Performance Evaluation of Organic dyes utilized for 3-G DSSC Applications: A Review

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# = Performance Evaluation of Organic dyes utilized for 3-G DSSC Applications: A Review

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## Abstract:

Solar energy is a substantial renewable energy resource that is produced by the sun's electromagnetic radiation. It is an inexhaustible, nontoxic, and clean energy source. According to studies, solar energy can provide about 1,000 times the energy that is currently being consumed. A solar cell is an electrical device that makes use of the photovoltaic effect to convert light energy directly into electricity. A Dye-Sensitized Solar Cell (DSSC) is a third-generation solar cell that functions due to the interactions between the cell's anode and cathode. This in addition to the nanoparticles coated with a light-sensitive dye surrounded by an electrolyte completes the structure of a DSSC. This review presents a comprehensive take on the enumerate organic dyes available for purpose of sensitisation of light for DSSC applications. Furthermore, this review also consists of a detailed assessment of the various components utilized to complete the structure of a DSSC along with their functions.

# Introduction:

Sustainable development demands the maintenance of the number of resources required by society to stay afloat as a whole. This step also ensures that future generations are not deprived of the necessities that we have effortless access to currently. The three dimensions of this type of development under this formulation are economic, social, and environmental. One such resource that forms the backbone of society is energy. The globe's requirement for electrical energy is on an indefinite steep rise. On the contrary, the exigency for electrical energy across the world is still met using the help of conventional fossil fuels. It is estimated

that by the next thirty years, the requirement for electricity will trifold [1-3]. Inarguably, modern society demands a source for the production of clean renewable energy to meet the ends on a day-to-day basis [4,5]. To achieve the said goal, it is now essential to meet the ever-increasing energy demand by exploring energy sources that are in bulk, inexhaustible, eco-friendly, and nearly seamless [6,7].

In today's world, there are an array of renewable energy sources available that sport both pros and cons. Some of the renowned renewable energy sources include wind energy, geothermal energy, tidal energy, biomass, small-hydel, and solar energy [8-11]. Out of all of these options, solar energy seems to be promising in nature as it is reported that  $430 \times 10^{18}$  joules of energy given out by just an hour of sunlight on our planet is almost on par with the global energy consumption of our entire planet for an entire year [12, 13]. Further strengthening the foundation, solar energy can be harnessed with ease using a photovoltaic system [14]. There are three distinct generations of photovoltaic cells, namely, Silicon wafer-based solar cells of the first generation; followed by CIGS, CdTe, and GaAs of the second generation; and lastly, quantum dot solar cells, multiple junction solar cells, perovskites, and DSSCs of the third generation [15, 16].

The DSSC first grabbed the attention of the masses in the early 1990s due to its eco-friendly nature, economical production cost, reputable energy conversion efficiency, and straightforward procedure of construction [17-29]. In addition to the achievement of an efficiency exceeding 13% on the lab-scale basis, a DSSC is also capable of reflecting stability for around an entire decade in outdoor conditions. Moreover, they can also easily adapt to dim, artificially lit, and partially shadowed conditions making them highly versatile [30-34].

The reasons mentioned above make the study of the 3G DSSC a worthwhile cause. This review paper will be focusing on the various organic dyes available for the sensitization of light for DSSC applications.

# **Basic components of DSSC:**

The components of a DSSC consist of

- A counter-electrode.
- A photo-anode.
- An electrolyte
- Dye-sensitizer



Figure 1: Schematic diagram of a DSSC [35].

A DSSC comprises of a photo-anode and a counter electrode between which an electrolyte is injected [35]. The photo-anode is coated with a film of nanomaterials whose structure could be in the form of nanorods [36], nanodots [37], nanotubes [38], nanothorns [39], nanocones [40], nanoleaves [41].

However, it is important to note that the morphology of each nanomaterial is dependent on a variety of factors. These structures are said to be acquired via a process that involves interactivity between the size and molecular interactions [42- 44]. These nanomaterials can be based on metal oxides such as ZnO [45], TiO<sub>2</sub> [46], CeO<sub>2</sub> [47], SnO<sub>2</sub> [48], and much more. Interestingly, these nanomaterials can also be a composite of two or more compounds [49] and can even be doped in certain percentages [50]. The synthesis of the nanomaterials can be carried out using methods such as hydrothermal, sol-gel, sol, solution combustion synthesis, electro-deposition, microwave method [51], ultrasound-assisted mechanical mixing method [52], solvothermal method [53]. The synthesized nanoparticles are soaked in a dye that could be chlorophyll, anthocyanin [54], or organic-based [55] for dye-sensitization. The dye acts as the most essential component of the system as it absorbs photons from the sunlight and releases electrons that traverse through the circuit to the counter-electrode for electricity generation. As the dye forms the most essential part of the DSSC and organic dyes outshine the rest of the available options in terms of the efficiency values obtained [56], this review will be focusing on the various types of organic dyes utilized for DSSC applications.

# Dye:

Needless to mention, the dye or sensitizer acts as the heart of a DSSC. The selection of the dye varies the performance of the DSSC immensely without a doubt. An ideal dye must be able to absorb all light below a wavelength of around 915 nanometres [57-59].

It must also satisfy a few conditions such as:

- The anchoring group must be localized around the lowest unoccupied molecular orbital (LUMO), while the donor group needs to be localized around the highest occupied molecular orbital (HOMO).
- To reduce energy losses during the electron transfer reaction, the excited state's energy level must be matched to the conduction band (CB) of the desired nanomaterial.

- For the redox couple to efficiently regenerate the oxidized dye produced after the injection of electrons into the CB of nanomaterial, the HUMO must be below the energy level of the redox couple.
- To reduce the nonradiative decay of the excited state to the ground state, the aggregation must be avoided on the surface.
- The dye must also have good solubility in a variety of solvents [57-59]

From the early 2000s, it has been reported that there was an enhancement in the efficiency when organic dyes were utilized for dye-sensitization. It has also been reported that the structure of an organic dye can be altered with ease to increase the overall efficiency. Usually, the structure of an organic photo-sensitizer consists of a Donor-Acceptor,  $\pi$ -conjugated bridge (D- $\pi$ -A) system. The anchoring of the dye onto the synthesized nanomaterials is corroborated by the acceptor part of the sensitizer. The attributes of the D and A components of the photo-sensitizer to donate and accept electrons, respectively, lead to the  $\pi$  bridge's electronic characteristics to modulate the properties of the dye. The A component could be R–COOH, C<sub>4</sub>H<sub>3</sub>NO<sub>2</sub>, or C<sub>5</sub>H<sub>5</sub>NO<sub>3</sub>S<sub>2</sub> based while the  $\pi$  bridge could be based on C<sub>9</sub>H<sub>6</sub>O<sub>2</sub>, oligothiophene, or C<sub>12</sub>H<sub>9</sub>NO. Lastly, the donor part could be based on C<sub>4</sub>H<sub>11</sub>N or C<sub>1 2</sub> H<sub>1 1</sub> N moiety among others [60- 67].

# **Carbazole-based organic dyes:**

Carbazole dyes form a crucial class of organic compounds in DSSCs. Two organic dyes, namely, DRA-BDC and DTB-BDC were developed as dyes for application in DSSCs with the structure of D- $\pi$ -A. They consisted of rhodanine-3-acetic acid/thiobarbituric acid as the electron acceptor and N, N-butyl dicarbazole as the electron donor. Additionally, TiO<sub>2</sub> nanoparticles were utilized for the creation of the photo-anode.

It was observed by Abusaif et al. [68] that the DSSC fabricated with the DRA-BDC organic dye showed a higher fill factor (FF) of 0.79%, open-circuit voltage (Voc) of 589mV, efficiency of 1.16%, and short-circuit current density ( $J_{sc}$ ) of 0.00246 A/cm<sup>2</sup> when compared to the values obtained by the DSSC fabricated with the DTB-BDC organic photo-sensitizer. The DTB-BDC obtained values that were under par reflecting an efficiency ( $\eta$ ) of 0.58%,  $V_{OC}$  of 544 mV, and FF of 0.63% due to a low of  $J_{SC} = 0.00167$  A/cm<sup>2</sup>. The reason behind DRA-BDC outperforming DTB-BDC could because of a greater energy gap being present between the LUMO level and the TiO<sub>2</sub> conductive band level. This could be due to the presence of a higher number of linked anchor groups. This increased energy gap causes a greater number of electrons to enter the nanoparticles, which then increases the  $J_{SC}$ . In turn, this also increases the efficiency obtained by the DSSC [68].

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Figure 2: Chemical structure of the DRA-BDC and DTB-BDC organic dyes [68]

#### C220 dye:

The work conducted by James S. Bendall et al. [69] included equipping ZnO-TiO<sub>2</sub> nanowires as the photoanode for the fabrication of the DSSC. A newly synthesized C220 organic dye was utilized as the photosensitizer in this procedure. The driving factor for the charge injection was the energy offset of the C220 dye molecule's LUMO from the ZnO conduction band edge. The molecular structure of the dye revealed that the 4, 40 -didodecyl-4H-cyclopenta dithiophene (CPDT) segment was utilized as the spacer between the donor and acceptor architecture (D-p-A). The utilization of this dye in liquid electrolyte SCs, along with a ZnO layer that was created to have a high surface area as well as effective electron transport characteristics was considered to be novel. Additionally, the DSSC fabricated with the C220 dye yielded a FF of 0.606, an  $\eta$  of 2.53%, V<sub>oc</sub> of 0.8196 V, and J<sub>sc</sub> of 0.00508 A/cm<sup>2</sup>. [69, 70].



Figure 3: Molecular structure of C220 dye [69].

#### JK-16 and JK-17 organic dye:

The work conducted by Hyunbong Choi et al. [71] consisted of incorporating bisdimethylfluorenyl amino benzo[b]thiophene to synthesize an organic dye for an effective DSSC. It consisted of cyano acrylic acid as the electron acceptor and thiophene as the electron donor. The LUMOs and HOMOs of the JK-16 and JK-17 organic dyes were calculated. This reflected that the HOMO and LUMO were both delocalized over the pconjugated system via the dimethylfluorenyl amino group and benzo[b]thiophene, respectively. The JK-16 sensitized cell produced  $J_{SC}$  of 0.01533 A/cm<sup>2</sup>,  $V_{OC}$  of 740 mV, FF of 0.66, and an efficiency of 7.43%. Whereas the JK-17 dye showed a  $J_{SC}$  of 0.01266 A/cm<sup>2</sup>,  $V_{OC}$  of 670 mV, FF of 0.65, and an  $\eta$  of 5.49%. JK-17 dye's lower effectiveness as compared to JK-16 dye results from their distinct oxidation potential differences. JK-16 has a somewhat higher oxidation potential than JK-17. As a result, the driving power for the reduction of the oxidized dye will be increased [71].



Figure 4: The molecular structure of JK-16 and JK-17 dye [71]

# DN350 dye:

The work conducted by Shinji Higashijima et al. [72] showed that due to the bathochromic absorption band and inhibition of aggregation formation, the combination of rhodanine acceptor and dimethylfluorene-substituted indoline donor (DN350) produced a reaction with significantly greater efficiency than D205. The maximum short-circuit photo-current density was displayed by DN350 with a value of 13.07mA/cm<sup>2</sup> along with an efficiency of 5.55% and FF of 0.65 whereas D205 showed an  $\eta$  of 4.92%, J<sub>SC</sub> of 0.01102 A/cm<sup>2</sup>, and FF of 0.68. This showed a 13% improvement over D205 [72].

# **ADEKA-1 dye:**

The work conducted by Kakiage et al. [73] showed the accomplishment of more than 12% proficiency in the fabricated DSSC. ADEKA-1 had a trimethoxysilyl group as the anchor to the titanium dioxide electrode. This was known to adsorb on the electrode along with the development of three Si–O–Ti bonds. The adsorption of a carboxy dye such as ADEKA-2 on the titanium dioxide electrode was considered to initiate the formation of ester linkages between the carboxy and hydroxy groups on the surface of the electrode utilized. ADEKA-1-sensitized cells displayed marginally higher  $J_{sc}$  and  $V_{oc}$  values than ADEKA-2 carboxy DSSC. The ADEKA-1-sensitized cell showed a  $J_{sc}$  of 0.0161A/cm<sup>2</sup>,  $V_{oc}$  of 0.848V, FF of 0.762, and efficiency of 10.4 whereas the ADEKA-2 sensitized cell showed a  $J_{sc}$  of 0.0151A/cm<sup>2</sup>,  $V_{oc}$  of 0.821V, FF of 0.752, and  $\eta$  of 9.32 [73-77].

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Figure 5: The molecular structure of ADEKA-1 and ADEKA-2 dye [73]

#### **Porphyrin sensitizers**

The work carried on by Tachibana et al. [78] showed that organic photo-sensitizers known as porphyrin could be naturally occurring or can be produced artificially, and they all consist of a porphyrin ring as a part of their structural makeup. Four pyrrolic rings were joined by four methine bridges to make the macrocycle known as porphyrin. Because of their optical characteristics, the porphyrin-based dyes are eligible sensitizers for DSSC applications. It is possible to functionalize the macrocycle of the porphyrin structure, which will tune the two bands and produce a dye that is suitable for DSSC applications. In the work done by Bessho et al [79], a novel porphyrin-based dye was created and added to a D- $\pi$ -A dye architecture as a  $\pi$ -linker. This setting reflected an impressive efficiency of 11%. It is important to note that this was one of the first instances where a device fabricated with a porphyrin dye fetched an  $\eta$  of over 10%. Furthermore, the device achieved a J<sub>sc</sub> of 0.0186 A cm<sup>-2</sup>, V<sub>oc</sub> of 770 mV, FF of 0.764, and  $\eta$  of 10.9% [78, 79].



Figure 6: The chemical structure of porphyrin [78]

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## Coumarin

The work conducted by Waddell and Rehm et al. [80, 81] reflected that photosensitizers based on coumarin are attractive organic compounds that could be employed as a suitable dye for DSSC applications because of their fluorescent features, which are visibly light-based, of high quantum yield, and superior solubility. Appropriate LUMO level, longer stability when exposed to solar radiation, and better photovoltaic performance are properties that have been noted due to the donor moiety's superior photo response in the visible light range. [80, 81]. Impressively, an efficiency of 8.03% was acquired when 20.00 mM of  $C_{24}H_{40}O_4$  was employed as the redox electrolyte [82]. Additionally, the J<sub>sc</sub> was found to be 15.10 mA cm<sup>-2</sup>, V<sub>oc</sub> was found to be 0.68 V, FF was 69.8%, and  $\eta$  fetched a value of 7.17%. [82]



Figure 7: Molecular Structure of Coumarin dye [80]

#### **WS-9**

The work conducted by Wu et al. [83] involved the derivation of the WS-9 photo sensitizer from the trial and tested WS-2 organic dye by adding  $C_{10}H_{16}S$  into the  $\pi$ -architecture. Compared to the traditional D– $\pi$ -A dyes, the specific D–A– $\pi$ -A organic dyes showed a complex electronic transition absorption band because of the presence of a strong electron-withdrawing  $C_6H_4N_2S$  in the p-bridge. It was evident that WS-9 had very good antiagregation properties and performed consistently well with any co-adsorbent and dye bath solvent. For WS-9 obtained from  $CH_2Cl_2$ ,  $J_{sc}$  was observed to be 17.26 mA cm<sup>-2</sup>,  $V_{oc}$  was 692 mV, FF was 0.64%, and an efficiency of 7.63 was obtained. For WS-9 stained from  $CHCl_3$ ,  $J_{sc}$  was found to be 16.99 mA cm<sup>-2</sup>,  $V_{oc}$  was 689 mV, FF was 0.70%, and a  $\eta$  of 8.15% was obtained [83].

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Figure 8: Synthesis of WS-9 organic dye [83]

#### FNE92

The work by Jiang et al. [84] was carried out in five phases. Terthiophene 1 was linked as the starting core to create the double D- $\pi$ -A dye FNE92. The compound was created by coupling two triphenylamine donors with hexyloxy substituents to the twisted terthiophene backbone after regioselective dibromination. The N-bromosuccinimide (NBS) dibromination was then followed by Stille coupling with (5'-(1,3- dioxolan-2-yl) -[2,2'-bithiophen]-5-yl) Tributyl to provide a protective intermediate for 1, 3-dioxalane. As a result, the target dye FNE92 was obtained by the tandem reaction of deprotection and Knoevenagel condensation. The J<sub>sc</sub> of FNE92 was found to be 11.25 mA cm<sup>-2</sup>, V<sub>oc</sub> was 0.77 V, FF was 0.76, and  $\eta$  was found to be 6.6%.



Figure 9: Structure of dye FNE92 [84]

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Dye Used	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>-2</sup> )	FF	η (%)	Reference s
DRA-BDC	0.5890	2.46	0.790	1.16	[68]
C220	0.8196	5.08	0.606	2.53	[69]
JK-16	0.7400	15.33	0.660	7.43	[71]
JK-17	0.6700	12.66	0.650	5.49	[71]
DN350	0.6600	13.07	0.650	5.55	[72]
ADEKA-1	0.8480	16.1	0.762	10.40	[73]
ADEKA-2	0.8210	15.1	0.756	9.32	[73]
Porphyrin	0.7700	18.60	0.764	10.90	[79]
Coumarin	0.6800	15.10	0.698	7.17	[82]
WS-9	0.7700	11.25	0.760	6.60	[83]
FNE-92	0.7700	11.25	0.760	6.60	[84]
МК-2	0.7100	11.96	0.720	6.10	[84]
NKX-2677	0.6000	9.63	0.750	4.30	[84]
FNE91	0.6700	7.13	0.710	3.40	[84]
CAR-CN	0.7600	5.18	0.500	2.30	[85]
DPA-CN	0.8300	1.67	0.620	1.00	[85]
$N_1$	0.5700	9.06	0.670	3.55	[86]

# **Table 1:** Comparison of the performance of DSSCs fabricated with organic dyes by various researchers.

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N <sub>3</sub>	0.4610	6.90	0.590	0.19	[86]
CF <sub>3</sub>	0.5400	8.57	0.720	3.28	[87]
o-NO <sub>2</sub> Ph	0.5800	9.91	0.700	4.05	[87]
C220	0.8100	5.08	0.600	2.53	[88]
BH2	0.9700	4.30	0.310	0.13	[89]
BH6	0.9500	4.40	0.310	0.13	[89]
DN362	0.6500	11.48	0.700	5.15	[90]
NGnP3	0.9710	14.57	0.710	10.04	[91]
NGnP6	0.9670	14.54	0.710	10.05	[91]
МК-2	0.8140	15.80	0.753	9.68	[92]
JK-2	0.7020	14.90	0.720	0.72	[93]
DTS-Me2	0.6490	15.10	0.640	6.73	[93]
EB	0.5670	0.53	0.600	0.22	[94]
РСВ	0.6200	7.54	0.630	3.47	[94]
D-Dye	0.7100	9.50	0.720	5.10	[95]
M-Dye	0.6300	8.50	0.680	3.60	[95]
Car-CN	0.7660	5.18	0.508	2.37	[96]
Dpa-CN	0.8320	1.67	0.622	1.02	[96]
CBPTZ-O	0.7800	5.94	0.645	2.99	[97]
CBPTZ-M	0.8500	7.33	0.662	4.13	[97]
WS-2	0.6010	8.46	0.760	3.86	[98]
WS-9	0.6890	16.99	0.700	8.15	[98]
AP25	0.5270	19.90	0.650	6.80	[99]

Dye Used	V <sub>oc</sub> (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF	η (%)	References
N719	0.6400	4.470	0.640	0.930	[100]
Ru-D1	0.7400	6.280	0.310	1.460	[100]
Ru-D2	0.7000	6.010	0.250	1.130	[100]
Eosin-Y	0.5790	1.570	0.500	1.518	[101]
N3	0.6870	1.530	0.670	2.366	[101]

**Table 2:** Comparison of the performance of DSSCs fabricated with synthetic dyes by various researchers.

#### **Conclusion:**

To conclude, this review aimed towards the study of various organic dyes, their chemical structures, and performances when utilized for the purpose of the fabrication of a DSSC. While natural dyes that boast a high content of pigments such as anthocyanin are eco-friendly, they tend to yield a low efficiency when utilized as the dye for the fabrication of a DSSC. Over the years, synthetic dyes such as the N719 dye, black dye, Eosin-Y dye, etc have shown promising results, they are toxic in nature, and deplete the environment [102-105]. This review paper mainly focused on organic dyes that have caught the attention of innumerable researchers for their ease of synthesis, availability, and a reputable photoelectric conversion efficiency when used for the purpose of sensitization of light. In the past decade, researchers have worked effortlessly to introduce continuous innovation into the world of organic dyes for DSSC applications. While there is a lot more to achieve, the start has been promising.

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