

**Quinoidal Oligoquinoline: A Novel Quinodimethane Exhibiting High
Electroluminescence Efficiency and p-Channel Field Effect Charge Transport**

Christopher J. Tonzola, Jessica M. Hancock, Amit Babel and Samson A. Jenekhe

Department of Chemical Engineering and Department of Chemistry, University of
Washington, Seattle, Washington 98195-1750, U. S. A.

Single Crystal Structure. Single crystals of **5** suitable for the determination of X-ray crystal structure were grown by slow evaporation of CHCl₃/methanol solution. **5** was obtained as white needles and was found to have a monoclinic crystal with unit cell parameters: $a = 17.7390(7)$ Å, $b = 5.9890(2)$ Å, $c = 25.1160(10)$ Å, and $\beta = 120.6770(16)$. The space group was P c. The structure was refined to a final residual of $R_1 = 6.77\%$.

Materials. All reagents were purchased from Aldrich and used as received.

6,6'-Bis(2-(diphenylmethylene)-4-phenylquinoline) (5). 0.507 g (2.42 mmol) of 1,1-diphenylacetone (**3**), 0.475 g (1.21 mmol) of 3,3'-dibenzoylbenzidine (**4**), 3 g of diphenylphosphate, and 5 mL toluene were added to a dry reaction flask. The flask was purged with argon for 20 minutes and the temperature was gradually raised to 120 °C and stirred for 24 hr. The reaction mixture was precipitated into 10% triethylamine/ethanol and collected by vacuum filtration.¹⁰ The precipitate was passed through silica gel column via flash chromatography to remove impurities. The resulting product was then recrystallized twice from tetrahydrofuran/methanol solutions. 0.725 g (81 %) of **5** was recovered as white needles. ¹H-NMR (CDCl₃): δ ppm = 8.22 (d, 2H), 8.11 (s, 2H), 8.04

(d, 2H), 7.99 (s, 2H), 7.48 (m, 10H), 7.43 (m, 20H), 5.89 (s, 2H). HRMS (FAB) calcd for $C_{56}H_{40}N_2$ 740.9566, found 740.9562.

6,6'-Bis(2-(diphenylmethylene)-4-phenylquinoline) (6, BQPQ). 1.45 g (1.96 mmol) of **5** and 0.56 g (2.5 mmol) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone were refluxed in anhydrous acetonitrile under argon for 2 h. The resulting solid was collected by filtration, dried, and chromatographed in silica gel with CH_2Cl_2 . Products were then recrystallized twice from $CHCl_3/MeOH$ mixtures. 0.745 g (52 %) was recovered as a yellow solid. 1H -NMR ($CDCl_3$): δ ppm = 8.76 (d, 2H), 8.59 (s, 2H), 8.09 (d, 2H), 7.91 (s, 2H), 7.71 (m, 10H), 7.50 (m, 20H). HRMS (FAB) calcd for $C_{56}H_{38}N_2$ 738.9407, found 738.9405.

General. 1H NMR and ^{13}C -NMR spectra were recorded on a Bruker DRX-499 at 499 MHz using $CDCl_3$ as the solvent. Fourier transformation infrared (FT-IR) spectroscopy was done as a film on a KBr plate using a Perkin-Elmer 1720 FT-IT spectrometer. Thermogravimetric analysis of the molecules was conducted on a TA Instruments Q50 TGA. A heating rate of 10 °C/min under flowing N_2 was used with runs being conducted from room temperature to 600 °C.

Photophysics. Optical absorption spectra were obtained by using a Lambda-900 UV/vis/near-IR spectrophotometer (Perkin-Elmer). Photoluminescence spectra were carried out on a PTI QuantaMaster model QM-2001-4 spectrofluorometer (Photon Technology International Inc. Ontario, Canada). To measure the PL quantum yields (ϕ_f), oligoquinoline solutions in spectral grade toluene were prepared. The concentration ($\sim 10^{-6}$ M) was adjusted so that the absorbance of the solution was lower than 0.1. A 5×10^{-6} M solution of 9,10-diphenylanthracene in toluene was used as a standard ($\phi_f = 0.93$). All the

solutions were degassed with high-purity nitrogen for at least 20 min before spectral acquisition.

Cyclic Voltammetry. Cyclic voltammetry experiments were done on an EG&G Princeton Applied Research Potentiostat/Galvanostat (Model 273A). Data were collected and analyzed by the Model 270 Electrochemical Analysis System Software on a PC computer. A three-electrode cell was used in all experiments as previously described.¹¹ Platinum wire electrodes were used as both counter and working electrodes and silver/silver ion (Ag in 0.1 M AgNO₃ solution, Bioanalytical System, Inc.) was used as a reference electrode. Ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as an internal standard and the potential values, thus, obtained in reference to Ag/Ag⁺ electrode were converted to the saturated calomel electrode (SCE) scale. Solution cyclic voltammetry was carried out on a millimolar solution of BQPQ in DMF solvent containing TBAPF₆ (0.1 M) as an electrolyte. The solution in the three-electrode cell was purged with ultrahigh-purity N₂ for 10-15 minutes before each experiment and a blanket of N₂ was used during the experiment.

Fabrication and Characterization of OLEDs. The OLEDs were fabricated using BQPQ as an emissive material. Indium-tin oxide (ITO)-coated glass substrates (Delta Technologies Ltd., Stillwater, MN) were cleaned sequentially in ultrasonic baths of 2-propanol/deionized water (1:1 volume) mixture, toluene, deionized water, and acetone, then dried at 60 °C in vacuum overnight. A ~1wt% poly(ethylenedioxythiophene)/poly(styrene sulfonate) blend (PEDOT) dispersion in water was filtered through a 0.45 μm PVDF syringe filter. A 40 nm thick layer was then spin cast onto the ITO-coated glass to act as a hole injection layer and dried at 200 °C for 15 minutes under vacuum. A

20nm thick poly(N-vinylcarbazole) (PVK) hole-transport/electron-blocking layer was spin coated from a 1 wt% toluene solution onto the PEDOT layer and dried at 60 °C for 4 hour under vacuum. Films (35-45 nm) of BQPQ were evaporated from resistively heated quartz crucibles at a rate of 0.2–0.3 nm/s in a vacuum evaporator (Edwards Auto 306) at a base pressure of $<3 \times 10^{-6}$ Torr onto the PVK layer. The chamber was vented with air to load the cathode materials, pumped down to $\sim 3 \times 10^{-6}$ Torr, and a 2 nm thick lithium fluoride layer followed by a 120nm thick aluminum layer were deposited through a shadow mask to form active diode areas of 0.2 cm². The film thicknesses were measured by an Alpha-Step 500 surface profiler (KLA Tencor, Mountain View, CA). Electroluminescence spectra were obtained using a PTI QM-2001-4 spectrofluorimeter. Current-voltage characteristics of the LEDs were measured using a HP4155A semiconductor parameter analyzer (Yokogawa Hewlett-Packard, Tokyo). The luminance was simultaneously measured using a model 370 optometer (UDT instruments, Baltimore, MD) equipped with a calibrated luminance sensor head (model 211) and a 5x objective lens. The device external quantum efficiency was calculated using procedures reported previously.¹⁴ All the device fabrication and characterization steps were done under ambient laboratory conditions.

Fabrication and Characterization of Thin Film Transistors. The thin film field-effect transistors were fabricated by using a bottom contact geometry. Heavily doped Si with a conductivity of 10³ S/cm was used as the gate electrode with a 300 nm thick SiO₂ layer as the gate dielectric. By means of photolithography and vacuum sputtering (2×10^{-6} Torr), two 90 nm thick gold electrodes (source and drain) with 10 nm thick Ti-W alloy adhesive layer were fabricated onto the SiO₂/Si substrates. A channel length (*L*) of 25 μm and a

channel width (W) of 500 μm were used. A gold contact pad was also deposited on the gate electrode to make ohmic contact. Electrical characteristics of the devices were measured using a Keithley 4200 semiconductor parameter analyzer (Keithley Instruments, Inc., Cleveland, OH). All fabrication and measurements were done under ambient laboratory conditions.

Surface Treatment of SiO₂ and Thin Film Deposition. SiO₂ surface was treated with hexamethyldisilazane vapor at 150°C for 5 min. The SiO₂ surface was characterized before and after modification by measuring the advancing contact angle of a water drop on the SiO₂ surface. Before treatment, the contact angle was around 10-15°, indicating a hydrophilic surface. After treatment with HMDS the water contact angle increased to 50°. The thin-films of BQPQ were deposited by vacuum evaporation ($<10^{-6}$ torr).

Table S1 Electroluminescent Properties of BQPQ OLEDs.

Device Structure ^a	V _{on} ^b (V)	Drive Voltage (V)	J _{max} ^c (mA/m ²)	L _{max} ^d (cd/m ²)	LE _{max} (@ L) (cd/A)	EL λ _{max}	CIE 1931 x,y
I BQPQ	2.2	5.3	234	180	0.1 (135)	512	0.27, 0.57
II BQPQ/TPBI	2.3	8	500	6030	5.0 (160)	507	0.25, 0.60
III PEDOT/PVK/BQPQ	3.5	11	202	1615	1.1 (804)	512	0.28, 0.59
IV PEDOT/PVK/BQPQ/TPBI	3.5	13.7	500	16265	5.9 (2035)	510	0.30, 0.58

^aAll devices used ITO as the anode and LiF/Al as the cathode. ^bTurn-on voltage (at which EL is visible to the eye). ^cCurrent Density. ^dLuminance.

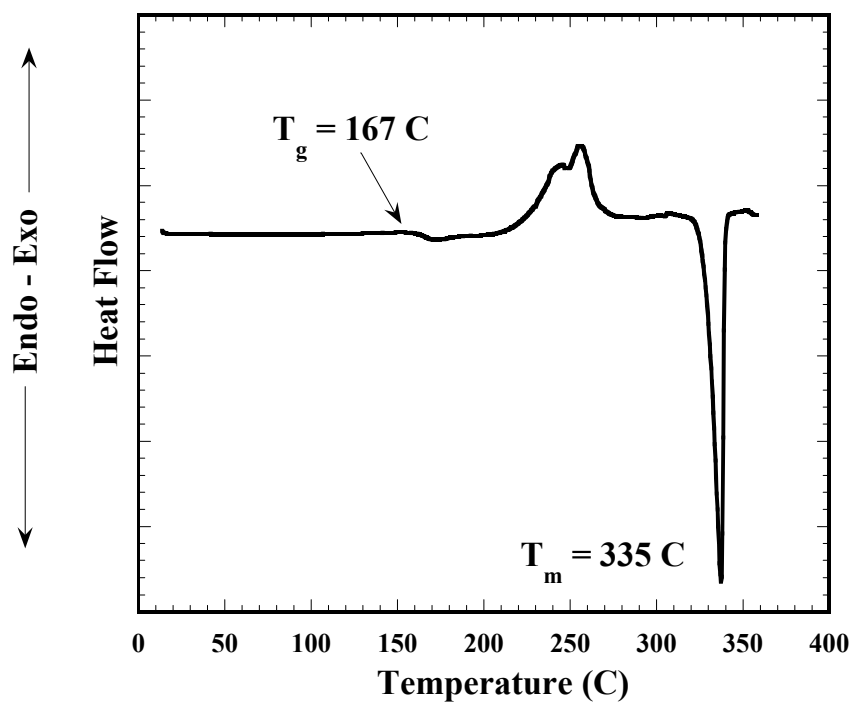


Figure S1 Second heating DSC scan of BQPQ at a heating rate of 10 °C/min in nitrogen.

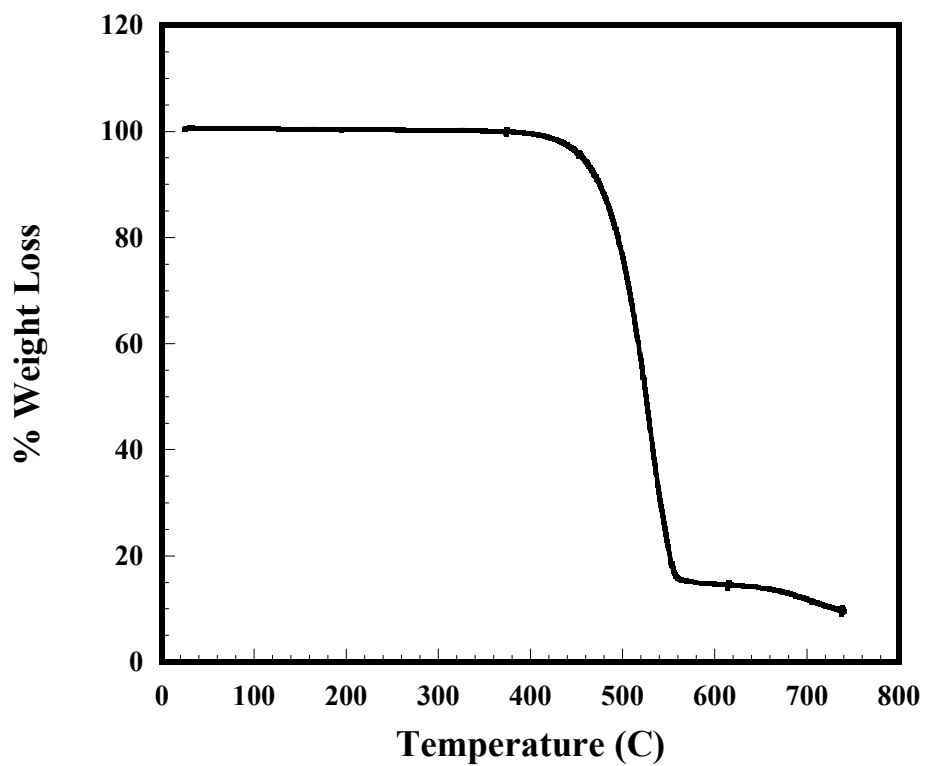


Figure S2 TGA scan of BQPQ at a heating rate of 10 °C/min in nitrogen.

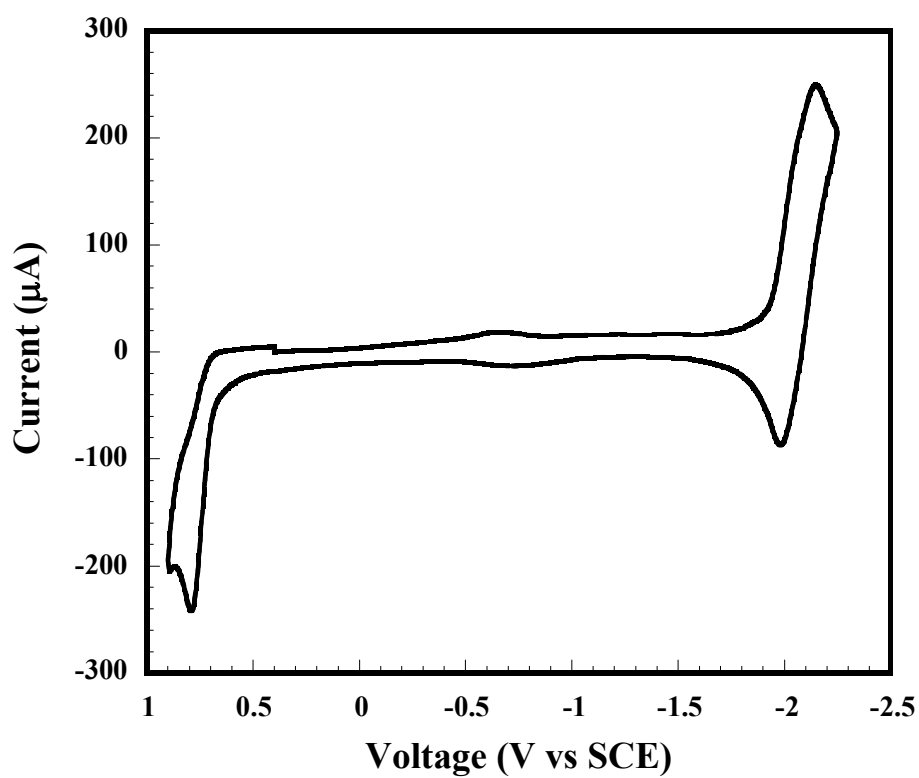


Fig. S3 Cyclic voltammogram of BQPQ in 0.1M in DMF/0.1 M TBAPF₆ MeCN.

Scan rate = 300 mV/sec.

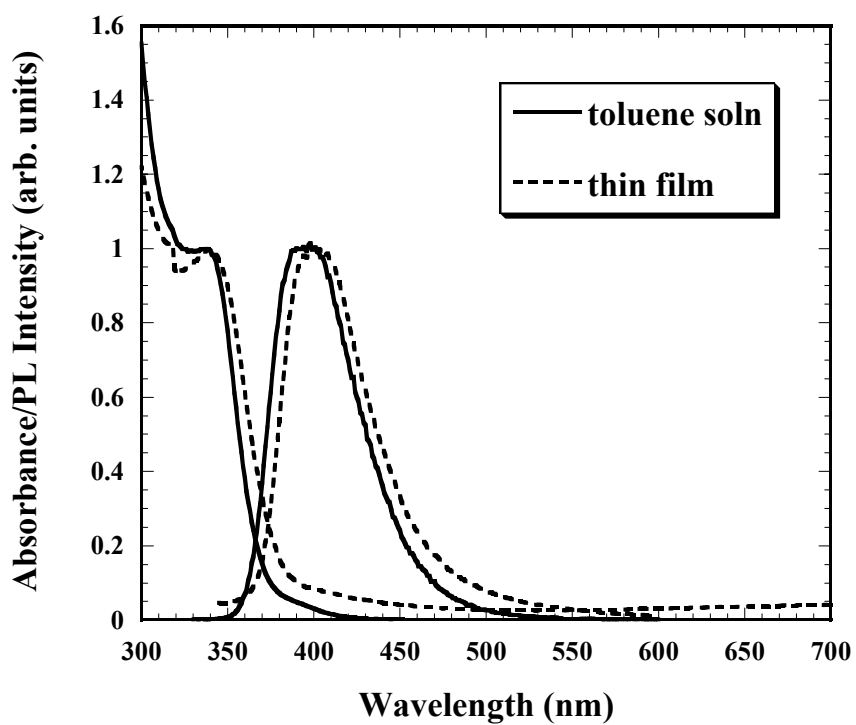


Fig S4 Absorption and photoluminescence (PL) spectra of **5** in 10^{-6} M toluene solution and as a thin film.

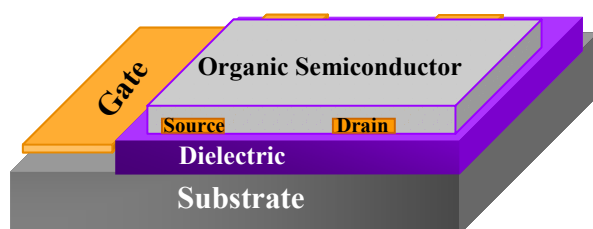


Figure S5 Device schematic of a bottom contact organic field-effect transistor (OFET).