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# A Novel Polythiophene Derivative as a Sensitive Colorimetric and Fluorescent Sensor for Anionic Surfactants in Water

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#### Abstract

А novel cationic polythiophene derivative, poly[N,N,N-trimethyl-4-(thiophen-3-ylmethylene)cyclohexanaminium chloride] (PTCA-Cl), has been prepared successfully and applied as a colorimetric and fluorometric probe for the detection of anionic surfactants. In paticular, a new method for the polymerization of cationic polythiophene derivatives is found, which has not been reported previously. The colorimetric and fluorescent of PTCA-Cl response to anionic surfactants have been investigated by absorption and emission spectroscopy. The sensing interaction can be apparently observed by naked eyes, which presents a great advantage for its practical applications. Moreover, the sensor (PTCA-Cl) shows a high selectivity to anionic surfactants in the presence of other negatively charged analytes and as well an high sensitivity with the detection limit at 10<sup>-9</sup> M by using fluorometry, which is the lowest ever achieved among all synthetic anionic surfactants sensors available by far. Therefore, the water soluble polythiophene derivative can be applied as a colorimetric and fluorescent probe for the detecting anionic surfactants with high selectivity and sensitivity.

Keywords: conjugated polymers; sensors; anionic surfactants; colorimetric sensing; fluorometric method

# Introduction

Surfactants are widely used in household cleaning detergents, personal care products and industries like textiles, paints, pesticide formulations, pharmaceuticals, mining, oil recovery and pulp and paper.<sup>1</sup> As a result, large amounts of surfactants are commonly discharged in large quantities to sewage treatment plants or directly to the aquatic environment in areas where there is no sewage treatment. In addition, anionic surfactants are the largest group of the surfactants and represent 70% of the annual surfactant production. Anionic surfactants deserve special interest since they impact on aquatic/terrestrial ecosystems and are used in large quantities in consumer products, which are discharged into the wastewaters after use. Thus they are becoming of the major components of environmental pollutants.<sup>2-6</sup> Therefore, it is becoming important to monitor easily the concentrations of anionic surfactants in water. Many well-known surfactant analysis techniques, such as the methylene blue method,<sup>7</sup> ion-selective electrodes,<sup>8-10</sup> gas chromatography/mass spectrometry,<sup>11-13</sup> high-performance liquid chromatography<sup>14,15</sup> and optical detection based on synthetic receptors,<sup>16-21</sup> capillary electrophoresis,<sup>22</sup> and so forth, have limitations in their applicability, owing tedious procedures, large necessary quantites of toxic solvents, irreproducibility, signal instability and unsatisfactory sensitivity and selectivity.<sup>23-28</sup> Thus, it is essential to develop new methods that could improve the simplicity, selectivity, and sensitivity of anionic surfactant detection in water, such as chromo- or fluorogenic methods. However, there are few reports on the use of UV or fluorescence changes to detect anionic surfactants.

Recently, a new sensory technology based on conjugated polymers has been developed in view of their signal amplification effect, and thus is sensitive to very minor perturbations.<sup>29,30</sup> Among the conjugated polymers, water-soluble conjugated polythiophenes with charged substituents have

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attracted increasing interest in recent years due to their unique chemical structures and optical properties.<sup>31-35</sup>

Among the various types of anion receptors, ammonium-based receptors have been studied extensively. Moreover, there have been many significant results from the application of new ammonium receptors to many anionic targets. Chun Li et al. recently reported a colorimetric and fluorescent method for the selective determination of anionic surfactants using ammonium-containing polythiophene derivative.<sup>36,37</sup> However, these systems involve a two-step process for the detection of anionic surfactants and an additional material is necessary for detection. Herein, we report the first example of an anionic surfactant-selective sensor only based on water soluble cationic polythiophene derivative (PTCA-Cl) (Scheme 1) without any additional material, which shows colorimetric changes and fluorescence enhancement in the presence of various of anionic surfactants. Compared to previous reports, this system is simpler and more effective in sensing anionic surfactants.

The colorimetric method provides unique advantages including visual detection and real-time in situ responses over fluorometric method. However, the limit of detection of the colorimetric method is only at 10<sup>-6</sup> M level due to the low sensitivity of absorption spectrometer relative to fluorometric detection. Thus, we report a selective and sensitive colorimetric and fluorescent dual method for the detection of anionic surfactants in water based on a cationic polythiophene derivative. The detection limit can be extended to be as low as of the order of 10<sup>-9</sup> M based on fluorometric method. In this paper, the simple, rapid, sensitive and selective method is based on conformationally flexible polythiophene derivative and complementary electrostatic interactions and does not require any additional material or chemical modification on the probe or target. In addition, a new method for the

polymerization of cationic polythiophene derivatives is found, which is supplementary for FeCl<sub>3</sub> oxidative polymerization.



Scheme 1. Synthetic route of PTCA-Cl

# Experimental

#### Materials

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All chemical reagents were common commercial level and used as received without further purification, (thiophene-3-ylmethyl) phosphonic acid diethyl ester (Scheme 1. Compound 2)<sup>38</sup> and 4-(dimethylamino) cyclohexanone (Scheme 1. Compound 1)<sup>39</sup> were prepared as reported previously.

#### Measurement

UV-vis spectra was recorded on a Shimadzu 3100 spectrometer Absorption and Fluorescence measurements were carried out on a Edinburgh Instruments Ltd-FLS920 fluorescence spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Bruker AV III 400MHz NMR spectrometer. Infrared spectra were recorded using Bruker Vertex 70 FT-IR spectrometer with KBr pellets. Gel permeation chromatography (GPC) measurements were performed with a Waters 2410 refractive-index detector at 35 °C, and THF was used as eluent at a flow rate of 1.0 mL/min. GPC

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data were calibrated with polystyrene standards. Mass spectra were obtained using a PerkinElmer Clarus500 Mass Spectrometer.

#### **Sample Preparation**

All tests described in this paper were carried out at room temperature in deionized water. In the experiments of titration with various anionic surfactants, the concentration of PTCA-Cl in colorimetric experiments and fluorometric experiments was 0.2 mM and  $0.1 \mu M$ , respectively.

#### Syntheses

### N,N-Dimethyl-4-(thiophen-3-ylmethylene)cyclohexanamine (3)

A mixture of 4-(dimethylamino)cyclohexanone (1.41 g, 10 mmol), 60% NaH (0.60 g, 15 mol) and THF (20 ml) was stirred for 30min under ice-water bath, and the flow of dry N<sub>2</sub> gas allowed for an inert atmosphere. Then compound **2** (2.34 g, 10 mol) was slowly dropped at 0 °C. After completion, the reaction mixture was warmed to room temperature and stirred further for 12 h. Then, the reaction mixture was poured into cold water and extracted with chloroform. The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated. The crude product was purified by chromatography on silica gel with n-hexane/acetate/methanol/triethylamine=30:5:2:1 as an eluent, and this afforded the pure substance as a colorless oil. (1.05 g, Yield: 48%). Ms: m/z = 221[M<sup>+</sup>]. FTIR (KBr, cm<sup>-1</sup>): 1639 (CH=C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm,  $\delta$ ): 7.21 (d, 1H, Th-C5-H), 6.99 (s, 1H, Th-C2-H), 6.98 (d, 1H, Th-C4-H), 6.13 (s, 1H, CH=C), 2.43 (m, 1H, CH), 2.27 (s, 6H, 2×CH<sub>3</sub>), 1.96-1.98 (m, 4H, 2×CH<sub>2</sub>), 1.31-1.40 (m, 4H, 2×CH<sub>2</sub>).

### N,N,N-Trimethyl-4-(thiophen-3-ylmethylene)cyclohexanaminium bromide (4)

Compound **3** (0.41 g, 18.6 mmol) and methyl bromide (0.35 g, 37.2 mmol) were dissolved in 15 ml CH<sub>3</sub>CN, and the reaction mixture was stirred at room temperature for 2 h, the solid was filtered and

washed with ether to obtained product **4** (0.42 g, 72%). Ms: m/z = 315[M<sup>+</sup>]. FTIR (KBr, cm<sup>-1</sup>): 1639 (CH=C). <sup>1</sup>HNMR (CDCl<sub>3</sub>, ppm, δ): 7.28 (d, 1H, Th-C5-H), 7.10 (s, 1H, Th-C2-H), 6.97 (d, 1H, Th-C4-H), 6.17 (s, 1H, CH=C), 3.08 (m, 1H, CH), 2.90 (s, 9H, 3×CH<sub>3</sub>), 2.42 (t, 2H, CH<sub>2</sub>), 2.17 (t, 2H, CH<sub>2</sub>), 1.93 (m, 2H, CH<sub>2</sub>), 1.42 (m, 2H, CH<sub>2</sub>).

#### Poly[N,N,N-trimethyl-4-(thiophen-3-ylmethylene)cyclohexanaminium chloride] (PTCA-Cl)

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Compound 4 (0.42 g, 1.33 mmol) and sodium lauryl sulfate (SLS) (0.38 g, 1.33 mmol) were added to 20 ml dry acetone, then the mixture was smashed by the ultrasonic vessel for 30 min. The acetone was removed by rotary evaporator, and then the white solid was obtained which was compound 4/SLS ion-pair complex. This ion-pair complex was dissolved in dry chloroform (20 ml) to give a translucent liquid. Anhydrous ferric chloride (0.86 g, 5.3 mmol) was suspended in 20 ml dry chloroform and stirred for 30 min under nitrogen, and then the above resulting translucent liquid was added dropwise. The mixture was stirred at room temperature for 24 hours. Treatment of the reaction mixture with methanol (25 ml) resulted in the precipitation of the polymer and then filtered. The filter cake and 1 ml hydrazine were mixed in 50 ml methanol and stirred overnight. The solution was filtered and evaporated to dryness. The resulting polymer was washed six times with a saturated solution of tetrabutylammonium chloride in methanol, until the absorbance remained unchanged. Then PTCA-Cl (0.17 g, 47%) was obtained after Soxhlet extraction with a mixed solvent (acetone:methanol=4:1) to remove impurity and oligomer. FTIR (KBr, cm<sup>-1</sup>): 1635 (CH=C). <sup>1</sup>HNMR (CDCl<sub>3</sub>, ppm, δ): 7.09 (s, 1H, Th-C4-H), 6.15 (s, 1H, CH=C), 3.17 (m, 1H, CH), 2.94-3.02 (s, 9H, 3×CH<sub>3</sub>), 2.05 (t, 2H, CH<sub>2</sub>), 1.89 (t, 2H, CH<sub>2</sub>), 1.09 (m, 2H, CH<sub>2</sub>), 1.07 (m, 2H, CH<sub>2</sub>). GPC: Mn=8310g/mol, PDI=1.73.

# **Results and discussion**

Scheme 1 displays the synthetic route of polymer PTCA-Cl. 1 was coupled with phosphonate 2 using a witting-Horner reaction to afford 3. Originally, we wanted to prepare the water soluble polymer PTCA-Cl by using the usual FeCl<sub>3</sub> polymerisation of monomer 4, but it failed. However, anionic surfactant SLS was introduced into the mixture of compound 4 and acetone which led to the formation of a compound 4 / SLS ion-pair complex. Then removed the solvent acetone to give white solid ion-complex. The resulting ion-pair complex as the monomer was polymerized using FeCl<sub>3</sub> in chloroform and then by anion exchange to afford PTCA-Cl. In this method, the ion-pair complex possesses a good solubility in organic phase, therefore, it can be easily dissolved in chloroform and readily polymerized. What's more, it is noted here that dodecyl sulfate ion can be easily exchanged with chloride ion from tetrabutylammonium chloride because the maximum absorption of the polymer solution tends to be almost unchanged after four times of exchange. PTCA-Cl displayed maximum absorption peak at 489 nm in UV-visible spectra and maximum emission peak at 589 nm in water (Fig. S1).

Fig. 1a illustrates absorption spectra of water soluble PTCA-Cl upon addition of different amounts of sodium dodecylbenzenesulfonate (SDBS). It is clearly seen that upon the addition of increasing amounts of SDBS caused a decrease in absorption at 489nm with a concomitant increase at 434nm. Simultaneously, a naked-eye color change from red to yellow was observed (Fig. 1a, S2), signifying that SDBS could cause the dissociation of PTCA-Cl aggregates. The same phenomenon was also observed upon sodium dodecyl sulfonate (SDS), sodium lauryl sulfate (SLS) and sodium dodecyl carboxylate (SDC) (Fig. S2, S3). And the ratio of absorbance measured at 489 nm and 434 nm (A<sub>489</sub>/A<sub>434</sub>) versus the increasing amounts of SDBS was all gradually decreased (Fig. 1b), and the

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detection limit is evaluated to be 10<sup>-6</sup> M. The blue shift caused by addition of SDBS should be attributed to a decrease in conjugation length.<sup>40</sup> arising from the dissociation of the PTCA-Cl aggregates and the conformation change of PTCA-Cl. The electrostatic interaction between the negatively charged sulfonate groups of the surfactants and the positively charged PTCA-Cl would be the driving force and the synergistic effect due to the hydrophobic interaction between alkyl chains in surfactants plays an important part in promoting the dissociation of PTCA-Cl aggregates. The PTCA-Cl aggregates were dissociated into nonaggregated PTCA-Cl chains with random-coiled conformation.<sup>33</sup> These interactions shift the  $\pi$ - $\pi$ \* transition to shorter wavelengths and lead to a color change of the solution from red to light yellow. To further prove that the transition to shorter wavelengths and the color change is due to the disassembly of PTCA-Cl, temperature dependent absorption spectra of PTCA-Cl were also measured (Figure S4, Supporting Information). The results declared clearly that after the temperature was up to 60 °C, the maximum absorption of PTCA-Cl was blue-shifted gradually, signifying the PTCA-Cl aggregates were being dissociated into non-aggregated PTCA-Cl chains with random-coiled conformation. The spectral characteristic supported the standpoint that the addition of anionic surfactants promoted the disassembly of PTCA-Cl aggregates.

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Figure. 1 (a) Variation in the absorption spectra and colorimetric response of PTCA-Cl (0.2 mM) in water with increasing concentrations of SDBS as indicated. (b) The relationship between  $A_{489}/A_{434}$  and the concentration of SDBS from 0.001 to 0.1 mM.

It is well known that fluorometric method has an advantage in extending the detection limit over colorimetric method due to the high sensitivity of fluromrtric methods relative to absorption spectroscopy. And PTCA-Cl examined here can give a strong emission in dilute solution and excellent signal. Fig. 2 displays emission spectra of PTCA-Cl in aqueous solution in the absence and in the presence of different amounts of SDBS. Upon addition of increasing amounts of SDBS, the emission intensity at 589 nm enhanced gradually, indicating that the fluorometric detection of SDBS is possible. The similar results also happened on SDS, SLS and SDC (Fig. S5). Though the specific reason for this phenomenon was unclear, according to our current knowledge, the electrostatic and hydrophobic cooperative interaction between anionic surfactants and cationic PTCA-Cl could lead to increase in vibrational structure, probably due to the backbone being more rigid.<sup>41</sup> In addition, the polymer chains are aggregated in the absence of surfactant, but that the addition of surfactant results in a disassembly of the aggregates, it is the reason for the blue-shift in absorbance, which could also explain the increase in emission intensity. This approach shows very high sensitivity due to the extremely low background noise. The detection limit can be extended to the of order of 10<sup>-9</sup> M, being  $10^3$  times lower than that based on colorimetric method.

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Figure. 2 Emission spectra of the PTCA-Cl in the absence and the presence of increasing amounts of SDBS. [PMTPA] = $0.1\mu$ M, Excitation wavelength: 450 nm.

To address the specificity of the cationic polythiophene PTCA-Cl toward anionic surfactants, absorption spectra and colorimetric response of the PTCA-Cl probe upon addition of SDBS, sodium dodecyl sulfonate (SDS), sodium lauryl sulfate (SLS), sodium dodecyl carboxylate (SDC), cetyltrimethylammonium bromide (CTAB), OP-10, and simple ions including K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>,  $\Gamma$ , SO4<sup>2-</sup>, CO3<sup>2-</sup>, NO3<sup>-</sup>, PO4<sup>3-</sup> and HPO4<sup>2-</sup>, were examined under identical conditions. It was found that the absorbance of PTCA-Cl at 489 nm was changed distinctly only for anionic surfactants, whereas upon addition of cationic, non-ionic surfactants and simple ions, the absorbance remained basically unchanged (Fig. 3a). What's more, most of the solutions remained red except for those containing anionic surfactants, which gave light yellow (SDBS), yellow(SLS) and light orange (SDS) solutions (Fig. 4). It is also confirmed that only anionic surfactants induced distinct enhancement in emission intensity by fluorometric approach (Fig. 3b). Moreover, it is found that the response concentration of SDC is higher than that of SDBS, SLS and SDS (see Fig. S3), which

should be attributed to the difference of the charged moieties in surfactants. These results are in good agreement with the previous observations that sulfonate has a strong affinity for quaternary ammonium group in PTCA-Cl with respect to carboxylate and phosphate.<sup>42</sup> Moreover, the effect of hydrophobic anion BF4<sup>-</sup> were examined (see supporting information, Fig. S6), the blue shift and colour change were also observed, however, the sensitivity was not higher than that of anionic surfactants, but it also supported the standpoint of deaggregation mechanism. Notably, the most dramatic effects are observed for anionic surfactants from these results, and hence we can clearly come to the conclusion that PTCA-Cl probe exhibits satisfied selectivity toward anionic surfactants. In order to further verify the feasibility of the present method, anionic surfactant in source water was detected. In this case, a certain known amount of SDBS (0.01 and 0.05 mM) was added to source water and the concentration was determined by using a suitable calibration curve. The recovery in percentage was determined to be 93% and 92%, respectively. These relatively good results indicate that this approach would be useful in detection of anionic surfactants.

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**Figure. 3** (a) Relative absorbance of the PTCA-Cl in water in the presence of various analytes. [PTCA-Cl] = 0.2 mM; [SDBS] = [SDS] = [SLS] = [CTAB] = [Triton X-100] = 0.1 mM; [SDC] = [simple ions] = 0.6 mM. (b) Emission intensity of PTCA-Cl versus the concentrations of surfactants as indicated. [PTCA-Cl] = 0.1  $\mu$ M. Excitation wavelength: 450 nm.



**Figure. 4** Changes in the color of PTCA-Cl in water induced by the addition of various analytes. [PTCA-Cl] = 0.2 mM; [SDBS] = [SLS] = [SDS] = [CTAB] = [OP-10] = 0.1mM; [simple ions] = 0.6 mM.

# Conclusions

In conclusion, we have developed a simple and convenient colorimetric and fluorescent sensor for anionic surfactants in water based on a novel cationic polythiophene derivative PTCA-Cl. This methodology does not require any chemical modification of the probe or the analytes and is based on conformational change of the conjugated backbone of cationic PTCA-Cl. Absorption and emission spectra can be applied to monitoring the conformational change of PTCA-Cl, realizing the colorimetric and fluorometric detection of anionic surfactants. This cationic polymer exhibited selective and color changes as well as fluorescence changes when exposed to anionic surfactants. And the fluorescent detection limit to anionic surfactants can be extended to as low as 10<sup>-9</sup> M. Moreover, the PTCA-Cl is a novel cationic polymer, which has not been reported so far. And the new synthetic method is first reported in this paper, which can be applied in other similar cationic polyelectrolytes. We believe that PTCA-Cl will not only provide a simple, convenient and sensitive approach for sensing anionic surfactants, but also develop various inexpensive means for the rapid detection and identification of target nucleic acids, proteins or other biological molecules.

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Scheme 1



# A Novel Polythiophene Derivative as a Sensitive Colorimetric and Fluorescent Sensor for Anionic Surfactants in Water

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we have developed a a sensitive colorimetric and fluorescent sensor for anionic surfactants in water based on a novel cationic polythiophene derivative, which has not been reported so far, especially, a new method for the polymerization of cationic polythiophene derivatives is found.