

## Quinone based oligomeric sensors as colorimetric probes for cyanide anion: Effects of solvent medium and substituent on sensing

P. Madhusudhana Reddy<sup>a,1</sup>, Shih-Rong Hsieh<sup>b,1</sup>, Wan-Chi Wu<sup>a</sup>, Chi-Jung Chang<sup>a,\*</sup>,  
Yi-Shao Chen<sup>a</sup>, Ming-Ching Lee<sup>b</sup>

<sup>a</sup> Department of Chemical Engineering, Feng Chia University, 100, Wenhwa Road, Seatwen, Taichung 40724, Taiwan, ROC

<sup>b</sup> Department of Surgery, Taichung Veterans General Hospital, 1650 Taiwan Boulevard Section 4, Taichung 40705, Taiwan, ROC

### ARTICLE INFO

**Keywords:**  
Oligomer  
Sensor  
Anion  
Substituent  
Solvent

### ABSTRACT

The main objective of the present study is to understand the structure-property relationships of sensor capable of colorimetric response, upon the addition of particular anions, due to hydrogen-bonding association between sensor and anion. Further, hydrogen-bonding association between sensor and anion, and thereby colorimetric response of the receptor in various solvent media was also targeted. For this, we have synthesized chloro-substituted quinone based oligomer sensor (QO-Cl) and cyano-substituted quinone based oligomer sensor (QO-CN), which contain the thiourea as a binding site. These oligomeric sensors were exploited as colorimetric sensors for cyanide anion [CN<sup>-</sup>]. Further, the sensing abilities of these sensors for CN<sup>-</sup> recognition in various solvents were monitored to investigate the influence of solvent on the hydrogen bonding association between sensor and anion. Our colorimetric and spectrometric results unveiled that the QO-CN sensor has shown the better binding constant ( $K_{QO-CN-CN^-} = 39,317 \text{ M}^{-1}$ ) and detection of limit (DOL = 1.2  $\mu\text{M}$ ) for CN<sup>-</sup> than that of QO-Cl, ( $K_{QO-Cl-CN^-} = 1950 \text{ M}^{-1}$ ; DOL = 69  $\mu\text{M}$ ). This can be attributed to the higher electron withdrawing nature of  $-\text{C}\equiv\text{N}$  than the moderately electron-withdrawing substituent Cl.

### 1. Introduction

Anions have been gained significant attention because of their vital roles in a wide spectrum of applications including environmental, industrial, biological, and medical ones [1]. Among various anions, the cyanide anion [CN<sup>-</sup>] is one of the most detrimental because of its well-known toxicity to biological and environmental systems [2]. Therefore, the scientific community is interested in the development of facile methods, which are highly sensitive, differentiating, fast, and dynamic in various solvent media, for the recognition and sensing of CN<sup>-</sup> [3].

In spite of the availability of various methods, such as spectral, voltammetry, electrochemical and ion chromatography for the recognition of CN<sup>-</sup> ions [4–10], still, there is a great demand for facile, fast, low cost and instrument-free methods for the detection of CN<sup>-</sup> ions. In this context, the colorimetric method can be greatly exploited as a top priority for the sensing of ions and thus, the development of colorimetric sensors for scientists is still a challenging area. These colorimetric sensors offer most valuable advantages such as cost-effectiveness, rapidity, real-time monitoring, lack of equipment required, and being naked eye detectable [11]. Basically, the colorimetric anion

sensors can be divided into two categories, such as neutral or positively charged sensors. The neutral sensor can make the hydrogen bonding interactions with the anion, whereas the positively charged sensor can make the electrostatic interactions with the anion. Moreover, there is also a possibility of deprotonation of the acidic hydrogen of the receptors in some cases [12].

In neutral anion sensors, sensors with urea or thiourea moieties can act as appropriate binding sites for most of the anions [13–15]. Therefore, urea or thiourea have been taken as good hydrogen bond donors for the construction of anion sensors that may bind anions by two hydrogen bonds of the (thio)-ureido  $-\text{NHs}$  [12]. Further, the binding abilities of these sensors can also be tuned through the insertion of electron-withdrawing substituents (EWS) or electron-donating substituents (EDS) onto the molecular framework of the sensor [16]. The insertion of such EWS or EDS on to the sensors can influence the polarization of N–H fragment of a receptor and thus the H-bond donor tendencies are varied. Besides, it is also known that the effects of the polarity of solvent can also play a fundamental role in governing anion binding and selectivity [16,17]. Therefore, it is very important to have detailed knowledge of the effects of substituents and type of solvent on

\* Corresponding author.

E-mail address: [changcj@fcu.edu.tw](mailto:changcj@fcu.edu.tw) (C.-J. Chang).

<sup>1</sup> These authors contributed equally to this work.

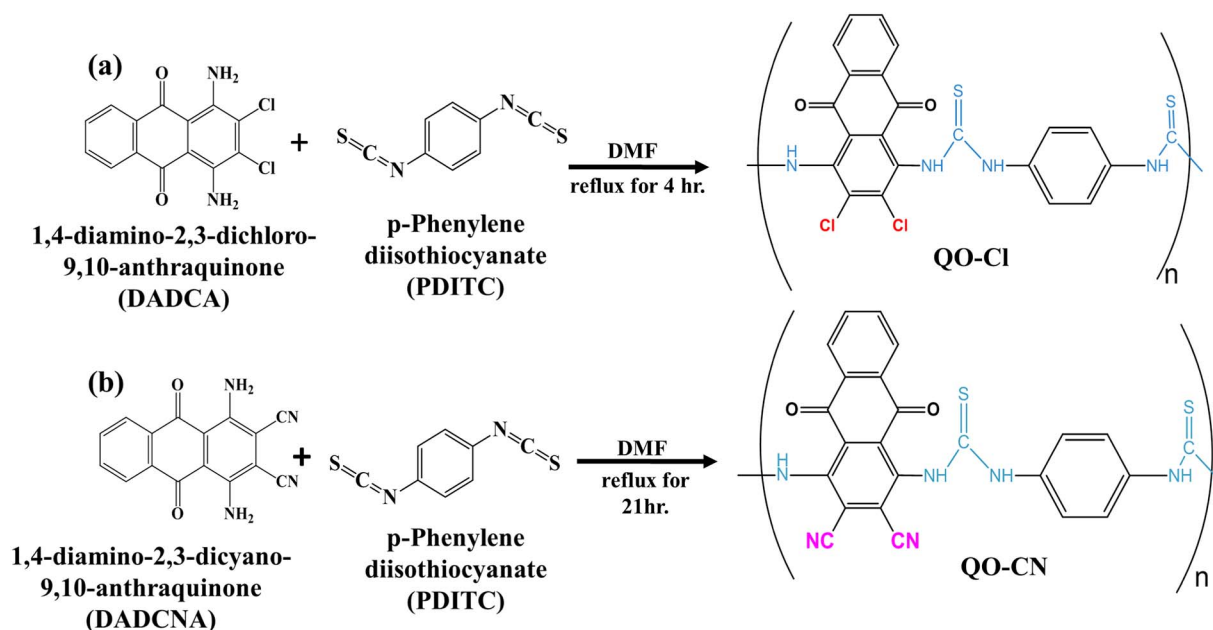


Fig. 1. Schematic illustration for the synthesis of the receptors, QO-Cl (a) and QO-CN (b).

the sensing abilities of sensors to design the potential sensor. Further, to the best of our knowledge, most of the developments of  $\text{CN}^-$  sensors are focused on small molecules [18–21], while polymeric sensory materials are relatively less explored to the best of our knowledge [22]. Further, the sensors based on quinone based polymers is rarely explored.

In view of this, we have developed two colorimetric sensors, such as chloro-substituted quinone based oligomer sensor Fig. 1 (QO-Cl) and cyano-substituted quinone based oligomer sensor (QO-CN), which contain the thiourea as a binding site. Further, we have evaluated the sensing of  $\text{CN}^-$  anions with these H-bond-donating receptors, whose binding tendencies are varied due to the presence of highly EWS ( $-\text{C}\equiv\text{N}$ ) and moderately EWS (Cl), and how such features ultimately influence the selectivity of anion recognition processes. In addition, the recognition of  $\text{CN}^-$  anions was observed by naked-eye detection, with a color change from purple to dark yellow for QO-Cl solution and blue to greenish blue for a QO-CN solution. Further, we have also evaluated the sensing abilities of these sensors in different solvent media ((DMSO, THF, 10% aq. DMSO (DMSO:H<sub>2</sub>O; 90:10 v/v) and 10% aq. THF (THF:H<sub>2</sub>O 90:10 v/v)). Therefore, the present study can provide some useful information for further development of new high-performance polymer based sensors for environmentally and biologically important anions.

## 2. Experimental

### 2.1. Materials

1,4-diamino-2,3-dichloro-9,10-anthraquinone (DADCA) and 1,4-diamino-2,3-dicyano-9,10-anthraquinone (DADCNA) was purchased from TCI Chemicals. Tetrabutylammonium cyanide (TBACN), tetrabutylammonium thiocyanate (TBASCN), tetrabutylammonium acetate (TBAAcO) and tetrabutylammonium fluoride (TBAF) were purchased from Aldrich. Tetrabutylammonium hydrogensulfate (TBAHSO<sub>4</sub>) and dimethyl sulfoxide (DMSO) were received from Sigma-Aldrich. Tetrabutylammonium bromide (TBABr) was provided by the Alfa Aesar. Tetrahydrofuran (THF) and dimethylformamide (DMF) were supplied by Macron fine chemicals. p-Phenylene diisothiocyanate (PDITC) was received from Acros organics. All the chemicals were re-ceived at their highest purity and used without further purification.

### 2.2. Instrumentation

Absorption measurement were carried out on HR4000 high-resolution UV-Vis spectrometer (Labguide Co.). Hitachi F-7000 fluorescence spectrophotometer with xenon lamp (150 W) as the light source was used to measure the fluorescence intensity measurements. Agilent Technologies DD2 spectrometer (600 MHz) was used to record the <sup>1</sup>H NMR spectra in *d*<sub>6</sub>-DMSO. Shimadzu SSU 8000 spectrometer was used to collect the FT-IR spectra.

### 2.3. Synthesis of QO-Cl and QO-CN

For the synthesis of QO-Cl sensor, DADCA (1 mmole) was dissolved in 20 mL of DMF solution. To this solution PDITC (1 mmole) was added and subsequently this mixture was allowed for reflux for 4 h under inert atmosphere. After the reaction completed, diethyl ether was added to the reaction mixture and filtered to collect the purple color QO-Cl. The number average molecular weights (M<sub>n</sub>), weight average molecular weights (M<sub>w</sub>) and dispersity indexes (M<sub>w</sub>/M<sub>n</sub>) were determined by gel permeation chromatography (GPC) using THF as a solvent. The M<sub>w</sub> and M<sub>n</sub> were 3125 g mol<sup>-1</sup> and 3105 g mol<sup>-1</sup> respectively. Further, QO-Cl was characterized by FT-IR (Fig. S1a) and <sup>1</sup>H NMR (Fig. S2a). FT-IR (KBr): 3460, 3405, 1642, 1541, 1502, 1257, 1100 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ 7.416–8.259 (m, 8H), 9.154 (s, 2H), 10.112 (s, 4H).

QO-CN was prepared by dissolving DADCNA (1 mmole) in 20 mL DMF solution. To this solution PDITC (1 mmole) was added and this mixture was allowed for reflux for 21 h under inert atmosphere. Upon completion of the reaction, the excess solvent was removed using rotary evaporator. The M<sub>w</sub>, M<sub>n</sub> and M<sub>w</sub>/M<sub>n</sub> were determined by the GPC using THF as a solvent. The M<sub>w</sub> and M<sub>n</sub> were 3208 g mol<sup>-1</sup> and 3081 g mol<sup>-1</sup> respectively. The obtained blue color solid was washed with pentane and finally the product was dried for further characterization. FT-IR (KBr) (Fig. S1b): 3425, 2220 (characteristic band for CN), 1625, 1575, 1526, 1257, 1114 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) (Fig. S2b): δ 6.987–9.981 (m, 8H), 8.942 (s, 2H), 9.982 (s, 4H).

Download English Version:

<https://daneshyari.com/en/article/7826416>

Download Persian Version:

<https://daneshyari.com/article/7826416>

[Daneshyari.com](https://daneshyari.com)