

Supplementary Information File

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Real-Time Optical Detection of Mercury Contamination in Drinking Water using Amphiphilic Recognition Probe at Liquid Crystal/Aqueous Interface

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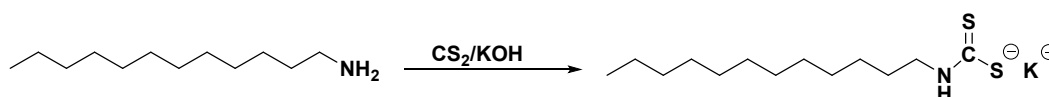
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1. Instrumentation

A polarizing microscope (B-510 POL, Optika, Italy) was used to image the optical textures of the 5CB film with a 10X objective and digital camera (CP6 Optika, Italy) at a resolution of 3072 x 2048 pixels, a gain of 1.2X, and a shutter speed of 1/10 s. Data analysis was performed according to the following procedure- Images of the LCs were first acquired using a polarizing optical microscope (POM) and then processed using Adobe Photoshop software to measure the intensity. Microsoft Excel and Origin 7.0 software were used for the numerical analysis, including the calculation of limit of detection (LOD) and reusability. We employed NMR instrument (Avance Neo 600 MHz, Bruker Insta Scientific) operating at 600 MHz to elucidate molecular structures and dynamics. The infrared spectra were recorded using an instrument (IR Spirit A224159, Shimadzu, Japan).

2. Synthesis of amphiphilic Dodecyldithiocarbamate surfactant derivatives (DDC)

20 ml of dry tetrahydrofuran (THF) were used to dissolve the primary n-dodecyl amine and KOH pellets (0.20g, 3.6mmol) were added to make the medium basic. After two hours of stirring, all of the KOH pellets were dissolved. Then, the resulting solution was placed in an ice bath and CS₂ (0.48 mL, 8.0 mmol) was gradually added with stirring. The reaction mixture was further stirred for 2 h. Then, we vacuumed out the solvent and washed it with diethyl ether and allowed it to dry. This compound was able to be dissolved in a range of organic solvents, including chloroform (CHCl₃), tetrahydrofuran (THF), dichloromethane (DCM), and acetonitrile, and it also formed a colloidal suspension in water.



Scheme 1: Reaction condition -Dry THF (solvent), Temp (0-5⁰C)

Yield: 60%. IR (cm⁻¹): 3206(N-H_{str}); 2929, 2847 (C-H_{str}); 1578 and 1371 (N-C=S_{str}), 1008 and 960 (C-S_{str}). NMR: ¹H NMR (600 MHz, CDCl₃, ppm): 5.74 (s, 1H, NH), 3.54 (t, 2H, -NCH₂), 1.71–1.26 (m, 20H, (CH₂)₁₀), 0.88 (t, 3H, CH₃); ¹³C NMR (150 MHz, CDCl₃, ppm): 211.60 (-CS₂), 48.21 (-NCH₂), 29.67 (-CH₂), 29.38, 28.99- 22.69 (-CH₂)_n, 14.12 (-CH₃).

3. Characterization of amphiphilic Dodecyldithiocarbamate surfactant derivatives (DDC)

The detailed characterization of the developed probe was performed using ^1H and ^{13}C nuclear magnetic resonance (NMR) and Infra-red (IR) spectroscopic techniques to confirm the molecular structure and purity of the probe.

The ^1H NMR spectrum of DDC in CDCl_3 exhibits peaks at δ 5.74(s), 3.54(t), 1.71-1.26(m) and 0.88(t) with 1, 2, 20 and 3 protons respectively attributed to $-\text{NH}$, $-\text{NCH}_2$, $-(\text{CH}_2)_{10}$ and $-\text{CH}_3$ protons respectively.

The ^{13}C NMR spectrum of DDC in CDCl_3 exhibits characteristic peaks of $-\text{CS}_2$, $-\text{NCH}_2$, long aliphatic carbons $-(\text{CH}_2)_n$, and $-\text{CH}_3$ protons at δ 211.60, 54.46, 31.25-22.05 and 13.91 respectively.

The position of peaks in ^1H and ^{13}C NMR and expected number of protons in ^1H NMR spectrum confirm the molecular structure and purity of the synthesized probe.

The absorption bands appearing at 3206; 2929, 2847; 1578 and 1371; 1008 and 960 in the FT-IR spectrum of DDC are attributed to $\nu(\text{N-H}_{\text{str}})$, $\nu(\text{C-H}_{\text{str}})$, $\nu(\text{N-C=S}_{\text{str}})$ and $\nu(\text{C-S}_{\text{str}})$ modes respectively. The occurrence of characteristic $-\text{NH}$ stretching vibration bands at 3206 cm^{-1} and strong absorption of $-\nu(\text{N-C=S}_{\text{str}})$ at 1578 and 1371 cm^{-1} clearly reveal the formation of $-(\text{NH-CS}_2)$ polar head group of the amphiphile whereas strong absorption bands at 2929 and 2847 cm^{-1} confirms the presence of non-polar part *i.e.* long aliphatic chains of the probe.

4. Supplementary figures

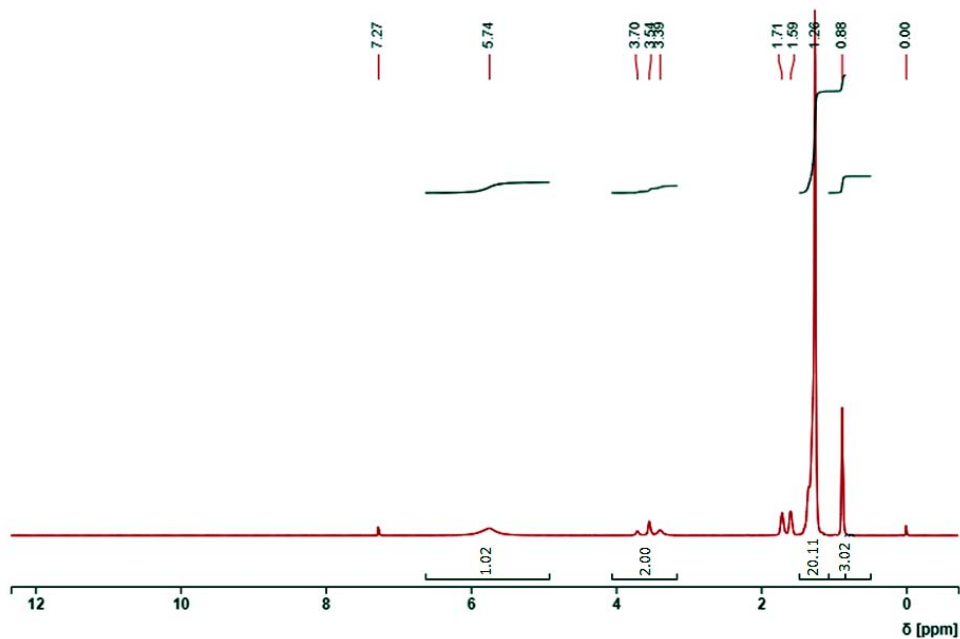


Figure S1. ^1H NMR spectra of DDC in CDCl_3 .

^1H NMR (600 MHz, CDCl_3 , ppm): 5.74 (s, 1H, NH), 3.54 (t, 2H, $-\text{NCH}_2$), 1.71–1.26 (m, 20H, $(\text{CH}_2)_{10}$), 0.88 (t, 3H, CH_3).

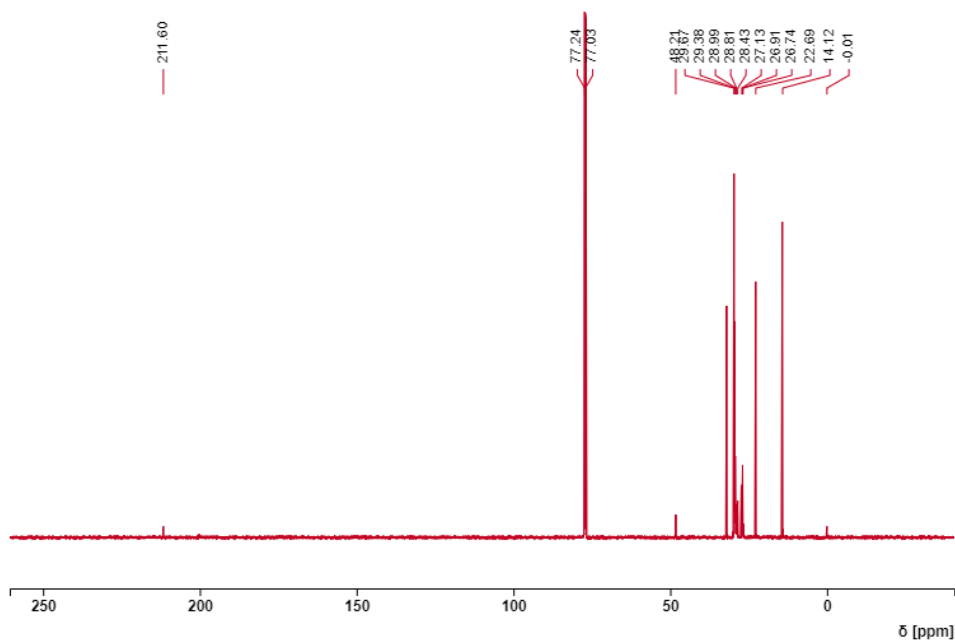
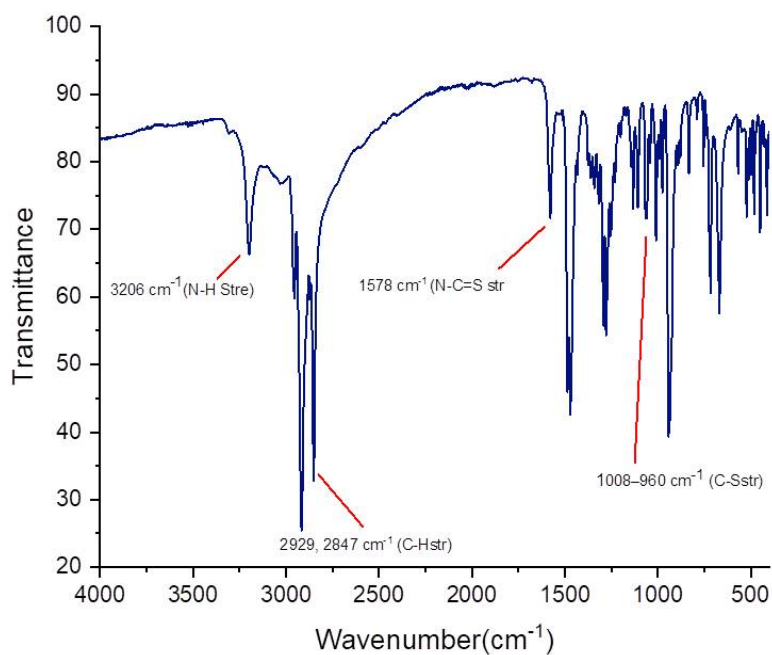


Figure S2. ^{13}C NMR spectra of DDC in CDCl_3 .

^{13}C NMR (150 MHz, CDCl_3 , ppm): 211.60 ($-\text{CS}_2$), 48.21 ($-\text{NCH}_2$), 29.67 ($-\text{CH}_2$), 29.38, 28.99–22.69 ($-\text{CH}_2$)_n, 14.12 ($-\text{CH}_3$).



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Figure S3. IR spectra of DDC surfactant

IR (cm⁻¹): 3206(N-H_{str}); 2929, 2847 (C-H_{str}); 1578 and 1371 (N-C=S_{str}), 1008 and 960 (C-S_{str}).

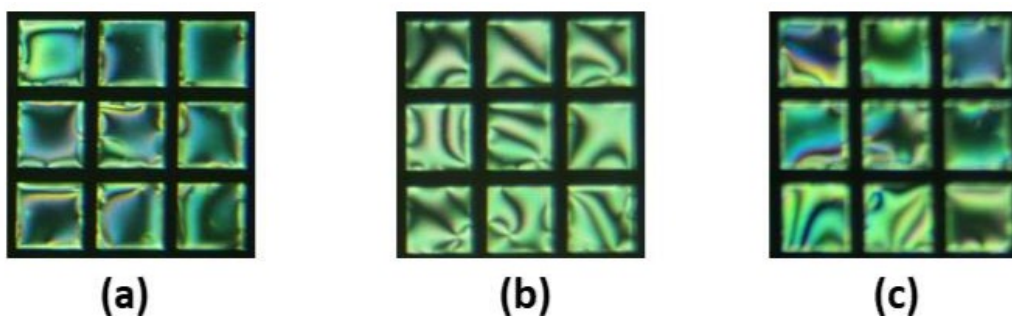


Figure S4: Cross-polarized optical pictures of 5CB doped with 0.4 mM of surfactant (DDC) submerged in an aqueous solution containing 1.0 mM of (a) HgSO₄ (b) HgCl₂ (c) Hg(NO₃)₂

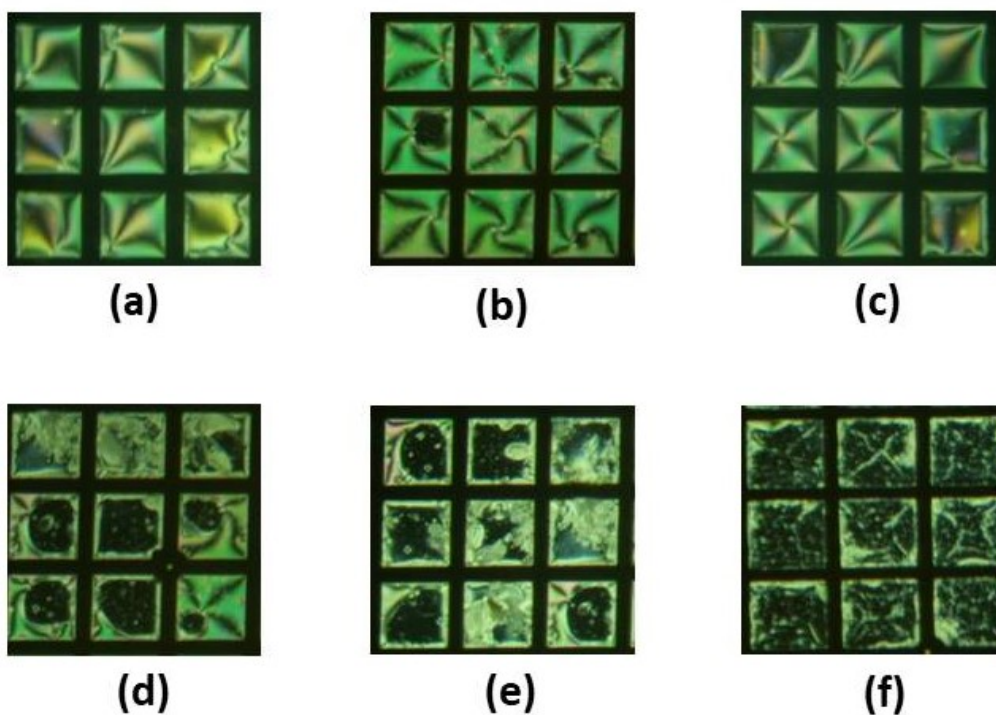


Figure S5: The stability assessment of LC-based sensors involved utilizing pre-prepared sensors stored in an air environment for varying durations **(a)** 1 Day **(b)** 2 Day **(c)** 3 Days **(d)** 4 Days **(e)** 5 Days **(f)** 6 Days

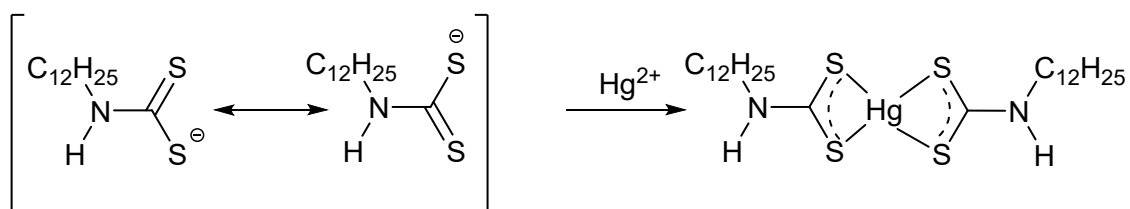


Figure S6: Resonance Hybrid Structure of DDC and Hg-DDC Complex
