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**Research Article**

# Synthesis of sensitizer containing triphenylamine as donor group and investigation of solar cell applicability

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## ABSTRACT

Developing technology and the increase in the world population increase the need for energy day by day. Renewable energy sources provide an affordable, eco-friendly way to meet this need. Solar energy, which is a renewable energy source, has sufficient capacity to obtain more affordable and clean energy compared to other sources. Researchers are interested in triphenylamine and its derivatives because of their numerous uses in solar cells, electronics, and medicine. This study, solar cell applicability was investigated by synthesizing an organic dye, in which the dye contains triphenylamine as the donor group and the hydroxyl group as the acceptor group that provides binding to $TiO_2$. FTIR, MS, NMR, and UV-Vis spectroscopy are used to identify the compound's (srl-2) structure. With srl-2-based DSSC and AM (amplitude modulation) irradiation (100 mW/cm$^2$), a PCE (photoelectric conversion efficiency) value of 0.01% was attained.

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## INTRODUCTION

Energy has an important priority in human life. Climate change, an increase in $CO_2$ emissions, the effects of mining fossil fuels and the increase of the world population, meeting the increasing energy need with the development of technology are the most urgent environmental problems. These problems can be solved with renewable energy sources[1,2].

Photovoltaics is one among these sources that is quite prominent. Dye sensitized solar cells (DSSCs), one of the most well-known third-generation PV technologies, are becoming a popular option because of its remarkable performance under indoor/diffused light-harvesting conditions, ease of fabrication, low production cost, color tunability, flexibility of integration into a range of substrates, and less environmental issues [2-4].

Solar energy is the most plentiful natural resource on the planet when it comes to renewable energy sources. Photovoltaic (PV) devices are used to convert sunlight into thermal or electrical energy, generating solar energy. Solar energy is simple to use, clean, discreet, inexhaustible, long lasting, and reliable. Due to these benefits, solar energy is a major component that is practical for supplying the world's rising electricity demand, which is being driven by an increase in population and the development of infrastructure [5].

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The potential of DSSCs in harvesting artificial/indoor light has been effectively proven by Michael Grätzel, Anders Hagfeldt, and colleagues [3]. By cosensitizing two triphenylamine sensitizers, they were able to successfully produce DSSCs with an efficiency of 28.9% in ambient light. Additionally, Tingare et al. reported on a series of acetylene bridged anthracene sensitizers that, when exposed to T5 fluorescent illumination, obtained a power conversion efficiency of 28.56% [6].

Numerous studies on various DSSC components, including as sensitizers, semiconductor metal oxides, and redox electrolytes, have been conducted thus far. Sensitizers are among the most significant components that have the ability to affect the overall performance of DSSC among all of these.

Common photosensitizers in DSSC include metal complexes including ruthenium-based polypyridyl systems, porphyrins, phthalocyanines, and metal-free organic dyes.

Ruthenium-based sensitizers exhibit outstanding photovoltaic performance compared to organic dyes

[7]. Nevertheless, there is little widespread use of paints based on ruthenium in DSSC applications. It pollutes the environment due to its high cost of manufacture and toxicity. In order to create dye-sensitizing solar cells that work, numerous organic dyes that do not contain metals are being tried [8].

Therefore, as prospective sensitizers in DSSC, metal-free dyes from various classes—such as coumarins, merocyanines, indolines, hemicyanines, perylenes, oligothiophenes, xanthenes, dialkylamines, phenothiazines, tetrahydroquinolines, carbazoles, and triphenylamines—have attracted increased attention [2].

Triphenylamine is frequently utilized in organic photovoltaic functional materials because it is a superior electron donor. TPA's nonplanar structure inhibits aggregation. It also shown excellent hole-transport characteristics. In DSSCs, triphenylamine-based dyes are frequently used and have high conversion efficiencies [9, 10].

Numerous organic photoelectric devices, such as organic light-emitting diodes (OLEDs) [11], organic field effect transistors (OFETs) [12], and perovskite solar cells (PSCs) [13,] employ triphenylamine (TPA). Recent investigations revealed that due to the benefits of low excitation energy, tiny light damage, strong penetrability, etc., possessed a promising use in biological probes and drug targeting domains [14].

Although there is a need to adjust their chemical and physical properties to increase the efficiency of solar cells, triphenylamine dyes have made significant progress as sensitizers in DSSCs [9].

In this work, organic electronic materials with a high absorption band in the visible spectrum and an anchor group attached to the triphenylamine structure are synthesized and used in solar cells.

## MATERIALS AND METHODS

### Materials

All chemical was of reagent quality and came from Fluka and Merck. The appropriate drying agents were used to distill solvents before they were used. Unless otherwise noted, the use of commercially available reagents without further purification. Column chromatography was performed using Merck's silica gel 60 (0.04-0.063 mm). To prepare 4-(Diphenylamino)benzaldehyde synthesis, the Vilsmeier-Haack reaction—which is commonly employed to make aryl aldehydes—was applied. [22].

The reaction of 2- (2-aminoethoxy) -ethanol with 4- (Diphenylamino) benzaldehyde was carried out using Knoevenagel reaction conditions.

### Equipment

FT-IR spectra were recorded on a Spectrum One Perkin Elmer FT-IR spectrophotometer utilizing ATR. At the YTU - BITUAM (Yıldız Technical University Science and Technology Application and Research Center), Turkey, GC-MS mass spectra were recorded and the mass spectra were obtained using an Agilent 6530 + Agilent HPLC LCMS QTOF. $CDCl_3$ solutions were used to record $^1$H-NMR spectra using a Varian 500 MHz spectrometer.

### Synthesis

#### *Synthesis of 4-(N,N-diphenylamino)benzaldehyde (srl-1)*

Phosphorous oxychloride ($POCl_3$) (4.85 g, 52.0 mmol) was added dropwise to the mixture of triphenylamine (4.9 g, 0.02 mmol) and N, N-dimethylformamide (40 mL) at 25°C. For eight hours, the reaction mixture was heated to 80 °C while being stirred. The reaction mixture was allowed to cool to room temperature. After cooling down to room temperature, the reaction mixture was poured into 50 mL cold water and acidized with dilute hydrochloric acid and extracted with using 50 milliliters of dichloromethane. Anhydrous $MgSO_4$ was used to dry the combined organic layer, and it was then filtered and evaporated at lower pressure. The residue was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate to afford compound **1** (3.38 g, 61%) as a pale yellow solid. Characteristic C-H aldehyde peaks were visible in the FTIR spectrum of 4-(Diphenylamino)benzaldehyde (1) at 2806–2739 cm$^{-1}$ and the aromatic C–H peak was visible at 3037 cm$^{-1}$. The presence of the carbonyl group C=O signal at 1686 cm$^{-1}$ provides evidence that the structure was formed.

#### *Synthesis of 4- (Diphenylamino) 2- {2-benzylideneamino] ethoxy} ethanol (srl-2)*

Add 30.0 mL of toluene to 4- (Diphenylamino) benzaldehyde (0.26 g, 95.2 mmol) and stir for 10 minutes under nitrogen gas. Then, 2- (2-aminoethoxy) -ethanol (0.095 mL, 1.80 mmol) and catalytic amount of piperidine are added onto the mixture and it is refluxed at 120 ° C for 24 hours. After the reaction is terminated, it is brought to room temperature and extracted with diethyl ether. The obtained product was purified by column chromatography with n-hexane: chloroform (1: 2), dried in a vacuum oven to obtain orange solid (0.19 g, 55%). $C_{23}H_{24}N_2O_2$ (2) Mp. 145 °C. UV-Vis (MeOH): λmax/nm (logε/dm$^3$mol$^{-1}$cm$^{-1}$): 352 (4.89), 300 (4.52). FT-IR max/cm$^{-1}$: 3270 (-OH), 3037 (Ar-CH),2868 (Aliphatic-$CH_2$), 1125, 1114 (C-O-C), 1566 (C=N), 1489 (Aromatic C=C); $^1$H NMR ($CDCl_3$, 500 MHz), δ(ppm): 7.71 - 6.85 (m, 14H), 9.74 (2, 1H), 3.87 (d, 2H), 3.28 (s, 1H), 3.72 - 3.62 (m, 6H); GC-MS m/z: Calc. 360.45. Found: 361.19 [M$^+$].

## RESULTS AND DISCUSSION

### Synthesis and Characterization

4-(Diphenylamino)benzaldehyde was synthesized via the Vilsmeier-Haack reaction, which is frequently employed to produce aryl aldehydes.4-(diphenylaminobenzaldehyde) compound was synthesized in 61% yield by mixing the starting material triphenylamine in DMF and adding phosphoryl chloride under reflux for 24 hours. The reaction of 2-(2-aminoethoxy)-ethanol with 4-(Diphenylamino) benzaldehyde was carried out using Knoevenagel reaction conditions. 4-(diphenylaminobenzaldehyde) compound and 2-(2-aminoethoxy)-ethanol compound were mixed in toluene under reflux for 24 hours and 4-(diphenylamino) 2-{2-benzylideneamino]ethoxy}ethanol compound was synthesized in 55% yield. The synthesized compounds were purified by column chromatography (Fig. 1).

In the IR spectrum of triphenylamine, one of the starting materials, the aromatic C-H peak was observed at 3033 cm$^{-1}$ and the aromatic C=C stretching peak at 1582 cm$^{-1}$.

In the IR spectrum of 4-(Diphenylamino)benzaldehyde (**srl-1**), characteristic C-H aldehyde peaks were observed at 2806 - 2739 cm$^{-1}$, and aromatic C-H peak at 3037 cm$^{-1}$. The presence of the carbonyl group C=O peak at 1686 cm$^{-1}$ supports the formation of the structure.

In the IR spectrum of the 2-(2-aminoethoxy)-ethanol compound; The range of 3600 – 3100 cm$^{-1}$ stretching vibration of the –OH group, N-H symmetrical stress peaks at 3356 cm$^{-1}$, the stretching vibration of the aliphatic $CH_2$ group at 2856 cm$^{-1}$, C-O-C at 1119 cm$^{-1}$ and 1062 cm$^{-1}$ group of peaks are observed.

The FTIR spectra of 4-(diphenylamino) 2-{2-benzylideneamino]ethoxy}ethanol (**srl-2**); The peak at 3270cm$^{-1}$, the stretching vibration of the –OH group, the stretching vibration of the aliphatic $CH_2$ group at 2868 cm$^{-1}$ and the peaks of the C-O-C group at 1125 cm$^{-1}$ and 1114 cm$^{-1}$ are observed. C=N imine and aromatic C=C peaks at 1566 cm$^{-1}$ and 1489 cm$^{-1}$ indicate the formation of the structure.

The compound dissolves well in typical polar organic solvents such ethanol, methanol, and chloroform. The ligand's UV-vis spectra showed two different kinds of transitions (Fig. 2), the first of which was caused by transitions with molecular orbitals that could be attributed to the π-π* transition and occurred in the 210–260 nm region. The second kind of transition, where the bands widen, occurs in the 270–310 nm region and is attributed to the n-π* transition.

The molecular ion peaks in the mass spectra of srl-2 appear at *m/z* 361,19 [M + H]$^+$.and *m/z* 428.11 [M + H]$^+$. The mass spectral data confirms the proposed structure of srl-2.

According to 1H NMR, the material with the aromatic protons shown in their respective areas and a hydroxyl group connected as an anchor group to the triphenylamine structure (srl-2) was pure. In the $^1$H NMR spectrum of the 2, peaks are observed in the range of 7.71 to 6.85 ppm

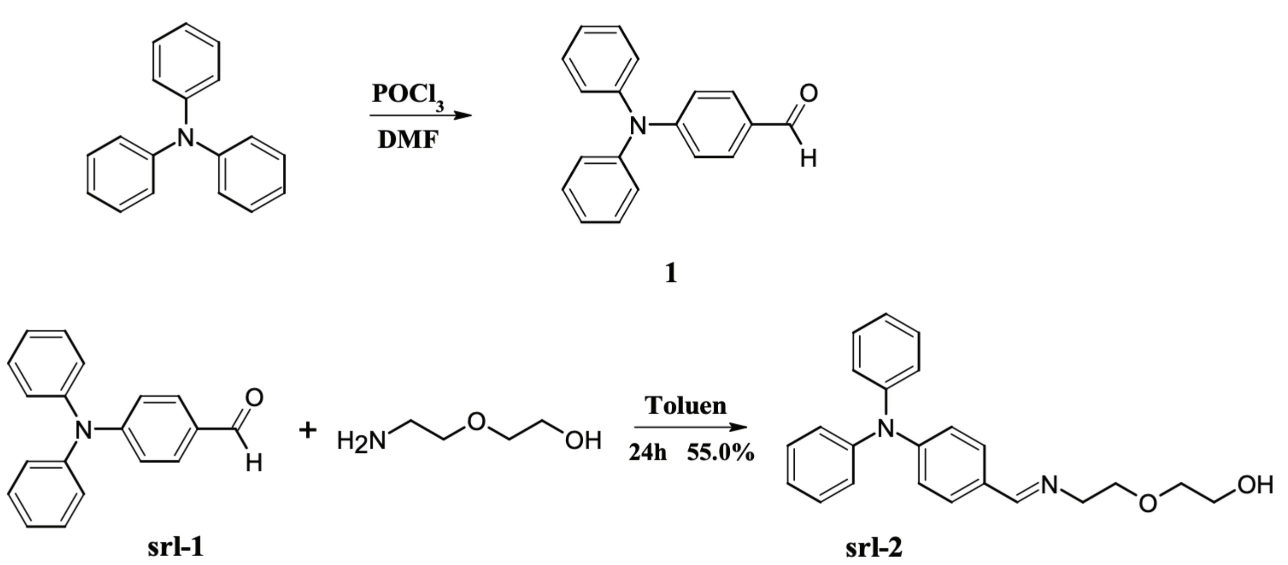


**Figure 1.** Synthesis of compound **2.**

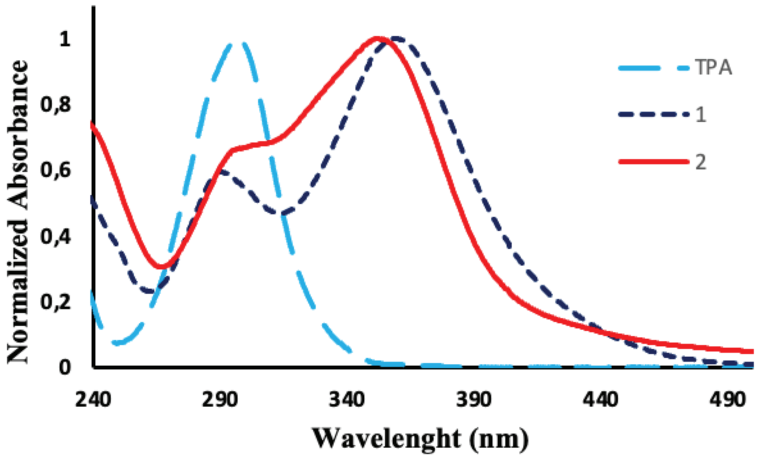


**Figure 2.** Normalized absorption spectra of TPA, srl-1 and srl-2 in methanol.

for the 14 protons of the triphenylamine ring system. The peak at 9.74 ppm is the 1 protons of the CH-N group and 3.87 ppm is for the 2 protons of the N-$CH_2$ group. The signal at 3.82 ppm is that of the C-OH group, whilst the resonances at 3.72 - 3.62 ppm are for the 6 protons of the $CH_2$-O-$CH_2$-$CH_2$.

### Fabrication and Characterization of DSSCs

For DSSCs fabrication, two transparent $TiO_2$ pastes were deposited using Doctor Blade's method on the conductive side of a FTO (Fluorine-doped Tin Oxide) substrate, as reported earlier [23]. The coated FTO substrates were immersed in a 0.3 mM dye solution in EtOH to create the dye-sensitized (**2**) $TiO_2$ films (photoanodes). Casting from a platinum paste solution was used to create the Pt counter electrodes on the FTO substrates. Surlyn film was used to seal the photoanode and counter electrode. Through a hole drilled in the counter electrode, the redox electrolyte was introduced between the electrodes. Using a potentiostat/galvanostat, the current density-voltage (J-V) characteristics were examined under AM 1.5 global one sun illumination (100 mW $cm^{-2}$) from a solar simulator.

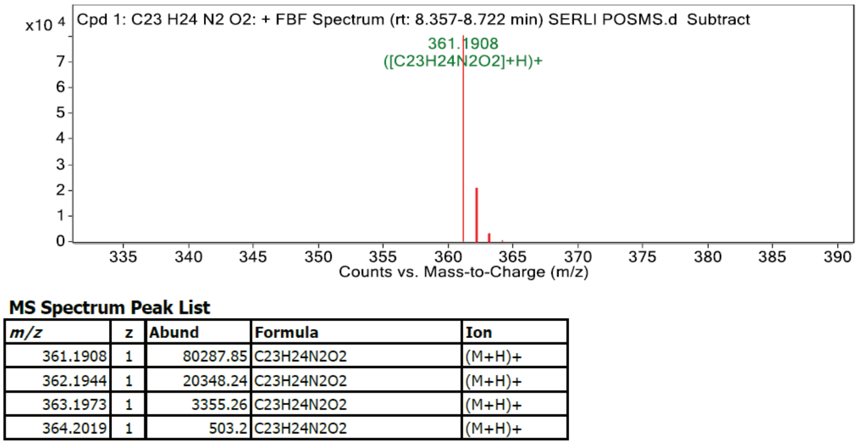
The photovoltaic cell efficiency (η), fill factor (FF), maximum power ($P_{max}$), current at the maximum power point (Imp), voltage at the maximum power point ($V_{mp}$), short-circuit current ($I_{sc}$), and open-circuit voltage ($V_{oc}$) all affect the solar cell's electrical performance. Equations 1 and 2 are used to determine the solar cell efficiency and fill factor, respectively:

$$\boldsymbol{\eta} = \frac{P_{max}}{P_{in}} = \frac{I_{sc} \cdot V_{oc} \cdot FF}{P_{in}} \tag{1}$$

where the I-V curve measurement is typically used to determine the FF, which is provided by

$$FF = \frac{I_{mp} \cdot V_{mp}}{I_{mp} \cdot V_{oc}} \tag{2}$$

The maximum product of current and voltage is divided by the incoming solar power to obtain the conversion efficiency of sunlight to electrical energy.



**MS Spectrum Peak List**

| m/z | z | Abund | Formula | Ion |
|---|---|---|---|---|
| 361.1908 | 1 | 80287.85 | C23H24N2O2 | (M+H)+ |
| 362.1944 | 1 | 20348.24 | C23H24N2O2 | (M+H)+ |
| 363.1973 | 1 | 3355.26 | C23H24N2O2 | (M+H)+ |
| 364.2019 | 1 | 503.2 | C23H24N2O2 | (M+H)+ |

**Figure 3.** Mass spectrum of compound srl-2.

In Figure 4, x-axis shows voltage and y-axis shows current. Figure 4a) shows the reference DSSC measurement result in light and dark. The photovoltaic efficiency of the reference DSSC is 0.08% when measured in the light, and 0.01% when measured in the dark.

Figure 4b shows the prepared compound srl-2 DSSC measurement result in light and dark. The photovoltaic efficiency of the srl-2-based DSSC device is slightly above 0.01% when measured in the light, and its photovoltaic efficiency is 0.01% when measured in the dark.

Considering the contribution of the produced srl-2 based DSSC device to Jsc, Voc and FF values, it was observed that a PCE value of 0.01 was obtained.

In general, TPA-based sensitizers have the ability to lessen aggregation and let excited dye molecules to inject electrons into the $TiO_2$ conduction band across the interface.

The reason for this low efficiency value is the π-conjugation system that provides electron conduction. It could be understood as the incompleteness of the material we create. This work demonstrates how the performance of sensitized solar cells is enhanced by direct electron transfer from the donor group to the anchor group in the sensitizing structure. This result shows that the conjugation system, which provides direct electron transfer from the donor group to the anchor group in the sensitizing structure, is at least as important as the donor and anchor group.

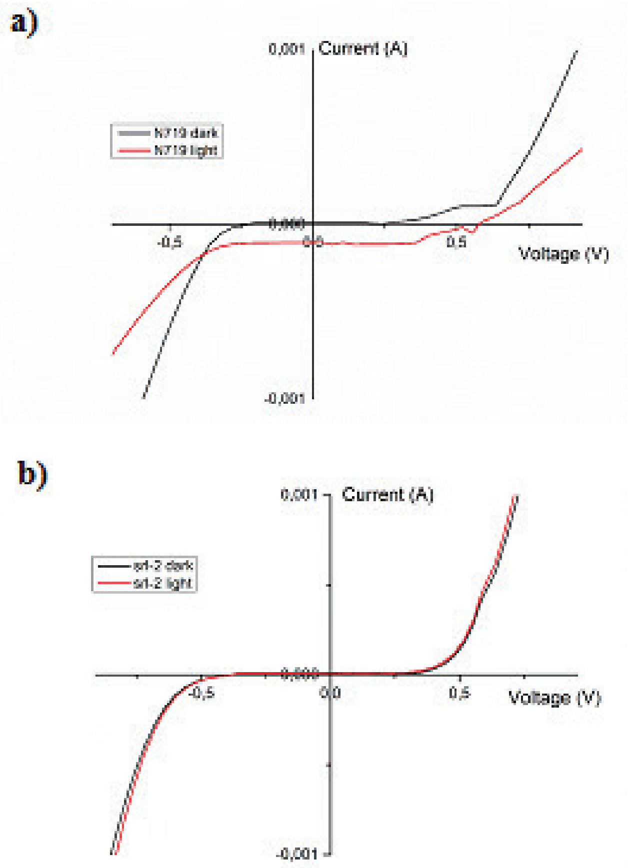


**Figure 4.** a) Graph of reference DSSC in light and dark, b) Graphic of the prepared compound srl-2 DSSC in light and dark.

In order to increase the weak electron injection capacity, conjugation can be achieved by adding an ethylene or acetylene bridge between the donor group and the anchor group. It is thought that the potential can be increased by adding different anchor groups such as "carboxyl", "cyano" or "phosphonite", in addition to the "hydroxyl" anchor group, in order to form a solid bond with the semiconductor oxide film and to conduct the electron to the conduction band of $TiO_2$ in a healthy way. To improve the inadequate photosensitization, the structure can be modified to include two triphenylamine or phenyl modified triphenylamine sensitizers to increase the number of donor groups. Alternatively, this synthetic material can be utilized as a ligand to manufacture phthalocyanine, which has a high light absorption capacity in the red and near-infrared spectrum regions, as I intend to do in my next study. Thus, I strongly believe that it can serve as a potential candidate for a high-performance solar cell with suitable structural features.

## CONCLUSION

In this study, sensitizer srl-2 containing hydroxyl group as anchor was synthesized. The DSSC devices were manufactured using these sensitizers, and the I-V values were recorded. In the study, photovoltaic efficiency of 0.01% was measured. The reason for this low efficiency value is the π-conjugation system that provides electron conduction. It can be interpreted as the lack of completeness in the substance we synthesize. This result reveals how direct electron transfer from the donor group to the anchor group in the sensitizing structure leads to an increase in the performance of sensitized solar cells. Like metal complexes, porphyrins and other organic dyes, triphenylamine organic dyes also suffer from a variety of scientific issues with respect to higher efficiency. The primary issues can be summed up as follows: dye aggregation on the $TiO_2$ surface; charge recombination at the $TiO_2$/electrolyte interface; absence of absorption in the near infrared region; and mismatch in energy levels between the dyes, $TiO_2$, and electrolyte. The bathochromic shift of the absorption maxima is one of the most crucial problems to improve the DSCs performance. It is still difficult to determine how to make metal-free organic dyes in DSSCs more efficient and how to adapt the technology to multijunction solar cells.

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## DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

## CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

## ETHICS

There are no ethical issues with the publication of this manuscript.

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