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# An investigation of the role the donor moiety plays in modulating the efficiency of 'donor-π-acceptor-π-acceptor' organic DSSCs

Kwang-Won Park [a, 1], Luis A. Serrano [b, 1], Sungwoo Ahn [a], Myung Hoon Baek [a], Alan A. Wiles [b], Graeme Cooke [b, *], Jongin Hong [a, **]

[a] Department of Chemistry, Chung-Ang University, Seoul, 06974, Republic of Korea
[b] WestCHEM, School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK

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ABSTRACT

Three 'D-π-A-π-A' based dyes have been synthesized featuring MeO-, MeS- and $Me_2N$- as donor residues and benzothiadiazole and cyanoacrylic acid residues as acceptor units. UV–vis spectroscopy, solution electrochemistry and DFT modelling indicated that the $Me_2N$- residue has the most significant effect on optical and redox properties of a photosensitizer. DSSCs with the $Me_2N$- functionalized dye gave the highest power conversion efficiency of the series ($\eta = 5.61\%$), presumably due to the better donor ability of this unit, which promotes more effective intramolecular charge transfer (ICT) characteristics.

## 1. Introduction

Dye-sensitized solar cells (DSSCs)[1] continue to be intensively studied as potential alternatives to silicon-based photovoltaic devices due to their distinctive features including low cost fabrication and ability to function under low-light conditions.[2] In particular, metal-free organic photosensitizers for DSSCs have become increasingly attractive and offer several advantages over their transition metal-incorporating brethren including cost-effective modular synthesis and higher molar extinction coefficients.[3] The majority of organic dyes reported to date feature a donor-π bridge-acceptor (D-π-A) architecture,[4] with triarylamine-based moieties being commonly used as the D moiety because of their convenient synthesis and interesting electron donating properties.[5] Cyanoacrylic acid residues have been used extensively as the A unit due to their facile synthesis from aldehyde residues and ability to simultaneously act as a $TiO_2$ anchoring unit. Various π-conjugated bridging units including aromatic, heteroaromatic or alkyne residues have been introduced to induce efficient charge separation between D and A units.[6] Recently, additional subordinate A units,[7] such as benzothiadiazole, have been incorporated as an electron trap to promote charge separation and electron migration to the second A unit in a D-π-A-π-A structure.[8]

In the D-π-A structure, the D units play an important role in determining the optical characteristics of the dye and, as a result, research has been diverted towards investigating the role differing D units have in modulating the absorption characteristics of the dyes and DSSC performance.[9] In this study, we report the facile synthesis of three 'D-π-$A_1$-π-$A_2$' organic dyes (**LS-385**, **LS-386** and **LS-387**, Scheme 1). In order to promote planarity between the D and $A_1$ residues an acetylene linker group has been included.[10] We have also investigated how the differing D groups (MeO-, MeS- and $Me_2N$-) affect the properties of their parent dyes and resulting DSSC devices.

## 2. Results and discussion

### 2.1. Synthesis

The three dyes were synthesized according to Scheme 1. Sonogashira reactions provided the building blocks **3**, **6** and **9** in respectable yields. Suzuki coupling reactions with 4-formylphenyl boronic acid provided the aldehyde-functionalized units (**4**, **7** and

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* Corresponding author.

** Corresponding author.

*E-mail addresses:* Graeme.Cooke@glasgow.ac.uk (G. Cooke), hongj@cau.ac.kr (J. Hong).

[1] These authors made equal contribution to this article.

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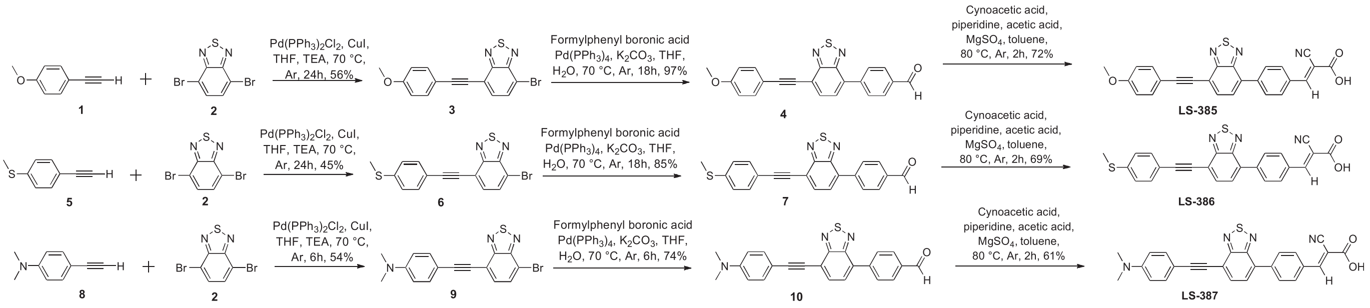

**Scheme 1.** Synthesis of dyes.

**10)** in good yields, which upon subsequent Knoevenagel condensation with cyanoacetic acid, yielded dyes **LS-385**, **LS-386** and **LS-387** in respectable yields.

### 2.2. Characterization

Fig. 1 shows the UV–vis absorption spectra of the three dyes in DMF solution and deposited as $TiO_2$ films. The absorption band around 300 nm is likely due to a $\pi$-$\pi^*$ transition of the conjugated aromatic moieties, and the molar extinction coefficient for this wavelength decreases in the order of **LS-387** > **LS-386** > **LS-385**. The distinct absorption band in the visible region is attributed to the intramolecular charge transfer (ICT) between the D and A moieties. The stronger electron donating ability of the $Me_2N$-moiety induces a bathochromic shift in the longest wavelength absorption of around 45 nm. This is also confirmed by electronic absorption spectra from the TDDFT calculations (see Supporting Information, Fig. S1). Compared with the spectra in DMF solution, the absorption bands of the dyes adsorbed onto $TiO_2$ exhibit significant spectral broadening and larger red-shifts because of the interaction of the anchoring groups with the surface of $TiO_2$ and the *J*-aggregation of photosensitizer molecules. This trend follows the order **LS-387** > **LS-386** > **LS-385**.

The electrochemical behavior of the three compounds was explored by cyclic voltammetry (CV) and square wave voltammetry (SWV) (Supporting Information, Fig. S2). The SWV experiments provided the estimated ionization potential (IP) and electron affinity (EA) energies in Table 1.[11] The $E_{fund}$ ($E_{fund} = \text{IP} - \text{EA}$) of **LS-385** and **LS-386** are similar (2.5 eV), however, dye **LS-387** possesses a lower value of 2.22 eV, presumably due to the stronger electron donating nature of the $Me_2N$- residue.

**Table 1**
SWV derived redox potentials of the dyes and their estimated EA/IP energies.

| Dyes | $E_{red}$(V) | $E_{ox}$(V) | EA (eV) | IP (eV) |
|---|---|---|---|---|
| **LS-385** | −1.66 | 0.79 | −3.14 | −5.59 |
| **LS-386** | −1.57 | 0.80 | −3.23 | −5.60 |
| **LS-387** | −1.68 | 0.41 | −3.12 | −5.21 |

### 2.3. Theoretical calculations

DFT and TDDFT calculations were performed to understand the electronic structure and optical properties of the dyes. We defined six bond lengths denoted as $d_1$ to $d_6$ to point out the relationship between bond length and electron donating ability for the given molecule (Fig. 2). Table 2 summarizes these bond lengths from the ground state optimized geometries. Among them, $d_1$ values between molecules differ significantly because of the various atomic radii of oxygen, sulfur and nitrogen. These $d_1$ values are very consistent with the covalent bonding radius of C—O (1.421 Å),[12] C—N (1.471 Å)[13] and C—S (1.77 Å)[14] single bonds in ascending order. Relatively short bond lengths in the DFT calculations might originate from hybridization between $sp^2$ and $sp^3$ carbons.[15] Recently, we reported that bond length values obtained from DFT calculations have strong correlation with the electronic and optical properties as well.[16] Interestingly, **LS-387** has the shortest bond lengths of $d_2$ to $d_6$, compared with those of other dyes, whereas no apparent difference between **LS-385** and **LS-386** was observed. We think that such a change in bond length is related to the donor strength of nitrogen, implying extensive delocalization throughout the molecule.[16,17] Accordingly, **LS-387** is expected to result in the best DSSC performance of this series of dyes.

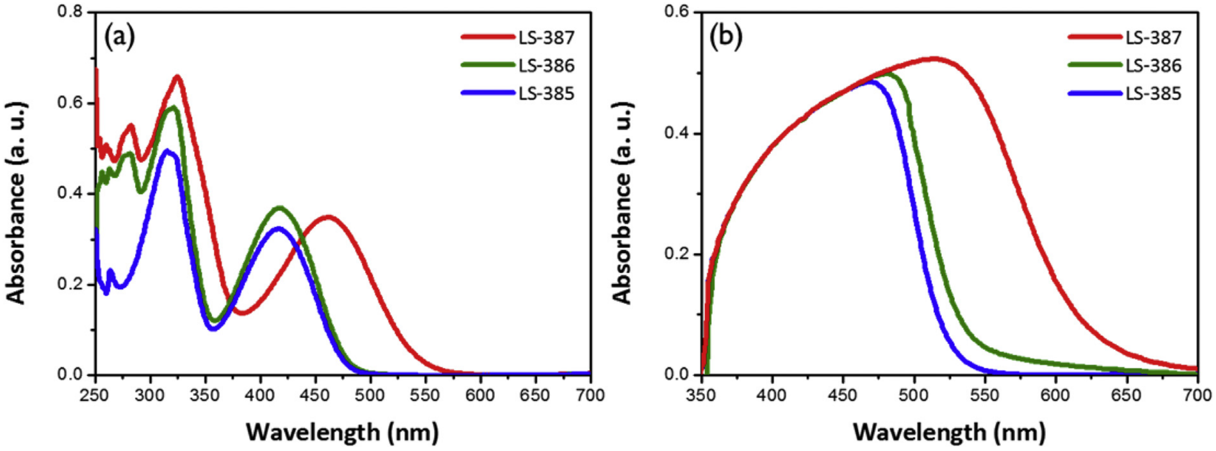

**Fig. 1.** UV–vis absorption spectra of each dye (a) in DMF solution ($1 \times 10^{-5}$ mol $L^{-1}$) and (b) adsorbed onto transparent $TiO_2$ film.