



# Liquid crystal based sensor system for the real time detection of mercuric ions in water using amphiphilic dithiocarbamate



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## ABSTRACT

We developed a simple, sensitive, label-free and real time detection method for mercuric ions ( $\text{Hg}^{2+}$ ) in water using liquid crystals (LCs). In this system, newly synthesized amphiphilic potassium N-methyl-N-dodecylthiocarbamate (MeDTC) was doped in 4-cyano-4'-pentyl biphenyl (5CB) LC, which align LC molecules at aqueous interface and polar head group of the amphiphile acts as mercuric ion specific chelating ligand. When this sensor system was incubated in the aqueous solution containing  $\text{Hg}^{2+}$  ions, a dark to bright transition of the image of LCs was observed. This was caused due to rapid and stable complex formation between dithiocarbamate chelating group of MeDTC with  $\text{Hg}^{2+}$  ions at aqueous interface, which disrupted the orientation of LCs giving bright texture. The limit of detection of the system for aqueous  $\text{Hg}^{2+}$  ion is  $0.5 \mu\text{M}$ . This sensor did not respond to other metal ions like  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , which are common environmental interference in water. We also demonstrated that this sensor is capable of detecting  $\text{Hg}^{2+}$  ions in real water samples (tap water). The very simple and effective procedure reported here should facilitate the development of real time, portable and reliable LC based sensor for mercury pollution control.

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## 1. Introduction

Contamination of water with heavy metal (HM) ions has been a major concern throughout the world for several decades [1]. The toxicity of HM ions is due to the bond formation of heavy metals with thiol-group of proteins. These ions when enter the cell, can disrupt biological events and cause significant oxidative damage; they are also carcinogenic. Among various heavy metals mercuric ion ( $\text{Hg}^{2+}$ ) is one of the highly toxic metal ion, that has serious deleterious effects on human health, especially in the central nervous system [2]. Therefore, the need for sensors that can make real time measurements of  $\text{Hg}^{2+}$  in water at low concentrations are desirable for maintaining safe water supplies to avoid the effect of this HMs on human health and environment. Currently, there are many well established techniques to accurately detect  $\text{Hg}^{2+}$  such as atomic absorption spectrometry [3], inductively coupled plasma mass spectroscopy [4], electrochemical method [5], atomic

fluorescence spectrometry [6], potentiometric ion selective electrode method, etc. [7]. However all of them need sophisticated instrument and are time consuming and expensive which make them inconvenient for fast, real-time, and continuous monitoring of  $\text{Hg}^{2+}$  in environmental, biological and industrial samples.

Recently, liquid crystals (LCs) have proved themselves as a fresh entrant for developing innovative sensing systems [8–10]. The alignment of LC molecules is extraordinarily sensitive to molecular and chemical binding events and these events combined with the long range orientational order in LC materials produce amplified optical signals [11,12]. The detection through LC based sensor can be carried out in ambient light without applying electrical current or molecular labeling and their optical signals can be easily observed with naked eyes. These important characteristics of LC based sensors make them well suited for simple detection, direct transduction, high sensitivity and low-cost assays [13–21]. The LC-based sensor has been applied for the detection of different biological and chemical molecules such as DNA [22–24], proteins [25–27], enzymes [28,29], proteases, [30,31] viruses, [32,33] organophosphates, [34–37], aldehydes [38,39] and amines [40,41]. Recently, label-free biosensors have been reported utilizing an amphiphilic block copolymer that consists of a side-group liquid crystalline polymer block

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poly(4-cyanobiphenyl-4-oxyundecylacrylate) (LCP) and poly(acrylic acid) (PAA) block [42–47]. The PAA and LCP blocks act as recognition and transducer elements in the biosensor. The selectivity and sensitivity of LC based sensors for detection of HM ions have been proved by different workers in some of their reports [48–51]. In these reports, different principals of LC based sensing have been applied to detect HM ions. For example, Hu et al. developed a LC-based sensor for the detection of  $\text{Cu}^{2+}$  ions in an aqueous solution using surface immobilized urease [48]. When the sensor was immersed in a urea solution, the surface immobilized urease produced a shift in the optical response of LCs from bright to dark transition. The presence of  $\text{Cu}^{2+}$  effectively inhibited the activity of urease, which caused another reorientation of LCs from homeotropic to planar so a dark to bright transition of LC image was observed. Yang et al. reported an LC based sensor to detect  $\text{Hg}^{2+}$  ions by using surface immobilized oligonucleotide as recognition units through the specific binding of  $\text{Hg}^{2+}$  with two DNA thymine (T) bases [49]. The target-induced DNA conformational changes in the presence of  $\text{Hg}^{2+}$  from hairpin structure to duplex-like complex, which disrupts the orientation of LCs leading to dark to bright optical signal. This optical signal of LC sensor has limit of detection (LOD) 0.1 nM with good specificity to  $\text{Hg}^{2+}$ . However, this system requires additional procedures of immobilization of oligonucleotide on glass surface to fabricate a LC cell. Jang et al. developed a real time analytical method for the detection of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  ions using the optical response of stearic acid doped 4-cyano-4'-pentyl biphenyl (5CB) droplet patterns [50]. In the presence of these metal ions, the acid doped 5CB droplet patterns appeared from dark to bright with a fan-shaped texture, which corresponds to the planar orientation of 5CB at the LC/aqueous interface. This dark to bright transition of the LC patterns was caused by coordination of metal ions to the deprotonated carboxylate moiety, followed by the sequential interruption of the self-assembled stearic acid at the LC/aqueous interface. In this system, no optical response was observed for higher concentration of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  ions. More recently, Chen et al. developed a LC sensor system for detecting  $\text{Hg}^{2+}$  ion in aqueous solutions [51]. In this system, 5CB was doped with a  $\text{Hg}^{2+}$  specific sulfur- and nitrogen-containing ligand 5-(pyridine-4-yl)-2-(5-(pyridin-4-yl)thiophen-2-yl)thiazole (ZT). When the system was immersed in the solution containing  $\text{Hg}^{2+}$ , the complex of ZT and  $\text{Hg}^{2+}$  formed in LCs, which disrupted the orientation of LCs and lead to a dark to bright transition of the LC image. The LOD of the system to  $\text{Hg}^{2+}$  was 10  $\mu\text{M}$  and was found to be highly specific towards  $\text{Hg}^{2+}$ . In this system, the ligand ZT has no amphiphilicity therefore  $\text{Hg}^{2+}$  ions have to diffuse from water to LCs for the observation of bright textures.

Dithiocarbamates are a group of organic ligands with dithio-atoms as metal ion chelators. These dithio-atoms (soft bases) has strong and selective chelating ability towards specific metal ion species (soft acids) like mercury, gold, silver etc. according to hard and soft acid base (HSAB) principle [52]. Therefore, these reagents have been employed in the determination and separation of toxic mercury ions in trace and ultra-trace amount. The detection and determination of mercury ions by dithiocarbamate ligands has been well established by various methods like colorimetry, fluorimetry, spectroscopy, voltammetry, etc. [53,54]. To the best of our knowledge, the specific binding selectivity of dithiocarbamates has never been employed in the LC sensor system for detecting mercuric ions so far.

In this study, we proposed a new approach to fabricate a label free, real time LC based sensors in aqueous solution by designing and synthesizing novel amphiphile that can align LC molecule at aqueous interface and can also selectively interact with target analytes (mercuric ions here). In order to realize the sensor, we synthesized; potassium N-methyl-N-dodecylthiocarbamate

(MeDTC) that can self-assemble at the LC/aqueous interface and induce a homeotropic anchoring of 5CB, giving dark appearance. A bright texture corresponding to a planar orientation of the LCs was observed when the sensor was incubated with aqueous solution of mercuric ions. The optical and orientational changes of the LC patterns were attributed to the interaction of the mercuric ions with dithio-chelating group and the consequent interruption of the self-assembled LCs at the LC/aqueous interface.

## 2. Materials and methods

### 2.1. Materials

Glass microslides were obtained from blue star, Mumbai, India. Nematic liquid crystal 5-cyanobiphenyl (5CB), octadecyltrichlorosilane (OTS), N-methyldodecylamine, carbon disulfide, potassium hydroxide, transmission electron microscope grids of copper (100 square mesh), all metal salts i.e. chlorides of  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  and lead nitrate were purchased from Sigma–Aldrich (India) and were used as received. All solvents used in this study were purchased from Merck chemicals and are of HPLC grade.

### 2.2. Synthesis of DTC

N-methyldodecylamine (0.75 g, 5.0 mmol) was dissolved in 45 mL of dry THF and KOH pellets (0.28 g, 5.0 mmol) were added. The mixture was stirred for 6 h until all KOH pellets was dissolved. The solution thus obtained was kept on ice bath and  $\text{CS}_2$  (0.61 mL, 10.0 mmol) was added drop wise. The reaction mixture was further stirred for 4 h. The solvent was removed under vacuum and the yellow product thus obtained was washed with diethyl ether and dried under vacuum.

Yield: 1.36 g, 87%. IR (KBr): 2929, 2847  $\nu(-\text{CH}_{\text{str}})$ ; 1371  $\nu(\text{C}-\text{N})$ , 1008–960  $\nu(\text{C}-\text{S})$ .  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  4.00 (t, 2H,  $-\text{NCH}_2$ ), 3.47 (s, 3H,  $-\text{NCH}_3$ ), 1.58–1.24 (m, 20H,  $-(\text{CH}_2)_{10}$ ), 0.85 (t, 3H,  $-\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  213.42 ( $\text{CS}_2$ ), 54.46 ( $-\text{NCH}_2$ ), 41.30 ( $-\text{NCH}_3$ ), 31.25 ( $-\text{CH}_2$ ), 28.97 ( $-\text{CH}_2$ ), 28.67 ( $-\text{CH}_2$ ), 26.69 ( $-\text{CH}_2$ ), 26.47 ( $-\text{CH}_2$ ), 22.05 ( $-\text{CH}_2$ ), 13.91 ( $-\text{CH}_3$ ).

### 2.3. Preparation of OTS-coated glass slides

At first, glass slides were cleaned using piranha solution, (70%  $\text{H}_2\text{SO}_4$ /30%  $\text{H}_2\text{O}_2$ ), for 2 h (caution: piranha solution is extremely corrosive and must be handled carefully), washed subsequently with distilled water, ethanol, and methanol, and dried under nitrogen. The cleaned substrates were then stored overnight in an oven at 120 °C. To functionalize the glass slides with OTS, the cleaned glass slides were immersed into an OTS (0.12 mL)/n-heptane (60 mL) solution for 30 min. Then the substrates were rinsed with methylene chloride and dried under stream of  $\text{N}_2$ . TEM copper grids (100 square meshes, Sigma–Aldrich India) were cleaned sequentially in ethanol and methanol, dried under nitrogen, and heated at 100 °C for 24 h to evaporate residual solvent.

### 2.4. Preparation of optical cells

Nematic LC, 5CB doped with different wt% of MeDTC was prepared by mixing 50  $\mu\text{L}$  of 5CB with respective wt% of MeDTC dissolved in ethanol. This solution was heated up to isotropic point of 5CB (36 °C) and then solvent (ethanol) was removed by vacuum evaporation. To prepare LC sensor standard procedure [50,51] was followed wherein a TEM grid was placed on the top of an OTS coated glass slide (1.0 cm  $\times$  1.0 cm each) and approximately 0.5  $\mu\text{L}$  of 5CB doped with 0.05 wt % of MeDTC was dispensed into the TEM grid.

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