



# The effect of the number, position, and shape of methoxy groups in triphenylamine donors on the performance of dye-sensitized solar cells



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## ABSTRACT

Four new organic photosensitizers (**SH-11–14**) that introduced methoxy groups as an additional donor were synthesized, and used in dye-sensitized solar cells. The dyes were designed in order to investigate the effects on the dye photophysical properties and the cell photovoltaic performance, by the number, position, and shape of methoxy groups introduced at the *para*-/*ortho*- and *para*-/*meta*- and *para*- (open or closed ring shape) positions on the triphenylamine donor. The introduction of methoxy groups led to bathochromic shift of the absorption spectrum, and enhancement of the molar extinction coefficient of the dyes. Their introduction decreased the amount of dye adsorbed on TiO<sub>2</sub> surface, due to the increased steric hindrance. As their number increased, an open-circuit voltage value decreased. All things considered, the dye (**SH-14**) with closed ring shape shows the best conversion efficiency of 6.01% under AM 1.5G conditions (**N719** dye's 7.59% under the same conditions).

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## 1. Introduction

Since Grätzel et al. reported Ru-based photosensitizers in 1991, dye-sensitized solar cells (DSSCs) have been considered as promising converters of solar energy, due to their low-cost fabrication, environmental friendliness, and high power conversion efficiency [1]. As one of the most important components in DSSCs, the photosensitizer plays a crucial role in achieving high DSSC efficiency. Thus, many photosensitizers, such as ruthenium complex dyes, metal-free organic dyes containing diverse molecular structures, and organometallic dyes that employ porphyrins or phthalocyanines, have been extensively studied by researchers around the world [2]. So far, Ru complex sensitizers (N3, **N719**, and black dye) and organic dyes containing triphenylamine (TPA) moiety have been reported to give high power conversion efficiencies of over 11% and 10% under AM 1.5G irradiation, respectively [3].

Recently, the highest efficiency of over 12% has been achieved from DSSCs co-sensitized by zinc porphyrin sensitizers (YD2-*o*-C8 and Y123) [4]. Porphyrin-based photosensitizer efficiencies have sharply improved in recent years, by the intense efforts of countless research scientists to achieve high efficiency [2c].

Although metal-free organic dye efficiencies are somewhat lower than those of Ru complex photosensitizers and zinc porphyrin photosensitizers, organic dyes as alternatives to metal complex photosensitizers are still promising candidates for the photosensitizers of DSSCs, due to their many advantages, such as relatively low cost, simple synthetic route, high molar extinction coefficient, diversity of molecular structure, and environmental friendliness. Until now, organic dyes of diverse structures containing carbazole [5], coumarin [6], fluorine [7], indoline [8], perylene [9], phenothiazine [10], phenoxazine [11], squaraine [12], tetrahydroquinoline [13], and triphenylamine [3d,14] have been extensively studied. Among them, triphenylamine-based and quinoxaline-based organic dyes showed higher efficiency compared to those of different structures [3d,3e].

TPA-based organic dyes are still under intense academic investigation, due to their prominent electron donation and hole-

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transport ability [15,2d]. To improve DSSC efficiency, photosensitizers are required to have bathochromic shifts, broad absorption spectra, and/or enhancement of molar extinction coefficients. To attain this end in most organic dyes (D- $\pi$ -A structure) having push-pull structure, two strategies were adopted: extending the  $\pi$ -conjugation length of molecule (D- $\pi$ - $\pi$ -A structure), and introducing an additional donor (AD) to the main donor (D) (AD-D- $\pi$ -A or D-D- $\pi$ -A structure). However, organic dyes having D- $\pi$ - $\pi$ -A structure can have close  $\pi$ - $\pi$  aggregation, which can lead to self-quenching, and reduction of electron injection into TiO<sub>2</sub> [16]. Compared to D- $\pi$ - $\pi$ -A structure, organic dyes with AD-D- $\pi$ -A structure benefit from the lower possibility of close  $\pi$ - $\pi$  aggregation. They can also have the advantages of bathochromic shift of the absorption spectrum, and enhancement of the molar extinction coefficient [17]. Therefore, organic dyes with AD-D- $\pi$ -A structure have recently been studied by several groups [17,18]. The aforementioned researches were oriented to the effects of the introduction of sterically bulky moieties, such as carbazole, diphenylamine group, alkoxy substituted phenyl group, and heterocyclic ring, as additional donors at the *para*-position of the TPA donor part. However, their introduction to the TPA donor part decreased the amount of dye adsorbed on TiO<sub>2</sub> surface, due to the increased steric hindrance.

Therefore, to minimize this drawback, we designed and synthesized four new TPA-based organic dyes (**D1** [19] that has been previously published, **SH-11**–**14** as shown in Fig. 1). The dyes have AD-D- $\pi$ -A structure, which has the TPA moiety as a main electron donor (D), methoxy groups as an additional electron donor (AD), furan moiety as a  $\pi$ -bridge ( $\pi$ ), and a cyanoacrylic acid group as an electron acceptor (A). The methoxy groups as an additional donor can lead not only to bathochromic shift of the absorption spectrum and enhancement of the molar extinction coefficient, but also to relatively smaller steric hindrance, compared to the sterically bulky moieties. The effects of the number, position, and shape of the methoxy groups attached to the TPA donor part were investigated by the dye photophysical and electrochemical properties, and the cells photovoltaic performance. To the best of our knowledge, this is the first report studying the effects of the introduction of an additional donor of various number, position, and shape to the TPA donor moiety for efficiency improvement. To gain further insight into their effects, density functional theory (DFT) calculations of all the dyes were carried out, using the B3LYP/6-31G(d,p) level. Electrochemical impedance spectroscopy (EIS) was

used to study their interfacial charge transfer. The synthetic routes of the new dyes are depicted in Scheme 1.

## 2. Experimental section

### 2.1. Materials and reagents

All reactions were performed under nitrogen atmosphere. 3,4-Dimethoxyaniline, 6-amino-1,4-benzodioxane, 2,4-dimethoxyiodobenzene, and 4-bromoaniline from TCI and 4-iodoanisole, KI, CuI, 1,10-phenanthroline, tetrakis(triphenylphosphine)palladium(0), 5-formyl-2-furan-boronic acid, cyanoacetic acid, and piperidine from Sigma-Aldrich were purchased and used as received without further purification. All solvents (toluene anhydrous, tetrahydrofuran anhydrous, and acetonitrile anhydrous) were obtained from Sigma-Aldrich and used as received. Other chemicals were reagent grade and used without further purification.

### 2.2. Analytical instruments and measurements

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 300 and 500 MHz (Seoul National University National Center for inter-University Research Facilities) with the chemical shifts against TMS. Mass spectra were measured with a JEOL JMS-600W mass spectrometer (Seoul National University National Center for inter-University Research Facilities). Elemental analyses were carried out with a Flash EA 1112 elemental (C,N,S) analyzer. UV-vis spectra and photoluminescence spectra were recorded on a Hewlett-Packard 8452A spectrophotometer and Shimadzu RF-5301PC spectrofluorometer, respectively. Cyclic voltammetry spectra were obtained using a three-electrode cell with a 273A (Princeton applied research, Inc.). The measurement was carried out using an Ag wire (Ag/Ag<sup>+</sup>), a glassy carbon and a platinum wire as a reference, a working and a counter electrode, respectively, in CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 M tetrabutylammonium tetrafluoroborate as a supporting electrolyte. A standard ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple was used to calibrate the oxidation peak. Photocurrent-voltage (*I*-*V*) measurements were performed using a Keithley model 2400 source measure unit. Incident photon-to-current conversion efficiency (IPCE) was measured as a function of wavelength from 300 nm to 1000 nm using a specially designed IPCE system for the dye-sensitized solar cell (PV measurements, Inc.).

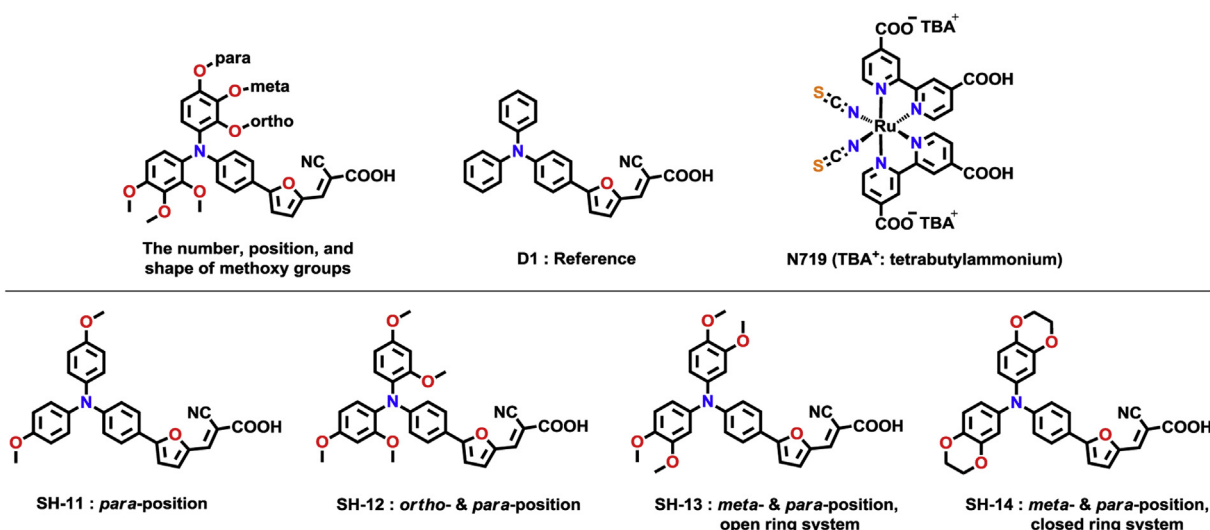


Fig. 1. Molecular structures of **D1**, **N719**, **SH-11**, **SH-12**, **SH-13**, and **SH-14**.

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