



저작자표시-비영리-변경금지 2.0 대한민국

이용자는 아래의 조건을 따르는 경우에 한하여 자유롭게

- 이 저작물을 복제, 배포, 전송, 전시, 공연 및 방송할 수 있습니다.

다음과 같은 조건을 따라야 합니다:



저작자표시. 귀하는 원저작자를 표시하여야 합니다.



비영리. 귀하는 이 저작물을 영리 목적으로 이용할 수 없습니다.



변경금지. 귀하는 이 저작물을 개작, 변형 또는 가공할 수 없습니다.

- 귀하는, 이 저작물의 재이용이나 배포의 경우, 이 저작물에 적용된 이용허락조건을 명확하게 나타내어야 합니다.
- 저작권자로부터 별도의 허가를 받으면 이러한 조건들은 적용되지 않습니다.

저작권법에 따른 이용자의 권리는 위의 내용에 의하여 영향을 받지 않습니다.

이것은 [이용허락규약\(Legal Code\)](#)을 이해하기 쉽게 요약한 것입니다.

[Disclaimer](#)

Master's Thesis
석사 학위논문

Effective doping of donor-acceptor copolymer

Geon-Hee Nam(남 건 희 南 建 僖)

Department of
Energy Science & Engineering

DGIST

2021

Master's Thesis
석사 학위논문

Effective doping of donor-acceptor copolymer

Geon-Hee Nam(남 건 희 南 建 僖)

Department of
Energy Science & Engineering

DGIST

2021

Effective doping of donor-acceptor copolymer

Advisor: Professor Chiyoung Park
Co-advisor: Professor Jongmin Choi

by

Geon-Hee Nam
Department of Energy Science & Engineering
DGIST

A thesis submitted to the faculty of DGIST in partial fulfillment of the requirements for the degree of Master of Science in the Department of Energy Science & Engineering. The study was conducted in accordance with Code of Research Ethics¹

01. 04. 2021

Approved by

Professor Chiyoung Park (Advisor)	(signature)
Professor Jongmin Choi (Co-Advisor)	(signature)

¹ Declaration of Ethical Conduct in Research: I, as a graduate student of DGIST, hereby declare that I have not committed any acts that may damage the credibility of my research. These include, but are not limited to: falsification, thesis written by someone else, distortion of research findings or plagiarism. I affirm that my thesis contains honest conclusions based on my own careful research under the guidance of my thesis advisor.

Effective doping of donor-acceptor copolymer

Geon-Hee Nam

Accepted in partial fulfillment of the requirements for the degree of Master of Science.

11. 16. 2020

Head of Committee Prof. Chiyoung Park (signature)

Committee Member Prof. Jongmin Choi (signature)

Committee Member Prof. Jiwoong Yang (signature)

MS/ES
201911065

남 건 희. Geon-Hee Nam. Effective doping of donor-acceptor copolymer. Department of Energy Science & Engineering. 2021. 10p. Advisors Prof. Chiyoung Park, Co-Advisors Prof. Jongmin Choi

ABSTRACT

Molecular doping is effective method for changing the electrical and physical properties of organic semiconductors. However, the mechanism of doping process was not certainly discovered and moreover the doping efficiency of the donor-acceptor copolymer was low. Herein, we synthesized diketopyrrolopyrrole based donor-acceptor copolymers and investigated the doping efficiency of each polymer by UV-Vis, FT-IR, and EPR spectroscopy. The TBD2F polymer which added thiophene linker with DPP based polymer, could be doped effectively by F4TCNQ molecular dopant. Moreover, the 2D-GIXD was measured to analyze the dopant position at polymer crystalline phase. From the result we could speculate that by dopant located at alkyl chain region of polymer crystalline matrix, the efficient doping enabled.

Keywords: Molecular doping, Copolymer, Organic semiconductor

List of Contents

Abstract	i
List of contents	ii
List of tables	iii
List of figures	vi
I. Introduction	
1.1 Organic semiconductors	1
1.2 Doping of organic semiconductors	1
1.2.1 Mechanisms of molecular doping	1
1.2.2 Doping of copolymer	2
II. Results and discussion	
2.1 Molecular structures	3
2.2 UV-Visible spectroscopy	3
2.3 Fourier transform infrared spectroscopy	4
2.4 Electron paramagnetic resonance spectroscopy	5
2.5 2-D Gazing incident X-ray diffraction	6
III. Conclusion	

List of Tables

Table 1. The summarized parameters about d-spacing and π - π stacking.

List of Figures

Figure 1. The molecular structure of 3 polymer and dopant (a). The energy level of corresponding polymers and dopant.

Figure 2. The UV-Vis absorption spectroscopy of DPP-DTT (a), BD2F (b), and TBD2F (c). For each spectrum, the pristine polymer (black), after doping (red), after chloroform washing (blue), and after dedoping (green) was shown.

Figure 3. FT-IR spectra of DPP-DTT (black), BD2F (blue), and TBD2F (red).

Figure 4. EPR spectra of DPP-DTT (a), BD2F (b), and TBD2F (c). The intensity of paramagnetic resonance after chloroform washing and dedoping was additionally illustrated in order to show the effective dedoping of TBD2F.

Figure 5. 2D-GIXD images of each pristine polymers and doped ones. For TBD2F, the dedoped and annealed states were additionally indicated due to further analysis.

I. INTRODUCTION

1.1 Organic semiconductors

Organic semiconductors (OSCs) are widely investigated to be applicable for photovoltaics, photodetectors, light-emitting diodes, and transistors. [1-3] These electronic devices were firstly investigated with inorganic semiconductors which had superior performance than organic counterparts. Only some organic electronic devices could be commercialized such as organic light-emitting diode (OLED) which had advantages of visibility, low energy consumption, and viewing angle. [3] Instead of competing with inorganic one, OSCs are finding its way into the wearable, disposable, or lightweight electronics

The working principle of OSC is resembled the inorganic semiconductor. As the semi-infinite atoms arrangement forms the valence and conduction band in inorganic semiconductor, the numerous number of conjugated monomer forms each same band in OSC. Because the π -orbital composes these band structure and electronic charges travel in this orbital passage, the structure of conjugated π -orbital was important to use for various organic electronics.

1.2 Doping of organic semiconductors

The molecular doping enables to change the mechanical and electrical conductivity of OSC. For example, to the organic thermoelectric generator, the electrical conductivity could increase by proper doping to the matrix semiconductor. [4] Because of the charges generated by charge transfer, electrical conductivity can be enhanced. Other application of doping is doping induced solubility control (DISC), which enables the patterning of OSCs. [5]

1.2.1 Mechanism of molecular doping

The number of literatures explained the relation of dopant and OSC, and generally their interaction was understood by two mechanisms, integer charge transfer (ICT) and charge transfer complex (CTC) formation. [6] In general, for p-type OSC, the electron transferred from the donor OSC to strong acceptor dopant. The HOMO of OSC donated the electron to the LUMO of dopant by lowering the energy. On the other hand, if the HOMO of OSC is lower than the LUMO of dopant, the orbital hybridization will occur so the electron transfers from

HOMO of OSC to HOMO of hybridized orbital. This description is intuitive, however, this do not correspond to all OSC-dopant system nor can predict which mechanism to be followed. For instance, the HOMO of quaterthiophene (4T) was slightly higher than the LUMO of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), although the CTC occurred between two molecules. [7] Likewise, the principles of doping and the interaction between OSC matrix and dopant need to be investigated.

To identify the doping mechanism, UV-Visible (UV-Vis) spectroscopy and Fourier transform infrared (FT-IR) spectroscopy were widely used with the specific peaks indicating the degree of charge transfer. For the UV-Vis spectra, the clear F4TCNQ anion peaks appear around 830 nm, meaning that the electrons completely transferred to F4TCNQ (ICT). The CTC can be determined by the hybrid orbital peaks around 1600 nm, and cannot find the F4TCNQ anion peak. [6] Meanwhile, more quantitative analysis is possible by FT-IR spectroscopy. The neutral F4TCNQ peak appears at $2,227\text{ cm}^{-1}$, and fully ionized F4TCNQ anion peak appears at $2,194$ and $2,188\text{ cm}^{-1}$. [6] The ICT is identified from the anion peak, and by confirmation of the relative position between $2,227$ and $2,194\text{ cm}^{-1}$, the degree of charge transfer can be quantitatively calculated.

1.2.2 Doping of copolymer

Copolymer is composed of different monomer units in order to control the physical or electrical properties. The well-known high mobility up to $10\text{ cm}^2\text{ V}^{-1}\text{ S}^{-1}$ donor-acceptor (D-A) copolymer, poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno [3,2-b]thiophene)] (DPP-DTT), has a low HOMO energy level of -5.2 eV . Due to the energy offset was mismatched with widely used molecular p-dopant F4TCNQ, DPP-DTT should only be doped by dopant with deeper LUMO level. [8] Herein, even using a diketopyrrolopyrrole based D-A-D-A copolymer, the efficient doping by F4TCNQ was demonstrated. We speculated that this can be achieved by long alkyl chain, which enable to make enough spaces to locate F4TCNQ anion.

II. RESULT AND DISCUSSION

2.1 Molecular structure

The structure of polymer and dopant molecule was shown at Figure 2a. The polymer MECT-29DPP-BD2F (hereafter BD2F) and MECT-29DPP-TBD2F (hereafter TBD2F) was synthesized by Yun-Hi Kim at Gyungsang National University. For two of polymer, donor unit was based on cyclopentadithiophene (CDT) and acceptor units were base on DPP and benzothiadiazole (BTZ). The difference of two polymer is the thiophene linker on both side of benzothiadiazole. The DPP-DTT was used as reference DPP polymer. The energy level of 3 polymers represented at Figure 2b. In terms of energy offset, only the DPP-DTT can be ICT and other 2 polymers should CTC.

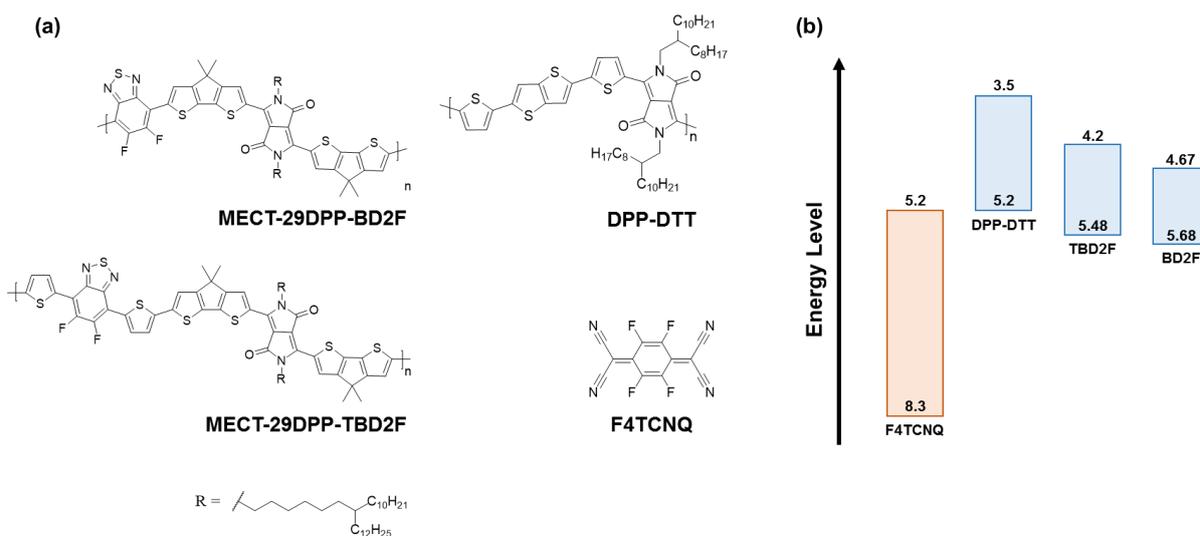


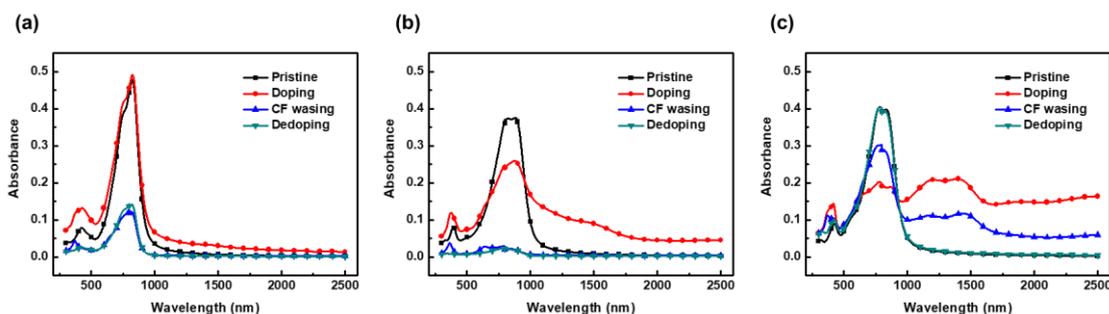
Figure 1. The molecular structure of 3 polymer and dopant (a). The energy level of corresponding polymers and dopant.

2.2 UV-Visible spectroscopy

The UV-Vis spectroscopy showed the insight whether the molecules were doped or not. In the Figure 2, the UV-Vis spectra of pristine, doped, washed by chloroform, and dedoped was represented. In the spectra of the DPP-DTT, the spectrum was not changed after F4TCNQ doping and after washing the intensity of main peak at ~800 nm was drastically decreased. This indicated that the DPP-DTT was not doped by F4TCNQ so that the existing DPP-DTT film was erased after chloroform washing by the high solubility of DPP-DTT at chloroform.

Meanwhile the BD2F showed the difference between the pristine and doped film. The new peak at 1,000-1,500 nm induced by the polaron which is the result of doping with F4TCNQ. However, after the chloroform washing, the BD2F film also washed out which can be inferred by the weak doping mechanism. In the TBD2F case, the strong polaron peak was shown after doping and the main polymer peak at ~800 nm was recovered after chloroform washing. We speculated that because the TBD2F doping was ICT mechanism, the solubility at chloroform was sharply decreased, so the TBD2F film was not washed by chloroform. This could be supported my spectrum of dedoping. The dedoping process removed the F4TCNQ at polymer film with basic solution. (Ethylene-diamine:Acetone (1:10 v/v%) in this paper) The spectrum of DPP-DTT and BD2F could not recover the pristine polymer peak after dedoping process, however, the TBD2F showed the almost identical spectra after dedoping. The entire TBD2F film was not erased after chloroform washing due to the high doping intensity, so the film restored the original absorption spectrum after the dedoping process.

Figure 2. The UV-Vis absorption spectroscopy of DPP-DTT (a), BD2F (b), and TBD2F (c). For each spectrum,



the pristine polymer (black), after doping (red), after chloroform washing (blue), and after dedoping (green) was shown.

2.2 Fourier transform infrared spectroscopy

More quantitative understanding of doping intensity was conducted by FT-IR spectroscopy. The doped films of each polymer were summarized at Figure 3. It was clearly seen that for the DPP-DTT, the peak of anion C-N vibration cannot be seen at $\sim 2190\text{ cm}^{-1}$. This agreed with previous UV-Vis spectra, which indicated that the DPP-DTT was not doped by F4TCNQ. The BD2F and TBD2F had peak at 2192 cm^{-1} , and the TBD2F had more intense peak at 2187 cm^{-1} . Some papers demonstrated that the intensity of this two peak could be varied by the position of anionic dopant molecules. [9, 10] We could speculate that the dopant position of BD2F and TBD2F was different, probably due to by the presence of thiophene linker.

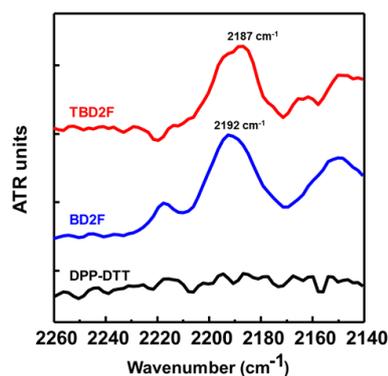


Figure 3. FT-IR spectra of DPP-DTT (black), BD2F (blue), and TBD2F (red).

2.3 Electron paramagnetic resonance spectroscopy

To identify doping intensity, the electron paramagnetic resonance (EPR) spectroscopy was also conducted. The DPP-DTT showed insignificant paramagnetism after doping, which corresponded with previous results. For both BD2F and TBD2F, paramagnetic response can be seen after doping while the intensity is much higher at the TBD2F. The more paramagnetic resonance ensured the more electron transferred from polymer to dopant. The dedoping process of TBD2F also showed that the film recovered the original properties by removal of F4TNCQ dopant.

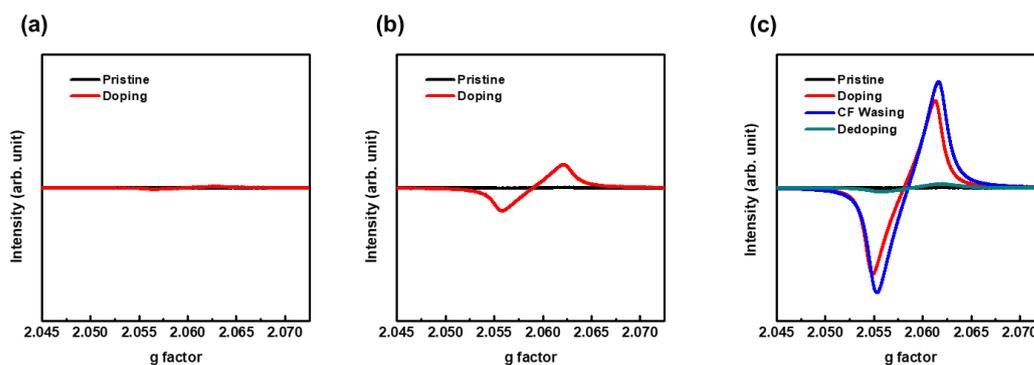


Figure 4. EPR spectra of DPP-DTT (a), BD2F (b), and TBD2F (c). The intensity of paramagnetic resonance after chloroform washing and dedoping was additionally illustrated in order to show the effective dedoping of TBD2F.

2.3 2-D Gazing incident X-ray diffraction

To understand how the polymer crystallinity was changed after doping, the 2D-GIXD was measured. The clear edge-on structure was clearly shown at all 2D-GIXD images. (Figure 5) We also calculated the d-spacing and π - π stacking to verify the position of dopant anion. (Table 1) The parameters of doped BD2F and dedoped d-spacing were could not be found, because of the low crystallinity induced by doping and dedoping process, therefore we compared the parameters of TBD2F with DPP-DTT. The all parameters of DPP-DTT increased due to the intercalation of dopant at the polymer backbone and alkyl chain. However, only the d-spacing increased after doping for TBD2F, while π - π stacking remained constant after doping, dedoping and annealing. We speculated that the dopant of TBD2F only intercalated to the alkyl chain, and this enabled the strong doping intensity as previous reports suggested. Also because the difference between two new polymers, BD2F and TBD2F, was the thiophene linker, the free volume of alkyl chain region allowed the highly doped film. We carefully suggested that this phenomenon originated from the large number of stabilized dopant anion by free space near the alkyl chain. More sophisticated analysis must be achieved to investigate the behavior of dopant and polymer matrix.

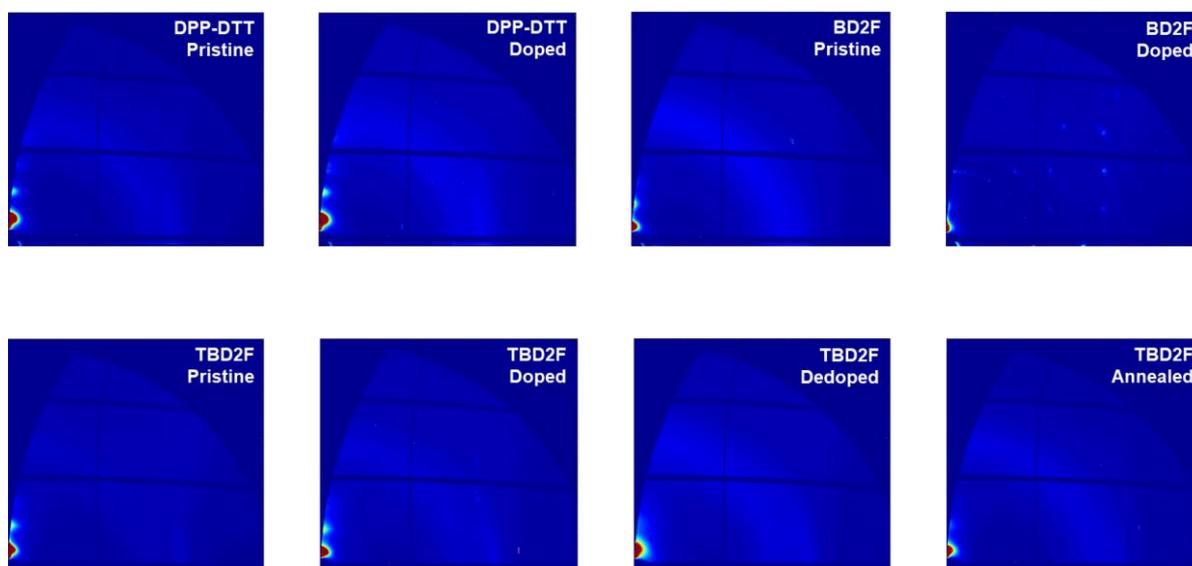


Figure 5. 2D-GIXD images of each pristine polymers and doped ones. For TBD2F, the dedoped and annealed states were additionally indicated due to further analysis.

	DPP-DTT		BD2F		TBD2F			
	Pristine	Doped	Pristine	Doped	Pristine	Doped	Dedoped	Annealed
d-spacing	20.94	21.33	25.81	-	23.91	25.08	-	21.98
π - π stacking	3.84	3.90	3.79	-	3.69	3.68	3.68	3.68

Table 1. The summarized parameters about d-spacing and π - π stacking.

III. CONCLUSION

In this paper, we studied the mechanism for doping of donor-acceptor copolymer, focused on the position of dopant molecules in polymer matrix. By using newly synthesized molecules, we successfully doped the donor-acceptor copolymer with F4TCNQ which hardly doped the general copolymer. The effective doping of TBD2F was identified by UV-vis, FT-IR, and EPR analysis while the DPP-DTT, well-known copolymer, showed the extremely low doping efficiency even the matched energy offset with F4TCNQ. Also the origin of different doping efficiency was investigated by 2D-GIXD. The results indicated that the high doping efficiency of TBD2F could be caused by the free volume at the alkyl chain region. This research presented the insight of doping mechanism in the view of polymer structure, enabling the design of polymer matrix for effective doping.

References

- [1] Jansen-van Vuuren, R. D., Armin, A., Pandey, A. K., Burn, P. L., & Meredith, P. "Organic photodiodes: the future of full color detection and image sensing." *Advanced Materials*, 28(24), 2016, pp. 4766-4802.
- [2] Torsi, L., Magliulo, M., Manoli, K., & Palazzo, G. "Organic field-effect transistor sensors: a tutorial review." *Chemical Society Reviews*, 42(22), 2013, pp. 8612-8628.
- [3] Park, J. S., Chae, H., Chung, H. K., & Lee, S. I. "Thin film encapsulation for flexible AM-OLED: a review." *Semiconductor science and technology*, 26(3), 2011, pp.034001.
- [4] Patel, S. N., Glauddell, A. M., Kiefer, D., & Chabinyk, M. L. "Increasing the thermoelectric power factor of a semiconducting polymer by doping from the vapor phase." *ACS Macro Letters*, 5(3), 2016, pp. 268-272.
- [5] Kim, J., Kang, M., Cho, J., Yu, S. H., & Chung, D. S. "Doping–Dedoping Interplay to Realize Patterned/Stacked All-Polymer Optoelectronic Devices." *ACS applied materials & interfaces*, 11(20), 2019, pp. 18580-18589.
- [6] Jacobs, I. E., & Moulé, A. J. "Controlling molecular doping in organic semiconductors." *Advanced Materials*, 29(42), 2017, pp. 1703063.
- [7] Henry, M., Georg, H., Stefanie, W., Johannes, F., Andreas, O., Katrein, S., Berthold, W., Martin, O., Christian, R., Steffen, D., Daniel, T., Norbert K. & Ingo, S. "Charge-transfer crystallites as molecular electrical dopants." *Nature communications*, 6(1), 2015, pp. 1-11.
- [8] Yevhen, K., Tim, E., Ivan, R., Mahmoud, A.-H., Marcus, B., Uwe, L., Manfred, S., Kirill, L. G., Tetyana, B., Vasiliy, B., Denis, V. A., Dimitri, A. I., Florian, G., Sibylle, G., Gotthard, S., Brigitte, V., Riccardo, D. P., & Anton, K. "High Conductivity in Molecularly p-Doped Diketopyrrolopyrrole-Based Polymer: The Impact of a High Dopant Strength and Good Structural Order." *Advanced Materials*, 28(28), 2016, pp. 6003-6010.
- [9] Zapata-Arteaga, O., Dörfling, B., Perevedentsev, A., Martín, J., Reparaz, J. S., & Campoy-Quiles, M. "Closing the Stability–Performance Gap in Organic Thermoelectrics by Adjusting the Partial to Integer Charge Transfer Ratio." *Macromolecules*, 53(2), 2020, pp. 609-620.
- [10] Hase, H., O'Neill, K., Frisch, J., Opitz, A., Koch, N., & Salzmänn, I. "Unraveling the Microstructure of Molecularly Doped Poly (3-Hexylthiophene) by Thermally Induced Dedoping." *The Journal of Physical Chemistry C*, 122(45), 2018, pp.25893-25899.

요 약 문

도너-어셉터 공중합체의 효과적인 도핑

분자 도핑은 유기 반도체의 전기적 및 물리적 특성을 변경하는 효과적인 방법입니다. 그러나 도핑의 메커니즘이 확실하게 발견되지 않았고, 더욱이 아직까지는 도너-어셉터 공중합체가 낮은 도핑 효율을 보이고 있다. 따라서 이 논문에서 우리는 diketopyrrolopyrrole 기반으로 합성된 도너-어셉터 공중합체를 UV-Vis, FT-IR, EPR 분광법을 통해 각 고분자의 도핑 효율을 분석하였다. DPP 기반 폴리머와 함께 thiophene 링커를 추가 한 TBD2F 폴리머는 F4TCNQ 분자 도펀트에 의해 효과적으로 도핑 될 수 있음을 확인하였다. 또한 2D-GIXD 를 이용하여 고분자 결정상의 도펀트 위치를 분석했습니다. 그 결과로부터 우리는 폴리머 결정질 매트릭스의 알킬 사슬 영역에 위치한 도펀트에 의해 효율적인 도핑이 가능하다고 추측 할 수 있었습니다.

핵심어: 분자 도핑, 공중합체, 유기반도체