# Narrow Bandgap Polymers: Poly-4-dicyanomethylene-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (PCDM)

**John P. Ferraris* and Tim L. Lambert**

*Department of Chemistry, The University of Texas, Dallas, PO Box 830688, Richardson, Texas 75083-0688, USA*

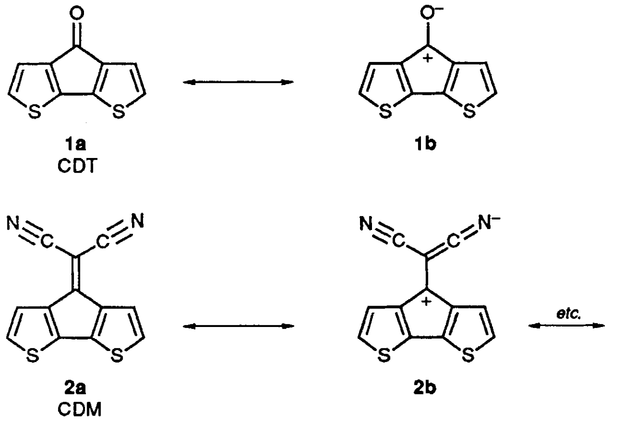
An electroactive polymer with a bandgap of ≈0.8 eV has been obtained from the monomer 4-dicyanomethylene-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene.

Polymers which have low bandgaps ($E_{gap} < 1.5$ eV) in their neutral state remain a desired goal in the field of electroactive materials and several approaches to these have been proposed.[1] We have recently identified another strategy for obtaining such materials which is based on using monomers of reduced aromaticity[2] whose decreased HOMO–LUMO separations[3] can be carried over into their polymers. Our first approximation[4] to such systems was poly-4*H*-cyclopenta[2,1-*b*; 3,4-*b'*]dithiophen-4-one, **1a** (PCDT) which displayed an $E_{gap} \leqslant 1.2$ eV, surpassed only by polyisothianaphthene (PITN) (and its derivatives)[5] and poly-dithieno[3,4-*b*;3',4'-*d*]thiophene[6] with $E_{gap} \approx 1$ eV. The CDT monomer should possess reduced aromaticity (lowered HOMO–LUMO gap[3]) to the extent that its primary resonance contributor, **1b**, participates and pushes the fused ring structure toward a 12 π electron system. Such participation is suggested by the strong red shifts of the lowest π–π* absorption observed by Koster and Janssen[7] when **1** is dissolved in acidic media.

We now report that the strategy for **1** has led to the title compound, **2** (PCDM), an electroactive polymer with a bandgap below 1.0 eV and we describe a Hückel molecular orbital interpretation for its reduced $E_{gap}$.

The dicyanomethylene group in CDM[†] (**2**) is a stronger electron-withdrawing substituent than the carbonyl in **1** and should enhance the participation of **2**'s primary resonance contributor, **2b**, to the overall structure of the molecule. This in turn is expected to reduce the HOMO–LUMO separation in the monomer, and the $E_{gap}$ in its polymer, PCDM.

The UV–VIS spectrum of CDM displays a 100 nm (0.48 eV) red shift of the long wavelength absorption band compared to CDT (**1**: $\lambda_{max} = 472$ nm, $\varepsilon = 1250$; **2**: $\lambda_{max} = 576$ nm, $\varepsilon = 1450$).



**1a** CDT

**1b**

**2a** CDM

**2b**

---

[†] CDM was prepared in 93% yield *via* a piperidine catalysed Knoevenagel condensation between CDT and malononitrile and displayed satisfactory analytical and spectral characteristics.

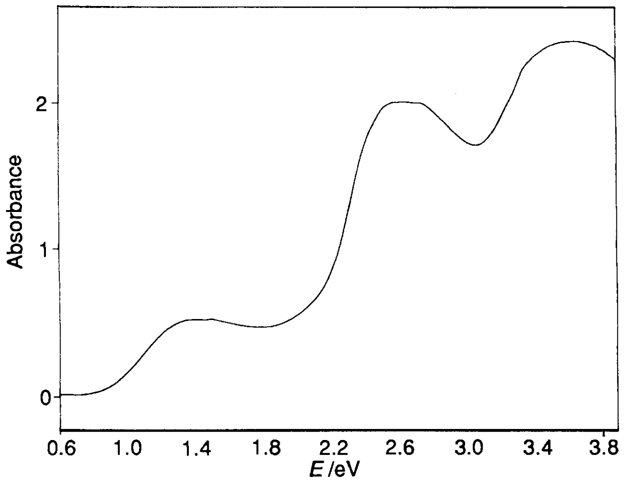


**Fig. 1** Absorption spectrum for poly-**2** (PCDM)

This band was assigned as a π–π* absorption for **1**.[4] We also assign the analogous absorption in **2** to a π–π* transition based on the presence of structure in this band, its 20 nm red shift from hexane to methanol, and by analogy with **1**. Upon polymerization this band shifts to 950 nm in neutral PCDM, a red shift of ≈0.9 eV compared to the monomer and similar in magnitude and direction to that observed upon polymerization of CDT.

The UV–VIS–near IR spectrum‡ of neutral PCDM (Fig. 1) shows the long wavelength band edge ($E_{gap}$) at ≈0.8 eV, making it one of the lowest bandgap polymers reported to date. Cyclic voltammetry (CV) of PCDM yields a peak anodic potential ($E_{pa}$) of +0.76 V *vs.* standard calomel electrode (SCE).§ For comparison, PCDT and polybithiophene (PBT) display $E_{pa}$ at +0.75[4] and +0.70[8] V *vs.* SCE, respectively. The anodic and cathodic CV¶ of PCDM (Fig. 2) show both oxidation and reduction of the polymer.|| The difference in the threshold potentials for hole (p-doping) and electron (n-doping) injection is ≈0.3 V, comparable to that of PITN,[5] and indicative of a narrow $E_{gap}$ material.[9] However, whereas PITN is unstable to n-doping,[5] PCDM remains stable to both p- and n-doping after repeated anodic and cathodic cycling.

The comparable $E_{pa}$ values for CDM, CDT and bithiophene (BT) (1.31, 1.25,[4] 1.2–1.28[4,10] V *vs.* SCE, respectively) and their corresponding polymers (see above) may appear surprising since electron-withdrawing groups in the 3-position of thiophene monomers normally increase $E_{pa}$ considerably.[11] These similarities are readily explained, however, by considering the symmetry of the HOMOs. Fig. 3 displays the frontier orbitals for the bithiophene and our fused bithiophene, CDM.

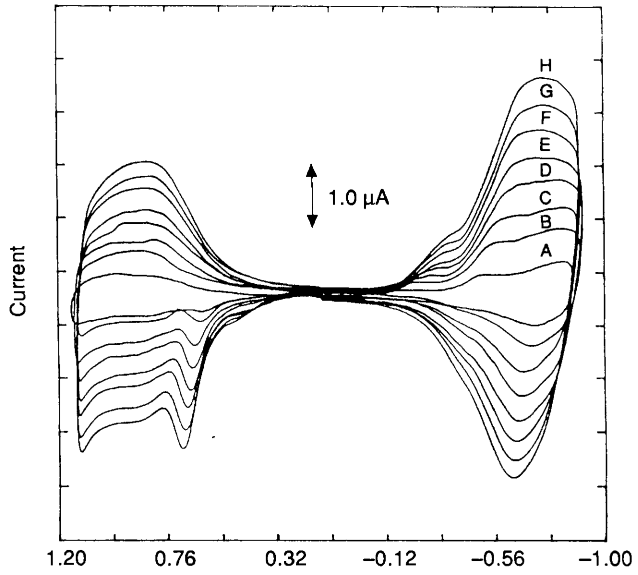


**Fig. 2** Cyclic voltammogram of PCDM as a function of scan rate showing p- and n-doping: (A) 10; (B) 20; (C) 30; (D) 40; (E) 50; (F) 60; (G) 70; (H) 80 mV s$^{-1}$

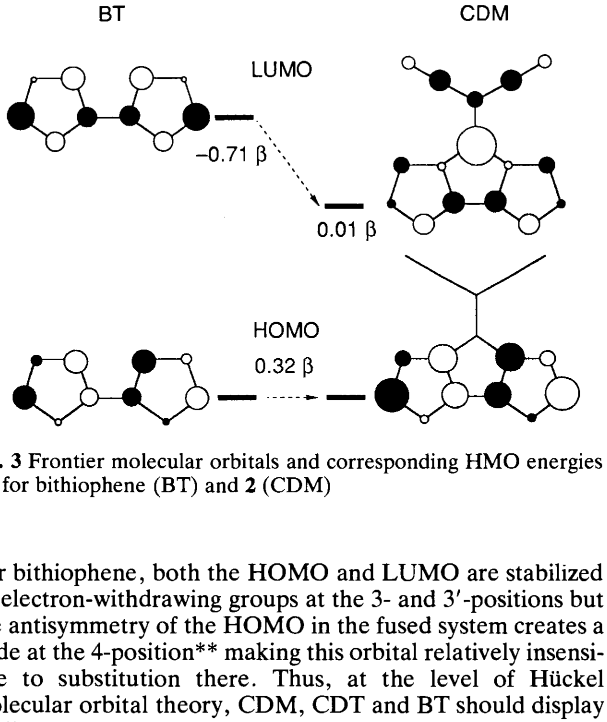


**Fig. 3** Frontier molecular orbitals and corresponding HMO energies (β) for bithiophene (BT) and **2** (CDM)

For bithiophene, both the HOMO and LUMO are stabilized by electron-withdrawing groups at the 3- and 3′-positions but the antisymmetry of the HOMO in the fused system creates a node at the 4-position** making this orbital relatively insensitive to substitution there. Thus, at the level of Hückel molecular orbital theory, CDM, CDT and BT should display similar $E_{pa}$. The $E_{pa}$ values of their respective polymers should also group at some lower value. The symmetric LUMOs for both systems are stabilized by substitution with electron-withdrawing groups. This is manifested by lowered half-wave reduction potentials and smaller $E_{gap}$ values. The $E_{1/2}$ for CDM, CDT and BT are −0.78,[12] −1.17[13] and −2.2 V[14] *vs.* SCE, respectively, while the corresponding polymer $E_{gap}$ values are 0.8, 1.2[4] and 2.0 eV.

In conclusion, Hückel molecular orbital theory satisfactorily explains the electrochemical features of CDM, CDT, BT and their polymers. Our model, which uses the development of non-aromaticity as a guide in the design of narrow $E_{gap}$ polymers, has led us to one of the lowest $E_{gap}$ polymers

---

‡ PCDM was grown galvanostatically onto indium tin oxide (ITO) coated glass electrodes at 750 mA cm$^{-2}$ for 3 min from 0.01 mol dm$^{-3}$ solutions of CDM in nitrobenzene containing 0.1 mol dm$^{-3}$ tetrabutylammonium tetrafluoroborate (TBATFB), and then electrochemically reduced at +2.8 V *vs.* Li/Li$^+$.

§ PCDM was grown on a 100 μm diameter Pt disk electrodes from 0.1 mol dm$^{-3}$ solutions of CDM in nitrobenzene containing 0.1 mol dm$^{-3}$ TBATFB and then rinsed with nitrobenzene. The $E_{pa}$ was determined by extrapolating to zero scan speed a series of CVs taken between 0.0 and +1.2 V *vs.* SCE.

¶ The potential was scanned from +0.16 to +1.16 to −0.89 to +0.16 V *vs.* SCE.

|| We have not identified the source of the oxidation wave peaking ≈0.5 V *vs.* SCE following each cathodic scan but note that it appears only if a cathodic scan precedes an anodic scan. This oxidation wave shows no discernible reduction. It appears associated with the adsorbed polymer rather than an impurity in solution since its current is linearly related to scan rate.

** HMO calculations were performed using $h_S = 1$, $k_{C\text{-}S} = 0.68$, $h_C = 0$, $h_N = 1.5$ and $k_{C\text{-}N} = 1$.

known to date, PCDM, with $E_{gap} \approx 0.8$ eV. Furthermore, this polymer appears stable to both p- and n-doping.††

Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Dr. Jacob Lin of Polytronix, Inc. for the continued generous provision of ITO electrodes.

*Received, 13th May 1991; Com. 1/02221K*

## References

1 J. L. Bredas, A. J. Heeger and F. Wudl, *J. Chem. Phys.*, 1986, **85**, 4673; J. M. Toussaint, F. Wudl and J. L. Bredas, *J. Chem. Phys.*, 1989, **91**, 1783; J. M. Toussaint, B. Themans, J. M. Andre and J. L. Bredas, *Synthetic Metals*, 1989, **28**, 205; J. L. Bredas, *J. Chem. Phys.*, 1985, **82**, 3808; A. K. Bakhashi and J. Ladik, *Solid State Commun.*, 1988, **65**, 1203; J. L. Bredas, *Synthetic Metals*, 1987, **17**, 115; M. Kertesz and Y. S. Lee, *J. Chem. Phys.*, 1987, **91**, 2690; K. Tanaka, K. Ueda, T. Koihe, M. Ando and T. Yamabe, *Phys. Rev. B*, 1985, **32**, 4279; K. Tanaka, S. Yamanaka, K. Ueda, T. Shinji and T. Yamabe, *Synthetic Metals*, 1987, **20**, 333; K. Tanaka, S. Wang and T. Yamabe, *Synthetic Metals*, 1989, **30**, 57; K. Tanaka, M. Murashima and T. Yamabe, *Synthetic Metals,* 1988, **24**, 371; F. Wudl, M. Kobayashi and A. J. Heeger, *J. Org. Chem.*, 1984, **49**, 3382.

2 T. L. Lambert and J. P. Ferraris, *Polym. Materials Sci. Eng.*, 1991, **64**, 332.

3 Z. Zhou and R. G. Parr, *J. Am. Chem. Soc.*, 1989, **111**, 7371.

4 T. L. Lambert and J. P. Ferraris, *J. Chem. Soc., Chem. Commun.*, 1991, 752.

5 M. Kobayashi, N. Colaneri, M. Boysel, F. Wudl and A. J. Heeger, *J. Chem. Phys.*, 1985, **12**, 5717; Eur. Pat. Appl. No. 87311095.1 (1987).

6 (*a*) C. Taliani, G. Ruani, R. Zamboni, A. Bolognesi, M. Catellani, S. Desti, W. Porzio and P. Ostoja, *Synthetic Metals*, 1989, **28**, C507; (*b*) A. Bolognes, M. Catellani, S. Desti, R. Zamboni and R. Taliani, *J. Chem. Soc., Chem. Commun.*, 1988, 245.

7 (*a*) P. B. Koster and M. J. Janssen, *J. Chem. Soc., Perkin Trans. 2*, 1976, 323; (*b*) P. B. Koster, J. Runsink and M. J. Janssen, *J. Chem. Soc., Perkin Trans. 2*, 1979, 393.

8 '*Handbook of Conducting Polymers*', ed. T. A. Skotheim, Dekker, New York, 1986, p. 302.

9 J. Kaufman, T. C. Chung and A. J. Heeger, *Solid State Commun.*, 1983, **47**, 585.

10 A. Amer, A. Burkhardt, A. Nkansah, R. Shabana, A. Galal, H. B. Mark, Jr., and H. Zimmer, *Phosphorus, Sulfur and Silicon*, 1989, **42**, 63.

11 R. J. Waltman, A. F. Diaz and J. Bargon, *J. Electrochem. Soc.*, 1984, **131**, 740; 1452.

12 Our measurements.

13 P. B. Koster, M. J. Janssen and E. A. C. Lucken, *J. Chem. Soc., Perkin Trans. 2,* 1974, 803.

14 M. Mastrogostino and L. Saddu, *Electrochim. Acta*, 1990, **35**, 463.

---

†† Preliminary 2-probe dc conductivities of compressed pellets of undoped PCDM were $\gtrsim 10^{-7}$ s cm$^{-1}$.