LINZ LECTURES

Lecture 1. The Development of Organic Conductors: Metals, Superconductors and Semiconductors

Lecture 2A. Introduction and Synthesis of Important Conjugated Polymers

Lecture 2B. Solid State Polymerization

Lecture 3. Fullerene Chemistry

Lecture 3B. Molecular Engineering

Lecture 3B. Molecular Engineering of Conjugated Polymers for OE

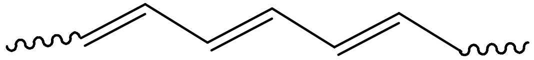
Processing Design

Bandgap Design

N-Dopable Design

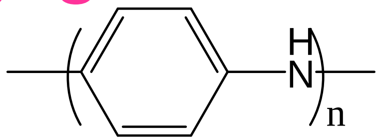
Self-Dopable and Water Solubility Design

The Most Popular Conjugated Polymers

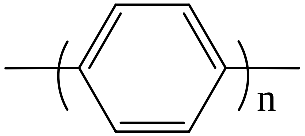


(CH)x

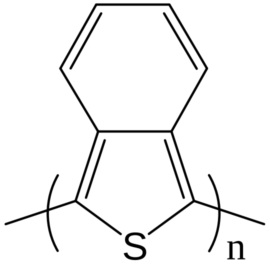
PA



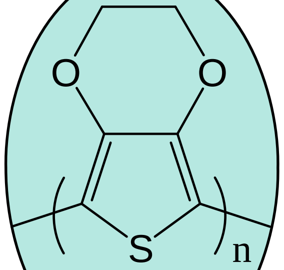
PANI



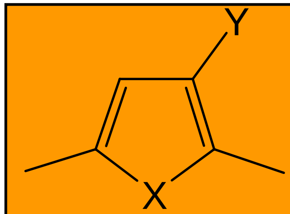
PPP



PITN

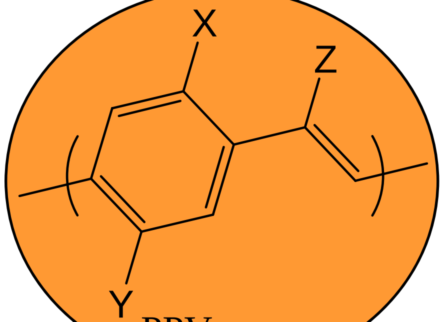


PEDOT

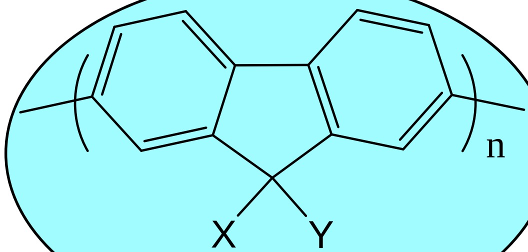


X = S, NH, NR; Y = H, R, Ph, etc

PT, PPy, etc



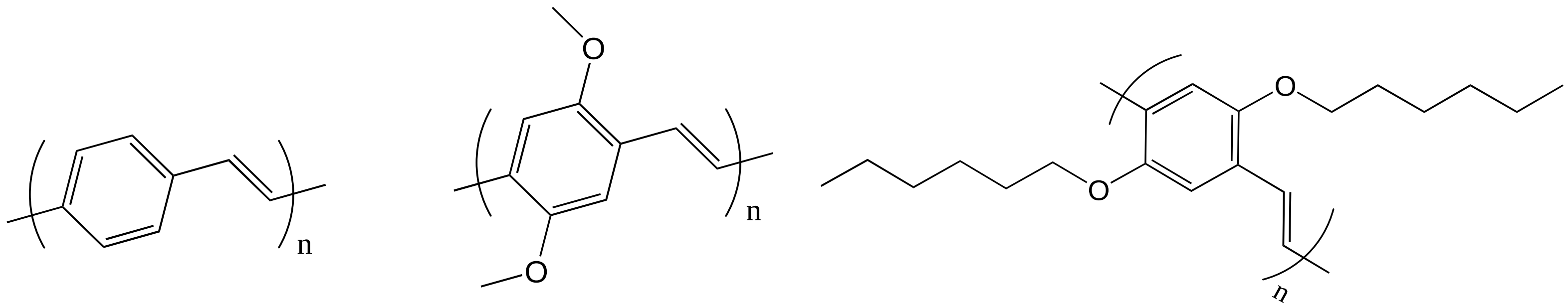
PPVs

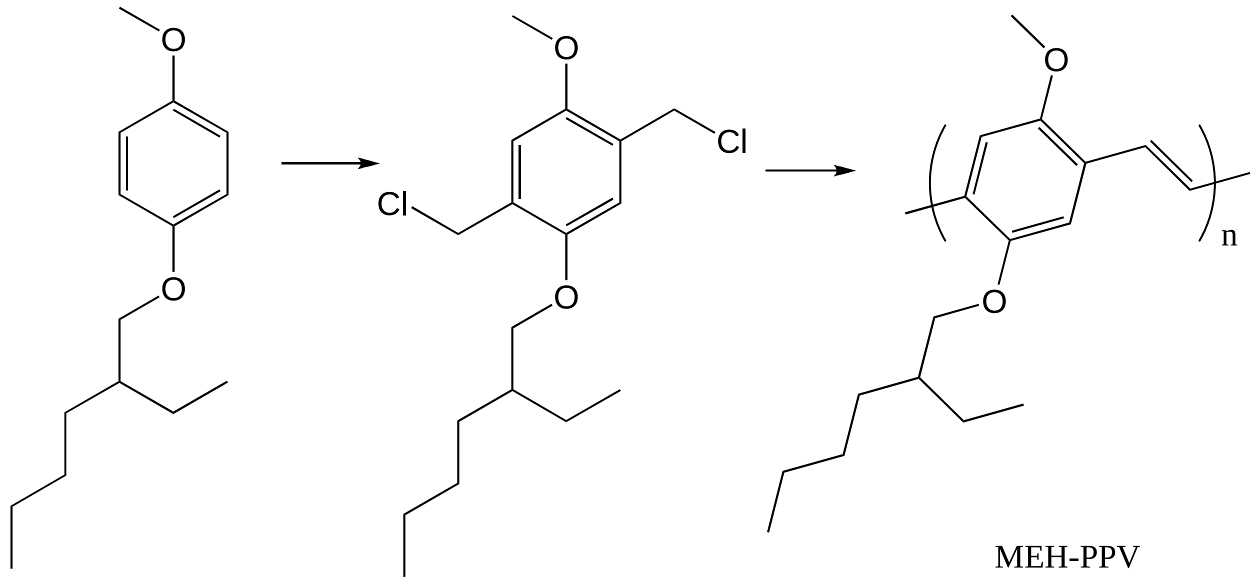


PFs

THE DRIVE TOWARD PROCESSING

The Evolution of Processable PPV as an Example



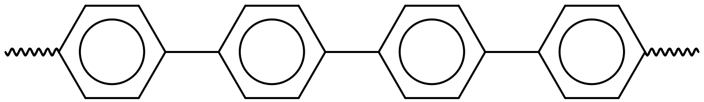
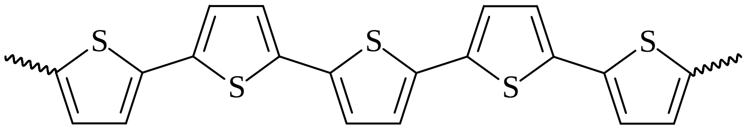
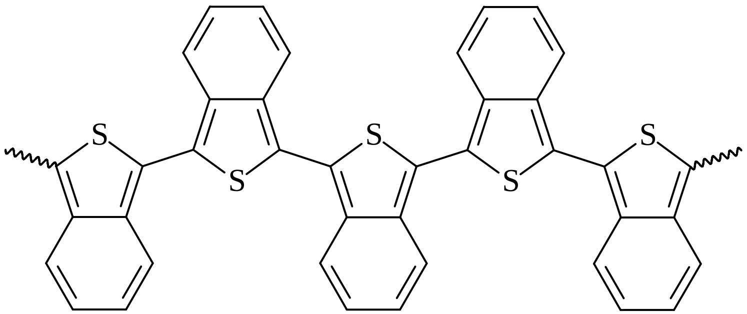


MEH-PPV

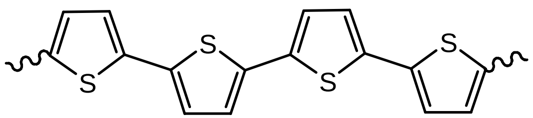
F. Wudl, P.-M. Alleman, G. Srdanov, Z. Ni, D. McBranch in “Materials for Nonlinear Optics” S. Marder, J.E. Sohn. G.D. Stucky, Eds; American Chemical Society Symposium Series, 1991. pp 683-686.

Designing the Semiconductor Gap

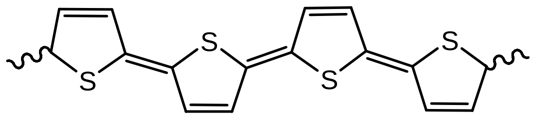
The Bandgaps of Conducting Polymers
(π–π*)

Polymer	ΔE Gap, eV
	ca. 3.0
	ca. 2.1
	ca. 1.5
	ca. 1.1

The Concept of Low Bandgap Based on Benzenoid and Quinoid Equivalence

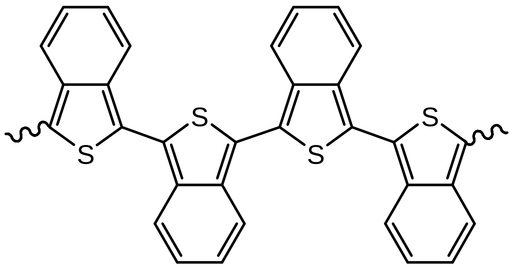


T_A

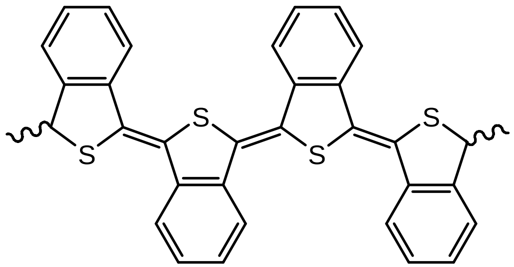


T_B

$E_A << E_B$



I_A



I_B

$E_A \sim E_B$

Poly(isothianaphthene). Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 3382–3384.
The Electronic and Electrochemical Properties of Poly(isothianaphthene). Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 5717–5723
Bredas, J.-L.; Heeger, J. A.; Wudl, F. *J. Chem. Phys.***1985**, *85*, 4673

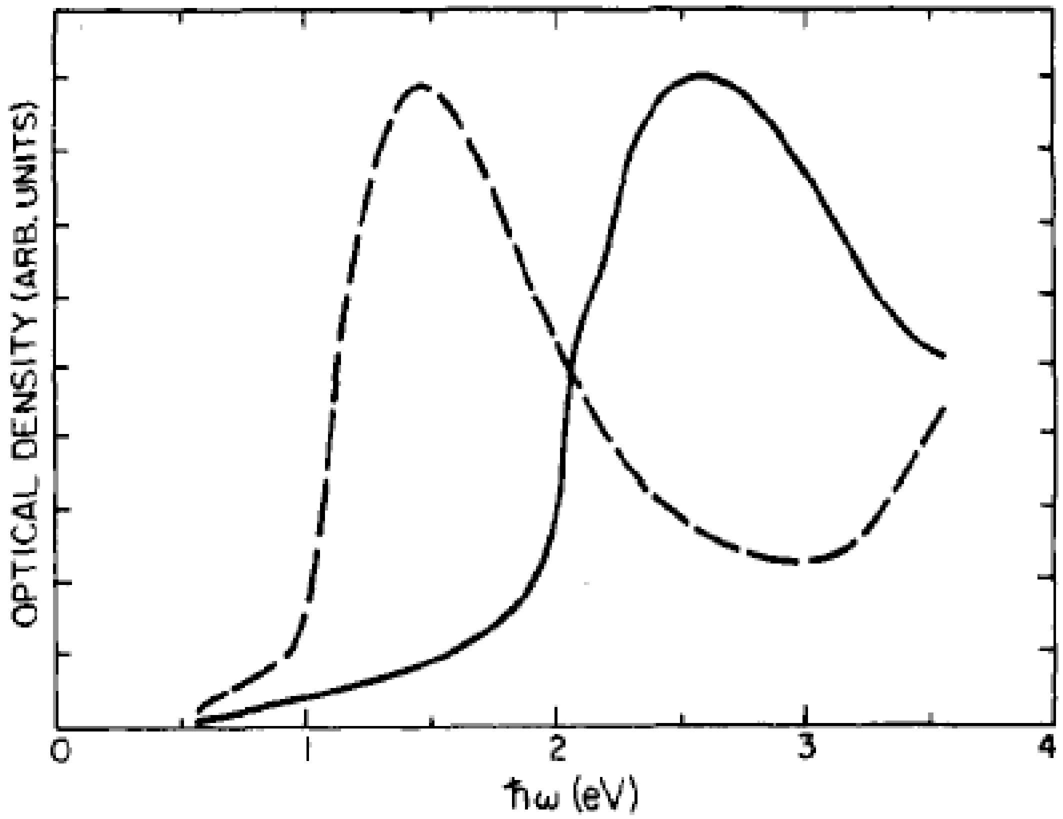


Figure 13. Absorption coefficients of polythiophene (solid curve) and poly(isothianaphthene) (dashed curve).

Transparent to the Human Eye

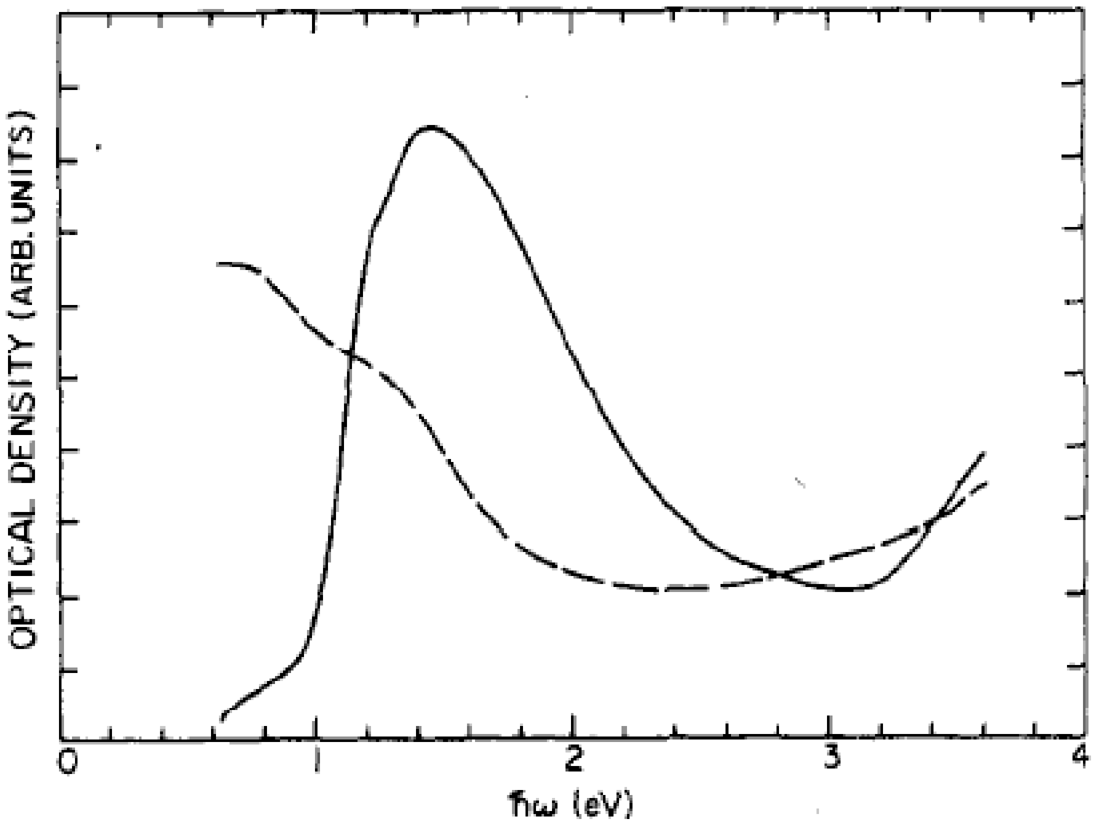
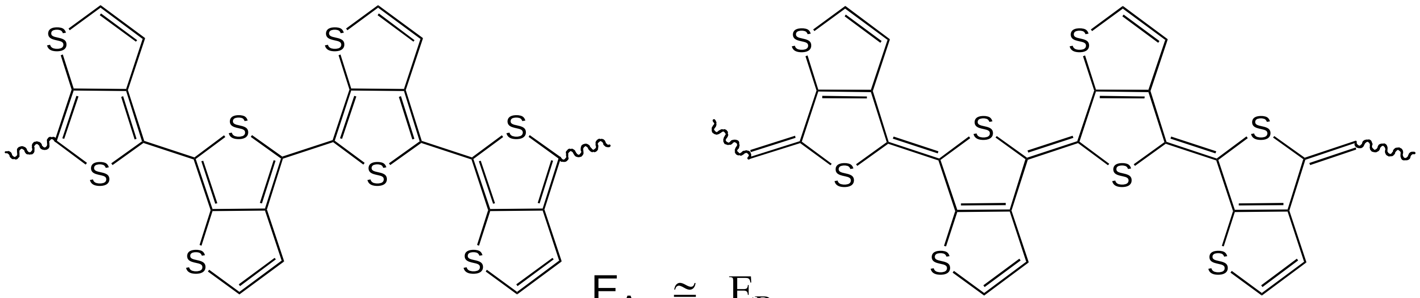
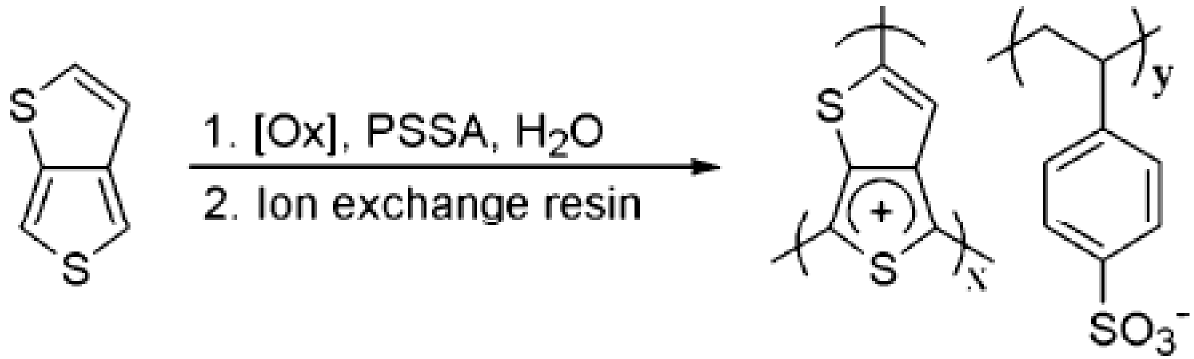


Figure 14. Spectral changes associated with the observed color change on doping; absorption spectrum of PITN after electrochemical compensation (solid curve) and after in situ electrochemical doping (dashed curve) (see text).

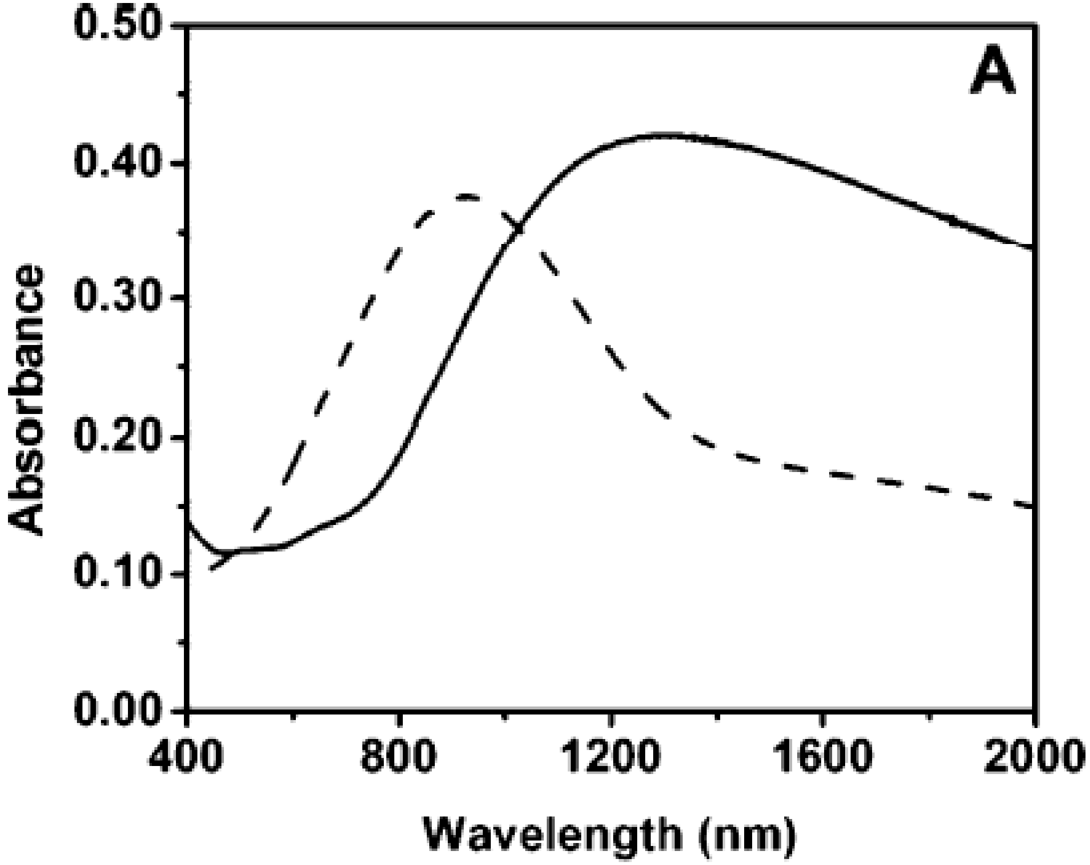
Application of the Concept to a PEDOT Analog



T_A T_B

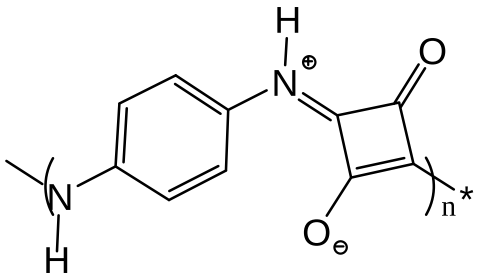


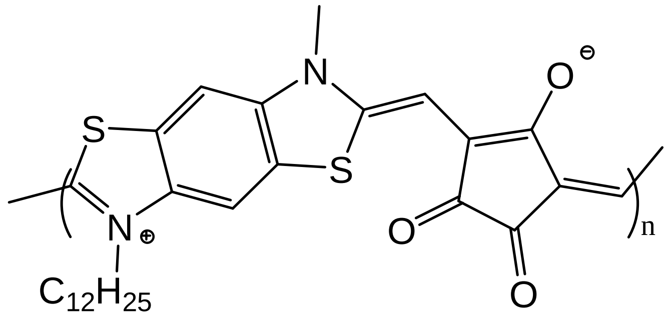
B. Lee, V. Seshadri, G. A. Sotzing *Langmuir* **2005,** *21,* 10797



B. Lee, V. Seshadri, G. A. Sotzing *Langmuir* **2005,** *21,* 10797

The Concept of Low Bandgap Based on Intramolecular Donor-Acceptor Interactions





Eg ca 0.5 eV

Havinga, E.E.; Pomp, A.; Ten Hoeve, W.; Wynberg, H. *Synthetic Metals*, **1995**, *69*, 581

Havinga, E.E.; Pomp, A.; Ten Hoeve, W.; Wynberg, H. *Polym. Bull.*, **1992**, *29*, 119

J. Eldo and A. Ajayaghosh *Chem. Mater.* **2002,** *14*, 410-418

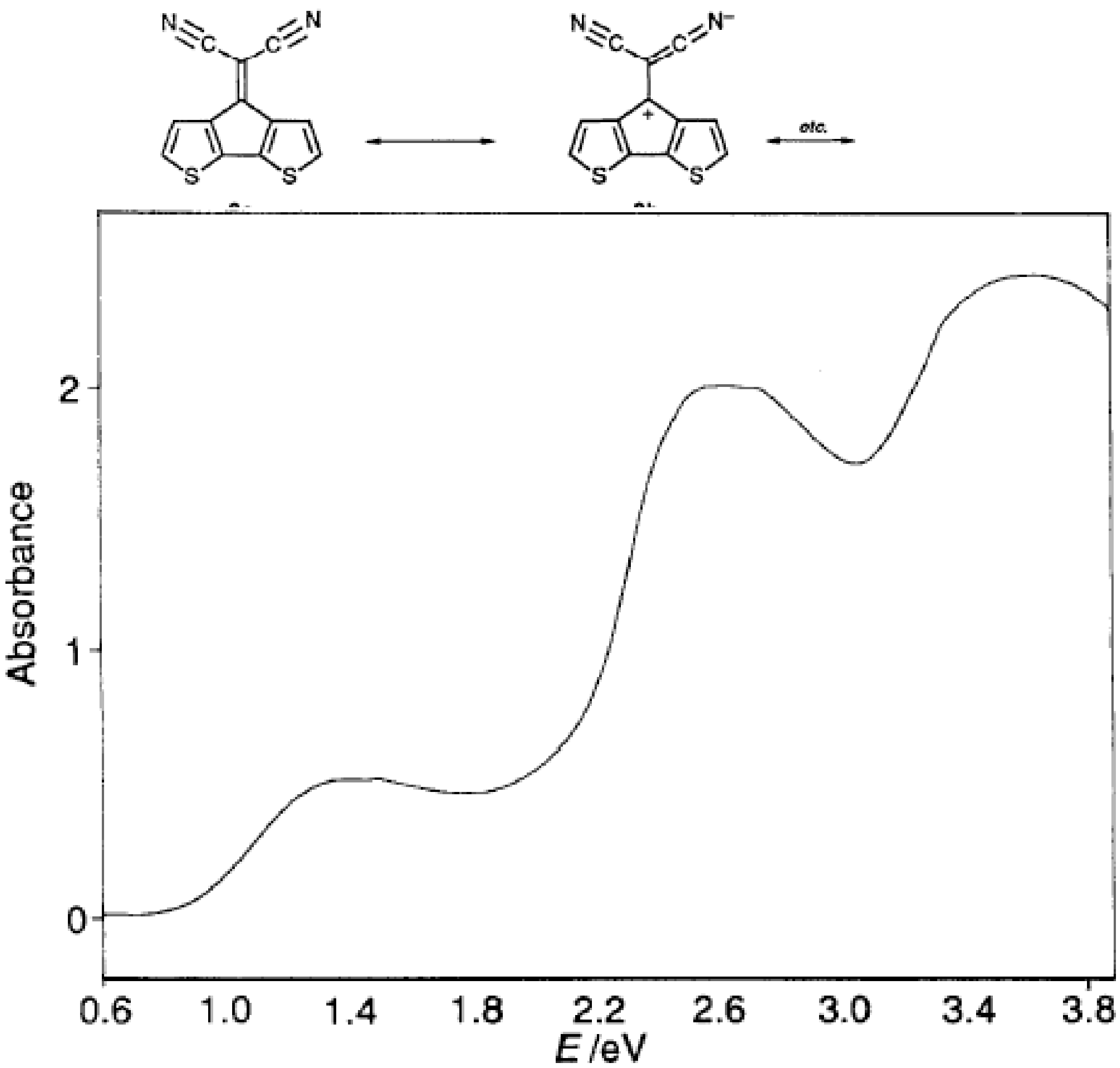
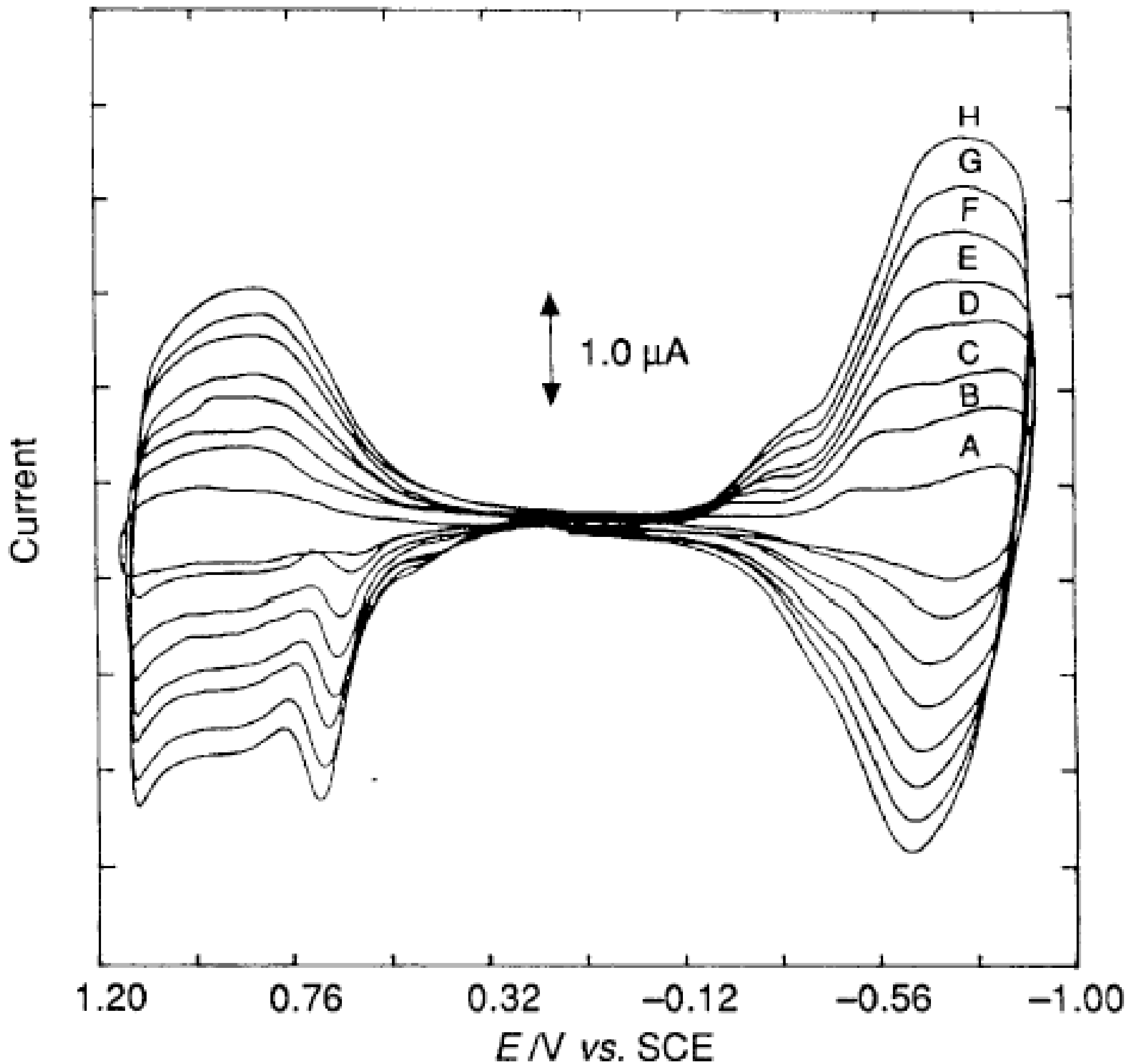


Fig. 1 Absorption spectrum for poly-**2** (PCDM)

J. P. Ferraris and T. L. Lambert *J. CHEM. SOC., CHEM. COMMUN.*, 1991, 1268



J. P. Ferraris and T. L. Lambert *J. CHEM. SOC., CHEM. COMMUN.*, 1991, 1268

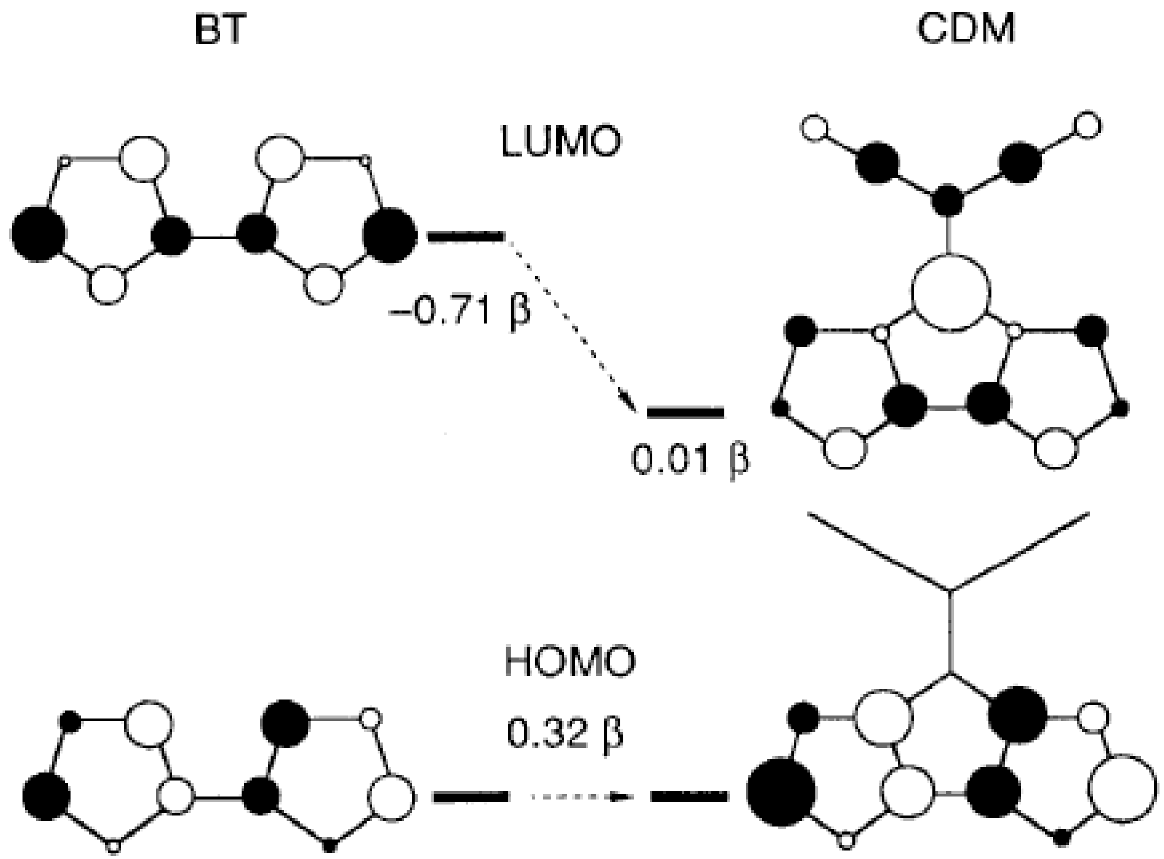
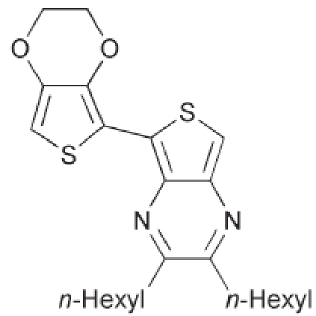


Fig. 3 Frontier molecular orbitals and corresponding HMO energies (β) for bithiophene (BT) and **2** (CDM)

J. P. Ferraris and T. L. Lambert *J. Chem. Soc., Chem. Commun.*, **1991**, 1268



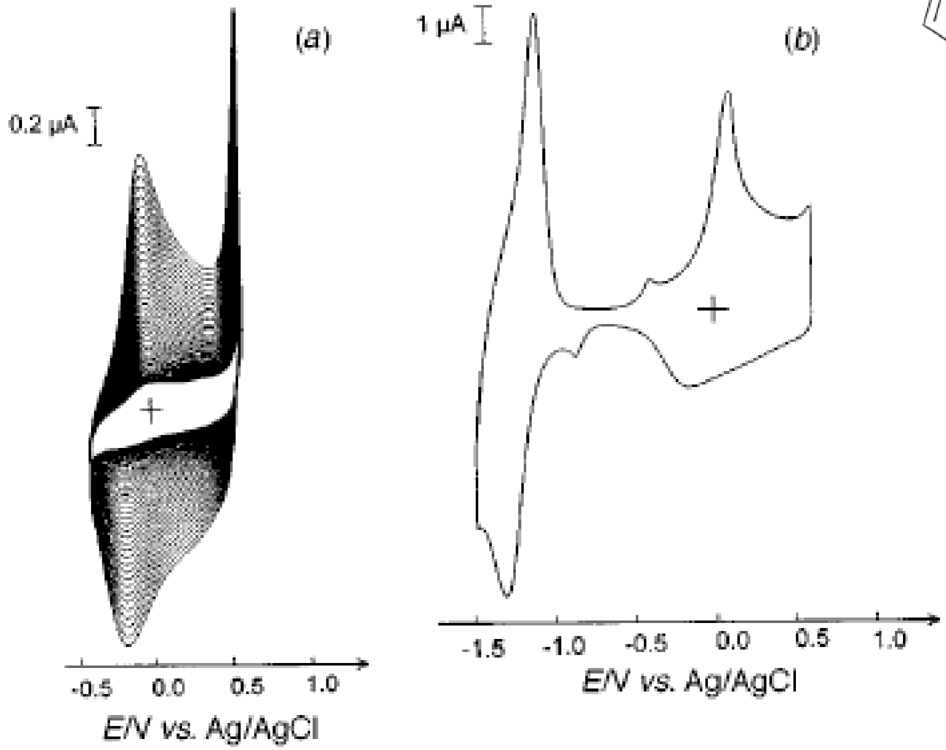
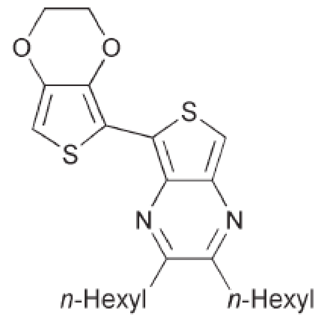


Fig. 1 (*a*) Potentiodynamic electropolymerization of **1** on Pt, t × 10^{-4} M substrate in 0.10 M Bu_4NPF_6–MeCN, scan rate 100 mV s^{-1}. (*b*) Cyclic voltammogram of poly(1) in 0.10 M Bu_4NPF_6–MeCN, Pt electrodes, scan rate 100 mV s^{-1}.

Said Akoudad and J. Roncali *J. C h e m.Soc. Chem. Commun.,* **1998**, 2081



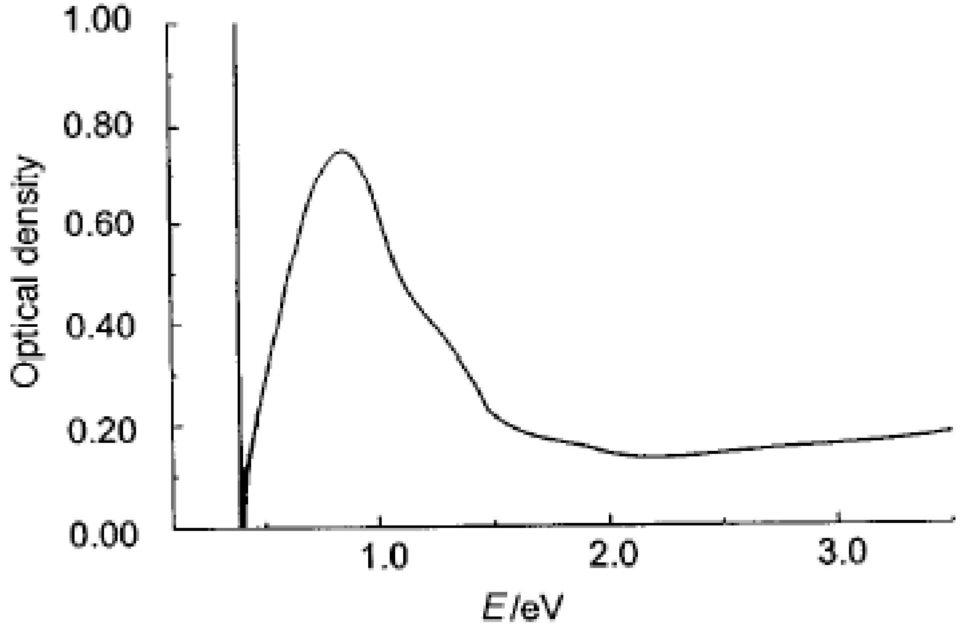
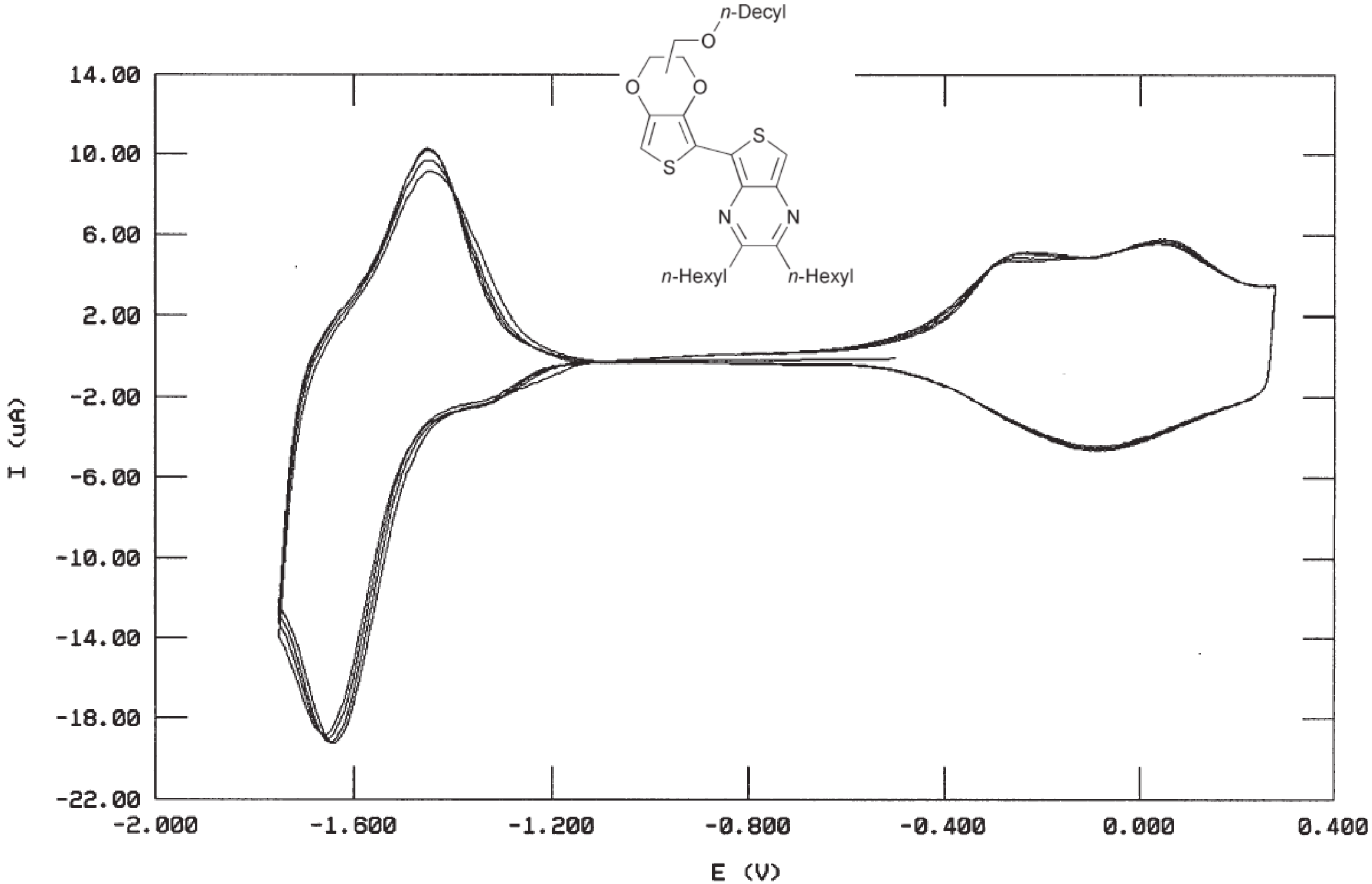
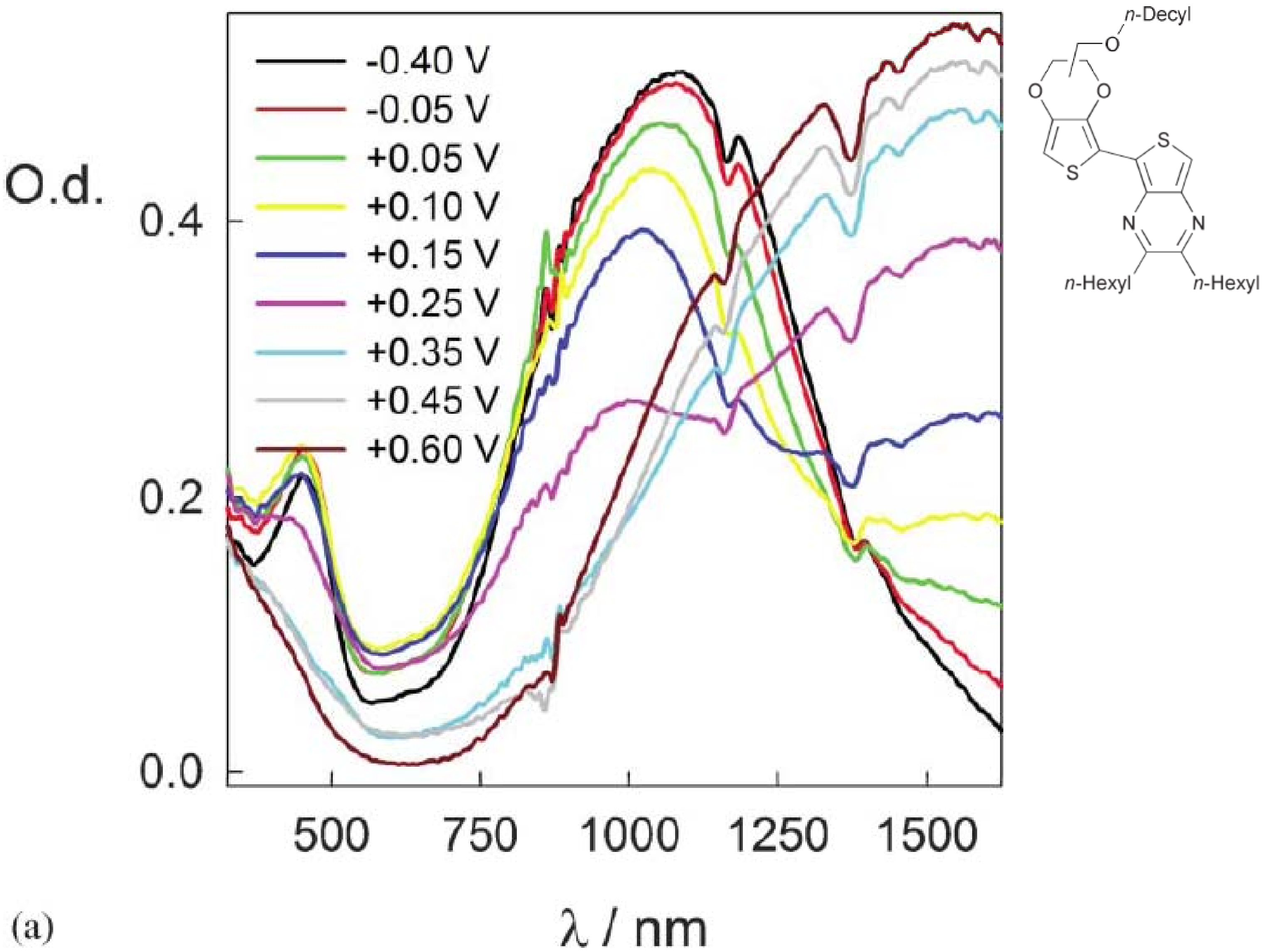


Fig. 2 Optical spectrum of neutral poly(**1**) on ITO (the straight line at 0.40 eV is due to ITO absorption)

Said Akoudad and J. Roncali *J. C h e m.Soc. Chem. Commun.,* **1998**, 2081



I. F. Perepichka, E. Levillain and J. Roncali *J. Mater. Chem.*, **2004**, *14*, 1679

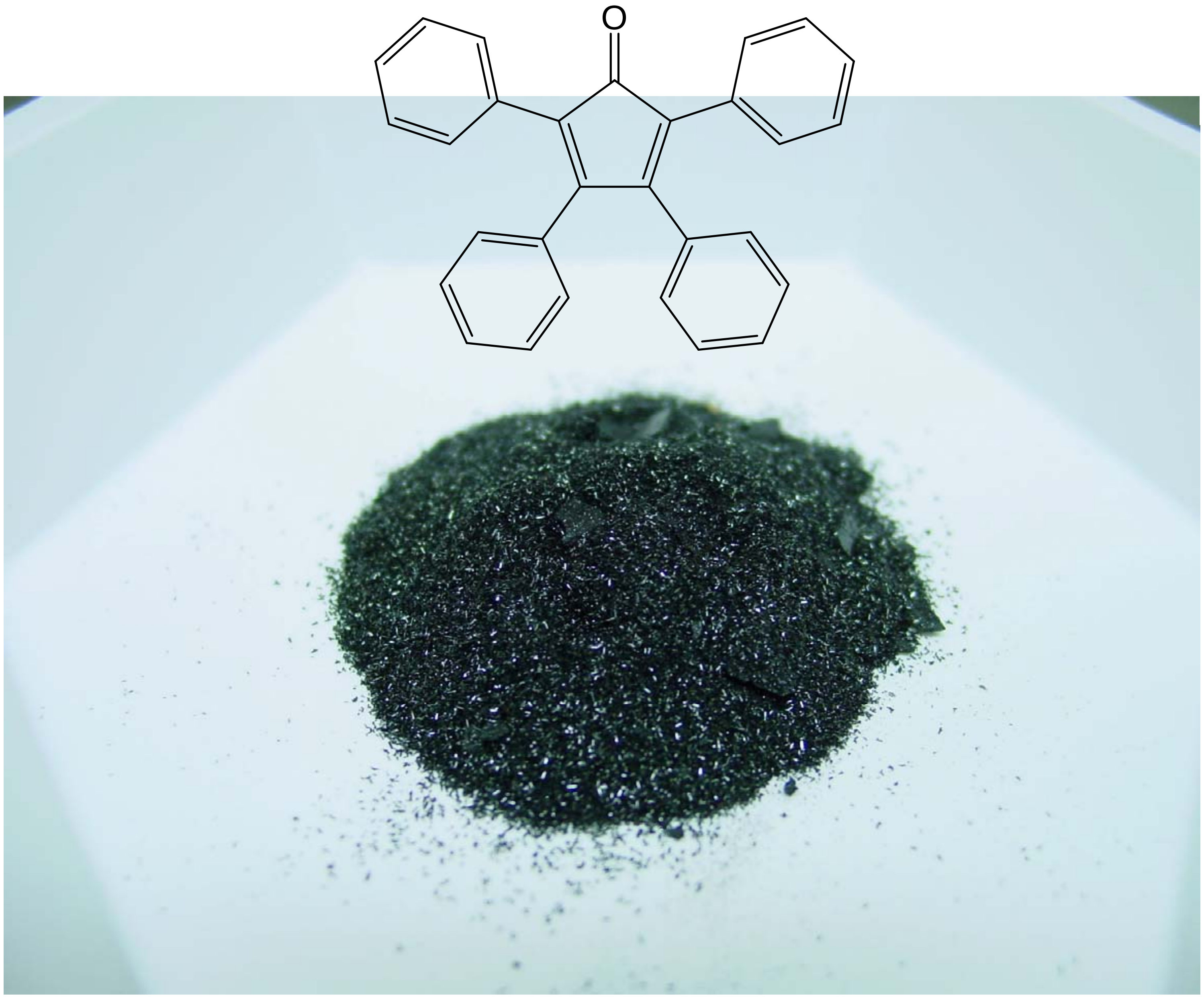


I. F. Perepichka, E. Levillain and J. Roncali *J. Ma t e r. C h e m*., **2004**, *14*, 1679

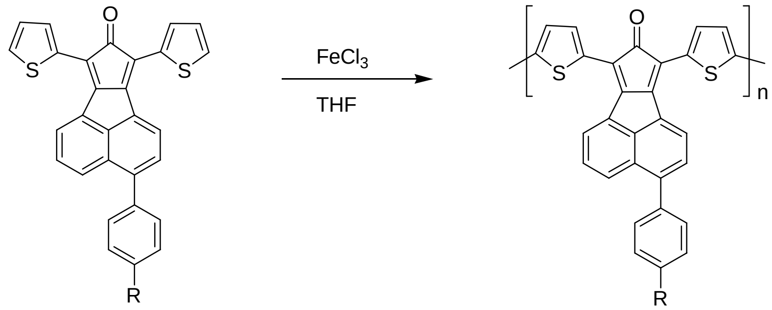
The Concept of Low Bandgap Polymer Based on Small Bandgap Monomer

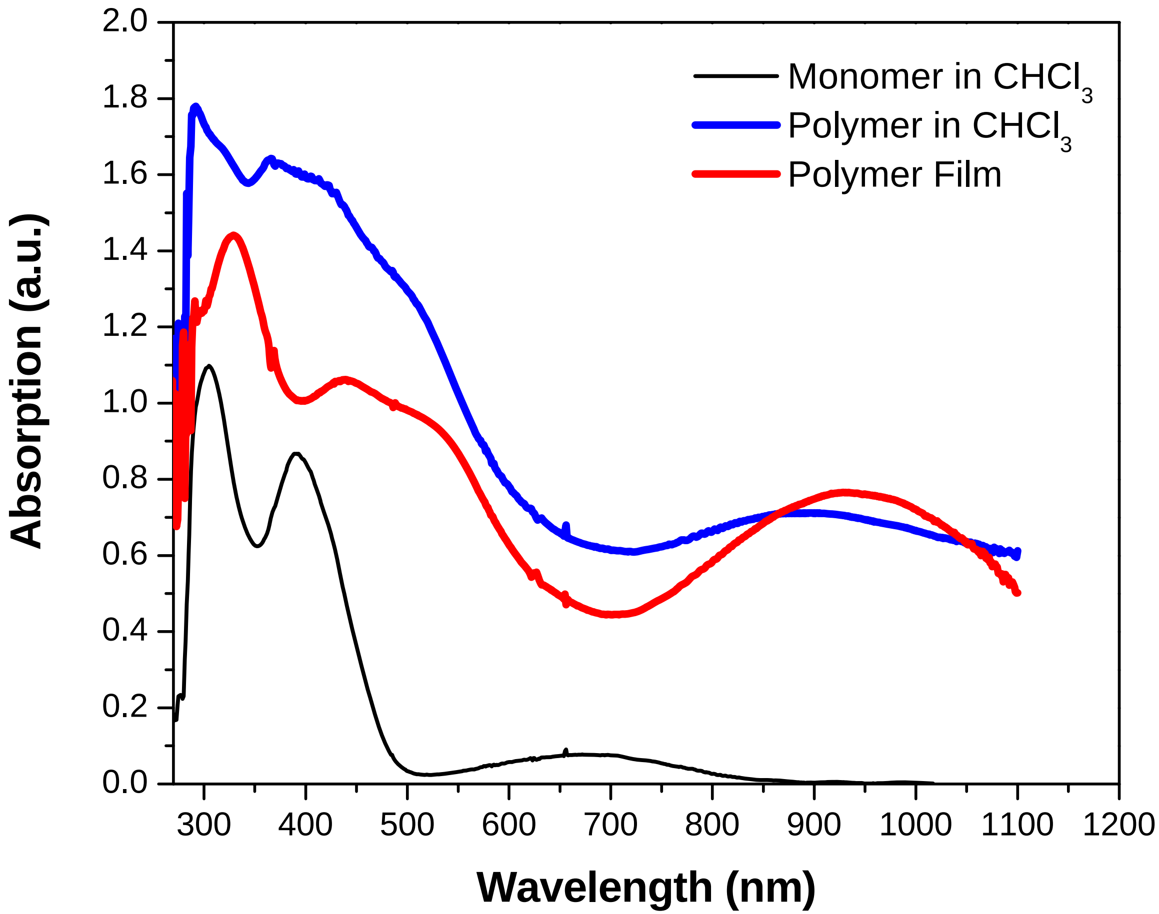
If the monomer units have a small HOMO-LUMO gap, it stands to reason the incorporation into a conjugated backbone ought to produce an even smaller bandgap polymer

An Example of a Very Low Bandgap Molecule



A New Polymer with a 0.9 eV Bandgap

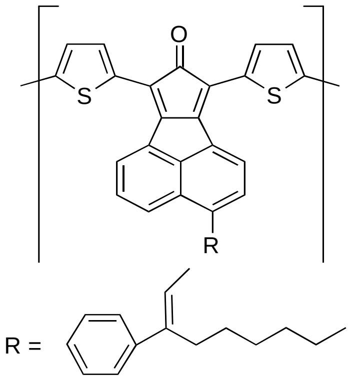


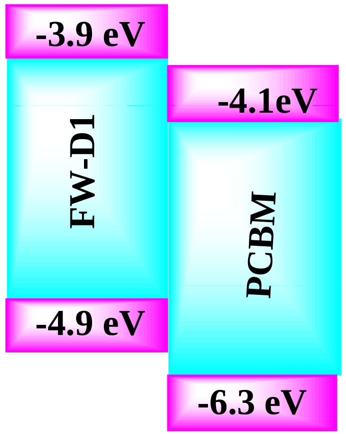


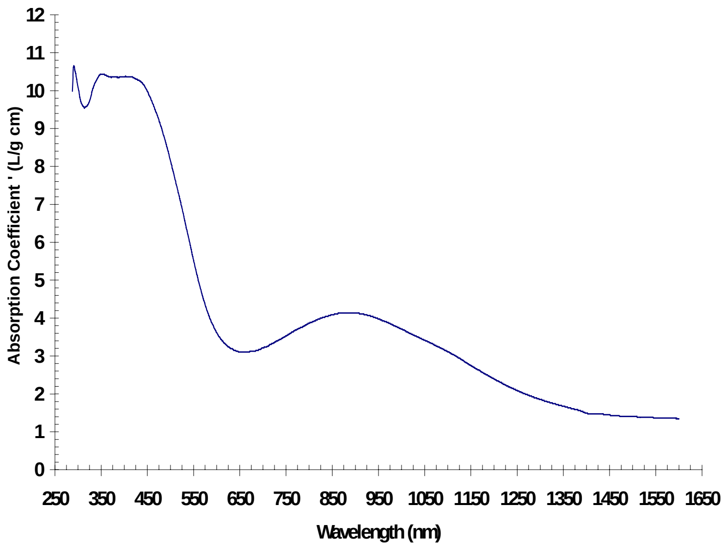
Wes Walker

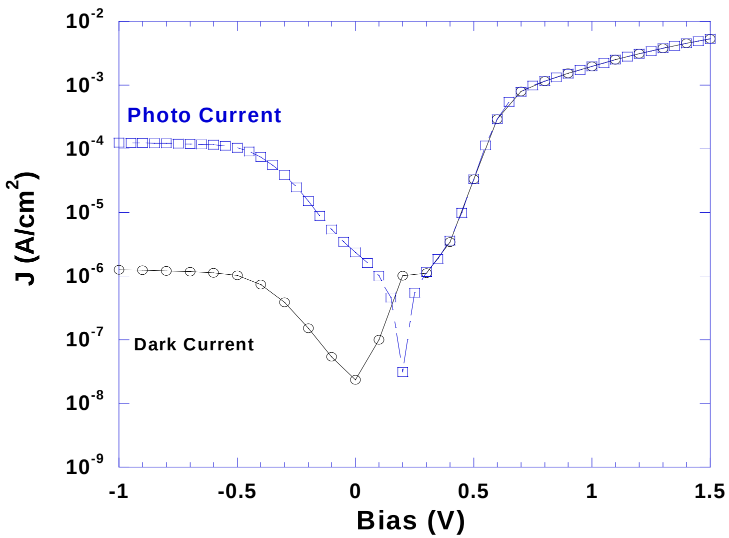
Satish Patil

Materials with Spectral Response: 400nm ~ 1400nm

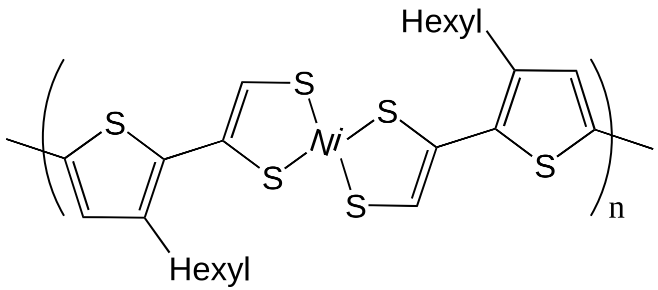


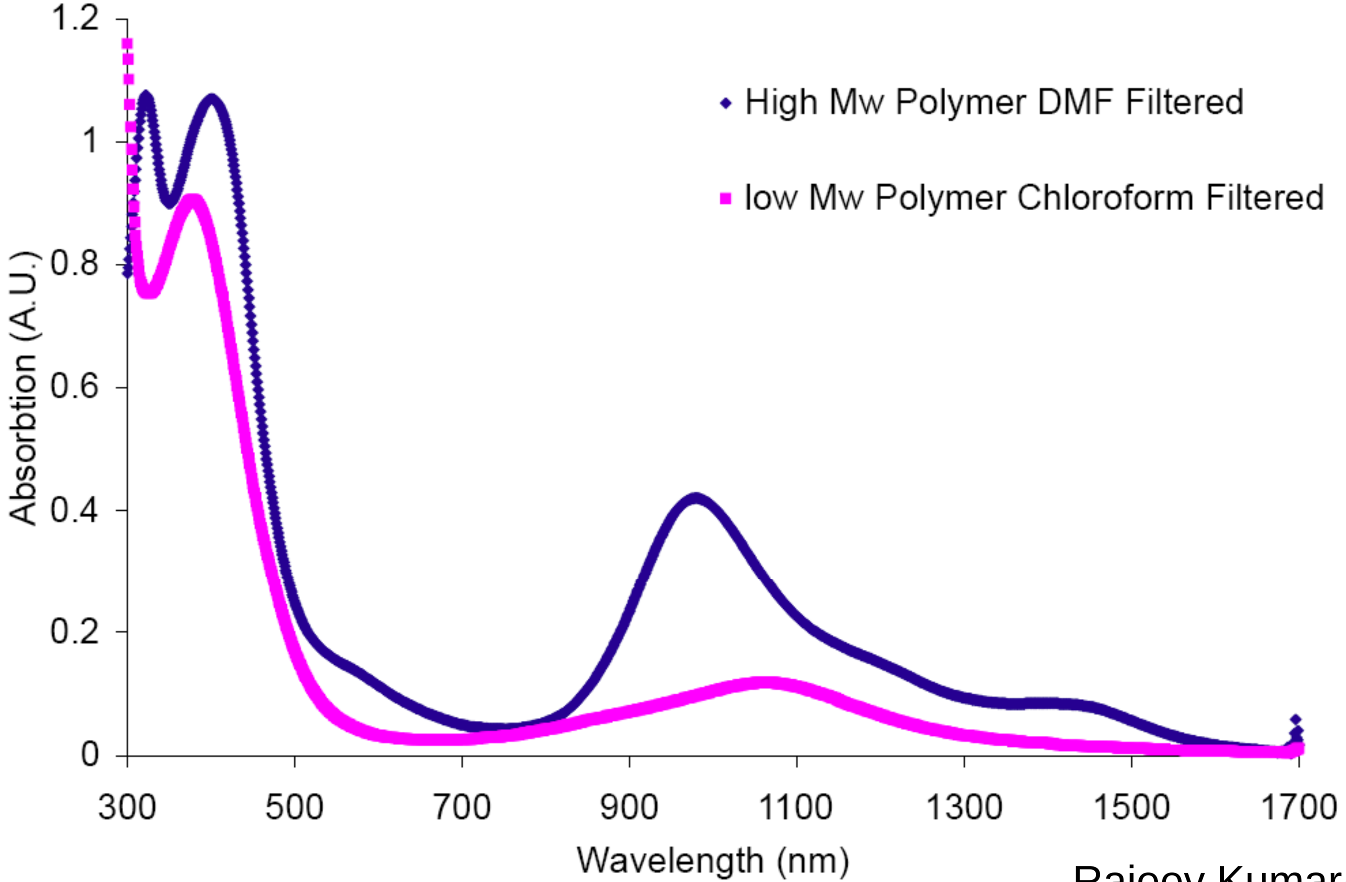






Preliminary Results

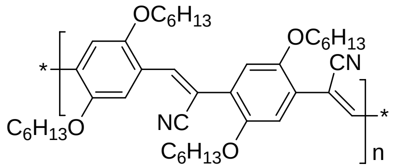




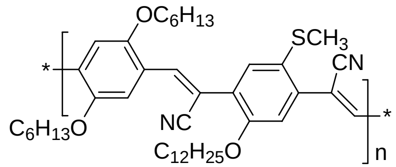
Rajeev Kumar/Britt Veldman

The Drive Toward *n*-Dopable Polymers

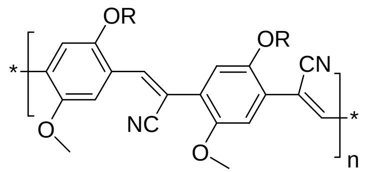
The Drive Toward *n*-Dopable Polymers



CN-PPV1 (E_g = 2.1 eV)
λ_{PL} = 710 nm

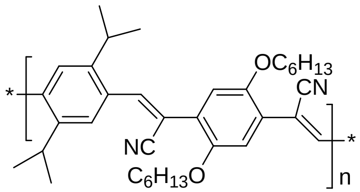


CN-PPV2 (E_g = 2.2 eV)
λ_{PL} = 610 nm

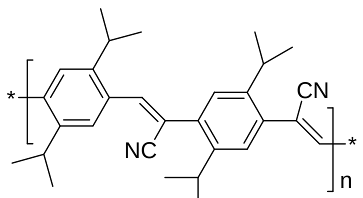


R = C_8H_{17}
R = $C_{10}H_{21}$
R = $C_{12}H_{25}$
R = $C_{16}H_{33}$

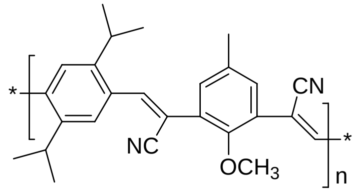
E_g = 2.0 eV
λ_{PL} = 611nm
λ_{EL} = 603-618 nm



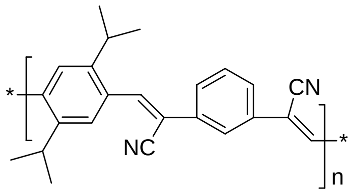
CN-PPV3 (E_g = 2.85 eV)
λ_{PL} = 516 nm; λ_{EL} = 510 nm



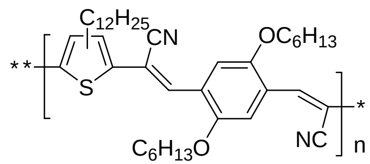
CN-PPV4 (E_g = 3.2 eV)



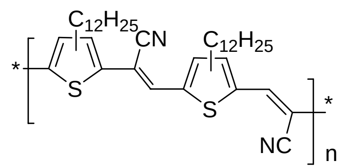
CN-PPV5 (E_g = 3.05 eV)



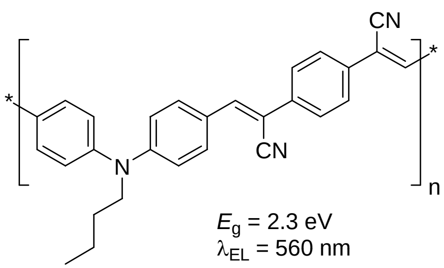
CN-PPV6 (E_g = 2.7 eV)



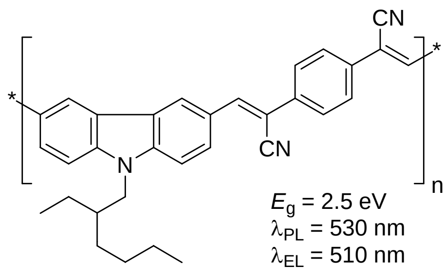
CN-PT-*co*-PPV (E_g = 1.8 eV)
λ_{PL} = 840 nm; λ_{EL} = 730 nm



CN-PT (E_g = 1.55 eV)
λ_{PL} = 950 nm

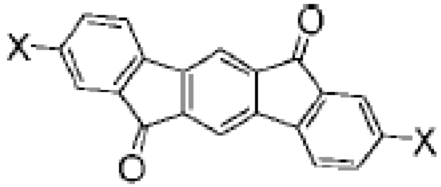


E_g = 2.3 eV
λ_{EL} = 560 nm

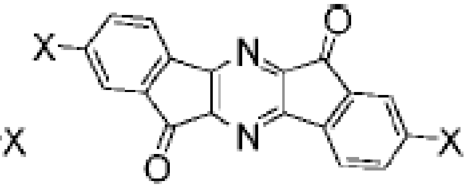


E_g = 2.5 eV
λ_{PL} = 530 nm
λ_{EL} = 510 nm

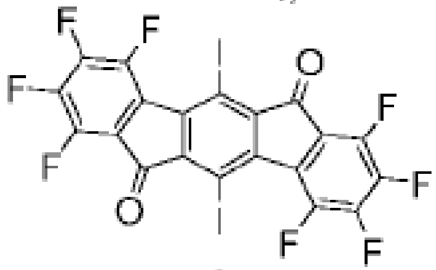
N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, A. B. Holmes Efficient Light-Emitting Diodes Based on Polymers with High Electron Affinities *Nature* **1993**, *365*, 628-630



1a; X = H
1b; = F
1c; = Cl
1d; = Br



2a; X = H
2b; = F



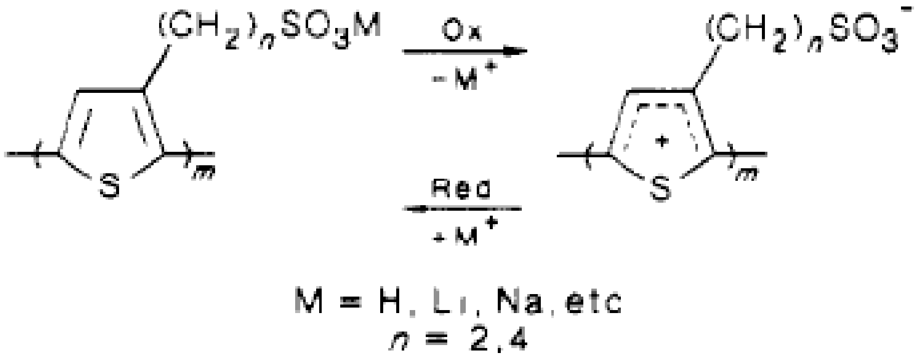
3

compound	surface	mobility, $cm^2\ V^{-1}\ s^{-1}$	on/off ratio	threshold, V
1a	HMDS	no gate effect		
1b	bare	1.9×10^{-4}	6×10^3	+88
	HMDS	0.17	2×10^7	+69

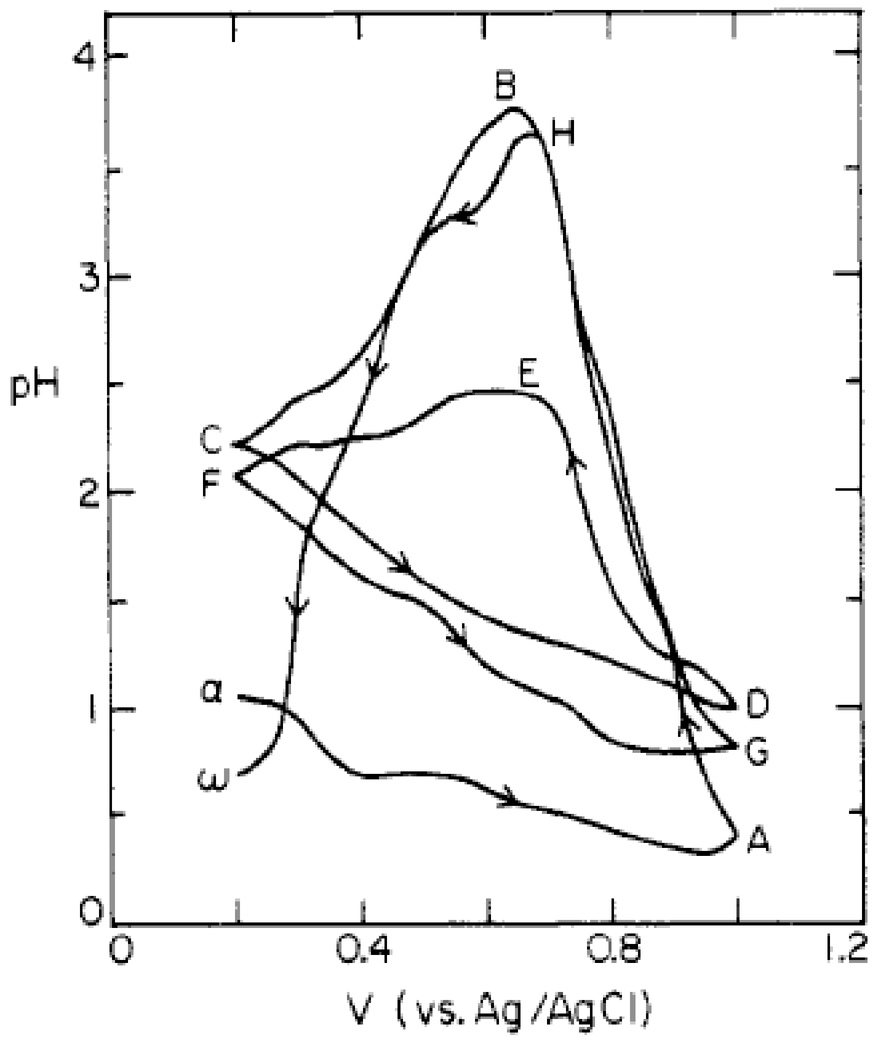
T. Nakagawa, D. Kumaki, J. Nishida, S. Tokito, Y. Yamashita *Chem. Mater.* **2008,** *20,* 2615–2617

Self-Doping and Water Solubility

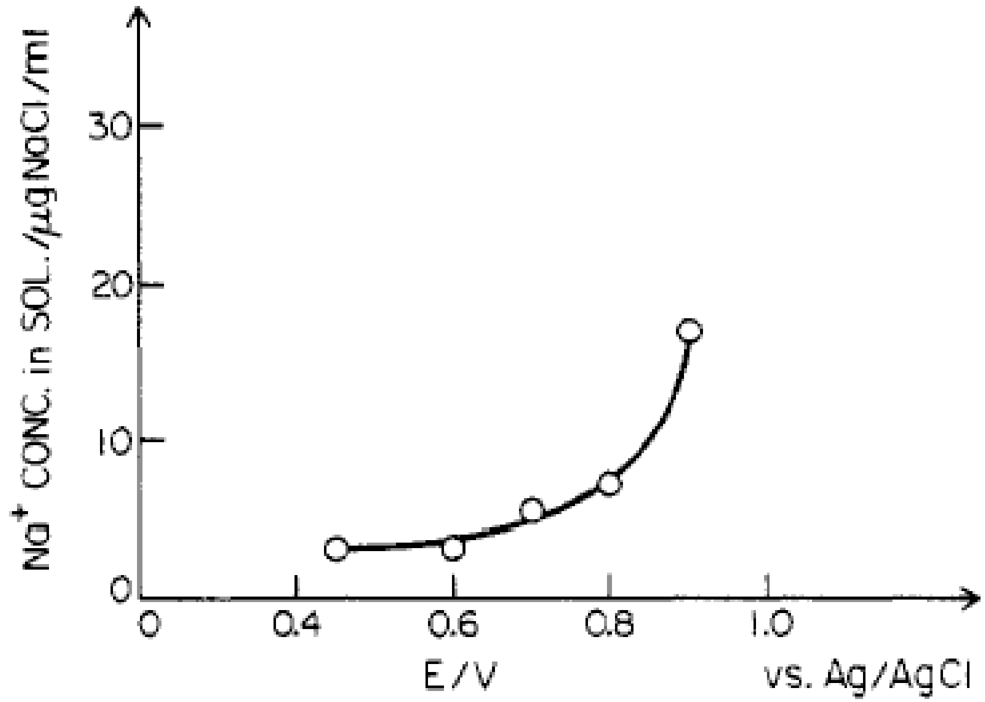
Self-Doping Conducting Polymer/Water Soluble Conducting Polymer



Ikenoue, Y.; Chiang, J.; Patil, A. O.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1988**, *110,* 2983–2985

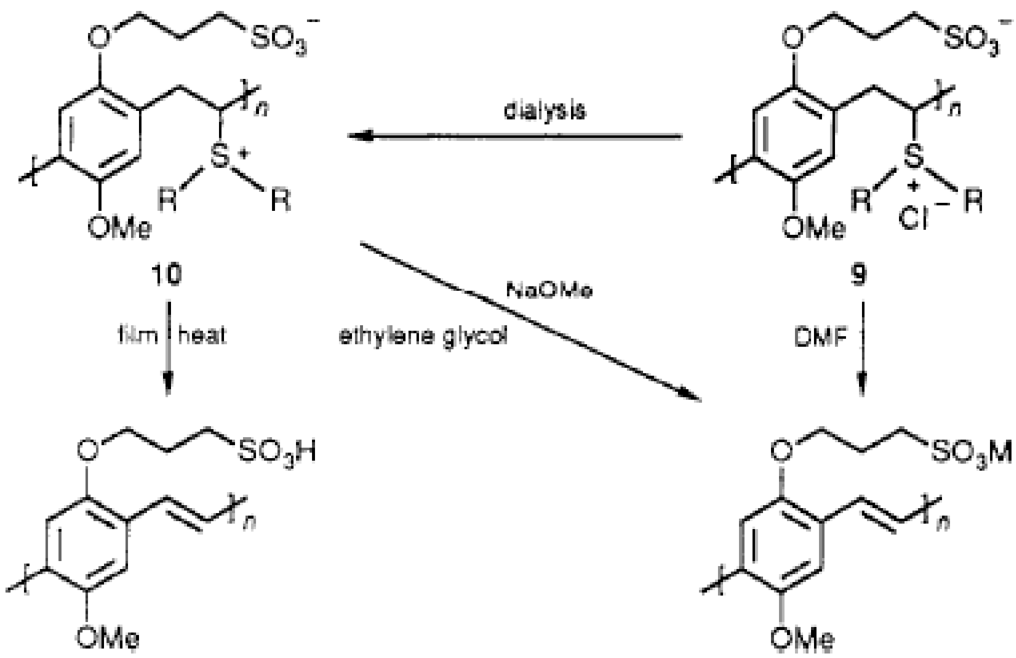


Ikenoue, Y.; Chiang, J.; Patil, A. O.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1988**, *110,* 2983–2985



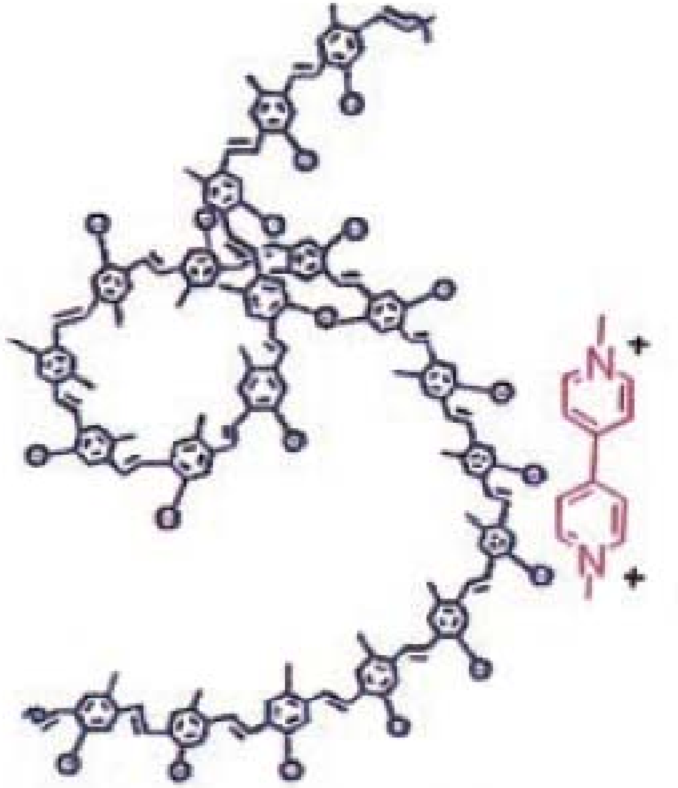
Ikenoue, Y.; Chiang, J.; Patil, A. O.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1988**, *110,* 2983–2985

A Water-Soluble PPV



S. Shi, F. Wudl *Macromolecules* **1990,** *23*, 2119

“Superquenching of a Water-Soluble PPV

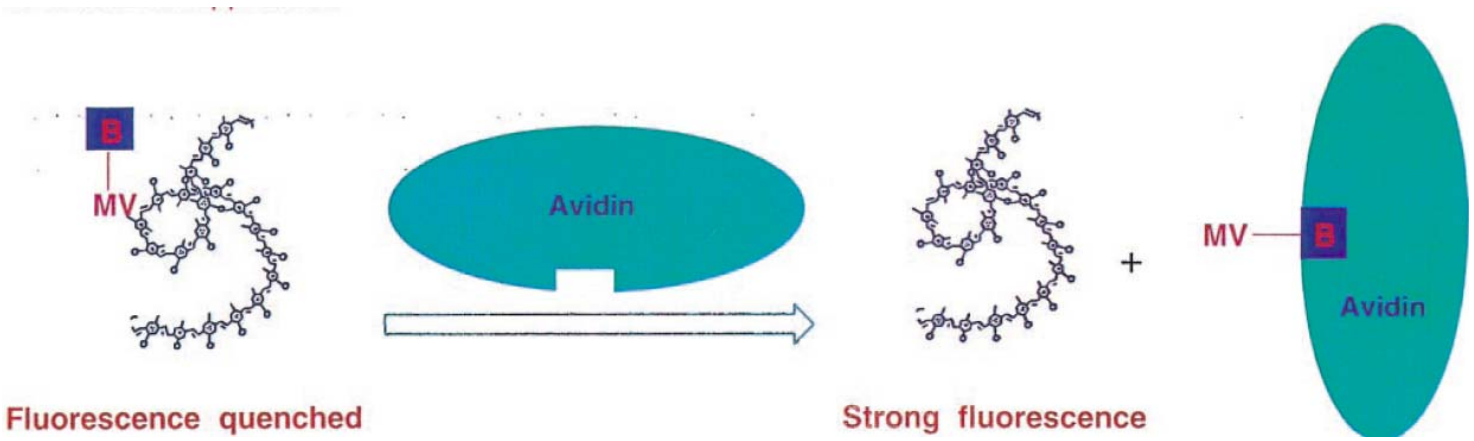


MPS-PPV / MV^{2+}

$K_{SV} \sim 10^7$

L. Chen, D. W. McBranch, H.-L. Wang, R. Helgeson§, F. Wudl, G. Whitten *PNAS*, **1999**, 12287

Biosensor Application



L. Chen, D. W. McBranch, H.-L. Wang, R. Helgeson§, F. Wudl, G. Whitten *PNAS*, **1999**, 12287

Summary

By application of simple design concepts conjugated poly processable, controllable Eg, n-dopable and water-soluble conjugated polymers could be prepared and applied to organic electronics and biology

The End

Thanks!