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# A novel dibenzosuberenone bridged D-A- $\pi$ -A type dye: Photophysical and photovoltaic investigations



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#### ABSTRACT

In this study, a novel dibenzosuberenone based organic dye comprising triphenylamine (TPA) as the electron-rich unit and a dibenzosuberenone as the central core and an additional acceptor and, benzene as the  $\pi$  linker unit, and an aldehyde as the electron-deficient unit to form  $\pi$ -conjugated donoracceptor- $\pi$ -bridge-acceptor (D-A- $\pi$ -A) system was designed. The dye was successfully synthesized by Suzuki coupling reaction using a novel one pot approach, i.e. two different aryl boronic acids containing electron withdrawing group (EWG) and electron donating group (EDG) at para positions were added to the reaction medium at the same time. As expected, three different coupling products were obtained in one-pot/one step. Structures of synthesized compounds were fully characterized by NMR, IR, HRMS UV-Vis, and fluorescence spectroscopy techniques. The photophysical and photovoltaic properties of the dye were elucidated and, DFT theoretical calculations were performed to support the investigations. The dye showed red shift of absorption and emission maxima, 388 and 571 nm, respectively. Moreover, a medium fluorescence quantum yield (0.27) and a very large Stokes shift (183 nm) of the dye was also found. The calculated HOMO and LUMO energies of the ground state optimized geometry of the dye were -5.360 and -2.521 eV, respectively, and the bandgap was 2.838 eV. The power conversion efficiency (%) value for the dye were also calculated as 3.01%. The findings provide a beneficial reference to the development of organic dyes containing dibenzosuberenone groups in more efficient dyes for DSSCs.

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#### 1. Introduction

Organic dyes have attracted attention because of their flexibility in design and synthesis. Organic luminescent materials exhibit excellent potential as a low-cost, environmentally-friendly and sustainable alternative [1]. Due to their interesting physical and chemical properties, organic fluorescent compounds have drawn attention in recent decades [2]. They are widely used in diverse fields including organic light-emitting diodes (OLEDs) for electroluminescent devices, photovoltaic cells, organic electronics [3], fluorescent dyes [2], chemical sensors [4], and bio-imaging [5]. Organic dyebased D- $\pi$ -A conjugated systems, with the donor (D) and acceptor (A) groups and the linking  $\pi$ -bridges, have highlighted its importance in many disciplines of science due to their special photophysical properties. This hybrit skeletons have been widely used in materials chemistry due to their excellent optical properties including organic light-emitting diodes (OLEDs), dye-sensitized solar cells (DSSCs) [6], nonlinear optical materials, fluorescence imaging, and memory [6,7]. These systems have also displayed very im-

\* Corresponding Author. E-mail address: musa.erdogan@kafkas.edu.tr portant photophysical properties, such as a wide absorption, large stokes-shift, easily tunable fluorescence, as well as excellent nonlinear optical qualities [8]. Up to now, it was reported that organic dyes such as  $D-(\pi-A)_2$ ,  $D-\pi-A$ ,  $D-D-\pi-A$ ,  $D-A-\pi-A$  and  $(D-\pi-A)_3L_2$  [9]. Among these dyes, a novel concept,  $D-A-\pi-A$  conjugate system, has been demostrated to provide extensive advantages, such as wide absorption and emission bands in UV-visible region, efficient intramolecular charge transfer, easily tunable molecular orbital energy levels and optoelectronic properties, and the narrow bandgap energy for harvesting more NIR light [9-12]. Thus, the use of "D- $A-\pi-A$ " organic sensitizers have been regarded as a promising approach to increase cell efficiency and improve photovoltaic performances in a solar cell instead of traditional  $D-\pi-A$  ones [9,13].

As already known, the photovoltaic performance of a DSSC is strongly dependent on the sensitizers, which play a very important role in sunlight harvesting, charge generation, and charge transport [14]. Thus, the optoelectronic quality of the photosensitizer is of paramount importance to the photovoltaic performance of a DSSC [15]. Normally, dye types are divided into two classes as metalbased and metal-free organic dyes [9,14]. Unlike the metal-based dyes, the metal-free organic sensitizers have a number of advantages, such as environmental friendliness, high molar extinction coefficient, good flexibility of molecular tailoring, tunable spectral properties, relatively high efficiency, and low cost [13,14,16]. So far, power conversion efficiencies (PCEs) of 14% have been reached for those based on metal-free organic dyes [17]. Therefore, the D-A- $\pi$ -A photosensitizers have been observed as promising candidates to increase the cell efficiency [18].

However such studies are scarce in the literature, and it is important to discover novel D-A- $\pi$ -A based dyes. To the best of our knowledge, the dibenzosuberenone-based dyes with different aromatic linkers have not been reported. In this study, we report for the first time novel dibenzosuberenon-based dye **10** (Scheme 3), in which dibenzosuberenone is used as an additional acceptor, triphenylamine is used as donor, benzene is a  $\pi$ -spacer, and aldehyde is an acceptor/anchor.

#### 2. Experimental Section

#### 2.1. General

All reactions were carried out under nitrogen and monitored by TLC thin layer chromatography (TLC) method and spots were visualized by UV irradiation. All solvents were dried and distilled before use. Melting points are uncorrected. IR spectra were recorded on Perkin Elmer FT-IR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Nuclear magnetic resonance spectrometer (Bruker-400 spectrometer) using CDCl<sub>3</sub> as solvent. Tetramethylsilane (TMS) was used as an internal standard. All spectra were recorded at 25 °C and coupling constants (J values) are given in Hz. Chemical shifts are given in parts per million (ppm) relative to the residual solvent peak (CHCl<sub>3</sub>: 7.26 ppm for <sup>1</sup>H and 77.36 ppm for <sup>13</sup>C-NMR). Mass spectra were determined on an Agilent Technologies 6530 Accurate-Mass Q-TOF-LC/MS. TLC was performed on silica gel 60 HF254 aluminium plates (Fluka). Fluorescence analyses were carried out on a Shimadzu RF-5301PC spectrofluorometer. Fluorescence quantum yield (QY) of the dye 10 was performed through the Parker-Rees equation [19]. J-V measurements were carried out according to the method reported in our previous study [15]. The geometry and electronic properties of the compound 9 and the dye 10 were performed with the Gaussian09 W program package. The quantum-chemical calculations were performed with Gaussian09 W software by using density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods with B3LYP/6-311++G(2d, 2p) basis set [20].

#### 2.2. Synthesis and characterization

The key compounds **2**, **3** and **4** were synthesized according to procedures the literature [21].

# 2.2.1. 3,7-Dibromo-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-one (2)

3,7-Dibromo-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-one (**2**) [21]: white crystals from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (1:3), mp 159-161 °C (lit [22] mp 160 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ = 8.11 (d, *J* = 1.8 Hz, 2H), 7.54 (dd, A part of AB system, *J* = 8.0 Hz, 1.8, 2H), 7.11 (d, B part of AB system, *J* = 8.0 Hz, 2H), 3.15 (s, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ = 192.3, 140.7, 139.4, 135.4, 133.4, 131.2, 120.8, 34.2.

2.2.2.

## 3,7,10,11-Tetrabromo-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-one (3)

3,7,10,11-Tetrabromo-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-one (**3**): The compound **3** [22] was moved onto the next reaction without purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.21 (d, *J* = 2.0 Hz, 2H), 7.69 (dd, A part of AB system, *J* = 8.2 Hz, 2.0 Hz, 2H), 7.28 (d, B part of AB system, J = 8.2 Hz, 2H), 5.70 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 189.0$ , 138.6, 135.9, 135.6, 134.5, 132.6, 124.0, 51.4.

#### 2.2.3. 3,7-Dibromo-5H-dibenzo[a,d][7]annulen-5-one (4)

3,7-Dibromo-5H-dibenzo[a,d][7]annulen-5-one (**4**): white solid, mp 266-268 °C (lit [22] mp 267 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =8.35 (d, *J* = 2.0 Hz, 2H), 7.74 (dd, A part of AB system, *J* = 8.3 Hz, 2.0 Hz, 2H), 7.42 (d, B part of AB system, *J* = 8.3 Hz, 2H), 7.01 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 203.2, 139.6, 135.5, 133.9, 133.4, 132.9, 131.4, 123.7.

## 2.2.4. Synthesis of dicoupling products via Suzuki coupling reaction of dibromobenzosuberenone 4 with arylboronic acids **5** and **8**

Dibromobenzosuberenone **4** (1.49 g, 4.09 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (142 mg, 0.122 mmol) was added into a 100 mL two-necked flask, followed by addition of 40 mL of dry DME. A solution of (4-(diphenylamino)phenyl)boronic acid (**8**) (1.42 g, 4.91 mmol), (4-formylphenyl)boronic acid (**5**) (0.736 g, 4.91 mmol) ve Na<sub>2</sub>CO<sub>3</sub> (1.30 g, 12.28 mmol) in degassed water (20 mL) was added and, all the solution was refluxed for 18 h under nitrogen atmosphere. The mixture was added to 100 mL of ice-water, and the DME was then evaporated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 75 mL). The combined organic layers were washed with water, dried with MgSO4, filtered, and then concentrated. The crude product was purified by column chromatography on silica gel eluted with the mixture of solvents (25% EtOAc/*n*-hexane).

1. Fraction: 3,7-Bis(4-(diphenylamino)phenyl)-5*H*-dibenzo[*a*,*d*][7]annulen-5-one (**9**): yield 39%, 1.10 g, yellow crystals, mp 239-241 °C (239-241 °C [15]), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ = 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), 7.20-7.13 (m, 10H), 7.10 (s, 2H), 7.08-7.03 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ = 193.1, 148.1, 147.7, 141.1, 138.9, 133.9, 133.4, 131.9, 131.3, 130.1, 129.6, 128.2, 128.0, 124.9, 123.8, 123.4. IR (KBr, cm<sup>-1</sup>): 3065, 3055, 3032, 1737, 1626, 1587, 1515, 1483, 1385, 1331, 1315, 1286, 1269, 1233, 1175, 1073, 1028, 964, 835. HRMS (Q-TOF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>51</sub>H<sub>37</sub>N<sub>2</sub>O: 693,2906, found: 693,2934.

Fraction: 4-(7-(4-(diphenylamino)phenyl)-5-oxo-5H-2 dibenzo[*a*,*d*][7]annulen-3-yl)benzaldehyde (**10**): yield 26%, 589 mg, yellow crystals, mp 216-218 °C, <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 10.08$  (s, 1H), 8.56 (d, I = 1.9 Hz, 1H), 8.49 (d, I = 1.9 Hz, 1H), 8.00 (d, *I* = 8.2 Hz, 2H), 7.95-7.84 (m, 4H), 7.71-7.56 (m, 4H), 7.32-7.26 (m, 2H), 7.19-7.11 (m, 8H), 7.09-7.02 (m, 4H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 192.52$ , 191.85, 148.00, 147.47, 145.44, 141.22, 139.66, 138.72, 138.68, 135.57, 135.03, 133.49, 132.87, 132.17, 131.92, 131.88, 130.62, 130.45, 130.41, 130.03, 129.42, 129.24, 127.93, 127.80, 127.67, 124.74, 123.50, 123.32. IR (KBr, cm<sup>-1</sup>): 3062, 3031, 2992, 2926, 1735, 1689, 1640, 1587, 1518, 1484, 1421, 1397, 1331, 1276, 1267, 1238, 1209, 1195, 1165, 1072, 1045, 027, 1013, 967, 914, 881, 855, 826, 755, 731, 695. HRMS (Q-TOF): m/z [M+H]+ calcd. for C<sub>40</sub>H<sub>28</sub>NO<sub>2</sub>: 554,21200; found: 554,21176.

3. *Fraction*: 4,4'-(5-oxo-5*H*-dibenzo[*a*,*d*][7]annulene-3,7diyl)dibenzaldehyde (**7**): yield 15%, 250 mg, brown solid, <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 10.10 (s, 2H), 8.57 (s, 2H), 8.01 (d, *J* = 7.9 Hz, 4H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 7.9 Hz, 4H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.19 (s, 2H). ). <sup>13</sup>C NMR spectrum could not be obtained due to strong aggregation even in different polar solvents. IR (KBr, cm<sup>-1</sup>): 3006, 2987, 2958, 2919, 2849, 2747, 1691, 1679, 1643, 1603, 1572, 1464, 1419, 1392, 1366, 1336, 1309, 1275, 1260, 1215, 1166, 1048, 821, 764, 750, 694. HRMS (Q-TOF): m/z [M+H]<sup>+</sup> calcd. for C<sub>29</sub>H<sub>19</sub>O<sub>3</sub>: 415,13342; found: 415,13318.

#### 2.3. Preparation of the DSSC devices

DSSC device was prepared using the method previously reported in our study [15]. According to this, Zn<sub>2</sub>SnO<sub>4</sub> nanowires were synthesized on gold-coated (3 nm) Si substrates. This process is able to reliably reproduce nanowire films roughly 20  $\mu$ m thick. The nanowires are then transferred into fluorine-doped tin oxide (FTO) substrates and annealed at 500 °C for 4 h to transform the precursor on FTO into a Zn<sub>2</sub>SnO<sub>4</sub> film. The annealed FTO substrates with the nanowires are placed in a suspension of the dye 10 and allowed to soak for 24 h. Immediately upon removal from the the dye 10 suspension, the substrates were dried with  $N_2$  gas and secured against a  $Cu_2S$  counter electrode containing a polysulfide electrolyte (0.25 M  $\text{Na}_2\text{S}$  and 0.1 M NaOH in 18  $\text{M}\Omega$ water). The Cu<sub>2</sub>S counter electrodes were fabricated. 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). Solar cell devices were prepared using the dye 10 solution as a sensitizer.

#### 3. Results and discussion

#### 3.1. Synthesis

Organic based dyes are not only cheaper and easier to synthesize but are also incredibly malleable in their structure and properties [23]. Triphenylamine (TPA) as a hole transport materials was used as electron donors in organic dyes due to high charge carrier mobility, oxidation potentials, improved film forming capacity and high solubility for good pore filling capability [24,25]. On the other hand, fluorescent organic compounds containing aldehyde functional groups are widely used as bisulfite sensors [26-28].

Herein, a new dibenzosuberenone-based organic photosensitizer **10** of the type D-A- $\pi$ -A were designed and synthesized with TPA as the electron donor, an additional dibenzosuberenone entity as a mild electronwithdrawing linkage and an aldehyde moiety as the electron-withdrawing and anchoring group. 3,7-Dibromodibenzosuberenone **4** was synthesized in three steps starting from dibenzosuberone **1** by electrophilic aromatic substitution with Br<sub>2</sub>/AlCl<sub>3</sub>, following radical bromination with NBS, and subsequent dehalogenation with NaI-promoted elimination according to the published method (Scheme 1) [21]. 3,7-Dibromodibenzosuberenone **4** was used as the key compound that allowed us to prepare coupling products **7**, **9** and **10**. For the synthesis of the target product **10** considering the monocapling procedures in the literature [29-31], the monobromide **6** was firstly synthesized in very low yield (15%). It was seen in the <sup>1</sup>H NMR spectra of the crude product that product **7** was also formed as a byproduct while the starting material **4** remained unreacted in excess amounts (Scheme 2). In addition, it was observed that the isolation of **6** was difficult due to the solubility problems of the compounds in the crude product.

For all these reasons, the method was changed, and the synthetic method represented in Scheme 3 was applied for the synthesis of the compound **10**. To the best of our knowledge, this method has not been reported before in the literature. The Pd-catalyzed Suzuki coupling reaction of dibromide **4** (1.0 equiv.) with two different phenyl boronic acids, (4-formylphenyl)boronic acid (**5**) (1.2 equiv.) and (4-(diphenylamino)phenyl)boronic acid (**8**) (1.2 equiv.), in the presence of Na<sub>2</sub>CO<sub>3</sub> in DME/H<sub>2</sub>O (v/v: 2/1) at 100 °C for 24 h afforded the corresponding dibenzosuberenone derivatives **7**, **9** and **10**.

With this approach, three different products **7**, **9**, and **10** were obtained with a one-pot/one-step synthesis strategy and then isolated. In our previous study, the D-A-D- type dye **9** was obtained according to the method in the literature [32] and its photovoltaic properties were investigated [15]. It is seen in Scheme 3 that the compound **9** has the highest reaction yield as 39%. It shows that the Suzuki coupling reaction is at higher yields with boronic acides bearing electron-donating substituents. With this approach, the target product **10** was obtained with yield 26%. The main purpose of this synthetic approach was to obtain the product **10**. Here we report the investigation of the photophysical properties, DFT calculations and photovoltaic properties of this newly obtained D-A- $\pi$ -A-based product **10**.

The newly synthesized compounds were characterized by <sup>1</sup>H, <sup>13</sup>C NMR and FT-IR spectroscopy. The purity of the samples was analyzed by HRMS analysis and the melting points were also determined (see Supporting Information).

#### 3.2. Photophysical properties

The synthesized dye **10** was evaluated for photophysical characteristics such as, absorption ( $\lambda_{max, abs}$ ), emission ( $\lambda_{max, ems}$ ), Stokes shift and fluorescence quantum yield ( $\Phi_F$ ). Figure 1-2 shows normalised absorption and emission spectra of the synthesized dye **10**. The dye **10** had three distinct bands in its absorption spectra at 271, 331 and 388 nm, which may be derived from the  $n-\pi^*/\pi-\pi^*$  transitions on triphenylamine, dibenzosuberenone, and benzaldehyde fragments in the structure of the dye **10**. The dye **10** also exhibited in emission maxima in 571 nm. Stokes shift for the dye



Scheme 1. Synthesis of the key structure 3,7-dibromodibenzosuberenone 4.



Scheme 2. Procedure for the synthesis of the monobromide 6.



Scheme 3. Synthesis of the dye 10.

**10** was found as 183 nm. Fluorescence quantum yield of the dye **10** was calculated as 0.27 by using Parker-Rees equation against quinine sulfate in  $H_2SO_4$  (0.5 M) as a standard ( $\Phi_F = 0.546$ ) [19]. Table 1 summarizes the results of some photophysical properties of the dye **10**, and also other dibenzosuberenone-based dyes that we had synthesized in our published previous studies.

As expected, in comparison to the other dyes, which have been investigated in our previous study as a dihydropyridazinedibenzosuberenone derived dyes [33], the installation of the dye **10** leads to a red-shift of the emission maximum up to 20 nm. The Stokes shift was shifted by 53 nm in comparison to the dihydropyridazine-dibenzosuberenone derived dyes for the dye **10** (Table 1). In comparison with dye **9**, dye **10** shows an increase of Stokes shifts up to 29.1 nm. In comparison with dye **9**, addition of the aldehyde group to dye **10** led to a red shift of the absorption (up to 7.9 nm) and emission maxima (up to 37 nm) due to the large  $\pi$ -conjugated skeleton electron delocalization from donor to acceptor in D-A- $\pi$ -A conjugated system. Moreover, the dye **10** showed a very high Stokes shift (183 nm) and a good fluorescence quantum yield (0.27), which might be because the lone electron

#### Table 1

#### Some photophysical properties of the dye 10.

Compounds	UV absorption <sup>a</sup> $\lambda_{max}/nm$ ( $\epsilon$ (M <sup>-1</sup> , cm <sup>-1</sup> ))	Fluorescence <sup>a</sup> $\lambda_{max}/nm (\lambda_{exc} /nm)$	Stokes shift <sup>b</sup> (nm)	Quantum yields <sup>c</sup> $(\Phi_F)$	Study
dye 10	271 (24800), 331 (21200), 388 (16400)	571 (380)	183	0.27	current study
dye 9	380.1	534 (360)	153.9	0.07	also, our previous study[15]
dihydropyridazine- dibenzosuberenone derived dyes	389-446	494-551	96-130	0.18-0.99	our previous study[33]

<sup>a</sup> The spectra were recorded in  $CH_2Cl_2$  solutions at rt (c = 5  $\mu$ M)

 $^{b}$  Stokes shift =  $\lambda$   $_{max\,(ems)}$  -  $\lambda$   $_{max\,(abs)}$ 

<sup>c</sup> The fluorescence quantum yields ( $\Phi_F$ ) of the compounds were calculated using quinine sulphate in 0.5 M H<sub>2</sub>SO<sub>4</sub> ( $\Phi = 0.546$ ) as the standard [19].



Figure 1. UV-Vis spectrum of the dye 10 in  $CH_2Cl_2$  at rt (c = 5  $\mu M).$  Ambient (right) images of the dye 10 in  $CH_2Cl_2.$ 

pairs of the nitrogen atoms enhanced the intramolecular charge transfer (ICT) as well as partially quenched the fluorescence. Moreover, the dye **10**, with high emission and absorption maxima values and a very large Stokes shift, is of great importance for dye applications.

#### 3.3. Theoretical investigation

In order to explore the electronic structure of the dye 10, density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations were performed using the Gaussian 09 at the B3LYP/6-311++G(2d, 2p) level [20]. For the dye **10**, the highest occupied molecular orbitals (HOMOs) were mainly localized on the TFA moiety, while the lowest unoccupied molecular orbitals (LUMOs) were more shifted to the CHO acceptor unit and on the dibenzosuberenone core. Figures (Figure 3-5) illustrate the electron density distribution of the HOMO and the LUMO and the optimized structures for compound 7 and the dye 10. The orbital distributions of TPA and CHO groups are conjugated through their dibenzosuberenone cores in the middle, and these groups formed branched or butterfly-shaped conjugations over almost the entire molecules. Hence, the length of  $\pi$ -conjugation increases with the addition of TPA and CHO units. The calculated HOMO and LUMO energies of the ground state optimized geometry of the dye 10 were -5.360 and -2.521 eV, respectively. The calculated HOMO and LUMO gap of the dye 10 is 2.838 eV.

Comparing the compound **7** and **9**, [32] the dye **10** has the lowest HOMO-LUMO band gap (2.838 eV) (Table 2), which means that



**Figure 2.** Fluorescence spectrum of the dye **10** in CH<sub>2</sub>Cl<sub>2</sub> at rt (c = 5  $\mu$ M) ( $\lambda_{exc}$  = 380 nm). Fluorescence (right, under 365 nm UV light) images of the dye **10** in CH<sub>2</sub>Cl<sub>2</sub>.



Figure 3. The HOMO (lower), LUMO (upper) orbitals and bandgap energy of the compound 9 at the B3LYP/6-311++G(2d, 2p) level.

Table 2		
TDDFT study of compounds	<b>7</b> , the dye <b>9</b> and the dye <b>1</b>	D.

Compounds	HOMO (eV)	LUMO (eV)	$\Delta E (eV)$
7	-6.350	-2.778	3.572
dye 9ª	-4.870	-1.750	3.120
dye 10	-5.360	-2.521	2.838

<sup>a</sup> See reference[32] for DFT study of the dye 9.



**Figure 4.** The HOMO (lower), LUMO (upper) orbitals and bandgap energy of the dye **10** at the B3LYP/6-311++G(2d, 2p) level.

the  $\pi$ -electron transition of the dye **10** is the easiest. This situation may be the major reason why the dye **10** exhibited the longest fluorescence emission wavelength and Stokes shift among these compounds. However, the LUMO (-2.521 eV) is lowered compared to **9** (-1.750 eV) because of the electron deficient nature of the CHO unit. This low lying LUMO in dye **10** facilitates faster and greater extent of charge transfer from donor to acceptor in the excited state, resulting in a lower HOMO-LUMO gap and a redshift in the absorption spectrum as compared to **9**. Such results of electron distributions, the transferring electrons through D-A- $\pi$ -A system can facilitate electron injection from the excited state of the sensitizer to TiO<sub>2</sub>.

#### 3.4. Photovoltaic properties

The current-voltage (J-V) characteristics of the DSSC device under illumination of AM 1.5 G (100 mW/cm<sup>2</sup>) is shown in Figure 6, and the device photovoltaic statistics such as short-circuit current density ( $J_{SC}$ ), open-circuit voltage (Voc), fill factor (FF) and photovoltaic conversion efficiency (PCE) are summarized in Table 3.



Figure 6. J-V for the devices base on the dye 10.

The PCE value is the product of  $V_{OC}$ ,  $J_{SC}$ , and FF. Calculations of PCE were made according to the method reported in the literature [15]. A good photovoltaic performance of the DSSC the dye **10** exhibited a maximal PCE of 3.01% with a  $J_{SC}$  of 9.44 mA/cm<sup>2</sup>, a  $V_{OC}$  of 0.65 V and a FF of 49%, under the illumination of AM1.5, 100 mW/cm<sup>2</sup> lamp. In comparison with the dye **10**, the **9** exhibited a PCE of 2.54% with a  $J_{SC}$  of 7.31mA/cm<sup>2</sup>, a  $V_{OC}$  of 0.65 and a FF of 50%, under the same experimental conditions.

Compared with the dye **9**, the photovoltaic performance significantly raised by adding an EWG, such as aldehyde (-CHO) in the scaffold for the dye **10**.

This may be because the stronger acceptor of the dye 10 has a narrower band gap and wider absorption spectrum, which adequately enhanced the  $J_{SC}$ .



Figure 5. Optimized structures of the compound 9 (upper) and the dye 10 (lower).

Table	3			
-				

Current-voltage characteristics of DSCs sensitized with 9 and 10.						
	J <sub>SC</sub> (mA/cm <sup>2</sup> )	V <sub>OC</sub> (V)	$J_{MP}$ (mA/cm <sup>2</sup> )	$V_{MP}$ (V)	FF (%)	Power conversion efficiency (%)
Dye <b>10</b>	9.44 7 31	0.65	6.67 5.17	0.45 0.46	49 0 50	<b>3.01</b> 2.38 <sup>a</sup>
- )						

<sup>a</sup> See reference [15] for photovoltaic investigation of the dye 9.

These results indicate that the bond of aldehyde group onto skeleton of the dye **10** increased  $J_{SC}$  and PCE. Because, the EWG depressed the bandgap of the dye **10**, causing the dye to absorb longer-wavelength light and thus increasing  $J_{SC}$ . The difference between the HOMO-LUMO bandgap of these two dyes is 0.282 eV. As well known, the incentive to dye regeneration and electron injection is reliant upon the HOMO and LUMO energy levels of sensitizers. The results demonstrate that this type of designs on dibenzosuberenone-based can greatly improve the photovoltaic properties.

#### 4. Conclusion

In conclusion, a new fluorescent organic dye, named by dye 10, containing a dibenzosuberenone motif as central core based on a D-A- $\pi$ -A configuration was designed, synthesized and characterized. The dye was successfully synthesized using Suzuki coupling reaction in a different approach, namely one pot two different aryl boronic acids containing EWG and EDG at para positions were added to the reaction medium at the same time. As expected, three different coupling products were obtained in a one-pot/one step. Due to the presence of a strong electron-donating TPA unit, a dibenzosuberenone as the central core and an additional acceptor, and and an aldehyde as the electron-deficient unit in the  $\pi$ bridge, the dye 10 exhibits much enhanced absorption (388 nm) and emission (571 nm) of long wavelength photons compared with the D-A-D dye 9 and the dyes reported in our previous studies. In addition, the dye 10 has a very large Stokes shift (183 nm), which emphasizes its potential applications such as fluorescence sensors, biological image and optoelectronic materials. The computational studies demonstrate that the HOMO energy level of the dye 10 are localized on the TPA unit, and the LUMO energy level are mainly localized on the acceptor moieties, dibenzosuberenone and benzaldehyde units. Comparing other derivatives 7, 9, the dye 10 has the lowest HOMO-LUMO band gap (2.838 eV), which means that the  $\pi$ -electron transition of the dye **10** is the easiest. The photovoltaic studies of the dye also afforded maximum conversion efficiency of 3.01%. Using our synthetic strategy, it is possible to design and synthesize novel D-A- $\pi$ -A type materials that have high potential in applicable optoelectronic devices. The results reported herein reveal that these dibenzosuberenone based organic dyes are also promising molecular materials in the progress on photosensitizers for DSSC.

#### **Declaration of Competing Interest**

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### **CRediT** author statement

Musa Erdoğan: This paper is a single-author study. Everything was done by the author.

#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.130056.

#### References

- N.M. Sarih, P. Myers, A. Slater, B. Slater, Z. Abdullah, H.A. Tajuddin, S. Maher, White Light Emission from a Simple Mixture of Fluorescent Organic Compounds, Scientific Reports 9 (2019) 1–8.
- [2] Y. Bai, K. Yu, H. Pan, D.-B. Dang, One new dicoumarol-based fluorescent compound: Synthesis, crystal structure and metal ions recognition, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 113 (2013) 257–260.
- [3] Z. Zhao, J.W. Lam, B.Z. Tang, Tetraphenylethene: a versatile AIE building block for the construction of efficient luminescent materials for organic light-emitting diodes, Journal of Materials Chemistry 22 (2012) 23726–23740.
- [4] A. Zhu, J. Pan, Y. Liu, F. Chen, X. Ban, S. Qiu, Y. Luo, Q. Zhu, J. Yu, W. Liu, A novel dibenzimidazole-based fluorescent organic molecule as a turn-off fluorescent probe for Cr3+ ion with high sensitivity and quick response, Journal of Molecular Structure 1206 (2020) 127696, doi:10.1016/j.molstruc.2020.127696.
- [5] L. Xiong, M. Yu, M. Cheng, M. Zhang, X. Zhang, C. Xu, F. Li, A photostable fluorescent probe for targeted imaging of tumour cells possessing integrin αvβ3, Molecular BioSystems 5 (2009) 241–243.
- [6] S.A. Al-horaibi, A.A. Alrabie, M.T. Alghamdi, F.H. Al-Ostoot, E.M. Garoon, A.S. Rajbhoj, Novel hemicyanine sensitizers based on benzothiazole-indole for dye-sensitized solar cells: Synthesis, optoelectrical characterization and efficiency of solar cell, Journal of Molecular Structure 1224 (2021) 128836, doi:10.1016/j.molstruc.2020.128836.
- [7] T. Wang, X. Hao, L. Han, Y. Li, Q. Ye, Y. Cui, D-A-*π*-A Carbazole Dyes Bearing Fluorenone Acceptor for Dye Sensitized Solar Cells, Journal of Molecular Structure 1226 (2021) 129367, doi:10.1016/j.molstruc.2020.129367.
- [8] P. Das, A. Kumar, A. Chowdhury, P.S. Mukherjee, Aggregation-induced emission and white luminescence from a combination of π-conjugated donor–acceptor organic luminogens, ACS Omega 3 (2018) 13757–13771.
- [9] Y. Li, J. Liu, D. Liu, X. Li, Y. Xu, DA-π-A based organic dyes for efficient DSSCs: A theoretical study on the role of π-spacer, Computational Materials Science 161 (2019) 163–176.
- [10] T. Zhang, H. Han, Y. Zou, Y.-C. Lee, H. Oshima, K.-T. Wong, R.J. Holmes, Impact of thermal annealing on organic photovoltaic cells using regioisomeric donor-acceptor-acceptor molecules, ACS Applied Materials & Interfaces 9 (2017) 25418–25425.
- [11] X. Wang, J. Yang, H. Yu, F. Li, L. Fan, W. Sun, Y. Liu, Z.Y. Koh, J. Pan, W.-L. Yim, A benzothiazole–cyclopentadithiophene bridged D–A–π–A sensitizer with enhanced light absorption for high efficiency dye-sensitized solar cells, Chemical Communications 50 (2014) 3965–3968.
- [12] C. Qin, A. Islam, L. Han, Incorporating a stable fluorenone unit into D-A-π-A organic dyes for dye-sensitized solar cells, Journal of Materials Chemistry 22 (2012) 19236–19243.
- [13] J. Yang, P. Ganesan, J. Teuscher, T. Moehl, Y.J. Kim, C. Yi, P. Comte, K. Pei, T.W. Holcombe, M.K. Nazeeruddin, Influence of the donor size in D- π-A organic dyes for dye-sensitized solar cells, Journal of the American Chemical Society 136 (2014) 5722–5730.
- [14] M.S. Abusaif, M. Fathy, M.A. Abu-Saied, A.A. Elhenawy, A.B. Kashyout, M.R. Selim, Y.A. Ammar, New carbazole-based organic dyes with different acceptors for dye-sensitized solar cells: Synthesis, characterization, dssc fabrications and density functional theory studies, Journal of Molecular Structure 1225 (2021) 129297, doi:10.1016/j.molstruc.2020.129297.
- [15] M. Erdogan, S. Horoz, Synthesis and characterization of a triphenylamine-dibenzosuberenone-based conjugated organic material and an investigation of its photovoltaic properties, Journal of Chemical Research (2020) 1747519820938022.
- [16] J. Liu, Y. Luo, L. Li, G. Wang, X. Wang, Y. Chen, B. Liu, Photovoltaic Performance of 4, 8-Bis (2'-ethylhexylthiophene) thieno [2, 3-f] benzofuran-Based Dyes Fabricated with Different Donors in Dye-Sensitized Solar Cells, ACS Omega (2020).

- [17] Y.-H. Chen, V.S. Nguyen, H.-H. Chou, Y.S. Tingare, T.-C. Wei, C.-Y. Yeh, Anthracene Organic Sensitizer with Dual Anchors for Efficient and Robust Dye-Sensitized Solar Cells, ACS Applied Energy Materials 3 (2020) 5479–5486.
- [18] J. Yang, X. Wang, W.-L. Yim, Q. Wang, Computational study on the intramolecular charge separation of DA-π-A organic sensitizers with different linker groups, The Journal of Physical Chemistry C 119 (2015) 26355–26361.
- [19] G.A. Crosby, J.N. Demas, Measurement of photoluminescence quantum yields. Review, J. Phys. Chem. 75 (1971) 991–1024, doi:10.1021/j100678a001.
- [20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.E. Peralta Jr., F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, in: Gaussian, Inc, Gaussian, Wallingford CT, 2010, p. 09. Revision C.01.
- [21] R.C. Chadwick, V. Kardelis, S. Liogier, A. Adronov, Synthesis of Conjugated Polymers Containing DIBAC-Derived Triazole Monomers, Macromolecules 46 (2013) 9593–9598.
- [22] Y. Wei, C.-T. Chen, Doubly ortho-linked cis-4, 4 '-bis (diarylamino) stilbene/fluorene hybrids as efficient nondoped, sky-blue fluorescent materials for optoelectronic applications, Journal of the American Chemical Society 129 (2007) 7478–7479.
- [23] X. Shi, Y. Yang, L. Wang, Y. Li, Introducing asymmetry induced by benzene substitution in a rigid fused  $\pi$  spacer of D- $\pi$ -A-Type solar cells: a computational investigation, The Journal of Physical Chemistry C 123 (2019) 4007–4021.
- [24] P. Agarwala, D. Kabra, A review on triphenylamine (TPA) based organic hole transport materials (HTMs) for dye sensitized solar cells (DSSCs) and perovskite solar cells (PSCs): evolution and molecular engineering, Journal of Materials Chemistry A 5 (2017) 1348–1373.

- [25] G. Sevinc, B. Kücüköz, A. Elmalı, M. Hayvalı, The synthesis of -1, -3, -5, -7, -8 aryl substituted boron-dipyrromethene chromophores: Nonlinear optical and photophysical characterization, Journal of Molecular Structure 1206 (2020) 127691, doi:10.1016/j.molstruc.2020.127691.
- [26] C. Yin, X. Li, Y. Yue, J. Chao, Y. Zhang, F. Huo, A new fluorescent material and its application in sulfite and bisulfite bioimaging, Sensors and Actuators B: Chemical 246 (2017) 615–622.
- [27] G.J. Mohr, A chromoreactand for the selective detection of HSO 3- based on the reversible bisulfite addition reaction in polymer membranes, Chemical Communications (2002) 2646–2647.
- [28] X. Liu, Q. Yang, W. Chen, L. Mo, S. Chen, J. Kang, X. Song, A ratiometric fluorescent probe for rapid, sensitive and selective detection of sulfur dioxide with large Stokes shifts by single wavelength excitation, Organic & Biomolecular Chemistry 13 (2015) 8663–8668.
- [29] L. Ding, M. Wu, Y. Li, Y. Chen, J. Su, New fluoro-and chromogenic chemosensors for the dual-channel detection of Hg2+ and F, Tetrahedron Letters 55 (2014) 4711–4715.
- [30] Y. Jiang, M. Fang, S.-J. Chang, J.-J. Huang, S.-Q. Chu, S.-M. Hu, C.-F. Liu, W.-Y. Lai, W. Huang, Towards Monodisperse Star-Shaped Ladder-Type Conjugated Systems: Design, Synthesis, Stabilized Blue Electroluminescence, and Amplified Spontaneous Emission, Chemistry A European Journal 23 (2017) 5448–5458, doi:10.1002/chem.201605885.
- [31] J. Liu, L. Li, R. Xu, K. Zhang, M. Ouyang, W. Li, X. Lv, C. Zhang, Design, Synthesis, and Properties of Donor-Acceptor-Donor' Asymmetric Structured Electrochromic Polymers Based on Fluorenone as Acceptor Units, ACS Applied Polymer Materials 1 (2019) 1081–1087.
- [32] L. Wang, L. Wang, J. Huang, G. Yu, Synthesis and Characterization of Dibenzo [a, d] cyclohepten-5-one Derivatives for Light-Emitting Diodes, Chinese Journal of Chemistry 33 (2015) 948–954.
- [33] M. Erdogan, A. Dastan, Design, synthesis, and characterization of a new class of efficient dihydropyridazine-dibenzosuberenone derived fluorescent dyes and investigation of their some photophysical properties, Tetrahedron 76 (2020) 131271, doi:10.1016/j.tet.2020.131271.