ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

CALIX[4]PYRROLE BASED SENSORS AND SUPRAMOLECULAR POLYMERS

Ph.D. THESIS

Samet YUVAYAPAN

Department of Chemistry Chemistry Programme

DECEMBER 2019



ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

CALIX[4]PYRROLE BASED SENSORS AND SUPRAMOLECULAR POLYMERS

Ph.D. THESIS Samet YUVAYAPAN (509142015)

Department of Chemistry Chemistry Programme

Thesis Advisor: Assoc. Prof. Dr. Abdullah AYDOĞAN

DECEMBER 2019



<u>ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ</u>

KALİKS[4]PİROL TEMELLİ SENSÖRLER VE SUPRAMOLEKÜLER POLİMERLER

DOKTORA TEZİ

SAMET YUVAYAPAN (509142015)

> Kimya Anabilim Dalı Kimya Programı

Tez Danışmanı: Doç. Dr. Abdullah AYDOĞAN

ARALIK 2019



Samet YUVAYAPAN, a Ph.D. student of ITU Graduate School of Science Engineering and Technology with student ID 509102066, successfully defended the thesis entitled "CALIX[4]PYRROLE BASED SENSORS AND SUPRAMOLECULAR POLYMERS" which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

· · · ·	A 1 •	
I DOCIC	Advisor ·	
1 110315	AUVISUI .	

Assoc.Prof. Dr. Abdullah AYDOĞAN Istanbul Technical University

Jury Members	:	
--------------	---	--

Assoc.Prof. Dr.İ. Volkan KUMBARACI Istanbul Technical University

Prof. Dr. Kasım Şener Yıldız Technical University

Prof. Dr. Turan Öztürk Istanbul Technical University

Prof. Dr. Amitav Sanyal Bogazici University

.....

.....

.....

.....

Date of Submission : 14.11.2019 Date of Defense : 30.12.2019



To my family and my fiancee,



FOREWORD

First of all, I would like to thank my supervisor Abdullah AYDOĞAN for his guidance, patience, and his support during all stages of mydissertation. I could not imagine to finish this thesis without his supervision. I'am honored for being his first graduating Ph.D. student. I also need to thank to the thesis committee members Ibrahim Volkan KUMBARACI and M. Kasım ŞENER for their valuable helps, critical comments and most importantly their understandings. Also, I would like to thank my colleagues Yonca ALKAN GÖKSU and Sana AMHARAR for their support and assistance. Finally, I would like to thank specially Semanur ŞEN for being with me during difficult times. I also thank to Scientific Research Projects Coordination Unit of Istanbul Technical University (Grant Number: TDK-2017-40643) and The Scientific and Technological Research Council of Turkey (TUBITAK 118Z327) for their financial supports.

December 2019

Samet YUVAYAPAN (M.Sc. Chemist)



TABLE OF CONTENTS

<u>1</u>	Page
FOREWORD	ix
TABLE OF CONTENTS	xi
ABBREVIATIONS	. xiii
LIST OF TABLES	XV
LIST OF FIGURES	xvii
SUMMARY	. xix
ÖZET	. xxi
1. INTRODUCTION	1
1.1 Purpose of Thesis	2
2. COUNTER CATION DEPENDENT AND STIMULI RESPONS	IVE
SUPRAMOLECULAR POLYMERS CONSTRUCTED	BY
CALIX[4]PYRROLE BASED HOST-GUEST INTERACTIONS	3
2.1 Introduction	3
2.2 Results and Discussion	5
2.3 Conclusions	14
2.4 Experimental Section	14
2.4.1 General Information	14
2.4.2 Synthesis	15
2.4.2.1 Compound 1	15
2.4.2.2 CTAOH	15
2.4.2.3 Compound 2a	16
2.4.2.4 Compound 2b	16
3. SUPRAMOLECULAR CALIX[4]PYRROLE POLYMERS FROM	Α
COMPLEMENTARY PAIR OF HOMODITOPIC HOST-GU	EST
MOLECULES	17
3.1 Introduction	17
3.2 Experimental	19
3.2.1 General Considerations	19
3.2.2 Synthesis and Characterization	19
3.2.2.1 Compound 5	19
3.2.2.2 Compound 2[59]	19
3.2.2.3 Compound 1	20
3.3 Results and Discussions	20
3.4 Conclusion	26
4. CALIX[4]PYRROLE DECORATED CARBON NANOTUBES ON PAI	PER
FOR SENSING ACETONE VAPOR	27
4.1 Introduction	27
4.2 Materials and Methods	29
4.2.1 General Considerations	29
4.2.2 Synthesis of Compound 3	29
4.2.3 Noncovalent functionalization of SWCNT	30

1,2, 11 doneddion o'r puper benborb	9
4.2.5 Sensing measurements	1
4.3 Results and Discussion	2
4.4 Conclusion	С
5. CONCLUSION	3
REFERENCES	5
CURRICULUM VITAE	5



ABBREVIATIONS

: Carbon Nuclear Magnetic Resonance Spectroscopy
: Deutareted Chloroform
: Dichloromethane
: Chloroform
: Methanesulfonic Acid
: Carbon Nano Tube
: Critical Polymerization Concentration
: Cetrimonium cation
: Cetrimonium Hydroxide
: Cetrimonium Acetate
: Copper(2)sulfate pentahydrate
: Dichloromethane
: Diffusion-Ordered NMR Spectroscopy
: Degree of Polymerization
: Fourier Transform Infrared Spectrophotometer
: Hydrogen Nuclear Magnetic Resonance Spectroscopy
: Methyl Alcohol
: Nuclear Overhauser Effect Spectroscopy
: Room Temperature
: Scanning Electron Microscope
: Single-Wall Carbon Nano Tube
: Tetrabuthylammonium Cation
: Tetrabuthylammonium hydroxide
: Tetrahydrofuran
: Volatile Organic Compound
: Specific Viscosity



LIST OF TABLES

Page

 Table 1: Response and recovery times of pristine SWCNT and 3@SWCNT paper sensors.

 35





LIST OF FIGURES

Page

Figure 2.1:Structures of carboxylic acid (1), carboxylate-functional	lized
calix[4]pyrroles (2) and the counter cation dependent supramoled	ular
Figure 2.2. Synthesis of 1 and 2 i) $CuSO(\bullet5(H_2O))$ sodium accordate/THE RT	
h. ii) In MeOH. RT. 1 h.	6
Figure 2.3: Partial ¹ H NMR spectra (500 MHz) of a) 1, b) 2a, c) 2b and d) CTA	AOH
recorded in CDCl ₃ at 25 °C. * denotes residual solvent peaks	7
Figure 2.4: ¹ H NMR spectra (CDCl ₃ , 500 MHz, 25 °C) of 2a at diffe	erent
concentrations: a) 12, b) 35, c) 125, d) 191 mM. * denotes resi	dual
solvent peaks	8
Figure 2.5: Partial ¹ H NMR spectra (CDCl ₃ , 500 MHz, 25 °C) of 2b at diffe	erent
concentrations: a) 12, b) 35, c) 125, d) 190 mM. * denotes resi	dual
solvent peaks	8
Figure 2.6: Specific viscosity (Vs) changes of 2a and 2b plotted against mono	omer
concentration in CHCl ₃ at 25 °C.	10
Figure 2.7: SEM images of gold-coated (a) fiber drawn from a 251 mM Cl	HCl ₃
solution of 2b, and (b) supramolecular polymer gel obtained <i>via</i> free	eze-
supremolecular gel obtained from a 251 mM CHCle solution of 2b s	1 01
$25 ^{\circ}\text{C}$ (d) $50 ^{\circ}\text{C}$ (e) Temperature dependent viscosity change of a	158
mM CHCl ₂ solution of 2b	130
Figure 2.8: Partial ¹ H NMR spectra (500 MHz) of a) $2a$ (100 mM, 0.5 mL)	after
addition of equimolar b) CH ₃ SO ₃ H. d) TBAOH. and d) CH ₃ S	O ₃ H
recorded in CDCl ₃ at 25 °C.	12
Figure 2.9: Specific viscosity changes of CHCl ₃ solutions 2a a) (100 mM)	upon
incremental addition of CH ₃ SO ₃ H, b) (257 mM) upon incremental	ental
change in the temperature	13
Figure 3.1: Chemical structures and pictorial representations of 1 and 2,	and
illustration of the linear supramolecular polymers formed by the l	10st-
guest interaction constructed by anion recognition between 1 and 2.	18
Figure 3.2: Structures of octamethylcalix[4]pyrrole (3), azide- and alk	yne-
Final 2.2 III NDAP $(500 \text{ MH} \text{ CDC} \text{ 25.00})$ $(4 \text{ and } 5, \text{ respectively})$.	21
Figure 3.3: "H NMR spectra (500 MHz, CDCl ₃ , 25 °C) of (a) 2; (b) 1, and (b) mixture of 10 mM 1 and 2. * denotes solvent residual nearly	(c) a
Figure 3.4. The stacked ¹ U NMP spectra (500 MHz, CDC), 25 °C) of solutions	44
Figure 3.4. The stacked in NWK spectra (500 WHz, CDC13, 25°C) of solutions (50 mM) after addition a) 0.10 b) 0.25°C) 0.50°d) 0.75° and e)	1 00
(50 mW) after addition a) 0.10, b) 0.25, c) 0.50, d) 0.75 and c) equivalents of 2	23
Figure 3 5. Partial ¹ H NMR spectra (CDCl ₂ 500 MHz 25 °C) of equimolar mixe	tures
of 1+2 and 3+TBAOAc at different concentrations: a) 8 b) 15 c) 3	1. d)
83, e) 125, and e) 198 mM	23

Figure 3.6: Specific viscosity (V _s) changes of CHCl ₃ solutions at 25 °C: (a) 1 (76 mM)
upon incremental addition of 2, (b) equimolar 1+2 plotted against
monomer concentration, (c) equimolar 1+2 (142 mM) upon incremental
change in the temperature of solution. (d) Concentration dependence of
diffusion coefficient D (500 MHz, 19°C) of equimolar 1+2 in CDCl ₃ 25
Figure 4.1: Structure of octamethylcalix[4]pyrrole
Figure 4.2: Synthesis of pyrene-functionalized calix[4]pyrrole
Figure 4.3: ¹ H NMR spectrum of 3 recorded in CDCl ₃ (* denotes the residual solvent
and H ₂ O peaks) 32
Figure 4.4: Illustration of calix[4]pyrrole decorated SWCNT (3@SWCNT)
Figure 4.5: (a) SEM image (scale bar denotes 250 nm) and (b) thermogravigrams of
3, SWCNT and 3@SWCNT
Figure 4.6: Responses of SWCNT and 3@SWCNT towards 60 ppm at 25 °C (a)
acetone, (b) MeOH, (c) EtOH, (d) THF, (e, f) resistance changes of
3@SWCNT and SWCNT, and (g) comparison of the response differences.
Figure 4.7: Responses of 3@SWCNT on paper chip to different concentrations of
acetone at 25 °C
Figure 4.8: Resistance changes of SWCNT and 3@SWCNT upon exposing relatively
non-polar VOCs

CALIX[4]PYRROLE BASED SENSORS AND SUPRAMOLECULAR POLYMERS

SUMMARY

Calix[4]pyrroles have gained attention because of their ease of synthesis and modifications. They are macrocylic compounds having four pyrrol units connected to each other *via* sp³ hybridized carbon atoms. In addition to these facts, they have anion binding ability in organic solvents, which cause them to change their conformation from 1,3-alternate to cone in which anion bound pyrrole rings of calixpyrrole are directed towards the anion. Aside from that, cation– π interaction between cations and π -electron system of cone-shaped calix[4]pyrroles are also well known.

In the literature, there are scarce examples of supramolecular polymers based on anion recognition ability of calix[4]pyrroles. Eventhough, carbon nanotube based sensors, that detect vapors of different organic solvents, are highly popular in the literature, there are few examples of vapor sensors obtained by non-covalent interaction between single walled carbon nanotubes (SWCNTs) and synthetically modified calix[4]pyrroles.

Three different manuscripts have been published during this Ph.D. work and contents of which were presented in three seperate chapters. Chapter 2 and 3 of this thesis are about supramolecular polymers based on modified calix[4]pyrroles and their anion binding ability. On the other hand, Chapter 4 is about a paper-based asetone vapor sensor fabricated by the deposition of calix[4]pyrrole-functionalized SWCNTs on a filter paper.

In Chapter 2, counter cation dependent and stimuli responsive supramolecular polymers constracted by carboxylate-functinalized calix[4]pyrroles are demonstrated. Unlike literature examples of supramolecular polymers derived from different supramolecular hosts and guests, the present work demonstrates the supramolecular polymers formed by an AB-type monomer which was synthesized by a click reaction between an alkyne-functionalized calix[4]pyrrole and 10-azido-decanoic acid. Using the advantages of the dynamic interaction between calix[4]pyrroles and carboxylate anions, the obtained supramolecular polymers were found to show dependency to temperature in terms of degree of polymerization that was succesfully altered by the addition of organic acids and subsequent addition of an appropriate base.

In Chapter 3, supramolecular calix[4]pyrrole polymers from a complementary pair of homoditopic host-guest molecules are demonstrated. Aside from the first part of the thesis, a triazole bridged bis-calix[4]pyrrole (bis-C4P) was synthesized *via* a click reaction between azide- and alkyne-functionalized calix[4]pyrroles. Additionally, a bis-carboxylate salt was synthesized by an acid-base reaction between suberic acid and tetrabuthyammonium hydroxide. They are further used to construct AA-BB type, linear, thermo responsive supramolecular polymers *via* host–guest interactions between bis-C4P and the carboxylate units of tetrabuthyammonium suberate.

Thermoresponsiveness of supramolecular polymers was measured and observed by temperature dependent specific viscosity measurements. It was found that, high molecular weight supramolecular aggregates present in low temperatures due to the dynamic nature of non-covalent interactions between bis-C4P and bis-carboxylate units.

The Chapter 4 of the thesis details the fabrication of a paper-based aceton vapour sensor derived by π - π interactions between the side walls of SWCNT and pyrene-functionalized calix[4]pyrrole. Their sensitivity and performance to different volatile organic compounds were measured by monitoring the resistance changes of paper sensor.

KALİKS[4]PİROL TEMELLİ SENSÖRLER VE SUPRAMOLEKÜLER POLİMERLER

ÖZET

Literatürde bulunan diğer supramoleküler ev sahiplerinin aksine kaliks[4]piroller, gerek sentezlerindeki kolaylık gerekse sentetik olarak modifikasyonlarındaki çeşitlilik nedeniyle önem kazanmışlardır. Kaliks[4]piroller, sp3 hibritleşmiş karbon atomuyla birbirlerine bağlanmış dört adet pirol halkasından oluşan makro halkalı yapılardır. Bunlara ek olarak, kaliks[4]pirollerin organik çözücü ortamında anyonları bağlama yeteneği mevcuttur. Anyon bağlandıktan sonra kaliks[4]pirol'ün formasyonunun 1,3-alternatif'ten konik formasyona dönüştüğü bilinmektedir. Ayrıca, anyonla bağlanma sırasında kaliks[4]pirole ait NH'ların anyona doğru yöneldiği bilinmektedir. Anyon bağlandığında, anyona eşlenik olan katyonların ise kaliks[4]pirole ait π -elektron bulutuyla olan etkileşimini de göz ardı etmemek gerekir.

Literatürde kaliks[4]pirollerin anyon bağlama yeteneği üzerine kurulmuş supramoleküler polimer örneklerine çok fazla rastlanmamaktadır. Supramoleküler polimer örneklerine bakıldığında, kaliks[4]pirol üzerine kurulmuş monomerlerle elde edilen bu polimerlerin yaygın organik solventlerdeki çözünürlükleri oldukça düşüktür. Buna ek olarak, supramoleküler polimerlerin polimerizasyon dereceleri yani tekrar eden monomer sayısı oldukça düşüktür.Bir diğer önemli husus ise supramoleküler polimer oluşumunu gerçekleştiren ev sahibi yapı ile misafir yapı arasındaki bağlanma va da etkilesim sabitinin düsük olusudur. Tezin diğer bir bölümünü göz önünde bulunduracak supramoleküler kümelerin olursak, olușmasında kullanılan monomerlerin çeşitli kimyasal reaksiyonlar kullanılarak, inşasının dışında, farklı uçucu organik solvent buharlarının tanınmasında ve algılanmasında kullanılan karbon nanotüp temelli sensörlerin örneklerine sıkça rastlanmaktadır. Ancak sentetik olarak modifiye edilmiş kaliks[4]piroller ile karbon nanotüp arasındaki kovalent olmayan etkileşimlerle kağıt üzerine üretilmiş organik sensör örneklerine rastlanmamaktadır.

Tezde üç farklı yayın sunulmaktadır. Ilk çalışma ve ikinci çalışma, modifiye edilmiş kaliks[4]pirollerden ekde edilen supramoleküler yapı oluşturmak için kullanılan monomerlerin, kendisiyle ve diğer monomer ile olan anyon bağlama yeteneği sayesinde elde edilen supramoleküler polimerler ile alakalıdır. Tezde yer alan üçüncü çalışma, piren ile modifiye edilmiş kaliks[4]pirol ile tek duvarlı karbon nanotüp'ün (SWCNT) kovalent olmayan etkileşimlerle modifiye edilmesiyle oluşan kağıt üzerine fabrikasyonu yapılmış aseton buharı sensörleri hakkındadır.

Tezde yer alan ilk çalışmada, katyona ve çeşitli dış uyarılara karşı tepkili supramoleküler polimerler, kaliks[4]pirollerin sentetik olarak modifiye edilmesiyle oluşan monomerlerden sentezlenmişlerdir. Literatürdeki ev sahibi-misafir etkileşimleri temeline uygun olarak sentezlenen supramoleküler polimerlerin aksine, tezin ilk çalışmasında sunulan supramoleküler polimerler, anyon tanımlama yeteneğine uygun olarak sentezlenmişlerdir. Alkin ile fonksiyonlanmış kaliks[4]pirol ile 10-azidodekanoik asit arasındaki klik reaksiyonuyla AB-tipi monomerler sentezlenmiştir. Elde edilen supramoleküler polimerlerin polimerleşme derecesi ¹H- NMR yöntemiyle bulunmuştur. Bunu takiben polimerleşme derecesi sıcaklık değişimleriyle beraber değişim göstermiştir. Aynı zamanda, supramoleküler polimerlere organik asit gibi dış bir uyarıcı (kimyasal) eklendiğinde anyon bağlamasına dayalı etkileşimin bozulduğu (ev sahibi yapı ile misafir yapı arasındaki H-bağı.) yani supramoleküler polimer formasyonunun kırıldığı tespit edilmiştir. Tersine, formasyonu bozulan supramoleküler polimerlerin oluşumu tetrabütilamonyum türevi organik baz eklenmesiyle (ev sahibi yapı ile misafir yapı arasındaki H-bağı kurulması.) eski haline dönmüştür.

Tezin üçüncü bölümünde, tamamlayıcı ev evsahibi ve misafir moleküllerinin etkileşimleriyle elde edilmiş supramoleküler polimerler sunulmuştur. Tezin ikinci bölümünden farklı olarak, bu bölümde sunulan supramoleküler polimerizasyon iki farklı homoditopik monomer ile gerçeklestirilmiştir. Ev sahibi homoditopic monomer, alkin ile fonksiyonlanmış kaliks[4]pirol ile azid ile fonksiyonlanmış kaliks[4]pirolün arasındaki klik reaksiyonuyla sulu THF çözücüsü içinde sentezlenmiştir. Misafir homoditopik molekül ise, metil alkol içindeki, süberik asit ile tetrabütilamonyum hidroksit arasındaki basit asit-baz reaksiyonuyla sentezlenmiştir. Elde edilen monomerler ile, AA-BB tipi, AA (bis-kaliks[4]pirol) ve BB (bis-karboksilat), doğrusal ve sıcaklık değişimine duyarlı supramoleküler polimerler hazırlanmıştır. Elde edilen supramoleküler polimerlerin sıcaklığa karşı tepkileri, farklı sıcaklıklarda yapılan spesifik viskozite ölçümleriyle belirlenmiştir. Bu ölçümlerde, sıcaklığın artmasıyla birlikte, supramoleküler polimer formasyonunun derecesi düşmüştür. Baska bir devisle tekrar eden monomerlerin sayısında düsüs gerceklesmistir. Bunun sebebi kovalent olmayan etkileşimlerin yüksek sıcaklıklarda azalması olarak bulunmustur. Kovalent olmayan etkilesimlerin sıcaklıkla azalmasıyla doğrusal olan supramoleküler etkileşimler azalmış dolayısıyla supramoleküler polimerin yapısı kısmi olarak bozulmaya uğramıştır. Elde edilen supramoleküler polimer yapılarının büyüklükleri DOSY NMR metoduyla tespit edilmiştir. Yüksek molekül ağırlıklı supramoleküler kümeler; bis-kaliks[4]pirol ve bis-karboksilat anyonu arasındaki kovalent olmayan etkileşimlerin dinamik doğası sayesinde, düşük sıcaklıkta elde edilmistir.

Tezde yer alan üçüncü çalışmada, selülöz kağıt üzerine yığınlanmış aseton buharı sensörleri sunulmaktadır. Bu sensörler, piren ile fonksiyonlanmış kaliks[4]pirol ile tek duvarlı karbon nanotüpün yan duvarının kovalen olmayan etkilesimler $(\pi - \pi$ etkileşimleri) ile hazırlanan maddenin selülöz kağıt üzerine basit bir süzme ile stoklanması sonucunda elde edilmişlerdir. Elde edilen sensörlerin çeşitli uçucu polar ve polar olmayan organik solventlerin buharlarına karşı hassasiyeti ve algılama kapasitesi çalışılmıştır. Sensörlerin elektirik direncindeki değişimleri sayesinde bahsedilen organik cözücülerin buharlarına karsı verdikleri tepkiler ölcülmüstür. Ölçümler sonucunda kağıt üzerine üretilen sensörün, karbon nanotüpe kıyasla polar olmayan solventlere karşı tepki vermediği aksine, polar solventlere karşı tepkili olduğu bulunmustur. Polar solventler kıyaslandığında kağıt üzerine üretilen sensörün aseton buharına tepkinisin diğer polar solventlere kıyasla daha fazla olduğu tespit edilmiştir. Şeçicilik tespitinin ardından, üretilen sensörün tespit miktarı aseton buharının artan konsantrasyonuna karşı test edilmiştir. Elde edilen sonuçlardan, sensörün düşük miktarda aseton buharına karşı tepki verdiği anlaşılmıştır. Bunlara ek, sensörün tekrar kullanılabilirliği test edilmiştir. İlk ölçümden sonra kullanılan sensor, bir hafta aradan sonra aynı miktar aseton buharına maruz bırakılmıştır ve ölçümlerde herhangi bir değişimin olmadığı görülmüştür. Tüm veriler göz önüne alındığında, tekrar kullanılabilir, seçici ve hassas aseton buharı sensörü. Karbon nanotüp ve piren ile fonksiyonlamış kaliks[4]pirol arasındaki kovalen olmayan etkileşimlerle sentezlenip, selülöz kağıt üzerine fabrikasyonu yapılmıştır.



1. INTRODUCTION

Supramolecular polymer chemistry combines the skill sets of polymer science and supramolecular chemistry. Simply, the supramolecular polymers can be defined as complexation of any type of molecular components *via* reversible bonds. In other saying, non-covalent interactions.

In a wide aspect of definition, supramolecular polymers are formed by monomeric units that are gathered together *via* directional and reversible non-covalent interactions such as multiple hydrogen bonding, metal coordination, host-guest interactions, and aromatic π - π stackings. Monomers that are used to construct linear supramolecular polymers can be classified into five major types which are AA-type, AB-type, AA/BBtype, ABBA-type and aromatic stacking type. AA-type monomers are kind of a selfcomplexing dimers that are mostly encountered in multiple-hydrogen-bonding systems. The AB-type monomers are named as heteroditopic monomers that bring each moiety tohether in a head-to-tail manner. For complexation of supramolecular aggregates, AB-type and AABB-type monomers have been extensively used. Unlike conventional polymers, supramolecular polymers may exhibit unique properties like self-healing, thermo- and stimuli-responsiveness.

Constructing supramolecular polymers by using the innate anion binding ability of calix[4]pyrroles (C4Ps) have not been fully studied in constrast to other supramolecular hosts such as crown ethers, calixarenes, cyclodextrins and pillar[5]arenes that have been exploited extensively. C4Ps can bind anions in common organic solvents selectively. In a matter of years, C4Ps have been utilized as ion selective optical and electroactive sensors, anion extractants, anion seperating solid supports, trans membrane ion transporters, molecular containers and nano sensors. On the other hand, utilization of C4Ps in supramolecular polymer chemistry has been scarcely reported. In fact, there are examples of supramolecular assemblies of C4Ps which are functionalized by tetrathiofulvane, bis(dinitrophenyl)-meso-substituted units. But, they have been found to posess low polymerization degrees and low solubilities in common organic solvents. However, AB type supramolecular polymers

with high solubility and high degree of polymerization (DP) were successfully achived based on anion recognition ability of C4Ps studied in this thesis without requiring other functional monomers. In addition to that, AA-BB type supramolecular assemblies were also prepred by following the same unique ability in which bis-host and biscarboxylates are the main components.

Another ability of C4P was alsocombined with singe-walled carbon nanotubes (SWCNTs) to fabricate paper-based sensors for the detection of volatile organic compounds (VOCs). SWCNTs have been extensively used in the literature for sensing VOCs because of their large surface area and high electrical conductivity. On the other hand, C4Ps can interact with neutral substrates both in solid state and solution. Taking these advanteges in account, non-covalent functionalization of SWCNTs with a pyrene modified C4P was achieved. The structure of modified SWCNT was characterized by scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Then, this modified SWCTN was used to fabricate a paper-based sensor to measure the VOC sensing ability in a sealed gas chamber with the aid of a multimeter connected to this system.

1.1 Purpose of Thesis

The main purpose of the thesis is the preparation and characterization of supramolecular polymers based on the anion recognition/binding ability of calix[4]pyrroles, which have limited examples in the literature. These supramolecular polymer systems have been expected to be responsive against different stimuli such as temperature and chemicals. Another purpose of thesis is the production and characterization of a paper-based sensor based on calix[4]pyrrole-modifed single-walled carbon nanotubes and their utilization in the sensing of volatile organic vapors *via* measuring the changes in the resistance of this modified SWCNT During this thesis, various spectroscopic methods (¹H-NMR, ¹²C-NMR, FT-IR, DOSY NMR) and chromatographic-purification techniques were performed for the characterizations and measurements. This thesis was organized in a manner that each chapter has its own introduction and list of references. In addition to that, second and fourth chapters were dedicated for experimental, results and discussion sub-chapters.

2. COUNTER CATION DEPENDENT AND STIMULI RESPONSIVE SUPRAMOLECULAR POLYMERS CONSTRUCTED BY CALIX[4]PYRROLE BASED HOST-GUEST INTERACTIONS¹

2.1 Introduction

Highly complicated and ordered materials having stimuli-responsiveness are ubiquitous in biological systems, in which the reversible interactions play a critical role. Development of new materials with unique properties requires the understanding of reversibility and responsiveness. At this junction, supramolecular chemistry provides a platform to develop advanced and sophisticated materials with unconventional properties. Supramolecular polymers, constructed from low molecular weight monomers with the aid of reversible noncovalent interactions, are kind of responsive polymers that can be sensitive to solvent, concentration, pH, temperature and chemical stimuli.[1, 2] Numerous types of forces, such as hydrogen bonding, metal-ligand coordination, and hydrophobic and donor-acceptor interactions are employed to engineer supramolecular polymers.[3-7] Among these, host-guest interactions have been widely utilized to construct supramolecular polymers by using various macrocyclic hosts such as crown ethers[8], calixarenes[9], cyclodextrins[10], cryptands[11, 12] and pillar[5]arenes.[13, 14] In this context, a number of guest molecules (e.g., adamantane, anthracene, charged-naphthalenes, -amines, -imidazoles, and viologens) have been used as neutral or positively charged guest species when they incorporated into the structures of above mentioned host molecules. Supramolecular chemistry of anionic dimers, trimers and tetramers are widely investigated.[15] However, pHand thermo-responsive high performance supramolecular polymers based on the recognition of anionic guest species have not been fully exploited yet.

¹ This chapter is based on the paper "Counter Cation Dependent and Stimuli Responsive Supramolecular Poylmers Constructed by Calix[4]pyrole Based Host-Guest Interactions" by **Yuvayapan S.**, Aydoğan A., European Journal of Organic Chemistry; vol. 2019, 633-639.



Figure 2.1: Structures of carboxylic acid (1), carboxylate-functionalized calix[4]pyrroles (2) and the counter cation dependent supramolecular polymerization of 2a and 2b.

Calix[4]pyrroles, known as selective anion receptors that recognize anions (e.g., fluoride, chloride, and acetate) well in organic media, have been widely employed as anion extraction agents[16-20], anion separating solid supports[21], ion transporters[22], electroactive, optical anion sensors[23-27] and ion-pair receptors.[28] Calix[4]pyrroles have also been used as building blocks to construct functional assemblies with complementary guest species. For instance, Sessler and coworkers reported heterocomplementary subunits consisting of a tetrathiafulvalenecalix[4]pyrrole functionalized and glycol diester-linked bis-2,5,7trinitrodicyanomethylenefluorene-4-carboxylate bis(dinitrophenyl)-mesoor substituted calix[4]pyrrole.[29, 30] These monomers were found to produce short oligomers stabilized by hydrogen bonding and donor-acceptor charge transfer interactions. An imidazolium-functionalized calix[4]pyrrole in the form of its bromide salt was also used to produce a supramolecular polymer via recognition of both the anion and imidazolium cation. Unfortunately, this system was suffered from low solubility in organic solvents such as CHCl₃ and CH₂Cl₂.[31] Although the above resulting supramolecular assemblies were found to show dynamic guest dependent structural transformations and good fidelities, these systems suffered from either complicated synthetic steps, low degrees of supramolecular polymerization[29, 31] or higher critical supramolecular polymerization concentrations (CPC).[32] Calix[4]pyrrole based, counter cation dependent, dual responsive, and high performance supramolecular polymers with low CPC have not been reported yet.

Structural analyses of supramolecular monomers reported earlier reveals that, for an A–B type monomer, favouring the formation of linear supramolecular polymers with low CPC can be achieved by using long and flexible alkyl chain linkers between host and guest moieties.[33-35] On the basis of these findings, we report here the design and synthesis of a novel, dual responsive and counter cation dependent supramolecular polymer, which was constructed from a heteroditopic A–B type calix[4]pyrrole monomer (2) by utilizing the reversible host-guest interactions between the calix[4]pyrrole core and its tethered carboxylate unit (Figure 2.1). The effect of counter cation on the properties of supramolecular polymers was also investigated by using two different ammonium cations, namely tetrabutylammonium (TBA) and cetyltrimethylammonium (CTA). When CTA was used as counter cation, the long alkyl chain was envisioned as the basis of high solubility and enhancements in the properties of supramolecular polymers (e.g., viscosity, drawing fibers and gel formation) *via* additional hydrophobic interactions between long alkyl chains of CTA which was a direct part of supramolecular polymer through cation– π interactions.

2.2 Results and Discussion

Preparation of carboxylate-functionalized calix[4]pyrroles 2a and 2b starts with the synthesis of corresponding carboxylic acid functionalized calix[4]pyrrole 1 as illustrated in Scheme 1. Sharpless and co-workers introduced the "Click Chemistry" as a term describing the reactions displaying high yields with tolerance to a wide range of substrates and solvents under mild conditions.[36] Therefore we followed the click reaction strategy to obtain calix[4]pyrrole 1 starting from an alkyne-functionalized calix[4]pyrrole and an azido compound having a carboxylic acid functionality. To do so, alkyne-functionalized calix[4]pyrrole 3[19] was dissolved in THF and reacted width 4[37] in the presence of an aqueous solution of CuSO₄•5(H₂O) and sodium ascorbate at room temperature. After completion of the reaction, crude products were extracted with methylene chloride and precipitated from hexane after workup. This was yielded 1 in 96% as a pale yellow solid. Once we have the carboxylic acid-

functionalized calix[4]pyrrole **1** in hand, it was treated with TBAOH or cetyltrimethylammonium hydroxide (CTAOH) [38, 39] to obtain **2a** and **2b**, respectively. For instance, a methanol solution of **1** treated with equimolar TBAOH to give essentially pure **2a** quantitatively in 1 h after removal of the solvent. **2b** was also obtained in the same manner when **1** reacted with CTAOH.



Figure 2.2: Synthesis of 1 and 2. i) CuSO₄•5(H₂O), sodium ascorbate/THF, RT, 48h. ii) In MeOH, RT, 1 h.

Characterizations of the precursor **1** and carboxylate-functionalized target compounds (**2a** and **2b**) were carried out using ¹H and ¹³C NMR spectroscopy, as well as low- and high-resolution mass spectroscopy. For example, ¹H NMR analysis of compound **1** revealed the *CH* protons of triazole ring at 7.59 ppm as a singlet peak. Pyrrole *NH* proton signals were observed at 7.23 and 7.12 ppm as two distinctive resonance signals, reflecting the asymmetric nature of the compound **1**. Similarly, the presence of multiplet and triplet peaks at 5.92 and 5.67 ppm was attributed to the *CH* protons of pyrrole ring (Figures 2.3a).



Figure 2.3: Partial ¹H NMR spectra (500 MHz) of a) 1, b) 2a, c) 2b and d) CTAOH recorded in CDCl₃ at 25 °C. * denotes residual solvent peaks.

¹H NMR measurements can also be used to obtain important information regarding the complexation behavior of supramolecular monomers.[40] Therefore, ¹H NMR spectra of **2a** and **2b** in CDCl₃ (12 mM) were compared with the ones that of precursor **1** and CTAOH. As shown in Figure 2.3, while pyrrole N*H* resonance signals of **1** were observed as two distinct peaks at 7.12 and 7.23 ppm, in the case of **2a** they were found to be shifted downfield to 9.55 ppm as a single broad peak. In contrast, pyrrole C*H* proton signals of **2a** appeared to be shifted upfield from 5.91 ppm to 5.78 ppm (*cf*. Figure 2.3a and 2.3b). When a calix[4]pyrrole was bound to an anion these lower and upper field peak shifts are known as typical.[41] Parallel to the above results, similar peak shifts were observed in the case of **2b**. For instance, pyrrole N*H* peaks of **2b** were observed at 11.09 and 11.27 ppm, pyrrole C*H* proton resonances gave rise around 5.66 ppm (*cf*. Figure 2.3a and 2.3d). These results clearly indicate that **2a** and **2b** exhibit intermolecular interactions *via* complexation of pyrrole NHs and tethered carboxylate units.

Since the counter cations of **2a** and **2b** are different, their effect on the self-assembly process was investigated by using ¹H NMR spectroscopy. An inspection of Figure 2.3b reveals that while the methylene protons connected to the nitrogen atom of TBA resonate at 3.06 ppm, in the case of CTA resonance signals of the same protons appear as a broad peak at 2.23 ppm. Similar to this observation, resonance signals belonging to the methyl protons of CTA gave rise as a very broad peak at 1.90 ppm (Figure 2.3c). On the other hand, methyl and methylene protons connected to the nitrogen atom of CTAOH gave resonance signals originally at 3.38 and 3.26 ppm, respectively (Figure 2.3d). When a calix[4]pyrrole is bound to an anion it adopts a cone conformation while

forming a "cup-like" π electron cloud by means of oriented pyrrole rings.[32] Upfield chemical shifts belonging to methyl and methylene protons of CTA clearly indicate that calix[4]pyrrole core of **2b** acts as an ion pair receptor for both tethered carboxylate unit and CTA, binding the ammonium cation of CTA *via* cation– π interactions and the tethered carboxylate *via* hydrogen bonding.[31, 42] This was also supported by the existence of correlated 2D-NOESY signals between the methyl protons of CTA and pyrrole CH protons of calix[4]pyrrole core.



Figure 2.4: ¹H NMR spectra (CDCl₃, 500 MHz, 25 °C) of 2a at different concentrations: a) 12, b) 35, c) 125, d) 191 mM. * denotes residual solvent peaks.



Figure 2.5: Partial ¹H NMR spectra (CDCl₃, 500 MHz, 25 °C) of 2b at different concentrations: a) 12, b) 35, c) 125, d) 190 mM. * denotes residual solvent peaks.

Variable concentration ¹H NMR analyses provide important insights into the selfassembly behavior of supramolecular aggregates in solution.[43] Although the

calix[4]pyrroles 2a and 2b were expected to form monomers and short oligomers at low concentrations, they were anticipated to self-assemble into higher order aggregates at elevated concentrations to give supramolecular polymers. This is because of an association constant ($K_a = 1.77 \times 10^3 \pm 24.6 \text{ M}^{-1}$ in CDCl₃) between calix[4]pyrrole and tethered carboxylate unit and the existence of a long flexible alkyl chain linker. In accordance, concentration-dependent ¹H NMR analyses of **2a** and **2b** were carried out in CDCl₃. As shown in Figures 2.4 and 2.5, calix[4]pyrroles 2a and 2b behave differently when their NMR spectra were compared under the same concentrations. For instance, while pyrrole NH proton resonance signals of 2a were observed at 9.55 ppm, in the case of **2b** these signals were found to resonate at 11.09 and 11.27 ppm at 12 mM concentrations (cf. Figures 2.4a and 2.5a). The corresponding signals undergo a downfield shift (10.70 ppm) as the concentration of 2a was increased to 191 mM. These peaks were found to resonate at 11.09 and 11.27 ppm and to be not effected over the course of above concentration increment in the case of **2b** (cf. Figures 2.4d and 2.5d). Another result that can be inferred from the concentration-dependent ¹H NMR spectra is that as the concentrations of 2a and 2b were increased gradually, all proton signals become broader, indicating the formation of higher order supramolecular aggregates in solution. In the case of 2b these peak broadenings were significantly enhanced when compared to 2a.

Two-dimensional diffusion ordered NMR (DOSY) can be utilized to investigate the self-assembly process of monomers and to compare the sizes of supramolecular aggregates quantitatively by using diffusion coefficients.[44] Therefore, concentration-dependent DOSY experiments of **2a** and **2b** were performed. Specifically, weighted average diffusion coefficients were measured as 6.81×10^{-10} and 4.79×10^{-10} m²s⁻¹ for 12 mM **2a** and **2b** solutions, respectively. When the concentration was increased, diffusion coefficients of the **2a** (300 mM) and **2b** (191 mM) were found to be decreased to 1.20×10^{-10} and 1.04×10^{-10} m²s⁻¹, respectively. These sharp decreases in the diffusion coefficients indicate the existence of higher order supramolecular polymers at elevated concentrations of **2a** and **2b**.



Figure 2.6: Specific viscosity (*V*s) changes of 2a and 2b plotted against monomer concentration in CHCl₃ at 25 °C.

Viscosity is a direct index for the formation of polymers. Therefore, viscosity measurements were also carried out by using an Ubbelohde semi-micro dilution viscometer to analyze further the supramolecular polymers obtained from **2a** and **2b**. As shown in Figure 2.6, a double-logarithmic plot of specific viscosity (V_s) versus concentration changes of monomers exhibited viscosity transitions. At low concentration ranges, the curve has a slop of 1.05. As the concentrations increased gradually, the slopes of curves approach 2.72 and 3.09 for **2a** and **2b**, respectively. The linear relationship (slope of 1.05) between concentration and viscosity indicates the presence of monomers and oligomers with constant sizes for both **2a** and **2b**. Whereas, exponential relationships (slopes of 2.72 and 3.09) are indicative for the formation of supramolecular polymers in which the size of supramolecular aggregates exhibited a nonlinear change with concentration increments. The CPCs for the monomers **2a** and **2b** in CHCl₃ were found to be about 43 and 32 mM, respectively, as evidenced from clear changes of slopes occurring at these concentrations, indicating transition from oligomeric and cyclic species to highly ordered supramolecular polymers.


Figure 2.7: SEM images of gold-coated (a) fiber drawn from a 251 mM CHCl₃ solution of 2b, and (b) supramolecular polymer gel obtained *via* freeze-drying of the same solution. Reversible sol-gel transition of supramolecular gel obtained from a 251 mM CHCl₃ solution of 2b at (c) 25 °C, (d) 50 °C. (e) Temperature dependent viscosity change of a 158 mM CHCl₃ solution of 2b.

NMR analyses and viscosity measurements reveal that 2b exhibits a better performance in the properties of supramolecular polymer when it was compared with **2a**. This is because **2b** exhibits notable enhanced peak broadenings when the 1 H NMR spectra of equimolar high concentration solutions of 2a and 2b were compared (cf. Figures 2.4d and 2.5d). 2b also shows broader peaks than 2a even at low concentrations that can be judged from Figures 2.4a and 2.5a and lower diffusion coefficient during DOSY NMR analyses. Additionally, a higher curve slope (m=3.09 and 2.72 for 2b and 2a, respectively) was obtained in the case of viscosity measurements. Furthermore, a binding constant because of the interaction between the π -electron cloud of cone-shaped carboxylate-bound calix[4]pyrrole 3 and the ammonium cation of cetyltrimethylammonium acetate (CTAOAc) (cf. Figures 2.3c and 2.3d) was calculated to be $K_a = 1.13 \times 10^2 \pm 0.87 \text{ M}^{-1}$ in CDCl₃, indicating that CTA becomes a direct part of supramolecular polymer. This was also supported by NOESY NMR analyses of 10.2 and 191 mM CDCl₃ solutions of **2b**. The correlated 2D-NOESY signals between methylene units of CTA were found to be enhanced at high concentration. All of these results let us to conclude that the presence of long alkyl chains of CTA provides additional hydrophobic interactions, as the supramolecular polymer of 2b grows. These enhanced properties were also found to be reflected in the degree of polymerization (DP). DP values of **2b** were estimated to be at least 40% higher than those of **2a**.

Since 2b exhibits better supramolecular polymerization performance, a high concentration solution of **2b** was used to draw rod-like fibers. Scanning electron microscopy (SEM) images of fibers are shown in Figure 2.7a and revealed fibers with diameters of 9.03 and 4.06 µm, providing direct evidence for the formation of supramolecular polymers with high degree of molecular weights.[45] After heating to 50 °C, the gel obtained from a 230 mM CHCl₃ solution of 2b dissociated into a solution. Cooling the solution to 25 °C afforded the reformation of supramolecular gel (cf. Figures 2.7c and 2.7d). The SEM image of a freeze-dried gel sample exhibited a paraffin like network structure (Figure 2.7b). Thermo-responsive behaviour of the supramolecular polymer formed by 2b was also supported by variable temperature viscosity measurements. As illustrated in Figure. 2.7e, Vs of a 158 mM CHCl₃ solution of 2b was found to be 4.04 at 25 °C. When the temperature of the solution was increased to 50 °C, it was measured as 1.1. 2a also showed a similar result when it was exposed to variable temperature viscosity measurements (Figure 2.9b). These sharp viscosity decreases reflects the dynamic nature of noncovalent interactions between calix[4]pyrrole and carboxylate units, and the presence of high molecular weight supramolecular polymers at low temperatures.



Figure 2.8: Partial ¹H NMR spectra (500 MHz) of a) 2a (100 mM, 0.5 mL), after addition of equimolar b) CH₃SO₃H, d) TBAOH, and d) CH₃SO₃H recorded in CDCl₃ at 25 °C.

Calix[4]pyrroles **2a** and **2b** contains tethered carboxylate units. Carboxylate salts can be protonated by adding an acid, thus destroying the host-guest interaction between calix[4]pyrrole core and the carboxylate unit and making the supramolecular

aggregates disassemble. Hence, the reversible supramolecular polymer–monomer transition could be achieved by changing pH. Evidence for this was provided by chemical shift changes in ¹H NMR spectra (Figure 2.8). When equimolar CH₃SO₃H was added to a CDCl₃ solution of monomer **2a** (100 mM), pyrrole NH resonances were found to be shifted from 10.56 to 7.35 and 7.25 ppm, indicating the disruption of host-guest interaction between calix[4]pyrrole and carboxylate units. However, the chemical shift reversed back to 10.33 ppm after addition of equimolar TBAOH which is an indication of the reestablishment of complexation between the same host-guest units. When the resulting solution was treated with CH₃SO₃H again, the corresponding NH proton signals were observed at 7.19 ppm as a broad singlet, showing that this process can be repeated over the course of consecutive acid base treatments.



Figure 2.9: Specific viscosity changes of CHCl₃ solutions 2a a) (100 mM) upon incremental addition of CH₃SO₃H, b) (257 mM) upon incremental change in the temperature.

The pH responsiveness of **2a** was also confirmed by viscosity measurements which were carried out with a 100 mM CHCl₃ solution of **2a** while increasing the concentration of CH₃SO₃H gradually (Figure 2.9a). As the concentration of acid was increased, V_s of the solution decreased gradually, since the H-bonding interactions between calix[4]pyrrole core and the carboxylate unit were broken step by step. These studies clearly indicate that the supramolecular polymerization of **2** can be controlled by changing the pH of solution. DOSY NMR analyses also support these findings. While the diffusion coefficient of a 100 mM CDCl₃ solution of **2a** was determined as 2.62×10^{-10} m²s⁻¹, after treatment with equimolar CH₃SO₃H it was found to be 4.04×10^{-10} m²s⁻¹.

2.3 Conclusions

In conclusion, here we showed the synthesis and characterization of a carboxylic acidfunctionalized calix[4]pyrrole with a long alkyl chain linker between the calix[4]pyrrole core and carboxylic acid unit. This calix[4]pyrrole then converted to its corresponding carboxylate derivatives (as TBA and CTA salts) by treatment with either TBAOH or CTAOH. The resulting heteroditopic A–B type supramolecular monomers consisting of a calix[4]pyrrole core and a tethered carboxylate unit with two different counter cations were found to self-assemble into the higher order aggregates at elevated concentrations to give pH- and thermo-responsive supramolecular polymers which was evidenced by various techniques such as NMR spectroscopy, viscosity measurements and SEM analyses. When CTA was used as the counter cation, it was shown to be a direct part of the supramolecular polymers formed. The present work demonstrates the first example of stimuli responsive and counter cation dependent supramolecular polymers based on calix[4]pyrroles and their anion recognition ability.

2.4 Experimental Section

2.4.1 General Information

All solvents were dried before use according to standard literature procedures. Unless specifically indicated, all other chemicals and reagents used in this study were purchased from commercial sources and used as received. ¹H, ¹³C, DOSY and NOESY NMR spectra were recorded on Agilent VNMRS 500 spectrometers using TMS as an internal reference. Mass spectra were measured on a Thermo Scientific TSQ Quantum GC and Micromass Autospec Ultima. Viscosity measurements were carried out with an Ubbelohde micro dilution viscometer (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 293 K in chloroform. Melting points were determined using a Gallenkamp instrument with 1°C/min. temperature increment under ambient conditions. The Compounds **3**[19], **4**[37] and CTAOAc[46] were synthesized according to previously reported literature procedures.

2.4.2 Synthesis

2.4.2.1 Compound 1

3 (830 mg, 1.52 mmol) and 10-azidodecanoic acid (**4**) (328 mg, 1.54 mmol) were dissolved in THF (20 mL). Then, the solution of Na-ascorbate (664mg, 3.35mmol) in 1mL water was added to reaction mixture dropwise followed by addition of solution of CuSO₄•5H₂O (418mg, 1.68mmol) in 1mL water. The reaction mixture was stirred at room temperature for 24h. After the completion of the reaction solvent was removed under reduced pressure. Then the crude mixture was dissolved in DCM (30mL) and washed with water three times. This was followed by washing the organic phase with 0.1N HCl (30mL) and brine (30mL). Excess solvent was removed under vacuum after drying the organic phase with anhydrous Na₂SO₄. Resulting viscous solution was added dropwise into excess hexane, causing the precipitation of 1 as a pale yellow solid (1.11 g, 96%). Melting point: > 224 °C (decomposes). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ =7.59 (s, 1H, triazole–CH), 7.23 and 7.12 (br s, 4H, NH), 6.94 and 6.86 (d, 4H, benzene-CH), 5.92 (m, 6H, pyrrole CH), 5.67 (t, J=3 Hz, 2H, pyrrole CH), 5.19 (s, 2H, -OCH₂-), 4.36 (t, J=7.2 Hz, 2H, -CH₂-), 2.35 (t, J=7.5 Hz, 2H, -CH₂-), 1.92 (br m, 2H, -CH₂-), 1.86 (s, 3H, -CH₃), 1.64 (br m, 2H, -CH₂-), 1.52 (br s, 18H, $-CH_3$), 1.33 ppm (br m, 10H, $-CH_2$ -). ¹³C NMR (126 MHz, CD₃CN): $\delta =$ 186.56, 144.30, 140.50, 138.50, 136.77, 128.46, 122.37, 113.85, 105.72, 102.79, 62.20, 53.41, 50.40, 44.00, 35.18, 33.31, 31.58, 29.65, 28.56, 26.30, 24.63 ppm. LRMS: *m/z* 758.26 [M–H]⁺. HRMS: *m/z* calcd for C₄₆H₆₀N₇O₃⁺, 758.47578; found 758.48012. Elemental analysis: calculated for C₄₆H₅₉N₇O₃: C 72.89, H 7.85, N 12.93; found C 72.63, H 8.02, N 12.86.

2.4.2.2 CTAOH

CTAOH was prepared according to a previously reported procedure with slight changes.[39] A glass column (1 cm diameter) packed with 5 g commercial anion exchange Amberlyst A-26 (OH⁻) form was washed with MeOH (100 mL). Methanol solution of CTABr (100 mg in 10 mL) was passed slowly through the column four times. After washing the column with 10 mL of MeOH, the combined eluates were evaporated, and the obtained residue was dried under high vacuum to give CTAOH quantitatively as a white solid. ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 3.53$ (m, 2H, –CH₂–), 3.47 (s, 9H, –CH₃), 1.75 (br m, 2H, –CH₂–), 1.36 (br m, 4H, –CH₂–), 1.26 (br s, 22 H, –CH₂–), 0.88 (t, J=7 Hz, 3H, –CH₃).

2.4.2.3 Compound 2a

To a methanol solution of **1** (502mg, 0.66 mmol) tetrabuthylammonium hydroxide (1M, 0.66 mL, in MeOH) was added dropwise. After addition was complete, the reaction mixture was stirred at room temperature for 1h. Excess methanol was removed and the resulting solid washed with diethyl ether followed by drying under vacuum afforded **2a** as a white solid (632 mg, 95%). Melting point: > 213 °C (decomposes). ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 10.42$ (br s, 4H, NH), 7.72 (s, 1H, triazole –CH), 6.86 and 6.81 (d, 4H, benzene–CH), 5.88-5.65 (m, 8H, pyrrole–CH), 5.19 (s, 2H, –OCH₂–), 4.40 (t, *J*=7.2 Hz, 2H, –CH₂–), 2.92 (m, 8H, –CH₂–), 1.91 (t, *J*=7.5 Hz, 2H, –CH₂–), 1.27-1.83 (m, 51H, meso–CH₃ and –CH₂–), 0.97 ppm (t, *J*=7.3 Hz, 12H, –CH₃). ¹³C NMR (126 MHz, CDCl₃): $\delta = 186.6$, 144.3, 140.5, 138.7, 136.8, 128.5, 122.4, 113.9, 105.7, 102.8, 53.4, 50.4, 44.0, 35.2, 33.3, 31.6, 29.7, 28.6, 26.3, 24.6, 22.7, 14.1. ppm. LRMS: *m/z* 756.403 [M]⁻. HRMS: *m/z* calcd for C₄₆H₅₈N₇O₃⁻, 756.46013; found 758.46125. Elemental analysis: calculated for C₆₂H₉₄N₈O₃: C 74.51, H 9.48, N 11.21; found C 74.93, H 9.79, N 11.14.

2.4.2.4 Compound 2b

This compound was prepared from **1** (126.5 mg, 0.42 mmol) and CTOH (318 mg, 0.42 mmol) using the same procedure that was used to produce **2a**. The product was a white solid (431 mg, 98%). M.p. > 213 °C (decomp). Melting point: > 198 °C (decomposes). ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 11.45$ and 11.27 (br s, 4H, NH), 7.86 (br s, 1H, triazole–CH), 6.88 (m, 4H, benzene–CH), 5.60-5.83 (br m, 8H, pyrrole–CH), 5.31 (s, 2H, –OC*H*₂–), 4.40 (t, J= 7.3 Hz, 2H, –C*H*₂–), 2.33 (t, J= 7 Hz, 2H, –C*H*₂–), 2.23 (br s, 2H, –NC*H*₂–), 1.90 (br m, 9H, –NC*H*₃), 1.84 (s, 3H, –C*H*₃), 1.69-121 (m, 60H, meso–C*H*₃ and –C*H*₂–), 0.89 ppm (t, J= 7 Hz, 3H, –C*H*₃). ¹³C NMR (126 MHz, CDCl₃): $\delta = 178.0$, 156.2, 143.5, 141.3, 140.0, 138.2, 128.8, 123.9, 114.2, 103.5, 100.8, 66.1, 62.4, 51.0, 44.2, 34.8, 32.0, 29.7, 26.1, 24.9, 22.7 ppm. LRMS: *m*/*z* 756.412 [M][–]. HRMS: *m*/*z* calcd for C₄₆H₅₈N₇O₃[–], 756.46013; found 758.46084. Elemental analysis: calculated for C₆₅H₁₀₀N₈O₃: C 74.96, H 9.68, N 10.76; found C 75.16, H 9.87, N 10.28.

3. SUPRAMOLECULAR CALIX[4]PYRROLE POLYMERS FROM A COMPLEMENTARY PAIR OF HOMODITOPIC HOST-GUEST MOLECULES²

3.1 Introduction

Advanced electronic, photonic functional materials and a wide range of applications of plastic products have been made possible by adopting the tailored properties of synthetic polymers into the commodity materials. During the last three decades, supramolecular polymerization has emerged as an alternative synthetic method in spite of the improved synthesis of bulk plastic materials. This is because, supramolecular polymers integrate the attractive features of conventional polymers with reversibility through non-covalent interactions while permitting thermodynamic control at molecular level. Linear supramolecular polymers have attracted strong attention because of their promising new properties and relative simplicity in preparation. To date, a number of host building blocks (crown ethers[8, 47], cyclodextrins[10, 48], pillar[5]arenes[49], calixarenes[50], etc.) and guest species (neutral or cationic) have been widely used for the construction of linear supramolecular polymers via a number of recognition motifs (e.g., $\pi - \pi$ stacking, host-guest interactions, metal coordination, hydrophobic interactions, and hydrogen bonding). However, anion-recognition based supramolecular polymers are relatively rare in the literature. This is because, host molecules recognizing cationic species benefit from both electrostatic and hydrogenbonding interactions. Whereas, those that recognize anions rely primarily on hydrogen-bonding to stabilize their complexes with anions. Therefore, a number of research groups have designed quite effective and elegant anion receptors to overcome the weak anion-receptor interactions. [51, 52] At this junction, calix [4] pyrroles that can bind anions selectively in organic media[41], emerged as molecules of particular interest because of their simple preparation, ease of functionalization and tunable anion

² This chapter is based on the paper "Supramolecular Calix[4]pyrrole Polymers from a Complementary Pair of Homoditopic Host-Guest Molecules " by **Yuvayapan S.,** Aydoğan A., Chemical Communication, vol. 55, 8800-8803.

binding characteristics. They have been used for several applications, including as ionpair receptors, anion selective sensors[53], anion-specific switches[54], extractants[16], explosive detectors[55], and in reversible cross-linking of copolymers.[56]

However, supramolecular polymers based on the anion recognition ability of these tetrapyrrolic macrocycles are limited. For instance, tetrathiafulvalene- and imidazolium-functionalized calix[4]pyrroles were utilized to obtain supramolecular assemblies.[29-31] Although these systems were found to show good fidelities, they suffered from either low degree of polymerization (DP) or high critical supramolecular polymerization concentrations (CPC) along with low solubility in organic media. To overcome these relative deficiencies, we reported A–B type heteroditopic systems and demonstrated their supramolecular polymerizations through calix[4]pyrrole- anion interaction.[32, 57]



supramolecular polymer

Figure 3.1: Chemical structures and pictorial representations of 1 and 2, and illustration of the linear supramolecular polymers formed by the host-guest interaction constructed by anion recognition between 1 and 2.

Although, above a few examples are studied, linear supramolecular polymers fabricated from homoditopic monomers based on anion recognition ability of calix[4]pyrroles are not reported, while condensation polymerization of two difunctional monomers is widely used in the synthesis of traditional linear polymers. Here we present more of our efforts toward the formation of AABB type linear supramolecular polymers from self-assembly of complementary homoditopic monomers (**1** and **2**) based on the anion recognition ability of calix[4]pyrrole (Figure 3.1).

3.2 Experimental

3.2.1 General Considerations

All solvents were dried before use according to standard procedures. Unless specifically indicated, all other chemicals and reagents used in this study were purchased from commercial sources and used as received. ¹H and ¹³C NMR spectra were recorded on Agilent VNMRS 500 spectrometers using TMS as an internal reference. DOSY NMR spectra were recorded on a Bruker Ascend 500 MHz spectrometer. Mass spectra were measured on a Thermo Scientific Thermo Q Exactive HR mass spectrometer equipped with a LC unit. Viscosity measurements were carried out with an Ubbelohde micro dilution viscometer (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 293 K in chloroform. Melting points were determined using a Gallenkamp instrument with 1 °C/min. temperature increment under ambient conditions. Compounds 6 was synthesized according to previously reported literature procedures. [24]

3.2.2 Synthesis and Characterization

3.2.2.1 Compound 5

To a solution of 4[58] (1.15 g, 2.04 mmol) dissolved in 50 mL DMF, NaN₃ (605 mg, 10.2 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 24h while keeping from light. After the reaction was complete, DMF was removed under vacuum. The resulting crude material was dissolved in CH₂Cl₂ and washed with water three times. The organic layer was dried over Na₂SO₄ and the solvent was removed under vacuum, yielding the calix[4]pyrrole 5 as a light brown solid (960 mg, 98%). M.p.: decomposes over 208 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 1.10-1.13$ (m, 2H, –CH₂–), 1.25-1.29 (m, 2H, –CH₂–), 1.41-1.53 (br m, 23H, meso–CH₃ and –CH₂–), 1.78-1.82 (m, 2H, –CH₂–), 3.17 (t, J = 8 Hz, 2H, –CH₂–), 5.88 (s, 8H, pyrrole–CH), 7.00 (br, 4H, NH). ¹³C NMR (126 MHz, CDCl₃): $\delta = 138.4$, 137.3, 103.7, 102.8, 51.3, 40.4, 38.7, 35.2, 29.1, 27.0, 23.8. HRMS (ESI): m/z calcd for C32H44N7 [M+H]+ : 526.36527; found: 526.36537.

3.2.2.2 Compound 2[59]

To a methanol (2 mL) solution of suberic acid (535 mg, 3.07 mmol), methanol solution of tetrabutylammonium hydroxide (1 M, 6.14 mL) was added dropwise. The reaction mixture was stirred at room temperature for 3h. Removal of methanol followed by

drying in vacuo afforded 2 quantitatively as a white solid. ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 0.98$ (t, J=7 Hz, 24H, -CH₃), 1.29 (m, 4H, -CH₂--), 1.43 (m, 16H, -CH₂--), 1.61-1.67 (br m, 20H, -CH₂--), 2.14 (t, J=8 Hz, 4H, -CH₂--), 3.34 (q, 16H, -CH₂--). ¹³C NMR (126 MHz, CDCl3): $\delta = 179.3$, 58.8, 49.9, 39.7, 30.5, 27.7, 24.1, 19.8, 13.7. HRMS (ESI): m/z calcd for C₃₂H₇₂N₂ [M]⁺2: 242.28423; found: 242.28421 (as tetrabutylammonium cation in positive ionization mode).

3.2.2.3 Compound 1

In a flask, 5 (272.6 mg, 0.52 mmol) and 6 (272.06 mg, 0.52 mmol) were dissolved in THF (50 mL). A freshly prepared aqueous solution of sodium ascorbate (226 mg, 1.14 mmol; 1 mL) was added, followed by an aqueous solution of copper(II) sulfate pentahydrate (272 mg, 0.57 mmol; 1 mL). The mixture was stirred for two days at ambient temperature. THF was removed under vacuum and the remaining crude mixture was dissolved in CH₂Cl₂ and washed with water three times. The organic layer was then dried over Na₂SO₄ and the excess of solvent was removed under vacuum. Tar material was removed by precipitation from diethyl ether. Supernatant was concentrated and precipitation from hexane afforded the compound 1 as a yellow solid (423 mg, 78%). M.p.: decomposes over 223 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 1.42-1.44$ (br m, 4H, -CH₂-), 1.50-1.52 (br m, 44H, meso-CH₃ and -CH₂-), 1.79-1.87 (br m, 4H, -CH₂-), 2.19 (br m, 4H, -CH₂-), 4.27 (t, J = 7 Hz, 2H, -CH₂-), 5.87-5.90 (m, 16H, pyrrole CH), 7.01 (br m, 8H, NH), 7.50 (s, 1H, -CH). ¹³C NMR (126 MHz, CDCl₃): $\delta = 173.6, 138.4, 137.1, 136.1, 123.4, 102.9, 65.8, 57.6, 51.9, 50.3,$ 40.4, 38.7, 35.2, 29.1, 26.8, 25.8, 23.7, 15.3. HRMS (ESI): m/z calcd for C₆₅H₈₃N₁₁O₂ [M]⁺: 1050.45400; found: 1050.68069.

3.3 Results and Discussions

Towards these aims, an azide-functinalized calix[4]pyrrole **5** was prepared through a substitution reaction starting from its precursor *meso*-n-alkylbromo calix[4]pyrrole **4**. The target triazole bridged bis-calix[4]pyrrole (**1**) was synthesized *via* a click reaction based on Huisgen 1,3-dipolar cycloaddition[60] starting from **5** and alkyne-functionalized calix[4]pyrroles **6**[24] (Figure 3.2).



Figure 3.2: Structures of octamethylcalix[4]pyrrole (3), azide- and alkynefunctionalized calix[4]pyrroles (4 and 5, respectively).

The homoditopic guest molecule 2, consisting bis-carboxylate units (as tetrabutylammonium salts) was prepared by reacting suberic acid with tetrabutylammonium hydroxide in methanol. After preparation, host-guest complexation between 1 and 2 was investigated by using ¹H NMR spectroscopy. As shown in Figure. 3.3, upon addition of equimolar guest molecule 2 into a 10 mM CDCl₃ solution of **1**, pyrrole–NH and –CH resonance signals were found to exhibit downfield and upfield shifts. For instance, while the pyrrole NH proton resonance signals belonging to 1 were observed at 7.01 ppm, after addition of equimolar 2 these signals were found to give rise around 7.71 ppm. Similarly, pyrrole CH peaks of 1 were found to shifted upfield by 0.06 ppm. These chemical shifts are typical when a calix[4]pyrrole is bound to an anion showing the complexation between calix[4]pyrrole units of 1 and carboxylate moieties of 2.[41] After complexation, the emergence of a new broad resonance signal at 7.71 ppm belonging to pyrrole-NH protons was attributed to the deshielding effect because of the H-bonding interaction between pyrrole NHs and carboxylate anions. Note that the association constant (K_a) between an analogous calix[4]pyrrole (3) and tetrabutylammonium acetate (TBAOAc) was calculated to be as high as $1.65 \times 10^3 \pm 54.3 \text{ M}^{-1}$ in CHCl₃. This binding affinity laid an important foundation for the preparation of AABB type supramolecular polymers using homoditopic host-guest molecules. Additionally, resonance signals in the ¹H NMR spectrum belonging to the equimolar mixture of 1 and 2 were found to be significantly broader when compared with the ones that of free 1 and 2. These peak broadenings were considered as an indication of the existence of higher order aggregates in the solution.



Figure 3.3: ¹H NMR spectra (500 MHz, CDCl₃, 25 °C) of (a) 2; (b) 1, and (c) a mixture of 10 mM 1 and 2. * denotes solvent residual peak.

To analyse the complexation behaviour between 1 and 2 further, a series of 50 mM solutions of 1 were prepared with non-stoichiometric amounts of 2 (from 10.06 to 35.22 mM) and the ¹H NMR spectra were recorded at 25 °C. As shown in Figure 3.4, an increment in the concentration of 2 with respect to 1 shifts the equilibrium toward the formation of longer linear supramolecular polymers as inferred from downfield shift of pyrrole NH protons from 7.49 to 8.57 ppm. Absence of pyrrole NH protons around 7.01 ppm during the increasing concentration of 2 indicates the fast-exchange complexation occurred between 1 and 2 on the ¹H NMR time scale. Likewise, β pyrrolic CH resonance signals of 2 were also exhibited a gradual upfield shift from 5.73 to 5.83 ppm. The resonance signals of the mixture broadened during the incremental addition of 2 which was attributed to the formation of linear supramolecular polymers. The presence of longer aggregates upon increase in the concentration of 2 was also confirmed by changes in the specific viscosity (V_s) . To do so, while keeping the concentration of 1 constant at 76 mM in CHCl₃, equivalent of 2 was increased gradually from 0 to 1. During this increment V_s of the solution was found to change from 0.25 to 0.63 (Figure 3.6a).

To verify that the above NMR signatures and viscosity measurements correspond to a supramolecular polymer formation, concentration-driven measurements were also undertaken. We first studied changes during concentration dependent ¹H NMR analyses which can provide important perception about the self-assembly behaviour of supramolecular polymers in solution.[40]



Figure 3.4: The stacked ¹H NMR spectra (500 MHz, CDCl₃, 25 °C) of solutions of 1 (50 mM) after addition a) 0.10, b) 0.25, c) 0.50, d) 0.75 and e) 1.00 equivalents of 2.



Figure 3.5: Partial ¹H NMR spectra (CDCl₃, 500 MHz, 25 °C) of equimolar mixtures of 1+2 and 3+TBAOAc at different concentrations: a) 8, b) 15, c) 31, d) 83, e) 125, and e) 198 mM.

An equimolar solution of **1** and **2** was expected to give higher order supramolecular aggregates when the concentration of solution is increased. It is well known that the formation of supramolecular polymers with high DPs can be achieved by means of a large binding constant or high monomer concentrations. Equimolar mixture of **1** and **2** meet these criteria because of a binding constant between the model compounds **3** and TBAOAc $(1.65 \times 10^3 \pm 54.3 \text{ M}^{-1} \text{ in CDCl}_3)$ and possibility of preparing high concentrated solutions in chloroform. In accordance with above expectations, when concentration of a equimolar mixture of **1** and **2** was increased from 7.85 to 198 mM (Figure 3.5) all peaks belonging to supramolecular polymer were found to be broadened. Meanwhile, pyrrole NH resonance signals shifted downfield from 7.62 to

9.83 ppm as the concentration increases. This was thought to reflect the presence of shorter oligomeric or cyclic species in the solution at low concentrations and formation of longer supramolecular polymers at high concentrations.

The equimolar mixture of **1** and **2** consists of calix[4]pyrrole cores and carboxylate units. Hence, the DP could be estimated using the isodesmic model in conjunction with the affinity constant between the model compounds **3** and the acetate anion (as tetrabutylammonium salt).[61-63] The resulting value, corresponding to the average number of subunits in the supramolecular polymer, was estimated to be ~26 at a concentration of 198 mM in CHCl₃ at 25 °C. When isodesmic model was used, the degree of polymerization belonging to an AA-BB type supramolecular polymer system is estimated by an equation (DP=(K_a2C)^{1/2}, since host is in H–H form) [63] which converges to large values at high concentrations. This approach ignores the attenuation because of the presence of cyclic oligomers and reduction in the association constant as the supramolecular polymer grows. Therefore, chemical shifts of pyrrole NH resonance signals belonging to **1+2** (Figure 3.5A) were compared with the ones that of model system **3**+TBAOAc (Figure 3.5B). The differences in the chemical shifts and their effects on DP was listed and revealed that DP of **1+2** is ~10% lower than the estimations based on isodesmic model at high concentrations.

We also corroborated the concentration-driven polymerization by following the changes in the specific viscosity. For that purpose viscosity measurement were carried out in CHCl₃ using an Ubbelohde semi-microdilution viscometer. The double-logarithmic plot of specific viscosity versus concentration (Figure 3.6b) reveals an initial slope (1.04) consistent with existence of noninteracting monomeric units with constant size that changes to a value (2.12) indicative to linear polymers with higher DP. This transition occurs at around 30 mM and, based on the prior reports on supramolecular polymers, was assigned to the critical polymerization concentration (CPC).[64] When compared with previous calix[4]pyrrole based supramolecular polymer systems, the CPC value of this homoditopic **1** and **2** system could be considered as the lowest concentration since the supramolecular monomers of our previous reports were constructed over heteroditopic monomer units with 33 and 118 mM CPCs.[32, 57]

Additionally, an increment in the repeating units of supramolecular polymer is expected to lead to a sharp decrease in the diffusion coefficient (D) of solution.

Therefore, we carried out two-dimensional diffusion-ordered ¹H NMR (DOSY) experiments to study the self-aggregation of linear supramolecular polymer **1**+**2**. For that purpose, equimolar **1** and **2** solutions in CDCl₃ at varying concentrations exposed to DOSY analyses (Figure 3.6d). Specifically, as the concentration of **1**+**2** increased from 8 mM to 198 mM, the diffusion constant of solution decreased significantly from 7.28×10^{-10} to 2.11×10^{-10} m² s⁻¹ at 19 °C. This result let us to conclude that the significant decrease in the diffusion coefficient with increasing concentration indicates the formation of supramolecular polymers with larger DP at high concentrations.



Figure 3.6: Specific viscosity (V_s) changes of CHCl₃ solutions at 25 °C: (a) 1 (76 mM) upon incremental addition of 2, (b) equimolar 1+2 plotted against monomer concentration, (c) equimolar 1+2 (142 mM) upon incremental change in the temperature of solution. (d) Concentration dependence of diffusion coefficient D (500 MHz, 19°C) of equimolar 1+2 in CDCl₃.

Thermo responsive behavior of the supramolecular polymer formed by 1+2 was also investigated by temperature dependent viscosity measurements. Figure 3.6c shows the specific viscosity dependence of a 142 mM CHCl₃ solution of 1+2 upon change in temperature. While the specific viscosity of the solution was 2.90 at 25 °C it was found to decrease sharply to 1.76 when the temperature was increased to 50 °C. These findings were also thought to reflect the presence of high molecular weight supramolecular aggregates at low temperatures and the dynamic nature of noncovalent interactions between 1 and 2. Since 1+2 has decent solubility and attains longer supramolecular aggregates in CDCl₃, rod-like fibers were also pulled successfully from a highly concentrated solution. A scanning electron microscopy (SEM) image of a fiber is shown in Picture3.1 and revealed a fiber with a diameter of ~5 μ m, providing direct evidence for the formation of a supramolecular polymer with high molecular weight.[47, 49]



Figure 3.7: SEM images of a gold-coated fiber drawn from a high concentrated CHCl₃ solution of equimolar 1+2.

Supramolecular polymerization of 1+2 was also tested by using different solvents. Variable concentration ¹H NMR spectra of equimolar 1+2 recorded in CD₂Cl₂ and CD₃CN revealed that the linear supramolecular polymers may also be formed in aforementioned solvents as inferred from concentration dependence of pyrrole NH resonance signals or peak broadenings as observed in the case of CDCl₃.

3.4 Conclusion

In conclusion, linear supramolecular polymers can easily be formed driven by the hydrogen bonding interactions between calix[4]pyrrole NHs and carboxylate units of homoditopic host **1** and guest **2** molecules. A combination of ¹H-, DOSY NMR analyses, and viscosity measurements revealed that while equimolar **1**+**2** form cyclic species at low concentrations, it was found to form linear supramolecular polymers when the concentration exceeds the CPC. In addition, rod-like fibers were also drawn successfully from a highly concentrated solution of **1**+**2**, thus providing direct evidence for the formation of supramolecular polymers with high DP. Considering the ease in preparation and the thermoresponsive behaviour of the resultant supramolecular polymer, the present study illustrates the first example of a AABB type supramolecular polymer based on the anion recognition ability of calix[4]pyrroles. Effect of different alkylammonium salts on the formation of calix[4]pyrrole supramolecular polymers is in due course.

4. CALIX[4]PYRROLE DECORATED CARBON NANOTUBES ON PAPER FOR SENSING ACETONE VAPOR³

4.1 Introduction

Since Pauling's report it has well known that several volatile organic compounds (VOCs) exist in the exhaled breath of human.[65] Abnormal concentrations of these compounds are markers of oxidative damages and have also been linked to medical conditions, such as sickle cell disease, asthma, breast and lung cancer, sleep apnea, kidney failure, cystic fibrosis, and diabetes.[66] Increased level of ketonic bodies (e.g., acetoacetic acid, β -oxybutyric acid and acetone) in blood is connected to diabetic ketoacidosis known to be an acute side effect of diabetes mellitus. Among the several biomarkers, excessive acetone circulating in the blood is excreted from lung after the fatty acid oxidation in diabetes and ketonic lack of insulin.[67] Hence, VOCs can be used as disease-specific biomarkers for non-invasive detection from breath. Towards this goal selective detection of VOCs are critically important to medical applications. Gas chromatographic techniques are reliable, highly sensitive and well-established technologies for analyzing and identification of VOCs.[68] Bulky and expensive instrumentations, requirement to highly trained technicians cause these techniques to have some limitations. Sensors based on changes in either electrical, optical, or gravimetric signals also have several drawbacks such as portability, calibration, limited shelf time, and ease of use.

Carbon nanotubes (CNTs), one of the nanostructured forms of carbon, have shown promise for utilization in chemical sensing[69-71] because of their extremely sensitive conductance change in the local chemical environment.[72-74] Besides, large surface area, high electrical conductivity and room temperature gas sensing properties of CNTs allow these materials to be an emerging class of sensors. Although resistivity based CNT sensors offer tremendous advantages when they compared to other

³ This chapter is based on the paper "Calix[4]pyrrole Decorated Carbon Nanotubes on Paper for Sensing Acetone Vapor " by Baysak E., **Yuvayapan S.,** Aydoğan A., Hizal G., Sensors and Actuators B:Chemical, vol. 258, 484-491.

methods for detecting VOCs, they also have some drawbacks such as expensive device fabrication, low stability of CNT-based dispersions, and low solubility of CNTs in common solvents. To overcome these drawbacks CNT sensors on paper have been developed and used as simple, multipurpose, flexible and disposable alternative device systems.[75-77] Because of their versatile properties, paper based substrates have been utilized as energy storage devices, active matrix displays, circuit, and gas sensors.[76-80] In this context, Swager et al. mechanically drew CNTs on different type of papers and used as NH₃ sensor.[77] Han et al. prepared sensors based on CNT-on-paper and CNT-cellulose composites to utilize these materials as NH₃ chemiresistors.[81] Similarly, paper based CNT sensors were also used for the selective detection of VOCs.[76-82] Recently, Kim et al. reported CNT coated paper sensors for the detection of damages in structural components by using electrical resistance tomography.[75] Solid composites of CNTs with supramolecular hosts were also utilized to detect VOCs. Swager et al. reported a rapid prototyping of CNTs on paper and their use in the selective sensing of solvent vapors.[83]



Figure 4.1: Structure of octamethylcalix[4]pyrrole.

Octamethylcalix[4]pyrrole (1) is a commercially-available supramolecular host that can bind anions (e.g., fluoride, chloride, and acetate) selectively in organic media.[41] Functionalized calix[4]pyrroles can be used as electro active and chromogenic sensors[24, 84-86] as well as selective anion extractants.[16, 17, 87] The binding of neutral substrates both in solution and in the solid state was also reported by Sessler et all.[88] Recent advances on CNT based paper sensors and the recognition of neutral substrates with calix[4]pyrroles prompted us to design a sensor for selective sensing of VOCs on the basis of molecular recognition of neutral substrates and chemiresistive response of single-walled carbon nanotubes(SWCNTs).



Figure 4.2: Synthesis of pyrene-functionalized calix[4]pyrrole.

In this study, we present the preparation of a SWCNT-on-paper chemiresistor decorated with calix[4]pyrroles and its use in the selective sensing of acetone vapor. The first step in this work involves the synthesis of a pyrene-functionalized calix[4]pyrrole (**3** in Figure 4.2) and noncovalent immobilization of **3** on SWCNTs.[89-92] Noncovalent functionalization of SWCNTs with calix[4]pyrrole **3** were characterized by scanning electron microscopy (SEM) and thermogravimetric analysis. This new calix[4]pyrrole decorated SWCNT was used as a chemiresistor to sense acetone selectively over a series of VOCs.

4.2 Materials and Methods

4.2.1 General Considerations

Unless specifically indicated, all chemicals and solvents used in this study were purchased from commercial sources and used as received. Compound **2** was prepared according to literature procedure.[93] ¹H and ¹³C NMR spectra were used in the characterization of products recorded on an Agilent VNMRS 500 MHz nuclear magnetic resonance spectrometer using a residual protio solvent as the reference. Mass spectra were measured on a Thermo Scientific TSQ Quantum GC and Micromass Autospec Ultima. Melting point was determined on an Electrothermal Gallenkamp apparatus. Thermogravimetric analyses were performed using a PerkinElmer Diamond TG/TDA at a 10 °C min⁻¹ heating rate under a flowing N₂ atmosphere. SEM analysis was carried out by using FEI Quanta FEG 250 SEM in ESEM mode. An Agilent 34401A bench multimeter equipped with a glass solvent vapor chamber was used for VOCs sensing experiments. The HPLC grade VOCs that are used in this work contains less than 0.5% relative humidity (RH).

4.2.2 Synthesis of Compound 3

Acid 2 (300 mg, 0.65 mmol), 1-pyrenemethanol (167 mg, 0.72 mmol), and 4dimethylaminopyridine (DMAP) (8 mg, 65.5 µmol) were dissolved in 15 mL dry methylene chloride under N₂ atmosphere. At this point, dicyclohexylcarbodiimide (DCC) (135 mg, 0.65 mmol) mixed in 3 mL dichloromethane was added to the mixture. The reaction mixture stirred for 24 h and the insoluble matter was filtrated off. The resulting filtrate was collected and was washed with first 0.1 N HCl (20 mL), followed by saturated NaHCO₃ (20 mL), and then finally water (20 mL). The organic layer was then dried over Na₂SO₄⁻ The excess solvent was removed under vacuum to afford a concentrated solution. Dropwise addition of this crude mixture to cold methanol caused the precipitation of pure **3** as a white solid (305 mg, 69%). M.p.: Decomposes at 226 °C, ¹H NMR: (600 MHz, CDCl₃): δ = 8.25-7.98 (m, 9H; ArH), 7.37 (s, 2H; NH), 7.02 (s, 2H; NH), 5.94-5.88 (m, 8H; pyrrole CH and CH₂), 5.77-5.51 (m, 2H; pyrrole CH), 1.81 (s, 2H; CH₂), 1.42 (s, 3H; CH₃), 1.26 (s, 18H; CH₃). ¹³C NMR: (126 MHz, CDCl₃): δ = 139.22, 138.38, 137.90, 131.94, 131.32, 130.74, 129.66, 128.23, 127.96, 127.76, 127.35, 126.14, 125.60, 125.47, 124.60, 122.89, 65.99, 35.14, 34.93, 28.97, 27.99, 26.91 ppm. LRMS (ESI): m/z (%): 672.35 (60) [M]–. HRMS (ESI): m/z calcd for C45H44N4O2 [M]–: 672.3464; found: 672.3458.

4.2.3 Noncovalent functionalization of SWCNT

To a round-bottomed flask CoMoCat SWCNTs (Southwest Nano Technologies, 10 mg) and **3** (50 mg) (**3** to nanotubes ratio: 5, w/w) and 100 mL of dry THF were added. The resulting mixture was sonicated for 30 min. in a low-power sonic bath and stirred vigorously for additional three days at room temperature. To remove unattached calix[4]pyrrole, the mixture was filtered with a 0.2 μ m Teflon membrane and washed with excess THF. The recovered black powder was then dried under vacuum at 35 °C for 24 h. This afforded 13.4 mg of functionalized SWCNTs (**3**@SWCNT).

4.2.4 Fabrication of paper sensors



Figure 4.3: Photographs of 3@SWCNT on filter papers with 0.9 cm diameter: (a) 1.18 mg/cm^2 , (b) 0.39 mg/cm^2 , and (c) 0.28 mg/cm^2 .

Whatman filter papers were cut into circular pieces (thickness=180 μ m, pore size=11 μ m, diameter=0.9 cm) which were further placed at the bottom of 2 mL syringes. 3.0,

1.0 and 0.7 mL suspensions of 3@SWCNT (2.5 mg/10 mL in CH₂Cl₂) were passed through filter papers individually. The impregnated papers were then dried under vacuum at 35 °C for 24 h (Figure 4.1).



4.2.5 Sensing measurements

Figure 4.4: Sketch (top) and photograph (bottom) of VOCs sensing system.

VOCs sensing measurements were carried out using a system as shown in Figure 4.4 The system consists of a 0.16 L sealed gas chamber and a multimeter connected to a computer. The used multimeter was equipped with a two-probe system having 0.5 mm aperture with a magnetic aperture slider ensuring the application of constant force. Paper sensor was fixed onto glass lamella in the gas chamber with the aid of magnetic aperture slider. After fixation of the paper sensor, gas chamber was sealed with the aid of a rubber stopper and this device setup was used for the sensing of VOCs. Gas chamber was repeatedly flashed with dry air (1000 mL/min) before and after every sensing measurement. Liquid VOCs fed into the gas chamber at 25 °C with the aid of a calibrated syringe.[73-82] The analyte VOCs were calculated to reach 99% of target concentration less than 15 s in the sensing chamber. The resistance of sensor was monitored by using a HP 34401A multimeter and recorded as a function of operating time by a computer software. Sensing performance of paper sensors assessed by applying a constant voltage across the two-probe system and monitoring the change in the resistance upon exposure to the target analytes under ambient conditions. All measurements performed in triplicates by using the paper sensor shown in Pic. 4.1a with a 1.18 mg/cm² **3**@SWCNT. The sensing response $\Delta R/R_0$ (%) was calculated by

measuring the normalized difference in resistance before (R₀) and after (R) the exposure to the VOCs: $\Delta R/R_0$ (%) = [(R-R₀)/R₀]×100. The Paper sensors were exposed to the analytes for three minutes followed by a three minutes dry air ventilation to attain the recovery of base resistivity. The response time of the sensors was calculated based on the time needed to reach 90% sensor output when the sensor attains its steady state.

4.3 Results and Discussion

Figure 4.2 provides the preparative chemistry of compound **3**. The synthesis of pyrenefunctionalized calix[4]pyrrole **3** was achieved by an esterification reaction of corresponding carboxylic acid calix[4]pyrrole (**2**) [93] and 1-pyrenemethanol in CH₂Cl₂. Purified **3** was obtained *via* precipitation in methanol with a 69% yield.



Figure 4.5: ¹H NMR spectrum of 3 recorded in CDCl₃ (* denotes the residual solvent and H₂O peaks).

Figure 4.3 shows the ¹H NMR spectrum of **3**. An inspection of the ¹H NMR spectrum of **3** reveals the aromatic pyrene proton resonances between 7.98 and 8.75 ppm as multiplet peaks. Pyrrole NH protons gave rise at 7.37 and 7.02 ppm. Similarly, pyrrole CH protons were observed as two distinct set of resonance signals around 5.98 ad 5.53 ppm. These findings corroborated with ¹³C NMR data and mass spectroscopy analysis results were consist of the expected structure of calix[4]pyrrole **3**.



Figure 4.6: Illustration of calix[4]pyrrole decorated SWCNT (3@SWCNT).

Once we prepared the pyrene-functionalized calix[4]pyrrole **3**, efforts were shifted to noncovalent functionalization of SWCNTs. The strategy for the noncovalent sidewall modification of CNTs with proteins, biopolymers and polymers based on the affinity of pyrene for CNTs is well known in the literature.[89-91, 94] From the perspective of π - π stacking of organic molecules and SWCNTs, pyrene-functionalized calix[4]pyrrole **3** is expected to interact with SWCNTs as shown in Figure 4.4. For that purpose, SWCNT and **3** were allowed to stir for three days in THF followed by ultrasonication for 30 min. This was expected to provide noncovalent functionalization of the side walls of SWCNTs.



Figure 4.7: (a) SEM image (scale bar denotes 250 nm) and (b) thermogravigrams of 3, SWCNT and 3@SWCNT.

SEM is used to characterize 3@SWCNT on paper. SEM image of 3@SWCNT on paper revealed interconnected and tangled bundles with diameter ranging from 12 to 46 nm (Figure. 4.5a). SEM-EDS (Energy Dispersive Spectrometer) profile of 3@SWCNT showed presence of nitrogen in the nanotube matrix which was considered as an indication for the existence of calix[4]pyrrole units on the surface of SWCNTs. The actual noncovalent functionalization of SWCNTs with pyrenefunctionalized calix[4]pyrroles were also characterized by thermogravimetric analysis. As shown in Figure 4.5b, upon heating to 600 °C, a 75% mass loss was observed when compound **3** was exposed to thermal analysis. In the case of pristine SWCNT an 8% mass loss was detected at the same temperature margin. Meanwhile, **3**@SWCNT revealed a 23% mass loss when heated to the same temperature. This mass loss corresponds to a 15% noncovalent-functionalization of SWCNT by pyrene-functionalized calix[4]pyrrole **3**.

The uniformity of 3@SWCNT paper sensor was tested by both resistivity measurements and SEM analyses. Paper sensor resistance versus amount of **3**@SWCNT per unit area was plotted. A linear correlation was observed between the amount of 3@SWCNT and the resistance of paper sensor. As the amount of 3@SWCNT increases the resistances of sensor was found to decrease linearly. An inspection of the SEM images belonging to two different points of 3@SWCNT paper sensor was also revealed similar distribution of **3**@SWCNT on paper sheet. The results were thought to reflect the uniformity of paper sensors fabricated by using 3@SWCNT and filter paper. The shelf life of **3**@SWCNT paper sensor was also analyzed. For that purpose, 3@SWCNT paper sensor was exposed to 60 ppm acetone vapor seven days after the first exposure. After one week no significant difference in the resistance change, response and recovery times of sensor were observed against acetone vapor. After analyzing the properties of 3@SWCNT, we evaluated the performance of this material as a chemiresistive vapor sensor by monitoring their response towards various polar and non-polar VOCs (e.g., acetone, methanol, ethanol, THF, toluene, methylene chloride, hexane, and diethyl ether). For that purpose, resistance changes of paper chips (a, b, c and d in Pic. 4.1) were monitored under an air atmosphere to attain the baselines prior to the VOCs sensing measurements. Once, the sensors exhibited a stable value of base resistance, VOCs were introduced in to the gas-sensing chamber. Sensing measurements revealed that 3@SWCNT paper sensors has better response for polar VOCs against non-polar analytes when it compared with the paper sensor fabricated from pristine SWCNT.



Figure 4.8: Responses of SWCNT and 3@SWCNT towards 60 ppm at 25 °C (a) acetone, (b) MeOH, (c) EtOH, (d) THF, (e, f) resistance changes of 3@SWCNT and SWCNT, and (g) comparison of the response differences.

Figure 4.6 shows the normalized response, $\Delta R/R_0$ (%), of pristine SWCNT and **3**@SWCNT on paper upon exposure to 60 ppm VOCs. An inspection of this data reveals that **3**@SWCNT exhibit reproducible responses towards each analytes. The responses of **3**@SWCNT towards polar VOCs (e.g., acetone, ethanol, methanol, and THF) exhibits three notable features.

	SWCNT				3@SWCNT			
VOC	Response	time	Recovery	time	Response	time	Recovery	time
	(s)		(s)		(s)		(s)	
Acetone	34		39		37		85	
MeOH	35		31		36		158	
EtOH	69		36		71		78	
THF	23		37		24		85	

Table 1: Response and recovery times of pristine SWCNT and 3@SWCNT paper sensors.

First, the sensor exhibit a fast response followed by slow response before attaining the base resistivity. Response and recovery times of paper chips are listed in Table 1. The recovery of the baseline during the VOCs exposure cycles implies the stability of the sensor and its recycling potential. For instance, pristine SWCNT shows a response

towards acetone in 34 s and attains its base resistivity in 39 s. Meanwhile, the response time of 3@SWCNT is 37 s and the recovery of base resistivity takes 185 s. These results reveal that while calix[4]pyrrole decorated SWCNT paper sensor is as fast as pristine SWCNT in terms of the response time, it displays prolonged duration for the recovery of base resistivity against acetone vapor. Similar response time and base resistivity recovery trends were also observed for other VOCs listed in Table 1.

Second, 3@SWCNT on paper shows a selectivity for acetone against other analytes when compared with pristine SWCNT (Figure 4.6a). While resistance change decreases were observed for THF (2.7%) and EtOH (1.2%), a 1.7% response increase was observed in the case of MeOH (Figure 4.6b-4.6d). The detection response of 3@SWCNT was enhanced notably when treated with acetone. Figure 4.6a shows a 3% resistance change when pristine SWCNT was used as a sensor. In the case of 3@SWCNT a 14.6% response was observed. This increment corresponds to 12.1% resistance increase (Figure 4.6g) and six fold enhancement in the detection. Increased resistance change responses for polar solvents are also correlated with the binding strength of 1 against polar solvent molecules.[88]

Third, while short recovery time delays were observed when pristine SWCNT paper sensor was exposed to VOCs, the recovery duration of baseline was longer in the case of **3**@SWCNT sensor. The reason for these delays was attributed to the presence of calix[4]pyrrole units in the SWCNT matrix. The interaction between VOC molecules and calix[4]pyrroles increased the retention of solvent molecules on SWCNT and therefore, deferred the baseline recovery time.

Interaction of VOCs with SWCNT could be either non-directional, dispersion and electrostatic forces or directional forces such as H-bonding and charge transfer[95]. Since non-directional interactions between carbon based nanotubes and the gas molecules are week in general[96, 97], SWCNT sensor response is expected to be higher for VOCs containing lone-pair electrons or aromatic π -electrons. This also emphasizes the importance of electrostatic forces and vapor polarizability.[98] Accordingly, polar VOCs used in this work such as acetone, methanol and ethanol showed better resistance increases while low responses were observed for the relatively non-polar VOCs (e.g., hexane and diethyl ether). These results suggest that vapor polarizability is key to **3**@SWCNT sensor function. There are several publications suggesting the chemical interaction between acetone and carbon nanotubes. During these experimental and theoretical studies curvature of nanotube

surfaces, topological defects and disorders were reported as important factors producing perturbations in the conductance and capacitance of SWCNTs.[97, 99, 100] Furthermore, the presence of oxygen functionalities has been shown to effect the interaction of acetone with carbonaceous surfaces [97, 99, 101] because of the purification of carbon nanotubes by oxidative methods.[102] Assembled structures of nanotubes consist of bundles due to van der Waals forces. Multiple adsorption sites are favored due to the bundled structure of nanotubes. Endohedral sites, grooves, and external walls of SWCNTs were reported as the domains where the acetone adsorptions could take place. Presence of oxygen functionalities was also found to prevent the access of acetone to endohedral sites of SWCNTs.[103] It was also reported that cryogenically adsorbed acetone on SWCNTs desorbs as an intact molecule, implying that the SWCNT acetone interaction is chemically reversible due to the dispersion forces and absence of significant charge transfer or polarization.[103] Borguet et al. also reported the strong correlation between physisorption energy and sidewall curvature of SWCNTs and the dependence of favorable endohedral and encapsulated interactions to the diameter of SWCNTs.[103]

On the basis of preceding discussions and the results of theoretical calculations and experimental studies, both the chemisorption and physisorption mechanisms could take place in the case of sensing of acetone with 3@SWCNT paper sensor. It was reported that the oxygen present in the CoMoCat SWCNTs is most likely as salts, metal oxides and not oxygen containing functional groups.[104] Additionally, when **3**@SWCNT was exposed to acetone, recovery of the baseline in a short time span and not requiring any other special techniques (e.g., UV light[104]) suggest us that the dispersion forces could play an important role in the sensing mechanism although the chemisorption mechanism is not very pronounced. The enhanced resistance increase of 3@SWCNT paper sensor for ethanol and acetone was considered as a result of the interaction between calix[4]pyrrole units and these VOCs. Association constants for 1 with ethanol and acetone in benzene are reported as $12.7 \pm 1.0 \text{ M}^{-1}$ and $2.2 \pm 0.2 \text{ M}^{-1}$, respectively[88]. 3@SWCNT paper sensor absorbs these VOCs with a better efficiency because of the binding of neutral gas molecules by calix[4]pyrrole units. Although calix[4]pyrrole has a stronger affinity towards EtOH, the strong interaction between EtOH and SWCNT enhances the response of pristine SWCNT as well. In contrast, pristine SWCNT was found to exhibit a week response (3%) for acetone. Thus, the presence of calix[4]pyrrole units increases the response of **3**@SWCNT paper sensor notably for acetone (14.6%) when it compared with pristine SWCNT. Additionally, the slow response of **3**@SWCNT paper sensor while attaining the base resistivity was attributed to the presence of calix[4]pyrrole units and their interaction with VOC molecules.

Statistical analysis of the measurements was also carried out. Accordingly, responses of 3@SWCNT paper sensor were measured independently, in triplicates, by injecting the 60 ppm VOCs at 25 °C (Figure 4.6g). Additionally, the sensor was also exposed to 60 ppm acetone vapor in repeating cycles. Analysis of the results revealed that the errors associated with the sensing measurements are less than 10%.

The effect of relative humidity on 3@SWCNT paper sensor was also evaluated. For that purpose, resistance changes, response and recovery times were tested through dynamic absorption-desorption cycles of 60 ppm acetone, with RH being gradually increased from 0.5 to 95%. Repeatable resistance changes (30 ± 2 ohm), response times (37±3 s), and recovery times (85±5 s) were observed until 80% RH. At 80% RH level, response of 3@SWCNT paper sensor increased to 251 ohm from 241 ohm. Additionally, while the response and recovery times were found to prolonged (49 and 180 s, respectively), the base resistivity increased to 221 ohm. Similar response behaviors were also observed when 3@SWCNT paper sensor was exposed to acetone vapor containing 85% RH. At this point, although the base resistivity is 221 ohm, the resistance change was calculated as 30 ohm. At 90% RH level, the resistance change was found to 24 ohm, meanwhile the response and the recovery times were measured as 74 and 180 s, respectively. These results show that 3@SWCNT paper sensor can be effective until 85% RH, although the base resistivity was increased by 10 ohm. The responses of **3**@SWCNT were also measured upon change in the RH without acetone gas. While $\sim 2\%$ response changes were obtained until 80%, an increase in the base resistivity was observed after 80% relative humidity level with 2 ohms of resistance increase. The observed resistance increases upon exposure to H₂O molecules seem to be correlated with theoretical calculations and experimental demonstrations.[74, 105-107] The electrical conduction of carbon nanotubes is dominated by holes. They also show a global p-type semiconducting behavior. The adsorbed H₂O molecules on the surface of carbon nanotube behave like electron donors, and reduces the hole density of p-type nanotubes, finally leading to the increase of resistance. After this point, they became less obvious with increase of RH due to the high H₂O vapor levels while requiring longer recovery time to reach steady state. At 80% RH and thereafter, the recovery process does not seem to reach the initial resistance value within three minutes.



Figure 4.9: Responses of 3@SWCNT on paper chip to different concentrations of acetone at 25 °C.

The sensing capability of 3@SWCNT on paper chip was also tested for detecting acetone gas. Figure. 4.7a shows the change of resistance $[\Delta R/R_0(\%)]$ with the injection of saturated acetone vapor into the chamber, corresponding to the increase of acetone concentration from 20 ppm to 500 ppm. After first injection (20 ppm) the change of resistance is 3.9%. The subsequent addition of the acetone vapors result in significant resonance changes indicating the selective and enhanced sensing by the sensor. Stepwise increase of the concentration revealed 33.8% resonance change at 500 ppm acetone vapor, which is 8.6 times higher than the initial response. Moreover, the detection limit of 3@SWCNT paper sensor was calculated as low as 13 ppm from the data present in Figure 4.7b. The relationship between acetone concentration and the resistance change was found to in a logarithmic fashion between 0 and 500 ppm as shown in Figure 4.7b. An inspection of Figure. 4.7b reveals an approach to linear response between 0–100 ppm. The nonlinear concentration-dependent response of paper based SWCNT gas sensors at high concentration ranges are reported in the literature. [73, 76, 77] **3**@SWCNT paper sensor seems to attain saturation at elevated concentrations[108] that can be potentially observed as the sensor is exposed to a large amount of analyte. Additionally, the choice of paper and their physical properties such as chemical impurities and optical brighteners on the surface of cellulose could be considered as some of the factors affecting the performance of the sensor.[77]



Figure 4.10: Resistance changes of SWCNT and 3@SWCNT upon exposing relatively non-polar VOCs.

The response of paper chips to other relatively non-polar VOCs were also measured (Figure. 4.8) within the margin of the same concentration which is 60 ppm. **3**@SWCNT demonstrates lower efficiency and no selectivity for these analytes. While, toluene, diethyl ether and hexane were found to show higher resistance changes, methylene chloride exhibit very small resistance changes for both SWCNT and **3**@SWCNT paper sensors. Moreover, **3**@SWCNT elicits resistance change decreases for all selected VOCs except toluene. The data present in Figure 4.8 is also consistent with the expected affiliation of these molecules with calix[4]pyrrole. Nonpolar nature of these molecules prevents them to interact with calix[4]pyrrole molecules via hydrogen bonding and might cause decrease in the absorption efficiency of the paper sensor.

4.4 Conclusion

In conclusion, we have demonstrated the fabrication of SWCNT based paper sensors via deposition of a noncovalent calix[4]pyrrole functionalized SWCNT on commercial filter paper by a simple and versatile filtration process. Effective solvent absorption and selective VOC interaction of SWCNT with the aid of calix[4]pyrrole **3** allow the paper sensor to be fabricated easily and to be post treatment free. Paper sensors fabricated by using **3**@SWCNT were used as chemiresistors to sense VOCs at 25 °C and exhibited selectivity for the detection of acetone in the concentration ranging from 20 to 500 ppm with a logarithmic fashion. The ease of synthesis of **3** and fabrication of present SWCNT based paper sensor lead us to suggest that the paper sensor

fabricated by using calix[4]pyrrole decorated SWCNTs could find practical application in the chemiresistive sensing of acetone vapor.





5. CONCLUSION

Two main conlusions could be drawn from the overall of the thesis. The first one is related to Chapter 2 and 3 and reflects the supramolecular polymerization performance of monomers that are constructed based on C4P cores. The supramolecular polymers obtained by both AB-type (C4P-carboxylate) and AA-BB-type (bis-C4P and biscarboxylate) monomers have been proven to have high solubility in chloroform and high degree of polymerization (DP) at elevated concentrations in contrast to other literature examples of supramolecular polymers derived by anion-C4P interactions. The formation of supramolecular polymers with high molecular weight was ultimately demonstrated via drawing rod-like fibers from highly concentrated solutions of above monomers. Additionally, in Chapter 2, an improved performance in supramolecular polymerization was achieved in chloroform by using CTA as counter cation due to the cation $-\pi$ interactions. All the supramolecular polymers were found to show thermoresponsiveness that is proved by temperature dependent specific viscosity measurements. In addition to that, supramolecular polymers in Chapter 2 showed chemi-responsiveness which was achieved via addition of an organic acid (CH_3SO_3H) followed by addition of a base (TBA) into the solution of supramolecular polymer. After addition of CH₃SO₃H, head-to-tail noncovalent interactions between supramolecular aggregates were broken which was restored by the addition of the base. Both the thermo- and chemi-responsiveness of the supramolecular polymers were monitored by ¹H-NMR analyses.

In Chapter 4 it was shown that paper-based sensors can be fabricated easily by a simple deposition of SWCNTs, that are functionalized with pyrene-modified C4P via non-covalent interactions, onto a commercial filter paper. Paper sensors fabricated in this way were used as chemiresistors to sense VOCs at room temperature, and showed distinct sensitivity for acetone vapor in different concentrations ranging from 20 to 500 ppm. Considering the ease of synthesis, facbication and the performance of sensors it was concluded that C4P-modified SWCNTs are suitable for practical applications for chemiresistive sensing of acetone vapor.



REFERENCES

- [1] L. Yang, X. Tan, Z. Wang, and X. Zhang. (2015). Supramolecular Polymers: Historical Development, Preparation, Characterization, and Functions, *Chemical Reviews*, vol. 115, no. 15, pp. 7196-7239.
- [2] X. Yan, F. Wang, B. Zheng, and F. Huang. (2012) Stimuli-responsive supramolecular polymeric materials, *Chemical Society Reviews*, vol. 41, no. 18, pp. 6042-6065.
- [3] C. Lu, M. Zhang, X. Yan. (2018) Fluorescent Metallacage-Core Supramolecular Polymer Gel Formed by Orthogonal Metal Coordination and Host– Guest Interactions, *Journal of the American Chemical Society*, vol. 140, no. 24, pp. 7674-7680.
- [4] A. Lavrenova, D. W. R. Balkenende, Y. Sagara, S. Schrettl, Y. C. Simon, and C.Weder, (2017). Mechano-and Thermoresponsive Photoluminescent Supramolecular Polymer, *Journal of the American Chemical Society*, vol. 139, no. 12, pp. 4302-4305.
- [5] A. Samanta, M. Tesch, U. Keller, J. Klingauf, A. Studer, and B. J. Ravoo, (2015).Fabrication of Hydrophilic Polymer Nanocontainers by Use of Supramolecular Templates, *Journal of the American Chemical Society*, vol. 137, no. 5, pp. 1967-1971.
- [6] Y. Han, Y. Tian, Z. Li, and F. Wang, (2018).Donor-acceptor-type supramolecular polymers on the basis of preorganized molecular tweezers/guest complexation, *Chemical Society Reviews*, vol. 47, no. 14, pp. 5165-5176.
- [7] P. Liu, Z. Li, B. Shi, J. Liu, H. Zhu, and F. Huang, (2018). Formation of Linear Side-Chain Polypseudorotaxane with Supramolecular Polymer Backbone through Neutral Halogen Bonds and Pillar[5]arene-Based Host–Guest Interactions, *Chemistry – A European Journal*, vol. 24, no. 17, pp. 4264-4267.
- [8] B. Zheng, F. Wang, S. Dong, and F. Huang, (2012). Supramolecular polymers constructed by crown ether-based molecular recognition, *Chemical Society Reviews*, vol. 41, no. 5, pp. 1621-1636.
- [9] D.-S. Guo and Y. Liu, (2012). Calixarene-based supramolecular polymerization in solution, *Chemical Society Reviews*, vol. 41, no. 18, pp. 5907-5921.
- [10] A. Harada, Y. Takashima, and H. Yamaguchi, (2009).Cyclodextrin-based supramolecular polymers, *Chemical Society Reviews*, vol. 38, no. 4, pp. 875-882.
- [11] X. Ren, J. Zhang, M. Cheng, Q. Wang, J. Jiang, and L. Wang, (2018). Supramolecular systems constructed by crown ether-based cryptands, *Tetrahedron Letters*, vol. 59, no. 23, pp. 2197-2204.
- [12] C. Yao, J. Zhang, Q. Sun, Y. Pan, (2018). A Four-Armed Unsymmetrical Cryptand: From Two Different Host–Guest Interactions to Responsive Supramolecular Polymer, *Macromolecular Rapid Communications*, vol. 39, no. 1, pp. 1700218-1700218,.

- [13] C. Li, (2014).Pillararene-based supramolecular polymers: from molecular recognition to polymeric aggregates, *Chemical Communications*, vol. 50, no. 83, pp. 12420-12433,.
- [14] H. Li, W. Chen, F. Xu, X. Fan, (2018). A Color-Tunable Fluorescent Supramolecular Hyperbranched Polymer Constructed by Pillar[5]arene-Based Host–Guest Recognition and Metal Ion Coordination Interaction, *Macromolecular Rapid Communications*, vol. 39, no. 10, pp. 1800053-1800053.
- [15] Q. He, P. Tu, and J. L. Sessler, (2018).Supramolecular Chemistry of Anionic Dimers, Trimers, Tetramers, and Clusters, *Chem*, vol. 4, no. 1, pp. 46-93.
- [16] A. Aydogan, (2016).Synthesis and characterisation of a calix[4]pyrrole functional polystyrene via 'click chemistry' and its use in the extraction of halide anion salts, *Supramolecular Chemistry*, vol. 28, no. 1-2, pp. 117-124.
- [17] A. Aydogan, D. Coady, A. Akar, S. K. Kim, (2008).Poly(methyl methacrylate)s with pendant calixpyrroles: polymeric extractants for halide anion salts, *Chemical Communications*, no. 12, pp. 1455-1457.
- [18] S. K. Kim, J. Lee, N. Williams, B. Hay, (2014).Bipyrrole-Strapped Calix[4]pyrroles: Strong Anion Receptors That Extract the Sulfate Anion, *Journal of the American Chemical Society*, vol. 136, no. 42, pp. 15079-15085.
- [19] A. Aydogan and A. Akar, (2012).Tri- and Pentacalix[4]pyrroles: Synthesis, Characterization and Their Use in the Extraction of Halide Salts, *Chemistry – A European Journal*, vol. 18, no. 7, pp. 1999-2005.
- [20] X. Chi, G. M. Peters, C. Brockman, V. M. Lynch, and J. L. Sessler, (2018). Controlling Structure Beyond the Initial Coordination Sphere: Complexation-Induced Reversed Micelle Formation in Calix[4]pyrrole-Containing Diblock Copolymers, *Journal of the American Chemical Society*, vol. 140, no. 41, pp. 13219-13222.
- [21] C. Zhou, HaoTang, S. Shao, and S. Jiang, (2006).Calix[4]pyrrole-Bonded HPLC Stationary Phase for the Separation of Phenols, Benzenecarboxylic Acids, and Medicines, *Journal of Liquid Chromatography & Related Technologies*, vol. 29, no. 13, pp. 1961-1978.
- [22] M. Yano, C. C. Tong, M. E. Light, F. P. Schmidtchen, and P. A. Gale, (2010). Calix[4]pyrrole-based anion transporters with tuneable transport properties, *Organic & Biomolecular Chemistry*, vol. 8, no. 19, pp. 4356-4363.
- [23] E. Baysak, S. Yuvayapan, A. Aydogan, and G. Hizal, (2018).Calix[4]pyrroledecorated carbon nanotubes on paper for sensing acetone vapor, *Sensors and Actuators B: Chemical*, vol. 258, pp. 484-491.
- [24] A. Aydogan, A. Koca, M. K. Şener, and J. L. Sessler, (2014).EDOT-Functionalized Calix[4]pyrrole for the Electrochemical Sensing of Fluoride in Water, *Organic Letters*, vol. 16, no. 14, pp. 3764-3767.
- [25] D. Sareen, J. H. Lee, H. Hwang, S. Yoo, and C.-H. Lee, (2016).Ion-mediated single-molecular optical switching and sensing based on the fluorophore-tethered calix[4]pyrrole, *Chemical Communications*, vol. 52, no. 34, pp. 5852-5855.
- [26] S. K. Kim, H. G. Lee, J. H. Oh, M. H. Lee, J. L. Sessler, (2017). A fluorogenic calix[4]pyrrole with a small rigid strap showing different fluorescent responses to anions, *Supramolecular Chemistry*, vol. 29, no. 9, pp. 651-657.
- [27] D. Stefani, M. Perrin, A. C. Aragones, Z. Futera, (2018). Mechanical Tuning of Through-Molecule Conductance in a Conjugated Calix[4]pyrrole, *ChemistrySelect*, vol. *3*, no. 23, pp. 6473-6478.
- [28] R. Molina-Muriel, G. Aragay, E. C. Escudero-Adán, and P. Ballester, (2018). Switching from Negative-Cooperativity to No-Cooperativity in the Binding of Ion-Pair Dimers by a Bis(calix[4]pyrrole) Macrocycle, *The Journal of Organic Chemistry*, vol. 83, no. 21, pp. 13507-13514.
- [29] S. Bähring, L. Martin-Gomis, G. Olsen, K. A. Nielsen, (2016).Design and Sensing Properties of a Self-Assembled Supramolecular Oligomer, *Chemistry – A European Journal*, vol. 22, no. 6, pp. 1958-1967.
- [30] J. S. Park, K. Y. Yoon, D. S. Kim, J. L. Sessler (2011). Chemoresponsive alternating supramolecular copolymers created from heterocomplementary calix[4]pyrroles, *Proceedings of the National Academy of Sciences*, vol. 108, no. 52, pp. 20913-20917.
- [31] A. Aydogan and J. L. Sessler, (2014). An imidazolium-functionalized selfassembling calix[4]pyrrole, *Chemical Communications*, vol. 50, no. 88, pp. 13600-13603.
- [32] S. Amharar, S. Yuvayapan, and A. Aydogan, (2018). A thermoresponsive supramolecular polymer gel from a heteroditopic calix[4]pyrrole, *Chemical Communications*, vol. 54, no. 7, pp.829-832.
- [33] S. Dong, Y. Luo, X. Yan, F. Huang, (2011). A Dual-Responsive Supramolecular Polymer Gel Formed by Crown Ether Based Molecular Recognition, *Angewandte Chemie International Edition*, vol. 50, no. 8, pp. 1905-1909.
- [34] F. Wang, J. Zhang, X. Ding, S. Dong, Y. Yu, (2010).Metal Coordination Mediated Reversible Conversion between Linear and Cross-Linked Supramolecular Polymers, Angewandte Chemie International Edition, vol. 49, no. 6, pp. 1090-1094.
- [35] N. Yamaguchi and H. W. Gibson, (1999). Stabilities of cooperatively formed cyclic pseudorotaxane dimers, *Chemical Communications*, no. 9, pp. 789-790.
- [36] H. C. Kolb, M. G. Finn, and K. B. Sharpless, (2001).Click Chemistry: Diverse Chemical Function from a Few Good Reactions, *Angewandte Chemie International Edition*, vol. 40, no. 11, pp. 2004-2021.
- [37] E. Riva, I. Wilkening, S. Gazzola, L. Smith, M. Tosin, (2014). Chemical Probes for the Functionalization of Polyketide Intermediates, *Angewandte Chemie*, vol. 126, no. 44, pp. 12138-12143.
- [38] F. Al-Ali, A. Brun, F. Rodrigues, G. Etemad-Moghadam, and I. Rico-Lattes,(2003). New Catanionic Amphiphiles Derived from the Associative Systems (α-Hydroxyalkyl)-phosphinic or (α-Hydroxyalkyl)-phosphonic Acid/Cetyltrimethylammonium Hydroxide. Preparation, Characterization, and Self-Organization Properties, *Langmuir*, vol. 19, no. 17, pp. 6678-6684.
- [39] E. Alcalde, I. Dinarès, A. Ibáñez, and N. Mesquida, (2012). A Simple Halideto-Anion Exchange Method for Heteroaromatic Salts and Ionic Liquids, *Molecules*, vol. 17, no. 4.

- [40] Y. Liu, Z. Wang, and X. Zhang, (2012). Characterization of supramolecular polymers, *Chemical Society Reviews*, vol. 41, no. 18, pp. 5922-5932.
- [41] P. A. Gale, J. L. Sessler, V. Král, and V. Lynch, (1996).Calix[4]pyrroles: Old Yet New Anion-Binding Agents, *Journal of the American Chemical Society*, vol. 118, no. 21, pp. 5140-5141.
- [42] C. Caltagirone, N. L. Bill, D. E. Gross, M. E. Light, J. L. Sessler, and P. A. Gale, (2010).Bis-cation salt complexation by meso-octamethylcalix[4]pyrrole: linking complexes in solution and in the solid state, *Organic & Biomolecular Chemistry*, vol. 8, no. 1, pp. 96-99.
- [43] N. Yamaguchi, D. S. Nagvekar, and H. W. Gibson, (1998).Self-Organization of a Heteroditopic Molecule to Linear Polymolecular Arrays in Solution, *Angewandte Chemie International Edition*, vol. 37, no. 17, pp. 2361-2364.
- [44] N. L. Strutt, H. Zhang, M. A. Giesener, J. Lei, and J. F. Stoddart, (2012). A self-complexing and self-assembling pillar[5]arene, *Chemical Communications*, vol. 48, no. 11, pp. 1647-1649.
- [45]N. Yamaguchi and H. W. Gibson, (1999).Formation of Supramolecular Polymers from Homoditopic Molecules Containing Secondary Ammonium Ions and Crown Ether Moieties, *Angewandte Chemie International Edition*, vol. 38, no. 1-2, pp. 143-147.
- [46] S. Debnath, A. Dasgupta, R. N. Mitra, and P. K. Das, (2016).Effect of Counterions on the Activity of Lipase in Cationic Water-in-Oil Microemulsions, *Langmuir*, vol. 22, no. 21, pp. 8732-8740.
- [47] H. Li, X. Fan, M. Qi, Z. Yang, H. Zhang, and W. Tian, (2016). Supramolecular Alternating Polymer from Crown Ether and Pillar[5]arene-Based Double Molecular Recognition for Preparation of Hierarchical Materials, *Chemistry – A European Journal*, vol. 22, no. 1, pp. 101-105.
- [48] P. Shen and L. Qiu, (2018).Dual-responsive recurrent self-assembly of a supramolecular polymer based on the host–guest complexation interaction between β -cyclodextrin and azobenzene, *New Journal of Chemistry*, vol. 42, no. 5, pp. 3593-3601.
- [49] H. Li, Y. Yang, F. Xu, T. Liang, H. Wen, and W. Tian, (2019). Pillararenebased supramolecular polymers, *Chemical Communications*, vol. 55, no. 3, pp. 271-285.
- [50] J. H. Lee, J. Park, J.-W. Park, H.-J. Ahn, J. Jaworski, and J. H. Jung, (2015). Supramolecular gels with high strength by tuning of calix[4]arenederived networks, *Nature Communications*, vol. 6, no. 1, pp. 6650-6650.
- [51] S. Bähring, H. D. Root, J. L. Sessler, and J. O. Jeppesen, (2019).Tetrathiafulvalene-calix[4]pyrrole: a versatile synthetic receptor for electron-deficient planar and spherical guests, Organic & Biomolecular Chemistry, vol. 17, no. 10, pp. 2594-2613.
- [52] P. A. Gale, E. N. W. Howe, X. Wu, and M. J. Spooner, (2018). Anion receptor chemistry: Highlights from 2016, *Coordination Chemistry Reviews*, vol. 375, pp. 333-372, 2018.

- [53] E. Mulugeta, Q. He, D. Sareen, J. H. Oh, C-H. Lee, (2017).Recognition, Sensing, and Trapping of Bicarbonate Anions with a Dicationic meso-Bis(benzimidazolium) Calix[4]pyrrole, *Chem*, vol. 3, no. 6, pp. 1008-1020.
- [54] R. Dutta, D. Firmansyah, J. Kim, H. Jo, K. M. Ok, and C.-H. Lee, (2018). Unexpected halide anion binding modes in meso-bis-ethynyl picketcalix[4]pyrroles: effects of meso- π (ethynyl) extension, *Chemical Communications*, vol. 54, no. 57, pp. 7936-7939.
- [55] E. H. Witlicki, C. Johnsen, M. V. Solano, K. A. Nielsen, A. H. Flood, (2017).Enhanced detection of explosives by turn-on resonance Raman upon host–guest complexation in solution and the solid state, *Chemical Communications*, vol. 53, no. 79, pp. 10918-10921.
- [56] E. S. Silver, B. M. Rambo, C. W. Bielawski, and J. L. Sessler, (2014).Reversible Anion-Induced Cross-Linking of Well-Defined Calix[4]pyrrole-Containing Copolymers, *Journal of the American Chemical Society*, vol. 136, no. 6, pp. 2252-2255.
- [57] S. Yuvayapan and A. Aydogan, (2019).Counter Cation Dependent and Stimuli Responsive Supramolecular Polymers Constructed by Calix[4]pyrrole Based Host-Guest Interactions, *European Journal of Organic Chemistry*, vol. 2019, no. 4, pp. 633-639.
- [58] A. Aydogan, G. Lee, C.-H. Lee, and J. L. Sessler, (2015). Reversible Assembly and Disassembly of Receptor-Decorated Gold Nanoparticles Controlled by Ion Recognition, *Chemistry – A European Journal*, vol. 21, no. 6, pp. 2368-2376.
- [59] N. Kiriyama, M. Ebihara, T. Udagawa, and H. Miyaji, (2016).Selforganization of dipyridylcalix[4]pyrrole into a supramolecular cage for dicarboxylates, *RSC Advances*, vol. 6, no. 24, pp. 19794-19796.
- [60] Z. P. Demko and K. B. Sharpless, (2002). A Click Chemistry Approach to Tetrazoles by Huisgen 1,3-Dipolar Cycloaddition: Synthesis of 5-Acyltetrazoles from Azides and Acyl Cyanides, *Angewandte Chemie International Edition*, vol. 41, no. 12, pp. 2113-2116.
- [61] B. Xia, B. Zheng, C. Han, F. Huang, (2013). A novel pH-responsive supramolecular polymer constructed by pillar[5]arene-based host– guest interactions, *Polymer Chemistry*, vol. 4, no. 6, pp. 2019-2024.
- [62] H. W. Gibson, N. Yamaguchi, and J. W. Jones, (2003).Supramolecular Pseudorotaxane Polymers from Complementary Pairs of Homoditopic Molecules, *Journal of the American Chemical Society*, vol. 125, no. 12, pp. 3522-3533.
- [63] F. Huang, D. S. Nagvekar, X. Zhou, and H. W. Gibson, (2007). Formation of a Linear Supramolecular Polymer by Self-Assembly of Two Homoditopic Monomers Based on the Bis(m-phenylene)-32-crown-10/Paraquat Recognition Motif, *Macromolecules*, vol. 40, no. 10, pp. 3561-3567.
- [64] O. A. Scherman, G. B. W. L. Ligthart, R. P. Sijbesma, and E. W. Meijer, (2006). A Selectivity-Driven Supramolecular Polymerization of an AB Monomer, *Angewandte Chemie International Edition*, vol. 45, no. 13, pp. 2072-2076.

- [65] L. Pauling, A. B. Robinson, R. Teranishi, and P. Cary, (1971).Quantitative Analysis of Urine Vapor and Breath by Gas-Liquid Partition Chromatography, *Proceedings of the National Academy of Sciences*, vol. 68, no. 10, pp. 2374-2376.
- [66] C. L. Whittle, S. Fakharzadeh, J. Eades, and G. Preti, (2007). Human Breath Odors and Their Use in Diagnosis, *Annals of the New York Academy* of Sciences, vol. 1098, no. 1, pp. 252-266.
- [67] P. Mayes,(2000). *Harper`s Illustrated Biochemistry*. New York: McGraw-Hill Companies Inc..
- [68] M. Phillips, (1997).Method for the Collection and Assay of Volatile Organic Compounds in Breath, *Analytical Biochemistry*, vol. 247, no. 2, pp. 272-278.
- [69] M. Meyyappan, (2016).Carbon Nanotube-Based Chemical Sensors, *Small*, vol. *12*, no. 16, pp. 2118-2129.
- [70] S. Salehi, E. Nikan, A. A. Khodadadi, and Y. Mortazavi, (2014).Highly sensitive carbon nanotubes–SnO2 nanocomposite sensor for acetone detection in diabetes mellitus breath, *Sensors and Actuators B: Chemical*, vol. 205, pp. 261-267.
- [71] G. P. Evans, D. J. Buckley, N. T. Skipper, and I. P. Parkin, (2014).Singlewalled carbon nanotube composite inks for printed gas sensors: enhanced detection of NO₂, NH₃, EtOH and acetone, *RSC Advances*, vol. 4, no. 93, pp. 51395-51403.
- [72] J. Li, Y. Lu, Q. Ye, M. Cinke, J. Han, and M. Meyyappan, (2003).Carbon Nanotube Sensors for Gas and Organic Vapor Detection, *Nano Letters*, vol. 3, no. 7, pp. 929-933.
- [73] S. Ammu, V. Dua, S. H. Agnihotra, S. K. Manohar, (2012).Flexible, All-Organic Chemiresistor for Detecting Chemically Aggressive Vapors, *Journal of the American Chemical Society*, vol. 134, no. 10, pp. 4553-4556.
- [74] D. R. Kauffman and A. Star, (2008).Carbon Nanotube Gas and Vapor Sensors, Angewandte Chemie International Edition, vol. 47, no. 35, pp. 6550-6570.
- [75] B. Kim, Y. Lu, T. Kim, J.-W. Han, M. Meyyappan, and J. Li, (2014).Carbon Nanotube Coated Paper Sensor for Damage Diagnosis, ACS Nano, vol. 8, no. 12, pp. 12092-12097.
- [76] L. R. Shobin and S. Manivannan, (2015).Carbon nanotubes on paper: Flexible and disposable chemiresistors, *Sensors and Actuators B: Chemical*, vol. 220, pp. 1178-1185.
- [77] K. A. Mirica, J. G. Weis, J. M. Schnorr, B. Esser, and T. M. Swager, (2012). Mechanical Drawing of Gas Sensors on Paper, *Angewandte Chemie International Edition*, vol. 51, no. 43, pp. 10740-10745.
- [78] D.-H. Kim, Y-S. Kim, J. Wu, (2009).Ultrathin Silicon Circuits With Strain-Isolation Layers and Mesh Layouts for High-Performance Electronics on Fabric, Vinyl, Leather, and Paper, *Advanced Materials*, vol. 21, no. 36, pp. 3703-3707.
- [79] P. Andersson, D. Nilsson, M. Chen, (2002). Active Matrix Displays Based on All-Organic Electrochemical Smart Pixels Printed on Paper, *Advanced Materials*, vol. 14, no. 20, pp. 1460-1464.

- [80] L. Hu, J. W. Choi, Y. Yang, S. Jeong, Y. Cui, (2009). Highly conductive paper for energy-storage devices, *Proceedings of the National Academy of Sciences*, vol. 106, no. 51, pp. 21490 -21494.
- [81] J.-W. Han, B. Kim, J. Li, and M. Meyyappan, (2014). A carbon nanotube based ammonia sensor on cellulose paper, *RSC Advances*, vol. 4, no. 2, pp. 549-553.
- [82] X. Dou, J. Wang, X. Lu, M. Zhang, Y. Quin, Z-X. Guo, (2016). A convenient approach to producing a sensitive MWCNT-based paper sensor, *RSC Advances*, vol. 6, no. 113, pp. 112241-112245.
- [83] K. A. Mirica, J. M. Azzarelli, J. G. Weis, J. M. Schnorr, and T. M. Swager, (2013). Rapid prototyping of carbon-based chemiresistive gas sensors on paper, *Proceedings of the National Academy of Sciences*, vol. 110, no. 35, pp. 3265-3270.
- [84] T. Guinovart, D. Hernandes-Alonso, P. Blondeau, P. Ballester, (2016).Recognition and Sensing of Creatinine, *Angewandte Chemie International Edition*, vol. 55, no. 7, pp. 2435-2440.
- [85] R. Nishiyabu and P. Anzenbacher, (2006).1,3-Indane-Based Chromogenic Calixpyrroles with Push–Pull Chromophores: Synthesis and Anion Sensing, *Organic Letters*, vol. 8, no. 3, pp. 359-362.
- [86] A. S. F. Farinha, M. R. C. Fernandes, and A. C. Tomé, (2014). Chromogenic anion molecular probes based on β,β'-disubstituted calix[4]pyrroles, *Sensors and Actuators B: Chemical*, vol. 200, pp. 332-338.
- [87] A. Aydogan, D. J. Coady, S. K. Kim, A. Akar, J. L. Sessler, (2008).Poly(methyl methacrylate)s with Pendant Calixpyrroles and Crown Ethers: Polymeric Extractants for Potassium Halides, *Angewandte Chemie International Edition*, vol. 47, no. 50, pp. 9648-9652.
- [88] W. E. Allen, P. A. Gale, C. T. Brown, V. M. Lynch, and J. L. Sessler, (1996). Binding of Neutral Substrates by Calix[4]pyrroles, *Journal of the American Chemical Society*, vol. 118, no. 49, pp. 12471-12472.
- [89] X. Lou, R. Daussin, S. Cuenot, C. Bailly, R. Jerome, (2004).Synthesis of Pyrene-Containing Polymers and Noncovalent Sidewall Functionalization of Multiwalled Carbon Nanotubes, *Chemistry of Materials*, vol. 16, no. 21, pp. 4005-4011.
- [90] R. J. Chen, Y. Zhang, D. Wang, and H. Dai, (2001).Noncovalent Sidewall Functionalization of Single-Walled Carbon Nanotubes for Protein Immobilization, *Journal of the American Chemical Society*, vol. 123, no. 16, pp. 3838-3839.
- [91] F. J. Gómez, R. J. Chen, D. Wang, R. M. Waymouth, and H. Dai, (2003). Ring opening metathesis polymerization on non-covalently functionalized single-walled carbon nanotubes, *Chemical Communications*, no. 2, pp. 190-191,.
- [92] H. Durmaz, A. Dag, U. Tunca, and G. Hizal, (2012).Synthesis and characterization of pyrene bearing amphiphilic miktoarm star polymer and its noncovalent interactions with multiwalled carbon nanotubes, *Journal of Polymer Science Part A: Polymer Chemistry*, vol. 50, no. 12, pp. 2406-2414.
- [93] A. Aydogan, J. L. Sessler, A. Akar, and V. Lynch, (2008).Calix[4]pyrroles with Long Alkyl Chains: Synthesis, Characterization, and Anion Binding Studies, *Supramolecular Chemistry*, vol. 20, no. 1-2, pp. 11-21.

- [94] P. Petrov, F. Stassin, C. Pagnoulle, and R. Jérôme, (2003). Noncovalent functionalization of multi-walled carbon nanotubes by pyrene containing polymers, *Chemical Communications*, no. 23, pp. 2904-2905.
- [95] K. Parikh, K. Cattanach, R. Rao, D.-S. Suh, A. Wu, and S. K. Manohar, (2006). Flexible vapour sensors using single walled carbon nanotubes, *Sensors and Actuators B: Chemical*, vol. 113, no. 1, pp. 55-63.
- [96] J. Zhao, A. Buldum, J. Han, and J. P. Lu, (2002).Gas molecule adsorption in carbon nanotubes and nanotube bundles, *Nanotechnology*, vol. 13, no. 2, pp. 195-200.
- [97] N. Chakrapani, Y. M. Zhang, S. K. Nayak, J. A. Moore, Y. Y. Choi, (2003). Chemisorption of Acetone on Carbon Nanotubes, *The Journal of Physical Chemistry B*, vol. 107, no. 35, pp. 9308-9311.
- [98] G. U. Sumanasekera, B. K. Pradhan, H. E. Romero, K. W. Adu, and P. C. Eklund, (2002). Giant Thermopower Effects from Molecular Physisorption on Carbon Nanotubes, *Physical Review Letters*, vol. 89, no. 16, pp. 166801-166801.
- [99] Y.-h. Shih and M.-s. Li, (2008). Adsorption of selected volatile organic vapors on multiwall carbon nanotubes, *Journal of Hazardous Materials*, vol. *154*, no. 1-3, pp. 21-28.
- [100] E. S. Snow and F. K. Perkins, (2005). Capacitance and Conductance of Single-Walled Carbon Nanotubes in the Presence of Chemical Vapors, *Nano Letters*, vol. 5, no. 12, pp. 2414-2417.
- [101] S. Kwon, R. Vidic, and E. Borguet, (2003). The effect of surface chemical functional groups on the adsorption and desorption of a polar molecule, acetone, from a model carbonaceous surface, graphite, *Surface Science*, vol. 522, no. 1-3, pp. 17-26.
- [102] X. Feng, C. Matranga, R. Vidic, and E. Borguet, (2004). A Vibrational Spectroscopic Study of the Fate of Oxygen-Containing Functional Groups and Trapped CO2 in Single-Walled Carbon Nanotubes During Thermal Treatment, *The Journal of Physical Chemistry B*, vol. *108*, no. 52, pp. 19949-19954.
- [103] D. Kazachkin, Y. Nishimura, S. Irle, K. Morokuma, R. D. Vidic, and E. Borguet, (2008). Interaction of Acetone with Single Wall Carbon Nanotubes at Cryogenic Temperatures: A Combined Temperature Programmed Desorption and Theoretical Study, *Langmuir*, vol. 24, no. 15, pp. 7848-7856.
- [104] R. J. Chen, N. R. Franklin, J. Kong, J. Cao, H. Dai, (2001).Molecular photodesorption from single-walled carbon nanotubes, *Applied Physics Letters*, vol. 79, no. 14, pp. 2258-2260.
- [105] J.-W. Han, B. Kim, J. Li, and M. Meyyappan, (2012). Carbon Nanotube Based Humidity Sensor on Cellulose Paper, *The Journal of Physical Chemistry C*, vol. 116, no. 41, pp. 22094-22097.
- [106] H. Zhao, T. Zhang, R. Qi, J. Dai, S. Liu, and T. Fei, (2017).Drawn on Paper: A Reproducible Humidity Sensitive Device by Handwriting, *ACS Applied Materials & Interfaces*, vol. 9, no. 33, pp. 28002-28009.
- [107] A. Zahab, L. Spina, P. Poncharal, and C. Marlière, (2000). Water-vapor effect on the electrical conductivity of a single-walled carbon nanotube mat, *Physical Review B*, vol. 62, no. 15, pp. 10000-10003.

[108] F. Tsow, E. S. Forzani, and N. J. Tao, (2008).Frequency-Coded Chemical Sensors, *Analytical Chemistry*, vol. 80, no. 3, pp. 606-611.





CURRICULUM VITAE



Name Surname : Samet Yuvayapan Place and Date of Birth :Bursa-1987 E-Mail : <u>sametyuvayapan@gmail.com</u>

EDUCATION:

Ph.D.: Chemistry, Istanbul Technical University, Graduate School of Science, Engineering and Technology (2013-2019)

M.Sc.: Chemistry, Istanbul Technical University, Graduate Schol of Science, Engineering and Technology (2011-2013)

B.Sc.: Chemistry, Faculty of Arts and Sciences, Dumlupinar University (2005-2009)

PROFESSIONAL EXPERIENCE :

2014-2019 Research Assistant, Chemistry, Istanbul Technical University **2012-2014** Research Assistant, Chemistry, Istanbul University

PUBLICATIONS FROM THESIS :

 Yuvayapan S., Aydoğan A., Counter Cation Dependent and Stimuli Responsive Supramolecular Poylmers Constructed by Calix[4]pyrole Based Host-Guest Interactions, European Journal of Organic Chemistry; vol. 2019, 633-639

- Yuvayapan S., Aydoğan A., Supramolecular Calix[4]pyrrole Polymers from a Complementary Pair of Homoditopic Host-Guest Molecules, Chemical Communication, vol. 55, 8800-8803.
- Baysak E., Yuvayapan S., Aydoğan A., Hizal G., Calix[4]pyrrole Decorated -Carbon Nanotubes on Paper for Sensing Acetone Vapor, Sensors and Actuators B:Chemical, vol. 258, 484-491.

OTHER PUBLICATION(s):

 Amharar S., Yuvayapan S., Aydoğan A., A thermoresponsive supramolecular polymer gel from a heteroditopic calix[4]pyrrole, Chemical Communication, vol. 54, 829-832