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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 π–π* 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.

1. Introduction

Several detection technologies based on different physico-chemical 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 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

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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 ^{13}C NMR spectra were recorded in DMSO-d_6 or $CDCl_3$ 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 H_2SO_4 (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 $BaSO_4$. 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 ($TBAPF_6$) 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^+ ($AgNO_3$ 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 N_2. 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 N_2 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), NaN_3 (16.38 g, 252 mmol), NH_4Cl (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 $\approx$ 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). ^{13}C 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 (ν_{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, $COOCH_3$), 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). ^{13}C 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 CH_2Cl_2 (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

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