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Short communication

A novel azathia-crown ether dye chromogenic chemosensor for the selective detection of mercury(II) ion

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Abstract

A novel azathia-crown ether dye was synthesized and characterized and its binding ability with metal ions was investigated via UV–vis spectroscopy. When a series of alkali-metal, alkaline earth metal and transition metal ions were mixed with the dye in acetonitrile, only Hg^{2+} induced a large blue shift from 478 nm to 369 nm corresponding to a distinct color change from red to yellow, which made it possible to distinguish Hg^{2+} from other metal ions by the naked-eye. The excellent Hg^{2+}-selectivity of the dye was attributed to the formation of a 1:2 dye:Hg^{2+} coordination complex which was demonstrated by means of a Job's plot.

Keywords: Azathia-crown ether; Naked-eye; Chemosensor; Chromophore; Selectivity

1. Introduction

Heavy metal mercury is one of the highly toxic environmental pollutants derived from both natural and industrial sources. Mercury(II) ion or the lipophilic methylmercury derivative can accumulate in the organs of living things through food chain, doing huge harm to human being and the nature [1]. Thus, effective detection of mercury is of great significance for biochemistry, environmental science and medicine, and considerable effort has been devoted to this regard. Though many sophisticated analytical techniques for mercury detection such as atomic absorption spectrometry [2], atomic fluorescence [3], inductively coupled plasma mass spectrometry [4] have been established, most of them are time-consuming or require expensive equipment. So it is still a challenge to develop rapid and inexpensive methods for monitoring this dangerous and widespread global pollutant. Currently, chemosensors based on molecular recognition are emerging as a very important research area within the field of supramolecular chemistry [5–7], which allow the detection of guest by binding-induced changes in spectroscopic or electrochemical properties [8–12]. Among many Hg^{2+}-selective chemosensors developed so far, chromogenic receptors are especially attractive because substrate determination can be carried out by the "naked-eye" without the use of instrumentation [13–15].

As a receptor, azathia macrocycle has received increasing attention due to its strong ability to coordinate with heavy and transition metal ions such as Cu^{2+}, Fe^{3+}, Hg^{2+} [16,17]. On the other hand, *p*-nitroazobenzene is a frequently used and easy-to-make chromophore. Potent electron-withdrawing group ($-NO_2$) and long π-conjugation system make the optical signals easy to detect. Here, we reported a novel chromogenic chemosensor (**6**) composed of azathia macrocycle and *p*-nitroazobenzene, which showed high selectivity for Hg^{2+} and made it possible to specifically detect Hg^{2+} by the naked-eye.

2. Experimental

2.1. General

Twice-distilled water was used throughout all experiments. All the materials used were of analysis grade quality obtained

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from commercial sources and used without further purification except when specified. Both pyridine and acetonitrile were refluxed with calcium hydride and distilled at normal pressure. Anhydrous potassium carbonate was dried at 200 °C (normal pressure) for 3 h. Melting points were determined on a XRC-I melting point apparatus and were uncorrected. The IR spectra were obtained on a Perkin Elmer 16PC FT-IR spectrometer with the samples in KBr pellets. ^{1}H NMR spectra were performed on a Varian UNITY INOVA-400 MHz spectrometer or Bruker AVANCE AV II-400 MHz spectrometer in $CDCl_3$ and chemical shifts (δ) were reported relative to Me_4Si as internal standard. UV–vis spectra were measured on a TU–1901 UV–vis spectrophotometer (Beijing Purkinje General Instrument). Mass spectra (MS) were recorded on an API-3000 LC/MS/MS spectrometer.

2.2. Synthesis of **1–6**

2.2.1. Preparation of β,β′-dichlorodiethyl ether (**1**) [5]

To 47 mL (500 mmol) of diethylene glycol was added slowly 80 mL (1100 mmol) of thionyl chloride at 86 °C. Because a lot of gas came into being when thionyl chloride met water, care must be taken to avoid fast addition. The reaction mixture was stirred at constant temperature for 18 h. Meanwhile, the resulting gas was guided to basic solution. Then the mixture was cooled and distilled at reduced pressure (15 mmHg). Collecting distillate of 96 °C afforded 425 mmol (85%) of colorless liquid **1**. ^{1}H NMR (ppm, $CDCl_3$, 400 MHz): δ 3.66–3.63 (t, 4H, $ClCH_2$), 3.80–3.77 (t, 4H, OCH_2). MS (*m/z*): 142 $[M]^+$.

2.2.2. Preparation of β,β′-dimercaptodiethyl ether (**2**) [25]

To a solution of sodium sulfide (96 g, 400 mmol) dissolved in 60 mL of water, 45 mL of carbon disulfide (600 mmol) was added dropwise at room temperature. Then the reaction mixture was warmed to 40 °C and stirred for 6 h. The excess carbon disulfide was removed by distillation at normal pressure. Then the procreant turkey red liquid was diluted with 125 mL of water, giving a transparent solution.

Compound **1** (20 g, 140 mmol) was added dropwise to the aqueous sodium trithiocarbonate obtained above at 20 °C. Then the reaction mixture was allowed to stir for 5 h at 65 °C. The resulting basic solution was extracted three times with ether after cooling to remove unreacted material and other nonacid impurity. Then sulfuric acid (3 mol L^{-1}) was added to the aqueous layer to adjust pH to 2–3, and the acidic aqueous medium was extracted four times with ether. The combined extract was washed with water until it became neutral and dried over anhydrous magnesium sulfate. Distillation at reduced pressure (15 mmHg) after removing solvent gave **2** as a colorless but quite odoriferous liquid (84 mmol, 60%). b.p. 110 °C (15 mmHg). ^{1}H NMR (ppm, $CDCl_3$, 400 MHz): δ 1.56–1.52 (t, 2H, SH), 2.62–2.57 (m, 4H, SCH_2), 3.51–3.48 (t, 4H, OCH_2). MS (*m/z*): 137 $[M-1]^-$.

2.2.3. Preparation of N,N′-phenyldiethanolamine (**3**) [26]

To a 500-mL three necked round-bottomed flask at room temperature was added 48 mL (500 mmol) of aniline and 89 mL (1200 mmol) of 2-chloroethanol. With stirring, 160 mL of aqueous solution of sodium hydroxide (44 g, 1100 mmol) was added dropwise to the mixture described above at 50 °C in the course of 4 h. Temperature rose gradually because the reaction was exothermic. Stirring was continued for an additional 6 h at 110 °C. Nitrogen atmosphere was required during the whole course. On standing for a night, the organic layer was separated and recrystallized from ethanol/water (1:4, v/v), giving **3** as a slightly yellow crystal in 86% yield. M.p. 57–58 °C. ^{1}H NMR (ppm, $CDCl_3$, 400 Hz): δ 4.64 (br, 2H, OH), 3.41–3.38 (t, 4H, NCH_2), 3.53–3.50 (t, 4H, OCH_2), 6.58–6.54 (t, 1H, ArH), 6.69–6.67 (d, 2H, ArH), 7.15–7.11 (t, 2H, ArH). MS (*m/z*): 182 $[M+1]^+$.

2.2.4. Preparation of N,N-bis[2-(p-tolylsulfonoxy)ethyl]-benzenamine (**4**) [26]

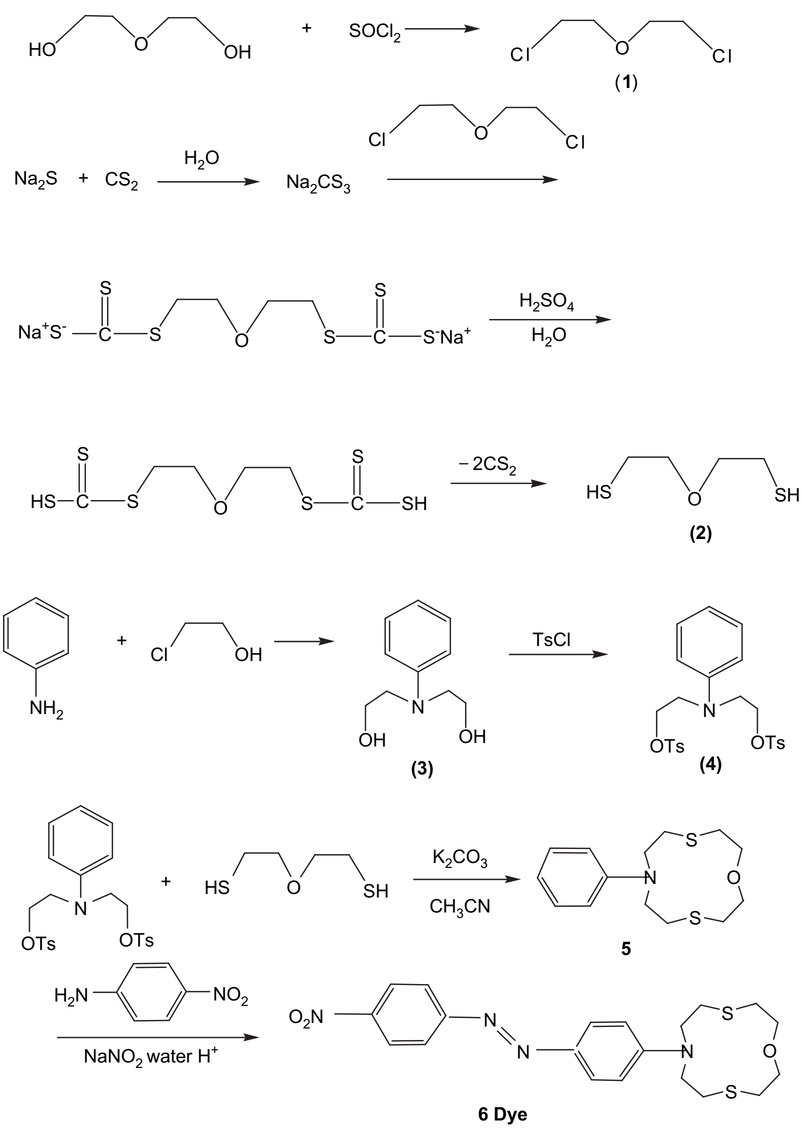
Dry compound **3** (46 g, 250 mmol) and 120 mL of anhydrous pyridine were added to a 500-mL three necked round-bottomed flask with an ice–salt bath, and then 96 g (500 mmol) of *p*-toluenesulfonyl chloride was introduced with vigorous stirring under nitrogen atmosphere. Stirring was continued for 4 h, during which the temperature was controlled to −5 to 5 °C. A yellow solid crystallized after the reaction solution was poured to 2 L of ice-water. The crystal was filtered, washed with ice-water and dried over anhydrous magnesium sulfate. Recrystallization from ethanol afforded a white crystal **4** in 60% yield. M.p. 91–92 °C. ^{1}H NMR (ppm, $CDCl_3$, 400 Hz): δ 2.42 (s, 6H, CH_3), 3.58–3.55 (t, 4H, NCH_2), 4.12–4.09 (t, 4H, OCH_2), 6.53–6.51 (d, 2H, ArH), 6.78–6.76 (t, 1H, ArH), 7.18–7.14 (t, 2H, ArH), 7.29–7.27 (d, 4H, ArH), 7.72–7.69 (d, 4H, ArH). MS (*m/z*): 490 $[M+1]^+$.

2.2.5. Preparation of 10-phenyl-1,7-dithia-4-oxa-10-aza-12-crown-4 (**5**) [17,27]

Dry potassium carbonate (10 g, 70 mmol) and 250 mL of anhydrous acetonitrile were added to a 500-mL three necked round-bottomed flask, and then 100 mL of anhydrous acetonitrile solution of **4** (13.5 g, 28 mmol) and 50 mL of anhydrous acetonitrile solution of **2** (5.72 g, 40 mmol) were simultaneously added dropwise. The reaction mixture was heated and refluxed for 25 h under nitrogen atmosphere. Potassium carbonate was filtered off after the reaction completed. The solvent was evaporated and semi-solid product was obtained. This crude product was purified by column chromatography on silica gel using petroleum ether/toluene (1:5, v/v) as eluent. A white crystal was obtained in 30% yield after distillation to remove solvent. M.p. 100–101 °C. IR (KBr, ν_{max}/cm^{-1}): 1315 (Ar–H), 1287 (C–N). ^{1}H NMR (ppm, $CDCl_3$, 400 MHz): δ 2.82–2.80 (t, 4H, CH_2), 2.92–2.89 (t, 4H, CH_2), 3.77–3.72 (m, 8H, CH_2), 6.68–6.64 (t, 3H, ArH), 7.23–7.19 (t, 2H, ArH). MS (*m/z*): 284 $[M+1]^+$.

2.2.6. Preparation of dye (**6**) [16,28]

With stirring, 7 mL of aqueous solution of sodium nitrite (4.1 g, 48 mmol) was slowly added to the solution of *p*-nitroaniline (6.5 g, 47 mmol) dissolved in 15 mL of water and 10.5 mL (36%) of hydrochloric acid (Scheme 1). The reaction



Scheme 1. The synthetic route of **6**.

temperature was controlled below 5 °C with an ice bath, during which diazonium salt precipitation appeared soon. Stirring was continued for another 15 min. Then the mixture was diluted to 250 mL with water.

To a 50-mL three necked round-bottomed flask was introduced 0.8 g (2.8 mmol) of **5** and 17 mL of the solution described above, and then 3 mL of aqueous solution of potassium acetate (0.38 g, 3.9 mmol) was added dropwise. The reaction temperature was controlled below 5 °C with an ice bath and stirring was continued for 30 min. The reaction mixture was filtered to afford a solid, which was washed with water, acetic acid (10%) and water/ethanol sequentially and dried at room temperature. Recrystallization from methylbenzene obtained a red crystal **6** in 46% yield. IR (KBr, ν_{max}/cm^{-1}): 1514, 1336 (NO_2), 1348 (Ar–N), 1269 (C–N). ^1H NMR (ppm, $CDCl_3$, 400 MHz): δ 2.93–2.78 (m, 8H, CH_2), 3.96–3.77 (m, 8H, CH_2), 6.77–6.75 (d, 2H, ArH), 6.98–6.96 (d, 2H, ArH), 7.97–7.95 (d, 2H, ArH), 8.36–8.32 (d, 2H, ArH). MS (*m/z*): 433 $[M+1]^+$.

3. Results and discussion

3.1. Photophysical property

The absorption spectrum of **6** in acetonitrile was characterized by an intense absorption at 478 nm with the molar extinction coefficients (ε) of 3.3×10^4 ($L\,mol^{-1}\,cm^{-1}$) (Fig. 1), which was ascribed to the intramolecular charge transfer (ICT) from the electron-rich macrocycle moiety (donor end) to the electron-deficient azobenzene moiety (acceptor end) [18].

3.2. Titration experiment of Hg^{2+}

The complexation ability of **6** ($2 \times 10^{-5}\,mol\,L^{-1}$) with Hg^{2+} was investigated by means of the UV–vis absorption technique. In our present experiments, $Hg(ClO_4)_2$ as a Hg^{2+} source was gradually added to the acetonitrile solution of **6**. The changes in the UV–vis spectrum of **6** upon addition of

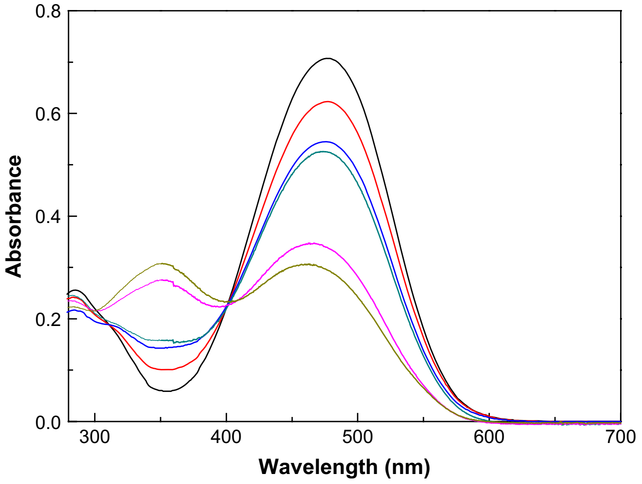


Fig. 1. UV–vis titration of **6** (2×10^{-5} mol L^{-1}) with $Hg(ClO_4)_2$ (0–5 equiv) in acetonitrile.

Hg^{2+} are presented in Fig. 1. Along with the increase of concentration of mercuric perchlorate, the intensity of absorption peak at 478 nm decreased gradually, and a new band at 369 nm appeared and increased gradually with an isosbestic point at 400 nm, which indicated the formation of a new compound. The fact suggested that the presence of Hg^{2+} influenced the ICT between the electron-rich macrocycle moiety and the electron-deficient azobenzene moiety. Judging from the titrations, the strong complexation of **6** to mercury(II) permitted the Job's plot method to be used in the detection of the stoichiometry for complexation, which was found to be 1:2 (**6** to Hg^{2+}) (Fig. 2). As shown in the schematic drawing (Scheme 2) [19], one Hg^{2+} might be bound to sulfur and nitrogen atoms (within the macrocycle) site [16,20] reducing the ICT [21,22], and the other Hg^{2+} might be bound to the −N=N− site [23,24] simultaneously that also reduced the ICT [19]. Thus, the degree of the ICT was diminished hugely via double diminution, which contributed to the extraordinarily large blue shift of the absorption band from 478 nm to 369 nm.

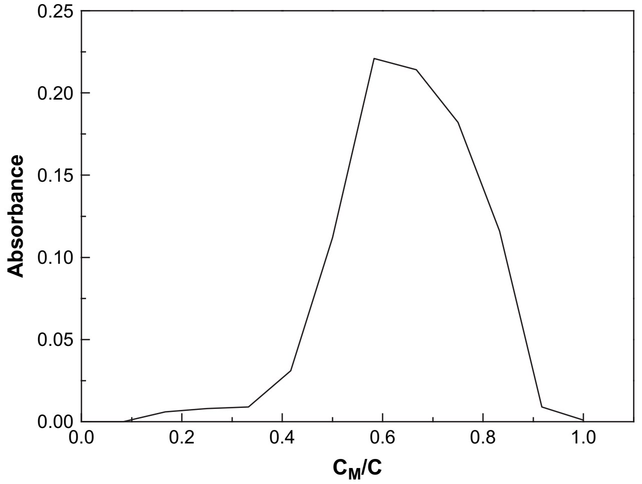
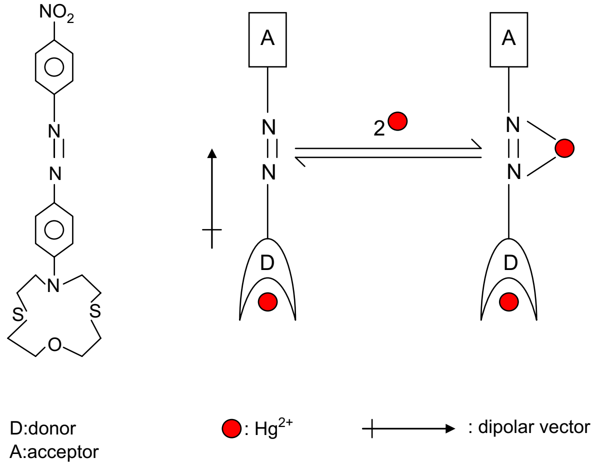


Fig. 2. Job's plot.



Scheme 2. The sensing process of **6** with Hg^{2+}.

3.3. Selectivity

For an excellent chemosensor, high selectivity is a matter of necessity. To examine the selectivity of **6**, we investigated its affinity for different alkali, alkaline earth and transition metal ions. The results are depicted in Figs. 3 and 4. Notably, the addition of Hg^{2+} (5 equiv) induced obvious spectral changes of **6**. Furthermore, the large blue shift ($\Delta\lambda = 109$ nm) resulted in a very noticeable color change from red to yellow. The addition of Ag^{+} (5 equiv) caused less pronounced blue shift ($\Delta\lambda = 8$ nm) and the intensity of absorption peak at 478 nm decreased noticeably, but the color of **6** in acetonitrile didn't change. While the addition of 5 equiv of Ca^{2+}, Cu^{2+} or Ba^{2+} increased the absorbance of **6** largely, the absorption position or the color of **6** in acetonitrile changed negligibly. As can be seen from Figs. 3 and 4, neither the spectral properties of **6** nor the color of the solution changed remarkably upon addition of other selected cations. Apparently, **6** can recognize

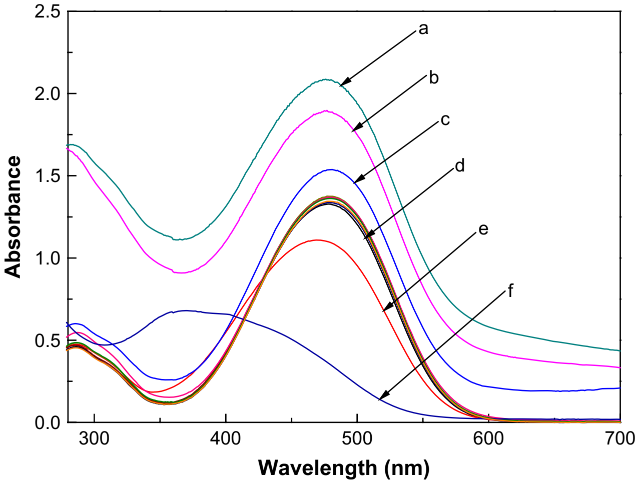


Fig. 3. UV–vis spectrum of **6** (4×10^{-5} mol L^{-1}) in acetonitrile before and after the addition of different metal ions (5 equiv, all as nitrates): (a) **6** + Ca^{2+}, (b) **6** + Cu^{2+}, (c) **6** + Ba^{2+}, (d) **6**, **6** + Na^{+}, **6** + K^{+}, **6** + Mg^{2+}, **6** + Zn^{2+}, **6** + Ni^{2+}, **6** + Pb^{2+}, **6** + Cd^{2+}, (e) **6** + Ag^{+}, (f) **6** + Hg^{2+}.

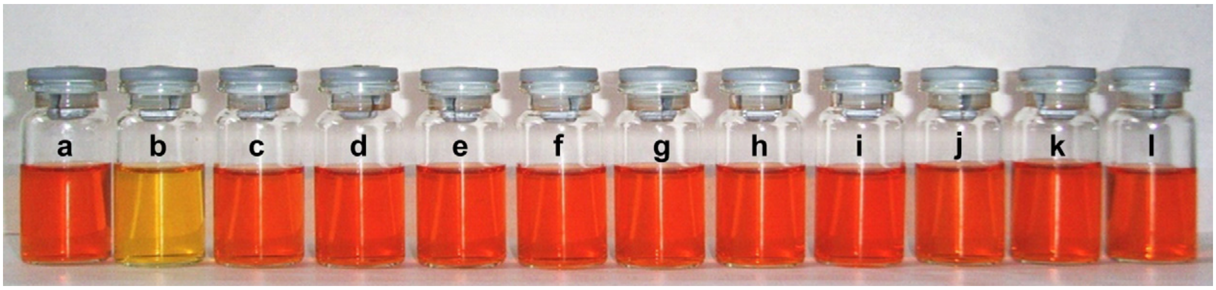


Fig. 4. Color changes (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.) of **6** in acetonitrile upon addition of various metal ions (5 equiv, all as nitrates): (a) only **6**, (b) **6** + Hg^{2+}, (c) **6** + Ag^{+}, (d) **6** + Mg^{2+}, (e) **6** + Na^{+}, (f) **6** + Ca^{2+}, (g) **6** + Zn^{2+}, (h) **6** + Pb^{2+}, (i) **6** + Ba^{2+}, (j) **6** + Cu^{2+}, (k) **6** + Ni^{2+}, (l) **6** + Cd^{2+}.

Hg^{2+} specifically in the presence of other metal ions studied. In addition, ‘‘naked-eye’’ detection can be made possible by the distinct color change of the solution. According to the theory of soft and hard acid–base, sulfur is a soft base, and nitrogen is a middle-intensity base. Among the selected metal ions, Hg^{2+} is the softest acid. So Hg^{2+} should form its most stable complex with sulfur and nitrogen atoms by comparison. As a result, Hg^{2+} may be bound to sulfur and nitrogen atoms (within the macrocycle) site and the –N=N– site selectively.

4. Conclusion

In summary, the synthesis, characterization and metal recognition property of **6** as a novel colorimetric chemosensor for Hg^{2+} were reported in this paper. The binding of Hg^{2+} gave rise to distinct color change from red to yellow, which made it possible to detect Hg^{2+} by the naked-eye. The high selectivity of **6** for Hg^{2+} over other metal ions tested is very advantageous in environmental sensing applications. Further study will address its quantitative analysis and application to real samples. Meanwhile, substituting electron-donating group such as $-N(CH_3)_2$ for electron-withdrawing group $-NO_2$ for the comparison is in progress.

Acknowledgments

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