

# Novel Thermally Stable Blue-Light-Emitting Polymer Containing N,N,N',N'-Tetraphenyl-Phenylenediamine Units and Its Intramolecular Energy Transfer

Hongchao Li, Yufeng Hu, Yanguang Zhang, Dongge Ma, Lixiang Wang,\* Xiabin Jing, and Fosong Wang

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

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A novel thermally stable and soluble blue-light-emitting polymer containing bulky N,N,N',N'-tetraphenyl-phenylenediamine (TPPA) and phenylenevinylene (PV) moieties, **P1**, was synthesized by the Wittig condensation reaction in a good yield (over 80%). The resulting polymer possesses a high molecular weight ( $M_w = 68\,200$ ) and excellent thermal stability ( $T_g = 179\text{ }^\circ\text{C}$ ). A blue light with the maximum emission peak at 430 nm in solution and 450 nm in film was observed when excited at different wavelengths where TPPA and PV moieties display their own absorption peak, indicating the existence of intramolecular energy transfer between them. The preliminary single-layer light-emitting device with a configuration of ITO/**P1**/Mg–Ag emitted a bright blue light with an emission peak at 442 nm. The maximum brightness and electroluminescent efficiency reach 144 cd/m<sup>2</sup> and 0.2 cd/A, respectively.

Tremendous progress has been made since the discovery of conjugated polymers capable of serving as the active component in light-emitting diodes (LEDs).<sup>1–5</sup> Blue-light-emission, usually difficult to achieve in inorganic semiconductors, can be sought in conjugated polymers with large energy gaps.<sup>6–8</sup> In the literature, several strategies have been developed to achieve efficient blue light in PPV derivatives. One approach to achieving blue emission is to insert a flexible nonconjugated spacer into the backbone,<sup>9–14</sup> which provides a direct control of the conjugation length and improves the processibility. However, it usually reduces the glass

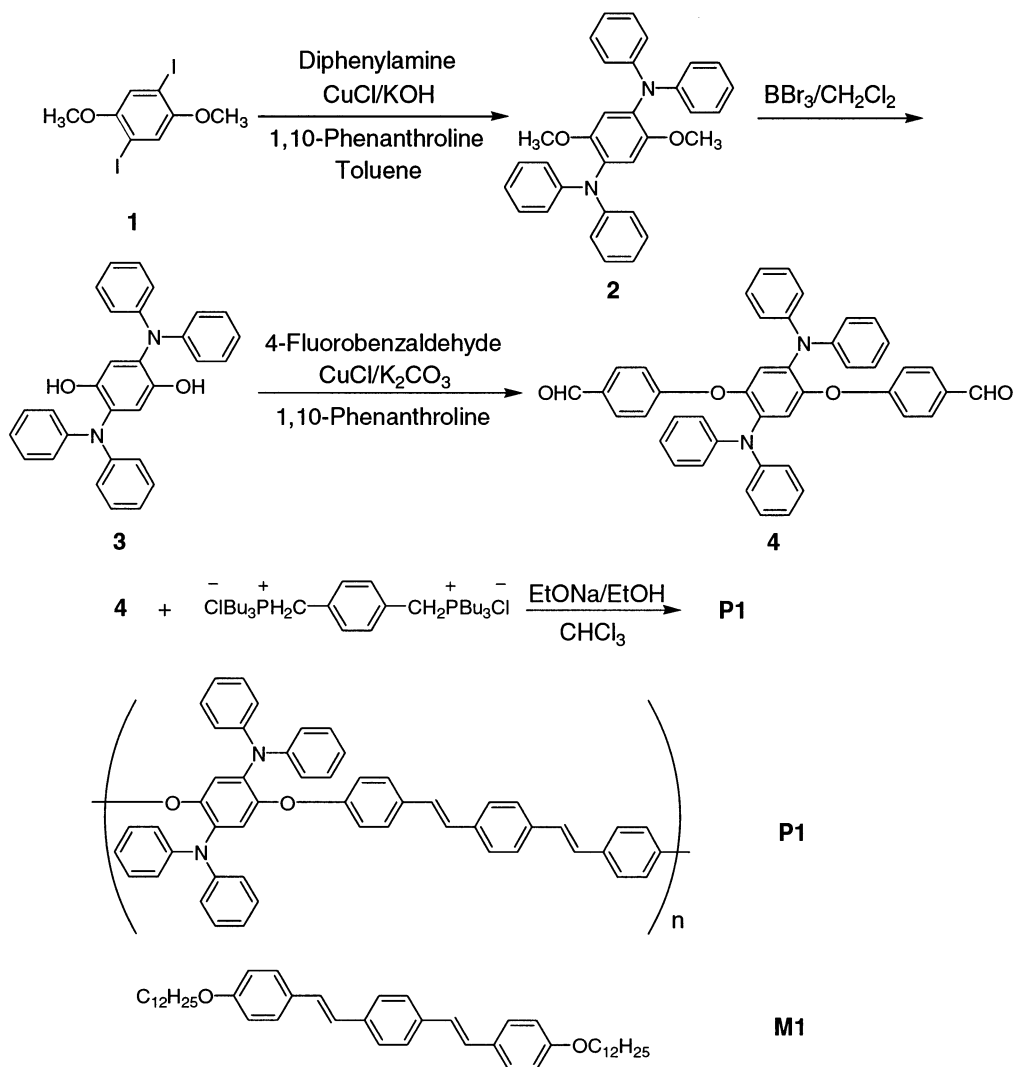
transition temperature ( $T_g$ ), decreases the mobility of the charge carriers, and thus leads to a high threshold voltage, which generally causes damage to the device. An alternative approach is to incorporate molecular linkage<sup>15,16</sup> (such as sulfonylene and organosilicon), an *m*-phenylene unit,<sup>17–19</sup> or a nonconjugated rigid spacer (such as adamantane)<sup>20</sup> instead of a flexible spacer into the conjugated backbone, which not only fixes the effective conjugation length but also maintains the thermal stability. Recently, some groups have reported on poly(arylene ether)s containing charge transport units as blue-light-emitting materials and found that these polymers show both high thermal stability and good charge-transporting properties.<sup>21,22</sup> However, most of the studies are limited to design the bipolar polymers, being capable of transporting both electrons and holes.

In this communication, we report a novel thermally stable blue-light-emitting poly(arylene ether) containing N,N,N',N'-tetraphenyl-phenylenediamine (TPPA) and phenylenevinylene (PV) moieties in the backbone (**P1** in Scheme 1). The design and synthesis of the polymer are based on the following considerations. (i) The ether linkage in the backbone provides a means to increase the thermal stability and adjust the length of conjugation, i.e., to achieve the blue emission. (ii) Incorporation of the TPPA moiety as a hole-transporting block into the polymer backbone provides the possibility to improve the hole-transporting ability of the resulting polymer, because TPPA and its derivatives have been widely incorporated into the polymer backbone used as active materials or hole-transporting components in LEDs.<sup>23–25</sup> (iii) The introduction of TPPA moiety as more bulky group is expected to realize the efficient intramolecular energy transfer from TPPA moiety to PV unit and to reduce the self-quenching of excitons caused by the interchain interaction, and thus enhance the PL efficiency.<sup>26</sup>

\* Corresponding author. Fax: +86-431-5685653. E-mail: lixiang@ciac.jl.cn.

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Scheme 1. Synthesis and Structure of **P1** and Model Compounds

Synthesis of the polymer **P1** is depicted in Scheme 1. The key monomer, compound **4**, was synthesized from compound **1**,<sup>27</sup> which reacted with diphenylamine by the Ullmann reaction<sup>28</sup> to give compound **2**. After demethylation, compound **3** was obtained and then coupled with 4-fluorobenzaldehyde to yield dialdehyde monomer **4** in a good yield. The polymer **P1** was prepared by Wittig condensation reaction. It should be pointed out that the polymerization reaction was carried out by using tributyl phosphonium salt instead of triphenyl phosphonium salt as monomer with the aim to improve the solubility of phosphonium salt in chloroform and to increase the molecular weight. Minimizing the amount of ethanol in solvents would be helpful to prevent the precipitates of resulting polymers in solvents and to achieve high molecular weights. The polymer was isolated by precipitation from ethanol twice prior to drying in a vacuum at room temperature. **P1** was obtained as light-yellow powder in over 80% yield. Its structure was confirmed by <sup>1</sup>H NMR, FT-IR, and elemental analysis. The elemental composition of **P1** (anal. calc. for C<sub>52</sub>H<sub>38</sub>O<sub>2</sub>N<sub>2</sub>:

C, 86.30; H, 5.29; N, 3.87; found C, 86.66; H, 5.10; N, 3.75) is in agreement with that of its repeating units. The newly formed peak at about 955 cm<sup>-1</sup> in FT-IR indicates exclusive trans-olefin bonds.

The molecular weight of **P1** was determined by gel permeation chromatography (GPC) using polystyrene as standard and THF as eluent. It has a weight-average molecular weight (*M<sub>w</sub>*) of 68 200 with a polydispersity of 2.7. The resulting polymer possesses excellent thermal stability. **P1** displays a glass transition temperature (*T<sub>g</sub>*) at 179 °C and an onset thermal decomposition temperature (*T<sub>d</sub>*) above 350 °C, indicating that the introduction of aromatic ether linkage in the backbone provides the improved thermal stability.

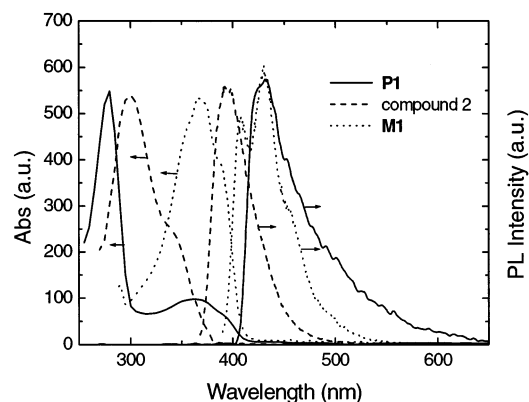
**P1** was readily soluble in common organic solvents, such as chloroform, 1,2-dichloroethane, THF, etc. Transparent, uniform, and pin-free thin film on a variety of substrates can be obtained by spin coating **P1** solution in chloroform or THF. Under excitation of 365 nm, bright blue fluorescence was observed both in solution and in film.

Figure 1 shows the UV-Vis spectra of **P1**, compound **2**, and model **M1** in THF solution. It can be seen that **P1** displayed two absorption peaks at 280 and 365 nm, whereas compound **2** and **M1** showed maximum ab-

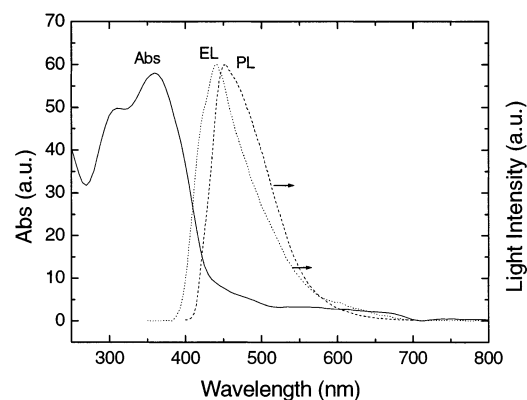
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**Figure 1.** UV-Vis and PL spectra of **P1**, compound **2**, and **M1** in THF solution.

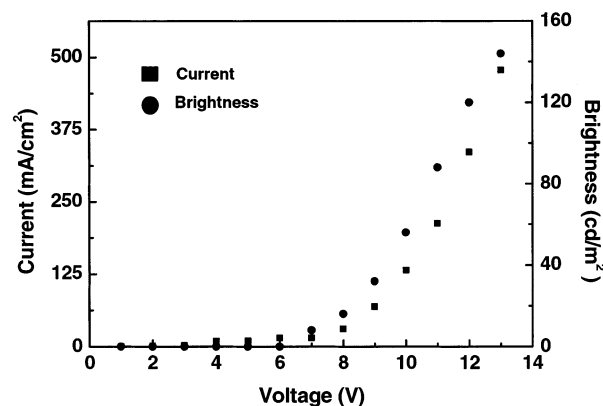


**Figure 2.** UV-Vis (solid line) and PL (dashed line) spectra of **P1** film, and EL spectrum (dotted line) of device ITO/**P1**/Mg-Ag.

sorptions at 300 and 366 nm, respectively. Therefore, the first absorption peak of **P1** can be assigned to TPPA units by considering the electron-donating effect of methoxy substituents of compound **2**. The peak at longer wavelength may be attributed to the  $\pi$ - $\pi^*$  transition of the conjugated moieties. It is interesting to notice that **P1** displayed its maximum absorption at almost the same wavelength as that of **M1**, indicating that their effective lengths of conjugation are identical. The band-gap calculated from the edge of absorption spectrum of solution was about 3.0 eV, which is ideal for achieving blue light emission.

The photoluminescence spectra of **P1**, compound **2**, and model **M1** in solution were shown in Figure 1. In THF solution and excited at 365 or 300 nm, compound **2** showed only a fixed emission peak at 390 nm, whereas **M1** exhibited a more resolved emission spectrum with two peaks at 400 and 430 nm. Under the excitation of 365 nm, polymer **P1** showed a maximum emission at about 430 nm, implying that the chromophore is the PV moieties and that the ether linkage prevents the extension of conjugation. When excited at 280 nm, where the TPPA units showed a very strong absorption, **P1** displayed the only emission peak at 430 nm, and no emission from the TPPA moieties at about 390 nm was observed, indicating the existence of the intramolecular energy transfer from the TPPA moieties to the PV units.

The UV-Vis and PL spectra of **P1** film spin-coated on a quartz substrate are given in Figure 2. Similar to that of the solution, the absorption of the film showed two peaks at 300 and 360 nm, attributed to TPPA and



**Figure 3.** Current-brightness-voltage characteristics of ITO/**P1**/MgAg.

PV units, respectively. **P1** film gave a bright blue fluorescence with the emission peak at 450 nm under the excitation of either 300 nm or 360 nm, implying that the energy transfer between TPPA and PV moieties also occurred in the film state. Because the intramolecular energy transfer is helpful to improve the emission efficiency, **P1** will be expected to display high quantum efficiency.

To investigate its electroluminescent property, the single layer device with a configuration of ITO/**P1**/Mg-Ag (**P1** film thickness is about 200 nm) was fabricated and evaluated. Figure 3 gives the current-brightness-voltage characteristics of the device. The single-layer device has a turn-on voltage at about 7 V, which is lower than that of the reported blue-light-emitting polymers,<sup>6,8,10,15</sup> indicating that the incorporation of TPPA units reduces the turn-on voltage. Bright blue electroluminescence was observed, and the maximum brightness of 144 cd/m<sup>2</sup> and electroluminescent efficiency of 0.2 cd/A were obtained. Figure 2 also shows the electroluminescence spectrum, which showed a maximum emission located at about 442 nm, indicating a pure blue light emission.

In conclusion, we have synthesized a novel soluble blue-light-emitting polymer, **P1**, by the Wittig condensation reaction. The polymer displays a high molecular weight and excellent thermal stability. A blue light emitting with the emission peaks at 430 nm in solution and 450 nm in film were observed when excited at different wavelengths where TPPA and PV display their own absorption peak, indicating existence of intramolecular energy transfer between TPPA and PV moieties. The single layer LED device emitted a pure bright blue light with an emission peak at 442 nm and with low turn-on voltage of 7 V. Further investigations, such as optimizing device structure, will be required to improve the EL properties of the novel polymer.

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**Supporting Information Available:** Experimental details and 400 MHz <sup>1</sup>H NMR and FT-IR spectrum of the polymer (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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