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Synthesis and Photophysics of New Donor-Acceptor Copolymers Based on Fluorene and Phenylquinolines

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Synthesis and Photophysics of New Donor-Acceptor Copolymers Based on Fluorene and Phenylquinolines

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*The synthesis and photophysics of two new donor-acceptor conjugated A-B type copolymers based on conjugated 2,6-disubstituted-4-phenyl-quinoline and 2-substituted-4-phenyl-quinoline, and 9,9-dialkyl-fluorene linked through the 1,4 and 1,3,5 phenyl rings via the Friedländer condensation and Suzuki coupling reaction are presented. The band gap energy of the polymers **1** and **2** measured from the thin films were 430 nm and 380 nm corresponding to 2.88 eV and 3.26 eV, respectively. The photoluminescence (PL) spectra of the thin films of the polymers **1** and **2** showed maximum peaks at 427 and 397 nm corresponding to the deep blue and UV ranges respectively. The red shift of the polymer **1** relative to the polymer **2** can be accounted for by the increased conjugation length because the quinoline unit is oriented to include the phenyl ring in the backbone of polymer **1**. Both polymers have similar trends of irreversible oxidation. The ionization energy of polymers **1** and **2** were measured by cyclic voltammetry (CV) and were found to be 5.60 and 5.65 eV, respectively.*

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INTRODUCTION

Conjugated polymers with donor-acceptor architectures are currently of interest for their potential applications in advanced semiconducting electronic devices such as polymeric light-emitting diodes (PLEDs) and organic solar cells [1]. Donor-acceptor type conjugated polymers have their own characteristic properties because the built-in intramolecular charge transfer can enhance the advantage of manipulation of the electronic structure (HOMO/LUMO levels), leading to small band gap semiconductors [2]. Since the potential utilization of polyquinolines was first introduced by Stille and coworkers [3], a variety of conjugated polyquinoline have been extensively designed, synthesized and characterized with the aim of achieving stable PLEDs with high brightness and external quantum efficiency (EQE) [4]. Most conjugated polyquinolines are known to be thermally stable semiconducting materials and well investigated as an excellent electron-acceptor which can be utilized in photonic and electronic application like PLEDs [5]. Previous studies have shown that 4-phenyl or alkyl quinolines are excellent building blocks for the design of electron-acceptor (n-type) conjugated linear-chain polymers and dendrimers with high electroluminescence [6], electron transport [7], electrochemiluminescence (ECL) [8], nonlinear optical [9], and other advanced electronic properties. However, hole injection and electron donating properties of the 4-phenyl and alkyl quinolines still need improvement [10]. One of the challenges of improving hole injection and transport (electron-donating) properties are introducing donor architectures such as polyfluorene [11]. Polyfluorenes have been shown to be p-type (hole transport) conducting polymers, and have been recently used in PLEDs by copolymerizing with an electron-deficient (n-type) building block while retaining the blue emission to improve the electron-transport properties [12].

In this paper, we report the syntheses and photophysics of two new donor-acceptor polymers based on 2,6-disubstitued-4-phenyl-quinoline or 2-substitued-4-phenyl-quinoline and 9,9-dialkyl-fluorene linked via 1,4 or 1,3,5 connecting phenyl rings as shown in Figure 1. The quinoline moiety was chosen as the acceptor building block because it showed good electron transport (n-type) properties in oligoquinoline [13], and polyquinoline based PLEDs [14]. Different configurations

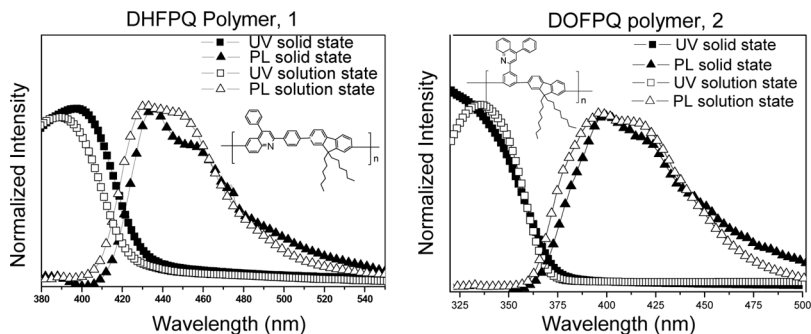


FIGURE 1 (a) Normalized optical absorption and PL emission spectra of 10^{-5} M solutions in CHCl_3 and thin films of copolymer **1** and **2**. The excitation wavelength was 350 nm. Normalized PL emission spectra of the polymer thin films annealed at 100°C in air.

of the quinoline units were introduced to control chain rigidity and conjugation length. 9,9-Dialkyl-fluorene was chosen as the donor building block.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a JEOL (Japan), JNM ECP-400 at 400 MHz or a Bruker-AF301 at 300 MHz. The spectra were recorded using CDCl_3 as the solvent at room temperature. Cyclic voltammetry (CV) experiments were performed using a Perkin ElmerTM Potentiostat/Galvanostat Model 263A. A three-electrode cell was used in all experiments. Platinum wire was used for counter electrodes. Working electrodes were made of indium-tin-oxide (ITO) and Ag/AgCl (a saturated 3.5 M KCl solution) was used as a reference electrode. The polymer was coated onto the ITO working electrode by spin coating of the viscous polymer solution in CHCl_3 . Electrolyte solutions of 0.1 M Bu_4NClO_4 in DMF were used in our experiments. Cyclic voltammograms were obtained at a scan rate of 50 mV/sec. UV-vis spectra were recorded on a UV-1601 PC, UV-visible spectrophotometer (SHIMADZU). Photoluminescence spectra were measured on a RF-5301 PC spectrofluorophotometer (SHIMADZU).

Polymerization of **6** with **7** by Suzuki Coupling

6-Bromo-2-(4-bromo-phenyl)-4-phenylquinoline, **6**, was prepared according to the literature methods [15]. To a two necked flask, 0.5 gram

(0.995 mmol) of 9,9-dihexyl-fluorene-2,3-bis(trimethylene boronate), (0.44 g, 0.995 mmol), 1 mol% of tetrakis(triphenylphosphine) palladium(0) (0.012 g) were dissolved in dry toluene (6 mL) at 60°C under an argon atmosphere. Aliquat 336 (0.01 mL) in 0.5 mL of dry toluene and 4 mL of 2M K₂CO₃ were added via syringe. The reaction mixture was heated at 80°C for 48 h. The polymerization mixture was extracted with a solution of EDTA in CHCl₃. Volatiles were removed under reduced pressure. The reaction mixture was slowly poured into 500 mL of methanol. The precipitated polymer was filtered off and further purified by soxhlet extraction through methanol for 24 h to remove low molecular weight oligomers and inorganic impurities. The resulting polymer was redissolved in chloroform and recrystallized from methanol. The precipitated polymer was collected, vacuum filtered, and dried in a vacuum oven to yield 0.62 g (66%). ¹H NMR (400 MHz, CDCl₃): δ 8.38 (1H, bs), 8.20 (1H, bd), 8.12–7.61 (17H, m), 2.04 (4H, bs), 1.08 (16H, bs), 0.76 (6H, bs) ppm. ¹³C NMR (CDCl₃): δ156.0, 148.5, 147.8, 144.1, 138.6, 137.5, 136.5, 124.4, 130.2, 129.7, 128.5, 128.2, 127.8, 127.2, 126.9, 126.0, 125.4, 124.3, 123.5, 35.7, 31.7, 29.1, 28.9, 22.7, 14.1 ppm. Tg: 168°C. IR (KBr) = 3058.63 (aromatic C–H), 2924.27 (aliphatic C–H), 1588.72 (C=N) cm⁻¹.

Synthesis of 10 via Friedländer Synthesis

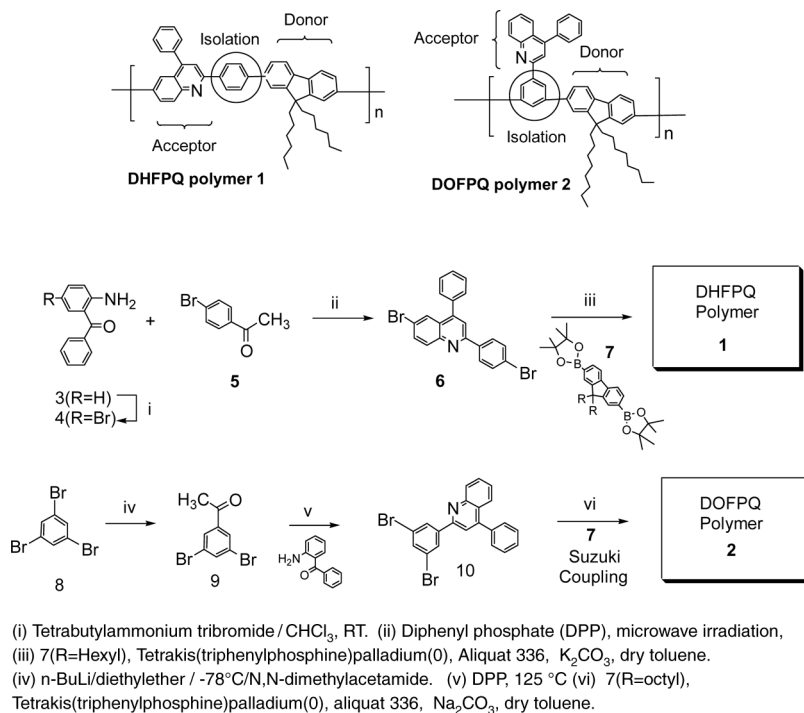
3,5-Dibromoacetophenone, **9** was prepared as described in the literature [16] with 62% yield. To a 500 mL round bottomed flask was added 5.12 g (18.5 mmol) of **9** (MW=292.8 g mol⁻¹), 4.04 g (20.5 mmol) of 2-aminobenzophenone (MW=197.24 g mol⁻¹), and 18.6 g (74.3 mmol) of diphenyl phosphate (MW=250.19 g mol⁻¹). Reaction mixture was stirred and heated slowly to 150°C and allowed to run overnight. 400 mL of CH₂Cl₂ was added. CH₂Cl₂ layer was washed twice with 200 mL of 10% aqueous NaOH solution and then washed five times with 300 mL of water. CH₂Cl₂ layer was dried over MgSO₄ and roto-evaporated to give a crude oil which was purified by column chromatography using silica gel (50:50 hexanes:chloroform, v/v) to give 6.19 g of light orange solid in 77% yield. m.p. = 183–184°C. ¹H NMR (300 MHz, CDCl₃): δ 8.32 (1H, s), 8.26 (1H, d), 7.94 (1H, d), 7.79 (2H, m), 7.58 (8H, m) ppm. ¹³C NMR (75 MHz, CDCl₃): δ153.56, 149.83, 148.70, 142.97, 138.00, 134.58, 129.96, 129.53, 129.31, 128.71, 130.24, 128.67, 127.06, 126.15, 125.75, and 123.48 ppm. IR (KBr) = 3083.90 (aromatic C–H), 1580.43 (C=N), 1540.71, 853.07 cm⁻¹. Mass spectrum: CIMS, m/s 439 (M⁺).

Polymerization of 2-(3,5-Dibromophenyl)-4-Phenylquinoline, **10**, with 9,9-Dioctyl-Fluorene-2,3-bis(Trimethylene Boronate) by Suzuki Coupling

The following reagents were added to a 500 mL of round bottomed flask under a blanket of argon: 1.311 g (2.35 mmol) of 9,9-dioctyl-fluorene-2,3-bis(trimethylene boronate) (MW = 558.4 g mol⁻¹), 1.036 g (2.36 mmol) of 2-(3,5-dibromophenyl)-4-phenylquinoline (MW = 439.1 g mol⁻¹), 5.15 g (48.6 mmol) of Na₂CO₃ (MW = 105.88 g mol⁻¹), 0.176 g of aliquot 336, 35 mL of toluene, and 24 mL of water. After stirring this reaction mixture under argon, 58.31 mg (0.05 mmol) of tetrakis(triphenylphosphine)palladium(0) was added. Reaction mixture was refluxed for 3 days then washed with three times of 200 mL water. Toluene layer was separated and dried over MgSO₄, then filtered to remove MgSO₄. The volatiles were rotoevaporated to give a crude product. The product was dissolved in THF, precipitated dropwise into MeOH, and repeated three times. 1.201 g of polymer was isolated in 51.2% yield. Further purification of 0.61 g of crude polymer by soxhlet extracted with acetone for three days, leaving 0.58 g polymer, having removed 4.6% of the mass as oligomers. ¹H NMR (300 MHz, CDCl₃): δ 8.51 (2H, m), 7.70 (15, m), 7.19 (2H, m), 2.09 (4H, bs), 1.12 (24H, m), 0.69 (6H, m) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 157.12, 151.93, 148.90, 149.38, 143.05, 140.39, 40.49, 55.57, 140.40, 140.15, 138.40, 130.20, 129.62, 128.66, 128.64, 126.49, 125.94, 125.72, 125.51, 121.89, 120.15, 119.70, 31.74, 30.10, 29.26, 23.95, 22.59, and 14.03 ppm. IR (KBr) = 3060.53 (aromatic C–H), 2925.49 (aliphatic C–H), 1587.85 (C=N), 1542.55, 1466.76, cm⁻¹.

RESULTS AND DISCUSSION

The synthetic approaches to polymers **1** and **2** are illustrated in Scheme 1. The synthetic strategy for the preparation of **1** involved the introduction of bromine functionality on the amino benzophenone ring of commercially available 2-aminobenzophenone, **3**, in tetrabutylammonium tribromide/CHCl₃ solution [17]. Friedländer condensation between **4** and 4-bromoacetophenone, **5**, in the presence of diphenylphosphate (DPP) gave 6-bromo-2-(4-bromophenyl)-4-phenylquinoline, **6** which was immediately reacted with 9,9'-dihexylfluorene-2,7-bis-(trimethylene boronate), **7** to obtain polymer, **1**, in 66% yield (Scheme 1). The synthesis of polymer **2** started from the acetylation reaction of commercially available 1,3,5-tribromobenzene, **8**, using one equivalent *n*-BuLi, and *N,N*-dimethylacetamide in diethylether at -78°C. 3,5-Dibromoacetylbenzene, **9**, was obtained in 62% yield. Condensation of **9** with 2-aminobenzophenone in the presence of



SCHEME 1 Molecular structures and synthetic route of polymers **1** and **2**.

DPP at 120°C gave 2-(3,5-dibromo-phenyl)-4-phenylquinoline, **10** in 80% yield. The acetyl carbonyl peak (1710 cm⁻¹) of **5** and **9** completely disappeared in the FT-IR spectra and new strong imine functional peaks from the quinoline ring (1400–1600 cm⁻¹) were observed in **6** and **10**. ¹H and ¹³C NMR are another excellent confirmation method of the completion of the cyclization reaction to produce the quinoline moiety *via* Friedländer condensation. The three protons and carbon of the acetyl group also completely disappeared in the ¹H and ¹³C NMR of **6** and **10**. DOFPQ polymer **2** was successfully obtained in 51.2% yield by treating **10** with 9,9'-dioctyl-fluorene-2,3-bis(trimethylene boronate), Na₂CO₃, aliquot 336 and tetrakis(triphenyl phosphine) palladium(II) (Scheme 1). Both polymers **1** and **2** were soluble in a number of organic solvents such as CH₂Cl₂, toluene, THF and ethyl acetate and were characterized using FT-IR, ¹H and ¹³C NMR which are in good agreement with the proposed structures of **1** and **2**.

ABSORPTION AND PHOTOLUMINESCENCE SPECTROSCOPY

The UV-vis and photoluminescence (PL) spectra of the two copolymers in dilute CHCl_3 solution ($1 \times 10^{-5} \text{ M}$) and in thin films are shown in Figure 1. In thin films, the band gap energies of the polymers were estimated from the absorption edges and were found to be 430 nm and 380 nm, respectively. It is, of course, clear that the absorption edge of the solution phase was blue shifted due to the higher degree of the freedom in polymer chain geometry, allowing for twisting and blending. The PL spectra showed the maximum emission peaks of polymers **1** and **2** at 427 nm and 397 nm, respectively. The red shift of polymer **1** relative to that of polymer **2** is likely due to increased conjugation length in the monomer when the quinoline unit is included as part of the polymer backbone. We note that DOFPQ polymer **2** emits almost ultra-violet light. In order to estimate the ionization potential (IP) of the polymers, we performed cyclic voltammetry (CV), shown in Figure 2 and determined the IP of polymers **1** and **2** as 5.60 eV and 5.65 eV, respectively. It is likely that both polymers have similar trends of irreversible oxidation. From the measured values of the band gap energies and IP, the electron affinity (EA) of polymers **1** and **2** were calculated and were found to be 2.80 eV and 2.30 eV, respectively. The optical data as well as the electrochemical data are summarized and shown in Table 1.

GPC analysis of the polymer was determined on a Younglin 9200 GPC system equipped with RI750F detector using THF as solvent.

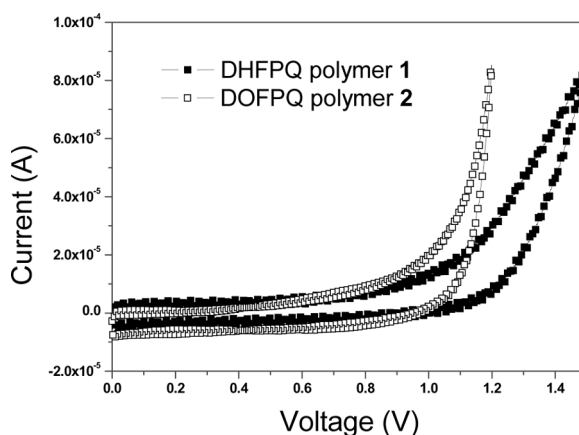


FIGURE 2 Cyclic voltammetry of oxidation of a 100-nano-thick polymer **1** and **2** film spin-coated over an ITO electrode with 0.1 M Bu_4NClO_4 in DMF as the supporting electrolyte. Scan rate 50 mV/s.

TABLE 1 Photophysical and Electrochemical Properties of Polymers **1** and **2**

Polymer	$\lambda_{\text{max}}^{\text{Abs}}$ (soln) (nm)	$\log \epsilon_{\text{max}}$ (10^5 M^{-1}) (cm^{-1})	$\lambda_{\text{max}}^{\text{abs}}$ (film) (nm)	$\lambda_{\text{max}}^{\text{PL}}$ (soln) (nm)	$\lambda_{\text{max}}^{\text{PL}}$ (film) (nm)	$E_{\text{ox}}^{\text{onset}}$ (V) ^a	IP (eV) ^b	E_{g} (eV) ^c	EA (eV) ^d
DHFPQ 1	389	0.93	397	432	435	0.80	5.60	2.80	2.80
DOFPQ 2	335	1.41	335	395	397	0.85	5.65	3.35	2.30

^aAll potentials are *vs* SCE reference.

^bIP were calculated from $\text{IP} = 4.8 + E_{\text{ox}}^{\text{onset}}$ (CV).

^c E_{g} was calculated from UV $\lambda_{\text{max}} = 1240/E_{\text{onset}}$, E_{onset} of **1** = 442 nm, E_{onset} of **2** = 374 nm.

^dEA = IP – E_{g} .

The weight-average molecular weights, based on polystyrene standards, were 35,000 for DHFPQ, **1** and 26,300 for DOFPQ, **2** with polydispersity indices ($M_{\text{w}}/M_{\text{n}}$) of 1.74 and 1.92, respectively. The thermal behavior of polymers **1** and **2** was measured by differential scanning calorimetry (DSC) analysis which was performed on a SETARAM DSC 131 at a heating rate of 10°C/min. Introduction of quinoline structure in the polyfluorene backbone significantly enhanced the thermal stability. DSC revealed that the glass transition temperatures (T_{g}) of DHFPQ, **1** and DOFPQ, **2** were 168 and 148°C which are much higher T_{g} than that of typical polyfluorene (55°C) [18]. Synthetic yields, molecular weights distribution, and thermal properties of DHFPQ, **1**, and DOFPQ, **2**, are summarized in Table 2.

SUMMARY

In summary, we described the syntheses and photophysics of two new donor-acceptor copolymers, **1** and **2**, containing phenyl quinolines and 9,9-di-*n*-alkyl fluorene units in the main chain. The band gap energies for polymers **1** and **2** were 2.88 and 3.26 eV, respectively. Emission peaks from PL measurements of polymers **1** and **2** were found at

TABLE 2 Molecular Weights Distribution and Thermal Properties of Polymers **1** and **2**

Polymer	Yield (%)	Mw ($\times 10^4$) ^a	$M_{\text{w}}/M_{\text{n}}^a$	DSC (T_{g} , °C)
DHFPQ 1	66	3.50	1.74	168
DOFPQ 2	51	2.63	1.92	148

^a M_{w} and PDI ($M_{\text{w}}/M_{\text{n}}$) of the polymers were determined by GPC using polystyrene as a standard.

427 nm (deep blue) and 397 nm (UV range), respectively. CV results estimate the IP of polymers **1** and **2** as 5.60 and 5.65 eV, respectively while EA was calculated as 2.8 and 2.3 eV, respectively. Optical data showed the emission wavelength could be controlled by incorporating or excluding the quinoline moieties into the backbone of the polymer. The PL spectra in Figure 1 shows that our material emits at near UV. This indicates that the fluorene-quinoline copolymers could be useful for developing UV emitting LED. We are currently investigating electroluminescent properties of these polymers.

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