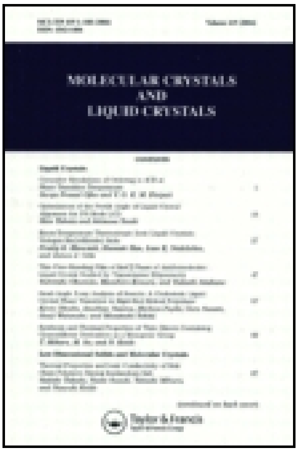

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A Highly Selective Detection Properties of 1,3-Bisdicyanovinylindane for Hg^{2+} Ion

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Efficient detecting and sensing function of metal ions are important aspects in the design of chemosensor for biological and environmental applications. Among the metal ions, the mercury pollution has been considered as important issue because of its severe genotoxic and neurotoxic effects. Therefore, many scientists have been devoted to the development of chemosensors for the detection of mercury ion with sufficient selectivity. In this work, we have synthesized new chemoesensor which is an appropriate compound due to solubility function in methanol or water under alkali solution. The complex properties for metal ions were examined by the measurements of optical spectrophotometer.

Keywords 1,3-Bisdicyanovinylindane; Job's method; mercury ion

Introduction

In recent years, the toxic metals such as Hg^{2+}, Zn^{2+}, Fe^{3+} *et al.* into the environment have become universal problems due to the rapid industrialization. If these toxic metals are exposed long-term into the environment, severe disease can be occurred. Thus, it is an important subject that the design and synthesis of new chemosensors suitable for environment are greatly of importance in the area of supramolecular chemistry due to their fundamental roles in chemical, biological, and environmental systems [1–3]. Since the discovery of crown ether by Pedersen, many researchers have studied on the chemosensors for metal ions because their detection can be applied to the areas of chemical, biological, and environment [4].

Among the toxic metal ions, Hg^{2+} has received great attention owing to this noxious transition metal, which is very harmful to human health. Hg^{2+} can be converted by bacteria into the methylmercury which is neurotoxic and can be implicated the cause of neurological damage [5–9]. Thus, plenty of effort has been made on the synthesis of selective detection sensor for Hg^{2+}. Because the Hg^{2+} was exposed in

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our surroundings such as air, water and soil. In addition, the detected Hg^{2+} should be used expensive instruments and should be spent for long time [10]. From these reasons, it is important of the development of chemosensor for Hg^{2+} ion detection properties.

In this work, we have synthesized 1,3-bisdicyanovinylindane dye as a colorimetric chemosensor that allows the color changes in addition of Hg^{2+}. The detection properties of this chemosensor were examined and determined. We have also monitored that Hg^{2+} titration was carried out with 1,3-bisdicyanovinylindane dye by job's plots.

Experimental

2.1. *Materials and Instrumentation*

1,3-indandion and malononitrile were purchased from Aldrich. All metal ions and solvents were purchased from Aldrich (USA) and Samchun (Korea). UV-Vis absorption spectra were recorded on Agilent 8453 spectrophotometer. Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Mass spectra were recorded on a Shimadzu QP-1000. Melting points were determined using an Electrothermal IA900.

2.2. *Synthesis of Dye Chemosensor*

A mixture of 1,3-indandion (3 mmol, 0.452 g) and malononitrile (9 mmol, 0.793 g) in ethanol (25 ml) was stirred at room temperature for 15 min. Then, as a catalyst sodium acetate (0.007 mmol. 0.574 g) has added into the mixture. The reaction mixture was refluxed for 3 h, until detected blue color change. After color change, the reaction mixture was cooled at room temperature. The resulting cooled blue solution was filtered to remove impurities such as 3-dicyanovinylindan-1-one. The filtrates were diluted with water and acidified using hydrochloric acid to give a white solid precipitate. The precipitate was filtered and then vacuum-dried [11]. The process scheme for 1.3-bisdicyanovinylindane was illustrated in Figure 1. Yield: 45.59% (0.33 g); m.p. 263–266°C; calculated for $C_{15}H_6N_4$: C, 74.37; H, 2.50; N, 23.13. Found: C, 74.78; H, 2.49; N, 23.48; m/z (M^+): 242.

2.3. *Stoichiometry Determination*

The complex stoichiometry was determined by job's method analysis [12–13]. The dye (1.0×10^{-4} M) and Hg^{2+} (1.0×10^{-4} M) solution were prepared in metanol/ water (2:1) mixed solution. Then, dye and Hg^{2+} solution were mixed in different

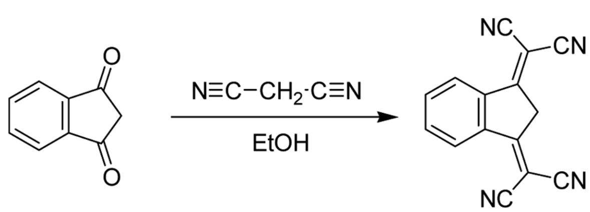


Figure 1. Synthesis of 1,3-bisdicyanovinylindane dye chemosensor.

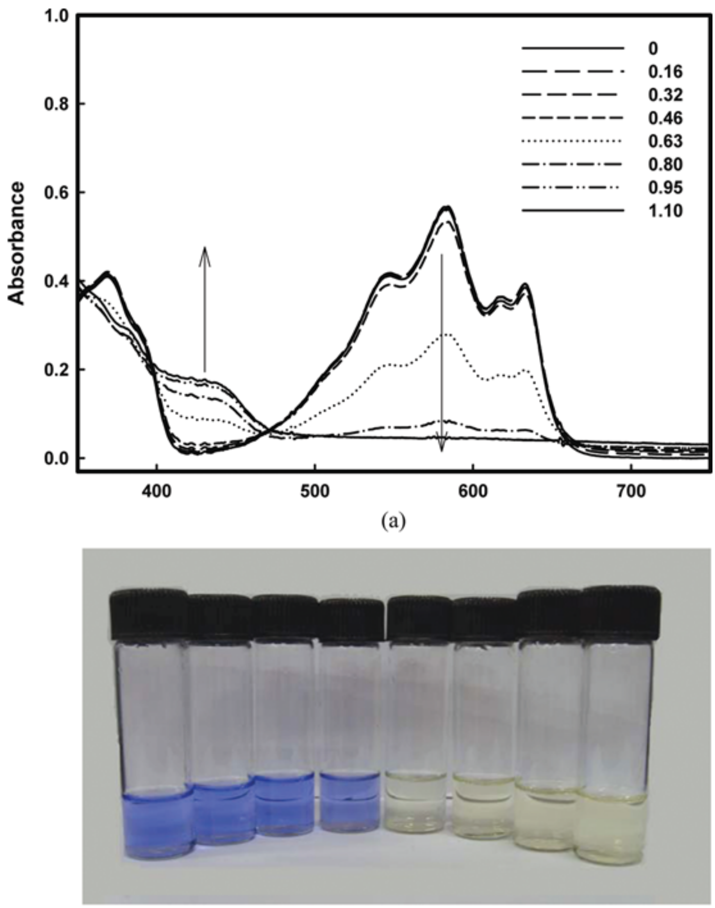
volume ratio such as 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1 using a total concentration of 1.0×10^{-4} M. Each mixture solutions were characterized at λ_{max} value using spectrophotometer. The complex ratio of this dye to Hg^{2+} was calculated using the following formula,

$$[ML] = \times F_{obs}/F_o \times [M], \times F_{obs} = F_o - F_{obs}$$

Where, F_o and F_{obs} were the absorption of metal ion addition (before and after) λ_{max} value into dye solution, respectively.

Results and Dicussion

In this work, 1,3-indandion and malononitrile were used to make 1,3-bisdicyanovinylindane which is new chemosensor for detecting Hg^{2+} ion. The absorbance of



(a)

(b)

Figure 2. UV-Vis absorption spectra of dye chemosensor (2.0×10^{-5} M) titrated with (a) Hg^{2+} (0–1.1 equiv) in methanol/water (ratio 2:1) and (b) color changing images.

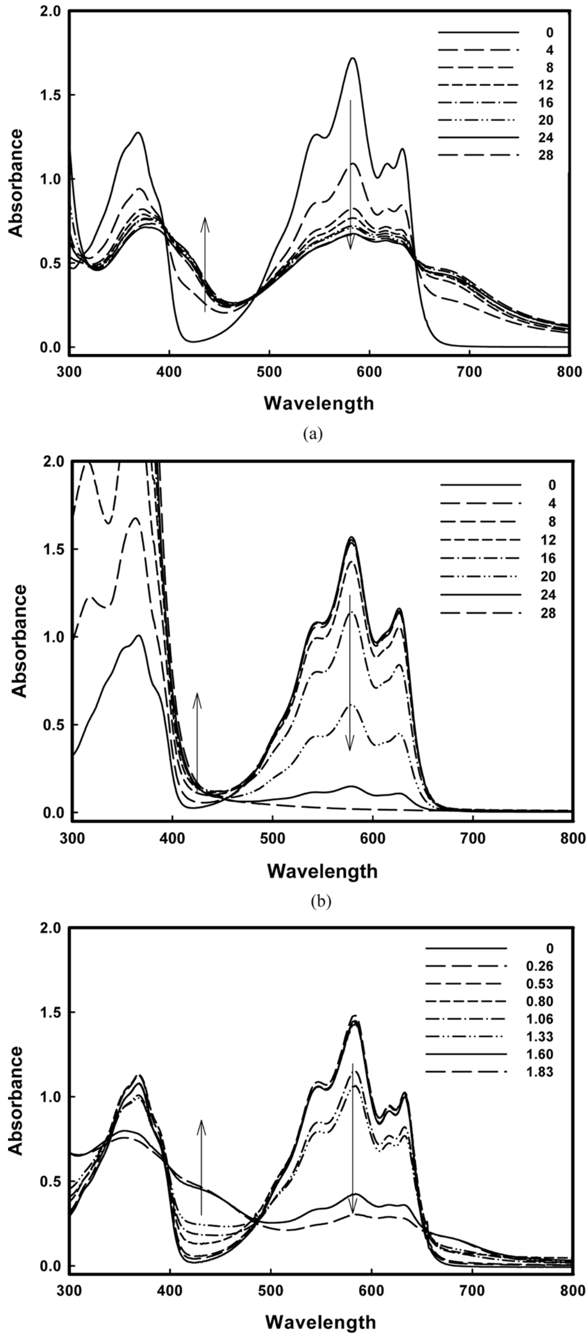


Figure 3. UV-Vis absorption spectra of dye chemosensor (4.0×10^{-5} M) titrated with metal ions in methanol/water (ratio 2:1): (a) Ag^{2+} (0–28 equiv), (b) Fe^{3+} (0–28 equiv), (c) Pd^{2+} (0–1.83 equiv).

1,3-bisdicyanovinylindane was investigated for the detection properties with various metal ions (Hg^{2+}, Zn^{2+}, Fe^{3+}, Ag^{2+}, Pd^{2+} Fe^{2+}, Ni^{2+}). These measurements were performed by adding various metal ions from 0 to 28 equivalents. The absorbance of 1,3-bisdicyanovinylindane with Hg^{2+} metal ion in water/methanol (2:1) and the color change behavior was showed in Figure 2. The main absorbance at 580 nm decreased, on the other hand absorbance at 400 nm increased; and then the isosbestic point was observed at 420 nm.

The absorbance of dye cheomosensor with Ag^{2+} and Fe^{3+} ions in water/methanol (2:1) was showed in Figure 3, respectively. The absorbance behavior of Ag^{2+}, Fe^{3+} and Pd^{2+} was similar spectral changes to absorbance value recorded to Hg^{2+} in Figure 2 with much smaller sensitivity. The main absorbance at 580 nm decreased, on the other hand absorbance at 400 nm increased and then the isosbestic point was observed at 420 nm. But, the absorbance of dye chemosensor with excessive Ag^{2+}, Fe^{3+} and Pd^{2+} ions was considered. The absorbance of dye chemosensor with other ions (Fe^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}) in water/methanol (2:1) did not indicate any absorption changes.

Comparison ratio of the absorption changes for dye chemosensor with other metal ions of 1 equivalent in methanol/water (2:1) was showed in Figure 4. The practical ability of dye chemosensor was showed by Hg^{2+}. Other metal ions such as Fe^{3+}, Ag^{2+}, Pd^{2+} were not detected by dye chemosensor, but the addition of excessive metal ions imparted a little change of absorption spectra. According to this finding, 'naked-eye' detection for Hg^{2+} ion with high efficiency can be expected from the distinct color change of the solution.

The complex stoichiometry was determined by job's method analysis. The job's plot result occurred by UV-vis absorbance changes of dye chemosensor was shown in Figure 5. From the Job's plot result, the inflection point was presented in $X = 0.5$ and the complex stoichiometry was determined as $M:L = 1:1$ [14–16].

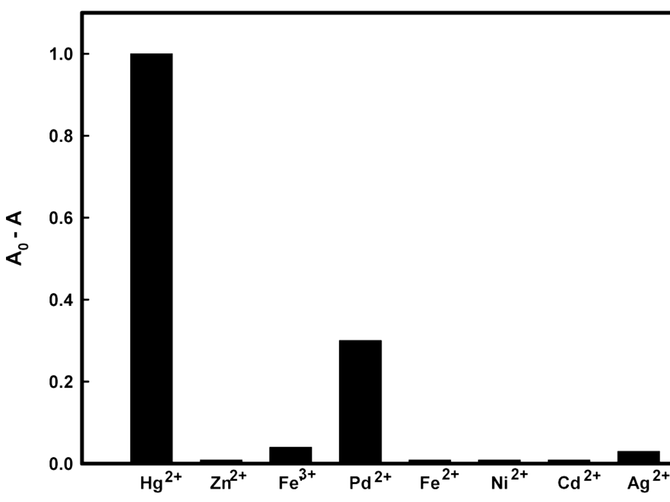


Figure 4. Comparison of absorption ratio for various metal ions (A and A_0 are the absorbance in the presence and the absence of metal ions, respectively at 583 nm).

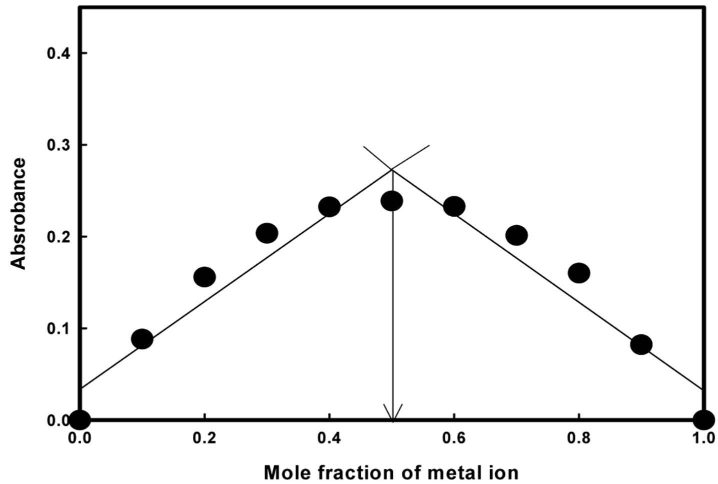


Figure 5. Job's plot of dye chemosensor for Hg^{2+} ion.

Conclusions

We had synthesized new colorimetric chemosensor, namely 1,3-bisdicyanovinylindane and experimentally examined selective functions for Hg^{2+}. Among the all metal ions used this study, the color change phenomenon of the chemosensor was clearly observed in a small amount of Hg^{2+} in methanol/water solution. From the Job's method, stable complex functions with Hg^{2+} of this dye chemosensor (1:1 complex ratio) were determined. From the findings, it is proposed that this dye chemosensor could be used as selective good chemosensor for Hg^{2+} in the detection of water pollution.

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