Poly(pyrazinoquinoxaline)s: New n-Type Conjugated Polymers That Exhibit Highly Reversible Reduction and High Electron Affinity

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Characterization

FT-IR spectra were taken on a Perkin Elmer 1720 FTIR spectrophotometer with KBr pellets. $^1$H NMR spectra were recorded on a Bruker-AV301 spectrometer at 300 MHz. Differential scanning calorimetry (DSC) analysis was performed on a TA instrument Q100 under N$_2$ at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) analysis was conducted with a TA instrument Q50 at a heating rate of 20 °C/min under a nitrogen gas flow.

UV-vis spectra were recorded on a Perkin Elmer Lambda 900 UV/VIS/NIR spectrophotometer. Photoluminescence spectra were measured on a PTI QuantaMaster model C-60/2000 spectrofluorometer (Photon Technology International Inc.). Cyclic voltammetry measurements were performed on an EG&G Princeton Applied Research Potentiostat/Galvanostat instrument (Model 273A) in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) in acetonitrile. Platinum (Pt) wire electrodes were used as both counter and working electrodes, and the Ag/Ag$^+$ electrode (Bioanalytical System, Inc.) was used as the reference. The
films of PZQP and PZQT were coated onto the Pt working electrode by dipping the Pt wire into 1.5 wt% formic acid solutions and dried under vacuum at 80 °C for 12 h.

**Computational Methods**

All of the calculations were performed on Gaussian03 by using density functional theory (DFT) B3LYP hybrid functionals with 6-31G basis set. The geometry and electronic properties were calculated for the isolated, infinite, one-dimensional polymers. The starting unit cell geometries were taken from the central part of corresponding oligomers, and then fully optimized to the equilibrium geometries inside a given lattice length on the constraints of periodic boundary conditions by assuming that the unit cell is repeated identically an infinite number of times along the translation vector. Both the lattice parameter and molecular structures were varied to locate the lowest energy position in the unit cell. Band structures were calculated along the k vector of these one-dimensional polymers with 30 k points after the optimization using the same level of theory. The lowest 4 unoccupied and highest 4 occupied bands in the first Brillouin zone were plotted. All the computed polymer orbital energies were directly used without further shifting or scaling. The effective masses were calculated at the top of the valence band and the bottom of the conduction band for all polymers.
Figure S1. FT-IR spectra of (a) PZQP (2a) and (b) PZQT (2b).
Figure S2. $^1$H NMR spectra of (a) PZQP (2a) and (b) PZQT (2b) in trifluoroacetic acid-d.
Figure S3. TGA thermograms of PZQP and PZQT.

Figure S4. Oxidation cyclic voltammograms of PZQP and PZQT thin films in TBAPF$_6$/acetonitrile.
Figure S5. Calculated band structures of (a) PZQP (2a), (b) PZQT (2b), (c) PZQP(5,10) (3a), and (d) PZQT(5,10) (3b).