Synthesis and Characterization of a New Phenanthrenequinoxaline-Based Polymer for Organic Solar Cells

Eunsol Jo,¹ Jong Baek Park,² Woo-Hyung Lee,¹ Ji-Hoon Kim,² In Hwan Jung,³ Do-Hoon Hwang,² In-Nam Kang¹

¹Department of Chemistry, the Catholic University of Korea, Bucheon, Gyeonggi-Do 14662, Republic of Korea ²Department of Chemistry, and Chemistry Institute for Functional Materials, Pusan National University, Busan 46241, Republic of Korea

³Division of Advanced Materials, Korea Research Institute of Chemical Technology (KRICT), Daejeon 34114, Republic of Korea Correspondence to: I.-N. Kang (E-mail: inamkang@catholic.ac.kr)

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ABSTRACT: Two donor-acceptor (D-A) conjugated polymers, PQx and PphQx, composed of alkylthienyl-substituted benzo[1,2-b:4,5-b']dithiophene (BDTT) as the electron donor and the new electron acceptors quinoxaline (Qx) or phenanthrenequinoxaline (phQx), were synthesized with Stille crosscoupling reactions. The number-averaged molecular weights (M_n) of PQx and PphQx were found to be 25.1 and 23.2 kDa, respectively, with a dispersity of 2.6. The band-gap energies of PQx and PphQx are 1.82 and 1.75 eV, respectively. These results indicate that, because phQx units have highly planar structures, their inclusion in D-A polymers will be a very effective method for increasing the polymers' effective conjugation

INTRODUCTION The development of polymer semiconductors is exciting because they enable the fabrication with printing techniques of polymer solar cells (PSCs).^{1,2} Recently, significant progress has been made in this field, and the power conversion efficiencies (PCEs) of PSCs have reached approximately 10% as a result of the development of new materials, device engineering, and the use of new processing techniques.³⁻⁶ Currently, most research is focused on the design and synthesis of new materials with low band gaps to enable efficient absorption over a broad range of the solar spectrum; other factors that must be considered in the molecular design include the requirements of a deeper highest occupied molecular orbital (HOMO) to produce a high open circuit voltage $(V_{\rm oc})$ and a high hole mobility for efficient charge transportation.^{7,8} The polymerization of donor (D) and acceptor (A) molecules results in a low band-gap polymer due to the formation of an intramolecular charge transfer (ICT) complex.9,10 High efficiency polymers require the appropriate donor and acceptor units, but unexplored

lengths. The hole mobilities of PQx and PphQx were determined to be 5.0×10^{-5} and 2.2×10^{-4} cm² V⁻¹ s⁻¹, respectively. A polymer solar cell device prepared with PphQx as the active layer was found to exhibit a power conversion efficiency (PCE) of 5.03%; thus, the introduction of phQx units enhanced both the short circuit current density and PCE of the device. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *00*, 000–000

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possibilities remain, so the search for new electron donor and electron acceptor molecules continues.

Quinoxaline units (Qx) are electron-withdrawing molecules because of the electron-withdrawing properties of the two sp² hybridized nitrogen atoms in the Qx units.¹¹⁻¹⁴ Furthermore, the phenyl rings in Qx units can easily be connected through an oxidative coupling reaction to form fused aromatic structures, the so-called phenanthrenequinoxaline (phQx) units. These phQx molecules exhibit higher planarity and better intermolecular packing due to their fused structure and extended conjugation length, which enhances the backbone planarity and $\pi - \pi$ stacking of the corresponding polymers.^{15–20} Therefore, phQx was thought to be a highly promising unit for the construction of donor-acceptor polymers. However, the highly fused rigid structure of phQx units leads to very poor solubility, which limits their applications in conjugated polymers. Recent work has shown that the rigid phQx unit can be copolymerized with a highly soluble

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1



SCHEME 1 Synthetic routes for the monomers.

donor counterpart, which improves its solubility.¹⁷⁻¹⁹ Liu et al. reported the improvement of the solubility of a phQxbased polymer by introducing alkyl side chains into the thiophene-linker units between the phQx acceptor and the benzo[1,2-b:4,5-b']dithiophene (BDT) donor unit.²¹ In this study, we synthesized a new soluble phQx unit by introducing four branched alkoxy side chains into the two fused phenyl rings of the phQx unit, then polymerized this unit with a alkylthienyl benzo[1,2-b:4,5-b']dithiophene (BDTT) donor to produce the D-A polymer PphQx. The addition of highly planar phQx groups to the polymer was expected to broaden the absorption band and enhance the carrier mobility and thus to improve the short circuit current (J_{sc}) without significant phase separation with $PC_{70}BM$ ([6,6]-phenyl C_{71} -butyric acid methyl ester). The optical, electrochemical, and photovoltaic properties of these polymers were investigated. For comparison, the tetra-alkoxy-substituted Qx-based BDTT polymer (PQx) was also synthesized with the same polymerization method.

EXPERIMENTAL

Instrumentations

¹H and ¹³C NMR spectra were recorded on Bruker ADVANCE 300 spectrometer, with tetramethylsilane as an internal reference. Elemental analysis was done by using PerkinElmer 2400 Series II CHNS/O Analyzer. The optical absorption spectra were measured by a Shimadzu UV-3100 UV-vis-NIR spectrometer. The number- and weight-average molecular weights of polymers were determined by gel permeation chromatography (GPC) on Viscotek T60A instrument, using chloroform as eluent and polystyrene as standard. The differential scanning calorimetry (DSC) was measured by using a TA Q100 instrument and operated under nitrogen atmosphere. Cyclic voltammetry was performed on an AUTOLAB/PG-STAT12 model system with a three-electrode cell in a solution of Bu₄NPF₆ (0.10 M) in acetonitrile at a scan rate of

50 mV/s. Polymer film coatings on ITO anode electrode were formed by spin-coating method.

Fabrication of the Organic Solar Cells

The devices were fabricated with the structure ITO/ PEDOT:PSS/polymer:PC70BM/Ca/Al. The PEDOT:PSS layer was spin-coated onto each ITO anode from a solution purchased from Heraeus (CleviosTM P VP AI4083) and baked for 20 min at 140 °C in glove box. Each polymer:PC70BM solution was then spin-coated onto the PEDOT:PSS layer. The polymer solution for spin-coating was prepared by dissolving the polymer (1 wt %) in chlorobenzene. Preannealing was not carried out. LiF and aluminum contacts were formed by vacuum deposition at pressures below 3×10^{-6} torr, providing an active area of 0.09 cm². Solar cell efficiencies were characterized under simulated 100 mW/cm² AM 1.5G irradiation from a Xe arc lamp with an AM 1.5 global filter. Simulator irradiance was characterized using a calibrated spectrometer, and the illumination intensity was set using an NREL certified silicon diode with an integrated KG1 optical filter. The EQE was measured by underfilling the device are a using a reflective microscope objective to focus the light output from a 100 W halogen lamp outfitted with a monochromator and optical chopper; the photocurrent was measured using a lock-in amplifier, and the absolute photon flux was determined using a calibrated silicon photodiode. All device fabrication procedures and measurements were carried out in air at room temperature.

Fabrication of Hole-Only Devices

The hole mobilities of the PQx1 and PQx2 films were determined by employing the space-charge limited current (SCLC) model to the J–V measurement of the device. The hole only devices were fabricated with the structure ITO/PEDOT:PSS/ polymers/Au. The hole mobilities of the fabricated devices were calculated from the SCLC by the following equation: JOURNAL OF Polymer



SCHEME 2 Synthetic routes for PQx and PphQx.

$$J_{\rm SCLC} = (9/8) e_{\rm r} e_0 \mu (V^2/L^3)$$

where e_r is the dielectric constant of the polymer layer, e_0 is permittivity of free space, μ is the SCLC mobility, *L* is the distance between the cathode and anode, which is equivalent to the film thickness, and *V* is the applied voltage.

Materials

See Supporting Information.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Monomers and Polymers

The synthetic routes for the monomers and polymers are shown in Schemes 1 and 2. As shown in Scheme 1, a branched alkyl group (3,7-dimethyloctyloxy) were introduced at the 3,4-positions of the two phenyl rings in the phQx unit to enhance the solubility of the D-A polymers. PQx and PphQx were obtained via Stille coupling reactions between compounds **12** and **11** and compounds **12** and **8**, respectively (Scheme 2). The weight average molecular weights

TABLE 1 Molecular Weights and Thermal Properties of the Synthesized Polymers

Polymers	<i>M</i> _n (g/mol)	<i>M</i> _w (g/mol)	Ð	Td _(5%) (°C) ^a
PQx	25.1K	66.9K	2.6	402
PphQx	23.2K	66.1K	2.6	416

^a Decomposition temperature at 5% weight loss.



 (M_w) of PQx and PphQx were determined by performing gel permeation chromatography (GPC) with a polystyrene standard in chloroform eluent, and were found to be 66.9 kDa (D = 2.6) and 66.1 kDa (D = 2.6), respectively. The synthesized polymers readily dissolve in chlorinated organic solvents such as chloroform and chlorobenzene and form good uniform thin films. The introduction of the 3,7-dimethyloctyl substituent was found to be sufficient to impart the required solubility to the polymers in these solvents. Thermal analysis of the polymers was conducted with thermogravimetric analysis (TGA), as shown in Supporting Information Figure S1. PQx and PphQx were found to exhibit sufficiently high decomposition temperatures ($T_{d(5\%)}$), 402 and 416 °C, respectively; PphQx is more thermally stable than PQx. The polymerization results for the synthesized polymers are summarized in Table 1.

Optical and Electrochemical Properties

The UV-visible absorption spectra of PQx and PphQx in dilute chloroform solutions and in thin films are shown in Figure 1; the absorption data for the polymers are summarized in Table 2. The UV-visible spectrum of the PQx thin film has two λ_{max} at 436 and 585 nm, and those of the PphQx thin film are at 443 and 593 nm, which is a common feature of donor-acceptor-type polymers.^{22,23}

The absorption peaks at the shorter wavelengths probably originate from the $\pi - \pi^*$ transitions of the polymer backbones, whereas the absorption bands at the longer wavelengths are probably due to ICT between the donor-acceptor molecules.^{24,25} The absorption bands of PphQx are red-

3



FIGURE 1 Normalized UV-visible absorption spectra of PQx and PphQx in (a) $CHCl_3$ solution and (b) thin films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shifted with respect to those of PQx for both the solution and thin film states because PphQx has a more planar geometry than PQx. The effect of the planar structure of the phQx units on the effective conjugation length of PphQx is greater than that of the Qx units on PQx, and this planarity also improves the strong interchain interactions of the PphQx backbone, and thus leads to a red-shift in its absorption bands. This result is consistent with those of other studies of phQx-based polymers.^{15–17} Further, the absorption intensity of PQx at 580 nm is higher than that of the short wavelength band (420 nm) in the thin film state, whereas the opposite trend was found for the absorption intensities of PphQx. This result suggests that the phQx accepting groups interfere more with the ICT between the D-A units in PphQx than is the case for the Qx groups in PQx. This difference is not yet well understood, but we suggest that it originates in the difference between the electron pulling abilities of the Qx and phQx groups.

The UV-visible absorption coefficients and photoluminescence spectra of the polymers are shown in Figure 2. The absorption coefficients and photoluminescence measurements were obtained from the same solution samples (chloroform solvent, 5×10^{-4} M), and the polymer solutions were excited at the λ_{max} of PQx and PphQx (559 nm for PQx, 570 nm for PphQx). The values of the absorption coefficients (α) of PQx and PphQx are similar because they have similar chromophore densities. The photoluminescence (PL) emission peaks of the PQx and PphQx solutions were found to be at 654 and 691 nm, respectively, as expected from their UVvisible spectra. Note that the PL intensity of PphQx is significantly lower than that of PQx; it is possible that the strong intermolecular interactions resulting from the introduction of the planar phQx units increase the PL quenching.^{26,27}

The HOMO levels of the polymer films were determined from cyclic voltammetry (CV) measurements by using the equation $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8)$ eV, where E_{ox} is the onset oxidation potential relative to the ferrocene external standard (Supporting Information Fig. S2).²⁸ The HOMO energy levels of PQx and PphQx are -5.40 and -5.40 eV, respectively. The optical band-gaps of the polymers were calculated from the absorption onsets of the polymers: PQx and PphQx have medium band-gaps of 1.82 and 1.75 eV, respectively. The calculated lowest unoccupied molecular orbital (LUMO) levels of the PQx and PphQx thin films were found to be -3.58and -3.64 eV, respectively, which are higher (by ~ 0.4 eV) than the value obtained for the acceptor PC₇₀BM ([6,6]-phenyl C_{71} -butyric acid methyl ester) (-4.30 eV) and suggest that the charge transfer from the two polymers to PC70BM should be facile. The optical and electrochemical properties of the polymers are summarized in Table 2.

Theoretical Calculations

The molecular structures of PQx and PphQx were optimized by using density functional theory (DFT) calculations. The electronic structures were modeled with density functional theory and the Gaussian 09 program at the B3LYP/6-31(G) level of theory.²⁹ To simplify the calculations, the 2ethylhexyl and 3,7-dimethyloctyl groups were replaced with methyl groups, and one repeating unit of each polymer was subjected to the calculations. Figure 3 shows the electron density distributions across the HOMO and LUMO, which were estimated from the results for one repeat unit. The

TABLE 2 Optical and Electrochemical Properties of POx and PphOx

Polymers	Solution (λ_{max} , nm)	Film (λ _{max} , nm)	E _g (eV) ^a	E _{HOMO} (eV)	E _{LUMO} (eV) ^b
PQx	426, 559	436, 587	1.82	-5.40	-3.58
PphQx	435, 570	443, 594	1.75	-5.40	-3.64

 $^{\rm a}$ Estimated from the onset of the absorption of the thin solid film $(E_{\rm g}=1240/\lambda_{\rm onset}).$

 $^{\rm b}$ Calculated from the optical band-gap energy. Values of the PphQx solar cell devices are higher.

JOURNAL OF POLYMER SCIENCE Chemistry



FIGURE 2 UV-visible absorption coefficients and PL intensities of polymers in chloroform solution at 5×10^{-4} M. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electron density distributions of the HOMO orbitals for the two polymers are delocalized along the polymer backbone, and the electron density of the LUMO is mainly located in the electron-accepting units (Qx for PQx and phQx for PphQx), which indicates that strong ICT states are possible in these D-A polymers. Furthermore, PQx is estimated to be a twisted structure from high dihedral angles (A1 = 40.6°, A2 = 36.6°) between phenyl rings and Qx. This distorted conformation of PQx is expected to disrupt the close-packing of



FIGURE 4 J-V characteristics of the (a) PQx/PC₇₀BM and (b) PphQx/PC₇₀BM devices. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the polymer chains, leading the blue-shift of absorption peak for PQx with respect to PphQx.

Space-Charge Limited Current Characteristics

We measured the hole mobilities of the polymer thin films by using the space-charge limited current (SCLC) method to characterize the vertical carrier transport properties of the organic photovoltaic (OPV) devices. To obtain the SCLC



FIGURE 3 Theoretical results for the model compounds: (a) chemical structures and (b) electron distributions of the HOMO/LUMO frontier orbitals. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Materials

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Polymer	Blend ratio	V _{oc} (V)	J _{sc} ₍ mA/cm²)	FF (%)	PCE (%)
PQx	1: 1	0.84	8.59	0.47	3.40 (3.36)
	1: 2	0.85	8.96	0.52	3.97 (3.92) ⁸
PphQx	1: 1	0.82	11.38	0.49	4.62 (4.59)

10.85

0.58

5.03 (4.98)^a

TABLE 3 Photovoltaic Properties of the Polymer/PC₇₀BM

 Devices

0.80

^a Average PCE value for five devices.

1:2

curves, hole-only devices were fabricated with the structure ITO/PEDOT:PSS/polymer/Au and the mobilities were calculated with the Mott-Gurney equation.³⁰ The voltage-current density curves of the fabricated hole-only devices are shown in Supporting Information Figure S3. The measured SCLC mobilities of the PQx and PphQx films were found to be 5.0 $\times 10^{-5}$ and 2.2 $\times 10^{-4}$ cm²/Vs, respectively.

The mobility of PphQx is slightly higher than that of PQx, which suggests that the polymer chain packing in PphQx is better than that in PQx.

Properties of the Photovoltaic Devices

PSCs were fabricated with the layered structure ITO/ PEDOT:PSS (60 nm)/polymer:PC₇₀BM (80 nm)/Ca/Al (100 nm). Figure 4 shows the *J*–*V* curves of the PSCs, and their photovoltaic parameters are summarized in Table 3.

The PCEs of the PQx and PphQx devices were found to be 3.97 and 5.03%, respectively, for a polymer:PC₇₀BM blend ratio of 1:2. The main difference between the PQx and PphQx devices was found in the short circuit current density (J_{sc}). Moreover, regardless of the blend ratio, the PphQx devices always exhibit higher J_{sc} values than the PQx devices. The J_{sc} values of PSCs are affected by many factors, including the light absorption of the active layer, the band-gap, the car-



FIGURE 6 External quantum efficiencies of the (a) $POx/PC_{70}BM$ and (b) PphQx/PC₇₀BM blend films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

rier mobility, and the active layer film formation properties. Given the optical band-gaps and hole mobilities of the polymers, the PphQx devices were expected to exhibit higher $J_{\rm sc}$ values than the PQx devices. The light absorption bandwidth and the hole mobility of PphQx (1.75 eV, 2.2 × 10⁻⁴ cm²V⁻¹s⁻¹) are slightly larger than those of PQx (1.82 eV, 5.0×10^{-5} cm²V⁻¹s⁻¹), which means that the $J_{\rm sc}$ and PCE.

To better understand the differences between the photovoltaic performances of the PSCs, AFM images of the surface morphologies of each solar cell device were obtained (Fig. 5). In general, nanoscale phase separation is required to overcome the short exciton diffusion lengths (\sim 10 nm) of donor polymers and provide efficient charge separation.³¹ The root-mean-square (RMS) roughnesses of the PQx:PC₇₀BM (1:2) and PphQx: PC₇₀BM (1:2) films were found to be 6.2 and 1.2 nm, respectively. Moreover, the phase separation in the PphQx:PC₇₀BM film is less than that in the



FIGURE 5 AFM tapping-mode height images of (a) POx/PC₇₀BM (1:2) and PphQx/PC₇₀BM (1:2). Scan size is $2 \times 2 \mu m$.

PQx blend film (Fig. 5). A smaller phase separation increases the total area for charge separation between the donor polymer and the PCBM acceptor, and leads to a higher photocurrent and a higher efficiency. Relatively high levels of phase separation are evident in the $PQx:PC_{70}BM$ blend film, which is likely to decrease the photocurrent density.

The EQE values of the PQx and PphQx solar cell devices were measured to evaluate their photo-responses as a function of wavelength, and are shown in Figure 6. The PQx and PphQx devices yield EQE plots that are similar to their UV-visible absorption spectra, which indicate that their excitons are mainly generated in the polymer phase (Fig. 1). The J_{sc} values calculated by integrating the EQE curves were found to be within 10% of the corresponding J_{sc} values obtained from the J-V curves. The spectral response of the PQx:PCBM (1:2) device shows that photons with wavelengths in the range 350–800 nm contribute significantly to the EQE, with a maximum EQE of 50% at 500 nm. The PphQx:PCBM (1:2) device exhibits a similar spectral response in the range 350–800 nm; however, a maximum EQE of 62% was obtained at 400 nm, which results in a much higher J_{sc} .

CONCLUSIONS

In conclusion, we have synthesized and characterized a new phQx-based D-A polymer. We found that the soluble phQx units in the polymer play a crucial role in its absorption spectra, energy levels, charge transport, blend film morphologies, and photovoltaic properties. Our preliminary results indicate that the tetra-alkoxy-substituted phQx acceptor unit has significant potential as a new building block for conjugated polymers for OPVs.

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