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Improving Organic Solar Cell Sustainability: Using Hansen Solubility Parameters to Enhance PTQ-10 Solubility in Green Solvents

Adam Wold

Department of Chemistry and Biochemistry
The University of North Carolina Asheville
One University Heights
Asheville, North Carolina 28804 USA

Faculty Mentor: Dr. Jeromy Rech

Abstract

Organic solar cells (OSC) are an emerging technology under the umbrella of renewable solar energy. While various research groups have demonstrated organic solar cells with champion efficiency over 20%, the materials used must be processed in problematic (e.g. expensive, toxic) solvents, often halogenated and aromatic like chlorobenzenes. The purpose of this work is to develop green solvent processable polymers to avoid problematic solvents by either (i) finding a new green solvent that can process already existing high-performance polymers, such as PTQ-10, a donor often used in OSC, or (ii) synthesizing new side chains for increased green processability. To do this we are using Hansen Solubility Parameters (HSPs) to model solubility of solvents and solutes on a three-dimensional graph. HSP values intermolecular forces mathematically and allows you to plot the strength of intermolecular forces. With these plots, this work will compare HSP values from PTQ-10 and green solvents to find new solvents to pair with PTQ-10. Previous works have utilized oligo(ethylene glycol) (OEG) side chains to modify PTQ-10's solubility, but it caused a decrease in efficiency of the solar cell. Building off this work, we decided to work on adding side chains with a long alkyl segment capped with either an ionic or polar head to increase the polarity of the HSP values. With PTQ-10's HSP values we created a list of potential solvents that are safer than the halogenated and/or aromatic solvents currently used. The first project resulted in three new green solvents that computational methods indicate should dissolve PTQ-10. The second project found that the addition of the new side chain does not work in regular S_n2 reaction conditions.

Introduction

People have become more aware of where their energy comes from, and how it affects the world they live in.[1] This attention is primarily aimed at the use of fossil fuels and how to cease their use. Fossil fuels, like coal and gas, are fuels formed hundreds of millions of years ago from the remains of living organisms. Currently, fossil fuels provide approximately 83% of the energy the world uses.[2] However, the hefty use of fossil fuels is unsustainable because these fuels are non-renewable. If we continue with the current rate of consumption, some estimates predict the exhaustion of fossil fuels by 2060.[3] Beyond the pressure of fossil fuels being a limited resource, there is also the environmental impact of burning these fuels. Fossil fuel consumption is one of the major driving forces behind climate change.[4]

As awareness of these problems become more widespread, people around the world have begun looking into energy alternatives for the future. Some of these renewable alternatives include hydropower, wind, and the most promising, solar. Solar is a promising option because it is available anywhere in the world and does not require extensive maintenance.[5] Most solar panels today are monocrystalline silicon solar panels, which can achieve up to a 25.6% efficiency.[6] These cells work through two different layers, one is a p-type (or acceptor) and the other is a n-type (or donor) as seen in **Figure 1**. When light hits the n-type layer, the electrons are dislodged and return along a loop as current to the receiver. [7]

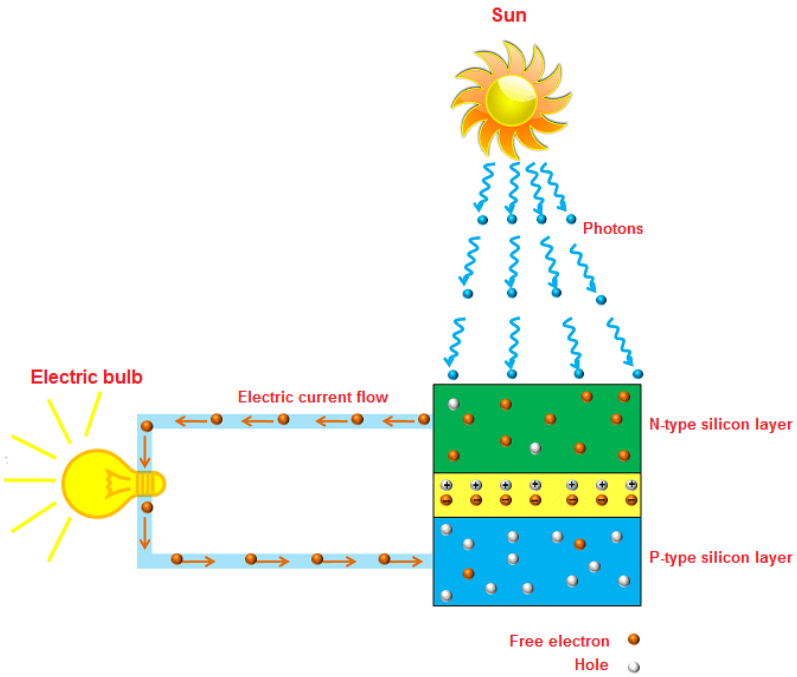


Figure 1. A visual representation of how silicon solar panels work.[8] These cells work through two different layers, one is a p-type, or acceptor, and the other is a n-type, or donor. When light hits the n-type layer, the electrons are dislodged and return along a loop as current to the receiver.

Recently there has been more interest in other types of solar cells including perovskites and polymer-based photovoltaics, or organic solar cells (OSC's). The interest in OSCs has risen because of their increase in efficiency.[9] OSCs work through conjugated polymers that are synthesized to generate excitons. Conjugated polymers are polymers that contain repeating π-bonds throughout the structure. With a combination of a donor polymer with an acceptor material (polymer or small molecule), excitons can be moved along the cell to form electricity. This mechanism is unique to OSCs and not used in the traditional solar cells, as monocrystalline silicon cells generate electrons/holes directly. These conjugated polymers have been researched for decades, since their low cost, flexibility, semi-transparency, and light weight makes them highly sought after.[10] These properties make them ideal for unique applications like portable solar chargers and greenhouse installations since the cells use a different part of the light spectrum than plants.[11] While this technology is relevant in academia, this technology has struggled to translate to commercial applications for a few major reasons. First, the larger molecules that have higher efficiencies also have an extremely high synthetic complexity, with several reactions that have a low yield. D18-Cl, the compound seen in **Figure 2B**, is one of the highest performing conjugated polymers with an efficiency of 18%. However, the synthetic route to make this compound is 28 steps long, with multiple steps taking over 20 hours.[9] The second reason is that the materials are not stable because they degrade when exposed to environmental conditions. The third reason is that these materials also require hazardous solvents like chloroform or dichlorobenzene to dissolve them, and these are not ideal for an industrial setting. With organic solar cells drastically increasing in efficiency over the last decade, the issues of synthetic complexity and hazardous solvents need to be addressed soon to allow commercial use. [12]

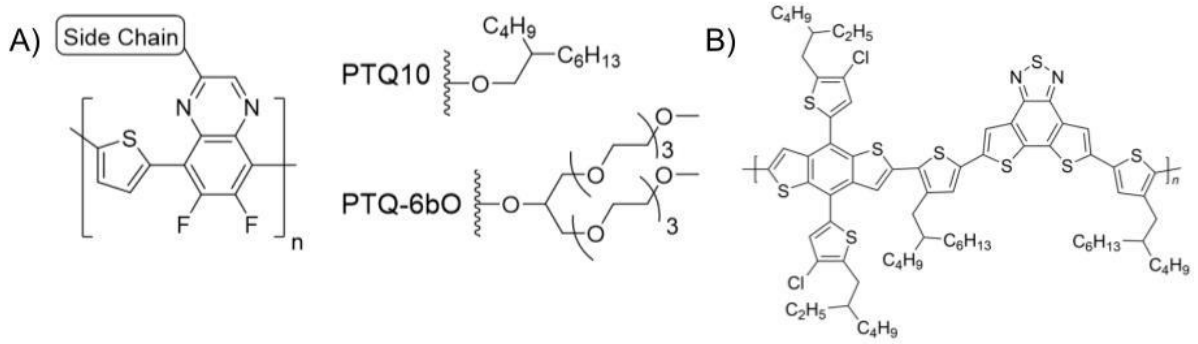


Figure 2. A) This is an image of PTQ-10, along with a derivative that has a new side chain to increase solubility. B) This is the structure of a D18-Cl monomer.

To address these issues, this work aims to create derivatives of PTQ-10 that are soluble in green solvents. PTQ-10, as shown in **Figure 2A**, is a synthetically easy-to-make solar cell donor, and its efficiency can beat 15%.[13] This makes it ideal since it is not a synthetically complex molecule, and it has an easy side chain to adjust to affect solubility. This side chain is easy to adjust because the reaction to add the side chain only requires an alcohol functional group, meaning any modifications that do not affect the alcohol will not affect the addition of the side chain. The synthetic route of PTQ-10 can be seen in **Figure 3**. There are only 5 steps and most of them have over an 80% yield which is significantly more efficient than the 28 step pathway to make D18-Cl.

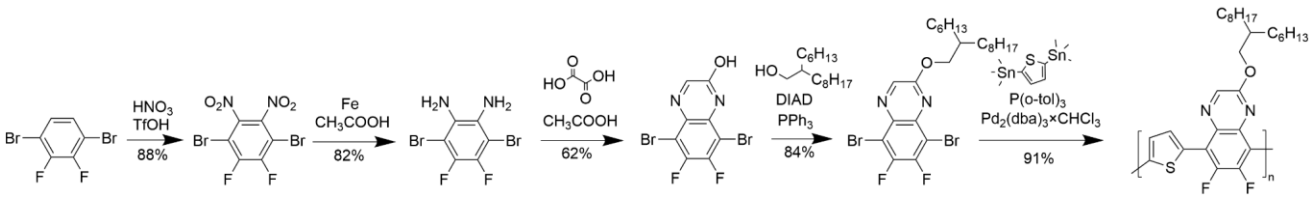


Figure 3. A common synthetic route to create PTQ-10.[13]

Green solvents are solvents that are environmentally friendly and safe. GlaxoSmithKline (GSK) rates solvents on a scale of one to ten for “greenness” based on factors like flammability, toxicity, environmental hazards, and ease of disposal.[14] Some examples of greener solvents include water, isopropanol, and ethanol.

To test PTQ-10 and derivatives solubility, previous studies have used Hansen Solubility Parameters.[12] HSP are a mathematical way to value the strength of intermolecular forces in molecules, and with this mathematical representation the solubility of a polymer in a given solvent can be determined. The HSP uses the premise of “like dissolves in like”, so the closer values are between a solvent and a solute, the more likely they are to be soluble.[15] To find these values experimentally, an amount of the compound is mixed in a solvent at a set temperature. This experimental procedure is commonly done with 10 mg of solute per 1 mL of solvent at room temperature. After this procedure you can blend two different solvents with different solubility parameters. As the ratio of solvents changes you can analyze which solvents the compound is most soluble in. This provides a spread of HSP values to test which is difficult to see with only individual solvents. After completing this process multiple times with different solvents you can find the exact mathematical values of your compound. HSP can be used computationally before experimentation to gain a general understanding of the HSP for a synthetic target. HSP can also be used after synthesis to selectively test green solvents that HSP indicates would work.

One goal of this study is to use HSP to guide two different processes. (i) The first process is to use the HSP values to find greener solvents for compounds that already exist. (ii) The second process is to design new materials, and then use HSP values to measure the change in solubility. In previous work, side chain adjustments to PTQ-10 were made to enhance solubility. The side chain used was an oligo(ethylene glycol) or OEG side chain seen in figure 2.[12] However these derivatives all showed decreased efficiency as the highest efficiency was 3.8%. They found that this decrease in efficiency was due to the increase of electronegative atoms, or oxygens, changing the electronic properties of the conjugated polymers. This study attempts to use side chains with ionic or polar groups at the end of the chain as seen in **Figure 4**. By using one electronegative atom, like nitrogen, this work hopes to find an increase in solubility like previous work, but without the decrease in efficiency due to the number of electronegative groups.

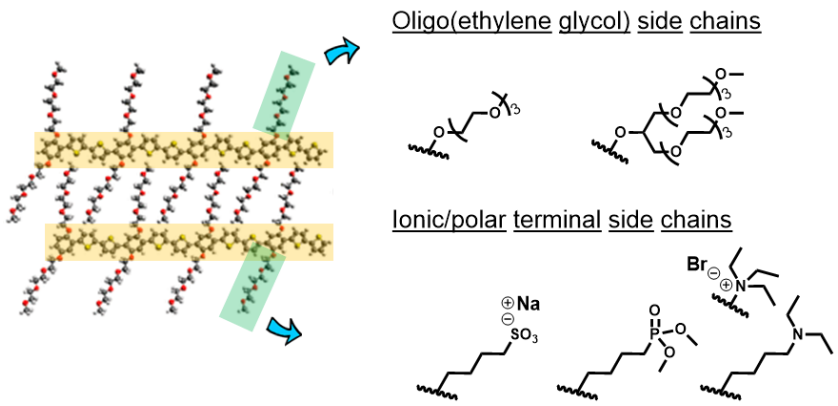


Figure 4. OEG side chains and the new proposed ionic/polar side chains.

Experimental

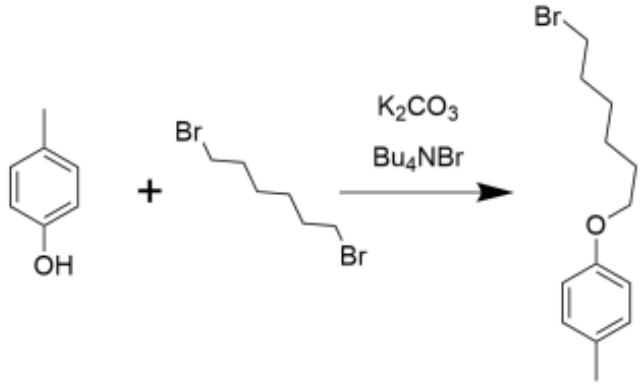
In this project there were two goals. The first was finding new green solvents for PTQ-10, in which a database was created containing HSP and greenness ratings for various solvents. The second goal was synthesizing a new material with increased solubility in green solvents, which relied on synthetic chemistry in laboratory experiments. The procedures for developing the database and laboratory experiments are listed below.

All chemicals were purchased from commercial sources (Sigma-Aldrich, Fisher, Acros, etc.) and were used as received except when specified. For reactions under argon, the reaction flask was evacuated via vacuum and refilled with argon three times.

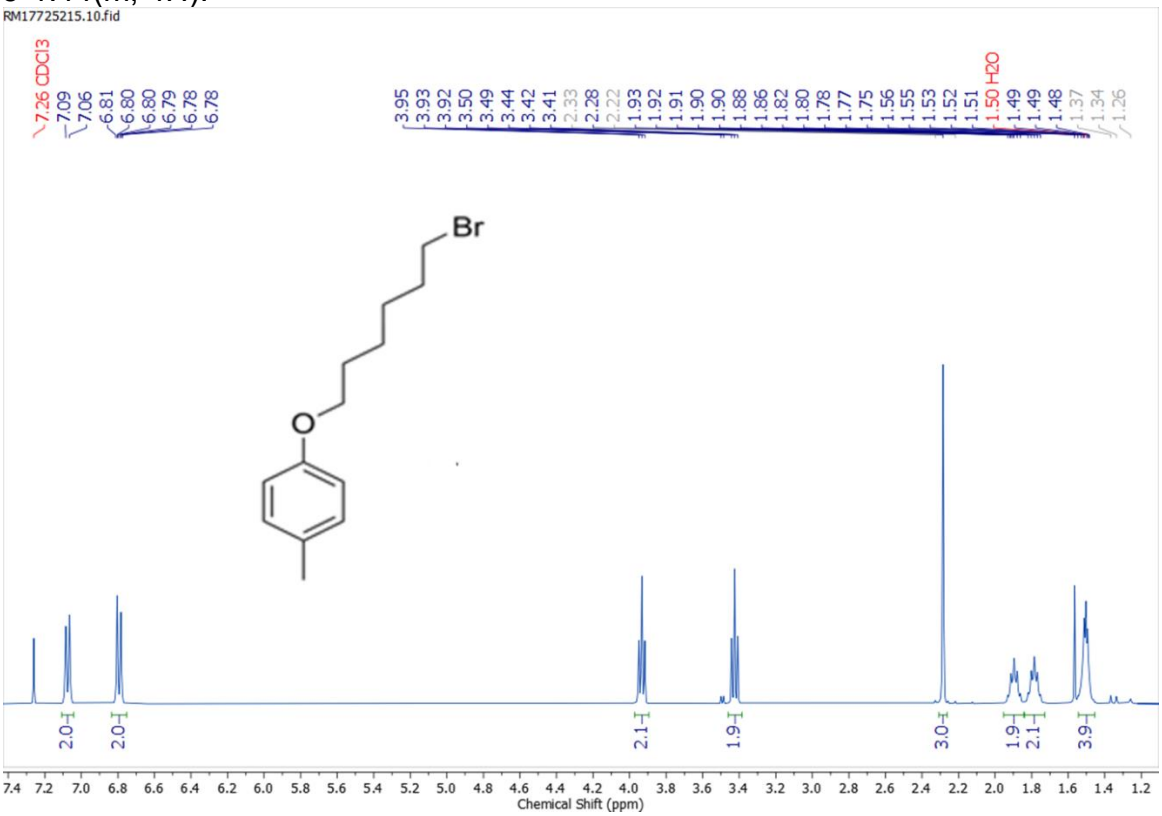
Solvent Database Development

A database was developed to document and compare screened solvent HSP values against PTQ-10's HSP values. The greenness ratings of various solvents were collected from a paper written by GlaxoSmithKline.[16] Greenness ratings were calculated based on scores across four categorized domains: waste, environment, health, and safety. The waste aspect takes into account recyclability, incineration, biotreatment, and VOC emissions. The environmental aspect considers air and aquatic impacts. The health aspect factors in exposure potential and health hazards. Finally, the safety aspect utilizes reactivity, stability, flammability, and explosivity. These categories were organized into a standardized system that rated each factor on a scale from 1 to 10. HSP values for these solvents were collected from a public access database.

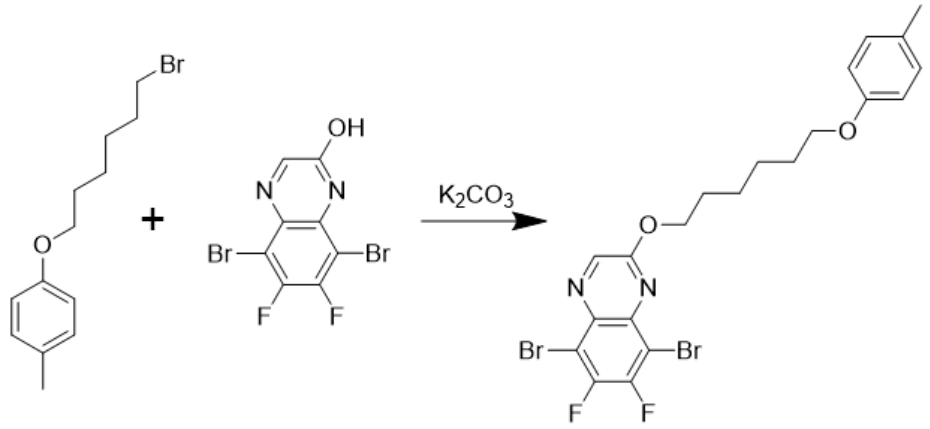
Synthesis of 1-((6-bromohexyl)oxy)-4-methylbenzene



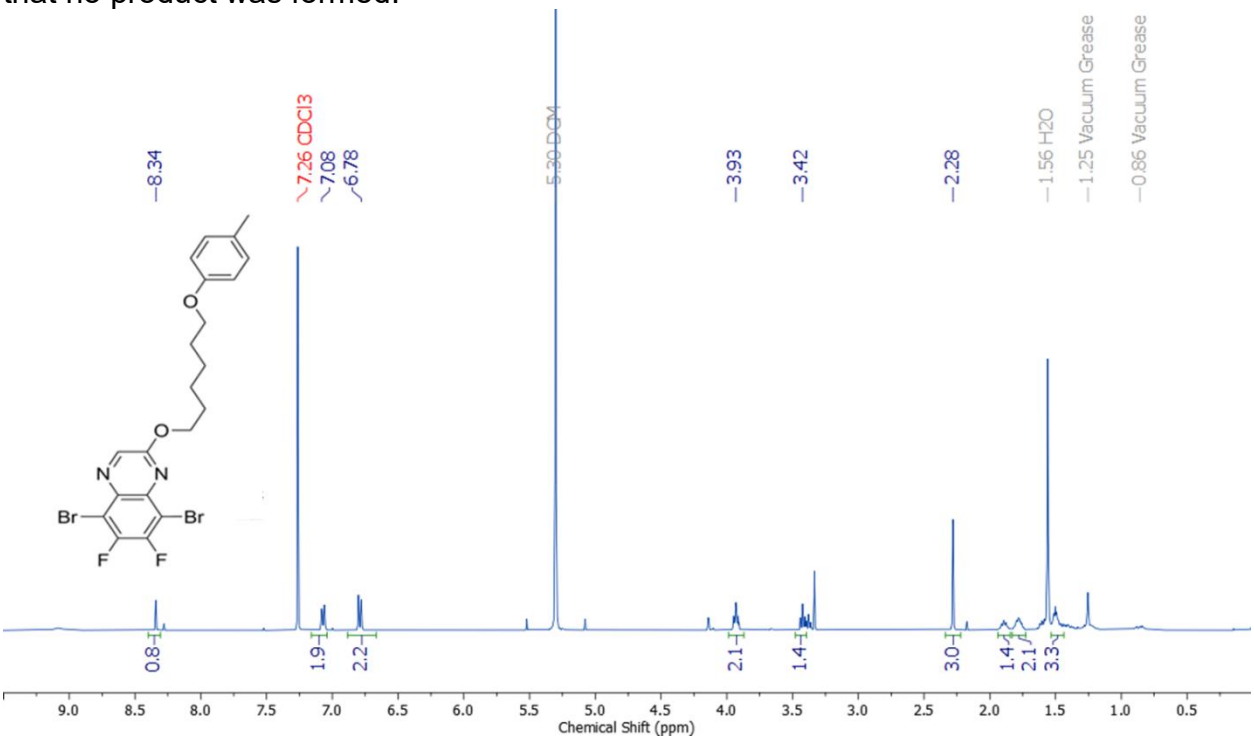
The synthesis of 1-((6-bromohexyl)oxy)-4-methylbenzene began with (0.779g, 7.20 mmol, 1 eq) of *p*-cresol, (2.26g, 16.2 mmol, 2.25 eq) of potassium carbonate, (0.142g, 0.440 mmol, 0.061 eq) of tetrabutylammonium bromide, and a stir bar were added to a three necked round bottom flask. The RBF was attached to a condensing column and put under argon. Once under argon (2.8 mL, 18.2 mmol, 2.5 eq) of 1,6-dibromohexane and 70 mL of acetone were syringed into the RBF. The reaction was then heated to 60°C for 48 hours. Once the reaction cooled down it was vacuum filtered and the liquid was rotovaped down. Once rotovaped down the yellow oil was separated from the clear liquid and vacuum distilled. The vacuum distillation was run at 80°C and a yellow liquid was collected. Yield 1.34g, 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (p.p.m.) 7.07 (d, 2H), 6.79 (d, 2H), 3.92 (t, 2H), 3.42 (t, 2H), 2.28 (s, 3H-1.83 (m, 2H), 1.83-1.73 (m, 2H), 1.55-1.44(m, 4H).



Synthesis of 5,8-dibromo-6,7-difluoro-2-((6-(p-tolyloxy)hexyl)oxy) quinoxaline



The synthesis of 5,8-dibromo-6,7-difluoro-2-((6-(p-tolyloxy)hexyl)oxy) quinoxaline began with (0.498g, 1.47 mmol, 1.0 eq) of 5,8-dibromo-6,7-difluoroquinoxalin-2-ol, (448mg, 1.68 mmol, 1.1 eq) of 1-[(6-Bromohexyl)oxy]-4-methylbenzene, and (198mg, 1.76 mmol, 1.2 eq) of potassium t-butoxide were added to a 2 necked 100 mL RBF and dissolved in 30 mL of methanol. The reaction was put at reflux for 12 hours and then cooled to room temperature. After cooling the reaction was mixed with saturated ammonium chloride, and then the product was extracted with dichloromethane. The extraction was washed with water and then dried with magnesium sulfate. After gravity filtration the liquid was rotovaped down to a yellow solid. A column was then run to purify the product in a solvent mixture of 5:1 Hexanes to Ethyl Acetate. After column chromatography, the fractions collected were analyzed with NMR and it was determined that no product was formed.



Results and Discussion

Solvent Database

To find a green solvent for PTQ-10, over 150 solvents were added to a database with their greenness ratings and HSP values. An image of this database is shown in **Figure 5**. The first four columns of numbers represent the greenness rating of 4 aspects collected by GlaxoSmithKline. These values are on a scale from 1 to 10, with 10 being the greenest a solvent can be. These 4 values were averaged together to then find the "total" column, for the total greenness of a solvent. To the right of these greenness columns are the three values for HSP. δD represents dispersion forces, δP represents polarity, and δH represents hydrogen-bonding. These three values would need to fall between the three ranges of PTQ-10 to be considered computationally soluble.

Solvent	Waste	Enviro	H Health	Safety	Total	δD	δP	δH
Glycerol	6	9	7	10	7.8	17.4	11.3	27.2
Lactic Acid	6	7.5	6.5	9	7.2	17	8.3	28.4
Propionic Acid	5.5	6.5	7	7.5	6.6	14.7	5.3	12.4
Glycerol triacetate	6.75	9.5	10	9.5	8.8	16.5	4.5	9.1
Formic Acid	5.75	8	4	7	6.0	14.6	10	14
Acetic Acid (glacial)	4.75	6	6	7	5.9	14.5	8	13.5
1,3-Propanediol	6	8	9.5	10	8.2	16.8	13.5	23.2
1-Pentanol	8	6.5	9.5	9.5	8.3	15.9	5.9	13.9
2-Ethyl hexanol	8.75	6	8.5	9	8.0	15.9	3.3	11.8

Figure 5. An image of the solvent database. It shows the GSK greenness values for waste, environment, health, safety, and average greenness. These values are also followed with the HSP values for dispersion, hydrogen bonding, and polarity.

From this computation, three new solvents were found to have HSP values that indicate solubility for PTQ-10 without modifications. These three solvents were glycerol triacetate, isobutyl acetate, and diethyl succinate.

As solvents are tested against PTQ-10 based on what computationally should work, an analysis of the accuracy with this computational method should be carried out. To verify the accuracy of this model, future work should involve testing the solubility of the compounds considered soluble, like glycerol acetate, isobutyl acetate, and diethyl succinate, and documenting how often the model is correct. Additional measurements documenting the amount of solvent needed per 10 mg of polymer would allow for a more thorough analysis of model accuracy, as higher amounts of solvent would imply worse solubility.

Synthesis of PTQ-10 Derivative

The complete synthesis of the PTQ-10 derivative is seen in **Figure 6**. In the synthesis of **8**, the procedure from literature was accurate and there was only a minor decrease in yield from 75% to 70%.[17] The synthesis of **9** did not yield the intended product determined by column chromatography.[18] Varying reaction conditions were changed, such as trying different bases like potassium carbonate and tert-butoxide, or methanol

and acetone as the solvent. Despite these varying conditions, the addition of the side chain to the quinoxaline core still did not work. After these tests didn't work we ran a TLC of **8** and found that there was a diprotected side chain that matched our peaks for the monoprotected side chain in proton NMR. With this impurity that was not removed with vacuum distillation, a solvent mixture was determined for column chromatography of **8**.

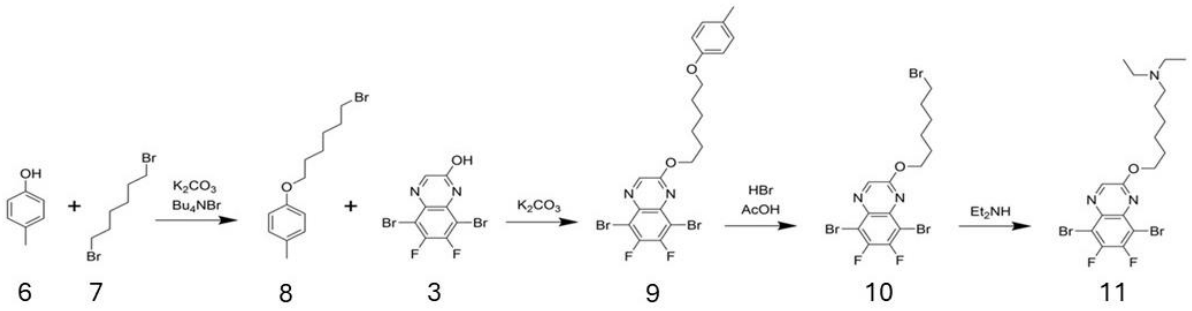


Figure 6. Synthetic scheme of the PTQ-10 derivative with the new alkyl chain with a polar group at the end.

The addition of the polar side chain is a synthetically difficult step to complete. This difficulty could be due to less acidity in the alcohol than expected, or a more thermodynamically unfavorable reaction than expected. With this synthetic route incomplete, the data and solubility of the new polymer was impossible to collect. The clearest step for future research is finding the problem with the synthesis of **9** to complete the rest of the synthesis. Two options for continuing synthesis include using the Mitsunobu found in previous literature or attempting a stronger base. Once this is complete, the new polymer should undergo solubility testing, and the solubility values should be compared against PTQ-10.

Conclusion

As the world moves towards a more sustainable future, it is important that the renewable energy sources that replace fossil fuels are green in every aspect. To initiate that process, this work brings attention to the problematic solvents used in the process of manufacturing organic solar cells. In order to enhance the sustainability of organic solar cells, we use Hansen solubility parameters to visualize and calculate solubility of the polymers used in organic solar cells.

We highlight two approaches to using HSP. (i) Use HSP to find new solvents on preexisting polymers to use greener solvents, and (ii) synthesize a novel polymer with a unique side chain to shift solubility towards greener solvents. For the former technique, an informational database containing greenness ratings and HSP values for over 150 solvents was created. These solvents were then compared to PTQ-10 based on their HSP values. Then, the solvents that showed solubility were filtered based on greenness scores from GlaxoSmithKline. For the latter technique, it was found that the addition of the novel side chain was unable to react with the quinoxaline core under preexisting

conditions. With varying compounds used to push the reaction forward and none working, it may require a new reaction to add these new side chains.

The next step for the first technique is testing solubility with the solvents recommended by the model with PTQ-10. With this experimental testing of solvents, the model should also be tested for its accuracy to determine if this computational method works. The next step for the second technique is to find reaction conditions that allow the novel side chain to react with the quinoxaline core.

Supplemental Information

Solvent Database: https://docs.google.com/spreadsheets/d/1BqM_VRZY1-zHy8eYb6_cqB_SpwuNo2sN/edit?usp=sharing&ouid=102743643841574691700&rtpof=true&sd=true

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