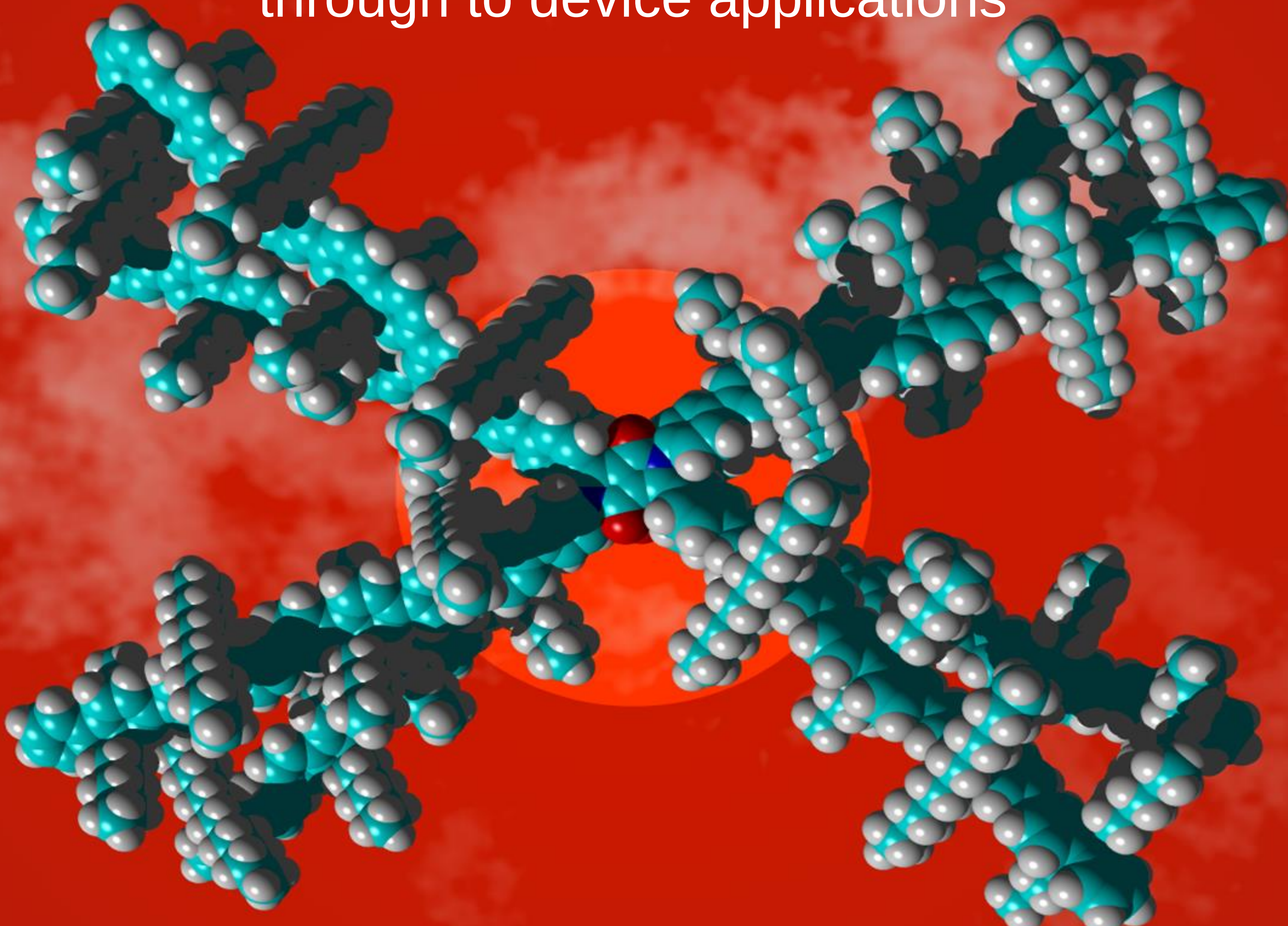
Complex conjugated architectures – from synthesis through to device applications



Acknowledgements

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NATO OTAN

THE ROYAL SOCIETY

RSC | Advancing the Chemical Sciences

The Leverhulme Trust

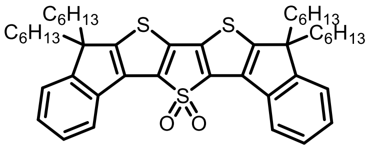
EPSRC

- Synthesis of small molecules, macromolecules and polymers: as organic semiconductors

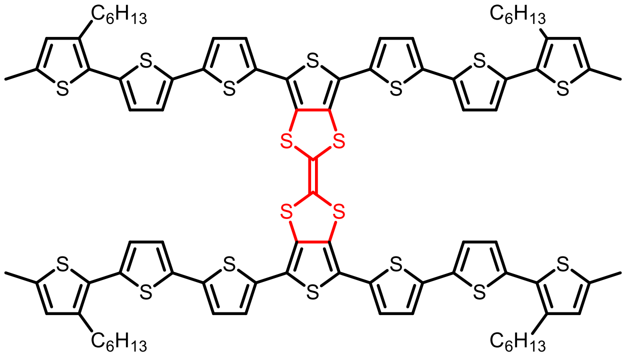
- Electrochemical characterisation

- Device fabrication (solar cells, OLEDs, sensors, OFETs, batteries/capacitors, hybrid MEMS devices)

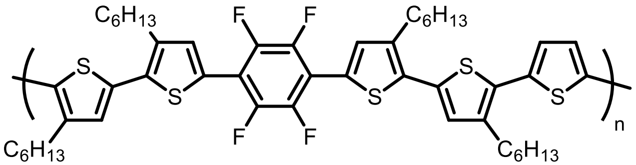
- Fundamental interest in non-covalent interactions and how they affect conformation



small molecules



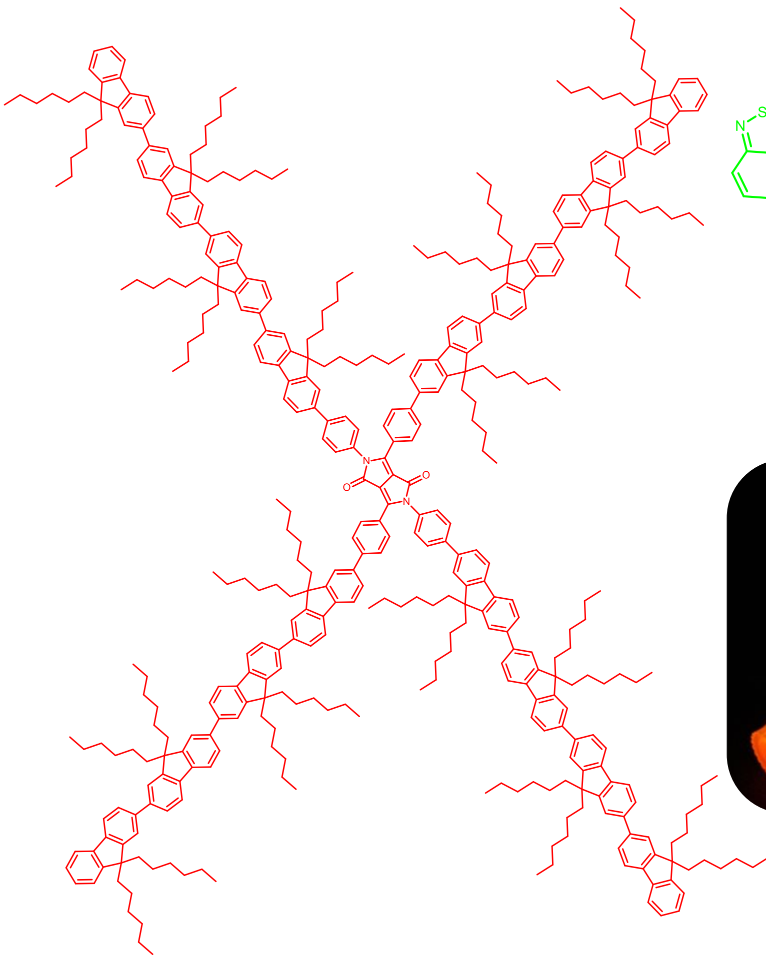
macromolecules

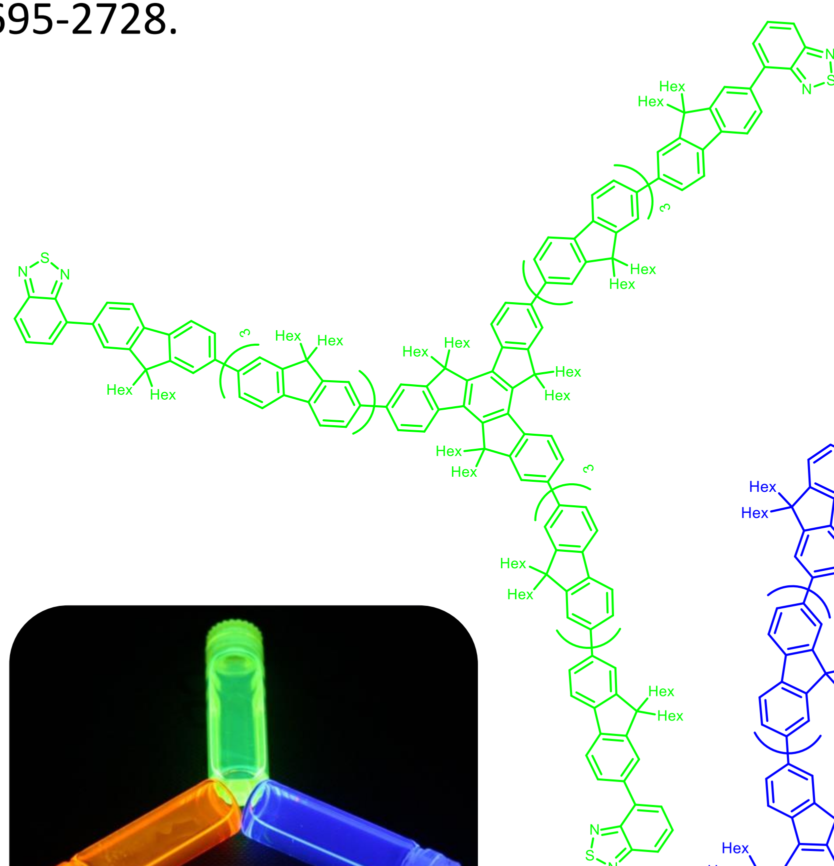


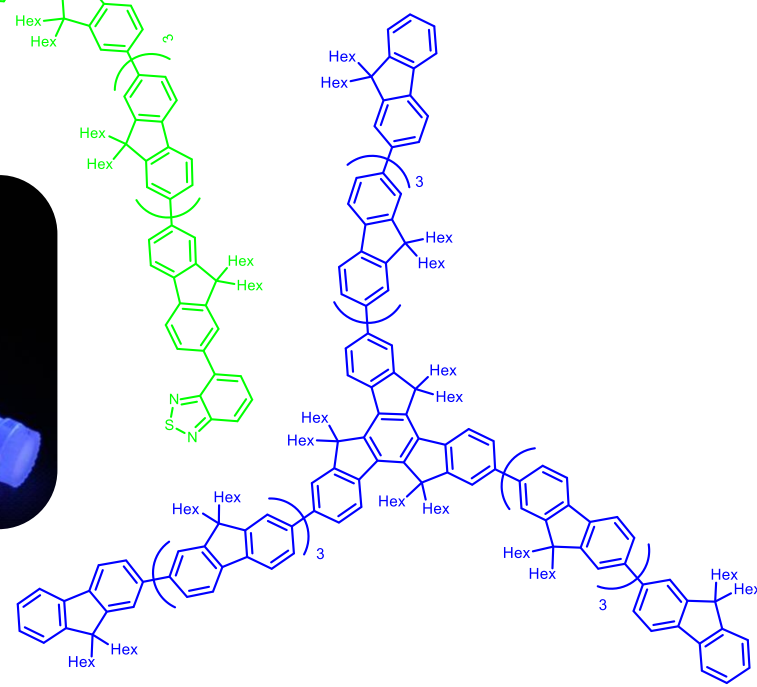
polymers

Star-shaped conjugated macromolecules

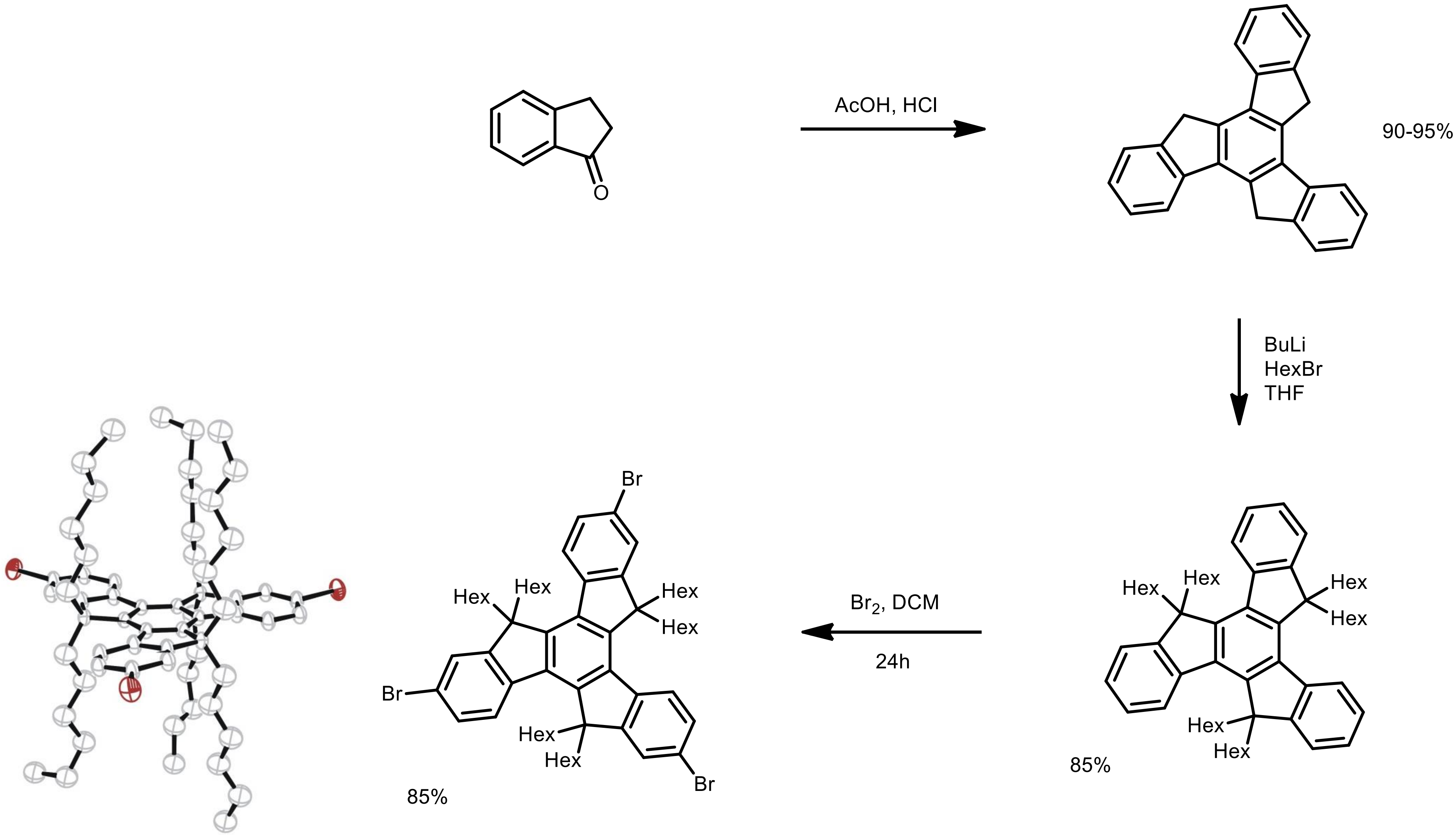
See: *Star-shaped π-Conjugated Oligomers and Their Applications in Organic Electronics and Photonics*, A. L. Kanibolotsky, I. F. Perepichka and P. J. Skabara, *Chem. Soc. Rev.*, 2010, **39**, 2695-2728.

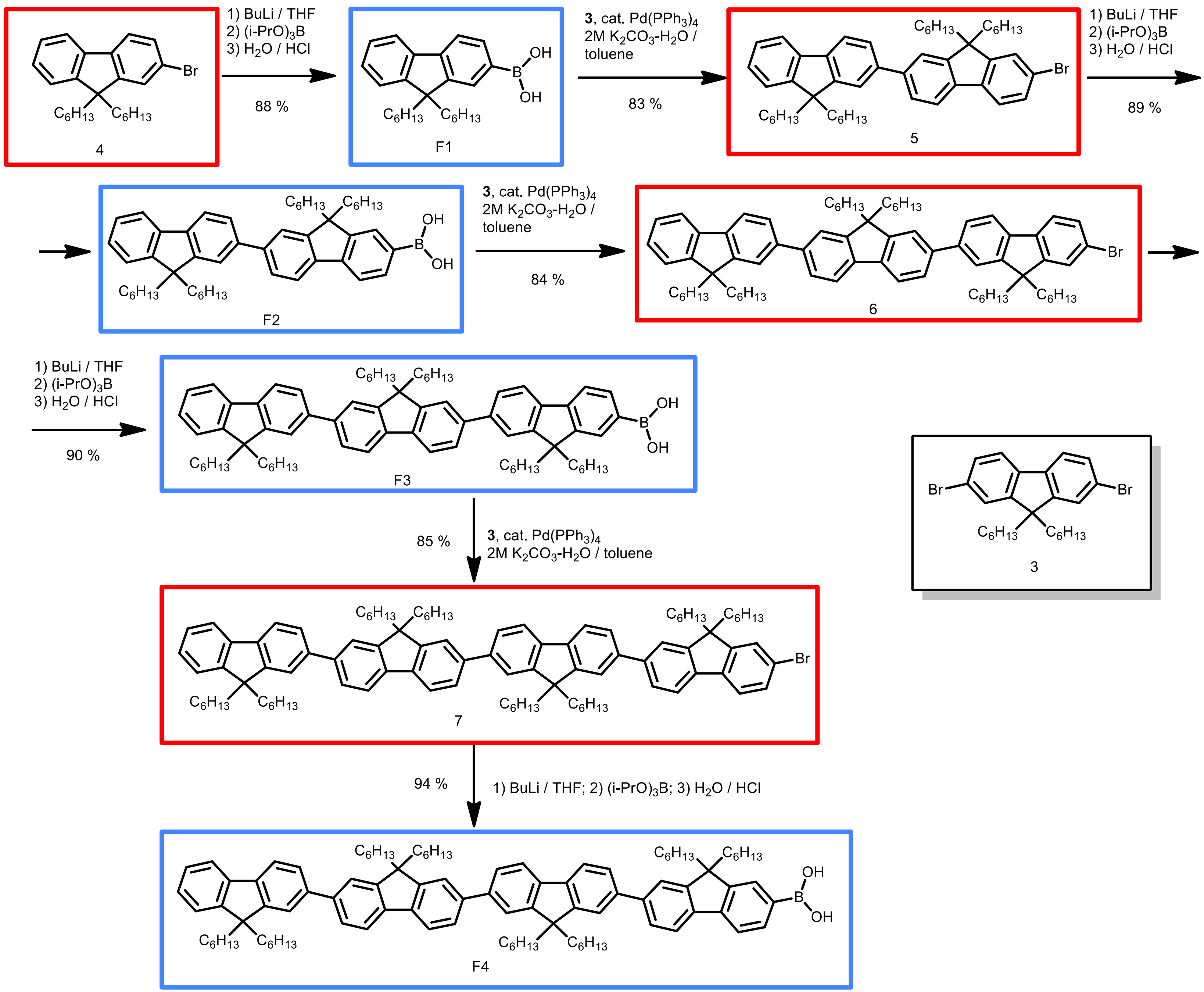






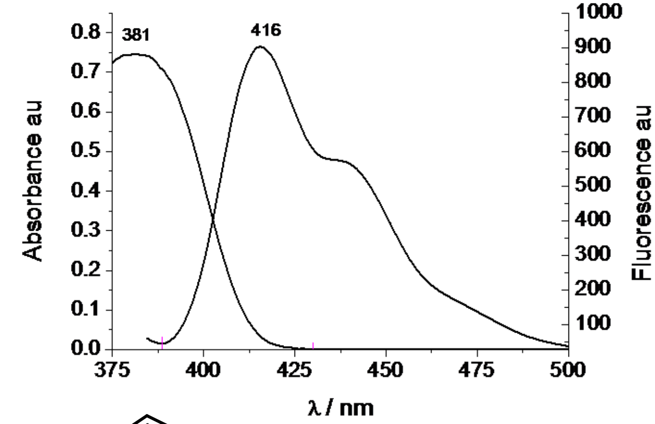
Star-shaped Oligofluorenes

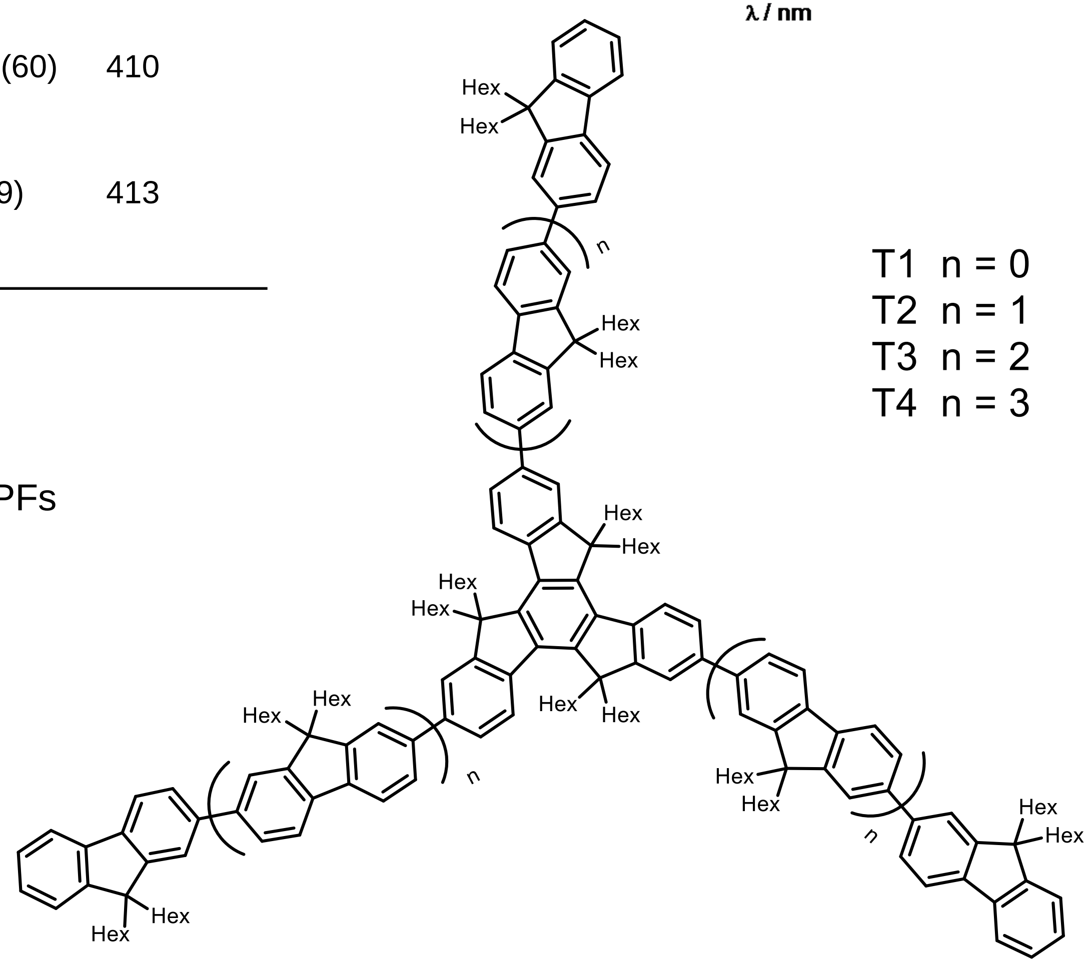




1) BuLi / THF
2) (i-PrO)3B
3) H2O / HCl
88 %
3, cat. Pd(PPh3)4
2M K2CO3-H2O / toluene
83 %
89 %
84 %
90 %
85 %
94 %
1) BuLi / THF; 2) (i-PrO)3B; 3) H2O / HCl
4
F1
5
F2
6
F3
7
F4
3
Br
OH
B
C6H13

cmpd	M_w, g mol^{-1}	λ_{abs}, nm film	λ_{PL}, nm (Φ_{PL}, %) film	TGA, °C [5% loss]
T1	1844.95	343	380sh, 398, 419.5 (43)	401
T2	2842.52	359	404, 425.5, 449 (51)	408
T3	3840.08	369	417sh, 436, 462sh (60)	410
T4	4837.65	372	422, 442, 467sh (59)	413



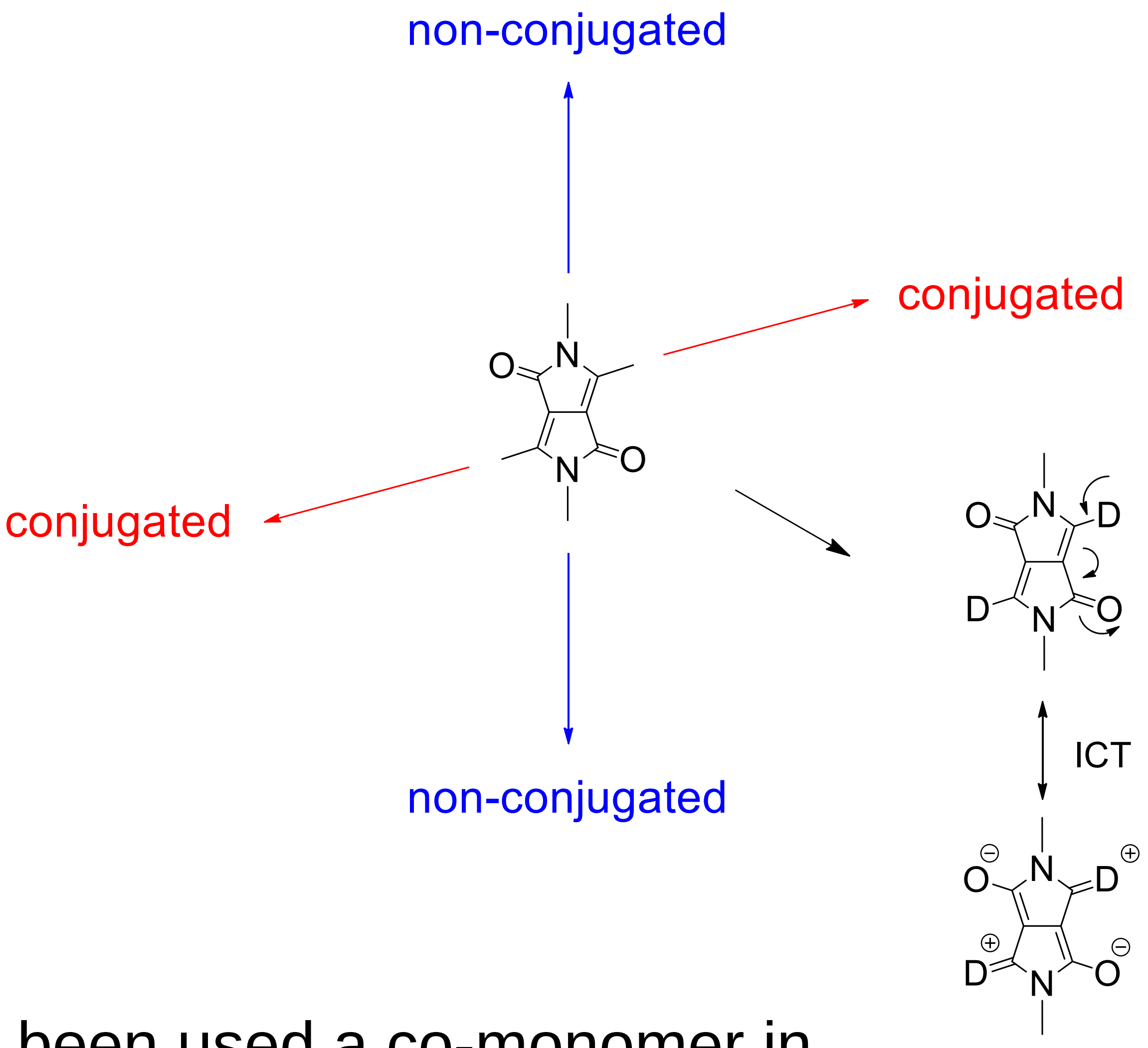


T1 n = 0
T2 n = 1
T3 n = 2
T4 n = 3

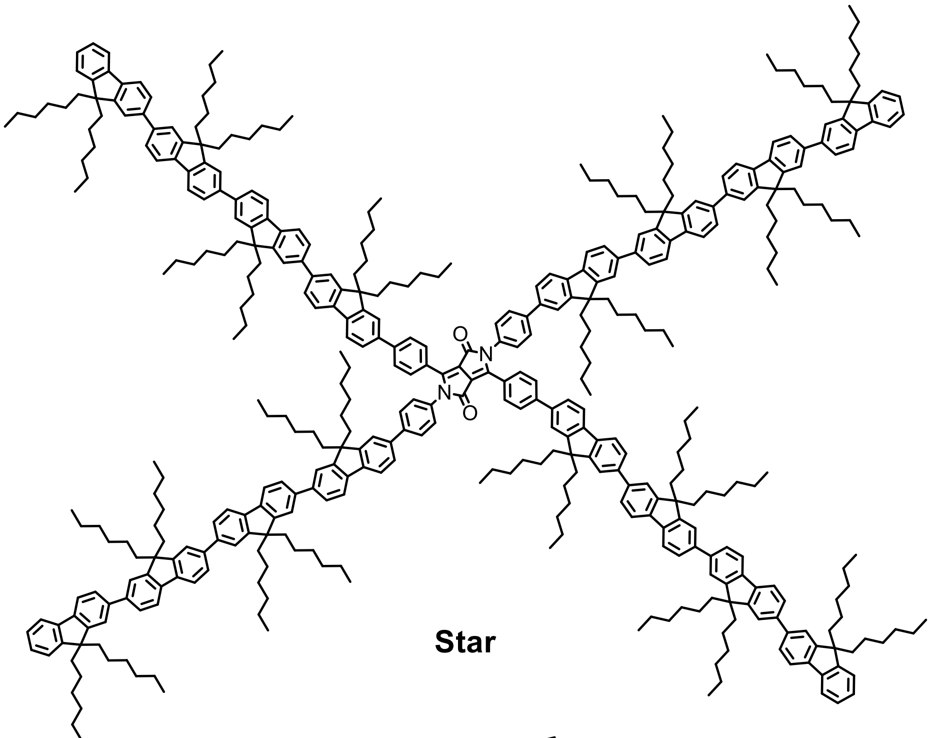
- Sharp PL characteristics
- Very accurate HOMO/LUMO levels
- PL efficiencies comparable to analogous PFs
- High degree of purity
- Good thermal stability
- Excellent solubility
- Improved stability over PFs
- **Synthetic reproducibility**

J. Am. Chem. Soc., 2004, **126**, 13695

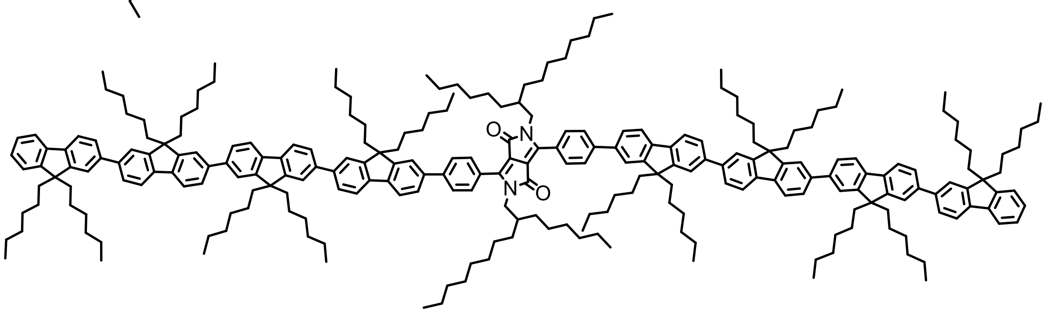
Alternative cores: 1,4-diketo-pyrrolo[3,4-*c*]pyrrole (DPP)



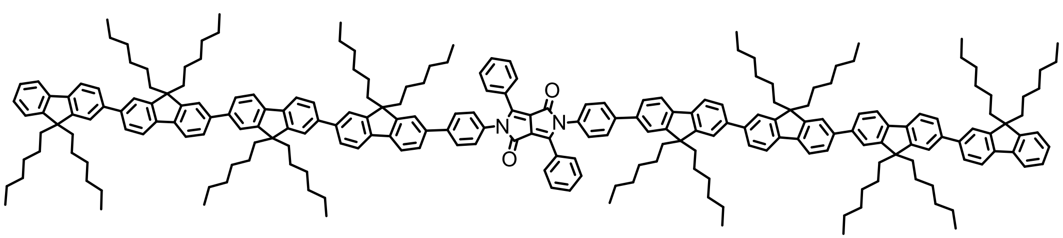
DPP has been used a co-monomer in materials for OPV, OFET and EL (red emitter)



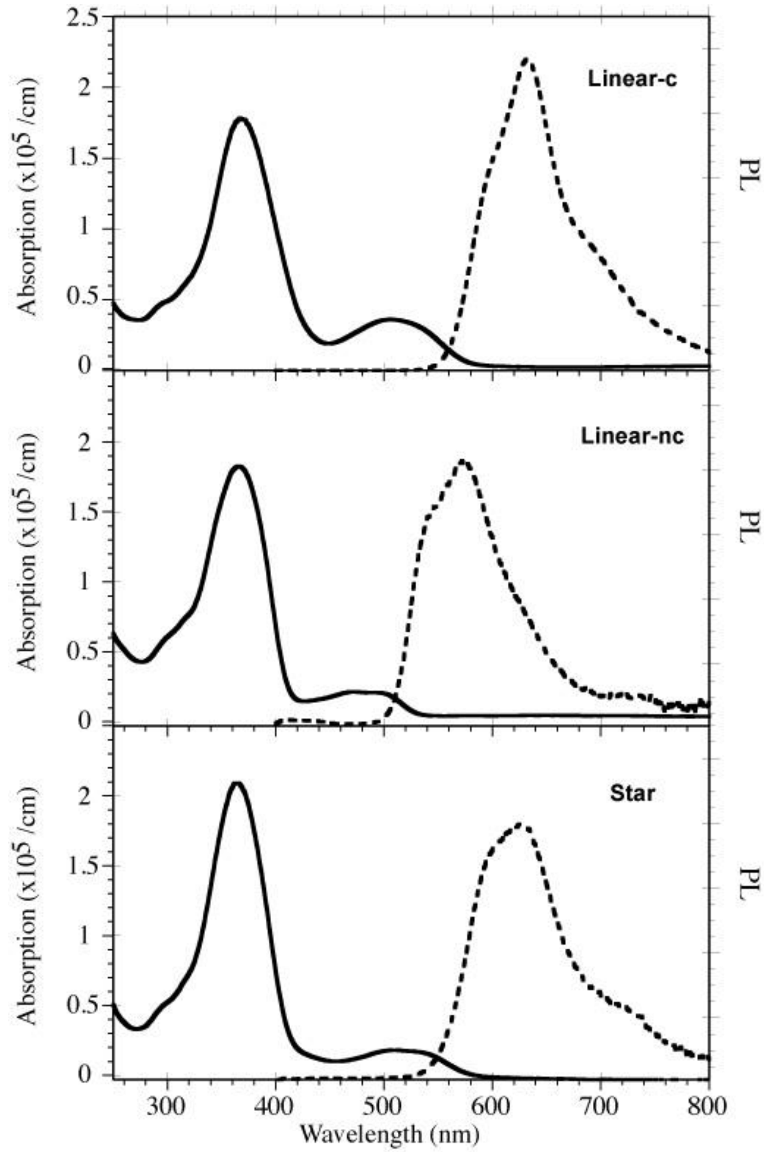
Star



Linear-c

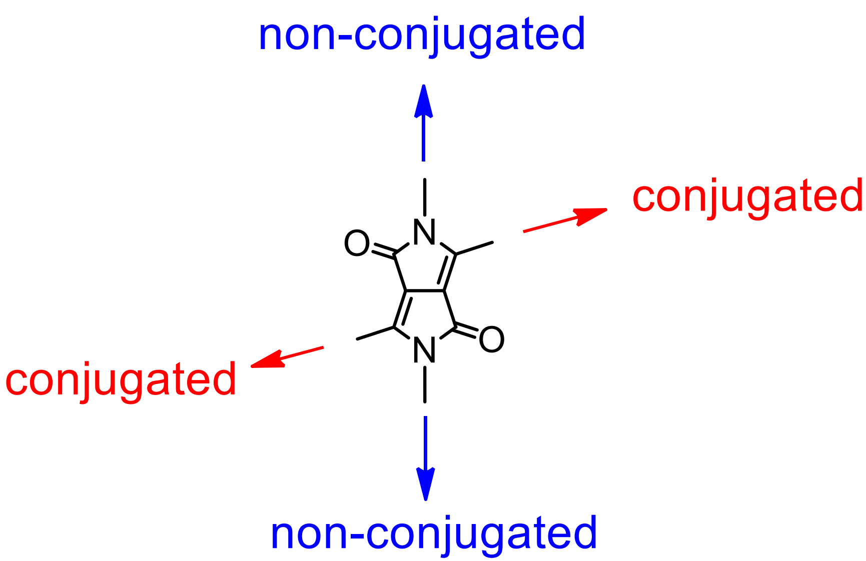


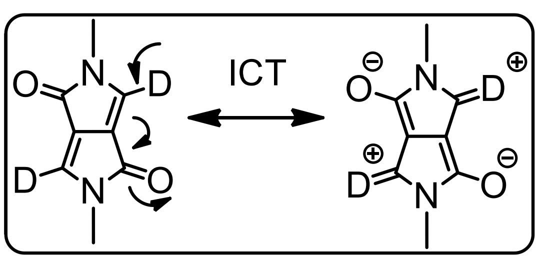
Linear-nc

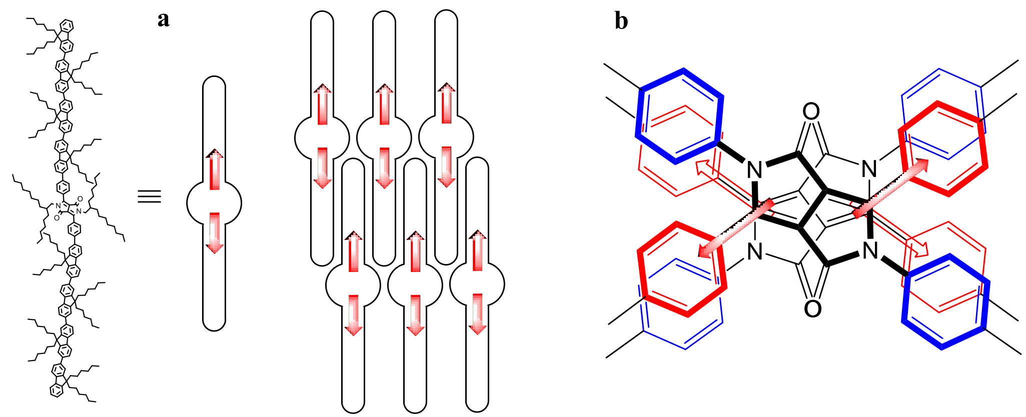


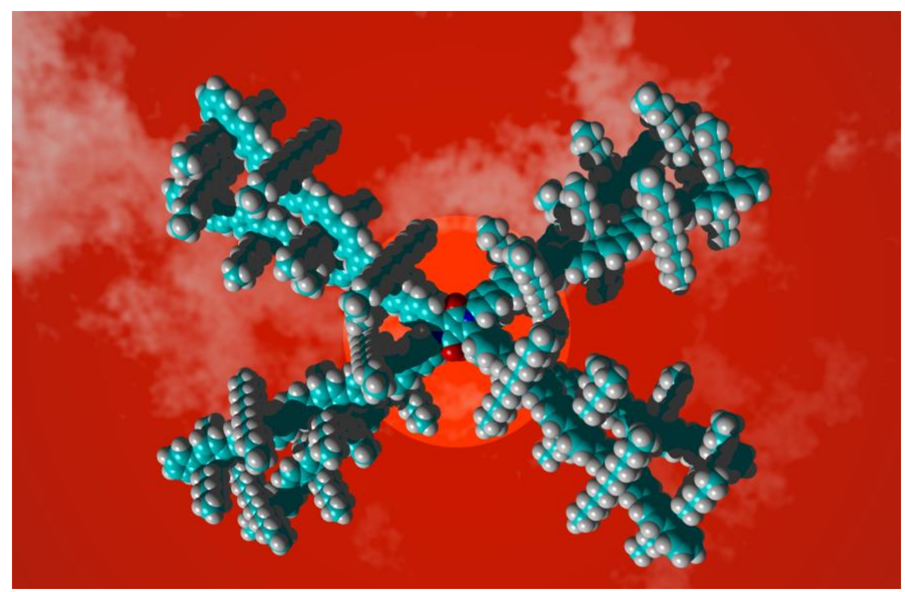
Charge transfer and aggregation

PLQY for neat films ranges 2-20% due to aggregation through dipole interactions.

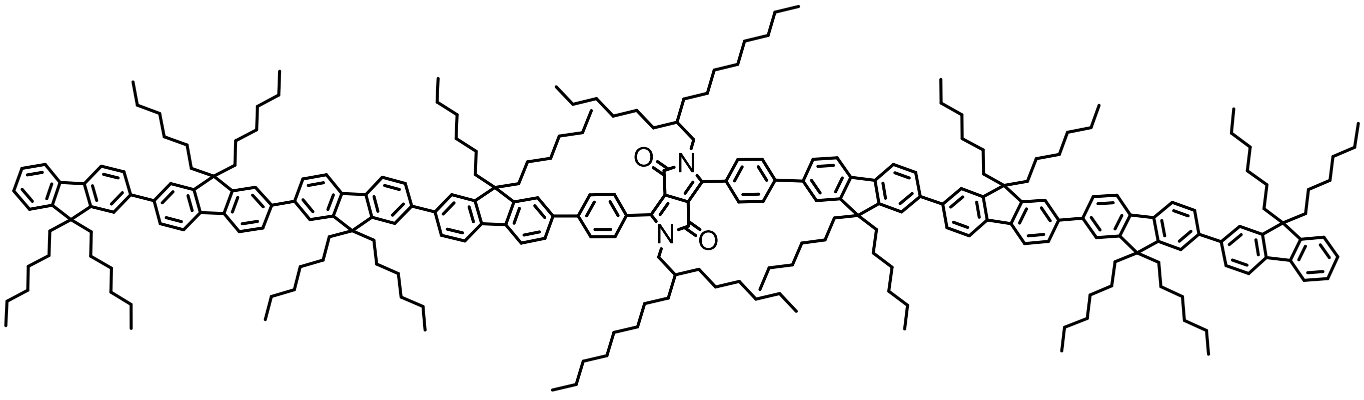


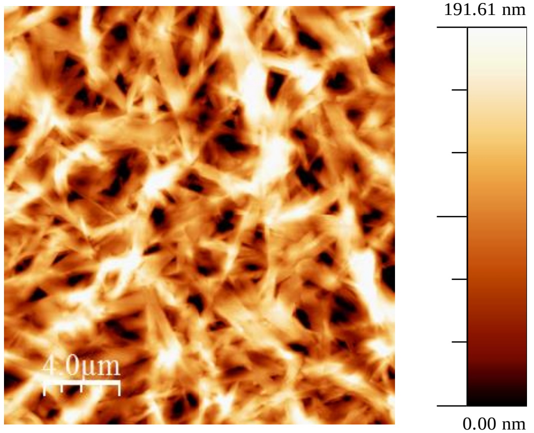






Adv. Mater. **2011**, *23*, 2093–2097

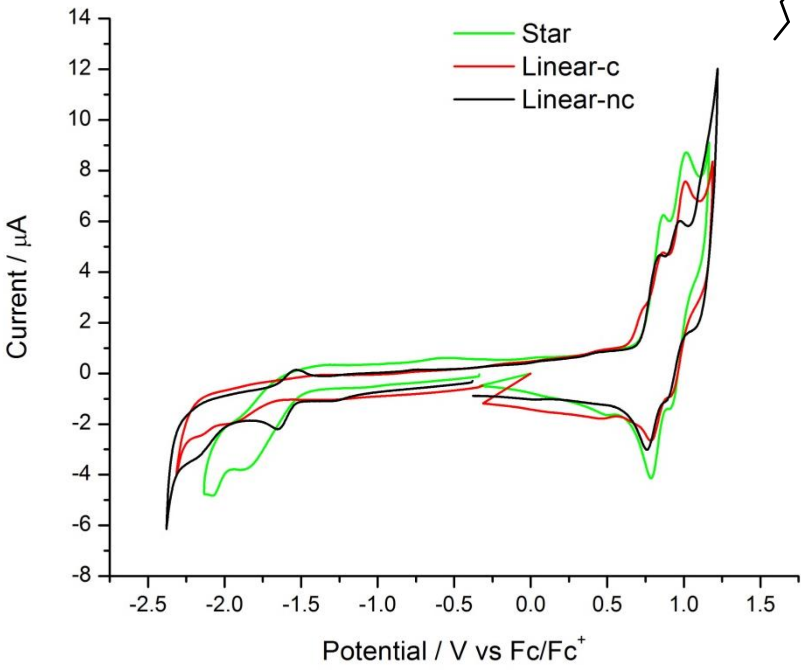


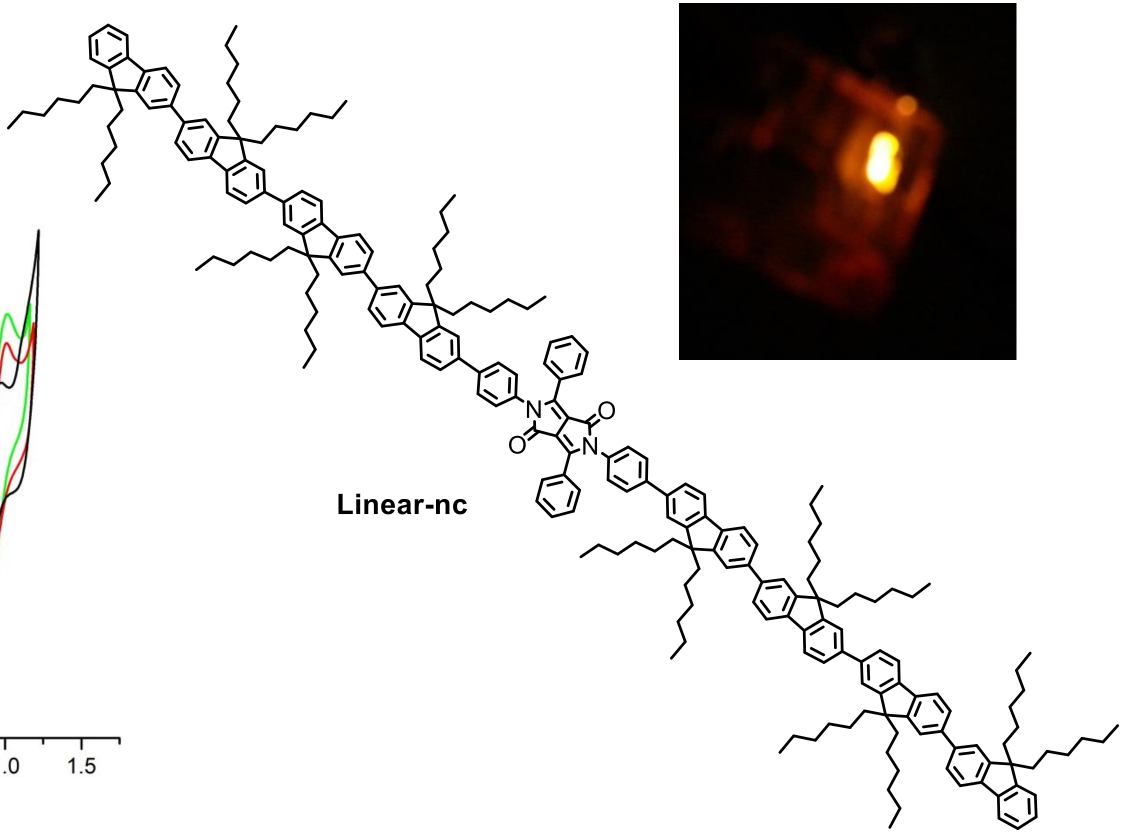


Isr. J. Chem., 2014, in press

Hole mobility **10^{-4} cm^2/Vs**

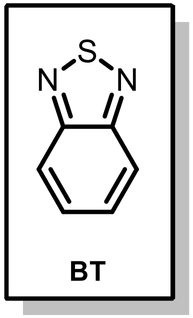
30mg of **Linear-c** in 1ml of chloroform, PFBT 20 seconds, annealed at 140 °C for 30 min

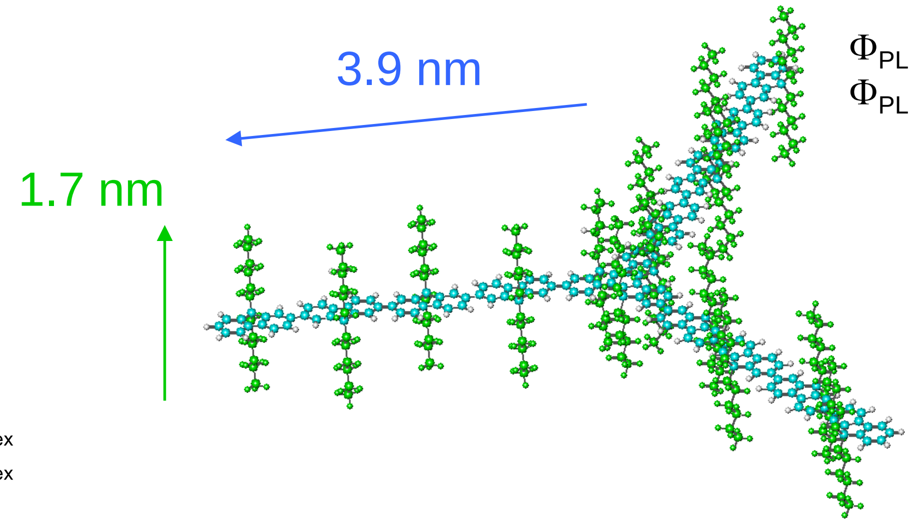


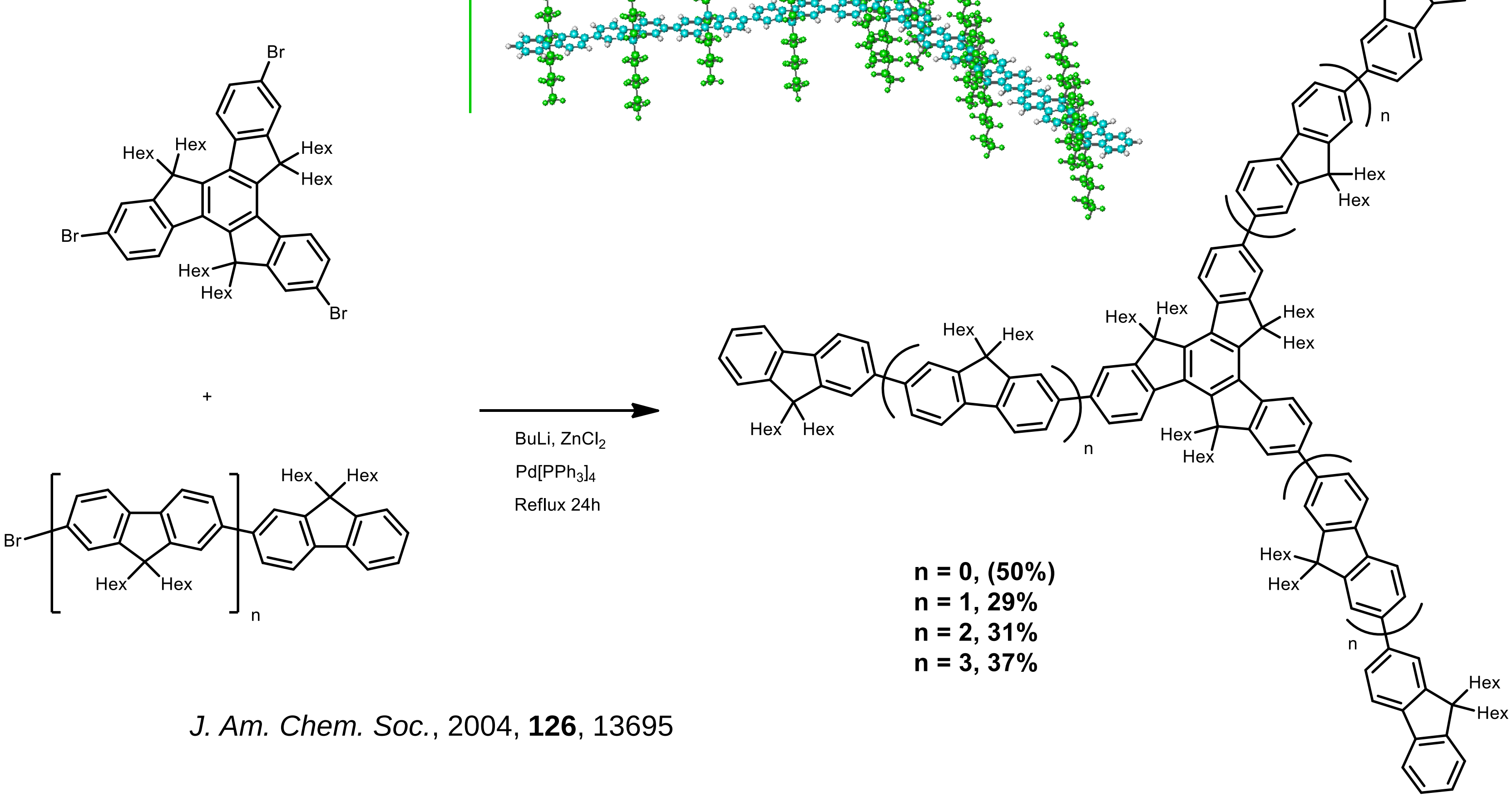


Linear-nc

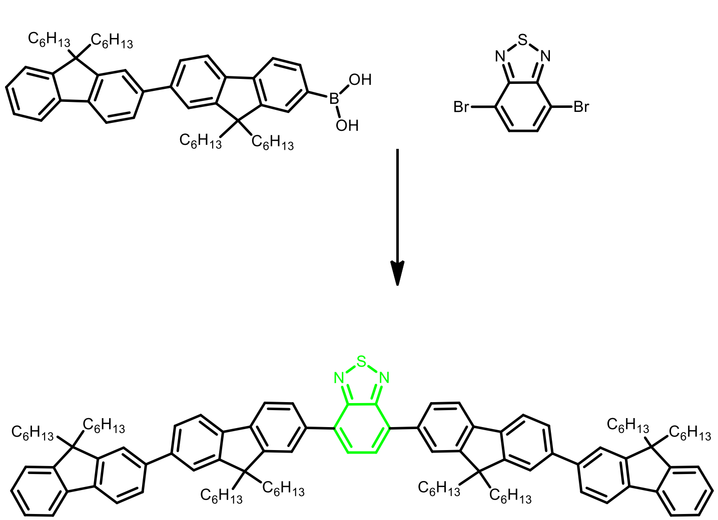
From blue to green: incorporating BT into oligofluorene-truxenes



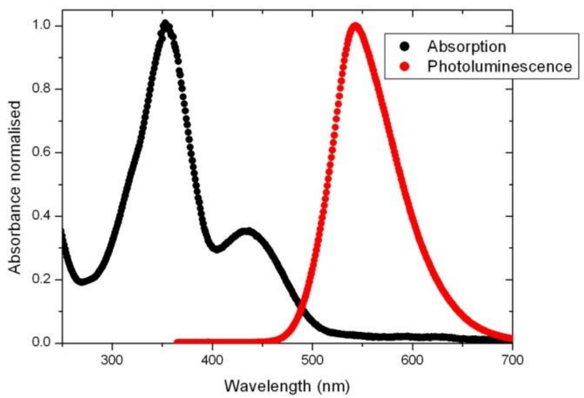


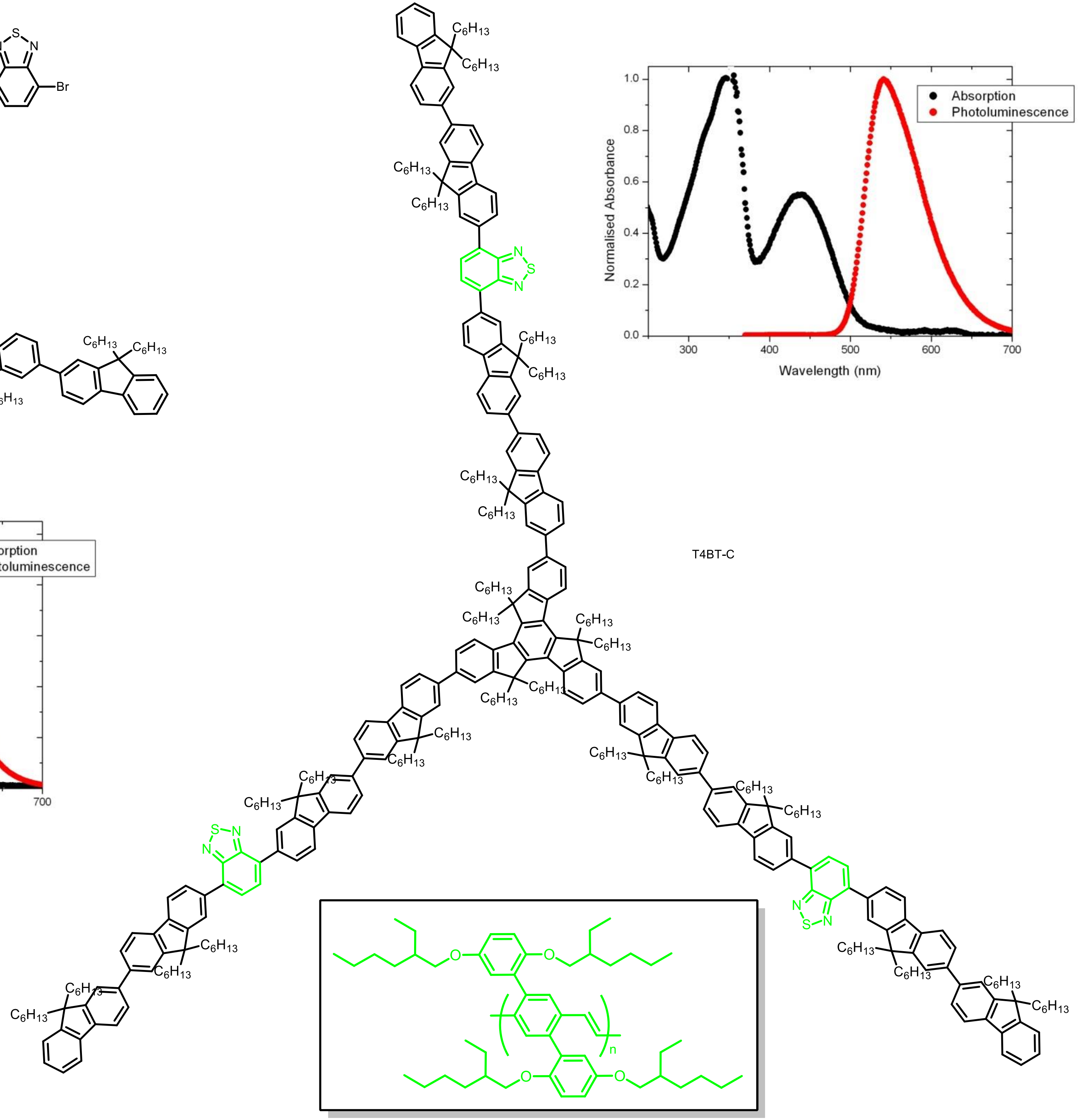


J. Am. Chem. Soc., 2004, **126**, 13695



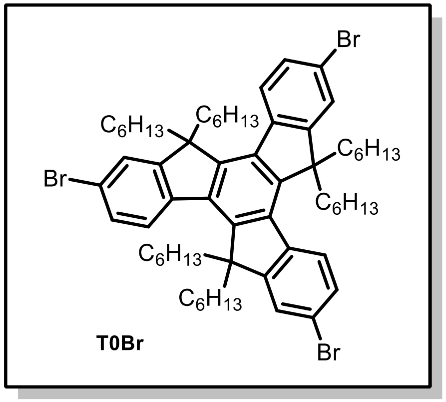
97.8%

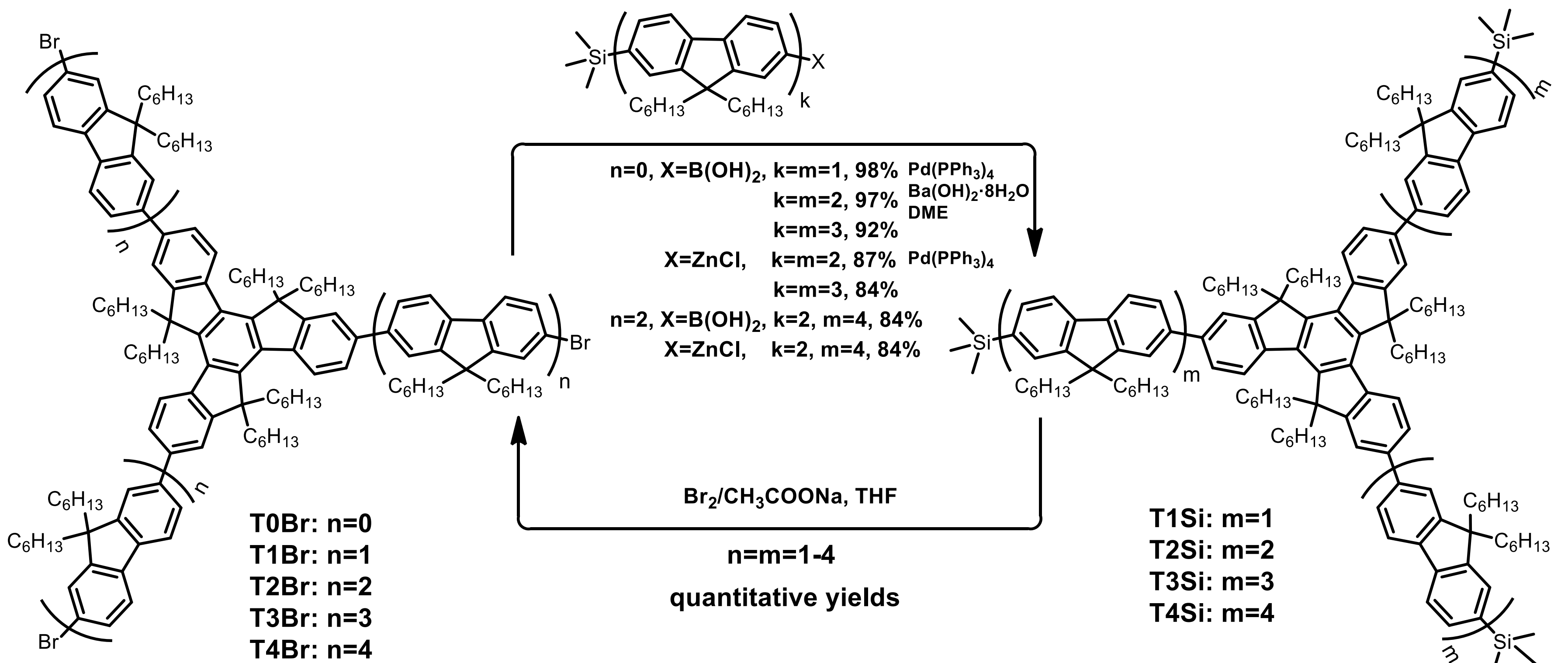




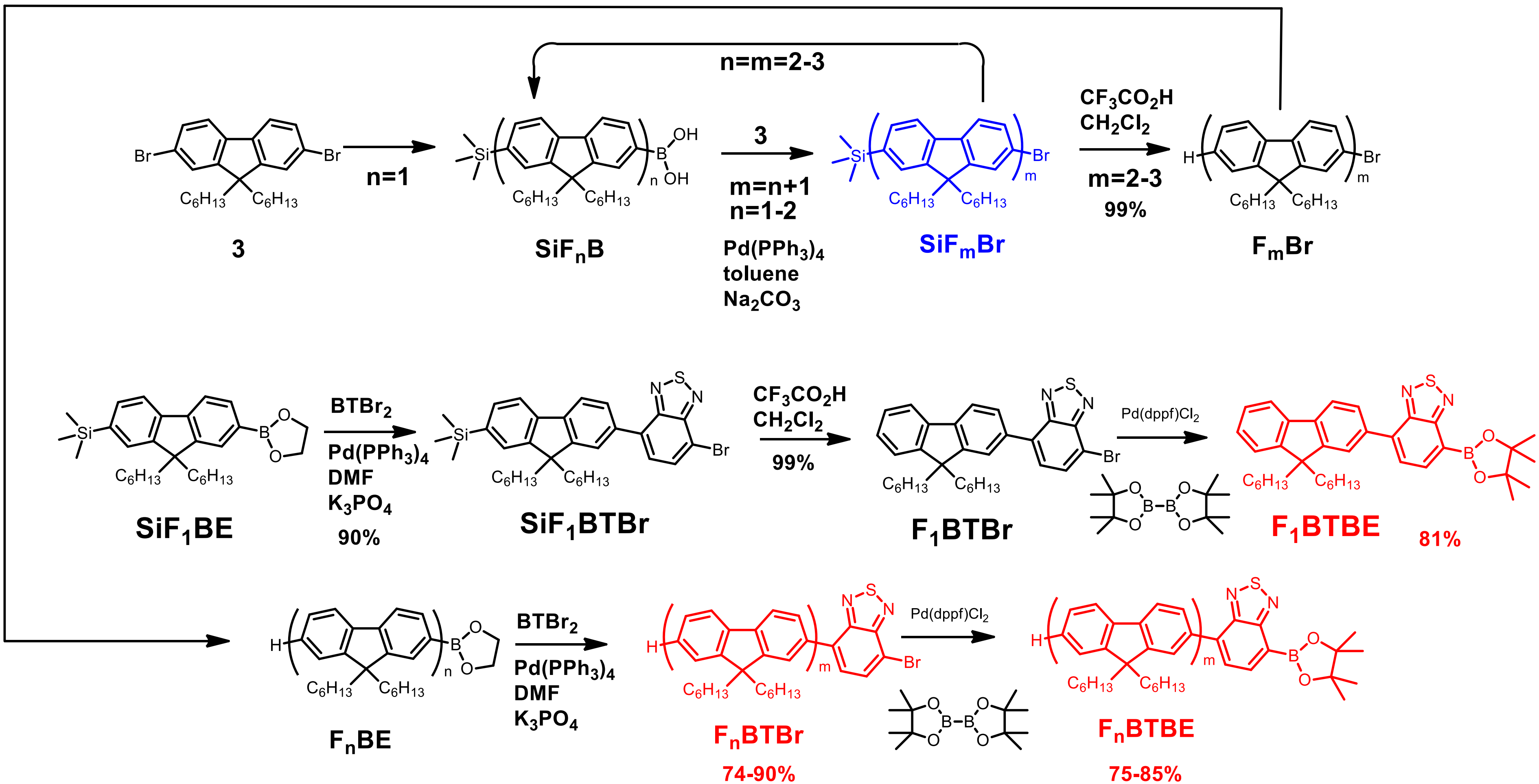
T4BT-C

Solid state PLQY for both compounds is ca. 88%
Fluorescence lifetime is ca. 4 ns for the star



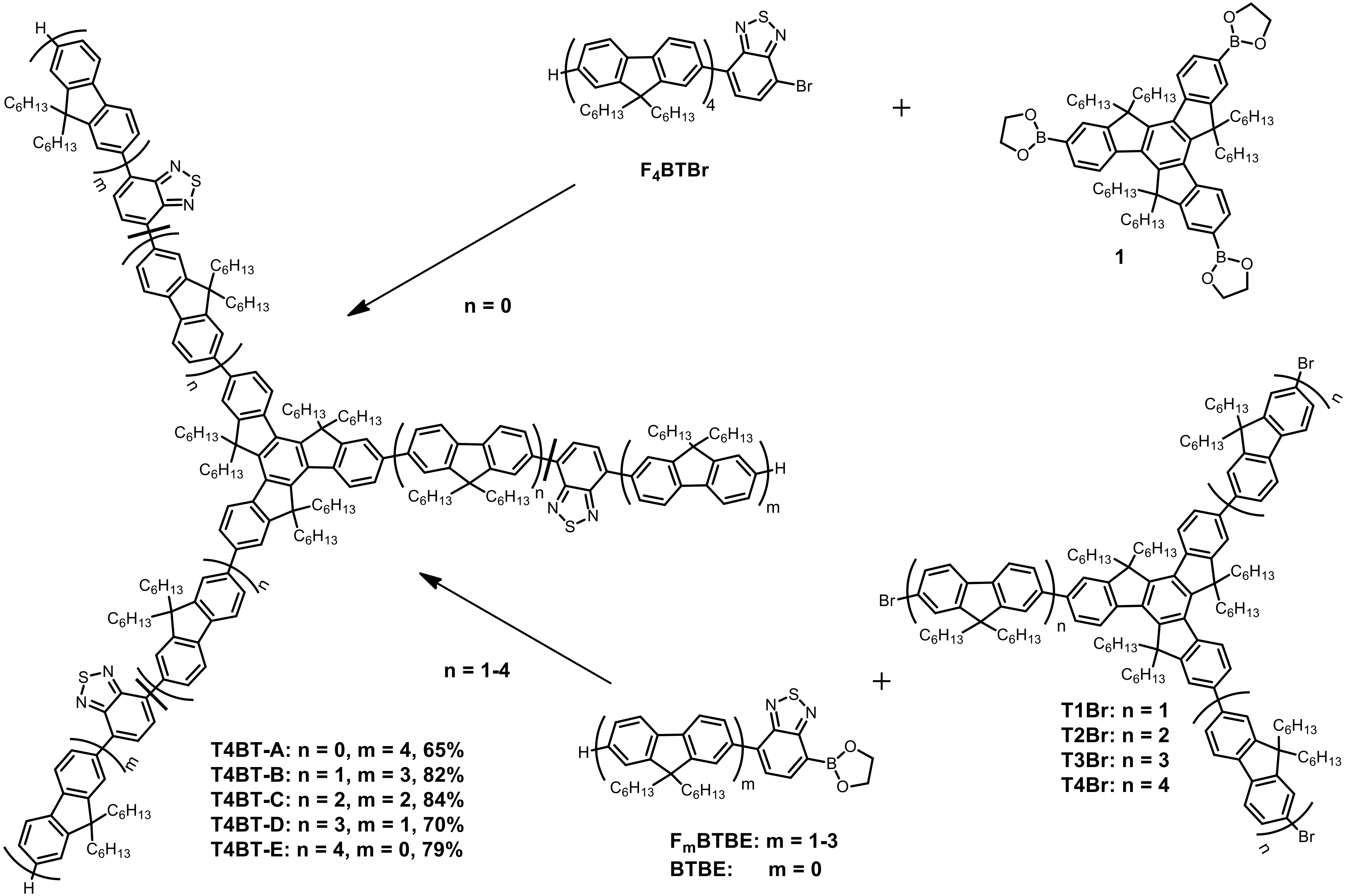


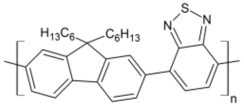
Synthesis of T1Si-T4Si by modified Suzuki coupling and bromination in mild conditions



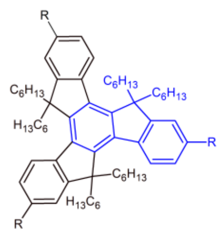
Synthesis of the oligofluorene-BT arm precursors F1BTBE - F3BTBE

New greens – BT series

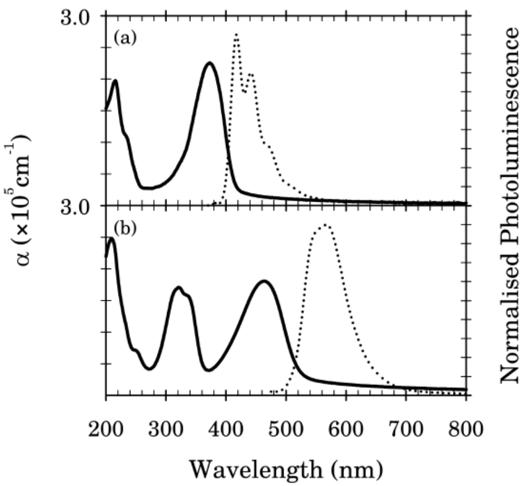


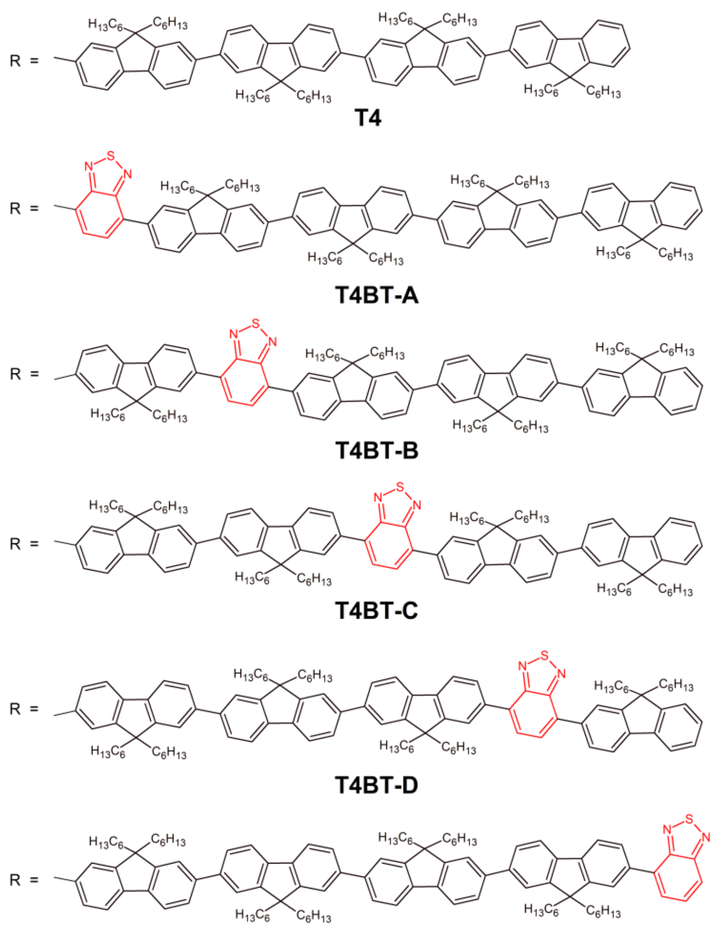


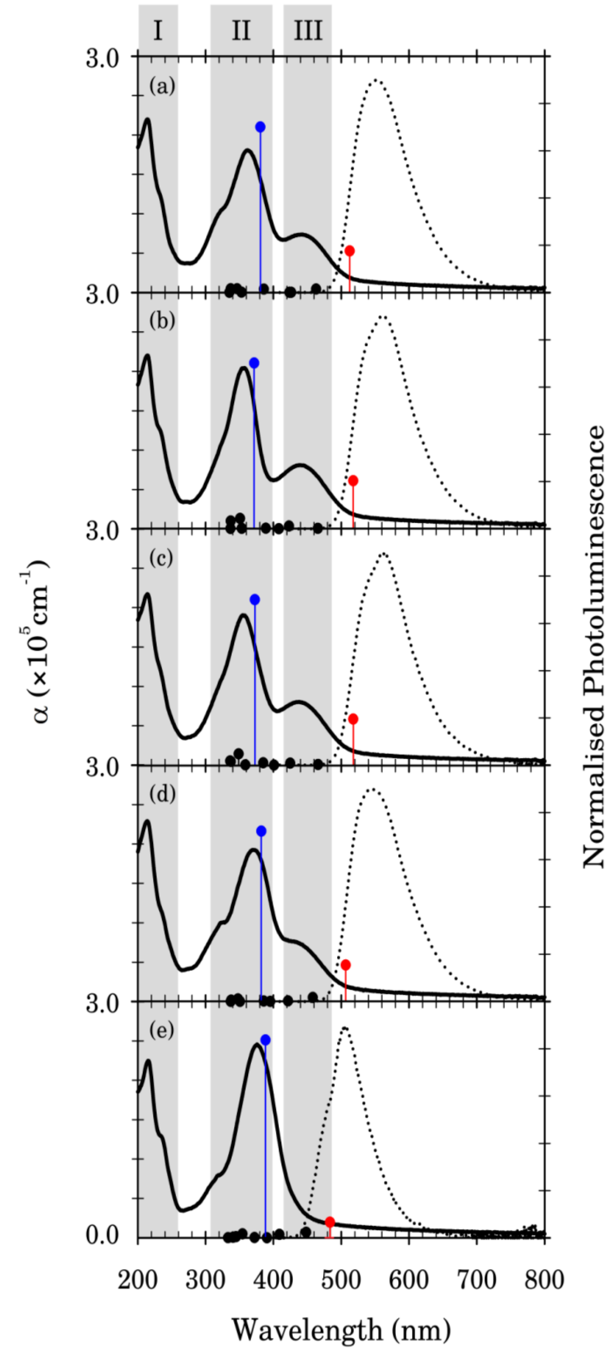
F8BT



Truxene Core





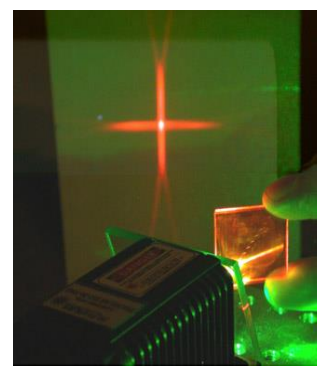


Adv. Funct. Mater., 2013, **23**, 2792

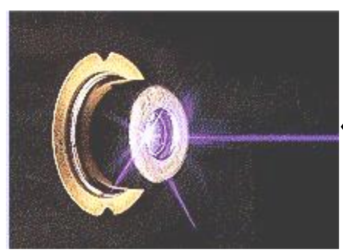
Shrinking Polymer Laser systems

1995 Regenerative amplifier
(Tessler)

~2000 Q-switched
Nd:YAG



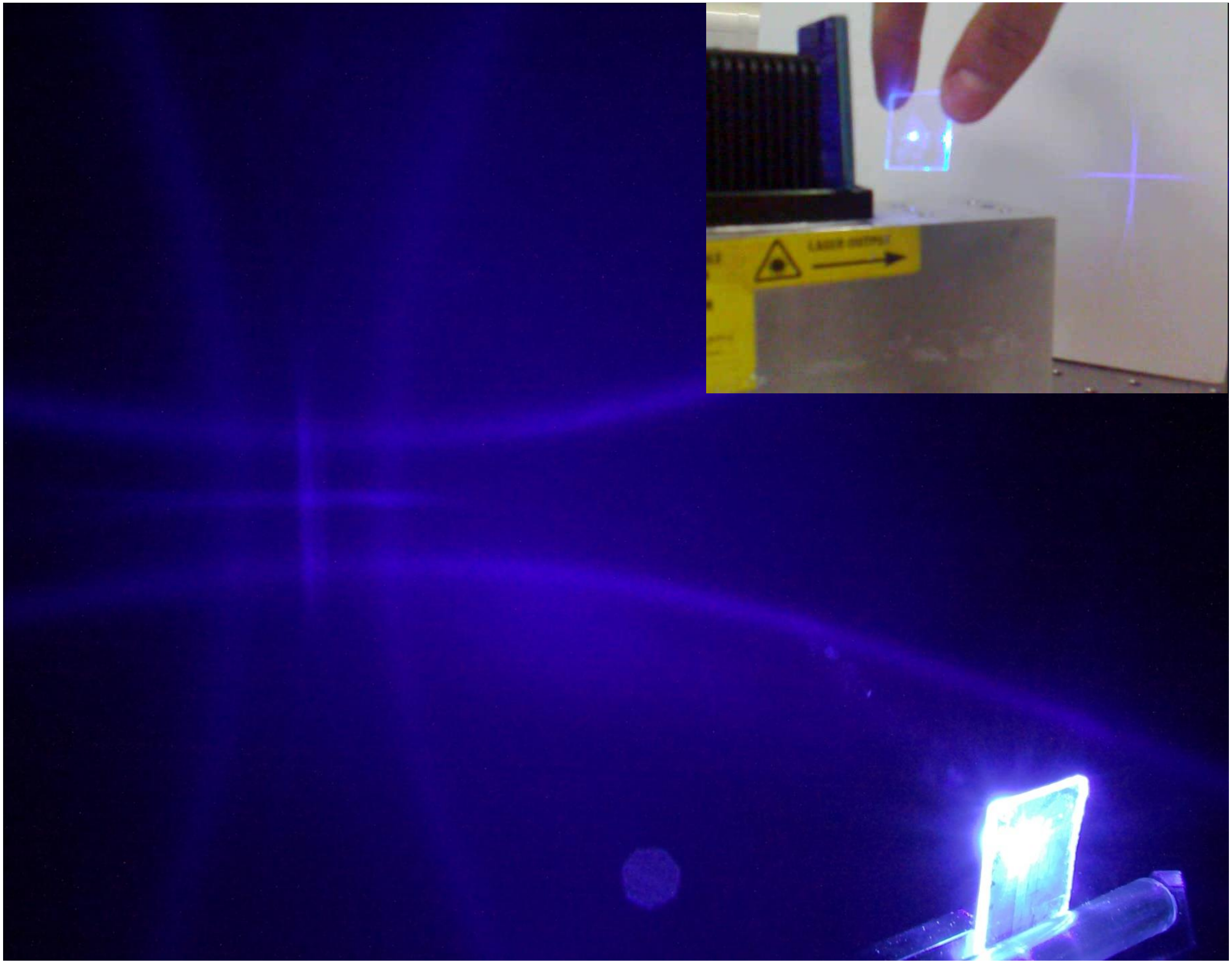
2003 Microchip laser



2006 Diode
pumped

2008 LED
pumped

Yang *et al*., App Phys Lett **92**, 163306 (2008)

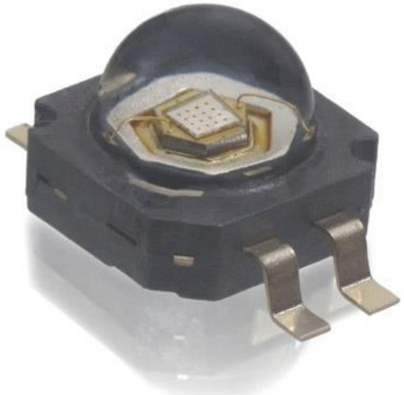


LED pumped polymer lasers

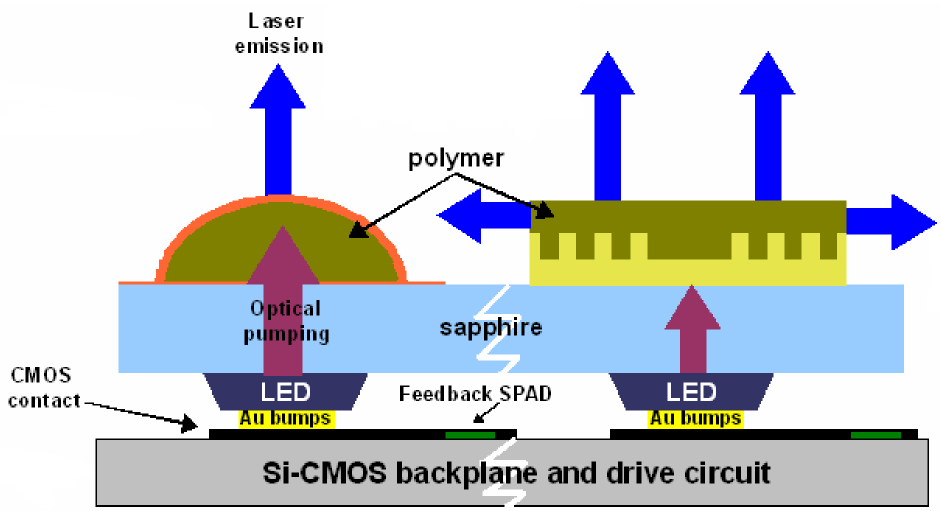
Advantages

- Exploits high mobility of III-V semiconductors
- Separates charge injection from gain medium
- Much lower cost than laser pumped system
- Very compact, electrically controlled

All the benefits from direct electrical pumping

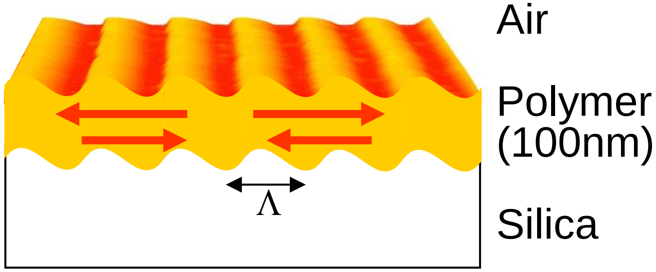


www.lumileds.com

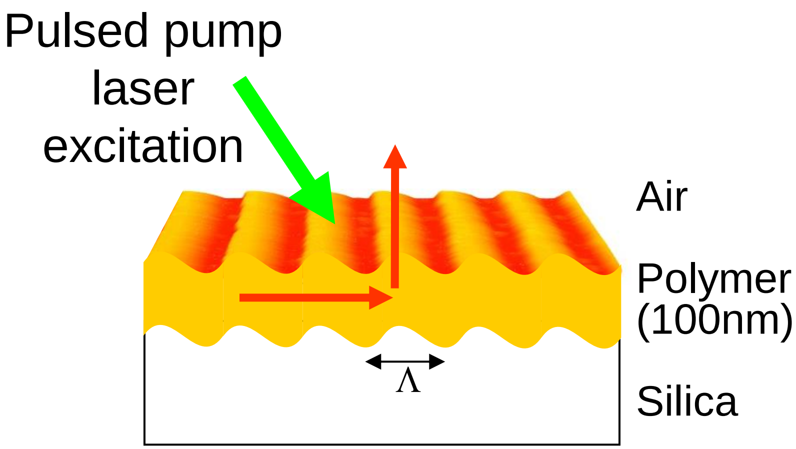


Surface-emitting distributed feedback lasers

$$m\lambda = 2n_{\text{eff}}\Lambda$$



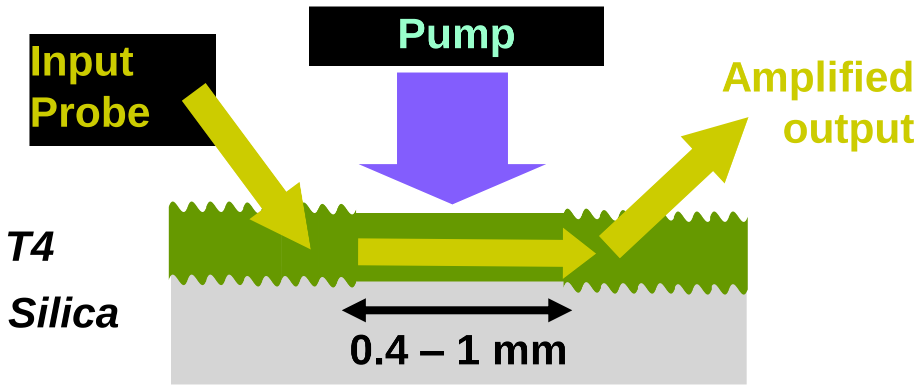
1st order scattering provides distributed feedback

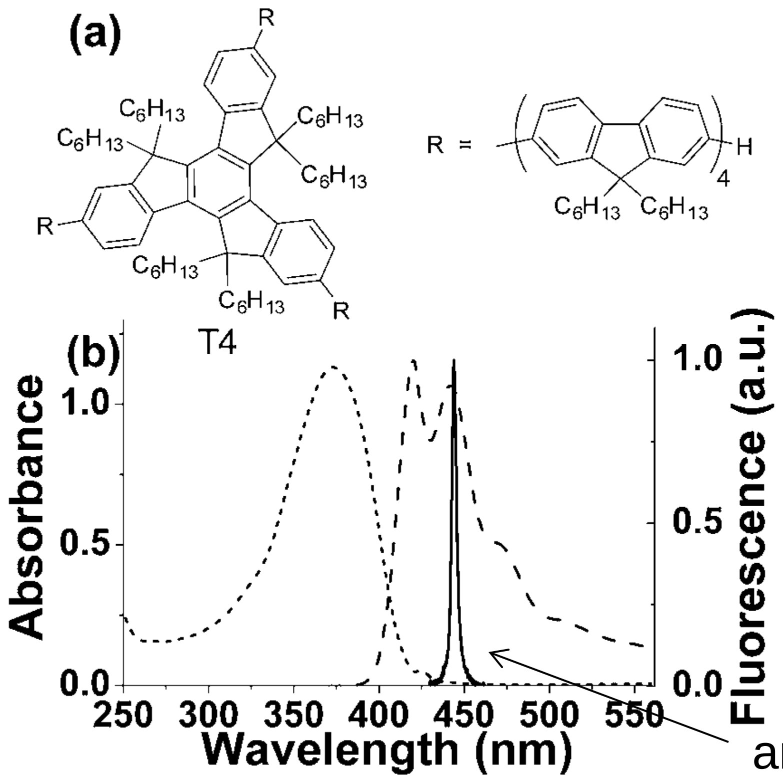


2nd order scattering provides surface output coupling

e.g. Phys Rev B **67**,165107 (2003); J Appl Phys **98**, 023105 (2005)

Truxene based lasers





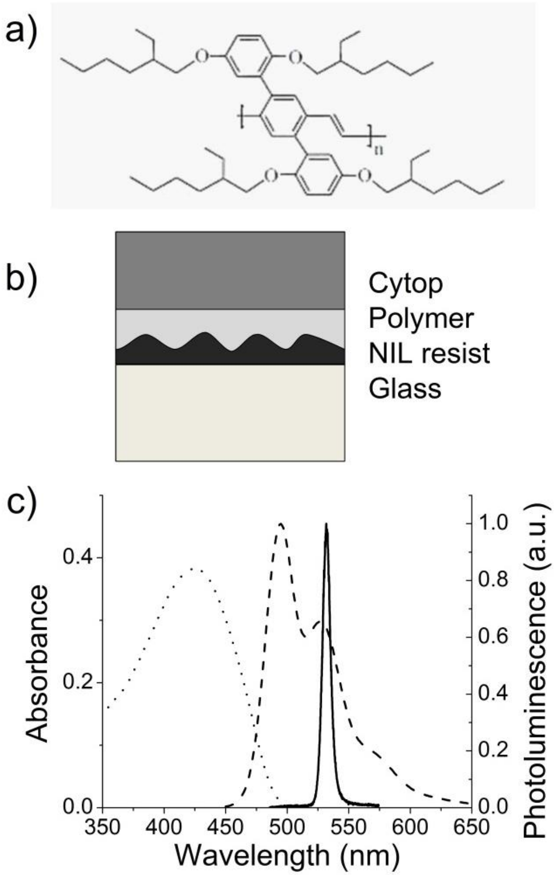
amplified spontaneous emission (ASE)

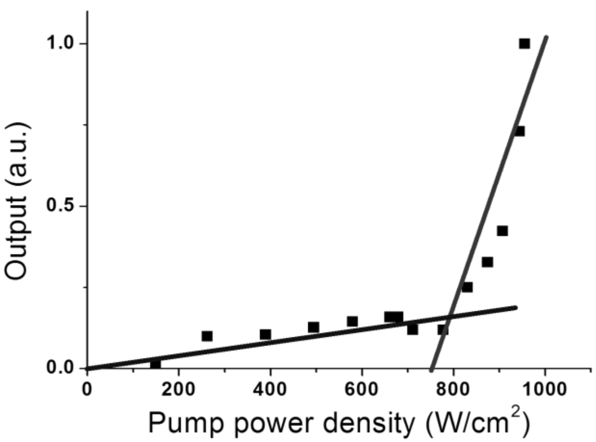
- T4 film (100-400 nm) forms optical waveguide
- Pump λ absorbed in ~100 nm
- Total internal reflection confines light in polymer film
- Signal amplified by 1000 times in 1 mm propagation through film
- T4 exhibits low-threshold (270 W cm^{-2}) and very low optical losses (2.3 cm^{-1}), one of the lowest report for an OSC

Appl. Phys. Lett., 2009, **94**, 243304.

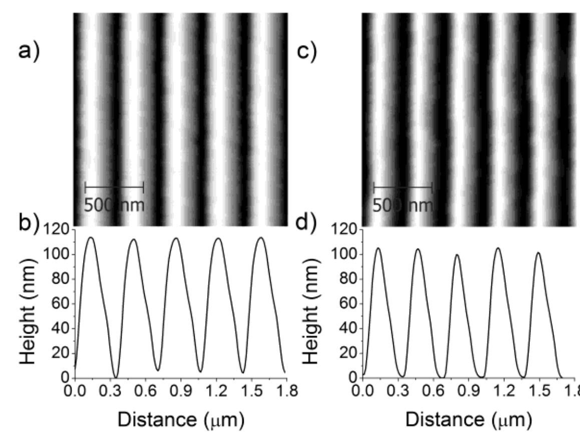
Nanoimprint lithography (NIL)

- Replicates a single high-quality master structure using a stamp-to-imprint procedure in a suitable photoresist under some combination of pressure and heat or UV illumination.
- Can be used as a roll-to-roll process.
- Low-cost.
- High volume.
- Commercial LED (Philips Luxeon Rebel royal blue) emitting at 448 nm; max power 1 kW/cm^2
- Previous lasing thresholds from NIL: 2 kW/cm^2

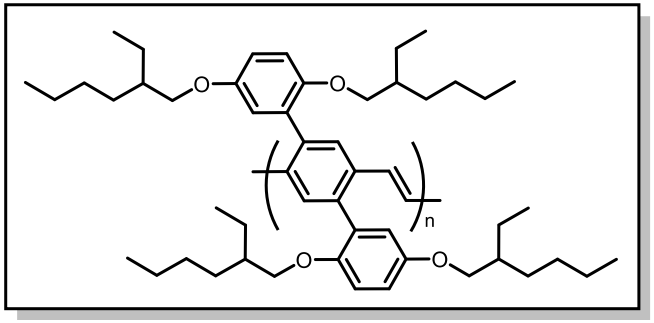




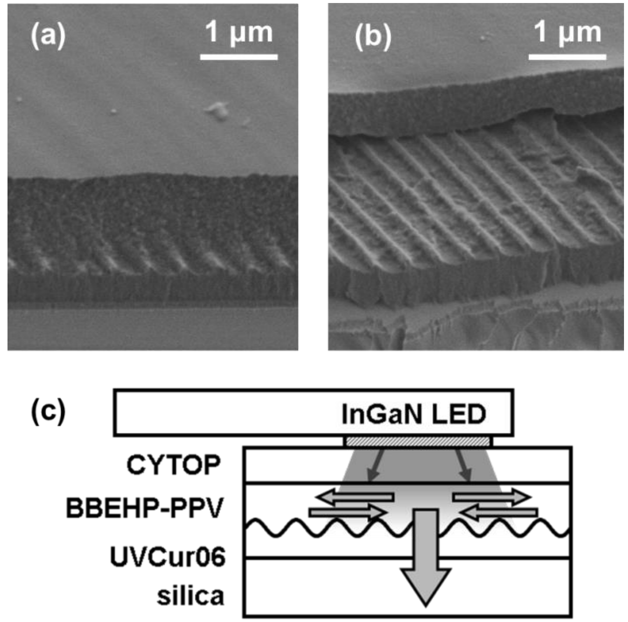
Threshold 770 W/cm^2

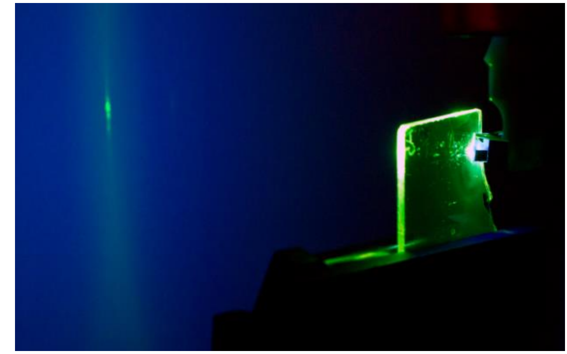


Case study on polymers: BBEHP-PPV



First synthesised and reported by:
A. Rose, Z. G. Zhu, C. F. Madigan, T. M. Swager, V. Bulovic, *Nature* **2005**, *434*, 876.





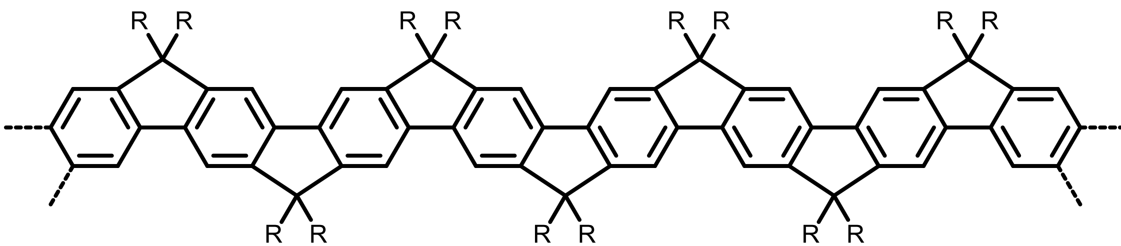
Plastic laser pumped by a cheap commercial LED!!!

Sample number	Isolation Method (from synthesis batch)	Appearance	*Mw*	*Mn*	PDI	ASE threshold [Wcm^{-2}]
1	Soxhlet, acetone (batch c)	Powder	28 430	28 270	1.01	488
2	Soxhlet, CH_2Cl_2 (batch d)	Powder	202 800	93 220	2.18	216
3	Soxhlet, CH_2Cl_2 (batch d)	Powder	341 300	68 860	4.96	167
4	Reprecipitation (batch b)	Powder	409 700	65 840	6.22	266
5	Soxhlet, CH_2Cl_2 (batch c)	Powder	463 300	77 570	6.0	270
6	Soxhlet, CH_2Cl_2 (batch b)	Powder	510 400	88 470	5.77	277
7	Reprecipitation (batch a)	Powder	582 800	54 790	10.6	302
8	**Soxhlet, CH_2Cl_2 (batch d)**	**Fibre**	**551 800**	**115 800**	**4.77**	**638**

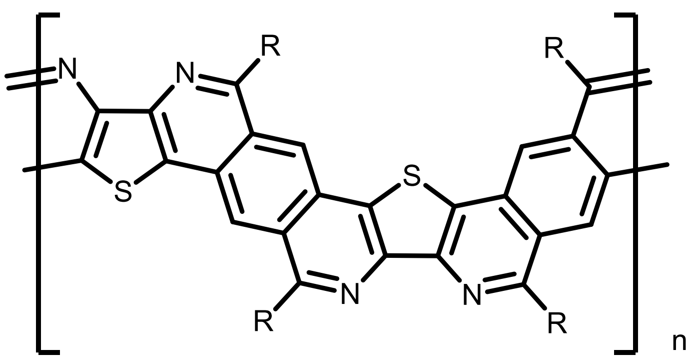
Advanced Materials, 2013, **25**, 2826-2830

Materials for organic solar cells and field effect transistors

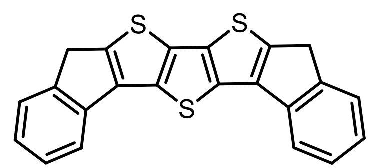
Towards planar structures
How important are non-covalent interactions vs covalent links?

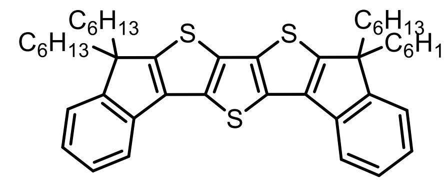


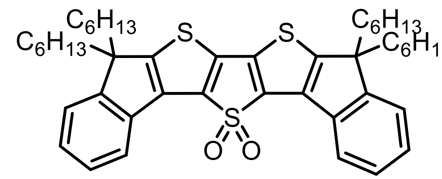
Scherf, Müllen
Ladders polymers – planar, but at the expense of bulky substituents to allow solubility



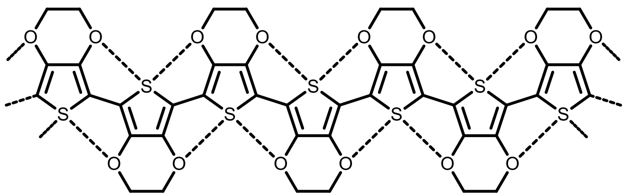
J. M. Tour, *J. Org. Chem.*, 2007, **72**, 7477.



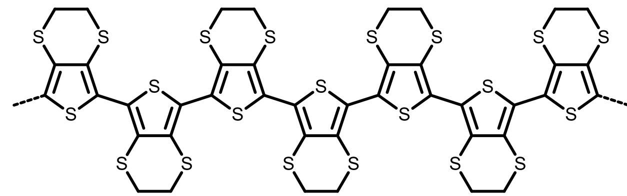




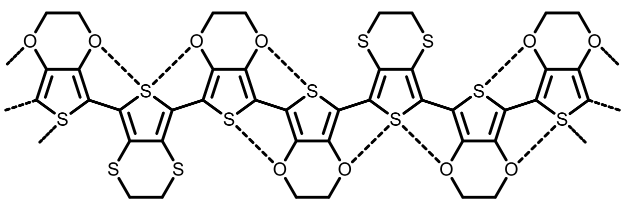
J. Mater. Chem., 2010, 20, 1112



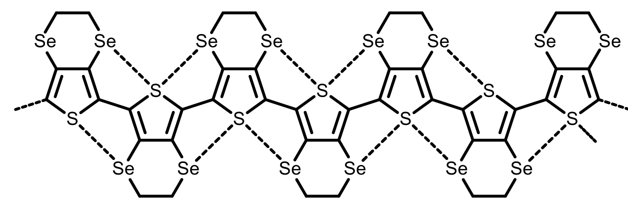
PEDOT
Eg = 1.6 eV



PEDTT
Eg = 2.2 eV

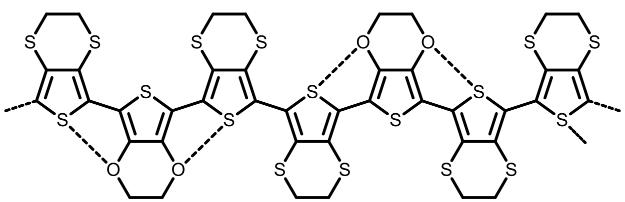


POSO
Eg = 1.6 eV



PEDST
Eg = 1.8 eV

Chem Mater., 2007, 19, 301



PSOS
Eg = 2.1 eV

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

Contact Radii :	C	H	F	S	N	O	Se	B
(Angstrom)	1.70	1.20	1.47	1.80	1.55	1.52	1.90	1.63

S---O interactions are 2.9-3.2 Å as opposed to 3.32 Å for S + O

Evidence: crystal structures, abs data, molecular modelling, systematic studies by structural variation

How significant are non-covalent interactions in conjugated polymers?

Pathways to exploitation:

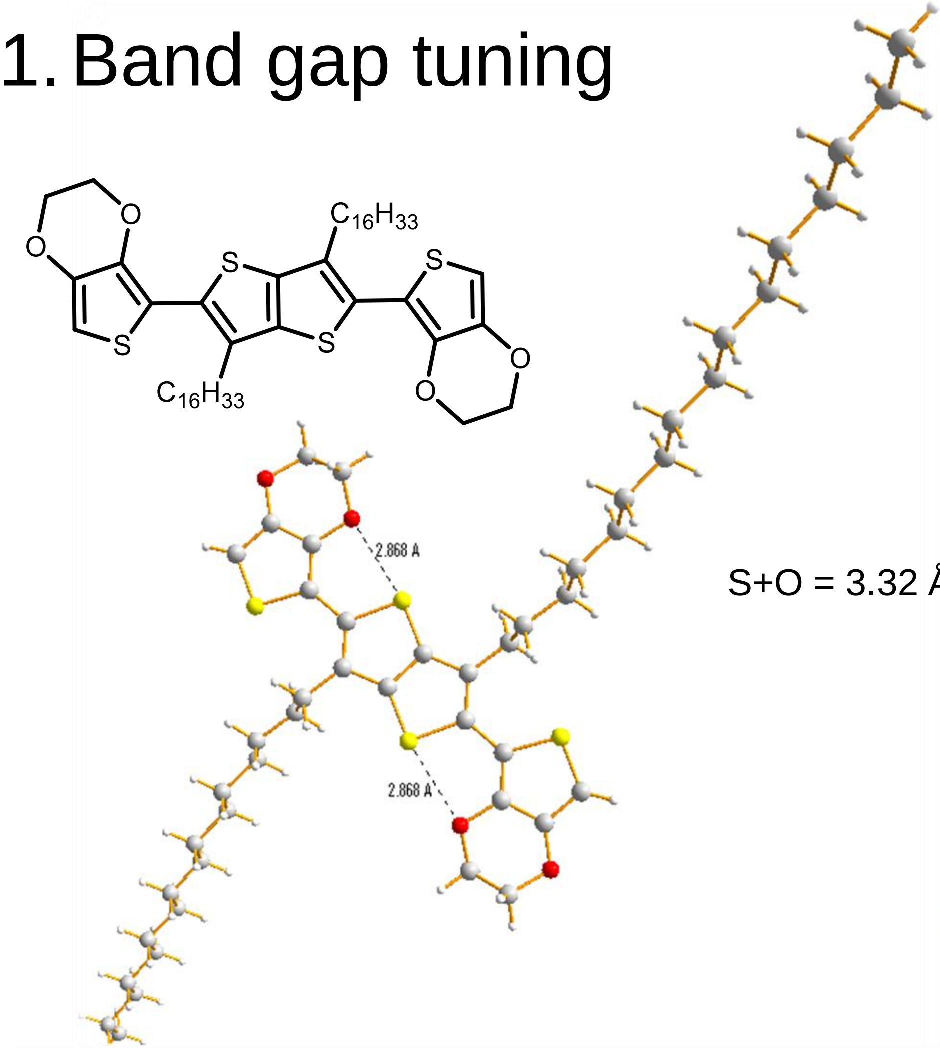
1. Band gap tuning

2. Enhanced stability of intermediate charged states

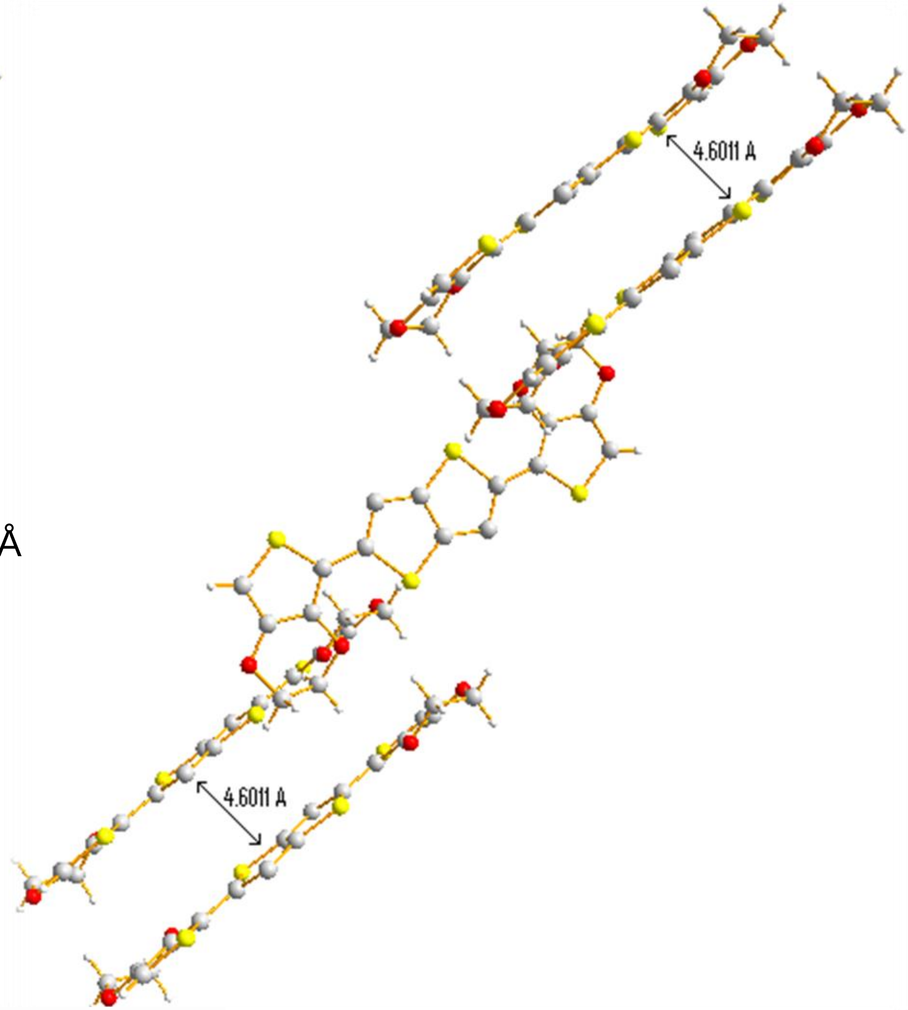
3. Processability

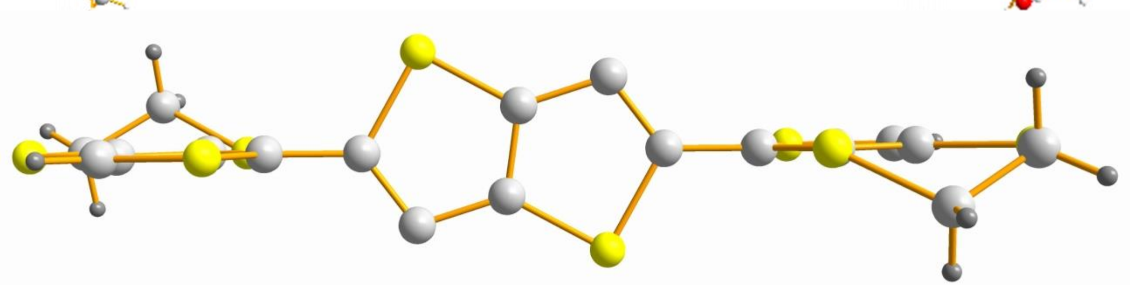
4. Efficient orbital overlap in the bulk in 2 or 3 dimensions

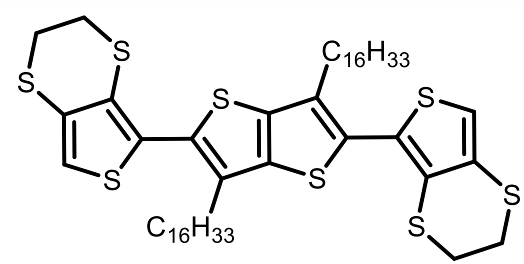
1. Band gap tuning



S+O = 3.32 Å



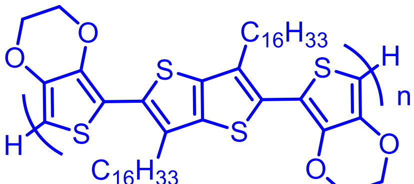




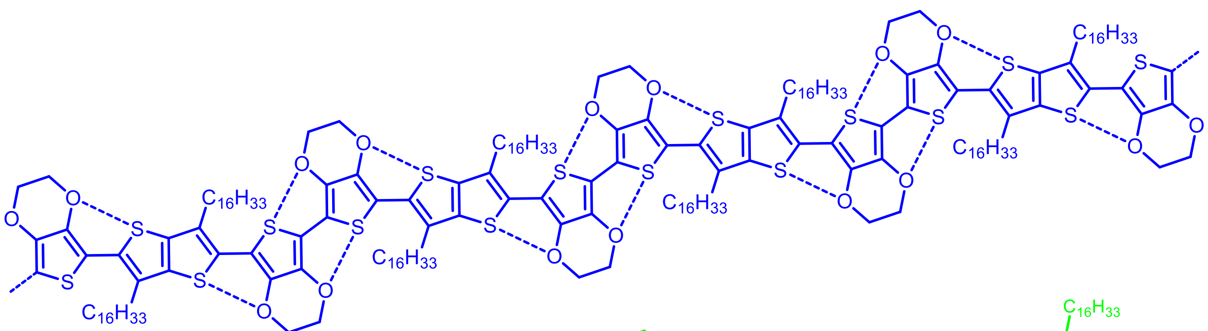
Chem. Mater., 2010, 22, 3000-3008

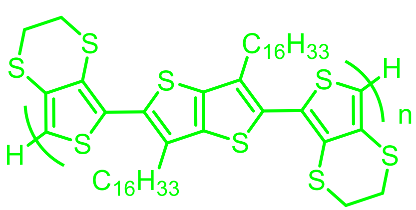
	E_{1ox} / V	E_{2ox} / V	E_{1red} / V	HOMO / eV	LUMO / eV	Electrochemical[a] HOMO-LUMO gap / eV	λ_{max} / nm
1	+0.46	+0.95	-1.98	-5.18	-2.97	2.21	347
2	+0.71/0.51	+1.00	-1.97	-5.42	-2.97	2.45	310

	E_{1ox}/ V	E_{2ox}/ V	E_{1red}/ V	HOMO / eV	LUMO / eV	[a] E_g eV
Poly(1)	-0.33	+0.31	-2.02	-4.24	-2.71	1.53
Poly(2)	+0.64/0.52	+0.74	-2.05	-5.39	-2.9	2.49

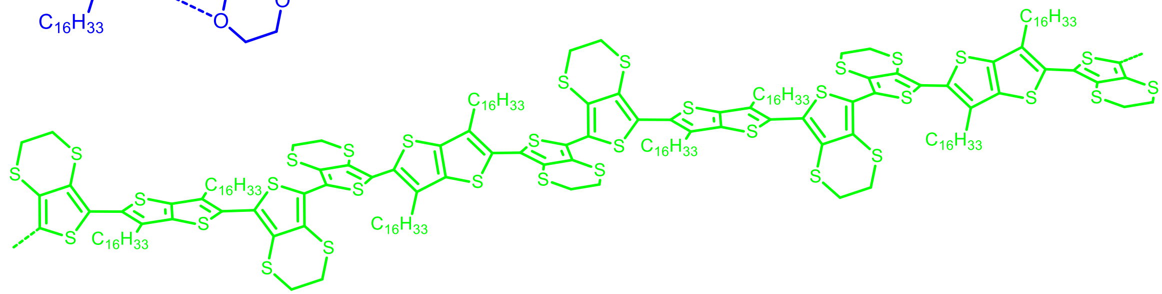


Poly(1)

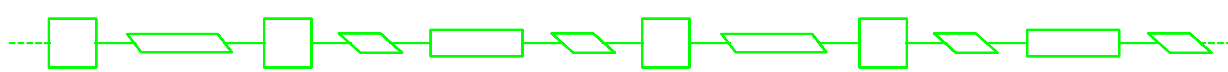




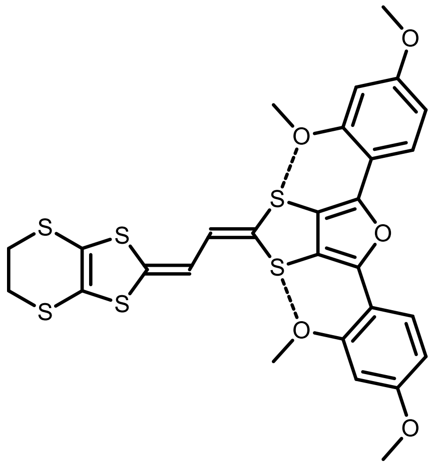
Poly(2)



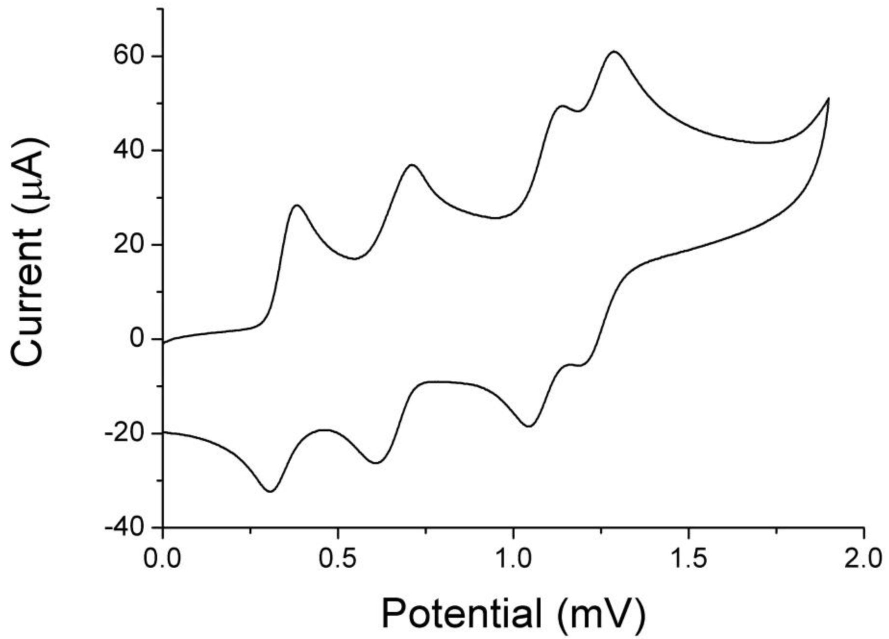
Chem. Mater., 2010, 22, 3000-3008

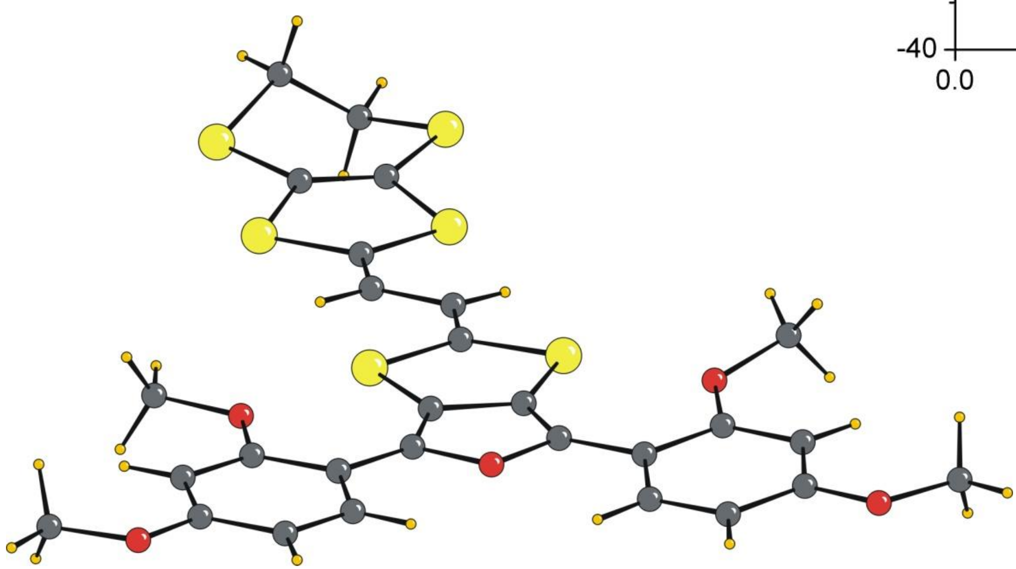


2. Enhanced stability of intermediate charged states



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



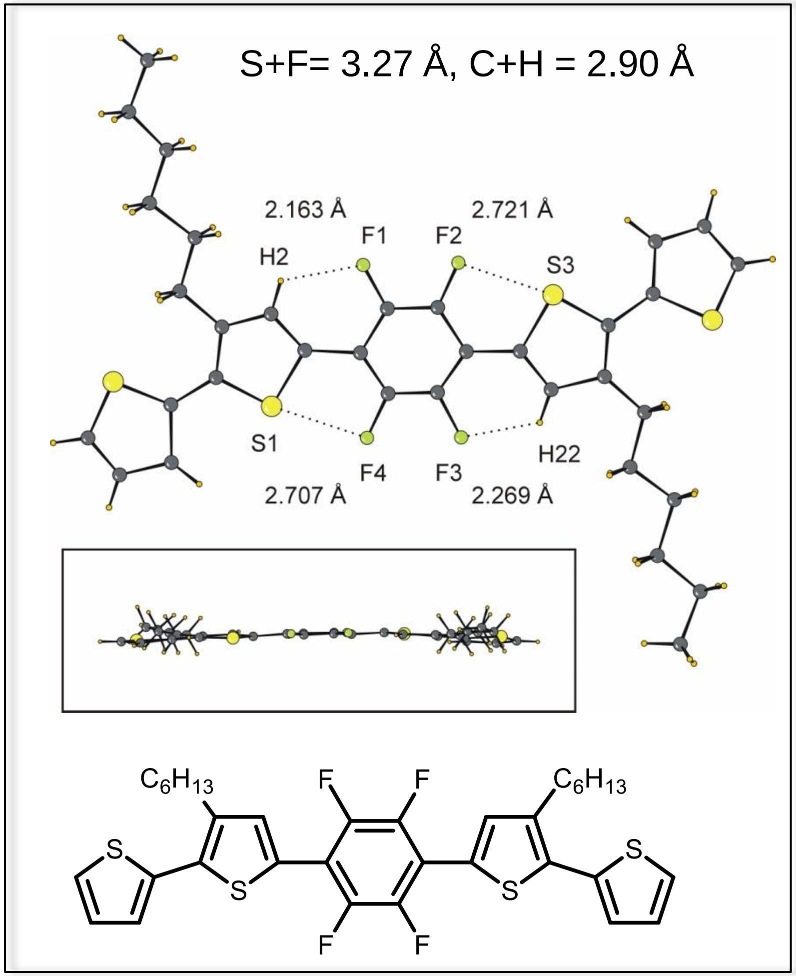


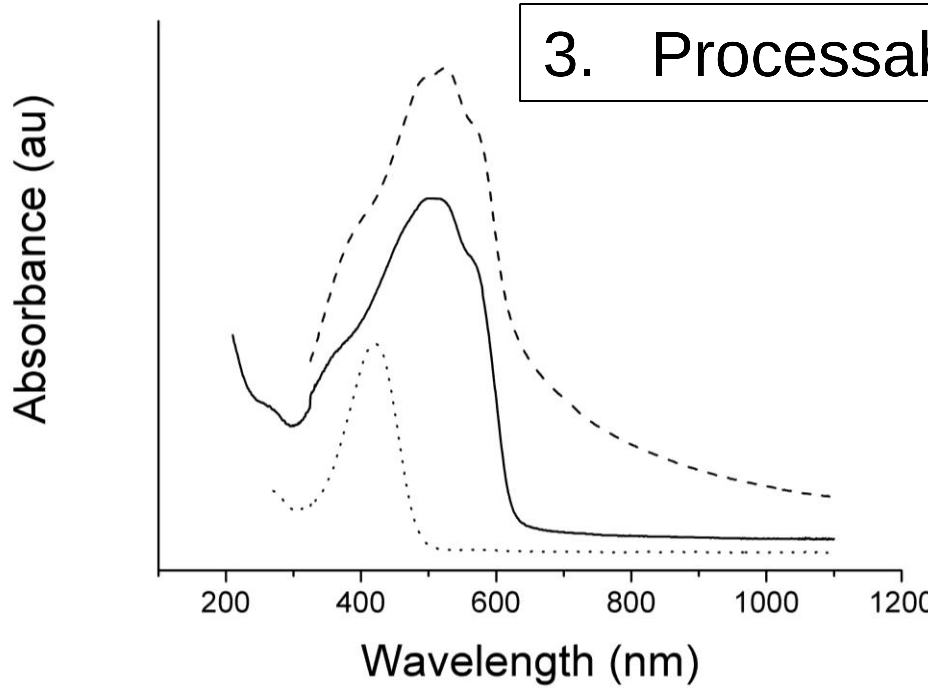
Tetrahedron Lett., 2004, **45**, 2535

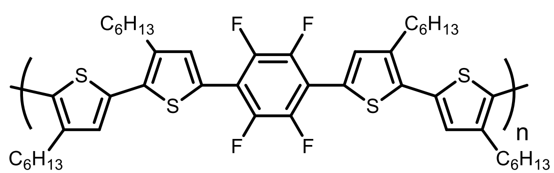
See also:

Chem. Soc. Rev., 2005, **34**, 69.

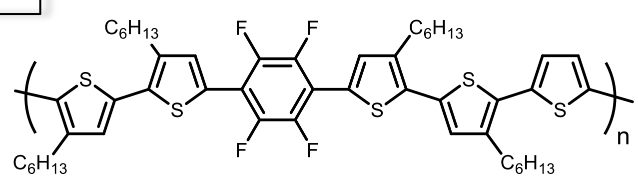
3. Processability







Dashed line
Electropolymerised
Solid state



Solid line – solid state
Dotted line – solution state

Mn = 10,500 (70 aryl units)

Excellent solubility

λ_{max} (solution) = 420 nm

λ_{max} (film) = 566 nm

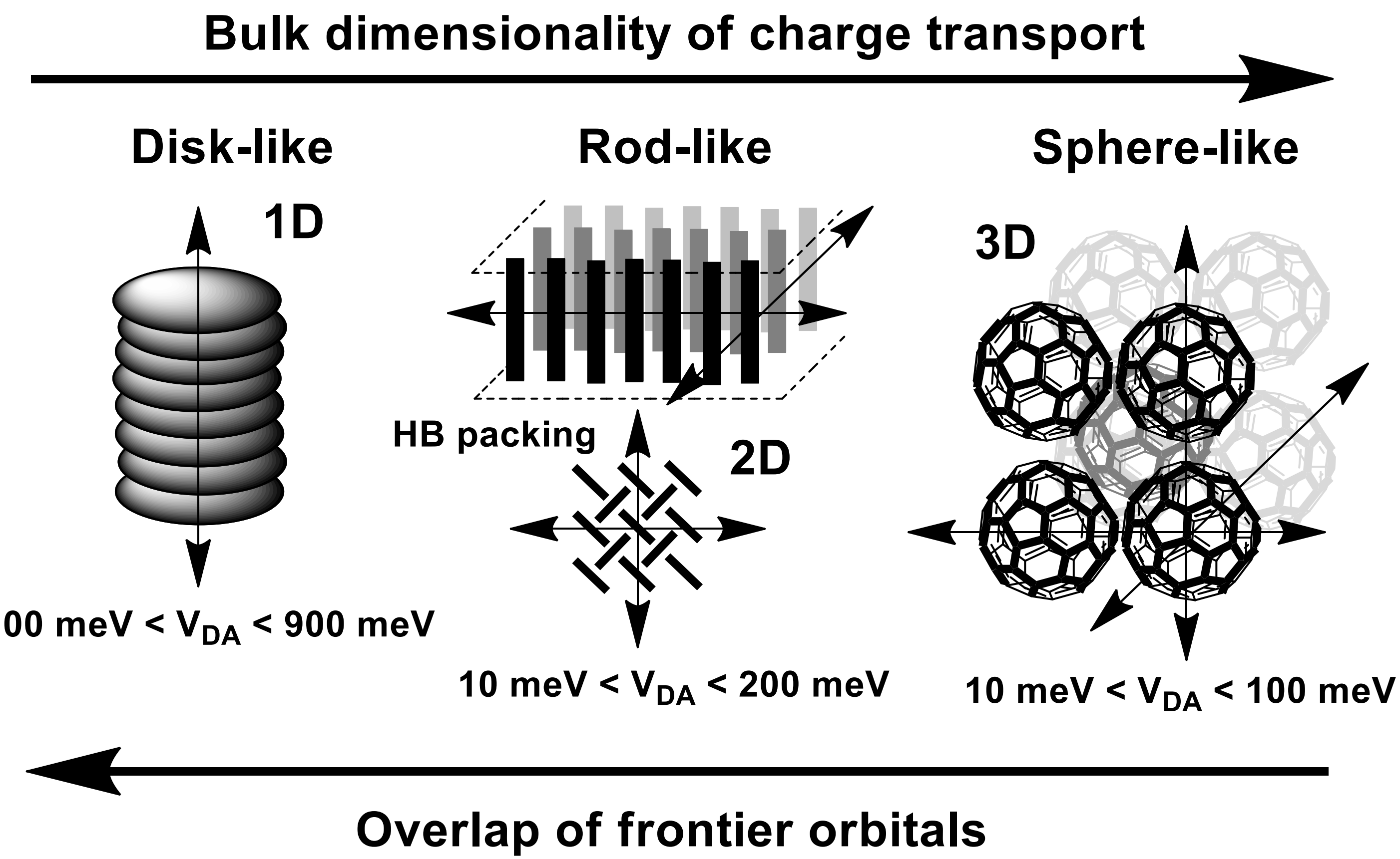
Mobility = 1 x 10^{-3} cm^2/Vs

On/off ratio $10^4 – 10^5$ Turn on voltage 2 V

Chem. Commun., 2005, 1465.

Chem. Mater., 2005, 17, 6567.

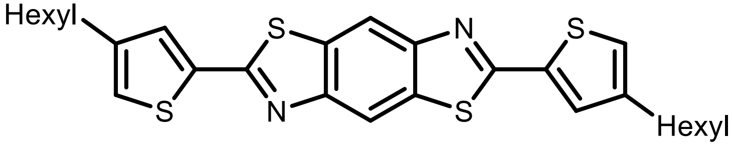
Charge transport in single molecule systems

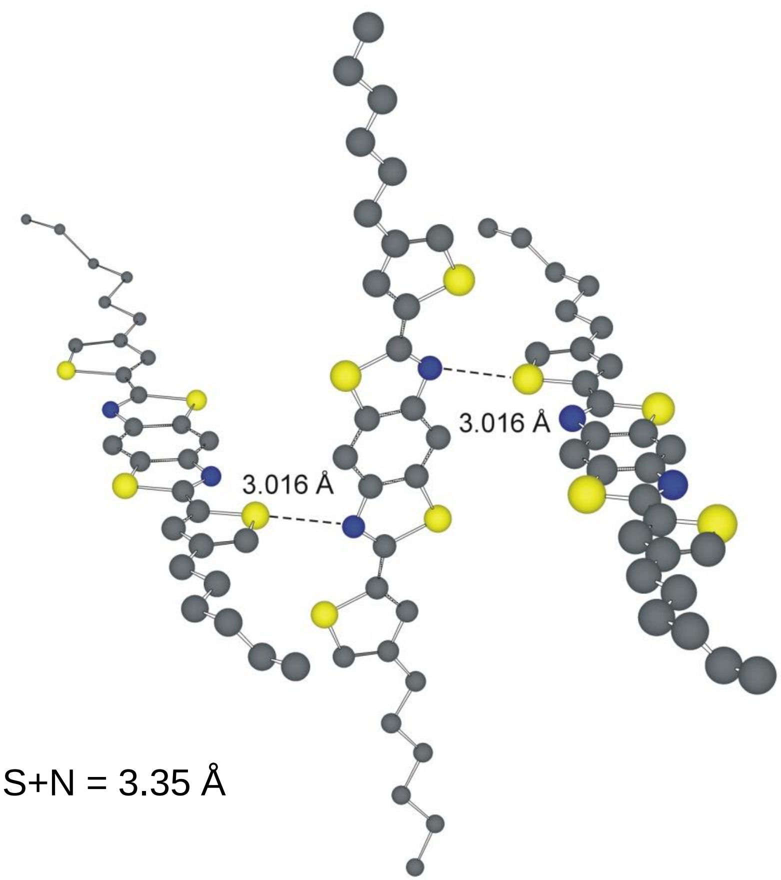


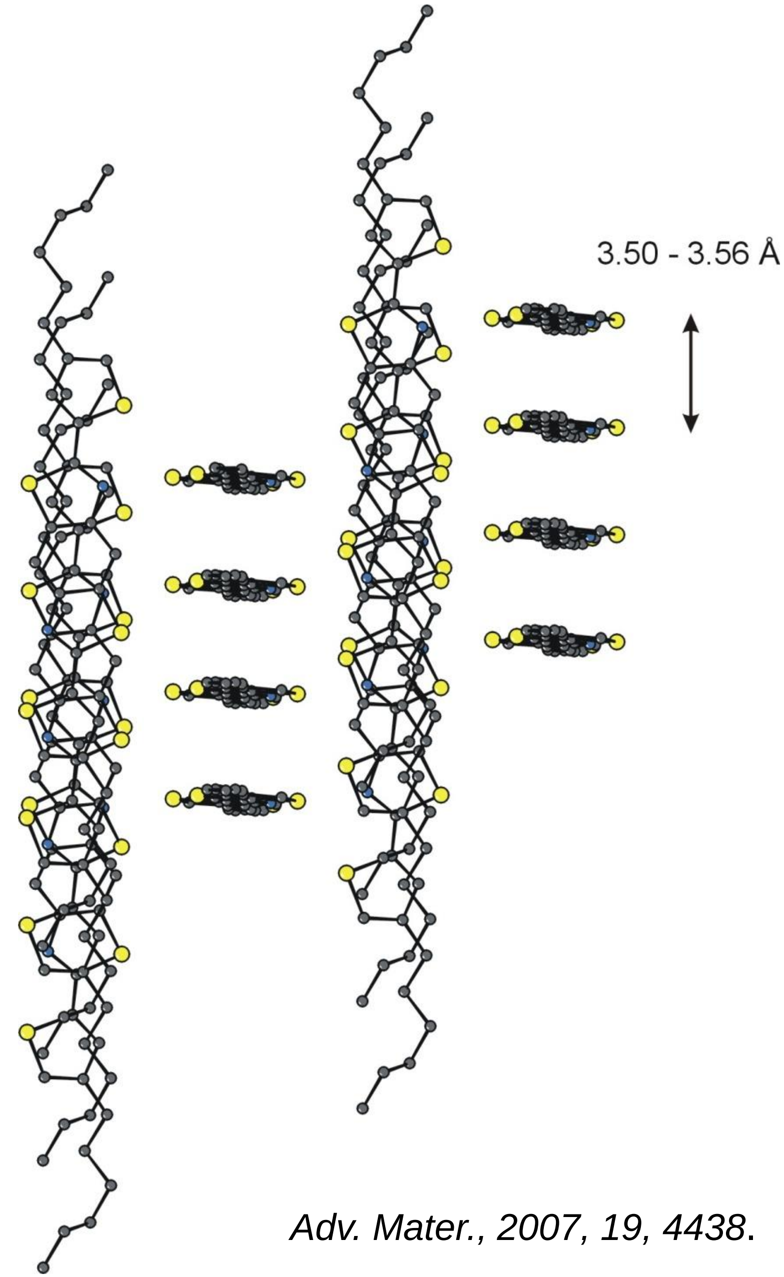
Schematic drawing of 1D, 2D, and 3D charge carrier materials with indicative values of transfer integrals. Values of transfer integrals, V_{DA}, should be considered as orders of magnitudes.

See: *Close Encounters of the 3D Kind – Exploiting High Dimensionality in Molecular Semiconductors*, Skabara, Arlin, Geerts, *Adv. Mater.*, 2013, **25**, 1948-1954.

4. Efficient orbital overlap in the bulk in 2 or 3 dimensions

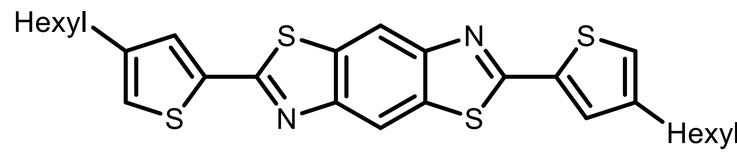




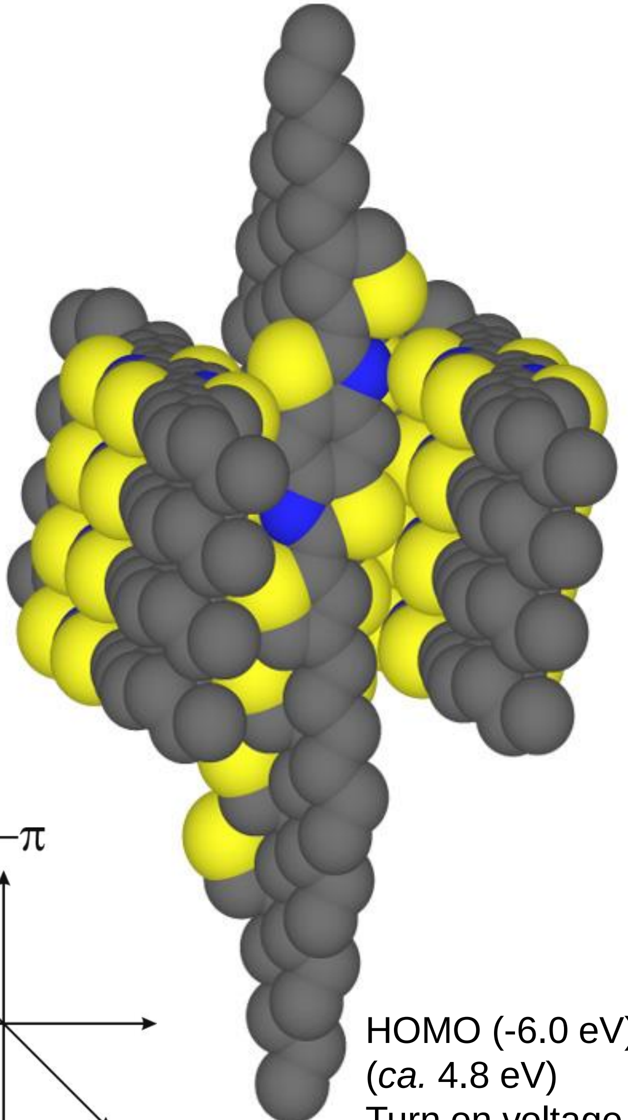


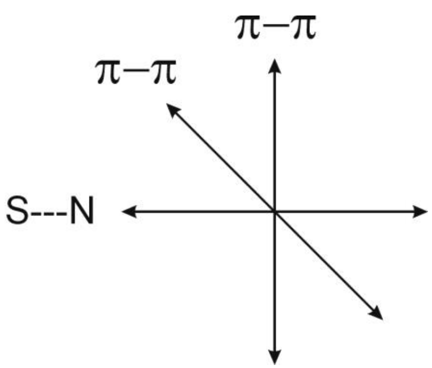
S+N = 3.35 Å

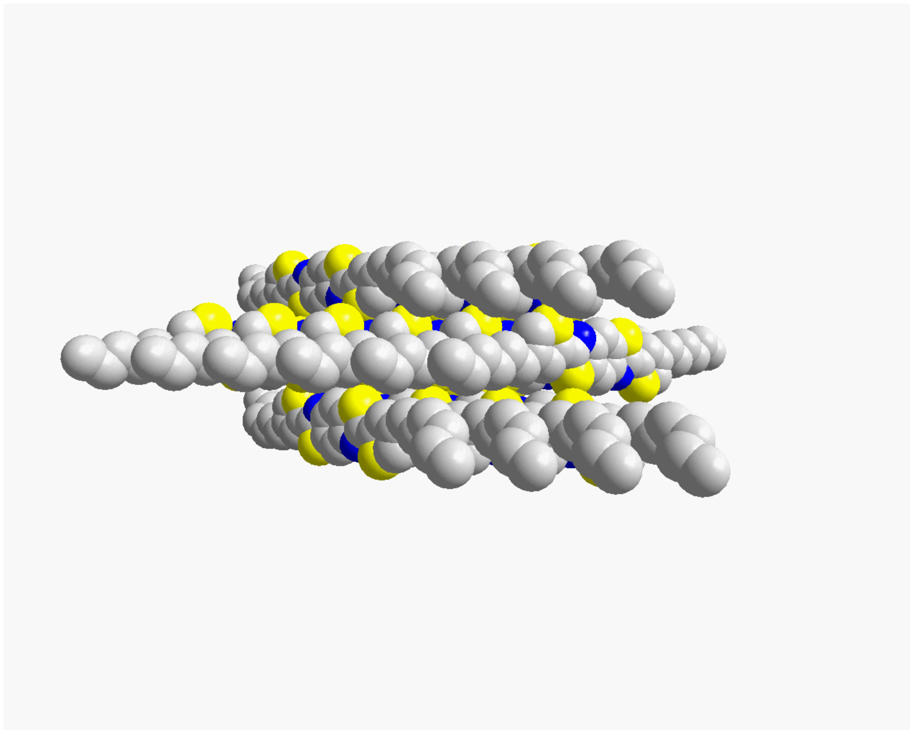
Adv. Mater., 2007, 19, 4438.



HOMO = -6.0 eV
LUMO = -2.7 eV







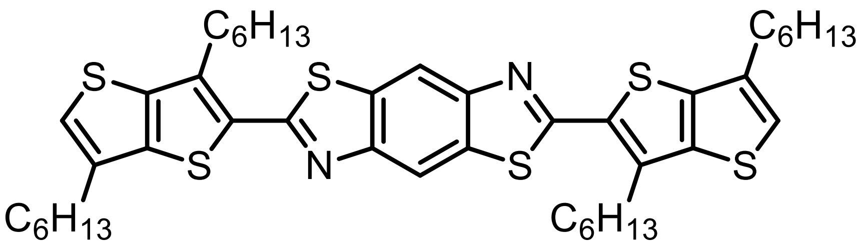
HOMO (-6.0 eV) appears to be far away from the Fermi level of Au (*ca.* 4.8 eV)

Turn on voltage -20 V

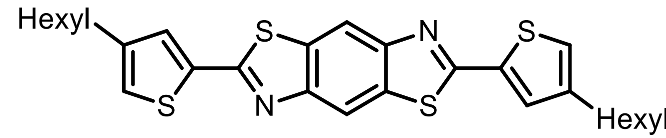
On/off ratio 10^5

Hole mobilities are approximately 0.01 cm^2/Vs (bottom gate, bottom contact)

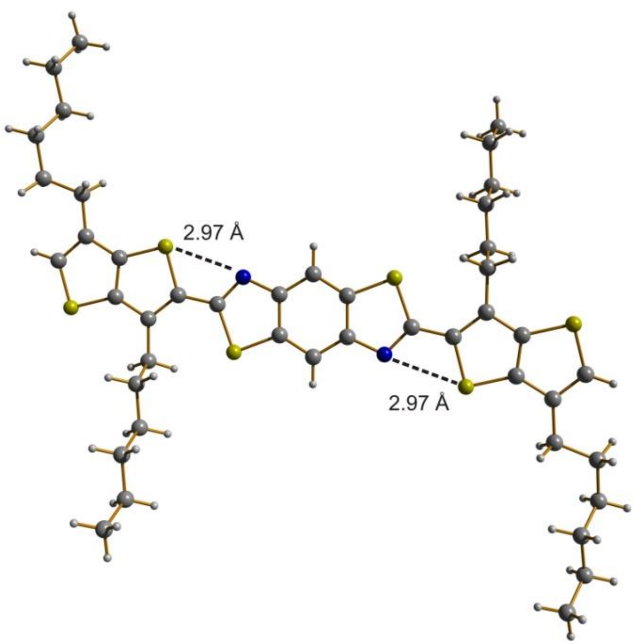
Adv. Mater., 2007, 19, 4438.



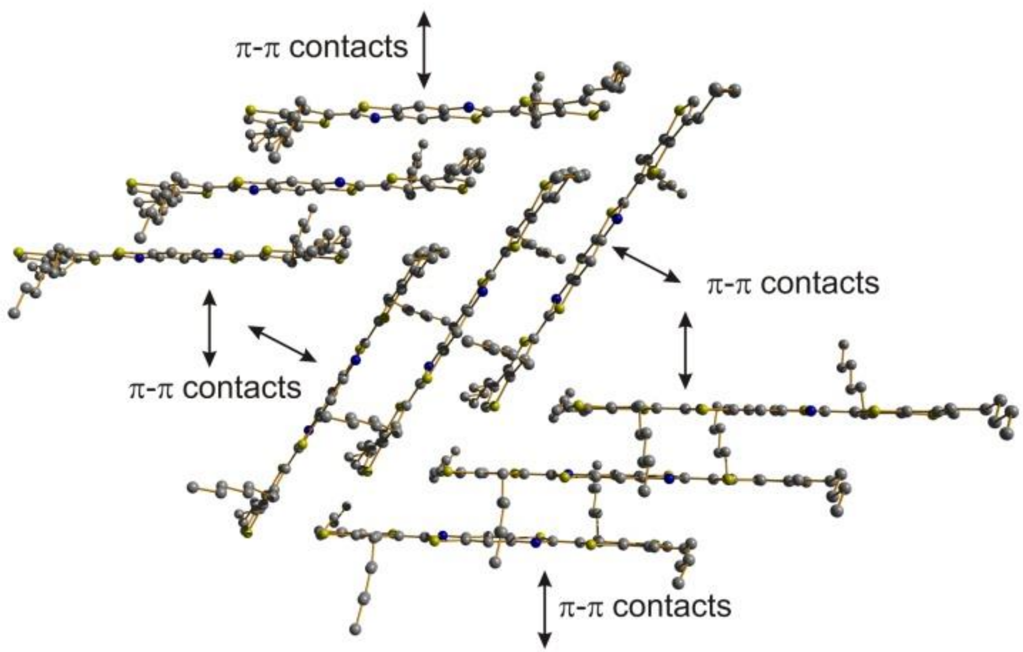
HOMO = -5.7 eV
LUMO = -2.9 eV



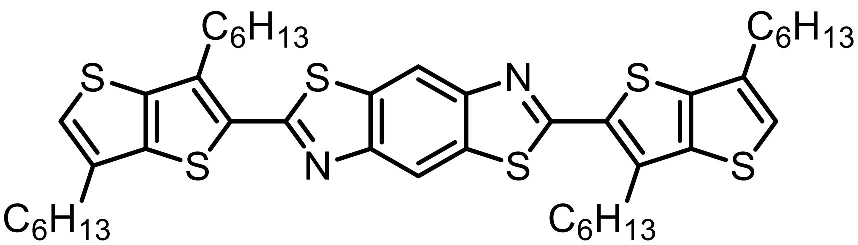
HOMO = -6.0 eV
LUMO = -2.7 eV



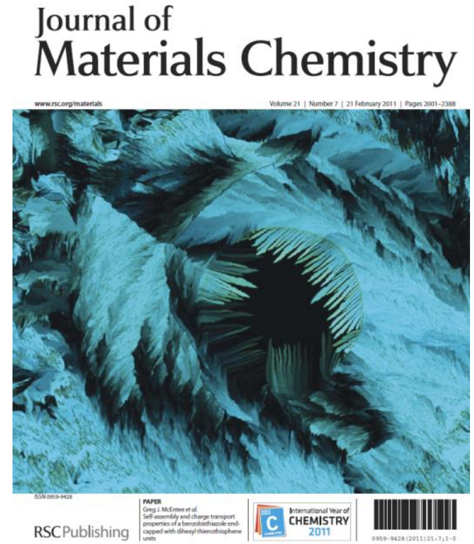
S+N = 3.35 Å

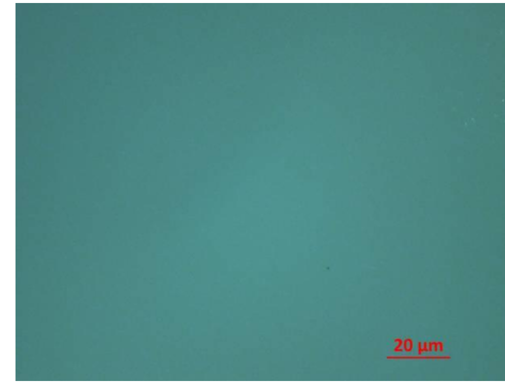


π–π = 3.52 Å

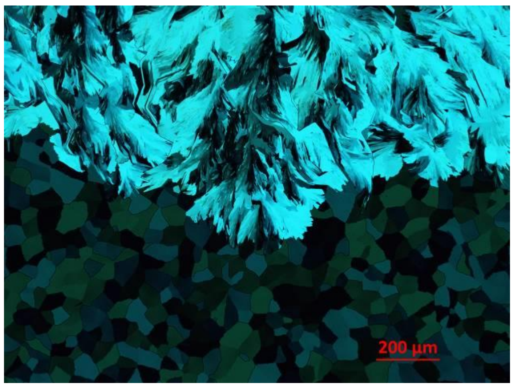


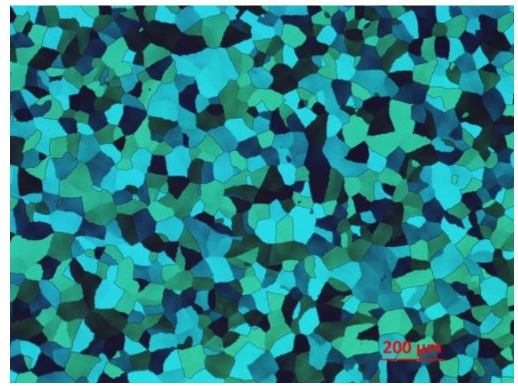
J. Mater. Chem., 2011, 21, 2091

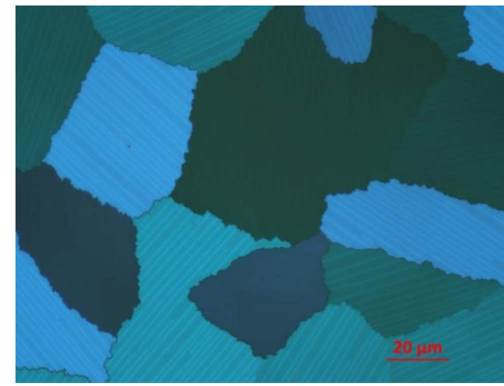




Before annealing
(50× magnification)



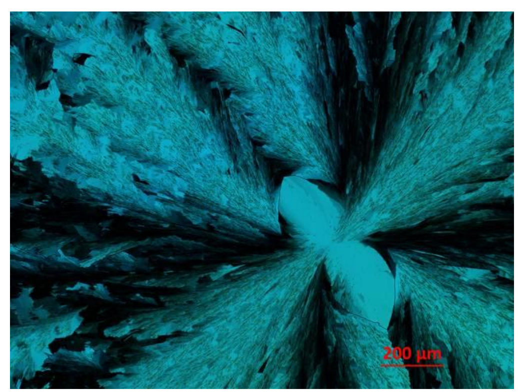


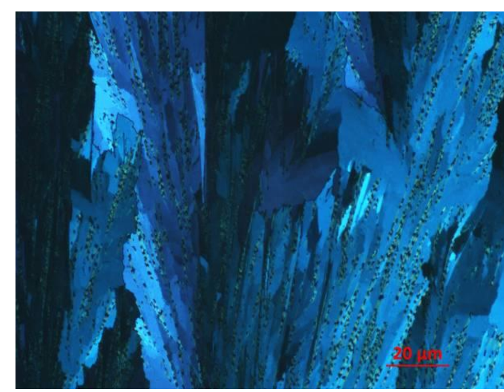


After annealing for 16 hours at 80˚C Phase 1 (crystal B) above, Phase 2 (crystal E) below

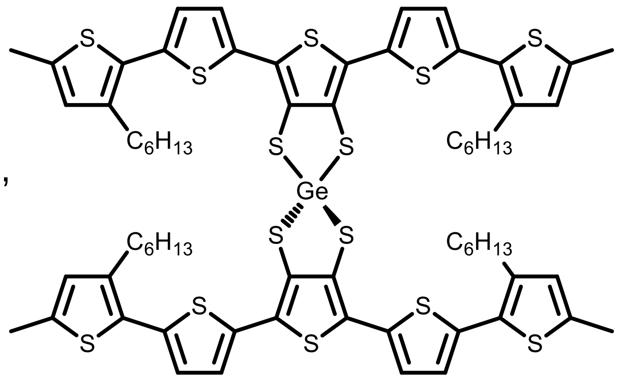
After annealing for a further 2 hours at 100˚C only Phase 2 persists.

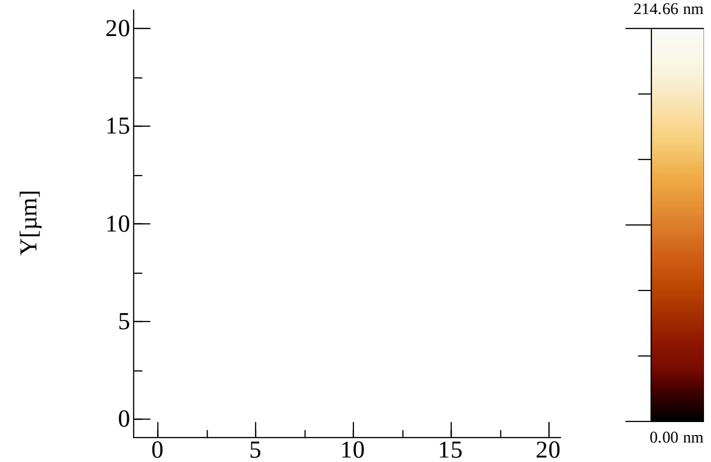
Hole mobilities of 3 x 10^{-3} cm^2 V^{-1} s^{-1}
after annealing at 70˚C for 15 hours
Bottom contact, top gate device
On/off ratio of 10^4 - 10^5
(slight drop in Phase 2 OFETs)

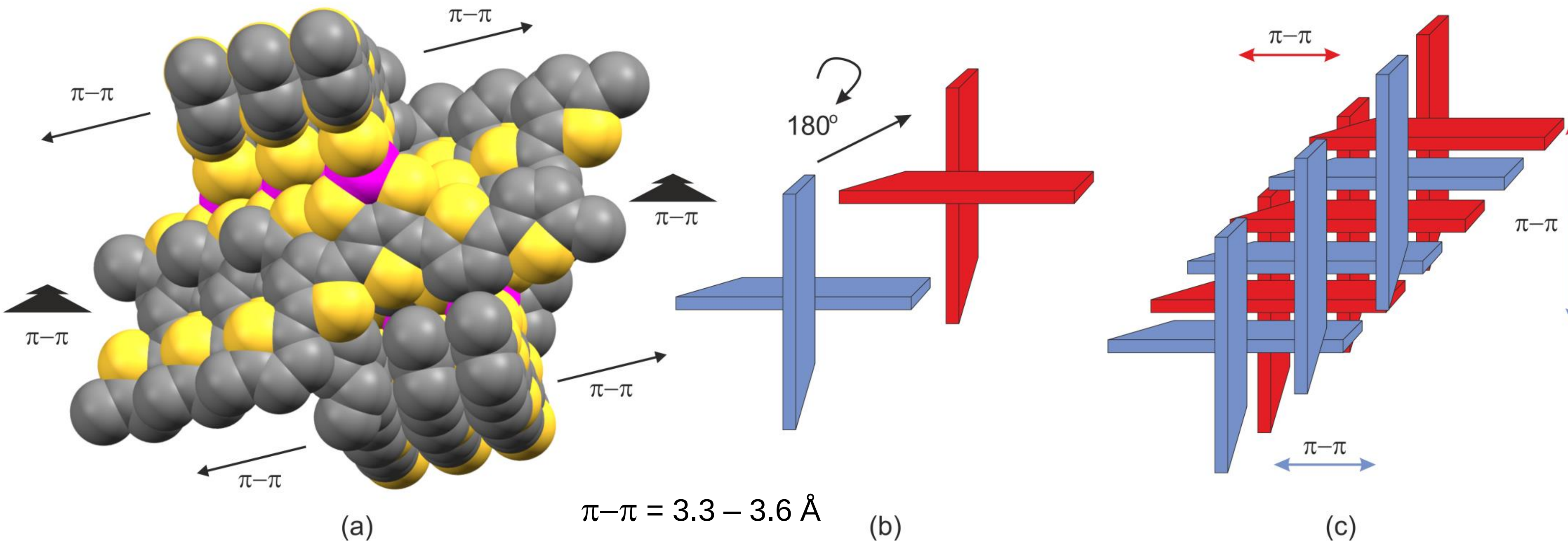




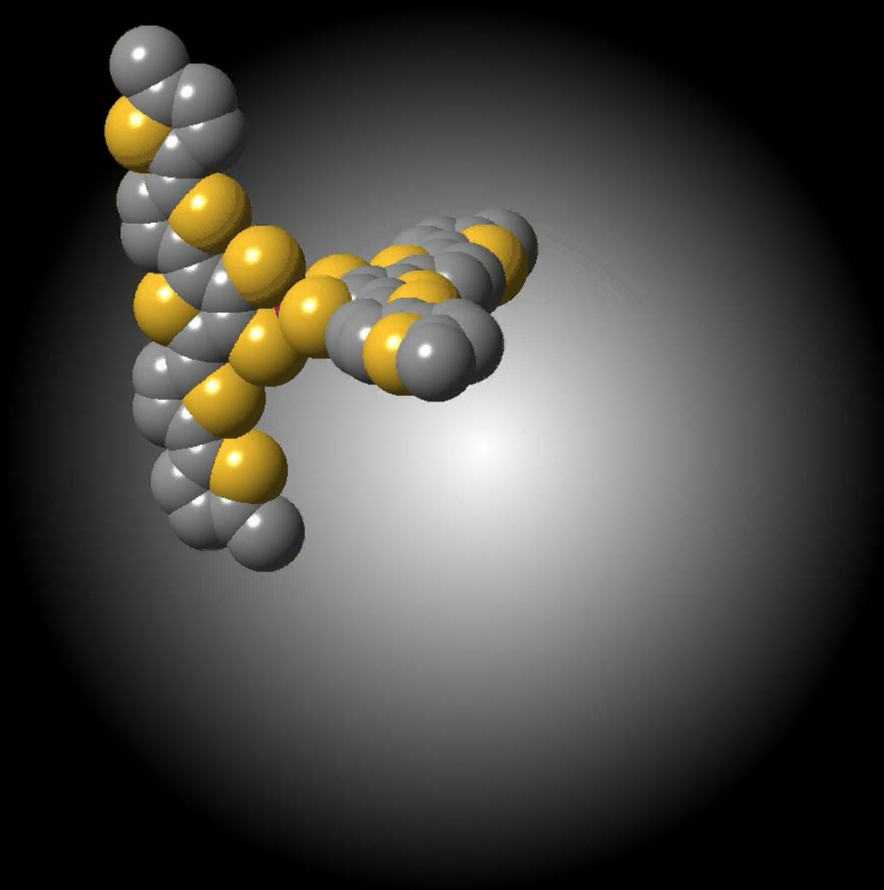
Angew. Chemie. Int. Ed., 2012, **51**, 4562

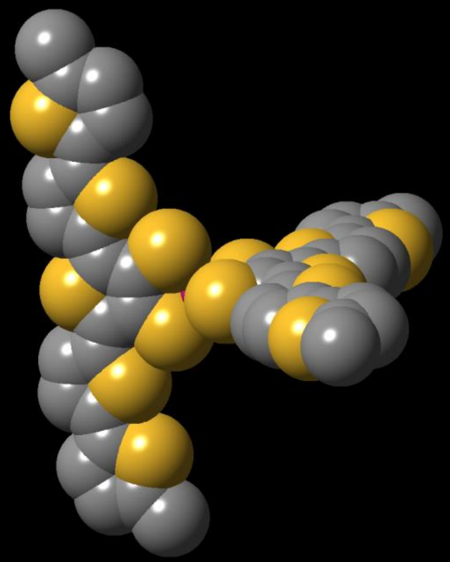


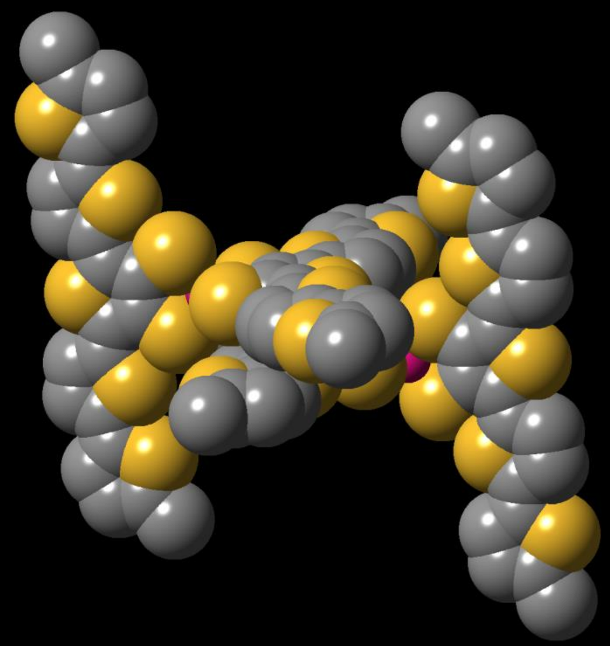


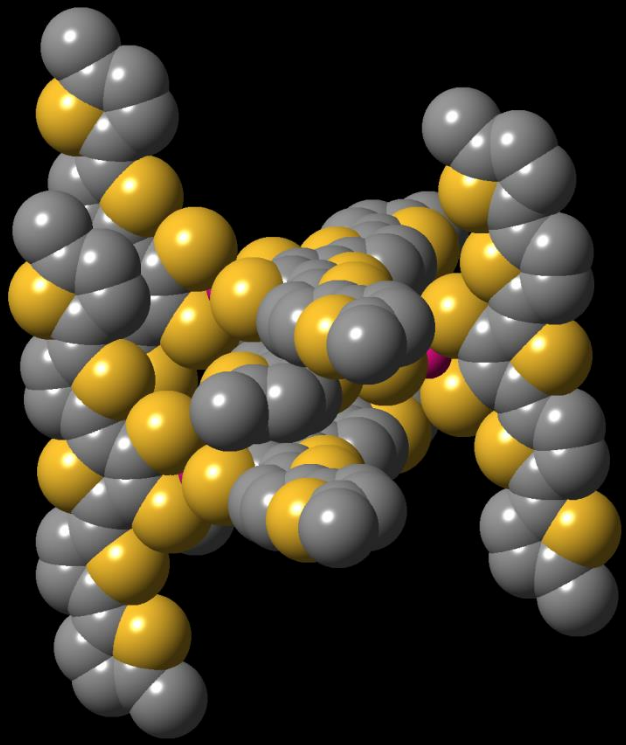


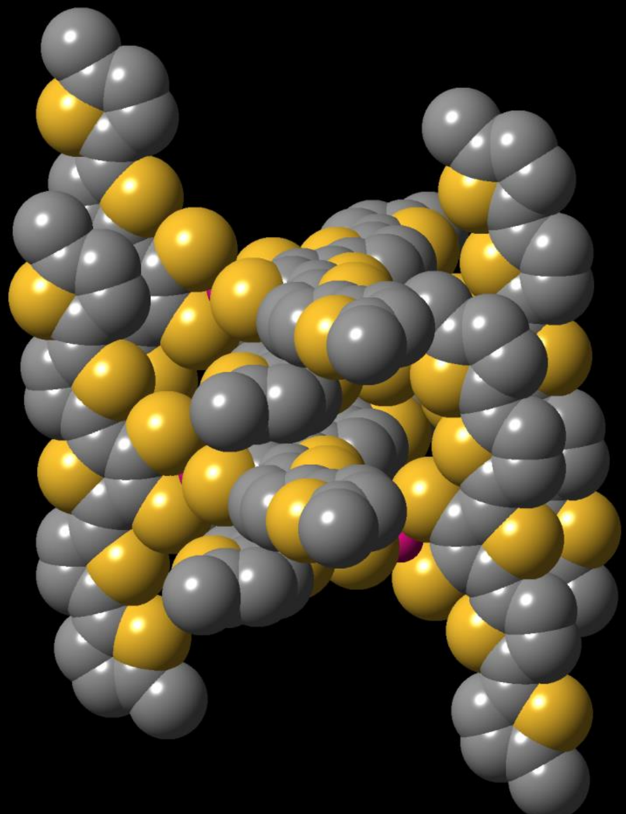
Self-assembly of cruciform 5T derivative: (a) packing structure derived from X-ray crystallography, showing π-stacking into and along the plane of the page (alkyl chains omitted; Ge atom coloured purple); (b) two orientations of the cruciform; (c) how these orientations interdigitate between horizontal chains to give a tightly packed structure with infinite π-stacks in two orthogonal directions.

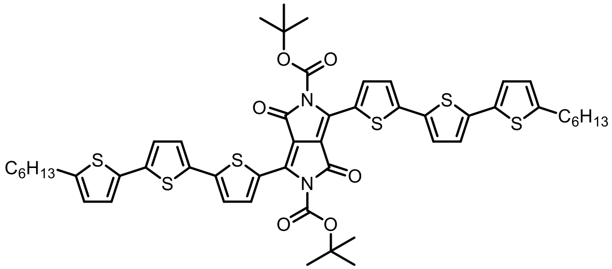






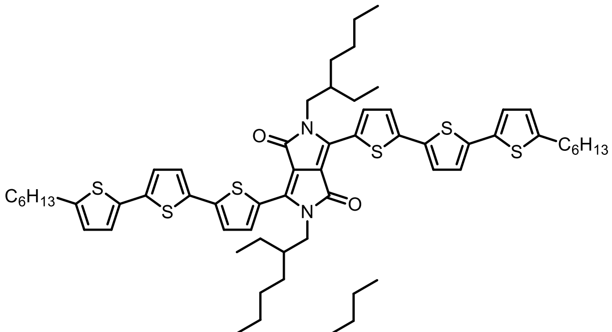






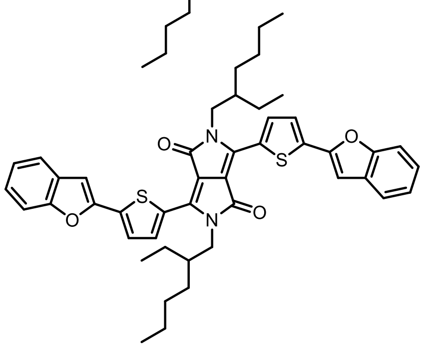
Nguyen et al., J. Phys. Chem. C, 2008, 112, 11545
2.3%

HOMO-LUMO gap 1.5 eV



Appl. Phys. Lett., 2009, 94, 103301
3.0%

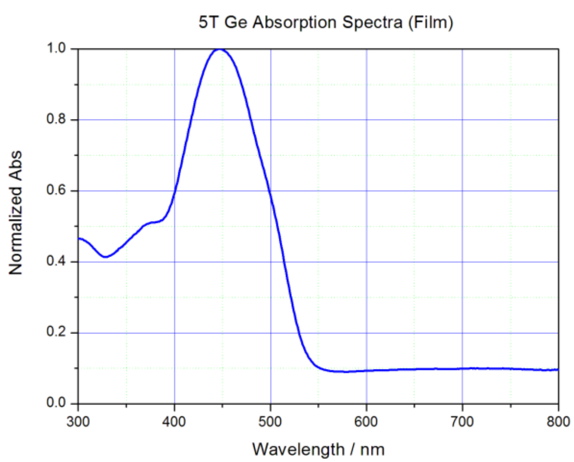
HOMO-LUMO gap 1.5 eV



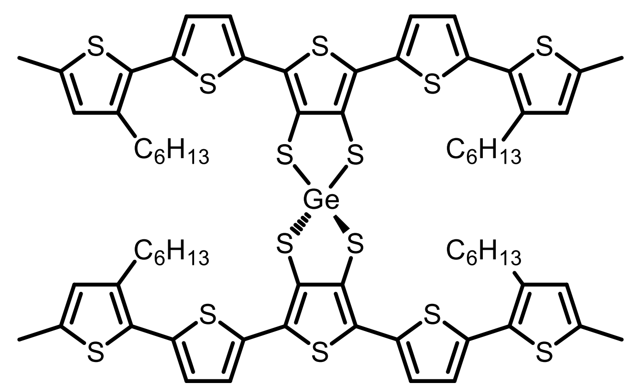
Adv. Funct. Mater., 2009, 19, 3063
4.5%

Adv. Energy Mater., 2011, 1, 610
5.2%

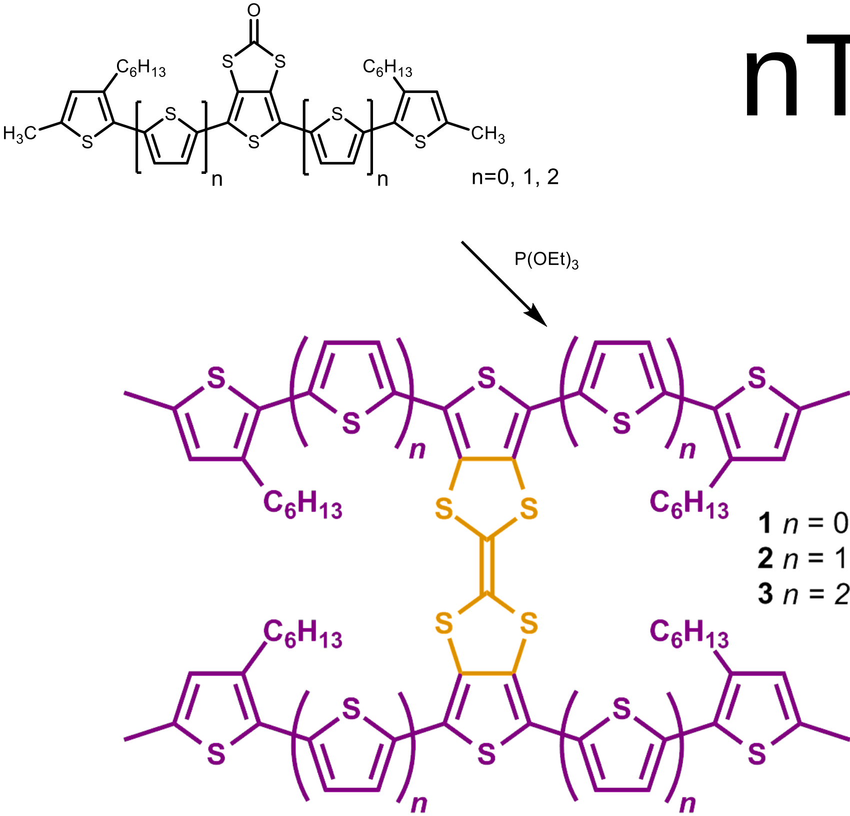
HOMO-LUMO gap 1.8 eV



J_{SC} = 9.57 mA cm^{-2}
V_{OC} = 0.63 V
FF = 0.37
PCE = 2.26%
E_g = 2.3 eV

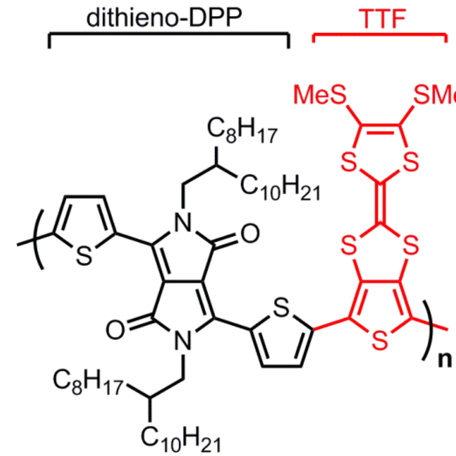


nT-TTF



1 *n* = 0
2 *n* = 1
3 *n* = 2

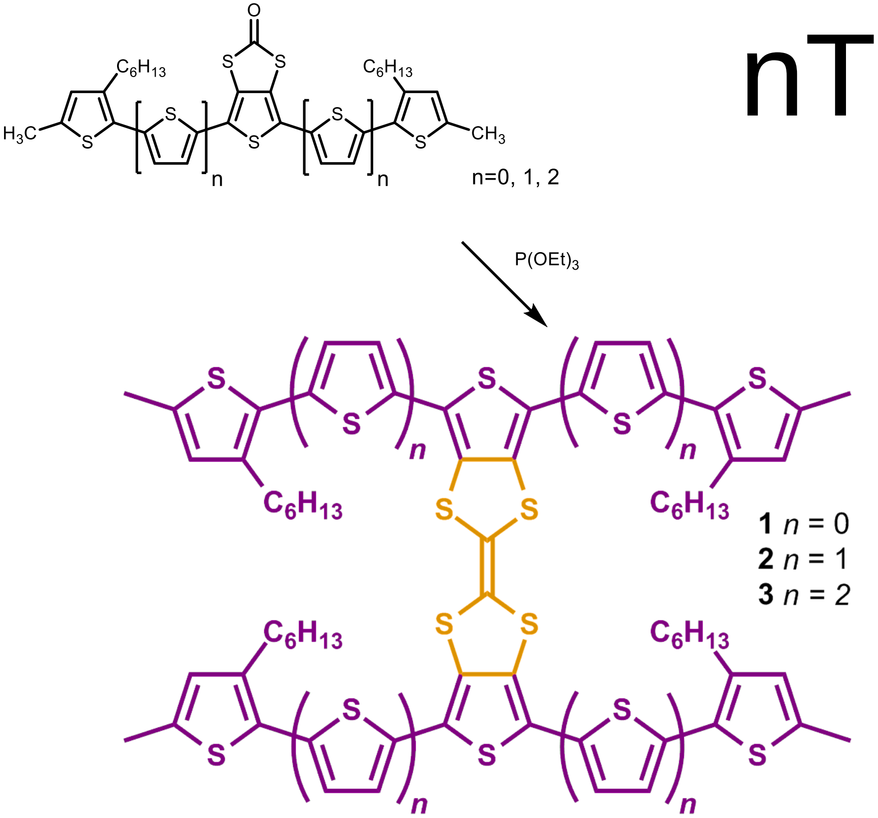
J. Mater. Chem. C, 2014, **2**, 2674

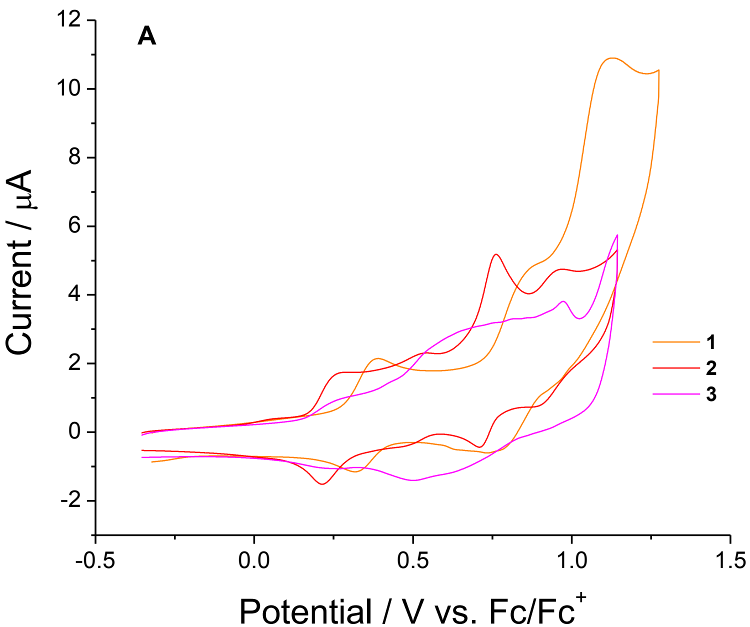


$\mu_h = 4 \pm 2 \times 10^{-2}\ cm^2\ V^{-1}\ s^{-1}$
air stable devices c.f. non-TTF analogue
J. Mater. Chem. 2012, **22**, 11310.

	1	2	3
λ_{max} (nm)	351	431	461
HOMO-LUMO gap (eV)	2.92	2.45	2.20
E_{1ox} (V)	+0.39/+0.32	+0.27/+0.21	+0.26/+0.23
E_{2ox} (V)	+0.86/+0.75	+0.54/+0.48[q]	+0.66/+0.49[q]
E_{3ox} (V)	+1.13/+1.02[q]	+0.76/+0.71[q]	+0.97/+0.94[q]
E_{4ox} (V)	-	+0.97/+0.89[q]	-
E_{red} (V)	-2.12[irr]	-2.19[irr]	-1.98[irr]
HOMO (eV)[a]	-5.06	-4.96	-4.95
LUMO (eV)[a]	-2.92	-2.81	-3.00
HOMO-LUMO gap (eV)[b]	2.14	2.15	1.95

nT-TTF





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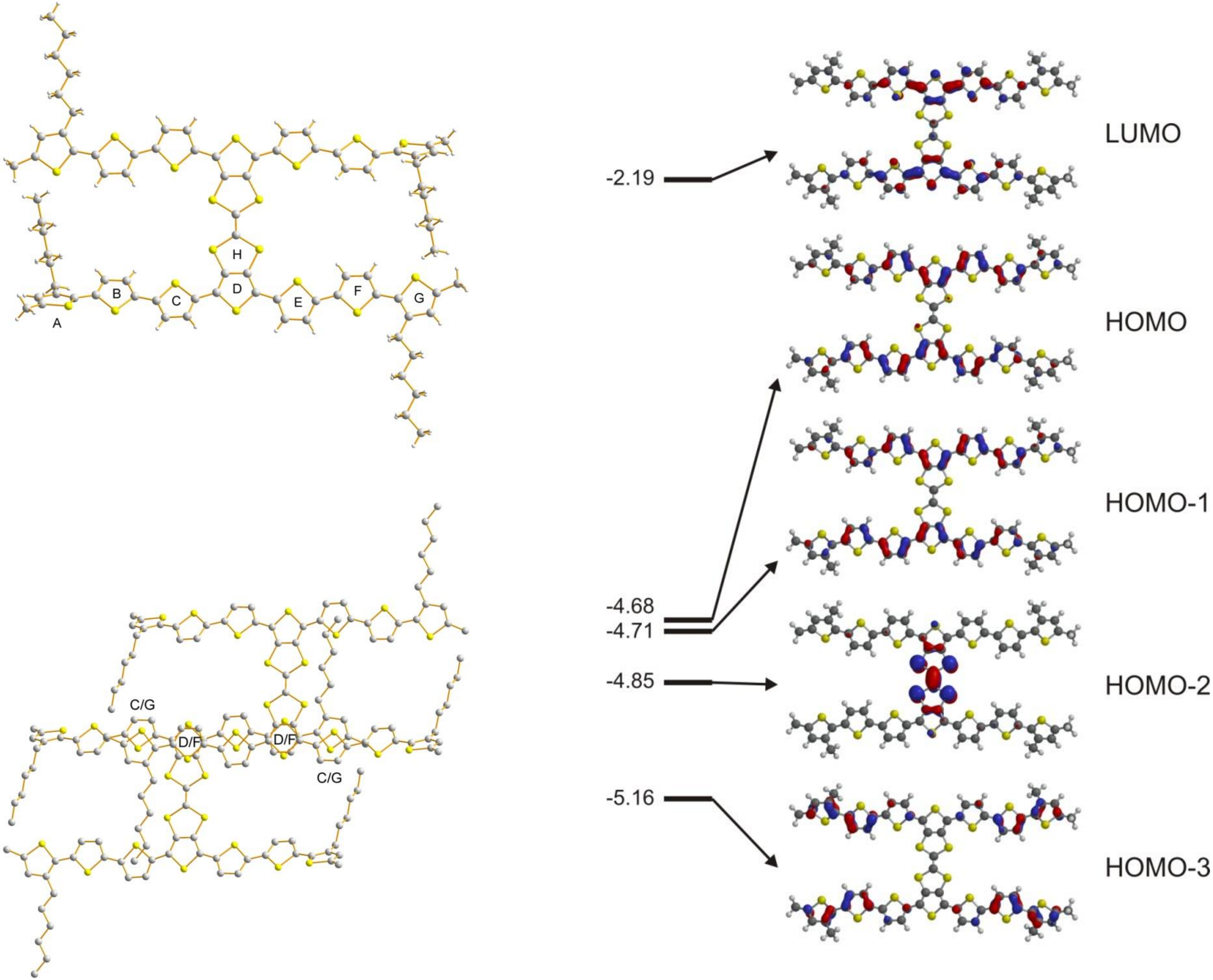
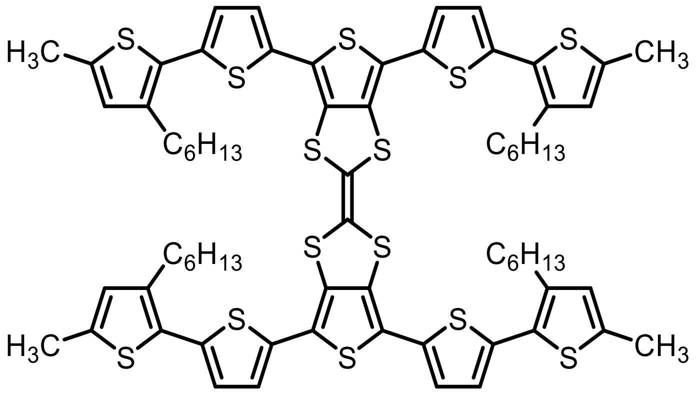
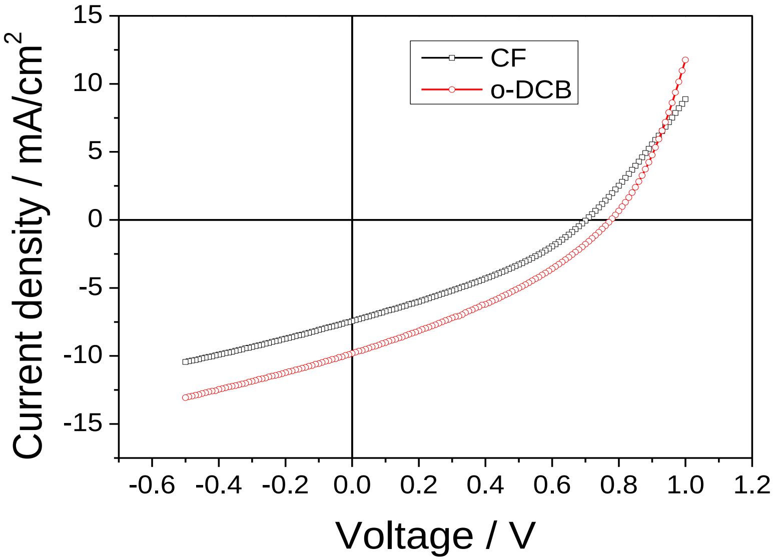
	1	2	3
λ_{max} (nm)	351	431	461
HOMO-LUMO gap (eV)	2.92	2.45	2.20
E_{1ox} (V)	+0.39/+0.32	+0.27/+0.21	+0.26/+0.23
E_{2ox} (V)	+0.86/+0.75	+0.54/+0.48[q]	+0.66/+0.49[q]
E_{3ox} (V)	+1.13/+1.02[q]	+0.76/+0.71[q]	+0.97/+0.94[q]
E_{4ox} (V)	-	+0.97/+0.89[q]	-
E_{red} (V)	-2.12[irr]	-2.19[irr]	-1.98[irr]
HOMO (eV)[a]	-5.06	-4.96	-4.95
LUMO (eV)[a]	-2.92	-2.81	-3.00
HOMO-LUMO gap (eV)[b]	2.14	2.15	1.95


H
B
C
D
E
F
G
A
C/G
D/F
D/F
C/G
-2.19
-4.68
-4.71
-4.85
-5.16
LUMO
HOMO
HOMO-1
HOMO-2
HOMO-3

5T-TTF



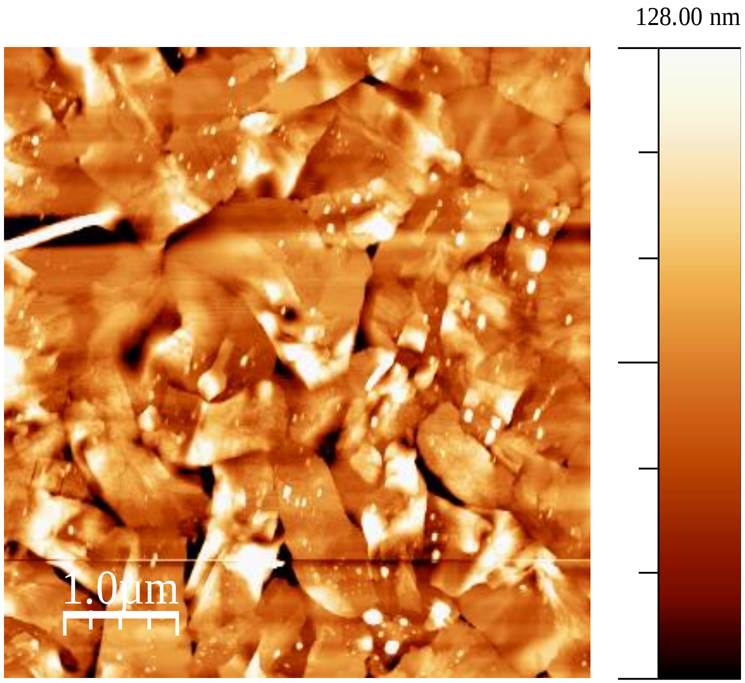
Eg = 2.45 eV



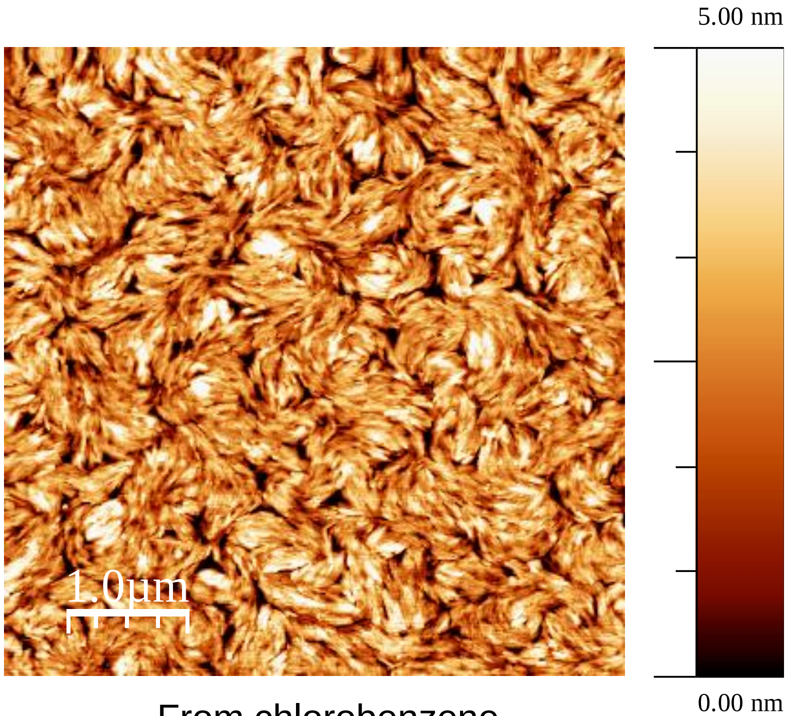
I/V curves of glass/ITO/PEDOT-PSS/**5T-TTF**: $PC_{71}BM$ (1:4)/Ca/Al configured photovoltaic cell

	Isc	Voc	FF	PCE (%)
From *o*-dichlorobenzene	9.81	0.78	0.33	2.5
From chloroform	7.44	0.70	0.33	1.7

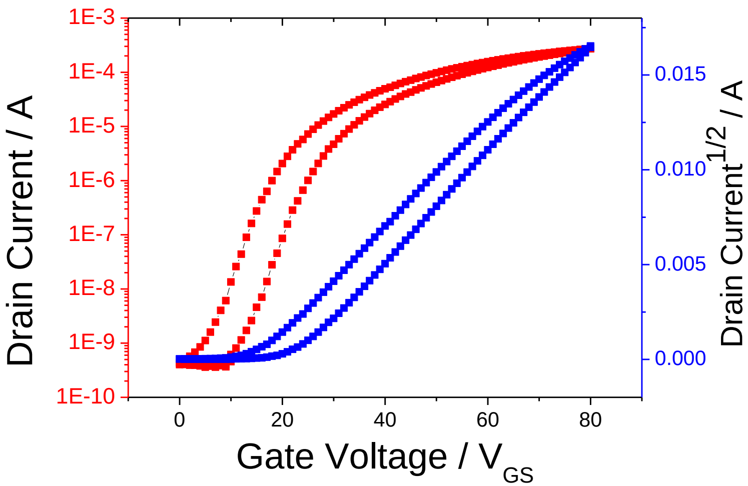
5T-TTF



From chloroform

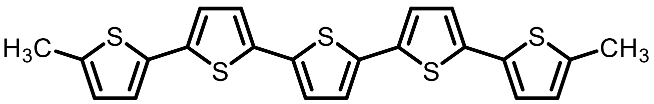


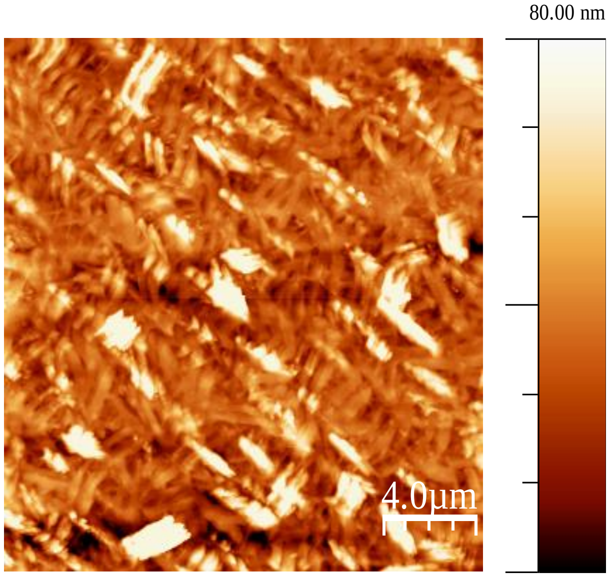
From chlorobenzene

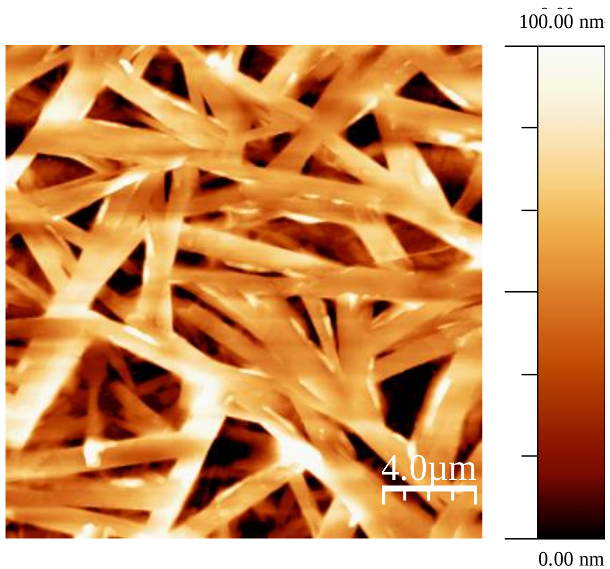


Hole mobility = 8.6 x 10^{-3} cm^2/Vs (OFET)
(TOF gave 1 x 10^{-5} cm^2/Vs)

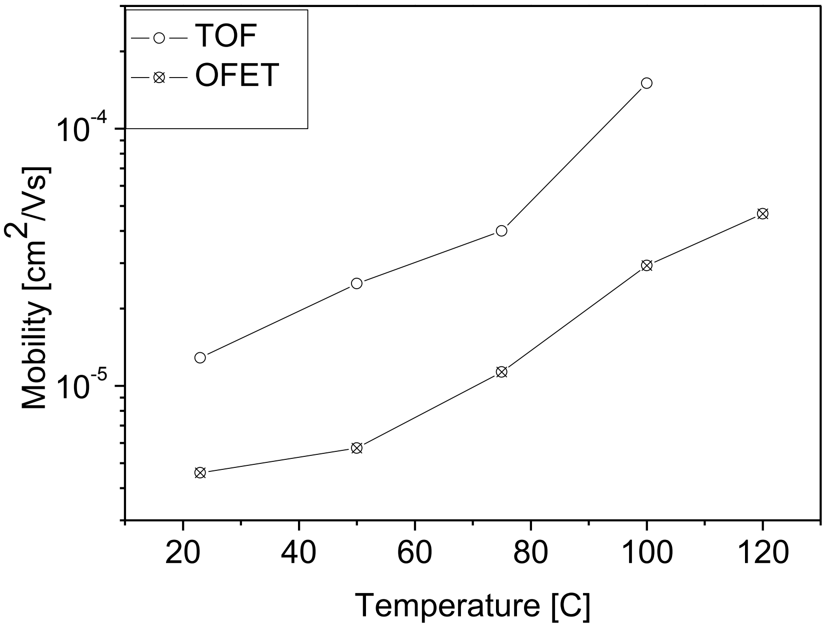
cf. hole mobility for end-capped quinquithiophene = 9 x 10^{-4} cm^2/Vs



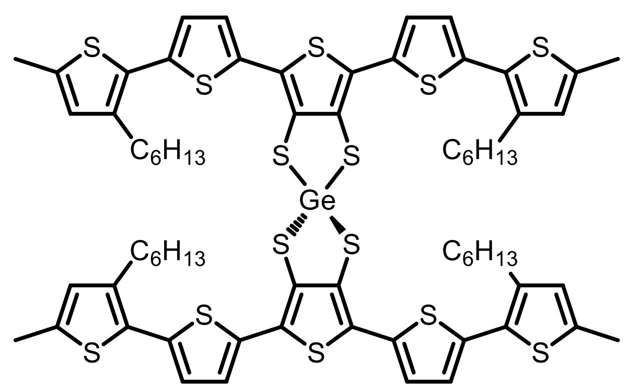




Tapping mode AFM images of **Ge-cruciform**: (top) annealed at 120 °C for 20 minutes after subsequent annealing at 50, 75, 100 for 20 minutes; (bottom) annealing straight to 120 °C for 20 minutes.



Temperature dependent mobility of step-annealed **Ge-cruciform** measured by time of flight and organic field effect transistor methods.



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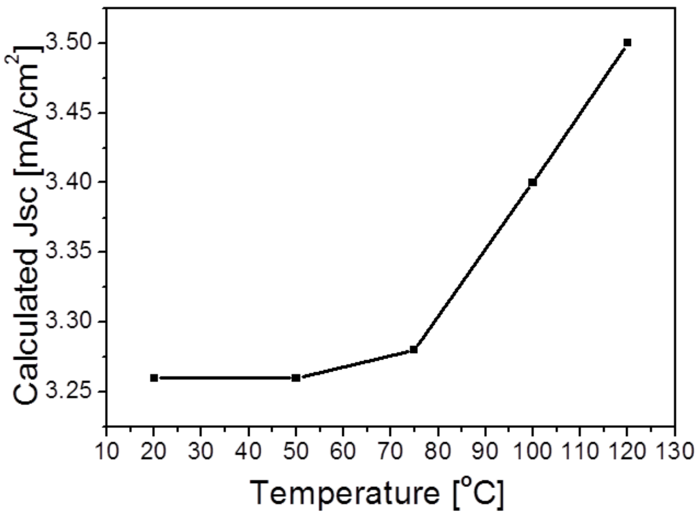
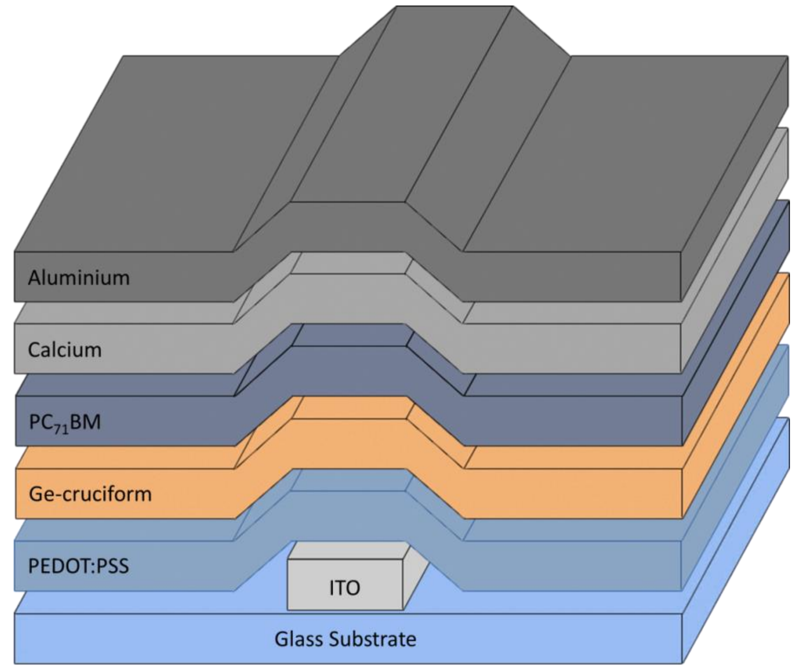
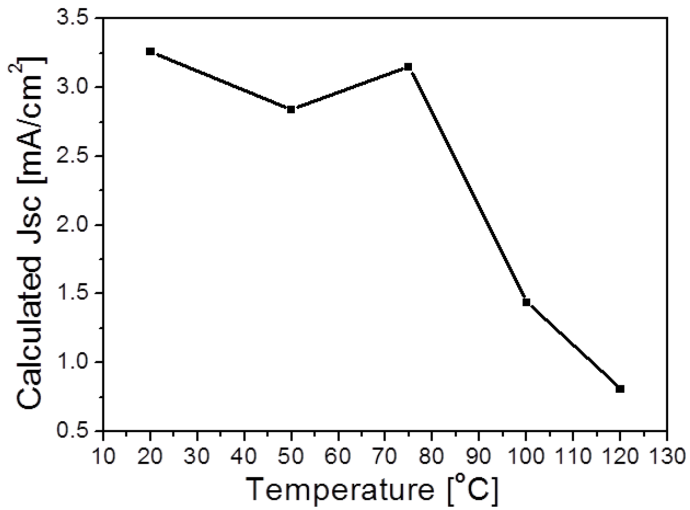




Device structure of a planar heterojunction used to determine the effect of annealing on short circuit current density.



Short-circuit current calculated for a single device measured at RT, then step-annealed at 50, 75, 100 and 120 °C with measurements taken between each temperature step of 20 minutes (top) and several individual devices annealed straight to a given temperature for 20 minutes (bottom).