Synthesis and Application of PDIB Nanostructures in Solar Cells

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SYNTHESIS AND APPLICATION OF PDIB NANOSTRUCTURES IN SOLAR CELLS

A Capstone Experience/Thesis Project

Presented in Partial Fulfillment of the Requirements for

the Degree Bachelor of Science with

Honors College Graduate Distinction at Western Kentucky University

By:

John T. Ferguson

*****

Western Kentucky University
2015

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ABSTRACT

Perylenediimide bridged silsesquioxane (PDIB) nanoparticles were synthesized by sol-gel processes as described by the Stöber method. These particles were synthesized homogeneously from solution and with the use of silica nanoparticles and bipyridine iodide bridged silsesquioxane (BPIB) nanoparticles as nucleation sites. The morphology of the resulting particles was confirmed by TEM and the presence of PDI confirmed by UV spectroscopy. Although further research will test all of the particles across a range of concentrations and sizes, the silica nucleated PDIB nanoparticles were analyzed in the active layer of bulk heterojunction organic photovoltaic devices in conjunction with P3HT polymer. Devices with the configuration of ITO/PEDOT:PSS/P3HT:(PDIB silane or nanoparticles)/calcium/aluminum prepared by spray-coating were observed to have higher power conversion efficiencies than the same devices prepared by spin-coating. Although the other nanoparticles remain untested, the silica-nucleated nanoparticle devices exhibit power conversion efficiencies of up to 3.13%. The increased performance of the devices containing nanoparticles is attributed to the morphology control of the active layer with thermally stable nanoparticles as opposed to allowing domain size to be controlled by phase-segregation in the active layer during annealing.

Keywords: PDI, Photovoltaics, Solar Cells, Silsesquioxane, Nanoparticles, OPV's
Dedicated to my grandfather, Bruce Ferguson
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My parents have always done the best for me and they deserve any credit that could possibly be accredited to me.
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CHAPTER 1

INTRODUCTION

Photovoltaic devices are a research area of great interest with numerous approaches currently being explored. One of the most important aspects of photovoltaic design concerns designing to perform under raw sunlight or concentrated sunlight.\(^1\) This is one way to reduce the cost of production for solar cells, as having them occupy a smaller area can maintain high efficiencies while decreasing material costs by use of lenses and mirrors for concentration. Although this approach is effective, concentrator systems are not feasible to be implemented on small scales and their dependence on orientation makes them effectively immobile. As a secondary approach for reducing material costs, many photovoltaic cells are designed to use thin films of material.\(^2\) These two techniques may even be used in conjunction with each other\(^3\) to further increase their cost efficiency; they still lack desirable features possible with organic materials.

Organic Photovoltaic (OPV) devices also use their materials very efficiently in thin films but, because of the flexibility found in organic materials these devices have the added benefit of being able to be manufactured as a flexible film.\(^4\) In addition to this allowing OPV’s to be placed on curved surfaces, this also significantly reduces structural material costs as inflexible devices need reinforcement to keep them rigid.
Although inorganic photovoltaics currently have higher power conversion efficiencies, OPV's have lower costs and less restrictive applications. To improve OPV's to a state of commercial viability, there are multiple sources of device inefficiency that need to be addressed. At the core of the OPV there needs to be a compound acting as an electron donor. An electron donor molecule can absorb the energy of onset photons to excite an electron from its highest occupied molecular orbital (HOMO) to its lowest unoccupied molecular orbital (LUMO). The excited electron and its positively charged hole left behind in the electron donor are collectively referred to as an exciton. For efficient power conversion an electron acceptor compound can be present to allow for exciton dissociation at the interface between the compounds. Devices may even be designed with a second electron acceptor\(^5\) or additional layers to improve charge separation and transport. The electron donor and acceptor compounds and any additional conductive layers must have compatible energy levels for efficient energy harvesting.\(^6\)

**The Process of Solar Energy Absorption**

For any donor material, the excitons created will have their energy dictated by the bandgap between the energy levels of the HOMO and LUMO. Incident photons can only excite an electron into an exciton if the photon’s energy is greater than or equal to the bandgap of the donor material. Consequently, the efficiency of the photovoltaic cell is constrained by the Shockley-Queisser Limit as to how well the bandgap of the electron donor compliments the solar spectrum.\(^7\) This sets a theoretical limit on device efficiencies with the greatest theoretical efficiencies possible for a bandgap of 1.1 eV.\(^7\) However, this calculation assumes no resistances in the cells and OPV's routinely have bandgaps of up to 2 eV to compensate for resistance\(^6\)
Harvesting the power of generated excitons into an electric current introduces further difficulties to hinder device performance. When a current is made as shown in Figure 1.1, the exciton will have to dissociate across the donor/acceptor interface (known as the heterojunction) in order for the excited electron to travel through the electron acceptor to the cathode while an electrode from the anode fills in the positively charged hole. In order for exciton dissociation to happen in place of recombination, the energy level of the LUMO in the donor must be greater than that of the acceptor by the exciton binding energy, typically 0.5 eV.\textsuperscript{[8]} Although the energy of the excitons is determined by the bandgap of the electron donor, the energy of the circuit after dissociation is limited to the bandgap across the heterojunction from the HOMO of the donor to the LUMO of the acceptor. Although a larger energy difference of the LUMO across the heterojunction better facilitates the dissociation,\textsuperscript{[8]} the difference should be minimized to not limit the output voltage of the devices. The energy of the HOMO of the acceptor needs be less than that of the donor so as to allow excitons in the acceptor to diffuse back across the interface and make reverse currents across the heterojunction energetically unfavorable.\textsuperscript{[6]}
The selection of electrodes for OPV’s also plays a significant role in device performance. The currents produced by photovoltaics will inevitably face resistance through the device. For this reason photovoltaic cells will produce a range of currents for different voltages. The maximum voltage at which the cell produces a current is known as the open circuit voltage and the maximum current that a cell will produce with no voltage requirement is known as the short circuit current. The open circuit voltage is limited by the bandgap across the heterojunction and is strongly influenced by the difference in the electron work function between the electrodes for bilayer OPV’s but despite trends cannot yet be accurately predicted for bulk heterojunction OPV’s.\textsuperscript{[6]}
Figure 1.2 shows a theoretical IV curve for an organic photovoltaic device showing the strength of any current that can be produced at a given voltage. The open circuit voltage is shown at the point $V_{OC}$ and the short circuit current is shown at the point $I_{SC}$. Between these two extremes the device is capable of producing currents with a voltage depending on their photovoltaic properties and configuration. The power (current multiplied by voltage) of any particular current produced by the device can be visualized as a rectangle on the IV curve bounded by the origin and the selected point. At the devices maximum output power $P_{max}$ the possible power conversion efficiency is maximized and outlined in blue in Figure 1.2.

![IV Curve of Photovoltaic Device Performance](image)

**Figure 1.2: IV Curve of Photovoltaic Device Performance**

The efficiency of the solar cell can be calculated in two manners from the IV curve. The efficiency of the power conversion is the simple ratio between the maximum power able to be produced by the cell and the power of all solar radiation across the cell area. The fill factor also looks at a ratio of power, but instead at the ratio of the maximum
power collected by the cell to the theoretical power of the open circuit voltage multiplied by the short circuit current,\cite{9} outlined in red in Figure 1.2. If the cell were able to produce a current of perfectly homogeneous voltage, the fill factor would be 100%.

In addition to measuring cell efficiency, IV curves can provide valuable information about the performance of the device tested. By analyzing the dependence of device performance on the intensity of irradiance and the voltage of the circuit it is possible to determine whether the device's losses are geminated.\cite{10} Non-geminated losses occur when the hole of an exciton is filled by an electron other than the one that created it. These losses are amplified by increased exciton formation and hinder device performance more greatly when more greatly irradiated. The relationship between light intensity and power conversion efficiency is also of interest to solar cells to be implemented in low-light or concentrated-light settings. Identifying major sources of inefficiency such as exciton recombination and charge carrier loss is critical to maximizing device performance.

Electrodes in OPV's must also be selected for their transparency. The nature of their design will always have one electrode blocking light reaching the active layer, so any opacity in the top electrode in the range of light absorbance for the electron donor subtracts from device performance.\cite{11} Transparency of the bottom electrode is not necessary for device performance, but partially transparent OPV's could have broader consumer applications on transparent surfaces such as windows.

**Organic Photovoltaic Device Configurations**

The transparency of the electron donor is not of consequence in a favorably oriented bilayer system. With onset solar radiation only having to pass through the anode
as shown in Figure 1.3, the electron acceptor and cathode cannot block light from reaching the donor. In a bilayer system, OPV’s have their active layer organized by having the electron donor and electron acceptor deposited as separate layers. This configuration ensures that each material is in complete contact with its respective electrode. However, the surface area of the heterojunction between the active layers is minimized, and these cells can exhibit open circuit voltages more strongly dependent on the factors of the heterojunction but typically with poorer fill factors.\textsuperscript{[12]} Regulating the exact thickness of the active layer(s) for morphology control in any OPV is crucial, and controlled by a number of factors.

![Figure 1.3: Cross-Sectional Diagram of Bilayer system](image)

The electron donating layer of bilayer-OPV’s is typically the one to physically absorb light for exciton formation. Increasing layer thickness will give diminishing returns for photon absorption, but the creation of a current from these excitons is still dependent on the exciton diffusion length. For this reason and because thicker layers equate to larger serial resistances it is not beneficial to make the active layer any thicker
than its exciton diffusion length\textsuperscript{[6]}, on the order of nanometers and dependent on a number of electrical factors including the conductance offset of the heterojunction.\textsuperscript{[13]}

The more common approach for OPV's is to have both donor and acceptor materials blended into a single layer so that there heterojunction is dispersed throughout as seen in Figure 1.4. This removes the limitation of the active layer to the exciton diffusion length and lets the thickness of the active layer be optimized around photon absorption and charge carrier mobility.\textsuperscript{[14],[15]} Even slight imperfections in the interfaces can create voids, interrupting charge transfer. By annealing a bulk heterojunction to near-melting temperatures after deposition, these voids can be removed, but the components of the active layer can reconfigure in the molten state and can cause undesirable morphology.\textsuperscript{[16]}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Cross-Sectional Diagram of Bulk Heterojunction System}
\end{figure}

The results of annealing create completely different problems for the configuration of bulk heterojunction OPV's. The abundance of interfaces maximize exciton dissociation but the chaotic morphology also hinders charge carrier mobility. The electrodes with their corresponding charge carrier component in the active layer will
consequently have less contact surface area. The phase segregation that comes along with annealing reduces the inter-facial area of the heterojunction while removing imperfections in all the contact areas.\[16],[17]

Device orientation should also be considered during annealing, as the components can separate out by density during the annealing process allowing for intermediates between bulk heterojunctions and bilayer systems.\[18] More crystalline donor and acceptor materials will undergo more extreme phase segregation during annealing but will also exhibit higher charge carrier mobilities, making the packing structures of the components with themselves and with each other critical to device performance.\[19]

**The Role of Nanoparticles**

Controlling the morphology of the active layer to benefit exciton dissociation and charge carrier mobility is one of the primary challenges for photovoltaics today. Extensive research has gone into the analysis of the annealed bulk heterojunction and the morphology of the polymers with different side chains and additives.\[20] By removing the role of molecular packing in the morphology control of the bulk heterojunction, donor and acceptor materials with high charge carrier mobilities but unfavorable phase segregation could be implemented efficiently into photovoltaic cells.

By incorporating one component of the active layer into nanostructures stable at the targeted annealing temperature control over the morphology of the active layer can be gained. Leaving the other component as polymer allows the annealing process to mold the polymeric component of the active layer around the nanostructured component for a highly organized system. Allowing the nanostructures to span the entire thickness of this
layer as shown in Figure 1.5 will guarantee each component complete contact with both electrodes while maintaining a high surface area at the heterojunction.

This allows for very crystalline components of the bulk heterojunction to be segregated into specifically-sized domains not dependent on their crystallinity. This morphology control can lead to a reduction of charge carrier loss and exciton recombination in any applicable OPV's.

**Homogeneous Silsesquioxane Nanoparticles**

One possible method to incorporate organic compounds in the active layer into nanoparticles of targeted dimensions is the incorporation of a silsesquioxane network as shown in Figure 1.6. Whereas silica networks condense to an SiO$_2$ structure, silsesquioxane networks incorporate an organic molecule to have a resulting structure of R-SiO$_{1.5}$. Bridging the molecule with linkers on either side to -triethoxysilane groups
allows for hydrolytic condensation to create a variety of different materials depending on reaction conditions.\textsuperscript{[21]}

![Diagram of Silica and Silsesquioxane Nanoparticles]

\textbf{Figure 1.6: Formation of Silica and Silsesquioxane Nanoparticles}

There exist many alternative methods for incorporating the photovoltaic materials into nanostructures, but silsesquioxane networks have some distinct advantages. The networks formed are thermally stable and capable of maintaining their structure through annealing. Having the photovoltaic material incorporated into the silsesquioxane monomer ensures that the material is distributed homogenously throughout the network instead of only on a surface. Longer molecules incorporated into these networks will also create pores, leading to greater surface areas which may increase the area of the heterojunction in the devices.\textsuperscript{[21]}

In solution with the presence of catalytic quantities of an acid or a base the silsesquioxane network will form via sol-gel processes. Porosity of the network determined by the length of the molecule bridging the triethoxysilane groups may cause the network to partially collapse upon drying.\textsuperscript{[21]} Stirring this solution and limiting or stopping the reaction before it reaches completion will create nanoparticles as described by the Stöber process.\textsuperscript{[22]} Because the length of the bridging group effects the nucleation,
porosity, and structural stability\textsuperscript{[23]} of the resulting nanoparticles, this method is limited in its applications to shorter bridging groups that can be modified at both ends.

Despite these few limitations, the Stöber process is very adaptable. Although it was originally implemented solely for the formation of pure silica nanoparticles, particles with numerous bridging groups have been synthesized in a variety of size ranges.\textsuperscript{[23]} Catalysis with either an acid or a base will facilitate the reaction, and the concentration of which has a direct influence to the particle size.\textsuperscript{[23]} The temperature of the reaction can also be used to control the porosity and textural properties of the network, leading to more amorphous networks formed at lower temperatures.\textsuperscript{[24]} The specifications of the linkers play a significant role in network formation. Longer, more flexible linkers on the bridging compound will increase the average pore size but their flexibility will also promote their collapse.\textsuperscript{[21]} Having -monoethoxysilane or -diethoxysilane linkers will lead to the formation of different polymer nanostructures.\textsuperscript{[25]}

Through the incorporation of multiple organosilanes, surfactants, surfaces, and additives a huge variety of materials have been synthesized with silsesquioxane networks.\textsuperscript{[26]} These methods allow for great control over the structural porosity of the networks and can alter the crystalline properties of the resulting materials.\textsuperscript{[27]} With careful consideration to the organic linkers of the monomer, the use of additives, and the reaction conditions of the particles, there is a considerable degree of control to the morphology of the active layer. Perylene diimide (PDI) was chosen as the electron acceptor to be modified because of its well studied photovoltaic performance, typically with poly(3-hexylthiophene) (P3HT). While the P3HT/PDI system uses inexpensive organic materials and has favorable bandgaps for solar energy, devices made typically
exhibit poor performance due to the trade-offs the PDI's crystallinity.\textsuperscript{[28]} Although PDI has been researched for its favorable energy levels, devices containing it typically have PCE's of less than 0.50%.\textsuperscript{[29],[30],[31]}

This method is not limited to any particular organic photovoltaic system. Although only applicable to molecules able to be bridged by silane linkers, the use of silsesquioxane nanoparticles for morphology control adds another dimension of manipulation for bulk heterojunction OPV's. Whereas the effects of annealing on phase segregation are a huge factor in designing bulk heterojunction OPV's, the incorporation of nanoparticles allows for these phase segregation properties to be very tightly controlled by particle size.
CHAPTER 2

EXPERIMENTAL METHODS

Objective

To create silsesquioxane nanoparticles, incorporating the electron acceptor perylene diimide to be used in the active layer of organic photovoltaic cells with poly(3-hexylthiophene). These silsesquioxane nanoparticles need to be thermally stable at up to 50° C to withstand annealing.

Materials

3,4,9,10-tetracarboxyanhydride perylene, 3-iodopropytriethoxysilane, 4,4’-dipyridyl, ammonium hydroxide (aqueous, 28%), ITO coated PET plastic, anhydrous ethanol, tetrahydrofuran, hexane, chloroform, dichloromethane, acetonitrile, poly(3-hexylthiophene), and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate were all purchased from Sigma Aldrich. 3-aminopropyltriethoxysilane and tetraethoxysilane were both purchased from Alfa Aesar.

Synthesis Method of Perylene Diimide Bridged Silane (PDIB Silane)

3,4,9,10-tetracarboxyanhydride perylene (2.94 g, 7.44 mmol) was added to a two-necked round bottom flask with anhydrous ethanol (100 mL). The flask was attached to a
water-jacket condenser, sealed with septa, and flushed with argon for 10 minutes. The flask and condenser were lowered into an oil bath at 85° C and allowed to stir while the temperature equilibrated. 3-aminopropyltriethoxysilane (6.00 g, 37.2 mmol) was added by syringe to the flask and the reaction was allowed to reflux for 20 hours.

The contents of the flask were filtered and the precipitate was collected. The precipitate was washed with anhydrous ethanol (50 mL) and anhydrous hexane (50 mL) to remove impurities. The precipitate was then dissolved in anhydrous chloroform and filtered to remove impurities. The filtrate product was rotovapped, collected into a vial, and then dried in a vacuum oven. The mass of the product was recorded, converted to molar quantities and compared to the initial quantity 3,4,9,10-tetracarboxyanhydride perylene. (Yield by mol= 41%)

1H-NMR (300MHz, CDCl3) \(\{\delta, \text{ppm}\} : 8.64 (2H, d), 8.57 (2H, d), 4.20 (4H, t), 3.82 (12H, q), 1.87 (4H, m), 1.21 (18H, t), 0.79 (4H, t); \)

FT-IR Peaks (cm\(^{-1}\)):
- 2943–2881 (C–H stretching of alkyl chains),
- 1693 (C=O carbonyl stretching),
- 1594–1654 (aromatic C–C stretchings),
- 1440 (N–C stretching from imide),
- 1342–1254 (Si–C stretchings) and
- 1075 (Si–O stretching);

Elemental analysis (%): experimental – C 63.15, H 6.33, N 3.49;
Calculated – C 63.13, H 6.31, N 3.51.

Scheme 2.1: Synthesis of PDIB Silane
Synthesis Method of Bipyridine Iodide Bridged Silane (BPIB Silane)

4,4'-dipyridyl (500. mg, 3.20 mmol) and anhydrous acetonitrile (20 mL) were added to a two-neck round bottom flask and attached to a water-jacket condenser. The flask and the condenser were sealed with septa, flushed with argon for 10 minutes, and lowered into an oil bath heated to 85° C and allowed to stir. 3-iodopropyltriethoxysilane (930 mg, 3.21 mmol) was injected by syringe and the reaction was allowed to reflux for 20 hours.

The solution was rotovapped and the precipitate was dissolved into anhydrous dichloromethane (20 mL). This solution was then vacuum-filtered to remove impurities and the filtrate rotovapped to yield a product which was collected into a vial and then dried with a vacuum oven. The mass of the product was recorded, converted to molar quantities, and compared to the initial quantity of 4,4'-dipyridyl. (Yield by mol= 76%)

$^1$H-NMR(300MHz, D$_2$O) {δ, ppm}: 8.80 (2H, d), 8.56 (2H, d-d), 8.24 (2H, d), 7.72 (2H, d-d), 4.70 (9H, s), 4.51 (4H, t), 2.00 (4H, m), 0.68 (1H, t)

![Scheme 2.2: Synthesis of BPIB Nanoparticles](image)

Synthesis Method of PDIB Nanoparticles

PDIB Silane (20.0 mg, 0.0250 mmol) was dissolved in anhydrous tetrahydrofuran (1 mL) in a vial with the aid of an ultrasonic bath. In a separate vial, anhydrous ethanol
(20 mL) and ammonium hydroxide (aqueous, 28%, 2 mL) were allowed to stir at 350 rpm. The tetrahydrofuran solution was withdrawn from the first vial by syringe and injected into the second vial through a 0.45 µm mesh filter. The reaction was capped and allowed to stir for 24 hours.

The solution was then centrifuged at 10,000 rpm for 10 minutes and the supernatant discarded. The precipitate was dispersed into ethanol (20 mL) with the aid of an ultrasonic bath and centrifuged again at 10,000 rpm for 10 minutes. The supernatant was discarded and the precipitate was dispersed in tetrahydrofuran (20 mL) using an ultrasonic bath and centrifuged once more at 10,000 rpm for 10 minutes. The supernatant was discarded and the precipitate was dried by vacuum oven before being collected into a vial. The mass of the nanoparticles was recorded and compared to the mass of the PDIB silane starting material (Yield by mass = 46%)

**Synthesis of TEOS-nucleated PDIB Nanoparticles**

Anhydrous ethanol (10 mL) and ammonium hydroxide (aqueous, 28%, 1 mL) were mixed in a vial and allowed to stir at 350 rpm. Tetraethoxysilane \{TEOS\} (0.1 mg) was injected into the solution and allowed to react for 20 hours.

The solution was centrifuged at 10,000 rpm for 10 minutes and the supernatant was discarded. The precipitate product was dried by vacuum oven and collected into a vial. The mass of the product was recorded and compared to the initial mass of tetraethoxysilane. (Yield by mass = 91%)

The resulting particles were used to nucleate PDIB nanoparticles. The dried TEOS particles were dissolved into the basic ethanol solution described in the synthesis
of PDIB nanoparticles and the same procedure followed. The mass of the particles was recorded and the change in the mass of the particles was calculated from the initial mass. This change in mass was compared to the mass of PDIB silane initially added. (Yield by mass = 30%)

**Synthesis of BPIB-nucleated PDIB Nanoparticles**

Deionized water (1 mL) was added to a vial with bipyridine iodide bridged trimethoxysilane (10 mg) and dissolved with the aid of an ultrasonic bath. Anhydrous ethanol (10 mL) and ammonium hydroxide (aqueous 28%, 1 mL) were added to a separate vial and allowed to stir at 350 rpm. The water solution from the first vial was added to the second vial by syringe through a 0.45 µm mesh filter. The solution was allowed to continue for 20 hours.

The solution was then centrifuged at 10,000 rpm for 10 minutes. The precipitate was dispersed into deionized water (10 mL) with an ultrasonic bath and centrifuged once more at 10,000 rpm for 10 minutes. This precipitate product was then collected and dried. (Yield by mass = 44%)

The resulting particles were used to nucleate PDIB nanoparticles. The dried BPIB particles were dissolved into the basic ethanol solution described in the synthesis of PDIB nanoparticles and the same procedure followed. The mass of the particles was recorded and the change in the mass of the particles was calculated from the initial mass. This change in mass was compared to the mass of PDIB silane initially added. (Yield by mass = 34%)
Fabrication of devices

Squares of ITO coated plastic (25x25 mm) were sequentially cleaned with isopropanol and acetone in an ultrasonic bath for 15 minutes. The plastic substrates were then placed inside a dry nitrogen atmosphere and spin coated with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) to form a 70 - 80nm thick layer. The devices were then annealed at 100° C for an hour.

A solution of chlorobenzene (2 mL) was prepared with a (1:1) blend of Poly(3-hexylthiophene-2,5-diyl) (P3HT) (10 mg) and PDIB nanoparticles (10 mg). This solution was then deposited by spin coating at 1000 rpm onto the device surface to leave an 80 – 100 nm thick active layer. Vinyl masks were then gently placed onto the active layer. Each mask left open space for 2x6 mm cathodes to be deposited in an equally-spaced grid on the surface of the device. The devices were then removed from the nitrogen atmosphere and flipped right-side-up in a vacuum evaporator. The vacuum evaporator was then used to deposit layers of calcium (80 nm) and aluminum (200 nm) into the 2x6 mm cells and the devices were then placed back into the dry nitrogen atmosphere. The devices were then annealed at 50° C for 10 minutes before being characterized in a solar simulator where dedicated electronic equipment varied the voltage across the devices while illuminated and recorded the currents produced at each voltage.
CHAPTER 3

RESULTS AND DISCUSSION

Perylenediimide bridged silane and bipyridine iodide bridged silane were both synthesized with propyl silane linkers as described. Using these organosilanes in conjunction with tetraethoxysilane, three different types of nanoparticles were made as depicted in Scheme 3.1. All three particle types feature a surface of hydrolyzed PDIB silane. Whereas the first particles were made using only PDIB silane, the other two particles were made by nucleating a layer of PDIB silane onto a silica or silsesquioxane core.

The full effect of the silsesquioxane core for the photovoltaic properties is not yet clear. While the size regularity of silica nanoparticles allows for a much greater control of the resulting particle size than those made without a nucleating agent, the amorphous structure of silica is suspected to be detrimental to charge carrier mobility.
Having a more crystalline core for the nanoparticles should result in a more crystalline shell of PDIB silsesquioxane. Whereas silica nanoparticles are amorphous, nanoparticles made from BPIB silane are more crystalline. With thicker layers around the core we hope to gather XRD data to confirm the effects of core crystallinity on the shell.

In Figure 4.1 the characteristic absorption peaks between 450 and 550 nm of PDI are seen in the silane precursor and all three species of nanoparticles. The highest wavelength absorption peak corresponds to the lowest energy of onset radiation that can be absorbed by the particles, also known as the bandgap. While the ratio of absorbance intensities changes across the particles, the fact that the peaks are not significantly shifted indicates comparable energy levels for the analytes. The bandgap is insufficient for predicting photovoltaic performance. Cyclic voltammetry will be needed to determine the
exact oxidation potential to see if how the HOMO and LUMO energy levels compare of the potential electron acceptors.

The most notable feature from the UV spectra is a significant lower-energy shift and broadening of the absorbance of BPIB silane nucleated PDIB nanoparticles. Due to the packing of these particles, less energy is necessary to excite an electron in the acceptor. Until analysis on the exact energy levels of these particles or photovoltaic data is collected, it is not known how this reduced bandgap will affect device performance. Its reduction in energy should correspond to a decreased open circuit voltage, but the improved compatibility with the solar spectrum should also increase the short circuit current.

![Figure 3.1: UV Spectra for PDIB Silane and all Species of Nanoparticles](image)

The appearance of all the nanoparticles synthesized was observed with a transmission electron microscope where the shadow of the nanoparticles in a well-focused beam of electrons is used to create an image. For adjusting the base concentration of the reactions to control the particle size, TEM data was crucial.
Although many of the particles shown feature a layered appearance, it should be noted that many of these effects are artifacts of sample preparation and should not be taken as empirical evidence of particle layering. To confirm the layering of the BPIB and silica nucleated particles, the UV spectra in Figure 4.1 were used to confirm the presence of PDIB silane. TEM samples were prepared before the addition of PDIB silane to confirm the morphology of the nucleating nanoparticles.

Images from Transmission Electron Microscopy

![Image of Transmission Electron Microscopy](image)

**Figure 3.2: Nucleation of PDIB Nanoparticles on Crystalline Impurities**

The nucleation of the PDIB nanoparticles proved to be a very sensitive process. In Figure 3.2 there are particles nucleated from solution (peripheral) but also many much
larger particles nucleated from crystals (center) presumed to be oxidized PDIB silane. Filtering all reactants through the 0.45 μm filter and limiting their exposure to oxygen and moisture helped remove these impurities from the reaction. These impurities collected with the product nanoparticles and they were avoided for our synthesis purposes.

With impurities removed from the solution other byproducts not of interest to our experiment still form. Sheets of unreacted PDIB silane remain in solution and appear to aggregate the smaller particles onto them as shown in Figure 3.3. These sheets can become tangled aggregates with stirring and will typically oxidize when drying. Dispersing the PDIB nanoparticles in tetrahydrofuran and centrifuging them again was necessary for the removal of these PDIB sheet byproducts.

Figure 3.3: PDIB Nanoparticles with unreacted PDIB Silane
With the removal of impurities and byproducts PDIB nanoparticles can be isolated as shown in Figure 3.4. As predicted by the length of the bridging group we observe the nanoparticles to have a porous appearance. This porosity of the silsesquioxane network also makes them fragile to drying and more likely to collapse when stressed than silica networks. The length of the bridging unit may also play a role in wide range of particle sizes. Although a change in reaction conditions, an additive compound, or a surfactant may be able to create particles of a tighter size range, we explored the use of nucleation agents to seed PDIB nanoparticles of more finely-controlled morphology.
As the original compound described by the Stöber method, TEOS readily forms homogenous silica nanoparticles in solution. Whereas silsesquioxane compounds can form crystalline or semicrystalline nanoparticles by a modified sol-gel synthesis, silica nanoparticles will always have an amorphous composition. Silica nanoparticles pictured in Figure 3.5 were originally selected as nucleation seeds for PDIB nanoparticles because of their regularity and control over size ranges, but ultimately their amorphous surface proved too great a challenge in our project. While PDIB did adhere to these particles, we now desire a more crystalline nanoparticle to enhance PDI charge carrier properties.

Figure 3.5: Silica nanoparticles made from TEOS
In Figure 3.6 PDIB sheets can be seen alongside silica nanoparticles covered with an irregular layer of PDIB silane and some much smaller PDIB silane nanoparticles. With centrifugation in tetrahydrofuran, the PDIB sheets and smaller PDIB silane nanoparticles are removed. The content of PDIB silane in the reaction was increased to attempt more thorough coverage on the particles but led to significant aggregation of the resulting particles.

Complete layers of PDIB onto the silica nanoparticles were attained and are isolated from impurities and byproducts in Figure 3.7. These layers reached any significant thickness however as using too much PDIB silane or initiating subsequent reactions onto the same particles only caused aggregation. Although the thinness of the
layer and amorphous qualities of the base silica nanoparticles are likely detrimental to device performance, these nanoparticles were synthesized with a very selective size range and a consistent (although thin) coating of PDIB silane.

Figure 3.7: Silica Nanoparticles with complete layer of PDIB silane

BPIB silane nucleates particles much more readily than PDIB silane and the particles are of a slightly more controlled size range in Figure 3.8. Byproducts of this reaction were not as difficult to remove as the sheets of PDIB silane, and centrifugation in water removed all unreacted BPIB material. The surface charges on the particles led to more particle aggregation being observed.
Despite the aggregative tendencies of BPIB nanoparticles, they appear to be more receptive to PDIB coatings than silica nanoparticles, likely due to a better agreement in crystal structures. Similar to the silica particles, these particles do not show a considerable change in size when coated with PDIB silane. The change in the appearance in their surface as shown in Figure 3.9 and the presence of PDI, although broadened, in the UV spectrum of the particles however confirm the presence of PDIB silane in the resulting particles.
Devices were fabricated with the silica-nucleated PDIB nanoparticles for analysis of their photovoltaic performance. Figure 3.10 shows IV curves from multiple devices containing different quantities of silica-nucleated PDIB Nanoparticles being mixed with 10 mg of P3HT in 2 mL of chlorobenzene for device spray coating as described by the experimental procedure. Typically, polymer:polymer bulk heterojunction OPV's are prepared by spin-coating where an excess of material in solution is deposited at the center of the surface and spun at high speeds to form a film by the centripetal forces. Although for polymer:polymer blends this method forms well-blended films by removing any material that does not adhere to the surface in a thin film, we postulate that this method could remove materials with a bias for polymer: nanostructure blends. Spray-coated
devices as featured in Figure 3.10 deposit the material for devices over an excess area without any removal of material from the device surface.

![IV Curves of Devices with varying concentrations of 100nm Silica-Nucleated PDIB Nanoparticles Prepared by Spray-Coating](image)

**Figure 3.10: IV Curves of Devices with varying concentrations of 100nm Silica-Nucleated PDIB Nanoparticles Prepared by Spray-Coating**

While the effect that spin-coating and spray-coating have on formation of polymer:nanostructure films is in need of further study, the preliminary effects on performance are clear. Figure 3.11 features IV curves from a device fabricated by spin-coating before and after annealing and in the absence of light. The annealed and illuminated spin-coated device attained a lesser open circuit voltage of 0.6 V and short circuit current density of 7 mA/cm$^2$. The devices prepared by spray-coating however demonstrate markedly higher efficiencies of up to 3.13% from their greater open circuit voltages and short circuit currents.
Figure 3.11: IV Curve of Device with 100nm Silica-Nucleated PDIB Nanoparticles Prepared by Spin-Coating
CHAPTER 4

CONCLUSION

Organic photovoltaic cells were made from PDIB silane nanoparticles nucleated with silica which demonstrated power conversion efficiencies of up to 3.13% with a spray-coating technique, outperforming spin-coating with the same materials. Two similar species of PDIB nanoparticles were also prepared and characterized by TEM, but photovoltaic data of these materials in devices has not yet been collected.

Bulk heterojunction OPV’s using PDI derivatives in conjunction with an electron-accepting polymer have shown poor power conversion efficiencies of less than 1 percent.\cite{28,29,30} The success of our P3HT-PDI nanoparticle system demonstrates the potential of silsesquioxane networks in photovoltaics applicable to numerous other OPV systems. Ideally, this methodology should be implemented with compounds eligible for a similar synthesis pathway and exhibiting good photovoltaic properties in bulk heterojunction only limited by unfavorable phase segregation in the active layer.

This methodology is adaptable to control the size range of the nanoparticles with the base concentration to better fit the dimensions of the active layer. Even though this sol-gel process is limited to particles below the micron size range\cite{22} that is still more than sufficient for organic photovoltaics which have thickness limited to nanometers by the exciton diffusion length.\cite{6}
This project can best be advanced by studying the photovoltaic performance of the pure PDIB nanoparticles and the PDIB nanoparticles nucleated with BPIB nanoparticles. Conductive nucleating agents may add for another way of aiding charge carrier mobility and should be explored with further research. Our results indicate that the morphology of the active layer can be controlled by incorporation of the electron acceptor in nanostructures for enhanced photovoltaic performance. Numerous factors in the synthesis of the nanoparticles and device fabrication still need to be explored to find the optimal methodology and full potential of this process.
References


