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Short communication

# Synthesis, photophysics and electroluminescence of new vinylene-copolymers with 2,4,6-triphenylpyridine kinked segments along the main chain

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ABSTRACT

Two new vinylene alternating copolymers **F** and **C** that contained 2,4,6-triphenylpyridine as a common moiety and fluorene or carbazole, respectively, as an alternating moiety were prepared by Heck coupling. They showed an outstanding thermal stability being stable up to approximately 350 °C and had relatively high glass transition temperatures (140 and 111 °C). The existence of the 2,4,6-triphenylpyridine kinked units along the polymer backbone caused a partial interruption of the $\pi$-conjugation. The copolymers emitted blue-green light with emission maximum at 446–464 nm and quantum yields of 0.52 and 0.28 in THF solution. The electrochemical properties of copolymers **F** and **C**, including HOMO and LUMO levels, were estimated from their cyclic voltammograms. Their electroluminescence (EL) emission maxima (greater than 500 nm) showed significant red-shifts relative to the PL maxima, which has been explained by the direct cross recombination transition between electrons and holes trapped on carbazole or triphenylpyridine subunits. Moreover, the emission colors transform gradually with increasing bias and approach to white color at about 30 ~ 35 V. The maximal luminance (maximal luminance efficiency) of the EL devices (ITO/PEDOT:PSS/**F** or **C**/Ca/Al) were 647 cd/m$^2$ (0.13 cd/A) or 615 cd/m$^2$ (0.10 cd/A), respectively.

## 1. Introduction

Conjugated polymers have been incorporated as active materials into several kinds of electronic devices such as transistors [1] and light-emitting diodes [2] (LEDs), including flexible displays [3]. Among the electroluminescent (EL) conjugated polymers poly(*p*-phenylenevinylene)s (PPVs) and poly(9,9-dialkylfluorenes) (PFs) have attracted the most general interest. Many different PPV derivatives have been synthesized in a number of ways [4]. Most of these polymers have low electron affinity. Conjugated polymers with high electron affinity are desired for certain applications, for example in LEDs. High electron affinity allows the fabrication of LEDs with good electron injection from stable cathodes like aluminum rather than the low work function metals required for more electron-rich polymers [5].

One way to achieve high electron affinity is to attach electron-withdrawing groups to the polymer like, for example, the cyano groups in poly[2,5-bis(hexyloxy)-1,4-phenylene-(1-cyanovinylene)] (CN-PPV) [5]. Another way is to use electron-deficient rings like pyridine in the polymer backbone [4]. Compared to benzene, pyridine is an electron-deficient aromatic heterocycle, with a localized lone pair of electrons in an sp$^2$ orbital on the nitrogen atom; consequently, the derived polymers have increased

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electron affinity [6], improved electron-transporting properties, and the symmetry of poly(phenylene) systems is broken. The application of pyridine as the $\pi$-deficient moiety is driven by the consideration that its homopolymer (PPy) has been used in blue-emitting devices [7,8] and that other pyridine-containing copolymers have been demonstrated to be highly luminescent [9]. In addition, introduction of the pyridinyl moiety in the polymer backbone not only increases the electron affinity of the polymer, which makes the polymer more resistant to oxidation and also gives the polymer better electron-transporting properties, but also avoids fluorescence quenching due to the intersystem crossing (ISC) effect of heavy atom [10]. Certain pyridine-containing conjugated polymers have been synthesized and characterized recently [11–13]. Moreover, poly(*p*-pyridylvinylene)polymers have been extensively investigated and present the advantages of facile n-doping (high electron affinity) and of tuning their electrooptical properties by coordination of different guests to the lone pair of nitrogen atoms [14–20].

The introduction of disorder to a conjugated system such as PF is one of the common approaches to suppress the long wavelength emissions, for example, 3,6-carbazole [21], quinoxaline or *N*,*N*′-diphenyl-*N*,*N*′-bis(4-phenyl)-1,1-biphenyl-4,4′-diamine (TPD) [22,23]. Moreover, the introduction of such a "kink" disorder on the conjugated polymer chain can efficiently depress the aggregation phenomena and its effect on the excimer formation. Poly(phenylene vinylene) derivative containing kinked 2,6-diphenylpyridine and 2,5-didodecyloxy-1,4-divinylbenzene repeat units was prepared and it was a green-yellowish emitting material [20,24].

In this investigation we describe the synthesis, characterization, photophysics, the redox and electroluminescent properties of two new vinylene alternating copolymers. They were successfully prepared by Heck coupling and contained the kinked 2,4,6-triphenylpyridine as a common moiety and fluorene or carbazole as alternating moiety. The alkyl side groups, which are attached to the fluorene or carbazole units, enhance the copolymer solubility. The existence of the pyridine units along the main chain is expected to improve the electron-transporting properties of the polymers. The introduction of carbazole units may also influence the HOMO energy level resulting in better hole-transporting ability for the polymer.

## 2. Experimental

### 2.1. Characterization methods

IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets. $^1$H NMR (400 MHz) spectra were obtained using a Brucker spectrometer. Chemical shifts ($\delta$ values) are given in parts per million with tetramethylsilane as an internal standard. UV–vis spectra were recorded on a Beckman DU-640 spectrometer with spectrograde THF. The PL spectra were obtained with a Perkin-Elmer LS45 luminescence spectrometer. The PL spectra were recorded with the corresponding excitation maximum as the excitation wavelength. TGA was performed on a DuPont 990 thermal analyzer system. Ground samples of about 10 mg each were examined by TGA and the weight loss comparisons were made between comparable specimens.

Dynamic TGA measurements were made at a heating rate of 20 °C /min in atmospheres of $N_2$ at a flow rate of 60 cm$^3$/min. Thermomechanical analysis (TMA) was recorded on a DuPont 943 TMA using a loaded penetration probe at a scan rate of 20 °C/min in $N_2$ with a flow rate of 60 cm$^3$/min. The TMA experiments were conducted at least in duplicate to ensure the accuracy of the results. The TMA specimens were pellets of 10 mm diameter and $\sim$1 mm thickness prepared by pressing powder of sample for 3 min under 8 kp/cm$^2$ at ambient temperature. The $T_g$ is assigned by the first inflection point in the TMA curve and it was obtained from the onset temperature of this transition during the second heating. Elemental analyses were carried out with a Carlo Erba model EA1108 analyzer.

To measure the PL quantum yields ($\Phi_f$) degassed solutions of the copolymers in THF were prepared. The concentration was adjusted so that the absorbance of the solution would be lower than 0.1. The excitation was performed at the corresponding excitation maximum and a solution in 1 M $H_2SO_4$ of quinine sulfate, which has $\Phi_f$ of 0.546 was used as a standard.

The oxidation and reduction properties of the polymers were measured with a cyclic voltammeter (model CV-50 W from BAS) under nitrogen atmosphere using a cyclic voltammetric potential excitation. The measuring cell comprised a glassy carbon coated with polymers (**F** or **C**) as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire electrode as the auxiliary electrode, supporting in 0.1 M $(n\text{-Bu})_4NClO_4$ in acetonitrile. The scan rate was 100 mV/s. The energy levels were calculated using the ferrocene (FOC) value of −4.8 eV with respect to vacuum level, which is defined as zero [25].

Double-layer EL devices with a configuration of ITO/PEDOT:PSS/**F** or **C**/Ca/Al were fabricated by successive spin-coating of poly(3,4-ethylenedioxythiophene) (PEDOT:PSS: Baytron P from Bayer) as hole-injection layer and **F** or **C** (30 mg/mL in chlorobenzene) as emissive layer onto ITO glass. Finally, calcium and aluminum was deposited as cathode via vacuum evaporation under $1.8 \times 10^{-6}$ Torr. The devices were fabricated in the ambient conditions and then their optoelectronic properties tested in a glove box filled with nitrogen. Device performance and electroluminescence spectra were investigated and recorded, respectively, using a combination of Keithley power supply (model 2400) and Ocean Optics usb2000 fluorescence spectrophotometer.

### 2.2. Reagents and solvents

*N*,*N*-Dimethylformamide (DMF) was dried by distillation over $CaH_2$. Triethylamine was purified by distillation over KOH. All other reagents and solvents were commercially purchased and were used as supplied.

### 2.3. Preparation of starting materials

#### 2.3.1. 2,6-Bis(4-bromophenyl)-4-phenylpyridine (1)

The preparation and characterization of this compound has been described in our previous publication [20].