Synthesis and characterization of a triphenylamine-dibenzosuberenone-based conjugated organic material and an investigation of its photovoltaic properties

Musa Erdoğan¹ and Sabit Horoz²

Abstract
3,7-Bis[4-(diphenylamino)phenyl]-5H-dibenzo[a,d][7]annulen-5-one, containing triphenylamine- and dibenzosuberenone-based donor-acceptor-donor (D-A-D) conjugated moieties, is synthesized in high yield by Suzuki coupling of 5H-dibenzo[a,d] [7]annulen-5-one with [4-(diphenylamino)phenyl]boronic acid. The most important part of the present study is the creation of a dye-sensitized solar cell structure using the synthesized organic molecule for the first time and the power conversion efficiency of this structure. Three solar cell devices are prepared and are named as first device, second device, and third device. The power conversion efficiency (%) value for first device, second device, and third device is calculated as 2.54, 2.38, and 2.54, respectively. Moreover, the chemical structure of the synthesized compound is determined by nuclear magnetic resonance, infrared, ultraviolet visible, fluorescence spectroscopy, and high-resolution mass spectrometry.

Keywords
characterization, dibenzosuberenone, D-A-D, D-π-A, photovoltaic, synthesis, triphenylamine

Introduction
The tricyclic structure of 5-dibenzo[2,3;4,5-dibenzotropone (5H-dibenzo[a,d][7]annulen-5-one) form has been utilized most in organic synthesis due to its symmetrical structure. This core skeleton is widely used, especially in materials chemistry, in photovoltaic applications, as a light-emitting diode, as an organic light-emitting diodes (OLED) in organic electronic applications, and in field-effect transistors, as well as in new bipolar molecular materials with high optoelectronic performances. In addition, the core skeleton has found various applications in polymer synthesis and in the formation of coordination cages. However, triphenylamine (TPA) derivatives are known for their strong electron-donor and blue light-emitting properties. TPA cores have shown exceptional properties, such as good solubility in organic solvents, hole-conducting properties, high electron mobility, two-photon absorption, and excellent optoelectronic properties.

Solar cells, including dye-sensitized solar cells (DSSCs), bulk heterojunction donor-acceptor blends, quantum dot solar cells, organic–inorganic hybrid perovskite solar cells, and tandem solar cells have received significant interest in the market for low-cost power and mobile energy generation. DSSCs, as a new form of green energy device, show important characteristics such as ease of manufacture, reasonably low manufacturing costs, low contamination, and good molecular design versatility. Photosensitizers play a critical role among all the components of DSSCs, being responsible for light harvesting and then passing electrons to a broad band gap of a semiconducting oxide. Therefore, optoelectronic activities of sensitizing dyes are essential for...

¹Department of Food Engineering, Faculty of Engineering and Architecture, Kafkas University, Kars, Turkey
²Department of Electrical and Electronics Engineering, Faculty of Engineering, Siirt University, Siirt, Turkey

Corresponding author:
Musa Erdoğan, Department of Food Engineering, Faculty of Engineering and Architecture, Kafkas University, Kars 36100, Turkey.
Email: musa.erdogan.kafkas@gmail.com
the photovoltaic efficiencies of a DSSC. Hence, molecular engineering of sensitizing dyes is one of the most productive ways of advancing DSSC performance. Owing to their simple growth and consistent efficiency, one of the most popular design approaches of metal-free organic dyes includes the use of D–π–A structures.26-27

Classic metal-free sensitizers are centered on the D–π–A method to accomplish productive separation and transfer of charges. Molecular engineering of donor groups has advanced from the use of a basic moiety of TPA to a moiety based on starburst phenylene, to regulate electronic grades or molecular configuration, and to provide efficient movement of charge.28 A π-tunneling device is a modern design function, affecting the highest energy occupied molecular orbital (HOMO)/lowest energy unoccupied molecular orbital (LUMO) energy levels or otherwise spectroscopic characteristics.29

Herein, we report on the synthesis of 3,7-bis[4-(diphenylamino)phenyl]-5H-dibeno[a,d][7]annulen-5-one (3) which has a D–A-D-based system and a high level of conjugation. In the molecular design of compound 3, TPA units were selected as the electron donor in the donor-acceptor conjugated system because of their propeller-like conformation and excellent hole-transporting ability. A dibenzosuberene ring containing a tropone core was selected as an acceptor in the donor–acceptor system due to its strong electron-withdrawing properties. A DSSC structure using the synthesized organic molecule 3 was fabricated for the first time and its power conversion efficiency (%) calculated. Moreover, the chemical structure of the synthesized compound 3 was determined by nuclear magnetic resonance (NMR), infrared (IR), ultraviolet (UV)-Vis, fluorescence spectroscopy, and high-resolution mass spectrometry (HRMS).

Results and discussion

Synthesis

Dibromodibenzosuberene (1) was synthesized according to a reported method2 and was used as the key structure allowing us to prepare dibenzosuberene derivative 3 (Scheme 1). Dibenzosuberene derivative 3 was synthesized in an excellent 95% yield (Lit.,20 yield 61%) by Suzuki coupling between 4-(diphenylamino)phenyl]boronic acid (2) and the dibromide 1.

NMR analysis

The 1H NMR spectrum of the compound 3 (Figure 1) having a symmetrical structure consists of sets of signals appearing in the aromatic region. The aromatic Ha protons are split into a doublet by the meta-coupling with the Hb protons 8.49 ppm (d, J = 1.9 Hz, 2Ha). The Hb protons resonate as a doublet of doublets at 7.78 ppm, due to coupling with the Hc and Ha protons (J = 8.1 Hz, J = 1.9 Hz). In addition, the Hd protons, one of the most specific peaks, resonate as a singlet at 7.10 ppm (s, 2H) due to the aromatic structure. The remaining aromatic ring protons resonate as multiplets 7.62–7.58 (m, 6H), 7.32–7.25 (m, 10H), 7.20–7.13 (m, 10H), and 7.08–7.03 (m, 4H) ppm. The carbonyl carbon, which is a characteristic peak in the 13C NMR spectrum of compound 3, resonates at 193.1 ppm. The proton-decoupled 13C NMR spectrum of compound 3 shows 16 carbon signals because of its symmetrical structure. The data were in very good agreement with previous data reported in the literature.20

Fourier transform infrared and HRMS analysis

The IR spectrum of 3 exhibited characteristic absorptions bands for aromatic C–H, C=O, aromatic C=C, and aromatic C–N bonds. The absorption bands at 3032, 3055, and 3065 cm−1 are attributed to aromatic C–H bending vibrations of compound 3. The absorption band at 1737 cm−1 is assigned to the stretching vibration of the carbonyl group, and those at 1483, 1515 and 1587 cm−1 are due to the aromatic C=C groups. The C–N stretch of the aromatic amines is observed at 1331–1233 cm−1. HRMS confirmed the constitution of compound 3. The HRMS results demonstrated excellent agreement between the calculated mass (693.2906) and the obtained mass (693.2934).

Photophysical properties

The result of the absorbance measurement on compound 3 is shown in Figure 2, with a large absorption peak at 380.1 nm being observed. This experimental observation is in accordance with the literature.20,21 The half-width full-width value for the absorption peak was determined as 46.7 nm. Considering the resulting peak position (380.1 nm), the energy band range of compound 3 is calculated as 3.26 eV.

As it is non-destructive and non-intrusive, photoluminescence (PL) is an essential technique for researching electronic equipment. In addition, the optical and electronic characteristics of a compound are closely related: a quantum system displays quantized energy states that are defined by the discrete wavelength of emission. The result of the PL measurement on compound 3 is shown in Figure 3. In the PL measurement, the excitation wavelength is 360 nm. As in absorption measurements, a wide PL band was observed at 534 nm and the half-width full width was detected as 76.6 nm. The observed PL wavelength corresponds to the emission of a blue-green color. This indicates that compound 3 can be used as a promising material in different optoelectronic technologies such as OLEDs, sensors, and solar cells.

There are significant benefits of organic molecules that are used in solar cell applications.30 Organic molecules, in fact, involve more adsorption layers than metal materials and absorb a wider range.31 The scope of organic materials is limitless and they can be quickly refreshed.32 Furthermore, curiosity in pure organic molecules is rising as computer simulations to model such compounds are simpler than using actual metal compounds. In addition, compound 3 showed red shifts of the absorption and emission maxima, which might be attributed to the large π-conjugated skeleton that is beneficial to electron delocalization. Moreover, a good fluorescence quantum yield (Φ = 0.070) and a large Stokes shift (153.9 nm) were demonstrated by compound 3.
which are highly desirable for dyes employed in photophysical applications.

**Photovoltaic properties**

In the light of the information given above, current density (J)–voltage (V) measurements were performed to examine the photovoltaic properties of three compound 3–based DSSC devices (see the “Experimental” section for details) and to calculate the power conversion efficiency (%) for each device. The resulting J-V plots are shown in Figure 4. The equations reported in our previous study were used to calculate the power conversion efficiency.

The obtained short-circuit current density (J_Sc), the open-circuit voltage (V_OC) current corresponding to the maximum power point (J_MP), the voltage corresponding to the maximum power point (V_MP), the fill factor (FF), and the power conversion efficiency (%) values for each device are given in Table 1.

The power conversion efficiency (%) values for the three devices were calculated as 2.54, 2.38, and 2.54 under illumination with a AM1.5, 100 mW/cm² lamp using the relation given in our previous study. It is well-recognized that the rate of electron transport in a solar cell configuration will impact the power conversion efficiency (%) value of an organic molecule sensitized solar cell device. The achieved high short-circuit current density value for the first device and the third device indicates that effectual injection of electrons occurs into the conduction band (CB) of a counter electrode (TiO₂) conduction band from the excited state of the organic molecule. Compared to the first and third solar cell devices, the second device has a
slightly lower \( J_{SC} \) value. One possible reason for the low \( J_{SC} \) value is the inadequate amount of compound 3 suspensions attached to the Zn$_2$SnO$_4$ the nanowires, which can be improved by adjusting the soaking time of nanowires in compound 3 suspensions. Consequently, this phenomenon carries off to achieve an enhanced power conversion efficiency of an organic molecule (compound 3)-sensitized solar cell device.

**Conclusion**

We have successfully synthesized and characterized the triphenylamine-dibenzosuberene derived D-A-D-based conjugated organic molecule 3. Compound 3 was synthesized in excellent yield via the Suzuki coupling reaction of \( 5H \)-dibenzo[a,d][7]annulen-5-one (1) with \[4-(diphenylamino)phenyl\]boronic acid (2). The synthesized molecule has an electron-rich triphenylamine unit acting as the electron donor (D) and an electron-deficient dibenzosuberene unit acting as an electron acceptor, assembled as a D-A-D-type compound with a highly \( \pi \)-conjugated skeleton. In addition, compound 3 has a large Stokes shift and good quantum yield. The most specific aspect of our current study was the use of the synthesized organic molecule 3 for the first time as a sensitizer in a DSSC structure. Three solar cell devices were prepared (first device, second device, and third device), with the power conversion efficiencies (%) calculated as 2.54, 2.38, and 2.54, respectively. The calculated power conversion efficiency (%) values can be considered as an indication that compound 3 is an effective sensitizer that can be used in DSSC devices.

**Experimental**

**General remarks**

The one- and two-dimensional \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Varian-400 or a Bruker-400 spectrometer in CDCl$_3$ using tetramethylsilane as the internal reference. All spectra were recorded at 25 °C and coupling constants (\( J \) values) are given in Hertz. Chemical shifts are given in parts per million (ppm). Abbreviations used to define the multiplicities are as follows: \( d \) = doublet; \( dd \) = doublet of doublets; \( m \) = multiplet. Mass spectra were recorded on an Agilent Technologies 6530 Accurate-Mass Q-TOF-MS. IR spectra were recorded on Perkin Elmer Fourier transform infrared (FT-IR) spectrometer. Absorption spectrometry was performed using a Perkin Elmer Lambda 35 spectrophotometer. Steady-state fluorescence measurements were conducted using a Shimadzu RF-5301PC spectrophotofluorometer. Absorbance and emission spectroscopy measurements were performed on 5 µm samples in CH$_2$Cl$_2$. The fluorescence quantum yield of compound 3 was calculated using the Parker–Rees equation and compared to a well-known reference, quinine sulfate, in aqueous solution (\( \Phi_F = 0.546 \), 0.5 M H$_2$SO$_4$) as the standard dye. The method we reported in our previous study was used for J–V measurements. Compound 3 as a suspension was used as the sensitizer.

**Synthesis of 3,7-bis[4-(diphenylamino)phenyl]-5H-dibenzo[a,d][7]annulen-5-one (3)**

To a 50-mL, two-necked, round-bottomed flask was added dibromodibenzosuberene (1) (0.45 g, 1.24 mmol) and Pd(PPh$_3$)$_4$ (42.8 mg, 0.037 mmol) in dimethyl ether (DME; 30 mL). A solution of \[4-(diphenylamino)phenyl\]boronic acid (2; 858 mg, 2.97 mmol) and Na$_2$CO$_3$ (393 mg, 3.71 mmol) in degassed water (15 mL) was added and the resulting mixture was refluxed for 24 h. The reaction mixture was quenched with water (20 mL) and extracted with CH$_2$Cl$_2$ (3 \( \times \) 20 mL). The combined organic layers were dried (Na$_2$SO$_4$), filtered, and evaporated. The crude reaction mixture was purified by column chromatography on silica gel (20% EtOAc/n-hexane). The obtained solid was recrystallized from CH$_3$Cl$_2$/n-hexane (9:1) to give 3,7-bis-[4-(diphenylamino)phenyl]-5H-dibenzo[a,d][7]annulen-5-one (3) (813 mg, 95%) as yellow crystals. M.p.: 240 °C. \(^1\)H NMR (400 MHz, CDCl$_3$): \( \delta = 8.49 \) (d, \( J = 1.9 \) Hz, 2H), 7.86 (dd, \( J = 8.1 \) Hz, 1.9 Hz, 2H), 7.62–7.58 (m, 6H), 7.32–7.25 (m, 10H), 7.10 (s, 10H).

| Device       | \( J_{SC} \) (mA/cm$^2$) | \( V_{OC} \) (V) | \( J_{MP} \) (mA/cm$^2$) | \( V_{MP} \) (V) | \( FF \) | Power conversion efficiency (%) |
|--------------|--------------------------|-----------------|--------------------------|-----------------|-------|-------------------------------|
| First device | 7.82                     | 0.65            | 5.53                     | 0.46            | 0.50  | 2.54                          |
| Second device| 7.31                     | 0.65            | 5.17                     | 0.46            | 0.50  | 2.38                          |
| Third device | 7.82                     | 0.65            | 5.53                     | 0.46            | 0.50  | 2.54                          |
Zn₂SnO₄ nanowires were synthesized on gold-coated (3 nm) Si substrates following a procedure published elsewhere. This process is able to reliably reproduce nanowires roughly 20 μm thick. The nanowires are placed in a suspension of compound 3 and allowed to soak for 24 h. Immediately upon removal from the compound 3 suspension, the substrates were dried with N₂ gas and secured against a Cu₂S counter electrode containing a polysulfide electrolyte (0.25 M Na₂S and 0.1 M NaOH in 18 MΩ water). The Cu₂S counter electrodes were fabricated following a procedure published elsewhere. The J-V value was measured immediately after device fabrication. Data are obtained using a monochromatic light source consisting of a 50 W tungsten-halogen lamp and a monochromator. The light beam is modulated by a chopper and a lock-in amplifier (Stanford Research SR830). Three solar cell devices were prepared using the compound 3 solution as a sensitizer. The three solar cell devices were named as first device, second device, and third device.

Declaration of conflicting interests
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ORCID iD
Musa Erdoğan https://orcid.org/0000-0002-6091-757X

Supplemental material
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