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# A rational design of high efficient and low-cost dye sensitizer with exceptional absorptions: Computational study of cyanidin based organic sensitizer

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ABSTRACT

We have computationally designed and characterized a series of new organic D−π−A architected dyes that have originated from cyanidin, which is vastly available in nature, for effective sensitization of DSSCs with absorption spectra extending up to near infrared region. Cyanidin acts as the donor group while cyanoacrylic acid and thieno [3, 2-b] thiophene are employed as the acceptor and π-spacer, respectively. Sensitization performance, depending on the substituted position of the π-spacer-acceptor (π-A) combination on cyanidin molecule, is examined by the results of density functional theory (DFT) and time dependent density functional theory (TDDFT) calculations. The calculated data of free energy change driving force ($\Delta G_{inject}$), electron regeneration driving force ($\Delta G_{regen}$), open circuit potential $eV_{OC}$ and light harvesting efficiency (LHE) suggest two preferred substitutions of π-A combination to cyanidin molecule that leads to an efficient DSSC. At LUMO the designed sensitizers have denser electron cloud towards acceptor group that leads to an efficient electron injection process. All π-A substitutions resulted a broader absorption spectrum with a redshift up to 2500 nm which is a significant improvement compared to the vast majority of reported sensitizers.

## 1. Introduction

The current global challenge is to meet the increasing global energy consumption with minimum disturbance to the environment. Solar energy provides a clean, abundant energy and is therefore, an excellent candidate for a future environmental friendly energy source.

The aim of solar cell research is to increase the solar energy conversion efficiency at low cost to provide a cost-effective sustainable energy source. In Switzerland, Gratzel and his co-researchers developed a solar cell using nanostructured electrodes combined with efficient electron injection dyes, named as the dye-sensitized nanostructured solar cell (DSSC) (Smestad and Gratzel, 1998).

Many forms of dyes have been studied for DSSCs application and in principle, they could be categorized into two, such as metal-based and metal-free organic dyes. The high cost and environmental hazards of these sensitizers compel the search for alternatives (Basheer et al., 2014; Narayan, 2011; Polo and Murakamiiha, 2006; Shalini et al., 2015; Torchani et al., 2015; van der Salm et al., 2015; Wongcharee et al., 2007; Ye et al., 2015).

An exciting approach in DSSC is the use of natural dye extracts as sensitizers which are more cost-effective and environmental friendly (Gomez et al., 2017; Narayan, 2012; Parisi et al., 2014; Shahid et al., 2013). Given the abundance and variety of natural dyes, a thorough understanding of their electronic structure and its energy levels are necessary to determine the potential of light harvesting and sensitizing abilities in order to perform in DSSCs (Basheer et al., 2014; Cheema and Delcamp, 2017; Gomez et al., 2017; Lim et al., 2015; Ye et al., 2015). According to the previous research, efficiencies of DSSCs based on natural sensitizers are still very low due to their poor light harvesting abilities. (Sugathan et al., 2015; Torchani et al., 2015). To improve its efficiency, the invention of natural dye-based new metal-free organic dyes, having improved optical properties with simple structures would be a resourceful approach.

Computational calculations play a significant role in designing new sensitizers, which provide a profound understanding of the correlation between optical properties and the chemical structures of the dyes (Pastore et al., 2013).

In this study, naturally abundant, widely tested, sensitizer cyanidin (Damit et al., 2017; Ekanayake et al., 2013; Gomez et al., 2017; Liu, 2008; Ludin et al., 2014; Shahid et al., 2013; Tennakone et al., 1997)

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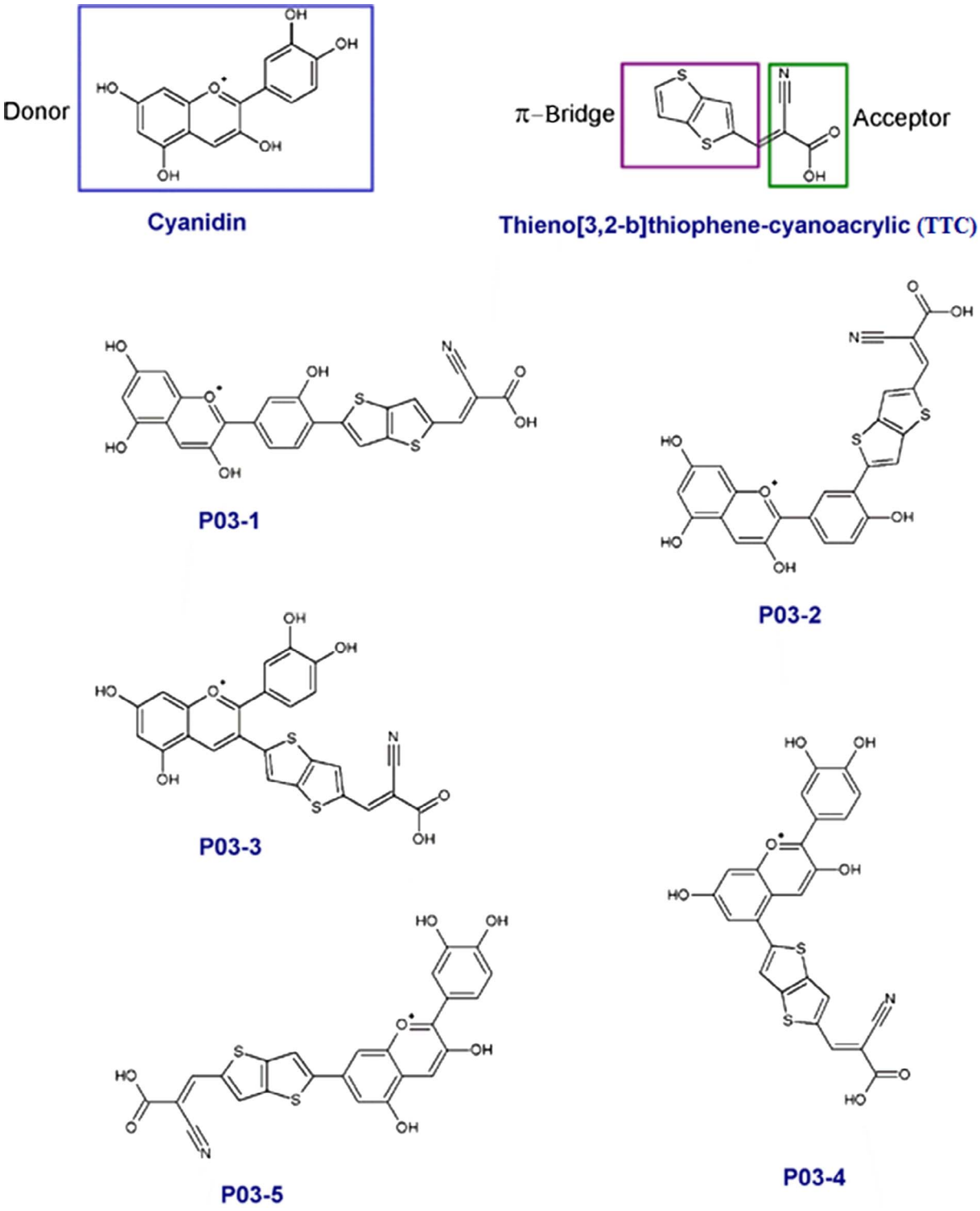


**Fig. 1.** Fundamental molecular structure of cyanidin, thieno [3, 2-b] thiophene cyanoacrylic acid (*TTC*), *P03-1*, *P03-2*, *P03-3*, *P03-4,* and *P03-5.*

based D-π-A architecture, a series of dyes coded as *P03-1*, *P03-2*, *P03-3*, *P03-4*, and *P03-5* are computationally designed (as shown in Fig. 1) and characterized as novel sensitizers in DSSC. This *P03* series of sensitizers are designed by combining electron rich cyanidin as the electron donor (D), promising electron acceptor cyanoacrylic acid group as the electron acceptor (A) and thieno thiophene moiety as the π-spacer (π). The thieno thiophene and cyanoacrylic acid are specially selected for this rational design by considering their recorded performance as π-spacer and acceptor group, respectively (Ahmad et al., 2013; Naik et al., 2017; Obotowo et al., 2016; Zhang et al., 2012).

## 2. Computational studies

### 2.1. DFT and TDDFT studies

We computed molecular structures of cyanidin, *TTC*, *P03-1*, *P03-2*, *P03-3*, *P03-4* and *P03-5* using Spartan'10 software (B. Deppmeier et al., 2011) to retrieve the molecular geometric coordinates and performed