

A New Polyquinoline Containing Spirobifluorene and Phenathiazine Units with Excellent Electroluminescence Properties

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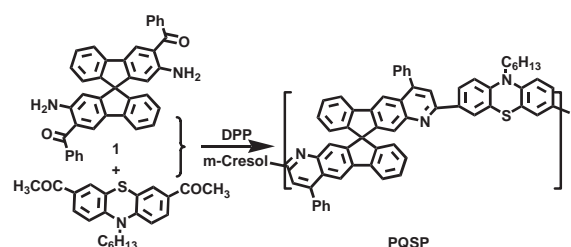
A new polyquinoline **PQSP** containing spirobifluorene and phenathiazine units was synthesized through the acid-catalyzed Friedländer condensation. **PQSP** showed strong yellow emission in solution and film. Excellent EL performances were obtained for **PQSP**. The devices based on **PQSP** showed a maximum external quantum efficiency of 0.63% and a maximum photometric efficiency of 1.85 cd/A. Pure yellow-green EL with narrow full width at the half-maximum (fwhm < 70 nm) and the highest maximum luminance (1768 cd/m²) among the currently reported polyquinolines was obtained for **PQSP**.

n-Type (electron acceptor, electron transport) polymeric semiconductors are urgently needed for developing more efficient and high performance plastic electronic and optoelectronic devices.¹ It has been well known that polyquinolines (PQs) are intrinsic good *n*-type semiconducting polymers.¹⁻⁷ Based on their optical and electric properties, polyquinolines have been studied for their potential uses in electroluminescent devices,¹⁻³ electrochromic cells,⁴ photovoltaic devices,⁵ chemosensors,⁶ and nonlinear optics.⁷ Many polyquinolines were developed since 1970s, and their electroluminescent and photophysical properties have also been recently investigated.¹⁻³ However, these polyquinolines showed poor electroluminescent performance (maximum luminance < 300 cd/m²) and broad electroluminescence because of the formation of aggregates and excimers in solid films even incorporating large hindrance substituents (long alkoxy or alkyl).

In this paper, we report a new polyquinoline containing spirobifluorene and phenathiazine units. It has been reported that spirobifluorene can be introduced into small compounds^{8,9} or polymeric chains^{10,11} to effectively suppress aggregate-forming tendency. Spiro-annulated molecules utilize the spiro-bridge to connect two perpendicular conjugated segments via a tetrahedral bonding atom at the center.^{8,9} The structural feature is expected to minimize the close packing of the polymer chains, thus reduces the formation of aggregates and interchain excimers, resulting in good solubility and significant increase in thermal stability and luminescent efficiencies. On the other hand, to properly balance the charge injection and transporting ability so as to achieve high efficiency in organic light-emitting diodes (OLEDs), hole transport groups (phenathiazine) are also introduced into the polymer chains.

The polymer was synthesized using a condensation scheme based on acid-catalyzed Friedländer reaction,¹ as shown in Scheme 1. The polymer was obtained with a yield of 93% by reacting an equimolar mixture of 2,7-diacetyl-10-*n*-hexylphenathiazine and the bis(*o*-aminoketone) monomer **1**¹⁰ in an acidic medium of diphenyl phosphate and *m*-cresol at 140 °C for 72 h

under argon. The structure of the polymer was checked by ¹H NMR spectroscopy.¹² The polymer is soluble in common organic solvents such as tetrahydrofuran (THF) and chloroform. Gel permeation chromatography combined with static laser scattering analysis with THF as an eluent yielded a weight-average molecular weight of 45000 with a polydispersity index of 1.24. Thermogravimetric analysis revealed that the polymer was thermally stable up to 370 °C. Differential scanning calorimetry showed a relatively high glass transition temperature at 222 °C.



Scheme 1. Synthesis of **PQSP**.

The absorption and photoluminescence (PL) properties of **PQSP** were investigated in THF solution and solid state, as illustrated in Figure 1. The polymer shows a solution PL efficiency of 0.16 in THF, measured relative to quinine bisulfate (in 1.0 M H₂SO₄). Absorption spectra in dilute solution and solid state are very similar, consistent with the absence of aggregation effects in their ground electronic states. The optical band gap (E_g^{opt}) of the polymer was determined to be 2.36 eV from the film absorption spectrum edge. In THF, **PQSP** emitted strong yellow-green fluorescence around 546 nm. PL emission spectrum showed a slight red shift by 4 nm in solid state relative to dilute solution, suggesting almost complete reduction of the aggregates and excimers. The polymer demonstrated narrow PL emission in solid state with a full width about 70 nm at half-maximum (fwhm).

Cyclic voltammetry was employed to investigate the redox behavior of the polymer dip-coated on a Pt disc. In Figure 2, **PQSP** showed reversible *n*-doping and *p*-doping processes. Re-

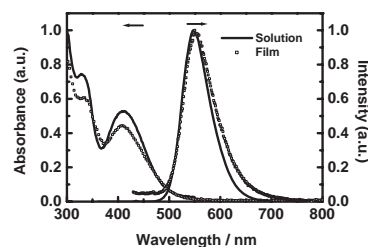


Figure 1. The optical absorption and PL spectra of **PQSP**.

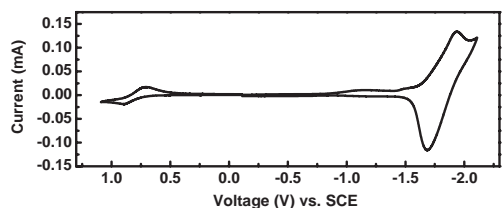


Figure 2. Cyclic voltammogram of PQSP.

garding the energy level of the SCE reference with the assumption that the energy level of SCE is 4.4 eV below vacuum,¹³ the LUMO and HOMO energy levels were calculated to be -2.94 and -5.07 eV from the onset potentials of the oxidation and reduction ($E_{\text{ox}}^{\text{onset}}$ and $E_{\text{red}}^{\text{onset}}$). The electrochemical band gap (E_{g}^{el}) of PQSP was estimated to be 2.74 eV according to the equation¹⁰ $E_{\text{g}}^{\text{el}} = E_{\text{ox}}^{\text{onset}} - E_{\text{red}}^{\text{onset}}$, close to that obtained by optical method. Its relatively high electron affinity and good solubility in organic solvents make them very attractive for use as electron transport materials in multilayer device architectures.¹ The polymer also demonstrated hole transport property with high HOMO energy level of -5.07 eV. These analyses suggested that PQSP was characteristic of bipolar property, which could obtain excellent EL performances when serving as emissive layer in OLEDs.

As previously reported, this kind of phenothiazine-phenylquinoline donor-acceptor polymer showed no emission in EL device.⁵ Surprisingly for this polymer, it is very easy to obtain yellow-green emission in several devices based on PQSP, as showed in Figure 3. The EL spectra of the devices based on the polymer are similar to PL spectrum of thin film and all show very narrow emissions (fwhm < 70 nm), further supporting the lack of interchain electronic interactions. Figure 4 showed the current voltage-brightness characteristic of the devices. For the device of ITO/PQSP (60 nm)/Alq (30 nm)/Al (100 nm), the turn-on voltage is 5 V, and the brightness reached 1768 cd/m² (the highest maximum luminance among the currently reported polyquinolines) at a bias voltage of 11.5 V and a current density of 204 mA/cm², corresponding to an external quantum efficiency of 0.2%. And the maximum external quantum efficiency is 0.37% at 694 cd/m² and 9.5 V. For the device of ITO/PEDOT (50 nm)/PQSP (60 nm)/Alq (30 nm)/Al (100 nm), the maximum external quantum efficiency and the maximum photometric efficiency reaches 0.63% and 1.85 cd/A at 140 cd/m² and 10.5 V, respectively. The higher efficiency than that of the device without PEDOT layer may be attributed to the good balance of charge transport and injection.

A new polyquinoline PQSP containing spirobifluorene and phenathiazine units was prepared via the acid-catalyzed Friedländer condensation. The incorporation of spiro moieties greatly

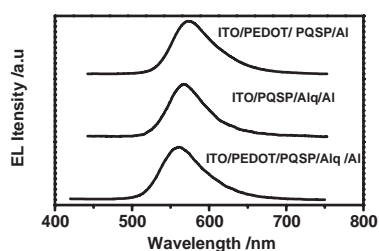


Figure 3. Normalized EL spectra of devices based on PQSP.

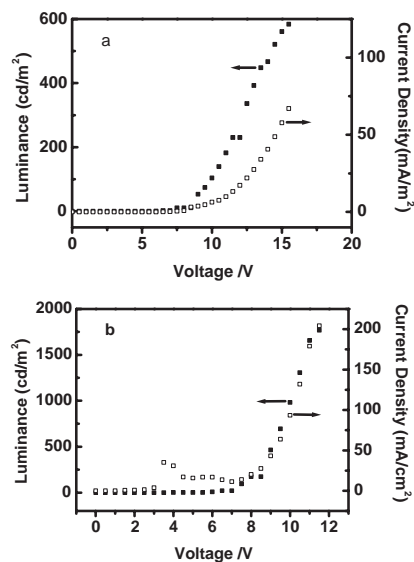


Figure 4. Current density and luminance versus applied voltage of ITO/PEDOT/PQSP/Alq/Al (a) and ITO/PQSP/Alq/Al (b).

suppressed the interchain interactions, leading to good solubility and a slight red shift in absorption and emission in film relative to dilute solution. The low-lying LUMO energy suggested that the polyquinoline was intrinsic *n*-type materials and might have potential for use as emissive layer and electron injection and transport layer in OLEDs. The devices based on PQSP showed a maximum external quantum efficiency of 0.63% and a maximum photometric efficiency of 1.85 cd/A. Pure yellow-green EL with narrow full width at the half-maximum (fwhm < 70 nm) and the highest maximum luminance (1768 cd/m²) among the currently reported polyquinolines was obtained for PQSP.

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- PQSP, ¹H NMR (300 MHz, CDCl₃): δ 0.75 (br, 3H), 1.03–1.26 (br m, 8H), 3.76 (br, 2H), 6.72 (br, 2H), 6.80 (d, 2H, $J = 6$ Hz), 7.09 (br, 2H), 7.32 (br, 2H), 7.49 (br, 2H), 7.60 (br m, 12H), 7.72 (br, 2H), 7.82 (br, 2H, $J = 5.7$ Hz), 8.23 (br, 2H).
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