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Synthesis and optoelectronic characterization of some triphenylamine-based compounds containing strong acceptor substituents

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ABSTRACT

Three novel triphenylamine-based compounds containing strong electron acceptor groups have been synthesized and their comparative photophysical properties are presented. These compounds were obtained by a two-step method: (i) triphenylamine compounds with one, two and three phenylacetylene arms were synthesized by Sonogashira reaction between iodine-substituted triphenylamines and phenylacetylene, followed by (ii) post-modification of these electron-rich alkynes by addition of the strong electron acceptor, tetracyanoethylene. Characterization of all oligomers was made by FTIR, ¹H-NMR, UV-vis and fluorescence spectroscopy. A bathochromic shifting of the UV and photoluminescence maxima was observed with the increase of the acceptor group number. The electrochemical behavior was studied by cyclic voltammetry. The cyclic voltammograms have evidenced that triphenylamine-phenylacetylene compounds undergo only oxidation processes while compounds modified with tetracyanoethylene show both oxidation and reduction peaks associated with donor and acceptor groups, respectively. The donor-acceptor compounds coordinate metal ions (i.e., Hg²⁺ and Sn²⁺) by cyano groups resulting in the decreasing of charge transfer band intensity, and they can be used as chemosensors.

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1. Introduction

Arylamine-based oligomers and polymers have attracted much attention in the last years due to their unique properties that allow them to have potential applications in organic electronics, photonics and spin electronics [1–3]. Particularly, triphenylamine-based oligomers have good hole-transporting properties, high light-emitting efficiencies, photoconductivity and photorefractivity, large two-photon absorption cross sections and stabilization effect of high-spin polyradicals in organic magnets. Due to the good electron-donating nature of triphenylamine (TPA), its oligomers and polymers have been widely studied as hole-transporting materials for a number of applications, such as xerography, organic field-effect transistors, photorefractive systems, light emitting diodes, etc. [4,5]. Many triphenylamine-based dyes are used in dye-sensitized solar cells as sensitizers [6–8]. These interesting properties are associated with the presence of TPA moiety that contains the nitrogen center linked to three electron-rich phenyl groups in a propeller-like geometry [9]. As a result, many TPA-based

oligomers with linear, dendrimer or star-shaped architectures have been synthesized and studied for various applications [10–20].

Since Gratzel et al. [21] have reported the first dye-sensitized organic solar cells, a considerable interest for small conjugated molecules having a donor- π -acceptor configuration has appeared. These compounds show intramolecular charge-transfer (ICT) interactions and efficient electron transfer from donor to acceptor upon photoexcitation, being promising candidates for building of the dye-sensitized and bulk heterojunction (BHJ) solar cells. As donor part, triphenylamine has been widely used in combination with directly attached cyanoacetic acid [22,23], quinoxaline [24], oxadiazole [25], dicyano- and tricyanovinyl [26–29] groups. Tetracyanoethylene (TCNE) is known to be a strong organic electron acceptor. The high reactivity of TCNE toward nucleophiles or electron-rich reagents allowed introducing strong acceptor moieties into organic molecules [30]. Diederich et al. [31–33] have recently reported that a variety of electron-rich alkynes reacted with TCNE to give donor-substituted 1,1,4,4-tetracyano-1,3-butadienes in excellent yields. Furthermore, the reaction was extended to other acceptor molecules, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ) or using another donors [34–37], or even to obtain polymers [38]. The new class of chromophores obtained by these reactions were characterized by intense ICT interactions with a strong absorption in the visible region and promising third-order nonlinear optics [39]. The absorption maxima of these

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materials are shifted in the 400–500 nm region of solar spectrum. In this paper, we report the synthesis of three new triphenylamine-based compounds containing strong donor and acceptor groups by post-modification of triple bonds with tetracyanoethylene. Relationship between chemical structures and optoelectronic properties of the compounds was investigated by spectral methods, such as $^1\text{H-NMR}$, FT-IR, cyclic voltammetry, UV–vis and fluorescence spectroscopy.

2. Experimental

2.1. Materials

Triphenylamine (TPA), phenylacetylene, $\text{PPh}_3\text{PdCl}_2$, CuI, triphenylphosphine (PPh_3) and tetracyanoethylene (TCNE) (all from Sigma-Aldrich) are commercial products and were used without further purification. Iodine derivatives; (4-iodophenyl)diphenylamine, bis(4-iodophenyl)phenylamine and tris(4-iodophenyl)amine were synthesized starting from triphenylamine, by iodination with KI/ KIO_3 at three molar ratios, as is described in the literature [40]. Solvents such as triethylamine, methylene chloride, acetic acid, and hexane were from commercial sources and used as received or dried by known methods. Carbon tetrachloride was purified by distillation at atmospheric pressure and dried on molecular sieves.

2.2. Instruments

The FT-IR spectra were recorded in KBr pellets on a DIGILAB-FTS 2000 spectrometer. UV–vis and fluorescence measurements were carried out in solution using spectrophotometric grade solvents, on a Specord 200 spectrophotometer and Perkin-Elmer LS 55 apparatus, respectively. The fluorescence quantum yields were determined by the integrating sphere method using an FLS 980 spectrometer and CHCl_3 as solvent. $^1\text{H-NMR}$ spectra were recorded at room temperature on a Bruker Avance DRX-400 spectrometer (400 MHz) as solutions in CDCl_3 , and chemical shifts are reported in ppm and referenced to TMS as internal standard. The cyclic voltammograms (CV) were recorded using a Bioanalytical System, Potentiostat–Galvanostat (BAS 100B/W) system. The electrochemical cell was equipped with three electrodes: a working electrode (Pt, $\phi=1.6$ mm), an auxiliary electrode (platinum wire), and a reference electrode (consisted of a silver wire coated with AgCl). Prior to the each experiment, Bu_4NBF_4 solution was deaerated by passing dry argon gas for 10 min. All measurements were performed at room temperature under argon atmosphere.

Compound 1. A mixture of $(\text{PPh}_3)_2\text{PdCl}_2$ (0.011 g, 0.015 mmol), CuI (0.018 g, 0.094 mmol), PPh_3 (0.017 g, 0.064 mmol), phenylacetylene (1 mL) and 2 mL triethylamine were introduced a 50-mL round-bottomed flask. The mixture was stirred under dry nitrogen at 50–60 °C for 1 h. Then, a solution of (4-iodophenyl)diphenylamine (1.5 g, 4.04 mmol) and TEA (6.5 mL) was added. After 12 h of stirring at 60 °C, TEA was removed by distillation and the solid product was dissolved in ethylic ether, washed with diluted HCl, water and dried over MgSO_4 . The product after purification by chromatography is viscous oil that crystallized in time. Yield, 74.3%. M.p.=79–80 °C. Anal. calcd for $\text{C}_{26}\text{H}_{19}\text{N}$ (345.445): C, 90.4; H, 5.54; N, 4.06 and found: C, 90.08; H, 5.40; N, 4.18.

FT-IR (KBr) ν , cm^{-1} : 3435, 3033–2853 (=C–H), 2202 (–C \equiv C–), 1588 (C=C, conjugated phenyl groups), 1488, 1316, 1277 (–CN stretching vibration), 1070, 1025, 831, 754, 689, and 497. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ , ppm: 7.52–7.48 (m, 4H), 7.41–7.20 (m, 9H), and 7.12–6.97 (m, 6H).

Compound 2. A 50-mL round-bottomed flask was equipped with a reflux condenser, a magnetic stirring bar and an inlet–outlet of inert gas and flushed with nitrogen. TEA (15 mL), $(\text{PPh}_3)_2\text{PdCl}_2$ (0.022 g, 0.031 mmol), CuI (0.036 g, 0.18 mmol),

PPh_3 (0.033 g, 0.12 mmol) and phenylacetylene (2 mL) were introduced and the mixture was stirred under dry nitrogen at 50–60 °C for 1 h. Then, a mixture of bis (4,4'-iodophenyl)amine (1.5 g, 3.01 mmol) and TEA (10 mL) was added. After 12 h of stirring at 60 °C, TEA was removed by distillation and the solid product was dissolved in ethylic ether, washed with diluted HCl, water and dried over MgSO_4 . After evaporation of solvent the crude product was purified by column chromatography to obtain a yellow crystalline product with 78.3% yield. M. p.=46–47 °C. Anal. calcd for $\text{C}_{34}\text{H}_{23}\text{N}$ (445.534): C, 91.65; H, 5.20; N, 3.14 and found: C, 91.48; H, 5.06; N, 3.02.

FT-IR (KBr) ν , cm^{-1} : 3437, 3050–2852 (=C–H), 2211 (–C \equiv C–), 1590 (C=C, conjugated phenyl groups), 1506, 1439, 1280 (–CN stretching vibration), 1025, 830, 754, 687, and 500. $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ , ppm: 7.51–7.49 (d, 8H), 7.40–7.37 (d, 4H), 7.31–7.29 (m, 6H), 7.11–7.09 (t, 3H), and 7.03–7.01 (d, 2H).

Compound 3. A 50-mL round-bottomed flask was equipped with a reflux condenser, a magnetic stirring bar and an inlet–outlet of inert gas and flushed with nitrogen. TEA (15 mL), $(\text{PPh}_3)_2\text{PdCl}_2$ (0.033 g, 0.047 mmol), CuI (0.054 g, 0.28 mmol), PPh_3 (0.051 g, 0.19 mmol) and phenylacetylene (3 mL) were introduced and the mixture was stirred under dry N_2 at 50–60 °C for 1 h. Then, a mixture of tris(4-iodophenyl)amine (2.13 g, 3.4 mmol) and TEA (10 mL) was added. After 12 h of stirring at 60 °C, TEA was removed by distillation and the solid product was dissolved in ethylic ether, washed with diluted HCl, water and dried over MgSO_4 . After evaporation of solvent the crude product was purified by column chromatography to obtain a yellow crystalline product (yield=65.4%). M.p.=201–202 °C. Anal. calcd for $\text{C}_{42}\text{H}_{27}\text{N}$ (545.646): C, 92.44; H, 4.99; N, 2.57 and found: C, 92.18; H, 4.78; N, 2.67.

FT-IR (KBr) ν , cm^{-1} : 3435, 3031–2937 (=C–H), 2207 (–C \equiv C–), 1589 (C=C, conjugated phenyl groups), 1505, 1317, 1287 (–CN stretching vibration), 833, 752, 686, and 512. $^1\text{H-NMR}$ (CDCl_3 , MHz) δ , ppm: 7.52–7.50 (m, 6H), 7.44–7.42 (d, 6H), 7.36–7.32 (m, 9H), and 7.07–7.05 (d, 6H).

Synthesis of M1, M2, and M3. To a solution of **1** (0.43 g, 1.24 mmol) in CCl_4 (15 mL) was added TCNE (0.16 g, 1.24 mmol). The mixture was stirred at reflux for 24 h in argon atmosphere. The solutions were filtered, and after evaporation of the solvent, the solid was dissolved in a minimal amount of CH_2Cl_2 , then *n*-hexane was added until precipitation started. Crystallization at 0 °C afforded the desired products. Compound **M1** was isolated pure in 63.7% yield as dark red solid. In the case of compounds **M2** and **M3** they were isolated in pure state in 63.1% and 63.4% yields, respectively, as red solids.

M1: M.p.=156–157 °C. FT-IR (KBr) ν , cm^{-1} : 3433, 3035–2923 (=C–H), 2220 (–C \equiv N–), 1587 (C=C, conjugated phenyl groups), 1487, 1336, 1204, 757, and 697. $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ , ppm: 7.73–7.71 (d, 2H), 7.66–7.62 (d, 2H), 7.57–7.52 (m, 3H), 7.42–7.38 (m, 4H), 7.28–7.21 (m, 6H), and 6.94–6.92 (d, 2H). ESI-MS=474.54.

M2: M.p.=109–110 °C. FT-IR (KBr) ν , cm^{-1} : 3434, 3049–2923 (=C–H), 2219 (–C \equiv N–), 1588 (C=C, conjugated phenyl groups), 1486, 1331, 1180, 756, 688, and 523. $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ , ppm: 7.37–7.64 (m, 4H), 7.57–7.52 (d, 8H), 7.35–7.33 (m, 6H), 7.22–7.16 (m, 3H), and 7.01–6.99 (d, 2H). ESI-MS=702.75.

M3: M.p.=142–143 °C. FT-IR (KBr) ν , cm^{-1} : 3427, 2222 (–C \equiv N–), 1590 (C=C, conjugated phenyl groups), 1499, 1326, 1181, 835, 757, 691, and 522. $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ , ppm: 7.74–7.66 (m, 69H), 7.55–7.52 (m, 6H), 7.36–7.35 (t, 9H), and 7.18–7.16 (d, 6H). ESI-MS=930.97.

3. Results and discussion

The steps for synthesis of the triphenylamine-based compounds starting from triphenylamine, are outlined in [Scheme 1](#).

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