Hemicyanines—potential heavy metal ion sensors

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Abstract: The synthesis of four hemicyanine dyes are reported. Varying the donor-acceptor properties of hemicyanine dyes has a drastic influence on the aggregation properties and photophysical properties. 4-(N, N-dimethyl)amino benzaldehyde, 4-nitro benzaldehyde and 4-hydroxy benzaldehyde are used as donors. Quaternary salts of 2- methyl benzothiazole with bromoacetic acid and methyl iodide are used as acceptors. Synthesis and characterization of the dyes were carried out. Preliminary studies shows that these compounds possess pH sensing as well as heavy metal ion sensing properties.

Keywords: Dyes, Hemicyanines, Heavy metal ion, Sensors

1. INTRODUCTION

Owing to the tremendous applications in the area of optoelectronic and biomedical devices, research in the area of chromophoric systems have gained lot of interest over the past several years [1-3]. Based on the type of electron donor and acceptor groups present in the chromophoric systems, they are further classified as cyanines, hemicyanines etc. If both donor as well as acceptor groups are heterocyclic they are referred to as cyanines. Amphiphilichemicyanines have been used as voltage sensitive fluorescent probes to record the fast changes in electrical membrane potential in neurons [4]. (Dibutylamino) stilbazoliumbutylsulfonate is a typical example of a hemicyanine dye frequently used as fluorescent probes. Their photophysical properties exhibit strong viscosity dependence as a result of which they are put forward to various applications in polymer science and analytical chemistry [5-6]. An explicit knowledge on the photophysical properties of hemicyanine dyes is essential while optimizing the design strategies of such probes for biological applications. Hemicyanines also find applications as materials for nonlinear optics and molecular electronics [7]. Metal ion sensing properties of crown ether appended hemicyanine based chromoionophores have been thoroughly investigated. Complexation of the chromoionophore with metal cations leads to dramatic changes in their absorption and emission properties, due to suppression of its intramolecular charge transfer [8-10]. Taking advantage of their immediate and sharp response to various metal ions they can be used to sense heavy metal ions.

Heavy metals pose serious threat to our environment due to their non-degradable nature. They have a tendency to bioaccumulate and biomagnify [11]. Monitoring the contaminants present in food,
drinking water and air is highly essential in order to ensure its quality [12]. Heavy metal ions are known for its toxicity among several other water pollutants like chemical fertilizers [13] or pesticides, plastic or waste [14] and pathogens [15]. But some of them are essential nutrient sources (for instance iron, cobalt, zinc), which can be poisonous at larger concentration [16]. Metals like cadmium, mercury and lead gets bioaccumulated into the food chain leading to major health problems like cancer or neurodegenerative diseases [17-18] even at very low concentrations [19-20]. These metal ions are introduced in ecosystem through vehicle emissions [21], coal-fired power plants and into marine environment from chemical, gold mining [22].

It is highly essential to provide a sensitive method for the detection of heavy metals. Recently several colorimetric probes have been developed for this purpose. Few complexes which are sensitive and selective towards heavy metals are reported [23-24]. In the present work we have synthesized few hemicyanine dyes (Figure 1) which binds with heavy metal ions like zinc, mercury, cadmium and lead. These molecules possess high molar extinction coefficients and good solubility in aqueous media. We have synthesised and characterized four benzothiazolium based hemicyanine dyes [25] and tested for its sensing towards heavy metals ions.

2. EXPERIMENTAL SECTION

2.1. Materials
All chemicals were purchased from commercial suppliers and used without further purification. All solvents were of analytical grade as well. Solvents used were distilled prior to use.

2.2. Synthesis of hemicyanine dyes (1-4)

**Hemicyanine dye 1-A** mixture of 3-(carboxymethyl)-2-methylbenzothiazoliumbromide salt (0.43g,1.5mmol) and N,N-dimethylaminobenzaldehyde (0.29g,1.5mmol) was refluxed in ethanol (38 mL) for 24 h in the presence of catalytic amount of piperidine (7μL,0.075mmol) to yield dye 1 (55% yield). IRmax: 2920(−C−Hstr), 1714(C=O), 1624(C=C), 1575, 1516, 1437(=C−H), 1377, 1337, 1268 and 913cm−1; ¹HNMR: ð7.195(1H), 6.6(1H), 5.9(2H), 3.09(2H), 1.53(3H); MS calculated for C19H19O2N2S [M−1]+ ion peak 337 found at 339.6.

Figure 1- Hemicyanine dyes
**Hemicyanine dye 2** - A mixture from prepared 3-(carboxymethyl)-2-methylbenzothiazoliumbromide salt (0.43 g, 1.5 mmol) and 4-hydroxybenzaldehyde (0.29 g, 1.5 mmol) was refluxed in ethanol (38 mL) for 24 h in the presence of catalytic amount of piperidine (7 μL, 0.075 mmol) to yield dye 2 (55% yield). IR \( \text{max} \): 3365 (−OH), 1731 (C=O), 1671 (C=C), 1440 (−C=H), 1370, 1259, 1219, 1149, 1039 and 949 cm\(^{-1}\); \(^1\)HNMR: δ 8.04 (1H), 4.22 (1H), 3.5 (1H), 3.2 (2H); MS calculated for C\(_{19}\)H\(_{19}\)O\(_2\)N\(_2\)S \([\text{M}-1]\) + ion peak 337 found at 339.6.

**Hemicyanine dye 3** - A mixture from prepared 3-(carboxymethyl)-2-methylbenzothiazoliumbromide salt (0.43 g, 1.5 mmol) and 4-nitrobenzaldehyde (0.29 g, 1.5 mmol) was refluxed in ethanol (38 mL) for 24 h in the presence of catalytic amount of piperidine (7 μL, 0.075 mmol) to yield dye 3 (60% yield). IR \( \text{max} \): 2960 (−C–Hstr), 1730 (C=O), 1659 (C=C), 1465 (−C=H), 1323, 1211, 1099, 1007 cm\(^{-1}\); \(^1\)HNMR: δ 8.07 (1H), 4.5 (1H), 3.5 (1H), 3.03 (2H), 1.6 (1H).

**Hemicyanine dye 4** - 2-methyl benzothiazoliummethiodide (0.43 g, 2 mmol) was refluxed with N,N-dimethylaminobenzaldehyde (0.29 g, 1.5 mmol) in methanol in the presence of piperidine (2 drops) for 48 h under nitrogen atmosphere. The crude product (45%) obtained was recrystallized from a mixture of chloroform and hexane. IR \( \text{max} \): 2885 (−C–Hstr), 1671 (C=C), 1531, 1487, 1442 (−C=H), 1381, 1343, 1265, 1125, 924 cm\(^{-1}\); \(^1\)HNMR (CDCl\(_3\)+ DMSO-d\(_6\)) 8 8.2–6.7 (1OH), 4.3 (3H), 3.0 (6H).

2.3. Results and Discussion

The hemicyanine dyes synthesized were further characterized using IR, NMR and Mass spectroscopic techniques as has been given in the experimental section. Preliminary absorption studies of the compounds were done. Absorption spectra of the dyes in acetonitrile were recorded. Absorption maxima of the dyes were found to be 514 nm (H1), 415 nm (H2) and 520 nm (H4) (see Figure 2) respectively and this is attributed to charge transfer.

![Figure 2. Absorption spectra of Hemicyanine1 (black), Hemicyanine2 (red), and Hemicyanine 4 (green).](image_url)

As a preliminary investigation these dyes were tested for their pH sensitivity. Small Whatman filter paper strips were cut and dipped into the stock solution of hemicyanine 1 to obtain pink paper strips. These strips were dipped in an acidic solution (pH = 2.6) The pink color vanished and the paper became colourless. Same paper strip when dipped into an alkaline solution (pH = 9) regained the pink colour. These changes are shown in Figure 3. These changes were attributed to the protonation-deprotonation of the dye molecule in presence of acidic/basic media. The lone pair of nitrogen plays a detrimental role in exhibiting such colour changes.
Absorption spectra was recorded to see if the dyes bind with heavy metal ions. The metal ions used were Cd$^{2+}$, Zn$^{2+}$, Hg$^{2+}$ and Pb$^{2+}$. Metal solutions are prepared in acetonitrile. In almost all the cases a gradual decrease in absorbance of the dyes is observed with increase in concentration of metal ions. Micromolar concentrations of metal ions were used. Figure 4 shows the absorption spectra of hemicyanine dye 2 in presence of heavy metal ions cadmium and lead. In the case of hemicyanine dye 1 complexation with cadmium and lead follows the same profile but on complexation with zinc a slight red shift is observed. Photophysical studies are underway to thoroughly understand the complexation properties thus making such dyes potential candidates as heavy metal ion sensors.

3. CONCLUSION

The synthesis of hemicyanine dyes has been carried out by varying the donor and acceptor groups. Preliminary absorption studies shows that they are sensitive to pH of the medium. They bind with heavy metal ions at micromolar concentrations. Changes in the absorption properties were observed. Detailed photophysical studies are in progress to better understand the complexation process.

ACKNOWLEDGEMENTS

The authors thank Mr. Nandakumar G., Research associate, Amrita School of Ayurveda, Amrita Vishwa Vidyapeetham, Amritapuri campus for the UV-Vis absorption studies reported in this work. The support provided by the Department of Chemistry, Amrita School of Arts and Sciences Amrita Vishwa Vidyapeetham, Amritapuri campus for the execution of this project is greatly acknowledged.
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