



# Synthesis and properties of novel fluoroionophores for Ag<sup>+</sup>-optode sensing based on oligophenylenevinylenes

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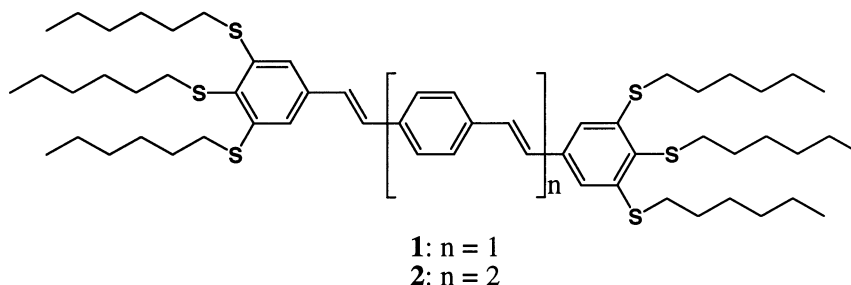
Received 31 May 2000; revised 13 September 2000; accepted 27 September 2000

## Abstract

Novel hexylsulfanyl substituted oligophenylenevinylenes have been designed and synthesized as fluoroionophores which selectively detect Ag<sup>+</sup> ions in membrane optode sensors. In addition, the 4-phenyl-ring oligomer-based optode sensor exhibits higher sensitivity than that of the 3-phenyl-ring counterpart. © 2000 Elsevier Science Ltd. All rights reserved.

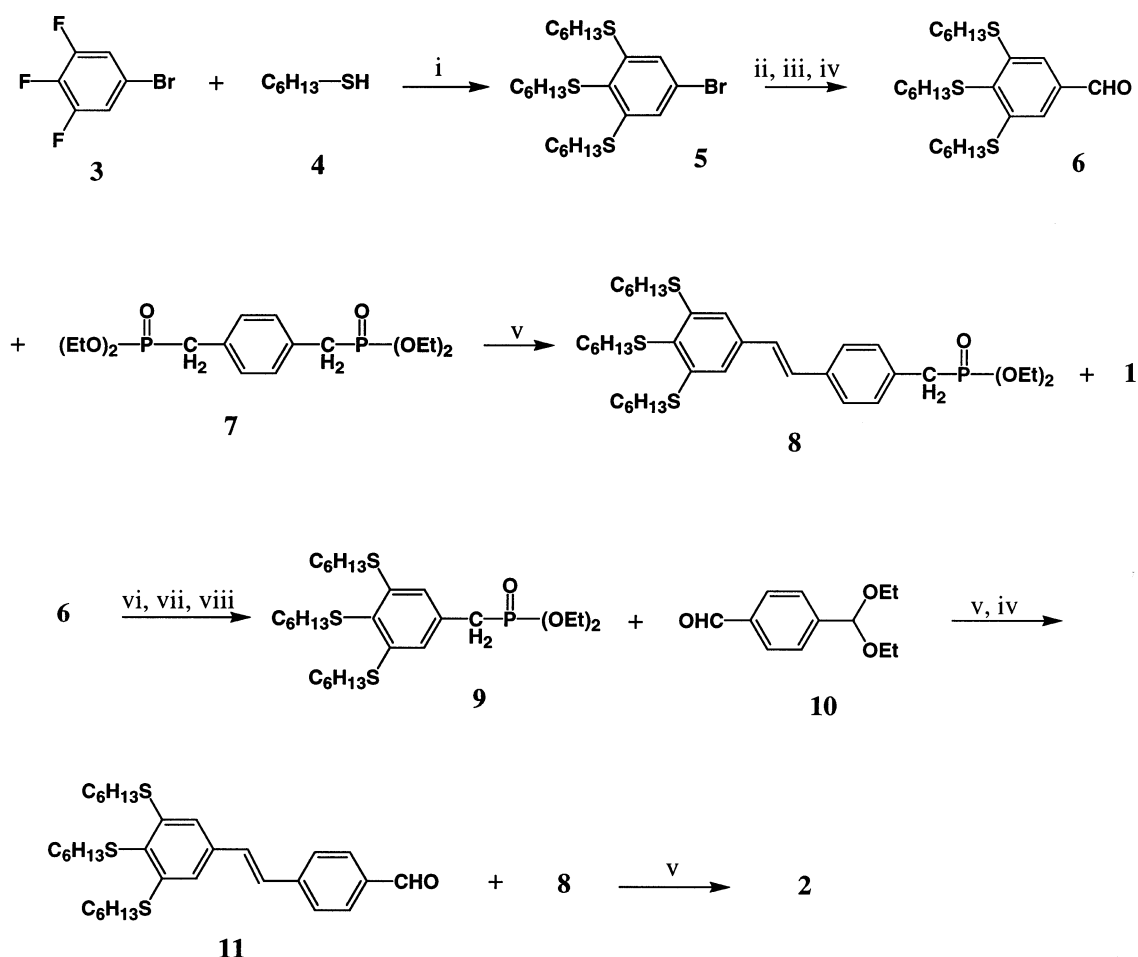
*Keywords:* oligomers; optical properties; fluorescence.

It is of great interest and challenge to design and synthesize fluoroionophores for sensing environmentally and/or biologically important cations.<sup>1,2</sup> In the course of our studies on the structure–property relationships of end-substituted oligophenylenevinylenes (OPV), we have found that planar OPVs, in particular the higher homologues, are highly fluorescent,<sup>3</sup> which indicated that they may be potentially useful fluorophores for sensing applications. With an incorporation of a specific ionophore onto the OPV framework, the spectral property/properties of OPV may be modified upon binding of the ionophore with a target ion which give(s) rise to a sensing mechanism. With this concept in mind, we have recently developed a novel I<sub>2</sub>-optode sensor with sensitivity down to 5×10<sup>-8</sup> M based on a polyalkenoxy-substituted 3-phenyl-ring OPV.<sup>4</sup> In a continuation of this, we report here our design, syntheses and optical properties of novel hexylsulfanyl-substituted OPVs **1** and **2** as well as their application in membrane optodes for Ag<sup>+</sup> ion sensing.



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The syntheses of the hexylsulfanyl substituted 3-phenyl-ring oligomer **1** and the 4-phenyl-ring oligomer **2** are shown in Scheme 1.<sup>5</sup> The three hexylsulfanyl substituents were incorporated by nucleophilic aromatic substitution of 1-bromo-3,4,5-trifluorobenzene **3**. Lithium–halogen exchange of **5** followed by the reaction with *N*-formylmorphine and hydrolysis afforded the corresponding tri-hexylsulfanyl substituted benzaldehyde **6**. Double Wadsworth–Emmons reactions of benzaldehyde **6** with bis-phosphonate **7** afforded the 3-phenyl-ring oligomer **1**. However, with an excess of bis-phosphonate **7**, both styrylbenzyl–phosphonate **8** and oligomer **1** could be isolated.<sup>6</sup> For the synthesis of the 4-phenyl-ring oligomer **2**, the key intermediate, mono-phosphonate **9** was prepared by  $\text{LiAlH}_4$  reduction of **6**, followed by chlorination with  $\text{SOCl}_2$  and then a Michaelis–Arbuzov reaction. The Wadsworth–Emmons reaction of **9** and terephthalaldehyde monodiethylacetal **10** followed by an acidic work up afforded the corresponding styrylaldehyde **11**. Oligomer **2** was finally obtained by the Wadsworth–Emmons reaction of **8** and **11**.



Scheme 1. Synthesis of hexylsulfanyl substituted oligophenylenevinylenes **1** and **2**, respectively. Conditions: (i)  $\text{K}_2\text{CO}_3$ , DMSO,  $140^\circ\text{C}$ , 50%; (ii) *n*-BuLi, THF,  $-78^\circ\text{C}$ ; (iii) *N*-formylmorphine; (iv) HCl, 80–95%; (v) NaH, DME, rt, 50–65%; (vi)  $\text{LiAlH}_4$ , THF,  $0^\circ\text{C}$ , 83%; (vii)  $\text{SOCl}_2$ , pyridine,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ , 60%; (viii)  $\text{P}(\text{OEt})_3$ ,  $150^\circ\text{C}$ , 69%

In view of the electronic absorption spectra of **1** and **2**, both oligomers show strong and intense low-lying absorption bands with apparent vibronic structures suggesting the coplanar conformation (Fig. 1) The absorption maximum of the higher homologous oligomer **2** ( $\lambda_{\text{max}} = 398 \text{ nm}$ ) is 11 nm red-shifted in  $\text{CHCl}_3$  with a concomitant increase in extinction coefficient ( $\epsilon_{\text{max}} = 6.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), compared to those of **1** ( $\lambda_{\text{max}} = 377 \text{ nm}$ ,  $\epsilon_{\text{max}} = 4.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). In addition, the fluorescence maxima of oligomer **2** are at longer wavelengths ( $\lambda_{\text{em}} = 420$  and  $444 \text{ nm}$  for **1** and  $441$  and  $469 \text{ nm}$  for **2**). With an incorporation of the hexylsulfanyl substituents, the fluorescence quantum yield of the three-phenyl-ring oligomer, **1** ( $\Phi = 0.15$ ) decreases substantially as compared to that of the unsubstituted counterparts;<sup>7</sup> however, there is a fourfold enhancement in the fluorescence quantum yield with an addition of a phenylenevinylene unit (**2**;  $\Phi = 0.65$ ).

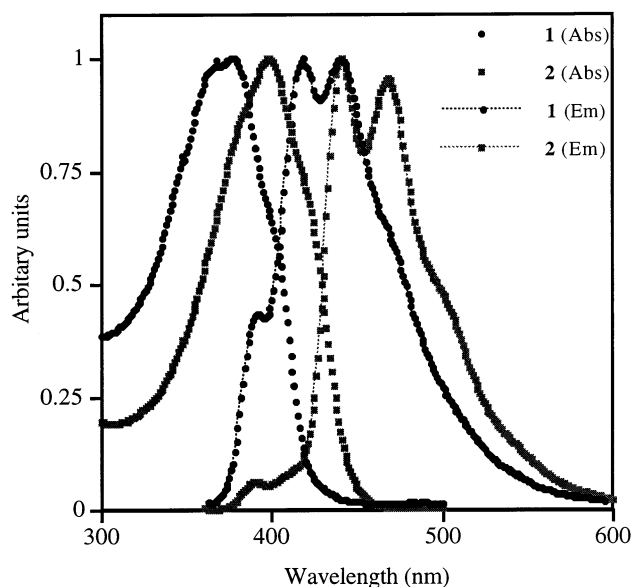


Figure 1. Normalized absorption and emission spectra of **1** and **2** in chloroform

To investigate the sensing properties of these OPVs towards various heavy metal ions, optode membrane sensors containing 3 wt% of oligomer **1** and **2** were fabricated.<sup>8</sup> It has been found that these OPV-based optode sensors show no significant change in fluorescence intensity upon contact with  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Co}^{2+}$  ions in the buffer solution  $\text{KNO}_3/\text{HNO}_3$ , respectively. However, there is a dramatic quenching in fluorescence intensity upon contact with  $\text{Ag}^+$  ions, suggesting that these OPV-based optode sensors are sensitive and selective to  $\text{Ag}^+$  ions. The fluorescence spectra of these optode sensors in response to various concentrations of  $\text{Ag}^+$  ions are shown in Figs. 2 and 3, respectively. It is evident that the **2**-based optode sensor exhibits higher sensitivity than that of its lower homologue.

In summary, novel hexylsulfanyl substituted oligophenylenevinylenes have been designed and synthesized as fluoroionophores for membrane optode sensing. It has been shown that these OPV-based optode sensors selectively respond to  $\text{Ag}^+$  ions. In addition, the 4-phenyl-ring oligomer-based optode sensor exhibits higher sensitivity than that of the 3-phenyl-ring counter-

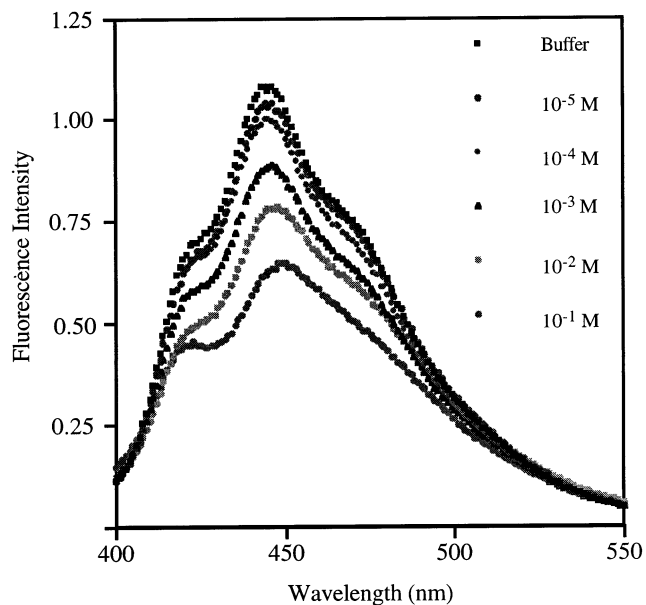


Figure 2. Fluorescence spectra of the 1-based optode sensor in various concentrations of  $\text{Ag}^+$  ions in 2 M  $\text{KNO}_3$  + 2 M  $\text{HNO}_3$  buffer solution with excitation at 383 nm

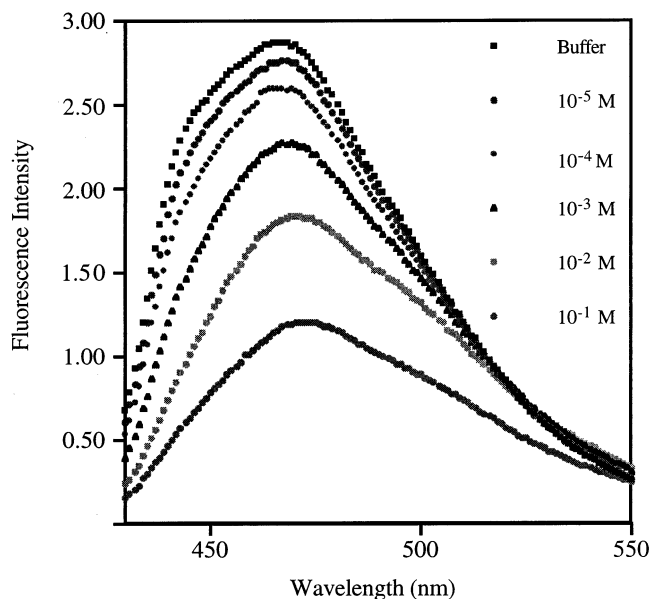


Figure 3. Fluorescence spectra of the 2-based optode sensor in various concentrations of  $\text{Ag}^+$  ions in 2 M  $\text{KNO}_3$  + 2 M  $\text{HNO}_3$  buffer solution with excitation at 398 nm

part. These OPV-based Ag-optode sensors show potential for practical applications. Further optimization of these hexylsulfanyl-substituted OPV-based optode sensors for  $\text{Ag}^+$  ion sensing is still under investigation.

## Acknowledgements

This work was supported by Faculty Research Grants (FRG/99-00/II-11) from Hong Kong Baptist University, and Competitive Earmarked Research Grant (HKBU 2054/98P).

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5. Spectroscopic data: **1**:  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (s, 4 H), 7.06 (s, 4H), 7.00 (s, 4H), 2.93 (t,  $J=7.29$  Hz, 8 H), 2.85 (t,  $J=7.29$  Hz, 4 H), 1.24–1.81 (m, 48H), 0.82–0.93 (m, 18H). MS (FAB)  $m/z$  979.7 ( $\text{M}^+$ ). Mp=85–88°C. **2**:  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (s, 8H), 7.13 (s, 2H), 7.06 (s, 4H), 7.00 (s, 4H), 2.93 (t,  $J=7.29$  Hz, 8H), 2.85 (t,  $J=7.29$  Hz, 4H), 1.24–1.78 (m, 48H), 0.84–0.90 (m, 18H). MS (FAB)  $m/z$  1081.0 ( $\text{M}^+$ ). Mp=49–54°C. The yields reported in Scheme 1 have not been optimized.
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