Heavy metal ion contamination may pose significant risks to the environment. Detection of mercury and its compounds in the environment is of great interest because of their high toxicity, wide usage in a number of industrial processes, and biomagnification in the food chain [1]. Once mercury is introduced into the food chains as a result of bioaccumulation, this environmental cycle causes serious threat to the human health and ecology [2, 3]. Despite the great efforts for the reduction of its industrial use, mercury pollution still continues through a variety of natural and anthropogenic sources [2-4]. To date, a number of Hg\(^{2+}\) ion detection methods have been examined and include colorimetric strategies [5-8] and fluroionophores [4, 9-12]. Anthraquinone dyes are the second most important class after azo dyes. Aminoanthraquinone dyes are the most important of the anthraquinone derivatives since most commercial anthraquinone dyes contain at least one amino substituent. For example, 1,4-diaminoanthraquinone is CI Disperse Violet 1. Anthraquinone derivatives have been widely utilized as chemosensors for several ions due to its high absorption coefficient and possibility of naked eye detection[13-15]. We have reported a number of different types of anthraquinone dyes for optical recording media [16-18]. Herein, we report new colorimetric chemosensor based on 1,2-specifically towards the Hg\(^{2+}\) ion. In addition, its solvatochromic properties were investigated by qualitative spectroscopic analysis.

A Highly Selective Ratiometric Chemosensor for Hg\(^{2+}\) Based on 1,2-Diaminoanthraquinone

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Abstract: A highly selective colorimetric chemosensor for Hg\(^{2+}\) based on 1,2-diaminoanthraquinone was investigated. 1,2-Diaminoanthraquinone showed color change only with Hg\(^{2+}\), but it showed no significant changes upon addition of other metal ions such as Fe\(^{3+}\), Na\(^{+}\), Mg\(^{2+}\), Pb\(^{2+}\), Cd\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\) and Zn\(^{2+}\). The solvatochromic responses of the 1,2-diaminoanthraquinone in several solvents of widely different polarities were measured; positive solvatochromism, with a large bathochromic shift, was observed from toluene to DMSO.

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In our present experiments, Hg(ClO\(_4\))\(_2\), was gradually added to the solution of AQ in DMSO as mercury source, and the coordination abilities of AQ with Hg\(^{2+}\) were investigated by UV-Vis spectroscopy.

Fig. 1 The changes in the absorption spectra of AQ (1 × 10\(^{-4}\) mol L\(^{-1}\)) upon titration with Hg\(^{2+}\) in DMSO.

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significant effect on the absorption spectrum of AQ. The superior selectivity of AQ for Hg$^{2+}$ in DMSO solution is evident from the absorption response of the metal ions, as illustrated in Fig. 2.

To investigate the role of complexation of functional groups with Hg$^{2+}$, we examine absorption change of 1-aminoanthraquinone. 1-Aminoanthraquinone did not have any change on the absorption spectra. These results indicated that the complexation between AQ and Hg$^{2+}$ is formed via two amino groups, not including carbonyl group. For the interpretation of the chromophoric system of AQ, the quantum chemical DMol$^3$ approach was used. All the theoretical calculations were performed by DMol$^3$ program in the Materials Studio 4.4 package [19-21] which is the quantum mechanical code using density functional theory. Perdew-Wang 1991 (PW91) function of generalized gradient approximation (GGA) level [22] was used to calculate the energy level of the frontier molecular orbital.

Fig. 3 shows the electron distribution of the HOMO and LUMO energy level of AQ. Comparison of the electron distribution in the frontier MOs reveals that the HOMO-LUMO excitation moves the electron distribution from two amino moieties to the acceptor, which showed a strong migration of intramolecular charge transfer character of AQ. Therefore, the electron donating two amino groups in the HOMO energy level is important for effective complexation with Hg$^{2+}$ in this system. As a result, the complexation of the Hg$^{2+}$ to the N atoms reduces the electron density on the N atoms and lowers the electron donating ability of two amino groups. The complex stoichiometry was determined by Job’s method analysis. From the Job’s plot result, the inflection point was presented in $[\text{Hg}^{2+}] / (\text{Hg}^{2+})+[\text{AQ}] = 0.5$ and the complex stoichiometry was determined Hg$^{2+}$: AQ = 1:1. The optimized AQ-Hg$^{2+}$ bidentate structure is shown in Fig. 4.

The $\lambda_{\text{max}}$ values of the solvent-dependent absorption of AQ in various solvents and $E_r(30)$ values are listed in Table 1. The results show that AQ exhibited strong solvatochromic properties.

**Table 1** $E_r(30)$ and $\lambda_{\text{max}}$ values of AQ in various solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$(nm)</th>
<th>$E_r$(kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>478</td>
<td>33.9</td>
</tr>
<tr>
<td>THF</td>
<td>500</td>
<td>37.4</td>
</tr>
<tr>
<td>EA</td>
<td>507</td>
<td>38.1</td>
</tr>
<tr>
<td>Acetone</td>
<td>508</td>
<td>42.2</td>
</tr>
<tr>
<td>DMF</td>
<td>530</td>
<td>43.2</td>
</tr>
<tr>
<td>DMSO</td>
<td>539</td>
<td>45.1</td>
</tr>
</tbody>
</table>
As the solvent polarity is increased, a bathochromic shift is observed (i.e., positive solvatochromism). The absorption maximum showed a shift with solvent polarity, which extended from 478 nm for toluene to 539 nm for DMSO. These spectral properties of AQ show a close similarity to that observed for solvatochromic dyes [23]. These features indicate a strongly allowed π-π* transition with charge transfer characters. The intramolecular charge transfer (ICT) interaction of AQ, that is from amino moiety to the carbonyl acceptor fragment is strongly enhanced upon excitation as evidence from the extreme bathochromic shift of the absorption maximum in polar solvents. The positive solvatochromism indicated that AQ has a large dipole moment in the excited state rather than in the ground state. To support this explanation, Pariser-Parr-Pople(PPP)-calculated dipole moment (μ, Debye) in the ground state and first excited singlet state of AQ are presented in Fig. 5.

Fig. 5 Effect of solvent polarity on the transition energy of AQ

The dependence of the absorption maximum of AQ on \( E_T(30) \) solvent polarity parameter can be fitted to almost linear function (Fig. 6). As the solvent polarity increased, a bathochromic shift observed.

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