INVESTIGATION OF PHOTOPHYSICAL PROPERTIES FOR POLY(PHENYLENE ETHYNYLENE)-BASED CONJUGATED POLYELECTROLYTES VIA CHAIN-GROWTH POLYMERIZATION

By

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To my family
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<th>Definition</th>
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<tr>
<td>CPDs</td>
<td>Conjugated polyelectrolyte dendrimers</td>
</tr>
<tr>
<td>CPEs</td>
<td>Conjugated polyelectrolytes</td>
</tr>
<tr>
<td>CPs</td>
<td>Conjugated polymers</td>
</tr>
<tr>
<td>CTP</td>
<td>Catalyst transfer polymerization</td>
</tr>
<tr>
<td>DAP or DArP</td>
<td>Direct arylation polymerization</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>Dppe</td>
<td>1,2-bis(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>Dppf</td>
<td>1,1’-bis(diphenylphosphino)ferrocene</td>
</tr>
<tr>
<td>ES</td>
<td>Excited state</td>
</tr>
<tr>
<td>FCS</td>
<td>Fluorescence correlation spectroscopy</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>GS</td>
<td>Ground state</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest occupied molecular orbital</td>
</tr>
<tr>
<td>MALDI-TOF</td>
<td>Matrix-assisted laser desorption ionization time-of-flight</td>
</tr>
<tr>
<td>Mn</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectroscopy</td>
</tr>
<tr>
<td>MV&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>Methyl viologen</td>
</tr>
<tr>
<td>PA</td>
<td>Polyacetylene</td>
</tr>
<tr>
<td>PANI</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbazole</td>
</tr>
<tr>
<td>PDA</td>
<td>Photo diode array</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity</td>
</tr>
<tr>
<td>PE</td>
<td>Phenyleneethynylene</td>
</tr>
<tr>
<td>PF</td>
<td>Polyfluorene</td>
</tr>
<tr>
<td>PI</td>
<td>Polyindole</td>
</tr>
<tr>
<td>PPE</td>
<td>Poly(paraphenylenethynylene)</td>
</tr>
<tr>
<td>PPE-SO3-</td>
<td>Sulfonated poly(phenyleneethynylene)</td>
</tr>
<tr>
<td>PPI</td>
<td>Polyisocyanide</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>PPP</td>
<td>Poly(paraphenylene)</td>
</tr>
<tr>
<td>PPV</td>
<td>Poly(paraphenylene vinylene)</td>
</tr>
<tr>
<td>PPy</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>PT</td>
<td>Polythiophene</td>
</tr>
<tr>
<td>PTI</td>
<td>Photon Technology International</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electron</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>STEM-EDX</td>
<td>X-ray spectroscopy</td>
</tr>
<tr>
<td>SV</td>
<td>Stern-Volmer equation</td>
</tr>
<tr>
<td>TBAF</td>
<td>Tetrabutylammonium fluoride</td>
</tr>
<tr>
<td>TCSPC</td>
<td>Time-correlated single photon counting</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TMS</td>
<td>Trimethylsilyl</td>
</tr>
<tr>
<td>TT</td>
<td>Tail-to-tail</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>( T )</td>
<td>Fluorescence lifetime</td>
</tr>
<tr>
<td>( \Phi )</td>
<td>Fluorescence quantum yield</td>
</tr>
</tbody>
</table>
Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

INVESTIGATION OF PHOTOPHYSICAL PROPERTIES FOR POLY(PHENYLENE ETHYNYLENE)-BASED CONJUGATED POLYELECTROLYTES VIA CHAIN-GROWTH POLYMERIZATION

By

Bethy Kim

August 2017

Chair: Kirk S. Schanze
Cochair: Lisa McElwee-White
Major: Chemistry

In the past several decades, conjugated polyelectrolytes (CPEs) have been intensively investigated due to their unique photophysical properties. Typically, palladium-catalyzed Sonogashira cross-coupling reactions are used for the synthesis of poly(phenylene ethynylene) (PPE)-based CPEs with diiodo- and diacetylene-functionalized monomers. However, the Sonogashira cross-coupling reaction is a step-growth polymerization. Therefore, it is difficult to control the polymer’s physical properties, such as molecular weight, polydispersity, and end-group fidelity. Also, when the reaction solution is exposed to the air, an acetylene homo-coupled structure can be formed in the polymer backbone. The acetylene homo-coupled structure may enhance the intramolecular π-stacking interaction and induce the aggregation of CPEs, resulting in fluorescence quenching by energy transfer of excitons to the lowest energy aggregation site traps. Therefore, the diiodo- and diacetylene-functionalized palladium catalyzed Sonogashira cross-coupling condition needs to be modified to diminish the acetylene homo-coupled structure in the polymer backbone.
In this dissertation, we focused on the synthesis of bi-functionalized AB-type PPE-based CPEs by chain-growth palladium catalyst-transfer polymerization (CTP) to reduce the homo-coupling defect. Chapter 2 described the synthesis of carboxylated PPE-based CPEs (chain-growth C-ab, step-growth S-ab, step-growth S-aabb, and step-growth S-aa). Due to the use of AB-type monomer, chain-growth PPE-based CPEs reduced the acetylene homo-coupled structure in the polymer backbone. Therefore, the C-ab showed improved fluorescence quantum yield ($\Phi = 35\%$ compared to the reported CPE, P1-O ($\Phi = 4\%$)). In chapter 3, di-, tri-, and tetra-functionalized carboxylated PPE-based CPEs (2Pd, 3Pd, and 4Pd, respectively) were prepared. Due to their unique core structures, the 2Pd showed linear, and 3Pd/4Pd showed star-shaped structures. In water, the 2Pd, and 4Pd showed fluorescence efficiency as $\approx 50\%$. However, the 3Pd CPE showed aggregation in water because of the planar core of polymer according to emission spectra and fluorescence quenching results compared to 2Pd and 4Pd CPEs. In chapter 4, PPE-based CPEs with sulfonated and imidazolium side groups (chain-growth/step-growth SO$_3$-Na, chain-growth/step-growth NR$_4$-Br) were synthesized by AB type palladium catalyzed CTP. In the case of sulfonated PPE-based CPEs, the chain-growth C-SO$_3$-Na showed well-structured absorption and emission spectra in aqueous solution. Also, the fluorescence quantum yield of C-SO$_3$-Na was obtained as $\Phi_{fl} = 30\%$. In the cases of C-NR$_4$-Br and S-NR$_4$-Br, the fluorescence quantum yield was obtained as $\Phi_{fl} = 33$ and 26% compared to previously reported imidazolium CPE, PIM-4 ($\Phi_{fl} = 34\%$). This result suggested that the bulky and positively charged imidazolium group may reduce aggregation, making it hard to observe the defect of the acetylene homo-coupled structure in the polymer backbone.
CHAPTER 1
INTRODUCTION

1.1 Conjugated Polymers

Conjugated polymers (CPs) have alternating multiple- and single-bonded backbones with π-delocalized electronic structures. In 1967, the first conjugated polymer, polyacetylene (PA), was reported by Hideki and Shirakawa (Figure 1-1).\textsuperscript{2-4} Followed by the first development of the PA, iodine-doped polyacetylene with high conductivity was discovered by Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa, who went on to win the 2000 Nobel Prize in Chemistry for their discovery.\textsuperscript{5-6} In subsequent years, various kinds of CPs have been investigated, such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PT), poly(paraphenylene) (PPP), poly(paraphenylene vinylene) (PPV), polyfluorene (PF), poly(phenylene ethynylene) (PPE), and polycarbazole (PC). (Figure 1-1).\textsuperscript{4,7}

\begin{figure*}[h]
\centering
\includegraphics[width=\textwidth]{conjugated_polymers.png}
\caption{Examples of conjugated polymers. Figure was reprinted from Hall with permission.\textsuperscript{5} Copyright 2010 The Royal Society of Chemistry}
\end{figure*}

CPs have features with linear and rigid backbones consisting of conjugated aromatic rings or multiple covalent bonds. Bunz and co-workers investigated the electrical properties of poly(phenylene ethynylene) (PPE) backbones to explain their optical behavior (Figure 1-2).\textsuperscript{4} The
single bond can easily rotate between the phenyl and ethynylene units in the PPE in the ground state. Therefore, the deviation from planarity between phenylene ethynylene (PE) units allows localization of electrons along the polymer backbone. Thus, the highest occupied molecular orbital (HOMO) of the polymer is stabilized, and the lowest unoccupied molecular orbital (LUMO) is destabilized. However, in the excited state, rotations around the PE units are not favorable due to their allenic structure, which prefers the planar structure upon releasing the twisted double bonds (Figure 1-2). As a result, the electrons can be delocalized through the polymer backbone. Thus, the HOMO-LUMO gap decreases as the planarity of the backbone increases, leading to lower energy needed to excite the electrons to the LUMO. Likewise, the conductivity of PPEs can be improved. There have been many efforts to develop synthetic methodology and to make use of PPEs in various organovoltaic materials and bio/chemo-sensing devices.

Figure 1-2. The structure of PPEs in the ground state (top) and the excited state (bottom). Figure was reprinted from Bunz et al. with permission. Copyright 2001 American Chemical Society
1.2 Conjugated Polyelectrolytes

1.2.1 Linear Conjugated Polyelectrolytes

Conjugated polyelectrolytes (CPEs) are polymers with π-delocalized electrons through the conjugated backbone and ionic side chains. Because of the ionic side chains, CPEs dissolve in polar organic solvents and aqueous solution. CPEs have been extensively studied because of their potential optical applications in sensing materials, photovoltaic devices, and organic light-emitting materials. Moreover, their water solubilizing ionic groups allow CPEs to be applied to bio-molecular targets. The coexistence of a hydrophobic backbone and hydrophilic ionic groups produce CPEs amphiphilic. Therefore, the CPEs have the ability to self-assemble and aggregate depending on the solvent polarity.

In 1987, Wudl, Heeger and colleagues published the first examples of CPEs, 3-(2-sulfonatoethyl) substituted, and 3-(4-sulfonatobutyl) substituted polythiophene. After their first reports of water soluble CPEs, various ionic side groups were introduced on the conjugated polymer backbones. In particular, sulfonate, carboxylate, phosphate, and alkyl ammonium, either linear or branched have been investigated for their photophysical properties in polar organic solvents and aqueous solution (Figure 1-3). The conjugated backbones, such as poly(phenylene ethynylene) (PPE), polyfluorene (PF), and polythiophene (PT), have been studied with cationic and anionic side chains. Furthermore, reviews on the applications of CPEs in organic photovoltaic devices have been published by Schanze, Reynolds, Cao, Scherf, and Bazan. Thus, CPEs soluble in polar organic solvents and water are promising materials for application in sensors and optoelectronic devices, as their structures can be tuned for targeted molecular recognition and photophysical properties.
1.2.2 Dendrimers and Star-shaped Conjugated Polyelectrolytes

The term “dendrimer” is derived from the Greek words Dendron and meros, which mean “tree” and “part,” respectively, because of their tree-like structures. A dendrimer consists of three architectural units: a surface functionalized group, interior branches, and a central core. Conjugated dendrimers are essential for applications in organic photovoltaics because of their well-defined shape-persistent structures, and optical properties.\(^\text{25}\)

Schanze and colleagues reported dendrimeric π-conjugated PPE-based CPEs that are surrounded by carboxylate groups. (Figure 1-4).\(^\text{26}\) This study demonstrated the amplified quenching effect of the dendrimeric CPEs, which is due to the interaction between CPEs and oppositely charged quenchers. However, unlike well-defined conjugated dendrimers, conjugated polyelectrolyte dendrimers (CPDs) are still ill-defined and poorly-controlled due to difficulties in predicting the accuracy of branching during synthesis.\(^\text{1}\) Considerable effort has been expended to improve synthetic methods and produce well-defined CPDs. Because photophysical properties of
CPDs are dependent on their terminal functional groups, introduction of various terminal functionalities on CPDs extends the possible application areas in sensing and photovoltaic devices.

Figure 1-4. Structure of dendrimeric conjugated polyelectrolyte. Figure was reprinted from Schanze et al. with permission. Copyright 2012 American Chemical Society

Star-shaped polymers are branched polymers consisting of linear chains connected to a core. The arms of a homogeneous star-shaped polymer are equivalent in structure and length. On the other hand, heterogeneous star-shaped polymers have arms with variable lengths and structures. Star-shaped polymers are prepared by either an arm-first or core-first pathway. Usually, the mono-functionalized living polymer is synthesized by the arm-first pathway. Each
activated arm terminus reacts directly with the polymer core to produce a star-shaped polymer. Because each terminus can be controlled, the arm-first pathway is the most popular synthetic route to prepare well-defined star-shaped polymers. In the core-first pathway, a multi-functionalized core reacts with multiple arms at the same time. A pioneering study of star-shaped polyamides was reported by Schaefgen and Flory in 1948. In 2006, Yoshida and colleagues reported the light-emitting properties of π-conjugated star-shaped polymers with a 1,3,5-triethynylbenzene cores and methoxy substituted oligo(p-phenyleneethynylene)s as arms.

In 2011, star-shaped glycosylated conjugated oligomers were reported by Liu and colleagues (Figure 1-5). In photophysical analysis, both the absorption and emission spectra of 4,4',4''-tris(4-(2-(4-(benzo[d]thiazol-2-yl)phenyl)-9,9'-bis(6-thiol-[β-D-glucose]-hexyl)-fluorene-7-yl)-phenylamine (TFBS) and 4,4',4''-tris(4-(2-(4-(benzo[d]thiazol-2-yl)phenyl)-9,9'-bis(6-N,N,N-trimethylammonium)-hexyl)-fluorene-7-yl)-phenylamine (TFBC) are almost the same in DMSO (λ_{abs} = 388 nm, λ_{em} = 660 nm and ϕ_{fl} = 0.09). (Figure 1-6). In water, the absorption maxima for TFBS and TFBC were observed at 384 and 388 nm, while the emission maxima were observed at 575 nm and 533 nm (TFBS and TFBC, respectively). The fluorescence quantum yields of TFBC and TFBS were 0.03 and 0.10, respectively, in water. Due to the hydrophilic glucose group, TFBS formed a self-assembled structure, which showed the two-photon absorption, while the two-photon absorption was not measurable in the case of TFBC because of its low fluorescence quantum yield in water.
1.2.3 Photophysical Properties of Conjugated Polyelectrolytes

The absorption and emission of light are typically explained by a Jablonski diagram (Figure 1-7). Once a molecule is excited from the ground state ($S_0$) to the excited state ($S_n$, $n = 1, 2, 3$, etc.), the molecule remains in the excited state until relaxation occurs. A Jablonski diagram
shows the relative vibrational and electronic energy modes of the ground and excited states. Each of the electronic energy levels contains several vibrational energy levels.

After excitation, molecules lose energy by either radiative or non-radiative decay. The radiative relaxation pathway involves fluorescence or photoluminescence. The non-radiative channel occurs through electron transfer, energy transfer, aggregation-induced quenching or fluorescence quenching. Typically, the emission spectrum is a mirror image of the absorption spectrum, displaced to longer wavelength. Excitation occurs from the lowest vibrational level of the ground state to an upper vibrational level of the excited state. The excited state rapidly undergoes vibrational relaxation to the lowest vibrational level prior to emission to an upper vibrational level in the ground state. Thus, the emission wavelengths are always longer than the absorption wavelengths, except for the case of excitation to \( \nu = 0 \) in the excited state and emission directly back to \( \nu = 0 \) in the ground state.
The photophysical properties of conjugated polyelectrolytes have been investigated according to their polymer backbones and ionic side chains.\textsuperscript{19, 22-24} The optical properties depend strongly on the solvent environment because of the cationic or anionic side groups.

Figure 1-8. PPE-SO\textsubscript{3}\textsuperscript{-}. (a) Absorption spectra and (b) fluorescence spectra. Figure was reprinted from Schanze et al. with permission.\textsuperscript{17} Copyright 2002 The Royal Society of Chemistry

A clear example of aggregation-induced self-quenching is shown in Figure 1-8, which was reported by Schanze and colleagues.\textsuperscript{34} Figure 1-8 shows the absorption and fluorescence emission spectra of PPE-SO\textsubscript{3}\textsuperscript{-} in methanol, 1:1 methanol:water, and in water. As the water content increases in the solution, the absorption and emission spectra of PPE-SO\textsubscript{3}\textsuperscript{-} were red-shifted (longer wavelength). Also, the emission spectra of PPE-SO\textsubscript{3}\textsuperscript{-} showed broad, ill-structured shapes, indicating aggregate formation. However, in methanol, the absorption and emission spectra were sharp, mimicking the spectra of a conjugated polymer in an organic solvent. Based
on these results, the \( \pi \)-stacking interaction between PPE-SO\(_3\) polymer chains are enhanced in water, thus inducing the fluorescence quenching.

1.3 Measurement of Aggregation in Aqueous Solution

Due to their amphiphilic nature (hydrophobic backbone and hydrophilic side chain), conjugated polyelectrolytes tend to aggregate in aqueous solution or polar organic solvents. The aggregation of conjugated polyelectrolytes has been extensively studied to gain a fundamental understanding of the amplified fluorescence quenching, as well as for applications in bio- and chemo-sensing and optoelectronic devices.\(^{16,35-37}\) There are several measurements to analyze the aggregation of conjugated polyelectrolytes in aqueous solution, including fluorescence quantum yield, fluorescence lifetime, fluorescence quenching, fluorescence correlation spectroscopy (FCS), and dynamic light scattering (DLS).

1.3.1 Fluorescence Quantum Yield and Fluorescence Lifetime

Measurement of fluorescence quantum yield and lifetime are valuable ways to characterize the fluorescence efficiency of conjugated polyelectrolytes. The fluorescence quantum yield (\( \phi \)) is the number of emitted photons relative to the number of absorbed photons. The fluorescence lifetime (\( \tau \)) is the average time that a molecule spends in the excited state before decaying to the ground state. The lifetime is determined by time-correlated single-photon counting (TCSPC)-coupled fluorescence lifetime spectrometry.

In 2014, Könen and Schanze reported the photophysical properties of carbon-, and oxygen-linked poly(phenylene ethynylene) (PPE) (Figure 1-9).\(^1\) Compared to the carbon-linked polymers (P1-C and P2-C), the oxygen-linked polymers (P1-O and P2-O) tended to aggregate in aqueous solution, as indicated by their broad and ill-structured emission spectra. Especially, in the case of P1-O, the fluorescence quantum yield was only 4\% (while both P1-C and P2-C
showed 16%), and the fluorescence lifetime (0.06 ns) was shorter than that of the P1-C polymer (0.43 ns) in water. They postulated that the oxygen may contribute to the planarity of PPE backbone, leading to formation of a hydrogen bond with the solvent. Therefore, the polymer chain of P1-O exhibit strong π-stacking interaction. Likewise, the fluorescence of P1-O was quenched by aggregation-induced fluorescence self-quenching.

Figure 1-9. Absorption and emission spectra of carboxylate PPE-based CPEs. Figure was reprinted from Schanze et al. with permission.© Copyright 2014 American Chemical Society
1.3.2 Stern-Volmer Fluorescence Quenching

Fluorescence quenching occurs via the processes of fluorescence resonance energy transfer, electron transfer, and intersystem crossing. Fluorescence quenching causes a decrease of the fluorescence efficiency. There are two ways to explain fluorescence quenching: dynamic quenching and static quenching (Figure 1-10).

![Diagram of Stern-Volmer fluorescence quenching](image)

**Figure 1-10.** Mechanism of Stern-Volmer fluorescence quenching. Figure was reprinted from Lakowicz with permission.\(^{33}\) Copyright 2007 Springer

Regarding dynamic quenching, also called collisional quenching, the excited molecules return to the ground state without photon emission because of collision with a quencher. In the case of static quenching, the excited molecules and quencher form a non-fluorescent complex, immediately. The Stern-Volmer (SV) equation 1-1 is:

\[
\frac{I_0}{I} = 1 + K_{sv}[Q]
\]

**(Equation 1-1)**

where \(I_0\) and \(I\) are the fluorescence intensities observed in the absence and presence of quencher, \([Q]\) is the quencher concentration and \(K_{sv}\) is the Stern-Volmer quenching constant.

A plot of \(I_0/I\) versus \([Q]\) is linear with a slope of \(K_{sv}\), which is used to characterize the quenching process. In the case of the CPEs in Figure 1-9, static quenching is dominant because of the opposite ionic charges of polyelectrolytes and the quencher (methyl viologen, Figure 1-11). Oxygen-linked P2-O had the largest \(K_{sv} (\sim 19 \times 10^6 \text{ M}^{-1})\), compared to the other
polyelectrolytes, indicating that P2-O is the most sensitive fluorophore to methyl viologen in aqueous solution.

\[
\text{H}_3\text{C} - \text{N} - \text{CH}_3
\]

Figure 1-11. Structure of methyl viologen (MV\(^{2+}\))

1.3.3 Fluorescence Correlation Spectroscopy (FCS)

The first report of fluorescence correlation spectroscopy (FCS) was in the 1970s by Madge, Elson, and Webb, who measured spontaneous fluctuations of fluorescence intensity.\(^{38}\) Figure 1-12 describes the working principles of FCS. FCS monitors the fluctuation of fluorescence intensity of molecules within a femtoliter excitation volume. Commonly, FCS is installed with confocal optics. The confocal volume, which means “in-focus” volume in a sample is detected by the confocal optics in FCS. FCS provides information regarding molecule diffusion behavior in solution, which is related to size and conformation.\(^ {39}\) In our work, we applied FCS to study the aggregation state and size of PPE-based CPEs.

Figure 1-12. Working principles for FSC. Adapted from Wu, D\(^ {39}\)
1.3.4 Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS) is a technique used to analyze the particle size distribution in solution. DLS is useful for characterizing particles such as proteins, nanoparticles, and polymers. DLS measurement is dependent on the size of the particle and the particle concentration. Also, time-dependent analysis of DLS provides information of aggregation of polymer particles in solution.

1.4 Synthetic Methodology for Conjugated Polymers

1.4.1 Preparation of Conjugated Polymers

Most commonly, poly(phenylene ethynylene)s (PPEs) are prepared by condensation reaction of a 1,4-diethynylbenzene with a 1,4-dihaloarene by the Sonogashira cross-coupling reaction or by alkyne metathesis. The Sonogashira cross-coupling reaction is a useful method for C (sp²)-C(sp) bond formation in the polymerization (Figure 1-13). However, in all cases, the polymerization occurs via a step-growth mechanism, in which there are challenges in molecular weight control, polymer dispersity, and end-group functionality.

![Figure 1-13. The Sonogashira cross-coupling reaction condition](image)

1.4.2 Mechanism of the Sonogashira Cross-coupling Reaction

The Sonogashira cross-coupling reaction proceeds at room temperature with a palladium catalyst, such as PdCl₂(PPh₃)₂, and copper (I) iodide (CuI) as a co-catalyst to increase the reactivity. Due to the combination of a palladium catalyst and a copper co-catalyst, it is difficult
to predict the exact mechanism of the Sonogashira cross-coupling reaction, although the generally proposed mechanism is shown in Figure 1-14.\textsuperscript{42}

Figure 1-14. A proposed mechanism for the Sonogashira cross-coupling reaction. Figure was reprinted from Najera et al. with permission.\textsuperscript{43} Copyright 2007 American Chemical Society

The pre-activated Pd\textsuperscript{0}L\textsubscript{2} catalyst is prepared from Pd(PPh\textsubscript{3})\textsubscript{4}, or PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}. The resulting Pd\textsuperscript{0}L\textsubscript{2} species is stabilized by amine or solvent molecules. After the Pd\textsuperscript{0}L\textsubscript{2} complex is formed, the palladium catalyst is oxidatively added to the aryl or vinyl halide (cycle A).

Meanwhile, in the copper co-catalyst cycle B, a copper acetylide is formed and undergoes transmetalation with the palladium catalyst to form a [Pd\textsuperscript{II}L\textsubscript{2}R\textsubscript{1}C\textequivCR\textsubscript{2}] complex. Finally, a reductive elimination of the cis-isomer produces the desired alkyne product. Unlike the palladium catalyst cycle mechanism, the copper co-catalyst cycle mechanism is not common.\textsuperscript{40}
However, it is considered that the π-alkyne copper complex increases the acidity of the terminal alkyne proton, and increases the reactivity. A recent study suggested that the amine can deprotonate the reactant and accelerate the reaction to form a reactive [Pd⁰L₂ (amine)] complex.⁴⁴

There are several reports that the undesired acetylene homo-coupled product is obtained by a copper-catalyzed reaction with oxygen in the reaction solution, which is called the Glaser reaction.⁴⁵ If oxygen is present in the Sonogashira cross-coupling reaction mixture, the Glaser homo-coupled product can be produced.⁴⁶ In the Glaser reaction mechanism, the deprotonated acetylene is coordinated to the Cu¹ catalyst (Figure 1-15). Then, the Cu¹ catalyst is oxidized by O₂ in the solution and is coordinated to one more equivalent of acetylene. Finally, two moles of acetylene molecules are reductively eliminated to form the homo-coupled product. Researchers have attempted to identify the homo-coupled product.⁴⁷ However, it is difficult to characterize the homo-coupled product in the polymer chain, because the acetylene homo-coupled structure may occur in only small portion of the polymer chain.

![Figure 1-15. Mechanism of Glaser–Hay coupling suggested by Vilhelmsen et al. Figure was reprinted with permission.⁴⁸ Copyright 2013, John Wiley and Sons](image)

1.4.3 Defects of the Homo-coupled Product

The previously discussed literature reported that the copper catalyst reacts with the diacetylene-functionalized monomer and produces the acetylene homo-coupled product when the reaction solution is exposed to the air.⁴⁶ The first observation of the homo-coupling reaction was
reported by Glaser in 1869.\textsuperscript{49} If the acetylene homo-coupled structure exists in the non-aggregated polymer chains, then the defect of homo-coupled structure affects to quench the fluorescence only from the polymer chain which contained the acetylene homo-coupled sites. However, if the polymer chains are aggregated, excitons can be transferred easily from acetylene homo-coupled sites to the aggregated trap sites. Thus, the fluorescence quenching may increase in aqueous solution if acetylene homo-coupled products are present.

The Sonogashira cross-coupling reaction can produce the acetylene homo-coupled structure with the diiodo- and diacetylene substituted AA + BB type monomers. Thus, to diminish the defect of an acetylene homo-coupled structure in the polymer chain, the polymerization conditions need to be changed to a bi-functionalized AB type monomer.

1.5 Well-defined Conjugated Polymer

1.5.1 Examples of Well-defined CPs

Well-defined CPs have controlled molecular weights, low polydispersity, and precisely controlled end group functionalities. To obtain the well-defined CPs, chain-growth mechanism, which has an ability to rigorously control the polymer’s physical properties, including molecular weights, polydispersity, and end-group fidelity, is widely used.\textsuperscript{5,45} Well-defined CPs are needed for sensors, organic light-emitting diodes, and organic semiconductors with improved optoelectronic properties.\textsuperscript{45} There have been many studies of the synthesis of the well-defined CPs, including polythiophenes, polyfluorenes, poly(phenylene ethynylene)s, and polyphenylenes, as well as donor-acceptor type copolymers (Figure 1-16).\textsuperscript{29,51-54}
The first example of a well-defined polymer, poly(3-hexylthiophene), was reported by McCullough and Yokozawa in 2004 (Figure 1-17 a).\textsuperscript{55-58} The nickel-catalyzed polymerization of 3-hexylthiophene gave a chain-growth type polymer with a controlled molecular weight ($M_n$) and narrow polydispersity ($D$). In Figure 1-17 b, the $M_n$ of the polymer increased linearly with monomer conversion ($\%$), while the $D$ remained relatively constant. These results suggested that the polymerization proceeded in a controlled, chain-growth pathway.

Yokozawa and co-workers reported chain-growth CTP using Suzuki-Miyaura cross-coupling polymerization (Figure 1-18).\textsuperscript{5} The polymerization was performed by reaction of borated thiophene and pre-initiated palladium catalyst. After successfully synthesizing the
polythiophene and polyfluorene homopolymers, the block co-polymer, polyfluorene-\textit{b}-polythiophene, was prepared by adding the thiophene monomer to the polyfluorene reaction solution without an additional pre-initiated palladium catalyst.

Figure 1-18. Synthesis of polythiophene and a block copolymers. Figure was reprinted from Yokozawa with permission.\textsuperscript{5} Copyright 2007 American Chemical Society

### 1.5.2 Example of Well-defined PPE Polymers

Chain-growth CTP of poly(phenylene ethynylene) (PPE) was reported by Bielawski and colleagues in 2013.\textsuperscript{41} The pre-activated Pd(P\texttextsuperscript{t}Bu\texttextsuperscript{3})(Br)(Ph) catalyst was used as an initiator under Sonogashira cross-coupling and Stille-type reaction conditions (Figure 1-19).

The polymerization followed the chain-growth pathway because of the linear relationship between the monomer conversion (%) and molecular weight (kDa) (Figure 1-19, A). Also, the molecular weight (M\textsubscript{n}) proportionally increases with the [monomer]\textsubscript{0}/[catalyst]\textsubscript{0} loading ratio (Figure 1-19, B). The chain-growth CTP also produce the PPE-\textit{b}-poly(fluorenyl ethynylene) block copolymer. First, the PPE polymer block was synthesized by AB type chain-growth CTP. Then, the fluorenyl ethynylene monomer was added to the PPE polymer reaction solution without additional palladium catalyst. Finally, the PPE-\textit{b}-poly(fluorenyl ethynylene) block copolymer was produced and characterized by GPC (M\textsubscript{n} = 10,500 g/mol and PDI = 1.40 (PPE block), M\textsubscript{n} = 16,000 g/mol and PDI = 1.55 (PPE-\textit{b}-poly(fluorenyl ethynylene) block co-
polymer). Thus, it has been confirmed that the pre-activated Pd(PtBu3)(Br)(Ph) catalyst produces a chain-growth type polymer by the catalyst-transfer polymerization.

Recently, Wu and colleagues published the synthesis of PPE-b-polysicyanide (PPI) block co-polymer with an air stable pre-activated palladium catalyst using chain-growth CTP (Figure 1-20 a). To obtain well-defined block co-polymer, 1-ethynyl-4-iodo-2, 5-bis(octyloxy)benzene was reacted with pre-activated palladium catalyst, [Pd(PtBu3)2(Cl)(C≡C-C4H9)], using Sonogashira cross-coupling reaction conditions to produce the PPE homo-polymer (Mn = 6,300 g/mol and PDI = 1.20). Then, decyl-4-cyanobenzoate was added to the reaction solution without additional palladium catalyst to obtain the PPE-b-PPI block co-polymer (Mn = 22,100 g/mol and PDI = 1.48). The molecular weight of PPE homo-polymer and PPE-b-PPI block co-polymer increased linearly with the [monomer]0/[catalyst]0 ratio and polydispersity
remained close to 1.00 (Figure 1-20 b), indicating the chain-growth polymerization mechanism.

Figure 1-20. Polymerization of PPE-\textit{b}-PPI block co-polymerization. Figure was reprinted from Wu et al. with permission.\cite{59} Copyright 2016 American Chemical Society

The absorption and emission spectra of the PPE homopolymer, PPI homopolymer, and PPE-\textit{b}-PPI block co-polymer exhibited different shapes, absorbance, and wavelengths (Figure 1-21). Due to the \(\pi\)-conjugated structure, the PPE homopolymer (poly-1\textsubscript{20}) has a strong absorption at 433 nm. The PPI homopolymer (poly-2\textsubscript{30}) absorbed at 253 nm and 364 nm, corresponding to the \(n-\pi^*\) transition of the C=N bond. The block copolymer, PPE-\textit{b}-PPI (poly(1\textsubscript{20}-\textit{b}-2\textsubscript{60})), absorbed 264 and 426 nm. In the emission spectra, the PPE homopolymer (poly-1\textsubscript{20}) emitted strong blue-green fluorescence at 483 nm. However, the block copolymer (1\textsubscript{20}-\textit{b}-2\textsubscript{60}) showed weak blue emission at 462 nm. A shorter wavelength emission of the block copolymer was due to the non-aggregated PPE block. The tail at longer wavelength corresponded to excimer-like emission of the aggregated PPI block. The fluorescence quantum yields of poly-1\textsubscript{20}, and poly(1\textsubscript{20}-\textit{b}-2\textsubscript{60}) were 0.82 and 0.38, respectively. Therefore, the fluorescence was quenched by aggregation in the block copolymer.
Figure 1-21. PPE (poly-120), PPI (poly-230) and PPE-b-PPI (poly(120-b-260)). (a) Absorption spectra of the PPE (poly-120), PPI (poly-230) and PPE-b-PPI (poly(120-b-260)). (b) Emission spectra of the PPE (poly-120) and PPE-b-PPI (poly(120-b-260)). Figure was reprinted from Wu et al. with permission. Copyright 2016 American Chemical Society

1.5.3 Examples of Well-defined Star-shaped CPs

Well-defined star-shaped polymers are known for their unique structural properties, reproducibility, high purity, and photophysical properties. In 2015, Huang and Keivanidis investigated well-defined star-shaped conjugated macroelectrolytes for polymer solar cells. In their work, the star-shaped monodisperse conjugated polyelectrolytes, TrNBr and TrOH, were prepared and characterized (Figure 1-22). TrNBr and TrOH have the same core in the polymer backbone. However, the TrNBr has a terminal cationic ammonium group, while the terminus of TrOH is a neutral diethanolamino polar group. Because of the cationic and polar side groups, both TrNBr and TrOH were soluble in a polar organic solvent such as ethanol. The star-shaped polymers were less aggregated than linear polymers in solution due to their three-dimensional structures. Indeed, TrNBr and TrOH showed improved process cycle efficiency (PCE) in photovoltaic device applications (4.88% and 4.74%, respectively).
Wu and colleagues prepared linear and star-shaped polyisocyanides using the chain-growth CTP method (Figure 1-23). To perform chain-growth polymerization, pre-activated air-stable di- and tri-functionalized palladium catalysts were prepared by the Sonogashira cross-coupling reaction with Pd(PEt\(_3\))\(_2\)Cl\(_2\) and 1,4-diethynylbenzene or 1,3,5-triethynylbenzene. The pre-activated palladium core reacted with an isocyanide monomer to afford the chain-growth type polymer. The di- and tri-functionalized polyisocyanides were characterized by GPC (Figure 1-24 a). The di-functionalized polyisocyanide (poly-f2\(\_60\)) had a M\(_n\) = 15,000 g/mol and PDI = 1.19 (the initial feeding ratio of [monomer]\(_0\)/[catalyst]\(_0\) = 60). The narrow polydispersity indicates a living chain-growth polymerization mechanism. The tri-functionalized
polyisocyanide (poly-g₂₃₀) also showed narrow polydispersity ($M_n = 12,000$ g/mol and PDI = 1.20; initial feeding ratio of [monomer]₀/[catalyst]₀ = 45).

In addition, $^{31}$P NMR spectroscopy was used to analyze the palladium catalyst initiator and the palladium catalyst on the polymer’s active site (Figure 1-24 b). The di-functionalized palladium initiator (1f) and the tri-functionalized palladium initiator (1g) each showed a single peak at 17.9 ppm corresponding to the phosphine group. After polymerization, the 17.9 ppm peak disappeared, and a new doublet peak appeared at 14.4 ppm. These results indicated that the palladium catalyst was transferred to the intramolecular polymer chain and was located at the reactive end of the polymer chain. Therefore, it was concluded that polymerization proceeded by a chain-growth catalyst-transfer pathway.
Figure 1-24. GPC and $^{31}$P NMR. (a) GPC trace for the di- (poly-f2$_{60}$) and tri-functionalized polymers (poly-g2$_{30}$). (b) $^{31}$P NMR di- (1f) and tri- (1g) Pd initiators and their polymers. Figure was reprinted from Wu et al. with permission.$^{62}$ Copyright 2014 American Chemical Society

Usually, PPE-based CPEs are prepared by a post-polymerization method, in which a neutral or organic soluble PPE polymer is synthesized first, and then the conjugated polyelectrolyte is obtained by hydrolysis, dialysis, and freeze-dry processes. Because the photophysical properties of PPE-based CPEs depend on their PPE backbones, it is important to optimize the synthetic conditions for the PPE backbone.

1.5.4 Chain-growth Catalyst-transfer Polymerization

Due to the ill-defined polymers and the homo-coupled side product, the step-growth Sonogashira coupling reaction condition needs to be modified. Recently, to obtain well-defined PPE polymers, the chain-growth catalyst-transfer polymerization (CTP) method has been introduced and used to prepare conjugated polymers such as polythiophenes, polyfluorenes, and polyphenylenes.$^{15}$
Figure 1-25. Proposed mechanism for chain-growth CTP. (A) Pre-activation of the Pd catalyst, (B) Initiation step of polymerization. (C) Propagation step, and (D) Termination step with acid or water.

In the chain-growth CTP mechanism (Figure 1-25), the palladium catalyst is oxidatively added to the polymer chain end, and walks through the polymer chain (chain-walk). There are two possibilities where the Pd\textsuperscript{II} catalyst can oxidatively add: ligand, to an intermolecular polymer chain end/monomer or to an intramolecular polymer chain end. Among the three possibilities, intramolecular oxidative addition is the most favorable due to a π-complex (4) formation by coordination of palladium to the phenyl ring at the polymer end. For this reason, it is preferred that the palladium is oxidatively added in intramolecular fashion. Also, it is known that the electron-rich phosphine ligand helps to form a stable π-complex between the Pd\textsuperscript{II} catalyst and the phenyl ring. Therefore, the palladium catalyst can walk through the intramolecular polymer chain following the living chain-growth mechanism. Generally, the polydispersity of chain-growth polymerization is close to 1.00. However, in the case of the chain-growth CTP, the
polydispersity is larger than 1.00, because the palladium forms a strong $\pi$-complex with the phenyl ring of the polymer chain end. Therefore, the oxidative addition of palladium catalyst to the polymer chain end occurs slowly, and this is the rate-determining step for CTP. Therefore, the slow oxidative addition step causes the broad polydispersity in chain-growth CTP.

### 1.5.5 Mechanistic Study of Chain-growth CTP

There are several features that define the chain-growth catalyst-transfer polymerization. First, the chain-growth CTP mechanism provides linear correlations between the Mn and monomer conversion (%) due to reactive species at the end of the polymer chain. Therefore, the length of the polymer chain can extend upon reacting with monomer. Also, the $\text{M}_n$ can be controlled based on the ratio of $[\text{monomer}]_0/[\text{catalyst}]_0$. The polydispersity of chain-growth CTP is close to 1.00. The polymer chain end group can be characterized by MALDI-TOF mass spectrometry, and the reactive palladium catalyst at the polymer chain end can be analyzed by $^{31}\text{P}$ NMR spectroscopy. Furthermore, in chain-growth CTP, the copolymer’s sequence should follow the order of monomer addition. Finally, the activated organometallic catalyst is oxidatively added in an intramolecular fashion.

There are examples to support the intramolecular oxidative addition of the catalyst. In 1976, Kumada and colleagues reported the unexpected double-substituted product with excess amounts of dichlorobenzene (Figure 1-26).\textsuperscript{64} The result suggested that the Ni catalyst reacts with the starting material twice before reacting with another molecule of starting material. In 2004, McCullough and colleagues also reported the double-substituted product with dibromothiophene (Figure 1-26).\textsuperscript{55} McCullough proposed that the intramolecular oxidative addition occurred between the Ni catalyst and the polymer chain end.
In 2010, Kiriy, Sommer, and Senkovsky studied poly(3-hexylthiophene) prepared by the Kumada catalyst-transfer polymerization. During the polymerization, the Ni catalyst walked along the intramolecular polymer chain and did not transfer to intermolecular polymer chains. This “chain-walk” occurred over a distance of one monomer unit. If the monomer length is longer than 1.1 Å, then the Ni catalyst could transfer to another polymer chain.

Figure 1-26. Major product via the double-substituted reaction. Figure was reprinted from Kiriy et al. with permission. Copyright 2010 American Chemical Society

Figure 1-27. Proposed mechanism of the unidirectional and random chain-walk pathway. Figure was reprinted from Kiriy et al. with permission.
To examine the direction of polymerization, two different directions of the catalyst chain-walk were proposed: unidirectional, and random (Figure 1-27).\textsuperscript{47,65} To predict the direction of chain-walking, Br-C\textsubscript{6}H\textsubscript{4}-Ni(dppe)-Br, which can be easily monitored by \textsuperscript{1}H NMR of the para-position phenyl ring, was prepared. For unidirectional chain-walk, the Ni catalyst moves in one direction to elongate the polymer length. For the random chain-walk pathway, the Ni catalyst moves in any direction, thus placing the benzene ring inside the polymer chain. The random chain-walking polymer had much higher probability because of the possibility to walk in both directions. However, experimentally, the unidirectional chain-walking polymer was the major product. It is because the Ni catalyst preferred to form a \( \pi \)-complex with thienyl ring than benzene ring. The catalyst-monomer \( \pi \)-complex is considered as a source of chain-walking. Therefore, it can be concluded that the polymer chain ends have different \( \pi \)-binding affinities to the Ni catalyst, and the different \( \pi \)-binding affinities determine the direction of the polymer elongation.

### 1.5.6 Analysis of the Well-defined CPs

In 2007, Higashimura and Yokozawa successfully synthesized polyfluorene, polyphenylene, and their copolymers by the Suzuki-Miyaura coupling reaction.\textsuperscript{5} They used end-group analysis to characterize the phenyl/hydrogen and phenyl/bromine end groups. In the initiation step of chain-growth polymerization, a phenyl group on the palladium catalyst forms a new bond to the monomer end by reductive elimination and oxidative addition of the palladium catalyst. The end group was analyzed by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry. As shown in Figure 1-28, the major peaks correspond to the phenyl/bromine polymer, and the minor peaks are due to the phenyl/hydrogen polymer. The numbers above the circles indicate the degree of polymerization (n). The mass spectrum
shows that all the polymers have a phenyl ring at one end, which explains the initiation step of polymerization. Because the polymerization precedes by the chain-growth pathway, the bromine remains at the other chain end. Hydrogen replaces the bromine when the polymerization is quenched by water.

Figure 1-28. MALDI-TOF mass spectrum of poly(9,9-dioctylfluorene). Figure was reprinted from Yokozawa with permission. Copyright 2007 American Chemical Society

1.5.7 Limitation of Chain-growth CTP

There are limitations to chain-growth CTP, including easy chain termination due to reactive species at the polymer chain end and a slow initiation step with pre-initiated catalyst. There is also a possibility of interrupting the chain propagation step via chain transfer and/or chain termination to monomer, oligomer, and solvents. The length of monomer also can be important in the intramolecular chain-walking of a catalyst. However, there are advantages of the chain-growth CTP mechanisms, including narrow polydispersity, introducing the desired polymer end group, and controllable polymer molecular weight.
1.6 Scope of the Present Study

The purpose of the current study is to synthesis of well-defined bi-functionalized AB type chain-growth PPE-based CPEs. In Chapter 2, carboxylate side chain PPE-based CPEs are prepared by an AB type chain-growth, an AB type step-growth, an AABB type step-growth, and a Glaser AA type step-growth polymerizations. The acetylene homo-coupled defect is demonstrated in comparison of four different types of polymers. In Chapter 3, carboxylate side group star-shaped PPE-based CPEs are designed and synthesized. The photophysical properties of star-shaped CPEs are characterized in polar organic solvents and aqueous solution. In Chapter 4, sulfonated and imidazolium side group PPE-based CPEs are synthesized by bi-functionalized AB type chain-growth CTP. Their photophysical properties are also measured and characterized in methanol and water.
CHAPTER 2
IMPROVED PHOTOPHYSICAL PROPERTIES FOR AB-TYPE CARBOXYLATE SIDE
CHAIN POLY(PHENYLENE ETHYNYLE)-BASED CONJUGATED
POLYELECTROLYTES BY CHAIN-GROWTH POLYMERIZATION

2.1 Background

In the past several decades, poly(phenylene ethynylene) (PPE)-based conjugated polyelectrolytes (CPEs) have been widely investigated due to their potential applications in sensing,\textsuperscript{21, 68-69} bio-imaging,\textsuperscript{70-72} and as suitable materials in organic photovoltaics.\textsuperscript{7, 23, 31, 73-78} In spite of the remarkable photophysical properties of PPE-based CPEs, the rigidity of the hydrophobic PPE backbone causes poor water solubility and aggregated structures due to \(\pi\)-stacking interactions between the polymer chains in aqueous solution.\textsuperscript{1, 17, 19, 79} In the aggregated structure, fluorescence is easily quenched by the rapid energy transfer of excitons to low energy aggregate state traps.\textsuperscript{1, 9, 17} Therefore, it is important to reduce the aggregation to improve the photophysical properties of PPE-based CPEs in aqueous solution.

We recently reported carbon- and oxygen-linked carboxylate side group PPE-based CPEs (P1-C and P1-O) which showed enhanced fluorescence properties in aqueous solution (Figure 2-1).\textsuperscript{1} Without a bulky and highly charged side group, the P1-C and P1-O showed increased fluorescence quantum yield in methanol (\(\Phi_f = 19\) and 18\%). In water, the P1-C exhibited \(\Phi_f = 16\%\) which was the improved fluorescence quantum yield compared to that of typical PPE-based CPEs (\(\Phi_f << 10\%)\textsuperscript{1} However, the P1-O showed \(\Phi_f = 4\%\) of fluorescence quantum yield, indicating the aggregation. It may be because the oxygen atom affected the planarity of the PPE backbone. Therefore, the planar backbone may exhibit an enhanced intermolecular \(\pi\)-stacking, which induced the aggregation in aqueous solution.
Defining the polymer's structure is crucial to understand the aggregation. Previously, carboxylate PPE-based CPEs were synthesized with AA + BB type monomers (diiodo- and diacetylene-functionalized compounds) by palladium-catalyzed Sonogashira cross-coupling reaction. Since the palladium-catalyzed Sonogashira cross-coupling reaction is a step-growth polymerization, it is hard to control the polymer's physical properties such as molecular weight, polydispersity, and end-group fidelity.\textsuperscript{80-81} It has also been reported that the copper catalyst reacts with the diacetylene-functionalized monomer and produces the acetylene homo-coupled products when the reaction solution is exposed to the air.\textsuperscript{46,49} If the acetylene homo-coupled structure exists in the non-aggregated polymer chains, then the defect of homo-coupled structure affects to quench the fluorescence only from the polymer chain which contained the acetylene homo-coupled sites. However, if the polymer chains are aggregated, excitons can be transferred easily from acetylene homo-coupled sites to the aggregated trap sites. Thus, the fluorescence quenching may increase in aqueous solution if acetylene homo-coupled products are present.

The AB type chain-growth catalyst-transfer polymerization (CTP) of PPE polymer was reported by Bielawski and colleagues in 2013.\textsuperscript{41} Since the PPE polymers were prepared by
Herein, we report a series of carboxylated PPE-based CPEs synthesis with four different “precursor route” polymerization pathways: an AB-type chain-growth CTP pathway (C-ab), an AB-type step-growth polymerization pathway (S-ab), an AABB-type step-growth polymerization pathway (S-aabb), and a Glaser AA-type step-growth polymerization pathway (S-aa) (Figure 2-2). The chain-growth polymer was prepared by Pd(P^tBu_3)(Pd)(Br) catalyzed CTP while the step-growth polymers were prepared by Pd(PPh_3)_4 catalyzed Sonogashira cross-coupling reaction. The AB-type chain-growth and AB-type step-growth polymerizations were monitored by time-dependent gel permeation chromatography (GPC). Also, the photophysical properties of the AB-type PPE-based CPE were investigated. Due to the AB-type monomer, chain-growth PPE-based CPE reduced the acetylene homo-coupled defect. Therefore, the newly synthesized chain-growth PPE-based CPE showed the improved fluorescence quantum yield (Φ = 35% compared to Φ = 4 (P1-O)^1).
2.2 Polymer Design and Preparation

2.2.1 Synthesis of the AB-type Monomer

Figure 2-3 shows the synthetic steps to obtain the AB-type monomer, didodecyl 2,2’-(2-ethynyl-5-iodo-1,4-phenylene)bis(oxy))diacetate (6). First, a commercially available hydroquinone reacted with 2-bromoacetaldehyde via a nucleophilic-substitution reaction. Then, the reaction mixture was acidified with 6 N HCl to afford 2,2’-(1,4-phenylenebis(oxy))diacetic acid (2). An esterification reaction of compound 2 with dodecyl alcohol resulted in the desired product, didodecyl 2,2’-(1,4-phenylenebis(oxy))diacetate (3) in a reasonable yield (80%). During the esterification reaction of compound 2, vaporized water was produced as a by-product and removed by Ar gas flow. After introducing an iodine on the phenyl ring (compound 4), a propargylic alcohol was substituted with one of the iodine atoms via the Sonogashira cross-coupling reaction. Finally, the alcohol group was reduced by manganese dioxide with a strong base to yield the desired AB-type monomer 6.

Figure 2-3. Synthesis of the AB-type monomer (6)
2.2.2 Synthesis of the AABB-type Monomer

A diacetylene-substituted monomer 8 was prepared from didodecyl 2,2'-(2,5-diiodo-1,4-phenylene)bis(oxy)diacetate (4) (Figure 2-4). The diiodo-substituted compound 4 reacted with two equivalents of trimethylsilyl acetylene in the Sonogashira cross-coupling reaction. Then, the trimethylsilyl (TMS) group was deprotected by reaction with tetrabutylammonium fluoride (TBAF). The remaining TBAF and its by-product were removed by column chromatography (dichloromethane as an eluent) to produce the desired diacetylene-functionalized monomer 8.

![Figure 2-4. Synthesis of the diacetylene-functionalized compound 8](image)

2.2.3 Preparation of the AB- and AABB-Type PPE Polymers

First, three different polymerization methods were considered to synthesize the PPE-based CPEs (Figure 2-5). C-ab and S-ab represent the chain-growth AB type and step-growth AB type PPE-based CPEs. S-aabb and S-aa represent the step-growth AABB type and step-growth AA type PPE-based CPEs.
The AB-type monomer, didodecyl 2,2’-(2-ethyl-5-iodo-1,4-phenylene)bis(oxy))diacetate (1) was polymerized in the presence of the pre-activated P(\(\text{Bu}\))_{3}\text{Pd}(\text{Ph})\text{Br} catalyst, following the chain-growth CTP mechanism to yield the C-ab ester polymer. The Pd(\(\text{PPh}_{3}\))\text{4} catalyzed Sonogashira cross-coupling reaction with the AB- and AABB-type monomers produced the S-ab and S-aabb ester polymers. The polar solvent and water-soluble CPEs were synthesized by hydrolysis of the ester units.

The polymerization of C-ab was monitored by time-dependent $^1\text{H}$ NMR to observe the disappearance of acetylene proton peak on the AB-type monomer (Figure 2-6). The time interval of the measurement was thirty minutes after the polymerization had begun. When the polymerization started, the singlet proton peak on the acetylene of the AB-type monomer appeared at 4.01 ppm. As the polymerization proceeded, the singlet proton peak of the acetylene
decreased in intensity, and eventually disappeared at the end of the polymerization. Each of the ester polymers was also characterized by $^1$H NMR spectroscopy to confirm the structure. The aromatic protons of the C-ab ester polymer, S-ab ester polymer, and S-aabb ester polymer appeared at 7.19, 7.17, and 7.11 ppm, respectively (Figure A-9, A-10, and A-11). The side chain’s proton peaks appeared at 4.0 – 5.0 ppm and 0.8 – 1.7 ppm as a multiplet. Also, each of the polyelectrolytes (C-ab, S-ab, and S-aabb) was characterized by $^1$H NMR in D$_2$O as a reference solvent (Figure A-13, A-14, and A-15). The aromatic proton of the CPEs appeared at 7.22 ppm (C-ab), 7.10 ppm (S-ab), and 7.15 ppm (S-aabb).

![Figure 2-6. Time-dependent $^1$H NMR for the chain-growth C-ab ester polymer. The time interval of the measurement was thirty minutes after the polymerization had begun](Image)

2.2.4 Characterization of Ester Polymers by GPC Analysis

The change in molecular weight of the C-ab ester polymer and S-ab ester polymer was monitored by time-dependent GPC (Figure 2-7). The molecular weight of C-ab ester polymer increased over time without overlapping GPC peaks, indicating a chain-growth mechanism. However, the molecular weight of S-ab ester polymer increased more gradually over time with
overlapping GPC peaks. The broad polydispersity (1.89) and overlapping GPC peaks of S-ab ester polymer indicated that the polymerization followed the step-growth mechanism. Both ester polymers were controlled to have a similar molecular weight of around $M_n = 8,000$ g/mol to obtain a reliable comparison of the photophysical properties. The relationship of molecular weight (Da) and monomer conversion (%) was plotted to verify the polymerization mechanism (Figure 2-8).

![Figure 2-7](image)

Figure 2-7. Time-dependent GPC trace for the C-ab ester polymer (left) and S-ab ester polymer (right). The arrow indicates the molecular weight increase direction. The time interval of the measurement was thirty minutes between each aliquot after the polymerization had begun.

![Figure 2-8](image)

Figure 2-8. Plots of monomer conversion (%) versus molecular weight (Da). (a) The chain-growth C-ab ester polymer, and (b) step-growth S-ab ester polymer.
If the polymerization mechanism follows the chain-growth pathway, the molecular weight increases in proportion to the monomer conversion. Because of this, the monomer was consumed as the polymer chain was lengthened in the case of the C-ab ester polymer. On the other hand, the molecular weight increases exponentially as the monomer conversion increases in the case of the S-ab ester polymer. In step-growth polymerization, various lengths of oligomers are formed at the initiation step. Then, the oligomers are combined at the propagation step. Therefore, the plot of molecular weight versus monomer conversion is not linear in the step-growth mechanism.

2.3. Photophysical Properties

2.3.1 Time-dependent Steady-state Absorption Spectra

Figure 2-9 shows the time-dependent steady-state absorption spectra of the C-ab ester and S-ab ester polymers. The time-dependent absorption spectra were obtained in chloroform every thirty minutes during the polymerization reaction. The absorption spectra of the C-ab ester and S-ab ester polymers were red-shifted as the molecular weight increased. During the polymerization, the absorption spectra of the C-ab ester polymer were red-shifted from 365 nm to 421 nm without absorption spectra overlapping while the absorption spectra of the S-ab ester polymer were red-shifted from 370 nm to 425 nm with absorption spectra overlapping. In both cases, shorter wavelength peak around 300 nm decreased and longer wavelength peak increased, as the conjugation length increased.
2.3.2 Steady-state Absorption and Emission Spectra

Figure 2-10 illustrates the absorption and fluorescence emission spectra of C-ab, S-ab, and S-aabb CPEs in water (pH = 8) and methanol. The area of fluorescence spectra represent the relative fluorescence quantum yield with OD = 0.1 at $\lambda_{\text{abs}} = 420$ nm. Water and methanol were selected as poor and good solvents based on previous work.\(^1\)

In methanol, the absorption maxima for C-ab, S-ab, and S-aabb were observed at 418, 433, and 433 nm while the emission maxima were observed at 459, 459, and 465 nm for the C-ab, S-ab, and S-aabb, respectively. In water, the absorption maxima were obtained at 413 (C-ab), 425 (S-ab), and 426 nm (S-aabb) while the emission maxima were at 461 (C-ab), 461 (S-ab), and 463 nm (S-aabb). The emission spectra of the C-ab showed the sharpest and most intense fluorescence emission spectra among the CPEs.
2.3.3 Fluorescence Quantum Yield, Lifetime, and Quenching

Fluorescence quantum yields of polymers were illustrated in Figure 11a. The fluorescence quantum yields of C-ab, S-ab, and S-aabb ester polymers showed $\Phi_{fl} = 88$, 87, and 89%, respectively, in THF. In methanol, the fluorescence quantum yields of CPEs were comparable ($\Phi_{fl} = 56$, 44, and 49% for C-ab, S-ab, and S-aabb, respectively). In water, the fluorescence quantum yields of C-ab, S-ab, and S-aabb were obtained as $\Phi_{fl} = 35$, 15, and 9%, respectively. The fluorescence of S-aabb was quenched about 90%, like as typical PPE-based CPEs. However, the C-ab and S-ab had improved fluorescence quantum yield compared to that of the S-aabb. Therefore, the AB-type chain-growth and step-growth CPEs can reduce the aggregation. Among the CPEs, the C-ab had the highest fluorescence quantum yield (35%).
Figure 2-11. Photophysical properties. (a) Fluorescence quantum yield of CPEs in water (pH = 8.0) and methanol. (b) Average fluorescence lifetime of CPEs in water and methanol. (c) Stern-Volmer quenching constant of CPEs in water and methanol.
Table 2-1. Optical properties of C-ab, S-ab, S-aabb in water (pH = 8.0) and methanol (H₂O (pH = 8)) and MeOH

<table>
<thead>
<tr>
<th>PPE</th>
<th>Abs.</th>
<th>λ_max (nm)</th>
<th>Em</th>
<th>Ksv (Q₉₀)</th>
<th>ε</th>
<th>Abs.</th>
<th>λ_max (nm)</th>
<th>Ksv (Q₉₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-ab</td>
<td>413</td>
<td>461</td>
<td>6.96(10.9)</td>
<td>16,800</td>
<td>418</td>
<td>459</td>
<td>4.95(5.85)</td>
<td></td>
</tr>
<tr>
<td>S-ab</td>
<td>425</td>
<td>463</td>
<td>4.17(13.7)</td>
<td>15,600</td>
<td>433</td>
<td>459</td>
<td>4.49(4.90)</td>
<td></td>
</tr>
<tr>
<td>S-aabb</td>
<td>426</td>
<td>463</td>
<td>8.29(11.3)</td>
<td>14,350</td>
<td>433</td>
<td>465</td>
<td>7.38(7.59)</td>
<td></td>
</tr>
</tbody>
</table>

a Contains 1 mg/mL NaOH. b The excitation wavelength corresponds to the wavelength of maximum absorption. c The Stern-Volmer constants (Ksv) are obtained from steady-state fluorescence emission quenching. d Q₉₀ represents the 90% quenching of fluorescence intensity. e Basic water (pH = 8) was prepared by adding NaOH.

Table 2-1 summarizes the absorption, fluorescence maxima, Stern-Volmer constants (Ksv), and UV-vis absorption coefficient (ε) results. CPEs have a similar absorption coefficient due to having the same PPE backbone. The fluorescence lifetime was obtained by time-correlated single photon counting (TCSPC) using a Fluo Time 100 (Picoquant). Figure 11b shows the average fluorescence lifetime of C-ab, S-ab, and S-aabb. The fluorescence decays of the C-ab, S-ab, and S-aabb showed multiexponential behavior, and with this CPEs, two exponentials were needed to fit the fluorescence decay. In water, longer lifetime (480, 490, and 510 ps for C-ab, S-ab, and S-aabb, respectively) was associated with the polymer relaxation and reorganization of the CPEs. Shorter lifetime (120, 40, and 20 ps for C-ab, S-ab, and S-aabb) was obtained in water by the emission from the excimer-like aggregation state traps. According to the fluorescence lifetime (τ₁ = 120 ps) of the C-ab, the excimers of the C-ab can live longer than that of the S-ab and S-aabb.
Table 2-2. Fluorescence lifetime of C-ab, S-ab, and S-aabb in water (pH = 8.0) and methanol

<table>
<thead>
<tr>
<th>CPE</th>
<th>solvent</th>
<th>$\lambda_{ex}$</th>
<th>$\tau_1$ [ns]</th>
<th>$A_1$ [%]</th>
<th>$\tau_2$ [ns]</th>
<th>$A_2$ [%]</th>
<th>$&lt;\tau&gt;$ [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-ab</td>
<td>H$_2$O</td>
<td>475</td>
<td>0.12</td>
<td>51</td>
<td>0.48</td>
<td>49</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>475</td>
<td>0.25</td>
<td>42</td>
<td>0.62</td>
<td>58</td>
<td>0.46</td>
</tr>
<tr>
<td>S-ab</td>
<td>H$_2$O</td>
<td>475</td>
<td>0.04</td>
<td>87</td>
<td>0.49</td>
<td>13</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>475</td>
<td>0.22</td>
<td>45</td>
<td>0.71</td>
<td>55</td>
<td>0.50</td>
</tr>
<tr>
<td>S-aabb</td>
<td>H$_2$O</td>
<td>475</td>
<td>0.02</td>
<td>98</td>
<td>0.51</td>
<td>2</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>475</td>
<td>0.22</td>
<td>40</td>
<td>0.71</td>
<td>60</td>
<td>0.52</td>
</tr>
</tbody>
</table>

*a* $<\tau>$ represents the average fluorescence lifetime.

Figure 2-12 illustrates the time-resolved ultrafast transient absorption (TA) spectra of C-ab, S-ab, and S-aabb. The time-resolve ultrafast transient absorption (TA) spectrum of C-ab resembles that of the S-ab and S-aabb indicating that laser pulse predominantly excites the PPE backbone. However, the transient spectra of C-ab, S-ab, and S-aabb after $\tau = 1.35$, 1.94, and 1.84 ps, respectively, showed different absorption intensities. Each lifetime slice was selected from the maximum wavelength of the absorbance. At $\lambda = 650$ nm, C-ab and S-ab exhibited stronger absorbance than that of the S-aabb. Figure 2-14b shows TA decay kinetics of the C-ab, S-ab, and S-aabb CPEs in water. The transient absorption kinetics of S-aabb and S-ab decayed much faster than the C-ab. In the cases of S-ab and S-aabb, the decay kinetics revealed that there were ultrafast components (< 2 ps) in the energy transfer process, which were associated to the rapid energy transfer of excitons to low energy aggregate state traps (Table 2-3). The decay of C-ab showed longer ultrafast components (2.16 ps) than that of S-ab and S-aabb.
Figure 2-12. Time-resolved ultrafast transient absorption spectra. (A) C-ab, (B) S-ab, and (C) S-aabb in water (pH = 8.0). All samples were prepared in an idealized solvent ratio of water (pH = 8) and methanol, such that their optical densities at 390 nm were equal to 0.4, with a path length of 2.0 mm in a quartz cell, which was constantly stirred throughout the data collection. The solution was degassed with nitrogen for twenty minutes.

Equation \( y=A_1e^{-x/t_1}+A_2e^{-x/t_2}+A_3e^{-x/t_3}+y_0 \) was used for the fitting.

As part of an investigation of aggregation, we examined the effect of methyl viologen (MV\(^{2+}\)) on the fluorescence quenching. Figure 11c shows the Stern-Volmer

Table 2-3. Transient decay kinetics of the C-ab, S-ab, S-aabb, and S-aa ester polymers in water.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( t_1 ) (ps)</th>
<th>( A_1 ) (%)</th>
<th>( t_2 ) (ps)</th>
<th>( A_2 ) (%)</th>
<th>( t_3 ) (ps)</th>
<th>( A_3 ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-ab</td>
<td>2.16</td>
<td>39</td>
<td>103</td>
<td>31</td>
<td>460</td>
<td>30</td>
</tr>
<tr>
<td>S-ab</td>
<td>1.82</td>
<td>48</td>
<td>72</td>
<td>26</td>
<td>410</td>
<td>26</td>
</tr>
<tr>
<td>S-aabb</td>
<td>1.12</td>
<td>57</td>
<td>44</td>
<td>34</td>
<td>410</td>
<td>9</td>
</tr>
</tbody>
</table>
fluorescence quenching constant of C-ab, S-ab, and S-aabb. Also, Figure S-15 illustrates the Stern-Volmer (SV) plots, which showed the fluorescence quenching efficiency of the C-ab, S-ab, and S-aabb depending on the concentration of MV$^{2+}$. In both methanol and water, the SV plot showed the upward curvature. In methanol, the quenching ability of MV$^{2+}$ for the C-ab, S-ab, and S-aabb were $K_{sv} = 4.95 \times 10^6$ M$^{-1}$, $4.49 \times 10^6$ M$^{-1}$, and $7.38 \times 10^6$ M$^{-1}$, respectively (Figure 11c). In water, the fluorescence of the S-aabb was quenched more efficiently than those of the C-ab and S-ab according to the calculated $K_{sv}$ value ($6.96 \times 10^6$ M$^{-1}$ for C-ab, $4.49 \times 10^6$ M$^{-1}$ for S-ab, and $8.29 \times 10^6$ M$^{-1}$ for S-aabb). It can be explained that polymer-quencher complexes were more likely formed in the case of S-aabb. Therefore, the exciton can be transferred from the polymer chain to the quencher and can quench the fluorescence intensity.

Figure 2-14. $K_{sv}$ plots. (a) and (b) C-ab, S-ab, and S-aabb in water (pH = 8.0) and methanol using MV$^{2+}$ as a quencher. Fluorescence quenching of 10μM CPEs with MV$^{2+}$ in 10 mM. The Stern-Volmer constants ($K_{sv}$) are obtained from the steady-state fluorescence emission quenching

2.3.4 Solvent-dependent Experiment

To examine the solvent dependency of the fluorescence intensity for the C-ab, S-ab, and S-aabb CPEs, water (pH = 8) and methanol mixed solutions were prepared with various volume
ratio (Figure 2-15). We expected that the CPEs would have the strongest fluorescence intensity in pure methanol, which is a good solvent. However, the CPEs showed the strongest fluorescence intensity in water and methanol mixture. The portion of water was different, depending on the CPE. In the case of S-ab and S-aabb, 20% water was needed to obtain the highest fluorescence intensity while C-ab needed 40% water to show the highest fluorescence intensity. In all cases, the lowest fluorescence intensity appeared in pure water.

Figure 2-15. Solvent dependent fluorescence intensity. (a) C-ab, (b) S-ab, and (c) S-aabb. (d) Optimized solvent volume ratio (%) for the maximum fluorescence intensity of C-ab, S-ab, and S-aabb
2.4 Nature of the Defect in the AABB-type Sonogashira Cross-coupling Reaction

2.4.1 Preparation of the Glaser AA-type Homo-coupled Polymer

Figure 2-16. Synthesis of the Glaser-type acetylene homo-coupled PPE-based CPE (S-aa)

Diacetylene-functionalized AA-type palladium-catalyzed Sonogashira cross-coupling reaction was designed to confirm the presence of acetylene homo-coupled defect (Figure 2-16). Since the Sonogashira cross-coupling condition also contains a copper catalyst, it can produce a Glaser-type acetylene homo-coupled polymer.\(^{82}\) The Glaser type S-aa was synthesized by 10 mol\% Pd(PPh\(_3\))\(_4\) catalyzed Sonogashira cross-coupling reaction. First, the AA type monomer, didodecyl 2,2'-(2,5-diiodo-1,4-phenylene)bis(oxy)diacetate (5) in THF was transferred to round-bottom flask. Then, 10 mol\% copper (I) iodide (CuI) and 10 mol\% Pd(PPh\(_3\))\(_4\) were added to the solution. To obtain the Glaser AA type polymer, the reaction flask was exposed to the air. After the reaction was done, the reaction solution was quenched by water to terminate the polymerization. Then, the crude product was precipitated with methanol to remove the remaining catalyst and oligomers. Finally, the desired orange-colored S-aa ester polymer was obtained in 47\% yield. The S-aa ester polymer (10 mg) was dissolved in 3mL of THF. A 2:1 ratio methanol (2 mL) and water (1 mL) was added to the solution. Afterwards, an excess of NaOH was added to the reaction solution. After hydrolysis, the desired S-aa CPE was obtained by dialysis and freeze-dry process. The S-aa ester polymer was characterized by \(^1\)H NMR spectroscopy (Figure A-12), and GPC (\(M_n = 38,000\) g/mol, PDI = 1.80).
2.4.2 Photophysical Properties of the Glaser AA-Type Polymer

The absorption and fluorescence emission spectra of C-ab ester, S-ab ester, S-aabb ester, and S-aa ester polymers in THF are compared in Figure 2-17. The absorption maxima of C-ab ester, S-ab ester, S-aabb ester, and S-aa ester polymers were obtained at 420, 420, 430, and 446 nm while the emission maxima were obtained at 463, 463, 466, and 544 nm, respectively. Table 2-4 summarizes the optical properties of the C-ab ester, S-ab ester, S-aabb ester, and S-aa ester polymer. The S-aa ester polymer showed significantly red-shifted absorption and emission spectra, indicating the aggregation. After hydrolysis, the S-aa CPE lost its fluorescence in water. This result suggested that the acetylene homo-coupled structure enhanced the fluorescence quenching by energy transfer of excitons to low energy aggregation state traps.

![Diagram](image)

Figure 2-17. Absorption and emission spectra of C-ab ester, S-ab ester, S-aabb ester, and S-aa ester polymers in THF ($\lambda_{ex} = 410$ nm)
Therefore, it can be concluded that the acetylene homo-coupled structure acts as a defect in the polymer chains. The S-aabb acquired a structural defect during the polymerization.

Table 2-4. Optical properties of the C-ab, S-ab, S-aabb, and S-aa ester polymers in THF

<table>
<thead>
<tr>
<th>Ester polymer</th>
<th>λ_{max} (nm)</th>
<th>λ_{max} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-ab</td>
<td>420</td>
<td>463</td>
</tr>
<tr>
<td>S-ab</td>
<td>420</td>
<td>463</td>
</tr>
<tr>
<td>S-aabb</td>
<td>430</td>
<td>466</td>
</tr>
<tr>
<td>S-aa</td>
<td>446</td>
<td>544</td>
</tr>
</tbody>
</table>

Using the long-wavelength UV lamp, the ester polymers of C-ab, S-ab, and S-aabb showed blue-green fluorescence (Figure 2-18) while the S-aa ester polymer showed green fluorescence. The CPEs of S-ab and S-aabb showed green fluorescence in aqueous solution while the C-ab CPE exhibited blue-green fluorescence. The S-aa CPE showed zero-fluorescence in water which indicates that fluorescence was totally quenched.

Figure 2-18. Fluorescence of the ester polymers in THF (left) and CPEs in water (right)

2.4.3 Illustration of the Defect of the Homo-coupled Structure

Figure 2-19 describes the defect of the acetylene homo-coupled structure in the S-aabb polymer. Ideally, in a good solvent, the polymer chain absorbs and emits light properly, even though the acetylene homo-coupled structure exists. In a poor solvent, however, the polymer chains are close enough to have a π-stacking interaction, leading to fluorescence quenching. Thus, the acetylene homo-coupled defect of the Sonogashira cross-coupling reaction leads to
significant fluorescence quenching in aqueous solution. Therefore, reducing the acetylene homo-coupled structural defect can improve the photophysical properties of PPE-based CPEs in aqueous solution. Furthermore, the improved fluorescence efficiency can allow PPE-based CPEs to be applied to various kinds of optical materials.

Figure 2-19. Illustration of the acetylene homo-coupled defect for the S-aabb CPE in good and poor solvents (a and b, respectively). Illustration of the C-ab CPE in good and poor solvents (c and d, respectively)

2.5 Conclusion

There are many efforts to increase fluorescence efficiency. Recently, the fluorescence efficiency of oxygen-linked PPE-based CPE (P1-O) was reported to increase in methanol, but it was easily quenched in water. The P1-O was synthesized by Sonogashira cross-
coupling reaction using diiodo- and diacetylene-functionalized monomers. Therefore, it was suggested that an acetylene homo-coupled structure may exist in the polymer backbones.

Herein, we investigated the acetylene homo-coupled defect which may exist in the AABB-type oxygen-linked PPE-based CPE. To examine the acetylene homo-coupled defect, we synthesized S-aa with acetylene monomers by the Pd(PPh<sub>3</sub>)<sub>4</sub> catalyzed Sonogashira cross-coupling reaction and characterized its photophysical properties. Consequently, S-aa lost fluorescence intensity in water. Therefore, the acetylene homo-coupled defect can affect to the photophysical properties of the AABB type PPE-based CPE in water. The bi-functionalized AB-type chain-growth PPE-based CPE (C-ab) was synthesized to minimize the acetylene homo-coupling defect. In conclusion, the well-defined C-ab showed the improved fluorescence quantum yield (Φ = 35% compared to Φ = 4 (P1-O))<sup>1</sup>.

2.6 Experimental

2.6.1 Instrumentation and Methods

<sup>1</sup>H NMR spectra were obtained with a Varian Gemini-300 spectrometer (300 MHz). The chemical shift (δ) is reported in parts per million (ppm) using CHCl<sub>3</sub> and D<sub>2</sub>O as internal references. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), and m (multiplet).

Gel permeation chromatography (GPC) analysis was carried out in a system composed of a Shimadzu LC-6D pump, Agilent mixed-D column and a Shimadzu SPD-20A photo diode array (PDA) detector, with THF as an eluent at a 1 mL/min flow rate at room temperature. Molecular weight calibration was effected by the linear polystyrene standard in THF.

Photophysical measurements were conducted with dry HPLC-grade THF as the solvent in 1 x 1 cm quartz cuvettes. UV-Vis absorption spectra were obtained on a Varian Cary 100 dual
beam spectrophotometer. Fluorescence emission spectra were recorded on a Photon Technology International (PTI) fluorimeter and collected at 90° relative to the excitation beam. The optical density of the sample solution was kept at \( \leq 0.1 \) at the excitation wavelength. Refractive index correction was applied to the sample and the standard solution for emission quantum yield measurements.

Fluorescence lifetime was measured via a Fluo Time 100 Fluorescence Lifetime Spectrometer (Pico Quant, USA). Fluorescence correlation spectroscopy (FCS) measurements were obtained on a homemade setup using a 405 nm diode laser (Coherent, CUBE) as the excitation light.\(^8\) Fluorescein (30 nM in 10 mM phosphate buffer, pH = 8) was used to calibrate the system. The concentration of the polymer samples was 5 \( \mu \)M.

Femtosecond-picosecond transient absorption spectroscopy was performed using the pump-probe technique, with a temporal resolution of less than 100 fs. The fundamental 800 nm laser beam generated by an Astrella Ti:Sapphire Amplifier with a 1 kHz repetition rate, as supplied by Coherent, was split into two beams. One beam was directed through a Coherent Oper A Solo Optical Parametric Amplifier, where the excitation wavelength was tuned to 390 nm for pumping. The other beam was focused onto a sapphire plate to produce a white light continuum for probing. Both beams were guided into a Helios femtosecond transient absorption spectrometer manufactured by Ultrafast Systems, where the pump passed through a chopper, reducing its repetition rate by half, and a neutral density filter to adjust the average power of the sample position to 100 \( \mu \)W.\(^7\) The probe beam passed through a computer-controlled delay stage before the two beams were overlapped. The total range of the delay stage allowed for continuous temporal probing relative to the pump pulse of up to 8 ns. Absorption spectra with and without pumping were collected at >1000 different time delays to produce an array of absorption
difference spectra. Chirp corrections were employed using software supplied by Ultrafast Systems. The corrected change in optical density at 650 nm with time was taken from the difference spectra to fit the kinetic traces for all polymers. This transition was assumed to correspond to the excited singlet state of the CPEs due to its relatively short lifetime and the absence of other positive changes in optical density. All samples were prepared in an idealized solvent ratio of water (pH = 8) and methanol, such that their optical densities at 390 nm were equal to 0.4, with a path length of 2.0 mm in a quartz cell, which was constantly stirred throughout the data collection.

### 2.6.2 Materials

All reactions were performed under a dry, argon atmosphere. Tetrahydrofuran (THF) and pentane were dried using solvent purification columns (Glass Contour) and were kept over 4Å molecular sieves under Ar gas. Unless otherwise indicated, all starting materials were purchased from commercial sources (Aldrich, Acros) and used without further purification. A Pd(PPh₃)₄ catalyst was purchased from the Strem Chemical Co. P'Bu₃Pd(Ph)Br was synthesized according to literature.³¹ Synthetic steps for diiodo- and di-acetylene functionalized monomers were followed according to literature.¹ 2,2'-(1,4-phenylenebis(oxy))diacetic acid (2), didodecyl 2,2'-(1,4-phenylenebis(oxy))diacetate (3), didodecyl 2,2'-(2,5-diiodo-1,4-phenylene)bis(oxy))diacetate (4), didodecyl 2,2'-(2,5-bis((triisopropylsilyl)ethyl)ynyl)-1,4-phenylene)bis(oxy))diacetate(7), and didodecyl 2,2'-(2,5-diethynyl-1,4-phenylene)bis(oxy))diacetate (8) were synthesized according to literature.¹ The step-growth S-aabb polymer was prepared according to literature.¹
2.6.3 Synthesis of Monomers

2,2’-(1,4-phenylenebis(oxy))diacetic acid (2). Hydroquinone (1 g, 9.08 mmol) was dissolved in water (50 ml). Then, an excess of NaOH was added to the solution. After stirring for thirty minutes at room temperature, 2-bromoacetaldehyde (2.79 g, 22.7 mmol) was added to the reaction mixture. The reaction mixture was refluxed for four hours, then cooled in an ice-bath. The white solid was filtered and washed with water and methanol. Then, the solid was dissolved in hot water and acidified with 6N HCl. The resulting white solid was collected by vacuum filtration, washed with cold water and dried under reduced vacuum to yield the product (1.4 g, 67% yield). \(^1\)H NMR (DMSO-d\(_6\), \(\delta\)ppm): 12.94 (s, 2H), 6.83 (s, 4H), 4.60 (s, 4H). See SI Fig. A-2 for the NMR spectrum.

Didodecyl 2,2’-(1,4-phenylenebis(oxy))diacetate (3). A mixture of 2,2’-(1,4-phenylenebis(oxy))diacetic acid (1.5 g, 6.6 mmol), dodecyl alcohol (25 g, 134 mmol) and 1mL of 85% phosphoric acid was heated at 150°C in a two-necked round bottom flask for six hours. The water which formed during the esterification reaction was removed by Ar gas flow. After the reaction had finished, the reaction mixture was poured into excess hot hexane and cooled overnight. The precipitated solid was filtered and recrystallized from isopropanol to yield the product (2.8 g, 80% yield). \(^1\)H NMR (CDCl\(_3\), \(\delta\)ppm): 6.85 (s, 4H), 4.58 (s, 4H), 4.20 (t, 4H), 1.65 (m, 4H), 1.27 (m, 36H), 0.89 (t, 6H). See SI Fig. A-3 for the NMR spectrum.

Didodecyl 2,2’-(2,5-diodo-1,4-phenylene)bis(oxy))diacetate (4). Didodecyl 2,2’-(1,4-phenylenebis(oxy))diacetate (1 g, 1.77 mmol) in CCl\(_4\) (10 mL) was prepared in a 25 mL round bottom flask. Iodine (0.449 g, 1.77 mmol) and bis(trifluoroacetoxy) (0.738 g, 1.72 mmol) were added to the flask, and the solution was stirred for six hours at room temperature. After the
reaction was finished, it was quenched by 5% NaHSO₃ (20 ml) and extracted by CH₂Cl₂ (DCM) three times. Then, the extracted solution was dried with anhydrous MgSO₄. The desired product was obtained as 1.64 g, 99% yield (white solid). ¹H NMR (CDCl₃, δppm): 7.18 (s, 2H), 4.61 (m, 4H), 4.20 (m, 4H), 1.65 (m, 4H), 1.25 (m, 36H), 0.87 (m, 6H). See SI Fig. A-4 for the NMR spectrum.

**Didodecyl 2,2'-(2-(3-hydroxyprop-1-yn-1-yl)-5-iodo-1,4-phenylene)bis(oxy))diacetate (5)**. Didodecyl 2,2'-(2,5-diiodo-1,4-phenylene)bis(oxy))diacetate (1 g, 1.22 mmol) was dissolved in THF (50 mL). Then, CuI (18 mg, 0.12 mmol) and Pd(PPh₃)₄ (34 mg, 0.12 mmol) were added to the solution. The reaction solution was cooled to 0°C for thirty minutes. Then, propargylic alcohol (24 μL, 1.83 mmol) was added dropwise to the solution. The reaction was stirred for twelve hours, and then was quenched by water. The organic compound was extracted with DCM, and dried over MgSO₄. The solvent was removed under a reduced vacuum. The crude product was purified by column chromatography (DCM and MeOH as eluents) to yield the pure compound (588 mg, 65% yield). ¹H NMR (CDCl₃, δppm): 7.40 (s, 1H), 7.30 (s, 1H), 4.99 (s, 4H), 4.27 (s, 2H), 4.13 (t, 4H), 1.60 (m, 4H), 1.43 (m, 4H), 1.26 (m, 32H), 0.88 (t, 6H). ¹³C NMR (CDCl₃, δppm): 124.86, 116.75, 67.04, 65.70, 51.70, 31.90, 29.33, 28.49, 25.79, 22.67, 14.11. MS (ESI) m/z ([M + NH₄]⁺ 760.3647. See SI Fig. A-5 and A-17 for the NMR spectra. See SI Fig. A-25 for MS spectrum.

**Didodecyl 2,2'-(2-ethynyl-5-iodo-1,4-phenylene)bis(oxy))diacetate (6)**. Didodecyl 2,2'-(2-(3-hydroxyprop-1-yn-1-yl)-5-iodo-1,4-phenylene)bis(oxy))diacetate (500 mg, 0.67 mmol) was dissolved in diethyl ether (10 mL) and methanol (5 mL). Then, MnO₂ (288 mg, 3.35mmol) and KOH (375 mg, 6.7 mmol) were added to the reaction solution four times every four hours. The
reaction flask was protected from the light using aluminum foil. After stirring, the reaction mixture was filtered over a celite bed. The clear solution was concentrated and purified by column chromatography (DCM and MeOH as eluents) to leave the pure product (400 mg, 82% yield). $^1$H NMR (CDCl$_3$, $\delta_{ppm}$): 7.40 (s, 1H), 7.38 (s, 1H), 4.99 (s, 4H), 4.13 (t, 4H), 4.01 (s, 1H) 1.60 (m, 4H), 1.43 (m, 4H), 1.26 (m, 32H), 0.88 (t, 6H). $^{13}$C NMR (CDCl$_3$, $\delta_{ppm}$): 125.06, 117.48, 67.20, 65.80, 32.07, 29.50, 28.68, 25.96, 22.85, 14.27. MS (ESI) m/z ([M+NH$_4$]$^+$) 730.3524. See SI Fig. A-6 and A-18 for the NMR spectrum. See SI Fig. A-26 for the MS spectrum.

**Didodecyl 2,2'-(2,5,-bis((triisopropylsilyl)ethynyl)-1,4-phenylene)bis(oxy))diacetate(7)$^1$.** Didodecyl 2,2'-(2,5-diiodo-1,4-phenylene)bis(oxy))diacetate (200 mg, 0.24 mmol) in THF (5 mL) and diisopropyl amine (2 mL) was degassed for thirty minutes. Then, Pd(PPh$_3$)$_4$ (42 mg, 0.03 mmol) and CuI (14 mg, 0.07 mmol) were added to the solution. Afterwards, trimethylacetylene (153 $\mu$L, 0.68 mmol) was added dropwise to the reaction mixture. The reaction mixture was stirred for twelve hours at room temperature. After the reaction was finished, it was quenched by adding 5% NaHSO$_3$ (20 mL) and extracted using CH$_2$Cl$_2$ three times. Then, the extracted solution was dried over anhydrous MgSO$_4$. Finally, the solvent was removed under reduced pressure, leaving the desired product (98 mg, 51% yield). $^1$H NMR (CDCl$_3$, $\delta_{ppm}$): 7.60 (s, 2H), 4.99 (s, 4H), 4.13 (t, 4H), 1.60 (m, 4H), 1.43 (m, 4H), 1.26 (m, 32H), 0.88 (t, 6H), 0.09 (s, 18H). See SI Fig. A-7 for the NMR spectrum.

**Didodecyl 2,2'-(2,5-diethynyl-1,4-phenylene)bis(oxy))diacetate (8)$^1$.** Didodecyl 2,2'-(2,5-bis((triisopropylsilyl)ethynyl)-1,4-phenylene)bis(oxy))diacetate (50 mg, 0.07 mmol) was dissolved in THF. Tetrabutylammonium fluoride (TBAF) solution 1.0 M in THF was then added

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to the solution. The reaction mixture was stirred for four hours, then extracted with DCM. The remaining TBAF and side product were removed by column chromatography to yield the product (25 mg, 58% yield). \(^1\)H NMR (CDCl\(_3\), \(\delta_{ppm}\)): 7.58 (s, 2H), 4.99 (s, 4H), 4.13 (t, 4H), 3.98 (s, 2H), 1.60 (m, 4H), 1.43 (m, 4H), 1.26 (m, 32H), 0.88 (t, 6H), 0.09 (s, 18H). See SI Fig. A-8 for the NMR spectrum.

### 2.6.4 Synthesis of the Palladium Catalyst

**P^3Bu_3Pd(Ph)Br\(^{41}\).** In a glove box, Pd(P^3Bu_3)\(_2\) (30 mg, 0.059 mmol) and a stir bar were added to a Schlenk flask. Then, bromobenzene (3 mL, 2.7 mmol) was added to the flask. The reaction mixture was heated at 70°C for three hours and the solvent was removed under vacuum. The remaining solid was washed with distilled pentane. An orange precipitate immediately formed. The orange precipitate was washed five times with 10 mL of pentane. The orange solid was dried under vacuum to yield an air- and water-sensitive palladium catalyst (9 mg, 36% yield). \(^1\)H NMR (C\(_6\)D\(_6\), \(\delta_{ppm}\)): 7.52 (d, 2H), 6.89 (m, 3H), 2.18 (d, 27H). See SI Fig. A-1 for the NMR spectrum.

### 2.6.5 Polymerization

**PPE COOC\(_{12}\)H\(_{25}\) (C-ab ester).** A solution of 20 mol% of CuI (3.1 mg, 0.017 mmol) and 20 mol% of triphenylphosphine (4.4 mg, 0.017 mmol) in THF (2 mL) was added to a flame-dried 50 mL Schlenk flask. A solution of monomer 6 (60 mg, 0.084 mmol) in dry THF (2 mL) was then added. After the solution was degassed using three vacuum-argon purge cycles, polymerization was initiated by adding a 2 mol% of PdPh(\(t\)-Bu\(_3\)P)Br (0.7 mg, 1.68 \(\mu\)mol) catalyst. The reaction mixture was stirred under argon for twelve hours at 50°C and quenched by water. The concentrated solution was precipitated with methanol to remove the remaining catalyst. The precipitated solid was collected by filtration and washed with methanol and cold acetone to yield
the C-ab ester polymer (14.5 mg, 30% yield) as a yellow solid. SEC: $M_n = 8$ kDa, $D (M_w/M_n) = 1.20$, $^1H$ NMR (CDCl$_3$, $\delta_{ppm}$): 7.10 (s, 2H), 4.77 (m, 4H), 4.21 (m, 4H), 1.65 (m, 4H), 1.25 (m, 36H), 0.88 (t, 6H). $^{13}C$ NMR (CDCl$_3$, $\delta_{ppm}$): 134.34, 129.12, 67.18, 65.58, 32.07, 29.82, 28.68, 26.00, 22.84, 14.27. See SI Fig. A-9 and A-19 for the NMR spectra.

**PPE COOC$_{12}$H$_{25}$ (S-ab ester)**. A flame-dried 50 mL Schlenk flask was filled with 10 mol% of CuI (0.8 mg, 0.042 mmol). A solution of monomer 6 (60 mg, 0.084 mmol) in dry THF (3 mL) was then added. After the solution was degassed using three vacuum-argon purge cycles, polymerization was initiated by adding 10 mol% Pd(PPh$_3$)$_4$ (9.7 mg, 0.008 mmol) catalyst. The reaction mixture was stirred under argon for twelve hours at 50°C and quenched with water. The concentrated solution was precipitated with menthol. The precipitated solid was collected by filtration and washed with methanol and cold acetone to yield the S-ab ester polymer (24 mg, 49% yield) as a yellow solid. SEC: $M_n = 8$ kDa, $D (M_w/M_n) = 1.8$, $^1H$ NMR (CDCl$_3$, $\delta_{ppm}$): 7.19 (s, 2H), 4.72 (m, 4H), 4.21 (m, 4H), 1.68 (m, 4H), 1.22 (m, 36H), 0.93 (t, 6H). $^{13}C$ NMR (CDCl$_3$, $\delta_{ppm}$): 134.21, 128.12, 67.14, 65.75, 32.07, 29.69, 28.69, 25.98, 22.84, 14.27. See SI Fig. A-10 and A-20 for the NMR spectra.

**PPE COOC$_{12}$H$_{25}$ (S-aabb ester)**. A flame-dried 50 mL Schlenk flask was filled with argon. A solution of monomer 4 (57 mg, 0.07 mmol) and 8 (44 mg, 0.07 mmol) in dry THF (3 mL) and diisopropylamine (1 mL) was added. Then, 10 mol% of CuI (0.7 mg, 0.035 mmol) was added. After the solution was degassed using three vacuum-argon purge cycles, polymerization was initiated by adding 10 mol% Pd(PPh$_3$)$_4$ (9.7 mg, 0.008 mmol) catalyst. The reaction mixture was stirred under argon for twelve hours at 50°C and quenched by adding water. The concentrated solution was precipitated with methanol. The precipitated solid was collected by filtration and washed with methanol and cold acetone to yield the S-aabb ester polymer (21 mg, 51% yield) as
a yellow solid. SEC: \( M_n = 8 \) kDa, \( D (M_w/M_n) = 1.9 \), \(^1\)H NMR (CDCl\(_3\), \( \delta \) ppm): 7.11 (s, 2H), 4.75 (m, 4H), 4.19 (m, 4H), 1.67 (m, 4H), 1.25 (m, 36H), 0.88 (t, 6H). See SI Fig. A-11 for the NMR spectrum.

**PPE COOC\(_{12}\)H\(_{25}\) (S-aa ester).** A flame-dried 50 mL Schlenk flask was filled with argon. A solution of monomer 8 (20 mg, 0.033 mmol) in dry THF (2 mL) and diisopropylamine (1 mL) was added. Then, 10 mol% CuI (3 mg, 0.017 mmol) was added. After the solution was degassed using three vacuum-argon purge cycles, polymerization was initiated by adding 10 mol% Pd(PPh\(_3\))\(_4\) (4 mg, 0.003 mmol) catalyst. The resulting reaction mixture was stirred under argon for twelve hours at 50°C and quenched by adding water. The concentrated solution was precipitated with methanol. The precipitated solid was collected by filtration and washed with methanol and cold acetone to yield the S-aa ester polymer (9 mg, 47% yield) as a yellow solid. SEC: \( M_n = 38 \) kDa, \( D (M_w/M_n) = 1.8 \), \(^1\)H NMR (CDCl\(_3\), \( \delta \) ppm): 7.11 (s, 2H), 4.75 (m, 4H), 4.19 (m, 4H), 1.67 (m, 4H), 1.25 (m, 36H), 0.88 (t, 6H). \(^{13}\)C NMR (CDCl\(_3\), \( \delta \) ppm): 134.26, 128.24, 67.20, 65.75, 32.07, 29.69, 28.69, 25.98, 22.84, 14.27. See SI Fig. A-12 and A-21 for the NMR spectra.

**2.6.6 Hydrolysis**

Approximately 20 mg of organic soluble ester polymer from the chain-growth and step-growth polymerizations were characterized by GPC and \(^1\)H NMR. The remaining material (10 mg) was dissolved in 3 mL of THF. A 2:1 ratio methanol (2 mL) and water (1 mL) was added to the solution. Afterwards, an excess of NaOH was added to the reaction solution. The solution became cloudy during the reaction. After twelve hours, 3 mL of water was added and the reaction mixture became clear. The solution was stirred at room temperature for five more hours to finish the hydrolysis reaction. After the reaction was done, THF was removed under reduced
pressure. The remaining solution was transferred to a 12 kDa molecular weight cutoff (MWCO) regenerated cellulose membrane (Fisher Scientific) to achieve further purification. After dialysis, the solution was filtered through a 1.0 μm glass fiber membrane and freeze dried for three days. The resulting polyelectrolytes were characterized by $^1$H NMR. Typical reaction yields were 90 – 95%.

\( C-ab. \) $^1$H NMR (D$_2$O pH = 8, $\delta_{ppm}$): 7.22 (s, 2H), 4.66 (m, 4H). $^{13}$C NMR (D$_2$O pH = 8, $\delta_{ppm}$): 131.34, 127.12, 67.18, 64.58, 32.07. Refer to spectra in A-13 and A-22.

\( S-ab. \) $^1$H NMR (D$_2$O pH = 8, $\delta_{ppm}$): 7.10 (s, 2H), 4.55 (m, 4H). $^{13}$C NMR (D$_2$O pH = 8, $\delta_{ppm}$): 134.34, 127.12, 67.18, 64.58, 32.07. Refer to spectra in A-14 and A-23.

\( S-aabb. \) $^1$H NMR (D$_2$O pH = 8, $\delta_{ppm}$): 7.15 (s, 2H), 4.58 (m, 4H) Refer to spectrum in A-15.

\( S-aa. \) $^1$H NMR (D$_2$O pH = 8, $\delta_{ppm}$): 7.07 (s, 2H), 4.55 (m, 4H). $^{13}$C NMR (D$_2$O pH = 8, $\delta_{ppm}$): 134.34, 129.12, 65.18, 64.58, 32.07. Refer to spectra in A-16 and A-24.
CHAPTER 3
DI-, TRI-, AND TETRA-FUNCTIONALIZED STAR-SHAPED POLY(PHENYLENE ETHYNYLENE)-BASED CONJUGATED POLYELECTROLYTES: SYNTHESIS, CHARACTERIZATION, AND PHOTOPHYSICAL PROPERTIES

3.1 Background

Conjugated polymers (CPs) have been studied for organic semiconductor applications, such as in solar cells, light-emitting diodes, bio/chemo sensors, and field effect transistors. 88-90 Among CPs, multi-dimensional π-conjugated polymers such as dendrimers and star-shaped polymers have been investigated due to their unique chemical structures, reproducibility, solution processability, and optoelectronic properties. 60, 91-92 The star-shaped polymer consists of a core part which creates the shape of the polymer and an arm part which determines the chemical or physical properties. Figure 3-1 shows the structure of the star-shaped polymer.

![Figure 3-1. Structure of the star-shaped polymer. Figure was reprinted from Skabara with permission. Copyright 2010 The Royal Society of Chemistry](image)

Typically, well-defined star-shaped conjugated polymers are prepared via divergent or convergent pathways. In the divergent method, there are several steps to complete the synthesis. First, the monomer of the arms is coupled to the core. Afterwards, the terminal arms are functionalized with the desired functionality. Then, the arms are extended from the star-shaped core. The convergent method proceeds by one synthetic step by a reaction of pre-activated...
oligomeric arms and the core. In 2014, Wu and colleagues demonstrated the synthesis of air-stable pre-activated di- and tri-functionalized palladium complexes for chain-growth catalyst-transfer polymerization (CTP). The tri-functionalized palladium catalyst which is the core of the star-shaped polymer reacts with isocyanide by a divergent pathway to produce the star-shaped polymer (Figure 3-2).

![Figure 3-2. Polymerization of star-shaped polyisocyanides. Figure was reprinted from Wu with permission.](image)

Herein, we describe the synthesis of pre-activated di-, tri-, and tetra-functionalized palladium complexes to obtain the linear (from the di-functionalized Pd initiator) and star-shaped (from the tri- and tetra-functionalized Pd initiators) carboxylate side group PPE-based CPEs. The pre-activated tri- and tetra-functionalized palladium complexes become the core of the star-shaped PPE polymers, while the pre-activated di-functionalized palladium complex becomes the core of the linear PPE polymer. In the previous chapter, we demonstrated the acetylene homo-coupled defect, which may affect the photophysical properties with enhanced the fluorescence quenching. In this chapter, the AB-type monomer, didodecyl-2,2\(^\prime\)-(2-ethynyl-5-iodo-1,4-phenylene)bis(oxy))diacetate reacts with the di-, tri-, and tetra-functionalized palladium complexes in order to avoid the acetylene homo-coupled defect via a divergent pathway.
following the chain-growth mechanism. Steady-state absorption and fluorescence emission spectra show that di-, tri-, and tetra-functionalized PPE-based CPEs have improved fluorescence efficiency (43–49%) in water.

3.2 Polymer Design and Preparation

3.2.1 Preparation of Di-, Tri-, and Tetra-Functionalized Palladium Initiators

Figure 3-3. Synthesis of di-, tri-, and tetra-functionalized palladium initiators

In the previous chapter, we demonstrated Pd(P^Bu3)2(Ph)(Br) catalyzed chain-growth CTP for linear AB-type carboxylate PPE-based CPEs. Here, we introduce the di-, tri-, and tetra-functionalized palladium complexes to use in the synthesis of star-shaped carboxylate side chain PPE-based CPEs. To synthesize the pre-activated di-, tri-, and tetra-functionalized palladium complexes, as illustrated in Figure 3-3, 1,4-diethynylbenzene, 1,3,5-triethynylbenzene, or
tetrakis(4-ethynylphenyl)methane is reacted with bis(triethylphosphine)palladium dichloride (Pd(PET)_3Cl_2) and copper (I) chloride (CuCl) co-catalysts. The mixture was stirred for twelve hours at room temperature, and then quenched with methanol. Finally, the air-stable crude palladium complex was purified by column chromatography. The resulting di-, tri-, and tetra-functionalized palladium complexes were characterized by ^1^H NMR spectroscopy (see SI, Figure B-1, B-2, and B-3). The di-, tri-, or tetra-functionalized palladium initiators are called 2Pd catalyst, 3Pd catalyst, or 4Pd catalyst, respectively. In the case of the 4Pd catalyst, a white-colored precipitate was observed during the reaction. However, the white solid disappeared after adding an excess of DCM when the reaction was finished.

3.2.2 Synthesis of Star-shaped Carboxylate Side Chain PPE-based CPEs

Di-, tri-, and tetra-functionalized star-shaped PPE polymers were synthesized by chain-growth CTP with the 2Pd catalyst, 3Pd catalyst, and 4Pd catalyst (Figure 3-4). The AB-type monomer didodecyl 2,2^(-(2-ethynyl-5-iodo-1,4-phenylene)bis(oxy))diacetate (7) was prepared to avoid the acetylene homo-coupled defect which was discussed in the previous chapter. Thus, didodecyl 2,2^(-(2-ethynyl-5-iodo-1,4-phenylene)bis(oxy))diacetate reacts in the presence of 2 mol% 2Pd catalyst, 2 mol% 3Pd catalyst, or 2 mol% 4Pd catalyst with triphenylphosphine and copper (I) iodide to produce the chain-growth polymer, 2Pd, 3Pd, or 4Pd ester polymer. The reaction mixture was stirred at 50^°^C for twelve hours and then quenched with water to eliminate the by-products to produce the desired 2Pd ester polymer (M_n = 6,500 g/mol, PDI = 1.23), 3Pd ester polymer (M_n = 11,000 g/mol, PDI = 1.31) or 4Pd ester polymer (M_n = 18,000 g/mol, PDI = 1.72). To measure the accurate molecular weight of the 3Pd ester and 4Pd ester polymers (which are multi-dimensional polymers), the molecular weight and polydispersity were monitored by GPC with a light-scattering detector (Figure 3-5).
Figure 3-4. Synthesis of di-, tri-, and tetra-functionalized star-shaped PPE ester polymers

Hydrolysis was carried out by the following specific procedure. First, the di-, tri-, and tetra-functionalized PPE polymers were dissolved in THF: water: methanol (2: 1: 0.5 volume ratio) with an excess of NaOH. The reaction mixture was stirred at 55°C for twelve hours. Then, 2 mL of water was added to the reaction mixture to complete the hydrolysis. After the hydrolysis was finished, the reaction mixture was transferred to a 12 kDa molecular weight cutoff (MWCO)
regenerated cellulose membrane for purification by dialysis to remove the remaining NaOH. To prevent possible aggregation, the purified solution was freeze-dried at -20°C for forty-eight hours. The resulting powder was fluffy and orange colored. The molecular weights and polydispersities of the conjugated polyelectrolytes were assumed to be the same as the corresponding ester polymers. Figure 3-6 shows the structures of 2Pd CPE, 3Pd CPE, and 4Pd CPE.

Figure 3-5. GPC analysis for the 2Pd ester polymer (red, $M_n = 6,500$ g/mol and PDI = 1.23), 3Pd ester polymer (green, $M_n = 11,000$ g/mol and PDI = 1.31), and 4Pd ester polymer (orange, $M_n = 18,000$ g/mol and PDI = 1.72)

Figure 3-6. Structures and fluorescence of the 2Pd CPE, 3Pd CPE, and 4Pd CPE polymers. The fluorescence of CPEs in water was measured using a long wavelength UV-lamp
3.3.3 Structural Characterization by $^1$H NMR Spectra

The structures of pre-activated 2Pd catalyst (4), 3Pd catalyst (5), and 4Pd catalyst (6) were characterized by $^1$H NMR spectroscopy in either CD$_2$Cl$_2$ or CDCl$_3$ (Figure 3-7). The methylene proton and methyl proton on the ethyl group appeared at 2.0 and 1.24 ppm as a multiplet. The proton on benzene appeared between 6.90 and 7.20 ppm. In the cases of the 2Pd catalyst and the 3Pd catalyst, the protons appeared as a singlet due to their equivalent positions on benzene. However, the proton of the 4Pd catalyst showed a multiplet peak because of the two different kinds of protons resulting from symmetry consideration.

![NMR Spectra](image)

Figure 3-7. $^1$H NMR. (a) The pre-activated 2Pd catalyst, (b) 3Pd catalyst, and (c) 4Pd catalyst

3.3. Photophysical Properties

3.3.1 Steady-state Absorption and Emission Spectra

Steady-state absorption and emission spectra of star-shaped ester polymers were measured in a THF solution (Figure 3-8). The absorption maxima for 2Pd, 3Pd, and 4Pd ester
polymers were observed at 415, 409, and 409 nm, while the emission maxima were observed at 466, 466, and 464 nm for the 2Pd, 3Pd, and 4Pd ester polymers, respectively.

Figure 3-8. Photophysical Properties. (a) Absorption and (b) emission spectra of the 2Pd ester, 3Pd ester and 4Pd ester polymers in THF. The CPEs were excited at $\lambda_{ex} = 410$ nm

As shown in Figure 3-9, the star-shaped CPE series absorbed at 418 (2Pd CPE), 420 (3Pd CPE), and 418 nm (4Pd CPE). The star-shaped CPEs emitted at different wavelengths, increasing with the number of polymer arms (455, 460, and 463 nm for 2Pd, 3Pd, and 4Pd CPEs, respectively). In water, the absorption spectrum of the 3Pd CPE showed a broad and long-tailed shoulder at 475 nm. This result suggested that the 3Pd CPE aggregated in water. Considering the core structure of the star-shape polymer, the 2Pd polymer and 3Pd polymer have a planar core, while the 4Pd polymer has a tetrahedral core. In case of the 2Pd polymer, the polymer chain is easily entangled due to its high flexibility. However, in the case of the 3Pd polymer, the arms are extended from a triangular-shaped core. Thus, the chance of entanglement is lower than that for 2Pd. Therefore, the planarity of polymer core may affect to form aggregation. Table 3-1 summarizes the optical properties of the star-shaped ester polymers and CPE polymers.
Figure 3-9. Photophysical properties. (a) Absorption and (b) emission spectra for 2Pd, 3Pd, and 4Pd CPEs in methanol. Absorption (c) and emission spectra (d) for 2Pd, 3Pd, and 4Pd CPEs in water. The CPEs were excited at $\lambda_{ex} = 420$ nm.

<table>
<thead>
<tr>
<th></th>
<th>THF (ester polymer)</th>
<th>MeOH (CPEs)</th>
<th>Water (CPEs)</th>
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<tbody>
<tr>
<td>PPE</td>
<td>Abs. $\lambda_{max}$ (nm)</td>
<td>PL $\lambda_{max}$ (nm)</td>
<td>Abs. $\lambda_{max}$ (nm)</td>
</tr>
<tr>
<td>2Pd</td>
<td>415</td>
<td>466</td>
<td>418</td>
</tr>
<tr>
<td>3Pd</td>
<td>409</td>
<td>466</td>
<td>420</td>
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<tr>
<td>4Pd</td>
<td>409</td>
<td>464</td>
<td>418</td>
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3.3.2 Fluorescence Quantum Yields and Stern-Volmer Constants

The fluorescence quantum yield indicates the ratio of photons emitted to photons absorbed. The fluorescence quantum yields of the star-shaped ester polymers and CPEs are
shown in Figure 3-10. Similar to the linear 2Pd ester polymer, the star-shaped 3Pd and 4Pd ester polymers have 80 – 90% quantum yields in THF while the CPEs have 59 – 73% and 43 – 50% quantum yields in methanol and water, respectively. The quantum yield results indicate that the 2Pd, 3Pd, and 4Pd CPEs have improved fluorescence efficiencies compared to the linear AABB-type step-growth polymer with 10% fluorescence efficiency in water.

As part of an investigation of aggregation, we examined the effect of methyl viologen (MV$_2^{2+}$) on the fluorescence quenching. Figure 3-11 illustrates the Stern-Volmer (SV) plots, which show the fluorescence quenching efficiency of the 2Pd, 3Pd, and 4Pd CPEs depending on the concentration of MV$_2^{2+}$.
Figure 3-11. Stern-Volmer plots of 2Pd CPE, 3Pd CPE, and 4Pd CPE in methanol (a) and water (pH = 8) (b). 10 μM of CPEs treated with methyl viologen. The $K_{sv}$ was obtained by the concentration range of a quencher from 1 to 5 μM.

In both methanol and water, the SV plot shows an upward curvature. In methanol, the quenching ability of MV$^{2+}$ for the 2Pd CPE, 3Pd CPE, and 4Pd CPE were $K_{sv} = 4.49 \times 10^6$ M$^{-1}$, $4.95 \times 10^6$ M$^{-1}$ and $7.79 \times 10^6$ M$^{-1}$, respectively. In water, the fluorescence of the 3Pd CPE was quenched more efficiently than those of the 2Pd CPE and 4Pd CPE according to the calculated $K_{sv}$ value ($5.49 \times 10^6$ M$^{-1}$ for the 2Pd CPE, $14.5 \times 10^6$ M$^{-1}$ for the 3Pd CPE, and $9.64 \times 10^6$ M$^{-1}$ for the 4Pd CPE). It can be explained that polymer-quencher complexes were more likely formed in the case of 3Pd CPE. Therefore, the exciton can be transferred from the polymer chain to the quencher and can quench the fluorescence intensity. Table 3-2 summarizes the fluorescence quantum yield and Stern-Volmer constant ($K_{sv}$) in methanol and water.
Table 3-2. Fluorescence quantum yield and Stern-Volmer constants ($K_{sv}$) of the 2Pd ester, 3Pd ester and 4Pd ester polymers in THF and CPEs in methanol and water ($pH = 8.0$). $Q_{90}$ represents the 90% quenching of fluorescence intensity. The $K_{sv}$ was determined by the concentration range from 0 to 5 μM of the Stern-Volmer plot.

<table>
<thead>
<tr>
<th>Ester</th>
<th>CPE (THF)</th>
<th>CPE (MeOH)$^a$</th>
<th>CPE (water)$^b$</th>
<th>CPE (MeOH)</th>
<th>CPE (water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Pd</td>
<td>0.86</td>
<td>0.68</td>
<td>0.48</td>
<td>4.49 (9.41)</td>
<td>5.49 (7.09)</td>
</tr>
<tr>
<td>3Pd</td>
<td>0.90</td>
<td>0.59</td>
<td>0.43</td>
<td>4.95 (8.41)</td>
<td>14.5 (4.79)</td>
</tr>
<tr>
<td>4Pd</td>
<td>0.85</td>
<td>0.73</td>
<td>0.49</td>
<td>7.79 (5.99)</td>
<td>9.64 (5.67)</td>
</tr>
</tbody>
</table>

$^a$ Contains 1mg/mL NaOH. $^b$ pH = 8 water was prepared by adding NaOH.

3.3.3 Fluorescence Lifetime

Table 3-3. Fluorescence lifetimes

<table>
<thead>
<tr>
<th>CPE</th>
<th>solvent</th>
<th>$\lambda_{em}$</th>
<th>$\tau_1$</th>
<th>$A_1$</th>
<th>$\tau_2$</th>
<th>$A_2$</th>
<th>$\tau_3$</th>
<th>$A_3$</th>
<th>$&lt;\tau&gt;$*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[nm]</td>
<td>[ns]</td>
<td>[%]</td>
<td>[ns]</td>
<td>[%]</td>
<td>[ns]</td>
<td>[%]</td>
<td>[ns]</td>
</tr>
<tr>
<td>2Pd</td>
<td>H$_2$O</td>
<td>450</td>
<td>0.32</td>
<td>6</td>
<td>0.08</td>
<td>17</td>
<td>0.05</td>
<td>77</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>450</td>
<td>0.70</td>
<td>12</td>
<td>0.02</td>
<td>88</td>
<td>-</td>
<td>-</td>
<td>0.10</td>
</tr>
<tr>
<td>Ester</td>
<td>THF</td>
<td>450</td>
<td>0.54</td>
<td>22</td>
<td>0.02</td>
<td>78</td>
<td>-</td>
<td>-</td>
<td>0.13</td>
</tr>
<tr>
<td>3Pd</td>
<td>H$_2$O</td>
<td>450</td>
<td>0.48</td>
<td>5</td>
<td>0.16</td>
<td>6</td>
<td>0.02</td>
<td>89</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>450</td>
<td>0.44</td>
<td>4</td>
<td>0.89</td>
<td>2</td>
<td>0.02</td>
<td>94</td>
<td>0.05</td>
</tr>
<tr>
<td>Ester</td>
<td>THF</td>
<td>450</td>
<td>0.58</td>
<td>1</td>
<td>0.16</td>
<td>99</td>
<td>-</td>
<td>-</td>
<td>0.16</td>
</tr>
<tr>
<td>4Pd</td>
<td>H$_2$O</td>
<td>450</td>
<td>0.42</td>
<td>2</td>
<td>0.03</td>
<td>98</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>450</td>
<td>1.14</td>
<td>25</td>
<td>0.48</td>
<td>75</td>
<td>-</td>
<td>-</td>
<td>0.06</td>
</tr>
<tr>
<td>Ester</td>
<td>THF</td>
<td>450</td>
<td>0.62</td>
<td>20</td>
<td>0.02</td>
<td>80</td>
<td>-</td>
<td>-</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Fluorescence lifetime was measured by determining the intensity of fluorescence as a function of time following instant excitation. We compared the fluorescence lifetimes for star-shaped PPE ester polymers and CPEs in MeOH and water (Table 3-3). The ester polymers exhibited 0.13 - 0.16 ns of the average fluorescence lifetime, whereas CPEs had 0.02 - 0.05 and
0.05 - 0.10 ns in water and methanol. The 3Pd CPE had the fastest lifetime at $\tau = 0.02$ ns in water and methanol which indicates the emission from aggregation sites.

### 3.3.4 Computational Results

Time Dependent Density Functional Theory (TDDFT) calculations were carried out to understand the aggregated structure of star-shaped PPE-based CPEs by Jason Zeman in Schanze group. The 2Pd CPE, 3Pd CPE, and 4Pd CPE were used for calculations (Figure 3-12).

![Diagram of structures](image)

Figure 3-12. Structures and fluorescence of the 2Pd CPE, 3Pd CPE, and 4Pd CPE polymers

Figure 3-13 shows the distribution of gyradius (radius of gyration) depends on the degree of polymerization which is from one to five. The gyradius of star-shaped CPEs increased as the degree of polymerization increased. A gyradius increment of the 4Pd CPE was smaller than those of the 2Pd CPE and 3Pd CPE which may be related to the three-dimensional structure of the 4Pd CPE. The gyration of the four side chains of the 4Pd CPE may require more energy than those of the two-dimensional 2Pd CPE and 3Pd CPE.
Figure 3-13. Distribution of the radius of gyration depend on the degrees of polymerization from one to five, for the 2Pd CPE (a), 3Pd CPE (b), and 4Pd CPE (c). Results were obtained from 1 ns of MD using the Universal Force Field (UFF).

The polymer structures of the 2Pd, 3Pd, and 4Pd CPEs were simulated using DFT calculation and the results are shown in Figure 3-14 and Table 3-4 (The solvent was implied in the calculations). The geometries for the CPEs were optimized by the B3LYP functional along with the 6-31G(d) basis set for all atoms. The $T_1 (\Delta\text{SCF})$ refers to the energy difference between the optimized singlet and triplet geometries. $S_1$ from TDDFT is a theoretical vertical excitation from the ground state to the singlet state while $T_1$ is from the ground state to the triplet state. Generally, $T_1 (\Delta\text{SCF})$ is smaller than $T_1$ because theoretical vertical excitation occurs not only from the ground state to the lowest vibrational level of the triplet but also to the second and third lowest vibrational levels. In the cases of the 2Pd, 3Pd, and 4Pd CPEs, $T_1 (\Delta\text{SCF})$ and $T_1$ were 1.78 and 1.68. It may be because when the triplet state polymer relaxes to the ground state, the geometry of the polymer may change, or because the triplet state polymer may not be the most stable geometry.
Figure 3-14. Optimized geometries of the 2Pd, 3Pd, and 4Pd CPEs simulated by DFT

Table 3-4. DFT calculation results

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HOMO</th>
<th>LUMO</th>
<th>gap</th>
<th>$T_1(\Delta\text{SCF})^a$</th>
<th>$S_1^b$</th>
<th>$T_1^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Pd CPE</td>
<td>-4.70</td>
<td>-2.15</td>
<td>2.55</td>
<td>1.78</td>
<td>2.24</td>
<td>1.63</td>
</tr>
<tr>
<td>3Pd CPE</td>
<td>-4.76</td>
<td>-1.97</td>
<td>2.79</td>
<td>1.76</td>
<td>2.47</td>
<td>1.72</td>
</tr>
<tr>
<td>4Pd CPE</td>
<td>-4.73</td>
<td>-1.92</td>
<td>2.81</td>
<td>1.76</td>
<td>2.50</td>
<td>1.75</td>
</tr>
</tbody>
</table>

$^aT_1(\Delta\text{SCF})$ refers to the energy difference between the optimized singlet and triplet geometries. $^bS_1$ from TDDFT is a theoretical vertical excitation from the ground state to the singlet state. $^cT_1$ from TDDFT is a theoretical vertical excitation from the ground state to the triplet state.

The images of the dynamics of solvent-free single molecule of 2Pd, 3Pd, and 4Pd CPEs were simulated by the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) II Forcefield (Figure 3-15). COMPASS can predict molecules’ structural, conformational, vibrational, and thermos physical properties. $^94$ The COMPASS II Forcefield is applied to minimize the bond stretching energy of molecules. In the absence of solvent
molecules, the images of 2Pd, 3Pd, and 4Pd CPEs’ dynamics show the polymer postures with minimizing the bond stretching energy.

Figure 3-15. Molecular dynamics. (a) solvent-free 2Pd CPE, (b) 3Pd CPE, and (c) 4Pd CPE. The simulation was carried out by the COMPASS II Forcefield

Calculations to predict the aggregation structure of 2Pd, 3Pd, and 4Pd CPEs in water was performed followed by 4 ns constant energy (NVE) annealing dynamics of energy minimization for 1 ns of constant temperature (NVT) dynamics. It is predicted that the linear 2Pd CPE has a well-organized or structured geometry (Figure 3-16). The 3Pd CPE also shows the organized geometry but less organized than 2Pd CPE. However, the 4Pd CPE displays the disorganized geometry. The simulation result suggested that the 2Pd and 3Pd CPE tend to aggregate in solution.
Figure 3-16. Aggregated structures. (a) 2Pd CPE, (b) 3Pd CPE, and (c) 4Pd CPE in water. The right side of the structures shows the geometry of star-shaped CPEs after 1 ns of NVT dynamics with 4 ns of NVE annealing.

Transient absorption (TA) spectra of the 2Pd, 3Pd, and 4Pd CPEs were shown in Figure 3-17. For TA measurement, polymer samples were dissolved in 95% water/5% methanol solvent to give an OD of 0.7 in a 2 mm cuvette. From the 2Pd CPE to the 4Pd CPE, the first two lifetimes significantly decreased but the third and longer lifetimes increased with increasing
disorganized aggregation. It seems that the 4Pd CPE showed decreased the short lifetime for singlet exciton decay by opening new pathways for energy transfer to the aggregate-trapped sites. The transient absorption kinetics for decay of the triplet state were measured at the constant wavelength, $\lambda_{\text{abs, max}}$ (590, 650, and 620 nm for 2Pd, 3Pd, and 4Pd CPEs, respectively). Table 3-5 summarized the fluorescence lifetime in the triplet state of CPEs. The 3Pd CPE showed the fastest lifetime component (with 0.19 ns) which indicates the significant decrease of the first two lifetimes in TA spectra.

Figure 3-17. Time-resolved transient absorption spectra after 250 ns time delay of the 2Pd CPE, 3Pd CPE, and 4Pd CPE in 95% water/5% methanol. Transient absorption decay kinetics for CPEs. It was taken at maximum absorbance: 590 (2Pd), 650 (3Pd), and 620 nm (4Pd)
Table 3-5. Summary of the triplet state decay lifetimes for the CPEs

<table>
<thead>
<tr>
<th>CPEs</th>
<th>τ₁</th>
<th>A₁</th>
<th>τ₂</th>
<th>A₂</th>
<th>τ₃</th>
<th>A₃</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Pd</td>
<td>5.40</td>
<td>0.33</td>
<td>70</td>
<td>3.29</td>
<td>279</td>
<td>96.38</td>
<td>0.755</td>
</tr>
<tr>
<td>3Pd</td>
<td>0.19</td>
<td>0.19</td>
<td>15</td>
<td>1.17</td>
<td>414</td>
<td>98.64</td>
<td>0.727</td>
</tr>
<tr>
<td>4Pd</td>
<td>8.20</td>
<td>0.79</td>
<td>115</td>
<td>9.95</td>
<td>580</td>
<td>89.26</td>
<td>0.757</td>
</tr>
</tbody>
</table>

3.3.5 DLS Analysis

Dynamic light scattering (DLS) is applied to estimate populations of CPEs’ aggregations for polymers. DLS provides an average hydrodynamic radius of polymers. DLS was utilized to determine the sizes and size distributions of 2Pd CPE, 3Pd CPE, and 4Pd CPE in water and methanol (Figure 3-18). The 1μM of 2Pd, 3Pd, and 4Pd CPEs was dissolved in water (pH =8) and methanol at room temperature. The average size (number) of 2Pd CPE, 3Pd CPE, and 4Pd CPE polymers were obtained as 21, 24, and 19 nm, respectively, in methanol. The sizes of CPEs in methanol is smaller than those of CPEs in water. In water, the average size (number) of 2Pd, 3Pd, and 4Pd CPEs exhibited 18, 44, and 68 nm, respectively. The DLS results in water showed that the hydrodynamic size increases in the order of the 2Pd, 3Pd, and 4Pd CPEs. This result is related to the simulation result of the aggregation images of the CPEs (Figure 3-16). As a result, the disorganized polymer (4Pd CPE) showed the highest hydrodynamic volume in water.
Figure 3-18. Number average size distributions of 2Pd CPE, 3Pd CPE, and 4Pd CPE in methanol (a) and water (b). Conditions: 1μM of CPEs in water (pH = 8) and methanol at room temperature. The pH =8 water was prepared by adding NaOH in water.

The number average size and the intensity average size of star-shaped CPEs are summarized in Table 3-6.

Table 3-6. Average particle size of star-shaped PPE-based CPEs in MeOH and water

<table>
<thead>
<tr>
<th>Polymer</th>
<th>MeOH</th>
<th>Water (pH = 8)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number average size</td>
<td>Intensity average size</td>
</tr>
<tr>
<td>2Pd CPE</td>
<td>21 (nm)</td>
<td>142 (nm)</td>
</tr>
<tr>
<td>3Pd CPE</td>
<td>24 (nm)</td>
<td>190 (nm)</td>
</tr>
<tr>
<td>4Pd CPE</td>
<td>19 (nm)</td>
<td>164 (nm)</td>
</tr>
</tbody>
</table>
3.4. Conclusion

In this chapter, we synthesized di-, tri-, and tetra-functionalized pre-activated palladium catalysts. The pre-activated palladium catalyst produced the chain-growth polymer with bi-functionalized AB-type monomer. Fluorescence quantum yield of 2Pd, 3Pd, and 4Pd CPEs were improved ($\Phi_{fl} = 43\% - 49\%$) in water compared to the AABB-type step-growth polymer ($\Phi_{fl} = 4\%$, discussed in chapter 2). The 2Pd and 3Pd CPEs showed the organized structure at the COMPASS II Forcefield simulation. The 4Pd CPE exhibited the disorganized geometry and large particle size in COMPASS II Forcefield simulation and DLS results. The emission spectra of 2Pd and 4Pd CPE showed similar shape and wavelength (460 and 463 nm) in water. In the time-resolved transient absorption spectra, from the 2Pd CPE to the 4Pd CPE, the first two lifetimes significantly decreased but the third and longer lifetimes increased with increasing disorganization. It seems that the 4Pd CPE showed decreased the short lifetime for singlet exciton decay by opening new pathways for energy transfer to the aggregate-trapped sites. Among the 2Pd, 3Pd, and 4Pd CPEs, the 3Pd CPE tended to aggregate in water according to absorption spectra, fluorescence lifetime, and fluorescence quenching results. Compared to the core of 2Pd CPE, the core of the 3Pd CPE was planar due to triangle shape. Therefore, the planar core of 3Pd CPE caused the polymer to aggregate in water, enhancing the $\pi$-stacking interaction between polymer chains.

3.5. Experimental

3.5.1 Instrumentation and methods

NMR spectra were measured on a Gemini-300 FT-NMR (300 MHz), a Mercury-300 FT-NMR, or an Inova-500 FT-NMR (500 MHz). The chemical shifts ($\delta$) are reported in parts per million (ppm) using CHCl$_3$ and D$_2$O as the internal reference. Splitting patterns are designated as
s (singlet), d (doublet), t (triplet), and m (multiplet). Gel permeation chromatography (GPC) analysis was carried out on a system composed of a Shimadzu LC-6D pump, Alient mixed-D column and a Shimadzu SPD-20A photodiode array (PDA) detector, with THF as an eluent at 1 mL/min flow rate at room-temperature. The system was calibrated against linear polystyrene standards in THF.

Photophysical measurements were conducted with dry HPLC-grade THF as the solvent in 1 x 1 cm quartz cuvettes. UV-vis absorption spectra were obtained on a Varian Cary 100 dual beam spectrophotometer. Fluorescence emission spectra were recorded on a Photon Technology International (PTI) fluorimeter and collected 90° relative to the excitation beam. The optical density of the sample solutions was kept at ≤0.1 at the excitation wavelength. Refractive index corrections were applied for samples and standard solutions for emission quantum yield measurements. Fluorescence lifetimes were measured via a Fluo Time 100 Fluorescence Lifetime Spectrometer (Pico Quant, USA). Fluorescence correlation spectroscopy (FCS) measurements were obtained on a homemade setup using a 405 nm diode laser (Coherent, CUBE) as the excitation light. Fluorescein (30 nM in 10 mM phosphate buffer, pH = 8) was used as the calibration for the system. The concentration of polymer samples was 5 μM.

Fluorescence lifetimes were measured using a Fluo Time 100 Fluorescence Lifetime Spectrometer (Pico Quant, USA). Fluorescence correlation spectroscopy (FCS) measurements were obtained on a homemade setup using a 405 nm diode laser (Coherent, CUBE) as the excitation light. Fluorescein (30 nM in 10 mM phosphate buffer, pH = 8) was used as the calibration for the system. The concentration of polymer samples was 5 μM. Femtosecond-picosecond transient absorption spectroscopy was performed using the pump-probe technique with a temporal resolution of less than 100 fs. The fundamental 800 nm laser beam generated by
an Astrella Ti:Sapphire Amplifier with a 1 kHz repetition rate, as supplied by Coherent, was split into two beams. One beam was directed through a Coherent Oper A Solo Optical Parametric Amplifier, where the excitation wavelength was tuned to 390 nm for pumping. The other beam was focused onto a sapphire plate to produce a white light continuum for probing. Both beams were guided into a Helios femtosecond transient absorption spectrometer manufactured by Ultrafast Systems, where the pump passed through a chopper, reducing its repetition rate by half, and through a neutral density filter to adjust the average power at the sample position to 100 µW. The probe beam passed through a computer-controlled delay stage before the two beams were overlapped. The total range of the delay stage allowed for continuous temporal probing relative to the pump pulse of up to 8 ns. Absorption spectra, with and without pumping, were collected at >1000 different time delays to produce an array of absorption difference spectra. Chirp corrections were employed using software supplied by Ultrafast Systems. The corrected change in optical density at 650 nm with time was measured from the difference spectra to fit the kinetic traces for all polymers. This transition was assumed to correspond to the excited singlet state of the CPEs due to its relatively short lifetime and the absence of other positive changes in optical density. All samples were prepared in an idealized solvent ratio of water (pH = 8) and methanol, such that their optical densities at 390 nm were equal to 0.4, with a path length of 2.0 mm in a quartz cell, which was constantly stirred throughout the data collection.

Computational calculations were performed by DFT. The geometry was optimized by the B3LYP functional with the 6-31G(d) basis set for all atoms by Charles J. Zeman.

3.5.2 Materials

All reactions were performed under a dry, argon atmosphere. THF was dried using solvent purification columns (Glass Contour) and 4Å molecular sieves. Unless otherwise
indicated, all starting materials were purchased from commercial sources (Aldrich, Acros) and were used without further purification. A Pd(PPh$_3$)$_4$ catalyst was purchased from Strem Chemical Co. Di-functionalized palladium initiator (4) and tri-functionalized palladium initiator (5) were synthesized according to literature.$^{62}$

### 3.5.3 Synthesis of Palladium Initiators

**Di-functionalized palladium initiator (4)**$^{62}$. 1,4-Diethynylbenzene (16 mg, 0.12 mmol) was treated with Pd(PPh$_3$)$_2$Cl$_2$ (140 mg, 0.31 mmol) in the presence of 3.6 mg of copper (I) chloride as a co-catalyst in a mixture of diethylamine (8 mL) and dichloromethane (8 mL). The mixture was stirred at room temperature for twelve hours. After the solvent was removed by evaporation under reduced pressure, the residue was purified by chromatography with petrol ether and dichloromethane as the eluent (v/v = 1/1) to yield the desired 2Pd catalyst as a yellow solid (68 mg, 63% yield). $^1$H NMR (CD$_2$Cl$_2$, $\delta$ ppm): 7.30 (s, 4H), 1.95 (m, 24H), 1.29 (m, 36H). See SI Fig. B-1 for the NMR spectrum.

**Tri-functionalized palladium initiator (5)**$^{62}$. 1,3,5-Triethynylbenzene (27 mg, 0.18 mmol) was treated with Pd(PPh$_3$)$_2$Cl$_2$ (2.23 mg, 0.54 mmol) in the presence of 5.3 mg of copper (I) chloride as a catalyst in a mixture of diethylamine (8 mL) and dichloromethane (8 mL). The mixture was stirred at room temperature for twelve hours. After the solvent was removed by evaporation under reduced pressure, the residue was purified by chromatography with petrol ether and dichloromethane as the eluent (v/v = 1/1) to yield a 3Pd catalyst as a yellow solid (150 mg, 65% yield). $^1$H NMR (CDCl$_3$, $\delta$ ppm): 6.95 (s, 3H), 1.99 (m, 36H), 1.20 (m, 54H). See SI Fig. B-2 for the NMR spectrum.

**Tetra-functionalized palladium initiator (6)**. Tetrakis(4-ethynylphenyl)methane (16 mg, 0.04 mmol) was treated with Pd(PPh$_3$)$_2$Cl$_2$ (83 mg, 0.21 mmol) in the presence of 1.2 mg of
copper (I) chloride as the catalyst in a mixture of diethylamine (8 mL) and dichloromethane (8 mL). The mixture was stirred at room temperature for twelve hours. After the solvent was removed by evaporation under reduced pressure, the residue was purified by chromatography with dichloromethane as the eluent to yield a 4Pd catalyst as a yellow solid (45 mg, 58% yield).

$^1$H NMR (CDCl$_3$, δ ppm): 7.09 (m, 16H), 1.96 (m, 48H), 1.20 (m, 72H). $^{13}$C NMR (CDCl$_3$, δ ppm): 144.89, 136.25, 128.25, 43.62, 12.35, 8.98. [M]$_{+}$ 1905.4057. See SI Fig. B-3 and B-10 for the NMR spectra. See SI Fig. B-17 for the MS spectrum.

3.5.4 Polymerization of Star-Shaped Polymers

**Di-functionalized PPE polymer (8).** Didodecyl 2,2’-((2-ethynyl-5-iodo-1,4-phenylene)bis(oxy))diacetate (60 mg, 0.084mmol) was dissolved in dry THF (3 mL) and diisopropyl alcohol (1 mL). After adding copper (I) iodide (3 mg, 0.001 mmol) and triphenylphosphine (3 mg, 0.001mmol), the reaction solution became a yellow color. Then, the solution of the 2Pd catalyst initiator (1.2 mg, 0.001 mmol) in THF (1mL) was slowly added dropwise to the reaction solution. The reaction mixture was stirred for twelve hours at 55°C. After the reaction was finished, THF and diisopropyl alcohol were removed under reduced pressure. Then, the product was dissolved in a minimum amount of chloroform and precipitated with excess methanol. The precipitated solid was collected by filtration and washed with methanol three times to yield a 2Pd ester polymer (65 mg, 62% yield). SEC: $M_n = 6.5$ kDa, $D$ ($M_w/M_n$) = 1.23, $^1$H NMR (CDCl$_3$, δ ppm): 7.32 (m, 2H), 6.85 (m, 2H), 6.68 (m, 2H), 4.73 (m, 4H), 4.20 (m, 4H), 1.64 (m, 4H), 1.25 (m, 32H), 0.89 (m, 6H). $^{13}$C NMR (CDCl$_3$, δ ppm): 137.89, 132.78, 67.85, 66.23, 32.78, 29.89, 28.17, 22.14. See SI Fig. B-4 and B-11 for the NMR spectra.

**Tri-functionalized PPE polymer (9).** Didodecyl 2,2’-((2-ethynyl-5-iodo-1,4-phenylene)bis(oxy))diacetate (30 mg, 0.04 mmol) was dissolved in dry THF (2 mL) and
diisopropyl alcohol (1 mL). After adding copper (I) iodide (1.5 mg, 0.008 mmol) and triphenylphosphine (2 mg, 0.008 mmol), the reaction solution became a yellow color. Then, a solution of the 3Pd catalyst initiator (1 mg, 0.008 mmol) in THF (1 mL) was slowly added to the reaction solution. The reaction mixture was stirred for twelve hours at 55°C. After the reaction was finished, THF and diisopropyl alcohol were removed under reduced pressure. Then, the product was dissolved in a minimum amount of chloroform and precipitated with excess methanol. The precipitated solid was collected by filtration and washed with methanol three times to yield a 3Pd ester polymer (18 mg, 30% yield). SEC: $M_n = 11$ kDa, $D (M_w/M_n) = 1.31$, $^1H$ NMR (CDCl$_3$, $\delta_{ppm}$): 7.25 (m, 2H), 4.78 (m, 4H), 4.32 (m, 4H), 1.65 (m, 4H), 1.48 (m, 32H), 0.89 (m, 6H). $^{13}C$ NMR (CDCl$_3$, $\delta_{ppm}$): 133.89, 131.23, 68.89, 67.12, 32.18, 30.28, 27.58, 26.45, 16.12. See SI Fig. B-5 and B-12 for the NMR spectra.

**Tetra-functionalized PPE polymer (10).** Didodecyl 2,2’-((2-ethynyl-5-iodo-1,4-phenylene)bis(oxy))diacetate (30 mg, 0.04 mmol) was dissolved in dry THF (2 mL) and diisopropyl alcohol (1 mL). After adding copper (I) iodide (1.5 mg, 0.008 mmol) and triphenylphosphine (2 mg, 0.008 mmol), the reaction solution became a yellow color. Then, the solution of the 4Pd catalyst initiator (0.8 mg, 0.008 mmol) in THF (1 mL) was slowly added dropwise to the reaction solution. The reaction mixture was stirred for twelve hours at 55°C. After reaction was finished, THF and diisopropyl alcohol were removed under reduced pressure. Then, the product was dissolved in a minimum amount of chloroform solution and precipitated with excess methanol. The precipitated solid was collected by filtration and washed with methanol three times to yield a 4Pd ester polymer (18 mg, 20% yield). SEC: $M_n = 18$ kDa, $D (M_w/M_n) = 1.72$, $^1H$ NMR (CDCl$_3$, $\delta_{ppm}$): 7.58 (m, 16H), 7.18 (m, 2H), 4.78 (m, 4H), 4.32 (m, 4H), 1.65 (m, 4H), 1.48 (m, 32H), 0.89 (m, 6H). $^{13}C$ NMR (CDCl$_3$, $\delta_{ppm}$): 127.18, 124.89,
3.5.5 Hydrolysis of Star-shaped PPEs

Approximately 30 mg of organic soluble ester polymers from chain-growth and step-growth polymerization were characterized by GPC and $^1$H NMR. The remaining material, 10 mg, was dissolved in 3 mL of THF. A 2:1 ratio of methanol (2 mL) and water (1 mL) was added to the solution. Afterwards, excess NaOH was added to the reaction solution, which became cloudy during the reaction. Then, 3 mL of water was added twelve hours later. The mixture became clear and was stirred at room temperature for five hours. After the reaction was finished, THF was removed under reduced pressure. The remaining solution was transferred to a 12 kDa molecular weight cutoff (MWCO) regenerated cellulose membrane (Fisher Scientific) for further purification. After dialysis, the solution was filtered through a 1.0 μm glass fiber membrane and was freeze dried for three days. The resulting polyelectrolytes were characterized by $^1$H NMR, and photophysical studies. The typical reaction yield was 90 - 95%.

$2Pd$ CPE. $^1$H NMR (D$_2$O pH = 8, δ$_{ppm}$): 6.89 (m, 2H), 4.28 (m, 4H). $^{13}$C NMR (CDCl$_3$, δ$_{ppm}$): 144.78, 140.86, 72.23, 68.18, 36.12. Refer to the spectra in B-7 and B-14.

$3Pd$ CPE. $^1$H NMR (D$_2$O pH = 8, δ$_{ppm}$): 6.48 (m, 2H), 4.19 (m, 4H). $^{13}$C NMR (CDCl$_3$, δ$_{ppm}$): 116.18, 112.12, 68.56, 65.21, 38.18. Refer to the spectra in B-8 and B-15.

$4Pd$ CPE. $^1$H NMR (D$_2$O pH = 8, δ$_{ppm}$): 7.56 (s, 2H), 4.30 (m, 4H). $^{13}$C NMR (CDCl$_3$, δ$_{ppm}$): 134.78, 130.21, 127.54, 67.78, 64.12, 37.12. Refer to the spectra in B-9 and B-16.
4.1 Background

Conjugated polyelectrolytes (CPEs) have been widely investigated in the field of optoelectronic applications due to their water solubility. Their unique photophysical properties can be applied to optical devices, such as novel bio- and chemo-sensors, molecular wires, and organic light-emitting devices. Various molecules including metal ions, organic ions, biomolecules, and biopolymers have been found to quench the fluorescence of CPEs with high sensitivity. This is referred to as amplified fluorescence quenching. The amplified fluorescence quenching occurs when the polymer-quencher complexes are formed. At the polymer-quencher complexes, the exciton is transferred from the polymer chain to the quencher. However, if the polymer chains are aggregated, the exciton is transferred from one polymer chain to another, thus reducing or eliminating the effect of the quencher. Therefore, it is important to reduce the polymer’s fluorescence self-quenching to increase the quencher’s quenching efficiency.

Recently, Schanze and colleagues published studies of the photophysical properties of poly(phenylene ethynylene) (PPE)-based CPEs. In their work, various kinds of anionic and cationic solubilizing groups, such as sulfonate, phosphonate, carboxylate, tetraaklyammonium, and imidazolium groups were investigated in terms of photophysical properties. For example, in 2002, they reported the photophysical properties of water-soluble sulfonated PPE-based CPE (PPE-SO₃⁻) (Figure 4-1).
Figure 4-1 shows the absorption and fluorescence emission spectra of PPE-SO$_3^-$ in methanol, 1:1 methanol: water, and in water. As the water content increases in the solution, the absorption and emission spectra of PPE-SO$_3^-$ are red-shifted (longer wavelength). Also, the emission spectra of PPE-SO$_3^-$ in water show broad, ill-structured shapes, indicating aggregate formation. However, in methanol, the absorption and emission spectra are sharp, mimicking the spectra of a conjugated polymer in an organic solvent. Based on these results, the π-stacking interaction between PPE-SO$_3^-$ polymer chains are enhanced in water, thus inducing the fluorescence quenching. The fluorescence quantum yields of PPE-SO$_3^-$ were $\Phi_f = 0.78$ and 0.10 in methanol and water, respectively.

Considerable efforts have been made to reduce aggregation in water by introducing bulky and highly charged ionic groups in the PPE backbone.$^{19,21}$ Parthasarathy and Schanze introduced
the imidazolium group on every phenyl unit (PIM-4) or on every other phenyl unit (PIM-2) in the PPE backbone (Figure 4-2). The imidazolium bulky group is capable of increasing electrostatic repulsion and decreasing the intermolecular π-stacking interaction due to positively charged ammonium group and its size. Therefore, PIM-4 showed better fluorescence quantum yield ($\Phi_f = 35\%$) than PIM-2 ($\Phi_f = 12\%$) in water.

![Figure 4-2. Structures of PIM-2 and PIM-4. (a) Normalized absorption and (b) fluorescence spectra of PIM-2 in MeOH (blue lines) and water (red lines). (c) Normalized absorption and (d) fluorescence spectra of PIM-4 in MeOH (green lines) and water (red lines). Figure was reprinted from Schanze with permission. Copyright 2015. The Royal Society of Chemistry](image)

In the previous reports, PPE-SO$_3^-$ and PIM-4 were synthesized by the AA + BB type (diiodo- and diacetylene-functionalized monomers) palladium-catalyzed Sonogashira cross-
coupling reaction. Since the Sonogashira cross-coupling reaction proceeds via a step-growth mechanism, PPE-SO$_3^-$ and PIM-4 had ill-defined physical properties, such as molecular weight, polydispersity, end-group fidelities. Also, the AABB-type Sonogashira cross-coupling condition can produce the acetylene homo-coupled Glaser product with the copper-catalyzed coupling reaction. The mechanism of the Glaser reaction is as follows. When the oxygen reduces the copper catalyst, two moles of diacetylene-functionalized monomer are coordinated to the copper. The two molecules of acetylene are reductively eliminated to produce the acetylene homo-coupled product. If the acetylene homo-coupled structure exists in the non-aggregated polymer chains, then the defect of homo-coupled structure affects to quench the fluorescence only from the polymer chain which contained the acetylene homo-coupled sites. However, if the polymer chains are aggregated, excitons can be transferred easily from acetylene homo-coupled sites to the aggregated trap sites. Thus, the fluorescence quenching may increase in aqueous solution if acetylene homo-coupled products are present.

Herein, we synthesized the bi-functionalized AB-type sulfonate and imidazolium side group PPE-based CPEs (Figure 4-3). The AB-type monomer reacts with Pd(P^tBu$_3$)(Pd)(Br) catalyst by the chain-growth catalyst-transfer polymerization (CTP) to yield the well-defined polymer. The previously used diiodo- and diacetylene-functionalized monomers were dissolved in water or dimethyl sulfoxide (DMSO). However, if water is used, the Pd(P^tBu$_3$)(Pd)(Br) catalyst can be decomposed in the case of chain-growth CTP. Therefore, the AB-type monomer should dissolve in distilled THF or DCM. To do this, the Na$^+$ ion of water-soluble sulfonated PPE polymer was exchanged to PPh$_4^+$ ion as a counterion while the Br$^-$ ion of water-soluble imidazolium PPE polymer was exchanged to BPPh$_4^-$ ion as a counterion.
To compare the photophysical properties, sulfonated C/S-SO$_3$-Na CPEs and imidazolium C/S-NR$_4$-Br were prepared (C and S represent a chain-growth polymer and step-growth polymer). The chain-growth polymer was synthesized via Pd(P$^t$Bu$_3$)(Pd)(Br) catalyzed CTP while the step-growth polymer was synthesized via Pd(PPh$_3$)$_4$ catalyzed Sonogashira cross-coupling reaction.

Steady-state absorption and emission spectra of the chain-growth and step-growth sulfonated and imidazolium PPE-based CPEs were characterized in methanol and water. In the case of sulfonated PPE-based CPEs, the chain-growth C-SO$_3$-Na had well-structured absorption and emission spectra in aqueous solution and showed an improved fluorescence quantum yield from $\Phi_f = 10\%$ (PPE-SO$_3$)$_2$ to 30%. Therefore, as discussed in chapter 2, the acetylene homo-coupled defect may affect the photophysical properties of the sulfonated PPE-based CPEs. On the other hand, C-NR$_4$-Br and S-NR$_4$-Br exhibited $\Phi_f = 33$ and 26% fluorescence quantum yields compared to PIM-4 ($\Phi_f = 34\%$). The bulky and positively charged imidazolium group may reduce aggregation, making it difficult to see the defect of the acetylene homo-coupled structure in the polymer backbone.
4.2 Polymer Preparation

4.2.1 Synthesis of the Sulfonated AB-Type Monomer

![Chemical reaction diagram]

The synthetic route for the sulfonated AB-type monomer started from commercially available compounds, hydroquinone (1) and 1,3-propanesultone under basic reaction conditions (Figure 4-4). After the nucleophilic ring-opening reaction, the water-soluble sulfonated compound 2 was obtained, which was iodinated to form compound 3. To obtain the organic-soluble compound 4, the sodium ion of compound 3 was exchanged with the PPh₄⁺ ion. A mixture of compound 3 and PPh₄Cl was stirred for twelve hours at room temperature to obtain the white, solid ion-exchanged product. The precipitate was filtered and washed with water to produce pure compound 4. A mono trimethylsilyl (TMS) acetylene substituted compound 5 was synthesized by the Sonogashira cross-coupling reaction. Finally, the TMS group was deprotected by anhydrous K₂CO₃ to produce the desired AB-type monomer 6.
4.2.2 Synthesis of the Imidazolium AB-Type Monomer

The imidazolium AB-type monomer (14) was prepared from a commercially available compound, 1,4-dimethoxybenzene (7) (Figure 4-5).

Figure 4-5. Synthesis of the imidazolium AB-type monomer

The first step was an iodination reaction of the starting compound (7). Purification of the iodination compound (8) was achieved by recrystallization. The methoxy groups on 1,4-diiodo-
2,5-dimethoxybenezene (8) were removed with boron tribromide (BBr₃) at 0 °C for twenty-four hours. Afterwards, 1,4-bis(3-bromopropoxy)-2,5-diiodobenzene (10) was obtained by a SN2 nucleophilic substitution reaction of 2,5-diiodobenzene-1,4-diol and 1,3-dibromopropane. The resulting compound (10) was reacted with 1-methyl-1H-imidazol in water, acetone, and methanol mixed solvent for twenty-four hours using reflux conditions to produce water-soluble compound (11). The crude product (11) was then used to synthesize the organic solvent soluble compound (12) without an additional purification step. The ion-exchange reaction of compounds 11 to 12 was performed by adding an excess of sodium tetraphenylborate (NaBPh₄) salt in water. After compound 12 precipitated, it was collected by filtration, and washed with water. After trimethylsilylacetylene substitution and trimethylsilyl group deprotection reaction, the desired imidazoliüm ionic chain AB-type monomer (14) was prepared and characterized by ¹H NMR spectroscopy (see SI, Figure C-13).

4.2.3 Polymerization of the Sulfonated PPE Polymer

The C-SO₃-PPh₄ and S-SO₃-PPh₄ PPE polymers were synthesized via two different polymerization pathways (Figure 4-6). The C-SO₃-PPh₄ was synthesized by 2 mol% Pd(P’Bu₃)(Ph)(Br) catalyzed chain-growth CTP pathway. The pre-activated palladium catalyst was freshly prepared from the reaction of Pd(P’Bu₃)₂ and bromobenzene. The bromobenzene and DCM were distilled under an Ar atmosphere before use. The AB-type monomer (6) was soluble in DCM. First, the AB-type monomer 6 in distilled DCM was transferred to dry Schlenk flask under argon atmosphere. Then, 20 mol% copper (I) iodide (CuI) and 20 mol% triphenylphosphine (PPh₃) were added to the solution and stirred for thirty minutes. The 2 mol% Pd(P’Bu₃)(Ph)(Br) was transferred to another Schlenk flask in grove box. Then, the Pd(P’Bu₃)(Ph)(Br) in DCM was dropwise to the reaction mixture via cannula transfer. After
adding the palladium catalyst, the color of the reaction solution turned from a dark yellow color to a fluorescent dark orange color during the polymerization. After twelve hours, the reaction solution was quenched by water to terminate the polymerization. Then, the crude product was precipitated with methanol to remove the remaining catalyst and oligomers. Finally, the desired orange-colored C-SO₃-PPh₄ was obtained in 67% yield. The S-SO₃-PPh₄ PPE polymer was prepared with 10 mol% Pd(PPh₃)₄ catalyzed Sonogashira cross-coupling reaction. After the polymerization was completed, the crude S-SO₃-PPh₄ was precipitated with methanol and centrifuged three times to achieve a pure polymer. The C-SO₃-PPh₄ and S-SO₃-PPh₄ were dissolved in THF and DCM. The GPC trace showed molecular weights and polydispersities of the C-SO₃-PPh₄ (Mₙ = 9,800 g/mol, PDI = 1.4, blue line) and S-SO₃-PPh₄ (Mₙ = 7,000 g/mol, PDI = 1.7, orange line) (Figure 4-9, a).

Figure 4-6. Polymerization of the C-SO₃-PPh₄ and S-SO₃-PPh₄ PPE polymers
4.2.4 Polymerization of the Imidazolium PPE Polymer

The chain-growth C-NR₄-BPh₄ was synthesized by 2 mol% Pd(P'Bu₃)(Ph)(Br) catalyzed CTP while the step-growth S-NR₄-BPh₄ was synthesized by 10 mol% Pd(PPh₃)₄ catalyzed Sonogashira cross-coupling reaction (Figure 4-7). Because the imidazolium ion is cationic, a BPh₄Cl salt was used for the ion-exchange reaction. The BPh₄⁺ exchanged monomer (14) was soluble in DCM. When the polymerization was completed, the reaction solution was quenched by water. Then, the concentrated crude polymer solution was precipitated with methanol three times and centrifuged to purify the polymer.

![Chemical structures and reaction schemes showing the synthesis of C-NR₄-BPh₄ and S-NR₄-BPh₄](image)

Figure 4-7. Polymerization of C-NR₄-BPh₄ and S-NR₄-BPh₄ PPE polymers

The C-NR₄-BPh₄ and S-NR₄-BPh₄ were dissolved in THF and DCM. The polymer chain was analyzed by GPC (Figure 4-8, b). C-NR₄-BPh₄ showed molecular weight of 5,800 g/mol,
and polydispersity of 1.49 (pink line) while S-NR₄-BPh₄ showed 7,100 g/mol, and 1.87 (gray line).

![Figure 4-8](image)

Figure 4-8. GPC analysis of polymers. (a) The chain-growth C-SO₃-PPh₄ (blue line) and step-growth S-SO₃-PPh₄ (orange line). GPC trace for (b) the chain-growth C-NR₄-BPh₄ (pink) and step-growth S-NR₄-BPh₄ (gray line). THF was used as eluent at 1mL/min flow rate.

### 4.2.5 Ion Exchange to Water Soluble Salts

Water soluble C-SO₃-PPh₄ and S-SO₃-PPh₄ polymers were prepared by an ion-exchange reaction from the tetraphenyl phosphonium ion to the sodium ion (Figure 4-9, a). When a sodium chloride (NaCl) aqueous solution was mixed with the yellow-colored C-SO₃-PPh₄ or S-SO₃-PPh₄ in dichloromethane, the ion-exchanged C-SO₃-Na or S-SO₃-Na polymers was transferred from the dichloromethane layer to the water layer, observed visually by color. After twelve hours, the yellow-colored water layer was filtered through a membrane filter (D = 0.45 μm) and dialyzed for two days. Finally, the solution of C-SO₃-Na and S-SO₃-Na was freeze-dried to prevent possible aggregation in aqueous solution and the desired product obtained as a yellow powder.

The ion-exchange for the C-NR₄-BPh₄ and S-NR₄-BPh₄ PPE polymers was carried out via a precipitation method (Figure 4-9, b). When the sodium bromide aqueous solution was added to the solution of C-NR₄-BPh₄ and S-NR₄-BPh₄ in dichloromethane, there was no visible
change between the organic layer and the water layer. It was suspected that C-NR₄-Br and S-NR₄-Br were soluble in the organic layer. Therefore, tetra-\textit{n}-butyl ammonium bromide (TBAB) was added to the solution to precipitate to obtain the C-NR₄-Br and S-NR₄-Br CPEs. First, C-NR₄-BPh₄ or S-NR₄-BPh₄ was dissolved in acetone. After TBAB was added to the solution, the reaction mixture was stirred for twelve hours to obtain the precipitate. Finally, the precipitate was filtered and washed with acetone to obtain the pure CPEs.

![Diagram of ion-exchange reaction](image)

**Figure 4-9.** Ion-exchange reaction. (a) C-SO₃-PPh₄ and S-SO₃-PPh₄ and (b) C-NR₄-Br and S-NR₄-Br

### 4.3 Photophysical Properties

#### 4.3.1 Steady-state Absorption and Fluorescence Emission Spectra of the Sulfonated Polymers

Steady-state absorption and fluorescence emission spectra of the C-SO₃-PPh₄ and S-SO₃-PPh₄ were measured in THF (Figure 4-10). The C-SO₃-PPh₄ absorbed at \( \lambda_{\text{abs}} = 358 \text{ nm} \) while the
S-SO$_3$-PPh$_4$ absorbed at $\lambda_{abs} = 365$ nm. The emission spectra of the C-SO$_3$-PPh$_4$ and S-SO$_3$-PPh$_4$ were obtained at 465 and 477 nm, respectively.

Figure 4-10. Photophysical properties. Absorption and fluorescence emission spectra of C-SO$_3$-PPh$_4$ and S-SO$_3$-PPh$_4$ in THF, together with a picture of (A) C-SO$_3$-PPh$_4$ and (B) S-SO$_3$-PPh$_4$. The polymers were excited at 380 nm

Steady-state absorption and fluorescence emission spectra of C-SO$_3$-Na and S-SO$_3$-Na CPEs were measured in methanol and water (the concentration of the molecules was adjusted to 10 $\mu$M). As shown in Figure 4-11 a, the absorption maxima of C-SO$_3$-Na and S-SO$_3$-Na were obtained at 414 and 441 nm while the emission maxima were obtained at 462 and 469 nm in methanol. In water, the C-SO$_3$-Na and S-SO$_3$-Na absorbed at 410/439 nm and emitted at 483/485 nm, respectively. The C-SO$_3$-Na showed a well-structured emission spectrum in water. The S-SO$_3$-Na showed the broad and long tailed emission spectrum in water, indicating aggregation. However, compared to previously reported PPE-SO$_3$ $^*$ ($\lambda_{em} = 550$ nm), the emission maxima of C-SO$_3$-Na and S-SO$_3$-Na were blue-shifted in water. This result suggested that the AB-type polymer reduces the aggregation. Also, the chain-growth C-SO$_3$-Na polymer has an ability to less aggregate in water than S-ab.
Figure 4-11. Optical properties. (a) Absorption spectra and (b) fluorescence emission spectra for C-SO$_3$-Na and S-SO$_3$-Na in methanol. (c) Absorption spectra and (d) fluorescence emission spectra for C-SO$_3$-Na and S-SO$_3$-Na in water (pH = 8), together with a picture of (E) S-SO$_3$-Na and (F) C-SO$_3$-Na in methanol, (G) S-SO$_3$-Na and (H) C-SO$_3$-Na in water. The CPEs were excited at 420 nm.

Table 4-1 summarizes the photophysical properties of sulfonated PPE polymers and CPEs. The fluorescence quantum yield of the C-SO$_3$-PPh$_4}$/ S-SO$_3$-PPh$_4$ in chloroform, and C-SO$_3$-Na/ S-SO$_3$-Na in methanol and water are summarized in Table 4-1. The C-SO$_3$-PPh$_4$ and S-
SO$_3$-PPh$_4$ showed $\Phi = 88$ and 81% fluorescence quantum yield, which is suggested that the polymers existed as an individual chain in THF. The fluorescence quantum yield of C-SO$_3$-Na and S-SO$_3$-Na were $\Phi = 33$ and 26% in water compared to the PPE-SO$_3^-$ ($\Phi = 10\%$). Thus, the fluorescence efficiency of the AB type polymer was improved than those of AABB type polymer in water.

Table 4-1. Summary of the optical properties and fluorescence quantum yield for C-SO$_3$-PPh$_4$/S-SO$_3$-PPh$_4$ and C-SO$_3$-Na/S-SO$_3$-Na in methanol and water

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Absorption (nm)</th>
<th>Emission (nm)</th>
<th>Fluorescence quantum yield ($\Phi$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-SO$_3$-PPh$_4$</td>
<td>CHCl$_3$</td>
<td>358</td>
<td>465</td>
<td>0.83</td>
</tr>
<tr>
<td>S-SO$_3$-PPh$_4$</td>
<td>CHCl$_3$</td>
<td>365</td>
<td>477</td>
<td>0.81</td>
</tr>
<tr>
<td>C-SO$_3$-Na</td>
<td>MeOH</td>
<td>414</td>
<td>462</td>
<td>0.43</td>
</tr>
<tr>
<td>S-SO$_3$-Na</td>
<td>MeOH</td>
<td>441</td>
<td>469</td>
<td>0.30</td>
</tr>
<tr>
<td>C-SO$_3$-Na</td>
<td>Water</td>
<td>410</td>
<td>483</td>
<td>0.33</td>
</tr>
<tr>
<td>S-SO$_3$-Na</td>
<td>Water</td>
<td>439</td>
<td>485</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Figure 4-12 shows the Stern-Volmer plots for C-SO$_3$-Na and S-SO$_3$-Na CPEs in methanol and water. In both solvents, the plots showed the upward curvature for the C-SO$_3$-Na and S-SO$_3$-Na CPEs. The Stern-Volmer constants of C-SO$_3$-Na and S-SO$_3$-Na were $K_{sv} = 1.79/2.16 \times 10^6$ M$^{-1}$ and $4.54/5.31 \times 10^6$ M$^{-1}$ in methanol and water. The quenching constants ($K_{sv}$) of C-SO$_3$-Na and S-SO$_3$-Na were smaller than those of PPE-SO$_3^-$ ($K_{sv} = 2.7 \times 10^7$ M$^{-1}$)$^{17}$, indicating less aggregation in water.
The photophysical properties of the C-NR₄-BPh₄ and S-NR₄-BPh₄ polymers were studied via absorption and fluorescence spectroscopy in THF (Figure 4-13). The absorption maxima of C-NR₄-BPh₄ and S-NR₄-BPh₄ were all obtained at 365 nm, indicating the π-π* transition. The emission maxima of C-NR₄-BPh₄ and S-NR₄-BPh₄ exhibited at 441 and 443 nm.

Steady-state absorption and fluorescence emission spectra of C-NR₄-Br and S-NR₄-Br were measured in methanol and water (the concentration of the molecules was adjusted to 20 μM). As shown in Figure 4-14, in methanol, the absorption maxima of the C-NR₄-Br and S-NR₄-Br were obtained at 413 and 426 nm. The fluorescence emission spectra of the C-NR₄-Br and S-NR₄-Br showed at λₑm,max = 447 and 452 nm. In water, the absorption maxima of C-NR₄-Br and
S-NR₄-Br were obtained at 421 and 435 nm while the emission maxima of C-NR₄-Br and S-NR₄-Br were obtained at 460 and 462 nm. The S-NR₄-Br exhibited red-shifted absorption and broad/long-tailed emission spectra compared to those of C-NR₄-Br in water and methanol due to aggregation.

Figure 4-14. Optical properties. (a) Absorption and (b) emission spectra of C/S-NR₄-Br in methanol. (c) Absorption and (d) emission spectra of C/S-NR₄-Br in water, together with a picture of (A) S-NR₄-Br and (B) C-NR₄-Br in methanol. (C) S-NR₄-Br and (D) C-NR₄-Br in water. Polymers were excited at 420 nm.

Compared to the optical properties of PIM-4 (λₘₐₓ ≈ 430 nm), the absorption maximum of C-NR₄-Br was blue-shifted about 9 nm while the S-NR₄-Br was red-shifted about 5 nm in water.
The fluorescence emission maxima of C-NR$_4$-Br and S-NR$_4$-Br (460 and 462 nm, respectively) differ by 6 and 2 nm than PIM-4 (466 nm) in water. We expected that C-NR$_4$-Br and S-NR$_4$-Br would have blue-shifted absorption and emission spectra compared to those of PIM-4, due to the minimized aggregation. According to the absorption and emission spectra of the C-NR$_4$-Br and S-NR$_4$-Br, the acetylene homo-coupled defect may not affect to photophysical properties of the imidazolium side group PPE-based CPEs. The bulky imidazolium solubilizing group may reduce the aggregation. Therefore, the acetylene homo-coupled defect is not clear in the case of imidazolium PPE-based CPEs. Table 4-2 summarizes the photophysical properties of the imidazolium side chain PPE-based CPEs in methanol and water.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Absorption (nm)</th>
<th>Emission (nm)</th>
<th>Fluorescence quantum yield (Φ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-NR$_4$-BPh$_4$</td>
<td>CH$_3$Cl</td>
<td>365</td>
<td>441</td>
<td>0.79</td>
</tr>
<tr>
<td>S-NR$_4$-BPh$_4$</td>
<td>CH$_3$Cl</td>
<td>365</td>
<td>443</td>
<td>0.75</td>
</tr>
<tr>
<td>C-NR$_4$-Br</td>
<td>MeOH</td>
<td>413</td>
<td>447</td>
<td>0.53</td>
</tr>
<tr>
<td>S-NR$_4$-Br</td>
<td>MeOH</td>
<td>426</td>
<td>452</td>
<td>0.48</td>
</tr>
<tr>
<td>C-NR$_4$-Br</td>
<td>Water</td>
<td>421</td>
<td>460</td>
<td>0.28</td>
</tr>
<tr>
<td>S-NR$_4$-Br</td>
<td>Water</td>
<td>435</td>
<td>462</td>
<td>0.25</td>
</tr>
</tbody>
</table>

The fluorescence-quenching experiments for C-NR$_4$-Br and S-NR$_4$-Br were investigated with pyrophosphate (PPi) as the quencher (Figure 4-15). The $K_{sv}$ of the C-NR$_4$-Br and S-NR$_4$-Br were obtained as $2.3 \times 10^5$ M$^{-1}$ and $3.2 \times 10^5$ M$^{-1}$ in methanol. In water, the $K_{sv}$ of the C-NR$_4$-Br and S-NR$_4$-Br were $1.2 \times 10^5$ M$^{-1}$ and $1.4 \times 10^5$ M$^{-1}$. According to Stern-Volmer constant, the C-NR$_4$-Br and S-NR$_4$-Br were more sensitive to the quencher in methanol than in water. This phenomenon was also observed in PIM-4 ($K_{sv} = 2.7 \times 10^5$ M$^{-1}$ in methanol and $1.3 \times 10^5$ M$^{-1}$ in water).
4.3.2 Fluorescence lifetime

The fluorescence decays of CPEs showed multiexponential behavior, and with C-SO$_3$-Na and S-SO$_3$-Na, three exponentials were needed to fit the decay. The fluorescence lifetime (at $\tau = 550$ and 470 ps) was occurred with the natural fluorescence decay of CPEs in water (Table 4-3). There was the shortest lifetime at $\tau = 20$ ps (for both C-SO$_3$-Na and S-SO$_3$-Na) in water. It is suggested that the shortest lifetime may be associated with energy transfer to excimer-like aggregate sites. The fluorescence decay was dependent on the solvent. In methanol, the longest fluorescence decay of C-SO$_3$-Na and S-SO$_3$-Na showed $\tau = 790$ and 730 ps while the shortest lifetime decay at $\tau = 410$ and 20 ps (for the C-SO$_3$-Na and S-SO$_3$-Na). Thus, CPEs tended to be more aggregated in water than in methanol compared to the shortest lifetime between in methanol and water.

The fluorescence decay of C-NR$_4$-Br and S-NR$_4$-Br also exhibited multiexponential behavior, and with the C-NR$_4$-Br, three exponentials were needed to fit the decay. The longest fluorescence lifetime (at $\tau = 780$ and 480 ps) was occurred in water with the polymer relaxation and reorganization of the CPEs (Table 4-3). There were shorter lifetimes at $\tau = 230$ and 20 ps (for C-NR$_4$-Br and S-NR$_4$-Br) in water. It is suggested that the shorter lifetime may be associated
with emission from the excimer-like aggregate sites. In methanol, the longest fluorescence lifetime of C-NR₄-Br and S-NR₄-Br showed τ = 680 and 590 ps while the shortest lifetime decay at τ = 20 and 8 ps (for the C-NR₄-Br and S-NR₄-Br). Figure 4-16 shows the average fluorescence lifetime of C-SO₃-Na/S-SO₃-Na and C-NR₄-Br/S-NR₄-Br in methanol and water.

Figure 4-16. Average fluorescence lifetime (τ) for sulfonated and imidazolium PPE-based CPEs in methanol (green bar) and water (pink bar)

Table 4-3 summarizes the fluorescence lifetime for the C-SO₃-Na/S-SO₃-Na and C-NR₄-Br/S-NR₄-Br in methanol and water.

Table 4-3. Fluorescence lifetime

<table>
<thead>
<tr>
<th>CPE</th>
<th>solvent</th>
<th>λₑm</th>
<th>τ₁ [ns]</th>
<th>A₁ [%]</th>
<th>τ₂ [ns]</th>
<th>A₂ [%]</th>
<th>τ₃ [ns]</th>
<th>A₃ [%]</th>
<th>&lt;τ&gt; [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-SO₃-Na</td>
<td>H₂O</td>
<td>450</td>
<td>3.03</td>
<td>2</td>
<td>0.55</td>
<td>6</td>
<td>0.02</td>
<td>92</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>450</td>
<td>0.79</td>
<td>22</td>
<td>0.41</td>
<td>78</td>
<td>-</td>
<td>-</td>
<td>0.20</td>
</tr>
<tr>
<td>S-SO₃-Na</td>
<td>H₂O</td>
<td>450</td>
<td>1.40</td>
<td>1</td>
<td>0.47</td>
<td>8</td>
<td>0.02</td>
<td>91</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>450</td>
<td>0.73</td>
<td>5</td>
<td>0.02</td>
<td>95</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>C-NR₄-Br</td>
<td>H₂O</td>
<td>450</td>
<td>0.78</td>
<td>1</td>
<td>0.23</td>
<td>22</td>
<td>0.007</td>
<td>77</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>450</td>
<td>0.68</td>
<td>10</td>
<td>0.02</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td>S-NR₄-Br</td>
<td>H₂O</td>
<td>450</td>
<td>0.48</td>
<td>5</td>
<td>0.02</td>
<td>95</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>450</td>
<td>0.59</td>
<td>5</td>
<td>0.008</td>
<td>95</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
</tr>
</tbody>
</table>

a Fluorescence decays are multi exponential.
4.4 Conclusion

In this chapter, we designed and synthesized the bi-functionalized AB-type monomers containing sulfonated and imidazolium groups. The newly designed organic-soluble AB-type monomers were prepared by an ion-exchange reaction from the water-soluble diiodo-functionalized compounds. Since the diiodo- and diacetylene-functionalized monomers (an AABB-type monomer) can produce the acetylene homo-coupled product in the Sonogashira cross-coupling reaction, the AB type monomer was utilized to the polymerization. The C-SO$_3$-Na and S-SO$_3$-Na showed improved fluorescence quantum yield ($\Phi = 33 \text{ and } 26\%$) compared to PPE-SO$_3^-$ ($\Phi = 10\%$) in water. Also, the C-SO$_3$-Na polymer has an ability to reduce the aggregation than S-SO$_3$-Na polymer according to fluorescence quantum yield and lifetime results. However, in the case of C-NR$_4$-Br and S-NR$_4$-Br, the photophysical properties were similar with as of PIM-4. It is possibly because the bulky imidazolium group reduces aggregation in the solution. Therefore, the acetylene homo-coupled defect is not clearly seen in the case of imidazolium PPE-based CPEs.

4.5 Experimental

4.5.1 Instrumentation and Methods

$^1$H NMR spectra were obtained with Varian Gemini 300 spectrometer (300 MHz). The chemical shifts ($\delta$) are reported in parts per million (ppm) using CHCl$_3$ and D$_2$O as the internal references. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), and m (multiplet).

Gel permeation chromatography (GPC) analysis was carried out on a system composed of a Shimadzu LC-6D pump, Agilent mixed-D column and a Shimadzu SPD-20A photodiode
array (PDA) detector, with THF as the eluent at 1 ml/min flow rate. Molecular weight calibration was affected by the linear polystyrene standards in THF.

Photophysical measurements were conducted with dry HPLC-grade THF as the solvent in 1 x 1 cm quartz cuvettes. UV-Vis absorption spectra were obtained on a Varian Cary 100 dual beam spectrophotometer. Fluorescence emission spectra were recorded on a Photon Technology International (PTI) fluorimeter and collected 90° relative to the excitation beam. The optical density of the sample solutions was kept at ≤ 0.1 at the excitation wavelength. Refractive index corrections were applied for the sample and standard solutions for emission quantum yield measurements. Fluorescence lifetimes were measured via a Fluo Time 100 Fluorescence Lifetime Spectrometer (Pico Quant, USA).

4.5.2 Materials

All reactions were performed under a dry and argon atmosphere. THF was dried using solvent purification columns (Glass Contour). Unless otherwise indicated, all starting materials were purchased from commercial sources (Aldrich, Acros) and used without further purification. A Pd(PPh₃)₄ catalyst was purchased from Strem Chemical Co. Water soluble sulfonated compound (2), diodo sulfonated compound (3), 1,4-diiodo-2,5-dimethoxybenezene (8), 2,5-diiodobenzene-1,4-diol (9), 1,4-bis(3-bromopropoxy)-2,5-diiodobenzene(10), water-soluble ammonium ionic compound (11) were prepared according to the literature.¹⁷,⁷³

4.5.2.1 Synthesis of the Sulfonated AB-Type Monomer

Water soluble sulfonated compound (2). 2,5-Diiodohydroquinone (7.24 g, 20 mmol) was dissolved in water (200 mL) with sodium hydroxide (2 g, 50 mmol). A solution of 1,3-propanesultone (6 g, 50 mmol) in dioxane (30 mL) was added to the solution. The reaction mixture was then stirred at room temperature for twelve hours. The reaction mixture was heated
at 100°C for thirty minutes more, and was then cooled down in the water bath. The concentrated crude product was purified with recrystallization from acetone. The resulting product was obtained as 8.5 g (68% yield).\textsuperscript{17} \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, \textdelta\textsubscript{ppm}): 7.30 (s, 4H), 4.05 (t, 4H), 2.64 (t, 4H), 2.00 (t, 4H). See SI Fig. C-1 for the NMR spectrum.

**Diiodo sulfonated compound (3).** Compound 2 (5 g, 36.2 mmol) was dissolved in glacial acetic acid (45 mL), water (3.5 mL) and concentrated sulfuric acid (1.5 mL). Then, iodine (11.8 g, 43.4 mmol) and KIO\textsubscript{3} (10.5 g, 43.4 mmol) were added to the reaction solution. The reaction mixture was refluxed for twenty-four hours. After the reaction was done, the solution was quenched by a saturated Na\textsubscript{2}SO\textsubscript{3} solution, extracted with dichloromethane, and dried over MgSO\textsubscript{4}. The solvent was removed under reduced pressure. The resulting solid was recrystallized from the THF/water mixture solution to yield the desired product as a yellow solid (7.5 mg, 64%).\textsuperscript{1}H NMR (CDCl\textsubscript{3}, \textdelta\textsubscript{ppm}): 7.05 (s, 2H), 4.01 (t, 4H), 2.97 (t, 4H), 2.28 (m. 4H).\textsuperscript{17} See SI Fig. C-2 for the NMR spectrum.

**Organic soluble sulfonated compound (4).** Sodium 3,3′-((2,5-diiodo-1,4-phenylene)bis(oxy))bis(propane-1-sulfonate) (179 mg, 0.27 mmol) was dissolved in deionized water (100 mL). After adding the tetraphenyl phosphonium chloride (123 mg, 0.32 mmol), the reaction mixture was stirred at room temperature for overnight. The tetraphenylphosphonium ion-exchanged compound 3 was then extracted with dichloromethane. The organic layer was washed with water, dried over MgSO\textsubscript{4}, filtered, and concentrated under reduced pressure to yield the desired product (300 mg, 87% yield). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, \textdelta\textsubscript{ppm}): 7.89 (m, 8H), 7.76 (m, 16H), 7.60 (m, 16H), 7.05 (s, 2H), 4.01 (t, 4H), 2.97 (t, 4H), 2.28 (m. 4H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, \textdelta\textsubscript{ppm}): 136.34, 134.34, 129.12, 117.65, 116.23, 68.18, 48.06, 25.35. MS (ESI) m/z ([M]\textsuperscript{−}) 604.8303. See SI Fig. C-3 and C-4 for the NMR spectra. See SI Fig. C-26 for the MS spectrum.
**Sulfonated TMS acetylene substituted compound (5).** The organic soluble diodo-sulfonated compound (3) (800 mg, 0.62 mmol) was dissolved in dichloromethane (10 mL) and diisopropyl amine (5 mL). Then, 10 mol% CuI (8 mg, 0.03 mmol) and 10 mol% Pd(PPh₃)₂Cl₂ (24 mg, 0.03 mmol) were added to the solution. The reaction mixture was cooled to 0°C for thirty minutes. Then, TMS acetylene (100 µL, 1.24 mmol) was added dropwise to the solution. The reaction solution was stirred at 50°C for twelve hours. After the reaction was done, the reaction mixture was quenched by water, extracted with dichloromethane three times, and dried over MgSO₄. Then, the solution was filtered and concentrated under reduced pressure to yield the desired product (300 mg, 46% yield). §H NMR (CDCl₃, δ ppm): 7.91 (m, 24H), 7.78 (s, 1H), 7.67 (m, 16H), 7.10 (s, 1H), 6.72 (s, 1H), 4.00 (t, 4H), 2.98 (t, 4H), 2.27 (t, 4H), 0.21 (s, 9H). §C NMR (CDCl₃, δ ppm): 137.23, 135.26, 131.23, 117.13, 116.25, 67.13, 62.16, 60.19, 56.12, 0.03. MS (ESI) m/z ([M]⁻) 574.9747. See SI Fig. C-5 and C-6 for the NMR spectra. See SI Fig. C-27 for the MS spectrum.

**AB-type sulfonated monomer (6).** The propargylic sulfonated compound (5) (352 mg, 0.29 mmol) was dissolved in a mixture of dichloromethane (10 mL) and methanol (10 mL). Then, anhydrous K₂CO₃ (404 mg, 4.64 mmol) was added to the solution. The solvent was removed under reduced pressure and purified with column chromatography. The desired product was a reddish-brown solid (190 mg, 83% yield). §H NMR (CDCl₃, δ ppm): 7.47 (m, 24H), 7.31 (s. 1H), 7.15 (m, 16H), 4.10 (t, 4H), 4.05 (s, 1H), 3.27 (t, 4H), 2.24 (t, 4H). §C NMR (CDCl₃, δ ppm): 137.23, 135.26, 131.23, 117.13, 116.25, 69.18, 64.89, 60.19, 54.12. MS (ESI) m/z ([M]⁻) 532.7692. See SI Fig. C-7 and C-8 for the NMR spectra. See SI Fig. C-28 for the MS spectrum.
4.5.2.2 Polymerization of Sulfonated PPEs

**C-SO\textsubscript{3}-PPh\textsubscript{4} Polymer via Chain-growth Polymerization.** The AB-type sulfonated compound (6) was dissolved in dichloromethane (3 mL) and diisopropyl amine (1 mL). Then, 20 mol% CuI (1.5 mg, 0.008 mmol) and 20 mol% PPh\textsubscript{3} (2 mg, 0.008 mmol) were added to the reaction solution. The reaction mixture became a red-colored solution. The reaction was carried out under an argon atmosphere in dry Schlenk flask. The 2 mol% Pd(P\texttextsubscript{t}Bu\texttextsubscript{3})(Ph)(Br) (0.7 mg, 0.8 μmol) was transferred to another dry Schlenk flask in the grove box. Then, Pd(P\texttextsubscript{t}Bu\texttextsubscript{3})(Ph)(Br) in THF (1 mL) was added dropwise to the reaction mixture via cannula transfer. After the reaction was stirred for twelve hours at 50°C, the reaction mixture exhibited a greenish-blue fluorescence under a long wavelength of the UV-lamp. The solvent was removed under reduced pressure. Then, the concentrated solution was precipitated with methanol three times to remove the by-product. The desired polymer was an orange solid (35 mg, 65% yield). GPC (THF): M\textsubscript{n} = 9,800 g/mol, PDI = 1.40. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, δ\textsubscript{ppm}): 7.47 (m, 24H), 7.31 (m, 1H), 7.15 (m, 16H), 4.10 (m, 4H), 3.27 (m, 4H), 2.24 (m, 4H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, δ\textsubscript{ppm}): 137.23, 135.26, 131.23, 117.13, 116.25, 69.18, 64.89, 58.76, 54.12. See SI Fig. C-9 and C-10 for the NMR spectra.

**S-SO\textsubscript{3}-PPh\textsubscript{4} Polymer via Step-growth Polymerization.** The AB-type sulfonated compound (6) was dissolved in DMC (3 mL) and diisopropyl amine (1 mL). Then, 10 mol% CuI (1.5 mg, 0.008 mmol) was added to the reaction solution. The reaction was carried out under an argon atmosphere in dry Schlenk flask. The reaction mixture became a red-colored solution. Then, 10 mol% Pd(PPh\textsubscript{3})\textsubscript{4} (0.4 mg, 0.8 μmol) was transferred to another dry flask. Then, the Pd(PPh\textsubscript{3})\textsubscript{4} in DCM (1 mL) was added to the reaction mixture by syringe. After the reaction was stirred for twelve hours at 50°C, the reaction solution exhibited a greenish-blue fluorescence under a long wavelength of the UV-lamp. The solvent was removed under reduced pressure. The concentrated...
solution was precipitated with methanol three times to eliminate the oligomer and catalyst. The desired polymer was an orange-colored solid (26 mg, 56% yield). GPC (THF): \(M_n = 7,000\) g/mol, PDI = 1.70. \(^1\)H NMR (CDCl\(_3\), \(\delta_{ppm}\)): 7.47 (m, 24H), 7.31 (m, 1H), 7.15 (m, 16H), 4.10 (m, 4H), 3.27 (m, 4H), 2.24 (m, 4H). \(^{13}\)C NMR (CDCl\(_3\), \(\delta_{ppm}\)): 137.23, 135.26, 131.23, 117.13, 116.25, 69.18, 64.89, 58.76, 54.12. See SI Fig. C-9 and C-10 for the NMR spectra.

**Ion Exchange to Water Soluble Salts.** The C/S-SO\(_3\)-PPh\(_4\) polymer (10 mg, 0.02 mmol) was dissolved in dichloromethane (10 mL). Then, sodium chloride (8 mg, 0.2 mmol) in water (5 mL) was added to the reaction solution. The reaction mixture was stirred for twelve hours at room temperature. Then, the water layer was filtered through a membrane filter (D = 0.45\(\mu\)m) and dialyzed for two days. During the dialysis process, the excess sodium hydroxide was removed. Afterwards, the reaction solution was filtered through 0.45\(\mu\)m Millipore filter paper. Finally, the filtered solution was freeze-dried, resulting in the desired product as 4.5 mg (45% yield). \(^1\)H NMR (CDCl\(_3\), \(\delta_{ppm}\)): 6.79 (m, 2H), 4.18 (m, 4H), 3.32 (m, 4H), 4.10 (m, 4H), 2.27 (m, 4H). \(^{13}\)C NMR (CDCl\(_3\), \(\delta_{ppm}\)): 119.86, 116.28, 65.08, 63.29, 53.89, 51.21. See SI Fig. C-11 and C-12 for the NMR spectra.

**4.5.2.3 Synthesis of the Imidazolium AB-Type Monomer**

**1,4-Diiodo-2,5-dimethoxybenezene (8).** 1,4-Dimethoxybenezene (5 g, 36.2 mmol) was dissolved in glacial acetic acid (45 mL), water (3.5 mL) and concentrated sulfuric acid (1.5 mL). Then, iodine (11.8 g, 43.4 mmol) and KIO\(_3\) (10.5 g, 43.4 mmol) were added to the reaction solution. The reaction mixture was refluxed for twenty-four hours. After the reaction was done, the solution was quenched by a saturated Na\(_2\)SO\(_3\) solution, extracted with dichloromethane, and dried over MgSO\(_4\). The solvent was removed under reduced pressure. The resulting solid was recrystallized from the THF/water mixture solution to yield the desired product as a yellow solid.
(10.5 mg, 75%).\textsuperscript{73} \textsuperscript{1}H NMR (CDCl\textsubscript{3}, δ\textsubscript{ppm}): 7.11 (s, 2H), 3.83 (s, 6H). See SI Fig. C-13 for the NMR spectrum.

\textbf{2,5-Diiodo-1,4-hydroquinone (9).} 1,4-Diiodo-2,5-dimethoxybenezene (10 mg, 0.03 mmol) was dissolved in DMF (5 mL). The solution was cooled to 0°C. Then, BBr\textsubscript{3} (7.5 μL, 0.06 mmol) was slow added to the solution. The reaction mixture was warmed to room temperature and stirred for six hours. After the reaction was done, the reaction solution was quenched with ice water. The crude product was recrystallized from isopropyl alcohol to yield the desired product (4.8 mg, 67% yield).\textsuperscript{73} \textsuperscript{1}H NMR (CDCl\textsubscript{3}, δ\textsubscript{ppm}): 7.29 (s, 2H). See SI Fig. C-14 for the NMR spectrum.

\textbf{1,4-Bis(3-bromopropoxy)-2,5-diiodobenzene(10).} 2,5-Diiodobenzene-1,4-diol (1 g, 2.76 mmol) was dissolved in dimethylformamide (60 mL). Then, anhydrous potassium carbonate (10 g, 0.07 mmol) and 1,3-dibromopropane (50 mL, 0.49 mmol) were added to the reaction mixture. The reaction solution was refluxed for seventeen hours at 65°C. After the reaction was done, the remaining potassium carbonate was filtered. Then, the reaction solution was extracted with chloroform, washed with water, and dried over MgSO\textsubscript{4}. The concentrated solution was purified with column chromatography (chloroform as an eluent).\textsuperscript{73} The desired product was obtained as 650 mg (54% yield).\textsuperscript{73} \textsuperscript{1}H NMR (CDCl\textsubscript{3}, δ\textsubscript{ppm}): 7.12 (s, 2H), 4.08 (t, 4H), 3.83 (t, 4H), 2.13 (m, 4H). See SI Fig. C-15 for the NMR spectrum.

\textbf{Water-soluble ammonium ionic compound (11).} 1,4-Bis(3-bromopropoxy)-2,5-diiodobenzene (155 mg, 0.17 mmol) was dissolved in acetone (5 mL), water (5 mL), and methanol (5 mL). Then, 1-methyl-1H-imidazole (5 mL, excess) was added dropwise to the solution. The reaction mixture was refluxed for eighteen hours. After the reaction was finished,
acetone and methanol were removed under reduced pressure. The crude compound then moved on to the next reaction without further purification.

**Organic soluble compound (12).** The crude water-soluble ammonium ionic compound (11) was dissolved in water (50 mL). Then, excess sodium tetraphenylborate was added to the solution. A white solid immediately formed in the solution. After twelve hours, the white solid was filtered and washed with water. Finally, a pure organic soluble ammonium ionic compound 12 was obtained (110 mg, 55% yield). $^1$H NMR (DMSO, $\delta_{ppm}$): 7.75 (m, 16H), 7.35 (m, 24H), 7.21 (m, 4H), 7.12 (m, 2H), 4.04 (m, 8H), 3.83 (s, 6H), 2.13 (m, 4H). $^{13}$C NMR (DMSO, $\delta_{ppm}$): 138.56, 135.18, 127.56, 123.32, 67.18, 48.16, 26.18. MS (ESI) m/z ([M]$^{+2}$) 610.1867. See SI Fig. C-16 and C-17 for the NMR spectra. See SI Fig. C-29 for the MS spectrum.

**Imidazolium TMS acetylene substituted compound (13).** An organic soluble diiodo-ammonium compound (12) (500 mg, 0.40 mmol) was dissolved in dichloromethane (10 mL) and diisopropyl amine (5 mL). Then, 10 mol% CuI (4.5 mg, 0.04 mmol) and 10 mol% Pd(PPh$_3$)$_2$Cl$_2$ (8.5 mg, 0.02 mmol) were added to the solution. The reaction solution was cooled to 0°C for thirty minutes. TMS acetylene (60 µL, 0.6 mmol) was added dropwise to the solution. Then, the reaction solution was stirred at 50°C for twelve hours. After the reaction was done, the solution was quenched with water, extracted with dichloromethane three times, and dried over MgSO$_4$. The solution was filtered and concentrated under reduced pressure to yield the desired product (160 mg, 46% yield). $^1$H NMR (CDCl$_3$, $\delta_{ppm}$): 7.91 (m, 8H), 7.79 (m, 16H), 7.65 (m, 16H), 6.84 (s, 2H), 4.17 (t, 4H), 3.27 (m, 4H), 2.97 (t, 4H), 2.24 (t, 3H), 1.36 (d, 18H). $^{13}$C NMR (CDCl$_3$, $\delta_{ppm}$): 138.35, 136.12, 127.12, 123.48, 67.18, 48.02, 26.18, 0.03. MS (ESI) m/z ([M]$^{+2}$) 574.9747. See SI Fig. C-18 and C-19 for the NMR spectra. See SI Fig. C-30 for the MS spectrum.
**AB-type monomer (14).** The propargylic alcohol-substituted compound (13) (45 mg, 0.02 mmol) was dissolved in dichloromethane (5 mL) and methanol (5 mL). Then, anhydrous K$_2$CO$_3$ (50 mg, 4.64 mmol) was added to the solution. The solvent was removed under reduced pressure and purified with column chromatography. The desired product was a reddish-brown solid (32 mg, 78% yield). $^1$H NMR (CDCl$_3$, δ ppm): 7.91 (m, 8H), 7.79 (m, 16H), 7.65 (m, 16H), 6.84 (s, 2H), 4.17 (t, 4H), 4.01 (s, 1H), 3.72 (s, 6H), 3.27 (m, 4H), 2.97 (t, 4H), 2.24 (t, 3H). $^{13}$C NMR (CDCl$_3$, δ ppm): 138.35, 136.12, 127.12, 123.48, 62.19, 58.38, 42.98, 26.32. MS (ESI) m/z ([M]$^+$2) 503.1065. See SI Fig. C-20 and C-21 for the NMR spectra. See SI Fig. C-31 for the MS spectrum.

4.5.2.4 Polymerization of Imidazolium PPEs

**C-NR$_8$-BPh$_4$ Polymer via Chain-growth Polymerization.** The AB-type ammonium compound (14) was dissolved in DCM (3 mL) and diisopropyl amine (1 mL). Then, 20 mol% CuI (1.5 mg, 0.008 mmol) and 20 mol% PPh$_3$ (2 mg, 0.008 mmol) were added to the reaction solution. The reaction was carried out under an argon atmosphere in dry Schlenk flask. The reaction mixture became a red-colored solution. The 2 mol% Pd(Ph)(Br)(P$^t$Bu$_3$) (0.4 mg, 0.8 μmol) was transferred to another dry Schlenk flask in grove bon. Then, the Pd(P$^t$Bu$_3$)(Ph)(Br) in DCM (1 mL) was added dropwise to the reaction mixture via cannula transfer. After the reaction mixture was stirred for twelve hours at 50°C, the reaction solution exhibited a greenish-blue fluorescence under a long wavelength of the UV-lamp. The solvent was removed under reduced pressure. Then, the concentrated reaction mixture was precipitated with methanol three times to eliminate the oligomer and catalyst. The desired polymer was an orange-colored solid (26 mg, 56% yield). GPC (THF): $M_n = 5,800$ g/mol, PDI = 1.49) $^1$H NMR (CDCl$_3$, δ ppm): 7.91 (m, 8H), 7.79 (m, 16H), 7.65 (m, 16H), 6.84 (m, 2H), 4.17 (m, 4H), 3.72 (m, 6H), 3.27 (m, 4H), 2.97 (m,
4H), 2.24 (m, 3H). $^{13}$C NMR (CDCl$_3$, $\delta_{ppm}$): 138.16, 134.34, 131.12, 67.56, 65.12, 33.18, 26.15, 24.89. See SI Fig. C-22 and C-23 for the NMR spectra.

**S-NR$_4$-BPh$_4$ Polymer via Step-growth Polymerization.** The AB-type ammonium compound (14) was dissolved in DCM (3 mL) and diisopropyl amine (1 mL). Then, 10 mol% CuI (1.5 mg, 0.008 mmol) was added to the reaction solution. The reaction was carried out under an argon atmosphere in dry Schlenk flask. The reaction mixture became a red-colored solution. The 10 mol% Pd(PPh$_3$)$_4$ (0.4 mg, 0.8 $\mu$mol) was transferred to another dry flask. Then, the Pd(PPh$_3$)$_4$ in DCM (1 mL) was added dropwise to the reaction mixture by syringe. After the reaction was stirred for twelve hours at 50°C, the reaction solution exhibited a greenish-blue fluorescence under a long wavelength of the UV-lamp. The solvent was removed under reduced pressure. Then, the concentrated reaction mixture was precipitated with methanol three times to eliminate the oligomer and catalyst. The desired polymer was an orange solid (26 mg, 56% yield). GPC (THF): $M_n = 7,100$ g/mol, PDI = 1.87. $^1$H NMR (CDCl$_3$, $\delta_{ppm}$): 7.91 (m, 8H), 7.79 (m, 16H), 7.65 (m, 16H), 6.84 (m, 2H), 4.17 (m, 4H), 3.72 (m, 6H), 3.27 (m, 4H), 2.97 (m, 4H), 2.24 (m, 3H). $^{13}$C NMR (CDCl$_3$, $\delta_{ppm}$): 138.16, 134.34, 131.12, 67.56, 65.12, 33.18, 26.15, 24.89. See SI Fig. C-22 and C-23 for the NMR spectra.

**Ion Exchange to Water Soluble Salts.** C/S-NR$_4$-BPh$_4$ (10 mg, 0.02 mmol) was dissolved in acetone (30 mL). Then, tetrabutylammonium bromide (TBAB) (8 mg, 0.2 mmol) was added to the reaction solution. The reaction mixture was stirred for twelve hours at room temperature. The precipitated solid was then filtered and washed with cold-acetone to yield the desired CPE (4.5 mg, 45% yield). $^1$H NMR (D$_2$O, $\delta_{ppm}$): 8.55 – 7.29 (m, 8H), 4.53 (m, 4H), 4.22 (m, 4H), 3.90 (m, 6H), 2.43 (m, 4H). $^{13}$C NMR (D$_2$O, $\delta_{ppm}$): 126.56, 123.18, 63.28, 38.16, 33.89, 32.58. See SI Fig. C-24 and C-25 for the NMR spectra.
APPENDIX A
SUPPORTING INFORMATION FOR CHAPTER 2

Figure A-1. $^1$H NMR spectrum of Pd(P$^t$Bu$_3$)(Ph)(Br) in C$_6$D$_6$

Figure A-2. $^1$H NMR spectrum of 2,2'-(1,4-phenylenebix(oxy))diacetic acid in CDCl$_3$
Figure A-3. $^1$H NMR spectrum of didodecyl 2,2$'$-(1,4-phenylenebis(oxy))diacetate in CDCl$_3$.

Figure A-4. $^1$H NMR spectrum of compound 4 in CDCl$_3$. 

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Figure A-5. $^1$H NMR spectrum of didodecyl 2,2$'$-((2-(3-hydroxyprop-1-yn-1-yl)-5-iodo-1,4-phenylene)bis(oxy))diacetate in CDCl$_3$

Figure A-6. $^1$H NMR spectrum of didodecyl 2,2$'$-((2-ethynyl-5-iodo-1,4-phenylene)bis(oxy))diacetate in CDCl$_3$
Figure A-7. $^1$H NMR of didodecyl 2,2'-(2,5-bis((triisopropylsilyl)ethynyl)-1,4-phenylene)bis(oxy))diacetate in CDCl$_3$.

Figure A-8. $^1$H NMR of compound 8 in CDCl$_3$. 
Figure A-9. $^1$H NMR spectrum of C-ab ester polymer in CDCl$_3$

Figure A-10. $^1$H NMR spectrum of S-ab ester polymer in CDCl$_3$
Figure A-11. $^1$H NMR spectrum of S-aabb ester polymer in CDCl$_3$

Figure A-12. $^1$H NMR spectrum of S-aa ester polymer in CDCl$_3$
Figure A-13. $^1$H NMR spectrum of C-ab in D$_2$O (pH = 8)

Figure A-14. $^1$H NMR spectrum of S-ab in D$_2$O (pH = 8)
Figure A-15. $^1$H NMR of S-aabb in D$_2$O (pH = 8)

Figure A-16. $^1$H NMR for S-aa in D$_2$O (pH = 8)
Figure A-17. $^{13}$C NMR of didodecyl 2,2'-(2-(3-hydroxyprop-1-yn-1-yl)-5-iodo-1,4-phenylene)bis(oxy))diacetate in CDCl$_3$

Figure A-18. $^{13}$C NMR of AB monomer in CDCl$_3$
Figure A-19. $^{13}$C NMR for C-ab ester polymer in CDCl$_3$

Figure A-20. $^{13}$C NMR for S-ab ester polymer in CDCl$_3$
Figure A-21. $^{13}$C NMR for S-aa ester polymer in CDCl$_3$

Figure A-22. $^{13}$C NMR for C-ab in D$_2$O (pH = 8)
Figure A-23. $^{13}$C NMR for S-ab in D$_2$O (pH = 8)

Figure A-24. $^{13}$C NMR for S-aa in D$_2$O (pH = 8)
Figure A-25. MS spectrum for didodecyl 2,2’-((2-(3-hydroxyprop-1-yn-1-yl)-5-iodo-1,4-phenylene)bis(oxy))diacetate

Figure A-26. MS spectrum of didodecyl 2,2’-((2-ethynyl-5-iodo-1,4-phenylene)bis(oxy))diacetate
APPENDIX B
SUPPORTING INFORMATION FOR CHAPTER 3

Figure B-1. $^1$H NMR spectrum of 2Pd catalyst (CD$_2$Cl$_2$, 300 MHz)

Figure B-2. $^1$H NMR spectrum of 3Pd catalyst (CDCl$_3$, 300 MHz)
Figure B-3. $^1$H NMR spectrum of 4Pd catalyst (CDCl$_3$, 300 MHz)

Figure B-4. $^1$H NMR spectrum of 2Pd ester polymer (CDCl$_3$, 300 MHz)
Figure B-5. $^1$H NMR spectrum of 3Pd ester polymer (CDCl$_3$, 300 MHz)

Figure B-6. $^1$H NMR spectrum of 4Pd ester polymer (CDCl$_3$, 300 MHz)
Figure B-7. $^1$H NMR spectrum of 2Pd CPE polymer (D$_2$O, 300 MHz)

Figure B-8. $^1$H NMR spectrum of 3Pd CPE polymer (D$_2$O, 300 MHz)
Figure B-9. $^1$H NMR spectrum of 4Pd CPE polymer (D$_2$O, 300 MHz)

Figure B-10. $^{13}$C NMR spectrum of 4Pd initiator (CDCl$_3$, 300 MHz).
Figure B-11. $^{13}$C NMR spectrum of 2Pd ester polymer (CDCl$_3$, 300 MHz).

Figure B-12. $^{13}$C NMR spectrum of 3Pd ester polymer (CDCl$_3$, 300 MHz).
Figure B-13. $^{13}$C NMR spectrum of 4Pd ester polymer (CDCl$_3$, 300 MHz).

Figure B-14. $^{13}$C NMR spectrum of 2Pd CPE (D$_2$O, 300 MHz).
Figure B-15. $^{13}$C NMR spectrum of 3Pd CPE (D$_2$O, 300 MHz).

Figure B-16. $^{13}$C NMR spectrum of 4Pd CPE (D$_2$O, 300 MHz).
Figure B-17. MS spectra for 4Pd initiator
Figure C-1. $^1$H NMR spectrum of SO$_3$Na salt (2) in CD$_2$Cl$_2$

Figure C-2. $^1$H NMR spectrum of diiodo SO$_3$Na salt (3) in CD$_2$Cl$_2$
Figure C-3. $^1$H NMR spectrum of $\text{SO}_3\text{PPh}_4$ salt (4) in CDCl$_3$

Figure C-4. $^{13}$C NMR spectrum of $\text{SO}_3\text{PPh}_4$ salt (4) in CDCl$_3$
Figure C-5. $^1$H NMR spectrum of $\text{SO}_3\text{PPh}_4$ salt with TMS acetylene (5) in CDCl$_3$

Figure C-6. $^{13}$C NMR spectrum of $\text{SO}_3\text{PPh}_4$ salt with TMS acetylene (5) in CDCl$_3$
Figure C-7. $^1$H NMR spectrum of SO$_3$PPh$_4$ AB monomer (6) in CDCl$_3$

Figure C-8. $^{13}$C NMR spectrum of SO$_3$PPh$_4$ AB monomer (6) in CDCl$_3$
Figure C-9. $^1$H NMR spectrum of SO$_3$PPh$_4$ polymer in CDCl$_3$

Figure C-10. $^{13}$C NMR spectrum of SO$_3$PPh$_4$ polymer in CDCl$_3$
Figure C-11. $^1$H NMR spectrum of SO$_3$Na polymer in D$_2$O

Figure C-12. $^{13}$C NMR spectrum of SO$_3$Na polymer in D$_2$O
Figure C-13. $^1$H NMR spectrum of 1,4-diiodo-2,5-dimethoxybenzene (8) in CDCl$_3$

Figure C-14. $^1$H NMR spectrum of 2,5-diiodobenzene-1,4-diol (9) in CDCl$_3$
Figure C-15. $^1$H NMR spectrum of 1,4-bis(3-bromopropoxy)-2,5-diiodobenzene (10) in CDCl$_3$

Figure C-16. $^1$H NMR spectrum of NR$_4$BPh$_4$ salt (12) in DMSO-d$_6$
Figure C-17. $^{13}$C NMR spectrum of NR$_4$BPh$_4$ salt (12) in DMSO-d$_6$

Figure C-18. $^1$H NMR spectrum of NR$_4$BPh$_4$ salt with TMS acetylene (13) in DMSO-d$_6$
Figure C-19. $^{13}$C NMR spectrum of NR$_4$BPh$_4$ salt with TMS acetylene (13) in DMSO-d$_6$

Figure C-20. $^1$H NMR spectrum of NR$_4$BPh$_4$ AB monomer (14) in CDCl$_3$
Figure C-21. $^{13}$C NMR spectrum of NR$_4$BPh$_4$ AB monomer (14) in CDCl$_3$

Figure C-22. $^1$H NMR spectrum of NR$_4$BPh$_4$ polymer in CDCl$_3$
Figure C-23. $^{13}$C NMR spectrum of NR$_4$BPh$_4$ polymer in CDCl$_3$

Figure C-24. $^1$H NMR spectrum of NR$_4$Br CPE polymer in D$_2$O
Figure C-25. $^{13}$C NMR spectrum of NR$_4$Br CPE polymer in D$_2$O

Figure C-26. MS spectrum of SO$_3$PPh$_4$ salt (4)
Figure C-27. MS spectrum of $\text{SO}_3\text{PPh}_4$ salt with TMS acetylene (5)

Figure C-28. MS spectrum of $\text{SO}_3\text{PPh}_4$ AB monomer
Figure C-29. MS spectrum of NR$_4$BPh$_4$ salt (12)

Figure C-30. MS spectrum of NR$_4$BPh$_4$ salt with TMS acetylene (13)
Figure C-31. MS spectrum of NR₄BPh₄ AB monomer
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BIOGRAPHICAL SKETCH

Bethy Kim was born in South Korea, Daejeon, one of the largest city in South Korea. At the age of nineteen, she went to Chung-Nam National University in Daejeon, where she earned her Bachelor of Science degree in chemistry and medicinal chemistry in summer of 2008. After graduation of Chung-Nam National University; she worked at anti-cancer center in Korea Research Institute of Chemical Technology (KRICT) for one year as a researcher. Later, she went to study abroad at the University of Houston. There, she earned her master degree in 2010. In 2012, she worked at petrochemical center at the LG Chemical company to develop the metallocene organo-catalyst.

Bethy enrolled the University of Florida’s graduate program in 2013. She joined the Prof. Kirk Schanze’s group in Department of Chemistry. Her research focused on the preparation of well-defined poly(phenyleneethylene) based conjugated polyelectrolytes with cationic or anionic side chain on the PPE backbones. She received her Ph. D. degree from the University of Florida in the summer of 2017.