May 2018

Main Group Element-containing Chromophores and Polyelectrolytes: Sulfur, Phosphorus and Gallium

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MAIN GROUP ELEMENT-CONTAINING CHROMOPHORES AND POLYELECTROLYTES: SULFUR, PHOSPHORUS AND GALLIUM

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
Wang Wan
May 2018

Accepted by:
Dr. Rhett C. Smith, Committee Chair
Dr. Andrew G. Tennyson
Dr. Jason D. McNeil
Dr. Daniel C. Whitehead
ABSTRACT

Research on chromophores and polyelectrolytes incorporating main group elements has attracted tremendous research interest and been investigated extensively in the past few decades. In the current contribution, potential applications of polyelectrolytes in ion-conductive/exchange materials, optoelectronics and as antibacterial agents are studied systematically. Several new classes of chromophores based on heterocycle (thiophene and pyrrole) motifs have been developed in this work, with potential use in various areas including organic photovoltaics, organic light-emitting diodes, chemical/bio-sensors, bio-imaging/labeling, etc.

In Chapter 2, a series of ten polythiophene derivatives is discussed. Each polymer in the series has a different percentage of carboxylic acid-bearing repeat units. The properties of these polymers are explored under neutral and anionic forms. The properties that are examined include UV-vis absorption and photoluminescence spectroscopy of films and solutions as well as solution aggregation measured by dynamic light scattering. All of these properties are strongly dependent both on protonation state and percentage of carboxylic acid/carboxylate side chains along the polymer backbone. The anionic form of each polythiophene derivative was then employed for layer-by-layer (LbL) film deposition with a cationic phosphonium polyelectrolyte. The film growth process is studied by spectroscopic techniques and film morphologies are examined by atomic force microscopy.

In Chapters 3 and 4, two series of tetraarylphosphonium polyelectrolytes (TPELs) has been discussed. This work involved developing new polymerization protocols for
using commercial diphenylphosphine and dihalides or readily-prepared bis(aryl triflate)s as monomers. The Ni- and Pd-catalyzed P–C coupling formation reactions produce degrees of polymerization up to 65. All TPELs have reasonable thermal stability in the range of 350–450 °C. The stability of the TPELs to alkaline solution is strongly depend on the spacer between adjacent phosphonium sites as well as counterions.

The work presented in Chapter 5 shows design and synthesis of two series of phosphonium polyelectrolytes (PELs) analogues. The polymerizations of diphosphines and α,α’-dibromo-p-xylene via SN2 reaction yielded phosphonium polymers with the degrees of polymerization higher than 10. The prepared polymers were employed for LbL self-assembly fabrication. The influences depending on spacer between charged sites and existence of hydrophobic side-chains have been investigated and compared systematically.

The Chapter 6 presents the work on a heavier analogue of BODIPY dye which presents strong visible light absorption and fluorescence emission. The new type of fluorescent dye has been prepared successfully with moderate yield ~ 44.2%. These new dyes exhibit strong visible light absorption and fluorescence emission (quantum yield up to 90 %). One member of this new chromophore family has been characterized by single crystal X-ray diffraction.
ACKNOWLEDGMENTS

First, I would like to give my sincere gratitude to my advisor: Dr. Rhett Smith. Without patient guidance and strong supporting, I could complete this dissertation smoothly and finish my Ph.D study successfully.

I would like to thank Dr. Tennyson, Dr. Whitehead and Dr. McNeil for being my committee members and taking the time to support my Ph.D study.

I would also like to thank my group members: Dr. Xiaoyan Yang Dr. Monte Bedford for the support in my research.

I really appreciate chemistry department of Clemson University for giving me opportunity to pursue Ph.D career.

Finally, I would like to show my appreciation to my family. They always support and comfort me when I have good and bad time.
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<td>$\lambda_{em}$</td>
<td>wavelength of emission</td>
</tr>
<tr>
<td>$\lambda_{max}$</td>
<td>wavelength of absorption</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>quantum yield</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
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<tr>
<td>BHJ</td>
<td>bulky-heterojunction</td>
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<tr>
<td>CDCl$_3$</td>
<td>chloroform-d$_1$</td>
</tr>
<tr>
<td>(CD$_3$)$_2$CO</td>
<td>acetone-d$_6$</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
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<tr>
<td>DFT</td>
<td>density functional theory</td>
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<tr>
<td>DLS</td>
<td>dynamic light scattering</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Optical band gap</td>
</tr>
<tr>
<td>$E_{IP}$</td>
<td>ionization potential</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
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<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
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<tr>
<td>HPPh₂</td>
<td>diphenylphosphine</td>
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<tr>
<td>LbL</td>
<td>layer-by-layer</td>
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<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
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<td>MeOH</td>
<td>methanol</td>
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<tr>
<td>$M_n$</td>
<td>number average molar mass</td>
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<tr>
<td>$M_p$</td>
<td>melting point</td>
</tr>
<tr>
<td>$M_w$</td>
<td>weight average molar mass</td>
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<td>$t$BuLi</td>
<td>$t$-butyllithium</td>
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<td>NBS</td>
<td>N-bromosuccinimide</td>
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<td>NMR</td>
<td>nuclear magnetic resonance</td>
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<td>OLED</td>
<td>organic light emitting diode</td>
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<tr>
<td>OPV</td>
<td>oligo(p-phenylenevinylene)</td>
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<td>PEL</td>
<td>Phosphonium polyelectrolyte</td>
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<tr>
<td>Pd(PPh₄)₄</td>
<td>tetrakis(triphenylphosphine)palladium(0)</td>
</tr>
<tr>
<td>Pd₂(dba)₃</td>
<td>tris(dibenzylideneacetone)dipalladium(0)</td>
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<td>PDI</td>
<td>polydispersity index</td>
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<td>PL</td>
<td>photoluminescence</td>
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PLED  polymer light emitting diode
ppm   parts per million
PT    polythiophene
$R_t$ retention factor
SDP   size distribution processor
$T_d$ decomposition temperature
TEA   triethylamine
$T_g$ glass transition temperature
TGA   thermogravimetric analysis
THF   tetrahydrofuran
TLC   thin layer chromatography
TMEDA tetramethylethylenediamine
TLC   thin layer chromatograph
TPEL  tetraarylphosphonium polyelectrolyte
UV-vis ultra-violet visible
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CHAPTER ONE
INTRODUCTION

Chromophore and Polyelectrolyte

Dipyrromethene derivatives

The compounds with diverse color and brightness are always attracting attention to grateful sense as well as their tremendous application in all fields. BODIPY is a typical family of colorful fluorescent compounds which has relatively outstanding stability and good intensity of emission. In a few decades after the first BODIPY was discovered and prepared on 1968 by Treibs and Kreuzer,\(^1\) while in following a few decades only a little study was focused on this novel type of compound. With the blossoming development of biochemistry and biological engineering after 1980s,\(^2\) the BODIPY had attracted people’s interest due to its sharp and intense photoluminescent emission and potential in bio-labeling and imaging.

The coordination compound of dipyrromethene (dipyrrin) and BF\(_2\) is the core of BODIPY dye. The substitution on the skeleton of dipyrrin ligand is variable and then the properties of the dye can be tunable, such as quantum yield and emission wavelength. Besides boron, some other metal centered derivatives of dipyrrin were also investigated, including main group metals (Al, Sn, Ga, In) and transition metals (Zn, Cu, Fe, etc).\(^3-13\)
Some of diamagnetic metal coordination complexes have unique properties in photophysics and chemical reactivities.\textsuperscript{14}

\[
\begin{align*}
\text{Scheme 1.1} & \quad \text{Synthetic routes to symmetric dipyrrin ligands} \\
\end{align*}
\]

In general, two types of dipyrrins including symmetric and asymmetric are designed and prepared in process of investigating their derivatives. For symmetric dipyrrin, one of the most widely used route is bimolecular condensation of 2-pyrrole-carbaldehydes (Scheme 1.1). The 5-substituted 2-pyrrole carbaldehydes processes homo coupling in strong acidic condition to form protonated dipyrrin salts, and then follow with deprotonation with ammonium hydroxide to yield neutralized dipyrrin ligands. The other route is to use two equivalences of 2-substituted pyrrole and one equivalence aldehyde to condense into aim dipyrrins under existence of catalytical amount of trifluoromethyl acetic acid. The most outstanding advantage of this route is that the substitution on meso-position is tunable by using different species of aldehyde. For asymmetric dipyrrins, the

\[
\begin{align*}
\text{Scheme 1.2} & \quad \text{Synthetic route to asymmetric dipyrrin ligands.}
\end{align*}
\]
most common and convenient method is shown in Scheme 1.2. The reaction is similar to Vilsmeier-Haak reaction. The pyrrole ring bearing aldehyde group reacts with trichlorophosphine oxide to form Vilsmeier reagent and then practice aromatic electrophilic substitution with other pyrroles to yield asymmetric products.

![Jablonski diagram illustrating radiative and non-radiative processes](image)

**Figure 1.1** Jablonski diagram illustrating radiative and non-radiative processes

For colored conjugated organic compounds, absorption and photoluminescence can be clearly explained by Jablonski diagram (Figure 1.1). The molecule absorbs photons of particular energy and the electrons on the ground states ($S_0$) are excited to higher energy level ($S_1$, $S_2$, etc.). In this transition, energy of photons is transferred to electrons inside the molecule. For the excited electrons, they can be relaxed via different routes. The first one is non-radiative vibrational relaxation, which happens among different vibrational level within a certain electronic level. The other important relaxation way is internal conversion. The excited electron in higher electronic state can process transition
to lower electronic level if vibrational energy levels of the two electron levels have overlap. The electrons in the lowest vibrational energy level of first excited electronic level transit back to ground state and extra energy is to emit as photon, which is observed as fluorescence. Fluorescence is commonly observed on the transition of first excited electronic state because non-radiative processes are more likely happened in higher excited electronic levels. Another uncommon radiative dissipation of energy of excited electron is phosphorescence. In the process of phosphorescence, the spin multiplicity of excited electron changes from singlet to triplet ($T_1$), which is indicated as intersystem crossing. The transition of excited triplet electron from $T_1$ to $S_0$ with emission of photon is forbidden based on Pauli exclusion principle. Compared to fluorescence, the process of phosphorescence is much slower with time scale in $10^{-3}$–$10^{-1}$ s.

Polythiophene

In the last three decades, polythiophenes have been investigated comprehensively due to their versatile applications in gene delivery agents, organic photovoltaics, chemical and biological sensor, dye-sensitized solar cell, theranostic drugs, optoelectronic devices and conductors. The backbone of polythiophene is considered to be constructed of coplanar thiophene rings, in which the extended π-conjugated system induces some interesting properties. Based on Hückel’s rule and comparison of the resonance energy of benzene (150.62 kJ/mol) to that of thiophene (121.34 kJ/mol), one concludes that thiophene is a typical aromatic system, so that the electrons of thiophene rings can be delocalized along the polymer chain. Delocalization of electrons decreases
the energy gap between the valence and conduction bands and thus enables the conjugated polymer to better conduct electricity. The lower gap between highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) allows the conjugated polymer to absorb energy in the range of visible light. Thiophene unit in polymer chains can be functionalized with diverse sidechains to tune the resultant optoelectronic properties.

Figure 1.2 shows the typical structure of organic photovoltaics. One of the most investigated moiety is the photoactive layer, which is comprised of donor and acceptor components. Polythiophene derivatives are ubiquitously used in the composition of polymer-fullurene bulky-heterojunction (BHJ) solar cells. Polythiophene with substituents on 3-position of each repeat unit, such as poly(3-hexylthiophene) (P3HT) and poly(3-carboxyalkylthiophene) (P3CAT) are examples of materials widely investigated for fabricating photoactive layers. Polythiophene-derivatized polyelectrolytes are explored in modifying interfaces among electrodes and active composite. A most extensively used cathode modifier, PSS-PEDOT, is comprised of an anionic polyelectrolyte poly(styrenesulfonate) (PSS) with the conjugated polymer poly(3,4-ethylenedioxythiophene) (PEDOT). Use of this layer can improve hole collection and enhances the open-circuit current (Voc) by improved ohmic contact with photoactive layers.
Figure 1.2 Typical structural layout of organic photovoltaics.

Polyelectrolytes

Polyelectrolyte is a special type of polymer which is bearing ionic segments in repeat unit, such as carboxylate, sulfate, ammonium, imidazolium, phosphonium, etc (Figure 1.3). Polymers featuring ionic functionalities, referred to as polyelectrolytes, ionenes or ionomers, represent a rapidly-growing research area. Some of the reasons for such widespread interest in ionic polymers include the fact that many are water-processable and exhibit better water solubility for biological applications, their composite films have high surface energies, and they can supramolecular assembly with other materials via ion-ion or ion-dipole interactions.
One notable yet still underexplored area of polyelectrolyte research is in the area of chromophore-derivatized or conjugated polyelectrolytes. These materials can exploit the desirable properties of polyelectrolytes for use in organic electronics and photonics. As an example, layers comprised of a mixture of anionic polyelectrolyte poly(styrenesulfonate) (PSS) with the conjugated polymer poly(3,4-ethylenedioxythiophene) (PEDOT) are ubiquitous in organic electronics. Several research teams including Buriak, Reynolds and Schanze, and Bazan, to name a few, have explored polyelectrolytes as components of organic photovoltaic cells and related devices. Notable improvements in device operation and interfacial effects can result from the incorporation of ionic polymers in place of neutral polymers.

Existing work on cationic polyelectrolytes most commonly has featured ammonium, pyridinium, imidazolium, guanidinium or phosphonium groups, each of which may be in the main chain or in side chain components. The Smith group’s
research on these materials has concentrated on properties and applications of phosphonium polyelectrolytes (PELs), some examples of which are displayed in Figure 1.3. Compared to ammonium salts, phosphonium salts often exhibit better thermal and chemical stability, making these particular species especially attractive in terms of performance under such duress over longer operational lifetimes. As an example of the thermal stability attainable, \textbf{R2} \textsuperscript{51} synthesized in Manners’ group is thermally stable up to 400 °C, and small molecular phosphonium salts represent the most thermally robust ionic liquids known.\textsuperscript{52} An example in which chemical stability is paramount is in an alkaline fuel cell, where the membrane must tolerate extended heating at temperatures up to 80 °C in the presence of aqueous hydroxide. The PEL \textbf{R1} \textsuperscript{53} has proven stable enough for test devices under such conditions, and recent advances in the preparation of tetraarylphosphonium polymers\textsuperscript{54} suggest that more advances are on the horizon in this area as structural elements leading to improved stability are identified. PELs also offer advantages in medicinal contexts. For example, PEL exhibit higher bactericidal activity\textsuperscript{55} and higher efficiency/lower toxicity to human cells in gene delivery\textsuperscript{56} versus ammonium analogues.

**Coupling reactions**

Metal catalyzed cross coupling reactions are very important in development of modern organic. This is one type of the most effective and tunable method to form carbon-carbon single bond. 2010 Nobel Prize in Chemistry was awarded to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki based on their great contribution on development
of palladium-catalyzed coupling reaction. All palladium catalyzed coupling reactions have similar cyclic mechanism, such as Stille reaction (Scheme 1.3) which was discovered and reported by John K. Stille in 1978.

![Scheme 1.3 Catalytical cycle of Stille coupling reaction.](image)

In these coupling reactions, one precursor is allyl/alkenyl/aryl halide or triflate. The first step of catalytical cycle is oxidative addition which cleavage is happened between sp2 hybridized carbon and halide/triflate then to form cis-tetravalent 16-electron Pd(II) complex. The other precursor is varying in different reaction and participates the second step which is called transmetallation. In this process the sp2 segment of metal based precursor is exchanged with halide/triflate group of former Pd(II) complex. The sp2 hybridized groups from two precursors coordinating with Pd(II) can be reductively eliminated to yield coupling product and the Pd(II) is reduced back to starting Pd(0) form. In the investigation from Dr. Heck, his group found that some of catalysts decomposed during the reaction even if it was under anaerobic condition.
Scheme 1.4 Proposed catalytical cycle of phosphorus-carbon coupling reaction.

The free phosphine in reaction system is also possible to proceed coupling with allylic/alkenyl/aryl halide/triflate. Similar to the C-C coupling, the first step of P-C coupling is oxidative addition. Under relatively high temperature, the free phosphine ligand has rapid exchange with palladium (II) additive. Then it is feasible that the coordinated phosphine and the R group process reductive elimination to yield phosphonium salt and original palladium (0) catalyst. By using phosphine free palladium ligand and only adding one species of desired phosphine, phosphonium products produced via phosphorus-carbon coupling reactions were obtained with outstanding selectivity and high yield. 44-45
Reference


34. Ouyang, J.; Xu, Q.; Chu, C.; Yang, Y.; Li, G.; Shinar J. Polymer 2004, 45, 8443–8450


CHAPTER TWO

INFLUENCE OF SIDECHAIN COMPOSITION ON POLYTHIOPHENE
POLYELECTROLYTE PROPERTIES AND THEIR SUPRAMOLECULAR
ASSEMBLY WITH PHOSPHONIUM POLYMERS

Introduction

Polythiophene derivatives (PTs, Chart 2.1A) (APT,\textsuperscript{1} P3CATs,\textsuperscript{2} P3(TBP)HT\textsuperscript{+}Br\textsuperscript{-},\textsuperscript{3}) are some of the most-studied organic conjugated polymers (CPs). They are components of many of the most efficient organic photovoltaic (OPV) cells known and have found a wide range of uses in optoelectronics as charge/electron injection layers (PTMAHT),\textsuperscript{4} components of efficient light-emitting diodes (PEDOT),\textsuperscript{5} and in field-effect transistors (P3HT),\textsuperscript{6} among a plethora of other applications available to these structurally-, electrochemically- and optically diverse materials.\textsuperscript{7-9}

Polyelectrolyte-bearing polythiophene backbones in particular have found use in colorimetric and fluorescent sensors. (PTAA,\textsuperscript{10} P1,\textsuperscript{11} P2,\textsuperscript{12} and as molecular delivery agents (PEI-co-PT,\textsuperscript{13} P4\textsuperscript{14}) via mechanisms based on the conformational changes of the PT derivatives when they complex with other species.

Several groups have studied how the presence of ionic sidechains influence the performance of PTs in optoelectronic contexts. Buriak’s group has investigated P3CATs in optoelectronic and molecular structural properties, as well as bulk hetero junction in OPV. P3CATs were processed in pyridine solution, and pyridine would be expected to deprotonate the carboxylic acid moieties, resulting in a pyridinium carboxylate salt.\textsuperscript{2} As the increasing of carboxyalkyl chain side-chains from propyl to hexyl, the UV-vis
absorption and photoluminescence emission of these P3CATs showed slightly red-shift and approximately unchanged, respectively. Inspired by these studies, we became interested in learning how the properties of PT are influenced by the sequential replacement of alkyl side chains with polar or ionic sidechains.

A)

B)
Supramolecular assemblies or complexes formed by the interaction of polyanions with polycations have drawn increasing interest. The ionic sites of a polyelectrolyte in a polyelectrolyte complex can be balanced either by the ionic moieties of the oppositely-charged polyelectrolyte (intrinsic sites), or by exogenous counterions (extrinsic sites) (Chart 2.2A). In layer-by-layer assembly, consecutive layer formation is driven by electrostatic affinities of ion-pairing interactions between opposite charged units, to form multilayers aggregation spontaneously. Charge compensation within the multilayer can be due to polyelectrolyte complexation (“intrinsic compensation”) plus additional neutralization by counterions within the film (“extrinsic compensation”). The match between the cation-cation distance ($d_{cc}$) and anion-anion distance ($d_{aa}$) can have a profound impact on the manner in which the polycation and polyanion assemble into polyelectrolyte complexes and layer-by-layer assembled films (Chart 2.2B). In our previous study on LbL film formation from LX and Pc12-100, we found that the number of methylene spacer in LX series (Chart 2.1B) would affect the amount of Pc12-100 and film roughness. Similar phenomena also found in LbL film of LO and Pc12-100. The proposed reason is that the spacer length affects dcc leading to match/mismatch of the $d_{aa}$. During the LbL process of LX/LO with Pc12-100, the mismatch of $d_{cc}$ and $d_{aa}$ requires more material to balance the charge which lead to higher absorbance.

In the course of this work we observed that the match of $d_{cc}$ and $d_{aa}$ dictates the ratio of polycation to polyanion and free ions was interpreted as improving the extent of intrinsic interactions and minimizing extrinsic sites in which counterions (in this case Na$^+$ and Br$^-$) remained associated with the polyelectrolyte backbone.
Herein we report on our efforts to evaluate the relationship between properties and the percentage of ionic or polar side-chains present in polythiophene derivatives. Photophysical properties, concentration-dependent aggregation in solution and thin film morphologies are reported for a series of ten polythiophene derivatives having variable percentage of polar or ionic sidechains in place of alkyl substituents. The anionic PT derivatives were also employed in layer-by-layer assembly of thin films with a
phosphonium polyelectrolyte to assess the effect of changing the average anion-anion distance ($d_{cc}$) while the cation-cation distance ($d_{aa}$) was held constant.

**Experimental**

*General Considerations.*

All air-sensitive reactions were performed in an MBraun UNILab glovebox under nitrogen. Anhydrous solvents were dried and degassed using an MBraun solvent purifier. Glass slides were purchased from Fisher Scientific. Other chemicals were used without further purification after purchased. All the NMR spectra were collected on a Joel ECX-300 MHz spectrometer operating at 300 MHz. UV-Vis absorption spectra were acquired on a Cary 50 Spectrophotometer. Photoluminescence (PL) spectra were obtained on a Varian Eclipse fluorimeter in quartz cuvettes with a pathlength of 1 cm. **Pc12, Pc12-100** and **LX5** were prepared as previously reported.\(^{20}\)

*Layer-by-layer technique.*

The procedure is similar with that published in our previous work.\(^{20-26}\) A glass microscope slide was cleaned by soaking in concentrated nitric acid, then sequential rinsing with deionized water and tetrahydrofuran. The slide was visually inspected for scuffs or scratches. Solutions of **LX5** and **Pc12-\text{y}** $(5\times10^{-4} \text{ M})$ were prepared in 50:50 acetonitrile:H$_2$O and 2:1 THF:water (pH of water adjusted to 9 with NaOH), respectively. For each film preparation, the slide was first dipped in the **LX5** solution then briefly shaken to remove excess solution droplets. The process was then repeated using the
**Pc12-y** solution. The spectrum of the slide was immediately collected using a Cary 50 UV-vis spectrometer with a scanning range of 275 to 800 nm. This procedure was repeated until the desired number of bilayers was obtained. *Layer films were prepared by W. Wan, X. Yang.*

*Atomic Force Microscopy (AFM).*

All AFM experiment were conducted using an AIST Smart SPM TM 1000 in semicontact mode within a 1 µm × 1 µm or 5 µm × 5 µm sample area using an aluminium tip (spring constant = 5 N/m, 160 kHz resonance frequency). Images were processed by AIST-NT and WSxM 5.0 Develop 7.0 software.27. *AFM data were collected in the laboratory of G. Chumanov with the assistance of L. Hu. Interpretation was performed by W. Wan and X. Yang.*

*Dynamic Light Scattering (DLS).*

Polymer samples were prepared in THF/diethyl ether (80:20), passed through a 0.2 µm PTFE filter, and placed in a 1 cm quartz cuvette. The autocorrelation function (ACF) of scattered light from a 20 °C sample was detected at 90° in a Beckman Coulter N4-plus analyzer. A CONTIN program was used to fit the ACF for size distribution analysis. Each datum point represents the mean diameter, with standard deviation, of intensity-based distribution calculated over 10 repetitions of acquisition. *AFM data were collected in the laboratory of S. Foulger with the assistance of Oleksandr Klep. Interpretation was carried out by M. S. Bedford and W. Wan.*
Computational Methods

The equilibrium geometries of molecules at ground states were optimized by using density functional theory (DFT) B3LYP/6-31G*.28 The polythiophenes are simplified to trimer to investigate energy level of neutral and ionic Pc12-y.

General Procedure for Hydrolysis of Pc12 to give Pc12-y.

To a solution of Pc12 in THF was added 20 wt.% NaOH(aq). The solution was then heated to reflux and stirred under nitrogen for the reaction times listed for each polymer Pc12-y listed below. After cooling to room temperature, the solution was made acidic (pH ~2) by careful addition of 3 M hydrochloride acid. The product was extracted from the aqueous fraction by use of dichloromethane/THF (3:1). The organic fraction was collected and all volatiles removed under reduced pressure. The product was washed with methanol (×3) and n-hexane (×3) then dried in a vacuum oven to yield the dark red solid.

Synthesis of precursors and polymer

1) Bromination of 2, 5-dibromo-thiophene-3-carboxylic acid (DBTAC):

Preparation followed a similar literature procedure with a modified recrystallization procedure.29, 30 N-bromo-succinimide (NBS) (15.3 g, 86mmol) and 3-thiophene-carboxylic acid (5.00 g, 39.0 mmol) was dissolved in 60 ml dry N, N-Dimethylformamide (DMF). The mixture was stirred at 55-60 ºC for 24 h, and then quenched by NaCl solution. The pure product was obtained via recrystallization in
ethanol/H₂O=4:1 and filtration (8.50 g, 76.2%). ¹H NMR (300 MHz, (CD₃)₂CO), δ (ppm): 7.56 (s, 1H). 13C NMR (75.5 MHz, CDCl₃), δ (ppm): Mp=178-179 ℃.

2) Esterification of dodecyl 2,5-dibromo-thiophene-3-carboxylate (C12):

Preparation followed a similar literature procedure with modified purification procedure.31 To a solution of DBTAC (1.43 g, 5.00 mmol) in anhydrous 30 ml DMF was adding anhydrous K₂CO₃ (2.07 g, 15.0 mmol) and 1-bromododecane (2.50 g, 10.0 mmol). The mixture was kept stirring at 85 °C overnight then quenched by 1 vol.% HCl solution. The solution mixture was extracted by dichloromethane twice. Combined organic phase was dried via rotary vapor to obtain crude product, and followed purification via silica-gel column chromatography using hexane/ethyl acetate 95:5 solvent system (ΔRf = 0.4) to yield the target as a white wax-like solid (1.82 g, 80.0%). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 0.88 (J=6.6 Hz, t, 3H ), 1.38 (m, 20H), 1.72 (J=6.6 Hz, quin., 2H), 4.26 (J=6.6 Hz, t, 2H), 7.34 (J=1.2 Hz, t, 1H). 13C NMR (75.5 MHz, CDCl₃), δ (ppm): 14.2, 22.8, 26.1, 28.6, 29.3, 29.4, 29.6, 29.7 (d), 32.0, 111.4, 119.0, 131.8, 132.1, 160.9. Mp= 39-40 ℃.

3) Synthesis of 2,5-bis-trimethylstannyl-3-hexylthiophene

Preparation followed a similar literature procedure.32 To a 250 mL round bottom flask 3-hexylthiophene (5.00 g, 29.7 mmol) and tetramethylethylenediamine (TMEDA) (13.5 ml, 3.00 equiv) were added into 150 ml of anhydrous hexane in N₂ atmosphere. After cooled to −78 °C with acetone/dry ice bath, t-BuLi (52.4 ml, 3.00 equiv.) was
added dropwise to the solution. After stirred for 24 h under protection of nitrogen atmosphere, the reaction mixture was cooled back to −78 °C and then added 92.0 ml of trimethyldichlorosilane solution (3.00 equiv.) to react overnight. The reaction mixture was quenched by NaHCO₃ (1 M) in ice bath and then washed by H₂O and brine. The organic phase was dried over MgSO₄ and evaporated by vacuum. The residual liquid was purified by flash chromatography on triethylamine pre-treated silica gel (90:10 hexane/triethylamine as eluent) to yield product as viscous light-yellow liquid (12.7 g, 86.6 %).

1H NMR (300 MHz, CDCl₃), δ (ppm): 0.26-0.51 (m, 18H), 0.94 (J=6.6 Hz, t, 3H), 1.36 (br, 6H), 1.64 (J=6.6 Hz, quin., 2H), 2.70 (J=6.6 Hz, t, 2H), 7.23 (J=1.2 Hz, t, 1H).

13C NMR (75.5 MHz, CDCl₃), δ (ppm): −10.5, −10.4, −10.3, −10.2, −8.0, −7.8, −5.7, −5.6, −5.5, −5.4, 14.3, 22.8, 29.6, 31.9, 32.4, 32.5, 137.6, 137.7, 143.2, 152.1.

4) Polymerization of Poly[(dodecyl-3-thiophenecarboxylate-2,5-diyl)-alt-(3-hexylthiophene-2,5-diyl)] (Pc12):

Polymers were prepared according previously reported methods with modification. In dry box, dodecyl/ethyl 2, 5-dibromo-thiophene-3-carboxylate (0.908 g, 2.00 mmol), 2, 5-bis-trimethylstannyl-3-hexylthiophene (0.988 g, 2.00 mmol), cupper(I) bromide (0.0580 g, 0.400 mmol), anhydrous potassium fluoride (0.232 g, 4.00 mmol) tetrakis-(triphenylphosphine)palladium(0) (Pd(Ph₃)₄) (0.116 g, 0.100 mmol) were mixed together with 15 ml solvent comprising of anhydrous THF/DMF 1:1 in 30 mL heavy wall pressure tube. The tube was sealed with a Teflon screw cap equipped with a Viton O-ring then heated with stirring under 110 °C for 20 h. The reaction mixture was
extracted by chloroform and then concentrated to 5 ml. Crude product was precipitated twice in methanol and collected by centrifuge to yield dark red solid (0.490 g, 53.0 %).

\[ ^1H \text{NMR (300 MHz, CDCl}_3\text{): } \delta (\text{ppm}): 7.00-7.50 (m, 2H), 4.15-4.35 (d-br, 2H), 2.45-2.85 (d-br, 2H), 1.10-1.80 (m-br, 28H), 0.80-0.95 (d-br, 6H). \]

Scheme 2.1. The hydrolysis of Pc12-0 produces Pc12-y, which have varying percentages (y) of repeat units with ionizable carboxylic acid sidechains.

Pc12-y.

The reaction time was controlled with 3 h increment reaction time time from 3 h to 24 h. Pc12 and Pc12-16 NMR spectra were acquired using CDCl₃ as solvent, while the NMR spectra for other Pc12-y polymer were acquired in THF-d₈ due differences in solubility. All \(^1\)H NMR spectra were collected as 300 MHz. An inset of the spectra is provided in Figure 2.1.
<table>
<thead>
<tr>
<th>Time (h)</th>
<th>x (%)</th>
<th>y (%)</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>0</td>
<td>Pc12-0</td>
</tr>
<tr>
<td>3</td>
<td>84</td>
<td>16</td>
<td>Pc12-16</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>40</td>
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</tr>
<tr>
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</tr>
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<tr>
<td>48</td>
<td>0</td>
<td>100</td>
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</table>

**Table 2.1** Relationship between reaction time and the percent of carboxylic acid sidechains in the neutral form of the polymer. Variables x and y are as defined in Scheme 2.1.

**Figure 2.1.** Progressive changes in the relevant region of the $^1$H NMR spectra as Pc12-0 is hydrolyzed. Spectra for 0% and 16% hydrolysis were acquired in CDCl$_3$, whereas the other spectra were acquired in THF-$d_8$ because the solubility changes as the percentage of units hydrolyzed increases.
Results and Discussion

Design and Synthesis

We previously reported polythiophene derivative Pc12-0 and the facile base-catalyzed hydrolysis of its ester side chains to yield Pc12-100 (Scheme 2.1). In the current case it was desired to produce materials in which known fractions of the ester side chains have been hydrolyzed in order to study the tunability of properties with variable occupancy of polar/ionizable units along the backbone. The percentage of ester units that were hydrolyzed was controlled by varying the hydrolysis time (Table 2.1), and quantified by integration of $^1$H NMR spectra (Figure 2.1). This was a simple process for accessing ten polythiophene derivatives, Pc12-y, where y is the percentage of repeat units containing carboxylic acid units in the neutral form of the polymer. This method was used to successfully access ten polythiophene derivatives having 0-100% carboxylic acid side chains. These units can be conveniently deprotonated to yield anionic, carboxylate-derivatized polyelectrolytes. Each site that is not hydrolyzed remains as the dodecyl ester. The dodecyl substituents were chosen to provide an initially very hydrophobic polymer that, upon hydrolysis to the carboxylic acid, will become very hydrophilic. This feature was incorporated with the aim of accentuating the differences in properties across the series. The direct attachment of the carbonyl carbon to the polythiophene backbone was likewise anticipated to maximize the extent to which the backbone system is perturbed upon deprotonation of the carboxylic acid moieties.
**Photophysical properties of Pc12-y**

The Pc12-y derivatives have different steric and electronic environments depending on the extent to which ester sidechains are hydrolyzed. Furthermore, the carboxylic acid units can be deprotonated to yield carboxylate-derivatized polyanions. Deprotonation would be expected to cause significant changes to the system of the backbone as well as to the inter/intrachain interactions both in solution and in films. It was therefore of interest to quantify the photophysical effects of varying the percentage of carboxylic acid side chains and the changes induced by subsequent deprotonation of those units (data are summarized in Table 2.2). The UV-vis wavelength of maximum absorbance ($\lambda_{\text{max}}$) for neutral Pc12-y derivatives increases by a modest 15 nm as the number of carboxylic acid sidechains increases (Figure 2.2, circular data markers). As one would anticipate, the effect is greater for the anionic (deprotonated) form of the polymers (Figure 2.2, triangular data markers). In the anionic form, the $\lambda_{\text{max}}$ smoothly increased by 59 nm, from 414 to 463 nm as the incidence of anionic sites increases.

<table>
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<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$E_{\text{g,soln}}$ (eV)</th>
<th>$E_{\text{g,film}}$ (eV)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$I_{\text{rel}}$ (%)</th>
<th>$\lambda_{\text{Abs}}$ (nm)</th>
<th>$E_{\text{g,soln}}$ (eV)</th>
<th>$E_{\text{g,film}}$ (eV)</th>
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<td>562</td>
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<td>ND b</td>
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</table>

Table 2.2 Selected photophysical data for the Pc12-y series.
The wavelength of maximum photoluminescence ($\lambda_{em}$, Figure 2.3A) is insensitive to the percent of carboxylic acid side chains in the neutral form, with $\lambda_{em}$ of 562-565 nm, within instrument uncertainty, for all materials. In contrast, the $\lambda_{em}$ for the anionic form increases by 41 nm, from 562 to 603 nm, as the percentage of anionic side chains increases. This observation suggests that increased stabilization of the singlet excited state is possible via delocalization over an increasingly large electron-rich carboxylate system in the anionic polymer than it is in the neutral form (Figure 2.7). Spartan DFT calculations on a unit of the polymer in ground and excited state in neutral and anionic form.

The excited state stabilization accompanying longer-wavelength photoluminescence often correlates with diminished photoluminescent quantum efficiency because a longer lifetime provides more time for nonradiative decay pathways such as collisional quenching. Such a correlation is indeed observed in the current case: the integrated photoluminescence output of neutral Pc12-y derivatives is essentially insensitive to the percent of carboxylic acid side chains, while the output for anionic forms decreases as the number of carboxylate units (and $\lambda_{em}$) increases (Figure 2.3B).
Figure 2.2 Relationship between maximum absorbance wavelength and percentage of carboxylic acid units in Pcl2-y polymers (5×10⁻⁵ M in THF) in neutral (circles) and anionic (triangles) forms.
Figure 2.3. Relationship between $\lambda_{em}$ (A) or integrated photoluminescence intensity (B) versus percentage of carboxylic acid units in Pc12-y in neutral (circles) and deprotonated (triangles) forms (1×10^-5 $M$ in THF).

Figure 2.4. Optical bandgap as a function of percentage of carboxylic acid/carboxylate units in Pc12-y polymers (5×10^-5 $M$ in THF). The inset equation refers to the trendline (black line) for data recorded for the anionic form.
Figure 2.5. Optical bandgap of polymer thin films versus percentage of carboxylic acid units.

Figure 2.6. Comparison of solution and thin film data for all samples. Dotted lines are meant as guides to the eye and do not imply a linear trend in the data. (In A-C, data collected for deprotonated polymers are represented as triangle data markers, those for neutral polymers as circular data markers. Hollow data markers are for solution data and filled data markers are for thin film data.)
Optical bandgaps can also be estimated from the red edge of UV-vis spectra. Herein, we define the optical bandgap as the energy at which the red edge absorbance is 5% of that at the $\lambda_{\text{max}}$. The optical bandgap was determined in this way for solutions (Figure 2.4) and thin films (Figure 2.5) for Pc12-y derivatives in neutral and anionic forms. In both solid and solution, the optical bandgap is higher for the neutral than for the anion form of the polymers. This can again be attributed to the presence of an extension of the $\pi$ system and stabilization of the LUMO afforded by carboxylate units in the anionic form. In solution the optical bandgap of neutral materials is not strongly influenced by the percentage of carboxylic acid sidechains. In contrast, there is a linear decrease in optical bandgap from 2.50 to 2.05 eV as the percentage of anionic side chains increases in the deprotonated form. These data compare well with calculated HOMO/LUMO gaps of 3.7 eV for model ester, eV for model carboxylic acid and 3.4 eV
for model carboxylate (Figure 2.7). The data are more difficult to interpret in the solid state. At higher percentages of carboxylic acid/carboxylate side chains both neutral and anionic forms of the polymers appear to show a decrease in optical bandgap as the percentage of anionic side chains increases (Figure 2.6). At higher percentages of ester side chains, the optical bandgaps appear to begin to go back down, in contrast to the solution measurements. This observation suggests that aggregation and strong ion pairing have a more significant impact than does the inherent backbone composition in the solid state.

Solution Aggregation of Pc12-y

Photon Correlation Spectroscopy requires careful method selection according to sample requirements. Although multiple angle DLS and static light scattering may result in increased resolution, in this case, measurements at a single angle were found suitable.\textsuperscript{34} Although suitable for the study of consistently polydisperse materials, the method of cumulants may otherwise be bypassed.\textsuperscript{35} Unimodal calculations are more easily attained, but intensity calculations based on size distribution avoid underlying assumptions. The single mode concept was challenged by the appearance of aggregates under certain conditions in the current study.\textsuperscript{26} When so, bimodal results tend to skew towards larger sizes since intensity of scattering from spheres of radius $r$ varies with $r^6$.\textsuperscript{36,37} As seen here (Figure 2.8), larger variations in size for neutral over anionic Pc12-y polymers corresponded with an expectation of intra– and inter–molecular interactions (Figure 2.9). What was proposed by the model was supported by the following events: large
aggregates with the greatest standard deviations occurred for 16% acidic side chains, which resulted from solvent hydrogen bonding, and for 60 and 67% conversions which occurred from attractive interactions between chains. Toward the smaller side, neutral polymers demonstrated dramatic size decreases (Pc12-72 and Pc12-76 at 0.005M, and Pc12-67, 0.02M) as solvent was excluded. The anionic polymers were conspicuously immune to these influences. Additionally, the 60 and 67% hydrolyzed AFM films show uniquely larger features (Figure S2.22). Neutral polymers demonstrate dramatic size decreases (Pc12-72, 0.005M and Pc12-67, 0.02M) as solvent is excluded.

The hydrodynamic radius (RH) distribution of each sample based on Size Distribution Processor (SDP) analysis are listed in Table 2.3. The functional side chain density is increased with reaction time of hydrolysis from esters. In acidic condition (Figure 2.8-circles), the aggregation size of polymers with percentage of hydrolysis around is relatively small. For those polymers, the steric repulsion among bulky dodecyl side-chains attached on repeat units inhibits polymer chain to aggregate together. The steric effect induced by long pairs of carboxyl group has the opposite effect to form larger aggregates as well. The particle radius of aggregated polymers is increasing with higher degree of hydrolysis, which is due to less steric effect from dodecyl side chains and inter-and intramolecular hydrogen bonding.\(^{38}\) The residual bulky alkyl side chains and long pairs on carboxyl group, however, are still react as counteractive to compact polymer chains. Therefore, the loose and large aggregation is preferred to construct for polymer chains.\(^{39}\) For the polymer with highest percent of hydrolysis, steric repulsion generated by alkyl side chains is weakened obviously as well as more hydrogen bonding

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assists polymer chains to coil tight, hence aggregation has compacted structure and smaller radius.\textsuperscript{40}

<table>
<thead>
<tr>
<th>Polymer</th>
<th>0.005 M neutral</th>
<th>0.020 M neutral</th>
<th>0.005 M anionic</th>
<th>0.020 M anionic</th>
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<tr>
<td>Pc12-16</td>
<td>1364; 24</td>
<td>502; 9</td>
<td>333; 2</td>
<td>395; 5</td>
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<td>215; 2</td>
<td>232; 2</td>
<td>147; 1</td>
<td>172; 1</td>
</tr>
<tr>
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<td>340; 3</td>
<td>335; 3</td>
<td>505; 5</td>
<td>387; 3</td>
</tr>
<tr>
<td>Pc12-60</td>
<td>1754; 36</td>
<td>1118; 9</td>
<td>315; 4</td>
<td>237; 1</td>
</tr>
<tr>
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<td>1335; 13</td>
<td>290; 4</td>
<td>333; 3</td>
<td>283; 3</td>
</tr>
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<td>602; 5</td>
<td>249; 2</td>
<td>240; 2</td>
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<tr>
<td>Pc12-76</td>
<td>632; 6</td>
<td>382; 4</td>
<td>248; 2</td>
<td>182; 3</td>
</tr>
<tr>
<td>Pc12-81</td>
<td>406; 7</td>
<td>946; 11</td>
<td>81; 1</td>
<td>168; 1</td>
</tr>
</tbody>
</table>

Table 2.3. Mean particle size of Pc12-y (0.005 M and 0.02 M) in 4:1 THF/Et\textsubscript{2}O in neutral form and anionic form as determined by dynamic light scattering, by intensity-based calculation, at 20 °C.

Figure 2.8. Relationship between the percentage of carboxylate sidechains and aggregate particle size in solutions of Pc12-y (0.005 M in 4:1 THF/Et\textsubscript{2}O) in neutral (circles) and deprotonated (triangles) forms.
The particle size distribution at basic condition (Figure 2.8-triangle) is attributed to a different mechanism even though it has similar trend as in acidic condition. Polymers have smaller aggregations at two ends of lowest and highest percentage of hydrolysis while increasing size at intermediate percentage, around 50-60%. In the polymer bearing the fewest ionic repeat units the influence is the same status as in acidic condition, in which the steric hindrance was the primary cause for forming large aggregates. With increasing anionic side chains, more ion-dipole interaction was strengthened and then maximized around 50% of carboxylate anions to polar ester side chains.39, 40

More dilute solutions produce larger particles, suggesting better solvation. The polymer chains could attract each other to build large particles via this effect. The size of aggregation in higher hydrolysis percent was diminished because intermolecular force was dominated by Coulombic repulsion between anionic sidechains. For particles with acid side chains and increasing functional side-chain density, DLS shows an initial decrease in size from increasing intramolecular H-bonding, followed by interchain H-bonding, in which increases size, and size collapse near 80%.27 For particles with increasing density of carboxylate chain, DLS shows an initial decrease in size from increasing intramolecular ion/dipole interaction, followed by growth from interchain ion/dipole aggregation, and size collapse near 80% due to charge repulsion.
Figure 2.9. Schematic representation of how interchain, intrachain and polymer-solvent interactions may vary as a function of % COOH in the backbone in neutral (A) and deprotonated (B) forms.

*Layer-by-layer assembly of Pc12-y and LX5.*
In prior work on the LbL assembly of anionic polythiophene derivatives with cationic polyelectrolytes, the anion-anion distance \( (d_{aa}) \) was found to play a significant role in the efficiency with which the two components form intrinsic binding pairs. The Smith group’s study of LbL assembly of LXs with Pc12-100 revealed that using LX5 as the cationic component led to films that exhibit a high absorbance per bilayer, which is desirable for improving the accuracy of film growth monitoring by UV-vis spectroscopy. Prior work has also demonstrated that the greater flexibility of the \((\text{CH}_2)_5\) backbone component of LX5 also facilitates access to conformations necessary for intrinsic charge-pairing (as summarized in Chart 2.2). LX5 was therefore selected as the cationic component for LbL film formation with the anionic form of Pc12-y.

The absorbance of the LbL film of Pc12-y with LX5 increases as the incidence of ionic units increase to 60% (Table 2.4). By comparing the \( \lambda_{\text{max}} \) of anionic Pc12-y (Table 2.2) and of LbL films (Table 2.4), the \( \lambda_{\text{max}} \) of the LbL films tend to be bathochromically shifted. This shift is due to the ion-ion interaction between LX and Pc12-y in LbL films, which stabilizes the \( \pi^* \) of Pc12-y. This effect is strengthened at higher percentages of anionic sites (Table 2.4).

Deposited layers are anchored by the electrostatic force of oppositely-charged sites of polyelectrolytes (intrinsic compensations). Ideally, each layer is deposited stoichiometric quantities of counterionic polyelectrolytes to coated film1. The amount of material deposited is influence by goodness of ion-ion distance \( (d_{aa} \text{ and } d_{cc}) \) matches as well as effective charge of polyelectrolytes. For Pc12-16 and -40, the negative charge of their chains is insufficient to adhere enough amount to cationic polymer via intrinsic
compensation. Therefore, less anionic chromophoric polyelectrolytes are deposited to construct films (Table 4), and extrinsic compensations from Na+ and Br- are required to stabilize film. With increasing of percent of hydrolysis from Pc12-48, the trend of absorbance tends to be a plateau after Pc12-67 in the range of 0.122-0.147, suggesting similar scarcity of intrinsic sites. For Pc12-y, aggregated polyelectrolytes can be attached to coated cationic surface by electrostatic interaction between opposite charge sites, and also the interaction among anionic polyelectrolytes, which accumulates more chromophoric anionic polymers (Figure 2.10A).

<table>
<thead>
<tr>
<th>% ionic Side Chains</th>
<th>Films</th>
<th>Absorbance (at $\lambda_{\text{max}}$)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>Pc12-16/LX5</td>
<td>0.016</td>
<td>427</td>
</tr>
<tr>
<td>40</td>
<td>Pc12-40/LX5</td>
<td>0.034</td>
<td>454</td>
</tr>
<tr>
<td>48</td>
<td>Pc12-48/LX5</td>
<td>0.087</td>
<td>451</td>
</tr>
<tr>
<td>60</td>
<td>Pc12-60/LX5</td>
<td>0.217</td>
<td>450</td>
</tr>
<tr>
<td>67</td>
<td>Pc12-67/LX5</td>
<td>0.192</td>
<td>450</td>
</tr>
<tr>
<td>72</td>
<td>Pc12-72/LX5</td>
<td>0.124</td>
<td>464</td>
</tr>
<tr>
<td>76</td>
<td>Pc12-76/LX5</td>
<td>0.122</td>
<td>461</td>
</tr>
<tr>
<td>81</td>
<td>Pc12-81/LX5</td>
<td>0.143</td>
<td>490</td>
</tr>
<tr>
<td>100</td>
<td>Pc12-100/LX5</td>
<td>0.147</td>
<td>462</td>
</tr>
</tbody>
</table>

Table 2.4. Absorbance and maximum absorbance wavelength for films comprised by 40 bilayers of Pc12-y and LX5
Figure 2.10. A) Relationship between the percentage of carboxylate sidechains and the absorbance (A) and $\lambda_{\text{max}}$ (B) of 40 bilayer-thick films made by LbL assembly of Pc12-$y$ (deprotonated form) with LX5
Conclusions

As a summary, the percentage of ionic side-chains present in polythiophene has an interesting effect on photophysical properties, aggregation particle size and LbL film assembly. Deprotonation of carboxylic units in polythiophene lead to a larger difference in photophysical properties and aggregation particle size compared to the original form. It was demonstrated that variation in the average anion-anion distance ($d_{cc}$) while keeping cation-cation distance ($d_{aa}$) constant has a great effect on the absorbance and $\lambda_{\text{max}}$ during LbL supramolecular assembly.

The properties of ionic polythiophene are strongly depend on ratio of charged side chains and testing conditions (such as pH), including photophysics, aggregation and electrostatic deposition.

In UV-vis and FL spectra, the \textbf{Pc12-100} has most obvious varying between acidic and basic condition for $\lambda_{\text{abs}}$ and $\lambda_{\text{em}}$ respectively. Increasing of carboxylate moieties leads to tremendous red shift of absorption (414 nm to 463 nm) and emission (562 nm to 603 nm) in basic condition, while only a little variation observed in acidic condition ($\Delta\lambda_{\text{abs}}=15$ nm and $\Delta\lambda_{\text{em}}=2$ nm). This observation approves the polyelectrolytes bearing thiophenyl carboxylate segments having potential application in tunable sensor. For aggregation of weak polyelectrolytes in solution phase, the pH and percent of ionisable side chain have complicated influence on the behavior of aggregating. The effectiveness of hydrogen bonding and dipole force can be modulated by tuning pH and degree of ionization.
These significant changes in photophysical behavior, band gap, aggregation and interaction with other macromolecules depending on the number of anionic sites present on the polymer sidechains should also serve as a cautionary note to those who work with potentially pH-sensitive materials. If conditions are not carefully selected, one may be measuring properties of a molecule that is in a different form than what is assumed, making it difficult to reproduce or appropriately interpret findings.

ATTRIBUTION OF WORK

My contribution to the work in this chapter consisted of synthesis, NMR, UV-vis absorption, fluorescence, DSC measurement, calculation. The other coworkers who are coauthors on the published portion of this chapter contributed to remaining areas of the study.
Reference


Figure S2.1 Proton NMR spectrum of DBTAC ((CD$_3$)$_2$CO, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.2 Carbon NMR spectrum of DBTAC ([CD$_3$)$_2$CO, 75.5 MHz]. Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.3 Proton NMR spectrum of C12 (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.4 Carbon NMR spectrum of C12 (CDCl3, 75.5 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.5 Proton NMR spectrum of 2,5-bis-trimethylstannyl-3-hexylthiophene (CDCl$_3$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.6 Carbon NMR spectrum of 2,5-bis-trimethylstannyl-3-hexylthiophene (CDCl₃, 75.5 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.7 Proton NMR spectrum of Pc12 (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.8 Proton NMR spectrum of Pc12-100 (THF-$d_8$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.9 Proton NMR spectrum of Pc12-16 (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.10 Proton NMR spectrum of Pc12-40 (THF-\textit{d}$_8$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.11 Proton NMR spectrum of Pc12-48 (THF-$d_8$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.12 Proton NMR spectrum of Pc12-60 (THF-$d_8$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
**Figure S2.13** Proton NMR spectrum of Pc12-67 (THF-\(d_8\), 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.14 Proton NMR spectrum of Pc12-72 (THF-\textit{d}_8, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.15 Proton NMR spectrum of Pc12-76 (THF-$d_8$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.16 Proton NMR spectrum of Pc12-81 (THF-$d_8$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S2.17 UV-vis spectra of Pc12-y in protonated form (5 × 10^{-5} M in THF) normalized to Abs_{max} = 1 for each spectrum.
Figure S2.18 UV-Vis spectra of Pc12-y in deprotonated form (5 × 10^{-5} M in THF) normalized to $\text{Abs}_{\text{max}} = 1$ for each spectrum.
Figure S2.19 Normalized FL spectra of Pc12-y excited at maximum absorbance wavelength ($\lambda_{a,a}$ in Table 2.1) in acidic THF solution at $1\times10^{-5}$ M demonstrating the insensitivity of fluorescence emission to the percentage of carboxylic acid sidechains in the neutral form of the polymer.
Figure S2.20 Normalized Photoluminescent spectra for deprotonated Pc12-y excited at maximum absorbance wavelength ($\lambda_{a,b}$ in Table 2.1) in THF solution at 1×10^{-5} M.
Figure S2.21 Photoluminescent spectra (normalized to $\lambda_{em,a}$ of Pc12-y = 1) of Pc12-y excited at maximum absorbance wavelength ($\lambda_{a,b}$ in Table 2.1) in basic THF solution at $1\times10^{-5}$ M.
Figure S2.22  5×5 µm AFM 2D-height (left column) and 3D (right column) images of Pc12-y hydrolyzed polyelectrolytes layered with LX5 processed by AIST software: Pc12-100/LX5 (A), Pc12-81/LX5 (B), Pc12-76/LX5 (C), Pc12-72/LX5 (D), Pc12-67/LX5 (E), Pc12-60/LX5 (F), Pc12-48/LX5 (G), Pc12-40/LX5 (H), Pc12-16/LX5 (I) and blank glass slide (J).
CHAPTER THREE
CONVENIENT ROUTE TO TETRAARYLPHOSPHONIUM POLYELECTROLYTES
VIA METAL-CATALYSED P–C COUPLING POLYMERISATION OF ARYL DIHALIDES AND DIPHENYLPHOSPHINE

Introduction

Polyelectrolytes and polyelectrolyte complexes have attracted widespread recent interest as potentially sustainable and green-processable/recyclable materials. Phosphonium polyelectrolytes specifically have also been explored for delivery of material to cells and as ion-transporting membrane component of alkaline exchange fuel cells. 1-7 Compared to alkylphosphonium polyelectrolytes, tetraarylphosphonium units ([PAr$_4$]$^+$) can be significantly more chemically stable, particularly to hydrolysis or nucleophilic attack.8-19 Furthermore, [PAr$_4$]$^+$ salts are the most thermally stable ionic liquids known,20 making these units excellent candidates for incorporation into polymers for high temperature applications.

The potential for TPELs to exhibit combined thermal and chemical stability led us to pursue simple transition metal-catalysed P–C bond-forming routes to tetraarylphosphonium polyelectrolytes (TPELs). In 2015, we reported the first such route$^{21}$ based on established small molecule chemistry.$^{15,16}$ Although this route to TPELs was successful, it requires the use of a bis(triarylphosphine) monomer (Scheme 3.1A). Such monomers generally require expensive organometallic reagents and time-consuming methodologies for their preparation, and there are few that are commercially available. Consequently, it is not practically feasible to rapidly and affordably prepare a
wide range of TPELs by this method. In our search for a more facile and affordable route to TPELs, we were inspired by a straightforward P–C coupling route to poly(triarylphosphine)s reported by Lucht in *This Journal* (Scheme 3.1B). This route exploits commercial aryl- or alkylphosphines and commercial aryl dihalides as coupling partners to yield polyphosphine analogues of polyaniline. We conceived of an analogous route to TPELs starting with commercial aryl dihalides and HPPH₂ (Scheme 3.1C).

In a 1980 report, Cristau et al. reported that HPPH₂ could be converted to tetraarylphosphonium salts in ~70% yield by NiBr₂-catalyzed coupling with o-, m- or p-tolylbromide (Scheme 3.1D). In order to extend this coupling methodology to a polymerization route capable of reasonable degrees of polymerization, however, the yield had to be significantly improved. The presumed stepwise pathway (Scheme 3.2) requires deprotonation of the [HPAr₃]+ resulting from the initial P–C bond-forming step prior to the second P–C bond-forming step, so we hypothesized that addition of a base might improve the reaction yield. As anticipated, simple addition of one equiv of diisopropylamine led to quantitative yields of the target [PAr₄]⁺ salts under the reported conditions. We also found that, in addition to the NiBr₂ catalyst used in the previous report, Pd₂(dba)₃ (dba = dibenzylideneacetone) was also an effective catalyst for the transformation shown in Scheme 3.1D. Having established appropriate conditions for high yield coupling, polymerization of HPPH₂ with several commercial dihalides was undertaken (Scheme 3.3) and properties of resultant polymers are summarized in Table 3.1.
Scheme 3.1. Established P–C coupling route to TPELs (A), and polyphosphines (B). The proposed new route to TPELs (C) employs chemistry similar to a little-explored synthesis (D) of small molecule [PAr₄]⁺ salts from HPPh₂.

**Experimental**

*General Considerations*

All air-sensitive reactions were performed in an MBraun UNILab glovebox under nitrogen. Anhydrous solvents were dried and degassed using an MBraun solvent purifier. Chemicals were used without further purification after purchased. All the NMR spectra were collected on a Joel ECX-300 MHz spectrometer operating at 300, 282 and 121 MHz.
for $^1$H, $^{19}$F and $^{31}$P, respectively. Thermogravimetric analysis (TGA) was performed on TA Instruments SDT Q600 from 25 °C to 800 °C with a heating rate of 20 °C min$^{-1}$. UV-Vis absorption spectra were acquired on a Cary 50 spectrophotometer. All NMR spectra were collected in CDCl$_3$. To assure that the $^{31}$P nuclei were fully relaxed between scans and thus provide accurate integrations, the spectra with 2 s, 4 s, 8 s and 10 s delay were compared. Integration of resonances in spectra collected with a 10 s delay are identical to those collected with an 8 s delay. As a result, $^{31}$P NMR spectra provided here were collected with a 10 s relaxation delay. To assure the accuracy of the chemical shift values, PPh$_3$ was added as an internal standard. The chemical shift of internal standard PPh$_3$ was set to $-4.7$ ppm.$^1$

*Calculation of degree of polymerization ($X_n$) and number average molecular weight ($M_n$)*

The method described here is similar to that which has been used in prior work.$^{2-4}$ In each $^{31}$P-NMR spectrum, the peak of phosphine oxide was identified at $\sim30.00$ ppm and the integrated area each of these peaks was normalized to 1.00 in the spectra provided in the supporting information. If the integration for the phosphonium unit is $x$, the degree of polymerization (the value of $n$ in the diagram below) is $x$ (because each polymer chain has on average one phosphine-oxide end group). The $M_n$ is then calculated by using this value of $n$ and the molecular weight of each repeat unit.

For **P3•Br** prepared by using Pd$_2$(dba)$_3$ as catalyst, 1.05 equivalents of diphenylphosphine was used to ensure conversion of -Br terminal groups into triarylphoshine and then phosphine oxide. Each polymer chain terminates in two
phosphine oxide groups. To determine the number average molecular weight in this case, integration of the signal attributable to the phosphine oxide moieties is normalized to 1.00. The degree of polymerization is then twice the integration of the resonance attributable to the main chain phosphonium moieties. The $M_n$ is then calculated by using the value of $2n$ and the molecular weight of each repeat unit.

\[
\text{NiBr}_2 \quad \text{Br}^- 
\]

*Nickel (II)-catalyzed synthesis of poly(phosphonium bromide)s*

**P1•Br**

Samples of 9,9-dioctyl-2,7-dibromofluorene (1.47 g, 2.69 mmol), diphenylphosphine (0.500 g, 2.69 mmol) and diisopropylamine (0.274 g, 2.69 mmol) were placed together in a 15 mL heavy-wall pressure tube under a nitrogen atmosphere. NiBr$_2$ (0.0600 g, 0.270 mmol) and 6 mL anhydrous ethylene glycol were then added, and the tube was sealed with a Teflon screw cap equipped with a Viton O-ring. The sealed tube was heated at 180 °C with stirring for 24 h. After cooling down to room temperature, the reaction vessel was opened to air and 50 mL dichloromethane (DCM) was added. The mixture and then washed with 1 M NaBr (50 mL×2). The organic layer
was dried over anhydrous MgSO₄ and concentrated to 10 mL by vacuum evaporation. The crude solution was added into 200 mL diethyl ether dropwise with stirring to yield a cloudy suspension. The solid was separated by vacuum filtration, and then dried in a vacuum oven overnight at 60 °C to give the desired product (1.36 g, 77.2%). ¹H NMR (300 MHz, CDCl₃) δ: 8.35-7.28 (br m, 16H), 2.53-0.32 (br m, 34H); ³¹P NMR (121 MHz, CDCl₃) δ: 30.39 (end groups), 26.13-23.01 (backbone phosphonium moieties). anal. calcd for repeat unit C₄₁H₅₀BrP•(H₂O) (ignoring end groups): C, 73.31; H, 7.80; found: C, 74.13; H, 7.89%

**P2•Br**

The synthetic procedure was the same as that used to prepare **P1•Br**, but using monomers as bis(4-bromophenyl) ether (0.882 g, 2.69 mmol) and diphenylphosphine (0.500 g, 2.69 mmol). The desired product was isolated as white powder (0.813 g, 61.1%). ¹H NMR (300 MHz, CDCl₃) δ: 7.98-6.86 (br m, 18H); ³¹P NMR (121 MHz, CDCl₃) δ: 29.51 (end groups), 24.78-20.87 (backbone phosphonium moieties). anal. calcd for repeat unit•(H₂O) formula C₂₄H₂₀BrO₂P (ignoring end groups): C, 63.87; H, 4.47; found: C, 62.10; H, 4.53%

*Palladium (0)-catalyzed synthesis of poly(phosphonium bromide)s*

**P1•Br**

The synthetic procedure was the same as NiBr₂ catalyzed **P1•Br**, but using Pd₂(dba)₃ (0.0270 mmol, 0.0280 g) as catalyst and reacting at 145 °C. The desired
product was obtained as light yellow powder (1.28 g, 66.6%). 1H NMR (300 MHz, CDCl3) δ: 8.07-7.38 (br m, 16H), 1.99-1.78 (br s, 4H), 1.29-0.36 (be m, 30H); 31P NMR (121 MHz, CDCl3) δ: 30.44 (end groups), 26.16-22.94 (backbone phosphonium moieties). anal. calcd for repeat unit•(H2O) formula C41H52BrPO (ignoring end groups): C, 73.31; H, 7.80; found: C, 73.20; H, 7.85%

P2•Br

The synthetic procedure was the same as NiBr2 catalyzed P2•Br, but using Pd2(dba)3 (0.0270 mmol, 0.0280 g) as catalyst and reacting under 145 °C. The desired product was obtained as yellowish white powder (0.822 g, 67.8%). 1H NMR (300 MHz, CDCl3) δ: 7.94-6.96 (br m, 18H), 31P NMR (121 MHz, CDCl3) δ: 29.29 (end groups), 24.51-20.72 (backbone phosphonium moieties). anal. calcd for repeat unit•H2O C24H20BrO2P (ignoring end groups): C, 63.87; H, 4.47; found: C, 62.75; H, 4.53%

P3•Br

The synthetic procedure was the same as Pd2(dba)3 catalyzed P1•Br, but using monomers as 3, 6-dibromo-9-phenyl-9H-carbazole (1.25 mmol, 0.500 g), diphenylphosphine (1.31 mmol, 0.244 g). Pd2(dba)3 (0.0130 mmol, 0.0120 g) as catalyst and reacting at 145 °C for 4 h. The desired product was obtained as light grey powder (0.468 g, 71.4%). 1H NMR (300 MHz, CDCl3) δ: 8.84-7.31 (br m, 21H); 31P NMR (121 MHz, CDCl3) δ: 30.88 (end groups), 27.02-23.89 (backbone phosphonium moieties).
Anal. calcd for monomer\((\text{H}_2\text{O})\) formula $\text{C}_{30}\text{H}_{23}\text{BrNOP} \text{(ignoring end groups)}$: C, 68.71; H, 4.42; N, 2.67; found: C, 68.81; H, 4.37; N, 2.75%

Anion exchange to prepare bis(trifluoromethane)sulfonimide salts

The bis(trifluoromethane)sulfonimide $[\text{NTf}_2]^-$ salts of the TPELs were prepared from the bromide salts (from NiBr$_2$-catalyzed routes for $\text{P1•Br}$ and $\text{P2•Br}$) via the procedures below. The degrees of polymerization reported for the bis(trifluoromethane)sulfonamide salts are slightly higher than those of the parent bromide salts in each case, presumably due to removal of some low molecular weight fractions in the rinsing of the bis(trifluoromethane)sulfonamide salts. The percentage of bromide anions that have been successfully exchanged by bis(trifluoromethane) sulfonimide anions was determined via C, H, N elemental microanalysis.

$\text{P1•[NTf}_2^-$

A sample of $\text{P1•Br}$ (0.100 g, 0.150 mmol) was dissolved in 50 mL H$_2$O/MeOH (1:1), and then added 10 mL bis(trifluoromethyl)sulfonimide lithium (0.100 g, 0.350 mmol) H$_2$O solution with stirring to form cloudy precipitation. The solid was separated by centrifugation. The supernatant liquid was removed by decantation and the sediment collected. The sediment was suspended in deionized water and collected by filtration two additional times, and the filtrand was dried in a vacuum oven at 100 °C for 24 h to obtain the anion-exchanged compound (0.131 g, 100%). The percentage of bromide counterions that had been replaced by ditriflamide was found to be 85.4% by elemental combustion microanalysis. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 8.43-7.29 (br m, 16H), 2.13-0.39 (br m,
$^{19}$F NMR (282 MHz) $\delta$: -78.57 (-CF$_3$); $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$: 29.48 (end groups), 26.58-23.34 (backbone phosphonium moieties). anal. calcd for monomer formula C$_{43}$H$_{50}$F$_6$NO$_4$PS$_2$ (ignoring end groups): C, 60.48; H, 5.90; N, 1.64; found: C, 62.26; H, 6.19; N, 1.45%.

**P2•[NTf$_2$]**

The procedure was the same as that used to prepare **P1•[NTf$_2$]** (0.117 g, 80.1%), but starting with **P2•Br** (0.100 g, 0.230 mmol). The percentage of bromide counterions that had been replaced by ditriflamide was found to be 82.0% by elemental combustion microanalysis. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.94-6.89 (br m, 18H); $^{19}$F NMR (282 MHz) $\delta$: -78.65 (-CF$_3$); $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$: 31.06 (end groups), 27.51-23.51 (backbone phosphonium moieties). anal. calcd for monomer formula C$_{26}$H$_{18}$F$_6$NO$_5$PS$_2$ (ignoring end groups): C, 49.29; H, 2.86; N, 2.21; found: C, 49.98; H, 2.97; N, 1.92%

**P3•[NTf$_2$]**

The procedure was the same as that used to prepare **P1•[NTf$_2$]** (0.102 g, 73.3%), but starting with **P3•Br** (0.100 g, 0.197 mmol). The percentage of bromide counterions that had been replaced by ditriflamide was found to be 98.5% by elemental combustion microanalysis. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 8.39-7.30 (br m, 21H); $^{19}$F NMR (282 MHz) $\delta$: -78.78 (-CF$_3$); $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$: 30.96 (end groups), 27.50-24.5 (backbone phosphonium moieties). anal. calcd for monomer formula C$_{32}$H$_{21}$F$_6$N$_2$O$_4$PS$_2$ (ignoring end groups): C, 54.39; H, 3.00; N, 3.96; found: C, 56.15; H, 3.11; N, 3.95%
Stability test under basic condition

To a 50 mL round bottom flask, 20.0 mg of the polymer dissolved in 1 mL dichloromethane was slowly evaporated so that the polymer thin film was coated homogeneously on the lower part of the inner wall of the flask. The polymer film was soaking in 25 mL of 1 M NaOH solution for 24 h. The remaining solid was collected and then dissolved in CDCl₃ to collect phosphorus-31 NMR spectra. Two more sets of experiments were conducted with the same protocol by using 1 M NaOH at 65 °C and 6 M NaOH at 65 °C, cooled to room temperature prior to collection of solids.

Results and Discussion

The NiBr₂-catalyzed polymerization reactions were carried out at 180 °C, while Pd₂(dba)₃-catalyzed (dba = dibenzylideneacetone) reactions were carried out at 145 °C, for 24 h. For P1, both aryl bromide and aryl iodide coupling partners were evaluated because aryl iodides generally give higher degrees of polymerization via C–C coupling reactions. At the elevated temperature employed for NiBr₂-catalyzed reactions, however, the aryl iodides screened underwent significant decomposition and were not useful coupling partners under these conditions.

The degrees of polymerization ($X_n$) and number average molecular weights ($M_n$) for polymers produced from aryl dibromides determined by analyzing the number of phosphine oxide end groups via NMR spectrometry, as summarized in Table 1. As with C–C coupling polymerizations, the degrees of polymerization ($X_n$) obtainable from
Pd$_2$(dba)$_3$-catalyzed P–C coupling polymerization reactions were notably higher than those obtained by the NiBr$_2$-catalyzed route (Table 3.1) These $X_n$ values are also notably higher than corresponding values for reported alkylphosphonium ionomers prepared via nucleophilic substitution-driven condensation polymerization of diphosphines with alkyl or benzyl bromides ($X_n$ generally $\leq 20$).

Scheme 3.2. Pathway to formation of [Ar$_2$PPh$_2$]$^+$ salts from HPPh$_2$.

Scheme 3.3. Synthesis of TPELs.
UV-vis absorption data (Table 3.1) confirm earlier indications that there is little or no-conjugation through the phosphonium moieties along the polymer backbone, as the absorption spectra are similar to those of the monomers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Catalyst</th>
<th>$M_n$ (kDa)</th>
<th>$X_n$</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$T_d$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1•Br</td>
<td>NiBr$_2$</td>
<td>11.1</td>
<td>17</td>
<td>331</td>
<td>344</td>
</tr>
<tr>
<td></td>
<td>Pd$_2$(dba)$_3$</td>
<td>15.0</td>
<td>23$^h$</td>
<td>332</td>
<td>328</td>
</tr>
<tr>
<td>P2•Br</td>
<td>NiBr$_2$</td>
<td>6.7</td>
<td>16</td>
<td>267</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>Pd$_2$(dba)$_3$</td>
<td>12.5</td>
<td>30</td>
<td>268</td>
<td>371</td>
</tr>
<tr>
<td>P3•Br</td>
<td>Pd$_2$(dba)$_3$</td>
<td>13.2</td>
<td>26</td>
<td>288</td>
<td>400</td>
</tr>
<tr>
<td>P1•NTf$_2$</td>
<td>NA$^e$</td>
<td>14.5</td>
<td>17</td>
<td>331</td>
<td>403</td>
</tr>
<tr>
<td>P2•NTf$_2$</td>
<td>NA$^e$</td>
<td>10.8</td>
<td>17</td>
<td>267</td>
<td>440</td>
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<tr>
<td>P3•NTf$_2$</td>
<td>NA$^e$</td>
<td>19.1</td>
<td>27</td>
<td>288</td>
<td>447</td>
</tr>
</tbody>
</table>

Table 3.1. Properties of TPELs

$^a$number average molecular weight determined by NMR end group analysis;  
$^b$degree of polymerization;  
$^c$wavelength of maximum absorption for the band attributable to the $\pi$-$\pi^*$ transition in the UV-vis spectrum in CH$_2$Cl$_2$.  
$^d$defined as the temperature at which 5% mass loss occurs under nitrogen as determined by thermogravimetric analysis.  
$^e$prepared via anion exchange with the corresponding poly(phosphonium bromide) made via NiBr$_2$ catalysis.  
$^h$average of two runs

The thermal stability of [PAR$_4$]$^+$ units was one of the motivating factors for incorporating them into TPELs, so thermogravimetric analysis was employed to determine the decomposition temperatures ($T_d$, Table 3.1) of P1-3. The bromide salts have reasonably good thermal stability ($T_d = 327-371$ °C) and decompose via thermal loss of HBr. Small molecular [PAR$_4$]$^+$ ditriflamide ([NTf$_2$]$^-$, Tf = –SO$_2$CF$_3$) salts have significantly better thermal stability compared to their halide analogues,$^{15}$ so P1-3•NTf$_2$ analogues were prepared by anion exchange in an effort to increase their thermal...
stability. Elemental microanalysis of the $\text{P1-3•NTf}_2$ indicated that $\geq 86.9\%$ of bromide counteranions had been replaced with $[\text{NTf}_2^-]$ counteranions in these materials. The thermal stabilities of $\text{P1-3•NTf}_2$ was improved as anticipated, with $T_d$ values of $>400\, ^\circ\text{C}$ for all of the materials.

Chart 3.1. Structure of $\text{FLoct}$, prepared via the method in Scheme 3.1A.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$[\text{NaOH}]$</th>
<th>$T, (°\text{C})$</th>
<th>$%$ decomp. ($\pm 5%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{P1•NTf}_2$</td>
<td>$1, M$</td>
<td>$20$</td>
<td>$0$</td>
</tr>
<tr>
<td></td>
<td>$1, M$</td>
<td>$65$</td>
<td>$7$</td>
</tr>
<tr>
<td></td>
<td>$6, M$</td>
<td>$65$</td>
<td>$26$</td>
</tr>
<tr>
<td>$\text{P2•NTf}_2$</td>
<td>$1, M$</td>
<td>$20$</td>
<td>$0$</td>
</tr>
<tr>
<td></td>
<td>$1, M$</td>
<td>$65$</td>
<td>$7$</td>
</tr>
<tr>
<td></td>
<td>$6, M$</td>
<td>$65$</td>
<td>$7$</td>
</tr>
<tr>
<td>$\text{P3•NTf}_2$</td>
<td>$1, M$</td>
<td>$20$</td>
<td>$0$</td>
</tr>
<tr>
<td></td>
<td>$1, M$</td>
<td>$65$</td>
<td>$0$</td>
</tr>
<tr>
<td></td>
<td>$6, M$</td>
<td>$65$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\text{FLoct}$</td>
<td>$6, M$</td>
<td>$60$</td>
<td>$100$</td>
</tr>
</tbody>
</table>

Table 3.2. Stability of TPEL films upon exposure to aqueous alkaline solutions for 24 h

Chemical stability, particularly to alkaline conditions and nucleophilic attack, is another potentially useful property of TPELs. A film of each polymer $\text{P1-3•[NTf}_2]$ was thus submerged in $\text{NaOH(aq)}$ for 24 h at room temperature or $65\, ^\circ\text{C}$. After exposure, each film was redissolved in $\text{CDCl}_3$ and analysed by NMR spectrometry to determine the percentage of phosphonium units that had decomposed (Table 3.2). It was observed that
**Floct** (Chart 3.1, $X^- = Br^-$ or $\text{[NTf}_2^-\text{]}$) undergoes complete decomposition via nucleophilic aromatic substitution ($S_{\text{NAr}}$) reaction upon heating to 60 °C in 6 $M$ NaOH ($aq$) for 24 h. The presence of electron donors, such as those present in P2 and P3, should slow down the $S_{\text{NAr}}$ reaction and afford greater stability; this was one of the primary motivations for selection of these targets. Films of P1-3•NTf$_2$ treated at room temperature do not undergo any detectable decomposition. The percentage of decomposition at 65 °C with 6 $M$ NaOH($aq$) is inversely related to the electron donating capacity of the substituent para- to the phosphonium site (Table 3.2). Notably, P3•NTf$_2$ undergoes very little if any decomposition under these conditions, making it the most chemically and thermally robust of the TPELs prepared.

**Conclusions**

A transition metal-catalysed P–C bond forming reaction was modified to allow the convenient preparation of tetraarylphosphonium polyelectrolytes (TPELs) from commercial aryl dihalides and diphenylphosphine. Both nickel and palladium catalysts are effective in C–P coupling reactions to yield polymers with degrees of polymerization up to about 30. Anion exchange of initial polymeric bromide salts allows ready access to ditriflamide salts having thermal stability of up to 460 °C. One TPEL prepared via this methodology is stable to heating at 65 °C in 6 $M$ NaOH($aq$) for at least 24 h, whereas alkylphosphonium polymers and even previously-reported TPELs undergo complete depolymerisation under these conditions. The improved stability suggests that P3•NTf$_2$ and similar TPELs may hold promise for use in alkaline fuel cell applications. The
synthetic protocol described herein promises to facilitate rapid access to a wide variety of thermally/chemically stability materials for a variety of applications

ATTRIBUTION OF WORK

My contribution to the work in this chapter consisted of: synthesis, NMR, UV-vis absorption, thermal stability, alkaline stability. The other coworkers who are coauthors on the published portion of this chapter contributed to remaining areas of the study.
References


12. G. W. Fenton and C. K. Ingold, *Journal of the Chemical Society* 1929, **2342-2357**.


**Figure S3.1** Proton NMR spectrum of compound P1-Br prepared by using NiBr₂ catalyst (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S3.2 Proton NMR spectrum of compound P2·Br prepared by using NiBr₂ catalyst (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S3.3 Proton NMR spectrum of compound P1•Br prepared by using Pd$_2$(dba)$_3$ catalyst (CDCl$_3$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S3.4 Proton NMR spectrum of compound P2•Br prepared by using Pd$_2$(dba)$_3$ catalyst (CDCl$_3$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S3.5 Proton NMR spectrum of compound **P3•Br** prepared by using Pd$_2$(dba)$_3$ catalyst (CDCl$_3$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S3.6 Proton NMR spectrum of compound P1•NTf₂ (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
**Figure S3.7** Proton NMR spectrum of compound P2•NTf₂ (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
**Figure S3.8** Proton NMR spectrum of compound P3•NTf₂ (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S3.9 Phosphorus-31 NMR spectrum of compound P1•Br prepared by using NiBr₂ catalyst (CDCl₃, 121 MHz). PPh₃ was used as an external standard and its chemical shift was normalized to –4.70 ppm.
Figure S3.10 Phosphorus-31 NMR spectrum of compound $\text{P}_2\text{Br}$ prepared by using NiBr$_2$ catalyst (CDCl$_3$, 121 MHz). PPh$_3$ was used as an external standard and its chemical shift was normalized to $-4.70$ ppm.
Figure S3.11 Phosphorus-31 NMR spectrum of compound $\textbf{P1} \cdot \text{Br}$ prepared by using $\text{Pd}_2(\text{dba})_3$ catalyst ($\text{CDCl}_3$, 121 MHz). $\text{PPh}_3$ was used as an external standard and its chemical shift was normalized to −4.70 ppm.
Figure S3.12 Phosphorus-31 NMR spectrum of compound P2•Br prepared by using Pd$_2$(dba)$_3$ catalyst (CDCl$_3$, 121 MHz). PPh$_3$ was used as an external standard and its chemical shift was normalized to −4.70 ppm.
Figure S3.13 Phosphorus-31 NMR spectrum of compound P3•Br prepared by using Pd$_2$(dba)$_3$ catalyst with a reaction time of 4 hours (CDCl$_3$, 121 MHz). PPh$_3$ was used as an external standard and its chemical shift was normalized to $-4.70$ ppm.
Figure S3.14 Phosphorus-31 NMR spectrum of compound $\text{P}1\cdot\text{NTf}_2$ (CDCl$_3$, 121 MHz). PPh$_3$ was used as an external standard and its chemical shift was normalized to −4.70 ppm.
**Figure S3.15** Phosphorus-31 NMR spectrum of compound P2•NTf₂ (CDCl₃, 121 MHz). PPh₃ was used as an external standard and its chemical shift was normalized to −4.70 ppm.
Figure S3.16 Phosphorus-31 NMR spectrum of compound $\mathbf{P3\cdotNTf_2}$ (CDCl$_3$, 121 MHz). PPh$_3$ was used as an external standard and its chemical shift was normalized to $-4.70$ ppm.
Figure S3.17 Fluorine-19 NMR spectrum of compound P1·NTf₂ (CDCl₃, 282 MHz).
Figure S3.18 Fluorine-19 NMR spectrum of compound \textbf{P2•NTf}_2 \textit{(CDCl}_3, 282 MHz)
**Figure S3.19** Fluorine-19 NMR spectrum of compound $\text{P3} \cdot \text{NTf}_2$ (CDCl$_3$, 282 MHz).
Figure S3.20. UV-vis absorption spectra of P1•X (X=Br, NTf₂) in dichloromethane. The metal listed in the legend is that which comprises part of the catalyst used to prepare the polymer.
Figure S3.21. UV-vis absorption spectra of $\text{P}_2\text{X}$ ($\text{X}=\text{Br, NTF}_2$) in dichloromethane. The metal listed in the legend is that which comprises part of the catalyst used to prepare the polymer.
Figure 3.22. UV-vis absorption spectra of $\text{P3} \cdot \text{X} \ (\text{X} = \text{Br, NTf}_2)$ in dichloromethane.
CHAPTER FOUR
CONVENIENT SYNTHETIC ROUTE TO TETRAARYLPHOSPHONIUM
POLYELECTROLYTES VIA PALLADIUM-CATALYZED P–C COUPLING OF
ARYL TRIFLATES AND DIPHENYLPHOSPHINE

Introduction

Polyelectrolytes have been attracting tremendous interest in recent decades due to the growing range of applications available based on their intriguing and unique properties.¹ Phosphonium-derivatized polyelectrolytes in particular have been investigated for application in diverse applications ranging from their use as antimicrobial agents and biodelivery vectors,²-¹³ ¹⁴-¹⁶ to materials and energy applications such as alkaline fuel cell membranes,¹⁷-²⁰ redox-active films,²¹,²² ordered optically-active materials²³-²⁵ and optoelectronic devices.²⁶

Compared to polyelectrolytes bearing alkyl phosphonium sites, tetraaryl phosphonium polyelectrolytes (TPELs) have demonstrated significantly improved thermal- and chemical (particularly alkaline) stability.²⁷,²⁸ Because of the advantageous properties of TPELs and their potential in practical applications, we were inspired to develop simple and convenient polymerization routes to TPELs based on transition metal-catalyzed P–C coupling.

There are at present three reported methods to prepare TPELs: one requiring multistep post-polymerization modification,²⁹ and two methods involving the much more efficient transition. There are at present three reported methods to prepare TPELs: one requiring multistep post-polymerization modification,²⁹ and two methods involving the
much more efficient transition metal-catalyzed P–C bond formation\textsuperscript{28,30} similar to the route that is the focus of the current contribution.

\[
\text{A) } \begin{array}{c}
\text{FG} \text{OTf} \text{ OTf} + \text{Ph}_2\text{PH} \\
\text{Pd(OAc)}_2 \\
\text{dppb, base} \\
\text{120 }^\circ \text{C}
\end{array} \rightarrow \begin{array}{c}
\text{FG} \text{PPh}_2
\end{array}
\]

\[
\text{B) } \begin{array}{c}
\text{FG} \text{OTf} \text{ OTf} + \text{Ph}_3\text{P} \\
\text{Pd}_3\text{(dba)}_3 \\
\text{145 }^\circ \text{C, 2 h}
\end{array} \rightarrow \begin{array}{c}
\text{FG} \text{PPh}_3
\end{array}
\]

\[
\text{C) } \begin{array}{c}
\text{Br} \text{Br} \text{arene} \text{arene} + \text{Ph}_2\text{PH} \\
\text{Pd}_3\text{(dba)}_3 \\
\text{base} \\
\text{145 }^\circ \text{C, 24 h}
\end{array} \rightarrow \begin{array}{c}
\text{Ph} \text{Br} \text{arene}_n \\
\text{Ph}
\end{array}
\]

\[
\text{D) } \begin{array}{c}
\text{TfO} \text{arene} \text{OTf} \text{ OTf} + \text{Ph}_2\text{PH} \\
\text{Pd}_3\text{(dba)}_3 \\
\text{base} \\
\text{145 }^\circ \text{C, 24 h}
\end{array} \rightarrow \begin{array}{c}
\text{Ph} \text{Tf} \text{arene}_n \\
\text{Ph}
\end{array}
\]

**Scheme 4.1:** Established P–C coupling to triarylphosphine (A) and tetraarylphosphonium salts (B). The reported coupling of aryl bromides with HPPh2 (C) inspired the new route to polymeric triflates (D).

In 2015 we reported the first transition metal-catalyzed P–C bond formation route to TPELs via coupling of bis(triarylphosphine) and aryl dihalide monomers.\textsuperscript{28} The scope and potential for commercialization of this methodology is limited by the expensive, multi-step methodologies required to prepare the requisite bis(triarylphosphine) monomers.\textsuperscript{31} We recently reported a significantly-simplified route to TPELs via direct Ni- or Pd-catalyzed P–C coupling polymerization of commercial aryl dihalides and diphenylphosphine (Scheme 4.1C).\textsuperscript{27} The use of aryl dihalides, however, is still relatively expensive and the halide counteranions need to be exchanged for other anions (i.e. triflate (‘OTf) or ditriflamide (NTf\textsubscript{2}−)) to obtain the most thermally robust materials. It is thus of interest to develop direct routes to TPELs bearing triflate couteranions in a single-step process.
Triflate is a common leaving group in well-established transition metal-catalyzed C–C coupling reaction, and more recently has found use in small molecule P–C coupling as well. In a 1996 report, Gilbertson et al. reported that aryl triflates can be converted to aryl diphenylphosphine derivatives in 80-90% yield employing a Pd$^{II}$-catalyst and diphenylphosphine (Scheme 4.1A). Furthermore, in 2007 Charette’s group reported that functionalized aryl triflates can be coupling efficiently with triphenylphosphine (Scheme 1B) to yield tetraarylphosphonium salts via a catalytic cycle summarized in Scheme 4.2.

Scheme 4.2. Proposed catalytic cycle for the P-C coupling reaction.

Charette further revealed that these coupling reactions are compatible with various functional electron withdrawing groups at positions para- and meta- to the coupling site. These promising small molecule proof-of-principle studies inspired us to explore coupling of aryl ditriflates with diphenylphosphine as a direct route to triflate TPELs (Scheme 4.1D). In addition to eliminating the anion exchange step, the triflate
monomers can be readily prepared from a wide variety of commercial bisphenol compounds. Bisphenols (notable bisphenol A (BPA)) are affordable and widely used in the industrial-scale production of polymers, and their facile, quantitative conversion to ditriflates via room-temperature esterification with triflic anhydride is well established.\textsuperscript{37} Herein, we report the development of a new P–C coupling route and its application to the preparation of eight structurally-diverse triflate TPELs. The relationship between structure and the thermal and alkaline stability of the materials is also discussed.

**Experimental**

*General Considerations*

All air-sensitive manipulations were performed in an MBraun UNILab glovebox under nitrogen. Anhydrous solvents were dried and degassed using an MBraun solvent purifier. NMR spectra were collected on a Joel ECX-300 MHz spectrometer operating at 300, 75.5, 282 and 121 MHz for $^1$H, $^{13}$C, $^{19}$F and $^{31}$P, respectively. Thermogravimetric analysis (TGA) was performed on TA Instruments SDT Q600 from 25 °C to 800 °C with a heating rate of 20 °C min$^{-1}$ under a N$_2$ atmosphere. Differential scanning calorimetry (DSC) was performed on TA Instruments SDT Q600 with a heat/cool/heat cycle at 5 °C min$^{-1}$, and the $T_g$ data reported in Table 4.1 are for the second scan (cooling and first/second heating curves are provided in the Supporting Information, Figure S4.50). UV-vis absorption spectra were acquired on a Cary 50 spectrophotometer. Phosphorus-31 NMR spectra were collected with a 10 s relaxation delay to obtain accurate integration of main chain versus end group resonances. The instrument was referenced to phosphoric
acid standard (0 ppm) and an additional PPh$_3$ external standard (~4.70 ppm) was employed to account for instrument drift.

Materials

Anhydrous ethylene glycol (99.8%, Sigma Aldrich), anhydrous pyridine (99.8%, Sigma Aldrich), 4,4’-(9-Fluorenylidene) diphenol (97%, Sigma Aldrich), 4,4’-(1-phenylethylidene) bisphenol (99%, Sigma Aldrich), 4,4’-Cyclohexylidenebisphenol (98%, Sigma Aldrich), 4,4’-Thiodiphenol (99%, Sigma Aldrich), Tris(dibenzylideneacetone)dipalladium(0) (97%, Sigma Aldrich), 4,4’-Dihydroxydiphenyl ether (98%, TCI America), 4,4-Dihydroxytetraphenylmethane (98%, TCI America), trimethylamine (99%, TCI America) 4,4’-Sulfonyldiphenol (99.7%, ACROS), diphenylphosphine (99%, STREM Chemicals), triflic anhydride (97%, STREM Chemicals), Lithium triflate (99%, STREM Chemicals), dichloromethane (99.5%, BDH Chemicals) were used without further purification.

General Route for the Synthesis of Bis(triflate) Monomers:

The general procedure that follows is based on a reported method.$^{37}$ To a 100 mL round bottom flask were added the requisite bisphenol (10.0 mmol) and anhydrous pyridine (40.0 mmol) dissolved in 10 mL dichloromethane (DCM) under a nitrogen atmosphere. The flask was cooled to 0 °C in an ice bath for 10 min and then a 10 mL DCM solution of triflic anhydride (40.0 mmol) was added slowly via cannula under a positive pressure of N$_2$. After stirring overnight, the reaction mixture was cooled in an ice
bath and 20 mL water was added to quench any remaining triflic anhydride. The mixture was extracted with 100 mL DCM. The DCM layer was subsequently washed with 50 mL 2 M HCl(aq), 50 mL 1 M NaCl(aq) and 50 mL deionized water. The DCM phase was concentrated to 10 mL under reduced pressure and further purified by passage through a 5 cm-high silica gel plug in a 30 mL fritted funnel to yield pure products. Yields and spectroscopic characterization data for each monomer follows.

4,4’-(propane-2,2-diyl)-bis(phenyl triflate) (M1)
Yield: 4.85 g (98.5%). $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 7.16-7.30 (m, 8H), 1.69 (s, 6H); $^{13}$C NMR (75.5 MHz, CDCl$_3$, $\delta$): 150.2, 147.8, 128.7, 125.2, 121.1, 120.9, 116.6, 112.4, 43.0, 30.8

4,4’-oxydiphenyl bistriflate (M2)
Yield: 3.825 g (82.0%). $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 7.05-7.10 (m, 4H), 7.26-7.30 (m, 4H); $^{13}$C NMR (75.5 MHz, CDCl$_3$, $\delta$): 156.2, 145.3, 125.2, 123.2, 121.0, 120.4, 116.7, 112.5

4,4’-(1-Phenylethylidene)-(bisphenyl triflate) (M3)
Yield: 4.89 g (88.5%). $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 7.03-7.35 (m, 13H), 2.20 (s, 3H); $^{13}$C NMR (75.5 MHz, CDCl$_3$, $\delta$): 148.9, 148.0, 147.2, 130.5, 128.5 (d), 125.2, 121.0, 116.7, 112.4, 52.2, 30.7

4,4’-Cyclohexylidene-bis(phenyl triflate) (M4)
Yield: 4.21 g (79.4%). \(^1\)H NMR (300 MHz, CDCl\(_3\), \(\delta\)): 7.16-7.34 (m, 8H), 2.26 (d, 4H), 1.53 (br s, 6H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\), \(\delta\)): 148.3, 147.6, 129.1, 125.1, 121.3, 120.9, 116.7, 112.4, 46.1, 37.3, 26.1, 22.7

4,4\(^{-}\)-(9-Fluorenylidene)-bis(phenyl triflate) (\(\text{M5}\))

Yield: 6.04 g (98.4%). \(^1\)H NMR (300 MHz, CDCl\(_3\), \(\delta\)): 7.81-7.84 (d, 2H), 7.26-7.47 (s, 10H); 7.15-7.18 (m, 4H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\), \(\delta\)): 149.6, 148.5, 145.8, 140.1, 128.3 (d), 125.9, 125.3, 121.3, 120.9, 120.6, 116.6, 112.2, 64.4

4,4\(^{-}\)-(Diphenylmethylene)-bis(phenyl triflate) (\(\text{M6}\))

Yield: 6.13 g (99.4%). \(^1\)H NMR (300 MHz, CDCl\(_3\), \(\delta\)): 7.12-7.36 (m, 18H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\), \(\delta\)): 147.8, 146.6, 145.2, 132.8, 130.8, 128.0, 126.7, 120.8, 120.5, 116.6, 64.3

4,4\(^{-}\)-Sulfonyldiphenyl bistriflate (\(\text{M7}\))

Yield: 5.07 g (98.6%). \(^1\)H NMR (300 MHz, CDCl\(_3\), \(\delta\)): 7.45-7.50 (m, 4H), 8.06-8.11 (m, 4H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\), \(\delta\)): 152.7, 141.0, 130.4, 125.0, 122.8, 120.7, 116.5, 112.2

4,4\(^{-}\)-Thiodipheyl bistriflate (\(\text{M8}\))

Yield: 4.79 g (99.2%). \(^1\)H NMR (300 MHz, CDCl\(_3\), \(\delta\)): 7.25-7.30 (m, 4H), 7.40-7.45 (m, 4H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\), \(\delta\)): 148.8, 135.7, 132.6, 125.0, 122.5, 120.8, 116.6, 112.2
General Procedure for Polymerization

The requisite bistriflate monomer (2.69 mmol), diphenylphosphine (0.525 g, 2.82 mmol), diisopropylamine (0.274 g, 2.69 mmol) Pd\(_2\)(dba)\(_3\) (0.0270 mmol, 0.0280 g) and 6 mL anhydrous ethylene glycol were mixed together in a 15 mL heavy-wall pressure tube sealed with a Teflon stopper and Viton O-ring under a nitrogen atmosphere. The sealed vessel was heated at 145 °C with stirring for 24 h. After cooling down to room temperature, the reaction vessel was opened to air and 50 mL DCM was added. The mixture was then washed with 0.5 \( M \) LiOTf\( \text{(aq)} \) (2×50 mL). The addition of triflate anions in the aqueous phase was undertaken as a precaution against any adventitious anion exchange. The organic layer was dried over anhydrous MgSO\(_4\) and concentrated to 10 mL under reduced pressure by rotary evaporation. The crude solution was slowly poured into 200 mL diethyl ether with stirring to yield a cloudy suspension. The solid was separated by vacuum filtration and dried in a vacuum oven overnight at 60 °C to give the desired product. The structure of each polymer is provided in Scheme 4.2 and characterization for each member of the series follow.

\( P1 \)

Yield: 0.947 g (69.4%). \(^1\)H NMR (300 MHz, (CD\(_3\))\(_2\)CO, \( \delta \)): 8.15-7.42 (br m, 18H), 1.88-1.61 (br, 6H); \(^{31}\)P NMR (121 MHz, (CD\(_3\))\(_2\)CO, \( \delta \)): 25.52 (end groups), 24.42-21.54 (backbone phosphonium moieties); \(^{19}\)F NMR (282 MHz, (CD\(_3\))\(_2\)CO, \( \delta \)): –78.44. Anal. calcd for monomer formula C\(_{28}\)H\(_{24}\)F\(_3\)O\(_3\)PS (ignoring end groups): C, 63.63; H, 4.58; found: C, 63.39; H, 4.60%

\( P2 \)
Yield: 0.680 g (51.1%). $^1$H NMR (300 MHz, (CD$_3$)$_2$CO, δ): 8.03-7.69 (br m, 14H), 7.69-7.45 (br, 4H); $^{31}$P NMR (121 MHz, (CD$_3$)$_2$CO, δ): 25.15 (ignoring end groups), 24.53-20.29 (backbone phosphonium moieties); $^{19}$F NMR (282 MHz, (CD$_3$)$_2$CO, δ): –78.52.

Anal. calcd for monomer formula C$_{25}$H$_{18}$F$_3$O$_4$PS (ignoring end groups): C, 59.76; H, 3.61; found: C, 60.02; H, 3.70%

$P_3$

Yield: 1.50 g (92%). $^1$H NMR (300 MHz, (CD$_3$)$_2$CO, δ): 8.05-7.03 (br m, 23H), 2.36-2.13 (br, 3H); $^{31}$P NMR (121 MHz, (CD$_3$)$_2$CO, δ): 24.86 (end groups), 23.60-21.46 (backbone phosphonium moieties); $^{19}$F NMR (282 MHz, (CD$_3$)$_2$CO, δ): –78.47. Anal. calcd for monomer formula C$_{33}$H$_{26}$F$_3$O$_3$PS (ignoring end groups): C, 67.11; H, 4.44; found: C, 66.88; H, 4.50%

$P_4$

Yield: 1.29 g (81.4%). $^1$H NMR (300 MHz, (CD$_3$)$_2$CO, δ): 8.13-6.95 (br m, 18H), 2.54-2.19 (br, 4H), 1.65-1.24 (br, 6H); $^{31}$P NMR (121 MHz, (CD$_3$)$_2$CO, δ): 25.35 (end groups), 23.34-22.76 (backbone phosphonium moieties); $^{19}$F NMR (282 MHz, (CD$_3$)$_2$CO, δ): –78.49. Anal. calcd for monomer formula C$_{31}$H$_{28}$F$_3$O$_3$PS (ignoring end groups): C, 75.33; H, 7.71; found: C, 74.13; H, 7.89 %

$P_5$

Yield: 1.120 g (64.1%). $^1$H NMR (300 MHz, (CD$_3$)$_2$CO, δ): 8.23-6.82 (br m, 26H); $^{31}$P NMR (121 MHz, (CD$_3$)$_2$CO, δ): 25.35 (end groups), 24.13-21.98 (backbone phosphonium moieties); $^{19}$F NMR (282 MHz, (CD$_3$)$_2$CO, δ): –78.42. Anal. calcd for
monomer formula C$_{38}$H$_{26}$F$_3$O$_3$PS (ignoring end groups): C, 70.15; H, 4.03; found: C, 69.37; H, 4.27%

**P6**

Yield: 1.50 g (85.5%). $^1$H NMR (300 MHz, (CD$_3$)$_2$CO, δ): 8.09-7.42 (br, 18H), 7.37-7.02 (br, 10H); $^{31}$P NMR (121 MHz, (CD$_3$)$_2$CO, δ): 26.21 (end groups), 23.61-21.20 (backbone phosphonium moieties); $^{19}$F NMR (282 MHz, (CD$_3$)$_2$CO, δ): −78.48. Anal. calcd for monomer formula C$_{38}$H$_{26}$F$_3$O$_3$PS (ignoring end groups): C, 69.93; H, 4.32; found: C, 69.38; H, 4.64%

**P7**

Yield: 0.719 g (50.6%). $^1$H NMR (300 MHz, (CD$_3$)$_2$CO, δ): 8.52-6.94 (br m, 18H); $^{31}$P NMR (121 MHz, (CD$_3$)$_2$CO, δ): 26.69 (end groups), 25.32-22.59 (backbone phosphonium moieties); $^{19}$F NMR (282 MHz, (CD$_3$)$_2$CO, δ): −78.63. Anal. calcd for monomer formula C$_{25}$H$_{18}$F$_3$O$_5$PS$_2$ (ignoring end groups): C, 54.54; H, 3.30; found: C, 57.02; H, 3.82%

**P8**

Yield: 0.424 g (30.4%). $^1$H NMR (300 MHz, (CD$_3$)$_2$CO, δ): 8.06-7.30 (br m, 18H); $^{31}$P NMR (121 MHz, (CD$_3$)$_2$CO, δ): 25.51 (end groups), 24.62-22.42 (backbone phosphonium moieties); $^{19}$F NMR (282 MHz, (CD$_3$)$_2$CO, δ): −78.52. Anal. calcd for monomer formula C$_{25}$H$_{18}$F$_3$O$_3$PS$_2$ (ignoring end groups): C, 57.91; H, 3.50; found: C, 59.47; H, 3.71%

*Procedures for Alkaline Stability Testing*
To a 50 mL round bottom flask was added a solution of 20 mg polymer powder dissolved in 0.2 mL DCM. The solution was evaporated slowly to coat a film homogeneously on the lower part of the inner wall of the flask. The polymer film was soaked in 1 M NaOH solution for 24 h. The organic material was extracted into 0.3 mL CH₂Cl₂, and 0.2 mL (CD₃)₂CO was added. This solution was characterized by NMR spectrometry. The protocol was repeated at 65 °C, with the only difference being that the solution was cooled to room temperature prior to extraction. Each trial of alkaline stability test was done in duplicate and the percentage of decomposition (% decomp.) data provided in Table 4.3 are the average values.

Results and Discussion

Synthetic Design and Characterization

The goal of the current work was to develop a P–C bond-forming route for the convenient preparation of tetraarylphosphonium polyelectrolytes (TPELs) using bis(aryl triflate)s and diphenylphosphine as the monomers.

On the basis of prior work in which different catalysts were evaluated for the preparation of TPELs,²⁷ tris-(dibenzylideneacetone) dipalladium(0) (Pd₂(dba)₃) was selected for the current work as well. Eight bisphenols bearing different functional groups were selected as starting materials for the bis(aryl triflate) monomers (Scheme 4.3). In order to evaluate the scope of the synthetic route, monomers that contribute electron-releasing substituents (as in P2 and P8), electron-withdrawing groups (as in P6), and a range of steric hindrance to conformational freedom (i.e., P1 versus P3-5) were targeted.
Polymerization reactions were carried out in anhydrous ethylene glycol because of its success in high-yield P–C coupling to form small molecular tetraarylphosphonium salts and its ability to solubilize previously-reported TPELs.\textsuperscript{2,36,38}

Polymerization of diphenylphosphine (1.05 equiv) with M1-M8 (1.00 equiv) catalyzed by Pd\textsubscript{2}(dba)\textsubscript{3} at 145 °C in ethylene glycol thus led to successful preparation of the target triflate TPELs as summarized in Scheme 4.3.

**Scheme 4.3** Synthesis of polymeric triflates.
The polymers were initially characterized via $^1$H, $^{19}$F, and $^{31}$P NMR spectra. The absence of a $^{31}$P NMR resonance for diphenylphosphine (a doublet at $-41.00$ ppm)\(^{39}\) in crude mixtures confirmed the consumption of HPPh\(_2\). Likewise, $^{19}$F NMR spectrometry confirms complete consumption of aryl-bound triflate units (appearing at about $-74.0$ ppm) and that ionic triflate groups (appearing at about $-78.5$ ppm)\(^{36,37}\) are the only fluorine-containing species detectable by NMR analysis (see Figure S4.33-4.40 in the Supporting Information).

Polyelectrolytes and related polymers can have very high affinity to GPC columns, sometimes requiring highly polar solvents such as formic acid for their elution.\(^{28,40,41}\) Following the techniques previously reported,\(^{42-44}\) NMR endgroup analysis was therefore selected as a convenient method to determine the $M_n$ of the TPELs.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (kDa)</th>
<th>$X_n$</th>
<th>$T_d$ ($^\circ$C)</th>
<th>$T_g$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>34.4</td>
<td>65</td>
<td>433</td>
<td>251</td>
</tr>
<tr>
<td>P2</td>
<td>16.6</td>
<td>33</td>
<td>441</td>
<td>260</td>
</tr>
<tr>
<td>P3</td>
<td>27.8</td>
<td>47</td>
<td>415</td>
<td>N/A</td>
</tr>
<tr>
<td>P4</td>
<td>11.9</td>
<td>21</td>
<td>373</td>
<td>N/A</td>
</tr>
<tr>
<td>P5</td>
<td>18.2</td>
<td>28</td>
<td>362</td>
<td>N/A</td>
</tr>
<tr>
<td>P6</td>
<td>13.0</td>
<td>20</td>
<td>374</td>
<td>N/A</td>
</tr>
<tr>
<td>P7</td>
<td>16.5</td>
<td>30</td>
<td>355</td>
<td>N/A</td>
</tr>
<tr>
<td>P8</td>
<td>32.1</td>
<td>62</td>
<td>384</td>
<td>244</td>
</tr>
</tbody>
</table>

*Table 4.1* General properties of triflate TPELs.
When equimolar amount of the bis(aryl triflate) and diphenylphosphine monomers were employed in the polymerization both aryl triflate end groups (evident in $^{19}$F NMR spectra) and phosphine oxide (evident in $^{31}$P NMR spectra) were observed. To simplify NMR endgroup analysis, a slight excess of diphenylphosphine monomer was employed, thus insuring that the end groups will be comprised almost entirely of phosphine moieties (confirmed by NMR spectra provided in the Supporting Information) that, upon aerobic workup, are transformed into phosphine oxide units (Scheme 4.4). This end group composition allowed for convenient determination of $M_n$ via $^{31}$P NMR end group analysis (Table 4.1). Accurate $^{31}$P NMR integrations were obtained by using a 10 s delay between scans following the reported procedure.$^{30}$ As expected, each polymer’s $^{31}$P NMR spectrum features a major resonance consistent with main chain phosphonium salt and a significantly smaller resonance consistent with a phosphine oxide. The main chain phosphonium resonance for P1-P8 is in the range of 20.29-25.32 ppm (Table 4.2) and the phosphine oxide end group is in the range of 24.86-26.69 ppm. The phosphonium and phosphine oxide resonances of P7 are both slightly down field of those for other known TPELs due to the presence of the electron-withdrawing sulfonyl substituent para- to the phosphorus nuclei.
Table 4.2 Phosphorus-31 NMR chemical shifts for P1-P8.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>δ of phosphonium (ppm)</th>
<th>δ of end group (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>22.87</td>
<td>25.52</td>
</tr>
<tr>
<td>P2</td>
<td>23.21</td>
<td>25.15</td>
</tr>
<tr>
<td>P3</td>
<td>23.08</td>
<td>25.32</td>
</tr>
<tr>
<td>P4</td>
<td>22.76</td>
<td>25.35</td>
</tr>
<tr>
<td>P5</td>
<td>23.02</td>
<td>25.35</td>
</tr>
<tr>
<td>P6</td>
<td>22.64</td>
<td>26.21</td>
</tr>
<tr>
<td>P7</td>
<td>24.41</td>
<td>26.69</td>
</tr>
<tr>
<td>P8</td>
<td>23.55</td>
<td>25.51</td>
</tr>
</tbody>
</table>

The observed $M_n$ values (Table 4.1) span a range from ~12-34 kDa, similar to those for TPELs prepared by coupling of HPPh$_2$ with aryl bromides. The variability of $M_n$ for the isolated polymers appears to depend more on the relative solubility of lower molecular weight fractions that are removed in the precipitation step than on the efficiency of the polymerization process itself, as crude analysis suggests that polymers as-formed have $M_n$ of about 20 prior to workup. An $M_n$ of about 20 is expected on the basis of the monomer feed ratios employed, assuming an essentially quantitative coupling efficiency. Polymer P2 was identified as a particularly attractive candidate for scale-up, so a 10 g sample of P2 was prepared to assess the scalability of the process. The synthetic efficiency and molecular weight of the larger batch of P2 were essentially identical to those of the smaller batch (see Figure S42B in the Supporting Information).
Thermal Stability and Transitions

Davis and coworkers\textsuperscript{45} demonstrated that tetraarylphosphonium salts are the most thermally stable ionic liquids known, so it was of interest to evaluate the thermal stability of P1-P8, and to study the effect of different repeat unit composition on thermal stability. Thermogravimetric analysis (TGA) was employed to determine the decomposition temperature ($T_d$) for each polymer. These data are summarized in Table 4.1.

Our previous work revealed that the counteranion has a significant effect on thermal stability of TPELs.\textsuperscript{27} In one case, for example, the TPEL having ditriflamide counteranions exhibited a $T_d$ of $\sim$460 °C while its bromide analogue had a $T_d$ of 400 °C. In addition to the counteranions, thermal stability should also be affected by the backbone composition.

Neutral polymers bearing spacers identical to those between phosphonium units in P1-P8 all have excellent thermal stability ($T_d > 400$ °C)\textsuperscript{46-50} and so their presence was not expected to diminish the inherent thermal stability of their composite TPELs. As anticipated, the $T_d$ values for P1-P8 are all relatively high, ranging from 355-441 °C. The lowest thermal stability is for P7. The diminished stability is attributable to the presence of two strongly electron-withdrawing groups on the same phenylene unit, an effect that has been observed in similarly-substituted TPELs previously.\textsuperscript{28}

Analysis of DSC data revealed that none of polymeric triflates has detectable glass transitions in the range of 20-200 °C. X-ray powder diffraction patterns for P1-P8 revealed that all the polymers are amorphous, consistent with the results from DSC.
**Chemical Stability**

The chemical stability of all TPELs has been investigated upon exposure to 1 \( M \) NaOH(aq) at room temperature and 65 °C. The percentage of phosphonium moieties that undergo decomposition in \( \text{P1-P8} \) are summarized in Table 4.3. Decomposition of 1,4-bis(triarylphosphonium)phenylene units upon exposure to alkaline solution is known to proceed via the SNAr mechanism depicted in Scheme 4.5A.\(^{28}\) The SNAr mechanism is facilitated by the presence of an appropriate leaving group positioned either *ortho-* or *para-* to a strongly electron-withdrawing substituent on an aryl ring.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>% decomp. (20 °C</th>
<th>% decomp. (65 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>11</td>
<td>67</td>
</tr>
<tr>
<td>P2</td>
<td>4</td>
<td>18</td>
</tr>
<tr>
<td>P3</td>
<td>10</td>
<td>72</td>
</tr>
<tr>
<td>P4</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>P5</td>
<td>20</td>
<td>22</td>
</tr>
<tr>
<td>P6</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>P7</td>
<td>55</td>
<td>88</td>
</tr>
<tr>
<td>P8</td>
<td>17</td>
<td>60</td>
</tr>
</tbody>
</table>

*Table 4.3* Stability of polymeric triflates upon exposure to aqueous alkaline solutions for 24 h

This is the situation in \( \text{P7} \), which consequently undergoes the greatest decomposition, with 55% decomposition occurring after only 24 h at room temperature, which we attribute to via the pathway shown in Scheme 4.5B. Decomposition of related ammonium polyelectrolytes has been misattributed to the inherent instability of sulfone
units to hydroxide.\textsuperscript{51} In contrast to P7, P2 has electron-releasing units \textit{para} to the phosphonium center and has significantly improved stability under alkaline conditions.

\begin{center}
\includegraphics[width=0.8\textwidth]{scheme_4.4.png}
\end{center}

\textbf{Scheme 4.4} Features of TPELs showing the formation of the phosphine oxide end groups used in calculation of degree of polymerization.

\begin{center}
\includegraphics[width=0.6\textwidth]{scheme_4.5.png}
\end{center}

\textbf{Scheme 4.5} Mechanism of decomposition for some phosphonium segments

\textit{UV-vis Absorption}

The maximum absorption peaks in the UV-vis absorption spectra for P1–P8 are located in the 220-230 nm range, attributable to the \( \pi-\pi^* \) transition of the backbone aryl units.\textsuperscript{38} These data agree with the fact that TPELs do not exhibit extended \( \pi \)-conjugation
along the backbone. In addition to the π-π* transition, the spectra for P2 and P8 exhibit absorptions at 268 and 300 nm, respectively. These can be attributed to n-p* transitions involving the oxygen- (P2) or sulfur- (P8) centered lone pairs.

Conclusions

A P–C bond-forming route to TPELs from bis(aryl triflates) and diphenylphosphine is reported. Eight triflate TPELs have been prepared via this route and their thermal and alkaline stability has been assessed. The polymerization route has been proven compatible and effective for a range of functional groups of interest in polymeric materials, including a sulfone, ether, and thioether. The TPELs have good thermal stability up to 441 °C. A relationship between the chemical composition of the backbone and the susceptibility of these materials to decomposition under alkaline conditions has been revealed. Tests of these materials as anion exchange membranes for alkaline fuel cell applications are currently underway.

ATTRIBUTION OF WORK

My contribution to the work in this chapter consisted of: synthesis, NMR, UV-vis absorption, thermal stability, alkaline stability. The other coworkers who are coauthors on the published portion of this chapter contributed to remaining areas of the study.
References


22. Khrizanforov, M. N.; Arkhipova, D. M.; Shekurov, R. P.; Gerasimova, T. P.; Ermolaev, V. V.; Islamov, D. R.; Miluykov, V. A.; Kataeva, O. N.; Khrizanforova,


Figure S4.1 Proton NMR spectrum of compound M1 (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
**Figure S4.2** Proton NMR spectrum of compound M2 (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.3 Proton NMR spectrum of compound M3 (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.4 Proton NMR spectrum of compound M4 (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.5 Proton NMR spectrum of compound M5 (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.6 Proton NMR spectrum of compound M6 (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.7 Proton NMR spectrum of compound M7 (CDCl₃, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.8 Proton NMR spectrum of compound M8 (CDCl$_3$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.9 Carbon NMR spectrum of compound M1 (CDCl₃, 75.5 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.10 Carbon NMR spectrum of compound M2 (CDCl₃, 75.5 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.11 Carbon NMR spectrum of compound M3 (CDCl₃, 75.5 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.12 Carbon NMR spectrum of compound M4 (CDCl₃, 75.5 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.13 Carbon NMR spectrum of compound M5 (CDCl₃, 75.5 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.14 Carbon NMR spectrum of compound M6 (CDCl₃, 75.5 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.15 Carbon NMR spectrum of compound M7 (CDCl₃, 75.5 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
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Figure S4.17 Fluorine-19 NMR spectrum of compound M1 (CDCl₃, 282 MHz).
Figure S4.18 Fluorine-19 NMR spectrum of compound \textbf{M2} (CDCl$_3$, 282 MHz).
**Figure S4.19** Fluorine-19 NMR spectrum of compound M3 (CDCl₃, 282 MHz).
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Figure S4.21 Fluorine-19 NMR spectrum of compound M5 (CDCl₃, 282 MHz).
Figure S4.22 Fluorine-19 NMR spectrum of compound M6 (CDCl₃, 282 MHz).
Figure S4.23 Fluorine-19 NMR spectrum of compound M7 (CDCl₃, 282 MHz).
Figure S4.24 Fluorine-19 NMR spectrum of compound M8 (CDCl₃, 282 MHz).
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Figure S4.26 Proton NMR spectrum of compound P2 prepared by using Pd$_2$(dba)$_3$ catalyst ((CD$_3$)$_2$CO, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.27 Proton NMR spectrum of compound P3 prepared by using Pd$_2$(dba)$_3$ catalyst (CD$_3$CO, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
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**Figure S4.29** Proton NMR spectrum of compound P5 prepared by using Pd$_2$(dba)$_3$ catalyst (CD$_3$CO, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.30 Proton NMR spectrum of compound P6 prepared by using Pd$_2$(dba)$_3$ catalyst ((CD$_3$)$_2$CO, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S4.31 Proton NMR spectrum of compound P7 prepared by using Pd₂(dba)₃ catalyst ((CD₃)₂CO, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.
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Figure S4.33 Fluorine-19 NMR spectrum of compound P1 ((CD$_3$)$_2$CO, 282 MHz).
Figure S4.34 Fluorine-19 NMR spectrum of compound P2 ((CD$_3$)$_2$CO, 282 MHz).
Figure S4.35 Fluorine-19 NMR spectrum of compound P3 ((CD$_3$)$_2$CO, 282 MHz).
Figure S4.36 Fluorine-19 NMR spectrum of compound P4 ((CD$_3$)$_2$CO, 282 MHz).
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Figure S4.38 Fluorine-19 NMR spectrum of compound P6 ((CD$_3$)$_2$CO, 282 MHz).
Figure S4.39 Fluorine-19 NMR spectrum of compound P7 ((CD$_3$)$_2$CO, 282 MHz).
Figure S4.40 Fluorine-19 NMR spectrum of compound P8 ((CD$_3$)$_2$CO, 282 MHz).
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**Figure S4.42.** A) Phosphorus-31 NMR spectrum of compound P2 prepared by using Pd₂(dba)₃ catalyst ((CD₃)₂CO, 121 MHz). PPh₃ was used as an external standard and its chemical shift was normalized to −4.70 ppm. B) Spectrum of a 10 g batch of P2 without added external standard.
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CHAPTER FIVE
LAYER-BY-LAYER SELF-ASSEMBLY OF PHOSPHONIUM POLYMERS WITH TUNABLE SIDE CHAINS AND SPACERS BETWEEN CHARGED SITES

Introduction

The intriguing physical properties of polyelectrolytes (alternatively called ionomers or ionic polymers) have led to their adaptation in an ever-expanding cadre of applications in recent years. Many polyelectrolytes can be processed from aqueous solution, making them attractive from an environmental and economic standpoint as well as rendering them suitable for biological applications. 1 Fluorescent sensors comprised by conjugated polyelectrolytes, for example can be used for detection of charged biomolecules (e.g., protein²-⁴ and DNA⁵-⁸) at low concentrations in biological milieu. The electrostatic interaction and supramolecular self-assembly endowed by ionic functionalities provides exciting opportunities for hierarchical assembly of films for optoelectronic⁹, ¹⁰ and electrochemical¹¹-¹³ devices as well.

One notable yet still underexplored area of polyelectrolyte research is in the area of chromophore-derivatized or conjugated polyelectrolytes (i.e., Chart 5.1). These materials can exploit the desirable properties of polyelectrolytes for use in organic electronics and photonics. As an example, layers comprised of a mixture of anionic polyelectrolyte poly(styrenesulfonate) (PSS) with the conjugated polymer poly(3,4-ethylenedioxythiophene) (PEDOT) are ubiquitous in organic electronics. Several research teams including Buriak,¹⁴-¹⁸ Reynolds and Schanze,¹⁹-²¹ and Bazan,²² to name a few, have explored polyelectrolytes as components of organic photovoltaic cells and related
devices. Notable improvements in device operation and interfacial effects\textsuperscript{17} can result from the incorporation of ionic polymers in place of neutral polymers.

![Chart 5.1 Anionic polyelectrolytes that have been used in layer-by-layer assembly with phosphonium polymers](image)

Phosphonium polyelectrolytes (PELs) incorporating chromophore-derivatized or conjugated moieties in the polymer main chain have been surprisingly scarce to date. This is especially surprising in light of the obvious applications (i.e., fluorescent sensors or optoelectronic films) in which these robust materials could find utility. The few examples of chromophore-derivatized PELs include R2,\textsuperscript{40} EGT1,\textsuperscript{36} SLK1\textsuperscript{37} and FL1-2 (Chart 5.2).\textsuperscript{33} All of these polymers exhibit significant absorption and photoluminescence in the UV-visible region of the spectrum, and some exhibit significant solvatochromic effects in response to changing polarity of their environment, making them possible elements of stimuli-responsive systems.\textsuperscript{38,39}
The Smith group’s work in the area of polyelectrolytes has primarily been on polymers that, like R2, feature both chromophores and phosphonium moieties in the polymer main chain. Such chromophore-derivatized polyelectrolytes were targeted as components of optically-active films that could be employed as elements of organic electronics or other photonic applications. One drawback is the synthetic pathways
requiring >10 steps for monomer synthesis to produce polymers such as \textbf{R2, EGT1,}^{36} \textbf{SLK1}^{37} would likely make them too expensive for practical application. It was therefore of interest to pursue phosphonium ionomers that, like \textbf{R2,}^{41} could be prepared from commercial monomers. We thus recently reported on the preparation of chromophore-derivatized \textbf{FLoct and FLone from commercially-available monomers.}^{33} \textbf{The monomers employed for those polymers were still relatively expensive, however, and the absorbance of films of these polymers was in the blue to UV region of the spectrum. More affordable commercially-available monomers 1,2-bis(diphenylphosphino)ethane, 1,1’-bis(diphenylphosphino)ferrocene, and 1,4-bis(diphenylphosphino)benzene were used to prepare \textbf{CAC1a-b (Chart 5.2)}^{42} with the aim of using them to prepare films with absorption farther into the visible region of the spectrum. Although \textbf{CAC1a-b do not themselves exhibit absorption in the visible region of the spectrum, they can still be used in the layer-by-layer assembly of films in which the alternate layers are comprised of commercially-available anionic conjugated polyelectrolytes such as polythiophene derivative \textbf{APT and poly}(p\text{-phenylene vinylene}) derivative \textbf{APPV (Chart 5.2). The investigation of the layer-by-layer assembly process involving \textbf{CAC1} revealed that polymers having flexible linkers, as are present in \textbf{CAC1a, exhibit significantly better substrate coverage and linearity of film growth as compared to more rigid materials such as \textbf{CAC1b.} }

The early findings from studies on the materials shown in Chart 5.2 and the existing literature on well-defined anionic\textsuperscript{43-45} and cationic\textsuperscript{46,47} polyelectrolytes drew our interest in further investigating the structure-property relationships that depend on the
spacer flexibility and distance between charges along the polymer backbone and side-chains connected in phosphonium polymer chains.

Herein we describe the preparation of two series of phosphonium polymers LX and LO and investigate how the spacer identity as well as hydrophobic side-chains influence properties such as degree of polymerization, the supramolecular layer-by-layer film growth process with anionic polythiophene derivative Pc12-100 (Chart 5.1), and the composition of LbL films. LX polymers (Scheme 5.1) have been designed bearing various spacer flexibility and distance between charges along the polymer backbone in phosphonium polymers; LO polymers (Scheme 5.1) are structural analogues of the LX series, but in which the phenylene units in LX have been replaced with 2,5-dioctyloxyphenylene units. Supramolecular-assembly of these PELs were examined and compared with the aim of sharpening the understanding of PEL structure-property relationships.

**Experimental**

General Considerations.

All air-sensitive reactions were performed in an MBraun UNILab glovebox under nitrogen. Anhydrous solvents were dried and degassed using an MBraun solvent purifier. Anionic polythiophene derivative Pc12-100 was prepared as described in Chapter2. Monomers M1 were obtained from Sigma-Aldrich or Strem Chemical. Glass slides were purchased from Fisher Scientific. Other chemicals were used without further purification.
after purchased. All the NMR spectra were collected on a Joel ECX-300 MHz spectrometer operating at 300 and 121.4 MHz for $^1$H and $^{31}$P, respectively.

*Layer-by-layer technique.*

Glass microscope slides were cleaned by concentrated nitric acid, rinsed with deionized water, and then with tetrahydrofuran (THF). The slide was visually inspected for scuffs or scratches. Solutions of $\text{LX}$ and $\text{LO}$ were prepared in CH$_3$CN/H$_2$O (4:1) and $\text{Pc12-100}$ ($5 \times 10^{-4}$ M) was prepared in THF/water (2:1). The pH of water used to prepare $\text{Pc12-100}$ solution was adjusted to 9 with NaOH to deprotonate carboxylic acid side chains. The slide was first dipped into the cationic polymer solutions then briefly shaken to remove any excess solution droplets. The process was then repeated using the $\text{Pc12-100}$ solution. The spectrum of the film was immediately collected using a Cary 50 UV-vis spectrometer with a scanning range of 275 to 800 nm. This procedure was repeated until the desired number of bilayers was obtained.

*Atomic Force Microscopy (AFM).*

All the AFM experiments were performed with an AIST SmartSPM™ 1000 instrument in semi-contact mode within $1 \times 1$ µm and $5 \times 5$ µm sample areas using an aluminium tip (spring constant = 5 N/m, 160 kHz resonance frequency). Images were processed by AIST-NT and WSxM 5.0 Develop 7.0 software (www.wsxmsolutions.com).
Synthesis of \textbf{LX1} \((n=1)\).

Monomers \(\alpha,\alpha'-\text{dibromo-}p\text{-xylene} \) (132 mg, 0.500 mmol) and bis(diphenylphosphino)methane (192 mg, 0.500 mmol) were placed in a heavy-walled glass pressure tube with \(N, N\text{-dimethylformamide (DMF, 10 mL) under nitrogen. The tube was sealed with an O-ring equipped Teflon screw cap. The tube was then heated to 90 °C for 24 h. After cooling the reaction vessel to room temperature, it was opened to air and 10 mL of diethyl ether was added. This yielded a white cloudy suspension that was collected by vacuum filtration. The crude product was then rinsed with 10 mL of diethyl ether (\times 3) and then dried in a vacuum oven for 48 h. The desired product was isolated as a white powder (0.332 g, 100\%).\) \(^1\)H NMR (300 MHz, (CD\(_3\))\(_2\)SO) \(\delta\): 8.45-7.15 (br m, 20H), 7.12-6.14 (br m, 4H), 6.03-3.70 (br m, 4H), 2.59-2.52 (br m, 2H); \(^{31}\)P\{\(^1\)H\} NMR (121.4 MHz, (CD\(_3\))\(_2\)SO) \(\delta\): 25.4-19.3 (main polymer peak) and 27.6 (end groups).

Anal. Calcd. for monomer formula C\(_{33}\)H\(_{34}\)Br\(_2\)P\(_2\)O\(_2\) (ignoring end groups): C, 57.91; H, 5.01; Found: C, 58.55; H, 5.34%.

Synthesis of \textbf{LX2} \((n=2)\).

This synthesis followed the same procedure as described for \textbf{LX1}, but using as monomers \(\alpha,\alpha'-\text{dibromo-}p\text{-xylene} \) (80 mg, 0.20 mmol) and 1,2-bis(diphenylphosphino)ethane (49 mg, 0.20 mmol). The product was isolated as a white powder (40 mg, 33\%). \(^1\)H NMR (300 MHz, (CD\(_3\))\(_2\)SO) \(\delta\): 8.5-7.4 (br m, 20H), 7.3-6.3 (br m, 4H), 5.3-4.1 (br m, 4H), 3.6-3.0 (br d, 4H); \(^{31}\)P\{\(^1\)H\} NMR (121.4 MHz, (CD\(_3\))\(_2\)SO) \(\delta\):
28.6 (main polymer peak) and 32.8 (end groups). Anal. Calcd. for monomer formula C_{34}H_{32}Br_2P_2 (ignoring end groups): C, 58.47; H, 5.20; Found: C, 59.27; H, 4.94%.

**Synthesis of LX3 (n=3)**

This synthesis followed the same procedure as described for LX1, but using as monomers α,α’-dibromo-p-xylene (132 mg, 0.500 mmol) and 1,3-bis(diphenylphosphino)propane (206 mg, 0.500 mmol). The product was isolated as a white powder (0.314 g, 92.9%). \(^1\)H NMR (300 MHz, (CD\(_3\))_2SO) δ: 8.1-7.6 (br m, 20H), 6.6-7.0 (br m, 4H), 5.1-4.6 (br m, 4H), 3.7-3.5 (br m, 4H), 1.8-1.6 (br d, 2H); \(^{31}\)P{\(^1\)H} NMR (121.4 MHz, (CD\(_3\))_2SO) δ: 25.4 (main polymer peak) and 26.4 (end groups); Anal. Calcd. for monomer formula C_{35}H_{34}Br_2P_2 (ignoring end groups): C, 59.01; H, 5.38; Found: C, 59.76; H, 5.49%.

**Synthesis of LX4 (n=4)**

This synthesis followed the same procedure as described for LX1, but using as monomers α,α’-dibromo-p-xylene (132 mg, 0.500 mmol) and 1,4-bis(diphenylphosphino)butane (213 mg, 0.500 mmol). The product was isolated as a white powder (0.321 g, 93.0%). \(^1\)H NMR (300 MHz, (CD\(_3\))_2SO) δ: 7.9-7.6 (br m, 20H), 7.8-7.7 (br m, 4H), 4.8-4.7 (br m, 4H), 3.1-2.9 (br m, 4H), 1.6-1.5 (br m, 4H); \(^{31}\)P{\(^1\)H} NMR (121.4 MHz, (CD\(_3\))_2SO) δ: 27.8 (main polymer peak) and 26.3 (end groups). Anal. Calcd. for monomer formula C_{36}H_{36}Br_2P_2 (ignoring end groups): C, 59.52; H, 5.55; Found: C, 60.88; H, 5.50%.
Synthesis of \textbf{LX5} \((n=5)\)

This synthesis followed the same procedure as described for \textbf{LX1}, but using as monomers \(\alpha, \alpha'\)-dibromo-\(p\)-xylene (132 mg, 0.500 mmol) and 1,5-bis(diphenylphosphino)pentane (220 mg, 0.500 mmol) The product was isolated as a white powder (0.349 g, 99.1%). \(^1\)H NMR (300 MHz, (CD\(_3\))\(_2\)SO) \(\delta\): 8.10-7.45 (br m, 20H), 7.31-6.57 (br m, 4H), 4.98-4.40 (br m, 4H), 3.00-2.68 (br m, 4H), 1.61-1.17 (br m, 6H); \(^{31}\)P\(\{^1\)H\}\) NMR (121.4 MHz, (CD\(_3\))\(_2\)SO) \(\delta\): 30.3-28.1 (main polymer peak); Anal. Calcd. for monomer formula C\(_{37}\)H\(_{42}\)Br\(_2\)P\(_2\)O\(_2\) (ignoring end groups): C, 60.01; H, 5.72; Found: C, 60.62; H, 5.95%.

Synthesis of \textbf{LX8} \((n=8)\)

This synthesis followed the same procedure as described for \textbf{LX1}, but using as monomers \(\alpha, \alpha'\)-dibromo-\(p\)-xylene(132 mg, 0.500 mmol) and 1,8-bis(diphenylphosphino)octane (241 mg, 0.500 mmol) The product was isolated as a white powder (0.359 g, 96.2%). \(^1\)H NMR (300 MHz, (CD\(_3\))\(_2\)SO) \(\delta\): 8.15-7.50 (br m, 20H), 7.12-6.65 (br m, 4H), 4.92-4.56 (br m, 4H), 3.01-2.65 (br m, 4H), 1.66-0.90 (br m, 12H); \(^{31}\)P\(\{^1\)H\}\) NMR (121.4 MHz, (CD\(_3\))\(_2\)SO \(\delta\): 30.8-26.0 (main polymer peak); Anal. Calcd. for monomer formula C\(_{40}\)H\(_{48}\)Br\(_2\)P\(_2\)O\(_2\) (ignoring end groups): C, 61.39; H, 6.18; Found: C, 63.07; H, 6.03%.

Synthesis of \textbf{LXPh}
This synthesis followed the same procedure as described for LX1, but using as
monomers α,α'-dibromo-p-xylene (132 mg, 0.500 mmol) and 1,4-
bis(diphenylphosphino)benzene (223 mg, 0.500 mmol). The product was isolated as a
white powder (0.336 g, 94.6%). $^1$H NMR (300 MHz, (CD$_3$)$_2$SO) δ: 8.38-7.49 (br m, 24H), 7.09-6.67 (br m, 4H), 5.53-5.10 (br m, 4H); $^{31}$P{$^1$H} NMR (121.4 MHz, (CD$_3$)$_2$SO δ: 27.3-25.9 (main polymer peak); Anal. Calcd. for monomer formula C$_{38}$H$_{36}$Br$_2$P$_2$O$_2$
(ignoring end groups): C, 61.14; H, 4.86; Found: C, 60.36; H, 5.04%.

Synthesis of LO2 ($n = 2$)

Monomers 2,5-bis(bromomethyl)-1,4-bis(octyloxy)benzene (234 mg, 0.450
mmol) and 1,2-bis(diphenylphosphino)-ethane (199 mg, 0.500 mmol) were placed in a
heavy-walled glass pressure tube with anhydrous $N$, $N$-dimethylformamide (DMF, 3 mL)
under nitrogen. The tube was sealed with an O-ring-equipped Teflon screw cap. The tube
was then heated to 90 °C with stirring for 15 h. After cooling the reaction vessel to room
temperature, it was opened to air. Then 10 mL of diethyl ether was added yielding a
white cloudy suspension from which the crude white solid was collected by vacuum
filtration. The crude product was then rinsed with 50 mL of diethyl ether (×3) while
stirring and dried in a vacuum oven for 48 h. The desired product was a white powder
(358 mg, 86.7%). $^1$H NMR (300 MHz, CDCl$_3$) δ: 8.71-7.29 (br m, 20H), 7.08-6.38 (br m, 2H), 5.48-4.40 (br m, 4H), 4.01-3.12 (br m, 4H), 3.11-0.52 (br m, 34H); $^{31}$P{$^1$H} NMR
(121.4 MHz, CDCl$_3$) δ: 29.5-27.0 (main polymer peak) and 33.3 (end groups). Anal.
Calcd. for monomer formula \( \text{C}_{50}\text{H}_{66}\text{Br}_2\text{P}_2\text{O}_3 \) (ignoring end groups): C, 64.10; H, 7.10; Found: C, 64.90; H, 7.12%.

_Synthesis of LO3 \((n = 3)\)._

The synthesis of _LO3_ involves same procedures as discussed for _LO2_. The monomers were 2,5-bis(bromomethyl)-1,4-bis(octyloxy)benzene (234 mg, 0.450 mmol) and 1,3-bis(diphenylphosphino)propane (206 mg, 0.500 mmol). The product was white powder (261 mg, 62.1%). \(^1\text{H} \text{NMR} \) (300 MHz, CDCl\(_3\)) \(\delta\): 8.49-7.31 (br m, 20H), 7.08-6.51 (br m, 2H), 5.60-4.30 (br m, 4H), 4.25-3.26 (br m, 6H), 3.25-0.52 (br m, 34H); \(^{31}\text{P} \{^1\text{H}\} \text{NMR} \) (121.4 MHz, CDCl\(_3\)) \(\delta\): 25.6 (main polymer peak) and 33.2 (end groups). Anal. Calcd. for monomer formula \( \text{C}_{51}\text{H}_{68}\text{Br}_2\text{P}_2\text{O}_3 \) (ignoring end groups): C, 64.42; H, 7.21; Found: C, 64.43; H, 7.23%.

_Synthesis of LO4 \((n = 4)\)._  

The synthesis of _LO4_ involves same procedures as discussed for _LO2_. The monomers were 2,5-bis(bromomethyl)-1,4-bis(octyloxy)benzene (234 mg, 0.450 mmol) and 1,4-bis(diphenylphosphino)butane (213 mg, 0.500 mmol). The product was a white powder (384 mg, 90.1%). \(^1\text{H} \text{NMR} \) (300 MHz, CDCl\(_3\)) \(\delta\): 8.70-7.31 (br m, 20H), 6.90-6.30 (br m, 2H), 5.60-4.30 (br m, 4H), 4.23-3.10 (br m, 8H), 2.95-0.62 (br m, 34H); \(^{31}\text{P} \{^1\text{H}\} \text{NMR} \) (121.4 MHz, CDCl\(_3\)) \(\delta\): 26.7 (main polymer peak) and 33.1 (end groups). Anal. Calcd. for monomer formula \( \text{C}_{52}\text{H}_{70}\text{Br}_2\text{P}_2\text{O}_3 \) (ignoring end groups): C, 64.73; H, 7.31; Found: C, 64.69; H, 7.38%.
Synthesis of LO₅ (n = 5).

The synthesis of LO₅ involves same procedures as discussed for LO₂. The monomers were 2,5-bis(bromomethyl)-1,4-bis(octyloxy)benzene (234 mg, 0.450 mmol) and 1,5-bis(diphenylphosphino)pentane (220 mg, 0.500 mmol). The product was a white powder (302 mg, 69.9%). ¹H NMR (300 MHz, CDCl₃) δ: 8.30-7.38 (br m, 20H), 7.10-6.30 (br m, 2H), 5.40-4.52 (br m, 4H), 4.45-2.10 (br m, 10H), 1.75-0.62 (br m, 34H); ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ: 28.0-23.5 (main polymer peak) and 33.0 (end groups). Anal. Calcd. for monomer formula C₅₃H₇₂Br₂P₂O₃ (ignoring end groups): C, 65.03; H, 7.41; Found: C, 64.47; H, 7.36%.

Synthesis of LO₈ (n = 8).

The synthesis of LO₅ involves same procedures as discussed for LO₂. The monomers were 2,5-bis(bromomethyl)-1,4-bis(octyloxy)benzene (234 mg, 0.450 mmol) and 1,8-bis(diphenylphosphino)octane (241 mg, 0.500 mmol). The product was a white powder (338 mg, 74.9%). ¹H NMR (300 MHz, CDCl₃) δ: 8.70-7.30 (br m, 20H), 7.10-6.28 (br m, 2H), 5.45-4.60 (br m, 4H), 4.49-1.60 (br m, 16H), 1.55-0.70 (br m, 34H); ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ: 28.2-25.2 (main polymer peak) and 33.3 (end groups). Anal. Calcd. for monomer formula C₅₆H₇₈Br₂P₂O₃ (ignoring end groups): C, 65.88; H, 7.70; Found: C, 65.83; H, 7.76%.

Synthesis of 1,4-bis(octyloxy)-2,5-xylenebis(triphenyl phosphonium bromide). (M₃)
Triphenylphosphine (101 mg, 0.385 mmol) and 2,5-bis(bromomethyl)-1,4-bis(octyloxy)benzene (99 mg, 0.190 mmol) were placed in a round bottom flask with 10 mL toluene. The reaction was refluxed at 90 °C for 20 h. After cooling, toluene was removed under reduced pressure yielding a white solid. 20 mL of diethyl ether was added to the flask and it was refluxed for 0.5 h. The product was washed by 40 mL of diethyl ether and separated by vacuum filtration. A white powder was obtained after vacuum drying for 48 h (74 mg, 37%). $^1$H NMR (300 MHz, CDCl₃) δ: 0.75-0.99 (t, 6H), 1.00-1.45 (m, 24H), 2.80-3.12 (t, 4H), 5.26-5.40 (d, 4H, $^4$J$_{HH}$ =12 Hz), 6.75 (s, 2H), 7.57-7.77 (m, 30H). $^{31}$P{$^1$H} NMR (121.4 MHz, CDCl₃) δ: 21.6. (Syntheses were carried out by M. S. Bedford, W. Wan, X. Yang and undergraduate co-authors C. A. Conrad, E. F. Colter and E. H. Freeman.)

Results and Discussion

Design and Synthesis

The aim of the current work was to assess the extent to which flexible hydrophobic side chains influence the properties of PELs, and PEL supramolecular assembly into layer-by-layer (LbL) films with polyanions. Two series of PELs (LXs, LOs, Scheme 5.1) was selected for this study on the basis of several considerations. Firstly, octyloxy side chains are anticipated to increase the solubility of the polymers in organic solvent and thus to improve processability. Secondly, side chains are well known to lower the glass transition temperature and decrease crystallinity, and the interplay of these established trends with the influence of inter-cation spacer had not been examined
for PELs. On the basis of prior studies on PELs, the improved solubility was also expected to lead to better film growth linearity for LbL self-assembly films and smoother/more uniform films. Finally, the LO backbone is identical to that of the LX polymer series, allowing direct comparison of data for the two series in the effort to derive more general structure-property correlations.

Scheme 5.1. Synthesis of LX and LO polymers with different lengths of alkylene spacers ‘X’ between phosphonium centers.

The selection of spacers (X in Scheme 5.1) between phosphonium units for the current study was made on the basis of two criteria. First, it was desirable for the diphosphine monomers (M1) to be commercially available for practical application of materials. Second, it was necessary to sample a range of flexibility and distance between phosphonium units. On the basis of these criteria, we selected the diphosphine monomers shown in Scheme 5.1. The comonomer M2 was selected because it is an affordable
commercial reagent, and it provides the same spacing between phosphonium units as present in CAC1 (Chart 5.2), which had previously shown outstanding layer-by-layer assembly with anionic polythiophene derivative APT (Chart 5.2). It was also anticipated that the rigid nature of the \( p \)-xylene chain component provided by M2 would help prevent the formation of cyclic oligomers of the type that were observed in preparation of R2, which has only flexible methylene units in spacers between phosphonium sites.

The polymerization of M1 and M2 (Scheme 5.1) proceeded readily upon heating at 90 °C under an atmosphere of dry nitrogen in DMF solution for 24 hours. Isolation was also straightforward and involved simple precipitation and rinsing with diethyl ether followed by drying in a vacuum oven to yield LX1-8, LXPh, and LO2-8, as white powders. The polymer composition was characterized by a combination of \(^1\)H and \(^{31}\)P NMR spectrometry (spectra are provided in the supporting information) and elemental microanalysis. The microanalysis data show excellent correlation of experimental and theoretical values considering the polydisperse nature of the materials and the presence of end groups that are not accounted for in the theoretical repeat unit formula. The solids are only sparingly soluble in acetonitrile, but have reasonable solubility in dimethylsulfoxide and are fully soluble in a water/acetonitrile mixture.

One challenging aspect of ionic polymers is that they are not easily analysed for molecular weight distribution by standard gel permeation chromatography (GPC) techniques. This is a result of their affinity to column media, although some researchers have reported success using formic acid in the mobile phase.\(^{53}\) NMR end group analysis
has therefore become the preferred method for obtaining reliable number average molecular weights ($M_n$) for phosphonium polyelectrolytes, which generally show a degree of polymerization of 14-25.\textsuperscript{33-36,37,42} On the basis of NMR end group analysis we were able to obtain the $M_n$ values and corresponding degrees of polymerization ($n$) provided in Table 5.1. Low intensities of end group resonances precluded successful determination of molecular weights for LX1, LX2 and LXPh. All of the phosphonium polyelectrolytes prepared in the analogous manner to LX polymers have exhibited values of $n$ between 16 and 21. On the basis of this data, the degrees of polymerization of LX1, LX2 and LXPh can be estimated to be not less than 19.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (Da)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LX1</td>
<td>9,700</td>
<td>14</td>
</tr>
<tr>
<td>LX2</td>
<td>11,900</td>
<td>17</td>
</tr>
<tr>
<td>LX3</td>
<td>$\geq$13,500</td>
<td>$\geq$19</td>
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<td>LX4</td>
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<td>$\geq$19</td>
</tr>
<tr>
<td>LX5</td>
<td>$\geq$14,100</td>
<td>$\geq$19</td>
</tr>
<tr>
<td>LX8</td>
<td>$\geq$14,900</td>
<td>$\geq$19</td>
</tr>
<tr>
<td>LXPh</td>
<td>11,400</td>
<td>15</td>
</tr>
<tr>
<td>LO2</td>
<td>11,900</td>
<td>12</td>
</tr>
<tr>
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<td>18,700</td>
<td>19</td>
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<tr>
<td>LO4</td>
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<td>17,300</td>
<td>17</td>
</tr>
<tr>
<td>LO8</td>
<td>11,000</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 5.1 Molecular weights and degrees of polymerization for LX and LO.
Layer–by-layer assembly of LO polymers with polyelectrolytes

The LbL assembly of LO polymers with Pc12-100 following the same procedure used for the LX polymers\textsuperscript{43} was undertaken to assess the influence of spacer on the LbL process and films. Film growth was monitored by UV-vis spectroscopy, and Figure 5.1 provides absorbance for 50-bilayer films made by LbL assembly of LO and LX polymers with Pc12-100. In contrast to the trends observed for LbL deposition of LX polymers, the linearity of film growth, amount of material deposited and the roughness of films were all independent of the spacer length when LO polymers were employed. This observation may suggest that octyloxy side chains counteract the difference of absorbance between odd and even number of methylene units in spacers of LO during LbL assembly with Pc12-100.

![Graph showing absorbance](image)

**Figure 5.1** UV-vis absorbance measurements of Pc12-100 accumulation in LbL-assembled films with LO (white) or LX (black) at 50 bilayers.
The plot of absorbance versus the number of methylene units between the phosphonium sites for each LbL film (Figure 5.1) reveals relatively uniform absorbance for films comprised of 50 bilayers with the exception of the polymer with three methylene units in its spacer for both LX and LO series. It was hypothesized that this behavior might be related to two influencing factors: 1) thermally-accessible polymer backbone conformation and 2) the extent to which the interion spacing ($d_{PP}$) of the PEL matches that of the Pc12-100 ($d_{OO}$). (Layer films were prepared by W. Wan, X. Yang and undergraduate co-author C. A. Conrad.)

Figure 5.2 Newman projection (left) and line-bond view of a segment of LX2 or LO2 (A) and a segment of LX3 or LO3 (B) demonstrate expected conformations. Structures for model compounds SM2, SM3, HH, HT and TT used in semi-empirical calculations are provided in (C).
As a result of the sterically-encumbered BnPh₂P-substituent flanking each side of the ethylene spacer in LO2/LX₂, one would expect the conformation about this spacer to be confined to a narrow range about the energy minimum of the anti-conformation about the C1-C2 bond (Figure 5.2A). In this conformation, the two phosphonium units are pointed in opposing directions about the linker. In contrast, the odd number of methylene units between phosphonium sites in LO3/LX₃ should lead to a lowest-energy conformation in which the two phosphonium units are directed in the same direction off of the backbone resulting from anti-conformations about both C1-C2 and C2-C3 bonds (Figure 5.2B). Semi-empirical calculations at the AM1 level support the lowest-energy conformations as expected for small molecular models BnPh₂P-C₂H₄-PPh₂Bn (SM₂, a model for LO2/LX2) and BnPh₂P-C₃H₆-PPh₂Bn (SM₃, a model for LO2/LX2, Figure 5.2C).

In order to better understand the extent to which the spacer length might influence the accessibility of anion-cation matching between LO/LX and Pc₁₂₋₁₀₀, the structure of Pc₁₂₋₁₀₀ must also be considered in more detail. There are three structural subunits in Pc₁₂₋₁₀₀ that are possible on the basis of the synthetic route used to prepare the polymer. These subunits result from either head-to-head (leading to subunit HH), head-to-tail (leading to subunit HT, the one most prevalent) or tail-to-tail (leading to subunit TT) coupling of the monomers, and lead to three different possible anion-anion distances along the backbone (Figure 5.2C). Semi-empirical (AM1) calculations were undertaken to assess the interaction of SM₂ and SM₃ with models for each of the possible structural subunits HT and TT. SM₂ and SM₃ were initially placed in their energy-minimized
geometries in the vicinity of the requisite oligothiophene, but no constraints were applied for calculations of the interactions. Representative optimized geometries are provided in Figure 5.3 and the values for $d_{PP}$, $d_{OO}$ and the difference between these interanion spacings ($\Delta_{OP}$) are summarized in Table 5.2.

From the data in Table 5.2, it is clear that there is a considerably better match of $d_{PP}$ to $d_{OO}$ for SM3 than for SM2 and the oligothiophene carboxylates in the calculated geometries. Since the HT geometry predominates in Pc12-100, the interaction between HT and the phosphonium models provide the best approximation for most of the sites in the LbL films. The geometries for SM2/HT (Figure 5.3A) and SM3/HT (Figure 5.3B) emphasize the improved interaction possible for SM3. In SM2/HT, not only is there a poor match in distances but there is also apparent steric deflection between O2 and one of the phenyl groups on P2 that leads to a deflection of the carboxylate away from the phosphonium site in SM2, leading to a longer $d_{OO}$ of 6.369 Å in SM2/HT versus that of 5.880 Å in SM3/HT.

Taken together, the absorption data and calculated interactions suggest that the optimal anion-cation spacing between Pc12-100 (approximated by HT) and LX3/LO3 (approximated by SM3) results in maximum intrinsic ion pairing and thus requires a smaller amount of Pc12-100 to achieve charge balance in the LbL films. Polymer rigidity and mismatched inter-ion distance along polymer backbones has also been observed to influence self-assembly and coacervate formation of, for example, chitosan (persistence length = 6.5 nm and inter-ion distance ~0.6 nm) with hyaluronic acid (persistence length = 4.0 nm and inter-ion distance ~1.3 nm) in which charges are twice as far apart.48-50
When charge matching is not possible due to this mismatch in inter-ion spacing, extrinsic sites occupied by non-polyelectrolyte-bound counterions are necessarily present so that one polymer is present in excess on a molar basis.\textsuperscript{51,52} The findings in the current study emphasize the potential to co-deposit rigid polyelectrolytes with variable interion distances as an additional avenue to control the polycation:polyanion ratio in LbL-assembled films.

<table>
<thead>
<tr>
<th>Pairing</th>
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<th>d_{OO}</th>
<th>Δ_{OP}</th>
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<td>1.717</td>
<td></td>
</tr>
<tr>
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<td>4.151</td>
<td>6.369</td>
<td>2.218</td>
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<tr>
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<td>2.336</td>
<td></td>
</tr>
<tr>
<td>SM3/HH</td>
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<tr>
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<td>5.880</td>
<td>0.632</td>
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<td>SM3/TT</td>
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<td>6.727</td>
<td>1.671</td>
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</tbody>
</table>

Table 5.2. Distances in optimized geometry from semi-empirical calculations at the AM1 level.
Figure 5.3 Optimized geometries obtained from semi-empirical calculations at the AM1 level: SM2 with HT (A) and SM3 with HT (B).
Conclusions

Spacer length and rigidity were proven to have significant influence on the properties of phosphonium polyelectrolytes, such as crystallinity and LbL supramolecular assembly. A dependence of film composition, film growth and surface roughness on spacer length and on whether the spacer had an odd or even number of methylene spacers was revealed. Nonpolar side chains reduce the thermal stability, crystallinity and glass transition temperatures of phosphonium polyelectrolytes. The presence of both ionic groups and hydrophobic segments/sidechains can facilitate domain segregation, which in turn drive film morphology and critical surface energy. The amount of material deposited in each layer of LbL self-assembled films of the phosphonium polymers with anionic polyelectrolytes was found to depend not only on flexibility of the backbone, but also on the inter-ion distance match between polyelectrolytes. The antimicrobial activity of the phosphonium polymers can also be related to structure, with hydrophobic sidechains and high cation density improving activity. Future work will build on the structure-property relationships elucidated by this work in an effort to rationally control surface morphologies, critical surface energies and self-assembly processes involving phosphonium polyelectrolytes.

ATTRIBUTION OF WORK

My contribution to the work in this chapter consisted of synthesis of anionic polymer, LbL fabrication and calculation. The other coworkers who are coauthors on the published portion of this chapter contributed to remaining areas of the study.
References


Supporting Information

Figure S5.1 Proton NMR spectrum of LX1 ((CD$_3$)$_2$SO, 300 MHz). Peak marked with an asterisk correspond to solvent signals.
Figure S5.2 Proton NMR spectrum of LX2 ((CD$_3$)$_2$SO, 300 MHz). Peak marked with an asterisk correspond to solvent signals.
Figure S5.3 Proton NMR spectrum of LX3 ((CD$_3$)$_2$SO, 300 MHz). Peak marked with an asterisk correspond to solvent signals.
Figure S5.4 Proton NMR spectrum of LX4 ((CD$_3$)$_2$SO, 300 MHz). Peak marked with an asterisk correspond to solvent signals.
Figure S5.5 Proton NMR spectrum of LX5 ((CD$_3$)$_2$SO, 300 MHz). Peak marked with an asterisk correspond to solvent signals.
Figure S5.6 Proton NMR spectrum of LX8 ((CD$_3$)$_2$SO, 300 MHz). Peak marked with an asterisk correspond to solvent signals.
Figure S5.7 Proton NMR spectrum of LXPh ((CD$_3$)$_2$SO, 300 MHz). Peak marked with an asterisk correspond to solvent signals.
**Figure S5.8** Proton NMR spectrum of Pc12 (CDCl₃, 300 MHz). Peak marked with an asterisk correspond to solvent signals.
Figure S5.9 Proton NMR spectrum of Pc12-100 (THF-d$_8$, 300 MHz). Peak marked with an asterisk correspond to solvent signals.
Figure S5.10 Phosphorous-31 NMR of compound LX1 ((CD$_3$)$_2$SO, 121 MHz)
Figure S5.11 Phosphorus-31 NMR of compound LX2 ((CD$_3$)$_2$SO, 121 MHz)
Figure S5.12 Phosphorous-31 NMR of compound LX3 ((CD$_3$)$_2$SO, 121 MHz)
Figure S5.13 Phosphorous-31 NMR of compound LX4 ((CD$_3$)$_2$SO, 121 MHz)
Figure S5.14 Phosphorous-31 NMR of compound LX5 \(((\text{CD}_3)_2\text{SO}, 121 \text{ MHz})\)
Figure S5.15 Phosphorous-31 NMR of compound LX8 ((CD$_3$)$_2$SO, 121 MHz)
Figure S5.16 Phosphorous-31 NMR of compound LXPh ((CD₃)₂SO, 121 MHz)
Figure S5.17 Proton NMR spectrum of LO2. Each peak marked with an asterisk correspond to a solvent signal.
Figure S5.18 Proton NMR spectrum of LO3. Peak marked with an asterisk correspond to solvent signals.
Figure S5.19 Proton NMR spectrum of LO4. Peak marked with an asterisk correspond to solvent signals.
Figure S5.20 Proton NMR spectrum of LO5. Peak marked with an asterisk correspond to solvent signals.
Figure S5.21 Proton NMR spectrum of LO8. Peak marked with an asterisk correspond to solvent signals.
Figure S5.22 Proton NMR spectrum of 1,4-bis(octyloxy)-2,5-xylene bis(triphenylphosphonium bromide). Peak marked with an asterisk correspond to solvent signals.
Figure S5.23 Phosphorus-31 NMR of compound LO2 (CDCl₃, 121 MHz).
Figure S5.24 Phosphorus-31 NMR of compound LO3 (CDCl3, 121 MHz).
Figure S5.25 Phosphorus-31 NMR of compound LO4 (CDCl3, 121 MHz).
Figure S5.26 Phosphorus-31 NMR of compound LO5 (CDCl₃, 121 MHz).
Figure S5.27 Phosphorus-31 NMR of compound L08 (CDCl$_3$, 121 MHz).
Figure S5.28 Phosphorus-31 NMR of M3(CDCl₃, 121 MHz)
**Figure S5.29** X-ray Powder Diffraction of LX polymers.
Figure S5.30. X-ray Powder Diffraction of LO polymers.
Figure S5.31 AFM (5x5 µm) 2D height images and 3D images of LbL films of LX with Pc12-100: LX1/Pc12-100 (A), LX2/Pc12-100 (B), LX3/Pc12-100 (C), LX4/Pc12-100 (D), LX5/Pc12-100 (E), LX8/Pc12-100 (F) and LXPh/Pc12-100 (G) and clean glass slide (H).
Figure S5.32 5×5 µm AFM 2D height images viewed from perpendicular to the film plane (left column) and 3D images (right column) of LO layer-by-layer with Pc12-100: LO2 (A), LO3-white (B), LO3-dark (C), LO4 (D), LO5 (E), LO8 (F) and clean glass slide (G).
CHAPTER SIX
HEAVIER MAIN GROUP ANALOGUES OF BODIPY

Introduction

Dipyrromethene (dipyrrin) has been widely studied as boron centered derivatives, 4-bora-3a,4a-diaza-s-indacene (BODIPY) (Figure 6.1) due to the distinctive photophysical properties and photochemical stability. BODIPYs are keeping attracting a lot of attention and widely investigated in the past three decades because of tremendous potential in biomedical\textsuperscript{1-8} sensing\textsuperscript{9-12} and optoelectronic\textsuperscript{13-20} applications. Besides BODIPYs, some other metal dipyrrinato complexes with fluorescent emission were also reported since 2004,\textsuperscript{21} including Zn (II)\textsuperscript{22-25}, Mg (II)\textsuperscript{26-27}, Ir (III)\textsuperscript{28}, Cu (II)\textsuperscript{29}, Al (II)\textsuperscript{30}, Sn (II)\textsuperscript{31-32}, etc.

Figure 6.1. Selected structure of BODIPY and coordination complexes of gallium (III) with N, N’ bidentate ligands

Coordination compounds of gallium (III) with NacNac species (e.g. Figure 6.1) were prepared and studied systematically.\textsuperscript{33-36} NacNac-Ga (III) complexes, however, didn’t have special property in photophysics in solution due to lack of chromophores and
conjugated structure along ligands. Dipyrrin is excellent candidate of chromophoric ligands because of their potential modification on backbone

![Diagram of GaDIPY]

**Scheme 6.1.** Formation and ORTEP representation of GaDIPY

The gallium coordination compounds are promising in a great deal of clinic research\(^{37-40}\) attracting plenty of attention as radiopharmaceuticals in application of radiolabeling large biomolecules\(^{41-44}\). As a hypothesis the gallium (III) might be possible to construct an N, N’ chelating complex with dipyrrins that having good photoluminescent properties. The first series of dipyrromethene coordination compound with gallium (III) was reported by Dr. Seth M. Cohen’s group on 2006.\(^{45-46}\) The synthetic route was using dipyrrin ligand and GaCl\(_3\) as starting materials under existence of triethylamie base, which is similar to traditional synthesis method of BODIPY. The pure product yielded was a 3-fold symmetric tris(dipyrrinato) with octahedral coordination geometry instead of a corresponding derivative of Cl-BODPY. This type of
tris(dipyrrinato) complexes have photoluminescence emission in green light range. The quantum yields, however, were not as high as other 1-fold and 2-fold bis(dipyrrinato) derivatives,\textsuperscript{22} in which only weak intensity of light was observed with UV light under room temperature (Φ=0.024). The formation of 3-fold complex can be contributed to larger radius of gallium atom endows higher coordination number. In order to obtain similar structure as BODIPY, we did some modification based on previous articles of coordination gallium complex\textsuperscript{37} and a relatively new route of quantitatively synthesizing of BODPY.\textsuperscript{47}

**Experimental**

All air-sensitive reactions were performed in an MBraun UNILab glovebox under nitrogen. Anhydrous solvents were dried and degassed using an MBraun solvent purifier. Chemicals were used without further purification after purchased. All the NMR spectra were collected on a Joel ECX-300 MHz spectrometer operating at 300 and 75 MHz for \textsuperscript{1}H and \textsuperscript{13}C, respectively. UV-Vis absorption spectra were acquired on a Cary 50 Spectrophotometer. Photoluminescence (PL) spectra were obtained on a Varian Eclipse fluorimeter in quartz cuvettes with a pathlength of 1 cm. Fluorescence spectra were recorded with a commercial fluorometer (Quantamaster, PTI, Inc.). Single crystal structure characterization was conducted using a Bruker D8 Venture singlecrystal diffractometer with an Incoatec Mo Kα microfocus source and Photon 100 CMOS detector. *The single crystal data was collected and resolved by Dr. Colin McMillen*

All DFT calculations were operated using Spartan ’16 software. The DFT calculation method is applying same as preview published reference.\textsuperscript{46} Equilibrium
geometry at ground state with density function B3LYP optimized in 6-31G* basis set and in vacuum.

**Synthesis procedure**

3,3',5,5'-tetramethyl-2,2'-dipyrromethene: The ligand was synthesized according to reference method.\(^{49-50}\) 3,5-dimethyl-1H-pyrrole-2-carbaldehyde (2.000 g, 16.24 mmol) was added to the mixture of 20 mL 48% HBr and 40 mL methanol. The reaction mixture was kept stirring and refluxing under protection of nitrogen flow for 2 hours. The precipitate in reaction mixture was separated via vacuum filtration and then rinsed with 200 mL diethyl ether to yield needle-like red crystal. The crystal product was suspended in 200 mL diethyl ether and 10 mL 28% ammonium hydroxide was added with stirring in the open air. The reaction mixture was kept stirring for 30 min and then washed with 3×50 mL deionized water. The orange diethyl ether solution was dried over anhydrous Na\(_2\)SO\(_4\). The organic solvent was evaporated via rotary evaporator to yield orange crystal (1.339 g, 82.44%). \(^1\)H NMR (300 MHz, CDCl\(_3\), 25 °C): δ 2.22 (s, 6H), 2.33 (s, 6H), 5.96 (s, 2H), 6.70 (s, 1H), 8.78 ppm (br, 1H). \(^1\)C NMR (75 MHz, CDCl\(_3\), 25 °C): δ 11.47, 16.24, 116.67, 117.23, 137.59, 138.60, 152.99 ppm. Anal. Calc’d for C\(_{13}\)H\(_{16}\)N\(_2\): C, 77.96%; H, 8.05%; N, 13.99%.

**GADIPY:**

Method I: 3,3',5,5'-tetramethyl-2,2'-dipyrromethene (0.800 g, 4.00 mmol) was dissolved in 15 mL anhydrous dichloromethane, after 1 M lithium bis(trimethylsilyl)amide in tetrahydrofuran (4.20 mL, 4.20 mmol) added, the reaction
mixture was kept stirring in N\textsubscript{2} at room temperature for 2 hours to yield the free base dipyrromethene solution. In a separate vessel, GaCl\textsubscript{3} (0.705 g, 4.00 mmol) and diphenylchlorophosphine (0.882 g, 4.00 mmol) were stirred in 20 mL CH\textsubscript{2}Cl\textsubscript{2} at room temperature for 1 hour to generate [Ph\textsubscript{3}PPPh\textsubscript{2}]\textsuperscript{+}[GaCl\textsubscript{4}] \textit{in situ}.\textsuperscript{51} The free base dipyrromethene solution was then added in one portion and stirring was continued overnight. Upon cooling to -40 °C, dark red needle-like crystals formed. The solution was decanted from the crystals and the crystals were rinsed with 10 mL toluene then 5 mL of refluxing CH\textsubscript{2}Cl\textsubscript{2}. After cooling this mixture to -40 °C for 2 h, the pure compound was separated via vacuum suction filtration and yielded as red small crystals. (0.606 g, 44.2 %)

Method II: To the solution of Ph\textsubscript{4}PCl (187 mg, 0.500 mmol) in 2 mL anhydrous DCM, GaCl\textsubscript{3} (88.1 mg, 0.500 mmol) was added and kept stirring 2h.\textsuperscript{52} The base-free 3,3',5,5'-tetramethyl-2,2'-dipyrrinato lithium (0.500 mmol) in 2 mL DCM was added to reaction mixture and stirred overnight in N\textsubscript{2} atmosphere. After the reaction completed the crude mixture was cooled down in -40 °C freezer and the crude product was isolated via vacuum filtration. The crude product was then heated with 3 mL DCM, and the pure compound was precipitated and separated by vacuum filtration after cooled in -25°C freezer over 2 h. (72 mg, 42.4 %)

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, 25 °C): δ 2.31 (s, 6H), 2.58 (s, 6H), 6.18 (s, 2H), 7.03 ppm (s, 1H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}, 25 °C): δ 11.80, 16.27, 119.36, 121.37, 134.88, 145.49, 159.43 ppm. Anal. Calc’d for C\textsubscript{13}H\textsubscript{15}Cl\textsubscript{2}GaN\textsubscript{2}: C, 45.94; H, 4.45; N, 8.24. Found: C, 96.01; H, 4.43; N, 8.20.
Result and Discussion

In this chapter, firstly free-base dipyrrinato lithium and tetraphenylphosphonium tetrachlorogallate ([Ph₄]•[GaCl₄]) were prepared as precursors, then followed with replacement reaction between these two complexes (Scheme 6.1). The new prepared 4,4-Difluoro-1,3,5,7-tetramethyl-4-gallium-3a,4a-diaza-s-indacene (GADIPY) presents extremely strong green fluorescence emission in different solvent from nonpolar to polar solvent, and the highest quantum yield was discovered in toluene solution. The single crystal of GADIPY suitable for X-ray diffraction analysis was obtained easily by recrystallization from CH₂Cl₂ or using vapor diffusion (CH₂Cl₂/pentane). Based on single crystal structure, all carbon and nitrogen atoms in the ligand are coplanar with gallium in the molecule, and two chloride atoms are symmetric toward the plane (supporting information). The length of Ga-N bond in GADIPY (1.896 Å) is much shorter than tris(dipyrrinato) gallium complexes (2.054 Å), which means strength of dipyrrin is much stronger than NacNac ligands.

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<th>λ_{em}</th>
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<td>382&lt;sup&gt;d&lt;/sup&gt;</td>
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Table 6.1. Collection of Photophysical Properties of GADIPY and References in Different Solvents
a: Reference standard sample to measure quantum yield. b: All data of BODPY is from references\textsuperscript{48}. c: Measured as crystalline status. d: Measured in THF ($1 \times 10^{-5}$ M) solution. e: Measured in hexane ($1 \times 10^{-6}$ M) solution.

**Figure 6.2** a) UV-vis absorbance spectra (blue-DCM, purple-hexane, red-toluene) and b) fluorescence spectra (in dichloromethane solution) of GADIPY (blue-excitation, orange-emission) at room temperature.

**Figure 6.3** Partial calculated energy level and frontier orbitals of Cl-BODIPY (right) and GADIPY (left).
Photophysical properties GADIPY have been investigated in different solvent with varying polarity from nonpolar to strong polar (Table 6.1). GADIPY shows strong absorption in the range of 490-500 nm ($\lambda_{\text{max}}$=494 nm, $\varepsilon$=5.1×10$^4$ M$^{-1}$·cm$^{-1}$ in DCM), which attributes to $\pi$-$\pi^*$ transition. Comparing to the BODIPY ($\lambda_{\text{max}}$=505 nm in DCM) with same skeleton structure, GADIPY has slightly hypsochromic shift (11 nm). For GADIPY, it displays absorption peak at 497 nm in toluene, which is bathochromically shifted 3 nm with respect to the solution of hexane and DCM. The GaDIPY presents remarkable green photoluminescence in different solution phases in the range of 499-505 nm. It is well-known that BODIPY dye series have typical small Stokes shift. The new prepared GADIPY has even smaller Stokes shift than the BODIPY with identical ligand (Table 6.1). The quantum yield of GADIPY was investigated by using fluorescein in 0.1 M NaOH as standard reference. The quantum yield of GADIPY is relatively high in different solvent varying from 0.71 to 0.91. In the same solvent, quantum yield ($\Phi$) of GADIPY (0.82 in DCM) slightly exceeds that of corresponding $F$-BODIPY (0.80 in DCM). Density functional theory (DFT) calculation shows that HOMO/LUMO energy gap of the GADIPY (3.0 eV) almost same as $Cl$- BODIPY (2.9 eV)/ $F$-BODPY (3.0 eV) (Figure 2), which is well matched experimental result.

**Conclusion**

In summary, the gallium analog of BODIPY has been prepared as an outstanding fluorophore successfully. Its structural property was characterized via crystallographic result, NMR structure and elemental analysis. The photoluminescent quantum yield of
GADIPY is extremely high in various solvent especially in toluene, and is comparable to corresponding BODIPY in the same solvent.

ATTRIBUTION OF WORK

My contribution to the work in this chapter consisted of: synthesis, NMR, UV-vis absorption, fluorescence, calculation. The other coworkers who are coauthors on the published portion of this chapter contributed to remaining areas of the study.
References


**Supporting Information**

**Figure S6.1.** $^1$H-NMR spectrum of dipyrrin 1 (CDCl$_3$). Each peak marked with an asterisk corresponds to a solvent signal.
**Figure S6.2.** $^{13}$C-NMR spectrum of dipyrrin 1 (CDCl$_3$). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S6.3. $^1$H-NMR spectrum of GADIPY 1 (CDCl$_3$). Each peak marked with an asterisk corresponds to a solvent signal.
Figure S6.4. $^{13}$C-NMR spectrum of GADIPY 1 (CDCl$_3$). Each peak marked with an asterisk corresponds to a solvent signal.
**Figure S6.5** UV-vis absorption spectra of **GADIPY 1** in dichloromethane (green), hexane (blue) and toluene (purple).
**Figure S6.6** Fluorescence spectra of **GADIPY 1** in hexane (up) and toluene (down)
**Crystallographic Data** Single crystal data was collected by Dr. Colin McMillen

**Crystal Structure Report for GaCl$_2$(C$_{13}$H$_{15}$N$_2$)**

A specimen of C$_{13}$H$_{15}$Cl$_2$GaN$_2$, approximate dimensions 0.041 mm x 0.044 mm x 0.167 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using an orthorhombic unit cell yielded a total of 25774 reflections to a maximum θ angle of 27.50° (0.77 Å resolution), of which 1738 were independent (average redundancy 14.830, completeness = 99.9%, $R_{int} = 4.25\%$, $R_{sig} = 1.70\%$) and 1521 (87.51%) were greater than 2σ(F$^2$). The final cell constants of $a = 11.1875(8)$ Å, $b = 7.2452(5)$ Å, $c = 17.2577(12)$ Å, volume = 1398.83(17) Å$^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8807 and 1.0000.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P n m a, with $Z = 4$ for the formula unit, C$_{13}$H$_{15}$Cl$_2$GaN$_2$. The final anisotropic full-matrix least-squares refinement on F$^2$ with 110 variables converged at $R_1 = 2.31\%$, for the observed data and $wR_2 = 5.35\%$ for all data. The goodness-of-fit was 1.088. The largest peak in the final difference electron density synthesis was 0.329 e/Å$^3$ and the largest hole was -0.306 e/Å$^3$ with an RMS deviation of 0.063 e/Å$^3$. On the basis of the final model, the calculated density was 1.614 g/cm$^3$ and F(000), 688 e$^-$. 

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Table 1. Sample and crystal data for D8_2279_WW_Dipy.

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<td>F(000)</td>
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table_2.png

Table 2. Data collection and structure refinement for
Theta range for data collection 2.36 to 27.50°

Index ranges -14<=h<=14, -9<=k<=9, -22<=l<=22

Reflections collected 25774

Independent reflections 1738 [R(int) = 0.0425]

Max. and min. transmission 1.0000 and 0.8807

Structure solution technique direct methods

Structure solution program SHELX-2014 (Sheldrick 2014)

Refinement method Full-matrix least-squares on $F^2$

Refinement program SHELXL-2014 (Sheldrick 2014)

Function minimized $\sum w(F_o^2 - F_c^2)^2$

Data / restraints / parameters 1738 / 0 / 110

Goodness-of-fit on $F^2$ 1.088

$\Delta/\sigma_{\text{max}}$ 0.001

Final R indices 1521 data; $R1 = 0.0231$, $wR2 = \_\_\_$
I > 2σ(I) 0.0514

R1 = 0.0297, wR2 =

all data 0.0535

Weighting scheme

w = 1/[σ²(Fo²) + (0.0218P)² + 1.0106P]

where P = (Fo² + 2Fc²)/3

Largest diff. peak and
hole

0.329 and -0.306 eÅ⁻³

R.M.S. deviation from
mean

0.063 eÅ⁻³

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for D8_2279_WW_Dipy.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

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Table 4. Bond lengths (Å) for D8_2279_WW_Dipy.

Ga1-N2   1.8949(19) Ga1-N1   1.898(2)
Ga1-Cl1  2.1694(5)  Ga1-Cl1   2.1694(5)
N1-C1    1.356(3)   N1-C4     1.408(3)
N2-C9    1.351(3)   N2-C6     1.405(3)
C1-C2    1.392(4)   C1-C10    1.493(3)
C2-C3  1.390(3)  C2-H2  0.95
C3-C4  1.419(3)  C3-C11  1.499(3)
C4-C5  1.390(3)  C5-C6  1.383(3)
C5-H5  0.95  C6-C7  1.424(3)
C7-C8  1.382(3)  C7-C12  1.492(3)
C8-C9  1.395(3)  C8-H8  0.95
C9-C13  1.492(3)  C10-H10A  0.98
C10-H10B  0.98  C10-H10C  0.98
C11-H11A  0.98  C11-H11B  0.98
C11-H11C  0.98  C12-H12A  0.98
C12-H12B  0.98  C12-H12C  0.98
C13-H13A  0.98  C13-H13B  0.98
C13-H13C  0.98

Table 5. Bond angles (°) for D8_2279_WW_Dipy.

N2-Ga1-N1  98.77(8)  N2-Ga1-Cl1  111.10(3)
N1-Ga1-Cl1  113.46(3)  N2-Ga1-Cl1  111.10(3)
N1-Ga1-Cl1  113.46(3)  Cl1-Ga1-Cl1  108.70(3)
C1-N1-C4  107.3(2)  C1-N1-Ga1  130.38(17)
C4-N1-Ga1  122.31(15)  C9-N2-C6  107.56(19)
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Table 6. Anisotropic atomic displacement parameters (Å²) for D8_2279_WW_Dipy.
The anisotropic atomic displacement factor exponent takes the form: 
-2π² [ h² a² * U₁₁ + ... + 2 h k a * b * U₁₂ ]

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<td>0.0175(12)</td>
<td>0</td>
<td>-0.0002(9)</td>
<td>0</td>
</tr>
<tr>
<td>C100</td>
<td>0.0161(12)</td>
<td>0.0434(17)</td>
<td>0.0339(15)</td>
<td>0</td>
<td>-0.0053(11)</td>
<td>0</td>
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<td>C110</td>
<td>0.0297(14)</td>
<td>0.0345(15)</td>
<td>0.0165(12)</td>
<td>0</td>
<td>-0.0001(10)</td>
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<tr>
<td>C120</td>
<td>0.0159(12)</td>
<td>0.0311(14)</td>
<td>0.0214(12)</td>
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<td>0.0001(10)</td>
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<td>C130</td>
<td>0.0194(13)</td>
<td>0.0502(18)</td>
<td>0.0173(12)</td>
<td>0</td>
<td>0.0010(10)</td>
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Table 7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) for D8_2279_WW_Dipy.

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<tr>
<th></th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq)</th>
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<tr>
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<td>0.047</td>
</tr>
<tr>
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<td>0.047</td>
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<tr>
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<tr>
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