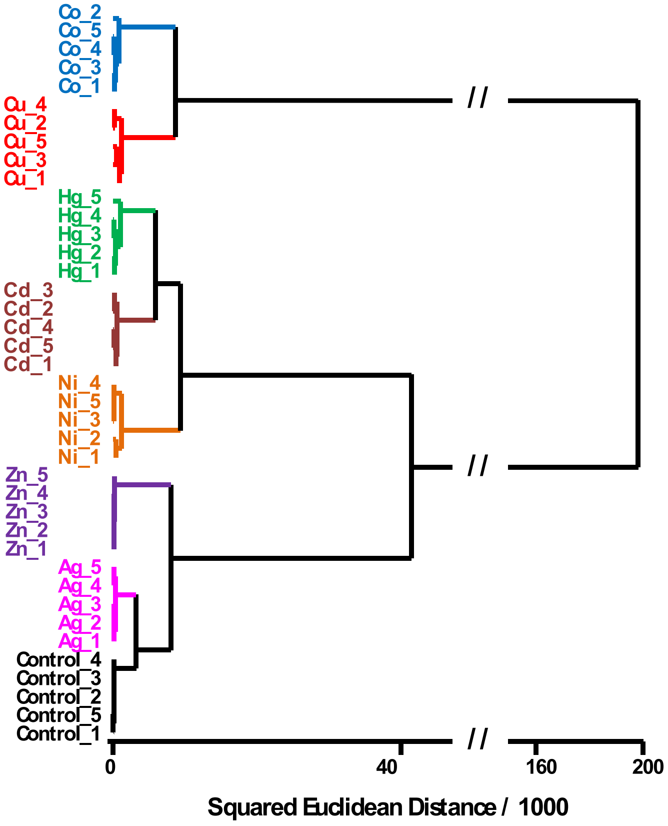


Fig. 2. HCA for seven heavy-metal ions at their wastewater discharge standard concentrations and a control.All experiments were run in quintuplicate trials. No confusions or errors in classification wereobserved in 40 trials. The HCA used minimum variance (that is, "Ward's Method") for clustering. A fulldigital database is provided in the Supporting Information.

Difference maps were obtained by taking the differences of the red, green, and blue (R, G, B) values from the before and after images. Therefore, the fluorescent response (color changes) was expressed using the Euclidean distance (ED), which could be defined by the following formula:

$$\sqrt{(\Delta R)^2+(\Delta G)^2+(\Delta B)^2}$$

The fluorescence changes of the array depend on the concentration of each heavy-metal ion, which allows simple estimation of the concentrations of heavy-metal ions and the detection limits of the method. Color differences for a representative analyte (Hg^{2+}) as a function of its concentration are shown in Fig. 3. A semi-quantitative interpolation of the heavy-metal concentration is obtained by comparing the color changes (that is., the total Euclidean distance of the measurement) with a set of known concentrations in the library. The sensor array paper showed good linear relationship between the color changes and Hg^{2+} concentrations at the range of 0.25–1.0 μM.

In real world use, the interference has to be concerned, in terms of both false positives from harmless cations and anions. The sensor array has been extensively tested against six common potential interfering agents: K^{+}, Na^{+}, Ca^{2+}, Mg^{2+}, SO_4^{2-}, and

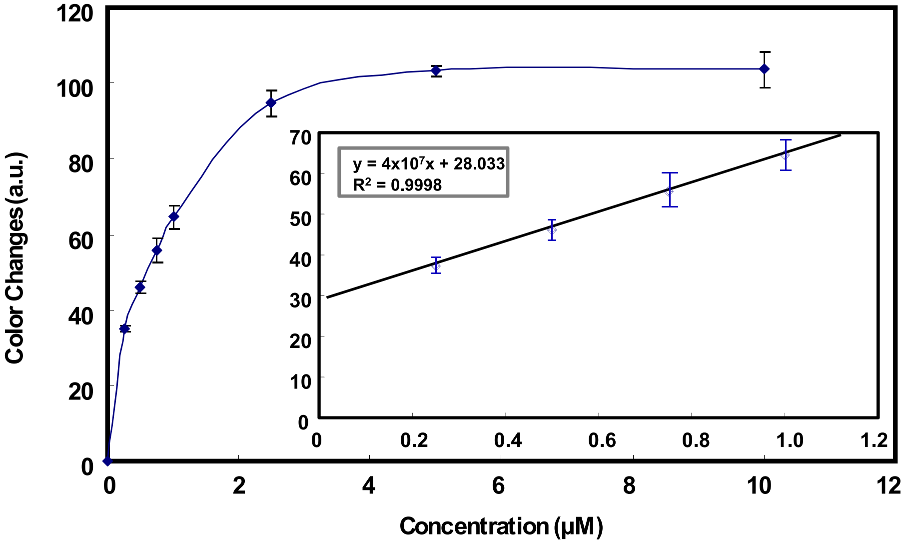


Fig. 3. The semi-quantitative analysis curve of Hg^{2+}. All experiments were run in triplicate trials.

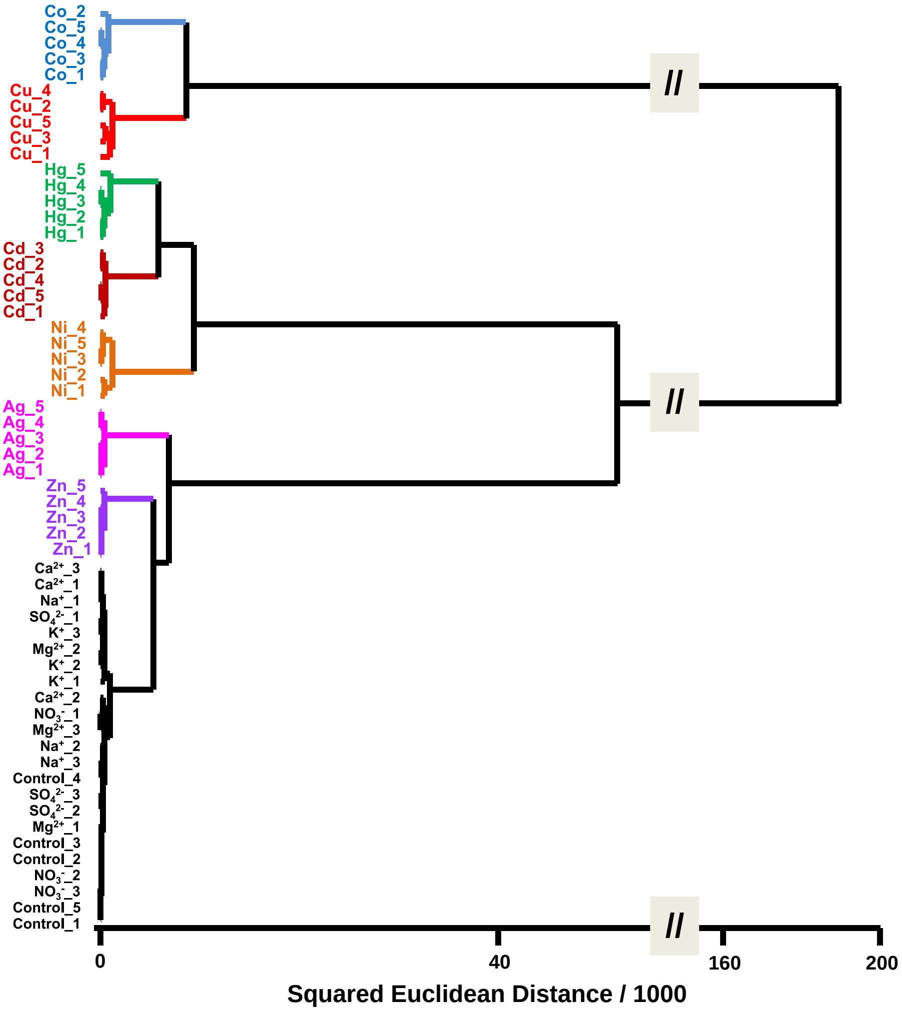


Fig. 4. HCA for seven heavy-metal ions at their wastewater discharge standard concentrations and a control as well as common interference ions, e.g., K^{+}, Na^{+}, Mg^{2+}, Ca^{2+}, SO_4^{2-}, NO_3^{-}, etc. All experimentswere run in quintuplicate trials except for triplicate trials for interferants. The HCA used minimumvariance (that is, "Ward's Method") for clustering.

NO_3^{-}, each at concentrations thousands of times higher than the eight heavy-metal ions tested. Little interference was observed, as shown in Fig. 4.

The tap water and sea water real samples were also evaluated directly after centrifuging at 10,000 rpm for 10 min. The ion contents in tap water and sea water were previously investigated

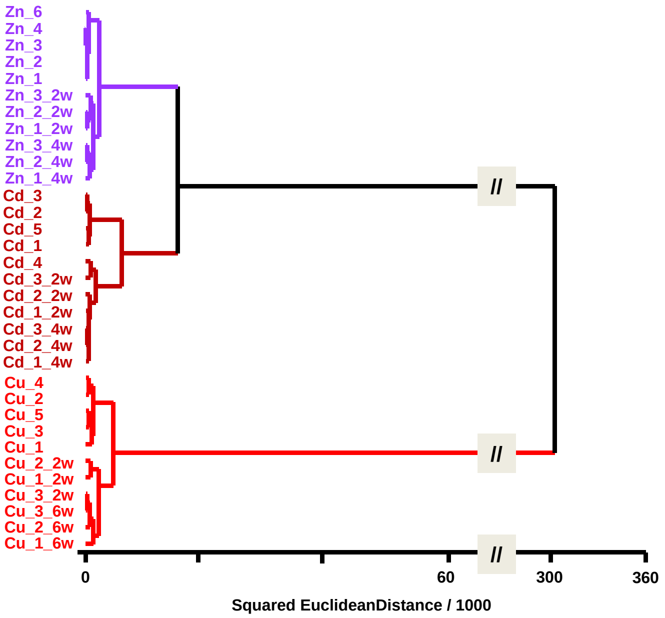


Fig. 5. HCA for three heavy-metal ions at their wastewater discharge standard concentrations using our sensor array paper stored under N_2 for 1, 2, and 4 weeks.

by ion-chromatography (Dionex ICS-1100) before any testing. Tap water (pH=6.8): Cl^-: 35.99 mg/L, NO_3^-: 38.75 mg/L; Sea water (pH=7.2): Cl^-: 15326 mg/L, NO_3^-: 685.7 mg/L; SO_4^{2-}: 1974 mg/L, Na^+: 5569 mg/L, K^+: 261.8 mg/L, Mg^{2+}: 1254 mg/L; Ca^{2+}: 246 mg/L. No significant heavy-metal ions were found in these two samples. The concentrated stock Cu^{2+} solution was then introduced, and the final concentration of Cu^{2+} in these real samples was at its wastewater discharge standard concentration. The HCA classified these spiked samples to the corresponding clusters (see the Supporting Information, Fig. S4). This partially proves the feasibility of our BODIPY-based DPA derivatives array paper for real sample testing. The discrimination of multi-ions in complex mixtures, however, still needs to be further investigated.

The batch-to-batch reproducibility of sensor array paper was investigated as well, and two batches prepared at different days showed similar responses to selected heavy-metal ions (see the Supporting Information, Fig. S5). The sensor array papers were stored in polyethylene bags under N_2 for 1, 2, and 4 weeks, and storage time has essentially no effect on the array responses, as shown in Fig. 5.

In summary, we have developed a library of fluorogenic indicators and created a fluorometric paper-based sensor to discriminate heavy-metal ions. By combining array technologies and pattern-recognition methods, we have applied our fluorometric paper-based sensor array to distinguish seven heavy-metal ions at their wastewater discharge standard concentrations. The indicators are based on BODIPY as the fluorophore and multi-pyridyl ligands as the metal-binding receptors. After the immobilization of indicators and the enrichment of analytes, seven heavy-metal ions could be distinguished using an array of 9 new indicators with the detection limit down to 10^{-7} M. The chemometric analysis revealed that the sensor array had a high dimensionality and, consequently, a strong capacity to distinguish heavy-metal ions at μM concentrations. We are now attempting to develop an inexpensive portable handheld device for detection of heavy-metal ions in resource-poor settings based on the array reported here (see the Supporting Information, Fig. S6).

Acknowledgments

We are grateful for financial support from the 973 program (2013CB933800). This work was also supported through the NSFC (Grant 21007067, 21177125, 21021004, 21222210) and by the 100 talents program, funded by CAS.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.02.073.

References

[1] W.W. Li, G.P. Sheng, R.J. Zeng, X.W. Liu, H.Q. Yu, Environ. Sci. Pollut. Res. 19 (2012) 1422–1431.
[2] G.F. Nordberg, B.A. Fowler, M. Nordberg, L. Frigerg, Handbook on the Toxicology of Metals, 3rd ed., Academic Press, Burlington, MA, 2007.
[3] R. McRae, P. Bagchi, S. Sumalekshmy, C.J. Fahrni, Chem. Rev. 109 (2009) 4780–4827.
[4] C. Orvig, M.J. Abrams, Chem. Rev. 99 (1999) 2201.
[5] I. Ali, H.Y. Aboul-Enein, Instrumental Methods in Metal Ion Speciation, CRC Press, Boca Raton, FL, 2006.
[6] P. Pohl, TrAC, Trends Anal. Chem. 28 (2009) 117–128.
[7] M. Ghaedi, H. Tavallali, A. Shokrollahi, M. Zahedi, M. Montazerozohori, M. Soylak, J. Hazard. Mater. 166 (2009) 1441–1448.
[8] M.D. Ioannidou, G.A. Zachariadis, A.N. Anthemidis, J.A. Stratis, Talanta 65 (2005) 92–97.
[9] S.P. Wang, E.S. Forzani, N.J. Tao, Anal. Chem. 79 (2007) 4427–4431.
[10] J.R. Kalluri, T. Arbneshi, S.A. Khan, A. Neely, P. Candice, B. Varisli, M. Washington, S. McAfee, B. Robinson, S. Banerjee, A.K. Singh, D. Senapati, P.C. Ray, Angew. Chem. Int. Ed. 48 (2009) 9668–9671.
[11] T. Lan, K. Furuya, Y. Lu, Chem. Commun. 46 (2010) 3896–3898.
[12] Y. Takahashi, H. Kasai, H. Nakanishi, T.M. Suzuki, Angew. Chem. Int. Ed. 45 (2006) 913–916.
[13] S.H. Lim, L. Feng, J.W. Kemling, C.J. Musto, K.S. Suslick, Nat. Chem. 1 (2009) 562–567.
[14] L. Feng, C.J. Musto, K.S. Suslick, J. Am. Chem. Soc. 132 (2010) 4046–4047.
[15] D.R. Walt, Chem. Soc. Rev. 39 (2010) 38–50.
[16] S.H. Shabbir, L.A. Joyce, G.M. Cruz, V.M. Lynch, S. Sorey, E.V. Anslyn, J. Am. Chem. Soc. 131 (2009) 13125–13131.
[17] A.W. Martinez, S.T. Phillips, G.M. Whitesides, E. Carrilho, Anal. Chem. 82 (2009) 3–10.
[18] T. Mayr, C. Igel, G. Liebsch, I. Klimant, O.S. Wolfbeis, Anal. Chem. 75 (2003) 4389–4396.
[19] Z. Wang, M.A. Palacios, P. Anzenbacher, Anal. Chem. 80 (2008) 7451–7459.
[20] M.A. Palacios, Z. Wang, V.A. Montes, G.V. Zyryanov, P. Anzenbacher, J. Am. Chem. Soc. 130 (2008) 10307–10314.
[21] M.A. Palacios, Z. Wang, V.A. Montes, G.V. Zyryanov, B.J. Hausch, K. Jursíková, P. Anzenbacher, Chem. Commun. (2007) 3708–3710.
[22] C.M. Cheng, A.W. Martinez, J.L. Gong, C.R. Mace, S.T. Phillips, E. Carrilho, K.A. Miria, G.M. Whitesides, Angew. Chem. Int. Ed. 49 (2010) 1–5.
[23] A.W. Martinez, S.T. Phillips, M.J. Butte, G.M. Whitesides, Angew. Chem. Int. Ed. 46 (2007) 1318–1320.
[24] A.W. Martinez, S.T. Phillips, G.M. Whitesides, P. Natl., Acad. Sci. USA 105 (2008) 19606–19611.
[25] O.A. Bozdemir, S. Erbas-Cakmak, O.O. Ekiz, A. Dana, E.U. Akkaya, Angew. Chem. Int. Ed. 50 (2011) 10907–10912.
[26] J.H. Olivier, J. Barberá, E. Bahaidarah, A. Harriman, R. Ziessel, J. Am. Chem. Soc. 134 (2012) 6100–6103.
[27] A.B. Nepomnyashchii, M. Bröring, J. Ahrens, A.J. Bard, J. Am. Chem. Soc. 133 (2011) 8633–8645.
[28] Z.C. Xu, J.Y. Yoon, D.R. Spring, Chem. Soc. Rev. 39 (2010) 1996–2006.
[29] X.J. Peng, J.J. Du, J.L. Fan, J.Y. Wang, Y.K. Wu, J.Z. Zhao, S.G. Sun, T. Xu, J. Am. Chem. Soc. 129 (2007) 1500–1501.
[30] F. Qian, C.L. Zhang, Y.M. Zhang, W.J. He, X. Gao, P. Hu, Z.J. Guo, J. Am. Chem. Soc. 131 (2009) 1460–1468.
[31] T. Rohand, W. Qin, N. Boens, W. Dehaen, Eur. J. Org. Chem. (2006) 4658–4663.
[32] T. Rohand, M. Baruah, W. Qin, N. Boens, W. Dehaen, Chem. Commun. (2006) 266–268.
[33] J.F. Hair, B. Black, B. Babin, R.E. Anderson, R.L. Tatham, Multivariate Data Analysis, 6th ed., Prentice Hall, Upper Saddle River, NJ, 2005.