

ฟลูออเรสเซนซ์คิโมเซ็นเซอร์จากสารประกอบคอนจูเกตพอลิฟีนิลีนเอไทม์ลีนที่มีหมู่ซาลิไซลด์  
ไฮด์สำหรับตรวจวัดแอนไอออน



นางสาวชนัญธิตา จงโวหาร



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต  
สาขาวิชาเคมี ภาควิชาเคมี  
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย  
ปีการศึกษา 2556  
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย



5471938123

Fluorescence chemosensors from conjugated phenylene ethynylene compounds  
containing salicylaldehyde group for anion detection.

Miss Chanantida Jongwohan



A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science Program in Chemistry  
Department of Chemistry  
Faculty of Science  
Chulalongkorn University  
Academic Year 2013  
Copyright of Chulalongkorn University

Thesis Title Fluorescence chemosensors from conjugated phenylene ethynylene compounds containing salicylaldehyde group for anion detection.  
By Miss Chanantida Jongwohan  
Field of Study Chemistry  
Thesis Advisor Assistant Professor Sumrit Wacharasindhu, Ph.D.  
Thesis Co-Advisor Associate Professor Mongkol Sukwattanasinitt, Ph.D.

---

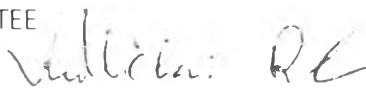
Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree



..... Dean of the Faculty of Science

(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE



..... Chairman

(Associate Professor Yudhichai Parasuk, Ph.D.)



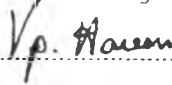
..... Thesis Advisor

(Assistant Professor Sumrit Wacharasindhu, Ph.D.)




..... Thesis Co-Advisor

(Associate Professor Mongkol Sukwattanasinitt, Ph.D.)



..... Examiner

(Associate Professor Voravee Hoven, Ph.D.)



..... External Examiner

(Sung Smarmoo, Ph.D.)



ขณัฎฐิตา จงโวหาร : ฟลูออเรสเซนซ์คีโมเซ็นเซอร์จากสารประกอบคอนจูเกตพอลิฟีนีลีนเอไธนีนลินที่มีหมู่ซาลิไซลัลดีไฮด์สำหรับตรวจวัดแอนไอออน. (Fluorescence chemosensors from conjugated phenylene ethynylene compounds containing salicylaldehyde group for anion detection.) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. สัมฤทธิ์ วัชรสินธุ์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ. ดร. มงคล สุขวัฒนาสินธุ์, 81 หน้า.

ฟลูออเรสเซนซ์โมเลกุลชนิดใหม่ เช่น พอลิฟีนีลีนเอไธนีนลินชนิดที่หนึ่งถึงสี่ และฟีนีลีนเอไธนีนลินชนิดที่หนึ่งและสอง ที่มีหมู่ซาลิไซลัลดีไฮด์เป็นองค์ประกอบในโครงสร้าง ถูกเตรียมมาเพื่อใช้เป็นตัวตรวจวัดหาไอออนของไซยาไนด์ พอลิฟีนีลีนเอไธนีนลินชนิดที่หนึ่ง สอง และพอลิฟีนีลีนเอไธนีนลินชนิดที่สามถูกสังเคราะห์ได้จาก แคลเซียมคาร์ไบด์ที่เป็นตัวให้แก๊สเอเซทิลีน ในขณะที่พอลิเมอร์แบบสลับชนิดที่สี่ถูกสังเคราะห์มาจาก อนุพันธ์ของไดโอน น้ำหนักโมเลกุลของพอลิเมอร์ดังกล่าวอยู่ในช่วง  $6.21 \times 10^3 - 1.86 \times 10^4$  ดาลตัน ส่วน โมเลกุลขนาดเล็ก หรือฟีนีลีน เอไธนีนลินชนิดที่หนึ่งและสอง ถูกสังเคราะห์จากปฏิกิริยาการเข้าคู่กัน ได้ผลิตภัณฑ์ร้อยละ 44 และร้อยละ 42 ตามลำดับ คุณสมบัติทางกายภาพของทั้งพอลิฟีนีลีน เอไธนีนลินทั้งสี่ชนิด และฟีนีลีนเอไธนีนลินทั้งสองชนิด มีความยาวคลื่นการดูดกลืนแสงสูงสุดอยู่ในช่วง 315-475 นาโนเมตร และคายแสงสูงสุดอยู่ในช่วง 363-508 นาโนเมตร อย่างไรก็ตามความสามารถในการให้สัญญาณฟลูออเรสเซนซ์ของพอลิฟีนีลีน เอไธนีนลินชนิดที่สองถึงสี่ กับไอออนลบทั้งสิบสองชนิดจะให้การเพิ่มสัญญาณฟลูออเรสเซนซ์ที่ต่ำในตัวทำละลายผสมระหว่าง เตตระไฮโดรฟิวเรนกับเฮกเซน บัฟเฟอร์ สำหรับในกรณีของพอลิฟีนีลีน เอไธนีนลินชนิดที่หนึ่งการเติมสารละลายไซเดียม ไซยาไนด์ที่ความเข้มข้น 1 ไมโครโมลาร์ สัญญาณฟลูออเรสเซนซ์จะเพิ่มขึ้น 9.69 เท่า แต่เนื่องจาก พอลิฟีนีลีน เอไธนีนลินชนิดที่หนึ่งมีความสามารถในการละลายในตัวทำละลายเตตระไฮโดรฟิวเรนจึงไม่สามารถนำมาใช้เป็นตัวตรวจจับได้ ในกรณีของโมเลกุลขนาดเล็ก (ฟีนีลีนชนิดที่หนึ่ง) มีความจำเพาะเจาะจงในการจับกับไอออนของไซยาไนด์ และความเข้มข้นต่ำสุดที่สามารถตรวจวัดได้อยู่ที่ 2.5 ไมโครโมลาร์ ในขณะที่ ฟีนีลีน เอไธนีนลินชนิดที่สอง มีความจำเพาะต่อไอออนลบน้อย แต่สามารถตรวจจับไอออนของฟลูออไรด์ออกจากเฮไลต์ไอออนตัวอื่นๆ โดยความเข้มข้นต่ำสุดที่สามารถตรวจจับได้อยู่ที่ 30 ไมโครโมลาร์ ดังนั้นในงานวิจัยนี้จึงใช้พอลิฟีนีลีน เอไธนีนลินชนิดที่หนึ่ง และฟีนีลีน เอไธนีนลินชนิดที่หนึ่งเป็นตัวตรวจจับไอออนของไซยาไนด์ และใช้ฟีนีลีน เอไธนีนลินชนิดที่สองตรวจจับไอออนของฟลูออไรด์ออกจากเฮไลต์ไอออนชนิดอื่นๆ

ภาควิชา เคมี  
สาขาวิชา เคมี  
ปีการศึกษา 2556

ลายมือชื่อนิสิต ทีตินา ขลิบ  
ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก \_\_\_\_\_  
ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม \_\_\_\_\_

# # 5471938123 : MAJOR CHEMISTRY

KEYWORDS: CYANIDE SENSOR / FLUORESCENSOR / SONOGASHIRA COUPLING

CHANANTIDA JONGWOHAN: Fluorescence chemosensors from conjugated phenylene ethynylene compounds containing salicylaldehyde group for anion detection.. ADVISOR: ASST. PROF. SUMRIT WACHARASINDHU, Ph.D., CO-ADVISOR: ASSOC. PROF. MONGKOL SUKWATTANASINITT, Ph.D., 81 pp.

The new fluorescence molecules PPE I – PPE IV and PE I and PE II, containing salicylaldehyde group as a receptor unit are prepared and the sensing ability toward  $\text{CN}^-$  are investigated. The homopolymer PPE I - II and random copolymer III are prepared from calcium carbide as the acetylene source while the alternate copolymer PPE IV are prepared from the corresponding diyne derivative. The molecular weights of PPEs are determined with GPC showing in the range of  $6.21 \times 10^3$  -  $1.86 \times 10^4$  Da. On the other hands, the small molecule PE I and PE II are prepared by Sonogashira coupling reaction to give the yellow solid in 44 % and 42% yield, respectively. The NMR spectroscopy and mass spectrometry data confirm the structures of PE I and PE II. The photophysical properties of PPEs and PEs showed absorption at ca. 315-457 nm and emission at 363-508 nm. However, the fluorescence sensing ability of PPE II, III and IV toward a variety of 12 anions shows small fluorescence enhancement signal in mixture of THF/ aqueous HEPES buffer. In case of PPE I, the addition of NaCN solution at 1 mM concentration increases the fluorescence signal of PPE I giving I/I0 ratio = 9.69. However, due to its poor solubility of PPE I, the sensing ability cannot be quantified and further investigated. In case of small molecule, PE I shows fluorescence enhancement specifically toward  $\text{CN}^-$  with the detection limits of  $2.5 \mu\text{M}$  while PE II gave a lower selectivity upon testing with the same set of anions. Interestingly, PE II shows specific fluorescence enhancement with  $\text{F}^-$  over other halide ion with the detection limits of  $30 \mu\text{M}$ . These results suggest the high potential use of PPE I and PE I for the detection of cyanide ion while the identification of  $\text{F}^-$  from other halide ion can be done with PE II.

Department: Chemistry

Field of Study: Chemistry

Academic Year: 2013

Student's Signature Chanantida

Advisor's Signature [Signature]

Co-Advisor's Signature [Signature]

173542247



## ACKNOWLEDGEMENTS

I wish to express my gratitude to my adviser, Assistant Professor Dr. Sumrit Wacharasindhu, my co-adviser Associate Professor Dr. Mongkol Sukwattanasinitt, invaluable guidance and encouragement throughout the course of this research.

I would like to gratefully acknowledge the committee, Associate Professor Vudhichai Parasuk, Associate Professor Voravee Hoven, and Dr. Sung Smanmoo for their comments, guidance and extending cooperation over my presentation. I would like to thank Dr. Anawat Ajavakom and Assistant Professor Dr. Paitoon Rashatasakhon for their attention and suggestions during our research group meeting.

Furthermore, I gratefully thank to my friends for their genuine, Ms. Nopparat Thavornsin, Ms. Manutchanok Boonsri, Mr. Janewit Khaokeaw, Mr. Thus La-ongnuan, Mr. Sattawat Dueansawang and everyone in MAPS group for spirit, smile, good wish and their helps in everything.

I would like to express my gratitude to Organic Synthesis Research Unit (OSRU), Department of Chemistry, Faculty of Science, Chulalongkorn University for providing the chemicals and facilities throughout the course of study.

This study is financially supported by the Thailand Research Fund (TRF-RSA5480004) and National Nanotechnology Center (NANOTEC), NSTDA (NN-B-22-FN9-10-52-06), Center for Petroleum, Petrochemicals and Advanced Materials, Chulalongkorn University. This work is part of the Project for Establishment of Comprehensive Center for Innovative Food, Health Products and Agriculture supported by the Thai Government Stimulus Package 2 (TKK2555, SP2), Asahi Glass Foundation, and also the National Research University Project of CHE (AM1006A).

Finally, I would like to express my thankfulness to my beloved parents who always stand by my side during both of my pleasant and hard time.



## CONTENTS

	Page
THAI ABSTRACT .....	iv
ENGLISH ABSTRACT .....	v
ACKNOWLEDGEMENTS .....	vi
CONTENTS .....	vii
CHAPTER I Introduction.....	1
1.1 Overview.....	1
1.2 Structures of fluorescence compounds.....	1
1.3 Introduction to fluorescence.....	3
1.4 Internal charge transfer.....	4
1.5 Literature review on fluorescence sensor for cyanide ion.....	5
1.6 Poly(phenylene ethynylene)s and their sensor applications .....	8
1.7 Literature review on sensor from poly(phenylene ethynylene)s .....	9
1.8 Objective of this work.....	11
CHAPTER II Experiment .....	13
2.1 Chemical and Materials .....	13
2.2 Analytical Instruments .....	13
2.3 Synthesis of monomer.....	14
2.3.1 Synthesis of diiodosalicylaldehyde (2a).....	14
2.3.2 Synthesis of dibutoxybenzene (2c).....	14
2.3.3 Synthesis of 1,4-dibutoxy-2,5-diiodobenzene (3c).....	15
2.3.4 Synthesis of 1,4-dibutoxy-2,5-bis(2-(trimethylsilyl)ethynyl)benzene (4c).....	16
1,4-dibutoxy-2,5-diiodobenzene (3c).....	16
2.3.5 Synthesis of 1,4-dibutoxy-2,5-diethynylbenzene (5c) .....	17
2.3.6 Synthesis of 8-octylsalicylaldehyde.....	17
2.3.7 Synthesis of 3,5-diiodo-4-octylsalicylaldehyde .....	18
2.3.8 Synthesis of 5-iodosalicylaldehyde (1d) .....	18
2.3.7 Synthesis of 2-hydroxy-5-(triethylsilyl)benzaldehyde (2d).....	19



1729542247

	Page
2.3.8 Synthesis of 2-hydroxy-5-ethynylbenzaldehyde (3d).....	19
2.4 Synthesis of Poly(phenylene ethynylene).....	20
2.4.1 Synthesis of PPE I.....	20
2.4.2 Synthesis of PPE III.....	21
2.4.3 Synthesis of PPE II.....	21
2.4.4 Synthesis of PPE IV.....	22
2.5 Synthesis of phenylene ethynylene.....	23
2.5.1 Synthesis of PE I.....	23
2.5.2 Synthesis of PE II.....	24
2.6 Photophysical properties.....	24
2.6.1 UV-Visible spectroscopy.....	24
2.6.2 Fluorescence spectroscopy.....	25
2.6.3 Fluorescence quantum yield.....	25
2.7 Fluorescence sensor study.....	25
2.7.1 Anion sensor.....	25
2.7.2 Surfactant study.....	26
CHAPTER III Results and Discussion.....	27
3.1 Cyanide fluorescence sensors from poly(phenyleneethynylene)s (PPEs) : PPE I, PPE II, PPE III, and PPE IV.....	27
3.1.1 Synthesis and characterization of PPE I, and PPE II.....	28
3.1.2 Synthesis and characterization of PPE III, and PPE IV.....	31
3.1.3 Molecular weight determination and photophysical properties of PPEs..	35
3.1.4 Sensing ability of PPE I, PPE II, PPE III, and PPE IV.....	37
3.2 Cyanide fluorescence sensors from PE I and PE II.....	40
3.2.1 Synthesis and characterization of PE I and PE II.....	40
3.2.2 Photophysical properties study of PE I and PE II.....	43
3.2.3 Screening of PE I and PE II toward anions.....	44
3.2.4 Fluorescence sensor study of PE I.....	45



1729542247



	Page
3.2.3 Fluorescent sensors study of PE II .....	51
CHAPTER IV CONCLUSION.....	58
REFERENCES .....	59
APPENDIX.....	63
VITA.....	81



## LIST OF TABLE

Table 1.1 Example of fluorescence sensor for amino acid and cyanide ion.....	7
Table 1.2 Example of fluorescence sensor form PPE.....	9
Table 3.1 Molecular weight, solubility, characteristics of polymer, and color under blacklight of all PPEs.....	36
Table 3.2 Photophysical properties of PE I and PE II .....	44
Table 3.3 Photophysical properties of PE I (5 $\mu\text{M}$ ) and PE II (5 $\mu\text{M}$ ) upon the addition of sodium cyanide (30 equiv) and sodium fluoride (60 equiv) in 10% HEPES buffer pH 7.4 10 $\mu\text{M}$ / 90% DMSO.....	57



## LIST OF FIGURE

<b>Figure 1.1</b> Molecular structures of some common $\pi$ -conjugated polymers.....	2
<b>Figure 1.2</b> Molecule structure of some common $\pi$ -conjugate molecules and their emission range in the visible region. ....	3
<b>Figure 1.3</b> Franck-Condon energy diagram explaining fluorescence process. [15, 16]..	4
<b>Figure 1.4</b> Potential energy surface of the ground state ( $S_0$ ) is excited to $S_1$ or $S_2$ and then relaxed to LE state, and ICT state (FC = Franck Condon). ....	5
<b>Figure 1.5</b> Fluorescence probe for the detection of cyanide ion .....	6
<b>Figure 1.6</b> Color changes of 4r solutions upon addition of cyanide ion and other anions under visible light. ....	6
<b>Figure 1.7</b> Structural model of poly(phenylene ethynylene).....	8
<b>Figure 1.8</b> Structure of PPE containing hydroxylamine (left) and fluorescence enhancement for $\alpha$ -hydroxyl carboxylic acid and L- isomer derivatives of <b>12r</b> (right). ....	10
<b>Figure 1.9</b> Fluorescence sensor model for the detection of cyanide ion. ....	11
<b>Figure 3.1</b> Structure of polymers PPE-I, PPE-II, PPE-III, and PPE-IV.....	28
<b>Figure 3.2</b> $^1\text{H}$ NMR of 3, 5-diiodosalicylaldehyde ( <b>2a</b> ).....	29
<b>Figure 3.3</b> $^1\text{H}$ NMR of <b>2b</b> and <b>3b</b> .....	30
<b>Figure 3.4</b> FT-IR spectrum of PPE I and PPE II.....	31
<b>Figure 3.5</b> $^1\text{H}$ NMR of 1,4-dibutoxybenzene ( <b>2c</b> ) and 2,5-dibutoxy-1,4-diiodobenzene ( <b>3c</b> ).....	33
<b>Figure 3.6</b> $^1\text{H}$ NMR of <b>4c</b> , and <b>5c</b> .....	34
<b>Figure 3.7</b> FT-IR spectrum of PPE III (red spectrum) compare with poly(phenylene ethynylene) (blue spectrum) which is no element of salicylaldehyde unit .....	35
<b>Figure 3.8</b> Emission spectra of the solution of PPE I and PPE II upon the addition of sodium cyanide (1 mM) in 90% THF/10 mM HEPES buffer pH 7.4 ( $\lambda_{\text{ex}}$ = 341 nm (PPE I) and $\lambda_{\text{ex}}$ = 365 nm (PPE II).....	37
<b>Figure 3.9</b> The polymer deflection caused by the diyne unit.....	38
<b>Figure 3.10</b> PPE II 50 $\mu\text{M}$ (left) and 100 $\mu\text{M}$ (right) upon the addition of NaCN and other anions 10 eq. ( $\lambda_{\text{ex}}$ = 365 nm).....	39



<b>Figure 3.11</b> PPE III (left) and PPE IV (right) 10 $\mu$ M upon the addition of NaCN and other anion(10 eq) in 90%THF/10 mM HEPES buffer pH 7.4 ( $\lambda_{ex}$ = 417 nm, $\lambda_{em}$ = 463) nm	39
<b>Figure 3.12</b> Structure of PE I and PE II.....	40
<b>Figure 3.13</b> $^1\text{H}$ NMR (400 MHz) spectra of starting material compound B and PE I ...	41
<b>Figure 3.14</b> $^1\text{H}$ NMR (400 MHz) spectra of 3d, 3c, and PE II .....	43
<b>Figure 3.15</b> Normalized absorption spectra PE I and PE II (10 $\mu$ M) in 90%DMSO/10 mM HEPES buffer pH 7.4 .....	44
<b>Figure 3.16</b> Emission spectrum of PE I (left) and PE II (right) at 5 $\mu$ M with 13 anions 2 eq and 30 eq, respectively in 90% DMS in HEPES buffer pH 7.4 .....	45
<b>Figure 3.17</b> Bar chart representing the fluorescence enhancement ( $I/I_0$ ) of PE I (5 $\mu$ M) upon the addition of sodium cyanide (2 eq) in HEPES buffer pH 7.4 (10 mM) in the presence of various surfactants (10 mM). The fluorescence intensity at the emission peak of each system was used.....	46
<b>Figure 3.18</b> Bar chart representing the fluorescence enhancement ( $I/I_0$ ) of PE I (5 $\mu$ M) upon the addition of sodium cyanide (2 eq) in HEPES buffer pH 7.4 (10 mM) in the presence of various surfactants (10 mM). The fluorescence intensity at the emission peak of each system was used.....	46
<b>Figure 3.19</b> The bars represent the fluorescence enhancement ratio ( $I/I_0$ ) of PE I (5 $\mu$ M) at various equiv of cyanide in DTAB (20 mM)/HEPES buffer pH 7.4 (10mM). .....	47
<b>Figure 3.20</b> Time-dependent changes in the fluorescence intensity of PE I (5 $\mu$ M) upon addition of cyanide 30 equivalent in DTAB (20 mM)/HEPES buffer pH 7.4 (10mM). ....	48
<b>Figure 3.21</b> Bar represent the fluorescence enhancement ratio ( $I/I_0$ ) of PE II (5 $\mu$ M ) at various pH of buffer (10 $\mu$ M in DTAB (20 $\mu$ M) upon the addition of CN- 60 equiv.....	48
<b>Figure 3.22</b> Fluorescence enhancement ratio ( $I/I_0$ ) of PE I in the presence of various anions. The data were based on the fluorescence intensity at 363 nm acquire from the solution in 10 $\mu$ M HEPES buffer pH 7.4 containing DTAB 20 $\mu$ M with PE I 5 $\mu$ M and anions 30 eq.....	49
<b>Figure 3.23</b> Fluorescence enhancement ratio ( $I/I_0$ ) of PE I in the presence of cyanide ion and another anion. The data were based on the fluorescence intensity at 363 nm acquire from the solution in 10 $\mu$ M HEPES buffer pH 7.4 containing DTAB 20 $\mu$ M with PE I 5 $\mu$ M and anions 0.15 mM.....	50



1729542247

<b>Figure 3.24</b> $^1\text{H-NMR}$ titration of PE I toward cyanide ion in $\text{DMSO-d}_6$ .....	51
<b>Figure 3.25</b> Emission spectrum of the solution of PE II $5\ \mu\text{M}$ (blue line) upon the addition of sodium fluoride 30 eq (orange line) in 10% HEPES buffer pH 7.4/10 $\mu\text{M}$ /90% DMSO.....	52
<b>Figure 3.26</b> Bar chart representing the fluorescence enhancement ( $I/I_0$ ) of PE II ( $5\ \mu\text{M}$ ) upon the addition of sodium fluoride (30 eq) in HEPES buffer pH 7.4 (10 mM) in the presence of various surfactants (10 $\mu\text{M}$ ).....	52
<b>Figure 3.27</b> Bar chart representing the fluorescence enhancement ( $I/I_0$ ) of PE II ( $5\ \mu\text{M}$ ) upon the addition of sodium fluoride (30 eq) in HEPES buffer pH 7.4 (10 mM) in the presence of various concentration of Brij.....	53
<b>Figure 3.28</b> Bar represent the fluorescence enhancement ratio ( $I/I_0$ ) of PE II $5\ \mu\text{M}$ and addition fluoride 30 eq at various pH of buffer (10 $\mu\text{M}$ in Brij (30 $\mu\text{M}$ ). .....	53
<b>Figure 3.29</b> The bars represent the fluorescence enhancement ratio ( $I/I_0$ ) of PE II ( $5\ \mu\text{M}$ ) at various equivalent of fluoride in Brij (30 $\mu\text{M}$ )/HEPES buffer pH 7.4 (10mM). .....	54
<b>Figure 3.30</b> Time-dependent changes in the fluorescence intensity of PE I ( $5\ \mu\text{M}$ ) upon addition of fluoride 60 equiv in Brij (20 $\mu\text{M}$ )/HEPES buffer pH 7.4 (10mM). .....	55
<b>Figure 3.31</b> Fluorescence enhancement ratio ( $I/I_0$ ) of PE II $5\ \mu\text{M}$ in the presence of various halide ions (300 $\mu\text{M}$ ). The color of PE II with various halide ion under backlight (inset).....	55
<b>Figure 3.32</b> Fluorescence enhancement ratio ( $I/I_0$ ) of PE II $5\ \mu\text{M}$ in the presence of fluoride ion and another halide ion (300 $\mu\text{M}$ ). .....	56
<b>Figure S.1</b> $^1\text{H-NMR}$ spectrum of 1,4-dibutoxybenzene (2c).....	64
<b>Figure S.2</b> $^{13}\text{C-NMR}$ spectrum of 1,4-dibutoxybenzene (2c).....	64
<b>Figure S.3</b> $^1\text{H-NMR}$ spectrum of bis-diiodo1,4-dibutoxybenzene .....	65
<b>Figure S.4</b> $^{13}\text{C-NMR}$ spectrum of bis-diiodo1,4-dibutoxybenzene (3c).....	65
<b>Figure S.5</b> $^1\text{H-NMR}$ spectrum of 1,4-dibutoxy-2,5-bis(2(trimethylsilyl)ethynyl)benzene .....	66
<b>Figure S.6</b> $^{13}\text{C-NMR}$ spectrum of 1,4-dibutoxy-2,5-bis(2(trimethylsilyl)ethynyl)benzene .....	66



1729542247

Figure S. 7 $^1\text{H-NMR}$ spectrum of 1,4-dibutoxy-2,5diethynylbenzene.....	67
Figure S. 8 $^1\text{H-NMR}$ spectrum of 3,5-diiodosalicylaldehyde.....	67
Figure S.9 $^{13}\text{C-NMR}$ spectrum of 3,5-diiodosalicylaldehyde.....	68
Figure S. 10 $^1\text{H-NMR}$ spectrum of 4-octylsalicylaldehyde.....	68
Figure S.11 $^1\text{H-NMR}$ spectrum of 3, 5-diiodo-4-octylsalicylaldehyde .....	69
Figure S.12 $^1\text{H-NMR}$ spectrum of 5-iodosalicylaldehyde .....	69
Figure S.13 $^{13}\text{C-NMR}$ spectrum of 5-iodosalicylaldehyde .....	70
Figure S. 14 $^1\text{H-NMR}$ spectrum of 5-(2-(trimethylsilyl)ethynyl)salicylaldehyde .....	70
Figure S.15 $^1\text{H-NMR}$ spectrum of 5-ethynyl salicylaldehyde .....	71
Figure S.16 $^1\text{H-NMR}$ spectrum of PE I.....	71
Figure S.17 $^{13}\text{C-NMR}$ spectrum of PE I.....	72
Figure S.18 $^1\text{H-NMR}$ spectrum of PE II.....	73
Figure S.19 $^{13}\text{C-NMR}$ spectrum of PE II.....	73
Figure S.20 MALDI-TOF-MS of PE II.....	74
Figure S.21 FT-IR spectrum of PPE I.....	74
Figure S.22 FT-IR spectrum of PPE II.....	75
Figure S.23 FT-IR spectrum of PPE III(c).....	75
Figure S.24 FT-IR spectrum of PPE IV.....	76
Figure S.25 GPC of PPE II.....	76
Figure S.26 GPC of PPE IV.....	77
Figure S.27 GPC of PPE III(a) .....	77
Figure S.28 GPC of PPE III(b).....	77
Figure S.29 GPC of PPE III(d).....	78
Figure S.30 GPC of PPE III(c).....	78
Figure S.31 Molar absorptivity of PE I.....	78
Figure S.32 Molar absorptivity of PE II .....	79
Figure S.33 Quantum yield of PE I toward $\text{CN}^-$ .....	79
Figure S.34 Quantum yield of PE II toward $\text{F}^-$ .....	79
Figure S.35 Fluorescence intensity of PE I (5 $\mu\text{M}$ ) at various equiv of cyanide in 99%DMSO/ HEPES buffer pH 7.4.....	80



**Figure S.36** Fluorescence intensity of PE II (5  $\mu\text{M}$ ) at various equiv of fluoride in 90%DMSO/ HEPES buffer pH 7.4. .... 80



## LIST OF SCHEME

Scheme 1.1 The mechanism of cyanide ion turn on of cumarin derivative <b>4r</b> .....	6
Scheme 1.2 Synthesis route of poly(phenylene ethynylene)s.....	9
Scheme 2.1 Synthesis of <b>2a</b> .....	14
Scheme 2.2 Synthesis of <b>2c</b> .....	14
Scheme 2.3 Synthesis of <b>3c</b> .....	15
Scheme 2.4 Synthesis of <b>4c</b> .....	16
Scheme 2.5 Synthesis of <b>5C</b> .....	17
Scheme 2.6 Synthesis of <b>2b</b> .....	17
Scheme 2.7 Synthesis of <b>3b</b> .....	18
Scheme 2.8 Synthesis of <b>1d</b> .....	18
Scheme 2.9 Synthesis of <b>2d</b> .....	19
Scheme 2.10 Synthesis of <b>3d</b> .....	19
Scheme 2.11 Synthesis of PPE I.....	20
Scheme 2.12 Synthesis of PPE III.....	21
Scheme 2.13 Synthesis of PPE II.....	21
Scheme 2.14 Synthesis of PPE IV.....	22
Scheme 2.15 Synthesis of PE I.....	23
Scheme 2.16 Synthesis of PE II.....	24
Scheme 3.1 Synthetic route of poly(phenylene ethynylene) PPE I.....	28
Scheme 3.2 Synthetic route of Poly(phenylene ethynylene) PPE I, and PPE II.....	29
Scheme 3.3 Synthetic route of Poly(phenylene ethynylene) PPE III.....	32
Scheme 3.4 Synthetic route of Poly(phenylene ethynylene) PPE IV.....	32
Scheme 3.5 Synthetic route of phenylene ethynylene PE I.....	41
Scheme 3.6 The mechanism of PE I toward cyanide ion.....	50



1728542247



## LIST OF ABBREVIATIONS

calcd	calculated
$^1\text{H-NMR}$	proton nuclear magnetic resonance
$^{13}\text{C-NMR}$	carbon-13 nuclear magnetic resonance
$\text{CDCl}_3$	deuterated chloroform
d	doublet (NMR)
dd	doublet of doublet (NMR)
t	triplet (NMR)
m	multiplet (NMR)
s	singlet (NMR)
$J$	coupling constant
FT-IR	fourier transform infrared spectroscopy
Hz	Hertz
Mg	milligram (s)
mL	milliliter (s)
mmol	millimole (s)
g	gram (s)
IR	infrared
H	hour (s)
Equiv	equivalent (s)
M.W.	molecular weight
M	molar
$\text{MHz}$	megahertz
Rt	room temperature
$m/z$	mass per charge
HRMS	high resolution mass spectrum



1729542247

TiHF	tetrahydrofuran
DMSO	dimethylsulfoxide
UV	ultraviolet
°C	degree Celsius
% yield	percentage yield
μM	micromolar (s)
μL	microliter (s)
δ	chemical shift
Φ	quantum yield
PPE	poly(phenylene ethynylene)
PE	phenylene ethynylene
K <sub>2</sub> CO <sub>3</sub>	potassium carbonate
DBU	1,8-Diazabicycloundec-7-ene
CuI	copper iodided
CH <sub>2</sub> Cl <sub>2</sub>	methylene chloride
M.W.	molecular weight
Pd	palladium
PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	bis(triphenylphosphine)palladium(II) chloride *
TMS	trimethylsilyl
TEA	triethylamine
Na <sub>2</sub> SO <sub>4</sub>	sodium sulfate
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	sodium thiosulfate
KI	potassium iodide
ppm	Parts per million
PPh <sub>3</sub>	triphenylphosphene
DMSO-d <sub>6</sub>	Deuterated dimethyl sulfoxide
N <sub>2</sub>	nitrogen gas
PE	phenylene ethynylene



$\text{NaHCO}_3$	sodium bicarbonate
ICT	internal charge transfer
$\epsilon$	Molar absorptivity
$\lambda$	Lambda

