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Synthesis and electrochemical characterization of new optoelectronic materials based on conjugated donor-acceptor system containing oligo-tri(heteroaryl)-1,3,5-triazines

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ABSTRACT

A series of novel oligoarylenes based on donor-acceptor system, containing triazine moiety as an electrontransporting central core, have been prepared by electrochemical polymerization. The redox behaviour of poly(2,4,6-tri[*p*-(2-(3,4-ethylenedioxythienyl))-phenyl]-1,3,5-triazine) was studied by cyclic voltammetry and triple in situ ESR/UV-vis-NIR spectroelectrochemistry to get more details on the type of charge carriers within the film. To obtain desired oligoarylenes, triazine-core monomers possessing various electrochromic side groups have been synthesized by the Stille cross-coupling methodology. The structures have been confirmed by ¹H NMR, ¹³C NMR, and elemental analysis. Monomers show good chemical stability in common organic solvents such as chloroform, dichloromethane or toluene and also exhibit excellent thermal stability over wide range of temperatures. Furthermore, their photophysical properties have been established with the use of fluorescence spectroscopy. Electrochemical results accompanied with fluorescence spectroscopy suggest that these derivatives of triazine can be successfully used in the fabrication of organic light-emitting diodes (OLEDs).

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1. Introduction

Donor-acceptor (D–A) systems, containing triazine unit as acceptor and heteroaryl group such as thiophen, furan or EDOT as donor, deserve much attention because of their high potential to be applied in molecular electronics and optoelectronic devices.

Over the past decade, considerable interest in the synthesis and characterization of compounds containing the 1,3,5-benzene or 1,3,5-triazine core has been observed [1]. Nevertheless, the application of the 1,3,5-triazine unit is advantageous over the 1,3,5-

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benzene core due to improved electron withdrawing properties and possessing of a larger nucleophilic susceptibility than the latter. In the field of supramolecular chemistry, triazine derivatives are commonly used, as they are well known to form hydrogen bonds and to favour p-p contacts, as recently shown to be involved in attractive anion-p interactions [2–4].

Furthermore, triazines have higher electron affinity (EA) values than 1,3,4-oxadiazoles (PBD) and 1,2,4-triazoles [5]; therefore they have been widely explored as building blocks for electron-transporting materials (ETMs) to be used for organic light-emitting diodes (OLEDs) [6–9]. Dendrimers containing triazine core are interesting because of their unique functional properties and potential applications in such fields as light power limiting, electroluminescence [10–14], medicine [15,16], and active materials in optoelectronic such as light-emitting and photovoltaic devices [6–9].

Importantly, the combination of triazine with an aryl group as for instance thiophene, furan or ethylenedioxythiophene improves chemical stability of the monomer and provides the polymer built from such monomers with enhanced mobility of the charge carrier. Polythiophene derivatives with optimized properties have been already used as active electrodes in several

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Scheme 1. Synthesis of monomers.

electrochemical/electronic devices [17,18]. It was also observed that poly(3,4-ethylenedioxy thiophene), PEDOT, is superior to its parent polythiophene in many categories crucial to organic electrochromic materials such as rapid switching and lower oxidation potential [19]. The low band gap of PEDOT allows the polymer to be almost transparent in the doped state and blue in the neutral state [20,21].

Increased understanding of conduction and redox-cycling processes of conducting polymers and oligomers has been achieved in the last decade by the application of in situ spectroelectrochemical techniques. Therefore the present work is focused on the newly synthesized star-shaped compounds with the central 1,3,5trazine ring and their analysis by voltammetry as well as by in situ UV-vis-NIR and EPR spectroelectrochemistry in order to follow different products of their electrochemical oxidation.

2. Experimental

2.1. Oxidative polymerization and spectroelectrochemistry

The cyclic voltammograms were obtained with a PAR 273 potentiostat (EG&G, USA) in a three-electrode system using platinum wires as working and counter electrodes and a silver wire as pseudo-reference electrode. Ferrocene (Fc) was added as the internal standard. Dichloromethane (DCM, dried) and acetonitrile (AN, puriss. absolute) both purchased from Fluka and ferrocene (p.a., \geq 98.0%) purchased from Merck were used as received. Tetrabutylammonium hexafluorophosphate (TBAPF₆, Fluka, dried under reduced pressure at 340K for 24h prior to use) was used as the supporting electrolyte. Polymer films were prepared by potentiodynamic polymerization of corresponding monomers on platinum-wire electrode in dichloromethane (DCM) solutions of 0.001 M monomer and 0.2 M supporting electrolyte by repetitive cyclic voltammetry. The so-prepared film was rigorously washed in a monomer-free electrolyte. The polymerization of **3c** was also done potentiostatically at 0.2 V vs. Fc/Fc⁺ in 0.2 M TBAPF₆/DCM using laminated conducting ITO-coated glass plate for spectroelectrochemistry of so-prepared polymer **p(3c)**. In situ ESR(electron spin resonance)/UV-vis-NIR spectroelectrochemical experiments were performed in the flat ESR cell filled with 0.2 M TBAPF₆/AN. The cell was filled and tightly closed in the glove box (water and oxygen content below 1 ppm) while the experiments were done in the optical ESR cavity (ER 4104OR, Bruker, Germany) outside the box. ESR spectra were recorded by the EMX X-band CW spectrometer (Bruker, Germany). UV-vis-NIR spectra were taken by TIDAS (J&M, Germany) spectrometer. Both the ESR spectrometer and the UV-vis-NIR spectrometer were linked to a HEKA potentiostat PG 285. Triggering was performed by the software package PotPulse 8.53 (HEKA Electronic, Germany).

2.2. Photophysical characterization

The electronic absorbance and fluorescence spectra were recorded on a Lambda UV/Vis spectrophotometer (Perkin Elmer) and a Fluoromax 3 spectrophotomether (Jobin Yvon), respectively. For the purposes of time-resolved fluorescence spectroscopy, the frequency doubled output (SHG) of a Titan Sapphire Laser (Tsunami 3960; Spectra Physics) was used to excite samples. The luminescence was detected in a right angle configuration to the incoming beam. A multichannel plate (ELD EM1-132/300; Europhoton GmBh) coupled to a FL920 fluorescence lifetime spectrometer (Edinburgh Instruments) was used for the signal detection. The time-resolved emission was collected in the time-correlated single photon counting mode. The fluorescence quantum yields were measured on a PL Quantum Yield measurement system C9920-02 with an integration sphere (Hamamatsu, Japan).

2.3. Synthesis

We designed the molecular structures of a group of monomers containing triphenyltriazine moieties and elaborated multiple-step reaction routes for their synthesis (Scheme 1). The cyclization of 4-bromobenzonitrile was achieved by the addition of trifluo-romethanesulfonic acid in chloroform, which gave arylbromide **2**. The palladium-catalyzed Stille cross-coupling reaction of derivative **2** with 2-(tributylstannyl)arylenes gave the desired products **3a–e** in yield of 59–82%. All the monomers were characterized by NMR spectroscopic methods and elemental analysis.

2.3.1. General

All chemicals, reagents, and solvents were used as received from commercial sources without further purification, except tetrahydrofuran (THF) and toluene, which were distilled over sodium/benzophenone. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on a Brucker 300 MHz and 250 MHz spectrometer. Chemical shifts are denoted in δ unit (ppm) and were referenced to internal tetramethylsilane (0.0 ppm). The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet) and m (multiplet). Preparative column chromatography was carried out on glass columns of different sizes packed with silica gel Merck 60 (0.035–0.070 mm).

2.3.2. Preparation of 2,4,6-tri(p-bromophenyl)-1,3,5-triazine (2)

Trifluoromethanesulfonic acid (6.00 g, 40 mmol) was quickly added to a vigorously stirred solution of 4-bromobenzonitrile (3.64 g, 20 mmol) in dry CHCl₃ (150 mL) at 0 °C. After stirring for 1 h, the solution was stirred for 24 h at room temperature. Then 150 mL of water was added and the mixture was stirred for 2 h. The solution was filtrated and the filtrate was washed twice by water and cold chloroform. The white microcrystals were dried in exsiccator (2.9 g, 80%, M_p > 320 °C).

2.3.3. General procedure for the preparation of 2,4,6-tri[p-(2-aryl)-phenyl]-1,3,5-triazine (**3a**-e)

To 2,4,6-tri(p-bromophenyl)-1,3,5-triazine (**2**) (1.09 g, 2.0 mmol) dissolved in 250 mL of anhydrous toluene under a nitrogen atmosphere was added a solution of 2-(tributylstannyl)aryl (6.6 mmol) and Pd(PPh₃)₄ (0.460 g, 0.4 mmol) in 150 mL of toluene. The resulting mixture was stirred for 4 days at 120 °C. After this time, the mixture was cooled down to room temperature. Water was added and the resulting solution was extracted three times with 50 mL portions of CHCl₃. The combined organic layers were washed with 50 mL of brine, dried over MgSO₄ and evaporated to dark brown oil. The crude product was purified by column chromatography (silica gel, hexane/AcOEt, 10:1).

2,4,6-*Tri*[*p*-(2-*thienyl*)-*phenyl*]-1,3,5-*triazine* (**3a**). Light yellow solid (M_p = 309–310 °C, 80%). ¹H NMR (300 MHz, CDCl₃) δ = 8.71 (d, *J* = 8.4 Hz, 6H); 7.77 (d, *J* = 8.4 Hz, 6H); 7.46 (dd, *J* = 3.6, 0.9 Hz, 3H); 7.36 (dd, *J* = 5.0, 0.8 Hz, 3H); 7.14–7.11 (m, 3H). ¹³C NMR (300 MHz, CDCl₃) δ = 171.0; 143.6; 138.2; 135.1; 129.6; 128.3; 126.0; 125.8; 124.2. Elemental analysis for: C₃₃H₂₁N₃S₃ Calc.: C, 71.32; H, 3.81; N, 7.56. Found: C, 71.47; H, 3.61; N, 7.68.

2,4,6-*Tri*[*p*-(2-*fury*])-*pheny*]-1,3,5-*triazine* (**3b**). Deep yellow solid ($M_p = 208-209 \degree C$, 76%). ¹H NMR (250 MHz, CDCl₃) $\delta = 8.80$ (d, J = 8.4 Hz, 6H); 7.88 (d, J = 8.4 Hz, 6H); 7.58 (d, J = 3.3 Hz, 3H); 6.56–6.54 (m, 3H). ¹³C NMR (250 MHz, CDCl₃) $\delta = 171.0$; 153.5; 143.0; 135.0; 134.4; 129.4; 123.8; 112.0; 107.0. Elemental analysis for: C₃₃H₂₁N₃O₃ Calc.: C, 78.09; H, 4.17; N, 8.28. Found: C, 78.41; H, 4.33; N, 8.11.

2,4,6-*Tri*[*p*-(2-(3,4-ethylenedioxythienyl))-phenyl]-1,3,5-triazine (**3c**). Braun solid (M_p = 156-157 °C, 82%). ¹H NMR (250 MHz, CDCl₃) δ = 8.71 (d, *J* = 8.3 Hz, 6H); 7.90 (d, *J* = 8.4 Hz, 6H); 6.39 (s, 3H); 4.39-4.28 (m, 12H). ¹³C NMR (250 MHz, CDCl₃) δ = 170.9; 142.4; 139.1; 137.1; 134.2; 129.2; 125.6; 117.0; 99.0; 64.8; 64.4. Elemental analysis for: C₃₉H₂₇N₃O₆S₃ Calc.: C, 64.18; H, 3.73; N, 5.76. Found: C, 64.31; H, 3.60; N, 5.98.

2,4,6-*Tri*[*p*-(2-*thiazolyl*)-*phenyl*]-1,3,5-*triazine* (**3d**). Yellow solid ($M_p = 282-284 \degree C$, 65%). ¹H NMR (250 MHz, CDCl₃) $\delta = 8.80$ (d, J = 8.4 Hz, 6H); 8.16 (d, J = 8.5 Hz, 6H); 7.96 (d, J = 3.2 Hz, 3H); 7.42 (d, J = 3.2 Hz, 3H). ¹³C NMR (250 MHz, CDCl₃) $\delta = 171.2$; 167.5; 144.2; 137.4; 137.3; 129.6; 126.8; 119.5. Elemental analysis for: C₃₀H₁₈N₆S₃ Calc.: C, 64.49; H, 3.25; N, 15.04. Found: C, 64.17; H, 3.62; N, 15.32.

2,4,6-*Tri*[*p*-(2-oxazolyl)-phenyl]-1,3,5-*triazine* (**3e**). Green solid ($M_p > 310$ °C, 59%). ¹H NMR (250 MHz, CDCl₃) $\delta = 8.87$ (d, *J* = 8.5 Hz, 3H); 8.68 (d, *J* = 8.3 Hz, 6H); 8.25 (d, *J* = 8.5 Hz, 3H); 7.39 (d, *J* = 8.2 Hz, 6H). ¹³C NMR (250 MHz, CDCl₃) $\delta = 171.7$; 161.6; 148.1; 139.1; 138.2; 133.7; 129.3; 126.5. Elemental analysis for: C₃₀H₁₈N₆O₃ Calc.: C, 70.58; H, 3.55; N, 16.46. Found: C, 70.37; H, 3.40; N, 16.72.

3. Result and discussion

3.1. Electropolymerization of monomers

Different processes during oxidation of compounds **3a–e** at a scan rate of $0.1 V s^{-1}$ were recorded in their dependence on the terminal arm moieties. Dominant dimerization reactions were observed for **3b**, **3d** and **3e** oxidation [22]. Only for monomers **3a** and **3c** the oxidation leads to the electrodeposition of an electroactive material on the electrode surface. The half-peak oxidation potential of the monomer **3a** is $E_{p/2} = 0.88 V vs$. Fc/Fc⁺ in DCM containing 0.2 M TBAPF₆. In the first cyclovoltammetric scan going to the anodic potentials up to 0.7 V vs. Fc/Fc⁺ no redox processes were observed within the potential region from $-0.6 V to +0.7 V vs. Fc/Fc^+$ (black line in Fig. 1a). Going to the region of the first oxidation peak for **3a** new redox processes are observable in the consecutive scans (2nd, 3rd and 4th cyclovoltammetric scan in Fig. 1a) and a fast adsorption on the working electrode takes place.

The further electropolymerization process made by potential scanning between -0.8 V and +1.1 V vs. Fc/Fc⁺ is shown in Fig. 1b (5th–9th cyclovoltammetric scan). The increase in current with every potential cycle, resulting from the redox processes of the



Fig. 1. Potentiodynamic polymerization of **3a** in 0.2 M TBAPF₆/DCM, scan rate 0.1 V s⁻¹. (a) Black line 1 – first cyclovoltammetric scan going to 0.7 V as reference, red line 2 – **3a** oxidation starting at –0.4 V, green line 3 – third CV scan in the same potential region, blue line 4 – fourth CV scan starting at 0.1 V and going both to the anodic and cathodic region. (b) Further potentiodynamic polymerization from 5th to 9th CV scan at starting potential of 0.1 V (all potentials are referred vs. Fc/Fc⁺, platinum-wire working electrode). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. (a) Cyclic voltammograms obtained during potentiodynamic polymerization of **3c** in 0.2 MTBAPF₆/DCM at scan rate of 0.1 V s⁻¹ in the potential region from -1.6 V to 0.25 V vs. Fc/Fc⁺ using starting potential -0.6 V for each CV scan (line numbers represent the corresponding CV scan). (b) CV trace of **p(3c)** in monomer-free 0.2 M TBAPF₆/AN electrolyte at scan rate of 0.1 V s⁻¹ (platinum-wire working electrode, 6 consecutive CV scans).

film, indicates a continual growth of conducting material on the electrode. Generally, very complex redox behaviour was observed both during electropolymerization of 3a and for prepared polymer film on the electrode. This indicates a wide variety of oxidation products. Different chain lengths, regions with various degrees of crystallinity as well as the presence of dimers are expected. Better and less ordered polymer structures of different crystallinity have been already reported for other polythiophene derivatives [23-26]. The presence of the segments of different effective conjugations also causes complexity of such electrochemically formed film [27]. Additionally, concerning the occurrence of new cathodic peak in the back scan with reduction potential strongly shifted to the negative potentials in comparison to the oxidation peak of 3a (peak marked with asterisk in Fig. 1b) we propose the presence of relatively stable short dimeric dicationic structures (sigma-dimers) within the film (for a review on self-association of radical ions see [28]). Concerning all observations and processes described above we can conclude that polymer film **p(3a)** prepared electrochemically represents a complex heterogeneous system.

In contrast to **3a** the oxidation potential of the monomer **3c** is much lower (half-peak potential $E_{p/2} = 0.11$ V vs. Fc/Fc⁺) and going up to 0.25 V vs. Fc/Fc⁺ only two new well-defined reversible redox couples arise at -0.35 V and 0.10 V vs. Fc/Fc⁺ upon repetitive cycling



Fig. 3. Cyclic voltammograms obtained during potentiodynamic polymerization of **3c** in 0.2 M TBAPF₆/DCM at scan rate of 0.1 V s^{-1} in the potential region from -1.6 V to 0.9 V vs. Fc/Fc⁺ using starting potential -0.6 V for each CV scan (line numbers represent the corresponding CV scan; first two CV scans were performed in broader potential region; platinum-wire working electrode).

in DCM containing 0.2 M TBAPF₆ (Fig. 2a). The polymerization made by potential scanning in this potential region leads to a fast adsorption on the working electrode resulting in a smooth film. In the next step, after washing in free monomer electrolyte, the film was redox cycled in 0.2 M TBAPF₆ in acetonitrile. During this pre-treatment process the rest monomers and short chains within the film are oxidized, which leads to further cross-linking within the film (Fig. 2b). The film prepared in such manner exhibits completely reproducible redox behaviour in 0.2 M TBAPF₆/acetonitrile electrolyte similar to the recently electrochemically synthesized polymers containing star-shaped molecules based on a triazine core substituted with short chain oligotiophene [29]. We observed two well-defined voltammetric main peaks with $E_{1/2} = -0.35$ V and $E_{1/2} = 0.10$ V vs. Fc/Fc⁺ with the peak separation of 0.02 V indicating well-defined adsorbed film and a reversible oxidation. The phenomenon we observed gives evidence for good stability and high conductivity of the film. It was recently confirmed that electropolymerization of star-shaped oligomers containing oligothiophene arms resulted in the formation of highly redox active, cross-linked hyperbranched



Fig. 4. UV–vis–NIR spectra measured in situ during the cyclic voltammetry of **p(3c)** deposited on ITO electrode in 0.2 M TBAPF₆/AN (scan rate $v = 0.002 V s^{-1}$) in the potential region from -0.8 V to +0.2 V vs. Fc/Fc⁺. 21 UV–vis–NIR spectra were recorded during cyclovoltammetric scan.



Fig. 5. (a) Spectroelectrochemical cell (1 – **p(3c)** deposited on ITO electrode, 2 – laminated ITO plate with a gold foil contact, 3 – Ag wire reference electrode, 4 – ESR flat cell). (b) Chronoamperometric ESR/UV–vis–NIR spectroelectrochemistry of **p(3c)** film on ITO electrode recorded in 0.2 M TBAPF₆/AN before (black lines) and after switching the potential (coloured lines). Insets in (b)–(f): corresponding ESR spectra measured after potential switch (experimental curves are marked with the corresponding applied potential in volts vs. Fc/Fc⁺). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

polymers, which led to systems with good conductivities, indicating the presence of multiple pathways for charge carriers provided by the branching units [30].

by cycling in the large potential region from -1.6 V to 0.9 V vs. Fc/Fc⁺ (Fig. 3) with a variety of redox processes. This indicates the forma-

tion of complex reaction mixture with cross-linked hyperbranched

structures, dimeric forms and multistep redox processes as will

be discussed below. It should be noted that very low solubility

of such highly cross-linked networks hindered detailed structural

Similar to **3a** complex redox behaviour was also indicated for **3c**

characterization in solution similar to other triazine-thiophene conjugated systems [29].

3.2. Spectroelectrochemistry of polymer p(3c)

The redox behaviour of polymer film **p(3c)** prepared by the electrochemical polymerization of **3c** in DCM solutions was studied by triple in situ ESR/UV–vis–NIR spectroelectrochemistry to get more details on the type of charge carriers within the film. Optically transparent indium tin oxide (ITO)-coated glass was used as electrode material. The UV–vis–NIR spectra taken simultaneously during cyclovoltammetry of $\mathbf{p(3c)}$ film in acetonitrile (AN) containing 0.2 M TBAPF₆ on ITO working electrode (scan rate 0.002 V s⁻¹) are shown in Fig. 4.

Absorbance maximum of neutral $p(3c)^0$ film was found at 520 nm confirming a high pi-conjugation length. Two polaroniclike transitions at 795 nm and 1300 nm are observed with a slight shift to higher energies by increasing potential. During further oxidation still at first oxidation peak several optical transitions are observed and they shift to higher energy up to stable 685 nm and 1137 nm. Concerning the literature data and the shape of the first oxidation peak measured for the investigated polymer film **p(3c)** we propose that the first voltammetric peak consists of two consecutive one-electron transfers. It was generally observed with long chain oligomers and other extended pi-systems that the simultaneous transfer of two electrons take place upon oxidation [31]. At a very low oxidation state the di-ionic spinless structures of the polymer chains are dominant. Simultaneously a small amount of polaronic states **p(3c)¹⁺** (ESR active states) is formed due to a comproportionation reaction with the neighbouring neutral segments. Formally this corresponds to a successive two-electron transfer with the first and second formal oxidation potentials in inverted order. Consequently at first oxidation peak the increase of ESR intensity is observed at the beginning of oxidation which then decreases upon further doping. By increasing the electrode potential to the value slightly behind the first peak a slight decrease of ESR intensity was observed confirming ESR silent character of dications p(3c)²⁺ [22].

At more anodic potentials in the region of the second voltammetric peak a new well-defined optical band at 940 nm appears upon oxidation accompanied with further small peaks at 1400 nm and new absorption above 1600 nm. This band is attributed to the ESR active trication **p**(**3c**)^{**3**+} as rapid increase of ESR intensity was observed at this stage of oxidation. By increasing the electrode potential further to the higher potentials (0.7 V vs. Fc/Fc⁺) new strong optical energy transition was observed at 815 nm (see Fig. 5d). Simultaneously the ESR intensity decreases going from the third to the fourth oxidation step confirming the formation of ESR silent tetracation **p(3c)**⁴⁺. This assignment was further supported by additional chronoamperometric ESR/UV-vis-NIR spectroelectrochemistry of p(3c) film on ITO electrode (Fig. 5) recorded in 0.2 M TBAPF₆/AN before and after switching from the certain potential to another one. Potential step chronoamperometry, switching between the various charged states, accompanied with ESR and UV-vis-NIR spectroscopy gives unambiguous attribution of experimental spectra to each redox state. ESR and UV-vis-NIR spectra were measured immediately after potential change to the fixed value. Fig. 5b shows experiment with potential step from -0.8 V (black line in UV-vis-NIR spectra) to -0.3 V vs. Fc/Fc⁺ (see four coloured UV-vis-NIR spectra immediately measured after potential change and corresponding ESR spectrum in Fig. 5b). Rapid and reversible changes were observed in a sub-second range after potential change confirming high redox stability and reversibility of the polymer upon anodic charging. Similar behaviour was found for switching between all redox states (Fig. 5b-f). A maximum ESR intensity was found for the tricationic state (Fig. 5c) while minimum ESR intensity was observed for neutral state and tetracation (Fig. 5d,f). These experiments confirm reversible redox behaviour of polymer **p(3c)** upon oxidation switching between all redox states even going up to tetracation.

3.3. Photophysical properties of triphenyltriazine derivatives

In order to establish the photophysical properties of the newly synthesized triphenyltriazines, electronic absorbance, molar extinction coefficient at the excitation wavelength, fluorescence



Fig. 6. Electronic absorbance, fluorescence excitation and emission spectra of 5×10^{-6} M solution of **3a** (TTT) in dichloromethane.

excitation and emission accompanied with quantum yield and fluorescence lifetime have been separately determined in CH₂Cl₂ for each compound. Electronic absorbance, fluorescence excitation and emission spectra of 5×10^{-6} M solution of **3a** in CH₂Cl₂ are presented in Fig. 6 and **3b** in Fig. 7. The electronic absorbance spectrum of compound **3a** exhibits two well-separated bands responsible for two electronically active transitions to the excited states. The first sharp band peaks at 265 nm as being consequence of $\pi - \pi^*$ transition and the second structureless responsible for $n-\pi^*$ transitions has maximum at 345 nm. Noticeable these compounds have high molar extinction coefficients indicating that the light is strongly absorbed at the excitation wavelength, which is desirable for optoelectronic application. As typically observed for free molecules in solution, the fluorescence excitation has the same shape and relative ratio between peaks as absorbance spectrum. Consequently, excitation of the molecule at 340 nm leads to the emission of fluorescence having the half width of 70 nm (determined by the fitting to the Lorentz function) in the range from 395 nm to 465 nm peaking at 425 nm (green light). High quantum yield being in the range from 0.36 to 0.42 depending on a derivative is another advantage supporting the idea of application these materials in optoelectronic.



Fig. 7. Electronic absorbance, fluorescence excitation and emission spectra of 5×10^{-6} M solution of **3b** (TFT) in dichloromethane.

Table 1

Maxima of electronic absorbance, fluorescence excitation and emission spectra accompanied with molar extinction coefficient at the excitation wavelength, quantum yield and fluorescence lifetime of all triphenyltriazine derivatives studied by steady-state and time-resolved fluorescence spectroscopy.

Compound	$\lambda_{abs}\left(nm\right)$	ε (L mol ⁻¹ cm ⁻¹)	$\lambda_{em}\left(nm ight)$	$\phi_{ m f}$	$\tau_{\rm f}({\rm ns})$
3a 3b 2a	265, 340 265, 345	26,780 32,930	415 425	0.36	1.65 2.29
3C	265, 365	38,460	450	0.42	2.33



Fig. 8. Electronic absorbance spectrum of 5×10^{-6} M solution of 3c (TET) in dichloromethane.

The decay of fluorescence of studied compounds excited at 350 nm and collected at emission wavelength of each derivative varies from 1.65 ns to 2.33 ns. All the photophysical properties for the derivatives studied by both steady-state and time-resolved fluorescence spectroscopy are gathered in Table 1.

3.4. Absorption properties

In the case of reference materials the spectra of the 2,4,6-tri[p-(2-(3,4-ethylenedioxythienyl))-phenyl]-1,3,5-triazine – TET (**3c**) reveal a progressive bathochromic shift of the absorption maxima with increasing length of the conjugative system exhibiting absorption maximum in the range from 230–270 nm to 340–390 nm (Fig. 8). This trend is in accordance with homologous series of conjugated oligothiophenes. Further, the thiophene derivatives of TTT (**3a**) show a similar intense absorption as compared to the latter oligothiophenes with a maximum absorption wavelength of 345 nm. For these reasons it has to be assumed that the donor-systems of the thiophenetriphenyltriazines are larger than the corresponding pristine oligothiophene moieties themselves. This assumption is further supported by the absence of any distinct absorption maxima in the region around 300 nm that could be attributed to the absorption of a triphenyltriazine moiety.

4. Conclusions

Based on an effective, iterative, palladium-catalyzed crosscoupling protocol, a homologous series of triphenyltriazine derivatives have been obtained in good yields. Triazine moiety as an electron-transporting central core, thought separated from the thiophene, furane, or EDOT groups by the *p*-phenylene spacers, can display excellent redox stability. Anodic oxidation of monomers **3a** and **3c** leads to the electrodeposition of an electroactive material on the electrode surface. Oligomers containing EDOT group provide the final polymer film with well-defined and reversible redox behaviour in contrast to the oligomers based on thiophene and furane. Spectroelectrochemical experiments confirm reversible redox behaviour of polymer **p(3c)** upon oxidation switching between all redox states even going up to tetracation. The electrochemical behavior of the oligothiophene–triphenyltrazines (**3a**) showed greater deviations from those of the corresponding linear oligothiophenes than expected at first instance.

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