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Synthesis, electrochemical, thermal and photophysical characterization of photoactive discotic dyes based on the tris-[1,2,4]-triazolo-[1,3,5]-triazine core

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ABSTRACT

This work presents the synthesis and characterization of compounds based on the heterocycle tris-[1,2,4]-triazolo-[1,3,5]-triazine (TTT) obtained by a new building block that can be applied to afford different discotic materials in one step. The thermal properties were evaluated by TGA and DSC and indicate very thermal stable compounds. The compounds exhibited absorption in the UV-B region (~280 nm) with molar absorptivity coefficients and radiative rate constants arising from spin and symmetry allowed $\pi - \pi^*$ electronic transitions. An emission located in the UV-A region (~363 nm) was observed, which was most likely due to a normal emission because no evidence of a charge-transfer mechanism in the excited state was observed. Spin-coated films indicate the presence of π -stacking in compounds presenting lower alkyl chains. Cyclic voltammetry measurements showed reduction and oxidation processes. The HOMO energy was obtained from the oxidation potential corresponding and the LUMO energy was found by subtracting its optical band gap from the HOMO value. In addition, *in situ* UV-Vis measurements were employed to evaluate the changes in the absorption spectra due to the changes in the electronic structure of the conjugated molecules under oxidative and reductive potentials. © 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Several detection technologies based on different physicochemical signal transmission mechanisms, such as colorimetry, metal oxide based devices, electrochemistry, chemiluminescence and semiconductor devices, have been developed in recent years [1]. However, these technologies are limited in their application due to lack of sensitivity, selectivity, or portability [2]. The most widely used techniques in optical sensors are optical absorption and luminescence [3]. As a means of controlling absorption and/or luminescence, molecular design plays a crucial role in providing the ability to control the properties of molecules via functionalization; for example, introducing heterocycles may confer high

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http://dx.doi.org/10.1016/j.dyepig.2016.06.041 0143-7208/© 2016 Elsevier Ltd. All rights reserved. luminescence [4,5]. Detection technology based on light-emitting molecules and semiconductors has been widely studied due to the low power consumption required, low cost and ease of use in sensors. In the presence of external agents, such as temperature and electric field, the orientation of these materials is altered, producing an optical signal that can be easily visualized [6]. Organic materials containing π conjugated bridges in its structure allow for photo- or electro-luminescence and charge transportation (organic semiconductor), thereby providing the ability to reversibly respond to external stimuli, such as chemical, electro-chemical, or photo-chemical stimuli.

These features make organic semiconductors good candidates for applications in molecular electronics, such as photoconductors, liquid crystals, organic light emitting diodes, solar cells and optical sensors [7–10]. In this context, discotic functional materials, discovered by Chandrasekhar et al. in 1977 [11], are now viewed as

2

the basis of a new generation of organic semiconductor compounds [12]. Discotic functional materials offer the advantage of highly ordered structures, which enable processing of the optical signals and storing of the electro-optic information, as well as excellent load carrying and thermal stability [13]. Combining these characteristics in a single molecule can enable new compounds with high charge mobility combined with light emission capability in the solid state or in solution: such compounds have potential applications in electroluminescent devices [6,14]. The last decade has seen growing interest in the synthesis of discotic compounds containing the heterocycle tris-[1,2,4]-triazolo-[1,3,5]-triazine (TTT) [15-18] because such discotic compounds are good candidates for use in functional discotic materials with luminescence and load carrying capacity. Some examples in the literature show highly stable phases for widely conjugated and luminescent compounds by adding to the ends of a greater number of aliphatic chains.

In this manner, new discotic compounds containing heterocyclic tris-[1,2,4]-triazolo-[1,3,5]-triazine (TTT) with a variable number of flexible alkoxy chains were synthesized and characterized. In addition, we studied the thermal, electrochemical and photophysical properties of the synthesized molecules.

2. Experimental

2.1. Materials and methods

All reagents were used as received. The solvents were purified before use, according to the procedure in the literature [19]. FTIR spectra were recorded on a Shimadzu IR Prestige-21 with a resolution of 4 cm⁻¹ using KBr pellets. The ¹H and ¹³C NMR spectra were recorded in DMSO-d₆ or CDCl₃ at 400 and 100 MHz, respectively. The chemical shifts (δ) are reported in parts per million (ppm) relative to TMS, and the coupling constants J are reported in Hertz (Hz). Spectroscopic grade solvents were used in the photophysical study. The UV-Vis absorption spectra in solution and in spin-coated films were acquired on a Shimadzu UV-2450 spectrophotometer, and the steady-state fluorescence spectra were measured on a Shimadzu spectrofluorometer model RF-5301PC. Spin coated films containing the tris-[1,2,4]-triazolo-[1,3,5]-triazines were prepared under vacuum using a Glove Box MBRAUN model MB 200B; silicon plates were used as the substrates for the films. The quantum yield of fluorescence (Φ_{FL}) was determined by applying the dilute optical method. Quinine sulfate (QS) in H₂SO₄ (0.5 mol L⁻¹) ($\Phi_{FL} = 0.55$) was used as the quantum yield standard [20]. The uncertainties related to the quantum yield of fluorescence ($\Delta \Phi_{FL}$) measurements using QS are in order of 6% [21,22]. The absorption spectra of the spin-coated films were measured on a Shimadzu UV2450PC spectrophotometer using an ISR-2200 integrating sphere. The baseline in the solid state was obtained using BaSO₄. The fluorescence spectra of the films were obtained with a solid sample holder at an angle designed to limit the reflected excitation beam from the emission monochromator.

The electrochemical measurements were performed using a Biologic potentiostat Model SP-200. The cyclic voltammetry experiments were performed using 0.1 mg mL⁻¹ solutions of the TTTs in 0.1 mol L⁻¹ tetra-*n*-butyl ammonium hexafluorophosphate (TBAPF₆) in dry dichloromethane as the supporting electrolyte, and the ferrocene/ferricenium (Fc/Fc⁺) redox couple was employed as the internal reference. The experiments were performed using a standard three-electrode cell with a circular glassy carbon electrode, a Pt-wire counter electrode and Ag/Ag⁺ (AgNO₃ 0.01 mol L⁻¹ in acetonitrile) as the reference electrode. All measurements were conducted in an electrolyte solution that had been purged with purified N₂. The spectroelectrochemical measurements were performed on a Shimadzu UV-1800 spectrofluorophotometer.

Optically transparent gold mesh was employed as the working electrode, a platinum wire was used as the auxiliary electrode, and Ag/Ag⁺ was employed as the reference electrode. Tetrabutylammonium hexafluorophosphate (0.1 mol L^{-1} in dichloromethane) was employed as the electrolyte. The spectra of the tris-[1,2,4]-triazolo-[1,3,5]-triazines were obtained by a constant potential with the aid of a coupled potentiostat. Low-resolution mass spectra were recorded on a Bruker Daltonics Autoflex apparatus for MALDI and on a Waters Micromass ZQ spectrometer for ESI/ApCI-ITD (Esquire 3000⁺ Bruker Daltonics). The thermal properties were investigated using differential scanning calorimetry on DSC-50 and SDT Q600 TA Instruments using a N₂ atmosphere with a flow rate of 100 mL min⁻¹ and a heating rate of 10 °C min⁻¹. The DSC curves were performed using two heating-cooling cycles in order to obtain the thermal transitions and the glass transition temperatures, respectively.

2.2. Synthesis

2.2.1. 5-(4-hidroxyphenyl)tetrazole (1)

4-Cyanophenol (10.01 g, 84 mmol), NaN₃ (16.38 g, 252 mmol), NH₄Cl (13.48 g, 252 mmol) and 100 mL of DMF were added to a round bottom flask. The mixture was kept under heating and stirring at 125 °C for 20 h. Next, the solution was poured into 300 mL of water and then acidified to pH ≈ 1 using HCl (6 mol L⁻¹). The precipitate formed was filtered and recrystallized from water, yielding 10.4 g (77%) of a crystalline orange solid. M.p.: 237–239 °C. FTIR (ν_{max} /cm⁻¹): 3367, 3099, 3065, 3021, 2937, 2847, 2743, 2632, 2494, 1647, 1615, 1599, 1515, 1471, 1415, 1379, 1280, 1249, 1181, 1154, 1061, 1025, 995, 918, 842, 792. ¹H NMR (DMSO-*d*₆, 400 MHz): 3.52 (broad, 1H, tet-H), 6.98 (d, *J* = 8.9 Hz, 2H, Ar–H), 7.89 (d, *J* = 8.9 Hz, 2H, Ar–H), 10.23 (broad, 1H, Ar–OH). ¹³C NMR (DMSO-*d*₆, 100 MHz): 115.3, 116.8, 129.4, 155.4, 160.8.

2.2.2. 5-(4-acetoxyphenyl)tetrazole (2)

5-(4-hydroxyphenyl)tetrazole (1) (5.02 g, 31 mmol) and 80 mL of water were added to a round bottom flask. To this suspension was added aqueous NaOH (3 mol L^{-1}) under magnetic stirring and at room temperature until the phenol is completely dissolved. Next, the solution was cooled in an ice bath, and then glacial acetic anhydride (3.37 g, 33 mmol) was slowly added. After complete addition, the system was stirred for 5 min in an ice bath and 15 min at room temperature. The suspension was then poured into 300 mL of ice/water, acidified to pH \approx 2, and then filtered. Recrystallization from water yielded 5 g (98%) of a crystalline white solid. M.p.: 182–183 °C (dec.) (lit. 182 °C) [10]. FTIR (*v*_{max}/cm⁻¹): 3072, 3017, 2924, 2859, 2775, 2724, 2630, 2485, 1756 (C=O), 1614, 1501, 1440, 1407, 1364, 1288, 1212, 1170, 1054, 1026, 1007, 994, 913, 850, 751. ¹H NMR (DMSO-*d*₆, 400 MHz): 2.33 (s, 3H, COOCH₃), 3.61 (broad, 1H, tet-H), 7.41 (d, *J* = 8.8 Hz, 2H, Ar–H), 8.10 (d, *J* = 8.8 Hz, 2H, Ar–H). ¹³C NMR (DMSO-*d*₆, 100 MHz): 21.5, 122.4, 123.7, 129.1, 153.2, 160.0, 169.7

2.2.3. Tris-(4-hydroxyphen-1-yl)-[1,2,4]-triazolo-[1,3,5]-triazine (4)

In a 3 neck round bottom flask equipped with condenser and under inert Ar atmosphere, a mixture of 5-(4-acetoxyphenyl)tetrazole (2) (1.84 g, 9 mmol), cyanuric chloride (0.55 g, 3 mmol) and anhydrous K_2CO_3 (4.98 g, 36 mmol) in 80 mL butanone was kept under vigorous stirring and reflux for 48 h. The hot mixture was filtered on Büchner funnel during washing with CH₂Cl₂ (3 × 20 mL). The protecting group acetyl was removed by adding 20 mL of distilled water and 30 mL of concentrated HCl to compound (3). The mixture was kept to reflux for 24 h and then cooled to room temperature and basified with NaOH solution (1 mol L⁻¹). The solid

formed was filtered and washed with water to give the desired product. Yield: 2.6 g (60%) of a light beige solid. M.p.: 120 °C (dec.) FTIR (ν_{max}/cm^{-1}): 3448, 1610, 1585, 1487, 1259, 1180, 831. ¹H NMR (DMSO- d_6 , 400 MHz): 8.60 (d, 6H, J = 8.43 Hz, Ar), 7.65 (d, 6H, J = 8.44 Hz, Ar), 4,60 (broad, OH). ¹³C NMR (DMSO- d_6 , 100 MHz): 175.7, 161.5, 159.6, 127.6, 122.0, 116.2.

2.2.4. General procedure to synthesize (5-7)

Tris-(4-hydroxyphenyl-1-yl)-[1,2,4]-triazolo-[1,3,5]-triazine **(4)** (3.01 g, 6.3 mmol), K_2CO_3 (2.76 g, 20.0 mmol), 19.5 mmol of the corresponding alkyl bromides and a catalytic amount of KI in 150 mL of butanone were added into a round bottom flask. The mixture was refluxed under vigorous stirring for 20 h. The K_2CO_3 was filtered, and then the solvent was evaporated at reduced pressure. The obtained product was extracted with a mixture of ethyl acetate/water. The organic phase was dried with sodium sulfate (Na₂SO₄). After filtration and solvent evaporation, the resulting solid was purified by column chromatography using silica gel and dichloromethane as eluent.

2.2.4.1. Tris-(4-octyloxyphen-1-yl)-[1,2,4]-triazolo-[1,3,5]-triazine (5). Yield: 60% of a dark beige solid. M.p.: 97–98 °C. FTIR (ν_{max}/cm^{-1}): 2924, 2854, 1595, 1483, 1255, 1180, 833. ¹H NMR (CDCl₃, 400 MHz): 8.08 (d, 6H, *J* = 9.06 Hz, Ar), 7.05 (d, 6H, *J* = 8.81 Hz, Ar), 4.05 (t, 6H, *J* = 6.55 Hz, -OCH₂-), 1.86 (quint, 6H, *J* = 8.06 Hz, -OCH₂CH₂-), 1.51–1.33 (m, 30H, -CH₂-), 0.93 (t, 9H, *J* = 7.05 Hz, -CH₃). ¹³C NMR (CDCl₃, 100 MHz): 162.0, 150.8, 140.5, 131.8, 115.8, 114.5, 68.2, 31.9, 29.4, 26.1, 22.7, 14.2. ESI Anal. Calcd. for C₄₈H₆₃N₉O₃: *m*/*z* 814.1; found *m*/*z* 814.6 [M+H]⁺.

2.2.4.2. *Tris*-(4-*decyloxyphen*-1-*yl*)-[1,2,4]-*triazolo*-[1,3,5]-*triazine* (6). Yield: 63% of a pale yellow solid. M.p.: 89–90 °C. FTIR (ν_{max}/cm^{-1}): 2924, 2852, 1610, 1595,1485, 1255, 1180, 833. ¹H NMR (CDCl₃, 400 MHz): 8.05 (d, 6H, *J* = 8.79 Hz, Ar), 7.02 (d, 6H, *J* = 8.79 Hz, Ar), 4.01 (t, 6H, *J* = 6.44 Hz, -OCH₂-), 1.81 (quint, 6H, *J* = 6.44, -OCH₂CH₂-), 1.49–1.24 (m, 42H, -CH₂-), 0.87 (t, 9H, *J* = 7.03 Hz, -CH₃). ¹³C NMR (CDCl₃, 100 MHz): 162.0, 150.8, 140.5, 131.8, 115.7, 114.5, 68.3, 32.0, 29.6, 29.4, 26.1, 22.7, 14.2. ESI Anal. Calcd. for C₅₄H₇₅N₉O₃: *m*/*z* 898.2; found *m*/*z* 898.7 [M+H]⁺.

2.2.4.3. *Tris*-(4-dodecyloxyphen-1-yl)-[1,2,4]-triazolo-[1,3,5]-triazine (7). Yield: 65% of a pale white solid. M.p.: 84–85 °C. FTIR (ν_{max}/cm^{-1}): 2918, 2848, 1610, 1585, 1487, 1259, 1180, 831. ¹H NMR (CDCl₃, 400 MHz): 8.10 (d, 6H, J = 8.79 Hz, Ar), 7.07 (d, 6H, J = 8.9 Hz, Ar), 4.06 (t, 6H, J = 6.74 Hz, $-OCH_2-$), 1.85 (quint, 6H, J = 7.91 Hz, $-OCH_2CH_2-$), 1.51 (m, 6H, $-CH_2-$), 1.31 (broad, 48H, $-CH_2-$), 0.91 (t, 9H, J = 6.74 Hz, $-CH_3$). ¹³C NMR (CDCl₃, 100 MHz): 162.0, 150.8, 140.4, 131.8, 115.7, 114.4, 68.2, 31.9, 29.7, 29.4, 26.0, 22.7, 14.1. ESI Anal. Calcd. for C₆₀H₈₇N₉O₃: *m*/*z* 982.4; found *m*/*z* 982.8 [M+H]⁺.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

The synthetic route for the preparation of all compounds is shown in Scheme 1.

The intermediate **1** containing the tetrazole ring was obtained from 4-cyanophenol under reflux with sodium azide and ammonium chloride in *N*,*N*-dimethylformamide. The next step was the acetylation of compound **1** using acetic anhydride and sodium hydroxide to yield compound **2**. To obtain the compound containing the tris-[1,2,4]-triazolo-[1,3,5]-triazine core (**3**), a procedure proposed by Huisgen was used [23]. This step involves the reaction of a tetrazole ring with cyanuric chloride, followed by HCl elimination. The reaction product undergoes ring thermolysis, followed by nitrogen elimination generating an iminonitrile, which cyclizes to produce the desired heterocycle [23,24]. Compound **4** was obtained in 60% yield by acid catalysed deprotection of the acetyl groups of precursor **3**.

Finally, to obtain the compounds **5**–**7**, an alkylation with three different alkyl bromides containing 8, 10, or 12 carbon atoms was performed via Williamson reaction in the presence of potassium carbonate to afford the final compounds with yields higher than 60%.

All compounds were characterized by ¹H and ¹³C NMR spectroscopies (Figs. S1-8). For compounds 5-7 the obtained NMR spectra in CDCl₃ showed a very similar profile (data not shown). For example, compound 7 exhibits two doublets with a coupling constant of 8.79 Hz centered at approximately 8.10 and 7.07 ppm relative areas to six hydrogens for each signal (AB system in Fig. S7), which is related to the phenyl rings attached to the TTT core. In addition, a triplet located at approximately 4.0 ppm with coupling constant of 6.74 Hz is observed, which is related to the six hydrogens (c) present in the methylene groups adjacent to the oxygen atoms in the alkyl portion of the molecule. In the region of 1.8 to 0.8 ppm, a set of signals related to 69 hydrogens is observed, which corresponds to the alkyl moiety of compound 7. In the ¹³C NMR spectrum (data not shown, Fig. S8), six different aromatic carbons were found, of which, the signals at 150.7 and 140.4 ppm were highlighted from the TTT system.

3.2. Photophysical characterization

Fig. 1 presents the electronic spectra of the TTTs **5–7** in dichloromethane. The relevant data from the UV-Vis absorption spectroscopy are summarized in Table 1. All compounds presented similar photophysical behavior in DMSO and DMF (Figs. S24–27). Form the Strickler-Berg relationship, it is possible to determine the pure radiative lifetimes (τ^0) and the radiative rate constants (k_e^0) [25]. In this relationship, the pure radiative lifetime can be defined as $1/k_e^0$, and the oscillator strength (f_e) can be obtained [26].

The tris-[1,2,4]-triazolo-[1,3,5]-triazines present absorption maxima in the UV-B region, below 300 nm (~280 nm), which is attributed to electronic transitions in the heteroaromatic portion of the molecule, as already observed in the parent compounds [16–18,27]. The molar absorptivity coefficient (ε) values for both absorption bands as well as the calculated radiative rate constants (k_e^0) for all of the compounds indicate that the spin and symmetry allowed electronic transitions were related to ${}^{1}\pi\pi^{*}$ transitions, where high values to the oscillator strength could be calculated, probably related to the rigidity of the TTT core. The absence of a shoulder on the absorption spectra located at higher wavelengths (>300 nm), as well as any evidence of solvatochromism allowed us to conclude that these compounds do not present an ICT character in the ground state [15]. Similar radiative lifetime values were obtained ($\tau^0 \sim 1$ ns) for all of the compounds, indicating that after radiation absorption, the fluorophores populate the same excited state.

The fluorescence emission spectra of tris-[1,2,4]-triazolo-[1,3,5]-triazines **5**–**7** in dichloromethane are also shown in Fig. 1. These compounds exhibited a similar photophysical behavior in both DMSO and DMF. The emission curves were obtained by exciting the compounds at the absorption maxima wavelength. The relevant data from fluorescence emission spectroscopy are listed in Table 1.

The changes in the chemical structure of the fluorophores do not appear to play a key role in the fluorescence maxima location, since the TTTs **5–7** present fluorescence emission in the UV-A region (~363 nm). Furthermore, the absent solvatochromism from the emission curves ($\Delta \lambda_{em} = 1$ nm) are indicating that no charge-

ARTICLE IN PRESS

A.G. Dal-Bó et al. / Dyes and Pigments xxx (2016) 1-8



Scheme 1. Synthetic route to obtain the tris-[1,2,4]-triazolo-[1,3,5]-triazines 5–7.



Fig. 1. UV-Vis absorption (left) and fluorescence emission (right) spectra for the tris-[1,2,4]-triazolo-[1,3,5]-triazines 5–7 in dichloromethane. Photophysical data for the precursor 4 is also presented for comparison (dotted lines).

Table 1

Relevant photophysical data of the UV-Vis spectra of **5**–**7**, where λ_{abs} is the absorption maxima (nm), ε is the molar absorptivity (×10⁴ L mol⁻¹ cm⁻¹), f_e is the calculated oscillator strength, k_e^0 (×10⁹) is the calculated radiative rate constant (s⁻¹), τ^0 is the inherent emission lifetime (ns), λ_{em} is the emission maxima (nm), $\Delta\lambda_{ST}$ is the Stokes shift (nm/cm⁻¹), and Φ_{FL} is the fluorescence quantum yield.

Solvent	Compound	λ_{abs}	ε	f_e	k _e ⁰	τ^0	λ_{em}	$\Delta\lambda_{ST}$	Φ_{FL}
Dimethylformamide	5	282	6.0	0.958	12.05	0.83	362	80/7836	0.10
	6	282	3.3	0.873	10.98	0.91	362	80/7836	0.10
	7	282	1.7	0.591	0.744	1.34	362	80/7836	0.10
Dimethylsulfoxide	5	282	4.8	0.905	11.38	0.88	363	81/7912	0.09
	6	282	3.4	0.897	11.28	0.89	363	81/7912	0.13
	7	282	3.0	0.792	0.997	1.00	363	81/7912	0.12
Dichloromethane	5	288	2.8	0.966	11.65	0.86	363	75/7174	0.15
	6	288	4.8	0.917	11.06	0.90	363	75/7174	0.22
	7	288	4.7	0.939	11.32	0.88	363	75/7174	0.23

transfer takes place in the excited state. On the other hand, in solution the alkoxy groups seems to play a significant role on the excited singlet state deactivation due to (i) the relative large Stokes shift (75–81 nm), although any evidence of charge transfer character was observed, which can be related to a non-radiactive energy loss due to conformational relaxation of the alkoxy chains present in the TTTs; and (ii) the low values to the fluorescence quantum yields (0.09–0.23), which can be related to non-radiactive pathways probably due to the free bond rotation of the benzene ring and alkoxy chains [17].

Compared to those of the solution spectra, the absorption maxima of the spin-coated films presented significant changes, showing a clear dependence on the alkyl chain length of the studied compounds (Fig. 2). The intense absorption located at 250 nm can probably be ascribed to the tristriazolotriazine moiety because it is known that spin-coated films can present blue-shifted bands relative to the maxima observed in solution [16]. In addition, a red shifted shoulder is observed in the DRUV spectra located at 337 nm (5), 328 nm (6) and 290 nm (7). Despite the absence of liquid crystalline behavior in these compounds, these results suggest the formation of aggregates in the ground state, probably via π -stacking between the heteroaromatic units. A higher alkyl chain does not allow a better interaction between the aromatic moieties, thereby increasing the absorption energy of the aggregate. In contrast, a lower alkyl chain allows a better interaction between the π systems, resulting in absorption at longer wavelengths.

The spin-coated films presented fluorescence intensity in the UV-A-blue regions with maxima located at 461 nm (5), 408 nm (6) and 380 nm (7), which are red shifted relative to the values

obtained in solution (~360 nm). A higher fluorescence emission could be observed in compound **7**, which has the higher alkyl chain. In contrast, spin-coated films containing compound **5**, which presents the lower alkyl chain, show a very weak fluorescence emission, similar to that observed for the parent compound **4** (Fig. 3c). As the formation of excimers via π -stacking are well known to suppress the emission in solids in similar compounds [16], the fluorescence emission spectra indicate that the π -stacking was sterically inhibited in compound **7**. In this manner, the weak emission from compounds **4** and **5** indicate that this π electronic interaction was not effectively suppressed and the formation of excimers via π - π stacking occurs in the excited state. In addition, it could be observed that the weaker the fluorescence emission is, the higher the fluorescence emission maxima is, as expected.

3.3. Thermal characterization

The thermal behavior of compounds **5**–**7** was investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The relevant data from DSC analysis are summarized in Table 2.

The thermal behaviors of the studied compounds **5–7** by DSC showed a similar tendency, as shown in Fig. 3. An increase of the aliphatic chain leads to a decrease in their respective melting points of 92.7 °C (**5**) to 85.5 °C (**7**). These compounds are also found to remain in a super-cooled state after fusing, i.e., cooling the material from its isotropic liquid state between two glass slides, no crystallization of the material is observed. For compound **7** (Fig. S18), during the first heating and cooling cycle, two transitions were



Fig. 2. Photophysical characterization of spin coated films containing tris-[1,2,4]-triazolo-[1,3,5]-triazines 5–7: (a) normalized DRUV, (b) transmittance and (c) fluorescence emission spectra. The inset presents the normalized emission of compounds 5–7. In all spectra, precursor 4 is also presented for comparison (dot lines).

ARTICLE IN PRESS

A.G. Dal-Bó et al. / Dyes and Pigments xxx (2016) 1-8



Fig. 3. First (left) and second (right) heating-cooling cycles of the DSC thermograms obtained for the compounds 5–7 at 10 °C min⁻¹.

Table 2

Thermal properties of the final compounds **5–7**, where T_d is the decomposition temperature, T_g is the glass transition temperature, and CrI & Cr II and I are the crystal phases and the isotropic liquid phase, respectively and ΔH is the enthalpy associated to the thermal event (J g⁻¹).

Compound	Transitions ^a ($\Delta H/J g^{-1}$)	$T_g (^{\circ}C)^b$	$T_d (^{\circ}C)^{c}$
5	Crl 73.6 °C (-4.87) Crll 92.7 °C (-6.37) I	41.6	396.1
6	Crl 72.3 °C (-4.47) Crll 85.8 °C (-2.61) I	36.3	398.2
7	Crl 59.4 °C (-1.81) Crll 85.5 °C (-11.59) I	36.7	392.8

^a Determined using DSC on heating at 10 °C min⁻¹

^b Glass transition temperature measured using DSC.

 c Temperature of decomposition obtained by TGA in atmosphere of N_{2} at 10 $^{\circ}C\mbox{ min}^{-1}.$

observed; the first is a crystal-crystal transition at 59.4 $^{\circ}$ C, and the second is the melting of the solid material at 85.5 $^{\circ}$ C (endothermic peak). In the later cooling, no exothermic peak related to crystal-lization is observed. In the second cycle, only one glass transition can be observed at 36.7 $^{\circ}$ C, which is typical for amorphous materials.

The degradation temperatures of **4**–**7** were evaluated by Thermogravimetric Analysis (TGA) under inert N₂ atmosphere (Fig. 4). To better visualize the thermal events, the DTG curves for all of the compounds were obtained from the TGA curves.



Fig. 4. Thermograms (TGA) and DTG curves of compounds 4-7.

The overall degradation process indicates that for compounds **5–7**, a main degradation event occurs with mass loss of approximately 70% at an initial decomposition temperature higher than 400 °C and a high maximum degradation rate located at 450 °C. Based on this phenomenon, the alkylation reaction appears to promote the thermal stability of these compounds because precursor **4** showed a significant decrease of the thermal stability with two decomposition processes located at 100 °C and 250 °C.

3.4. Electrochemical characterization

It can be observed from the cyclic voltammogram curves for compound **7** that a distinct anodic and cathodic behavior occurs (Fig. 5). A similar behavior was observed for compounds 5-6 (Figs. S20–21).

A reduction processes were observed located at peak potential of -1.12 V, -1.23 V and -1.37 V versus Ag/Ag⁺, and oxidation processes located at peak potential of 1.55 V, 1.47 V and 1.60 V versus Ag/Ag⁺ for **5**, **6**, and **7**, respectively. The results of the electrochemical study suggested that the tristriazolotriazine group potentially has electron-transporting characteristics [16]. The TTT series showed a more negative reduction with an increase of the



Fig. 5. Cyclic voltammogram of compound 7 on a glassy carbon electrode in 0.1 $TBAPF_6/CH_2Cl_2$ at 100 mV s⁻¹. The reduction region is also presented (inset).

Table 3

Optical and electrochemical properties of compounds **5–7**. Optical and electrochemical properties of compounds **5–7**, where E_{ox} is the onset potential of oxidation, E_{red} is the onset potential of reduction, I_p (HOMO) is the ionization potential, E_a (LUMO) is the electron affinity, E_g is the band gap, and λ_{onset} is the absorption onset wavelength.

Parameters	Compounds				
	5	6	7		
$\begin{array}{l} E_{ox}\left(V\right) \text{ vs. NHE}^{a}\\ E_{red}\left(V\right) \text{ vs. NHE}^{a}\\ I_{p}\left(HOMO\right)\left(eV\right)^{b}\\ \lambda_{onset}\left(nm\right)^{c}\\ E_{g}\left(eV\right)^{d}\\ E_{a}\left(LUMO\right)\left(eV\right)^{e} \end{array}$	1.60 0.53 6.04 336 3.69 2.35	1.56 -0.72 -6.00 334 3.71 -2.29	$1.64 \\ -0.76 \\ -6.08 \\ 334 \\ 3.70 \\ -2.38$		

Notes.

^a $E_{ox/red}$ (vs. NHE) = $E_{ox/red}$ (vs. Ag/Ag⁺) + 0.266.

^b $I_p = -(E_{ox} + 4.44) \text{ eV}.$

^c λ_{onset} : absorption onsets wavelength.

 d Optical band gap calculated on the low energetic edge of the absorption spectrum (Eg = 1240/ λ_{onset}).

 e $E_{g} = E_{a} - I_{p}$.

alkyl chain; this behavior results in higher LUMO levels [17]. The cyclic voltammogram of compound **4** (data not shown, Fig. S19) was obtained for comparison since it was used as a building block for the TTT series; the same voltammetric processes were observed, but at a lower potential, and a new oxidation process was observed, probably due to oxidation of the hydroxyl group. In addition, the onset potentials of oxidation (E_{ox}) and reduction (E_{red}) could be directly correlated to electron transfer at the HOMO (ionization potential) and LUMO (electron affinity), respectively. Therefore, Ag/Ag⁺ was used as the reference, and the potential found was normalized to NHE, using the Fc/Fc⁺ couple as an internal standard [25].

The electron affinity and ionization potential of **5–7** were calculated based on the optical and electrochemical data and are shown in the Table 3. The optical band gaps of TTTs **5–7** were obtained from the onset values of band in the UV-vis spectra, measured in the open circuit potential (OCP), as shown for compound **7** (Fig. 6). Once again, the parent compounds **5–6** presented a similar behaviour (Figs. S22–23). It was not employed the reduction potential obtained electrochemically in the calculation of the band gap. In this case, the process was not very pronounced, which would generate errors in the calculation of the LUMO energy value. Thus, the HOMO energy was obtained from the onset potential oxidation corresponding and the LUMO was found by subtracting its optical band gap from the HOMO value. The optical and

electrochemical data evaluated from these studies are summarized and compared in Table 3.

Compared to the optical excitation process, the electrochemical oxidation or reduction of the studied TTT series are significantly influenced by their dielectric environments and the Coulomb interactions associated with charge injection processes [28]. Spectrolectrochemical measurements were performed to obtain information about the species behavior in the oxidized and reduced form. The applied potentials were chosen before the peak, on the peak and after the peak position observed in the cyclic voltammetry (Fig. 5). In the corresponding spectrum obtained on OCP (Fig. 6) for compound 7, a strong absorption peak is observed in the range of approximately 240 nm-340 nm, which is attributed to $\pi\pi^*$ electronic transitions in the heteroaromatic portion of the molecule due to the high molar absorption coefficient [15,27]. Under the reduction potential the TTT series showed suppression and displacement of the absorption band to higher energy values (Fig. 6 and Figs. SI22-23). The oxidized species of 5-7 present differences in the absorption; when submitted to oxidizing potentials, the compounds showed suppression and displacement of the absorption band to lower energy values (Fig. 6 and Fig. SI22-23).

4. Conclusions

A series of compounds based in heterocycle tris-[1,2,4]-triazolo-[1,3,5]-triazine (TTT) was synthesized and characterized using FTIR, ¹H and ¹³C NMR and mass spectrometry (MS). Compounds **5–7** exhibited absorption maxima located around 280 nm, with molar absorptivity coefficient (ε) values related to $\pi\pi^*$ electronic transitions. Changes in the solvent polarity did not cause a significant solvatochromic effect (~6 nm), indicating a nearly absent chargetransfer state in the ground state. Compounds 5-7 exhibited emissions in the UV-A region (~360 nm), where the different alkoxy groups do not play a fundamental role in photophysics of these compounds in solution. A Stokes shift (75-81 nm) can be related to a non-radiative energy loss in the excited state, probably due to the alkoxy chains (conformational relaxation). Molecular π -stacking was inhibited in spin-coated films prepared using compound 7, improving the prospects for application of this compound as a good solid state emitter.

Spectroelectrochemical measurements showed changes in the absorption spectra due to changes in electronic structure under oxidation and reduction conditions. The electrochemical band gaps confirmed that the energy level required for the materials is compatible for building electronic devices.



Fig. 6. Spectroelectrochemistry in different potential regions for 7: (left) reduction potential, (right) oxidation potential, and (inset) OCP.

8

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A.G. Dal-Bó et al. / Dyes and Pigments xxx (2016) 1-8

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.06.041.

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