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13. ABSTRACT (Maximum 200 words) A new conjugated rigid-rod polyquinoline, poly (2,2'-p-phenylene)-6,6'-bis(4-(p-tert-butylphenyl)quinoline)), was synthesized and its thin film was used as the emissive layer in light-emitting diodes. The electroluminescent devices, also containing 1,1-bis(di-4-tolylaminophenyl)cyclohexane dispersed in polystyrene as the hole-transport layer, emitted bright yellow light ($\lambda_{max}=554$ nm) with a quantum efficiency of 0.16% photons/electron, and a luminance of 200 cd/m ² at a current density of 120 mA/cm ² . These results demonstrate that the new polyquinoline is a good n-type (electron transport) electroluminescent material.				
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Efficient Electroluminescence from a New Conjugated Rigid Rod Polyquinoline

By

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Efficient Electroluminescence from a New Conjugated Rigid-Rod Polyquinoline

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Abstract

A new conjugated rigid-rod polyquinoline, poly(2,2'-(*p*-phenylene)-6,6'-bis(4-(*p*-*tert*-butylphenyl)quinoline)), was synthesized and its thin film was used as the emission layer in light-emitting diodes. The electroluminescent devices, also containing 1,1-bis(di-4-tolylaminophenyl)cyclohexane dispersed in polystyrene as the hole-transport layer, emitted bright yellow light ($\lambda_{\text{max}} = 554 \text{ nm}$) with a quantum efficiency of 0.16% photons/electron and a luminance of 200 cd/m^2 at a current density of 120 mA/cm^2 . These results suggest that the new polyquinoline is a good n-type (electron transport) electroluminescent material.

Efficient Electroluminescence from a New Conjugated Rigid-Rod Polyquinoline

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Conjugated rigid-rod polyquinolines have excellent thermal stability and high mechanical strength.^{1,2} These intrinsic n-type semiconducting polymers³ have interesting electronic,^{2b} photoconductive,⁴ and nonlinear optical⁵ properties. Recently, they were also used as both the electron-transport layer and the emission layer in polyquinoline/poly(*p*-phenylenevinylene) heterojunction light-emitting diodes (LEDs).⁶ The attractive combination of excellent thermal, mechanical, and optoelectronic properties in conjunction with the synthetic flexibility and diversity of the conjugated polyquinolines have motivated our further exploration of their synthesis and electroluminescent device applications.

The conjugated rigid-rod polyquinolines have very limited solubility or are insoluble in common organic solvents. They are, however, highly soluble in common organic solvents as Lewis acid (GaCl₃, AlCl₃) or alkyl/aryl phosphate complexes.^{1a,2a} To simplify thin film processing of the polyquinolines for device applications, we decided to synthesize conjugated polyquinolines which may have an inherent solubility in organic solvents through side group substitution which could also influence the electronic structure and optical properties. A previous attempt at improving the solubility of rigid-rod polyquinolines by appending aryl ether groups to the polymer backbone via a fairly involved synthesis of the monomers was unsuccessful.⁷ In this paper, we report the synthesis, photoluminescence, and electroluminescence of a new conjugated polyquinoline, poly(2,2'-(*p*-phenylene)-6,6'-bis(4-(*p*-*tert*-butylphenyl)quinoline)) (Bu-PPQ, **2**). The related poly(2,2'-(*p*-phenyl)-6,6'-bis(4-phenylquinoline)) (PPPQ, **1**) is known to be only soluble in strong acids (methanesulfonic acid, trifluoroacetic acid, formic acid), di-*m*-cresyl

phosphate/*m*-cresol and Lewis acid/nitromethane solutions.² In Bu-PPQ (**2**), two *tert*-butyl groups were incorporated into the pendent phenyl groups of the polymer as shown in Scheme 1.

The new monomer 3,3'-di(4''-*tert*-butylbenzoyl)benzidine (**10**) was synthesized according to a modified literature procedure (scheme 1).^{1b} Treatment of bromide **3** with potassium cyanide in acetonitrile at room temperature afforded nitrile **4**⁸ in quantitative yield which on condensation with **5** in basic methanol yielded anthranil **6**.⁹ Reduction of the anthranil with iron and acetic acid⁹ followed by treatment with trifluoroacetate group gave **8**.^{1b} Coupling of **8** with half equivalent of hexamethylditin in dry toluene and using a palladium catalyst afforded biphenyl **9** (70% yield), which on reflux with potassium carbonate and ethanol for 8 hours to allow for the deprotection of the amino groups, yielded monomer **10** in quantitative yield.^{1b}

Polymerization of **10** with diacetyl benzene (**11**) was conducted in a *m*-cresol/diphenylphosphate medium at 140°C for 48 h to Bu-PPQ (**2**). After cooling, the polymerization dope was precipitated into ethanol-triethylamine.^{2b} The precipitated polymer was collected by suction filtration and continuously extracted for 24 h with an ethanol-triethylamine solution and dried in vacuo. The new polymer, obtained in essentially quantitative yield (>95%), with high thermal stability, was characterized by Fourier transform infrared (FT-IR), UV-Vis, and ¹H NMR spectroscopies, and by thermogravimetric analysis (TGA). Disappearance of carbonyl absorption bands of the monomers and appearance of new strong bands between 1600 and 1400 cm⁻¹ in the FT-IR spectra of the polymers confirmed the complete cyclization to form the quinoline rings.^{1,2} The low intrinsic viscosity of Bu-PPQ (1.28 dL/g in methanesulfonic acid at 30 °C) implied a low molecular weight; however, excellent film forming properties were obtained. The *tert*-butyl groups were intended to disrupt the coplanar array in the polymer chain through steric interference of the *tert*-butyl groups thereby preventing the dense packing of the chains in the solid state and consequently to influence the solubility and optical

properties. However, Bu-PPQ (2), had similar solubility properties as PPPQ (1). The photoluminescence and electroluminescence of Bu-PPQ were significantly different from those of PPPQ (1).

Thin films of Bu-PPQ for optical absorption and photoluminescence measurements were obtained by spin coating from its formic acid solution onto fused silica substrates. Then the films were dried in a vacuum oven at 60 °C overnight. Optical absorption spectra were obtained by using a Lambda-9 UV/Visible/Near-IR spectrophotometer (Perkin-Elmer). Steady-state photoluminescence studies were carried out by using a Spex Fluolog-2 Spectrofluorimeter. The films were positioned such that the emission light was detected at 22.5° from the incident beam. Electroluminescent devices were prepared and investigated as sandwich structures between aluminum (Al) and indium-tin oxide (ITO) electrodes. 1,1-Bis(di-4-tolylaminophenyl)cyclohexane (TAPC, **12**) dispersed in polystyrene (PS, **13**) was used as the hole-transport layer (chart 1). The TAPC:PS (50 wt.%) thin films (50 nm) were deposited onto ITO coated glass substrates by spin coating from dichloromethane solutions. Thin films (50 nm) of Bu-PPQ were spin coated from its formic acid solutions onto the TAPC:PS layer and dried at 60 °C in vacuum overnight. Finally, 100–130 nm aluminum electrodes were vacuum (5×10^{-6} torr) evaporated onto the resulting bilayers. The LED fabrication and characterization are similar to previously reported procedures.⁶ The EL quantum efficiencies of the diodes were estimated by using procedures similar to that previously reported.¹⁰ All the fabrication and measurements were done under ambient laboratory conditions.

Figure 1 shows the optical absorption, steady-state photoluminescence (PL), and electroluminescence (EL) spectra of Bu-PPQ. This polymer shows a strong absorption with a π - π^* transition at 399 nm. The optical absorption edge bandgap is 2.78 eV (446 nm). Bu-PPQ thus has identical absorption peak and bandgap as those of PPPQ which

were previously reported.^{2b} This suggests that the ground state electronic structure of PPPQ does not change with the introduction of the *tert*-butyl groups in Bu-PPQ.

Also shown in Figure 1 is the steady-state PL spectrum of Bu-PPQ thin film excited at 399 nm. The PL spectrum shows an emission peak at 554 nm. The yellow emission corresponds to a large Stokes shift of 155 nm (0.87 eV) which is characteristic of excimer emission of the solid film of many conjugated polymers.¹¹ The PL emission of Bu-PPQ showed a 20 nm blue shift compared to PPPQ (**1**) which has a PL emission peak at 574 nm. This indicates that the introduction of the *tert*-butyl groups in Bu-PPQ modifies the excited state electronic structure of the parent polymer PPPQ. That chain packing of conjugated polymers should significantly influence their excited state properties more than their ground state electronic properties has been predicted.¹¹

The EL spectrum of the device ITO/TAPC:PS/Bu-PPQ/Al at a bias voltage of 8 V is shown in Figure 1. The EL emission peak is at 554 nm. It can be seen that the EL spectrum is identical to the PL spectrum, indicating that the EL emission is from the Bu-PPQ layer only and that the electroluminescence and photoluminescence of Bu-PPQ originate from the same excited states.

Figure 2 shows the current-voltage and luminance-voltage characteristics of the EL device. The turn-on voltage of the ITO/TAPC:PS(50 nm)/Bu-PPQ(50 nm)/Al device was 8 V. It showed bright yellow color emission which can be clearly seen under the room light. The luminance of the device was 200 cd/m² at a current density of 120 mA/cm². The EL efficiency of the device was estimated to be 0.16% photons/electron. These values were about four times higher than those of PPPQ (**1**) under the same conditions. For example, the device ITO/TAPC:PS(50 nm)/PPPQ(50 nm)/Al had a luminance of 50 cd/m² at the same current density of 120 mA/cm². The large enhancement of electroluminescence in the *tert*-butyl substituted Bu-PPQ (**2**) compared to the parent polyquinoline **1** can be understood in terms of reduced concentration quenching of luminescence facilitated by increased interchain packing distances.^{11,12} The observed efficient electroluminescence in

the ITO/TAPC:PS/Bu-PPQ/Al devices imply that the emissive Bu-PPQ layer also exhibits good n-type (electron transport) characteristics in accord with prior finding for other polyquinolines.^{3,6}

In summary, a new electroluminescent, yellow light-emitting conjugated polymer, Bu-PPQ (**2**), was synthesized and characterized. Although the substitution of *tert*-butyl groups in Bu-PPQ did not improve its solubility in organic solvents, efficient electroluminescence with an EL quantum efficiency of 0.16% photons/electron and a luminance of 200 cd/m² was observed. The brightness and efficiency of light-emitting diodes from Bu-PPQ (**2**) were four times higher than those of PPPQ (**1**) with no *tert*-butyl substitution. These results also suggest that Bu-PPQ thin films exhibit good n-type (electron transport) characteristics in the EL devices. Studies in the synthesis and electroluminescence of other π -conjugated polyquinolines are in progress.

Acknowledgment

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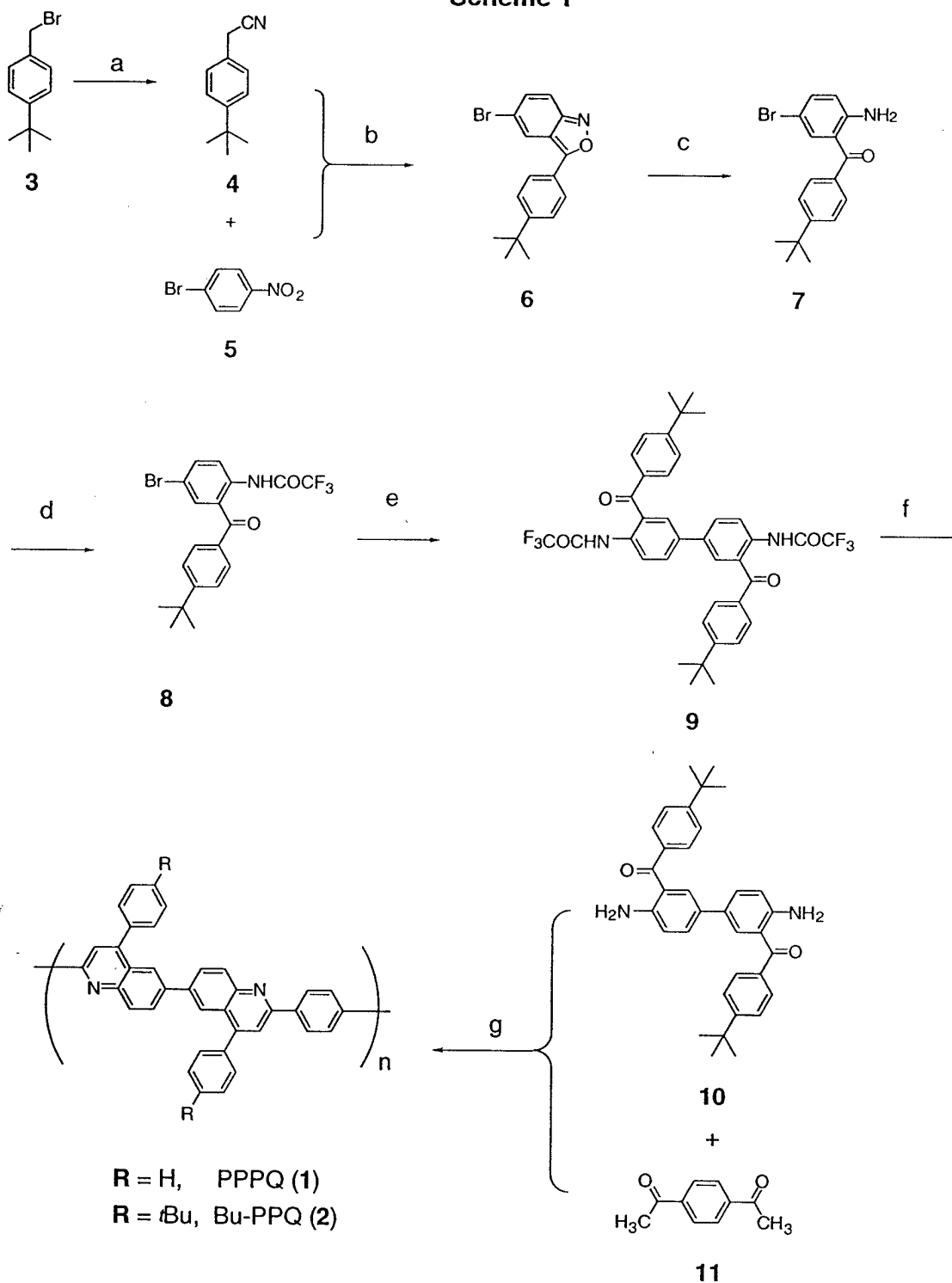
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Figure Captions

Figure 1. Optical absorption, photoluminescence (excited at 399 nm) and electroluminescence (8 V) spectra of Bu-PPQ thin films.

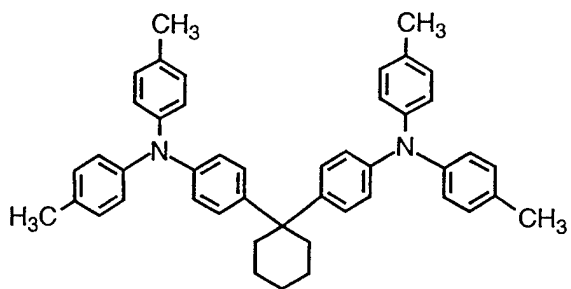
Figure 2. Current-voltage and voltage-luminance characteristics of the electroluminescent device ITO/TAPC:PS/Bu-PPQ/Al.

Scheme 1

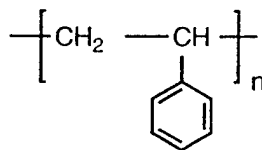


Reagents: a) KCN/ acetonitrile/ 18-crown-6. b) KOH/methanol/THF. c) Iron/acetic acid/ 80°C. d) Trifluoroacetic anhydride/ ether. e) Hexamethylditin/ Pd(PPh₃)₄/ toluene/ argon/ 90°C. f) K₂CO₃/ethanol/ 70°C. g) Diphenylphosphate/ *m*-cresol/ 140°C/ argon.

Chart 1



TAPC, 12



PS, 13

Figure 1

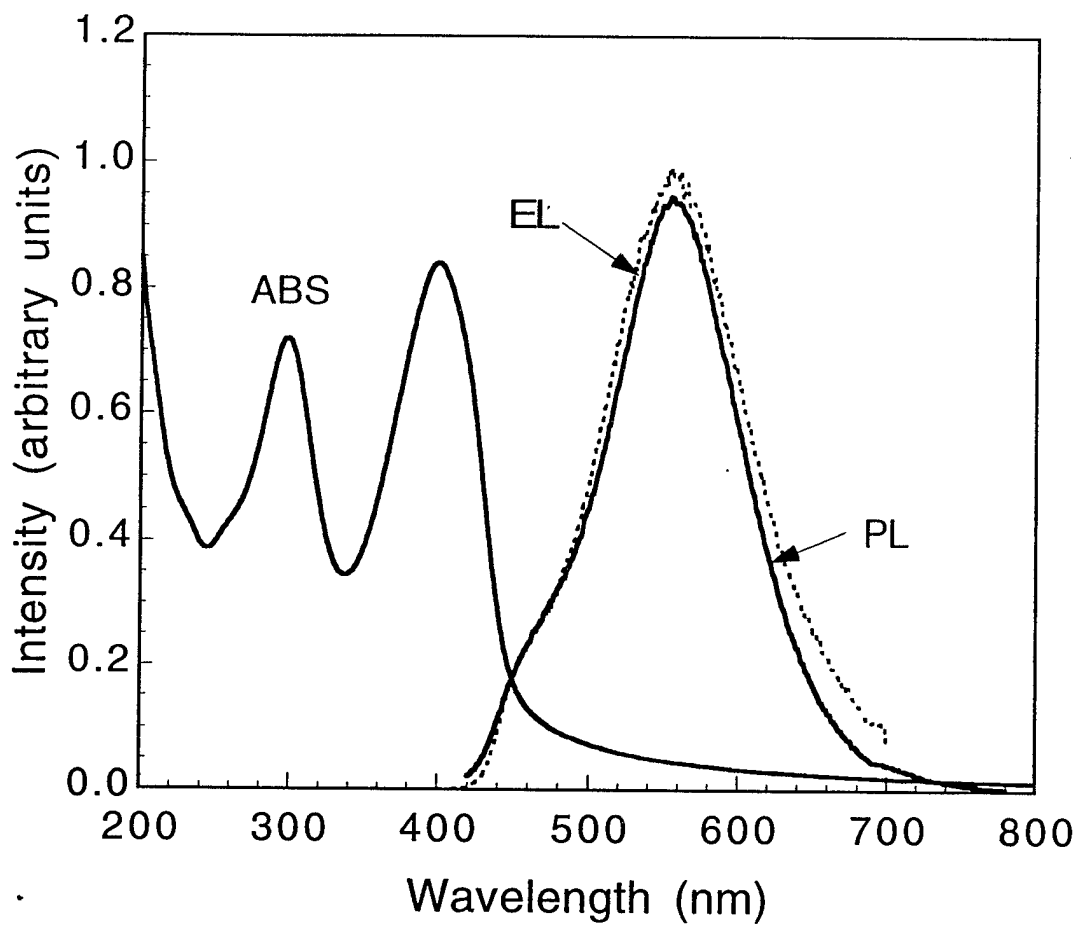


Figure 2

