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The Effect of Chemical Structure on the Photodegradation of Conjugated Polymers

1. Problem Identification

Conjugated polymers (CPs) are a significant group of semiconducting materials that possess remarkable optical and electrical characteristics similar to metals and inorganic counterparts. CPs have garnered significant attention from both the industrial and academic sectors because of their convenient processing and straightforward, cost-efficient, and versatile synthesis techniques. In recent years, significant advancements have been achieved in the field of CPs in areas such as biosensors, organic light-emitting diodes (OLEDs), transistors, photovoltaics (PVCs), solar cells, and batteries. However, further research efforts are still required to achieve a significant breakthrough in the commercialization of these technologies.

Conjugated polymer stability in various application fields, one of the most important market entry criteria, remains a significant concern and has received comparatively less attention in the literature. Although certain efforts have been made to mitigate the stability concern, including the implementation of air-stabilized electrode materials, inverted organic solar cell structures, and improved encapsulation techniques, the overall lifetime of CPs is still limited by the stability of the active parts. The process of oxidative degradation of the polymer's lifespan has been a subject of interest due to its significant impact on the CP's durability. Molecular oxygen (O₂), which makes up 21% of the Earth's atmosphere, is one of the main oxidizing agents.

The objective of this PoC is to gain a deeper understanding of the degradation of polymers with singlet oxygen, which involves modulating the π -bridge unit of the main polymer backbone with thiophene (T), selenophene (Se), and thiazole (Tz) to clearly understand how these bridge units affect the photochemical stability of polymers under ambient conditions besides their optical and electrochemical properties. Donor- π -acceptor (D- π -A) conjugated polymers, which consist of an electron-donating unit (D), an electron-accepting unit (A), and π -bridges which is the main focus of this study. These polymers have the advantage of having adjustable frontier energy levels, absorption spectra and charge mobilities. The fundamental optoelectronic characteristics of D- π -A polymers are mostly determined by the D and A components. However, the π -bridge species also have a significant impact on relieving the



steric tension of the polymer backbone, altering the molecular conformation, and influencing other behaviors. Thiophene is frequently employed as a π -bridge due to its ability to minimize distortion with adjacent groups, its moderate electronegativity, and its capacity for intermolecular S \cdots S non-covalent weak interactions.

Experimental group design and synthesize three donor-acceptor (D-A) types of conjugated polymers. All polymers contain a benzoxadiazole (BOz) -based acceptor group and a benzo[1,2-b:4,5-b']dithiophene (BDT)-based donor group with varying π -bridge groups. Thiophene, selenophene, and thiazole were incorporated into the polymer's main chains as π -bridge groups to investigate the effects of structural alterations on electrochemical and optoelectronic properties, and more importantly, examine the impact of these units on the photochemical stability of polymers.

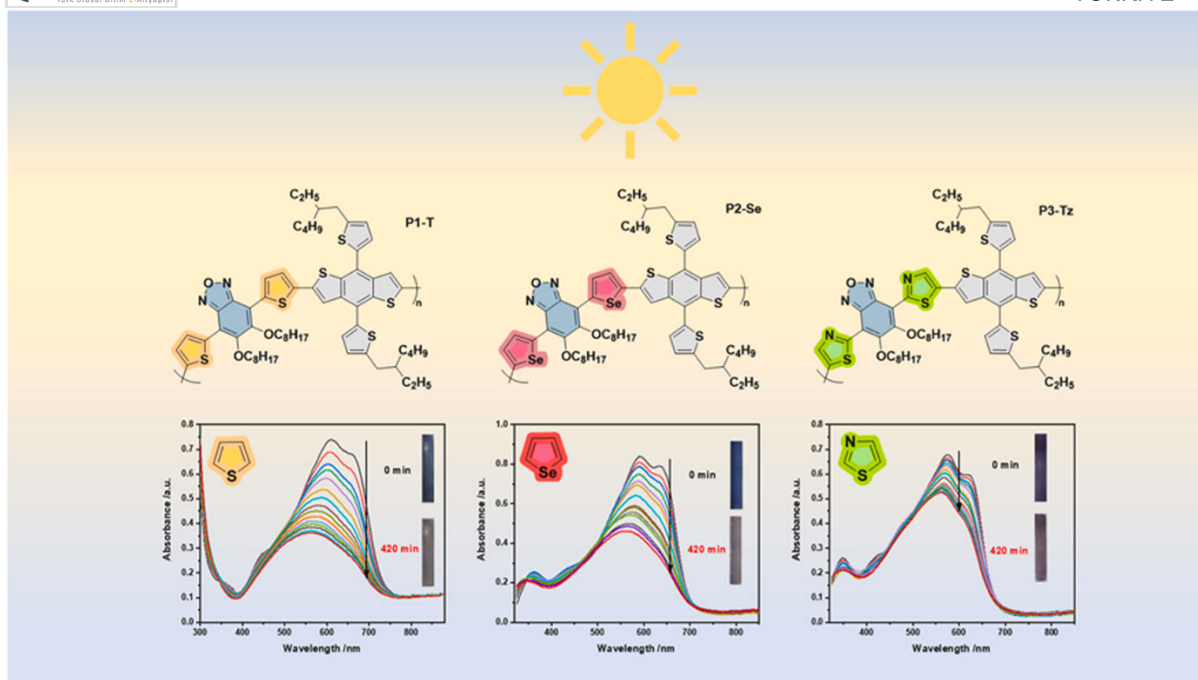
To find out how photooxidation works, this study utilized a variety of spectroscopic and computational methods, including Ultraviolet- visible (UV-vis), X-ray photoelectron spectroscopy (XPS), Fourier transmission infrared spectroscopy (FTIR) and Density Functional Theory (DFT).

Photochemical degradation studies were conducted both experimentally and theoretically with TD-DFT calculations at HPC resources to gain a more comprehensive understanding of how the bridge units thiophene, selenophene, and triazole on the main polymer backbone influence the photochemical stability of polymers under ambient conditions.

Comprehending the photochemical stability of these polymers is crucial for progressing their commercial uses, such as organic photovoltaics, OLEDs, and sensors. This study highlights the significance of choosing suitable π -bridges to improve the longevity and effectiveness of CPs, thus satisfying market requirements and broadening their possible applications. By this academic PoC, both experimental and theoretical group developed innovative ideas for the photodegradation of conducting copolymers. Experimental group learned how to perform useful representative theoretical experiments using HPC resources and our group acquired experience on the modeling of the photodegradation of polymers.

2. First Suggestion

This study aimed to examine the impact of photodegradation-induced structural alterations on the theoretical, electrochemical and optoelectronic characteristics of polymers, as well as their photochemical stability, using thiophene (T), selenophene (Se), and thiazole (Tz) as π -bridges. The polymers names as P1-T, P2-Se and P3-Tz. Theoretical calculations were performed by NCC expert.



Structures and UV-Vis spectras of three D- π -A polymers synthesized with thiophene, selenophene, and thiazole bridges. Different π -bridges significantly influence intrinsic properties and stability. Polymer with selenophene had the greatest red-shift in absorption onset and lowest band gap value. (<https://doi.org/10.1016/j.polymer.2024.127736>)

3. Solution Stage – I

To explain experimental degradation, DFT methods were employed to optimize different initial conformations to obtain the lowest energy structures. This was achieved by controlling the torsional angle between the bridge, donor and acceptor units in the initial structures. The objective was to identify the lowest energy geometry in the most stable conformation. The calculations for the monomers and trimers were performed by using the hybrid B3LYP functional and 6-311g(d) basis set with tight SCF convergence conditions in the Gaussian09 (Revision A.02) software package. To enhance computational efficiency, the long alkyl side chains are replaced with ethyl groups in the model structures, resulting in minimal impact on the optoelectronic characteristics. The optimized geometries for these model compounds were used to calculate the HOMO, LUMO, and the electrostatic potential surface (ESP). The band gap, E_g , values were determined using two distinct approaches. The first method involved calculating the energy difference between the HOMO and the LUMO levels for optimized ground state structures. The second method utilized the vertical excitation energy of the lowest singlet excited state (S_0 - S_1) through a time-dependent density functional theory (TD-DFT) approximation. The percentage of HOMO, LUMO, and reactivity indices on different units were analyzed by using Multiwfn. The energy difference between the neutral molecule and its anion in the ground state geometry was used to determine the vertical electron affinities (VEA). This was followed by the similar calculation for the neutral molecule and optimized anion geometry to calculate adiabatic electron affinities (AEA). The vertical

ionization potential (VIP) and adiabatic ionization potential (AIP) were also computed using the identical approximation. The internal electron and hole reorganization energies (λ_{reorg}) were determined. Bond dissociation energy for the alkoxy groups on BDT were compared. Trimers were subjected to calculations to determine their dipole moment (μ), isotropic polarizability (α), and hyperpolarizability (β). TRUBA and UHEM resources were used in all calculations.

4. Results and Achievements

The results of our research emphasize the crucial importance of the π -bridge in influencing the photochemical stability of conjugated polymers (CPs). The photochemical stability of the polymers differs depending on the π -bridges, despite the fact that they all contain the same electron withdrawing group (BOz) and electron donating group (BDT). The conjugated polymer films containing T and Se (**P1-T**, **P2-Se**) experienced a substantial reduction in the intensity of their peak absorption when exposed to light and air for up to 7 hours. In contrast, the peak intensity and characteristics of the thiazole counterpart (**P3-Tz**) only exhibited a minor change under the same conditions. The enhanced photostability of the **P3-Tz** polymer film can be ascribed to its notably deeper HOMO level and wider band gap when compared to P1-T and P2-Se. Theoretical calculations indicated the localization of HOMO on the donor groups in P3-Tz that resulted in the decreased reactivity of the bridge and acceptor groups towards electrophilic attack.

Studied electrical and optoelectronic characteristics of tetramer model compounds.

	HOMO	LUMO	$E_{\text{g}}^{\text{direct}}$	$E_{\text{g}}^{\text{optical}}$	VEA	AEA	VIP	AIP	$\lambda_{\text{reorg}}^{(b)}$	$\lambda_{\text{reorg}}^{(c)}$	Dipole Moment (μ)	Polarizability (α),	Hyperpolarizability (β) (a.u.)
P1-T	-5.07	-2.98	2.09	1.77	-2.414	-2.471	5.612	5.552	0.121	0.111	0.940	2891	16379
P2-Se	-5.07	-2.99	2.08	1.70	-2.474	-2.527	5.575	5.512	0.127	0.105	1.471	2397	24017
P3-Tz	-5.34	-3.17	2.16	1.85	-2.601	-2.688	5.871	5.809	0.120	0.087	0.685	2716	31544

The findings have significant implications for the marketing and implementation of CPs. Improved resistance to photodegradation increases the durability and dependability of CPs, rendering them more appealing for incorporation into organic solar cells, OLEDs, transistors, and other optoelectronic devices. The exceptional stability of the polymer based on thiazole indicates its potential for use in situations where prolonged exposure to light and air is unavoidable. This study emphasizes the significance of choosing suitable π -bridges to improve the stability and performance of CPs, hence facilitating their wider commercial acceptance and utilization in diverse high-tech industries.



The results were published in *Polymer* journal in October 2024 with title

Elif Demir Arabacı, Oguzhan Karakurt, Ali Cirpan, Erol Yildirim, Ahmet M. Onal “The Impact of π -Bridge Moiety as Selenophene, Thiophene, and Thiazole on the Photodegradation of Benzodithiophene-Based Conjugated Polymers”, *Polymer* 313 (2024) 127736

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5. HPC Benefits

TRUBA resources were used for all quantum chemistry calculations. Some of the analysis were also performed at TRUBA and UHEM resources such as reactivity and orbital distribution by using open source codes. In addition to use Gaussian Software, experimental group acquire knowledge on how to install and use open source codes in The TRUBA HPC center.

Dr. Elif Demir Arabacı, member of the experimental group supervised by Prof. Önal, attended theoretical chemistry laboratory regularly during the study to learn Density Functional Theory calculations by using HPC resources. One of her PhD thesis chapter constituted by these theoretical studies completed during the project. She is able to perform calculations independently without theoretical group support as a result of this study.

We showed that it is possible to model photodegradation and stability of polymers which is an important step for the development of green polymers.

6. Challenges

After light exposure of the polymers, many different products formed as a result of degradation. Although, we successfully predict stability order of polymers by using calculations at the HPC resources, it is not possible to calculate all products accurately. ReaxFF force field based calculations will be applied in the future projects.

Polymers in the calculations were selected as tetramers to use more accurate computational chemistry methods, thus molecular weights are not identical with experiments due to computational capacity. Still, prediction of band gaps is relatively successful which is the main parameter.

7. References



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