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NEW THIOPHENE BASED MATERIALS FOR EMISSIVE LAYERS OF ORGANIC LIGHT-EMITTING DIODES

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Optoelectronic display devices have gained an important role in the modern world. Digital displays based on organic light-emitting diodes are taking one of the leading places among other displays due to high contrast and high-quality color gamut. The relative novelty of the technology is the reason for the insufficient number of researched materials for use in layers of organic light-emitting diodes. This paper analyzes the properties of molecular structures based on thiophene heterocycles, as well as the feasibility of their use for displays on exclusively organic light-emitting diodes and in complex technologies, such quantum dots color converter.

Three thiophene structures of type T (thiophene), TB (thiophene-benzene), TPy (thiophene-pyrrole) were chosen for the study. Modeling and computing of characteristics of molecular structures was performed with the software for quantum chemical calculations Gaussian 09 due to the wide range of quantum chemical methods implemented in it, as well as high efficiency and convenient user interface.

With the help of the selected software, modeling of molecules, optimization by B3LYP methods, and the values of HOMO and LUMO energy levels were calculated. Emission and absorption spectra of T, TB and TPy type structures were obtained. Based on the obtained results, the possible application of structures in the emitting layers of organic LEDs was determined. T-type molecules can be used as a material for creating a self-emitting layer for organic light-emitting diodes in the visible wavelength range. Molecules of the TB-type are suitable for creating devices with radiation in the ultraviolet range. Molecules of the TPy-type have no prospects for use in direct OLED radiation, but their characteristics allow us to propose these structures as sources of exciting radiation for the creation of devices with light color conversion technologies.

Keywords: *digital display; organic light-emitting diodes; thiophene; quantum dots color converter; GAUSSIAN 09.*

Introduction

Main advantages of organic light-emitting diodes (OLEDs) in comparison with other types of LEDs are high energy efficiency and contrast, small structure thickness, large viewing angle, abundant color gamut [1]. The key to research is the emissive layer, as the efficiency, intensity, and color of the radiation depend on it. One of the possible directions is the study of the properties of substances based on various heterocyclic compounds, which can be used both for direct OLED radiation and in the latest hybrid technologies, which include the quantum dot color converter (QDCC).

The purpose of this work is to study thiophene-based structures that satisfy the basic requirements for an emitting layer: a band gap from 1 to 5 eV, absorption and emission spectra in the visible and ultraviolet ranges. The width of the band gap is determined by the difference between the energy levels of the HOMO and LUMO orbitals in the energy structure of molecules. Modeling and computing of characteristics of these molecules will allow us to determine the possibility of effective use of new substances that can improve the operating characteristics and emission and absorption spectra of organic LEDs. For the modeling and analysis of thiophene structures, the work uses the methods built

into the quantum chemical modeling system Gaussian 09 [2].

1 Preconditions and means for solving problem

Organic LEDs consist of several layers of organic and inorganic compounds. The combination of layers allows you to expand the spectrum by wavelengths, control the half-width of each spectrum or reduce energy losses. There are 8 main types of layers, each of which performs its function [3] (shown in Fig. 1):

1. Substrate. Performs the function of the foundation for an OLED. It does not directly participate in the processes that are the cause of radiation, therefore, the choice of both organic and inorganic structures is possible. The determining factors are the degree of transparency, refractive index, strength, which depend on the type of organic LED.

2. Anode, towards which electrons move inside the structure. The anode layer can be made of organic or inorganic compounds. Materials are selected that have high transparency, since the output radiation is directed towards the anode.

3. Hole Injection Layer (HIL). The presence of this layer improves the efficiency of injection of positive charge carriers - holes [4].

4. Hole Transport Layer (HTL). The main function is to transport holes from the injection layer to the emitting layer.

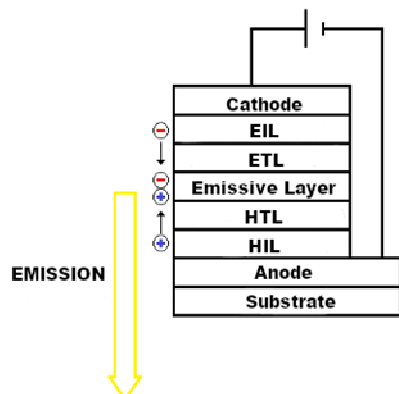


Figure 1. Structure of multilayer OLEDs

5. Emissive Layer. In this layer, the recombination of electrons and holes takes place, which is accompanied by the emission of a photon. Selecting the configuration of the molecular structure allows you to set the wavelength of radiation, which makes it possible to create LEDs with different wavelengths and radiation intensity.

6. Electron Transport Layer (ETL). Similarly to the hole transport layer, it performs the function of transporting electrons from the injection layer to the emitting layer.

7. Electron Injection Layer (EIL). The presence of this layer improves the efficiency of injection of negative charge carriers - electrons.

8. Cathode, from which electrons move inside the structure. It does not require the mandatory presence of organic molecules in the structure. It is possible to choose substances with a high degree of transparency for certain types of organic LEDs [3].

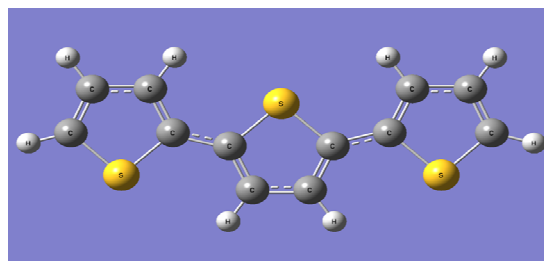
The main problem in the creation of organic LEDs is the insufficient research of materials for the manufacture of the emitting layer, since the most important processes (recombination of charge carriers and light emission) take place in this layer [5].

2 Solution

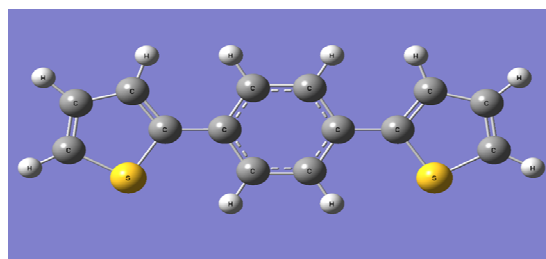
Three thiophene structures of type T (thiophene), TB (thiophene- benzene), TPy (thiophene-pyrrole) were chosen for the study. These molecules are simple for both research and synthesis, as they consist of three cycles, two of which are arranged symmetrically. The band gap of thiophene structures lies within defined limits (from 1 to 5eV), and the absorption and emission spectra are in the visible and near-ultraviolet ranges. Figures 2a, 2b, and 2c show T, TB, and TPy molecules, respectively, which were modeled and optimized in Gaussain 09 software.

The values of E_{HOMO} and E_{LUMO} in electronvolts were calculated using the corresponding built-in methods of the specified software. $E_g = E_{HOMO} - E_{LUMO}$ (gap width) was also calculated. The results are shown in Table 1 and in Fig. 3. The value for the HOMO and

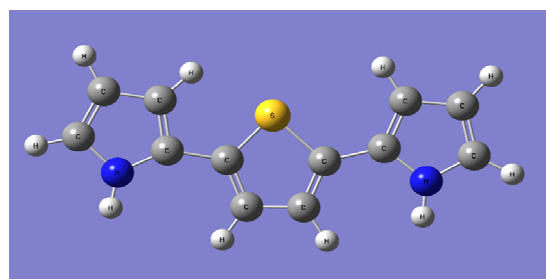
LUMO levels changes significantly depending on the molecular composition for the structures of the added rings (thiophene, pyrrole or benzene), which will be reflected in the ranges and positions of the emission and absorption spectra [6].



(a) Molecule T



(b) Molecule TB



(c) Molecule TPy

Figure 2. Researched molecular structures

3 Results and discussion

3.1 Absorption

Based on the optimized molecular structure, the absorption spectrum in the near-ultraviolet and visible light wavelength ranges was calculated by the TD-SCF method.

This method uses the calculation of spectra for unexcited molecules, the results of which are absorption spectra [6]. The results of the research carried out in the work are shown in Table 2 and on Fig. 4. The wavelengths for the maxima in the absorption spectrum fall on the border of the visible and near-ultraviolet ranges. For molecules of type T, the value lies in the visible range (violet color), for TB and TPy – in the near ultraviolet.

The value ϵ_a is the molar absorption coefficient at this wavelength. The molar absorption coefficient shows the optical density of a substance with a concentration of 1 mol/dm at an absorption layer thickness of 1 cm. The optical density (A) is a dimensionless quantity and is determined by the formula: $A = -\lg \frac{I}{I_0}$, where I – the intensity of the light beam falling on the substance, I_0 – the

intensity of the light beam that passed through the substance.

Table 1. Values of energy levels in molecules of type T, TB, TPy

Molecules	E_{HOMO} , eV	E_{LUMO} , eV	E_g , eV
T	-5.143	-1.687	3.456
TB	-4.544	-0.490	4.054
TPy	-4.599	-0.816	3.783

Table 2. Characteristics of the absorption spectra of the corresponding structures (T, TB, TPy)

Molecules	λ_{max} , nm	ε_a , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	OS
T	392.67	37403	0.9235
TB	328.57	36309	0.8961
TPy	353.78	27102	0.6691

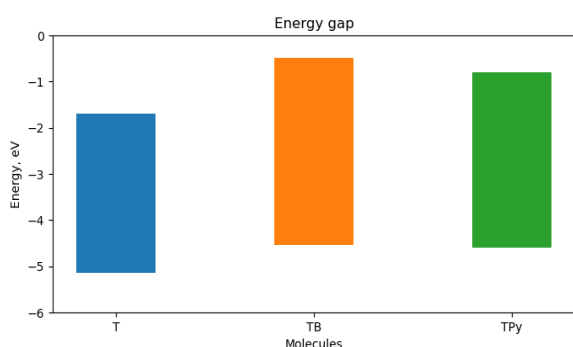
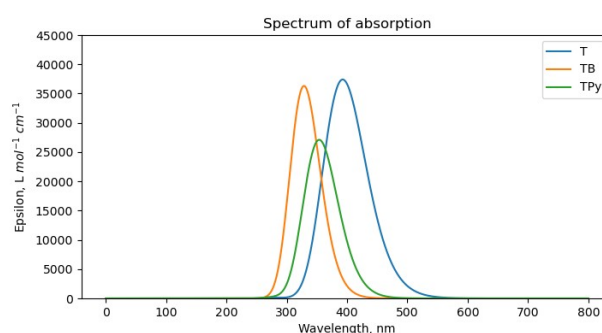


Figure 3. The position of the energy level of molecules T, TB, TPy

Figure 4. Molar absorption coefficient ε_a on the λ_{max} wavelength

The value ε_a depends only on the structure of the substance. For molecules with two thiophene heterocycles (T and TB), the values of the molar absorption coefficient are close to each other and differ significantly in comparison with a molecule with one thiophene heterocycle (TPy).

Oscillator strength (OS) in this case determines the probability of radiation absorption, which is the probability of transition between energy levels, at the wavelength corresponding to the absorption maximum, energy levels [3]. In the case of OLEDs, it is between the HOMO and LUMO levels. Analogously to the molar absorption coefficient, the value for a TPy molecule containing one thiophene heterocycle is significantly smaller.

The influence of different cycles in the structure of the structures can be seen on the graph of the dependence of the molar absorption coefficient on the wavelength (Fig. 4). The shift of the λ_{max} spectrum to the short-wavelength region from TB to T is due to the addition of bonds between molecules in additional cycles (bonds in the benzene, pyrrole, and thiophene cycles, respectively) [6].

3.2 Emission

The ZINDO method was used to determine the spectra of recombination radiation in the visible and near-ultraviolet ranges of the specified components. The ZINDO method examines the spectra of excited molecules, so the obtained data correspond to the

emission spectrum [2]. The main results are given in Table 3, the graphs are in Fig. 5.

For radiation, the maximum wavelength of the photoluminescence of the TB structure falls on the ultraviolet range, the TPy structure - the violet color of the visible range, the T structure - the blue color of the visible range.

In this case, ε_e corresponds to the molar emissivity coefficient. The corresponding increase in the coefficient difference for molecules of type TB and T indicates a more significant effect of the additional effect of the benzene cycle than that of the main thiophene cycle, as well as the influence of the width between the HOMO and LUMO levels.

The oscillator strength (OS), given in the table, determines the probability of emission of an excited molecule at the wavelength of the maximum emission intensity. The high power of the oscillator is an important criterion for the possibility of using the material in the radiating layer [6]. The difference between the values of the oscillator strength for different molecules is also explained by the influence of additional cycles [5]. Similarly to the absorption spectrum, there is a shift λ_{max} into the short-wavelength region from TB to T. For additional analysis, the Stokes shift (SS) was also determined, which is determined by the difference between the wavelengths of the maxima for radiation and absorption (Table 3).

The Stokes shift determines the amount of energy that is lost during nonradiative transitions of an excited atom. The value of the Stokes shift in units of

wavelength is the largest for a molecule of type T, whose emission and absorption maxima fall on the visible range of wavelengths [6].

Table 3. Characteristics of the emission spectra of the corresponding structures (T, TB, TPy)

Molecules	λ_{max} , nm	ϵ_e , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	OS	SS, nm
T	497.99	37459	0.8648	105.32
TB	368.72	43223	0.9662	40.15
TPy	407.68	30599	0.7554	53.90

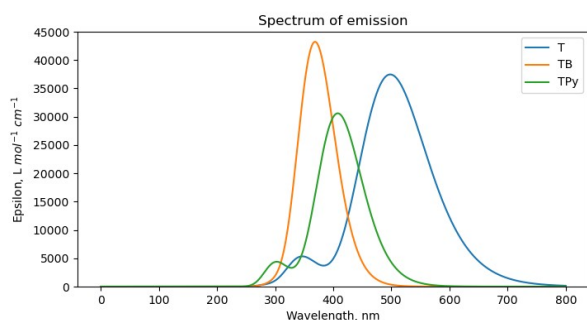


Figure 5. Molar emissivity coefficient ϵ_e on the wavelength λ_{max}

3.3 Analysis of application

The high oscillator strength (0.86) and the large half-width of the emission spectrum ($\Delta\lambda = 135$ nm) of the T-type molecules make it possible to directly use this material in emitting devices of the visible range based on organic light-emitting diodes: television screens, smartphones, computers, etc. The disadvantage is that most of the absorption spectrum falls into the visible range.

Molecules of the TB-type can be used in specialized organic light-emitting diodes for medical and biological purposes, the main requirements for which are radiation in the violet and ultraviolet ranges, as well as a small half-width of the spectra ($\Delta\lambda = 74$ nm, should not exceed 90 nm) [7]. Although the Stokes shift is relatively small (40 nm), the emission spectrum is quite narrow, and the probability of emission at the wavelength of maximum intensity is very high.

The shift of the radiation spectrum of the TPy-type molecule to the region of ultraviolet wavelengths is a significant drawback for the direct use of these structures for emitting devices in the visible range. However, these characteristics allow the use of these molecules in hybrid radiation technologies. One of the possible variants is the technology of quantum dots color converter, or QDCC [8].

The principle of QDCC operation is based on the possibility of converting absorbed radiation of a shorter wavelength by quantum dots into its own radiation of a longer wavelength. Due to the combination of an OLED and a QD layer, the whole device forms a green or red LED, which is a pixel in the display matrix [8]. As shown in Figure 6, color conversion can be divided into three main stages:

1. Absorption. Shorter wavelength radiation (blue and violet ranges of the visible spectrum) is absorbed by the layer of quantum dots. Absorption efficiency is defined as the ratio of the intensity of the absorbed radiation to the intensity of the initial radiation.

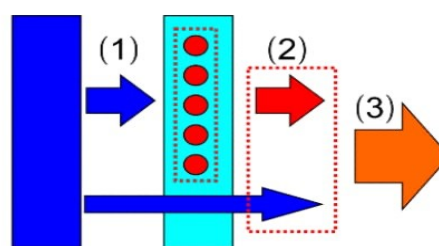


Figure 6. Principle of operation of QDCC [8]

2. Conversion. A layer of quantum dots changes the absorbed radiation of a shorter wavelength to its own radiation of a longer wavelength. The conversion efficiency is defined as the ratio of the intensity of the self-radiation of the quantum dots to the intensity of the absorbed radiation.

3. Radiation. Radiation occurs at the natural wavelength of the layer of quantum dots. At the output, the light of the initial wavelength is mixed with the converted light, which leads to a change in the color of radiation perception [9].

If the OLED emits a blue wavelength on a layer of quantum dots with its own red radiation, the human eye will perceive the output color of the radiation as orange (Fig. 6). The criteria for selecting LEDs for QDCC is peak emission in the blue or violet ranges, as well as absorption in the ultraviolet region [9].

Conclusion

The results of modeling and analysis confirm the possible use of thiophene structures in the production of OLEDs for use both in stand-alone devices and in color converters on quantum dots. The energy characteristics and spectra of thiophene structures of type T, TB and TPy satisfy the basic requirements for molecular structures in the emitting layers of organic LEDs. The stability of the structures and the simple synthesis add weight to the analysis and application of structures with the main thiophene ring between organic structures with different composition and structure.

The T-type molecules can be used as a material to create a self-emitting layer for organic light-emitting

diodes in the visible wavelength range. Molecules of the TB-type are suitable for creating devices with radiation in the ultraviolet range. Molecules of the TP-type have no prospects for use in direct OLED radiation, but their characteristics allow us to propose these structures as sources of excitation radiation for creating devices with light color conversion technologies.

References

- [1] V. C. Bender, T. B. Marchesan and J. M. Alonso, "Solid-State Lighting: A Concise Review of the State of the Art on LED and OLED Modeling," in *IEEE Industrial Electronics Magazine*, vol. 9, no. 2, pp. 6-16, June 2015. DOI: 10.1109/MIE.2014.2360324.
- [2] M. J. Firsich, G. W. Trucks, H. B. Schlegel and oth. Gaussian 09, Revision A.02, Wallingford CT, 2016.
- [3] B. Geffroy, P. le Roy, and C. Prat, "Organic light-emitting diode (OLED) technology: materials, devices and display technologies", *Polymer International*, vol. 55, is. 6, pp. 572-582, 2006. DOI: 10.1002/pi.1974
- [4] Dechun Z. *Chemical and photophysical properties of materials for OLEDs*. Woodhead Publishing Limited, 2013.
- [5] A. Laaperi, *Active matrix, organic light-emitting diodes (AMOLEDs) for displays*. Woodhead Publishing Limited, 2013.
- [6] N. Belghiti, M. Benani, S. Bouzzine, M. Hamidi, and M. Bouachrine, "The DFT chemical investigations of optoelectronic and photovoltaic properties of short-chain conjugated molecules", *Physical Chemistry Research*, vol. 2, pp. 11-20, 2014. DOI: 10.22036/PCR.2014.3819
- [7] T. Elze, C. Taylor, & P. J. Bex, "An evaluation of organic light emitting diode monitors for medical applications: great timing, but luminance artifacts", *Medical physics*, 40(9), 092701, 2013. DOI: 10.1118/1.4818056.
- [8] H. Zhiping, Y. Yongming, A. Muhammad Umair, P. Wenxiang, Zh. Shijie, and oth "Inkjet printed uniform quantum dots as color conversion layers for full-color OLED displays", *Nanoscale*, vol. 12, is. 3, pp. 2103-2110, 2020. DOI: 10.1039/C9NR09086J
- [9] C. Yan, X. Du, J. Li, X. Ding, Z. Li, and Y. Tang, "Effect of Excitation Wavelength on Optical Performances of Quantum-Dot-Converted Light-Emitting Diode," *Nanomaterials*, vol. 9, no. 8, p. 1100, Aug. 2019, DOI: 10.3390/nano9081100

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НОВІ МАТЕРІАЛИ НА ОСНОВІ ТІОФЕНУ ДЛЯ ВИПРОМІНЮВАЛЬНИХ ШАРІВ ОРГАНІЧНИХ СВІТЛОДІОДІВ

Оптоелектронні пристрої відображення інформації відіграють важливу роль у сучасному світі. Цифрові дисплеї на органічних світлодіодах посідають одне з провідних місць серед інших дисплеїв завдяки високій контрастності та якісній кольоропередачі. Відносна новизна технології є причиною недостатньої кількості досліджених матеріалів для використання в шарах органічних світлодіодів. У цій роботі проаналізовано властивості молекулярних структур на основі тіофенових гетероциклів, а також доцільність їхнього використання для дисплеїв на виключно органічних світлодіодах і в комплексних технологіях, таких як конвертер кольору на квантових точках.

Для дослідження було обрано три тіофенові структури типу Т (тіофен), ТВ (тіофен-бензол), ТРу (тіофен-пірол). Моделювання і дослідження молекулярних структур виконано за допомогою програмного пакету для квантово-хімічних розрахунків Gaussian 09 через широкий спектр реалізованих в ньому квантово-хімічних методів, високу ефективність та зручний інтерфейс користувача. В обраному програмному забезпеченні проведено моделювання молекул, оптимізація методами V3LYP та обраховано значення енергій НОМО та LUMO рівнів. Отримано спектри випромінювання та поглинання структур типу Т, ТВ та ТРу.

На основі отриманих результатів визначено можливе застосування структур у випромінювальних шарах органічних світлодіодів. Молекули типу Т можуть використовуватись як матеріал для створення самостійного випромінювального шару для органічних світлодіодів у видимому діапазоні довжин хвиль. Молекули типу ТВ придатні для створення пристроїв з випромінюванням в ультрафіолетовому діапазоні. Молекули типу ТРу не мають перспектив використання у безпосередньому випромінюванні OLED, проте їхні характеристики дозволяють пропонувати ці структури за джерела збуджуючого випромінювання для створення пристроїв з технологіями перетворення кольору світла.

Ключові слова: цифровий дисплей; органічний світлодіод; тіофен; конвертер кольору на квантових точках; Gaussian 09.

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