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

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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 2₁. 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. 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. \(^1\)H-NMR (CDCl₃): \( \delta \) 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$_2$Cl$_2$. Products were then recrystallized twice from CHCl$_3$/MeOH mixtures. 0.745 g (52 %) was recovered as a yellow solid. $^1$H-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.** $^1$H 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 ($\phi_l$), oligoquinoline solutions in spectral grade toluene were prepared. The concentration (~10$^{-6}$ M) was adjusted so that the absorbance of the solution was lower than 0.1. A 5 x 10$^{-6}$ M solution of 9,10-diphenylantracene in toluene was used as a standard ($\phi_l = 0.93$). All the
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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 AgNO\(_3\) 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 TBAPF\(_6\) (0.1 M) as an electrolyte. The solution in the three-electrode cell was purged with ultrahigh-purity N\(_2\) for 10-15 minutes before each experiment and a blanket of N\(_2\) 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 x 10^{-6} Torr onto the PVK layer. The chamber was vented with air to load the cathode materials, pumped down to ~ 3 x 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. 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 SiO$_2$ and Thin Film Deposition.** SiO$_2$ surface was treated with hexamethyldisilazane vapor at 150°C for 5 min. The SiO$_2$ surface was characterized before and after modification by measuring the advancing contact angle of a water drop on the SiO$_2$ 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.

<table>
<thead>
<tr>
<th>Device Structure</th>
<th>$V_{on}$ (V)</th>
<th>Drive Voltage (V)</th>
<th>$J_{\text{max}}$ (mA/m²)</th>
<th>$L_{\text{max}}$ (cd/m²)</th>
<th>LE$_{\text{max}}$ (@ L) (cd/A)</th>
<th>EL $\lambda_{\text{max}}$</th>
<th>CIE 1931 x,y</th>
</tr>
</thead>
<tbody>
<tr>
<td>I BQPQ</td>
<td>2.2</td>
<td>5.3</td>
<td>234</td>
<td>180</td>
<td>0.1 (135)</td>
<td>512</td>
<td>0.27, 0.57</td>
</tr>
<tr>
<td>II BQPQ/TPBI</td>
<td>2.3</td>
<td>8</td>
<td>500</td>
<td>6030</td>
<td>5.0 (160)</td>
<td>507</td>
<td>0.25, 0.60</td>
</tr>
<tr>
<td>III PEDOT/PVK/BQPQ</td>
<td>3.5</td>
<td>11</td>
<td>202</td>
<td>1615</td>
<td>1.1 (804)</td>
<td>512</td>
<td>0.28, 0.59</td>
</tr>
<tr>
<td>IV PEDOT/PVK/BQPQ/TPBI</td>
<td>3.5</td>
<td>13.7</td>
<td>500</td>
<td>16265</td>
<td>5.9 (2035)</td>
<td>510</td>
<td>0.30, 0.58</td>
</tr>
</tbody>
</table>

*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).