K_{ass}-controlled Hg^{2+} transport from Crystal Violet Lactone to Fluoran

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ABSTRACT

We have investigated the Hg^{2+} transport from Crystal Violet Lactone to Fluoran dye based on the association constant, K_{ass}. Upon addition of Hg^{2+}, the Crystal Violet Lactone shows a new peak at around 603 nm, and the color of the solution changed from colorless to blue. With the addition of Fluoran dye in this solution containing Crystal Violet Lactone and Hg^{2+}, the absorption intensity of Fluoran dye at 447 nm and 586 nm was all increased. So the color of solution gradually became black from blue color. From the changes of the ratio A$_{586}$/A$_{447}$, it is apparent that the Hg^{2+} in Crystal Violet Lactone–Hg^{2+} was transported to colored Fluoran. The Hg^{2+} transport from Crystal Violet Lactone to Fluoran dye was also carried out by the calculation of the association constant: the binding ability for the complex formation of Fluoran dye and Crystal Violet Lactone–Hg^{2+} is much greater in CH$_3$CN solution ($K_{ass} = 3.0 \times 10^4$ M^{-1}) than that of the Crystal Violet Lactone with Hg^{2+} ($K_{ass} = 1.2 \times 10^3$ M^{-1}).

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1. Introduction

The leuco triphenylmethanes are generally stable substance. The formation of colored materials from leuco bases such as Crystal Violet Lactone (CVL) and Fluoran is accomplished by treatment with acids such as acid clay, bisphenol A, acetic acid, or silicagel. CVL is one of most important phthalide dyes and extensively used in the pressure-sensitive or the carbonless copy as color formers and other digital printing outlet [1]. The process of the color formation using CVL consists of a ground-state dissociation of the C–O bond in the lactone ring (in the presence of a proton donor) resulting in the formation of the Crystal Violet cation [2]. The lability of the C–O bond under various influences makes CVL very attractive for various applications, such as a photopolymerization initiator [3,4] and the active ingredient in thermochromic coatings [5,6]. Although there are widespread uses of CVL, only a few studies have been carried out toward understanding the fundamental photophysics and the photochemistry of CVL and other phthalide-based color formers. The existing reports [7] give, however, incomplete or even misleading [3] insights into CVL spectroscopy. Therefore, fundamental studies on the photophysical properties of CVL and its derivatives are still crucial for the exploration of new functions and applications in CVL dye chemistry.

CVL shows bluish violet ($\lambda_{max} = 603$ nm), but is not fast to light. Oda's group observed a significant increase in the photostability of CVL by adding of various counterions [8,9]. Our group recently reported the ionochromic properties of CVL with metal cations [10]. It shows a good selectivity and sensitivity for Hg^{2+}. Fluoran dyes are well known as leuco dyes or colored cationic dyes for thermosensitive recording papers and have equilibrium between the colorless lactone form and the colored zwitterion form. The colored form of Fluoran has two distinctive absorption maxima in visible region. The two colors are complementary, and fortunately the two absorption maxima are nearly the same in absorbancy. As a result, a black hue can be obtained by the use of only one chromophore. That's why this compound is called One Dye Black (ODB). A new chromogenic chemosensor based on Fluoran derivatives was developed by Kim et al. [11,12]. It shows an extreme selectivity for Fe^{2+} and Fe^{3+}. The ion transport process plays an important role in the host–guest chemistry and molecular-level machine, the transfer of a guest ion from one host to another [13,14]. In the present paper, we demonstrate the active Hg^{2+} transport mediated by CVL and ODB system based on the absorption titration and the value of the association constant, K_{ass}.

2. Experimental

2.1. General

CVL was purchased from Aldrich. The other chemicals were of the highest grade available and were used without further

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purification. Absorption spectra were recorded on Agilent 8457 UV–vis spectrophotometer using 1-cm quartz cell. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using electron energy of 70 eV and the direct probe EI method. ^{1}H NMR, ^{13}C NMR spectra were recorded using a Varian Inova 400 MHz FT-NMR spectrometer with TMS as internal standard. Spectroscopic titrations were carried out according to the literature [10–12].

2.2. Determination of binding ratio and association constant

In our present experiments, Hg(ClO$_4$)$_2$ was gradually added into the solution of CVL as a mercury source, and the coordination abilities of CVL with Hg^{2+} were investigated by UV–vis spectroscopy. The binding stoichiometry of CVL with Hg^{2+} ions was determined by using Job plot [15,16] according to the method of continuous variations. For Job plot analysis, a series of solutions with varying mole fraction of Hg^{2+} were prepared by maintaining the total CVL and Hg^{2+} ion concentration constant (1×10^{-4} molL^{-1}), and the molar fraction of Hg^{2+} varied from 0.0 to 1.0. The association constant (K_{ass}) of CVL–Hg^{2+} and CVL–Hg^{2+}–ODB were calculated by the linear Benesi–Hildebrand expression [15,16] with the good linear correlation coefficient ($R = 0.9934$ for CVL–Hg^{2+} and 0.9980 for CVL–Hg^{2+}–ODB) as shown in Fig. 2.

2.3. Synthesis of ODB (Scheme1)

ODB was synthesized according to the literature method [17].
Yield: 58%, m.p. 187 °C; mass (m/z) 532(M$^+$); ^{1}H NMR (400 MHz, DMSO-d6): δ (ppm) 7.93 (d, $J = 7.56$, 1H), 7.76 (t, $J = 7.56$, 1H), 7.66 (t, $J = 7.36$, 1H), 7.41 (s, 1H), 7.26 (t, $J = 7.84$, 1H), 7.22(s, 1H), 6.99 (t, $J = 7.84$, 2H), 6.62 (t, $J = 7.04$, 1H), 6.55 (d, $J = 7.6$, 2H), 6.49 (d, $J = 8.08$, 2H), 6.43 (s, 1H), 6.41 (d, $J = 9.08$, 1H), 3.25 (t, $J = 7.6$, 4H), 2.21 (s, 3H), 2.07(s, 1H),1.48(m, 4H), 1.29(m, 4H), 0.87(t, 6H).
^{13}C NMR (400 MHz, DMSO-d6): δ (ppm), 13.78, 17.84, 19.63, 28.86, 30.59, 49.89, 83.55, 96.98, 104.1, 108.5, 114.63, 116.99, 118.32, 118.53, 119.49, 123.92, 124.45, 126.24, 128.59, 128.77, 129.94, 134.92, 135.40, 136.85, 145.25, 146.58, 149.63, 152.43, 152.49, 168.66.

3. Results and discussion

Upon addition of Hg^{2+} the CVL showed a new peak at around 603 nm in its absorption spectra, and the color of solution changed from colorless to blue (Fig. 1).

CVL showed a good selectivity for Hg^{2+} over the other metal cations. No significant absorption intensity changes were observed on the addition of Fe^{3+}, Cu^{2+}, Fe^{2+} and Al^{3+}, which makes it promising application in Hg^{2+} sensor [10]. The stoichiometry and association constant of the complex are established by use of the Benesi–Hildebrand method [15,16]. When assuming a 1:1 association between CVL and Hg^{2+}, the Benesi–Hildebrand expression is given as follows:

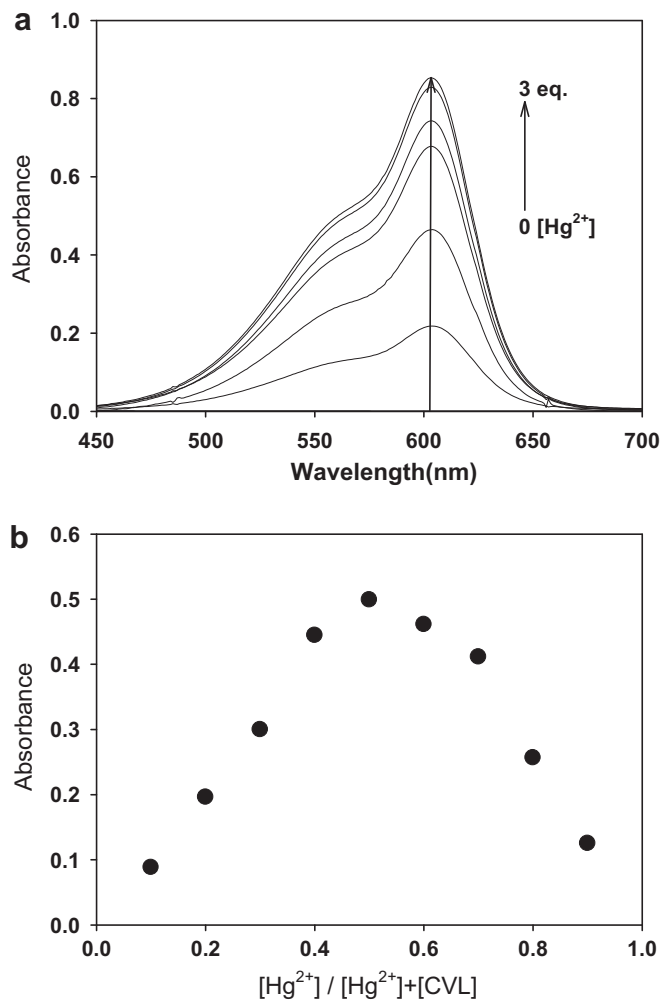**Fig. 1.** (a) Changes in UV–Vis spectra of CVL (1×10^{-5} molL^{-1} in CH$_3$CN) upon addition of Hg^{2+}. (b) Job plot of Hg^{2+} versus CVL ([Hg^{2+}] + [CVL] = 1×10^{-4} molL^{-1}).

$$\frac{1}{A - A_0} = \frac{1}{K_{ass}(A_{max} - A_0)\left[Hg^{2+}\right]} + \frac{1}{A_{max} - A_0}$$

In this equation, A$_0$ is the absorbance of CVL, A is the absorbance obtained with Hg^{2+}, A$_\infty$ is the absorbance obtained with excess amount of Hg^{2+}, K_{ass} is the association constant (M^{-1}), and [Hg^{2+}] is the concentration of Hg^{2+} added (M). According to the linear Benesi–Hildebrand expression, the measured absorbance [1/(A − A$_0$)] at 603 nm varied as the function of 1/[Hg^{2+}] in a linear relationship. The binding mode of CVL with Hg^{2+} from the results of absorption titration spectra (Fig. 1) was 1:1 with the binding constant of 1.2×10^3 M^{-1} (error limits <10%) (Fig. 2(a)).
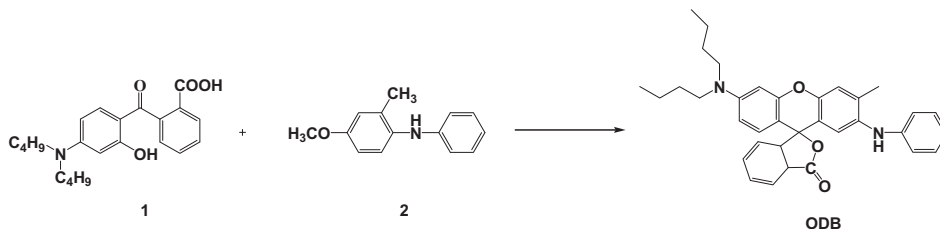

Scheme 1.
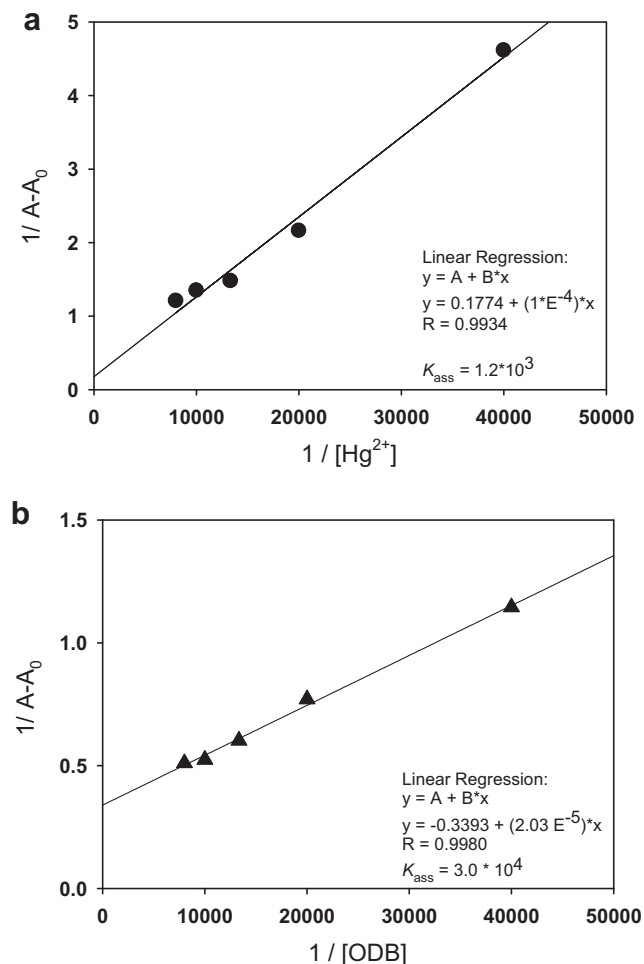
Fig. 2. Benesi−Hildebrand plot of (a) CVL with Hg^{2+} and (b) CVL−Hg^{2+} with ODB (λ_{max} = 603 nm for (a) and 586 nm for (b), correlation coefficient; (a) R = 0.9934, (b) R = 0.9980).

Job plot analysis of the UV−vis titration carried out in CH_3CN revealed a maximum at 50% mole fraction, in accord with the proposed 1:1 binding mode (Fig. 1(b)).

ODB was synthesized from 2-(4-(dibutylamino)-2-hydroxy benzoyl) benzoic acid **1** and 4-methoxy-2-methyl-N-phenylben zenamine **2** as starting materials using H_2SO_4 as catalyst (Scheme 1).
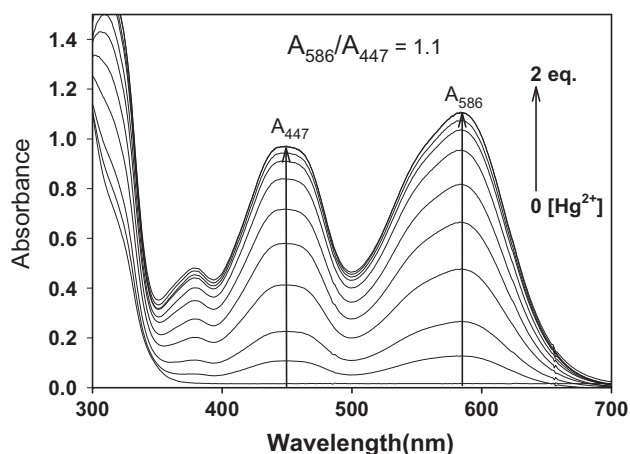
Fig. 3. Changes in UV−vis spectra of ODB (1×10^{-5} $molL^{-1}$ in CH_3CN) upon addition of Hg^{2+}.
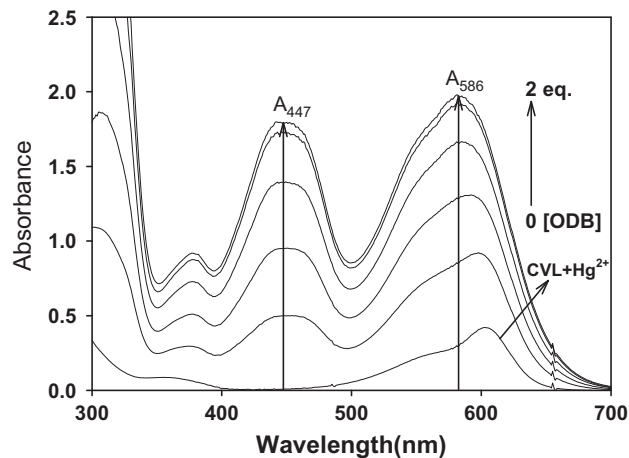

Fig. 4. Changes in UV−vis spectra of ODB (1×10^{-5} $molL^{-1}$ in CH_3CN) upon addition of Hg^{2+} to the solution of CVL−Hg^{2+}.

The recognition between ODB and Hg^{2+} was investigated by UV−vis spectroscopy in the CH_3CN solution. From the absorption spectrum of ODB in the CH_3CN solution, it was not found that an absorption band appeared in visible region, ODB solution was colorless. Fig. 3 shows the UV−vis spectra of ODB (1.0×10^{-5} $molL^{-1}$) upon addition of Hg^{2+}, in CH_3CN solution. Upon addition of Hg^{2+}, we found new absorption bands appeared including the absorption at wavelength peaked at 447 nm and 586 nm. The color changed from colorless to black. The color of 447 nm is complementary to the color of 586 nm. As a result, the black color hue can be obtained by use of only one dye molecule.

The Hg^{2+} transport ability of ODB containing CVL and Hg^{2+} was investigated in the CH_3CN solution (Fig. 4).

Fig. 4 shows the absorption band at λ_{max} = 603 nm for solution containing CVL and Hg^{2+}. While upon addition of ODB to CVL−Hg^{2+}, we also found new absorption bands appeared including the absorption at wavelength peaked at 447 and 586 nm, which is similar to Fig. 3.

Direct evidence for the decoloration of CVL and the coloration of ODB was obtained by plotting A_{586}/A_{447} (Fig. 5). As the ODB concentration increases, the ratio A_{586}/A_{447} decreases, the solution changing from blue to black solution. The A_{586}/A_{447} reached to 1.1 which is similar value with the ratio A_{586}/A_{447} of ODB−Hg^{2+}
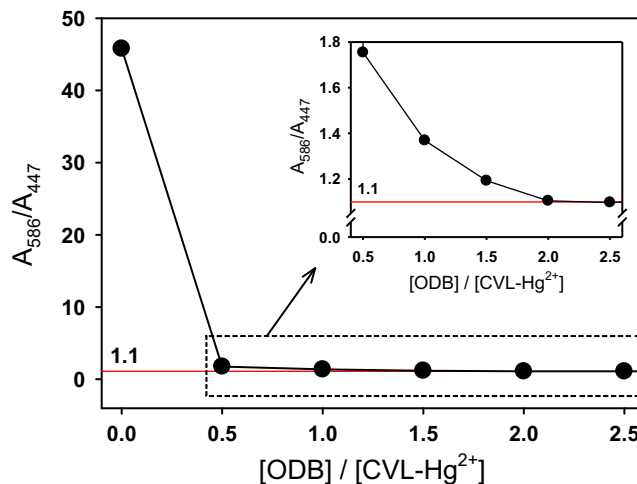
Fig. 5. Changes in absorption intensity ratio A_{586}/A_{447} obtained from absorption titration of ODB to CVL−Hg^{2+}.
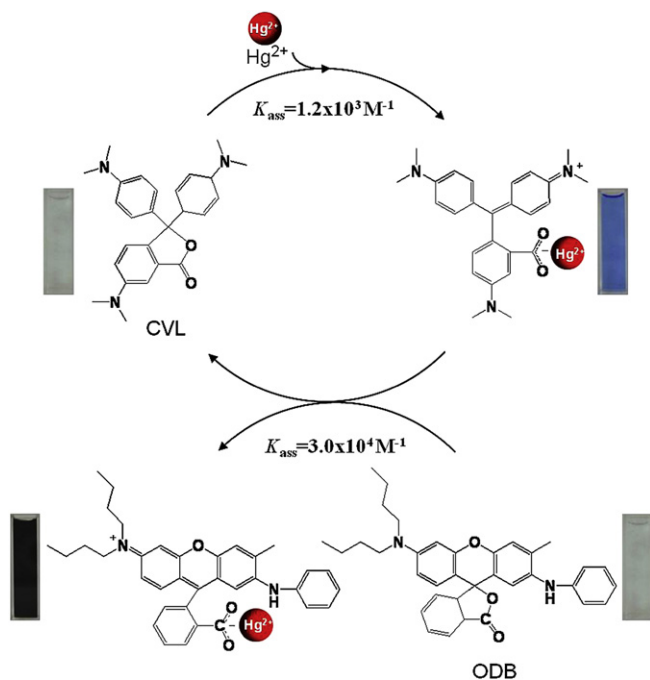
Fig. 6. Coloration and decoloration of CVL and ODB and their proposed Hg^{2+} ion transport.

binding up to 2 equiv of ODB. In order to understand the nature of Hg^{2+} transport ability from CVL to ODB, as well as binding mode of ODB with Hg^{2+} in the present system, the calculation of the association constant was carried out (Fig. 2(b)). From the absorption titration the association constant of ODB in CH_3CN with CVL–Hg^{2+} was calculated to be $3.0 \times 10^4 \, M^{-1}$, showing the high affinity of ODB than CVL for Hg^{2+}. It is apparent that the Hg^{2+} transport can be rationalized on the basis of the K_{ass} between CVL–Hg^{2+} and CVL–Hg^{2+}–ODB. Fig. 6 shows the coloration and decoloration of CVL and ODB and their proposed Hg^{2+} ion transport.

4. Conclusions

In summary, the Hg^{2+} transport ability from CVL to ODB was investigated based on the absorption titration and association constant. By adding of ODB to the solution containing CVL and Hg^{2+}, the color of the solution changed from blue to black. As the ODB concentration increases, the ratio A_{586}/A_{447} decreases to 1.1 which is the inherent A_{586}/A_{447} value of ODB with Hg^{2+}.

References

[1] National Cash Register. 3,3-bis(4-dimethylaminophenyl)6-dimethylaminophenyl phthalide. US Patent 2417897; 1945.
[2] White MA. The chemistry behind carbonless copy paper. Journal of Chemical Education 1998;75:1119–20.
[3] Kaneko Y, Neckers DC. Simultaneous photoinduced color formation and photoinitiated polymerization. Journal of Physical Chemistry A 1998;102: 5356–63.
[4] Nag AK. Photopolymerization of methyl methacrylate using crystal violet lactone–nitrobenzene complex as initiator. Indian Journal of Chemistry, Section A: Inorganic, Bio-inorganic, Physical, Theoretical & Analytical Chemistry 1994;33:658–60.
[5] Ma Y, Zhu B, Wu K. Preparation and solar reflectance spectra of chameleon-type building coatings. Solar Energy 2001;70:417–22.
[6] Ma Y, Zhang X, Zhu B, Wu K. Research on reversible effects and mechanism between the energy-absorbing and energy-reflecting states of chameleon-type building coatings. Solar Energy 2002;72:511–20.
[7] Allen NS, Hughes N, Mahon P. Photochemical fading and photostabilization of the crystal violet lactone color former system. Journal of Photochemistry 1987;37:379–90.
[8] Oda H, Kitao T. Contribution of counterions to the photofading of crystal violet lactone and related colorants. Journal of the Society of Dyers and Colourists 1989;105:257–61.
[9] Oda H, Kitao T. Photostabilisation of colorants for imaging and data recording systems: effect of metal carboxylates on the light fastness of colour formers. Dyes and Pigments 1991;16:1–10.
[10] Wang S, Hwang IJ, Gwon SY, Kim SH. Ionochromism of crystal violet lactone triggered by metal cations. Fibers and Polymers 2010;11:1198–200.
[11] Wang S, Gwon SY, Son YA, Matsumoto S, Hwang IJ, Kim SH. Highly selective colorimetric signaling of iron cations based on fluoran dye. Molecular Crystals and Liquid Crystals 2009;504:155–63.
[12] Wang S, Gwon SY, Kim SH. A highly selective and sensitive coloriletric chemosensor for Fe^{+2} based on fluoran dye. Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy 2010;76:293–6.
[13] Echegoyen L, Kaifer AE, editors. Physical supramolecular chemistry. London: Kluwer academic publishers; 1996.
[14] Müller TJJ, Bunz UHF, editors. Functional organic materials. Weinheim: Wiley-VCH; 2007.
[15] Kim HJ, Park JE, Choi MG, Ahn S, Chang SK. Selective chromogenic and fluogenic signaling of Hg^{2+} ions using a fluorescein-coumarin conjugate. Dyes and Pigments 2010;84:54–8.
[16] Jadhav JR, Bae CH, Kim HS. Fluorescence sensing of $H_2PO_4^-$ by a imidazolium-based cholestane receptor. Tetrahedron Letters 2011;52:1623–7.
[17] Yanagita M, Aoki I, Tokita S. New fluoran leuco dyes having a phenylenediamine moiety at the 6-position of the xanthene ring. Dyes and Pigments 1998; 36:15–26.