



# Synthesis and molecular properties of butterfly-shaped tetrathiophene derivatives



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## ARTICLE INFO

### Article history:

Received 9 October 2014

Received in revised form 16 January 2015

Accepted 1 February 2015

Available online 7 February 2015

### Keywords:

Butterfly-shaped

Organic synthesis

Thiophene

DFT calculations

## ABSTRACT

Four cross-conjugated butterfly-shaped molecules were designed and synthesized with the branched tetrakis(thiophene-2-yl)ethene or the planar naphthotetrathiophene as the donors and dicyanovinylene as the acceptor. Owing to the donor–acceptor conjugated structures, these molecules exhibited broad and strong absorbance in the UV–vis region. Their electrochemical and photophysical properties were studied; in addition, the UV–vis behaviors were also described by virtue of DFT calculations to further understand the origins of different absorption bands and efficient charge transfer was observed for given optical transitions from the ground states to the excited states in natural transition orbitals. Finally, these butterfly-shaped molecules were applied to fabricate organic photovoltaic devices and we believe the current work illustrated an efficient way for the design and synthesis of sophisticated structures with the tetrathiophene building blocks.

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## 1. Introduction

Thiophene and its derivatives are promising building blocks for the conjugated materials design and synthesis. Owing to their structural diversity, a variety of sophisticated thiophene-based  $\pi$ -conjugated materials have been synthesized.<sup>1–5</sup> 1,1,2,2-Tetra(thiophen-2-yl)ethene (TTE), as one of the thiophene tetramers, bears a branched structure with four thiophene units and a vinyl bridge. On the one hand, this  $\pi$ -extended conjugated structure guarantee it possess a lower band gap than that of the dithienylethylene and tetrathiophene.<sup>6</sup> On the other hand, TTE can be employed as a novel unit for sophisticated structure construction. Recently, we reported two novel dendrimers (16T and 20T) utilizing TTE as a dendron via Suzuki, and McMurry reactions;<sup>1</sup> the crystal results clearly presented hyperbranched configurations. When photocyclization was applied to TTE, the ring closure reaction may occur and a new flat and rigid  $\pi$ -conjugated thiophene-based building blocks could be synthesized, i.e., naphthotetrathiophene (NTT). This planar structure brought the effective extension of  $\pi$ -conjugation, exhibited strong aggregation and indicated a significant potential as a cruciform scaffold for  $\pi$ -electron materials.<sup>7</sup>

Nowadays, small molecules or oligomers with the donor–acceptor (D–A) conjugated systems have attracted more and more attentions<sup>8</sup> and have been extensively studied in various fields, such as dye sensitized solar cells,<sup>9</sup> nonlinear electro-optics,<sup>10</sup> organic photovoltaics,<sup>11</sup> and organic field-effect transistors.<sup>12</sup> These materials possess well-defined structures and single molecular weights, which make them simply reproducible. With the electron push–pull systems, these materials possess low-lying band gaps, resulting in extended absorption spectra. Meanwhile, the strong intermolecular interactions induced from the donor and acceptor moieties might favor the molecules forming ordered structures,<sup>8</sup> increasing the  $\pi$ -orbital overlapping and offering potential usage in organic electronics. Thiophene and its derivatives are always good candidates for the electron donors; as for the acceptor units, there are many options, such as tricyanofuran,<sup>13</sup> dicyanovinylene (DCV),<sup>12</sup> rhodanine,<sup>14,15</sup> cyanoacetate,<sup>14</sup> etc. DCV is considered as a strong electron-withdrawing group,<sup>16</sup> which can be prepared via simple Knoevenagel condensation between the corresponding C=O derivatives and malononitrile. Utilizing the DCV-based oligothiophenes, a good performance in organic photovoltaics was obtained by Heliatek GmbH.<sup>17</sup>

Based on our previous work, we wanted to further develop the tetrathiophene systems. Herein we reported the synthesis and characterization of four new butterfly-shaped molecules (TTE-DCV, NTT-DCV, TTET-DCV, and NTTT-DCV, in Fig. 1), which were composed of two different types of tetrathiophene building blocks. These molecules employed two TTE or NTT components as the  $\pi$ -

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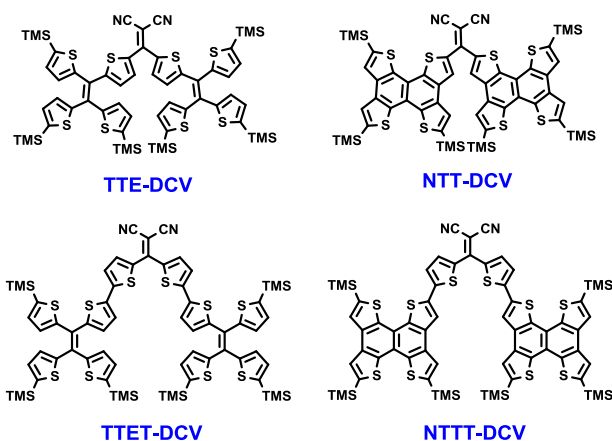


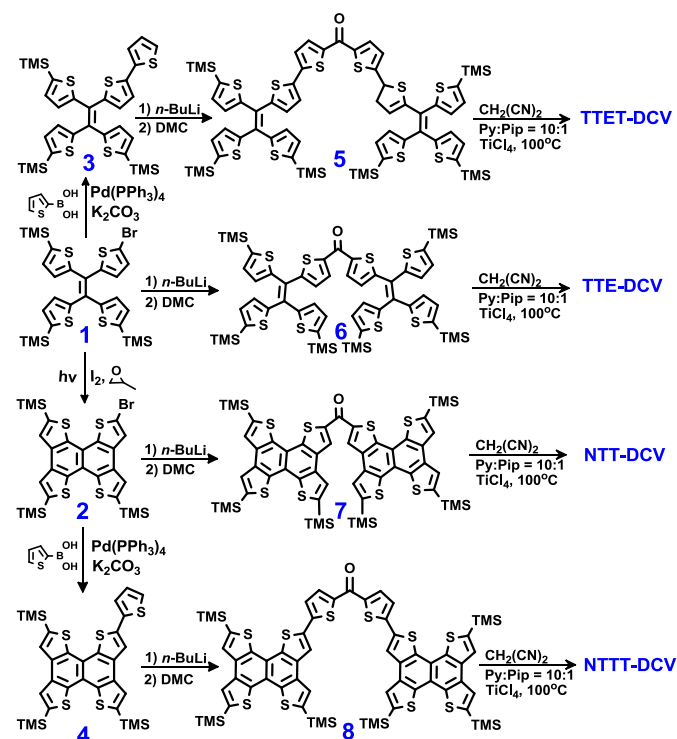
Fig. 1. Chemical structures of the tetrathiophene based butterfly-shaped molecules.

electron donors and DCV as the acceptor groups, respectively. Meanwhile, six TMS groups were incorporated into each molecule to assist the solubility and two more thiophene units were introduced into the **TTET-DCV** and **NTTT-DCV** to extend the conjugated ‘wings’ of the molecules. The spectroscopic and electrochemical data were collected and their absorption behaviors were further studied using the time dependent density functional theory (TD-DFT) calculation. In addition, these molecules were also fabricated into OPV devices with PC<sub>71</sub>BM as the acceptor, and **TTET-DCV** presented the best photovoltaic activity among these molecules in the preliminary results.

## 2. Results and discussions

### 2.1. Synthesis of molecules

The synthetic routes to all the four DCV molecules are outlined in Scheme 1. Starting from the crucial vinyl building unit TTE, the



Scheme 1. Synthetic routes for the DCV based compounds **TTE-DCV**, **NTT-DCV**, **TTET-DCV**, and **NTTT-DCV**.

mono bromo compound **1** could be synthesized according to the previous work<sup>1</sup> and via the irradiation under a medium pressure mercury lamp, the corresponding naphtho-unit (**2**) was obtained in high yield of 75%, which was the other important building block to construct the D–A molecules in this study. Via Suzuki cross coupling with the 2-thiophene boronic acid, another two units (**3** and **4**) were obtained from compound **1** and **2** in high yields of 85%<sup>1</sup> and 75%, respectively. Subsequently, these four basic building blocks (**1–4**) were employed for the Br/Li exchange or deprotonation in the presence of *n*-BuLi and the corresponding dimers (**5–8**) with ketone bridges were afforded by quenching the reactions with *N,N*-dimethylcarbonyl chloride (DMC) in high yields of 85%,<sup>1</sup> 93%,<sup>1</sup> 79%, and 72%, respectively. Finally, from the ketone precursors (**5–8**), the targeted butterfly-shaped D–A molecules were synthesized via the Knoevenagel condensation with the malononitrile in yields of 75%, 56%, 55%, and 30% for **TTE-DCV**, **NTT-DCV**, **TTET-DCV**, and **NTTT-DCV**, respectively. Due to the poor solubilities, the <sup>1</sup>H NMR spectra of compound **8** and the <sup>13</sup>C NMR spectra of compound **7**, **8**, and **NTTT-DCV** were not obtained.

### 2.2. Photophysical properties

All of the molecules were soluble with low concentrations in common organic solvents such as chloroform, dichloromethane, and toluene. UV–vis absorption spectroscopy was measured in both solutions ( $1 \times 10^{-5}$  M in chloroform) and solid thin films, which were shown in Fig. 2a and b, respectively. Detailed photophysical characterization results of these four DCV molecules were shown in Table 1. In solution, **TTE-DCV** and **TTET-DCV** exhibited similar absorption behaviors and four clear absorption bands were observed as following: 440–650 nm (Band-I), 330–440 nm (Band-II), 270–330 nm (Band-III), and 230–270 nm (Band-IV). Their molar extinction coefficients reached  $4 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup> at the maximum absorption wavelength, indicating these molecules should have good light-harvesting abilities. With one more thiophene introduced in between the DCV and TTE moieties, **TTET-DCV** exhibited bathochromic absorption behaviors compared to **TTE-DCV**, which could be attributed to the extended conjugation length. As for **NTT-DCV** and **NTTT-DCV**, three main absorption bands were shown up in the region of 420–620 nm (Band-I), 270–420 nm (Band-II), and 230–270 nm (Band-III), shoulder peaks at 330–420 nm were observed next to the Band-II for both of them. By replacing the TTE moieties with the planar NTT units, the molar extinction coefficients ( $\sim 6 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>) at the maximum absorption wavelength were increased almost 50% when compared with the corresponding TTE based molecules. In thin films, all of the compounds presented similar absorption behaviors to their solutions, but all absorption bands in solid state became broader. The maximum and onset absorption wavelengths of TTE based molecules in solid state were very close to that of their solutions (in Table 1), while the NTT based molecules presented obvious bathochromic shift in thin films. This phenomenon could be explained by the

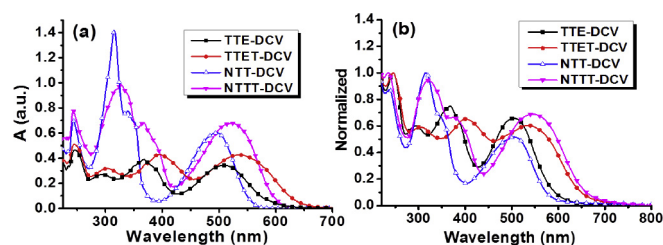


Fig. 2. UV/vis spectra for DCV based **TTE-DCV**, **NTT-DCV**, **TTET-DCV**, and **NTTT-DCV** in chloroform at room temperature (a) chloroform solution ( $[C]=1 \times 10^{-5}$  M) and (b) thin films.

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