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*

A novel tetraphenylquinodimethane based on electron-deficient 4-phenylquinoline oligomer displayed an unusually low ionization potential and was used as a p-channel semiconductor in thin-film transistors and as an emitter to achieve very bright and high efficiency green light-emitting diodes.

Fundamental interest in the molecular and electronic structures and the properties of quinoidal molecules, such as Theile's (**1a**) and Chichibabin's (**1b**) hydrocarbons and their derivatives (Fig. 1),[1–3] goes back over 100 years and remains strong in many areas of contemporary chemistry.[3–9] Stability and electron-accepting properties improved significantly in going from the tetraphenylquinodimethane **1a** to the corresponding tetracyano compound, 7,7,8,8-tetracyanoquinodimethane (TCNQ).[5] Numerous TCNQ derivatives and related quinoidal compounds have been extensively investigated as acceptor components of molecular metals and other functional organic materials.[4,6] More recently, π-stacked derivatives of quinoidal terthiophene **2** were found to be good n-channel semiconductors for organic field effect transistors (OFETs) with electron mobilities as high as 0.2 cm^2 V^{-1} s^{-1}.[7] Even longer quinoidal oligothiophenes of up to the hexamer were recently synthesized and shown to have unusual optical and redox properties.[8] Conjugated polymers with quinoidal bonding motif have also been of long interest as small band gap semiconductors, transparent conductors, and potential intrinsic conductors.[9] Very little is known about the light-emitting properties of quinodimethane compounds.[3–9] We are thus interested in exploring

electron-deficient rings, such as 4-phenylquinoline (**7**), as building blocks for new quinodimethane compounds that may be capable of ambipolar charge transport and high luminescence efficiency.

We report herein the synthesis, properties, and initial organic light emitting diode and thin-film transistor applications of a novel tetraphenylquinodimethane compound based upon the electron-deficient (n-type) 6,6′-bis(4-phenylquinoline) oligomer. 6,6′-Bis(2-(diphenylmethylene)-4-phenylquinoline) (BQPQ, **6**) was synthesized in two steps (Scheme 1). The aromatic precursor **5** was obtained in 81% by acid-catalyzed Freidlander condensation of 1,1-diphenylacetone (**3**) and 3,3′-dibenzoylbenzidine (**4**).[10] Dehydrogenation of **5** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gave the desired quinodimethane compound **6** in 52%. The structures of **5** and **6** were confirmed by ^{1}H NMR, mass spectrometry, and other methods. The X-ray single crystal structure of **5** also confirmed its structure.‡ The singlet resonance at 5.89 ppm in the ^{1}H NMR spectrum of **5** due to the methyne proton completely disappeared in the spectrum of **6**.

Cyclic voltammetry of BQPQ solution in *N,N*-dimethylformamide (DMF) showed a quasi-reversible one-electron reduction wave with a half-wave reduction potential ($E_{1/2}^{red}$) of −2.05 V (*vs.* SCE) and an onset reduction potential of −1.87 V. An irreversible oxidation wave, with an anodic peak at 0.79 V and an onset oxidation potential of 0.6 V, was also observed. Compared to the related aromatic oligoquinoline, 6,6′-bis(2,4-diphenylquinoline) (**7**),[11] BQPQ is reduced at a more negative potential and this is indicative of poorer electron-accepting properties. A similar comparison of the oxidation potential of BQPQ and the aromatic oligomer **7** shows that BQPQ has substantially better electron-donating properties. The electron affinity (EA) or LUMO
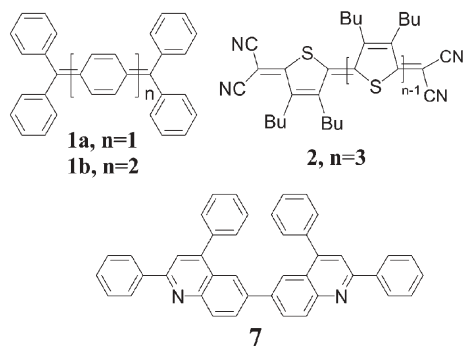
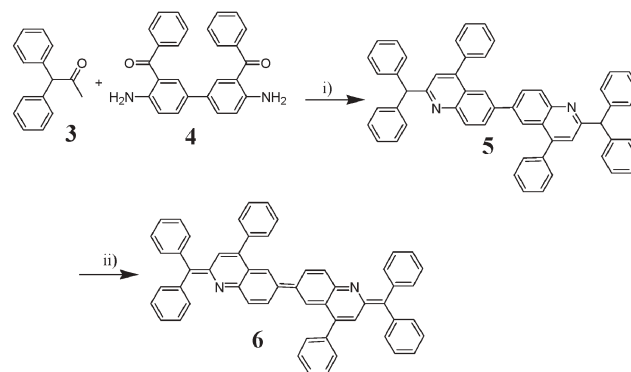**Fig. 1** Some known quinoidal and aromatic compounds.

Departments of Chemical Engineering and of Chemistry, University of Washington, Seattle, Washington, 98195-1750, USA.
E-mail: Jenekhe@u.washington.edu

† Electronic supplementary information (ESI) available: Complete synthetic and experimental data. See http://dx.doi.org/10.1039/b509322h

Scheme 1 Synthesis of compound **6** (BQPQ). *Reagents and conditions*: (i) diphenyl phosphate, toluene, 120 °C, 24 h; (ii) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, MeCN, reflux, 24 h.

level of BQPQ derived from the onset reduction potential is 2.5 eV and the ionization potential (IP) or HOMO energy level similarly estimated from the onset oxidation potential is 5.0 eV.[12] The electrochemical band gap ($E_g^{el} = IP - EA$) of BQPQ is thus 2.5 eV. The observed redox properties and the HOMO/LUMO energy levels of BQPQ are quite surprising since currently known quinodimethane compounds are usually better electron acceptors than the related aromatic compounds.[3–8] The HOMO level (5.0 eV) of BQPQ is 0.8 eV higher lying than the related aromatic compound **7**,[11] suggesting that it has far better electron donating or hole-injecting properties than **7**.

The optical absorption and photoluminescence (PL) spectra of BQPQ in dilute (2×10^{-6} M) toluene solution and as a thin film are shown in Fig. 2. The absorption spectrum in solution has a lowest energy absorption maximum (λ_{max}) at 430 nm (log ε = 3.7) and a more intense band centered at 320 nm (log ε = 5.8). A thin-film absorption spectrum with a nearly identical lineshape is seen; however, the lowest energy λ_{max} is red shifted to 440 nm. The optical band gap (E_g^{opt}) derived from the thin-film absorption edge is 2.54 eV, which is in good agreement with the electrochemical band gap E_g^{el} (2.5 eV). However, this E_g^{opt} value is significantly smaller than the 3.0 eV observed for the aromatic compound **7**.[11]

The PL emission spectrum of BQPQ in toluene solution (2×10^{-6}) is slightly structured, with the 0–1 and 0–2 transitions at 491 and 517 nm, respectively. This emission band is fairly broad with a full width at half maximum (FWHM) of 96 nm. The bright green PL emission in toluene has a PL quantum yield (ϕ_{PL}) of 69% and a lifetime (τ) of 2.5 ns. From the ϕ_{PL} value in solution and the lifetime τ we obtain the radiative lifetime (τ_0) of the emission band to be 3.6 ns according to $\phi_{PL} = \tau/\tau_0$. In the solid state, the PL emission spectrum loses vibronic structure and is centered at 531 nm with a FWHM of 89 nm. The red shift of the thin-film PL emission spectrum from that in solution is sufficiently small to preclude a need to invoke intermolecular emitting species such as aggregates or excimers.[13] With the measured lifetime (τ = 1.0 ns) of the PL emission of BQPQ thin films, the ϕ_{PL} value of thin films was estimated to be ~28%.

The intense green fluorescence of BQPQ thin films encouraged us to explore them in organic light emitting diodes (OLEDs).
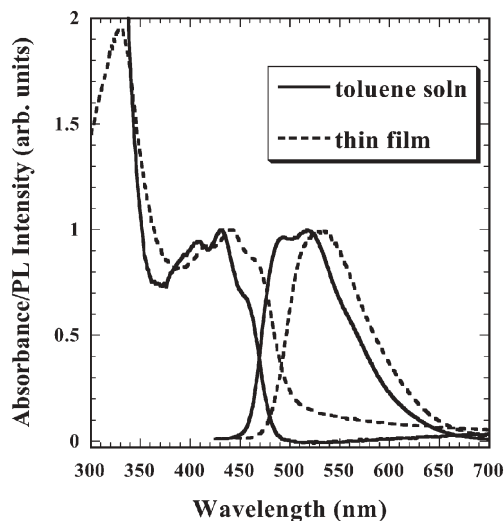
Four diode structures were constructed: ITO|BQPQ|LiF|Al (I), ITO|BQPQ|TPBI|LiF|Al (II), ITO|PEDOT|PVK|BQPQ|LiF|Al (III), and ITO|PEDOT|PVK|BQPQ|TPBI|LiF|Al (IV).[14] Representative EL spectra of BQPQ are shown in Fig. 3(a). Indeed, the EL spectra of all four types of diodes were identical to those in Fig. 3(a) and had an emission maximum at 507–512 nm. The EL spectra are only slightly blue shifted compared to the thin-film PL emission spectrum but the FWHM values of the EL and PL emission spectra are identical. The green electroluminescence of the four diodes had excellent CIE coordinates (x = 0.30, y = 0.58 for diode IV) indicative of pure green.

The four different diodes, including the single-layer device I, all had low turn-on voltages (2.2–3.5 V), implying that there is facile electron and hole injection into BQPQ. The increase in brightness and luminous efficiency from 180 cd m^{-2} and 0.1 cd A^{-1} in device I to 6030 cd m^{-2} and 5.0 cd A^{-1} in device II reveals that the role of TPBI is that of confinement of holes in BQPQ rather than improvement of electron injection since identical turn-on voltages (2.2–2.3 V) were observed in devices I and II. A similar comparison of the performance of device III (1615 cd m^{-2}, 1.1 cd A^{-1}) to device I shows that the PVK functions as an electron blocking layer that helps to confine electrons to BQPQ. Diode IV, whose current density–luminance–voltage characteristics are shown in Fig. 3(b), showed the best performance with a brightness of 16 255 cd m^{-2}. The maximum external quantum efficiency (EQE) of diode IV was 1.9% at a brightness of 2035 cd m^{-2} with a
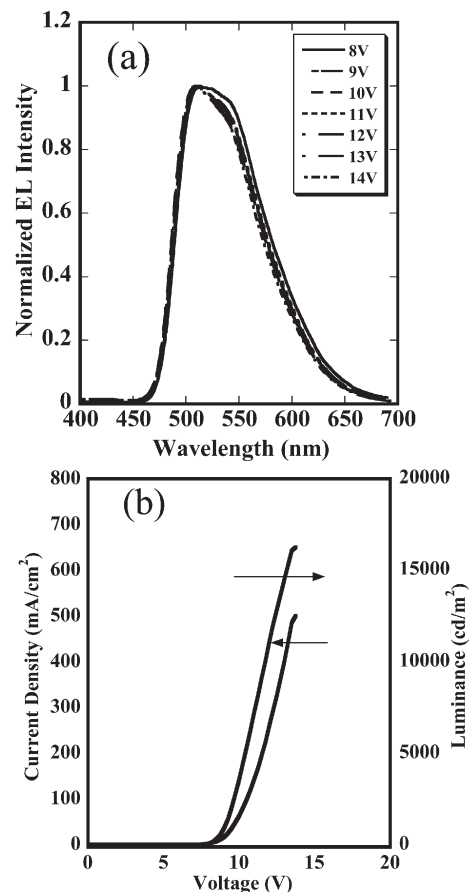

Fig. 3 (a) Electroluminescence spectra and (b) current density–luminance–voltage curves of diode IV.
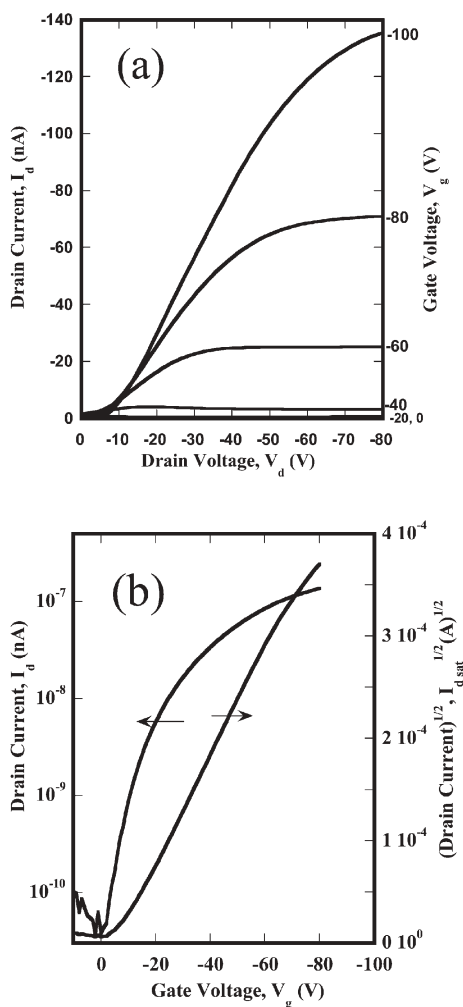

Fig. 2 Absorption and photoluminescence (PL) spectra of BQPQ in 2×10^{-6} M toluene solution and in thin film.

Fig. 4 (a) Output characteristics and (b) transfer characteristics of a BQPQ FET with HMDS treated SiO_2 gate dielectric.

observed p-channel field effect charge transport in BQPQ is consistent with the OLED results and the redox properties of this quinodimethane. The high fluorescence efficiency and low field effect carrier mobility of BQPQ indicate that the thin films are not highly crystalline.

In summary, we have described the synthesis and properties of a novel tetraphenylquinodimethane **6** (BQPQ) based on an electron-deficient 4-phenylquinoline oligomer. Very bright ($>16\,000\,\mathrm{cd\,m}^{-2}$) and efficient ($5.9\,\mathrm{cd\,A}^{-1}$) green electroluminescent diodes were realized from BQPQ. Its unusually low ionization potential (5.0 eV) facilitated the demonstration of p-channel thin-film transistors with a hole mobility of $4 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. Work in progress aims to synthesize tetracyano and other derivatives of quinoidal oligoquinolines as semiconductors for thin-film transistors and high performance OLEDs.

This work was supported by the NSF (CTS-0437912), the AFOSR (F49620-03-1-0162) and the NSF STC (MDITR).

Notes and references

‡ *Crystal data* for **5**: $C_{58}H_{42}Cl_6N_2$, $M = 979.64$, monoclinic, space group Pc, $a = 17.7390(7)$, $b = 5.9890(2)$, $c = 25.1160(10)$ Å, $\beta = 120.6771(16)°$, $V = 2294.88(15)$ Å^3, $Z = 2$, $D_c = 1.418$ Mg m^{-3}, $T = 130(2)$ K, $\mu = 0.418$ mm^{-1}, λ(Mo-Kα) = 0.71073 Å, 7818 refections, 3951 with $I > 2\sigma(I)$; R, wR ($I > 2\sigma(I)$) = 0.0677, 0.1386; R, wR (all) = 0.1616, 0.1680; $\chi = 0.4(1)$. CCDC 282777. See http://dx.doi.org/10.1039/b509322h for crystallographic data in CIF or other electronic format.

1 J. Thiele and H. Balhorn, *Chem. Ber.*, 1904, **37**, 1463.
2 A. E. Chichibabin, *Chem. Ber.*, 1907, **40**, 1810.
3 L. K. Montgomery, J. C. Huffman, E. A. Jurczak and M. P. Grendze, *J. Am. Chem. Soc.*, 1986, **108**, 6004.
4 T. Kawase, N. Ueno and M. Oda, *Tetrahedron Lett.*, 1992, **37**, 5405; S. Yoshida, M. Fujii, Y. Aso, T. Otsubo and F. Ogura, *J. Org. Chem.*, 1994, **59**, 3077.
5 L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.*, 1962, **84**, 3374.
6 See the Special Issue on Molecular Conductors:, *Chem. Rev.*, 2004, **104**, 4887–5782.
7 R. J. Chesterfield, C. R. Newman, T. M. Pappenfus, P. C. Ewbank, M. H. Haukaas, K. R. Mann, L. L. Miller and C. D. Frisbie, *Adv. Mater.*, 2003, **15**, 1278; T. M. Pappenfus, R. J. Chesterfield, C. D. Frisbie, K. R. Mann, J. Cascado, J. D. Raff and L. L. Miller, *J. Am. Chem. Soc.*, 2002, **124**, 4184; J. Casado, T. M. Pappenfus, K. R. Mann, E. Ortí, P. M. Viruela, B. Milián, V. Hernández and J. T. L. Navarrete, *Chem. Phys. Chem.*, 2004, **5**, 529.
8 T. Takahashi, K.-I. Matsuoka, K. Takimiya, T. Otsubo and Y. Aso, *J. Am. Chem. Soc.*, 2005, **127**, 8928.
9 S. A. Jenekhe, *Nature*, 1986, **322**, 345; W. C. Chen and S. A. Jenekhe, *Macromolecules*, 1995, **28**, 465.
10 A. K. Agrawal and S. A. Jenekhe, *Macromolecules*, 1993, **26**, 895.
11 A. P. Kulkarni, A. P. Gifford, C. J. Tonzola and S. A. Jenekhe, *Appl. Phys. Lett.*, 2005, **86**, 061106.
12 EA (eV) = E_{red}^{onset} (*vs.* SCE) + 4.4 and IP (eV) = E_{ox}^{onset} (*vs.* SCE) + 4.4, where the SCE energy level below vacuum is 4.4 eV. For details see: A. K. Agrawal and S. A. Jenekhe, *Chem. Mater.*, 1996, **8**, 579.
13 S. A. Jenekhe and J. A. Osaheni, *Science*, 1994, **265**, 765.
14 ITO is indium tin oxide, 1,3,5-tris(*N*-phenylbenzimidizol-2-yl)benzene (TPBI) is a hole-blocking layer, poly(ethylenedioxythiophene)|poly(styrene sulfonic acid) (PEDOT) is the hole injection layer, and poly(*N*-vinylcarbazole) (PVK) is the electron blocking layer. For details on our procedures for device fabrication and characterization of OLEDs, see: A. P. Kulkarni, Y. Zhu and S. A. Jenekhe, *Macromolecules*, 2005, **38**, 1553; X. Zhang and S. A. Jenekhe, *Macromolecules*, 2000, **33**, 2069.
15 For details on our procedures for OFET fabrication and characterization, see: A. Babel and S. A. Jenekhe, *J. Phys. Chem. B*, 2003, **107**, 1749; A. Babel and S. A. Jenekhe, *J. Am. Chem. Soc.*, 2003, **125**, 13656.

luminous efficiency of $5.9\,\mathrm{cd\,A}^{-1}$. The far superior performance of diode II compared to diode III means that the hole current is dominant and thus that the mobility of holes is greater than the electron mobility in BQPQ thin films.

Charge carrier transport in BQPQ was explored directly by investigating its semiconductor properties in bottom contact organic field effect transistors (OFETs) fabricated from gold source/drain electrodes, SiO_2 gate dielectric layer, and vacuum evaporated BQPQ thin films.[15] The BQPQ OFETs showed typical p-channel output characteristics with good drain current modulation. The saturation region field effect mobility of holes was found to be $9 \times 10^{-6}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. By modifying the gate dielectric with a silylating agent, hexamethyldisilazane (HMDS), the output and transfer characteristics of BQPQ OFETs (Fig. 4) significantly improved. In this case, the saturation region mobility of holes was $4 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ with an on/off ratio of 10^3. The large improvement in the OFET performance by HMDS surface modification of SiO_2 is a result of improved ordered packing into a morphology favorable to charge transport. n-Channel field effect charge transport was not observed in BQPQ OFETs in accord with the expected large barrier to electron injection from gold due to the small electron affinity (2.5 eV) of this quinodimethane. The