This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Pyrazino[2,3-g]quinoxaline-2,7-dione based π-conjugated polymers with affinity towards acids and semiconductor performance in organic thin film transistors

Jesse Quinn, Chang Guo, Lewis Ko, Bin Sun, Yinghui He and Yuning Li*

Pyrazino[2,3-g]quinoxaline-2,7-dione (PQx) was used as a building block for π-conjugated polymer semiconductors, which demonstrated a strong acid affinity by showing marked bathochromic shifts in their absorption spectra. These polymers exhibited semiconductor performance in organic thin film transistors (OTFTs). Copolymers of PQx and bithiophene exhibited electron-dominant ambipolar transport characteristics with electron mobilities of up to $4.28 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ and hole mobilities of up to $5.22 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ while copolymers of PQx and thiolo[3,2-b]thiophene exhibited hole-dominant ambipolar transport characteristics with hole mobilities of up to $4.82 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ and electron mobilities of up to $3.95 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$.

Introduction

Organic electronics have made great strides in recent decades. Certain characteristics of organic electronic devices such as flexibility and low-cost manufacturing make them ideal candidates for niche applications such as radio-frequency identification (RFID) tags, flexible displays, memory devices and sensors. Organic thin film transistors (OTFTs) have been extensively studied as essential components to integrated circuits (ICs), backplanes for displays, memory devices, and as chemosensors.  

Through rational structural design and optimization, polymer semiconductors based on the amide/imide-containing building blocks such as naphthalene diimide (NDI) and derivatives, diketopyrrolopyrrole (DPP), isoindigo (IID) and (3,7,8,9-tetraoxo-3,7-bis(2-oxoindolin-3-ylidene)benzo[1,2-b;4,5-b']difuran-2,6(3H,7H)-dione (IBDF) have exhibited high carrier mobilities in OTFTs. A recent work demonstrated that an OTFT sensor with an IID based-polymer showed promising sensitivity to heavy metals in both freshwater and saltwater, demonstrating the excellent environmental stability of amide/imide building blocks that are essential for sensor applications. 

Previously, we introduced an imide-containing building block, pyrimido[4,5-g]quinoxaline-4,9-dione (PQ, Fig. 1), for polymer semiconductors, which showed hole transport characteristics in OTFTs and strong response towards acids. However, the backbones of these polymers are not very coplanar due to the steric repulsion between the N-alkyl side chains on the PQ unit and the neighbouring thiophene units, which would hamper the charge transport along the polymer backbone and through the interchain π-π stacks. In this study, we report an isomer of PQ, pyrazino[2,3-g]quinoxaline-2,7-dione (PQx, Fig. 1), which places the N-alkyl substituents at a greater distance from the neighbouring thiophene units, achieving a highly coplanar polymer backbone. Quinoxalin-2(1H)-one or pyrazinimine (a half of the PQx structure) derivatives have been reported as candidates suitable as antitumor, antimicrobial, and antithrombotic agents. For this reason, it is expected that PQx-based polymers may also exhibit activities towards various chemical and biological analytes allowing for applications as OTFT based chemo- and bio-sensors.

Results and discussion

To the best of our knowledge, synthesis of the PQx moiety was only reported in one paper in 1970, where benzene-1,2,4,5-tetraamine and arylenediglyoxylates were condensed to form polymeric materials. Due to the extremely low solubility of these polymers, no definite structural assignments were made. In this study, a similar synthetic procedure for the synthesis of quinoxalin-2(1H)-one compounds is followed to synthesize the target 3,8-di(thiophen-2-yl)-1,6-dihydropyrazino[2,3-g]quinoxaline-2,7-dione (PQx2T-H) from 1,2,4,5-
benzenetramine tetrahydrochloride and 2-thiophene glyoxylic acid (Scheme 1). A similar amount of the isomeric by-product, iso-PQx2T-H, is expected to form during the reaction. However, the crude product mixture is insoluble in any solvents and thus was used for the next step without further purification. Alkylation of the crude PQx2T-H was conducted using 11- (bromo-methyl)tricosane in the presence of K₂CO₃ in DMF at 130 °C to afford PQx2T-24 in 9% yield. The alkylated by-product, iso-PQx2T-24, was probably produced based on the thin layer chromatography (TLC) analysis. However, this by-product could not be isolated from other impurities. Next, PQx2T-24 was brominated with N-bromosuccinimide (NBS) to obtain PQx2T-Br-24 in 64% yield. Polymers PQx2T-BT-24 and PQx2T-TT-24 were synthesized via Stille coupling polymerization of PQx2T-Br-24 with 2,5-bis(trimethylstanny)-2,2'-bithiophene and 2,5-bis(trimethylstanny)thieno[3,2-b]thiophene, respectively, and purified using Soxhlet extraction. Most of PQx2T-BT-24 (68%) was dissolved in refluxing chloroform, while 22% of this polymer was obtained by using 1,1,2,2-tetrachloroethane. Only the fraction extracted by chloroform was used for characterization. PQx2T-TT-24 showed much better solubility with 97% of it being extracted with chloroform. The number average molecular weight (Mn) and polydispersity index (PDI) were measured to be 24.6 kg mol⁻¹ and 7.86 for PQx2T-BT-24 and 14.4 kg mol⁻¹ and 2.05 for PQx2T-TT-24, respectively (ESI†). Data were obtained using high-temperature gel-permeation chromatography (HT-GPC) at 140 °C with 1,2,4-trichlorobenzene as an eluent and polystyrene as standards. The GPC trace for PQx2T-BT-24 appears to be a monomodal distribution, which might be due to the aggregation of polymer chains that have been often observed for conjugated polymers.36-40 As mentioned previously, PQx2T-BT-24 showed much poorer solubility than PQx2T-TT-24, indicating a stronger aggregation tendency of the former. The thermal stability of these polymers was characterized using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC, ESI†). PQx2T-BT-24 showed good thermal stability with a 5% weight loss temperature (T₅%) at 325 °C, while PQx2T-TT-24 showed slightly higher thermal stability with a T₅% at 332 °C. No noticeable endo- or exothermic transitions were observed on their differential scanning calorimetry (DSC) diagrams (ESI†).

A computational study was conducted using the density functional theory (DFT) with the D3LYP/6-31G(d) level of theory under tight convergence to investigate the geometry, molecular energy levels, and electron distributions of a simple 2,7-dithienyl-substituted PQx molecule, PQx2T-Me (Fig. 2). The optimized geometry results revealed that the PQx unit is coplanar and there is no twisting between the flanking thiophenes and the PQx unit. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) wavefunctions are evenly distributed throughout the molecule. The LUMO and HOMO energy levels of PQx2T-Me were calculated to be -2.75 eV and -5.53 eV, respectively. The LUMO energy level of PQx2T-Me is much lower than that of PQ2T-Me (-1.97 eV), indicating PQx is a stronger electron acceptor than PQ. To investigate the polymer geometry and molecular energy levels, the dimer of PQx2T-BT-Me and PQx2T-TT-Me were simulated (ESI†). The LUMO and HOMO energy levels were calculated to be 2.95 eV and 4.90 eV for PQx2T BT Me and -2.99 eV and -4.96 eV for PQx2T TT-Me, respectively. For both PQx2T BT Me and PQx2T TT Me, the LUMO wavefunctions are evenly distributed across the dimer. However, the HOMO wavefunctions appear largely distributed on the thiophene and thienothiophene moieties and only slightly scattered on the PQx moiety. The results suggest that the HOMO energy levels for both dimers are mostly influenced by the thiophene and/or thienothiophene units. The dihedral angles between the PQx unit and thiophene units in PQx2T-BT-Me were < 1°. However, greater twisting was observed between thiophene units with dihedral angles ranging from 6 to 8°. PQx2T-TT-Me was nearly coplanar with dihedral angles < 1° throughout the thiophene and thienothiophene units.
The surface morphology of the polymer thin films was characterized with atomic force microscopy (AFM) (Fig. 3). The polymer thin films were prepared under the same conditions as those used for the OTFT devices. In the AFM images of the PPQx2T-BT24 films annealed at 100, 150 and 200 °C, smooth surfaces with a low root mean squared roughness (Rq) of 0.5 nm were observed with very little difference. At 250 °C, the polymer thin film appears rougher with an increase of Rq to 1.1 nm. Under scrutiny, all PPQx2T-BT24 films are comprised of tiny grains, which is in agreement with its poor crystallinity verified by the X-ray diffractometry (XRD) (see below). On the other hand, the 100 °C-annealed PPQx2T-TT24 film shows distinct worm-like grains, indicative of its higher crystallinity. With increasing annealing temperature, the worm-like grains disappeared and pinholes formed concurrently. Layered structures comprising large pinholes are observed for the 250 °C-annealed film, which might cause the degraded OTFT performance at this annealing temperature.

The polymer thin films, which were prepared similarly as those for the OTFTs and AFM measurement, were subject to XRD measurement to study their crystallinity and molecular organization (ESI†). At all annealing temperatures (100, 150, 200 and 250 °C), PPQx2T-BT24 thin films showed no obvious diffraction peaks. In contrast, PPQx2T-TT24 thin film annealed at 100 °C exhibited a clear primary (100) diffraction peak at 2θ = 3.68 °, which corresponds to a d-spacing distance of 2.40 nm. When the annealing temperature was increased to 150 °C, the (100) peak shifted slightly to 2θ = 4.00 ° (d-spacing = 2.21 nm) accompanied by the appearance of a secondary (200) diffraction peak at 2θ = 7.84 °, indicating that long range ordering formed. At an annealing temperature of 200 °C, the intensity of both (100) and (200) peaks further increased and shifted to 2θ = 3.92 ° (d-spacing = 2.25 nm) and 2θ = 7.72 °, respectively. Further increasing the annealing temperature to 250 °C resulted in a decrease of intensity for the (100) peak and a decrease in the d-spacing to 2.21 nm (2θ = 4.00 °). However, the (200) peak became stronger and a tertiary (300) diffraction peak at 2θ = 11.52 ° can be seen. Transmission XRD measurements were also performed using polymer flakes (ESI†). PPQx2T-BT24 and PPQx2T-TT24 showed strong (100) peaks at 2θ = 3.31 ° and 3.63 °, which correspond to the inter-lamellar distances of 2.67 nm and 2.43 nm, respectively. The hump centred at 2θ = 23.58 ° observed for PPQx2T-BT24 could be assigned to the (10) peak originating from the co-facial π-π distance of adjacent polymer backbones, which was calculated to be 0.38 nm. In comparison, a much stronger (010) peak was observed for PPQx2T-TT24 at 2θ = 25.39 ° corresponding to a π-π distance of 0.35 nm. Thus, the higher crystallinity and a shorter π-π distance could be accounted for the higher charge mobility observed for PPQx2T-TT24. The higher crystallinity and a shorter π-π distance of PPQx2T-TT24 would be beneficial for efficient charge transport of this polymer.
The frontier energy levels of these polymers were determined from the oxidation and reduction onset potentials on their thin film cyclic voltammetry (CV) (ESI†). The HOMO and LUMO energy levels of PPQx2T-BT-24 are -5.54 eV and -3.59 eV, respectively. PPQx2T-TT-24 has a same HOMO energy level of -5.54 eV, but a slightly higher LUMO energy level of -3.52 eV. The electrochemical band gaps are thus 1.95 eV for PPQx2T-BT-24 and 2.01 eV for PPQx2T-TT-24. The greater electrochemical band gaps than the optical bandgaps are possibly caused by the large exciton binding energy that is typical of π-conjugated polymers.22

The UV-Vis-NIR absorption properties of PPQx2T-BT-24 and PPQx2T-TT-24 in chloroform and in thin films are shown in Fig. 4. In solution, PPQx2T-BT-24 showed a broad featureless absorption profile with the maximum absorption wavelength (λmax) to be 600 nm while a similar absorption profile and λmax of 598 nm were observed with the film. PPQx2T-TT-24 showed clearly two major peaks in both solution and film absorption profiles. The λmax in solution appeared at 627 nm along with a slightly weaker peak at 582 nm. From solution to film, positions of these two peaks (at 632 nm and 576 nm) changed very little. The optical band gaps of PPQx2T-BT-24 and PPQx2T-TT-24 calculated from the onset absorption wavelengths of their thin films are ~1.66 eV and ~1.82 eV, respectively. Compared to its analogous PQ polymer PPQ2T-BT-24, which has an optical band gap of 2.03 eV, PPQx2T-BT-24 has a much narrower band gap because PQx is a stronger electron acceptor than PQ, which resulted in more efficient intramolecular donor-to-acceptor charge transfer, and a more coplanar backbone.

As with PQ-based polymers,28 the basic 1,6-pyridyl nitrogen atoms of PQx are expected to allow the PQx-based polymers to interact strongly with acids. Similar behaviour has been reported for conjugated polymers and small molecules incorporating pyridine moieties43,44 and benzothiadiazoles.45–51 In contrast, azulene-based conjugated polymers and small molecules, which
do not contain a basic site, have also shown noteworthy responses to various acids. In all cases reversible bathochromic shifts in the absorption maxima occur with some cases reaching near infrared (NIR). To elucidate the acid effects of these PQx polymers, trifluoroacetic acid (TFA), which has a $pK_a$ of -0.25, was first tested. As shown in Fig. 5A, PPQx2T2BT24 exhibited a slight decrease in absorbance at a TFA concentration as low as 1 mM. With increasing TFA concentration, the $\lambda_{\text{max}}$ bathochromically shifted and the long wavelength tail intensified. At 500 mM TFA, the $\lambda_{\text{max}}$ appeared at ~840 nm. Further increasing the TFA concentration caused a bathochromic shift in the new $\lambda_{\text{max}}$ peak. At 2 M TFA, near the solubility limit for TFA in chlorobenzene, very little spectral change occurred and a largest solubility limit for TFA in chlorobenzene, very little spectral change occurred and a largest $\lambda_{\text{max}}$ of 846 nm was reached, which corresponds to a bathochromic shift of 246 nm from that of the solution without TFA. In the case of PPQx2T2TT24, a slight decrease in absorption also started at 1 mM TFA (Fig. 5B). A new $\lambda_{\text{max}}$ peak appeared at ~780 nm, similar to PPQx2T2BT24, but at a lower TFA concentration (50 mM) and a shorter wavelength. This new $\lambda_{\text{max}}$ peak bathochromically shifted up to 804 nm at 100 mM TFA. Surprisingly, the peak at 804 nm disappeared and a very intense peak appeared at ~900 nm as the TFA concentration increased to 500 mM. At 2 M TFA, the $\lambda_{\text{max}}$ shifted to 914 nm, which corresponds to a bathochromic shift of 287 nm from that of the solution without TFA.

The effect of boron tribromide (BBr3), a strong Lewis acid, on the absorption spectra of PPQx2T2BT24 (Fig. 5C) and PPQx2T2TT24 (Fig. 5D) was also studied. Both polymers at a BBr3 concentration of 1 µM show absorption spectra similar to those observed for TFA at a concentration of 50 mM, indicating a much stronger interaction of BBr3 with both polymers than that of TFA. At a BBr3 concentration of 4 µM, PPQx2T2BT24 bathochromically shifted with a $\lambda_{\text{max}}$ of 621 nm accompanied by the appearance of a strong absorption peak at 796 nm, which appears to be similar to that observed in the TFA solution at 500 mM. At a BBr3 concentration beyond 4 µM, precipitates formed, which are assumed to be the polymer-BBr3 complexes. For PPQx2T2TT24, at a BBr3 concentration of 6 µM, which is the maximum BBr3 concentration without formation of precipitates, the $\lambda_{\text{max}}$ bathochromically shifted to 846 nm, which is comparable to that observed for the TFA solution at 500 mM. In either case, with the addition of pyridine the original spectra of the pristine polymers could be completely recovered (Fig. 5C and D).

To reveal if the polymers have amplified sensitivity towards acids, the UV-Vis-NIR spectra of the monomer compound PQx2T24 solutions with various concentrations of TFA were measured. PQx2T24 showed a significant change at 25 mM TFA (Fig. 6). At 50 mM TFA, a broad featureless absorption peak with a $\lambda_{\text{max}}$ of 516 nm was observed. There was little change as the TFA concentration was increased up to 100 mM. With a higher TFA concentration of 1 M, three well-defined peaks at 473 nm, 505 nm, and 542 nm ($\lambda_{\text{max}}$) appeared. Further increasing the TFA concentration to 2 M, the absorption profile remained the same, but the overall intensity increased. The overall bathochromic shift from the absence of TFA to 2 M of TFA is ~88 nm. PPQx2T2TT24 clearly demonstrates an amplification effect since this polymer exhibited a dramatic spectra change at a much lower TFA concentration of ~1-5 mM than PQx2T2BT24. On the other hand, it appears that PPQx2T2BT24 has a similar sensitivity to TFA (at ~10-50 mM) compared to PQx2T2BT24. The reason for the dramatically different responses to acids observed for these two polymers is unclear. The basicity of the 1,6-nitrogen atoms in PQx in these two polymer should be similar because they have similar HOMO energy levels. As aforementioned, PPQx2T2BT24 might form chain aggregates in solution, which would hinder the access of TFA molecules to the polymer chains inside the aggregates, resulting in the low sensitivity of this polymer.

PPQx2T2BT24 and PPQx2T2TT24 were evaluated as channel semiconductors in bottom-gate, bottom-contact (BGBC) OTFT devices fabricated on dodecyltrichlorosilane (DDTS) modified SiO2/Si wafer substrates. Both polymers showed ambipolar charge transport characteristics with PPQx2T2BT24 being electron-dominant and PPQx2T2TT24 being hole-dominant (Fig. 7, Fig. S22, and Table S1). The electron-dominant transport behaviour of PPQx2T2BT24 is most likely due to its slightly lower LUMO energy level than that of PPQx2T2TT24, which facilitated electron injection and stabilized electron transport. For devices based on PPQx2T2BT24, the best performance was observed at 200 °C with the highest hole mobility of $5.22 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ (5.04 $\times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ in average) and the highest electron mobility of $4.28 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ (3.97 $\times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ in average). At a higher annealing temperature of 250 °C, both hole and electron mobilities decreased. For PPQx2T2TT24, the highest hole mobility of $4.82 \times 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$ (3.79 $\times 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$ in average) and the highest electron mobility of $3.95 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ (3.12 $\times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ in average) were achieved also at the annealing temperature of 200 °C. The electron transport characteristics of devices with PPQx2T2TT24 started to appear.
Fig. 7 Output (A) and transfer (B) curves of OTFT devices with PPQx2T5BT524 thin films annealed at 200 °C. Likewise, the output and transfer curves (C) of OTFT devices with PPQx2T5TT524 thin films annealed at 200 °C. Device dimensions: channel width ($W$) = 1000 µm; channel length ($L$) = 30 µm.

Conclusions

We report two polymers, PPQx2T5-BT-24 and PPQx2T5-TT-24, based on the new building block, pyrazino[2,3-g]quinoxaline-2,7-dione (PQx). These polymers showed dramatic bathochromic shifts in their UV-Vis-NIR absorption spectra in the presence of trifluoroacetic acid and the Lewis acid boron tribromide. In OTFTs, PPQx2T5-BT-24 exhibited electron-dominant ambipolar transport characteristics with hole mobilities of up to $4.82 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ and electron mobilities of up to $3.95 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$. Our preliminary results demonstrate that PQx is a promising new building block for polymer semiconductors for OTFTs that can be used for chemical and bio-sensors.

Experimental

Materials and Instrumentation

All chemicals were purchased from commercial sources and used without further purification. 11-(Bromomethyl)tricosane (C$_{24}$-Br) was synthesized using a method previously reported.$^{55}$ GPC measurements were performed on a Malvern SEC system using 1,2,4-trichlorobenzene as eluent and polystyrene as standards at 140 °C. TGA measurements were carried out on a TA Instruments Q500 at a temperature ramping rate of 10 °C min$^{-1}$ under nitrogen. DSC measurements were carried out on a TA Instruments Q2000 at a temperature ramping rate of 20 °C min$^{-1}$ under nitrogen. UV-Vis-NIR absorption spectra were obtained on a Thermo Scientific GENESYS™ 10S VIS spectrophotometer. Polymer solutions containing an acid were prepared by adding an intended amount of acid (TFA or BB$_3$) in chlorobenzene under nitrogen. The molar concentration of the pyrazino[2,3-g]quinoxaline-2,7-dione (PQx) units of the polymer was kept at ~$1 \times 10^{-5}$ M. CV experiments were carried out on a CHI600E electrochemical analyser using an Ag/AgCl reference electrode and two Pt disk electrodes as the working and counter electrodes in a 0.1 M tetrabutylammonium hexafluorophosphate solution in anhydrous acetonitrile at a scan rate of 50 mV s$^{-1}$. Ferrocene was used as the reference, which has a HOMO energy level of -4.8 eV.$^{56}$ NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer with chemical shifts relative to the residual chloroform in the deuterated solvent (7.26 ppm for $^1$H NMR and 77 ppm for $^{13}$C NMR). Reflection XRD diagrams of polymer thin films (~40 nm) spin-coated on dodecyltrichlorosilane-modified SiO$_2$/Si substrates and annealed at 100, 150, 200, and 250 °C for 30 min in nitrogen were obtained using a Bruker D8 Advance powder diffractometer with Cu K$\alpha$ radiation ($\lambda = 0.15406$ nm). Transmission XRD measurements were carried out on a Bruker Smart 6000 CCD 3-circle D8 diffractometer with a Cu K$\alpha$ (Rigaku) X-ray source ($\lambda = 0.15406$ nm) using polymer flakes stacked between two Mylar film substrates. AFM images were taken on polymer thin films spin-coated on the dodecyltrichlorosilane modified SiO$_2$/Si substrates with a Dimension 3100 scanning probe microscope. DFT calculations through Gaussian 09 Revision D.01$^{57}$ using the B3LYP/6-31G(d) level of theory under tight convergence were conducted to investigate the geometry, molecular energy levels, and electron distributions for the model compounds.

Synthesis of 3,8-di((thiophen-2-yl)-1,6-dihydropyrazino[2,3-g]quinoxaline-2,7-dione (PQx2TH)

A 100 mL two-neck round-bottom flask was charged with 1,2,4,5-benzenetetramine tetrahydrochloride (1.1 g, 3.92 mmol),
2-thiopheneglyoxylic acid (1.2 g, 7.84 mmol) and acetic acid (80 mL). The mixture was then refluxed for 16 h. Subsequently, the reaction mixture was cooled to room temperature, added to water, filtered and washed with methanol to afford a yellow/brown solid (0.84 g, 56%). Due to its poor solubility, this product was used for the next step without further purification. An isomeric by-product, iso-PQx2T5-H, is expected to form with a similar yield to that of PQx2T5-H and present in this crude product.

**Synthesis of 1,6-bis(2-decyltetradecyl)-3,8-di(thiophen-2-yl)-1,6-dihydropyrazino[2,3-g]quinoxaline-2,7-dione (PQx2T24)**

A 100 mL two-neck round-bottom flask was charged with the crude PQx2T2-H (0.81 g, 2.2 mmol) and potassium carbonate (1.49 g, 10.8 mmol) and purged with argon. N,N-Dimethylformamide (DMF) (24 mL) was added and the reaction mixture was heated to 80 °C and stirred for 1 h before 11j (bromomethyl)tricosane (4.49 g, 10.8 mmol) was added. The reaction mixture was stirred at the same temperature for an additional 48 h. After cooling, the reaction mixture was extracted with dichloromethane and the separated organic phase was washed with water. The combined organic phases were dried and the solvent was removed. The residue was purified by column chromatography using 33% dichloromethane in hexanes to give a yellow solid as the target product PQx2T24 with 2.24 g (21%) of the less soluble fraction upon removal of solvent in vacuo. Only the chloroform-extracted fraction was used for characterization. 1H-NMR spectrum is provided in ESI†.

**Synthesis of PPQx2T5BT24**

To a 25 mL Schlenk flask, PQx2T5-Br24 (101.3 mg, 0.084 mmol), 5,5′-bis(trimethylstannyl)-2,2'-bithiophene (41.3 mg, 0.084 mmol) and tri(o-tolyl)phosphine (P(o-tolyl))3 (2.1 mg, 0.007 mmol) were charged. After degassing and refilling argon three times, chlorobenzene (3 mL) and tris(dibenzylideneacetone)dipalladium (Pd(dba)) (1.5 mg, 0.002 mmol) were added. The reaction mixture was stirred at 130 °C for 72 h. Upon cooling to room temperature, the reaction mixture was poured into methanol (100 mL). The precipitate was collected by filtration and subjected to Soxhlet extraction with acetone, hexanes, and chloroform successively. Upon removal of solvent in vacuo, the chloroform extract gave 70 mg (68%) of PPQx2T5-BT24. Further extraction with 1,1,2,2-tetrachloroethane dissolved the remaining polymer, which gave 22 mg (21%) of the less soluble fraction upon removal of solvent in vacuo. Only the chloroform-extracted fraction was used for characterization. 1H-NMR spectrum is provided in ESI†.

**Fabrication and characterization of organic thin film transistors (OTFTs)**

A bottom-gate, bottom-contact (BGBC) configuration was used for all OTFT devices. The device fabrication procedure is as follows. A heavily n+-doped SiO2/Si wafer with ~300 nm-thick SiO2 was patterned with gold source and drain pairs by conventional photolithography and thermal deposition techniques. Next, the substrate was treated with Oz-plasma followed by cleaning with acetone and isopropanol via an ultrasonicating bath. Then the substrate was placed in a solution of dodecyltrichlorosilane in toluene (10 mg mL−1) at room temperature for 20 min followed by washing with toluene and drying under a nitrogen flow. Subsequently a polymer solution in chloroform (5 mg mL−1) was spin-coated onto the substrate at 3000 rpm for 60 s to give a polymer film (~40 nm), which was further subject to thermal annealing at various temperatures for 30 min in a glove box. All the OTFT devices have a channel length (L) of 30 μm and a channel width (W) of 1000 μm.
Devices were characterized in the same glove box using an Agilent B2912A Semiconductor Analyser. The hole and electron mobilities are calculated in the saturation regime according to the following equation:
\[
I_{DS} = \frac{C_{ox}}{2L} \mu (V_G - V_{th})^2
\]
where \(I_{DS}\) is the drain-source current, \(\mu\) is the charge carrier mobility, \(C_{ox}\) is the capacitance per unit area of the dielectric (11.6 \(\text{nF cm}^{-2}\)), \(W\) (1000 \(\mu\)m) and \(L\) (30 \(\mu\)m) are OTFT channel width and length, \(V_G\) is the gate voltage and \(V_{th}\) is the threshold voltage.

Acknowledgements

Financial support of this work by the Natural Sciences and Engineering Research Council (NSERC) of Canada (Discovery Grant #402566-2011) is acknowledged.

Notes and References
57 M. J. Frisch, *et al.* Gaussian 09, 2009 (see ESI for the full citation).
Graphical abstract

Pyrazino[2,3-g]quinoxaline-2,7-dione (PQx) is used as a building block for π-conjugated polymer semiconductors that demonstrate a strong acid affinity and ambipolar semiconductor performance in thin film transistors.