Electronic supplementary information (ESI)

Synthesis and characterization of β,β'-dimethylated dithieno[3,2-b:2',3'-d]pyrroles and their corresponding regioregular conducting electropolymers†

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1. Single crystal X-ray structure analysis of Me-DTP 5

Table S1 Crystallographic data of Me-DTP **5** (CCDC number: 2070707)

Bond precision:	C-C = 0.0025 Å	Wavelength=1.54184

Cell: a=14.1113(3) b=14.1996(3) c=6.88839(13)
alpha=90   beta=90   gamma=90

Temperature: 150 K

	Calculated	Reported
Volume	1380.26(5)	1380.26(4)
Space group	P n m a	P n m a
Hall group	-P 2ac 2n	-P 2ac 2n
Moiety formula	C16 H13 N S2	C16 H13 N S2
Sum formula	C16 H13 N S2	C16 H13 N S2
Mr	283.39	283.39
Dx,g cm-3	1.364	1.364
Z	4	4
Mu (mm-1)	3.350	3.350
F000	592.0	592.0
F000'	595.89	
h,k,lmax	17,17,8	17,17,8
Nref	1469	1461
Tmin,Tmax	0.547,0.718	0.788,1.000
Tmin'	0.404	

Correction method= # Reported T Limits: Tmin=0.788 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.995   Theta(max)= 74.038
R(reflections)= 0.0312(1298)   wR2(reflections)= 0.0866(1461)
S = 1.049   Npar= 98

Table S2: Relevant bond length distances in the X-Ray structure analysis of Me-DTP **5**.

Atom1	Atom2	Bond length (Å)
C12	C5	1.359(2)
C5	C9	1.429(2)
C9	C3	1.388(2)
C3	C3	1.418(2)
S1	C12	1.734(2)
S1	C3	1.726(2)
C5	C16	1.499(2)
C9	N3	1.389
N3	C1	1.431
C1	C14	1.374
C14	C10	1.384
C10	C13	1.373
C13	C6	1.369
C6	C7	1.385
C7	C1	1.370

Table S3: Relevant bond angles in the X-Ray structure analysis of Me-DTP **5**.

Atom1	Atom2	Atom3	Angle (deg.)
C12	C5	C9	108.8(1)
C5	C9	C3	115.2(1)
C9	C3	S1	110.3(1)
C3	S1	C12	90.58(7)
S1	C12	C5	115.1(1)
C12	C5	C16	125.1(1)
C16	C5	C9	126.0(1)
C5	C9	N3	135.4
N3	C9	C3	109.4
C9	C3	C3	107.1(1)
C9	N3	C1	126.4
N3	C1	C7	120.0
C1	C7	C6	119.8
C7	C6	C13	120.5
C6	C13	C10	119.3
C13	C10	C14	120.7
C10	C14	C1	119.5
C14	C1	C7	120.2

Table S4: Relevant torsion angles in the X-Ray structure analysis of Me-DTP **5**.

| Atom1	Atom2	Atom3	Atom4	Torsion angle (deg.)
S1	C12	C5	C16	-179.6(1)
C12	C5	C9	N3	-177.8
S1	C3	C3	S1	0.0(3)
C5	C9	N3	C1	-5.9
C9	N3	C1	C7	92.1
C9	N3	C1	C14	-87.9
C12	C5	C9	C3	0.0(2)
C5	C9	C3	C3	-178.2(1)
S1	C12	C5	C9	0.0(2)
C3	C3	C9	N3	0.2

Table S5 Inter- and intramolecular short contacts (below the sum of the corresponding atomic van der Waals radii) in the X-Ray structure analysis of Me-DTP **5**.

|	Atom1	Atom2	Length (Å)	Symm. op. M1	Symm. op. M2
InterM.	H13	C3	2.712	x,y,z	-1/2+x,1/2-y,1.5-z
	S1	S1	3.533	x,1/2-y,z	2-x,-1/2+y,-z
IntraM.	C1	C16	3.316		
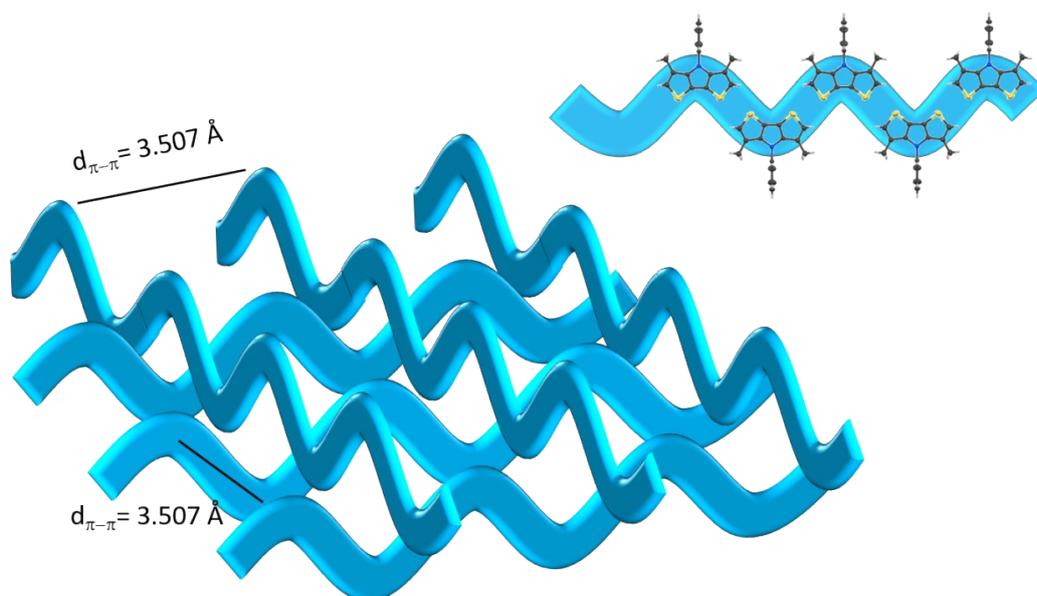
Fig. S1 Scheme of the organization of the π-delocalized systems in the crystal structure analysis of Me-DTP **5** (blue bands evolution in the symmetry (9 0 4) and (9 0 -4) planes).

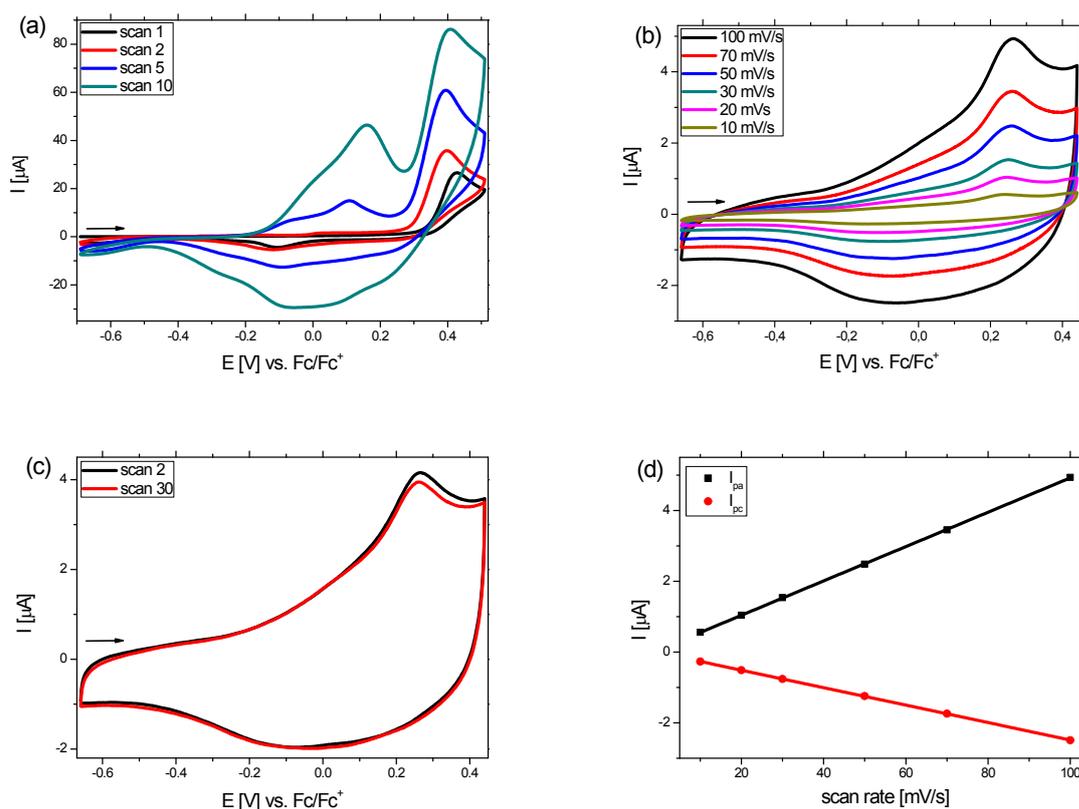## 2. General oxidative polymerization mechanism of DTP
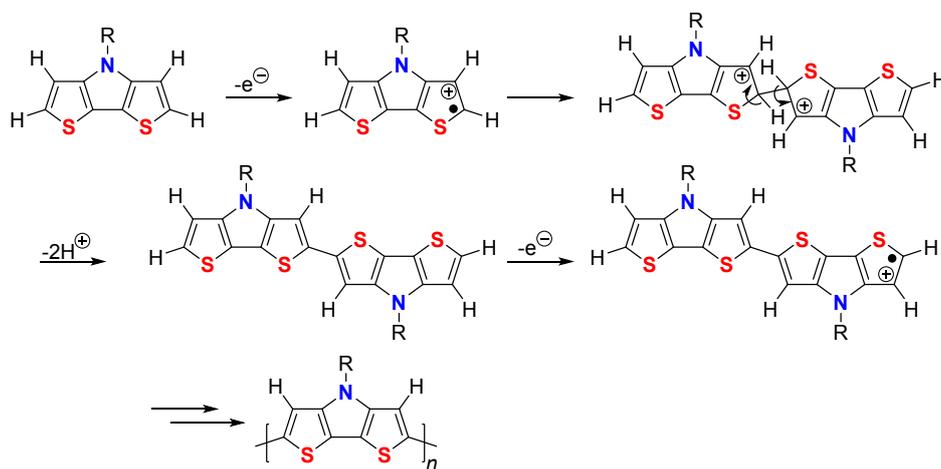
Scheme S1: Generally accepted oxidative polymerization mechanism of DTPs.[1]

3. Potentiodynamic electropolymerization of Me-DTPs 2, 4, 6, and 7 and characterization of the corresponding p(Me-DTP)s P2, P4, and P7
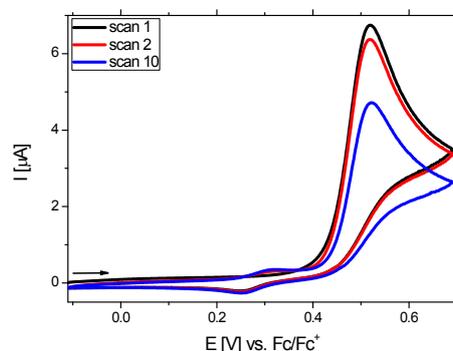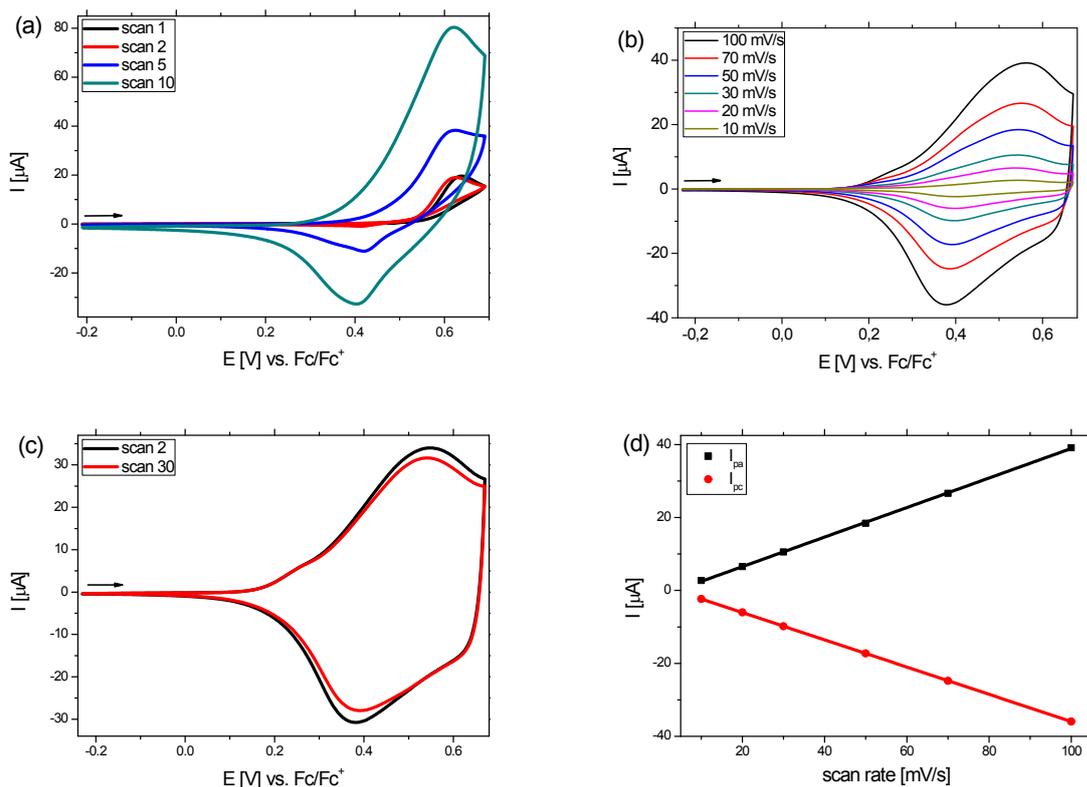

Fig. S2 Electropolymerization of Me-DTP monomer **6** with a 9-anthracenyl residue at the nitrogen.

Fig. S3 Electropolymerization of Me-DTP monomer **2** with a hydrogen residue at the nitrogen (a) and characterization of the obtained film **P2** using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents I_{pa} and the cathodic peak currents I_{pc} from the applied scan rate (d).
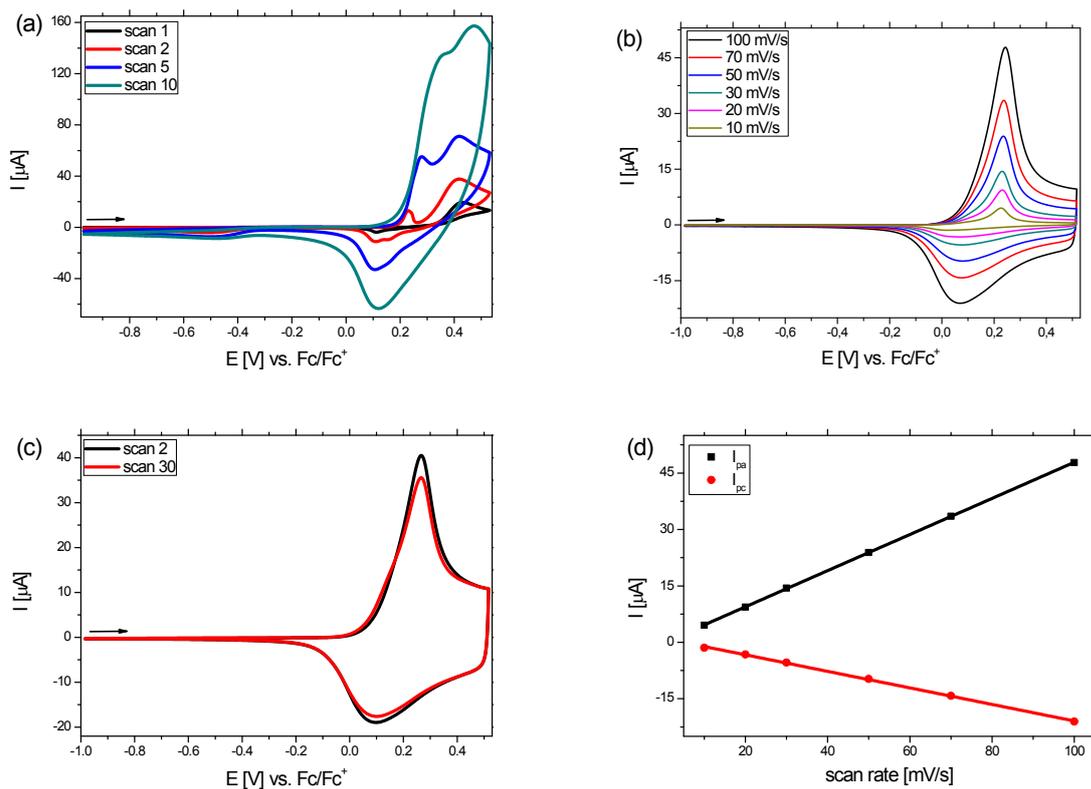
Fig. S4 Electropolymerization of Me-DTP monomer **4** with a hexyl residue at the nitrogen (a) and characterization of the obtained film **P4** using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents I_{pa} and the cathodic peak currents I_{pc} from the applied scan rate (d).

Fig. S5 Electropolymerization of Me-DTP monomer **7** with a benzoyl residue at the nitrogen (a) and characterize-ation of the obtained film **P$_{ec}$7** using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents I$_{pa}$ and the cathodic peak currents I$_{pc}$ from the applied scan rate (d).

4. DFT-calculation on a Me-DTP trimer
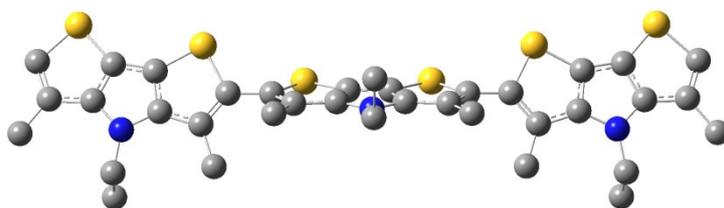
Fig. S6 Geometry optimized structures of Me-DTP trimer with ethyl residues at the nitrogens. Calculations were carried out with the Gaussian 09 program.[2] Geometry optimizations were performed via DFT methods using the M06-2X correlation/exchange functional[3] and the 6-311G basis set.
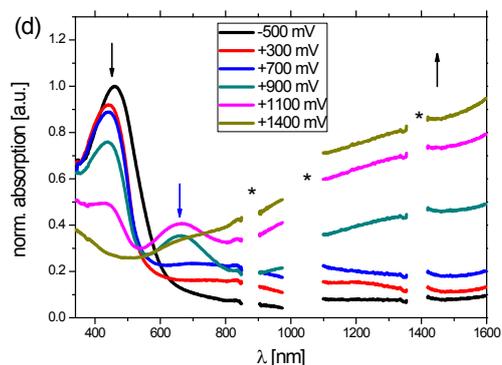
5. Spectroelectrochemical characterization of characterization Me-DTP polymers P4, P5, and P7
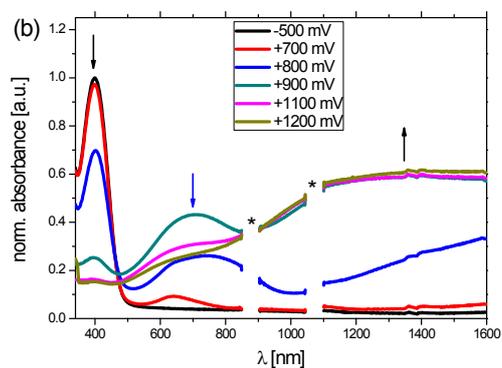
Fig. S7 UV-Vis-NIR spectra obtained from spectroelectrochemical measurements of films of p(Me-DTP) **P4**. Applied voltages are given vs. Ag/AgCl. Black arrows show the changes starting at low potentials. The blue arrow shows the further changes at high potentials. Artefacts due to switching of the detectors in the spectrometer are marked with * in the spectra.
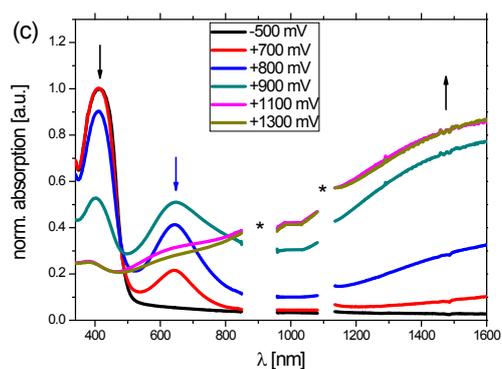

Fig. S8 UV-Vis-NIR spectra obtained from spectroelectrochemical measurements of films of p(Me-DTP) **P5**. Applied voltages are given vs. Ag/AgCl. Black arrows show the changes starting at low potentials. The blue arrow shows the further changes at high potentials. Artefacts due to switching of the detectors in the spectrometer are marked with * in the spectra.


Fig. S9 UV-Vis-NIR spectra obtained from spectroelectrochemical measurements of films of p(Me-DTP) **P7**. Applied voltages are given vs. Ag/AgCl. Black arrows show the changes starting at low potentials. The blue arrow shows the further changes at high potentials. Artefacts due to switching of the detectors in the spectrometer are marked with * in the spectra.

6. ¹H-NMR-spectrum of soluble polymer P4'
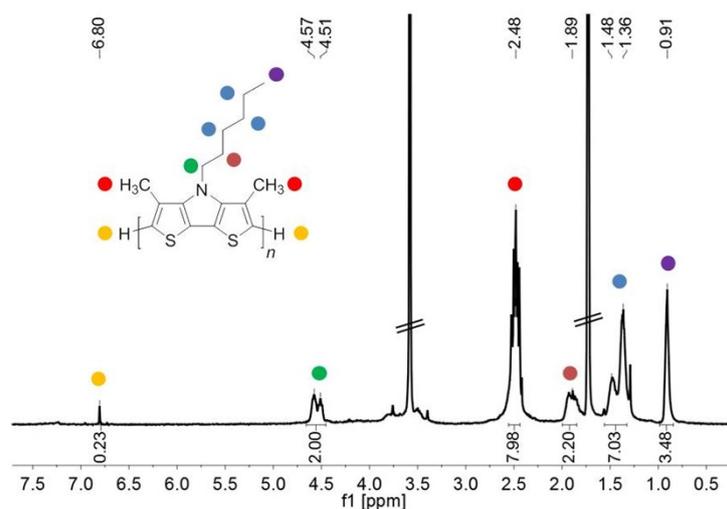
Fig. S10: ¹H-NMR spectrum in THF-d$_8$ of the soluble fraction of p(Me-DTP) **P4'** prepared by chemical oxidation with iron trichloride.

7. Absorption spectrum of soluble polymer P4'
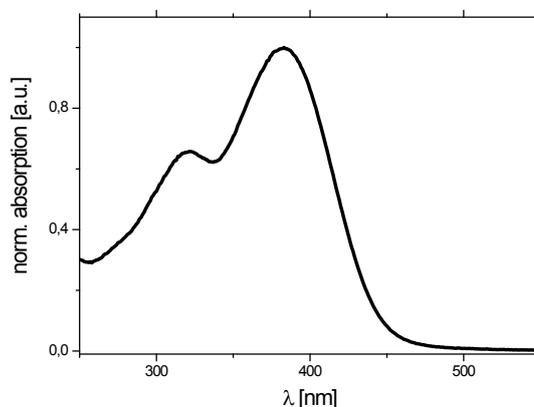
Fig. S11 Normalized UV-Vis absorption spectra of the soluble oxidatively prepared p(Me-DTP) **P4'** in THF solution.

Table S6: Optoelectronic properties of *N*-hexyl-substituted p(DTP) **P4** (electrochemically prepared) and **P4'** (prepared by chemical oxidation, soluble fractions).

P(Me-DTP)	E_{pa} [a] [V]	E_{onset} [V]	λ_{max} [nm]	λ_{onset} [nm]	HOMO[b] [eV]	LUMO[c] [eV]	E_g [eV]
P4	0.24	-0.03	400	475	-5.07	-2.77	2.40
P4'	0.28	0.02	383	444	-5.12	-2.33	2.79

Potentials are referenced vs. Fc/Fc⁺; *a* E_{pa}: anodic peak potential (scan rate 100 mV/s); *b* Redox potential of Fc/Fc⁺ is -5.1 eV on the Fermi scale; *c* The LUMO energy levels were calculated from the HOMO energy levels and the energy gaps E_g.

8. References

1   P. Audebert and F. Miomandre, Electrochemistry of Conducting Polymers in Handbook of Conducting Polymers, 3rd Edition, T. A. Skotheim, J. R. Reynolds (Eds), CRC Press, Boca Raton, USA, 2007, pp. 18-1.

2   M. J. Frisch, 2013, Gaussian, Inc., Wallingford CT.

3   H. Adams, R. A. Bawa, K. G. McMillan, S. Jones, *Tetrahedron: Asymmetry* **2007**, *18*, 1003-1012.