



A star-shaped sensitizer based on thienylenevinylene for dye-sensitized solar cells

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ABSTRACT

A novel star-shaped dye based on highly conjugated oligothienylenevinylene (nTV) bearing pendant solubilizing hexyl chains and end-capped with three tetramethylammonium cyanoacetates as anchoring groups has been synthesized. Its photovoltaic performance, in mesoporous TiO₂ dye-sensitized solar cell, has been tested under different experimental conditions. The best performances were obtained at longer adsorption times of 4 h using different electrolyte compositions, reaching up to 3.11% of efficiency.

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The global environmental issues and growing energy demand have greatly encouraged scientists and governments to explore and develop renewable and environmentally friendly energy sources. Solar photovoltaic (PV) electricity keeps growing and represents now the third source of the world-wide renewable energy in terms of installed capacity after hydro and wind power.¹ However, mainly due to the high-purity required for the inorganic silicon semiconductors in actual solar panels,² this technology still remains expensive in terms of price-per-KWh.

Alternative photovoltaic systems based on cheap materials and production processes such as dye-sensitized solar cells (DSCs) appear to be a promising route to produce competitive and cost-effective, new photovoltaic devices. DSCs were initially developed based on ruthenium(II)-polypyridyl complexes (such as N3, N719, or black dyes) as the active material³ adsorbed on nanocrystalline TiO₂ with validated conversion efficiencies up to 11% under simulated AM 1.5G illumination (100 mW cm⁻²). Metal-free organic donor-acceptor (D-A) dyes have attracted increasing attention due to their low cost, low-impact environmental pollution ('green dye'), high and tunable molar absorption coefficients, and easy modification of the molecular structures by design strategies.⁴⁻⁶ A porphyrin dye has recently achieved 11% solar-to-electric power conversion efficiency at simulated 1 sun solar irradiation in combination with a Cobalt (II/III) redox couple, which is the best-efficient free-metal organic DSC to date.⁷ This significant breakthrough has

strongly renewed the interest and perspectives for free-metal organic based DSC.

Conjugated oligomers are target compounds for many applications in material science⁸ due to their interesting optical, electrical, and optoelectronic properties. One type is star-shaped conjugated systems,⁹ in which identical arms are attached to a central core. Three-armed star with a benzene core (propeller shaped)¹⁰ has been widely used in material science as hole-blocking materials, in OLED,¹¹ liquid crystal,¹² as active materials for organic electronic devices such as BHJ solar cells¹³ or combined with fullerene in studies of photoinduced electron transfer.¹⁴ Finally, star-shaped systems substituted with carboxylate groups were used to produce metal-organic frameworks (MOFs).¹⁵

Recently we described new dyes for DSC where thienylenevinylene oligomers (nTV) of different lengths act as donor¹⁶ or bridge¹⁷ in D- π -A structures for DSCs. For instance, we have reported a linear 4-thienylenevinylene dye functionalized with cyanoacrylic acid as anchoring group (Chart 1) and its performance tested in mesoporous TiO₂ DSCs.¹⁸

We report herein on the successful synthesis and characterization of a star-shaped dye containing a benzene central core and three arms, each one formed by four thienylenevinylene oligomer units bearing pendant solubilizing hexyl chains and end-capped with three tetramethylammonium cyanoacetates as anchoring groups (Chart 2).

So far, most of the free-metal organic sensitizers previously studied and tested in DSCs are based on D-A, linear 'push-pull' type dyes. To date, very few works report on proof-to-principle

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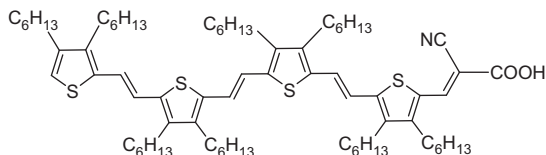


Chart 1. Molecular structure of a linear 4-thienylenevinylene dye sensitizer previously described and tested in DSCs in our group.

efficiency of multi-component, -light harvesting, and/or -anchoring dyes used in free-metal organic based DSCs, together with their structure shape relationship, such as star-shapes. To our knowledge only one example of a star-shaped molecule has been investigated as a dye for DSCs.¹⁹ The advantage (or disadvantage) to use these kinds of multi-component systems in DSCs, covalently assembled at the supramolecular level, still remains unclear. For example we need to tune the electrolyte so that electron injection to the TiO₂ conduction band is optimal while the bulky dye structure prevents recombination by maintaining the oxidized species in the electrolyte away from the titania surface, so that the photovoltage is not reduced. These features are investigated below by determination of the electrochemical, optical, and photovoltaic properties of this new star-shaped dye and its performance in DSCs under different experimental conditions.

The synthesis of dye **6** is depicted in Scheme 1. Tris(phosphonate) **1**²⁰ and 4TV-CHO **2**²¹ were prepared according to the procedure previously described in the literature. The first step involves the reaction of phosphonate **1** and 4TV-CHO **2** in THF with an excess of *t*-BuOK under Wittig–Horner conditions, affording triad **3** in 84% of yield. Subsequently, **3** was formylated via a Vilsmeier–Haack reaction in the presence of an excess of POCl₃/DMF at reflux in DCE overnight, affording (tris)aldehyde **4** in a 71% yield. The final step was a Knoevenagel condensation with cyanoacetic acid in the presence of a catalytic amount of piperidine to convert tris–aldehyde **4** into tris–cyanoacrylic acid **5**. Due to its dual amphiphilic behavior, a strong lipophilic central core induced by numerous side alkyl chains of 4TV skeletons and the hydrophilic behavior induced by the three surrounding cyanoacrylic acid polar tails, dye **5** has a strong tendency to precipitate in organic solvents such as CH₂Cl₂. In order to increase its solubility and make it more easy

to handle in common organic solvents, dye **5** was converted into its (tetramethylammonium) cyanoacetate salt **6**. The structure of dye **6**, as well as its precursors **3** and **4**, was confirmed by MALDI-TOF mass spectrometry as well as ¹H and ¹³C NMR, FT-IR, and UV–vis spectroscopies (see SI.). The thermal stability of dye **6** was studied by thermogravimetric analysis (TGA) under nitrogen, with a heating rate of 10 °C/min. Decomposition temperature (Td) was estimated as the temperature that is the intercept of the leading edge of the weight loss by the baseline of the TGA scans. Dye **6** is thermally stable with decomposition temperature higher than 378 °C (Fig. SI. 14).

The UV–visible spectra of dyes **3**, **4**, and **6** in CH₂Cl₂ are shown in Figure 1. They display the characteristic band of 4TV centered at around 545 nm. The maximum of absorption of dye **6** (549 nm, log ε = 4.78) is slightly red-shifted by 11 nm compared to compounds **3** and **4** (538 nm). This can be explained by the increase of conjugation induced by the terminal cyanoacetate groups. Moreover, it can be seen a broadening of the 4TV band in dye **6**, which is accompanied with a decrease of its extinction molar coefficient compared to **3** and **4** which suggests the tendency of dye **6** to form aggregates in organic solution. It is interesting to note that the absorption of **6** covers up to 700 nm, facilitating the absorption in this region of the solar emission. Utilization of materials that absorb light extending into the infrared range is one of the strategies to harvest more solar light and thereby to increase power-efficiency.²² The high molar extinction coefficient absorption bands are as well in favor of light harvesting and hence photocurrent generation.

The fluorescence emission spectroscopy was employed to get information about the excited state–solvent interactions. The emission maxima of dye **6** can be found at 750 nm (λ_{exc} = 549 nm) (Fig. SI.13). The optical band gap for dye **6** is 1.96 eV, and it was calculated by the intersection of absorption and emission spectra. The large Stokes shift of dye **6** (201 nm) can be attributed to the significant structural reorganization upon photoexcitation or to the charge transfer nature of the excited state. Upon adsorption onto TiO₂ the emission was totally quenched indicating an efficient photoinduced electron transfer process from dye **6** to the TiO₂ nanoparticles.

The redox properties of dye **6** were investigated through Cyclic Voltammetry (CV) and Osteryoung Square Wave Voltammetry

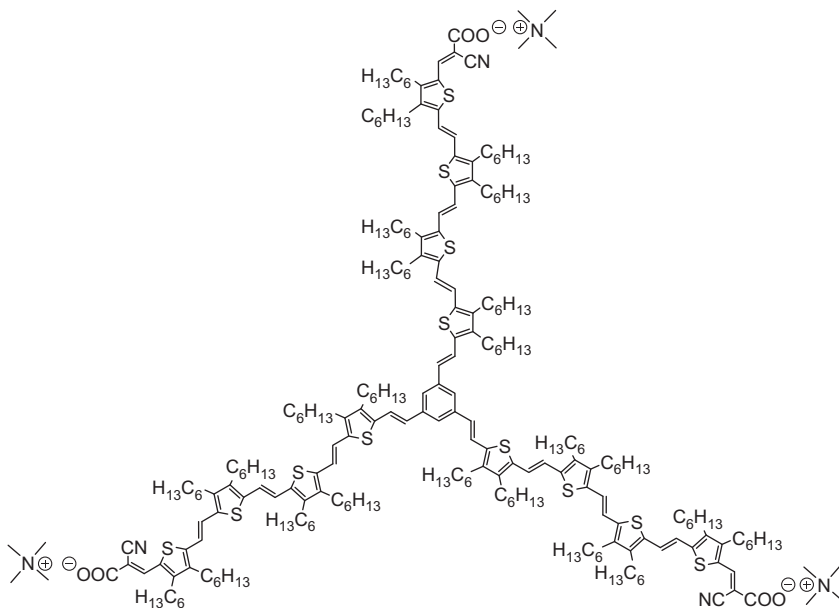


Chart 2. Molecular structure of the novel star-shaped sensitizer based on 4-thienylenevinylene studied in this work (dye **6**).

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