



EuroCC@Türkiye

This document is prepared by EuroCC@Türkiye for EuroCC2 under GA NO 101101903

## Design, Synthesis, and Theoretical Studies on the Random Copolymers for Organic Solar Cell Applications

### 1. Problem Identification

Researchers are exploring alternative, eco-friendly energy sources to address this challenge and meet our growing needs. Among the most promising options are solar cells, which can directly convert sunlight's abundant and renewable energy into electrical power. Conjugated polymers (CP) provide many advantages in organic photovoltaic technology, such as their lower production cost, lightweight, and flexibility. Thus, organic solar cells (OSCs) come to the forefront among other counterparts by enabling roll-to-roll production, output elasticity, and environmentally friendly production and annihilation methods.

Conjugated conducting polymers (CP) provide many advantages in organic photovoltaic technology, such as their low cost, light weight, and plastic behaviour. Organic solar cells (OSCs) should be improved compete with traditional cells by enabling roll-to-roll production, flexibility both electronically and mechanically, and environmentally friendly production and decomposition methods.

Donor-acceptor copolymerization is the widely used method for improving conjugated polymer systems. The backbone of the conjugated polymer is characterized by a repeating pattern of alternating electron-rich and electron-deficient units along the polymer's backbone. Donor-acceptor (D-A) conjugated polymers offer the following advantages: (a) showing a broad absorption spectrum with high extinction coefficients to collect solar photons, (b) showing favorable and tunable molecular energy levels that obtain matching with acceptors, (c) showing improved charge mobility, which helps with charge separation and transport processes.

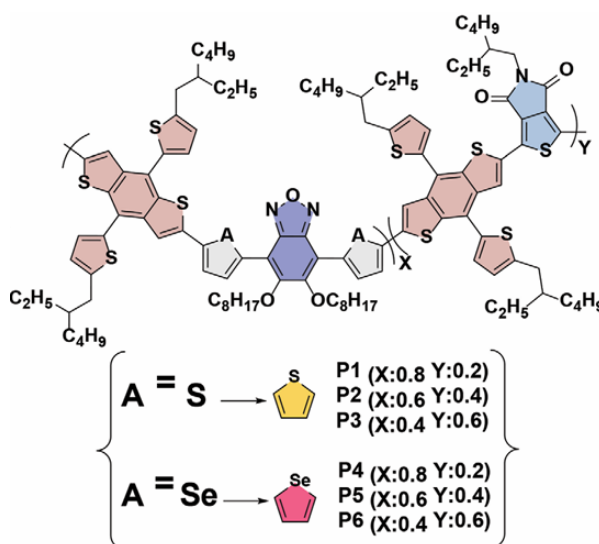
In this academic collaboration, six different new donor- $\pi$ -acceptor<sub>1</sub>- $\pi$ -donor-acceptor<sub>2</sub> type random co-polymer structures were prepared by using thiophene and selenophene bridges in polymer structures containing benzodithiophene (BDT) as donor and benzo [c][1,2,5]oxadiazole (BO) and thieno[3,4-c]pyrrole-4,6-dione (TPD) as two acceptors. The impact of the  $\pi$ -bridge and acceptor core ratios was thoroughly studied in terms of optical, electrochemical, and photovoltaic functionality in these designs. Theoretical studies were performed on these structures by our group. Next, the experimental group member is trained to learn how to design and evaluate efficiency of donor-acceptor type conducting polymers by using computational chemistry techniques at HPC center.

## 2. First Suggestion

Timeline	Tasks and Milestones
Month 1	Six different random copolymers P1-P6 were modelled and optimized at TRUBA and UHEM resources.
Month 2-6	Important molecular properties were calculated including band gap, polarizability, electrostatic potential surface, frontier orbitals and etc.
Month 3-5	Results such UV-Vis absorption spectra were compared with the experimental results and best candidates for the organic solar cell applications were selected. A manuscript submitted to the <i>Macromolecular Rapid Communications Journal</i> .
Month 6-12	Experimental group members were trained on the same system and their own diverse organic photovoltaic systems for the use of quantum chemistry in HPC resources for their own projects.

## 3. Solution Stage – I

To investigate how the acceptor unit ratio and replacement of aromatic bridge units impact the structural, electronic, and optical properties of the six polymers (P1-P6), density functional theory (DFT) calculations were carried out for the tetramer models.



P1-P6 conducting polymer structures

The chemical compositions of P1, P2, and P3 were modeled by incorporating a thiophene  $\pi$ -bridge, while P4, P5, and P6 were altered with a selenophene  $\pi$ -bridge in the theoretical models. The experimental compositions of P1, P2, and P3 consisted of first monomer with acceptor ratios of ratio of (X:0.8 Y:0.2), (X:0.6 Y:0.4), and (X:0.4 Y:0.6), respectively. Besides,



the experimental compositions of P4, P5, and P6 consisted of second monomer with ratio of (X:0.8 Y:0.2), (X:0.6 Y:0.4), and (X:0.4 Y:0.6).

Electrostatic potential surface (ESP), HOMO, and LUMO were computed for the optimized geometries of tetramers. The theoretical band gap ( $E_g$ ) was determined the optical band gap ( $E_g^{opt}$ ) obtained by computing the first vertical excitation energy of the lowest singlet excited state ( $S_0 \rightarrow S_1$ ) where singlet excited states were computed using time-dependent density-functional theory (TDDFT).

Vertical ionization potential (VIP) and adiabatic ionization potential (AIP) were determined by the energy difference between the neutral tetramer and the cation state of the optimized ground state geometry, followed by optimization of the cation geometry, respectively. Vertical hole reorganization energies ( $\lambda_{reorg}$ ) were determined.

Dipole moment ( $\mu$ ), isotropic polarizability ( $\alpha$ ), anisotropic polarizability ( $\beta$ ) and first-order hyperpolarizability ( $\gamma$ ) were calculated for the tetramers of P1-P6.

Orbital distributions and charge transfers between different units are determined.

## 4. Results and Achievements

This study showed that fine-tuning the energy levels and detailed band-gap engineering can be applied by controlling the bridge units for solar cell applications.

We showed that the open-circuit voltage ( $V_{OC}$ ), which is strongly correlated with the HOMO levels of the donor material, was enhanced with the increasing ratio of the TPD moiety. On the other hand, the short-circuit current ( $J_{SC}$ ), which is associated with the absorption ability of the donor material, was improved by the increasing ratio of BO moiety with the  $\pi$ -bridges.

The trend in bandgap increases observed among **P1** to **P3** or **P4** to **P6** in theoretical studies is consistent with the experimental results (**Table 3.4**). The small variations in band gap provided by thiophene and selenophene bridges indicate that the structure of the bridge may not be the primary determining factor for  $E_g$ . Instead, the structural composition of the polymers and donor-acceptor types play more crucial roles compared to the effect of bridge unit. Still, this study showed that fine-tuning the energy levels and detailed band-gap engineering can be applied by controlling the bridge units. The difference between the experimental and computational results can be attributed to the limitations in chain length and the interchain interactions that cannot be fully accounted for in theoretical calculations. Additionally, it should be noted that the composition of the P<sub>n</sub> and P<sub>nt</sub>, where n=1,2,3,4,5,6, were not perfectly identical due to computational capacity since it is impossible to reach an exact experimental ratio for a tetramer structure.



The results were published in July 2024 at

*“Design, Synthesis, and Theoretical Studies on the Benzoxadiazole and Thienopyrrole Containing Conjugated Random Copolymers for Organic Solar Cell Applications”*

Karakurt O., Oral P., Hacıoğlu S. O., Yılmaz E. A., Hacıfendioğlu T., Bicer U. I., Özcelik E., Özsoy G. H., Yildirim E., Toppare L. K., Çirpan A. **Macromolecular Rapid Communications**, 2024, 2400343.

With acknowledgment:

*The numerical calculations reported in this paper were partially performed at TUBITAK ULAKBİM, HighPerformance and Grid Computing Center (TRUBA resources) and National Center for High Performance Computing of Turkey (UHeM).*

## 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 construction of orbital surfaces.

Beyond this academic PoC study, we have published 5 other papers with the same group that include theoretical calculations in the last three years.

Oguzhan Karakurt, Elif Fatma Demirgezer, Murat Dastemir, Semih Can Cakmaktepe, Hector Miranda-Salinas, Erkan Aksoy, Andrew Danos, Andrew Monkman, Erol Yildirim, Ali Cirpan, Design and performance of sulfur and selenium-substituted triarylboron D3-A TADF emitters for OLED applications, *Organic Electronics* 134, 107130 (2024)

Sultan Taskaya Aslan, Eda Alemdar Yılmaz, Tuğba Hacıfendioğlu, Yasemin Arslan Udum, Levent Toppare, Erol Yildirim, Ali Cirpan, *European Polymer Journal*, 169, 111141 (2022)

ST Aslan, D Cevher, E Bolayır, GH Ozsoy, YA Udum, E Yildirim, et al., *Electrochimica Acta*, 398, 139298. (2022)

Cansu Zeytun Karaman, Seza Göker, Ümmügülsüm Şahin, Serife O Hacıoğlu, Sultan Taşkaya Aslan, Tuğba Hacıfendioğlu, Gönül Hızalan, Erol Yildirim, Ali Çirpan, Levent Toppare, , *Journal of Electroanalytical Chemistry*, 115483 (2021)

CZ Karaman, S Göker, SO Hacıoğlu, T Hacıfendioğlu, E Yildirim, et al, *Journal of The Electrochemical Society* 168 (3), 036514 (2021)

The difference of this study from the previous ones is the contribution of the students from experimental groups to theoretical studies. M.Sci. students Sevgi Aydın and Murat Dastemir took important duties and trained during all the calculations of this study. They can support experimental group without our support using their own HPC accounts. These students



learned how to construct their polymer structures by molecular modeling software, learn how to submit their own jobs to HPC and performed some analysis with the help of theoretical group. As a result, Çırpan and Toppare groups that are two of the most productive experimental groups from METU Chemistry Department become regular users of HPC opportunities by collaboration with Erol Yildirim. These groups are planning to utilize theoretical chemistry resources for their other studies such as OLEDs and non-fullerene acceptors.

## 6. Challenges

There is a difference between the experimental and computational results can be attributed to the limitations in chain length and the interchain interactions that cannot be fully accounted for in theoretical calculations by using quantum chemical calculations. Additionally, it should be noted that the composition of the P1-P6 copolymers were not perfectly identical with experiments due to computational capacity since it is impossible to reach an exact experimental ratio for a tetramer structure.

Since the experimental group did not have any computational background it was challenging to convince contribution of HPC resources to their device based studies. However, after successful calculation of experimental parameters and publication, our collaboration move forward.

## 7. References

- [1] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- [2] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys Rev B* 37 (1988) 785–789. <https://doi.org/10.1103/PhysRevB.37.785>.
- [3] A.D. Becke, Density-functional thermochemistry. I. The effect of the exchange-only gradient correction, *J Chem Phys* 96 (1992) 2155–2160. <https://doi.org/10.1063/1.462066>.
- [4] J.-L. Brédas, D. Beljonne, V. Coropceanu, J. Cornil, Charge-Transfer and Energy-Transfer Processes in  $\pi$ -Conjugated Oligomers and Polymers: A Molecular Picture, *Chem Rev* 104 (2004) 4971–5004. <https://doi.org/10.1021/cr040084k>.
- [5] B.H. Besler, K.M. Merz, P.A. Kollman, Atomic charges derived from semiempirical methods, *J Comput Chem* 11 (1990) 431–439. <https://doi.org/10.1002/jcc.540110404>.
- [6] T. Lu, F. Chen, Multiwfn: A multifunctional wavefunction analyzer, *J Comput Chem* 33 (2012) 580–592. <https://doi.org/10.1002/jcc.22885>.



[7] Oguzhan Karakurt, Pelin Oral, Serife Ozdemir Hacioglu, Eda Alemdar Yılmaz, Tuğba Hacıfendioğlu, Umran Isil Bicer, Egemen Ozcelik, Gonul Hizalan Ozsoy, Erol Yildirim, Levent Kamil Toppare, Ali Cirpan, Design, Synthesis, and Theoretical Studies on the Benzoxadiazole and Thienopyrrole Containing Conjugated Random Copolymers for Organic Solar Cell Applications, *Macromol. Rapid Commun.* 2024, 45, 2400343