



## SYNTHESIS AND ELECTRONIC PROPERTIES OF *TRIS*(4-FORMYLBIPHENYL-4-YL) AMINE AS A BUILDING BLOCK FOR COVALENT ORGANIC FRAMEWORKS AND FOR OPTOELECTRONIC DEVICES

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### Abstract

Herein is reported the preparation of a new triphenylamine derivative, the *tris*(4-formylbiphenyl-4-yl) amine (TFBA). This compound exhibits optoelectronic properties suitable for its use in Dye-Sensitized Solar Cells (DSSCs) and light emitting diodes. The electrochemical properties were studied by cyclic voltammetry (CV) and square wave voltammetry (SWV). At the same time, the symmetrical chemical structure of TFBA allows its utilization as a building block in Covalent Organic Frameworks (COFs) bringing additional properties and a wide range of applications to such materials.

**Keywords:** electrochemistry, fluorescence, COF's.

## 1 Introduction

Triphenylamine (TPA) and its derivatives have received a great deal of attention over the past decades as a new class of functional materials, (e.g. nonlinear optical [1], photorefractive [2], solar cells [3]) and hole transporting materials (HTMs) in organic light emitting diodes (OLEDs). [4] In addition, owing to its excellent thermal stabilities from its three-dimensional propeller structure, TPA is a good choice as the central core for Starburst molecules.

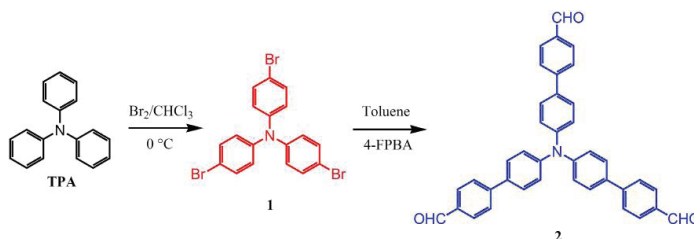
Furthermore, organic porous frameworks are technologically important materials with several functions and applications [5]. The pore surface forms a microscopic interface with gas or guest molecules, which is an important characteristic that determines the macroscopic nature of these materials in applications such as gas adsorption, molecular separation, catalysis and energy storage. Among these materials, covalent organic frameworks (COFs) are a class of porous materials that feature low weight elements and strong covalent linkages of their components, and they exhibit high flexibility in their molecular design, which allows the atomically precise integration of their building blocks

into porous structures [6]. Despite the availability of a variety of skeletons for COFs, control of the pore surface remains a significant challenge. Additionally, the organic linkers can be selected to have a determined property for a specific purpose.

One purpose of our research group is the design of dynamic systems that can respond to both physical and chemical stimuli in a reversible fashion and therefore they can be implemented in several applications at the same time. In this regard the synthesis of *tris*(4-formyl-biphenyl-4-yl) amine (TFBA) represents an starting point for the design of photoactive molecules capable of self-assembling and interacting covalently with other building blocks, for instance, for the preparation of novel COFs with not only great absorption properties but also with optoelectronic applications.

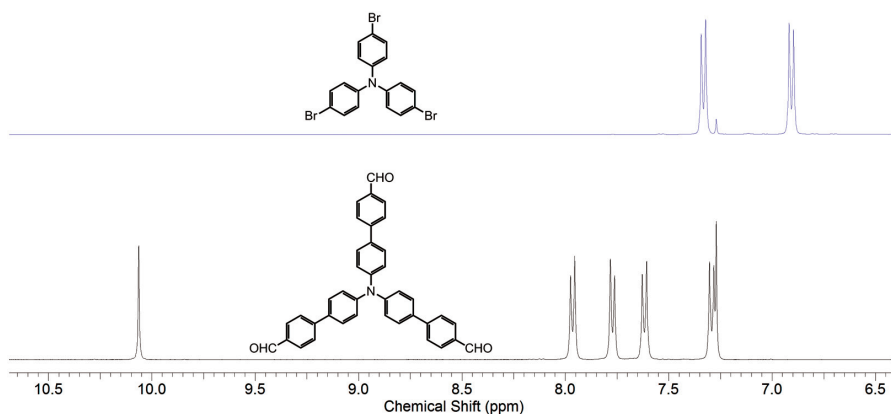
## 2 Results and discussion

Scheme 1 shows the synthetic pathway for the preparation of TFBA from TPA. This reaction can be optimized and accelerated by the introduction of microwave radiation (see experimental part).



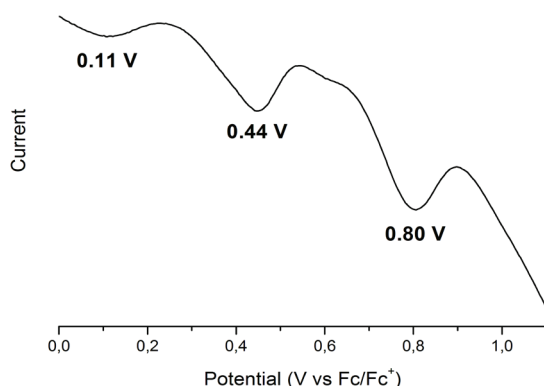
**Scheme 1.** Synthesis of compounds **1** and **2** from triphenylamine (TPA).

The  $^1\text{H-NMR}$  spectrum of compound 1 shows two doublets at 7.33 and 6.91 ppm ( $J=8.59$  Hz). Each of them integrates for 6 Hs. When going from compound 1 to compound 2, it is observed the appearance of three new signals, a singlet (10.06 ppm, 3H) and two doublets corresponding to the three aldehyde protons and to the inserted aryl moiety respectively (see Figure 1).



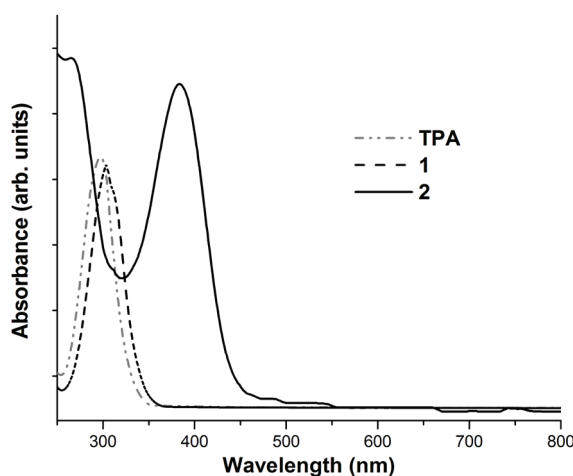
**Figure 1.**  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) spectra of up) compound **1** and below) compound **2**.

We study the electrochemical properties of compound **2** by using cyclic voltammetry (CV) and osteryoung square wave voltammetry (OSWV). This compound exhibits three reversible oxidation potentials (as determined by CV) at 0.11, 0.44 and 0.80 V (see Figure 2). These potentials contrast with the larger oxidation potential of compound **1** (+0.78 V) [7]. Clearly, compound **2** exhibits a low lying oxidation potential which makes it suitable for molecular electronic applications, DSSCs and OLEDs.



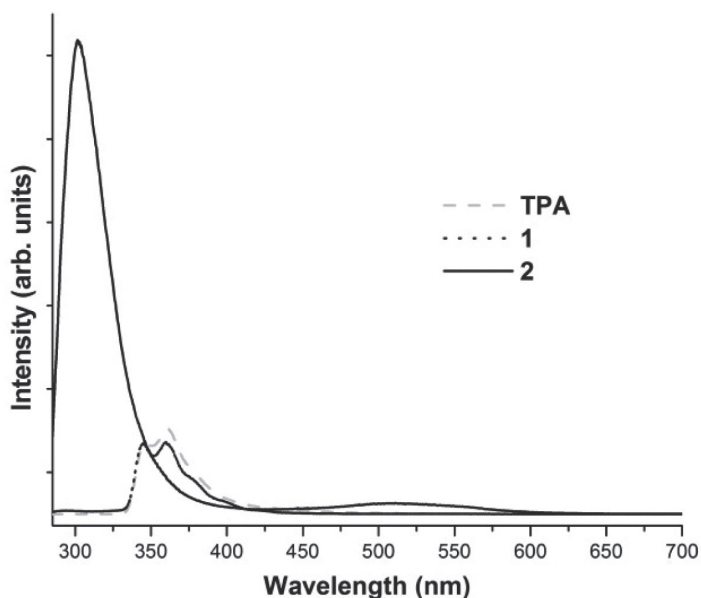
**Figure 2.** Osteryoung square wave voltammetry (OSWV) of compound **2** in 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>/THF with ferrocene as an internal standard. Scan rate = 100 mV/s.

UV/Vis absorbance experiments were measured in ethanol (see Figure 3). The substitution of -Br in the TPA framework causes a small shift of 5 nm while compound **2** exhibits a strong absorption peak around 382 nm attributed to the electronic  $\pi$ - $\pi^*$  transition. The large bathochromic shift of **2**, compared to TPA, is due to the larger conjugation of compound **2** that lowers the energy level of the  $\pi^*$  orbital. The optical band-gaps can be calculated from the spectral onset [8] resulting in 2.44, 2.71 and 1.86 eV for TPA, **1** and **2** respectively.



**Figure 3.** UV-vis spectrum of TPA and compounds **1-2**. Concentration of 0.7 mM in ethanol.

The emission spectrum (see Figure 4) of TFBA shows two peaks located around 300 nm and 515 nm, the former of larger intensity. Compounds TPA and **1** exhibit two peaks around 343 and 360 nm. These peaks are of lower intensity compared to TFBA. One possible reason for the large emission intensity in compound **2** compared to TPA, could be the larger conjugation through the carbon framework.



**Figure 4.** Fluorescence spectrum of TPA and compounds **1-2**. Concentration of 0.7 mM in ethanol. Excitation wavelength: 285 nm.

### 3 Conclusions

In conclusion, the *tris*(4-formyl-biphenyl-4-yl) amine is a symmetrical compound suitable as an organic linker in COFs, besides, its electronic properties such as lower HOMO-LUMO gap than TPA, its low oxidation potential, large emission and absorptions make of compound **2** an excellent candidate for DSSCs and OLEDs applications.

Further work is devoted to the synthesis of new TPA derivatives and the rational design and preparation of novel COFs.

### 4 Methodology

The starting materials were purchased from Sigma-Aldrich and used without any further purification. FT-IR spectra were taken in a Shimadzu FTIR-8400.  $^1\text{H}$  and  $^{13}\text{C}$  NMR were taken in a 400 MHz Bruker Ultra Shield spectrometer. UV-vis spectra were recorded in a UV-1700 PharmaSpec Shimadzu spectrophotometer. Fluorescence experiments were carried out in a FP-8500 Jasco spectrofluorometer. The synthesis of compound **2**, assisted by microwave irradiation, was performed using a Monowave 300 single-mode

microwave reactor. The reaction temperature was monitored by an internal fiber-optic (FO) temperature probe (ruby thermometer) protected by a borosilicate immersion well inserted directly into the reaction mixture. The reaction time refers to the hold time at the desired set temperature and not to the total irradiation time. Elemental analysis was performed in an analyzer Thermo Finnigan FlashAE1112 CHNS. Cyclic Voltammetry and Osteryoung Square Wave Voltammetry were performed in THF containing 0.1M of  $N(n\text{-Bu})_4\text{PF}_6$  as the supporting electrolyte. The concentration analyzed was about  $5.0 \times 10^{-4}$  M. A 2 mm diameter glassy carbon disk was used as the working electrode and a platinum wire as the counter electrode. A silver wire served as a pseudo reference electrode. A small amount of ferrocene was added at the end of each experiment and used as a reference for measuring the potentials.

***Tris(4-bromophenyl)amine (1)***: Triphenylamine (10 mmol) was dissolved in approximately 10 mL of chloroform after that the solution was cooled down to 0°C and kept under constant stirring. Then 50 mmol of bromine,  $\text{Br}_2$ , was added dropwise in the dark. Once the addition was completed the solution was stirred during 2 hours, time that it took for the reaction to be completed. The product was obtained in 89 % yield after recrystallization from  $\text{CHCl}_3$ -hot ethanol (1:3, v/v).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C, TMS,  $\delta$ ): 7.33 (d,  $J=8.59$ , 6H), 6.91 (d,  $J=8.59$ , 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C, TMS,  $\delta$ ): 146.02, 132.50, 125.60, 116.05. Elemental analysis calculated (%) for  $\text{C}_{18}\text{H}_{12}\text{Br}_3\text{N}$ : C 44.85, H 2.51, N 2.91; found: C 44.81, H 2.47, N 2.93.

***Tris(4-formyl-biphenyl-4-yl) amine (2)***: To a solution of the formerly prepared *tris*(4-bromophenyl)amine (0.5 mmol) and  $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$  (0.05 mmol) in toluene (5 mL) was added a solution of 4-formylphenylboronic acid (2.0 mmol) and  $\text{K}_2\text{CO}_3$  (2.5 mmol) in methanol (5 mL). The mixture was refluxed during 3 days. The reaction can alternatively be shortened heating the mixture by microwave radiation at 70 °C for 40 minutes. After that the reaction mixture was poured in 100 mL of a saturated solution of  $\text{NH}_4\text{Cl}$ . The compound was extracted with dichloromethane (4 x 50 mL) and washed with brine and dried with anhydrous sodium sulfate. After evaporation of the solvent the compound was purified by flash chromatography over silica gel using dichloromethane as eluent. The product was obtained in 74 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C, TMS,  $\delta$ ): 10.06 (s, 3H), 7.97 (d,  $J=8.03$ , 6H), 7.77 (d,  $J=8.03$ , 6H), 7.62 (d,  $J=8.78$ , 6H), 7.24-7.33 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C, TMS,  $\delta$ ): 191.45, 147.14, 145.97, 134.66, 134.14, 130.05, 128.07, 126.77, and 124.32. Elemental analysis calculated (%) for  $\text{C}_{18}\text{H}_{12}\text{Br}_3\text{N}$ : C 84.00, H 4.88, N 2.51; found: C 83.92, H 4.82, N 2.47.

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- [8] Band-gaps calculated from the spectral onset; band gap (eV)  $\approx$  1240/onset (nm).

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