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HYBRID ACTIVE LAYERS FOR ORGANIC SOLAR CELLS BASED ON BODIPY DERIVATIVES AND NICKEL PHTHALOCYANINE

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In response to the current challenges of organic photonics and the demand for organic photodetectors (OPDs) with a broadened spectral range and enhanced sensitivity, this work proposes hybrid non-fullerene systems that combine nickel (II) phthalocyanine (NiPc) metal complexes with boron-dipyrromethene (BODIPY)-based dyes. In this study, a heterostructure based on NiPc and a newly synthesised BODIPY derivative sensitiser (bThBODIPY) was developed and comprehensively evaluated. The bThBODIPY dye, belonging to the BODIPY family, exhibits an absorption maximum around 510 nm, whereas the newly synthesised BODIPY sensitiser demonstrates an absorption maximum near 600 nm. Both dyes form stable dark-red solid compounds that are readily soluble in common organic solvents (toluene, chlorobenzene, dichloromethane, chloroform, ethyl acetate), enabling the fabrication of homogeneous thin films resistant to subsequent thermal treatment. The photosensitivity of the fabricated devices was assessed on thin-film OPDs with the architecture ITO/PEDOT:PSS/NiPc: sensitiser:bThBODIPY/BCP/Al. The active layer was deposited by spin-coating, employing a pre-optimised NiPc-to-sensitiser ratio followed by post-deposition thermal annealing. Under illumination with the standard solar spectrum AM 1.5G (100 mW cm^{-2}), the fabricated device demonstrated stable photoelectrical parameters. Specifically, the fill factor (FF) reached 16.4 %, while the power conversion efficiency (PCE) was 0.32 %. The obtained results confirm the high potential of non-fullerene NiPc–BODIPY hybrid systems for extending the spectral sensitivity and improving the performance of organic photodetectors. Promising directions for further research include interface modification with selective buffer layers, the design of multi-sensitiser systems employing complementary dyes, and the development of architectures capable of harvesting the entire visible and near-infrared spectral regions. Promising directions for further research include interface modification with selective buffer layers, the design of multi-sensitiser systems employing complementary dyes, and the development of architectures capable of harvesting the entire visible and near-infrared spectral regions.

Keywords: *Heterostructure, solar cells, organic photodetectors, organic photovoltaic devices, BODIPY derivatives, nickel phtalocyanine.*
UDC: 620.9

Introduction

Organic solar cells based on bulk heterojunction (BHJ) architectures have attracted significant attention due to a number of advantages, including compatibility with solution-processing techniques, relatively low cost, and the possibility of large-scale manufacturing. In organic semiconducting materials,

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the phenomenon of photoconductivity is realized, which underlies the operation of organic photovoltaic devices. For most of these materials, the bandgap lies in the range of 1.5–3 eV, ensuring photosensitivity in the visible and near-infrared regions of the spectrum.

The mechanism of photoconductivity in organic semiconductors significantly differs from that in inorganic systems. In inorganic semiconductors, photogenerated electrons and holes are delocalized and freely migrate to the respective electrodes, forming an electrical current in the external circuit. In contrast, in organic materials, photoexcited electrons and holes are not fully delocalized, which leads to the formation of bound electron–hole pairs known as excitons. Their dissociation into free charge carriers occurs at phase boundaries or potential barriers and requires additional energy, known as exciton binding energy (Eb), which for most organic semiconductors is about 0.1–0.2 eV. This factor accounts for the lower power conversion efficiency (PCE) of OPVs compared to their inorganic counterparts.

Nevertheless, despite their lower energy performance, organic solar cells remain highly promising due to their cost-effectiveness, light weight, flexibility, and scalability for large-area fabrication. These advantages make OPVs a competitive technology for practical applications in renewable energy.

BODIPY derivatives [1, 2] exhibit strong absorption in the near-infrared region and emit narrow fluorescence bands with high quantum yields [12]. These dyes attract considerable interest owing to their unique molecular architecture, straightforward synthesis, strong absorption coefficients, delocalized molecular orbitals, and good solubility in a wide range of organic solvents [13]. BODIPY molecules are widely applied in organic electronics [14–16].

Nickel phthalocyanine (NiPc) is a promising photosensitive material for photovoltaic applications [5, 6]. Its derivatives are used as donor components in bilayer organic solar cell architectures, including dye-sensitized solar cells [17]. NiPc exhibits strong optical activity in the visible and near-infrared spectral regions, along with high thermal and chemical stability, making it suitable for hybrid organic–inorganic systems [18]. Furthermore, NiPc can be integrated into perovskite solar cell (PSC) architectures as an alternative to expensive and unstable materials such as Spiro-OMeTAD and PTAA [19].

BODIPY derivatives also play an important role as light-harvesting components in solar cells [20]. The combined application of BODIPY and NiPc-based components in solar cell structures facilitates efficient energy transfer from excited BODIPY fragments to the phthalocyanine center [24, 25]. The integration of boron-dipyrromethene derivatives with phthalocyanine frameworks enables the development of materials with extended spectral coverage, efficient energy transfer, and potential for multifunctional applications ranging from photovoltaics to biosensing [21].

In this study, a novel nickel phthalocyanine-BODIPY (NiPc-BODIPY) solution was prepared containing three iodine-substituted groups on the phthalocyanine macrocycle and one BODIPY fragment attached via an amide linkage. The photoactive properties of the conjugate were tested in a solar cell structure of the type: ITO/PEDOT:PSS/NiPc: sensitiser:bThBODIPY/BCP/Al [29].

2. Experimental part

Organic photodetectors were fabricated on glass substrates coated with a transparent conductive indium tin oxide (ITO, Ossila; sheet resistance <15 Ω/cm^2). Before the deposition of functional layers, the substrates were cleaned by sequential ultrasonic treatment in deionised water, acetone, and isopropanol (10 min each), followed by drying under an argon stream [18].

On the cleaned surface, a PEDOT:PSS (Ossila) layer was deposited by spin coating (https://www.ossila.com/products/spin-coater) at 4000 rpm for 60 s, followed by thermal annealing at 120°C for 15 min. The thickness of the resulting layer, measured using a profilometer (Precision Measurement – S lynx 2 Compact 3D Optical System), was 50 nm.

The active layer consisted of three components: nickel(II) phthalocyanine (NiPc) [5], a BODIPY sensitizer, and the dye bThBODIPY. Solutions were prepared in toluene with a molar ratio of NiPc:BODIPY:bThBODIPY = 1:1:1, which was found to be optimal in terms of spectral sensitivity and photocarrier generation. The films were deposited by spin coating at 2000 rpm for 60 s, followed by thermal annealing at 100 °C for 10 min. Profilometric analysis confirmed an active layer thickness of 400 nm, ensuring efficient absorption in the 300–800 nm range.

To form the exciton blocking and electron-transporting layer, bathocuproine (BCP) was deposited by thermal vacuum evaporation under a base pressure of ~10^{-5} Torr [7]. The BCP layer thickness was 70 nm, which satisfied the energy-level alignment requirements at the cathode interface.

The final step involved deposition of the aluminum cathode by thermal vacuum evaporation through a shadow mask, defining electrodes with an active area of 0.04 cm^2. The aluminum layer thickness was 200 nm, ensuring a stable ohmic contact [15].

As a result, a multilayer structure with precisely controlled parameters was fabricated:

ITO/PEDOT:PSS (50 nm)/NiPc:BODIPY:bThBODIPY (400 nm)/BCP (70 nm)/Al (200 nm).

Electrical characteristics of the fabricated photodetector structure were measured using a Hewlett Packard 4145A semiconductor parameter analyzer (see Fig. 2). Measurements were performed both in the dark and under illumination using a solar spectrum simulator (AM 1.5G standard, 100 mW/cm^2). Current-voltage (I–V) characteristics were recorded in the voltage range from –5 V to +5 V. Data acquisition was performed at 100 measurement points with a constant scan rate of 0.1 V/s, ensuring high resolution and minimizing noise contribution. This approach allowed investigation of the conductivity features under both forward and reverse bias, as well as comparison of dark and photocurrent responses with respect to applied voltage symmetry [24, 25]. The obtained results enabled the determination of key photosensitivity parameters and assessment of device stability under external illumination.

Fig. 1. Schematic structure of the organic photodetector

The spectral properties of the active layer were characterized using an AvaSpec-NEXOS™ optical spectrometer (Avantes) based on a symmetric Czerny–Turner configuration with a focal length of 75 mm. Measurements were carried out in the 300–1100 nm range, covering the ultraviolet, visible, and near-infrared regions.

Samples were prepared on transparent ITO substrates without the metallic cathode, which allowed direct transmission of light through the active layer. Transmission spectra were measured using a fiber-optic probe connected to a white light source and the spectrometer. A reference substrate without the active layer was used for calibration [27].

Absorbance A(λ) was determined as the negative decimal logarithm of the ratio between the transmitted light intensity through the sample and the intensity through the reference channel:

$$A(\lambda) = -\log_{10}\left(\frac{I(\lambda)}{I_0(\lambda)}\right),$$

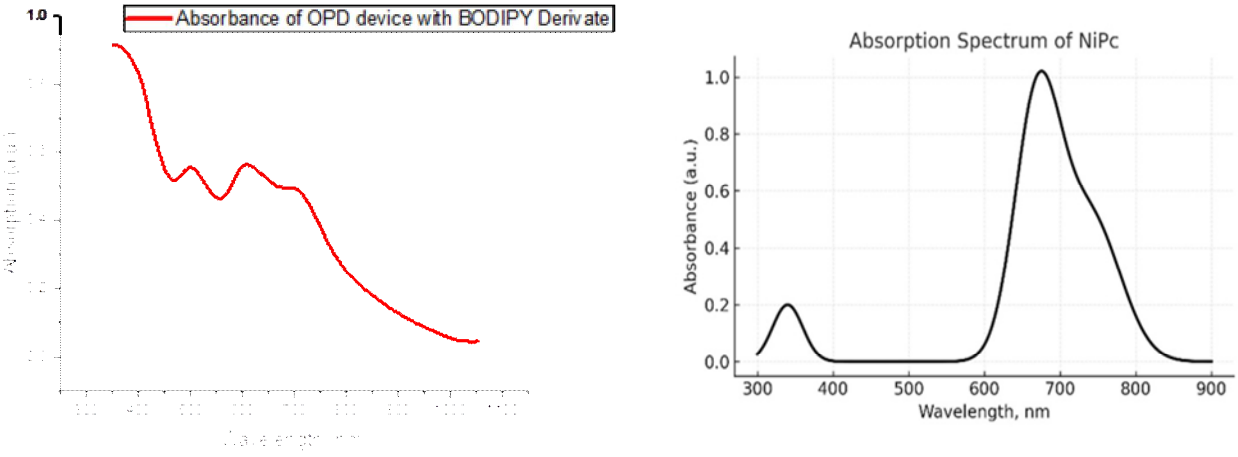
where $A(\lambda)$ – absorbance at wavelength λ;, $I(\lambda)$ – transmitted light intensity through the sample at λ; $I_0(\lambda)$ – reference intensity at λ.

The AvaSpec-NEXOS™ spectrometer provides an integration time down to 9 μs, a signal-to-noise ratio of ~375:1, and stray light levels below 0.1 %. This enables highly accurate spectral measurements even for thin organic films. To improve data reliability, each spectrum was averaged over three independent samples, and the results were normalized to the maximum intensity [12].

3. Results and discussion

The investigation of the electro-optical characteristics of the fabricated hybrid photodetectors was focused on studying the absorption spectral properties and electrical parameters of the structures under dark and illuminated conditions [23, 24]. Particular attention was given to analyzing the influence of BODIPY derivatives on device photosensitivity and comparing them with NiPc-only systems. This approach enables the evaluation of the effectiveness of molecular design of the active layer, the identification of key factors affecting photocarrier generation, and the justification of the proposed architecture for application in modern optoelectronic systems [8–10].

The absorption spectra of the fabricated hybrid sample containing a BODIPY derivative were measured in the wavelength range of 300–1100 nm (Fig. 2, *a*). The overall spectral profile indicates broadband photosensitivity, enabled by the molecular design of the active layer. Such a characteristic is highly promising for next-generation optoelectronic devices, including organic photodetectors, spectroscopic sensors, and energy conversion systems. The fabricated hybrid OPDs exhibited pronounced sensitivity in the 510–600 nm region, attributed to the absorption maxima of BODIPY and bThBODIPY dyes. This resulted in an extended absorption spectrum compared to pure NiPc (Fig. 2, *b*) [28], thereby enhancing photocarrier generation. Composition optimization revealed that a NiPc:sensitizer ratio of 1:2, combined with thermal annealing (100 °C, 10 min), provided the best performance.



a *b*

Fig. 2. Absorption spectra of the experimental structures ITO/PEDOT:PSS (50 nm)/NiPc:BODIPY:bThBODIPY (400 nm)/BCP (70 nm)/Al (200 nm) (a) and pure NiPc (b)[29]

The current–voltage (I–V) characteristics of the hybrid photodetector were investigated in the voltage range from –5 V to +5 V under dark conditions and illumination with a simulated AM 1.5 solar spectrum (100 mW/cm^2) (Fig. 3). The dark current showed low values across the entire bias range, from 10^{-8} A to 10^{-5} A, confirming effective suppression of thermally generated carriers and minimal leakage losses. The symmetry of the dark I–V curves indicates balanced charge transport and the absence of significant internal asymmetry.

Under illumination, a significant photocurrent increase was observed, reaching ~10^{-1} A at reverse bias. The nonlinear current growth with voltage confirms efficient photogeneration and extraction of charge carriers. The photocurrent-to-dark-current ratio exceeded 10^3 at –6 V, highlighting the high sensitivity and low noise level of the device [15].

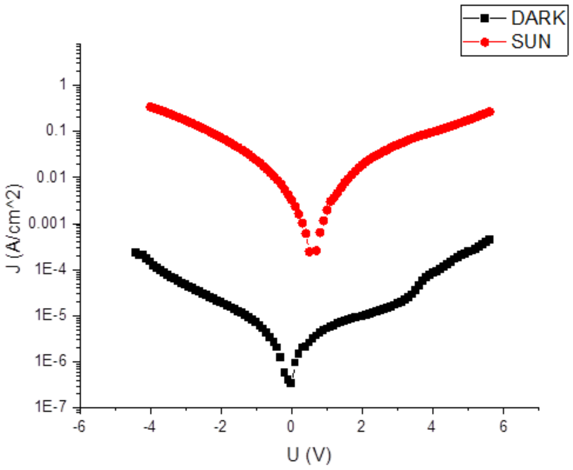


Fig. 3. Current-voltage characteristic demonstrating the dependence of photocurrent on applied bias

The fill factor (FF) is a critical parameter characterising the quality of photovoltaic conversion in organic solar cells. It is defined as the ratio of the maximum extractable power (P_max) to the product of the short-circuit current density (J_sc) and open-circuit voltage (V_oc)[30]

$$FF = \frac{P_{\max}}{V_{oc} \times I_{sc}} = \frac{V_{\max} \times I_{\max}}{V_{oc} \times I_{sc}}.$$

The FF can be affected by several factors, including carrier mobility limitations, non-ideal active layer morphology, contact losses, or charge recombination [21]. In the investigated device, based on BODIPY derivatives and nickel phthalocyanine, the fill factor was found to be 16.4 %.

The power conversion efficiency (PCE) is the key performance metric of photovoltaic devices and is defined by the equation:

$$\eta = \varphi \cdot A \cdot FF \cdot eV_{\max} / h\nu,$$

where J_sc – short-circuit current density (mA/cm^2); V_oc – open-circuit voltage (V); *FF* – fill factor, %; P_in – incident light power density (100 mW/cm^2 under AM 1.5 G illumination) [30].

For the organic solar cell based on the NiPc-BODIPY solution, the PCE reached 0.32 %. The Table demonstrate main parameters of prepared experimental device

Photoelectric parameters of the reference device

Parameter	Value	Unit
Current at maximum power(*I_m*)	64.9	mA
Voltage at maximum power(*U_m*)	0.2	V
Short-circuit current density (*J_sc*)	3.30	mA/cm^2
Open-circuit voltage (*V_oc*)	0.6	V
Fill factor (FF)	16,4	%
Power conversion efficiency (PCE, η)	0,32	%

The obtained results confirm the potential of the proposed structure for application in low-light optoelectronic systems. Further optimization of the active layer morphology and interface engineering may enhance the spectral selectivity and photosensitivity of the device

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References

[1] *Keremane K. S., Abdellah I. M., Eletmany M. R., Naik P., Anees P., Adhikari A. V. (2025). Push-pull carbazole twin dyads as efficient sensitizers/co-sensitizers for DSSC application: effect of various anchoring groups on photovoltaic performance. J. Mater. Chem. C., 13(18):9258–9275. DOI: 10.1039/D4TC04612A.*

[2] *Bogomolec M., Glavaš M., Škorić I. (2024). BODIPY Compounds Substituted on Boron. Molecules. 29(21):5157. DOI: 10.3390/molecules29215157.*

[3] *Akyol, B., Cokluk, E. M., Ayhan, M. M., Tuncel Kostakoğlu, S., & Gürek, A. G. (2024). Tuning the Photophysical Properties of BODIPY Dyes and Studying Their Self-Assembly via Hydrogen Bonding. ACS omega, 10(1), 1716–1726.*

[4] *Chapran M., Angioni E., Findlay N. J., Breig B., Cherpak V., Stakhira P., Tuttle T., Volyniuk D., Grazulevicius J. V., Nastishin Y. A., Lavrentovich O. D., Skabara P. J. (2017). An ambipolar BODIPY derivative for a white exciplex OLED and cholesteric liquid crystal laser toward multifunctional devices. ACS Appl. Mater. Interfaces. 9(5):4750–4757. DOI: 10.1021/acsami.6b13689.*

[5] *Kim Y. R., Lee S., Kim J., Oh J., Kim J.-H., Ki T., Oh C.-M., Hwang I.-W., Suh H., Lee K., Kim H. (2023). Photostable organic solar cells based on non-fullerene acceptors with an aminated bathocuproine electron transport layer. J. Mater. Chem. A, 11(9):4220–4230. DOI: 10.1039/D2TA09327H.*

[6] *Luo Y., Fang S., Zheng N., et al. (2020). High-performance organic photovoltaic materials based on phthalocyanine derivatives. ACS Appl. Energy Mater., 3(2):1694–1701.*

[7] *Chen X., Yu B., Wang J., et al. (2023). Recent advances in organometallic photodetectors. J. Mater. Chem. C, 11(6):1850–1858.*

[8] *Li X., Peng X. H., Zheng B. D., Tang J., Zhao Y., Zheng B. Y., Ke M. R., Huang J. D. (2018). Chem. Sci., 9(9):2098–2104. DOI: 10.1039/C7SC05115H.*

[9] *Haider M., Zhen C., Wu T., Liu G., Cheng H. M. (2018). J. Mater. Sci. Technol., 34(9):1474–1480. DOI: 10.1016/j.jmst.2018.03.005.*

[10] *Bertrand B., Passador K., Goze C., Denat F., Bodio E., Salmain M. (2018). Coord. Chem. Rev., 358:108–124. DOI: 10.1016/j.ccr.2017.12.007.*

[11] *Zhou W., Guo H., Lin J., Yang F. J. (2018). Iran Chem. Soc., 15:2559–2566. DOI: 10.1007/s13738-018-1444-6.*

[12] *Kim N. H., Kim D. IntechOpen. 2018. DOI: 10.5772/intechopen.80349.*

[13] *Harrath K., Talib S. H., Boughdiri S. J. (2018). Mol. Model., 24:279. DOI: 10.1007/s00894-018-3821-6.*

[14] *Ruan Z., Zhao Y., Yuan P., Liu L., Wang Y., Yan L. J. (2018). Mater. Chem. B, 6(5):778–786. DOI: 10.1039/C7TB02924A.*

[15] *Niu G., Wang S., Li J., Li W., Wang L. J. (2018). Mater. Chem. A, 6(11):4823–4830. DOI: 10.1039/C8TA00161H.*

[16] *Antina E., Bumagina N., Marfin Y., Guseva G., Nikitina L., Sbytov D. (2022). Telegin F. Molecules, 27(4):1396. DOI: 10.3390/molecules27041396.*

[17] *Spector D., Abramchuk D. S., Bykusov V. V., et al. (2024). Russ. Chem. Rev., 93(10):RCR5136. DOI: 10.59761/RCR5136.*

[18] *Liu Y., Li Y., Yang Y. (2018). Adv. Mater., 30(19):1800466. DOI: 10.1002/adma.201800466.*

[19] *Claessens C. G., González-Rodríguez D., Rodríguez-Morgade M. S., Medina A., Torres T. (2018). Chem. Rev., 118(6):2632–2708. DOI: 10.1021/acs.chemrev.7b00420.*

[20] *Wang X., Zhan X. (2018). Chem. Soc. Rev., 47(10):2939–2960. DOI: 10.1039/C7CS00858A.*

[21] *Li J., Zhao Y., Tan H., Hu Y., Yang Y. J. (2018). Mater. Chem. A, 6(5):2345–2361. DOI: 10.1039/C7TA11376A.*

[22] *Yum J. H., Jang S. R., Humphry-Baker R., Grätzel M., Nazeeruddin M. K. (2018). Energy Environ. Sci., 11(1):84–93. DOI: 10.1039/C7EE00239A.*

[23] *Zhang Q., Cao G. (2018). Nano Energy,13:509–522. DOI: 10.1016/j.nanoen.2015.02.028.*

[24] *Bizet C., Rio J., van Lier J. E. (2019). J. Porphyr Phthalocyanines, 23(01n03):1–15. DOI: 10.1142/S108842461930001X.*

[25] *Yanık H., Koca A., Gül A. (2020). Dyes Pigments, 174:108048. DOI: 10.1016/j.dyepig.2019.108048.*

[26] *Chen Y., Liu Y., Wang Y., Zhang J., Liu J. (2021). ACS Appl. Mater. Interfaces, 13(5):6789–6798. DOI: 10.1021/acsami.0c20456.*

- *[27] Rio J., Bizet C., van Lier J. E. (2018). New J. Chem., 42(3):2145–2153. DOI: 10.1039/C7NJ04238A.*
- *[28] Guseva G., Antina E., Marfin Y., Bumagina N. J. (2022). Photochem. Photobiol. A Chem., 429:113964. DOI: 10.1016/j.jphotochem.2022.113964.*
- *[29] Djurišić A. B., Kwong C. Y., Lau T. W., Liu Z. T., Kwok H. S., Lam L. S. M., Chan W. K. (2003). Spectroscopic ellipsometry of metal phthalocyanine thin films. Appl. Opt., 42(31):6382–6387. DOI: 10.1364/AO.42.006382.*
- *[30] Telegin F., Sbytov D., Nikitina L., Antina E. (2023). Electrochim. Acta, 446:141922. DOI: 10.1016/j.electacta.2023.141922.*
- *[31] Liu Y., Zhang H., Wang J., Zhao Y. (2024). Thin Solid Films, 794:140312. DOI: 10.1016/j.tsf.2024.140312*

ГІБРИДНІ АКТИВНІ ШАРИ ДЛЯ ОРГАНІЧНИХ СОНЯЧНИХ ЕЛЕМЕНТІВ НА ОСНОВІ ПОХІДНИХ BODIPY ТА ФТАЛОЦІАНІНУ НІКЕЛЮ

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У відповідь на сучасні виклики органічної фотоніки та потребу в органічних фотодетекторах(OPD) із розширеним спектральним діапазоном і високою чутливістю у роботі запропоновано гібридні безфулеренові системи, що об'єднують металокомплекси фталоціаніну з іоном Ni^{2+} та барвників на основі борон-дипірометену (BODIPY). У цьому дослідженні розроблено та всебічно оцінено гетероструктуру на основі нікель (II) фталоціаніну (NiPc) і новосинтезованого сенситайзера BODIPY та bThBODIPY. Барвник bThBODIPY, що належить до класу BODIPY, характеризується максимумом поглинання близько 510 нм, тоді як новосинтезований сенситайзер BODIPY має максимум поглинання в області 600 нм. Обидва барвники утворюють стабільні тверді сполуки темно-червоного кольору, які добре розчиняються в органічних розчинниках (толуен, хлорбензол, дихлорметан, хлороформ, етилацетат), забезпечуючи формування однорідних тонких плівок, стійких до подальшої термічної обробки. Фоточутливість виготовлених пристроїв оцінювали на тонкоплівкових органічних фотодетекторах з архітектурою ITO/PEDOT:PSS/NiPc:sensitizer:bThBODIPY/BCP/Al. Активний шар формували методом центрифугування, оптимізувавши співвідношення NiPc до сенситайзера та з післятермообробкою. Під освітленням стандартним сонячним спектром AM 1,5 G (100 мВт/см^2) виготовлений пристрій продемонстрував стабільні фотоелектричні параметри. Зокрема, заповнювальний коефіцієнт (fill factor, FF) становив 16,4 %, а ефективність перетворення потужності (power conversion efficiency, PCE) – 0,32 %. Отримані результати підтверджують високий потенціал безфулеренових гібридних сполук NiPc–BODIPY для розширення спектральної чутливості та підвищення ефективності органічних фотодетекторів. Серед перспективних напрямів подальших досліджень – модифікація міжшарових інтерфейсів селективними буферними шарами, розроблення мультисенситайзерних систем з барвниками, що доповнюють один одного, та інтеграція структур, здатних захоплювати весь видимий і ближній інфрачервоний спектри.

Ключові слова: *гетероструктура, сонячні комірки, органічні фотодетектори, органічні фотоелектричні пристрої, похідні BODIPY, фталоціанін нікелю.*