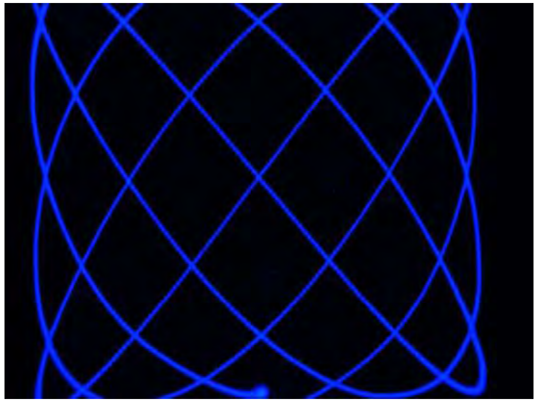
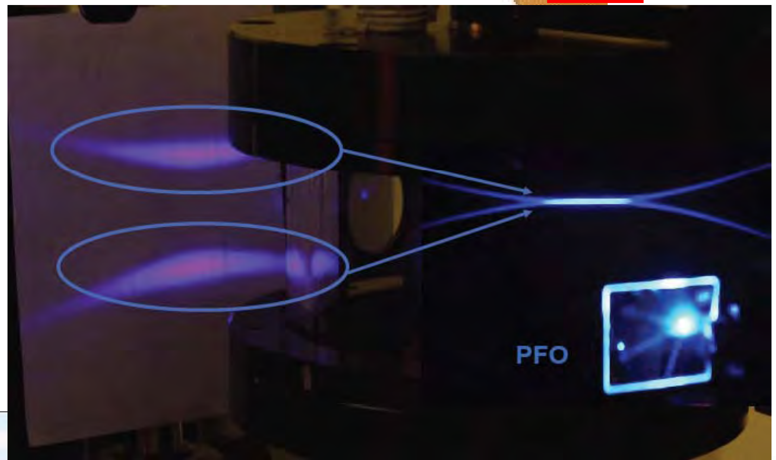
Peter Skabara

Electrochemical behaviour of multi- redox-active conjugated polymers

Applications





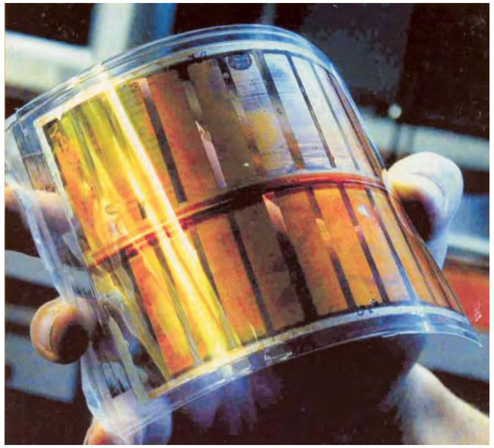
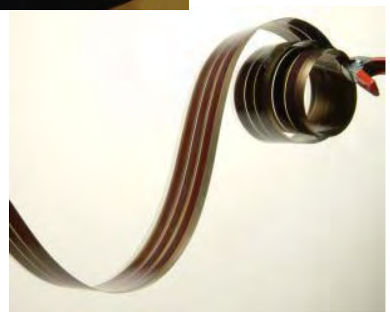
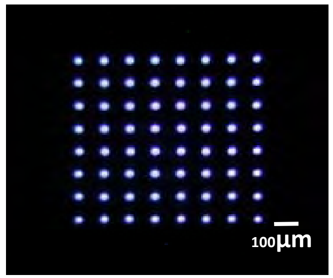
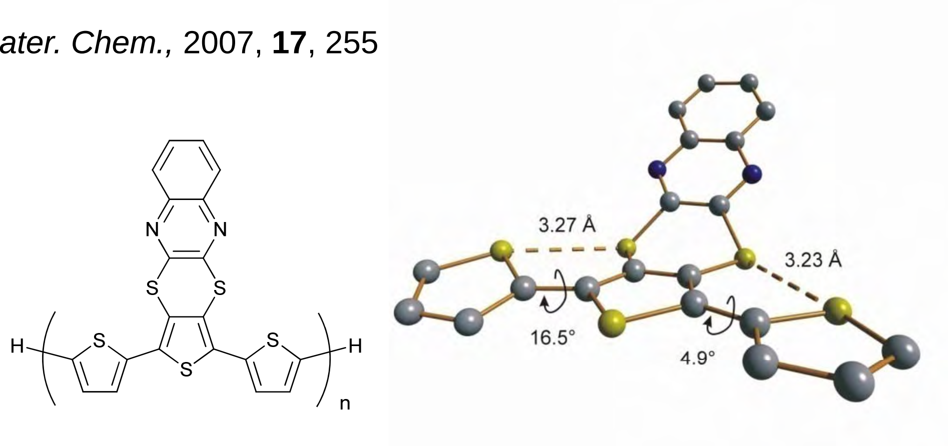


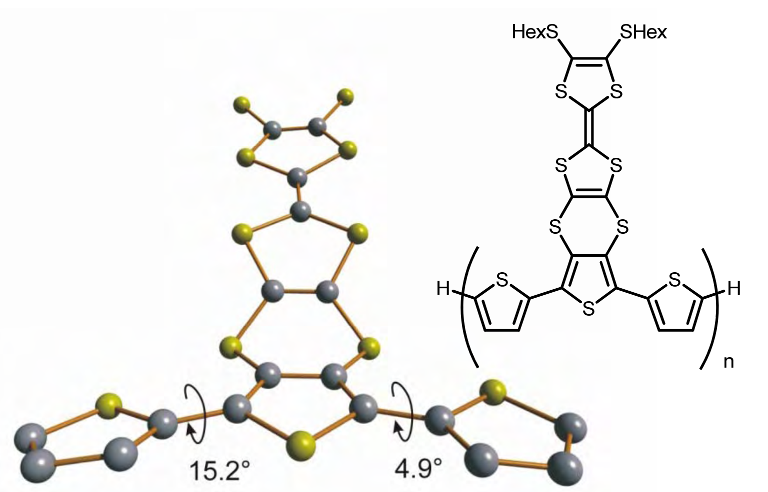

Figure 2. Flexible solar cell technology incorporated into a military tent



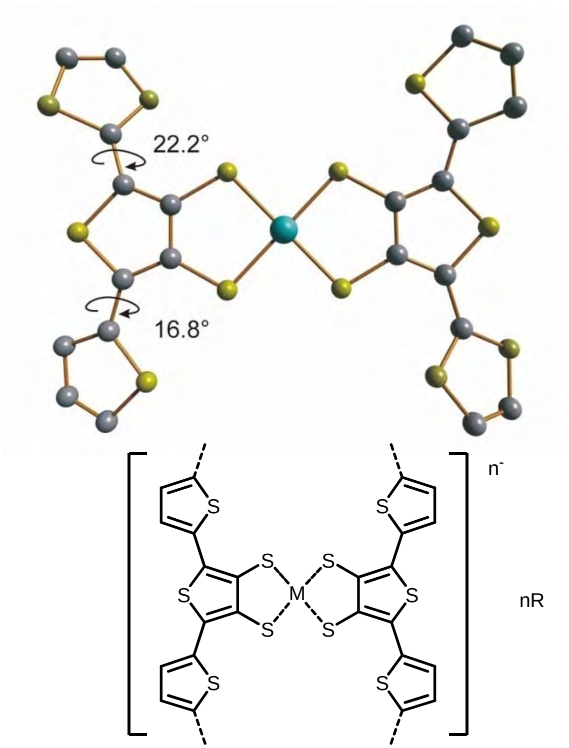


J. Mater. Chem., 2007, **17**, 255



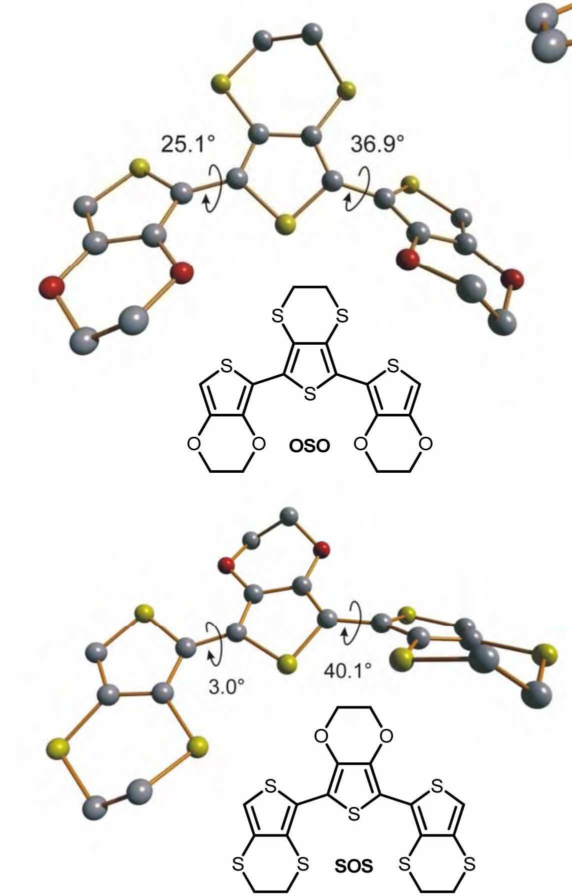


J. Phys. Chem. B, 2006, **110**, 3140
Chem. Commun., 2000, 1005

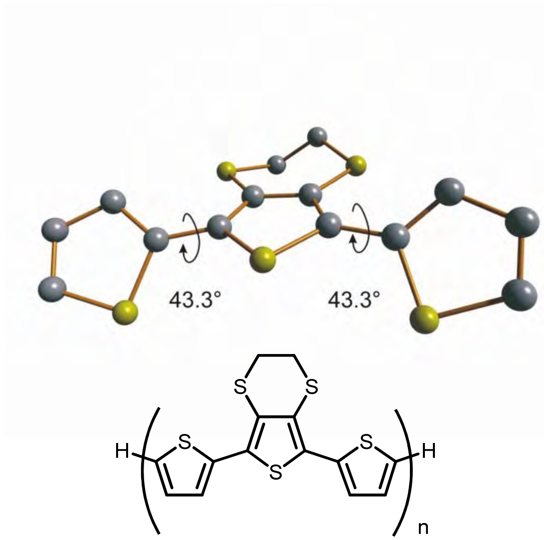


M = Ni, Au, Pd
R = PPN, *n*-Bu$_4$N, Na

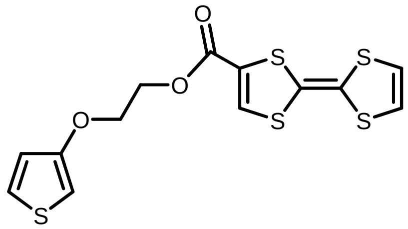
Chem. Commun., 2002, 2408



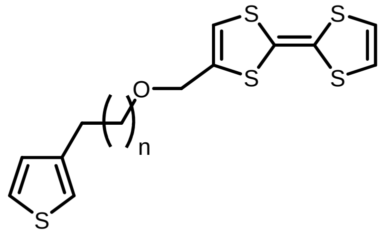
J. Mater. Chem., 2005, **15**, 4783



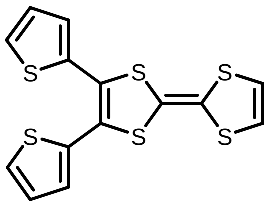
J. Mater. Chem., 2002, **12**, 500



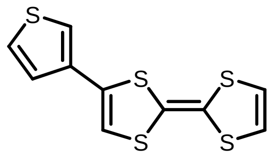
Bryce (Synth. Met., 1991, 39, 397)



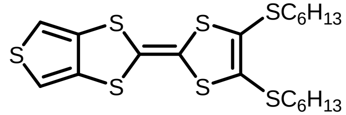
Roncali (Adv. Mater., 1998, 10, 541;
J. Phys. Chem. B, 1998, 102, 7776)



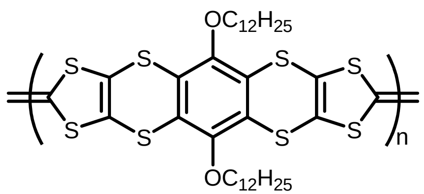
Underhill (J. Org. Chem., 1997, 62, 3098)



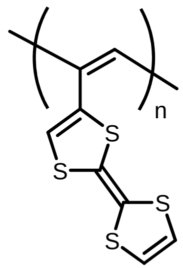
Skabara (J. Mater. Chem., 1998, 8, 1719)



Skabara (J. Mater. Chem., 1998, 8, 1719)



Müllen, J. Mater. Chem., 1995, 5, 1529



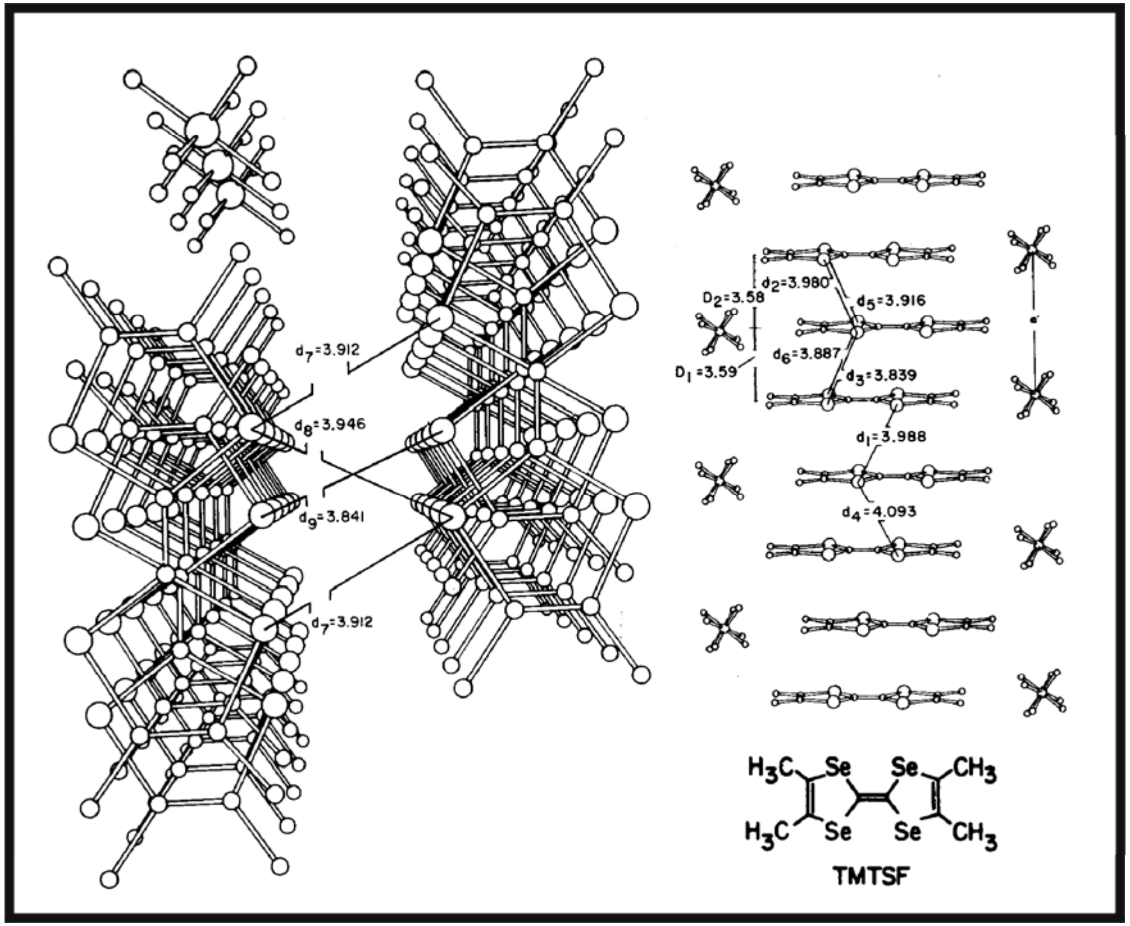
Yamamoto (Chem. Commun., 1999, 515)

TMTSF and the Bechgaard salts

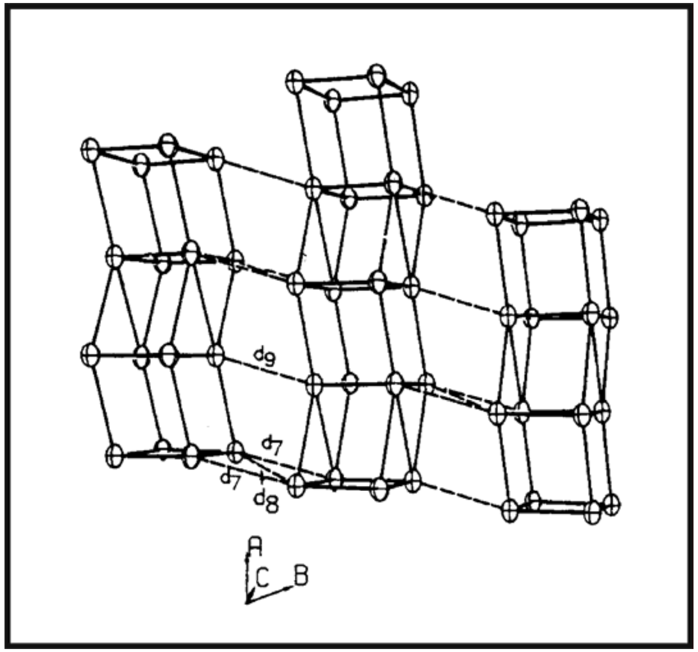
See: *Acc. Chem. Res.*, 1985, **18**, 261.

Salts grown by electrocrystallisation to give $[TMTSF]_2X$

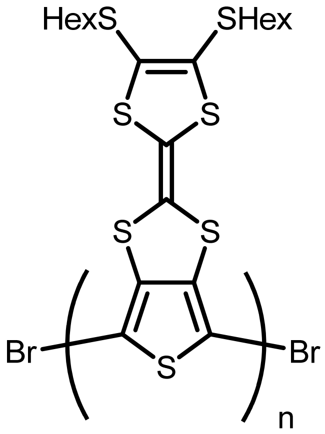
X = *e.g.*, BrO_4, ClO_4, PF_6, BF_4, NO_3, ReO_4



- Metals at room temperature
- Superconductors under pressure at low Ts
- Greater dimensionality through Se-Se contacts



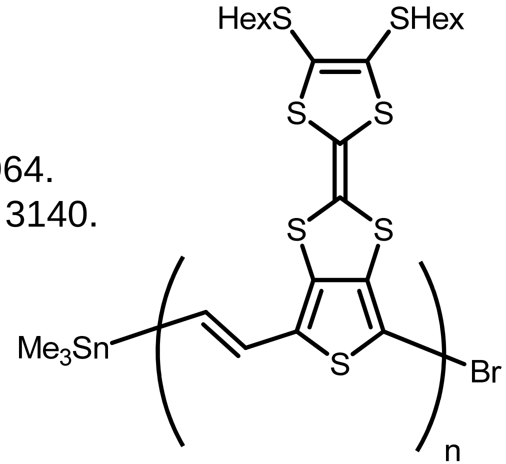
Polythiophenes incorporating fused TTFs



J. Mater. Chem., 2004, **14**, 1964.
J. Phys. Chem. B, 2006, **110**, 3140.

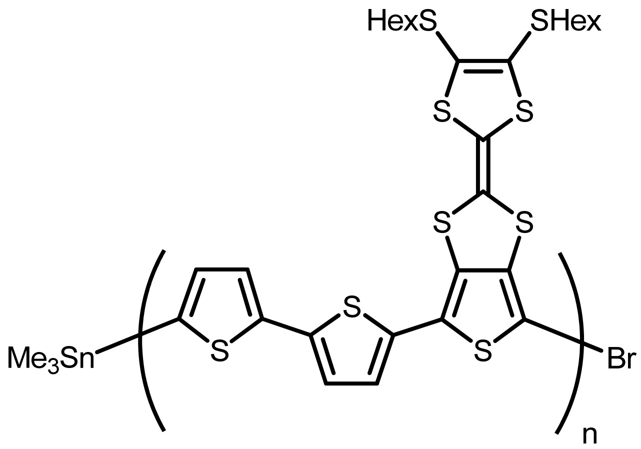
Optical band gap = 1.75 eV (solid film)

Electrochemical band gap = 1.82 eV



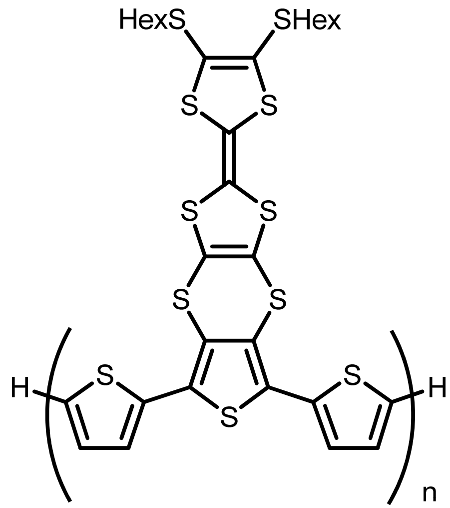
Optical band gap = 1.45 eV (solid film)

Electrochemical band gap = 1.44 eV



Optical band gap = 1.82 eV (solid film)

Electrochemical band gap = 1.83 eV



Optical band gap = 1.70 eV (solid film)

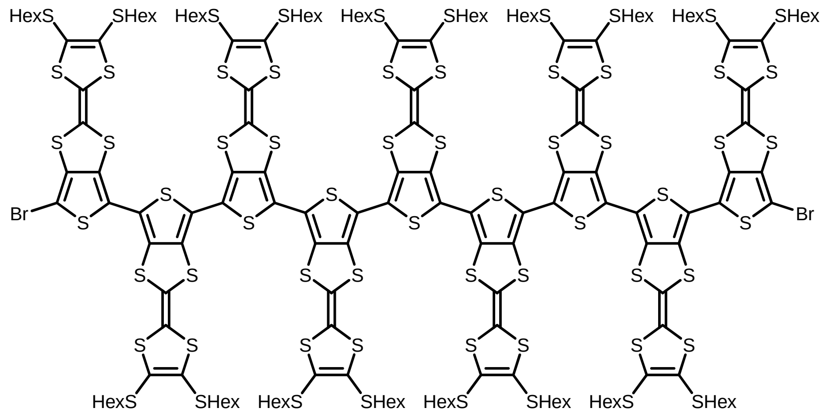
Electrochemical band gap = 1.81 eV

Soluble polymer using DMF/Toluene

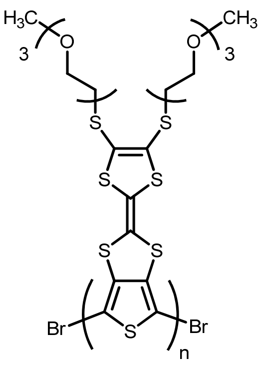
Good solubility in common solvents (chloroform, dichloromethane, THF)

GPC gives an average MW of *ca.* 4,500 – 9 repeat units (Polydispersity 1.32)

Exceptional doping levels



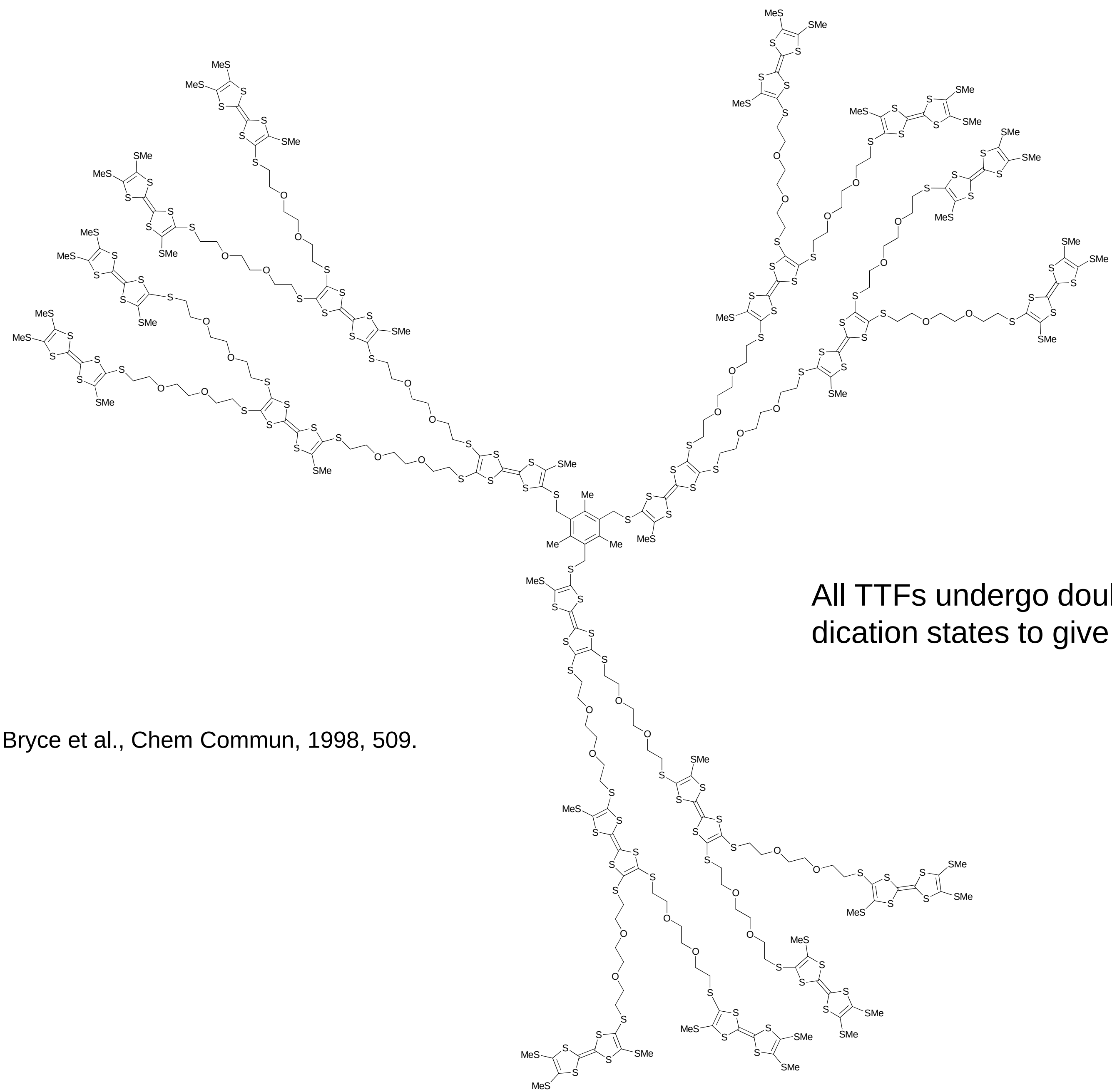
Alternative functionality provides MWs of around 250,000 and the polymer has excellent solubility.



Organic charge storage materials

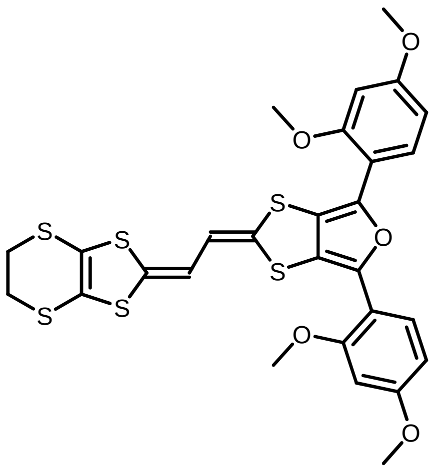
Advantages over conventional materials:

- Cost reduction
- Weight reduction
- Heavy metals elimination
- Flexibility
- Solution processability into thin films
- Potential compatibility with other (organic semiconductor) devices



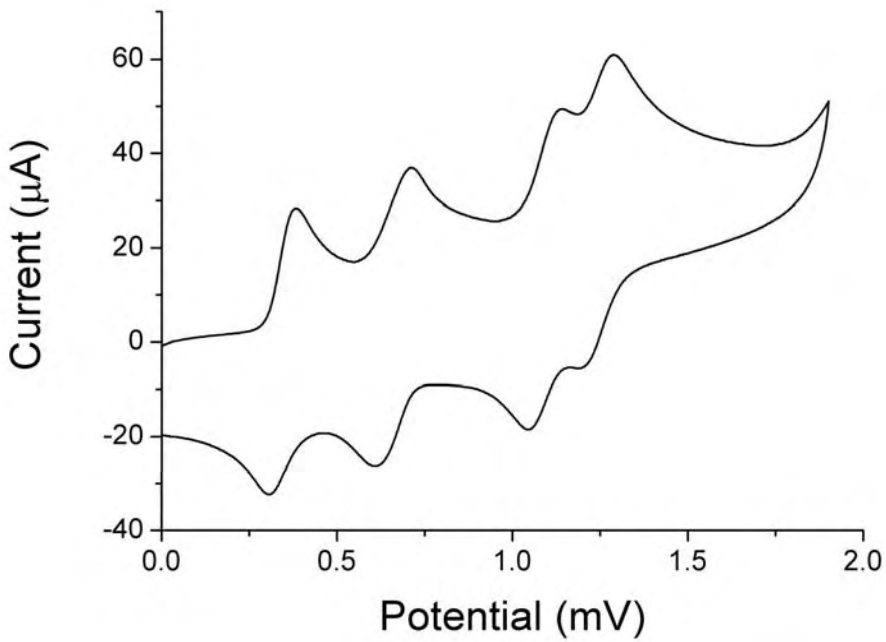
All TTFs undergo double oxidation to individual dication states to give a 42+ intermediate

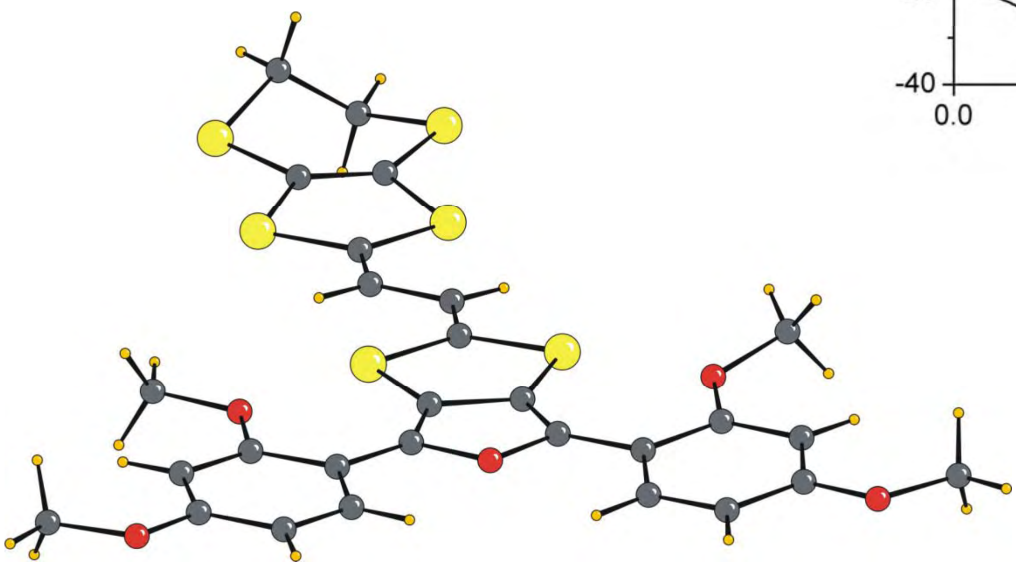
Bryce et al., Chem Commun, 1998, 509.



Tetrahedron Lett., 2004, **45**, 2535

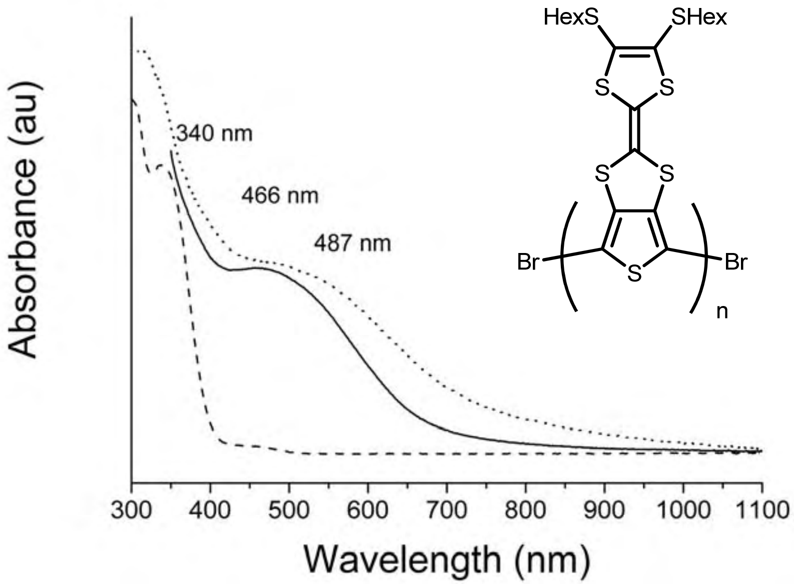
+0.34, +0.66, +1.09, +1.25 V *vs* Ag/AgCl

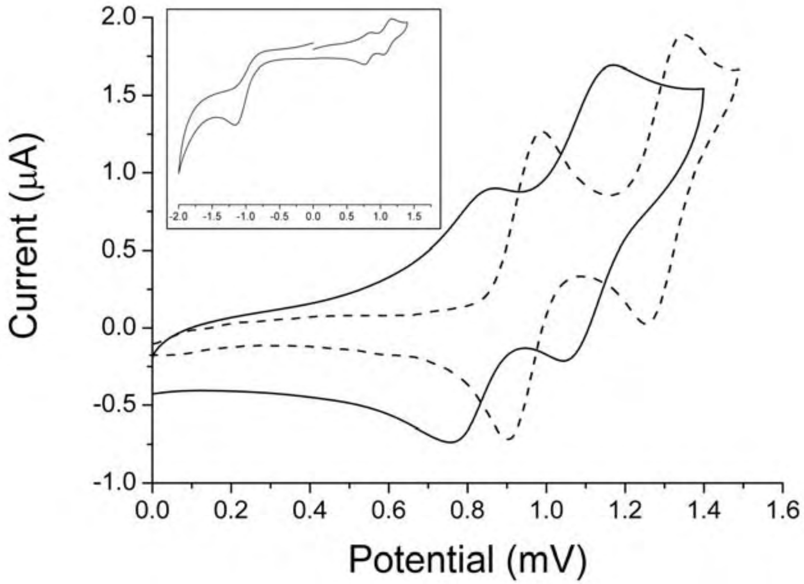




See also:*J. Mater.Chem*., 2004, **13**, 2490

Absorption Spectroscopy / CV



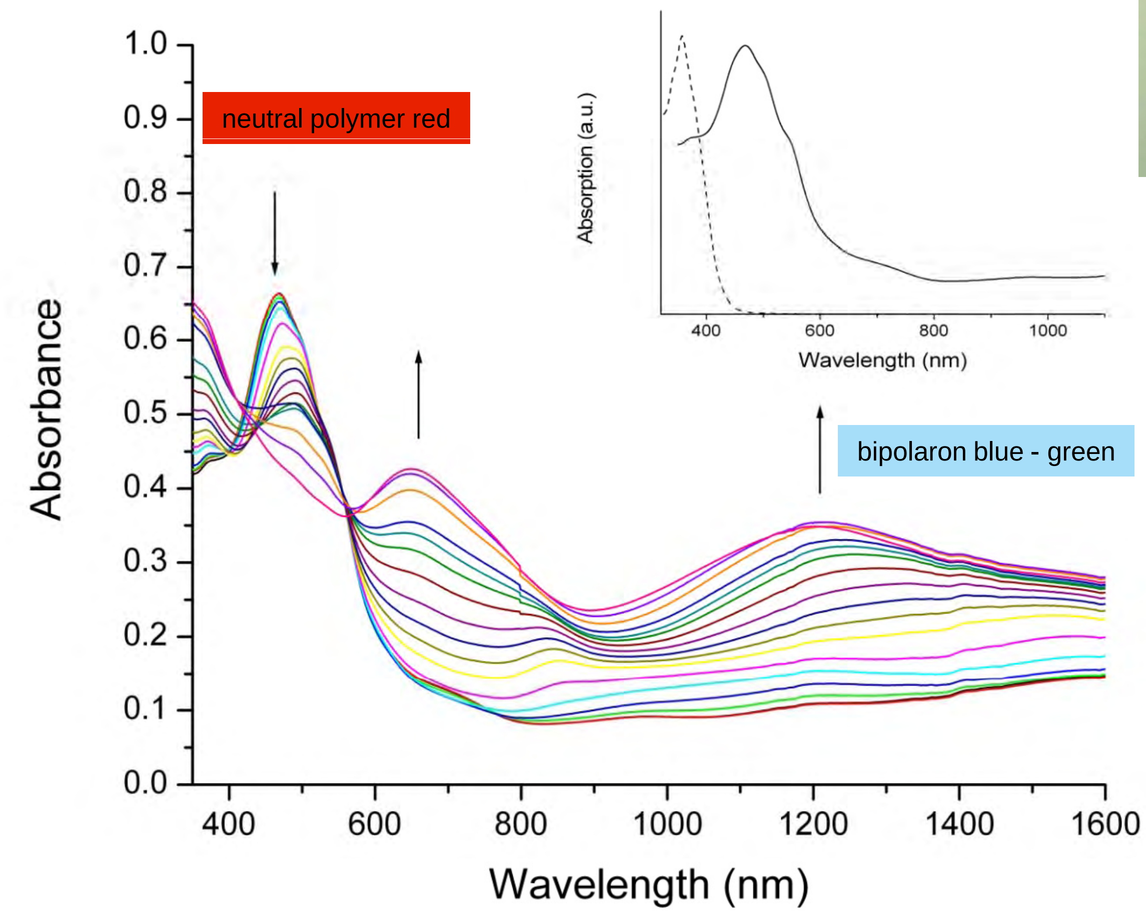


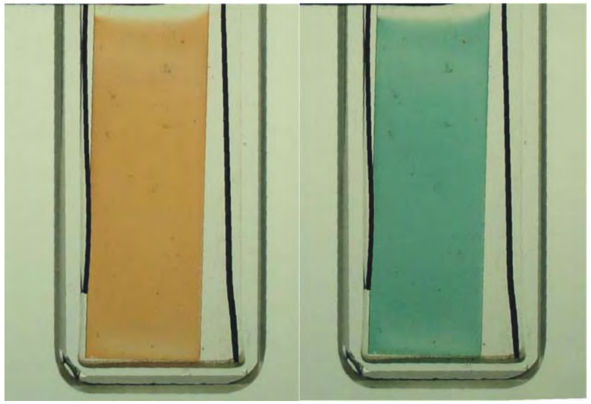
Optical band gap = 1.77 eV (solid film)

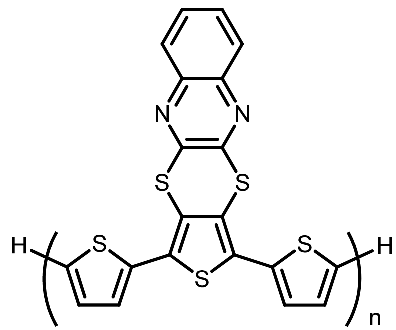
Electrochemical band gap = 1.82 eV

EPR spectroelectrochemistry: g = 2.0078 at 900 mV

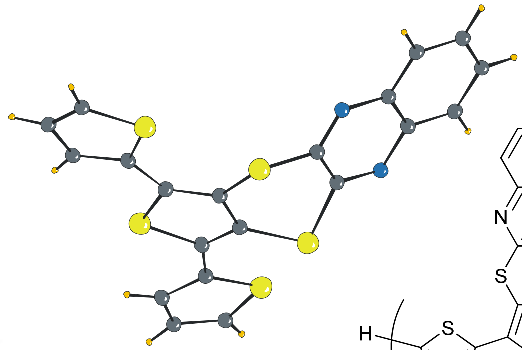
Spectroelectrochemistry

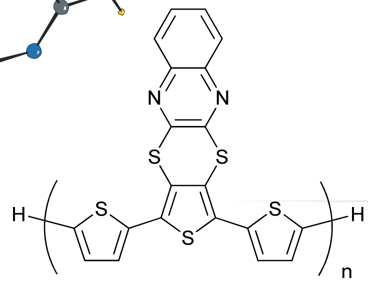


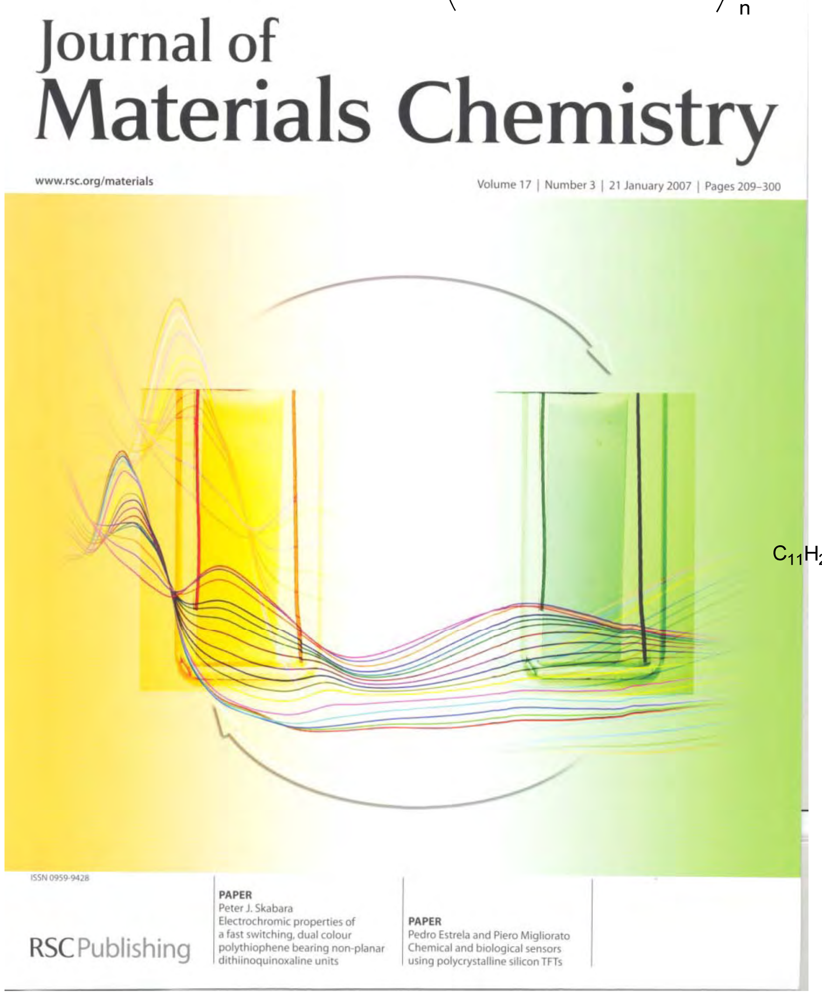




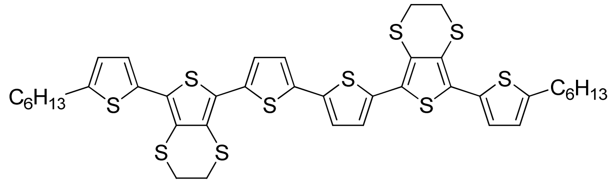
J. Mater. Chem., 2007, **17**, 255

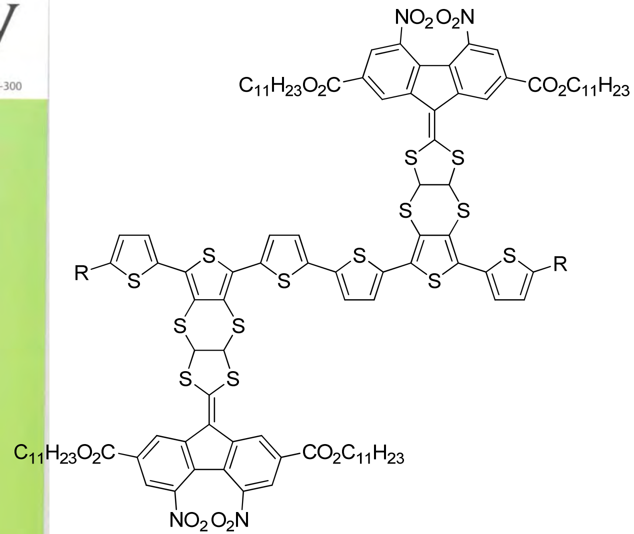


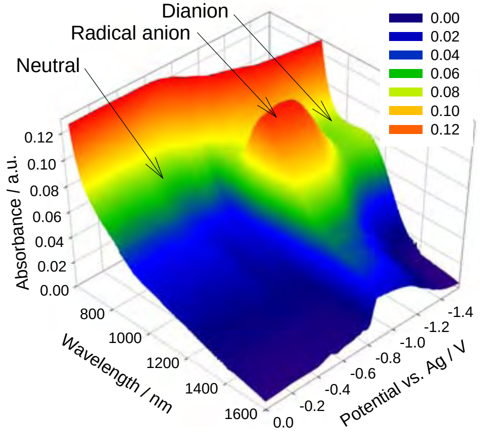


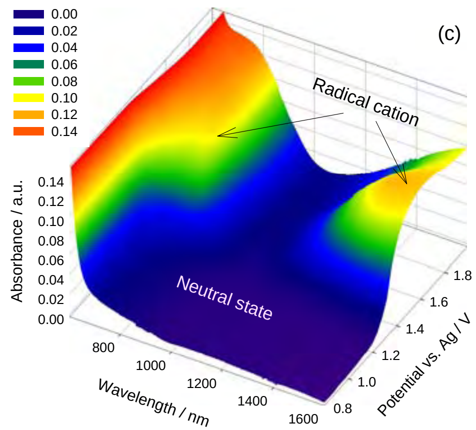


J. Mater. Chem. 2005, ***15***, *1446*

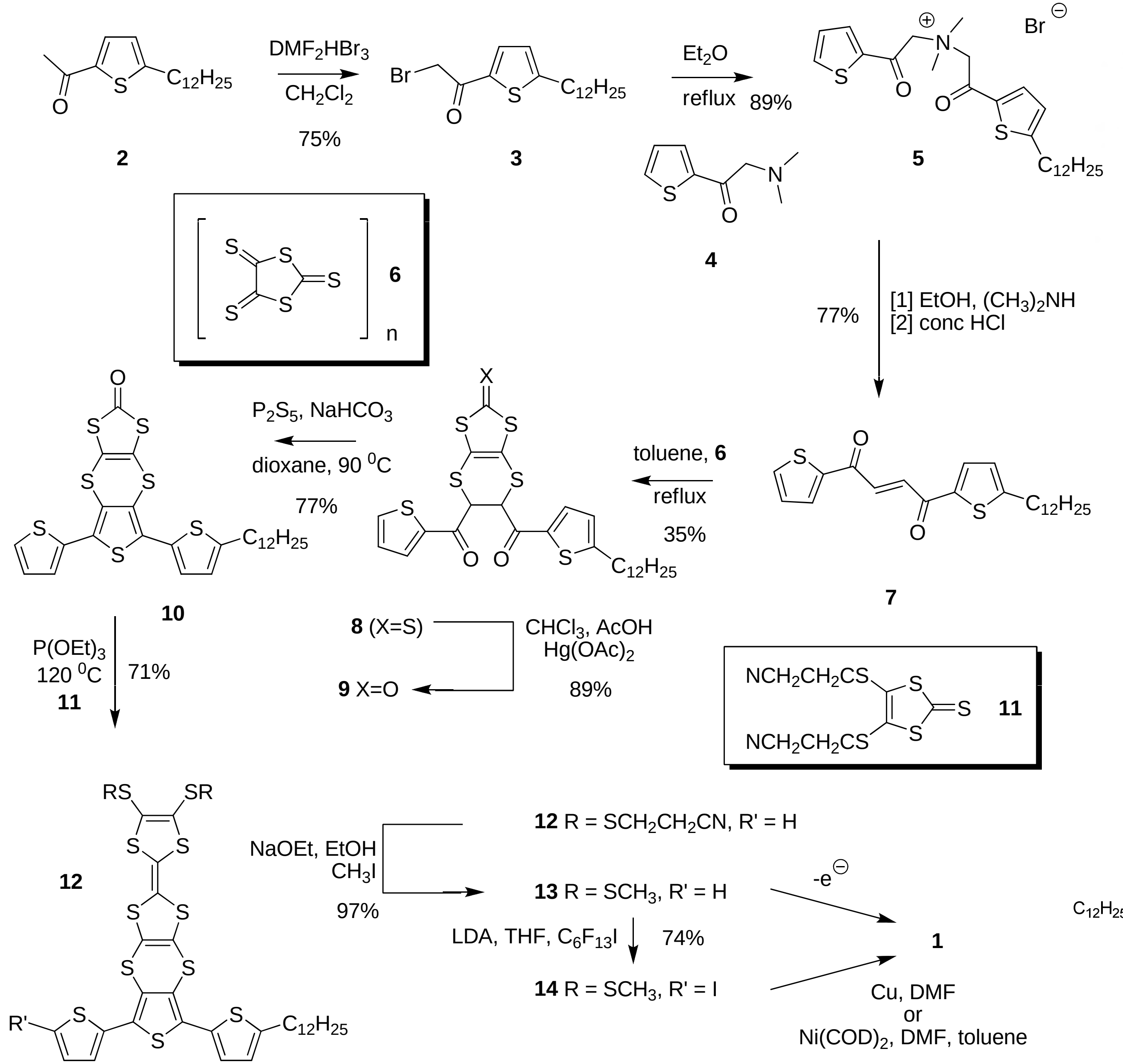


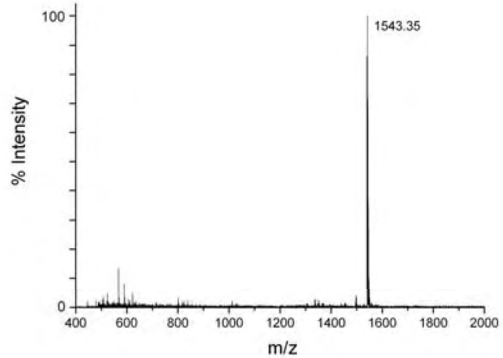


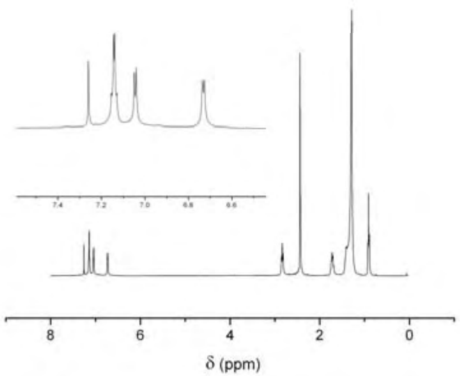


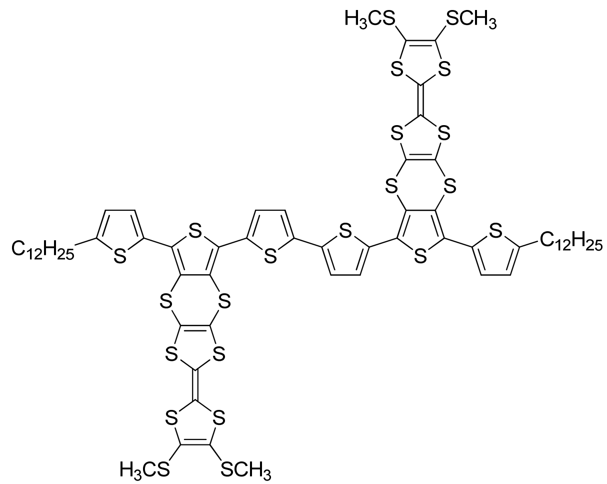


J. Mater. Chem., 2007, **17**, 1055



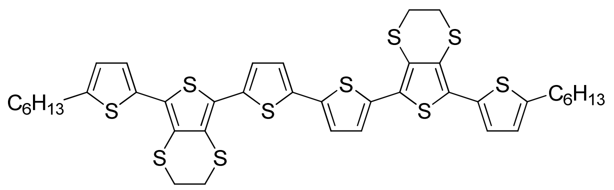


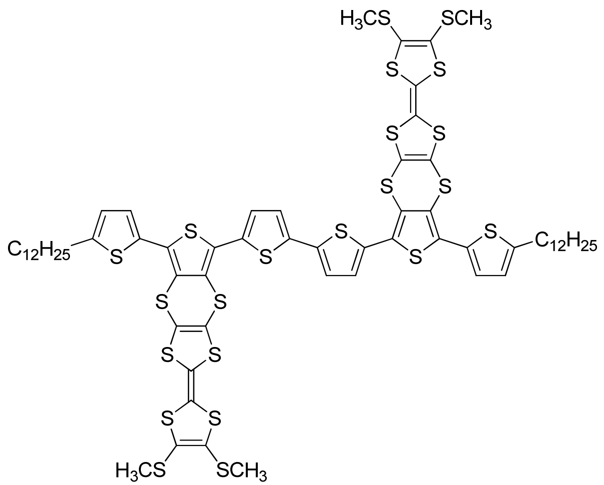


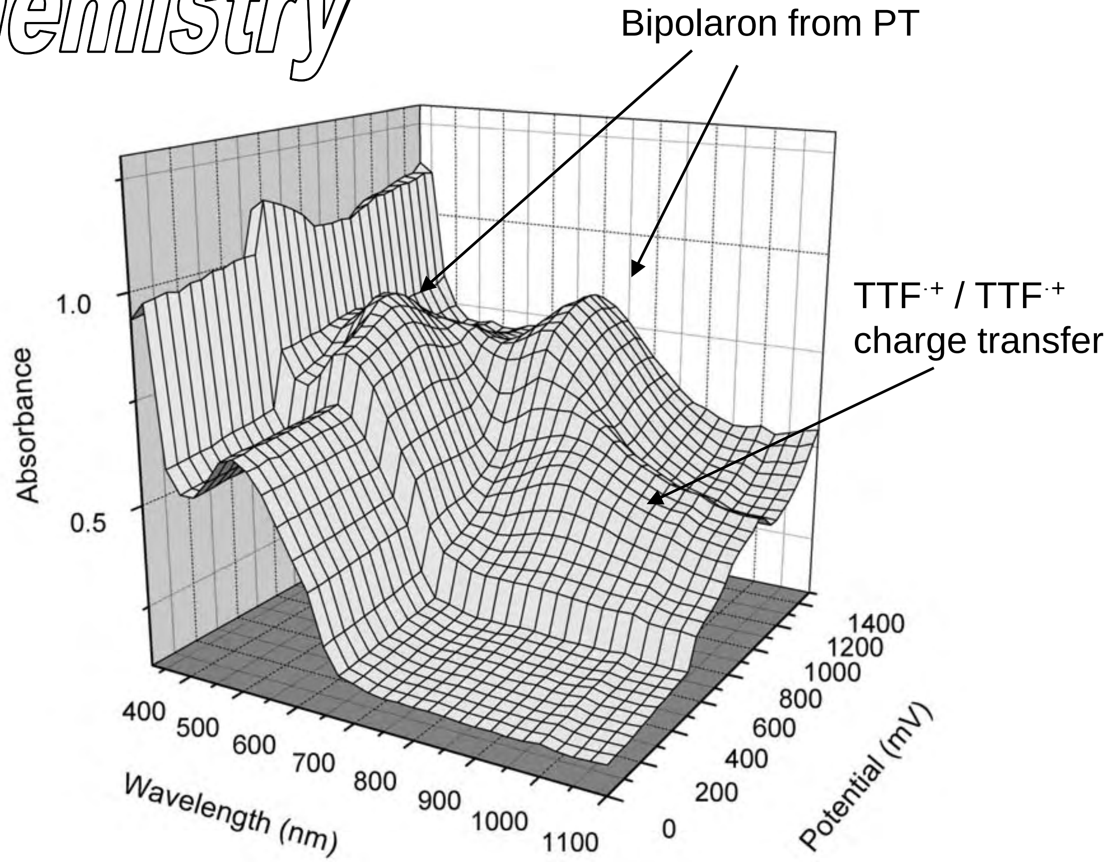


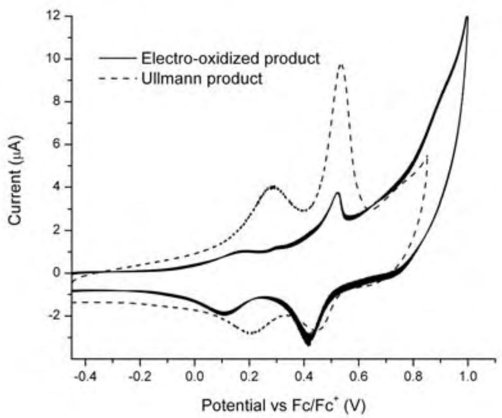
Organic Letters, 2007, 9, 1601

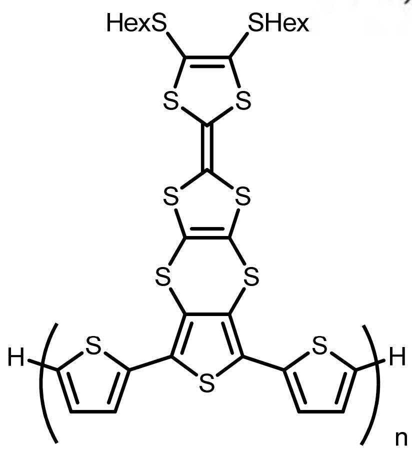
Spectroelectrochemistry



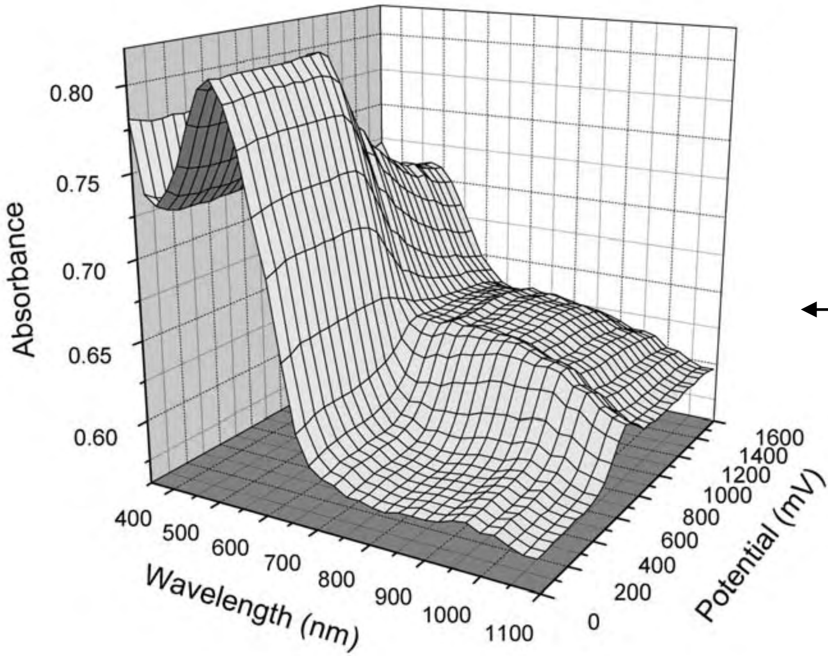


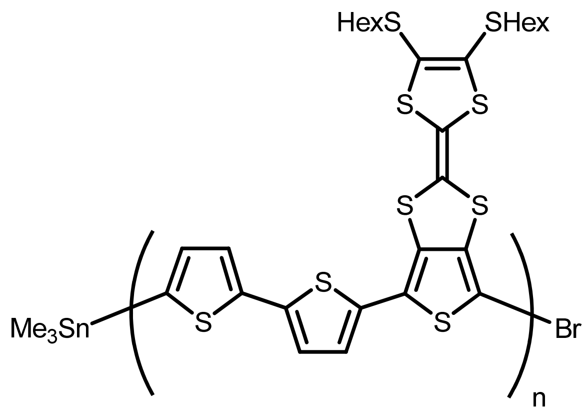


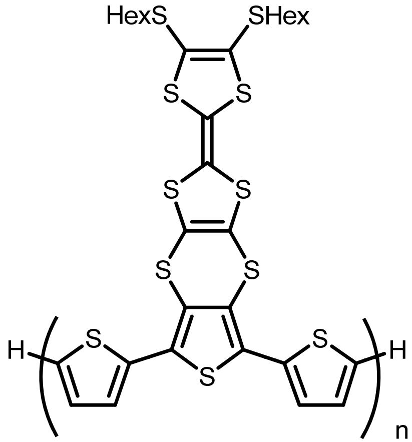


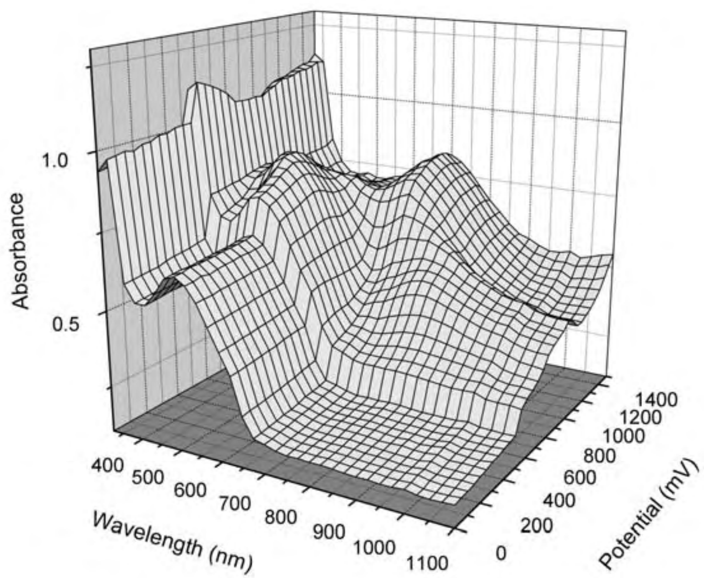


Spectroelectrochemistry

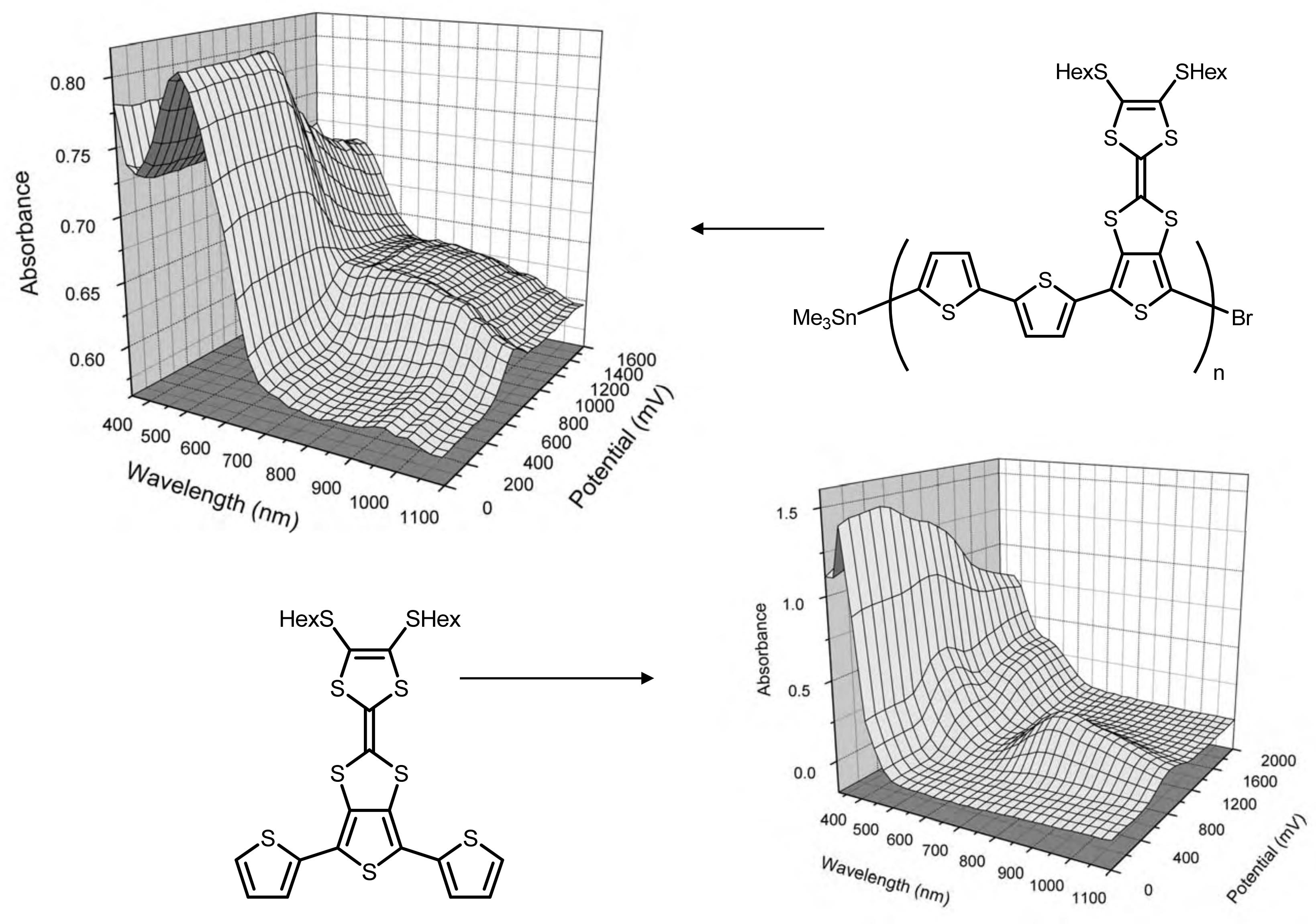


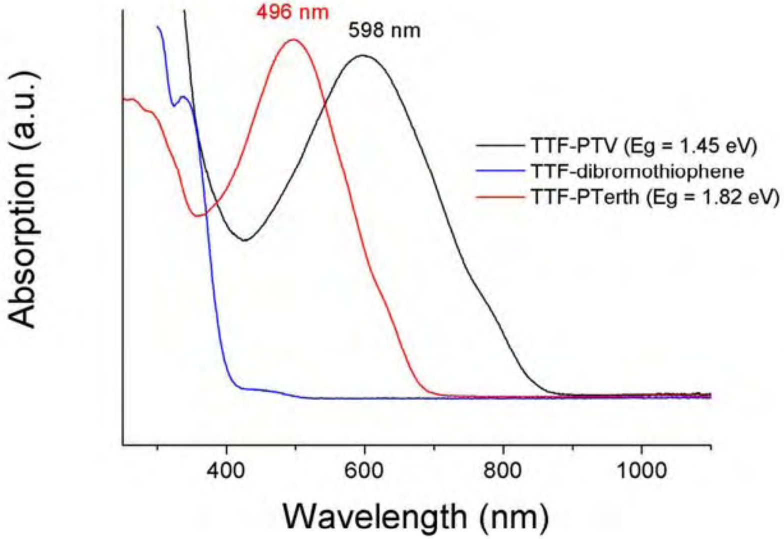




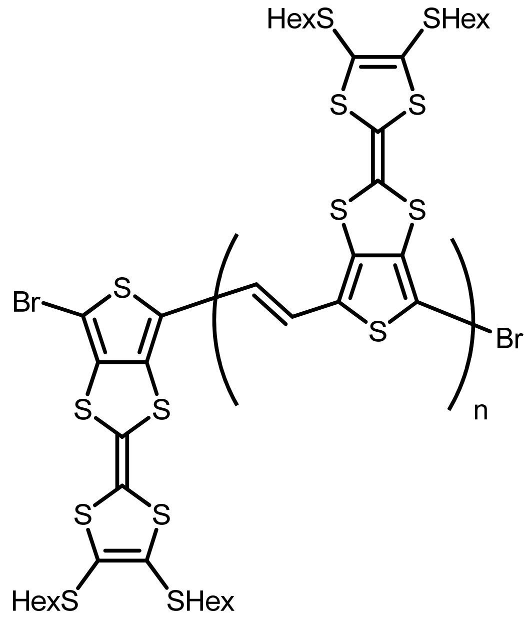


Spectroelectrochemistry

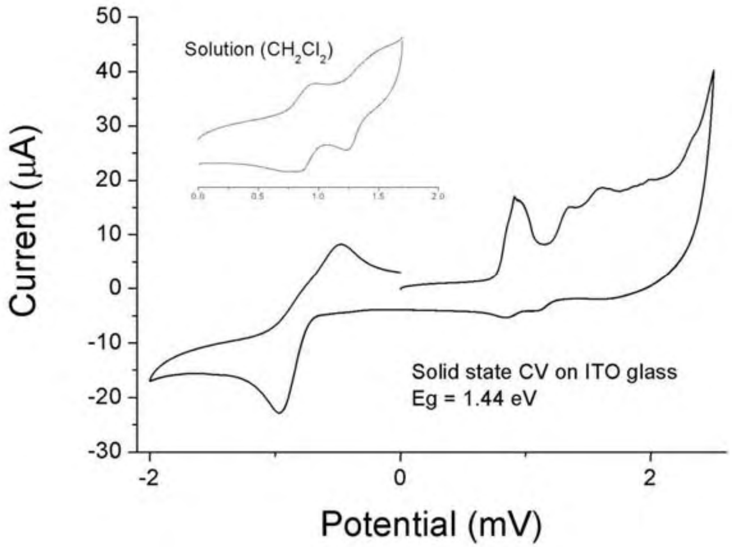




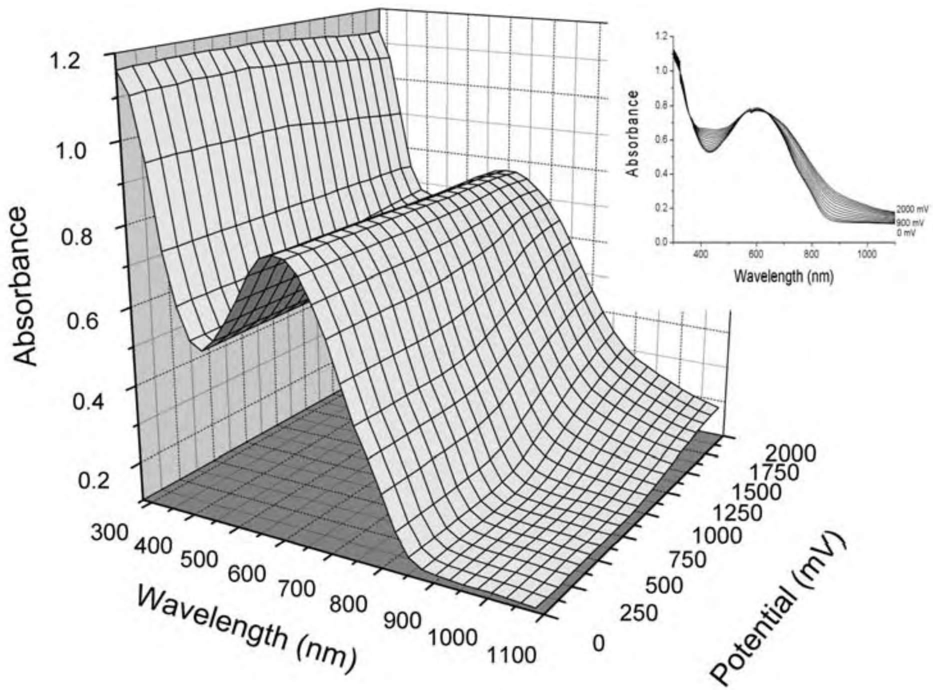
496 nm
598 nm
Absorption (a.u.)
TTF-PTV (Eg = 1.45 eV)
TTF-dibromothiophene
TTF-PTerth (Eg = 1.82 eV)
400
600
800
1000
Wavelength (nm)



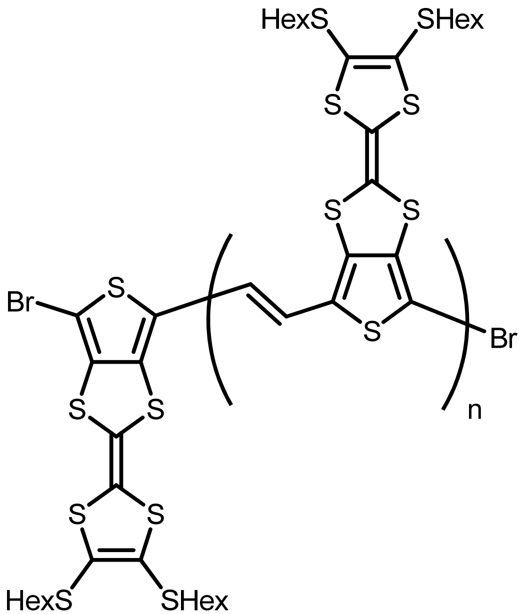
HexS
SHex
S
Br
n

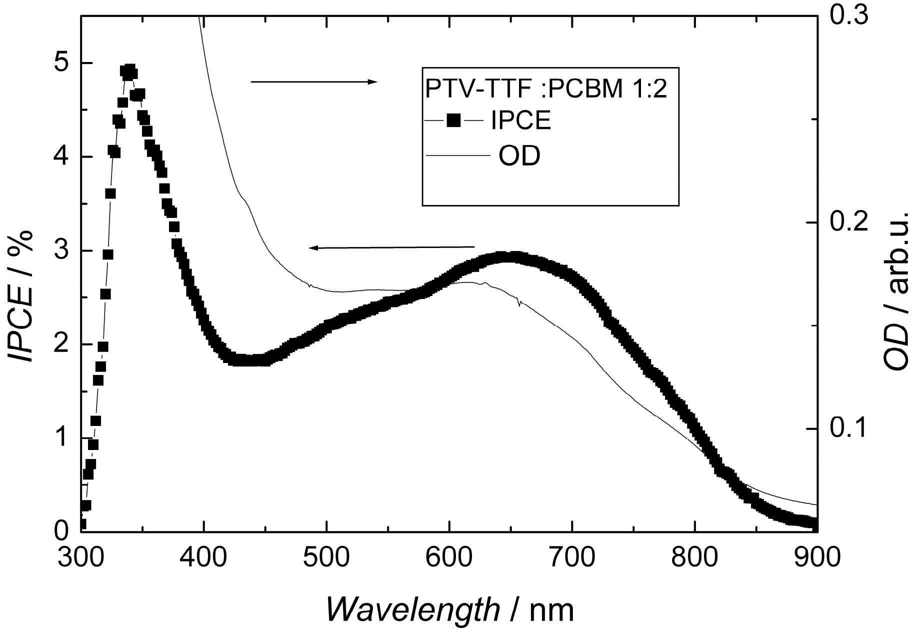


Current (μA)
Solution (CH_2Cl_2)
Solid state CV on ITO glass
Eg = 1.44 eV
-2
0
2
Potential (mV)



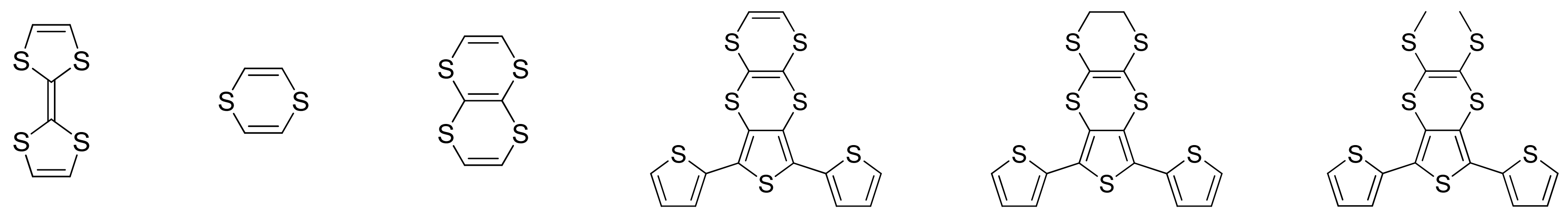
Absorbance
Wavelength (nm)
Potential (mV)
2000 mV
900 mV
0 mV



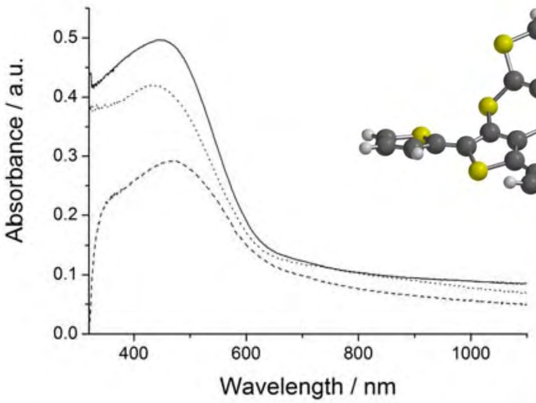


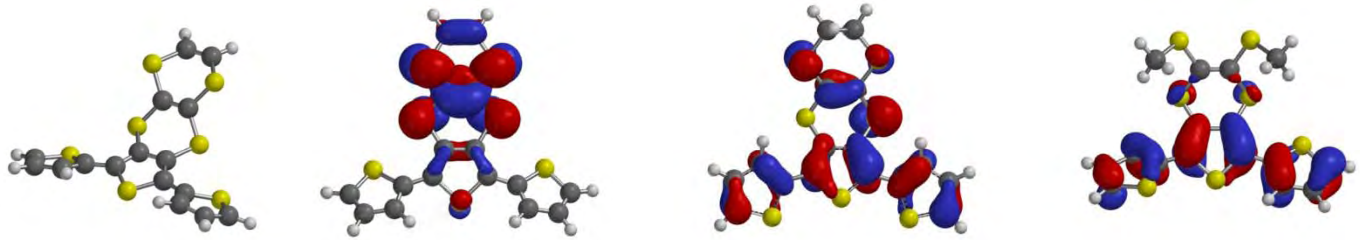
PCBM blends give good photovoltaic diodes, photocurrent until 850 nm, open circuit voltage reasonably high (comparable with P3HT). Power conversion efficiency 0.13%.

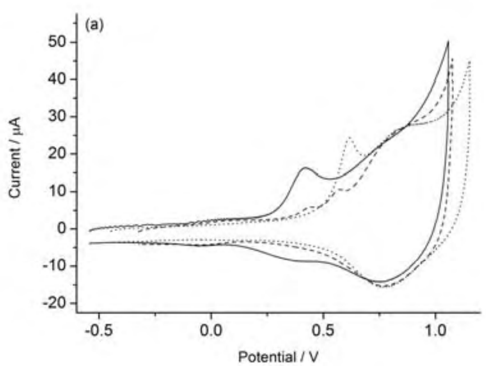
J. Phys. Chem. B, 2006, **110**, 3140.
Patent US20060289058A1 (2006).

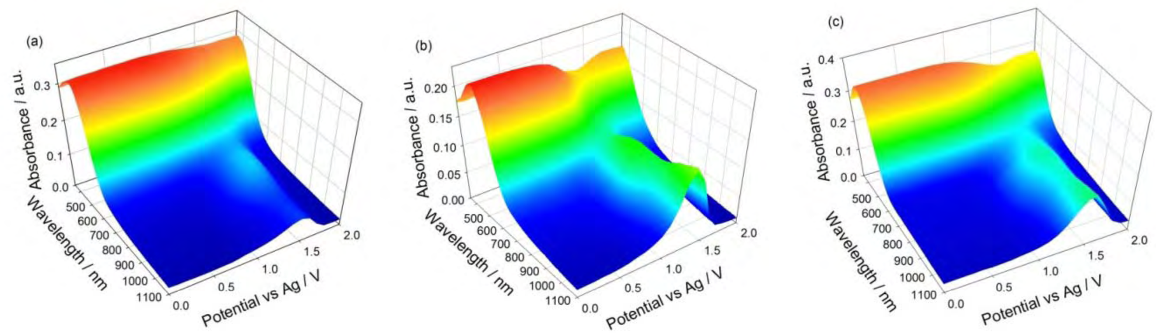


TTF 1,4-dithiin TTN 1 2 3







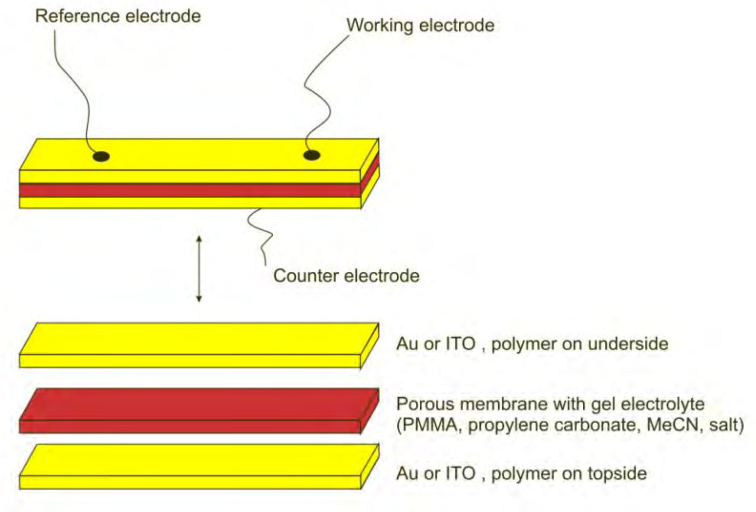


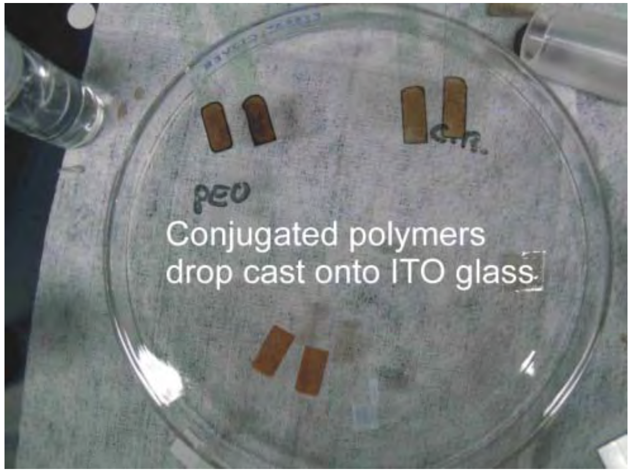
	E_{1ox}/V	E_{2ox}/V	E_{1red}/V	HOMO/eV	LUMO/eV	E_g/eV	λ_{max}/nm
Poly**1**	+0.42	+0.77	-1.97	-5.05	-3.01	2.04	436
Poly**2**	+0.56	+0.80	-1.82	-5.21	-3.14	2.07	471
Poly**3**	+0.60	+0.83	-1.93	-5.30	-3.19	2.11	450

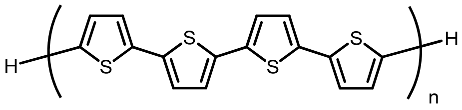
Types of Polymer	Charge Density (Ah/kg)	Specific Energy (Wh/kg)	Open Circuit Voltage (V)	Specific Power (W/kg)
Polyacetylene	100-300	100-300	3.5-3.9	up to 30,000
Polyaniline	50-150	100-350	1-4	
Polypyrrole	50-120	50-350	3-4	
Polythiophene	25-100	50-325	3.2-4.2	up to 90,000
Poly-*p*-phenylene	20-140	300	3.2-4.5	up to 320

Battery characteristics for a range of generic electroactive polymers.

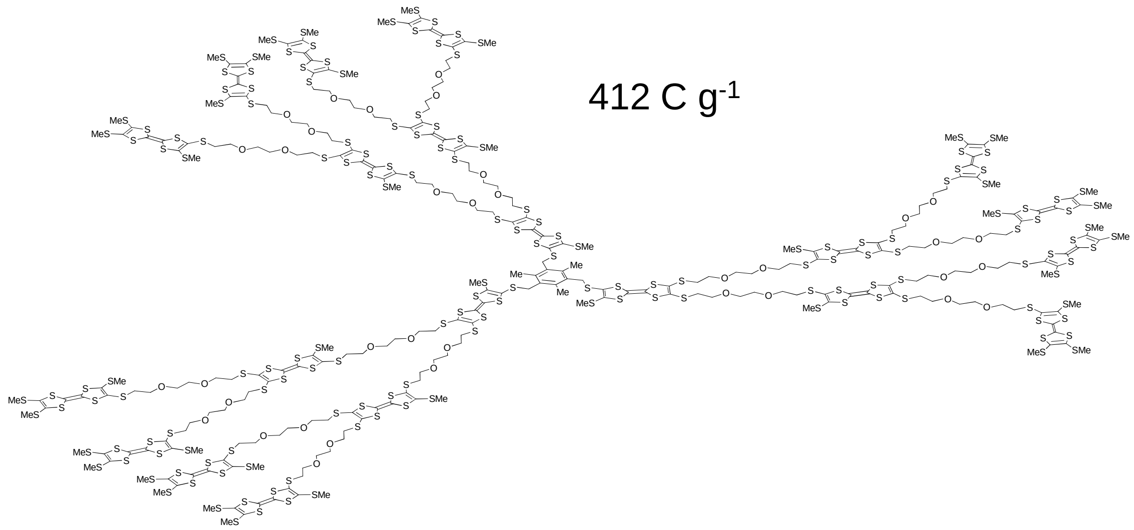
J. A. Irvine, D. J. Irvin, J. D. Stenger-Smith, in *Handbook of Conducting Polymers*, 3rd Edition ed., Taylor and Francis Group, Boca Raton, **2007**. P. Novak, K. Muller, K. S. V. Santhanam, O. Haas, *Chemical Reviews* **1997**, *97*, 207.



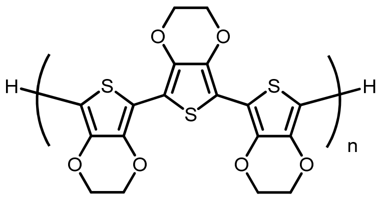




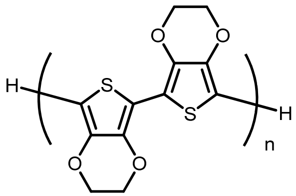
294 C g^{-1}



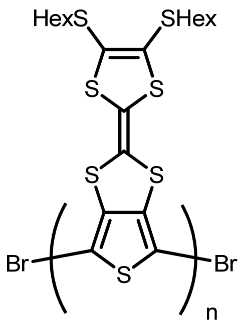
412 C g^{-1}



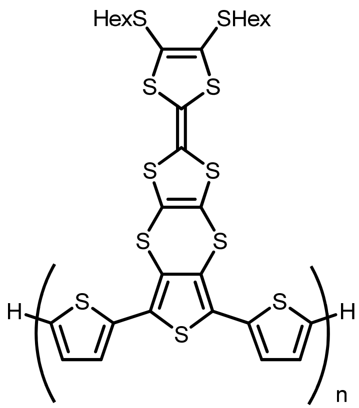
230 C g^{-1}



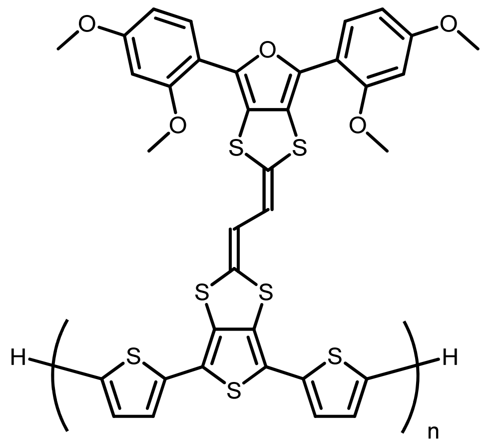
345 C g^{-1}



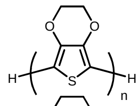
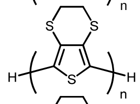
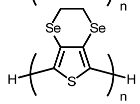
394 C g^{-1}

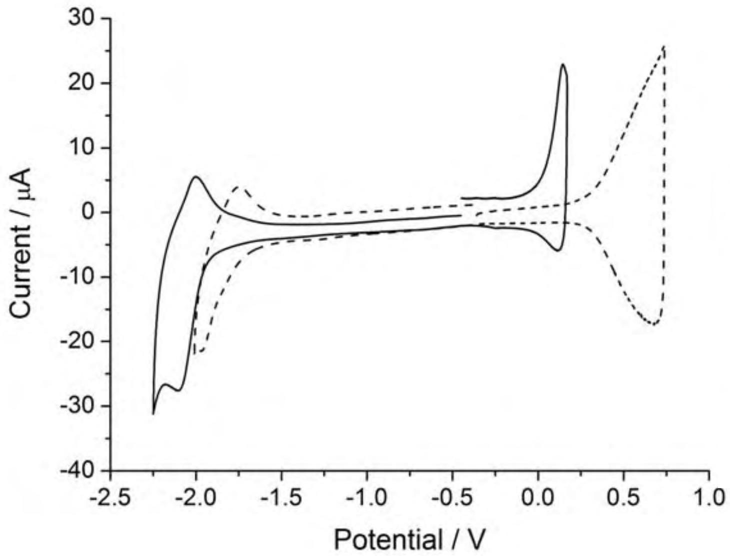


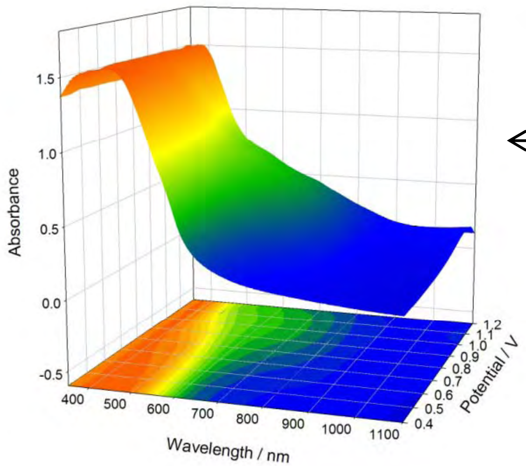
389 C g^{-1}



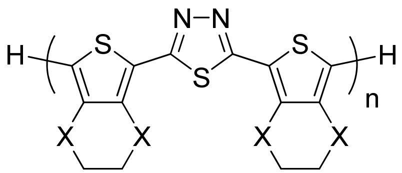
508 C g^{-1}

		HOMO (eV)	LUMO (eV)	E_g (echem, eV)	λ_{max} (nm)	E_g (optical, eV)
poly(**EDOT-TDA-EDOT**)		-4.7	-2.9	1.8	433, 572	1.83
poly(**EDTT-TDA-EDTT**)		-5.1	-3.2	1.9	512, 546, 593	1.89
PEDOT		-4.0	-2.7	1.3	578	1.6
PEDTT		-4.9	-2.75	2.15	441	2.2
PEDST		-4.8	-3.3	1.5	459	1.8



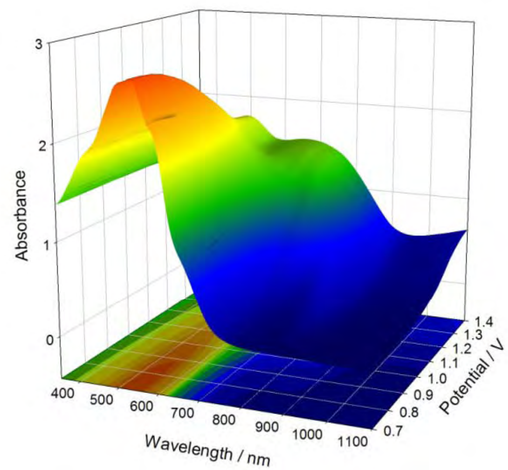


poly(**EDOT-TDA-EDOT**)

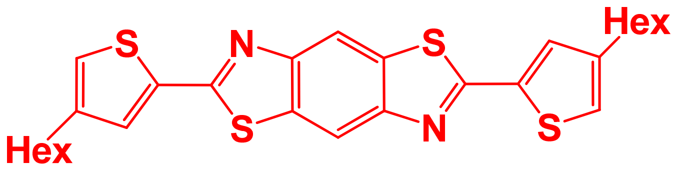


X = O or S

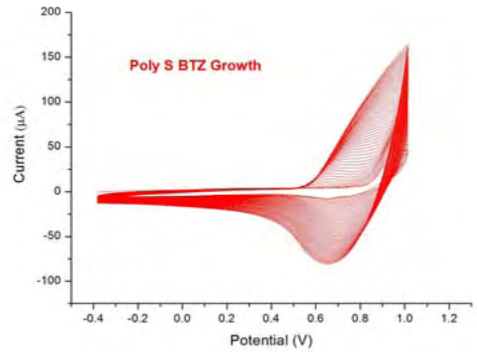
poly(**EDTT-TDA-EDTT**)

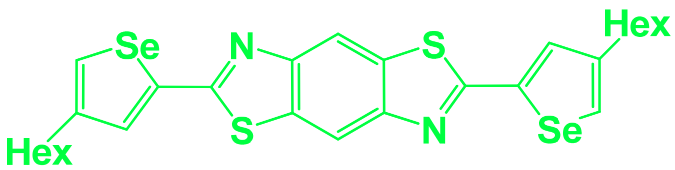


Benzobis(thiazole) cores

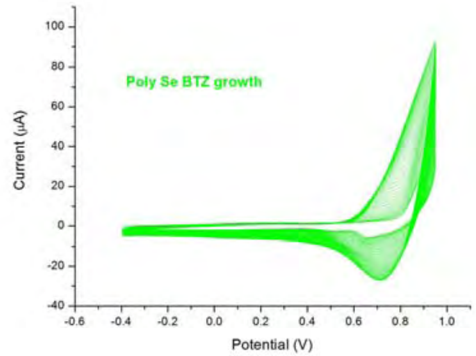


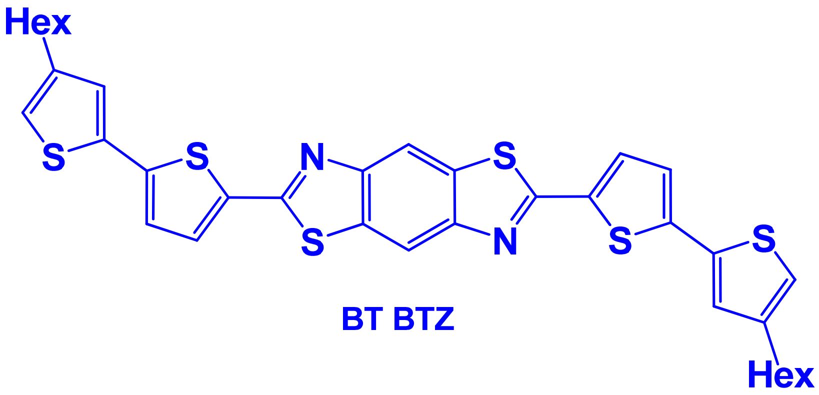
S BTZ



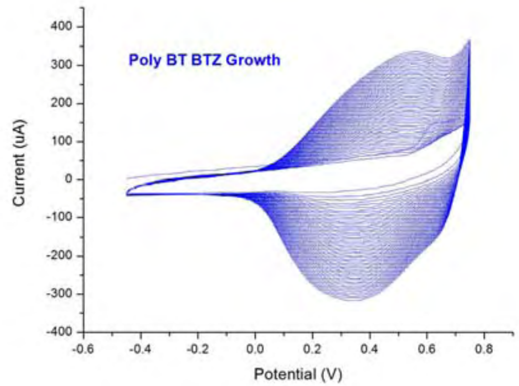


Se BTZ



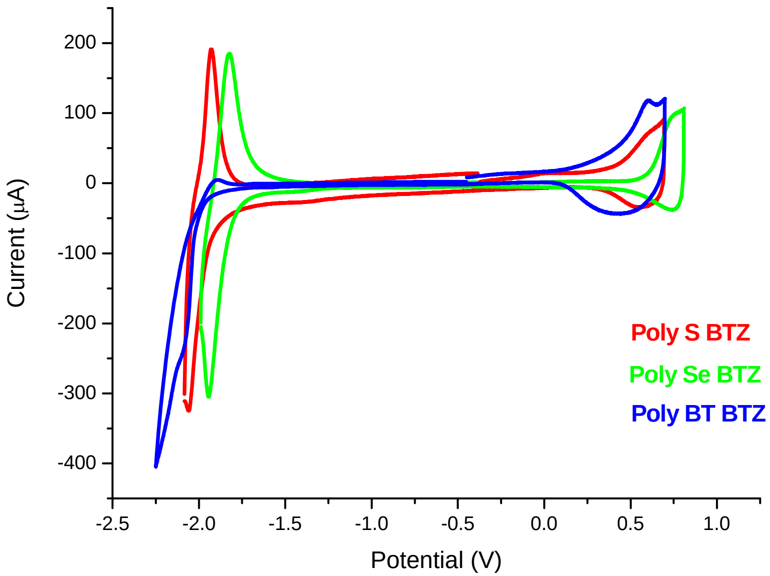


BT BTZ

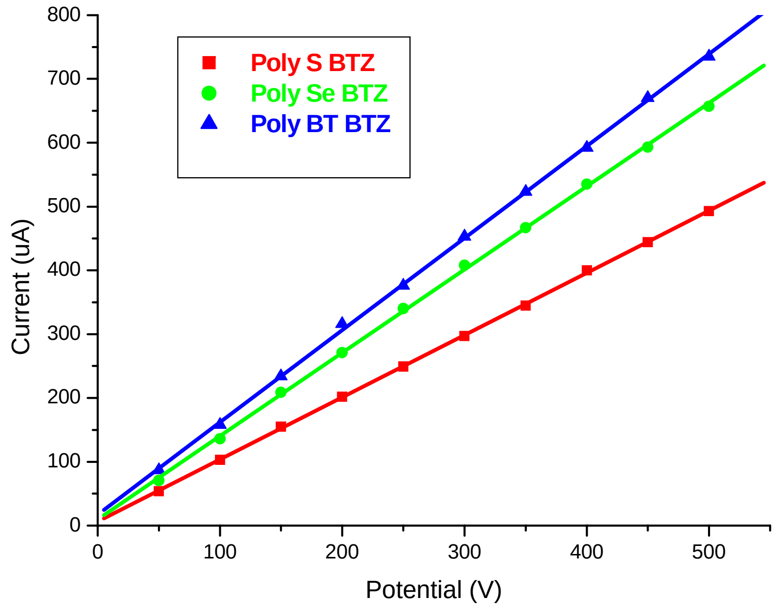


Monomer electrochemical polymerisation by repetitive cycling over the first oxidation wave. The data is referenced to the Fc/Fc+ redox couple.

Electrochemistry



Cyclic voltammograms of polymers as films on ITO glass. Experiments were conducted in monomer-free acetonitrile solution, under the same conditions as A. The data is referenced to the Fc/Fc+ redox couple.

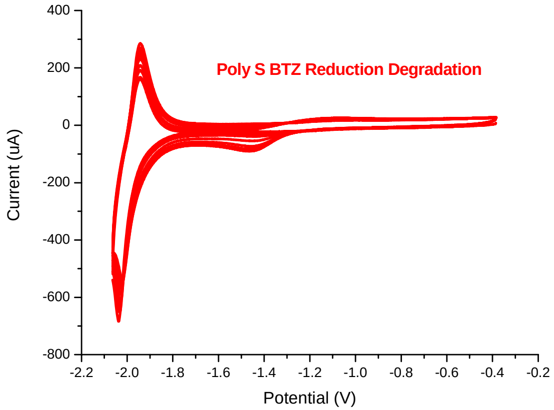


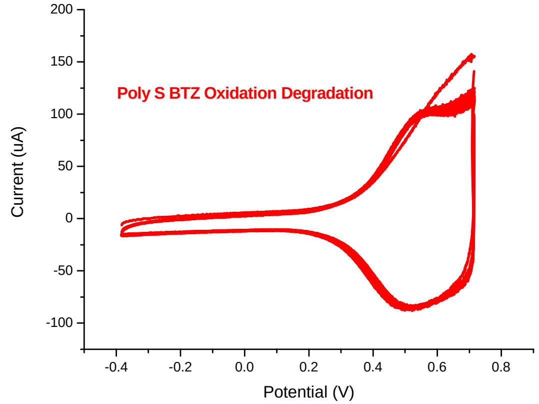
Plot of current versus scan rate for polymers

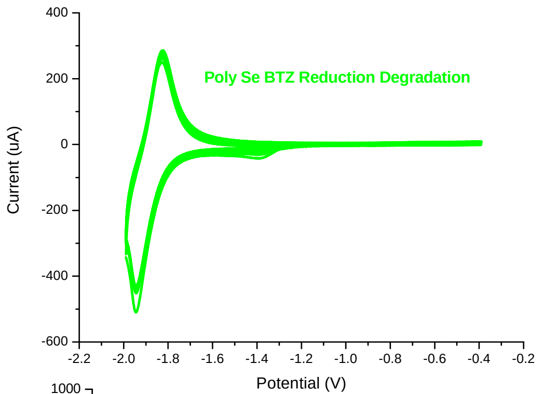
Polymers	E_{1ox}/V	E_{1red}/V	HOMO/eV[a]	LUMO/eV[a]	Eg/eV
Poly S BTZ	+0.61	-2.06	-5.2	-2.9	2.3
Poly Se BTZ	+0.74	-1.94	-5.4	-3.1	2.3
Poly BT BTZ	+0.60	-2.11	-4.9	-2.9	2.0

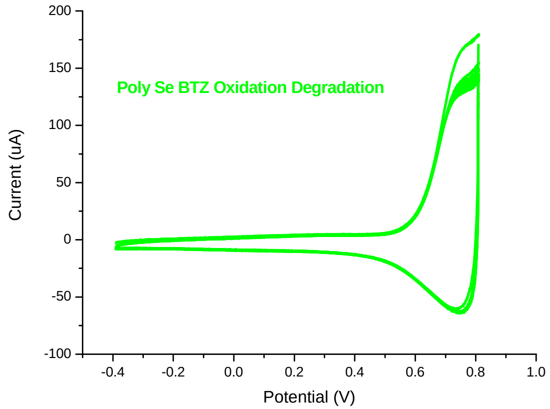
HOMO and LUMO values are calculated from the onset of the corresponding redox wave and referenced to ferrocene, which has a HOMO of -4.8 eV. Electrochemical band gap from the HOMO-LUMO separation.

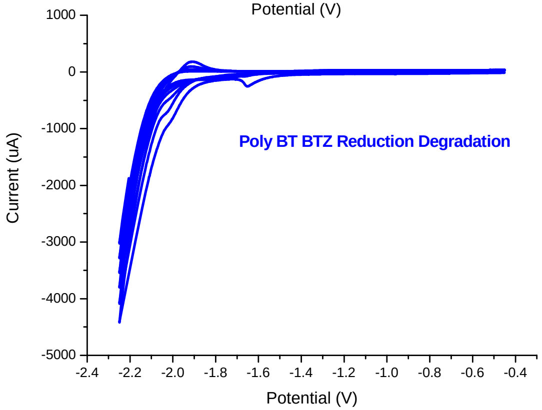
Electrochemistry

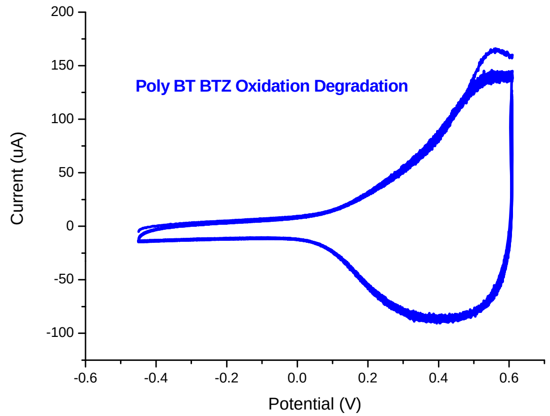












Acknowledgements

John Forgie
Hao Pang
Rory Berridge
Alexander Kanibolotsky
Lyudmila Kanibolotskaya
Sergey Gordeyev
Jan Lohr
Donna Roberts
Cristina Pozo-Gonzalo
Tahir Khan
Shaun Wright

Eric McInnes

Pierre Frère

Zuska Vobecka
Ivan Stibor
Serdar Sariciftci
Christoph Winder
Helmut Neugebauer
Antonio Cravino

Simon Coles
Mike Hursthouse
Ross Harrington
Bill Clegg

COST
European Science Foundation
ESF
The Royal Society
NATO OTAN
RSC Advancing the Chemical Sciences
The Leverhulme Trust
EPSRC

MC9 at

IUPAC CONGRESS 2009

3 – 7 August 2009, Glasgow, Scotland

RSC | Advancing the Chemical Sciences