



A NOVEL PREPARATION OF PQ DERIVATIVE

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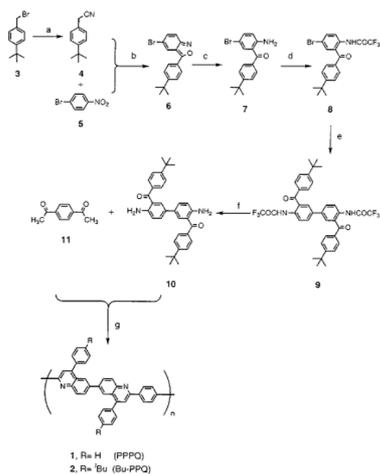
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ABSTRACT

A novel preparation of PQ derivatives through acid-catalyzed Friedlander reaction is described. The preparative procedure presented in this paper is operationally simple and environmentally good. The reaction media and the catalyst used can be recovered and reused for at least four times without loss in the catalytic activity.

Introduction-

As one of the most frequently used pathways to quinoline derivatives, the Friedlander synthesis is an acid or base catalyzed condensation followed by a cyclodehydration between an aromatic 2-aminoaldehyde or ketone with the carbonyl compounds containing a reactive α -methylene group.⁵ For instance, it has been reported that drops of concentrated sulfuric acid or 6 N hydrochloric acid can be used as efficient catalysts in the Friedlander condensation procedure.⁶ With this method, various structurally varied substrates can give the corresponding quinoline products in moderate to high yields. Unfortunately, this method involves the utilization of excessive glacial acetic acid as solvent or necessitates a metal bath to maintain the reaction temperature at as high as 200°C, thus making this method unsuitable for an up-scaling process.



Scheme 1.

Results and Discussion-

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

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 p-p* transition at 399 nm. The optical absorption edge band gap is 2.78 eV (446 nm). Bu-PPQ thus has absorption peak and band gap identical to 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.

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 room light. The luminance of the device was 280 cd/m² at a current density of 100 mA/cm². The EL efficiency of the device was estimated to be 0.26% photons/electron. These values were about six 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 45 cd/m² at the same current density of 100 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 [10, 11]. Observation of efficient electroluminescence in the ITO/TAPC:PS/Bu-PPQ/Al device implies that the emissive Bu-PPQ layer also exhibits good electron transport (n-type) characteristics, in accord with prior findings for other polyquinolines [3, 6].

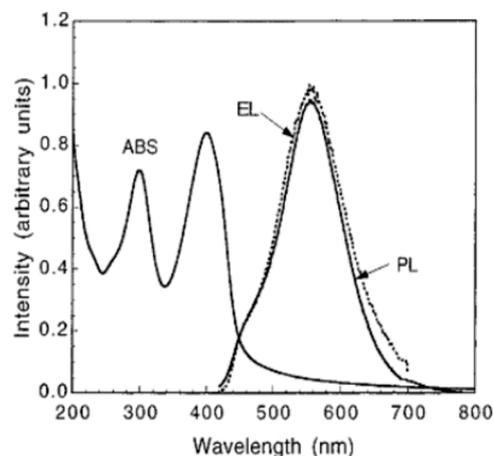


Fig. 1. Optical absorption, photoluminescence (excited at 399 nm) and electroluminescence (8 V) spectra of Bu-PPQ thin films.

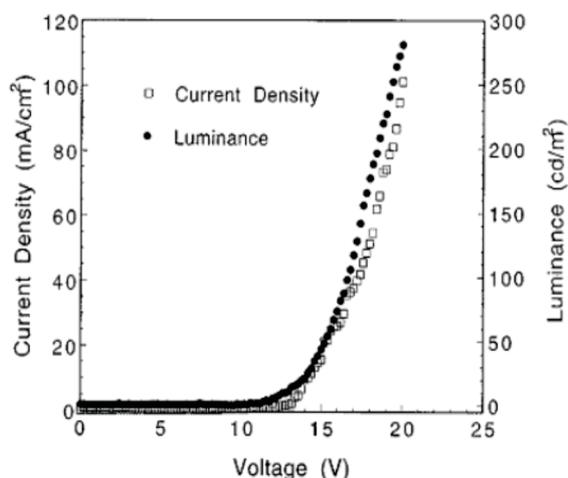


Fig. 2. Current–voltage and voltage–luminance characteristics of the electroluminescent device ITO/TAPC:PS/Bu-PPQ/Al.

Experimental-

4-tert-Butylbenzyl nitrile(4) was synthesized according to a literature procedure[8]. The other intermediates were synthesized by modifying literature procedures as is outlined below.

3-(p-tert-Butylphenyl)-5-bromoanthranil(6)[9]

To a solution of 360g KOH in methanol(500ml) and THF (100ml) was added with stirring and cooling, in an ice bath, 40g (0.23mol) of 4-tert-butyl benzyl nitrile (4) and a solution of 44g (0.23mol) 4-bromonitro benzene(5) in methanol(300ml) and THF (50ml). The mixture was stirred for 16h at room temperature and 1.5l of water was then added with stirring. The precipitate was isolated by filtration, washed with water, and dried. The product was further purified upon crystallization from hexane as pale yellow needles(50g, 70%). ¹HNMR(CDCl₃, 300MHz): δ 8.06(s, 1H), 7.95(d, 2H), 7.61(d, 2H), 7.55(d, 1H), 7.40(dd, 1H), 1.50(s, 9H). MS(EI) 331(71%), 329(64%), 57.10(100%).

2-Amino-5-bromo-4-tert-butylbenzophenone(7)[9]

A solution of 16.8g(51mmol) of 6 in 300ml of acetic acid was heated at 80°C, and 24g (8.5eq.) of iron filings was added over 4h, during which 30ml of water also added. The mixture was then cooled, diluted with 1l of water and extracted with ether (56100ml). The extract was washed with dilute sodium carbonate solution (26100ml) and brine (26100ml) and dried over magnesium sulfate. The ether was removed under reduced pressure to afford the product as bright yellow crystals (14g, 83%). ¹HNMR (CDCl₃, 300MHz): δ 8.58(d, 1H), 7.85(d, 1H), 7.80(dd, 1H), 7.75(d, 2H), 7.59(d, 2H), 1.40(s, 9H). MS(EI) 333(80%), 331(100%), 276(60%).

5-Bromo-2-(trifluoroacetamido)-4-tert butylbenzophenone(8) [1b]

To a solution of 9.5g(28.6mmol) of 7 in 350ml of freshly distilled (Na/benzophenone) diethyl ether was added 35g (0.21mol) of anhydrous sodium carbonate. The reaction mixture was cooled in an ice bath, and 30ml (0.21mmol) of freshly distilled trifluoroacetic anhydride was added drop wise as rapidly as possible while maintaining a gentle reflux. Upon completion of the addition, the ice bath was removed and the reaction mixture stirred for 1h. 500ml of water was added and the organic layer was separated and washed with brine (26100ml) and dried with magnesium sulfate. The solvent was removed under reduced pressure to afford the product(8) a slight brown needles (11.7g, 95%). ¹HNMR(CDCl₃, 300MHz): δ 8.58(d, 1H), 7.85(d, 1H), 7.80(dd, 1H), 7.75(d, 2H), 7.59(d, 2H), 1.40(s, 9H). MS(EI) 429(30%), 427(35%), 294(100%).

4,4'-Bis(trifluoroacetamido)-3,3'-di(para-tert butyl)benzoyl biphenyl(9)[4]

A heavy-walled flask (250ml) was charged with a solution of 0.64g (0.54mmol, 2mol%) of tetrakis(triphenylphosphine)palladium(0) in 50ml of freshly distilled (Na/benzophenone)deoxygenated toluene under argon. To the above was added a solution of 11.7g(27.3mmol) of 8 in 60ml of dry toluene. The reaction mixture was degassed and back-filled with argon three times, and stirred at 80°C. To this mixture was added dropwise over 1h a solution of 4.47g(13.6mmol) of hexamethylditin in 50ml of dry toluene. After heating for an additional 10h the reaction was cooled and the product isolated by suction filtration to afford the product 9 as a pale yellow powder (7.1g, 75%). ¹HNMR (CDCl₃, 300MHz): δ 8.70(d, 2H), 7.89(d, 2H), 7.80(dd, 2H), 7.72(d, 4H), 7.52(d, 4H), 1.40(s, 18H).

3,3'-Di(para-tert-butyl)benzoylbenzidine(10)

A mixture of 5.37g (7.7mmol) of 9 and 20g (144mmol) of anhydrous potassium carbonate in 200ml of ethanol and 100ml of water was refluxed for 6h. After cooling, the precipitate was isolated by suction filtration and then stirred in 150ml of water to dissolve any remaining potassium carbonate. Filtration and drying yielded 3.38g(87%) of 10. ¹HNMR(CDCl₃, 300MHz): δ 7.6(m, 6H), 7.89(m, 6H), 6.80(d, 2H), 6.0(s, 4H), 1.40(s, 18H).

Polymer 1 was synthesized according to the literature procedure [2]. The new polymer Bu-PPQ(2) was synthesized as follows. Equimolar amounts of both 3,39-bis(p-tert-butyl)benzoylbenzidine (0.28g) and p-diacetyl benzene (0.09g) were added along with 5.0g of diphenyl phosphate(DPP) and 10ml of freshly distilled m-cresol in a glass reactor fitted with mechanical stirrer, two gas inlets, and a side arm. The reaction mixture was purged with argon for 15min, and then the temperature was raised to 140°C under positive pressure of argon. The temperature was maintained for 48h, during which time small amounts of m-cresol to facilitate efficient stirring of the reaction mixture were added when ever it became highly viscous. After cooling, the polymerization mixture was slowly poured into a stirring solution of 500ml of ethanol/50ml of triethylamine. The precipitated polymer was collected by suction filtration: [η]=1.28dl/g(30°C, methanesulfonic acid). FT-IR (free standing film, cm⁻¹): 3056, 3028, 1585, 1572, 1541, 1486, 1353, 1182, 826, 587.

The LED fabrication and characterization are similar to previously reported procedures [6,12]. EL quantum efficiencies of the diodes were estimated by using procedures similar to those previously reported[13]. All the fabrication and measurements were done under ambient laboratory conditions.

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