พอลิไดแอเซทิลีนจากแอมฟิฟิลิกไดแอเซทิลีนและสมบัติการเปลี่ยนสีตามตัวทำละลาย

นางสาว ทิฆัมพร เอียดคง

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POLYDIACETYLENE FROM AMPHIPHILIC DIACETYLENE AND THEIR SOLVATOCHROMISM PROPERTY

Miss Thichamporn Eaidkong

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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By Miss Thichamporn Eaidkong
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ทิฆัมพร เอียดคง : พอลิไดแอเซทิลีนจากแอมฟิฟิลิกไดแอเซทิลีนและสมบัติการเปลี่ยนสีตามตัวทำละลาย (POLYDIACETYLENE FROM AMPHIPHILIC DIACETYLENE AND THEIR SOLVATOCHROMISM PROPERTY) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: อ.ดร. สัมฤทธิ์ วัชรสินธุ์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ.ดร.มงคล สุขวัฒนาสินิทธิ์, 62 หน้า

งานวิจัยนี้ได้พัฒนาการเตรียมกระดาษเปลี่ยนสีที่มีพอลิไดแอเซทิลีน (PDA) เป็นเซ็นเซอร์อาเรย์ สำหรับการตรวจวัดและการแบ่งแยกสารประกอบอินทรีย์ระเหย เซ็นเซอร์อาเรย์ของพอลิไดแอเซทิลีนที่เคลือบลงบนกระดาษเตรียมได้จากไดแอเซทิลีนมอนอเมอร์ 8 ชนิดที่มีโครงสร้างแตกต่างกัน โดย 10,12-เพนตะโคซะไดอายน์โนอิก แอซิดและ10,12-ไตรโคซะไดอายน์โนอิก แอซิดได้รับจากแหล่งการค้าพาณิชย์ ขณะที่ไดแอเซทิลีนมอนอเมอร์อีก 5 ชนิด (3-8) จะสังเคราะห์อย่างจำเพาะสำหรับงานวิจัยในครั้งนี้ เมื่อเตรียมไดแอเซทิลีนมอนอเมอร์ได้สำเร็จ ไดแอเซทิลีนมอนอเมอร์ทั้งหมดได้ถูกนำมาขึ้นรูปบนกระดาษกรองด้วยกระบวนการหยดและแห้ง จากนั้นได้ทำการฉายแสงด้วยรังสียูวีเพื่อให้ได้พอลิไดแอเซทิลีนอยู่บนกระดาษที่มีสีน้ำเงิน เมื่อเซ็นเซอร์อาเรย์ได้สัมผัสกับไอของสารประกอบอินทรีย์ระเหยที่แตกต่างกัน 18 ชนิดจะเกิดรูปแบบของสีที่ไม่ซ้ำกัน การเปลี่ยนสีของกระดาษที่มีพอลิไดแอเซทิลีนตรึงอยู่นั้นได้รับการประเมินโดยการวัดค่าความเข้มของ RGB ของรูปที่ได้จากกล้องดิจิตอลและสแกนเนอร์ ค่า RGB ที่ได้จาก PDAทั้ง 8 ชนิด, ไอของสารประกอบอินทรีย์ระเหย 18 ชนิดและการวัดหาค่า 12 ซ้ำ สามารถนำมาจำแนกทางสถิติได้เป็น 18 กลุ่ม โดยใช้วิธีการวิเคราะห์องค์ประกอบหลัก (PCA) ซึ่งกลุ่มเหล่านี้สอดคล้องกับตัวทำละลายอินทรีย์แต่ละชนิด การใช้แฟคทอเรียลดิสคริมิเนทอะนาไลซิส (FDA) สามารถลดจำนวนของพอลิไดแอเซทิลีนเซ็นเซอร์อาเรย์ให้เหลือเพียง 2 เซ็นเซอร์โดยยังคงมีความถูกต้องไว้ที่ 100 เปอร์เซ็นต์ นอกจากนี้ การใช้กระดาษเปลี่ยนสีที่มีพอลิไดแอเซทิลีนเป็นเซ็นเซอร์อาเรย์ มาจำแนกน้ำมันรถยนต์ชนิดต่างๆ ที่ได้จากหลายบริษัทเป็นผลสำเร็จ

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต
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THICHAMPORN EAIDKONG: POLYDIACETYLENE FROM AMPHIPHILIC DIACETYLENE AND THEIR SOLVATOCHROMISM PROPERTY. ADVISOR: SUMRIT WACHARASINDHU, Ph.D., CO-ADVISOR: ASSOC. PROF. MONGKOL SUKWATTANASINITT, Ph.D., 62 pp.

This research work deals with development of a paper-based polydiacetylene (PDA) sensor array for detecton and discrimination of volatile organic compounds (VOCs). The sensor array is generated from a combination of eight structurally diversed diacetylene (DA) monomers. 10,12-pentacosadiynoic acid (PCDA) and 10,12-tricosadiynoic acid (TCDA) are commercially available whilst the other five DA monomers **3**-**8** are synthesized specifically for this application. Once obtained, DA monomers were fabricated on filter paper by drop and dry process followed by UV irradiation to produce blue paper-based PDA. The sensor array gives a unique colorimetric pattern after being exposed to vapors of 18 different VOCs. The color transition is evaluated by measuring the RGB values of photographic images obtained from digital camera and scanner. Measurement of RGB intensities obtained from 8 PDAs × 18 VOC vapors × 12 replicated measurements could be statistically classified into 18 clusters by principal component analysis (PCA). Each cluster distinctly corresponds to each specific solvent. Factorial discriminate analysis (FDA) also cross validates that the reduced PDA sensing array containing only 2 sensing element can give with 100% discriminating accuracy. Moreover, discrimination of various automotive fuels obtained from various sources was accomplished using this paper based PDA sensor array.

Field of Study : Petrochemistry and Polymer Science	Student's Signature ....
Academic Year : 2010	Advisor's Signature ....
	Co-advisor's Signature ....

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CONTENTS

Pages

Pages

Pages

LIST OF FIGURES

Figure **Pages**

Figure **Pages**

Figure **Pages**

Figure **Pages**

LIST OF SCHEMES

LIST OF ABBREVIATIONS

Abs	Absorbance
MeCN	Acetonitrile
Å	Angstrom
B5	Biodiesel
brs	Broad singlet
^{13}C-NMR	Carbon nuclear magnetic resonance
cm	Centimeter
δ	Chemical shift
$CHCl_3$	Chloroform
J	Coupling constant
^{o}C	Degree Celsius
$CDCl_3$	Deuterated chloroform
DA	Diacetylene
CH_2Cl_2	Dichloromethane
D	Diesel
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
EtOH	Ethanol
EtOAc	Ethyl acetate
EDC	1-ethyl-3-(3′-dimethylamino) carbodiimide HCl salt
FDA	Factorial discriminate analysis
FID	Flame ionization detector
γ	Gamma ray
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
G95	Gasohol 95
G91	Gasohol 91
B91	Gasoline 91
E20	Gasohol
g	Gram
Hz	Hertz

LB	Langmuir-Blodgett
LS	Langmuir-Scheafer
MeOH	Methanol
μL	Microlitre
μW	Microwatt
mL	Millilitre
mmol	Millimole
M	Molar
nm	Nanometer
AE-PCDA	*N*-(2-aminoethyl) pentacosa-10,12-diynamide
Et-PCDA	*N*-(2-(ethylamino) ethyl) pentacosa-10,12-diynamide
Br-Et-AEPCDA	*N*- ethyl-2-pentacosa-10,12-diynamidoethanaminium bromide
DCC	*N,N′*-dicyclohexylcarbodiimide
NDIR	Non-dispersive infrared
NHS	*N*-hydroxysuccinimide
6,8-19DA	6,8-nonadecadiynoic acid
ppm	Part per million
PCDA	10,12-pentacosadiynoic acid
cm^{-1}	Per centimetre
M^{-1}	Per molar
π	Pi bond
PID	Photo-ionization detector
PDA	Polydiacetylene
PDAs	Polydiacetylenes
PCA	Principal component analysis
^{1}H-NMR	Proton nuclear magnetic resonance
RGB	Red, green, blue color
cm^2	Square centimeter
TIF	Tag image file format
THF	Tetrahydrofuran
TCDA	10,12-tricosadiynoic acid
UV/vis	Ultra violet-visible

λ	Wavelength
VOCs	Volatile organic compounds
w/v	Weight by volume

CHAPTER I

INTRODUCTION

1.1 Overview

In recent years, development of sensor for volatile organic compounds (VOCs) has gained numerous attentions due to environmental and public safety concern posed by exposure to these substances [1-11]. A variety of VOC-responsive sensor systems have been developed for potential application as “electronic noses”. These efforts have led to the discovery of a variety of small molecule and polymer-based sensory compounds and systems. Reported sensor arrays for VOCs employ a wide range of sensing materials including small organic compounds [12,13], inorganic compounds [2,8,9,14] and conjugated polymer [4,6,10,12]. Changes in optical, electrochemical, conducting, fluorescence and chromic properties of those materials after exposure to VOCs provide a signal for the detection and identification of analytes. However, industrial application of aforementioned sensors are limited because they are cumbersome, non-portable, require expensive instrumentation, and resulting data are difficult to analyze. Also, polymeric supporting materials are not environmentally friendly and a method for quantitative discrimination of multiple solvents has not been developed. Thus, with these limitations in mind, the aim of this work is to demonstrate a strategy to conveniently fabricate a PDA sensor array that is inexpensive, portable and able to rapidly and a reliably produce a quantitative analysis to distinguish multiple VOCs.

1.2 Polydiacetylene (PDA)

Polydiacetylene (PDA) is one of the most intriguing classes of conjugated polymers as it possesses unique chromic properties that can be developed into practical colorimetric transducers in biosensors and chemosensors [15-26]. PDA is an ene-yne π-conjugated polymer which is generally prepared from the topological polymerization of a diacetylene monomer under UV light or γ-ray irradiation. Its π-conjugated backbone which is the chromophore of this polymer can be disturbed by various external stimuli to cause changes in its backbone that affects electronic absorption and color.

1.2.1 Diacetylene monomer

Diacetylene (DA) monomer is an organic compound containing two conjugated triple bonds. The R groups in the structure (Figure 1.1) can be hydrophobic alkyl chain or hydrophilic functional group such as carboxylic acid, amine, amide or ester.

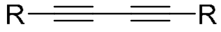
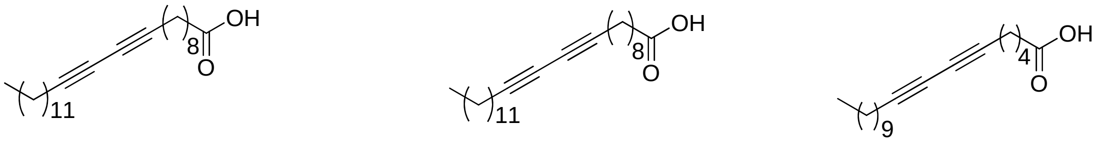


Figure 1.1 General structure of diacetylene monomer.

If both of two R groups in structure (Figure 1.1) are hydrophobic, the DA monomer is non-polar which normally have a low intermolecular interaction. These DA monomers usually have a low melting point and require a low temperature to form self assemblies. If both of two R groups are hydrophilic, the DA monomer is bipolar or bolaamphiphilic molecule which have a strong intermolecular interaction especially an intermolecular hydrogen bonding. This DA monomer can usually form self-assemblies in organic solvent [27,28]. If one R group is hydrophilic and the other one is hydrophobic, the DA monomer is amphiphilic. This DA monomer has a characteristic property that it can self-assemble in aqueous media [29].

1.2.2 Topological polymerization

Topological polymerization is a polymerization which requires precise prelignment of the monomer that is usually found in solid state crystal. The distance between diacetylene monomer which the polymerization occurs is ~5 Å and the orientation angle (θ) is ~ 45° relative to the translation axis (Figure 1.2). [30-36]



10,12-pentacosadiynoic acid (PCDA, 1)

10,12-tricosadiynoic acid (TCDA, 2)

6,8-nonadecadiynoic acid (6,8-19DA, 3)

Figure 1.2 Packing parameters: r = ~5 Å and θ = ~ 45° required for the topological polymerization of diacetylene monomers.

1.2.3 Forms of polydiacetylene

Polydiacetylene (PDA) materials have been prepared mainly in three froms: thin films (Langmuir-Blodgett (LB) or Langmuir-Scheafer (LS)), vesicle (liposome) and powder. For instance, PDA Langmuir films are fabricated by assembling amphiphilic diacetylene molecules at air/water interfaces, followed by photopolymerization. Several techniques have been utilized for making different types of thin flims on the surface [37,38]. PDA vesicle is one of the most widely used forms of polydiacetylene for sensor application. The lipid vesicles or liposomes are synthesized through self-asssembly of amphiphilic diacetylene monomer in water. The interest in these lipid vesicles is mainly related to the development into bio- and chemosensor [39-42]. The powders have been typically synthesized by a sol-gel process. Diacetylenic monomers were used as surfactants and co-assembled with silisesquioxanes. Diacetylene monomer can be directly incorporated into silisesquioxanes to form PDA nanocomposite powders [43].

1.2.4 Electronic absorption and optical properties

Optical absorption in polydiacetylene occurs *via* $\pi \rightarrow \pi^*$ absorption within the linear π- conjugated polymer backbone. Upon polymerization, frequently the first chromogenically interesting state of PDA appears blue in color. The exposure of PDA to environmental perturbations such as heat (thermochromism), mechanical stress (mechanochromism), solvent (solvatochromism), or ligand receptor (affinochromism) create a significant shift in absorption from low to high energy bands of the visible spectrum so the polydiacetylene transforms from blue to red color. The color transition resulted from changes in molecular conformation such as side chain packing, ordering and orientation that impart stresses on the polymer backbone, thus changing the electronic states and the corresponding optical absorption [44].

The peak associated with a blue phase appears at ~ 640 nm, while the peaks corresponding to the red phase occur at ~ 540 nm. A peak at ~ 600 nm has often been observed in the spectra and is attributed to an intermediate purple form between the red and the blue ones. However, it should be noted that this purple form is different from a real purple color derived from a mixture of blue and red forms [45]. It is different because color and peak in PDA are dependent on extent of polymerization, the structure of side chain, the form of material, and the exposure to environmental stimuli.

1.2.5 Chromisms of polydiacetylene

One of the most fascinating properties of PDA is its ability to change color upon its exposure to an external stimulant such as heat (thermochromism), organic solvents (solvatochromism), mechanical stress (mechanochromism), and ligand-receptor interactions (affinochromism). The color changes of polydiacetylenes involve a shift of the wavelength 640 nm to a band around 540 nm, resulting in a transformation of the material from blue to red.

Thermochromism

Thermochromism is one of the earliest reported chromatic properties of polydiacetylene [27,41,46-49]. It can be either reversible or irreversible depending on the interaction between the side chain substituent and side chain head groups, and enhancement of hydrogen-bonding interactions among the head groups. For example, Kim *et al.* had further compared PDA materials derived from diacetylene monomers capable of forming different numbers of hydrogen bonds [46]. PCDA (10,12-pentacosadiynoic acid) had a hydrogen-bonded carbonyl stretch, PCDA-aniline had hydrogen-bonded amide and carbonyl stretches, while PCDA-mBzA possessed all of the above three stretches. When heated up over 75°C, the hydrogen-bonded carbonyl stretch for PCDA slightly shifted to a higher wavelength with reduced strength which did not revert after cooling to room temperature. As a comparison, PCDA-mBzA maintained the hydrogen-bonding strength during the heating-cooling cycle. Thus, it was found that PDA from PCDA displayed irreversible thermochromism while PCDA-mBzA displayed reversible thermochromism (Figure 1.3).

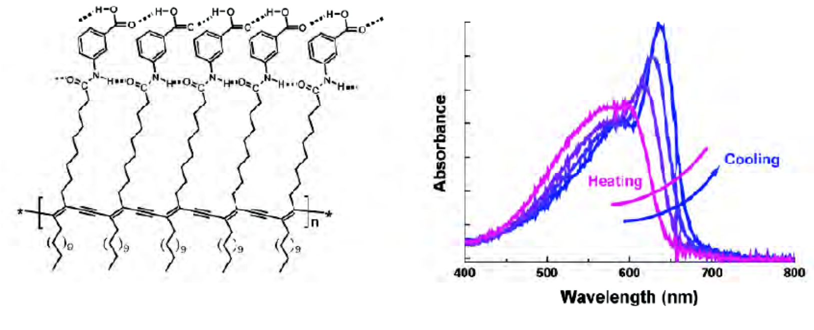


Figure 1.3 (a) Schematic illustration for the formation of a strong hydrogen-bonded network. (b) UV-vis spectra of reversible thermochromatic transition in PCDA-mBzA [46].

In 2001, Tachibana and co-worker synthesized a series of urethane-substituted diacetylene monomers (DA-mUPh) with different alkyl chain length (m=4, 5, and 6) in side-chain substituents of $(CH_2)_mOCONHC_6H_5$ to study the effect of alkyl chain length on polymerization [69]. The results showed that monomers were packed by hydrogen bonding between the urethane groups, but the arrangement of the diacetylene moieties depended on the alkyl chain length. They found that the DA-4UPh and DA-6UPh crystals polymerized upon γ-irradiation, while no polymerization occured in the DA-5UPh crystal. Thus the reactivity of the DA-mUPh crystals upon γ-irradiation was different depending whether the alkyl chain length (m) is odd or even. The difference can be explained by the distance between the neighboring carbon atoms of the diacetylene groups.

Mechanochromism

Mechanochromism is the phenomenon of color changes induced by mechanical force. An irreversible chromic transition of PDA single crystal which induced by mechanical stress was observed by Muller and Eckhardt [50]. Nallicheri and Rubner have incorporated diacetylenes in polyurethane segmented copolymers. In these materials, the optical properties of diacetylenes were linked with the mechanical properties of thermoplastic elastomers. The resulting of polyurethane elastomers containing polydiacetylene undergoes color changes that are coupled to elastomeric strain (mechanochromism) [51].

Affinochromism

The most attractive feature of polydiaceylene to be discovered in recent investigations concerns the new chromic changes promoted by interactions with biologically, environmentally or chemically interesting target molecules. Lee and co-worker observed that α-cyclodextrin (α-CD) disrupts the ordered structures of PDA derived from PCDA (10,12-pentacosadiynoic acid) by forming inclusion complexes. This result is shown the chromatic transition induced by interaction of PDA derived from PCDA with α-CD [52].

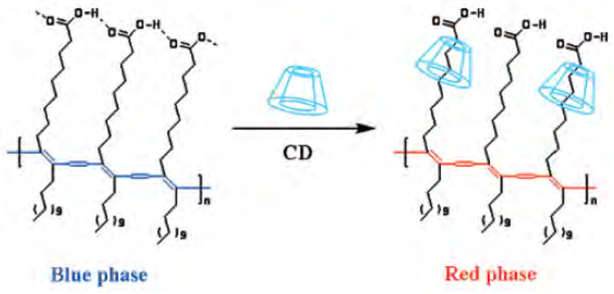


Figure 1.4 Schematic representation of the interaction between PDA and cyclodextrin.

Solvatochromism

Solvatochromism is one of the chromic properties of polydiacetylene. It is believed that solvation of polymer side chain in the presence of organic solvent caused a side chain disorder which affected the conjugation of polydiacetylene backbone. For example, Chances *et al.* reported that PDA with alkyl-urethane pendent groups in either a solution or a crystalline state exhibit a yellow to blue or red color transition upon exposure to various solvents depending on the nature of side chain substituents [53].

1.3 Volatile Organic Compounds (VOCs)

Volatile organic compounds (VOCs) are large group of carbon-based chemicals that easily evaporate at room temperature and which can affect the environment and human health. Along with carbon, they contain elements such as hydrogen, oxygen, fluorine, chlorine, bromine, sulfur or nitrogen.

Volatile organic compounds are released from burning fuel, such as gasoline, wood, coal, photocopiers or natural gas. They are also released from organic solvents, paints, glues, adhesives, varnishes and other products that are used and stored at home and at work.

1.3.1 Classification of volatile organic compounds

1.3.1.1 Non-chlorinated volatile organic compounds or non-halogenated hydrocarbons

The volatile organic compounds do not have chlorine atoms in their molecule. These substances are from the environment such as burning garbage, plastic materials, organic solvents and paint material such as fuel oils, gasoline, propane, 1,3-butadiene, hexane, formaldehyde, ethanol, methanol, toluene, benzene and xylene etc.

1.3.1.2 Chlorinated volatile organic compounds or halogenated hydrocarbons

The volatile organic compounds with chlorine atoms in the molecules are synthetic chemicals used in industry. These compounds are more toxic and more stable in the environment than non-chlorinated VOCs. Examples of substances in this group are dichloromethane, chloroform, propylene dichloride and bromomethane etc.

1.3.2 Health risks from volatile organic compounds

Each VOC has its own toxicity and potential for causing different health effects depending on the length and intensity of exposure.

Short-term (acute) effects include eye, nose, throat irritation, headaches and vomiting whilst **long-term (chronic) effects include** cancer, liver and kidney damage, and central nervous system damage.

1.3.3 Detection and measurement of volatile organic compounds

There are five methods to detect and measure the VOCs:

1. Gas chromatography (GC)
2. Flame ionization detector (FID)
3. Photo-ionization detector (PID)
4. Non-dispersive infrared (NDIR)
5. Combustion analyzer
6. Gas chromatography-mass spectrometry (GC-MS)

1.4 Literature surveys

Solvatochromism of polydiacetylene

Solvatochromism of polydiacetylene has been known for some time. The blue-to-red colorimetric transition occurs when PDAs are exposure to certain organic solvents. Mechanism underlying the change is the influence of organic solvent on the molecular order of PDA supramolecular. Despite this knowledge, only a minor effort has been given to the development of PDA sensor systems for differentiation of organic solvents.

In 2007, Kim and co-workers reported the production of PDA embedded electrospun fibers using electrospinning technique. A high surface area microfiber was obtained to make a colorimetric sensor array for common organic solvent [4]. The PDA-embedded fiber mats were prepared from four different DA monomers. Interestingly, polymer mats containing polydiacetylene shows different colorimetric responses after exposure to organic solvent such as chloroform ($CHCl_3$), tetrahydrofuran (THF), ethyl acetate (EA) and hexane (Figure 1.5). This observation of organic solvent induced the color transition suggests that the colorimetric response might depend on both nature of the organic solvent and structure of diacetylene monomers.

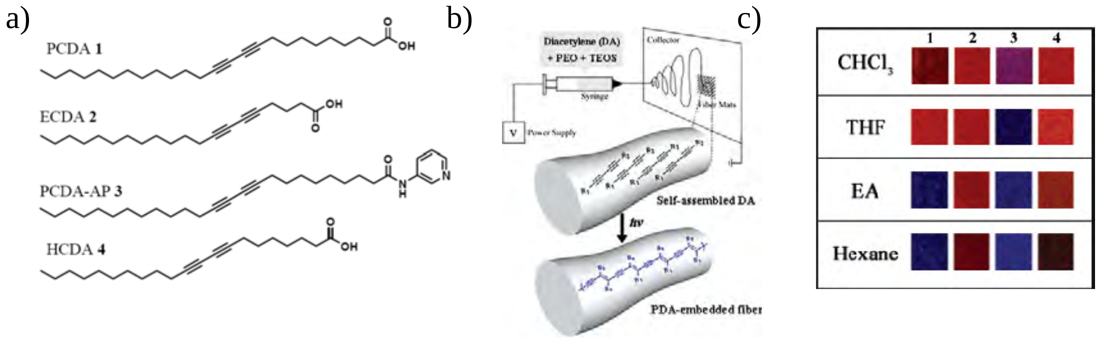


Figure 1.5 (a) Four types of diacetylene monomers, (b) scheme of presentation of PDA embedded electrospun fiber mats, (c) photographs of PDA embedded electrospun fiber mats prepared with DA monomer 1-4 upon exposure to organic solvent [4].

In 2009, Bubeck and co-workers reported the stability improvements of thin film of diacetylene derivatives TDA, HAD or AzoDA by means of hydrogen bonding with P4VP (poly(4-vinylpyridine)) as shown in Figure 1.6 [6]. The thin films were prepared using spin coating. These films showed that the stable hydrogen bonding complex can be used in photolithography. The sensor discriminated various organic solvents and gases based on the stimuli-induced color change of polydiacetylene.

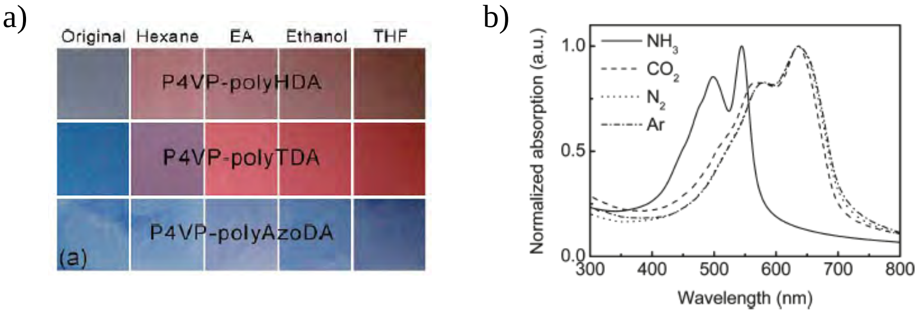


Figure 1.6 (a) Photographs of hydrogen-bonding complexes of P4VP-polyHDA, P4VP-polyHDA and P4VP-polyAzoDA before and after exposure to different organic solvents. (b) UV-vis absoptionspectra of P4VP-polyTDA films after after exposure to different gases [6].

In 2009, Kim and co-workers investigated colorimetric differentiation of organic solvent using PDA array [7]. A PDA embedded electronspun fiber mat prepared from PCDA-ABA (1) displayed no colorimetric change after exposure to common organic solvents. In contrast, a fiber mat prepared with PCDA-AN (2) underwent a solvent-sensitive color transition. Thus, sensitivity of the array could be adjusted by altering ratio of PCDA-ABA to PCDA-AN as shown in Figure 1.7.

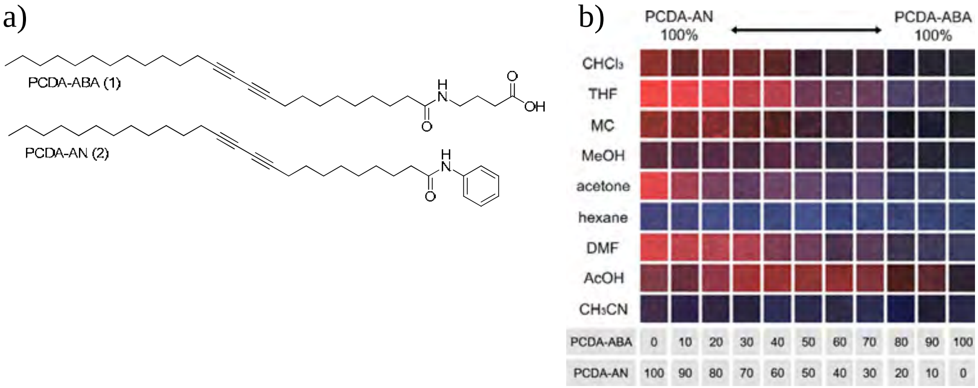


Figure 1.7 (a) Two types of DA monomers and (b) photographs of the polymerized PDA embedded fiber mats after exposure to organic solvent at 25°C for 30s [7].

In 2010, Zou and co-workers reported the development of polydiacetylene based sensitive colorimetric microarray sensor for the detection and identification of volatile organic compounds [10]. The PDA embedded-PDMS films were prepared by spin-coating method combined with the sol-gel process. The color changes of PDA films were monitored by UV-vis absorption spectra. PDA films derived from TCDA were found to be the most sensitive and displayed a color transition with all solvent except for acetonitrile while CNAPCDA showed a blue to purple with toluene only. (Figure 1.8)

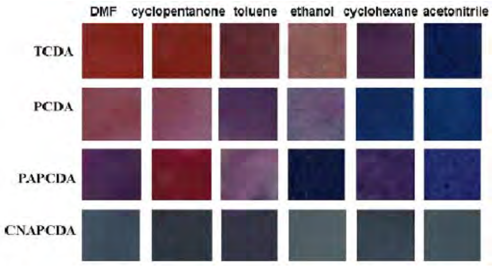


Figure 1.8 Photographs of the PDA films derived from TCDA, PCDA, PAPCDA and CNAPCDA after dipped in organic solvents at room temperature [10].

In 2011, Kim and co-workers reported the development of the colorimetric detection of fake and adulterated gasolines [54]. Color changes from blue to red were observed when PCDA (10,12-pentacosadiynoic acid) embedded electrospun fiber is exposed to fake gasoline (a mixture of thinner, toluene, and methanol) and adulterated gasoline (toluene or methanol added to commercial gasoline). The chromic transition occurs only when the protective matrix polymer is dissolved by the component of gasoline as shown in Figure 1.9.

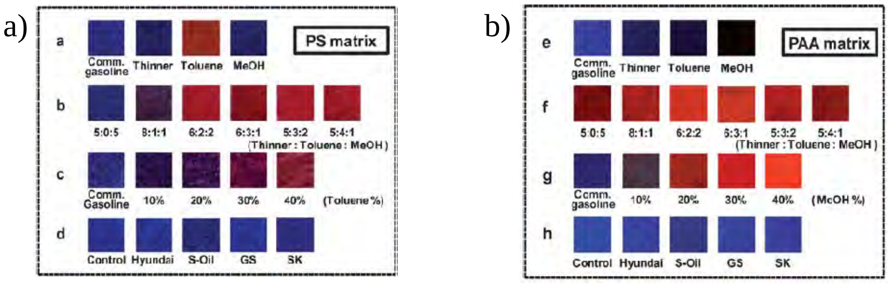


Figure 1.9 Photographs of PCDA embedded electrospun with a) polystyrene (PS matrix) and b) polyacrylic acid (PAA matrix) fiber mat after exposure to (a,e) commercial gasoline, thinner, toluene and methanol, (b,f) fake gasolines, (c,g) adulterated gasolines and (d,h) four commercial gasolines [54].

A review of existing colorimetric sensor array for detecting VOCs and related compound

In 2000, Suslick and co-worker reported a simple optical chemical sensing method that utilizes the color change induced in an array of metallopotphyrin dyes upon vapor phase ligands binding by taking the difference before and after exposure of scanned images of the sensor array [1]. The chemoselective response of a library of immobilized vapour-sensing metalloporphyrin dyes permits visual identification of a wide range of ligating (alcohols, amines, ethers, phosphines, phosphites, thioethers and thiols) and even weakly ligating (arenes, halocarbons and ketones) vapors. Unique color change signatures for analytes were obtained as shown in Figure 1.10. These unique color can be obtained at analyte concentrations below 2 parts per million and responses to below 100 parts per million have been observed.

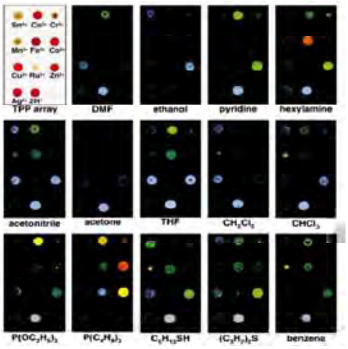
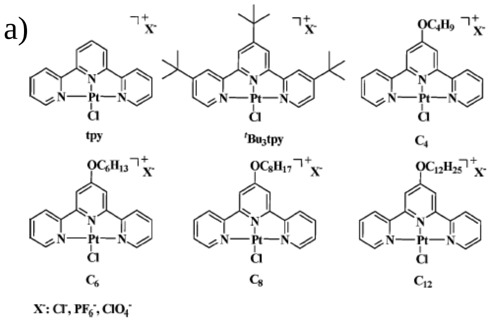


Figure 1.10 Color change profiles of a metalloporphyrin sensor array [1].

In 2008, Castellano and co-workers reported the vapochromic and vapoluminescent microarray for pattern recognition using eighteen volatile organic compounds (VOCs) of Pt^{II} terpyridyl chloride complexes as shown in Figure 1.11 [5]. As shown in Figure 1.12, the VOCs that induced the strongestvapochromic and vapoluminescent changes were those that contain lone pairs electron, for example acetonitrile, piperidine, and DMF.



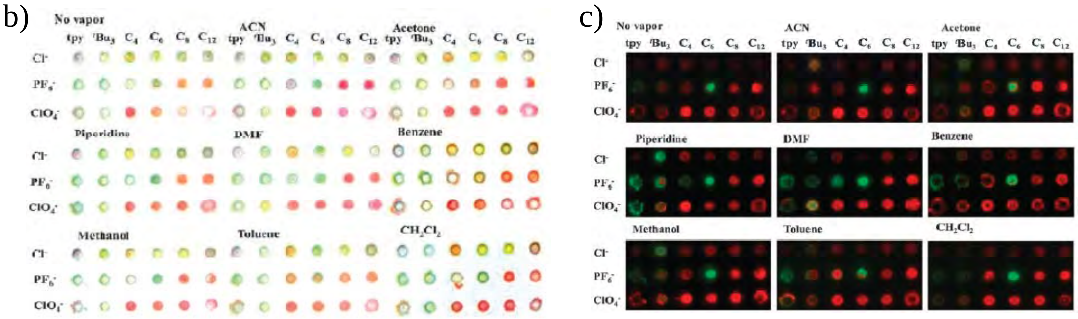


Figure 1.11 (a) Chemical structures of the Pt^{II} terpyridyl chloride salts used as cross-reactive microarray sensors. (b) Vapochromic colorimetric response of the Pt^{II} terpyridyl chloride based microarrays towards different VOCs. (c) Vapoluminescent response of the Pt^{II} terpyridyl chloride based microarrays towards different VOCs. The arrays were excited using a broadband UV lamp (300–400 nm, λmax = 365 nm) [5].

In 2010, Suslick and co-works reported a simple, inexpensive, portable and highly sensitive colorimetric sensor for detection of Triacetone triperoxide (TATP) vapor [12]. This colorimetric sensor array can detect even very low levels of TATP vapor from its acid decomposition product with limits of detection (LOD) below 2 ppb. They performed principal component analysis (PCA) to measure the array response at different concentrations of TATP. As shown in Figure 1.13, an excellent separation at low concentration was obtained from this plot. The PC1 accounts for 90.3% of variance and PC2 accounts for 4.6%. The sum of these variances is 94.9%.

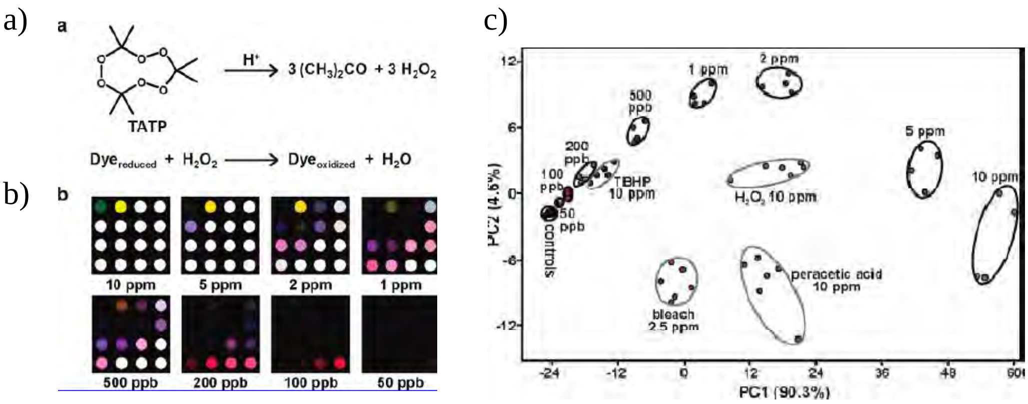
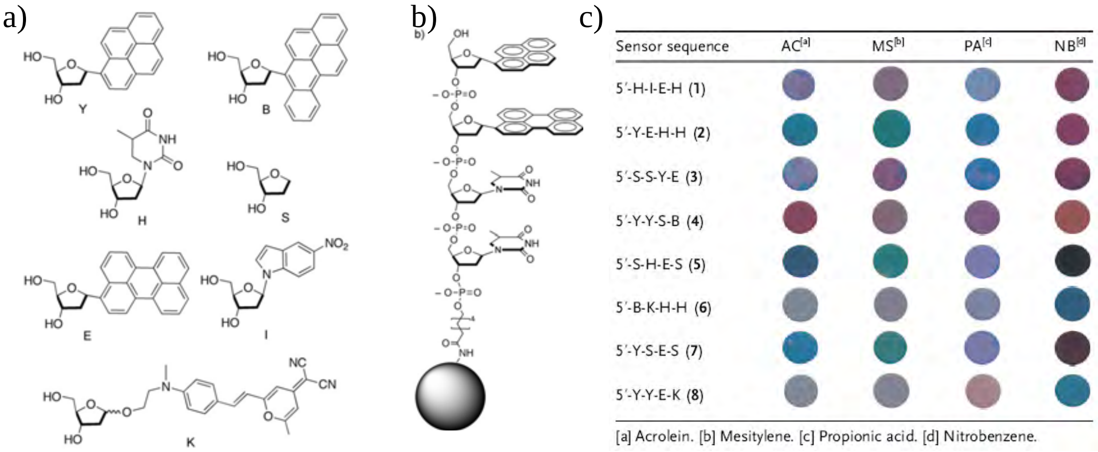


Figure 1.12 (a) Acid catalyzed decomposition of TATP. (b) color difference maps of TATP vapor at concentrations specified after 5 min (top row) and 10 min (bottom row) of exposure at 50% relative humidity and 298K. (c) Two-dimensional principal component analysis (PCA) plot [12].

In 2010, Kool and co-workers reported a rapid and easy synthesis of tetramer ODFs (oligodeoxyfluorosides) containing sequences of seven monomer such as four fluorophores (Y, E, B, K), a potential quencher (I), an abasic spacer (s), and a spacer/hydrogen-bonding element (dihydrothymidine, H) supported on poly(ethylene glycol) (PEG) – polystyrene (PS) beads by amide linkage [13]. These sensors were tested on vapors of four small molecules such as acrolein, mesitylene, propionic acid and nitrobenzene. The responses and reproducibility were further investigated quantitatively on the basis of the RGB value color-change profiles. The difference in colorimetric pattern was observed with presence of nitrobenzene vapor (Figure 1.13). They performed principal component analysis (PCA) for better understanding of the data relationships. The F1 accounts for 65.7% of variance and F2 accounts for 30.6%. The sum of these variances is 96.3%. Interestingly, the data for acrolein and nitrobenzene vapors show the largest spread in component values (Figure 1.14).



Sensor sequence	AC[a]	MS[b]	PA[c]	NB[d]
5′-H-I-E-H **(1)**	●	●	●	●
5′-Y-E-H-H **(2)**	●	●	●	●
5′-S-S-Y-E **(3)**	●	●	●	●
5′-Y-Y-S-B **(4)**	●	●	●	●
5′-S-H-E-S **(5)**	●	●	●	●
5′-B-K-H-H **(6)**	●	●	●	●
5′-Y-S-E-S **(7)**	●	●	●	●
5′-Y-Y-E-K **(8)**	●	●	●	●

[a] Acrolein. [b] Mesitylene. [c] Propionic acid. [d] Nitrobenzene.

Figure 1.13 (a) Fluorescent and nonfluorescent monomer employed as component of the library. (b) example of a sensor (5′-Y-E-H-H-3′) constructed on PEG-PS bead. (c) fluorescence images of ODF sensors after exposure to analyte vapors in gray color [13].

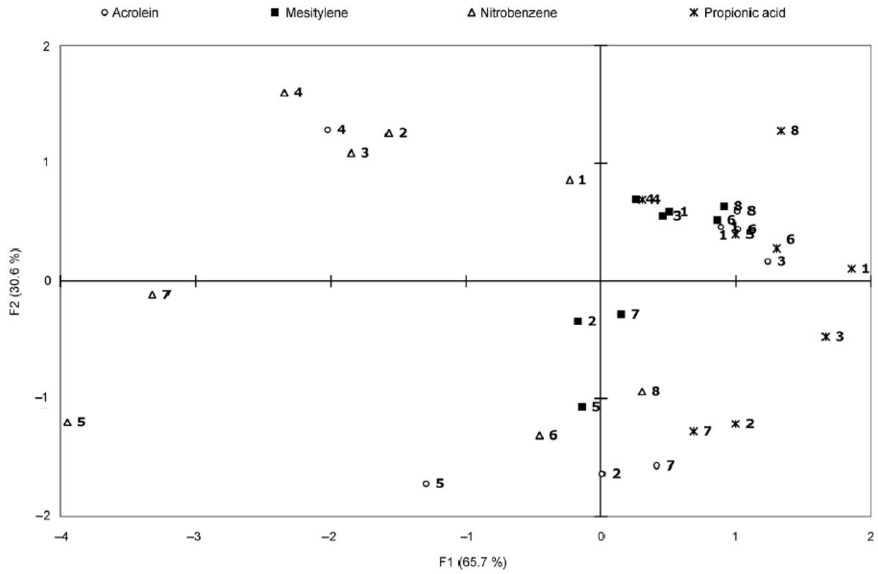


Figure 1.14 PCA score plot of ODF sensor responses upon exposure to four analyte. Each data point represents an average from 5 or 6 sensor beads [13].

A review of paper-based sensor array

Paper-based sensor arrays are very common in medical applications. The basic elements of these systems comprise patterned paper and a portable device that acquires images and transmits digital information (e.g. a digital camera, a camera-equipped cellular phone and scanner).

In 2008, Whitesides and co-workers described a prototype system for quantifying bioassays [55]. The system uses paper-based microfluidic devices for running multiple assays simultaneously, camera phones or portable scanners for digitizing the intensity of color associated with each colorimetric assay. The microfluidic devices were fabricated in paper using photolithography and were functionalized with reagents for colorimetric assays. This system gives accurate and quantitative results when detecting glucose and protein in urine which using small volumes of sample (≤ 5 μL). The combination of patterned paper, a portable method for obtaining digital images and a method for exchanging results of the assays with off-site diagnosticians offers new opportunities for inexpensive monitoring of health, especially in situations that require physicians to travel to patients to obtain diagnostic information that might be obtained more effective by less valuable personnel.

In 2009, Whitesides and co-workers continued to report 96- and 384-microzone plates fabricated in paper as alternatives to conventional multiwall plates fabricated in molded polymers [56]. The paper-based plates are fabricated by patterning sheets of paper by using photolithography. These plates are compatible with conventional microplate readers for quantitative absorbance and fluorescence measurements. The common biological stains such as Coomassie Brilliant Ble, Amaranth and bovine serum albumin (BSA) were tested. The demonstration of quantitative colorimetric correlation uses a scanner or camera to image the zones and to measure the intensity of color to make it possible to conduct assays without a microplate reader.

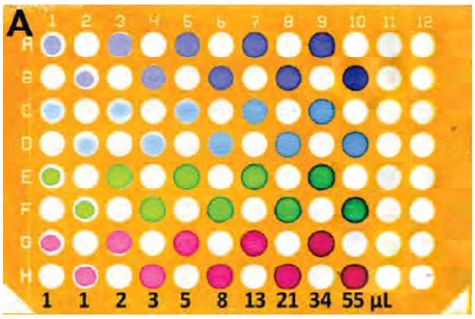


Figure 1.15 Paper plates for multizone assays produced using photolithography.

From the above review, solvatochromism of polydiacetlene was reported for some time but the first report using PDA array for the differentiation of VOCs were realized only recently by Kim and co workers [4,7,54]. Up to date, all the known literature works on this application share the same strategy which includes preparation of a PDA library embedded in various forms of supported polymers such as poly(4-vinylpyridine) spin-coating films [6], polyethyleneoxide electrospun fibers [7], polystyrene or polyacrylic acid [54]. Common disadvantages from those works are difficulty of the fabrication method, high cost as well as the requirement of polymeric support which is mostly considered to be environmentally unfriendly materials. Also, a method for quantitative discrimination, other than direct observation, has not been introduced. Therefore, the aim of this project is to demonstrate a strategy to conveniently fabricate PDA and develop a reliable quantitative analysis to distinguish a wide variety of VOCs.

1.5 Objectives and scope of the thesis

The objectives of this thesis are to study solvatochromism of polydiacetylene. To achieve the objectives, the work scope includes

1. Synthesis of amphiphilic diacetylene monomer and bolaamphiphilic diacetylene monomer
2. Characterization of diacetylene monomers
3. Preparation of paper based polydiacetylene
4. Study of polymerized polydiacetylene
5. Study of solvatochromism

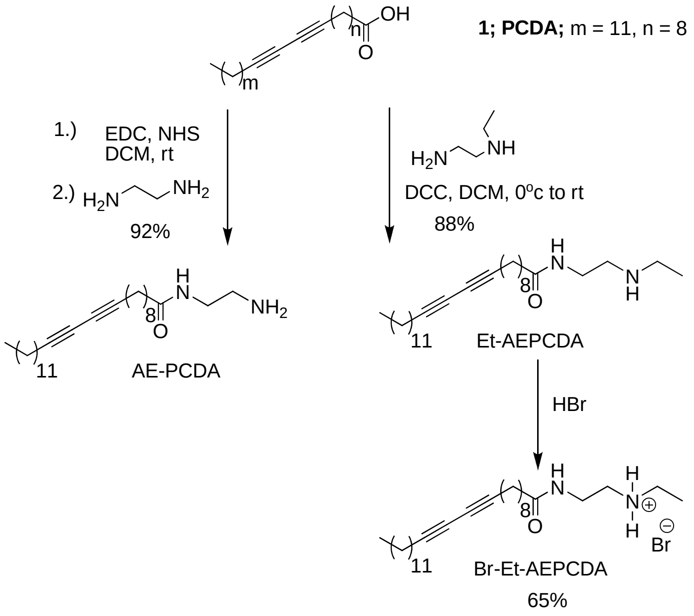
CHAPTER II

EXPERIMENTAL

2.1 Materials: 10,12-pentacosanoic acid (PCDA), 10,12-tricosadiynoic acid (TCDA) and 10-undecynoic acid were purchased from GFS Chemicals (USA). 6,8-nonadecadiynoic acid (6,8-19DA, 3) was prepared according to previous report [49]. Copper (I) chloride, *N*-hydroxysuccinimide (NHS), 1-ethyl-3-(3′-dimethylamino) carbodiimide HCl salt (EDC) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) were purchased from Fluka (Switzerland). Ethyldiamine, *N*′-ethylethylenediamine and 5-hexynoic acid were purchased from Aldrich (USA). All organic solvents for monomer synthesis and purification were purchased from TSL Chemicals (Thailand). For extraction and chromatography, solvents were commercial grade and distilled before use. Column chromatography was performed on Merck silica gel 60 (230-400 mesh; Merck) stationary phase. Analytical thin layer chromatography was performed on glass-blacked silica gel plates with F_{254} indicator.

2.2 Analytical instruments: The ^{1}H spectra were acquired by Varain Mercury 400 MHz NMR spectrometer (Varain, USA) and ^{13}C spectra were acquired by Bruker Mercury 400 MHz NMR spectrometer (Bruker, German) using the residual solvent proton resonance of $CHCl_3$ at 7.26 ppm and Methanol-D_4 at 3.34 as the reference. Mass spectra were obtained from Quattro micromass (Waters, France). The optical microscopy images were taken using Olympus DP72 equipped with 4X objective (Olympus, Japan). UV-irradiation was conducted using UV light source (TUV 15W/G15 T18 lamp; Philips, Holland). The photographic images were recorded by G11 Canon and CanoScanner LiDE 200 (Canon, Japan).

2.3 Synthesis of amphiphilic diacetylene monomers (4-6)



Scheme 2.1 Synthesis of amphiphilic diacetylene monomers.

2.3.1 *N*-(2-aminoethyl) pentacosa-10,12-diynamide (AE-PCDA, 4):

A solution of 1-ethyl-3-(3′-dimethylamino) carbodiimide HCl salt (EDC) (246.14 mg, 1.28 mmol) in methylene chloride (2 mL) was added dropwise into a solution of 10,12-pentacosadiynoic acid (PCDA) (400.00 mg, 1.07 mmol) in methylene chloride (5 mL). The mixture was stirred for 1 h at room temperature and was then added dropwise into a solution of *N*-hydroxysuccinimide (NHS) (147.77 mg, 1.28 mmol) in methylene chloride (2 mL) at room temperature. The reaction mixture was stirred at room temperature overnight. After that, water (20 mL) was added and the mixture was extracted with methylene chloride (25 x 3 mL). The organic phase was dried with sodium sulfate and rotary evaporated to yield the crude product as a white powder. Then the crude product was dissolved in methylene choloride (10 mL) and added dropwise in to a solution of ethylenediamine in methylene chloride (2 mL). After that, the mixture was kept stirred for 4 h at room temperature. Then the reaction was extracted with methylene chloride (25 x 3 mL). The organic phase was dried with sodium sulfate and rotary evaporated to yield the crude product as a white powder. The crude product was purified by column chromatography on silica gel eluted with a mixture of ethyl acetate and methanol (70:30) to give *N*-(2-aminoethyl) pentacosa-10,12-diynamide (AE-PCDA, **4**): (325 mg, 92% yield) as a white powder: mp 111-

114 °C. ^{1}H NMR (400 MHz,$CDCl_3$): δ (ppm): 0.87 (t, $-CH_3$, 3H, *J* = 6.8 Hz), 1.42 (m, 16-CH_2- , 32H), 2.18 (t,-CH_2-, 2H, *J* = 7.6 Hz), 2.23 (t, -CH_2-, 4H, *J* = 6.8 Hz), 2.84 (t, -CH_2-,2H, *J* = 5.7 Hz), 3.31 (q, -CH_2-, 2H, *J* = 5.8 Hz), 5.94 (brs, NHC=O, 1H). ^{13}C NMR (400 MHz,$CDCl_3$): δ (ppm): 173.6, 77.6, 77.5, 65.3, 65.3, 41.6, 41.6, 41.3, 36.8, 31.9, 29.6, 29.6, 29.5, 29.3, 29.2, 29.2, 29.1, 28.9, 28.9, 28.7, 28.3, 25.7, 22.7, 19.2, 19.2, 14.1. ESIMS *m/z* = 416.50, 438.47 and 439.34 corresponding to $[M]^+$, $[M-H+Na]^+$ and $[M+Na]^+$, respectively.

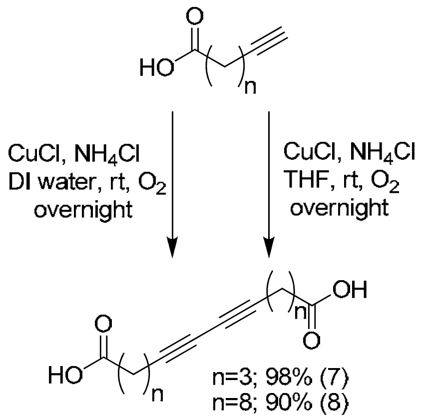
2.3.2 *N*-(2-(ethylamino) ethyl) pentacosa-10,12-diynamide (Et-AEPCDA, 5):

N,N′- dicylohexylcarbodiimide (DCC) (264.18 mg, 1.28 mmol) in methylene chloride (4 mL) was added dropwise into a solution of 10,12-pentacosadiynoic acid (PCDA) (400.00 mg, 1.07 mmol) in methylene chloride (7 mL). The mixture was stirred at 0 °C for 1 h. *N*-ethylethylenediamine (146 μL, 1.38 mmol) was added dropwise into the reaction mixture at room temperature. After that, the mixture was kept stirred at room temperature for overnight. The mixture was extracted with methylene chloride (25 x 3 mL). The organic phase was dried with sodium sulfate and rotary evaporated to yield the crude product as a white powder. The crude product was purified by column chromatography on silica gel eluted with a mixture of ethyl acetate and methanol (70:30) to give *N*-(2-(ethylamino) ethyl) pentacosa-10,12-diynamide (Et-AEPCDA, **5**): (417 mg, 88% yield) as a white powder: mp 64-66 °C. ^{1}H NMR (400 MHz,$CDCl_3$): δ (ppm): 0.86 (t, $-CH_3$, 3H, *J* = 6.8 Hz), 1.09 (t, $-CH_3$, 3H, *J* = 7.1 Hz), 1.33 (m, 16-CH_2- , 32H), 2.15 (t,-CH_2-, 2H, *J* = 7.6 Hz), 2.21 (t, -CH_2-, 4H, *J* = 6.9 Hz), 2.64 (q, -CH_2-,2H, *J* = 7.2 Hz), 2.74 (t, -CH_2-, 2H, *J* = 7.6 Hz), 3.329 (q, -CH_2-, 2H, *J* = 5.7 Hz), 4.75 (brs, -NH-, 1H), 6.11, (brs, NHC=O, 1H). ^{13}C NMR (400 MHz,$CDCl_3$): δ (ppm): 173.5, 77.6, 77.5, 65.3, 65.2, 48.4, 43.7, 38.7, 31.9, 29.6, 29.6, 29.6, 29.5, 29.5, 29.3, 29.3, 29.1, 29.2, 29.1, 28.9, 28.9, 28.8, 28.4, 28.3, 25.7, 22.7, 19.2. ESIMS *m/z* = 444.58 and 445.48 corresponding to $[M]^+$ and $[M+H]^+$, respectively.

2.3.3 *N*-ethyl-2-pentacosa-10,12-diynamidoethanaminium bromide (Br-Et-AEPCDA, 6):

N-(2-(ethylamino) ethyl) pentacosa-10,12-diynamide (400.00 mg, 0.90 mmol) was dissolved in chloroform and hydrobromic acid (HBr) (97.00 μL, 1.80 mmol). The mixture was stirred at room temperature for 1 h. The mixture was extracted with chloroform and water. The organic phase was dried with sodium sulfate and rotary evaporated to yield the crude product as a white powder and was dissolved in small amount of chloroform followed by slow addition of cool hexane at 0 °C and was dried in a vacuum oven at room temperature to give *N*-ethyl-2-pentacosa-10,12-diynamidoethanaminium bromide (Br-Et-AEPCDA, **6**): (307 mg, 65% yield) as a white powder: mp 115-118 °C. ^{1}H NMR (400 MHz,$CDCl_3$): δ (ppm): 0.88 (t, $-CH_3$, 3H, J= 6.8 Hz), 1.40, (m, 16-CH_2- , 32H), 1.62 (t, $-CH_3$, 3H, J = 7.2 Hz), 2.25 (m, 3-CH_2-, 6H), 3.12 (m, $-CH_2$-, 4H), 3.68 (q, $-CH_2$-,2H, J = 4.4 Hz), 7.65 (brs, NHC=O, 1H). ^{13}C NMR (400 MHz,$CDCl_3$): δ (ppm): 175.5, 77.7, 77.4, 65.3, 65.2, 47.9, 43.5, 36.5, 36.3, 31.9, 29.7, 29.6, 29.7, 29.5, 29.4, 29.2, 29.2, 29.1, 28.9, 28.9, 28.9, 28.3, 28.4, 25.6, 22.7, 19.2, 19.2, 14.1, 11.3. ESIMS *m/z* = 444.62 and 445.50 corresponding to $[M]^+$ and $[M+H]^+$, respectively.

2.4 Synthesis of bolaamphiphilic diacetylene monomers (7-8)



Scheme 2.2 Synthesis of bolaamphiphilic diacetylene monomers

2.4.1 5,7-dodecadiynedioic acid (7):

A solution of 5-hexynoic acid (400 μL, 3.60 mmol) in DI water (15 mL) in a three-neck round bottom flask was bubbled with oxygen gas at room temperature. Then copper (I) chloride (1790 mg, 18.10 mmol) and ammonium chloride (1930 mg, 36.00 mmol) were successfully added. After the reaction mixture was vigorously stirred for overnight, 10 mL of 1M hydrochloric acid cold solution was poured into the mixture and the precipitate was collected and dried under vacuum oven at room temperature to give 5,7-dodecadiynedioic acid (**7**): (393 mg, 98% yield) as a white powder: mp 137-139 °C. ^{1}H NMR (400 MHz,$CDCl_3$): δ (ppm): 1.79 (m, 2-CH_2-, 4H), 2.32 (t, -CH_2CO-, 4H, *J* = 2.33 Hz), 2.43 (t, -CH_2CH-, 4H, *J* = 2.43 Hz). ^{13}C NMR (400 MHz,$CDCl_3$): δ (ppm): 19.4, 25.0, 33.8, 51.7, 51.9, 67.1, 77.4, 175.5. ESIMS *m/z* = 220.46 corresponding to $[M]^-$

2.4.2 10,12-docosadiynedioic acid (8):

A solution of 10-undecynoic acid (200 mg, 1.1 mmol) in tetrahydrofuran (15 mL) in a three-neck round bottom flask was bubbled with oxygen gas at room temperature. Then copper (I) chloride (545 mg, 5.50 mmol) and ammonium chloride (590 mg, 11.00 mmol) were successfully added. After the reaction mixture was vigorously stirred for overnight, 10 mL of 1M hydrochloric acid cold solution was poured into the mixture and the precipitate was collected and dried under vacuum oven at room temperature to give 10,12-docosadiynedioic acid (**8**): (179 mg, 90% yield) as a white powder: mp 100-103°C. ^{1}H NMR (400 MHz,$CDCl_3$): δ (ppm): 1.51 (m, 6-CH_2-, 12H), 2.42 (t, -CH_2CO-, 4H, *J* = 2.24 Hz), 2.28 (m, 2-CH_2-, 4H, *J* = 2.28 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm): 19.5, 25.8, 29.3, 29.6, 29.8, 29.9, 30.0, 34.6, 66.2, 77.7, 175.9. ESIMS *m/z* = 360.51 corresponding to $[M]^-$

2.5 Colorimetric response of paper-based PDA sensor arrays

2.5.1 Fabrication of PDAs coated paper.

Diacetylene monomer was first dissolved in THF or chloroform (2% w/v) and 2 µL of the solution was dropped on a piece of filter paper (Whatman No.1 chromatography paper) using auto pipette. The paper was allowed to dry in the air at room temperature for 60 minute. Polymerization was conducted using a hand-held UV lamp (500 µW/cm^2) operating at a wavelength of 254 nm. The lamp were hung 10 cm above the white dots on filter paper. The samples were then irradiated for 1 min to provide multiple blue PDA dots.

2.5.2 Preparation of volatile organic compounds saturated vapors.

The eighteen common organic solvents were used in this work were AR grade i.e. pentane, hexane, cyclohexane, toluene, *o*-xylene, benzene, diethyl ether, dichloromethane (DCM), 2-propanol, tetrehydrofuran (THF), chloroform ($CHCl_3$), ethanol (EtOH), ethyl acetate (EtOAc), acetone, methanol (MeOH), acetonitrile (MeCN), dimethylformamide (DMF), dimethylsulfoxide (DMSO). The organic solvents (3 mL) were poured into Petri dish and kept for 60 minutes in close system. A filter paper containing the blue PDA dots was attached on the inside surface of a cover of a Petri dish containing saturated VOC vapor. The cover was then used to close the chamber tightly for 60 min at 30 °C. The cover was removed from the chamber and the photographic images of the PDAs dots were recorded using either scanner or digital camera. For the digital camera, the images were captured at the distance of 30 cm. Each image of PDAs dots were saved in TIF format and cropped into 0.5 x 0.5 cm^2 areas.

2.5.3 Image processing methods for screening.

A filter paper containing the blue PDA dots was attached on the inside surface of a cover of a chamber containing a VOC tested. The cover was then used to close the chamber tightly for 60 min at 30 °C. The cover was removed from the chamber and the photographic images of the PDAs dots were recorded using a scanner and digital camera. Each image of PDAs dots were saved in TIF format and cropped into 0.5 x 0.5 cm^2 areas.

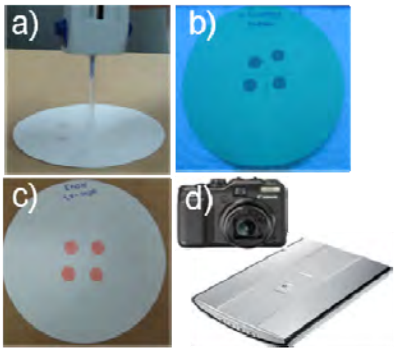


Figure 2.1 Process of colorimetric response of paper-based PDA sensor arrays for VOCs detection. (a) Drop and dry in the air (b) UV irradiation for 1 min (254 nm, 500 $\mu W/cm^2$) (c) exposure to saturated vapors of volatile organic solvents at 30 °C for 60 min (d) record with digital camera and scanner

2.6 Optical microscopic images.

The PDA test paper of before and after exposure to saturated VOCs vapors were recorded using Olympus DP72 equipped with 4X objective lens (Olympus, Japan).

2.7 Statistical analysis data

2.7.1 Color change profile.

For the histogram plot of color change profile of PDAs dots array (12 replicates), the digital and scanned images were quantified using AdobePhotoshop®. The use of 8-bit imaging digital camera and scanner produces red (255, 0, 0), green (0, 255, 0) and blue (0, 0, 255) values. Raw color images (TIF format) - the mean intensity in the red, green, blue channel was recorded and cropped into 0.5 x 0.5 cm^2 areas. The ΔRGB values were calculated by subtraction of RGB value before and after exposure to vapor of volatile organic compounds using the following equation:

$$\Delta \text{ RGB value} = \text{RGB}_{\text{value}} \text{ VOCs} - \text{RGB}_{\text{value}} \text{ blank}$$

Whereas; R = red, G = green and B = blue values. The ΔRGB of 12 replicated measurements were averaged and standard errors of each data set were determined.

2.7.2 Principal component analysis (PCA)

To carry out these quantitative analyses, PCA was performed with Unscrambler 9.7 software version, using the ΔR, ΔG, ΔB values as input. For the VOCs discrimination, data set were received from 8 monomers x18 VOCs x 12 measurements. In case of gasoline detection experiment, the dataset were obtained from 8 monomers x 10 gasoline vapors x 9 measurements.

CHAPTER III

RESULTS AND DISCUSSION

In the recent years, there are increasing concerns about the impact of volatile organic compounds (VOCs) which are considered as a serious pollution generated from industry or combustion engines, so the development of sensors for VOCs has gained interest due to environmental concern and public safety.

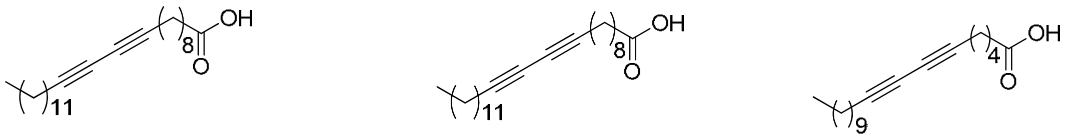
The development of efficient sensors for the detection of VOCs continues to be a significant scientific effort. Recently, diverse VOCs can be monitored using colorimetric sensor array system owing to VOC-induced color changes of sensors. The reported sensor elements are composed of arrays of metalloporphyrins, conducting polymers, metal oxides, solvatochromic dyes and pH indicators. However, colorimetric analysis methods derived from those sensors are difficult to implement and has slow response times which also require high temperature and expensive devices. Therefore, the challenge remains to improve the analysis method for VOC detection.

In this work, two series of diacetylene monomers such as amphiphilic and bolaamphiphilic diacetylene monomers will be synthesized. All prepared monomers will be deposited on paper and polymerized to obtain paper-based PDA sensor arrays. Solvatochromism of this PDA-based paper will be tested with various vapors of VOCs. As a result, they should display unique colorimetric patterns due to the structurally diverse diacetylene monomers. The colorimetric response patterns will be analyzed and differentiated using computer aid program. To expand the scope of this work, the colorimetric differentiation between gasoline vapors will be evaluated using the PDA test paper. The outcome from this work will provide a new sensor system for VOCs detection and identification that is inexpensive, portable and more rapid than conventional testing procedures.

3.1 Synthesis of diacetylene lipid monomers

3.1.1 Synthesis of amphiphilic acid monomers

PCDA (**1**) and TCDA (**2**) were acquired from GFS Chemicals and used without any purification. Next, 6,8-nonadecadiynoic acid (**3**) was prepared according to the literature via coupling reaction between iodoalkyne and alkynoic acid using copper-one catalyst [49] (Figure 3.1)



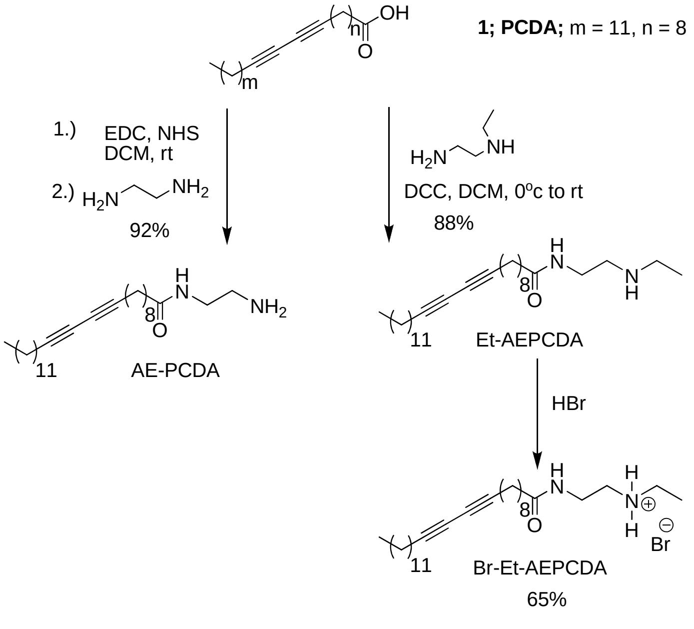
10,12-pentacosadiynoic acid (PCDA, 1)

10,12-tricosadiynoic acid (TCDA, 2)

6,8-nonadecadiynoic acid (6,8-19DA, 3)

Figure 3.1 Structure of PCDA (1), TCDA (2) and 6,8-19DA (3)

Series of amphiphilic diacetylene monomers such as *N*-(2-aminoethyl) pentacosa-10,12-diynamide (AE-PCDA,**4**), *N*-(2-(ethylamino) ethyl) pentacosa-10,12-diynamide (Et-AEPCDA, **5**) and *N*- ethyl-2-pentacosa-10,12-diynamidoethanaminium bromide, were synthesized using the condensation of PCDA (**1**) with aliphatic amines as show in scheme 3.1

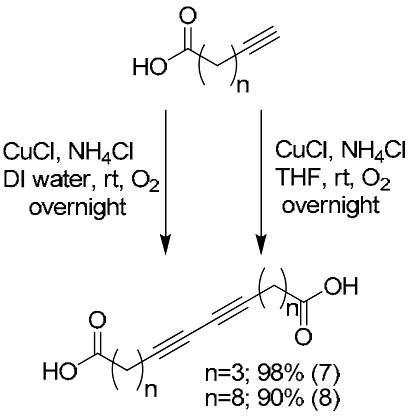


Scheme 3.1 Synthesis of amphiphilic acid monomers.

Diacetylene lipids AE-PCDA (**4**) and Et-AEPCDA (**5**) were prepared from PCDA (**1**) through straightforward amide coupling reaction. For AE-PCDA (**4**), commercially available PCDA was first converted into the activated ester PCDA-NHS using 1-Ethyl-3-(3′-dimethylamino) carbodiimide HCl salt (EDC) and *N*-hydroxysuccinimide (NHS) followed by the coupling reaction with ethylenediamine. AE-PCDA was isolated in high yield (92%) as a white solid after column purification. Similarly, diacetylene monomer carrying secondary amino group Et-AEPCDA (**5**) was synthesized in one step from coupling reaction of PCDA with an excess *N*-ethylethylenediamine in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) as a coupling agent. The target diacetylene monomer **5** was obtained as a white solid in an excellent yield (88%). Treatment of an excess hydrobromic acid to diacetylene lipid **5** (Et-AEPCDA) gave rise to the formation of secondary ammonium salt Br-Et-AEPCDA (**6**) in moderate yield (65%), as a white solid.

3.1.2 Synthesis of bolaamphiphilic acid monomers [57,58]

In the synthesis of balaamphiphilic diacetylene monomers (**7**-**8**), homocoupling reaction of terminal alkynoic acids mediated by copper (I) catalyst in the presence of oxygen gas were performed as depicted in scheme 3.2



Scheme 3.2 Synthesis of bolaamphiphilic acid monomers.

For diacetylene monomer 5,7-dodecadiynedioic acid (**7**), 5-hexynoic acid were treated with an excess of copper (I) chloride and ammonium chloride in the presence of oxygen gas at room temperature. The crude product from the reaction was simply purified by recrystallization with MeOH to give the desired product in 98% yield. Similarly, 10,12-docosadiynedioic acid (**8**) was prepared from 10-undecynoic acid by reacting with an excess copper (I) chloride and ammonium chloride under oxygen atmosphere at room temperature to obtain the target product in 90% yield.

3.2 Characterization of diacetylene lipid monomers

^{1}H and ^{13}C NMR and Mass spectra techniques were acquired to characterize all prepared diacetylene monomers (for the ^{13}C NMR and Mass spectra please see the appendix section). The results are in good agreement with the report literatures [57,58,59].

3.2.1 Characterization of amphiphilic diacetylene monomers

The ^{1}H NMR spectra of the amphiphilic diacetylene monomers (4-6) are shown in Figure 3.3. ^{1}H NMR spectra of AE-PCDA (**4**) and Et-AEPCDA (**5**) displayed the signals of -NH protons (u) in the chemical shift range of 6.0-6.2 ppm confirming the formation of C-N bond. The unusual strong down field of singlet signals at 7.4 ppm of Br-Et-AEPCDA (**6)** belong to N-H protons. This support the existence of secondary ammnonium salts of monomer **6**. Moreover, two methylene protons next to the amido nitrogen (v, w) of Et-AEPCDA (**5**) appeared at 3.4 and 3.2 ppm respectively while that of Br-Et-AEPCDA **6** slightly shifted to 3.6 and 2.8 ppm respectively due to the high electronegativity of ammnonium moiety. Besides, the signals of the methylene protons next to the carbonyl group of amide (t) of **4**-**6** are displayed similarly around 2.2 ppm. Most of the protons in the aliphatic chain (b-k, n-s) in all three products gave the similar pattern showing the signals in the range of 1.8 - 0.9 ppm.

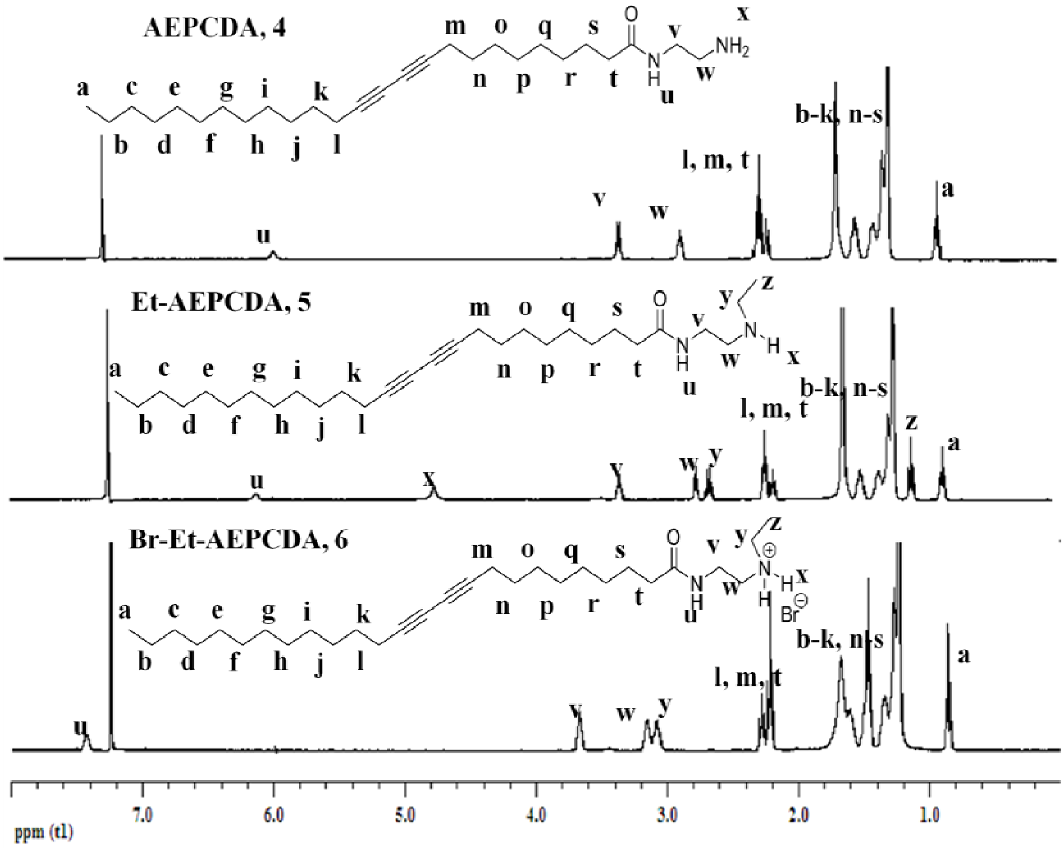


Figure 3.2 ^{1}H NMR spectra of the amphiphilic diacetylene lipids

3.2.2 Characterization of bolaamphiphilic diacetylene monomers

The ^{1}H NMR spectra of the bolaamphiphilic diacetylene monomers (**7**-**8**) are shown in Figure 3.4. The signals of methylene proton adjacent to the carbonyl group of the carboxylic acid (a) for 5,7-dodecadiynedioic acid (**7**) and 10,12-docosadiynedioic acid (**8**)appeared at the chemical shift of 2.2 ppm. The position of methylene proton connected to the acetylene appeared at 2.2-2.4 ppm. Most of the protons in the aliphatic chain in both products showed similar pattern in the range of 1.8-1.2 ppm.

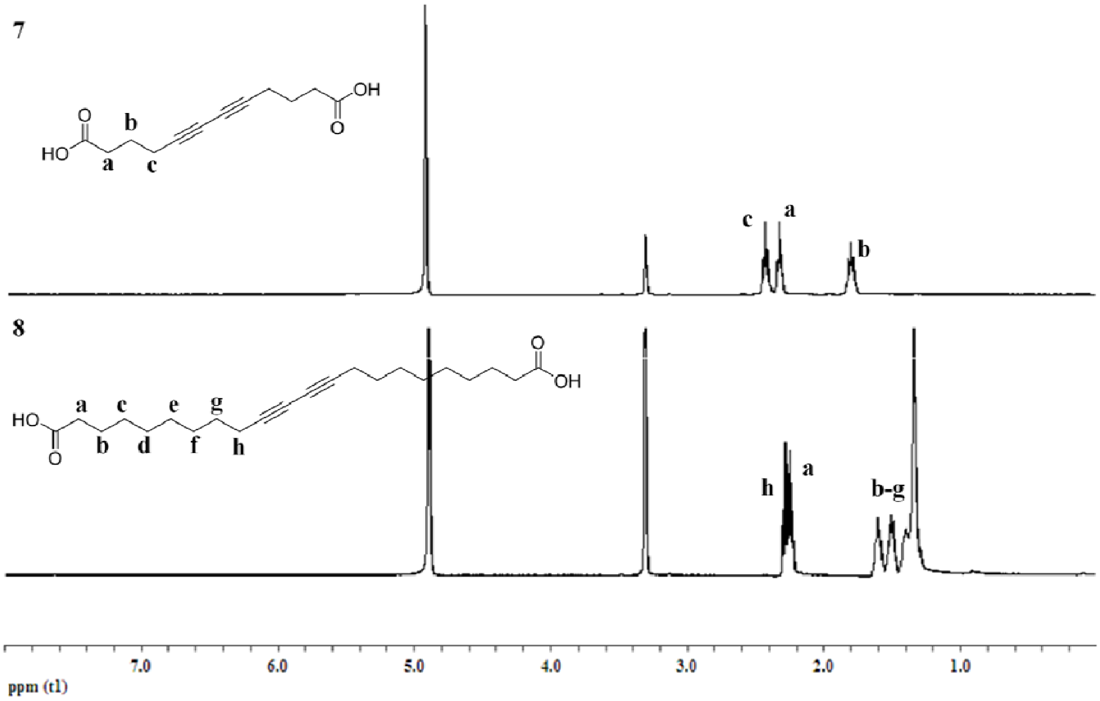


Figure 3.3 ^{1}H NMR spectra of the bolaamphiphilic diacetylene lipids

3.3 Fabrication of PDAs coated paper

Filter paper was used as a supporting material for PDA. It is chosen for many reasons such as wide availability, low cost, convenient storage and transport. Moreover, it is thin, lightweight, white and clean. Therefore, it is considered a good medium for colorimetric tests because it is able to provide strong contrasts with a colored substrate. Finally, it is safe after use because it is biodegradable and biocompatible. From the reasons described above, in this experiment, we decided to fabricate diacetyelene monomers on paper followed by UV irradiation to obtain a PDA-coated paper. The resulting PDA-coated paper will be tested with various common volatile organic solvents (VOCs).

The fabrication process was started by dropping a solution of each diacetylene monomer in 2-propanol in case of monomer **1**, **2**, **3**, **4**, **7** and **8** on to a piece of filter paper and dried in the dark at room temperature (Figure 3.4a). THF were used to dissolve monomer **5** and **6** due to solvent compatibility. The desired number of diacetylene dots can be created simply by repeating the dropping process on different locations on the filter paper as illustrated in Figure 3.4a. The resulting white paper containing multiple dots of diacetylene monomers were then irradiated with UV-light (254 nm) for 1 min to give blue dots of PDA (blank) as shown in Figure 3.4b. As depicted in Figure 3.4c and d, all diacetylene monomers (**1-8**) was deposited on filter papers and underwent polymerization to produce blue PDA-test papers. The appearance of blue color confirms the formation of cross-linked ene-yne π-conjugated PDA backbone. The only exception was bolaamphiphilic diacetylene monomer **7** which appeared as a red spot. The latter observation could be attributed to an improper packing parameter of diacetylene monomer which is caused by a short methylene linker between the head group and an acetylene unit (n = 3) [30-36, 69]. Pleasingly, the paper-based PDA did not change color from blue to red even after a month of storage on laboratory bench, suggesting a high degree of stability. As mention above, the aim of this research is to perform a colorimetric measurement of PDA-based paper upon exposure to VOC, therefore the images must be recorded. In our experiment, scanner and digital camera were use as the optical recorder and results from both sources were compared in Figure 3.4c and d. Obviously, the scanner showed the brighter images in the comparison with the photographic from the camera. The fade color obtained from scanner is probably due to the polarized light during the scan process. Camera, on the other hands, provided the better images showing the higher contrast that are similar to the observation by eyes. However, we reasoned that it is difficult to produce the same quality of photographs with the digital camera due to many variations during process of photo capture such as ambient light, camera resolution adjustment and the distance between object and lens.

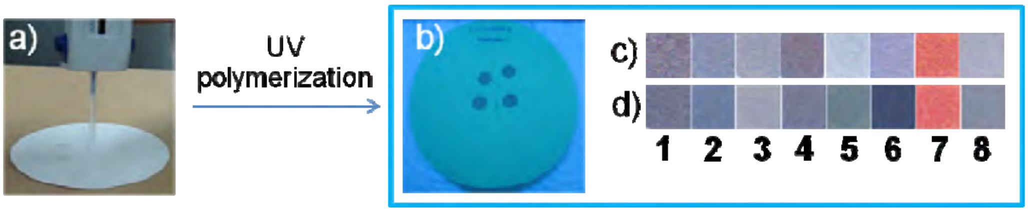


Figure 3.4 Fabrication of PDAs coated paper (a) drop and dry process, (b) exposure with UV light, (c) scanned images and (d) photographs of PDAs **1-8** after irradiated with UV light.

3.4 Colorimetric response of paper-based PDA sensor arrays

The solvent dependent color transition of PDA molecules is known to vary with PDA structure [4,6,7,10]. Therefore, identification of VOCs compounds would be possible using an array of structurally diverse PDA molecules. Ultimately, the resulting color response of PDA array with each solvent could create the unique patter leading to the discrimination among analytes. With eight kinds of paper-based PDA in hands, the solvatochromic investigation has begun by testing all prepared PDA test paper with vapors of common organic solvent including: pentane, hexane, cyclohexane, toluene, *o*-xylene, benzene, ethyl ether, dichloromethane (DCM), 2-propanol, tetrehydrofuran (THF), chloroform ($CHCl_3$), ethanol (EtOH), ethyl acetate (EtOAc), acetone, methanol (MeOH), acetonitrile (MeCN), dimethylformamide (DMF), dimethylsulfoxide (DMSO). Each PDA coated papers (8 kinds) were incubated with each vapor of VOCs (18 kinds) for 60 minutes and then 12 individual measurements were performed. The images were recorded using both scanner and digital camera. The acquired images were depicted in Figure 3.5.

The images from the scanner revealed that poly-PCDA (**1**) provided high selectivity when exposed to THF vapor developing a strong orange color (Figure 3.5a). However, it remained unchanged with the other vapors. The blue to red color transition was observed with poly-TCDA (**2**) displaying the red color with vapors of toluene, benzene, THF, $CHCl_3$ and DMF. Nevertheless, poly-TCDA displayed small or no color change with the others but purple was observed with *o*-xylene. Although, there is still no clear explanation for the color change of solvatochromism of PDA, it has been widely accepted that the chromic change is governed by the distortion of PDA back bone. We hypothesized the solvation of PDA head group and insertion of VOC molecule into the PDA head group on the surface of test paper led to the twist of conjugated backbone of PDAs. Therefore, intense blue PDA embedded on paper undergo chromic changes to red or purple. Therefore, the degree of color response of PDA immobilized paper would depend on the stress induced in the system. Interestingly, paper-based PDA derived from 6,8-19DA (**3**) was considered to be the most sensitive and displayed vivid red color on almost vapor of VOCs except hexane which is purple. Nevertheless, all the paper-tested prepared from AE-PCDA (**4**) showed dark blue colors with all VOCs tested but only $CHCl_3$ showed a red to purple transition. This result suggests that PDA derived from AE-PCDA were less sensitive and indicates that the molecularly ordered structure of polymerized AE-PCDA is stable and cannot be disturbed by most solvent vapors. For poly-Et-AEPCDA (**5**), red color were developed upon treatment with *o*-xylene, toluene, benzene, dichloromethane, 2-propanol, THF, chloroform, ethanol and methanol while it displayed purple color upon contacting with the vapors of cyclohexane, ethyl acetate and acetone. The other vapor did not induce the major chromic change upon contacting with poly-Et-AEPCDA test paper indicating such vapors could not disturb the self-assemble structure of poly-Et-AEPCDA on the paper surface. In case of poly-Br-Et-AEPCDA (**6**), vivid red color was observed with methanol while the blue to purple transition were detected with vapor of THF, chloroform, ethanol and DMF. It remains minimal or unchanged with others. The colorimetric pattern of polymer **7** was however, different from the other prepared polydiacetylene. It illustrated the color transition from red to orange with a variety of vapors such as 2-propanol, THF, chloroform, ethanol, ethyl acetate, acetone, methanol, acetonitrile, DMF and DMSO. The polymer **8** displayed the light red color on vapor of THF and DMF while the others are blue response. Pentane vapor did not found to induce blue to red color changes in all experiments.

On the other hand, the result from the camera is in accordance with the scanner, showing similar trend of chromic changes (Figure 3.5b). Again, the color appearance received form camera provides a better resolution which is similar to naked eye observation. As motioned earlier solvatochromism of PDA is associated with the conformational change caused by solvent perturbation or solvation of PDA into the head group. To explain the formation of unique colorimetric pattern, we believed that the amount of stress which induced the chromic changes in our system is dependent on the structure of diacetylene monomers and the nature of solvent effecting by vapor pressure, polarity of volatile organic solvent and structure of solvent.

Notably, the chromatic changes of PDA test paper, exposure to VOCs, are irreversible meaning that the color remained the same after a day of storage on laboratory bench. This behavior suggests the opportunity to use this sensor onsite and provides the consistency during the measurement. Importantly, the result up to this point indicates that array of PDA immobilized on paper are not only able to detect the vapor of VOCs by naked eyes observation but also generate unique colorimetric pattern when exposure to VOCs. Therefore, solvent discrimination and identification is possible.

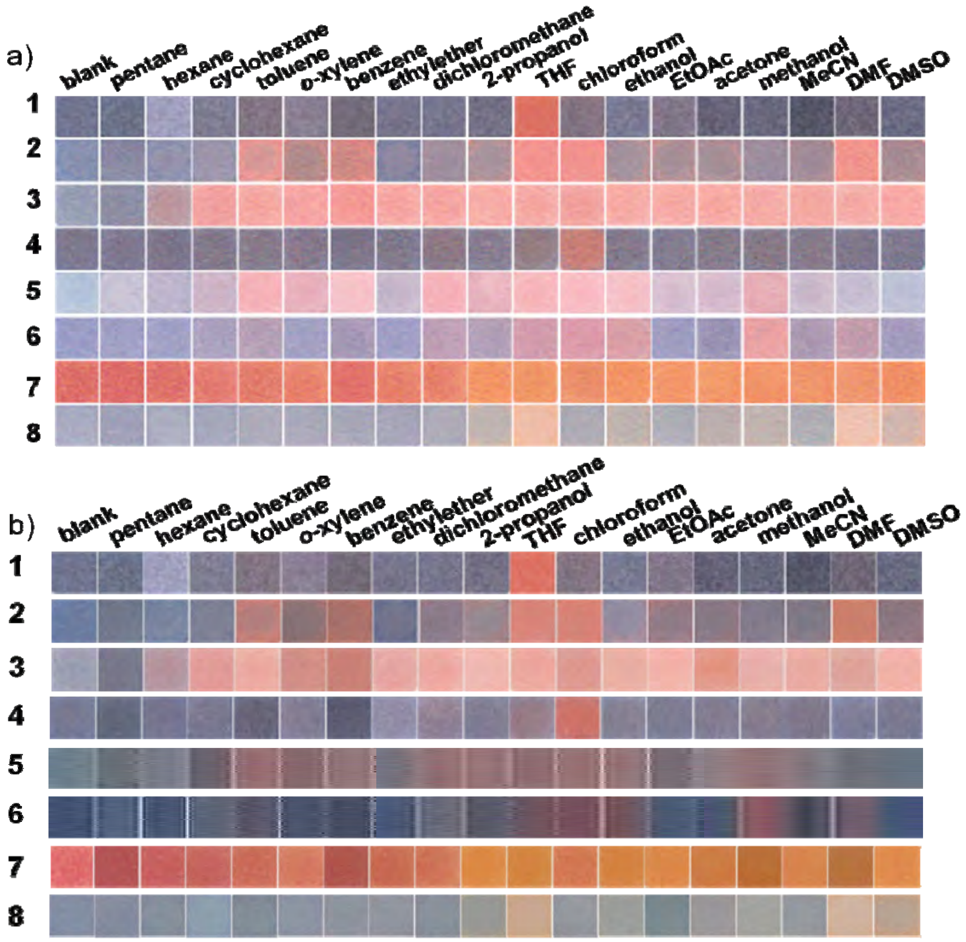


Figure 3.5 (a) Scanned images and (b) photographs of the paper-based PDA sensor array prepared from diacetylene monomers **1-8** before and after 60 min exposure to saturated vapors of volatile organic solvents at 30 °C. All images were acquired at 150 dpi.

3.5 Optical microscopic images

Optical microscope was used to characterize the surface of the paper-based PDA sensor array before and after exposure to VOCs vapors. The optical microscopic images of diacetylene – embedded paper derived from PCDA, TCDA, Br-Et-PCDA and monomer **8** after UV- irradiation for 1 minute (Figure 3.6 top panel). These purple and blue colors of PDA test paper confirmed that diacetylene monomers are able to deposit and polymerize on the filter paper. Valuable information was gained from these images. For PCDA and TCDA test papers, fiber of the paper surface was coated with intense blue color covered most area indicating an excellent immobilizability and polymerizability of monomers. Nevertheless, purple and pale blue were found in the case of poly-Br-Et-AEPCDA and **8** respectively with off-white area. These results are perhaps due to either poor deposition of diacetylene monomers or low degree of polymerization. The panel on the bottom of the figure showed the appearance of PDA paper after exposure to VOCs. After exposure to THF vapor for 60 min, optical microscopic of PDA immobilized papers, prepared from PCDA and TCDA, displayed the red color covered on the most area corresponding to the naked eye observation. On the other hands, blue to purple color change were observed in case of poly-Br-Et-AEPCDA. Interestingly, images from optical microscope showed that PDA test paper derived from diacetylene **8** appeared as green fiber upon incubating with THF vapor. Moreover, the results from the optical microscope indicated that the mode distribution of PDA in paper is not homogeneous but PDA exists as aggregates as shown in far right images of Figure 3.6.

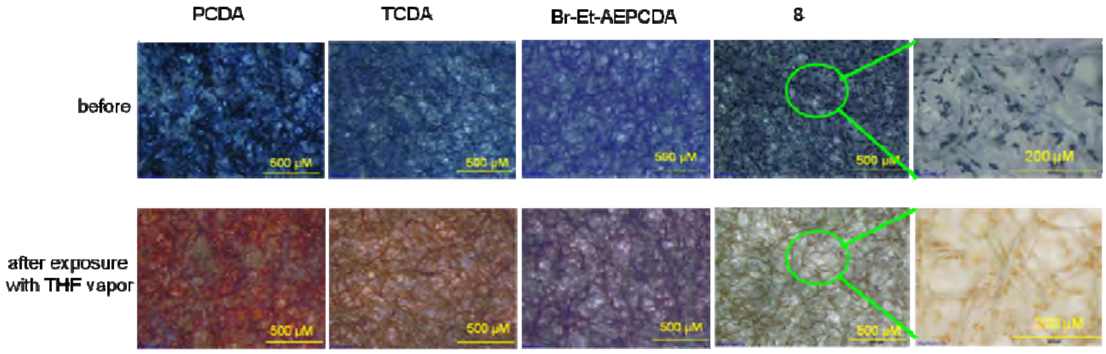


Figure 3.6 The photographs microscopic images of paper-based PDA before and after exposed to THF vapor for 60 min at 30 °C.

3.6 Color change profile

The images before and after vapor exposure (TIF format) were cropped in 0.5 × 0.5 cm^2. The cropped images in three channels (RGB) were merged using AdobePhotoshop® to obtain the final RGB pictures. The color change profile R, G, B was calculated for each polymer and averaged from 12 individual measurements. In order to quantify colorimetric response of PDA test paper, a color change profile was determined by subtracting the RGB values of the images before and after exposure of each PDA with VOCs vapor for 60 min at 30 °C. The quantitative results are shown in Figure 3.7.

First, the color change profile obtained from flat scanner images of PDA color before and after exposed to VOCs vapor is shown in Figure 3.7a. This histogram shows mostly red and green as positive value while blue were found as negative value. For example, in case of THF vapor, the proportion of ΔR was ca. 100 with PDA immobilized paper derived from PCDA (**1**) and 6,8-19DA (**3**), indicating the development of a strong red color. On the other hand, the proportion of ΔR displayed around 30 with polymer of TCDA (**2**), AE-PCDA (**4**) and monomer (**7**), indicating a small blue to red color change correspond to the observation by eyes. In case of PDA-based paper of polymer **5**, **6** and **8**, the proportion of ΔR was ca. 60. In case of chloroform vapor, the proportion of ΔR is ca. 80 with polymer of TCDA (**2**), 6,8-19DA (**3**), AE-PCDA (**4**), Et-AEPCDA (**5**) and Br-Et-AEPCDA (**6**). Low responses were detected when test paper exposed to vapor of pentane, hexane, cyclohexane and ether. They showed ΔR value below 10 with all paper-based PDA sensor array, resulting in the insignificant color change as previously observed by eyes (Figure 3.5). Interestingly, poly-6,8-19DA (**3**) was observed the high red color (ΔR ~ 90) almost all experiment with VOCs excepted pentane and hexane. It indicates a good sensitivity with organic solvent vapors. On the other hand, poly-AE-PCDA (**4**) gave less response to all VOCs vapor phase as it appeared as blue. Remarkably, this color change profile obtained from flat scanner produced a good reproducibility showing error bars below ~ 0.3.

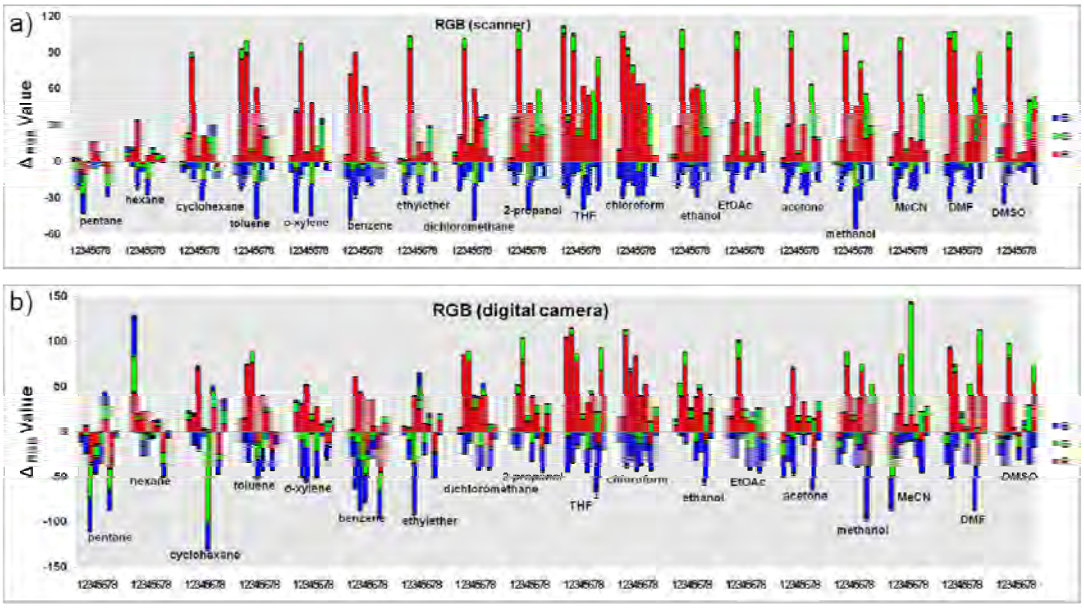


Figure 3.7 Quantitaive color change profile of paper-based PDA sensor array prepared from diacetylene monomers **1-8** after 60 min exposure to saturated vapors of volatile organic solvents at 30 °C obtained from (a) scanner and (b) digital camera. Error bars represent standard deviations of the intensity of each polymer.

The color change profiles received from digital camera of PDA-based paper before and after exposed to VOCs vapor are presented in Figure 3.7b. Even though it showed similar patterns with results from scanner but some colorimetric pattern profiles from vapors such as pentane, hexane, cyclohexane and ether, were quite unexpected. For example, those solvents triggered small blue to purple color change according to naked eyed observation but ΔR and ΔG were found in negative value while the ΔB was shown in positive value. Moreover, the ΔR obtaining from a camera generated typically low values in comparison with a scanner (below ~ 30) whereas the ΔB value has an approximate value. For example, polymer **2** and **3** showed ΔR from scanner was around 100 with toluene but ΔR from camera is 60. From the above observation, it indicated that color response from the camera has a lower sensitivity than flat scanner.

Even though both of two color changes profiles, from the scanner and the digital camera, are quite in good agreement with the observation by eyes but we reason that scanner have more consistent result than camera according to previous literatures and from above discussion [5,55,58]. Scanners are not only relatively inexpensive and portable but also the scanned images are always in focus, and the intensity of images is not affected by lighting condition. Digital cameras, on the other hand, have the disadvantage that the intensity of digital images is affected by lighting condition resulting in lower reproducibility.

3.7 Principal component analysis (PCA)

Even though the histogram of color change profile demonstrated differentiable pattern of chromic change toward each VOCs tested, principal component analysis (PCA) is always used to analyze the data of sensor array [3,12,13,60,61]. Without knowing the class to which the samples belong, PCA is a mathematical transformation used to establish samples classification by extracting highly correlated data from a large amount of correlated and non-correlated data and to group the samples with similar characteristics. To carry out this quantitative analysis, we input the ΔRGB color values from cropped images to generate a set of 5184 colorimetric data (18 VOCs x 12 replicates x 8 polymers x 3 values of each RGB) as a multivariate data matrix. Based on the data similarity of RGB values obtained from the scanner, the data in 24 variables (RGB values of 8 polymers) can be reduced to a two-dimension PCA score plot with clear 18 clusters for 18 VOCs (Figure 3.8a).

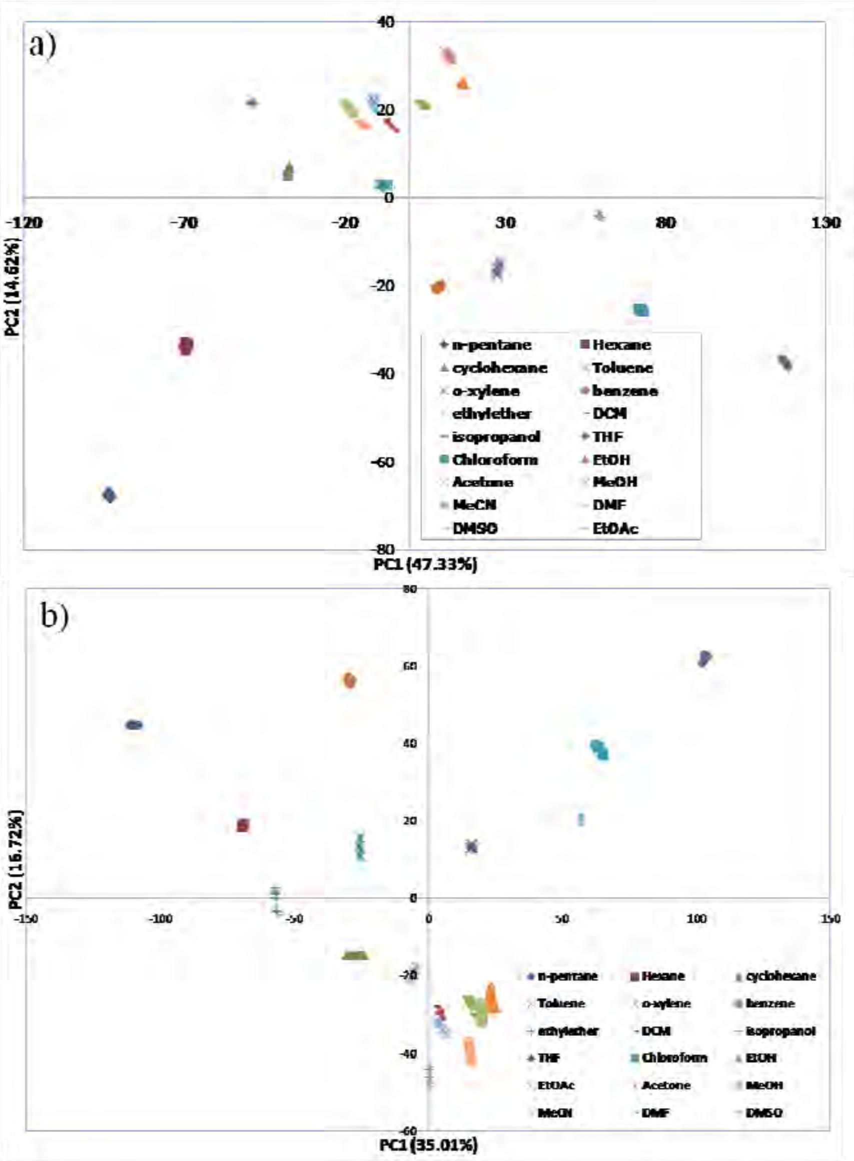


Figure 3.8 PCA score plot of paper-based PDA sensor array derived from polymer **1-8** form (a) scanner and (b) digital camera, upon exposure to 18 solvents. Each data point represents an average of RGB value obtained from 12 replications.

PCA score plot from scanner showed that the first component (PC1) accounts for 47.33% of variance, while the second component (PC2) accounts for 14.62%, providing the sum of these two PCs of 61.95%. Factorial discriminate analysis (FDA) is applied on selected principal component (PC) scores to test the discriminating accuracy of the sensor array. An accuracy levels of 100% obtained from FDA is achieved from the first two PC scores indicating an excellent discerned among 18 vapors of VOCs. On the other hand, PCA score plot from digital camera displayed the first component (PC1) accounts for 35.01% of variance, while the second component (PC2) accounts for 16.72%, providing the sum of these two PCs of 51.73%. An accuracy levels of 97.69% obtained from FDA is achieved from the first two PC scores.

Since it is not always the case that every variable is significant for the discrimination of the analysis, some of the data may represent noise and can negatively affect the analysis. For a sensor array, if the numbers of sensing elements can be reduced without deterioration of the discriminating performance, faster analysis would be achieved. In the attempt to reduce the sensing elements, PCA loading plot was used to identify the importance of each individual polymer toward each PC. The loading plot obtained from the polymer 6,8-19 DA (**3**) was the main contributor to PC1 while polymer **8** was showed the highest contributor to PC3 (Figure 3.9). PCA score plot from scanner, the first component (PC1) accounts for 67.08% of variance, and the second component (PC2) accounts for 30.06%, providing the sum of these two PCs of 97.14%. Pleasingly, the FDA cross-validation results also revealed 100% of the variance (Figure 3.9), the sensor array composed of polymer **3** and **8** displayed a better discriminating ability due to the reduction of non-informative and redundant data. Up to this point, PDA coated paper sensor array was successfully prepared and used for the VOCs discrimination. The color response was quantified using scanner and the data were statistically evaluated by PCA. This process had led to the complete distinguish of 18 different VOCs. In the comparison with previous report, our system showed the highest VOCs sensing capability and the quantitative analysis method was first established [4,6,7,10,54,].

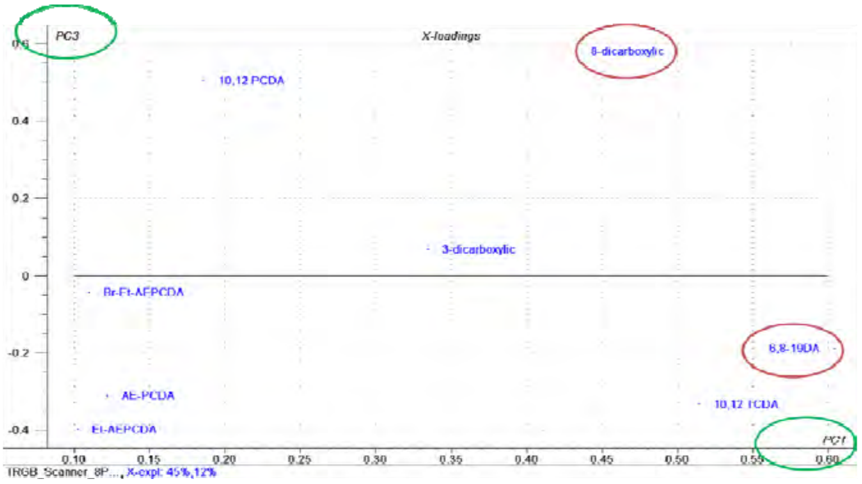


Figure 3.9 The loading plot obtained from the polymer 6,8-19 DA (**3**) and polymer **8**

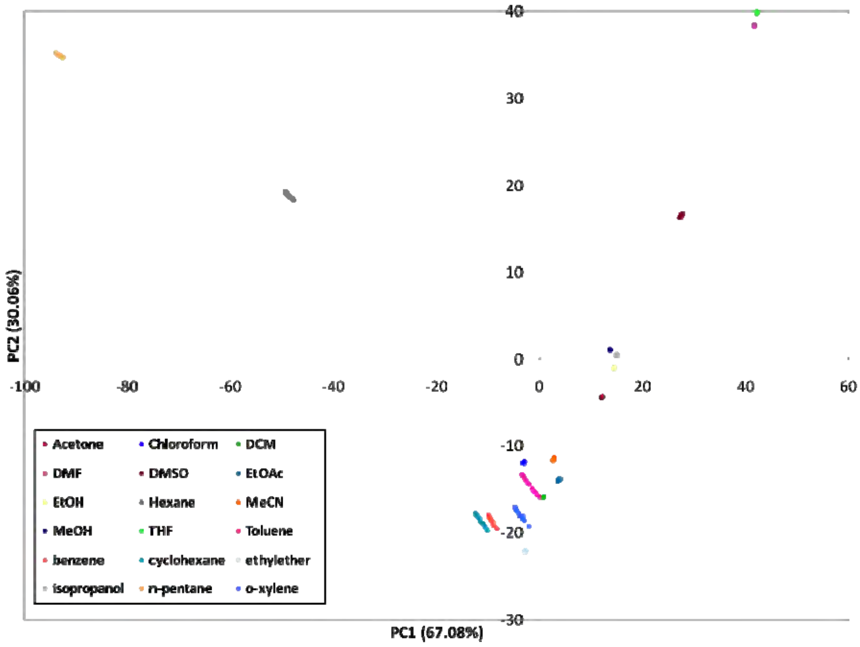


Figure 3.10 PCA score plot of paper-based PDA sensor array responses from scanner upon exposure to 18 solvents to two polymer; the polymer 6,8-19 DA (**3**) and polymer **8**. Each data point represents an average of RGB value obtained from 12 replications.

3.8 Gasoline detection

Gasoline is a petroleum-derived liquid mixture which is primarily used as a fuel in internal combustion engines. Since the first production of gasoline in 1900s, the hydrocarbon composition of gasoline was formulated and a variety of additives were used to adjust their properties. Therefore, gasoline formula is not uniform. In Thailand, many types of automotive gasolines have been used such as Gasohol 95 (G95), Gasohol 91 (G91), Gasoline 91 (B91), Diesel (D), E20 and Biodiesel (B5). Each one of them has to be used specifically in order to gain optimal energy performance. The components of gasohol are gasoline (90%) blend with ethanol (10%). Diesel fuel is a specific fractional distillate of petroleum fuel oil which used in diesel engines. E20 is a petrol fuel, which blends 20 percent ethanol with gasoline 80 percent, reduces hydrocarbon and carbon monoxide. Biodiesel refers to a vegetable oil or animal fat based diesel fuel consisting of long-chain alkyl esters. Biodiesel is typically made by vegetable oil and animal fat with an alcohol. B5 contains 5 percent biodiesel and 95 percent petroleum diesel.

Based on government regulations, different types of gasoline are differentiated using color additive to prohibit misuse. (figure 3.11). This easy and simple method allows differentiation by the naked eye, but the observation does not reflect chemical component within the gasoline. Nowadays, exact composition is analyzed using gas chromatography, IR spectroscopy and photothermal analysis [62-68]. These methods require complicated data analysis and expensive instrument. Therefore, the needs for inexpensive, portable and rapid gasoline testing remain challenging.

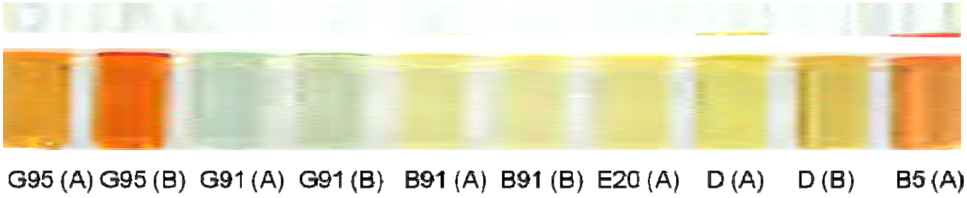


Figure 3.11 The appearance of commercial gasoline from Petroleum Authority of Thailand (A) and Esso company (B).

From the above results, the discrimination and identification of common volatile organic solvents has been successfully established using paper based-PDA sensor array derived from DA **1-8** in combination with the statistic data analysis. In this section, we will apply our developed analysis platform for the colorimetric differentiation between gasolines.

3.8.1 Colorimetric response

In this application, eight kinds of diacetylene monomers PCDA (**1**), TCDA (**2**), 6,8-19DA (**3**), AE-PCDA (**4**), Et-AEPCDA (**5**), Br-Et-AEPCDA (**6**), monomer **7** and monomer **8** were fabricated onto filter paper as previous discussed. We hoped that the color changes from blue to red of paper based PDA sensor upon exposure to a vapor of gasolines would occur due to the volatile organic compound component in gasoline. In this experiment, commercially available gasoline such as gasohol 95(G91), gasohol 91(G91), gasoline 91(B91), diesel(D), E20 and B5 from Petroleum Authority of Thailand (A) or Esso Company (B) will be tested under our developed method.

The color response upon exposure of PDA tested to 10 types of gasoline vapors were depicted in Figure 3.12. The blue to purple color change was observed with PDA **1** when exposed to vapor of four types of Gasohol while polymer **2**, **3**, **5** and **7** showed sensitivity when exposed to vapor of Gasohol 95 and Gasohol 91 from both companies. Polymer **2** showed the purple color after exposed to E20. Only PDA **3** was induced blue to red by Gasoline 91A, Gasoline 91B and E20 while PDA **5** showed blue to purple with Gasoline 91A, Gasoline 91B and E20. Notably, PDA paper array from polymer **4**, **6** and **8** typically showed low response with any gasoline. Moreover, non-response to vapor of Diesel and B5 appeared as the blue color in all of the experiments. From these results, we reasoned that the Gasohol 91, Gasohol 95 and E 20 typically induced strong color change. This can be explained by the fact that the content of EtOH played an important role in the color transition of array of PDA paper.

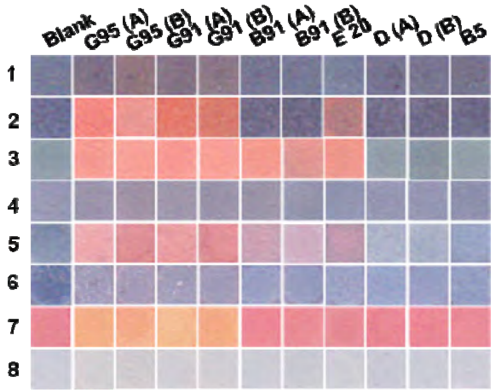


Figure 3.12 Scanned images of the PDA-based paper array prepared with diacetylene monomers **1-8** after exposed to vapors of gasoline for 60 min at 30 °C. Blanks refers to UV-irradiated DA-test paper with no exposure to gasoline.

3.8.2 Color change profile

The color change profiles of scanned images before and after exposure with 10 gasolines were shown in Figure 3.13. Typically, this histogram showed that red values were positive while blue values were negative. For example, polymer **2**, **3** and **5** showed a good response with gasohols (ΔR ca. 100), gasoline 91and E20 (ΔR ca. 50). The high red color values are positive which correspond to the observation by naked eyed. Otherwise, Diesel and B5 did not show the considerable color changes with any PDA test papers.

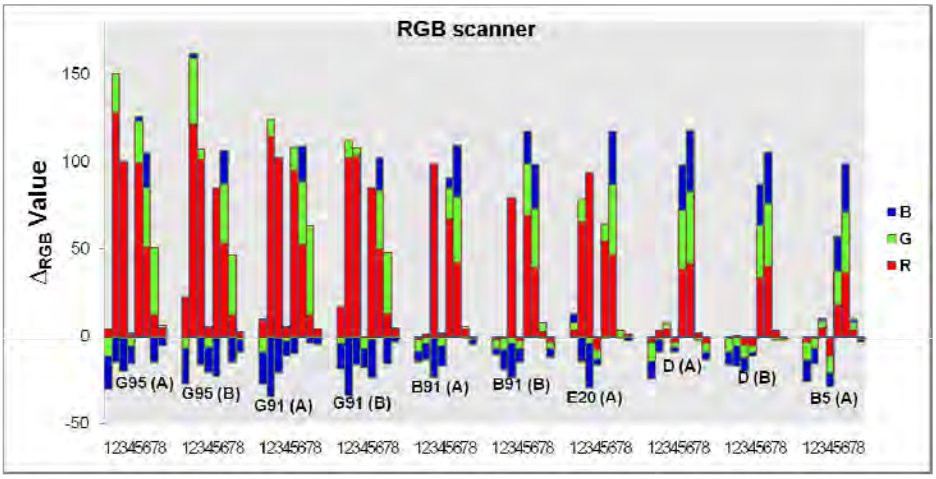


Figure 3.13 Quantitative color change profile of paper-based PDA sensor array prepared from diacetylene monomers 1-8 after 60 min exposure to gasolines at 30 °C. Error bars represent standard deviations of the intensity of each polymer.

3.8.3 Principal component analysis (PCA)

Although, the histogram plot showed the differentiate color pattern for gasoline detection, the relationship of on data set of 2160 (10 gasoline × 9 repeats × 8 polymers × 3 values of each RGB) was also further simplified using PCA technique. From PCA score plot, a total variance of 91.14% can be obtained from the first two PCs in which PC1 and PC2 contributed 80.20% and 11.74%, respectively (Figure 3.14). In the PCA score plot, the various gasolines of each company were discriminated. This color pattern induced by each gasoline due to properties of each grade of gasoline and additives which impart special properties to fuel in order to gain optimal engine performance.

The color change from PDA paper induced by B91(A), B91(B), E20(A), G91(A) and G91(B) showed a very good scattering. This indicated the ability to discriminate these gasoline form the remaining five gasolines, B5(A), D(A), D(B), G95(A) and G95(B), which were clustered more closely together. Unfortunately, the response from Gasohol 95 of both companies are overlapped, this is perhaps due to similar content of ethanol in each gasoline. The same happens to B5 (A) and D (B). This result indicates B5 has chemical and physical properties similar to conventional diesel fuel. Importantly, this is the first example to use paper based PDA sensor array to discriminate automotive fuels.

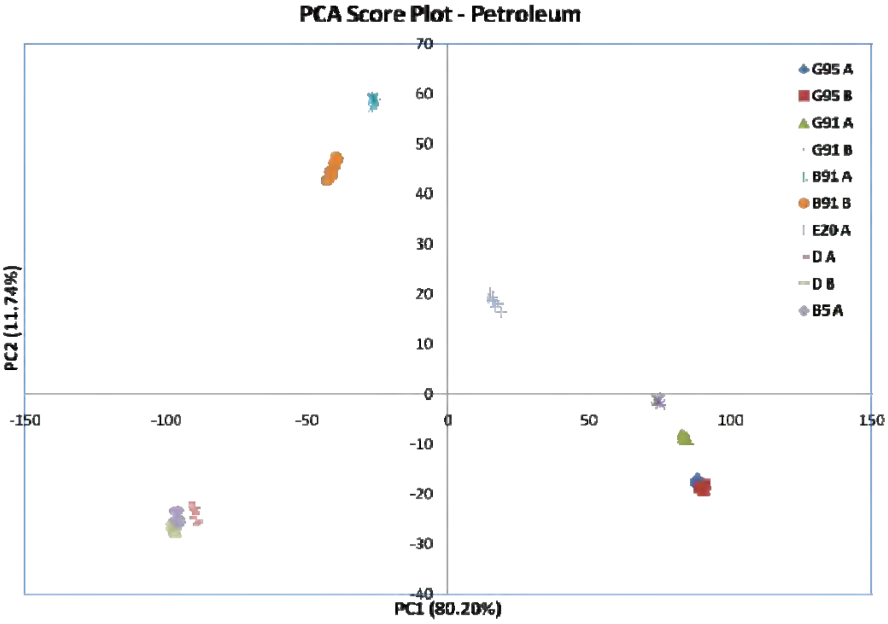


Figure 3.14 PCA score plot of ΔRGB data set obtained from paper-based PDA sensor array derived from polymer **1-8** upon exposure to 10 gasolines. Each data point represents an average of RGB value obtained from 9 replications.

CHAPTER IV

CONCLUSION

4.1 Conclusion

A new, low-cost and portable paper-based polydiacetylene (PDA) array for the detection and identification of VOCs and gasoline has been fabricated and developed.

Two series of amphiphilic (AE-PCDA (**4**), Et-AEPCDA (**5**), Br-Et-AEPCDA (**6**)) and bolaamphiphilic (monomer **7** and **8**) diacetylene monomers were successfully synthesized and characterized. Eight types of diacetylene monomers were fabricated on filter paper by drop and dry technique followed by UV irradiation to induce polymerization and generate PDA-coated papers.

Our PDA array showed unique colorimetric response to eighteen different volatile organic compounds (VOCs) in vapor phase. The color transition could be observed by naked eye. To quantitatively analyze the color transition, a scanner and a digital camera were selected as an optical recorder and the data subjected to principal component analysis (PCA). As a result, eighteen different VOCs vapor were differentiated with 100% accuracy.

In addition, using the same method, the array successfully differentiated ten different types of automotive gasoline from two commercial sources. Thus, we have developed a novel and economical method for detecting and differentiating VOCs in the environment with high accuracy. The work has excellent commercial potential and could be further developed into a platform for an onsite analysis of VOCs.

4.2 Suggestion for future works

To expand the scope of this work, our paper based polydiacetylene sensor can be applied for the detection of toxic gases releasing from industry i.e. acetylene, ammonia and nitrogen oxide etc. In addition, viability of papers should be investigated in order to see the effect of the matrix to colorimetric response of our PDA arrays.

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APPENDICES

APPENDIX A

NMR SPECTRA

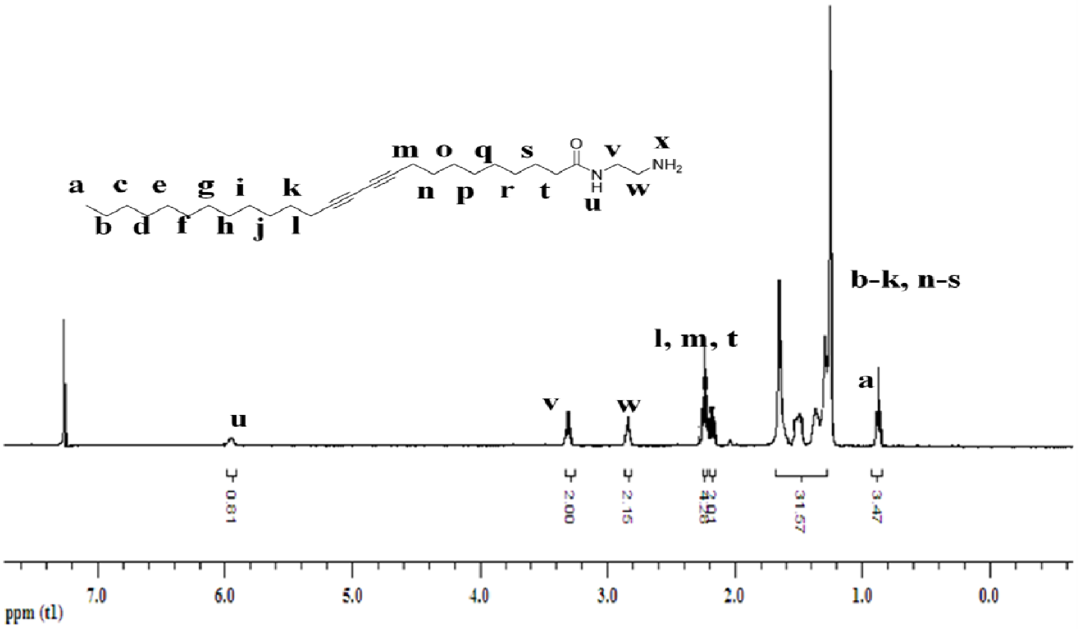

Figure A1 ^{1}H NMR spectrum of *N*-(2-aminoethyl) pentacosa-10,12-diynamide (AE-PCDA, 4)

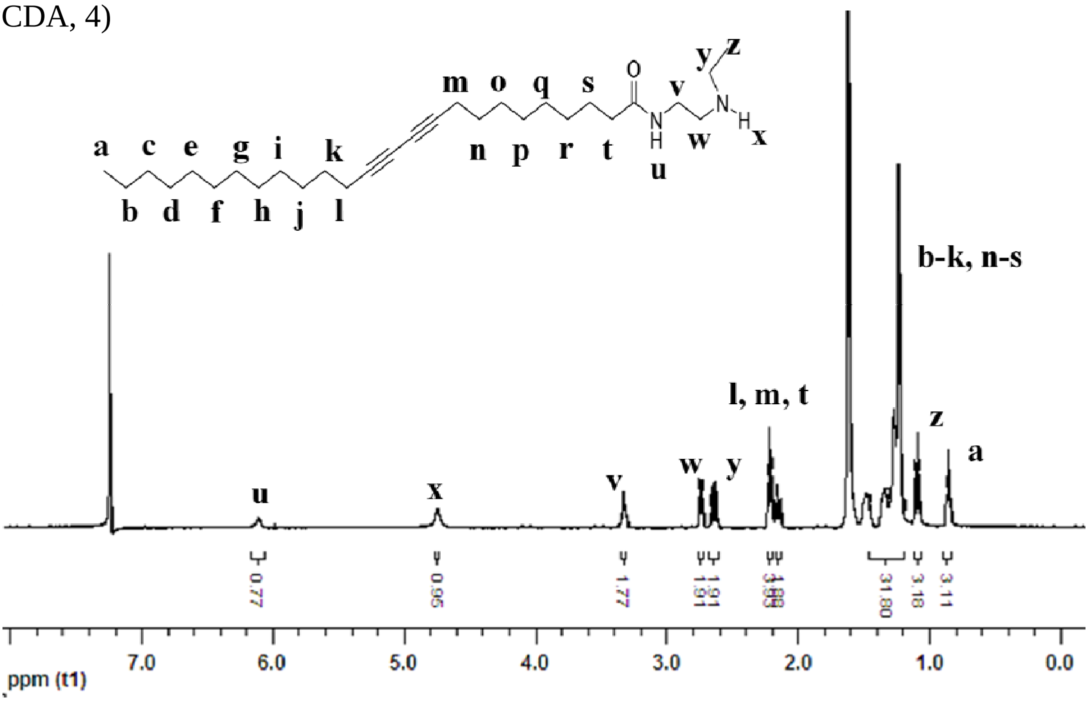

Figure A2 ^{1}H NMR spectrum of *N*-(2-(ethylamino) ethyl) pentacosa-10,12-diynamide (Et-AEPCDA, 5)

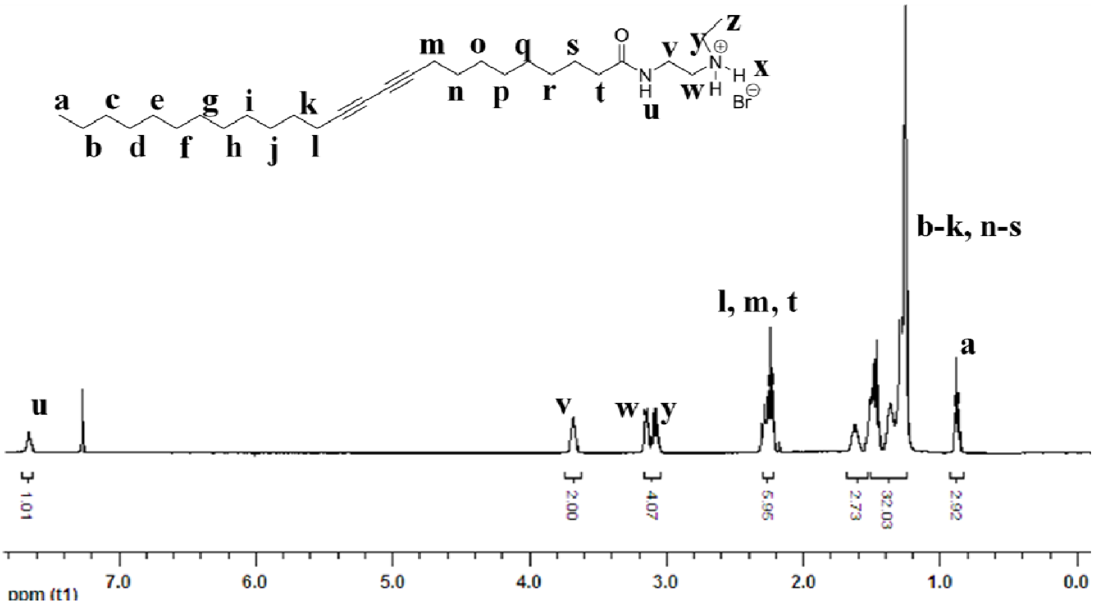

Figure A3 ^{1}H NMR spectrum of *N*-ethyl-2-pentacosa-10,12-diynamidoethanaminium bromide (Br-Et-AEPCDA, 6)

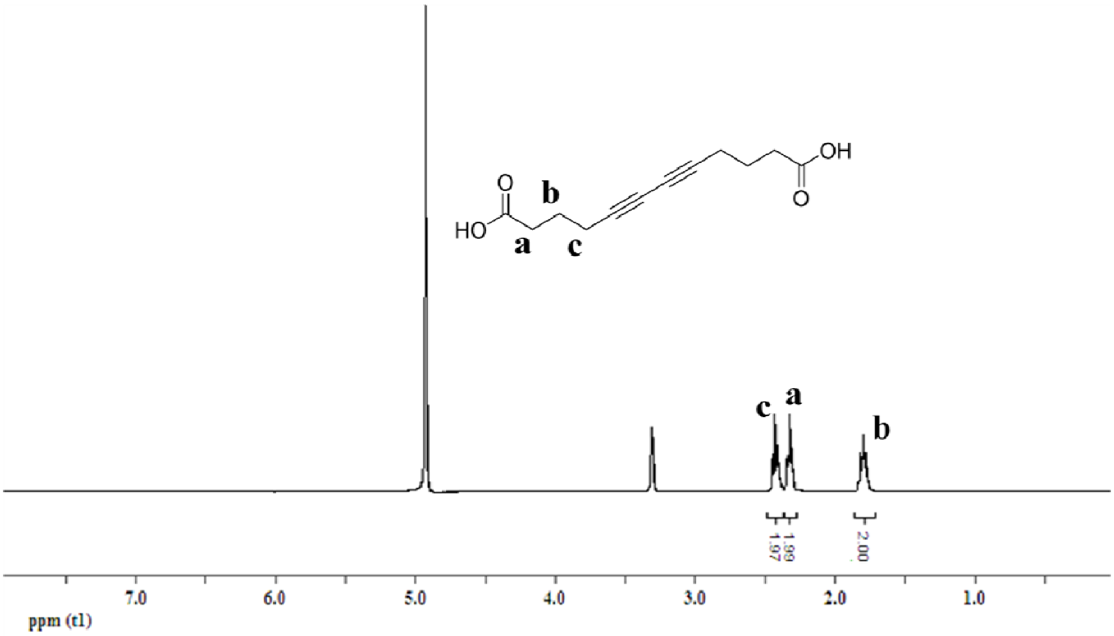

Figure A4 ^{1}H NMR spectrum of 5,7-dodecadiynedioic acid (7)

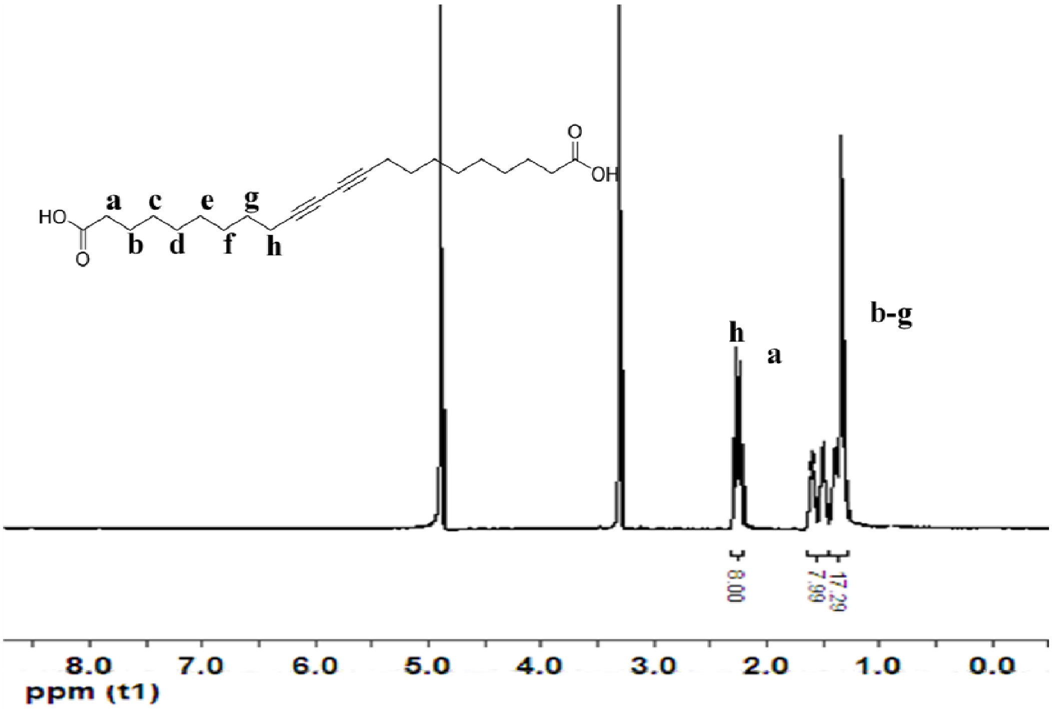

Figure A5 ^{1}H NMR spectrum of 10,12-docosadiynedioic acid (8)

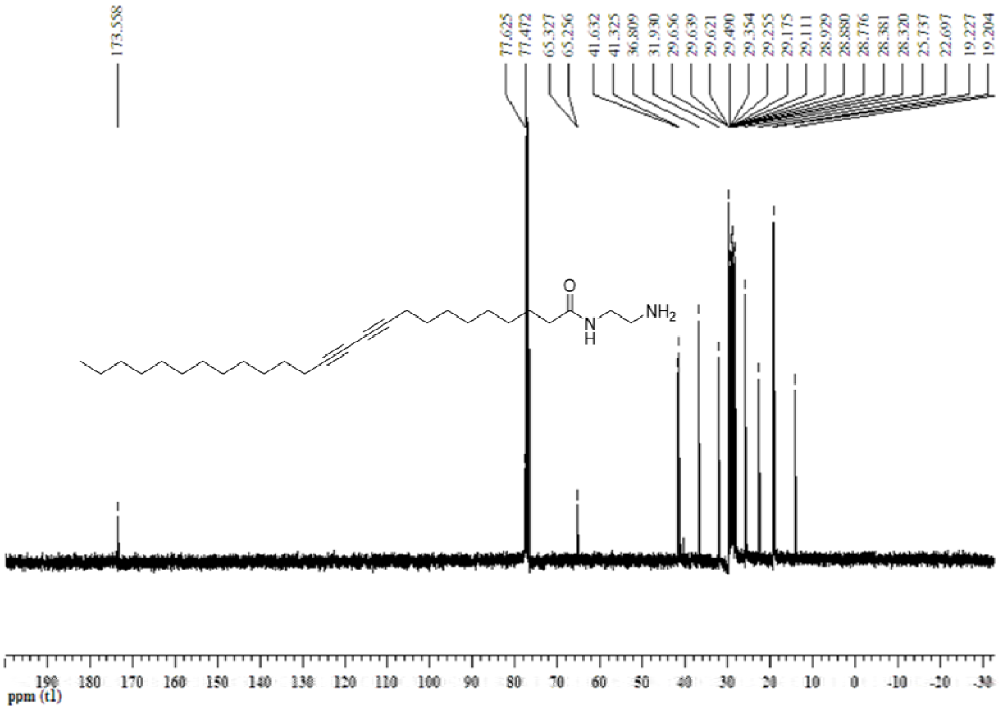

Figure A6 ^{13}C NMR spectrum of *N*-(2-aminoethyl) pentacosa-10,12-diynamide (AE-PCDA, 4)

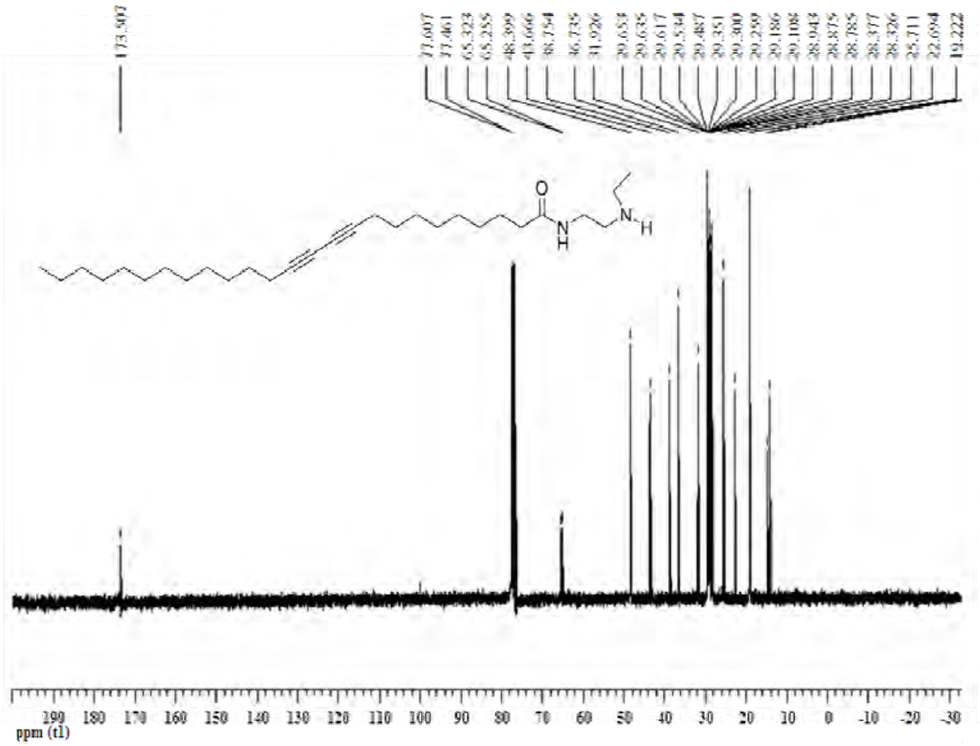

Figure A7 ^{13}C NMR spectrum of *N*-(2-(ethylamino) ethyl) pentacosa-10,12-diynamide (Et-AEPCDA, 5)

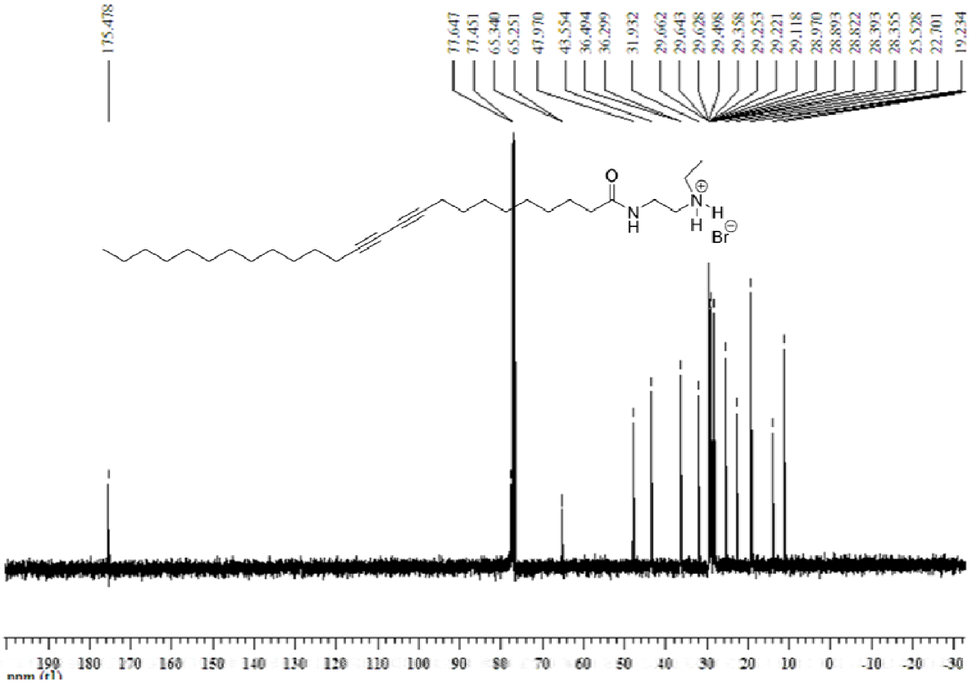

Figure A8 ^{13}C NMR spectrum of *N*-ethyl-2-pentacosa-10,12-diynamidoethanaminium bromide (Br-Et-AEPCDA, 6)

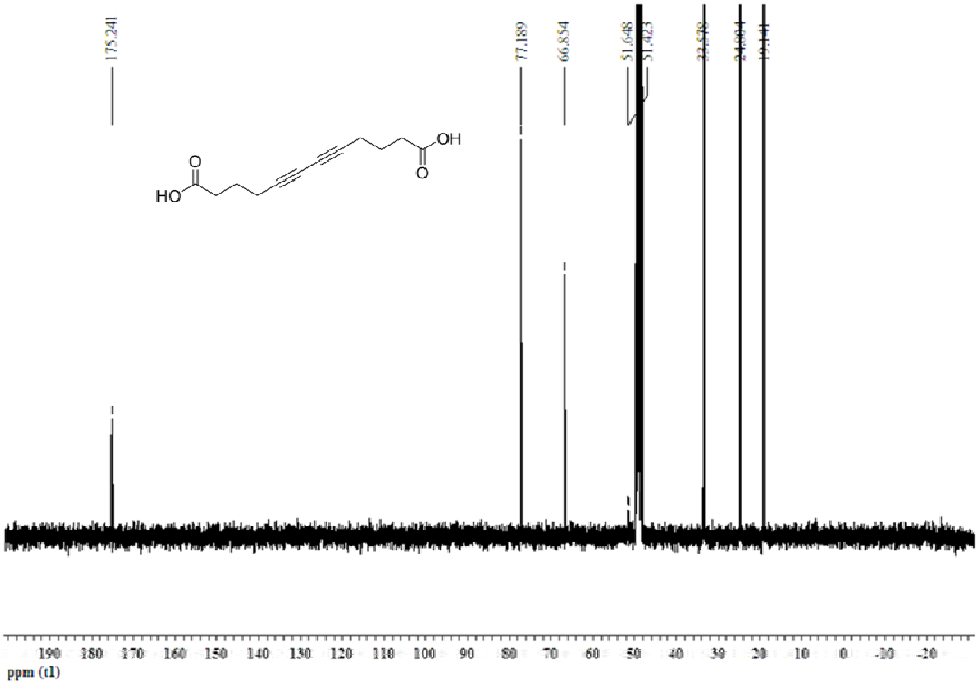

Figure A9 ^{13}C NMR spectrum of 5,7-dodecadiynedioic acid (7)

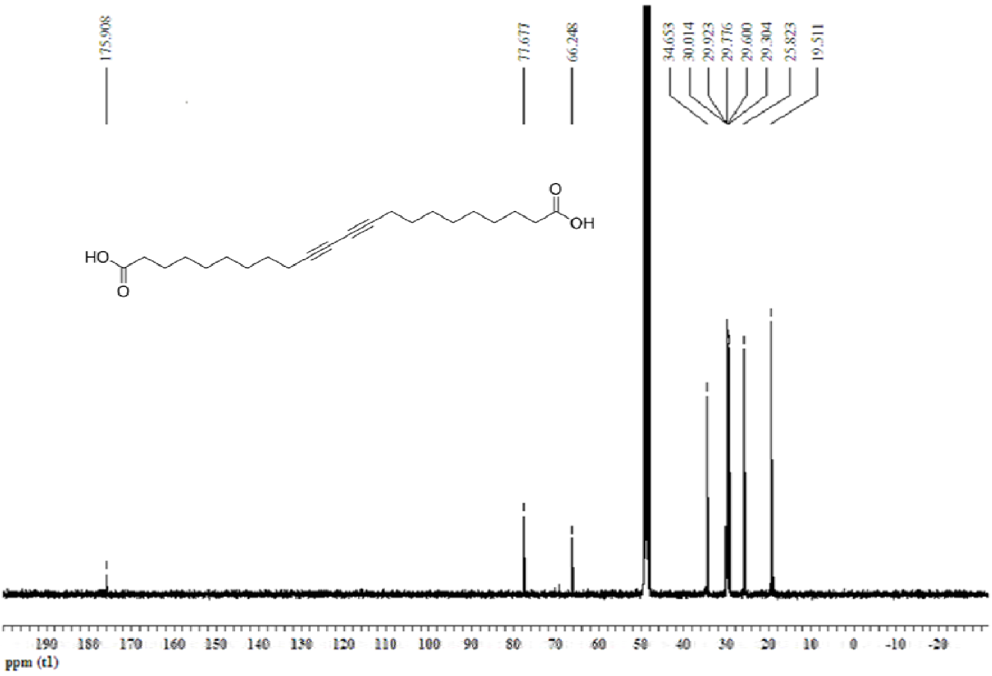

Figure A10 ^{13}C NMR spectrum of 10,12-docosadiynedioic acid (8)

APPENDIX B

MASS SPECTRA

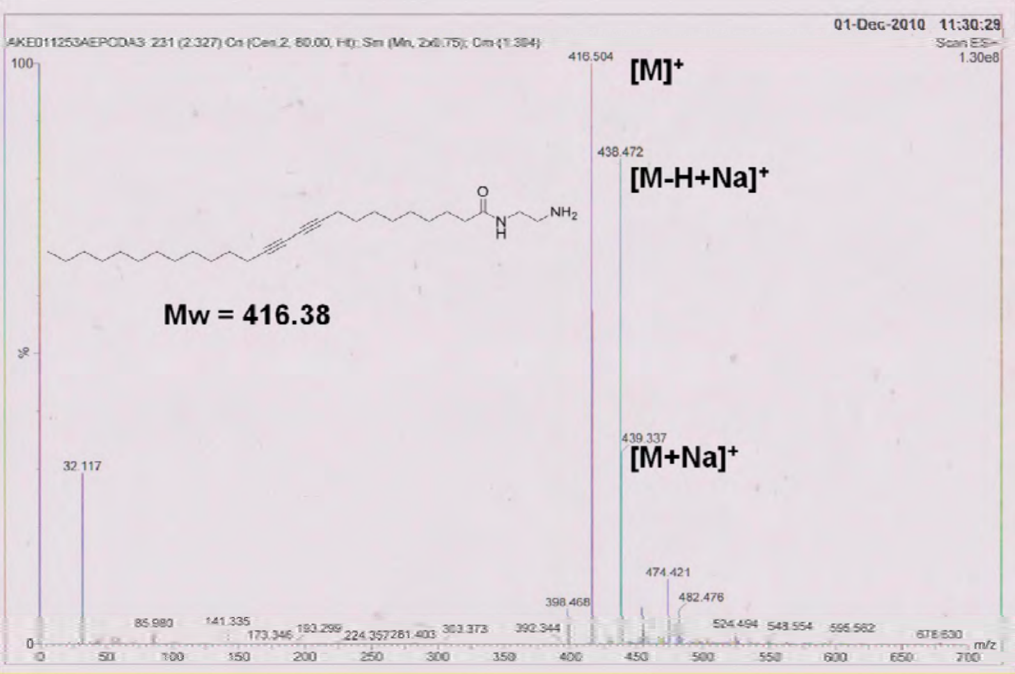

Figure B1 Mass spectrum (ESI+) of *N*-(2-aminoethyl) pentacosa-10,12-diynamide (AE-PCDA, 4)

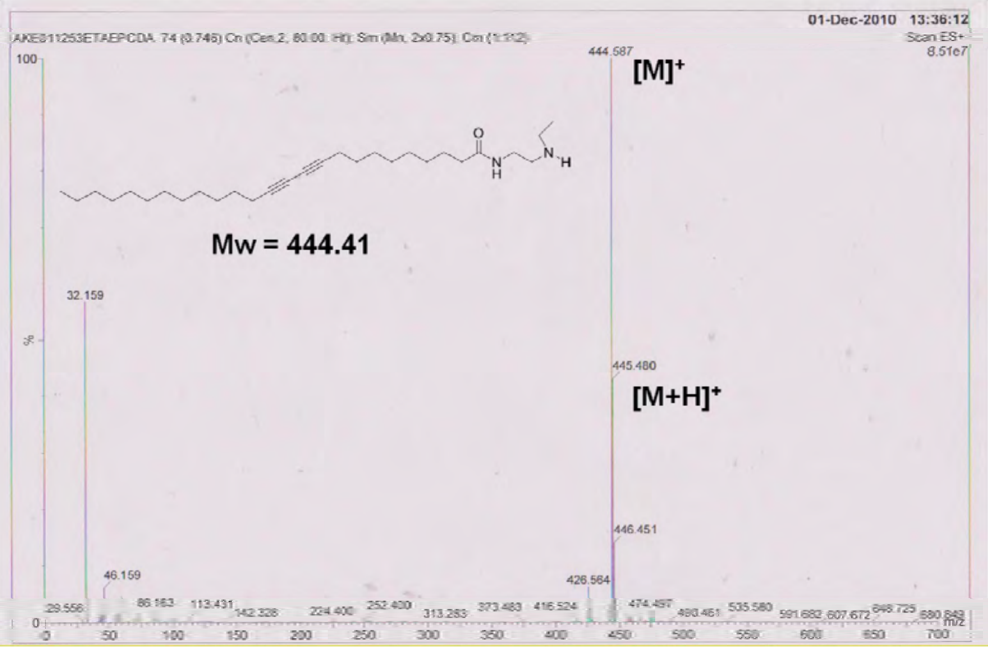

Figure B2 Mass spectrum (ESI+) of *N*-(2-(ethylamino) ethyl) pentacosa-10,12-diynamide (Et-AEPCDA, 5)

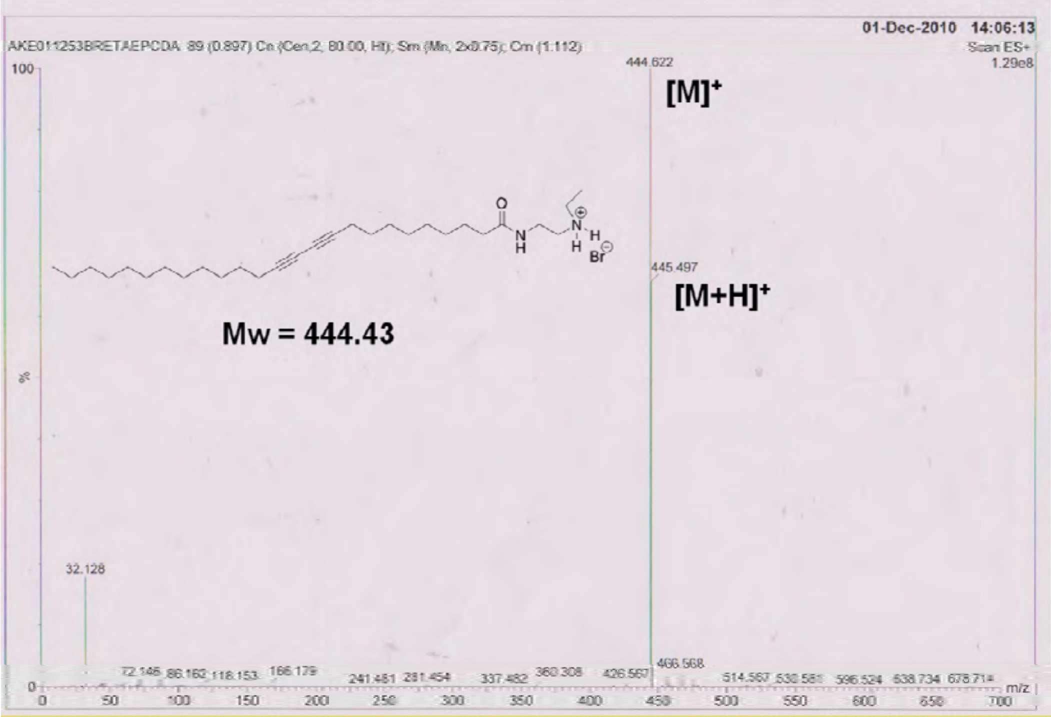

Figure B3 Mass spectrum (ESI+) of *N*-ethyl-2-pentacosa-10,12-diynamido ethanaminium bromide (Br-Et-AEPCDA, 6)

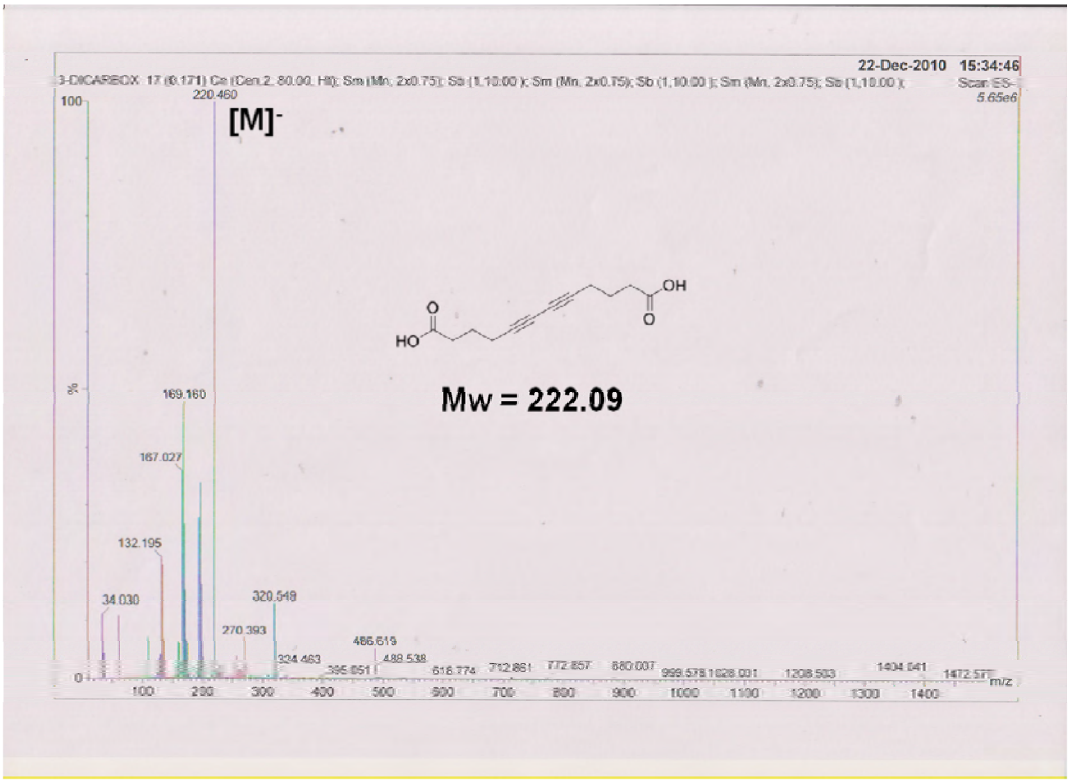

Figure B4 Mass spectrum (ESI-) of 5,7-dodecadiynedioic acid (7)

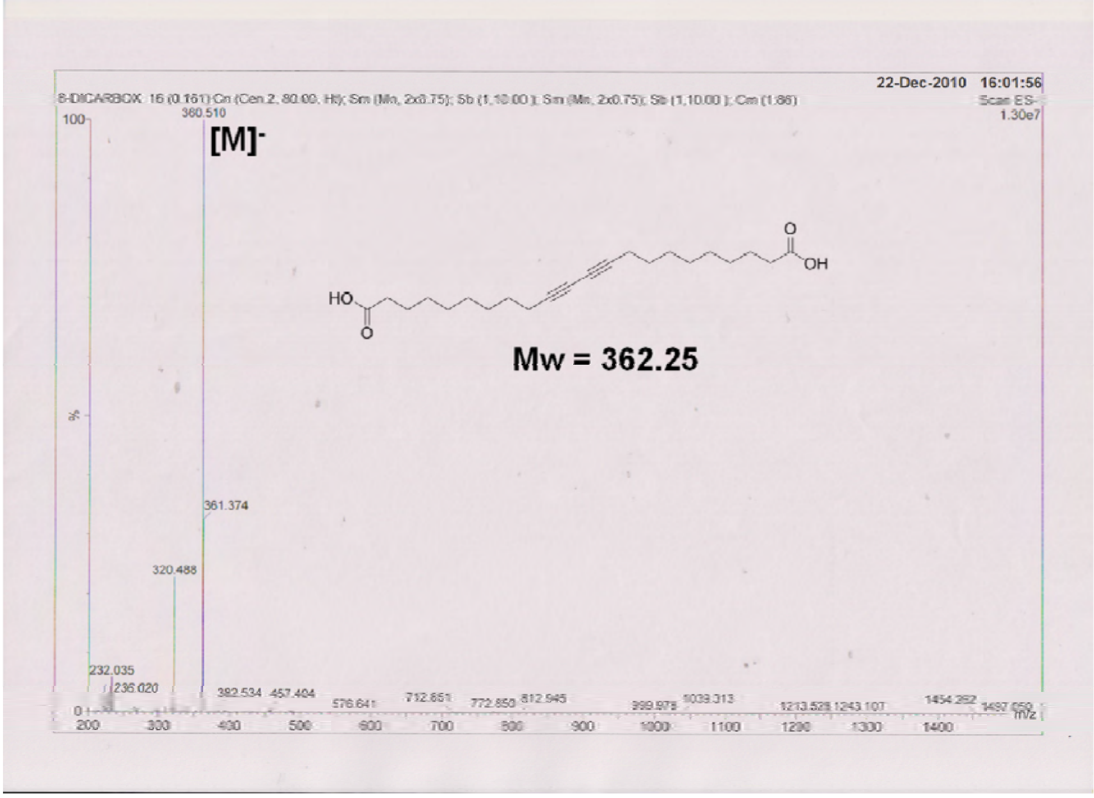

Figure B5 Mass spectrum (ESI-) of 10,12-docosadiynedioic acid (8)

VITAE

Miss Thichamporn Eaidkong was born on November 3rd, 1985 in Songkhla, Thailand. She received a Bachelor's Degree of Science, majoring in Chemistry from Faculty of Science, Srinakharinwirot University in 2007. She has been a graduate student studying Petrochemistry and Polymer Science as her major course from Faculty of Science, Chulalongkorn University and completed the program in 2011. During the master study, she had received a scholarship from the 90th anniversary of Chulalongkorn University Fund. Throughout master study, she had a great opportunity to present her work in poster session in the topic of "Colorimetric paper based array from polydiacetylenes: new sensor platform for volatile organic compounds" at the 7th International Symposium on Advanced Materials in Asia-Pacific (7th ISAMAP). And she had a chance to present her work in oral session in the topic of "Colorimetric paper based array from polydiacetylenes: new sensor platform for discrimination of volatile organic compounds" at Pure and Applied Chemistry International Conference (PACCON2011). The finance for joining the conference was supported by National Center of Excellence for Petroleum and Petrochemicals and Advanced Materials (NCE-PPAM), Chulalongkorn University. She graduated in 2011.

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