



# The effect of direct amine substituted push–pull oligothiophene chromophores on dye-sensitized and bulk heterojunction solar cells performance



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## ABSTRACT

The effect of direct amine substitution on the photovoltaic performance of donor–acceptor oligothiophenes in dye-sensitized and bulk heterojunction (BHJ) solar cells was investigated. These dyes have a common donor (di-*p*-tolylamino),  $\pi$ -bridge (terthiophene), and tunable acceptors to provide new materials for evaluation in dye-sensitized solar cells (DSCs) and BHJ solar cells. They were tested with liquid, ionic liquid, and metal-complex based electrolytes for DSCs and PC<sub>61</sub>BM for solution processable BHJ solar cells. Direct amine substitution of the oligothiophene resulted in a significant spectral red-shift, reduction in band-gaps and improved photovoltaic performance in DSCs but not for BHJ devices.

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## 1. Introduction

Organic-based photovoltaic devices (OPVs) are receiving significant attention due to their promise as low-cost, flexible power sources. They can be broadly classified into DSCs based on titanium dioxide (TiO<sub>2</sub>) films<sup>1</sup> and purely organic devices<sup>2</sup> that typically have a BHJ<sup>3</sup> or evaporated bilayer<sup>4</sup> active layer. The polythiophene P3HT has been the chromophore and hole transport material of choice in BHJ<sup>5,6</sup> and various permutations of donor–acceptor oligothiophenes have been used in organic-based DSCs.<sup>7</sup> In the field of BHJ OPVs the use of small molecules in place of P3HT has the potential to simplify synthesis and purification and enable greater control over energy levels and morphology.<sup>8–11</sup>

In our own development of small molecule chromophores/charge transport materials,<sup>12</sup> we have sought to design molecules based on a common core structure that, with simple modifications, can be used in both BHJ and DSC devices. Small molecules for BHJ and DSCs generally have a donor–acceptor structure to obtain

sufficient absorption of the visible spectrum that a polymer like P3HT achieves simply by its extended conjugation length. Reported donor–acceptor oligothiophenes exclusively use a triarylamine-type donor such that a phenyl (or related aromatic unit like fluorene) links the amine nitrogen to the thiophene.<sup>7,13,14</sup> In this report, we examine the strategy where the donor amine nitrogen is a direct substituent on the oligothiophene spacer and its effect on chromophores for applications in DSCs and BHJ devices. The new chromophores show significant spectral red-shifts, reduction in energy band-gaps, and superior DSC performance when compared in parallel with the triphenylamine equivalents. Here we have used a ditolylamino oligothiophene derivative with the direct substitution of the amine nitrogen on the oligothiophene and methyl groups at the *p*-positions to avoid the possible dimerization of the phenyl ring.<sup>15</sup>

We have synthesized three model examples (**1**, **2**, **3**) with this modification along with reference dyes (**R1**, **R2**) such that the length of conjugation between the amine nitrogen and acceptors is the same for all compounds. The structures are shown in Fig. 1. In the modified design, the acceptor groups were varied with cyano-carboxyvinylidene (**1**) used for DSCs and dicyanovinylidene (**2**), and diethylthiobarbituric acid (**3**) for BHJ devices. The compounds were synthesized following the method of Marder et al. who studied derivatives with two thiophene units as non-linear optical

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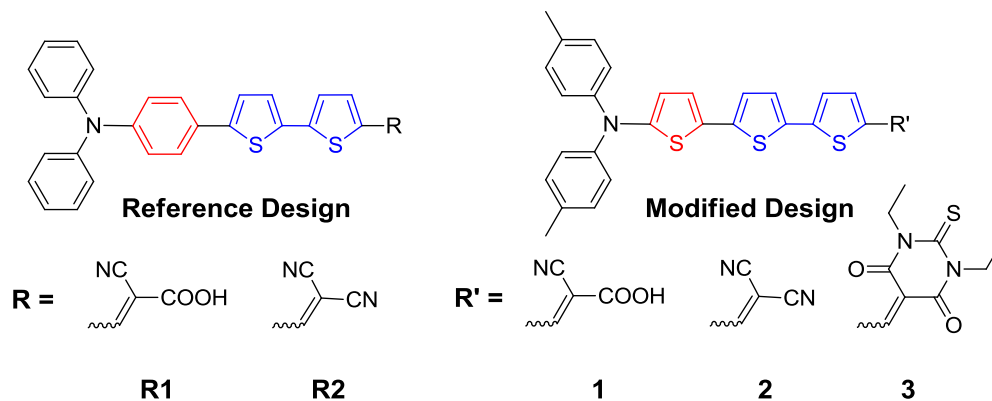


Fig. 1. Molecular structures of the investigated newly designed (**1**, **2**, and **3**) and reference (**R1** and **R2**) materials.

materials.<sup>16</sup> The molecules reported in this work were found to be highly soluble in a variety of conventional organic solvents, such as dichloromethane, chloroform, chlorobenzene, and toluene. High solubility is a desirable feature for the fabrication of solution-processable OPVs and precludes the need for inclusion of electroactively inert alkyl chains into the organic module. To the best of our knowledge, this is the first time that materials based on a common structural core have been evaluated in both DSCs and BHJ photovoltaic devices.

## 2. Results and discussion

### 2.1. Design concept and synthetic strategy

All the new materials were based on the D- $\pi$ -A modular design and have a common di-*p*-tolylamino donor, terthiophene as a  $\pi$ -bridge, and various acceptors to generate a set of organic dyes that were evaluated as organic semiconductor components for OPVs. In the modified design, replacement of the phenyl group with thiophene provided significant spectral red-shifts. This could be attributed to the lower aromaticity of thiophene, that is, advantageous for superior charge delocalization.<sup>17</sup> Furthermore, with the use of the strong aromatizable diethylthiobarbituric acid acceptor unit for BHJ design, we could expect bathochromic shifts in the absorption that might provide a higher molar extinction coefficient and narrower band gap. Intramolecular charge transfer (ICT) would be enhanced with the use of an acceptor fragment with increased acceptor strength, which in-turn would provide for greater light harvesting and perhaps better positioning of energy levels.

The synthesis involved the reaction of di(*p*-tolyl)-2-aminothiophene with *n*-BuLi and subsequent reaction with tributyltin chloride to give *N,N*-di-*p*-tolyl-5-(tributylstannyl)thiophene-2-amine. The stannane was then reacted with 5'-iodo-2,2'-bithiophen-5-carbaldehyde using bis(triphenylphosphine)palladium(II) chloride to provide the 5'-formyl-5-(*N,N*-di-*p*-tolylamino)-2,2':5'2''-terthiophene. This penultimate aldehydic component was a common synthon, which was condensed with cyanoacetic acid, malononitrile, and diethylthiobarbituric acid to give compounds **1**, **2**, and **3**, respectively. These new materials were prepared in moderate to high yields and their chemical structures were confirmed by <sup>1</sup>H NMR spectroscopy and mass spectrometry.

### 2.2. Optical properties

The comparative ultraviolet–visible (UV–vis) spectra of all the materials measured in solution and as thin films are shown in Figs. 2 and 3, respectively. Direct attachment of the diarylamino donor group to the terthiophene resulted in 42 nm and 30 nm

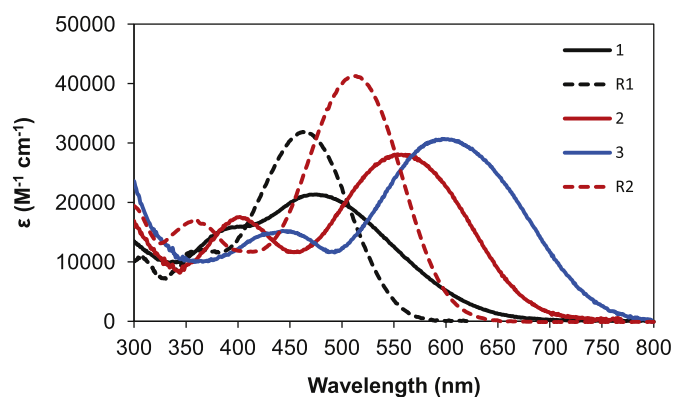


Fig. 2. Molar absorptivities of newly synthesized dyes **1–3** (thick lines) vs reference dyes **R1** and **R2** (dotted lines) in chloroform solutions.

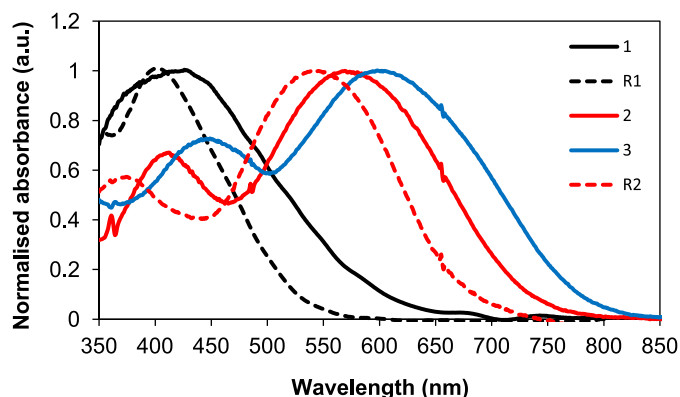


Fig. 3. Normalized film absorption spectra of newly synthesized dyes **1–3** (thick lines) vs reference dyes **R1** and **R2** (dotted lines); **R1** and **1** on 1.2  $\mu\text{m}$  thick  $\text{TiO}_2$  film and dyes **2**, **3**, and **R2** on glass substrates.

bathochromic shifts of solution and film absorption spectra, respectively, of compound **2** when compared with reference compound, **R2**<sup>12a</sup> that has a phenyl linker between the amine nitrogen and terthiophene unit. Similarly, the acid derivative **1** displays 16 nm and 22 nm red shifts of solution and film spectra when compared with the reference dye **R1**,<sup>18</sup> which has a phenyl group rather than thiophene between a diarylamino nitrogen and cyanoacetyldithiophene. The use of the strong acceptor group, diethylthiobarbituric acid, leads to a more marked red-shift of 46 nm and a 10% enhancement in the peak molar absorptivity of **3** compared with the dicyanovinylidene group in compound **2**. We

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