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Preparation of 4,4′-bis-(carboxyl phenylazo)-dibenzo-18-crown-6 dye and its application on ratiometric colorimetric recognition to Hg^{2+}

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ABSTRACT

A multifunctional dye, 4,4′-bis-(carboxyl phenylazo)-dibenzo-18-crown-6 dye (BCADC) was designed and prepared via diazotization and coupling reaction of dibenzo-18-crown-6 with p-amino benzoic acid. The dye, combining crown ether ring, azo and carboxyl group, exhibits well-defined Hg^{2+}-selective ratiometric colorimetric behavior, with the maximum absorbance peak changing from 354 nm to 408 nm exclusively. Under the optimum conditions, the recognition to Hg^{2+} has a linear range of 2.5–58 × 10^{-7} mol L^{-1} with a 0.9978 correlation coefficient. The method was applied to analyse 3 environmental water samples with a detection limit of 2.9 × 10^{-8} mol L^{-1} and a relative standard deviation (R.S.D.) lower than 3.7% (n = 5). The action mechanism between BCADC and metal ions was discussed by means of Job's plots and theoretical calculations.

1. Introduction

Hg^{2+} is one of the environmentally most toxic and dangerous heavy metal ions because of the high affinity for thiol groups in proteins and enzymes. Especially, Hg^{2+} can accumulate in the human body, which leads to the dysfunction of cells and consequently causes a wide variety of diseases in the brain, kidney, and central nervous system even in a low concentration [1,2]. However, despite the toxicity, mercury and mercuric salts are still widely used in industrial process and a high percentage of mercury contamination has happened here and there in many products of daily life such as paints, electronic equipment, and batteries [3,4]. Accordingly, the accurate and facile detection of Hg^{2+} is of great importance. Classic detection methods include atomic absorption spectrometry [5], X-ray fluorescence spectrometry [6] and electro-chromic techniques [7], most of them require the complicated instrumentation and involve some cumbersome laboratory procedures. Although several papers describe fluorescent chemosensors which offer the advantages of rapid, sensitive and nondestructive detection methods [8–10], these sensor systems for Hg^{2+} have typically suffered from unfavorable fluorescence quenching due to spin orbit interactions [11].

Recently, colorimetric sensors have drawn more and more attention to decrease the experimental cost, to simplify the sensing process, and even only to utilize naked eyes instead of the complex instrument [2,12,13]. However, the sensitivity of common colorimetric sensors is low and the detections are conducted in nonaqueous solutions. So in view of the selective signal of Hg^{2+} in aqueous solution, the present work concerns a multifunctional dye that exhibits high selectivity and sensitivity to Hg^{2+} achieved by using a crown-ether ring as the anchoring group with Hg^{2+} based on the oxygen affinity nature as well as the size of the mercuric ion [14], –N=N– group as the connecting group to reduce other coexisting ion interferences [15], and –COOH group to increase the solubility in aqueous solution.

On the basis of the ideas above, in this work, a multifunctional chemosensor 4,4′-bis-(carboxyl phenylazo)-dibenzo-18-crown-6 dye (BCADC) was selected and prepared (Scheme 1). The compound effectively signals Hg^{2+} exhibiting well-defined, visible, Hg^{2+}-selective ratiometric chromogenic behavior with the maximum absorbance at 354 nm decreasing and that at 408 nm increasing accordingly. The selectivity to Hg^{2+} was not significantly affected in the presence of common physiologically and environmentally important alkali, alkaline earth, rare earth and transition metal ions, such as K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Na^+, Ni^{2+}, Cd^{2+}, Ag^+, Cu^{2+}, Pb^{2+}, Al^{3+}, Co^{3+}, Fe^{3+}, Eu^{3+} and Dy^{3+}. The detection limit was 2.9 × 10^{-8} mol L^{-1}, which is comparable to the toxicity level of Hg^{2+} in drinking water (3.0 × 10^{-8} mol L^{-1}) defined by Word Health Organization (WHO) [16]. The action mechanism of BCADC and metal ions was discussed by means of Job's plots and theoretical calculations. The proposed method was applied in the analysis of Hg^{2+} in environmental aqueous samples and the results were satisfying.

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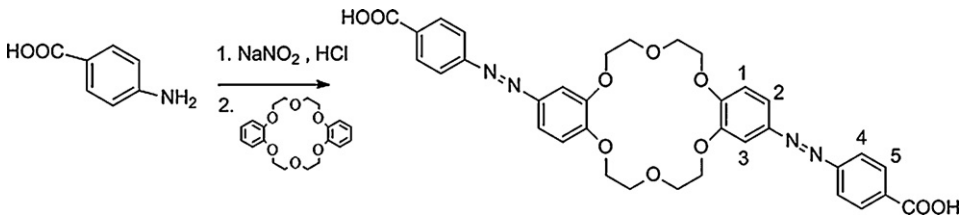

Scheme 1. Synthetic route and serial number of aromatic ring of the target compound.

2. Experimental

2.1. Reagents

Dibenzo-18-crown-6, *p*-amino benzoic acid and all the other chemicals were of AR grade and were used as received from Sinopharm Chemical Reagent Co. Ltd. Water used throughout was doubly deionized.

A 1.0×10^{-6} mol L^{-1} Hg^{2+} standard solution for testing was prepared in doubly deionized water at room temperature and diluted to appropriate concentration daily. 5.0×10^{-4} mol L^{-1} (BCADC) stock solution was prepared in DMSO at room temperature and stored at room temperature. NaAc–HAc or phosphate buffers were prepared by the mixture of 0.01 mol L^{-1} of HAc solution and 0.01 mol L^{-1} of NaAc solution or 0.01 mol L^{-1} Na_2HPO_4 solution and 0.01 mol L^{-1} KH_2PO_4 solution to the desired pH.

2.2. Apparatus

IR spectra were recorded on a Perkin Elmer Model 882 infrared spectrometer, mixed with KBr and pressed into pellets, scanning from 4000 to 500 cm^{-1}. ^1H NMR were recorded using a Bruker AMX-400 spectrometer operating at 400 MHz, with tetramethylsilane(TMS) as a reference and DMSO-d_6 as solvent. Elemental analysis was conducted using an Elemental Vario EL-III apparatus. UV–vis spectra were recorded on a Shimadzu UV-265 spectrometer using a 1-cm square quartz cell. All pH measurements were made with a PHS-25 pH meter.

2.3. Preparations of BCADC

As shown in Scheme 1, *p*-amino benzoic acid (0.686 g, 5 mmol) was dissolved in an ice–water solution of 15% sodium nitrite (0.38 g, 5.5 mmol). After cooling to 0 °C, the solution was added to concentrated hydrochloric acid (1.2 mL) and stirred for 30 min. The excess nitrous acid was destroyed with about 5 mg urea. The mixture was then added drop wise to 10 mL buffered aqueous solution (KH_2PO_4/Na_2HPO_4, pH 6) containing dibenzo-18-crown-6 (1.56 g, 5 mmol) and stirred for another 2 h at 0–5 °C. The resultant precipitate was filtered and purified by column chromatography on silica gel (eluent: petroleum methanol/ethyl acetate = 1:9) to provide light yellow crystal BCADC in the yield of 68.5%.

Mp, 202–203 °C; IR (KBr), υ (cm^{-1}): 2500–3500 (–COOH), 1697 (C=O), 1604 (N=N), 1258 (C–O–C). ^1H NMR (DMSO-d_6, 400 Hz) δ (ppm): 12.5 (s, 2H, COOH), 7.8 (d, J = 8.5 Hz, 4H, H^5), 7.5 (d, J = 8.4 Hz, 4H, H^4), 7.0–6.8 (m, J = 5.6 Hz, 6H, $H^{1,2,3}$), 4.1 (t, J = 2.7 Hz, 8H, CH_2), 3.9 (t, J = 2.5 Hz, 8H, CH_2). Anal. Calcd for $C_{34}H_{32}N_4O_{10}$: C, 62.19; H, 4.91; N, 8.53. Found: C, 62.73; H, 5.04; N, 9.01.

2.4. Procedures of detection

For Hg^{2+} detection, 1.0 mL HAc–NaAc (pH 5.0), 1.0 mL 5.0×10^{-4} mol L^{-1} of BCADC and 1.0 mL of the appropriate concentration of Hg^{2+} solution were transferred into a 10 mL volumetric flask. The mixture was stirred thoroughly and finally diluted to 10 mL with doubly deionized water. After incubating for 15 min, the absorbance spectra were measured from 250 nm to 500 nm and the band-slit was set as 2.0 nm. The ratio ($A_{408/354}$) of the absorbing intensity at 408 nm to that at 354 nm was used for quantitative analysis.

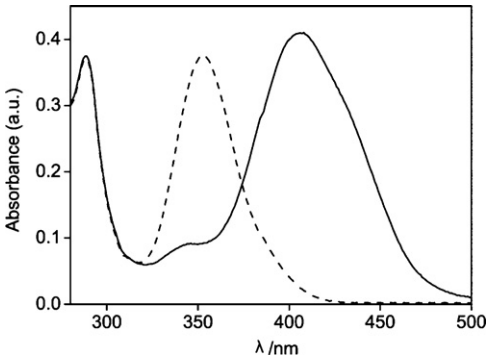

Fig. 1. UV–vis absorption spectra of BCADC in the absence (- - -) and presence (––) of Hg^{2+} ($C_{Hg^{2+}} = 5.8 \times 10^{-6}$ mol L^{-1}, pH 5.0; $C_{BCADC} = 5.0 \times 10^{-5}$ mol L^{-1}).

3. Results and discussion

3.1. The UV–vis absorption spectrum of BCADC

The UV–vis absorption spectra of BCADC in the absence and presence of Hg^{2+} in HAc-NaAc (pH 5.0) solutions were shown in Fig. 1.

It can be seen from Fig. 1 that BCADC has two absorbance peaks between 250 nm and 500 nm. The first absorption peak at 288 nm is attributed to the π–π electron transition in non-conjugated *p*-amino benzoic acid moiety. The second absorption peak at 354 nm results in the π–π electron transition in the huge π-conjugated system, N,N-di-phenyl azo, with ε_{max} about 7.5×10^4 L mol^{-1} cm^{-1}. In the presence of Hg^{2+}, the absorbance at 288 nm keeps unchanged nearly, however, the absorbance at 354 nm obviously red shifts to

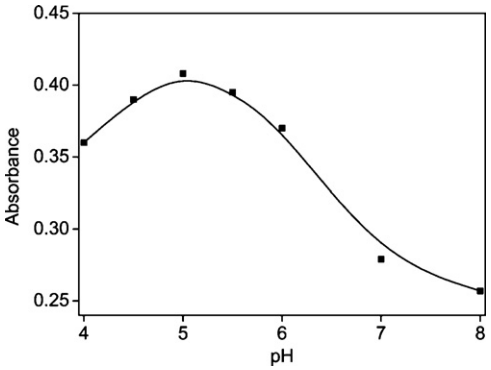

Fig. 2. Effect of pH on the absorbance of BCADC at 408 nm (pH 5.0; $C_{BCADC} = 5.0 \times 10^{-5}$ mol L^{-1}, $C_{Hg^{2+}} = 5.8 \times 10^{-6}$ mol L^{-1}).

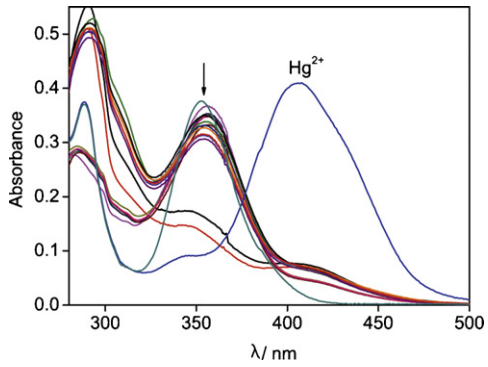

Fig. 3. Effect of different iron ions on the UV–vis absorbance spectrum of BCADC (from up to down: blank, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Na^+, Ni^{2+}, Cd^{2+}, Ag^+, Cu^{2+}, Pb^{2+}, Al^{3+}, Co^{3+}, Fe^{3+}, Eu^{3+} and Dy^{3+}), pH 5.0; $C_{BCADC} = 5.0 \times 10^{-5}$ mol L^{-1}.

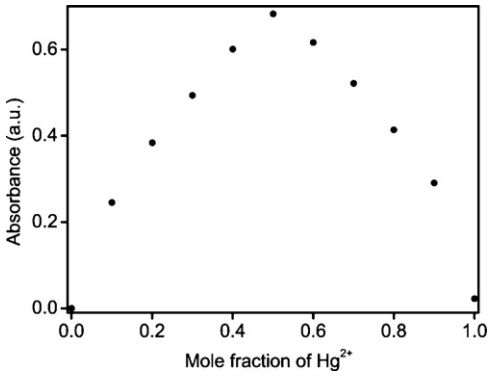

Fig. 6. Job's plot of BCADC–Hg^{2+} system. [BCADC] + [Hg^{2+}] = 6.0×10^{-5} mol L^{-1}, in aqueous 10% DMSO solution at pH 5.0.

408 nm, a visible spectrum, which allows a naked-eye detection of Hg^{2+} in aqueous solution.

3.2. Effect of pH value

As pH of the system has a significant influence on the interaction between BCADC and Hg^{2+} and the detection sensitivity, the effect of pH on the detection was investigated in the range of pH 4.0–9.0. As shown in Fig. 2, it can be easily seen that pH of the solution plays an important role in the interaction between BCADC and Hg^{2+}. The absorbance at 408 nm vary gradually with the decrease of pH and reaches the maximum when pH is ca 5.0. The reason may be that at pH < 5.0, oxygen atoms in crown ring are easily protonated, which reduces their coordination with Hg^{2+}. When pH is more than 5.0, the solubility of Hg^{2+} in aqueous solution decreases. Both above decrease the interaction between crown ether rings and Hg^{2+}, so the absorbance at 408 nm decreases.

3.3. Effect of coexisting foreign substances

To demonstrate the selectivity of BCADC for Hg^{2+}, we have investigated the colorimetric response of BCADC to other physiologically and environmentally important alkali, alkaline earth, rare earth and transition metal ions, such as K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Na^+, Ni^{2+}, Cd^{2+}, Ag^+, Cu^{2+}, Pb^{2+}, Al^{3+}, Co^{3+}, Fe^{3+}, Eu^{3+} and Dy^{3+} in aqueous solutions containing 5.0×10^{-5} mol L^{-1} BCADC at pH 5.0.

Fig. 3 shows the relative changes in the absorbance intensity of BCADC with the addition of 1 equiv of different metal ions. The additions of these metal ions except Hg^{2+} all show negligible red-shifts in the absorption of BCADC and the change in the absorbance intensity at 408 nm is less than 5% relative to Hg^{2+} at the same conditions. It means that the selectivity of BCADC to Hg^{2+} is well.

We also find that some high valence metal ions, especially rare earth elements, i.e., Eu^{3+} and Dy^{3+} can make the absorbance of BCADC at 354 nm quench. The reason may be that some high valence metal ions, i.e., Eu^{3+} and Dy^{3+} can coordinate with –N=N bond to make the terminal phenyl rings distorted. While in the

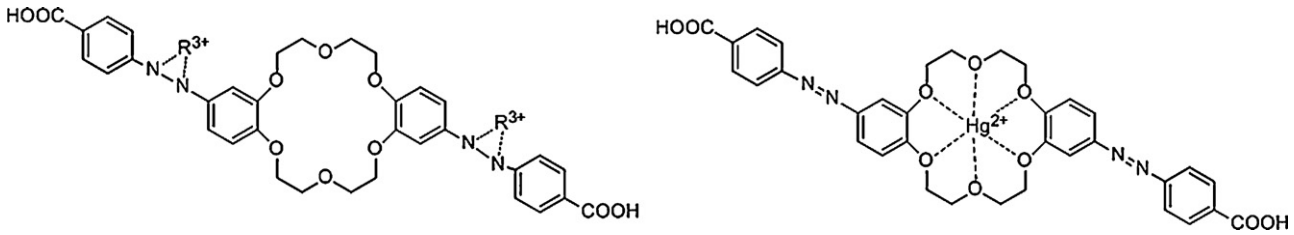

Fig. 4. The schematic diagram of the complex between BCADC and rare earth elements and Hg^{2+}.

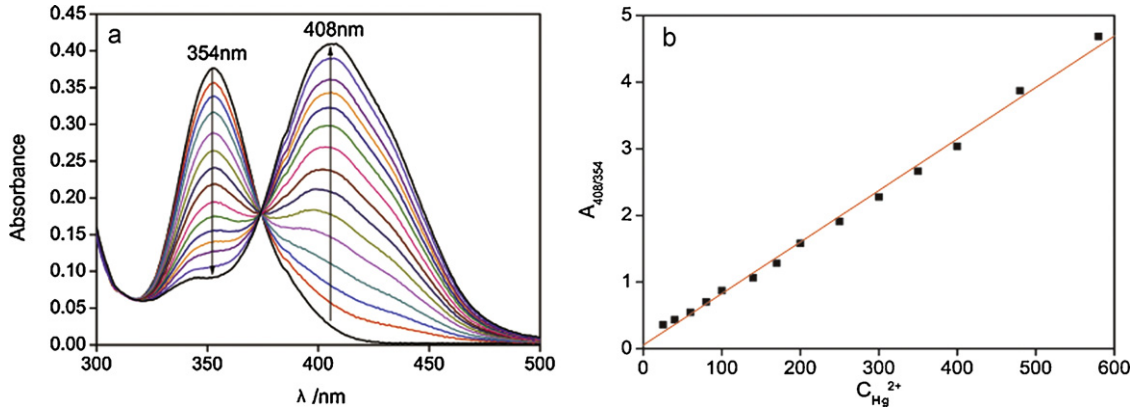

Fig. 5. (a) The absorbance spectra of BCADC in different Hg^{2+} concentrations: 0, 25, 40, 60, 80, 100, 140, 170, 200, 250, 300, 350, 400, 480, 580×10^{-7} mol L^{-1}. (b) The linear relationship between the $A_{408/354}$ of the system at 408 nm. pH 5.0; $C_{BCADC} = 5.0 \times 10^{-5}$ mol L^{-1}.

Table 1
Determination results for environmental water samples ($n = 5$).[a]

Samples[b]	$C_{Hg^{2+}}$ in sample[b] (10^{-9} mol L^{-1})	Spiked (10^{-9} mol L^{-1})	Found (10^{-9} mol L^{-1})	Recovery (%)	R.S.D. (%) ($n = 5$)
1(the Pi River)	425.1	500.0	881.6	95.3	2.0
2 (underground water)	948.4	500.0	1487.5	102.7	0.9
3 (tap water)	0.00	500.0	493.0	98.6	3.1

[a] pH 5.0; $C_{BCADC} = 5.0 \times 10^{-5}$ mol L^{-1}.
[b] The environmental water Hg^{2+} concentration determined using BCADC with the proposed method. The real values are the table values $\times 10^{-2}$ mol L^{-1} for the detected water samples were concentrated 100 times.

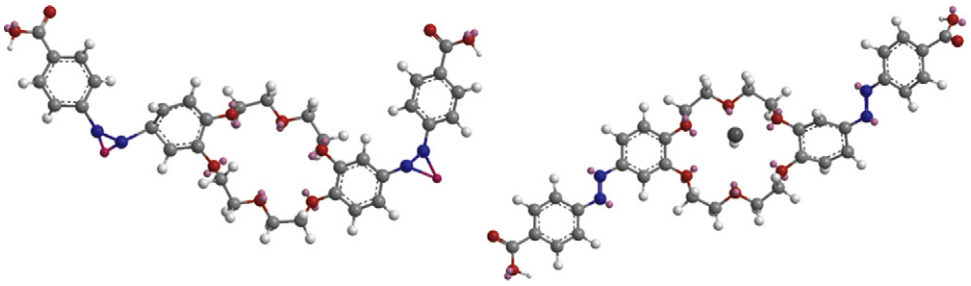

Fig. 7. The optimized structures of the complexes between BCADC and rare earth elements and Hg^{2+}.

presence of Hg^{2+}, Hg^{2+} can coordinate with oxygen atoms in crown ether ring, not with nitrogen atoms in –N=N bonds, based on the oxygen affinity nature as well as the size of the mercuric ion [14] (Fig. 4).

3.4. Analytical parameters and samples detection

Fig. 5a shows the absorbance spectra of BCADC at different concentrations of Hg^{2+} between 2.5×10^{-7} mol L^{-1} and 5.8×10^{-6} mol L^{-1}. From the spectra, the calibration graph, the detection limit and precision for Hg^{2+} detection under the optimum conditions can be obtained (Fig. 5b). A linear relationship between BCADC and Hg^{2+} concentration is exhibited in the range of 2.5–58 $\times 10^{-7}$ mol L^{-1} with a correlation coefficient of 0.9978. The regression equation is $A_{408/354} = -1.46 \times 10^{-1} + 7.73 \times 10^{-3}$ c (10^{-7} mol L^{-1}). Based on the definition of detection limit, three times of average deviation of absorbing intensity ratio ($A_{408/354}$) of the intensity at 408 nm to that at 354 nm in 20 blank samples without Hg^{2+} used here, the limit of detection (LOD) for Hg^{2+} is up to 2.9×10^{-8} mol L^{-1}, which is comparable to the toxicity level of Hg^{2+} in drinking water (3.0×10^{-8} mol L^{-1}) defined by Word Health Organization (WHO) [16].

To further evaluate the feasibility, the proposed method has been applied to analyse 3 environmental water samples from the Pi River, underground water and tap water in campus, respectively. All the samples were obtained by filtering several times and concentrated by 100 times. The Hg^{2+} concentrations in the sample are determined colorimetrically using a standard addition method by measuring $A_{408/354}$ of BCADC at 408 nm and 354 nm with the above mentioned procedures.

Table 1 shows the results obtained in the three independent samples above. For recovery studies, some known concentrations of Hg^{2+} were added to the environmental water samples and the total Hg^{2+} concentration determined following the method proposed above. The recoveries of different known amounts of Hg^{2+} spiked were obtained from 95.3% to 102.7% with a satisfying analytical precision (R.S.D. $\leq$ 3.7%), which validated the reliability and practicality of this method.

3.5. Mechanisms of the action

To investigate the nature of the bonding between BCADC and Hg^{2+}, the binding stoichiometry of BCADC with Hg^{2+} was determined by using Job's plot. For the Job plot analyses, a series of solutions with varying mole fraction of Hg^{2+} ions were prepared by maintaining the total BCADC and Hg^{2+} concentration constant (6.0×10^{-5} mol L^{-1}). The absorbance intensity at 408 nm was measured for each solution. A 1:1 stoichiometry, not 1:2 for the complex between BCADC and Hg^{2+}, drawn from Job's plots [17] in Fig. 6, confirms that Hg^{2+} coordinates with oxygen atoms in crown ether rings, not with nitrogen atoms in –N=N bonds, as proposed above.

Theoretical calculations have been carried out to further understand the nature of the bonding between BCADC and Hg^{2+}. The complexes shown in Fig. 4 were optimized using the B3LYP/6-31G level of theory and method implemented in the Gaussian 03 suite of program [18]. That Hg^{2+} can selectively coordinate with oxygen atoms in crown ether ring, not with nitrogen atoms in –N=N bonds, may be attributed to the oxygen affinity nature as well as the size of the mercuric ion [14]. As shown in Fig. 7, once the binding of Hg^{2+} with BCADC, the stability and conjugated system of the complex both increase owing to the formation of six rigid five-membered rings. So the absorbance of BCADC is red-shift. On the other hand, the coordination of some high valence metal ions such as Eu^{3+} and Dy^{3+} with –N=N bond makes the terminal phenyl rings distorted which results in the original conjugated system destroyed and so the absorbance at 354 nm deduced and even quenched.

4. Conclusions

In conclusion, we have designed and demonstrated the use of BCADC as a novel ratiometric colorimetric sensor for the detection of Hg^{2+} in aqueous solutions. BCADC displays unusual selectivity for Hg^{2+} due to the special oxygen affinity nature and size of mercury ion. Under the optimum conditions, the method has a linear range of 2.5–58 $\times 10^{-7}$ mol L^{-1} with a 0.9978 correlation coefficient. The limit of detection was 2.9×10^{-8} mol L^{-1} meeting the toxicity level of Hg^{2+} in drinking water (3.0×10^{-8} mol L^{-1}) defined by Word Health Organization (WHO) [16]. The presented method has been applied successfully to the determination of Hg^{2+} in environmental samples. The reaction mechanism between BCADC and metal ions was discussed by means of Job's plots and theoretical calculations. Further studies are in progress to explore the application of BCADC in detection of rare earth metals.

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