



Soluble acetylenic molecular glasses based on dithienyldiketopyrrolopyrrole for organic solar cells



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ABSTRACT

We present the synthesis and photovoltaic response of soluble glass-forming molecules containing a dithienyldiketopyrrolopyrrole core and difluorenylarylamino endgroups, linked through an acetylene bond. Introducing the 2,6-naphthylene moiety vs. 1,4-phenylene leads to an increased glass transition temperature (T_g) and hole mobility. Thus, $T_g = 107.7$ °C, $\mu_h = 7.95 \times 10^{-5}$ cm² V⁻¹ s⁻¹ for the 1,4-phenylene compound, while $T_g = 119.4$ °C, $\mu_h = 9.17 \times 10^{-5}$ cm² V⁻¹ s⁻¹ for the 2,6-naphthylene compound. Thermal annealing the as-cast films of both compounds below T_g resulted in little change in optical absorption. The preliminary characterization of the bulk hetero-junction solar cells showed that the 2,6-naphthylene compound generally provides a higher power conversion efficiency than the 1,4-phenylene compound, due probably to its enhanced hole transport. The photoluminescence experiments show a weak exciplex emission around 880 nm for the blends containing the new dyes and PC₆₁BM. The present work may be useful for further efforts toward high-performance cost-effective acetylenic organic semiconductors for organic solar cells with thermally stable morphology.

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1. Introduction

Organic semiconductors that contain an acetylene bond have received considerable interest as electron donors for organic bulk hetero-junction solar cells [1–6]. The choice of acetylene as a π -linkage may produce beneficial consequences: i) the weak electron-withdrawing nature due to the *sp*-hybridized carbon atoms may lead to a lower HOMO level, and ii) the conjugated cylinder-like π -electron density is more adaptable to conformational and steric constraints. Furthermore, based on judicious design, toxic stannyl intermediates or risky lithiation reactions can be avoided, thus providing a potentially “green” synthetic route [1c,6,7].

Recently we reported a crystalline conjugated molecule **DT-DPP(AAnAT)**₂ based on a dithienyldiketopyrrolopyrrole unit (**DT-DPP**) [8–10], featuring an acetylenic linkage (Fig. 1) [6]. The photovoltaic response of **DT-DPP(AAnAT)**₂ as well as the optical absorption of the as-cast thin film appeared sensitive to the

annealing temperature, while a PCE of 4.39% with $V_{oc} \approx 0.77$ V was obtained in a simple structure (ITO/PEDOT:PSS/**DT-DPP(AAnAT)**₂:PC₆₁BM/Al), without a high-boiling-point solvent additive or solvent vapor annealing. For instance, thermal annealing the active layer at a temperature of 70 °C led to decreasing of the PCE, which may arise from the high crystallization tendency of **DT-DPP(AAnAT)**₂, yielding unfavorable morphology with large domain sizes.

In this context, we further describe two acetylenic molecular semiconductors **1** and **2** with dithienyldiketopyrrolopyrrole as the core (See Fig. 2). Introducing the rigid, bulky and non-planar difluorenylarylamino endgroups is intended to improve the morphological stability of the resulting dyes [11]. As a result, compounds **1** and **2** have a high tendency to form amorphous films after spin-cast from solution, showing a high glass transition temperature (T_g) of 107.7 and 119.4 °C, respectively. Unlike **DT-DPP(AAnAT)**₂ (See Fig. 1) [6], thermal annealing the as-cast films of the new compounds below T_g produced little influence on the optical absorption. In addition to synthesis, the correlation between the molecular structures of both the compounds and electrochemical, hole transport and preliminary photovoltaic properties as well as optical absorption and morphology is discussed.

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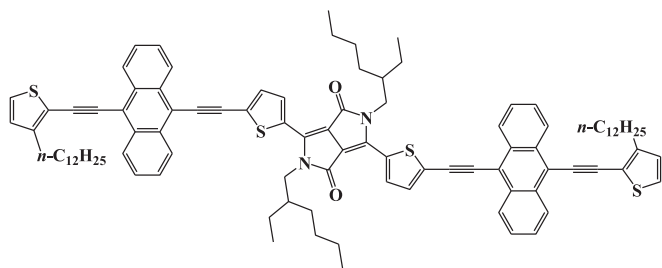


Fig. 1. Chemical structure of DT-DPP(AAnAT)₂.

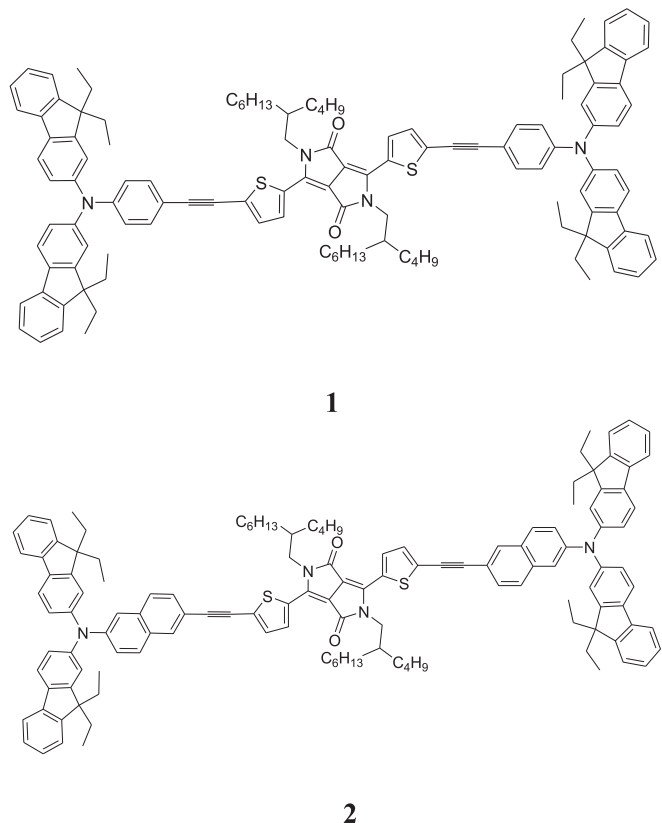


Fig. 2. Chemical structures of compounds **1** and **2**.

2. Results and discussions

2.1. Synthesis, thermal and optical properties

The synthesis of compounds **1** and **2** is straightforward and outlined in Fig. 3. Ullmann reaction of 6-bromonaphth-2-ylamine [14] with 2 eq. (9,9)-diethyl-2-iodo-fluorene yielded (6-bromonaphth-2-yl)-di(9,9-diethylfluorene-2-yl)amine. The resulting bromo triarylamine compound reacted with trimethylsilylacetylene via Sonogashira coupling, leading to 1-(6-di(9,9-diethylfluorene-2-yl)-aminonaphth-2-yl)-2-trimethylsilylacetylene. The ensuing detrimethylsilylation with K₂CO₃ in THF/methanol produced (6-di(9,9-diethylfluorene-2-yl)aminonaphth-2-yl)acetylene (**4**). Finally Sonogashira reaction of (4-di(9,9-diethylfluorene-2-yl)aminophenyl)acetylene (compound **3**) and compound **4** with 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-butyl)pyrrolo[3,4-*c*]pyrrole-1,4-(2*H*,5*H*)-dione afforded the target products **1** and **2**, respectively. The identity and purity of

compounds **1** and **2** are evidenced by TLC, ¹H NMR, MS (MALD-TOF) and microanalysis (See supporting information Fig. S1–3). The new dyes are well soluble in toluene, xylene and chlorinated solvents such as CH₂Cl₂ and chlorobenzene.

Thermogravimetric analysis reveals no mass loss for compounds **1** and **2** when heated up to ca. 300 °C. Both the new compounds form amorphous films after being spin-cast from solution (See Fig. S5 and S6). For the differential scanning calorimetry measurements, the samples are precipitated from CH₂Cl₂ solution by adding ethanol. In the first heating run, compounds **1** and **2** melt at 228.6 and 233.5 °C, respectively. Upon cooling, no crystallization is observed. When reheated, glass transition is clearly witnessed with a high T_g of 107.7 °C for compound **1** and 119.4 °C for compound **2** (Fig. 4).

Compounds **1** and **2** show similar absorption as films, as well as in dilute CH₂Cl₂ solution, featuring a sharp band between 300 and 450 nm and a broad charge-transfer band between ca. 500–700 nm (Fig. 5 and Table 1). The latter exhibits two absorption maxima at ca. 605 and 646 nm in the as-cast films, which are redshifted from ca. 600 and 634 nm in solution, respectively.

It is worth noting that introducing the 2,6-naphthylene group into compound **2** leads to an emerging absorption shoulder in the 400–420 nm region.

In contrast with other molecular organic dyes based on dithienopyrrolopyrrole [6,8,15], thermal annealing the as-cast films of compounds **1** and **2** produces little change in the absorption spectra (Fig. 5), even at a temperature over 100 °C, which may benefit from the stable amorphous morphology.

2.2. Electrochemistry

Cyclic voltammetry performed in CH₂Cl₂ in the presence of *n*-Bu₄NPF₆ as supporting electrolyte shows that compounds **1** and **2** undergo two consecutive reversible one-electron oxidations at ~0.90 V and 1.10 V vs. Ag/AgCl (Fig. 6 and Table 1). The electrochemical data gave estimated HOMO levels of –5.20 eV for **1** and –5.18 eV for **2**, with reference to the energy level of ferrocene. The LUMO levels were derived as –3.43 and –3.41 eV from the HOMO levels and the corresponding absorption onset of thin films.

2.3. Hole-mobility measurement

Single carrier hole-only devices (ITO/PEDOT:PSS/compound **1** or **2** or the blend with PC₆₁BM/MoO₃/Al) were fabricated. A vacuum-deposited molybdenum trioxide (MoO₃) layer was used as an electron-blocking layer at the cathode. At low voltages, the device current shows a clear quadratic dependence on the voltage, indicating a space-charge-limited current (Fig. 7). Consequently, fitting the *J*-*V* curve in accord with Mott-Gurney's square law, yielded a mobility value of 7.95 × 10^{–5} cm² V^{–1} s^{–1} for compound **1** and 9.17 × 10^{–5} cm² V^{–1} s^{–1} for compound **2** (eqn. (1), [16]). Blending compound **1** or **2** with the electron acceptor PC₆₁BM led to a reduction of hole mobility to 2.23 × 10^{–5} cm² V^{–1} s^{–1} (**1**:PC₆₁BM 1:3 w/w) and 5.14 × 10^{–5} cm² V^{–1} s^{–1} (**2**:PC₆₁BM 2:5 w/w), respectively.

$$J = \frac{9}{8} \varepsilon \mu \frac{V^2}{d^3} \quad (1)$$

where ε is the permittivity, $\varepsilon = \varepsilon_0 \varepsilon_r$ (ε_0 the permittivity of the free space, and ε_r the relative permittivity and is assumed to be approximately 3.0), d the thickness of the active layer, and V the effective voltage corrected by subtracting from the applied voltage (V_{appl}) the built-in voltage (V_{bi}) and the voltage drop (V_s) resulting from the series resistance.

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