

Optical Properties and Quantum-Chemical Calculations of Various Bithienyl Derivatives of Benzene, Triazine and Triphenyltriazine as Organic Light Emitting Diodes

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Abstract

Derivatives of tris (2,2-bithiophen-5-yl) derivatives based on a benzene, a triazine or a triphenyltriazine core are presented for optical light emitting diode functionality. Optical properties as well as their corresponding molecular energy levels were investigated by UV-VIS absorption supported by fluorescence spectra. Furthermore, DFT and TDDFT calculations for obtained materials are presented to supplement the experimental data. It is demonstrated that HOMO - LUMO orbitals are delocalized uniformly on aromatic core and bithienyl substituents. Additionally, an OLED was built using synthesized compounds to facilitate electron transport and act as light emitting layer. Optical and charge transport properties along with good electrochemical stability confirm potential application of bithiophene-aromatic hybrids in electrochromic devices, light emitting electrochemical cells and spintronics.

Keywords: Bithiophene; Fluorescence spectroscopy; DFT calculations; TDDFT simulations; OLED

Introduction

Symmetrical starting materials are useful building blocks for designing complex target molecules. The structural symmetry can be used to reduce the number of steps necessary for the synthesis of a target molecule. Symmetrical molecules are also often used as central cores in various oligomers [1].

Organic π -conjugated structures containing thiophene units play an important role in the search for new materials and their novel applications such as organic solar cells [2,3] or organic field effect transistors [4]. In this case, the interest in thiophenes is associated with high hole mobility. Thiophenes with well-defined chemical structures have recently attracted great attention not only as an example of model compounds for conducting materials, but also as a new class of functional π -electron systems [5-11]. Branched oligothiophenes based on central phenyl core have come to the fore over the last several years, acting both as monomers in cross-linked semiconducting polymers [12-15] and as components of conjugated dendrimers [16-18].

Some of the 2,4,6-trisubstituted-1,3,5-triazine derivatives exhibit properties characteristic for liquid crystalline materials and find applications in coordination chemistry and crystal engineering [19-22]. On the other hand, star-shaped systems possessing donor-acceptor intramolecular arrangement can exhibit strong internal charge transfer band at low energy levels and therefore, have found applications in organic solar cells [23].

Over the last decade, highly efficient blue OLEDs have attracted considerable attention due to their potential applications in full color ultra-thin flat panel displays [24-30]. Organic light sources are currently made from either low molecular weight organic materials or polymers. For the former, the layer structure of the OLED is usually deposited on a rigid base made from glass or metal [31-34].

In the current work a series of planar donor-acceptor systems based on an electron-withdrawing triazine core substituted at the 2,4 and 6

positions with various electron-donating bithiophene branches are presented. The optical, structural and functional properties of these systems are compared to a series of symmetric molecules based on benzene and triphenyltriazine core. They are connected to bithiophene units and derivatives containing triazine core. For a systematic study and rational of OLED functionality UV-Vis, steady-state and time-resolved fluorescence spectroscopy have been performed. The studies are supported DFT calculations and TDDFT simulations. Finally functionalizing studies of an OLED device using synthesized low molecular weight material as electron transport with the new compounds as light emitting layers are summarized.

All compounds studied in this work were obtained by the Stille cross-coupling methodology according to the procedure reported in our previous work [35].

Results and Discussion

Optical measurements

Optical studies reveal valence electron transition in the visible and UV regime. All reported bithiophene derivatives were studied using UV-VIS spectroscopy. Electronic absorption spectra collected for bithiophene derivatives in chloroform are presented in Figure

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1. In most cases, the bithiophenes exhibit a single $n \rightarrow \pi^*$ transition peak associated with heteroatoms present in chemical structure. However, for different cores the bithiophene absorption has different origin. As an electron-withdrawing moiety, 1,3,5-triazine, lowers the LUMO energy more than that of the HOMO, resulting in a decrease in HOMO–LUMO gap, which can be observed as a bathochromic shift in absorption. On the other hand, the electron-donating methoxy groups contributed to significantly lower effect on the absorption wavelength because of the weaker interaction between the substituents and HOMO orbitals, however, a clear hypsochromic shift was also observed in this case. Consequently, when compared absorption spectrum collected for phenyl bithiophene derivative K11 ($\lambda_{\text{max}}=360$ nm), to the absorption spectra collected for the derivatives containing 1,3,5-triazine in the core (K13, K14) a significant bathochromic shift of about 40 nm can be observed. When comparing bithiophene derivative K11 spectrum to those of methoxyphenyl derivatives, a hypsochromic shift of 5 nm and 15 nm can be observed for 1-methoxyphenyl and 1,3,5-trimethoxyphenyl derivative, respectively. A second additional band peaking at around 270 nm is observed for derivative K14. This peak can be ascribed to three additional phenyls present in the structure and additional λ_{max} transitions. The bithiophene have moderate molar extinction coefficients (ϵ) from 60.000 for phenyl bithiophene, through 89.000 for 1-methoxyphenyl up to high 99.000 determined for triazinebithiophene. The summary regarding photophysical properties determined using UV-VIS measurements are presented in Table 1.

All reported bithiophene derivatives were also studied using steady-state and time-resolved fluorescence spectroscopy. Steady-state fluorescence spectra collected for bithiophene derivatives in chloroform are presented in Figure 2. In most cases, a multi peak emission spectrum is observed, which is associated with emissions from locally excited state and intermolecular charge transfer state. Similarly to absorption spectra, also for fluorescence spectra a slight hypsochromic shift (2-8 nm depending on derivative and band) is observed for methoxyphenyl derivatives. A peak at 460 nm, common for all derivatives, can be associated with bithiophene moieties. Unlike methoxy group, the triazine moiety introduces much stronger effect on fluorescence. Consequently, K13 emission is shifted towards the red of around 30 nm. The multimodal spectrum character is also maintained in this case. Further 15 nm shift is observed for K14. This fact can be associated with extended conjugation due to additional phenyl rings. Nevertheless, also in this case a noticeable shoulder can be observed at wavelengths characteristic for bithiophene.

The methoxyphenyl derivatives exhibit much lower quantum yield (around 10%) when compared to quantum yields of triazine derivatives (40-60%). The methoxyphenyl derivatives fluorescence has significantly shorter decay times (200-600 ps), while for triazine derivatives decay times over 1 ns are observed. On contrary, the triazine derivatives have significantly lower Stokes shifts (~ 3000 cm^{-1}) and larger rates of the radiative processes, which confirm higher fluorescence quantum yields. On contrary, the methoxyphenyl derivatives have larger Stokes shifts (over 4000 cm^{-1}) and higher non-radiative deactivation rates. Particularly for the derivative K12 the non-radiative processes constant was high due to very low decay time (200 ps).

Quantum-chemical calculations

For a rational of the OLED characteristics of the novel thiophene derivatives, as presented in Figure 3 and in Figure 4, the experimental and TDDFT-derived absorption spectra stay in good agreement, even though the theoretical energy gaps are approximately 0.3 eV lower than the experimental values, which correspond to a 40 nm larger bathochromic

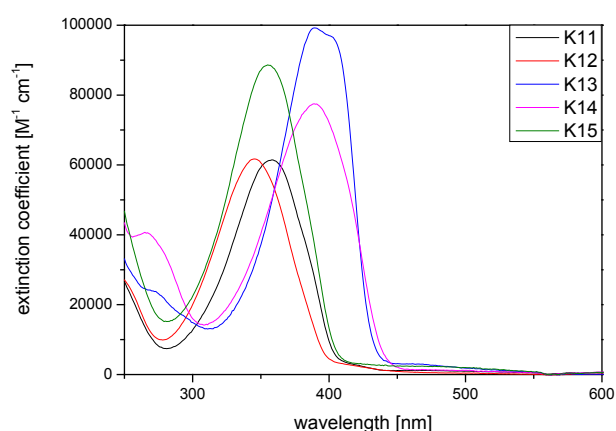


Figure 1: Electronic absorption spectra for all dyes in chloroform (in ex. coefficient units).

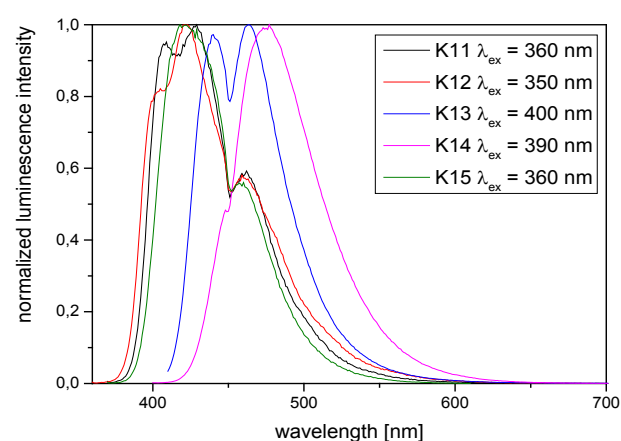


Figure 2: Normalized fluorescence emission spectra for all dyes in chloroform.

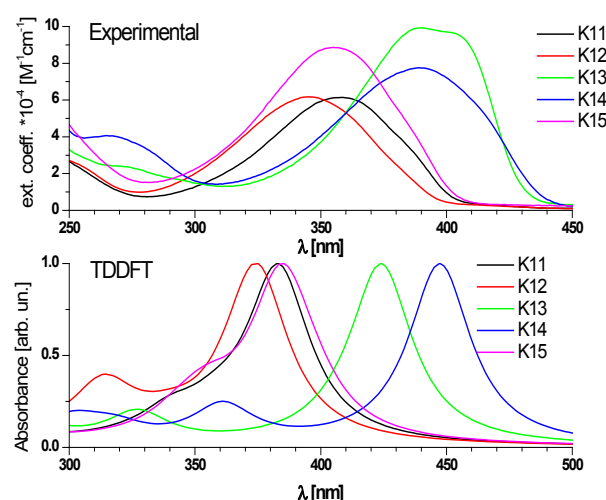


Figure 3: Experimental (top panel) and TDDFT (bottom panel) UV-VIS absorption spectra of the studied set of molecules.

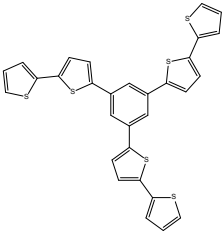
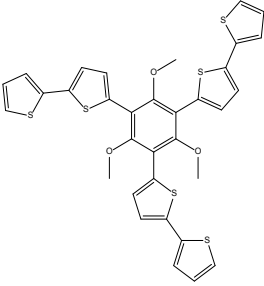
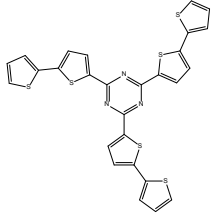
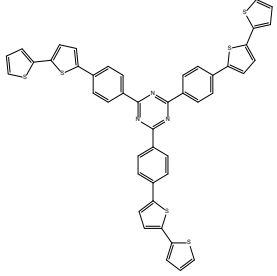
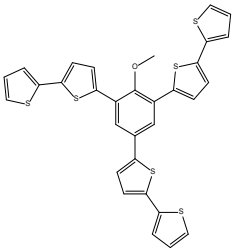
Name/Structure	λ_{ab} (nm)	ϵ (M ⁻¹ cm ⁻¹)	λ_{em} (nm)	Φ (%)	$\Delta\nu$ (cm ⁻¹)	τ (ns)	k_f (10 ⁹ s ⁻¹)	K_{nr} (10 ⁹ s ⁻¹)
K11 	360	61 000	408 428 462	11.7	3328	0.4	2.9	2.2
K12 	345	62 000	405 422 460	7.4	4294	0.2	3.7	46.3
K13 	390	99 000	440 463	41.7	2914	1.4	3.0	4.2
K14 	390	77 000	450 475	58.1	3419	1.1	5.3	3.8
K15 	355	89 000	420 458	12.7	4359	0.6	2.1	4.2

Table 1: Absorption and emission properties of the studied bistiophene derivatives.

shift. This energy gap underestimation is commonly encountered in DFT calculations. According to the TDDFT simulations, in all the molecules the first (i.e., of the lowest energy) absorption peak arises mainly from the HOMO-LUMO and HOMO-LUMO+1 transition.

All studied molecules are optically active i.e., absorb light in the UV or violet visible range and emit in the blue-violet spectral region. Among studied molecules, the triazine-based derivatives (K13 and K14) have significantly smaller energy gap than the other three derivatives. Based on the DFT HOMO-LUMO calculations presented in Figure 5, the difference in energy gap can be attributed mainly to the lower energy of the LUMO level in the triazine-centered molecules. Additionally, the orbital plots suggest another significant factor influencing the optical properties. The HOMO orbital delocalization observed for K13 and K14 encompasses all three side branches of the molecule, while in other compounds the delocalization is limited to two branches at most. This feature cannot result only from the steric hindrance of methoxy-groups twisting the side aromatic rings out of plane (K11 has no methoxy groups), but rather from the presence of the central triazine ring and its contribution to the HOMO orbital. According to the DFT calculated geometries, the dihedral angles between the central ring and the first aromatic ring in side branches are much smaller in the two triazine-based molecules (Tables 2 and 3) than in the benzene-centered ones. This difference influences the energy of frontier orbitals.

Similarly to TDDFT calculations for absorption spectra, the TDDFT-derived fluorescence emission spectra follow the same trend with approximately 0.3 eV difference between the triazine-containing molecules and those with benzene as the central ring. Similar difference can be observed in the experimental fluorescence spectra, where the triazine-containing molecules emit light at energy 0.15 eV lower than their benzene-based counterparts. For triazine-based bithiophenes, the fluorescence quantum yield is several times higher than for the benzene-centered ones, most likely due to the planar structure of the former allowing for efficient contribution of the π electrons to the optical transitions. As presented in Table 2, bithiophene substituted triazines also exhibit longer fluorescence decay times (1.4 ns for K14 vs. 0.2 ns for K12 and the domination of radiative over non-radiative processes).

OLED preparation and technical characterisation

The OLED devices of the various thiophene systems have been prepared according to the schematic device built-up sketched in Figure 6. Figure 6 highlights the layer structure of the OLED device with details on the used organic compounds and the function of each layer.

For functional studies, the device was connected to a DC. A blue light for the corresponding bithienyl derivatives was observed under such conditions. Figure 7 displays the working diode prepared using 2,4,6-Tris[p-(2,2-bithiophen-5-yl)-phenyl]-1,3,5-triazine and 1,3,5-tris(2,2-bithiophen-5-yl)-benzene as an active emitting layer. The hole-transport layer (HTL) was PEDOT: PSS poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) (Sigma-Aldrich).

OLED function tests were performed (Figure 7) varying the applied voltage from 0 to 24 V. Most OLEDs started normal light emittance with a yellow to orange color at 9 V improving the performance until 12-15 V, while the organic matrix started to emit light with blue color at 18-20 V, being the dominant light source at 24 V. No burning of any material has been detected up to the maximum voltage applied.

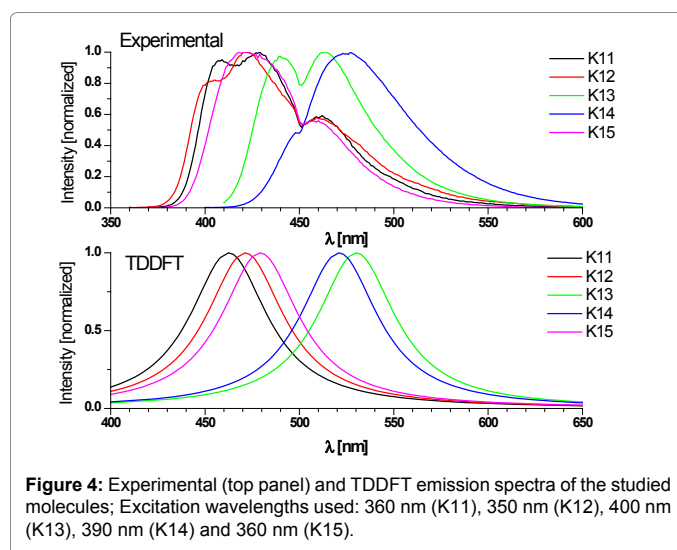


Figure 4: Experimental (top panel) and TDDFT emission spectra of the studied molecules; Excitation wavelengths used: 360 nm (K11), 350 nm (K12), 400 nm (K13), 390 nm (K14) and 360 nm (K15).

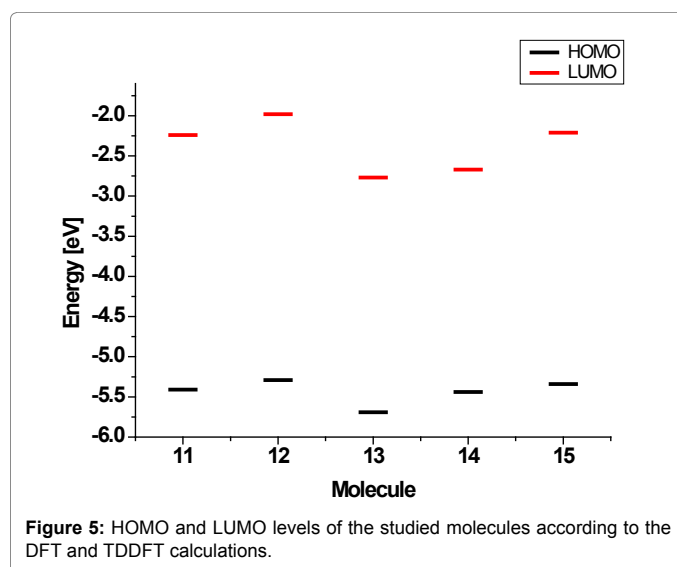


Figure 5: HOMO and LUMO levels of the studied molecules according to the DFT and TDDFT calculations.

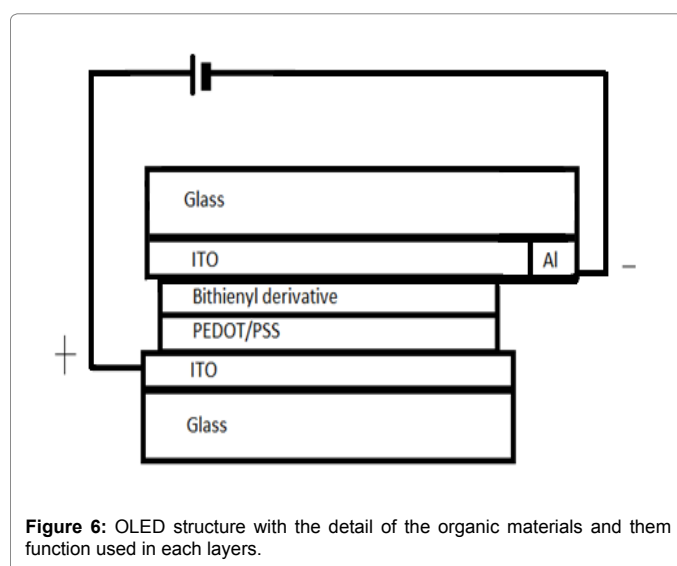


Figure 6: OLED structure with the detail of the organic materials and their function used in each layers.

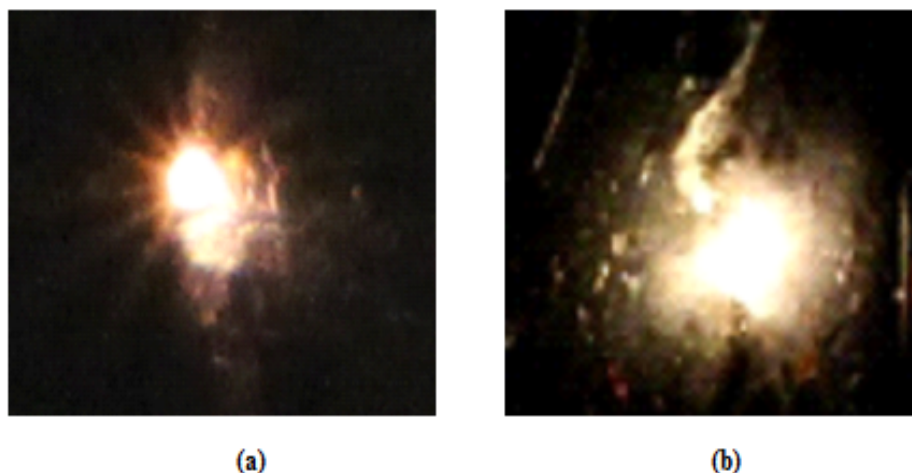


Figure 7: Effect with 12 V applied of the organic light-emitting diodes made from a) 2,4,6-Tris(2,2-bithiophen-5-yl)-1,3,5-trimethoxybenzene, b) 2,4,6-Tris(2,2-bithiophen-5-yl)-1-methoxybenzene.

	HOMO [eV]	LUMO (Eg-HOMO) [eV]	Eg (absorption) [eV/nm]	Eg (Emission) [eV/nm]	Dihedral angle in ground/excited state [deg]
K11	-5.41	-2.24	3.18/ 390	2.68/ 463	25/9
K12	-5.29	-1.98	3.31/ 375	2.63/ 471	54/34
K13	-5.69	-2.77	2.92/ 424	2.34/ 530	1/0
K14	-5.44	-2.67	2.77/ 448	2.38/ 521	1/0
K15	-5.34	-2.21	3.13/ 396	2.59/ 479	25/5

Table 2: Molecular parameters derived from (TD) DFT calculations.

Compound	HOMO	LUMO	HOMO – excited state	LUMO – excited state
K11				
K12				
K13				

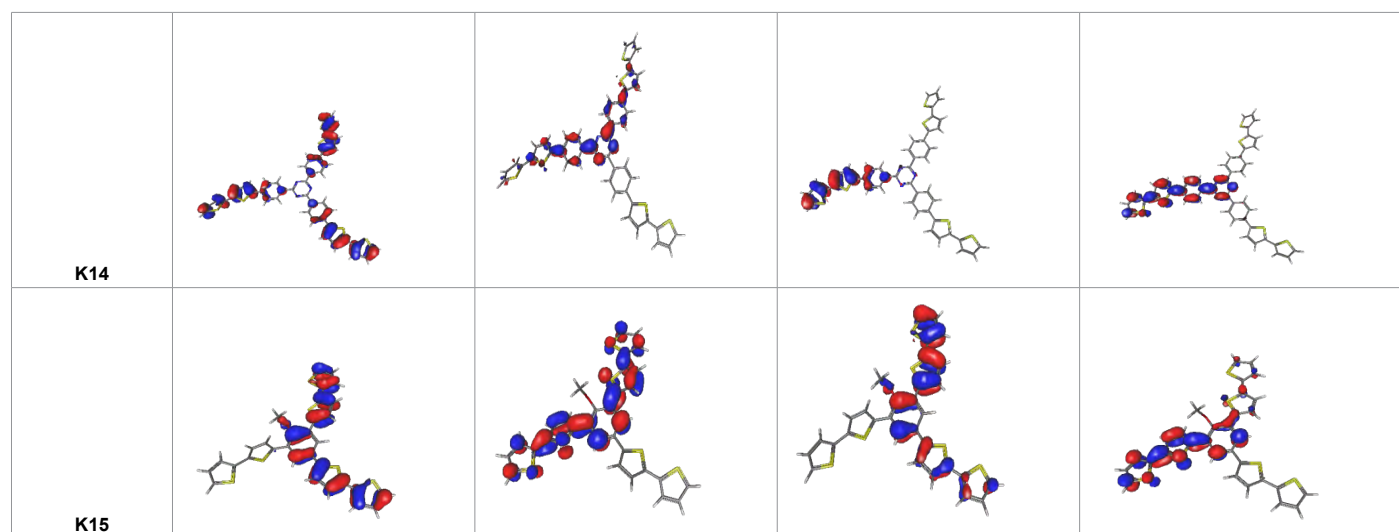


Table 3: DFT-derived HOMO and LUMO orbitals of the studied molecules.

Conclusions

In this work we have presented an extend study of photophysical, structural and theoretical characteristics of the new molecular materials based either on benzene, triazine or triphenyltriazine core, which was connected to bithiophene units for OLED fabrication. All studied molecules are optically active; absorb light in the UV or violet visible range and emit in the blue-violet spectral region. The replacement of the benzene by triazine increases the fluorescence quantum yield several times, most likely due to the planar structure of the former allowing for efficient contribution of the π electrons to the optical processes. Furthermore, we described DFT calculation and TDDFT simulations of presented materials, thus our experimental data is supported by quantum-chemical calculations. HOMO and LUMO orbitals are delocalized uniformly on benzene, triazine, triphenyltriazine core and bithienyl substituents. Theoretical calculation provided values for HOMO–LUMO gaps for neutral states of compounds. Therefore, the compounds described in this paper fulfill the technological requirements for materials to be successfully applied in the construction of organic–electronic devices as demonstrated by the OLED device presented in this paper. In order to verify the practical usefulness of the synthesized materials we built a prototype diode (OLED) using bithienyl derivatives of benzene and also bithienyl derivatives of triazine. Obtained OLEDs emitted yellow to orange light at a voltage of 12 V, clearly distinguishable from the blue light emitted at 22 V from the surrounding organic matrix.

Heterocyclic units can be used as innovative, efficient, cost-effective and environmentally friendly (mercury free) materials for light sources. These units can be flexibly designed and emit a broad spectrum of visible light, when appropriately tuned. The manufacturing of this type of light sources is one of the global research priorities, because it is based on a combination of new organic materials and economic production methods, thus enabling a variety of innovative products to be designed. Considerable progress in nanotechnology that has been made in recent years has resulted in the launch of the first electronic products made of organic materials.

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