

Synthesis and characterization of new highly soluble and thermal-stable perylene–PPV copolymers containing triphenylamine moiety

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Abstract

Three new copolymers containing poly(*p*-phenylenevinylene) (PPV) and triphenylamine (TPA) moieties carrying *N*-(*n*-butyl)-*N'*-ethoxy-1,6,7,12-tetra-(4-*tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxylic bisimide (PERY) pendant groups were successfully synthesized by Wittig condensation. The molar percentage of perylene pendants in copolymers was controlled by tuning the initial feed ratio of the perylene–bisaldehyde monomer. The structures and properties of three copolymers were characterized and evaluated by FT-IR, NMR, UV, FL, and photovoltaic analyses. The copolymers were highly soluble in conventional solvents such as toluene, CHCl₃, THF, DMF, etc., and they were thermally stable (≥ 396 °C). Three copolymers have emission spectra with characteristic features of the perylene unit, however, and their luminescence are largely quenched with the increasing amount of PERY units in copolymers. The photophysical study in solution has shown that singlet–singlet energy transfers from PPV backbone to perylene in the copolymers. The photovoltaic devices ITO/PEDOT:PSS/copolymers/Ba/Al were fabricated, and the energy conversion efficiency of the device is only about 0.0005%, further indicating that an efficient energy transfer has taken place from PPV to perylene in the copolymers.

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1. Introduction

In recent years, conjugated polymers and organic materials have attracted great interest due to their possible applications in light-emitting diodes and photovoltaic cells [1–8]. Poly(phenylenevinylene)s

(PPVs) are widely used in the manufacture of optical and electrical devices because of their electroluminescent activity and nonlinear optical responses [9–14]. Triphenylamine (TPA) and its derivatives, with excellent solubility, good stability, and high photoluminescent efficiency, have been extensively used as hole-transporting species in photoelectronic devices [15–17]. Perylenes are one kind of key chromophores for high-tech applications, spanning from electronic

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to biological fields such as optical switches, lasers, DNA/RNA probes, etc. Beside their conventional uses, perylenes are potential candidates as electron-active materials in organic photovoltaic solar cells [18–23]. Many types of PERY have been synthesized, but the expected low solubility of these molecules is a problem for synthesis, purification and applications in the devices. Therefore, work has shifted to more soluble perylenes [24]. Both PPV and perylene bisimide chromophores have been applied in bulk-heterojunction-like solar cell configurations as donor and as acceptor materials, respectively [9]. Attachment of perylene as pendant groups to the PPV backbone is thus of interest because the resulting polymer may show enhanced light-harvesting capacity due to synergistic interactions between the pendant groups and the conjugated backbones. In this paper, we present the synthesis and characterization of three copolymers containing PPV and TPA and different molar percentage of perylene bisimide moieties (Scheme 1). The molar percentage of perylene pendants in copolymers was controlled by tuning the initial feed ratio of the perylene-bisaldehyde monomer. The copolymers were good soluble in common organic solvents and were characterized by ^1H NMR, IR, UV–Vis, FL, TGA, and GPC analyses. Finally, three copolymers were incorporated into a photovoltaic cell by spin-casting the copolymers onto an ITO glass substrate and depositing an aluminum film on the top.

2. Experimental

2.1. Material

1-Methyl-2-pyrrolidinone (NMP) and dichloromethane (DCM) were refluxed with calcium hydride and distilled before used. 2,5-Di-*n*-octyloxy-1,4-xylenebis (triphenylphosphonium bromide) (**10**) were prepared refer to the literature [25]. *N,N'*-di(*n*-butyl)-1,6,7,12-tetra (4-*tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxylic bisimides (**6**) was prepared following a procedure described in the literature [26]. All other reagents and solvents were of analytical grade, and used as received without further purification.

2.2. Characterization

^1H NMR spectra were obtained with a Bruker AM-500 spectrometer. FT-IR spectra were recorded on a Nicolet Magna-IR550 in the region of 4000–

400 cm^{-1} using KBr pellets spectrophotometer. UV–Visible spectra were determined with a Varian Cary 500 spectrometer in chloroform solution. Photoluminescent spectra were recorded on Varian Cary Eclipse. Thermogravimetric analyses (TGA) was conducted in Mettler Toledo Thermal Analyzer SDTA 851° at a heating rate of 10 °C/min under nitrogen atmosphere. The molecular weights were determined by gel permeation chromatography (Waters HP/GPC), using THF as eluent and polystyrene standards of known molecular weights were used for calibration.

2.3. Synthesis of 4-methoxy-4',4''-diformyltriphenylamine **2**

To the mixture of 4-methoxytriphenylamine (1 g, 3.63 mmol) and 15 mL *N,N*-dimethyl-formamide cooled to 0 °C, phosphorus oxychloride (3.6 mL, 38.7 mmol) was added dropwise under the protection of nitrogen and then the mixture was reacted for 9 h at 95–100 °C. After cooling down to room temperature, the mixture was poured into 50 g ice and then filtered. The crude product was purified by column chromatography using chloroform and petroleum (1:2) as elute to obtain 1.61 g (38.2%). ^1H NMR (CDCl_3): δ = 9.89 (s, 2H), 7.74 (d, J = 8.63 Hz, 4H), 7.16 (d, J = 8.59 Hz, 4H), 7.05 (d, J = 8.71 Hz, 2H), 6.90 (d, J = 8.89 Hz, 2H), 3.79 (s, 3H).

2.4. Synthesis of 4-hydroxyltriphenylamine **3**

A mixture of 4-methoxytriphenylamine (3 g, 10.9 mmol), anhydrous aluminum chloride (3 g, 22.47 mmol), and toluene (60 mL) was stirred at 110 °C under argon for 4 h. The reaction mixture was cooled, then poured into water (20 mL), and adjusted to acidity with dilute HCl solution. And the reaction mixture was extracted with ethyl acetate, dried over anhydrous magnesium sulfate, and chromatography on silica gel with a mixture of petroleum and ethyl acetate (2:1) to give the yellow viscous liquid 2.11 g (75.3%). ^1H NMR (CDCl_3): δ 7.21 (m, 4H), 7.07 (m, 6H), 6.92 (t, J = 7.11 Hz, 2H), 6.83 (d, J = 8.90 Hz, 2H), 5.67 (s, 1H).

2.5. Synthesis of 4-hydroxyl-4',4''-diformyltriphenylamine **4**

To the mixture of 4-hydroxytriphenylamine (2 g, 38.7 mmol) and 30 mL *N,N*-dimethyl-formamide cooled to 0 °C, phosphorus oxychloride (7.2 mL,

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