Supplementary Material (ESI) for Chemical Communications

3,4-Vinylenedioxythiophene as a new EDOT analogue for thiophene-based π-conjugated systems

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ELECTRONIC SUPPLEMENTARY INFORMATION

EXPERIMENTAL PROCEDURES AND CARACTERIZATIONS

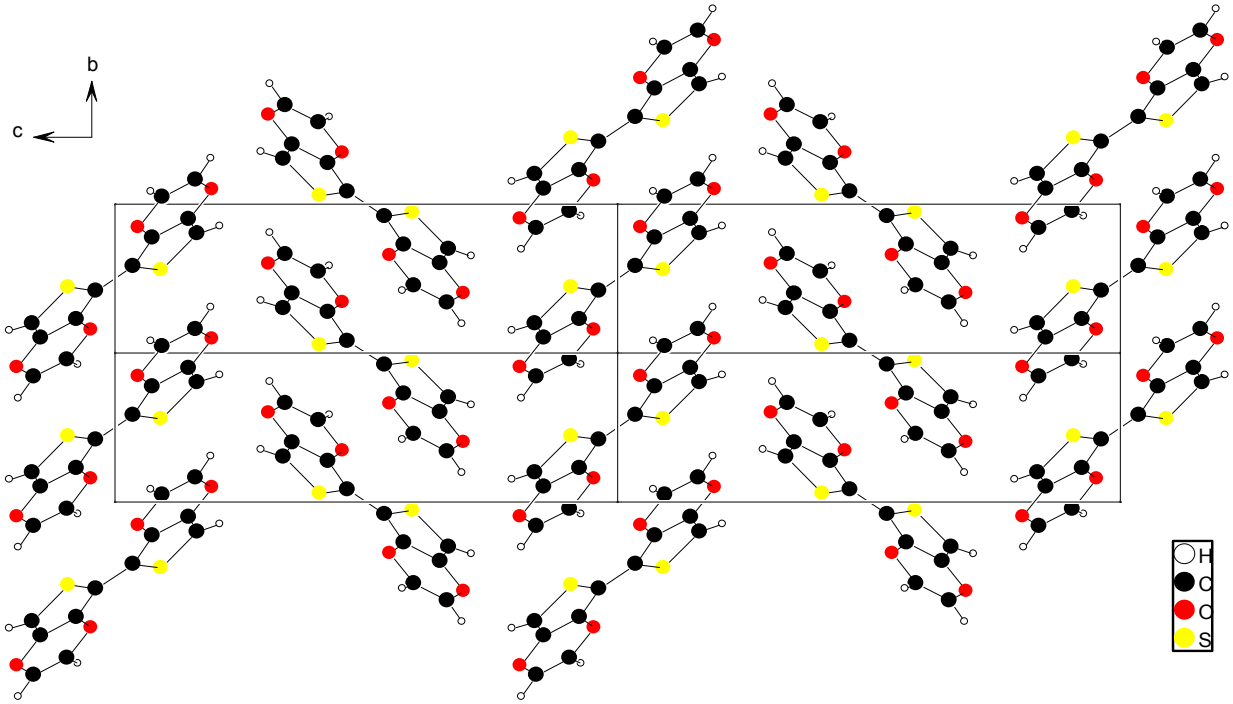
Electrochemical studies were performed in a standard three-electrode configuration under the argon blanket. The working electrode was a 1 mm Pt disk sealed in glass, the reference electrode was Ag/AgCl 0.1 M, the potential scans were performed with an EG&G 273 potentiostat. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (Fluka puriss, used as received). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE DRX 500 spectrometer operating at 500.13 and 125.7 MHz; δ are given in ppm (relative to TMS) and coupling constants (J) in Hz. Mass spectra were recorded under EI or FAB mode on a VG-Autospec mass spectrometer, under MALDI-TOF mode on a MALDI-TOF-MS BIFLEX III Bruker Daltonics spectrometer or under positive electrospray (ESI+) on a JMS-700 JEOL mass spectrometer of reversed geometry. UV-visible optical data were recorded with a Perkin-Elmer lambda 19 spectrophotometer. Melting points were obtained from a Reichert-Jung Thermovar hot-stage microscope apparatus and are uncorrected. Column chromatography purifications were carried out on Merck silica gel Si 60 (40-63 μm).

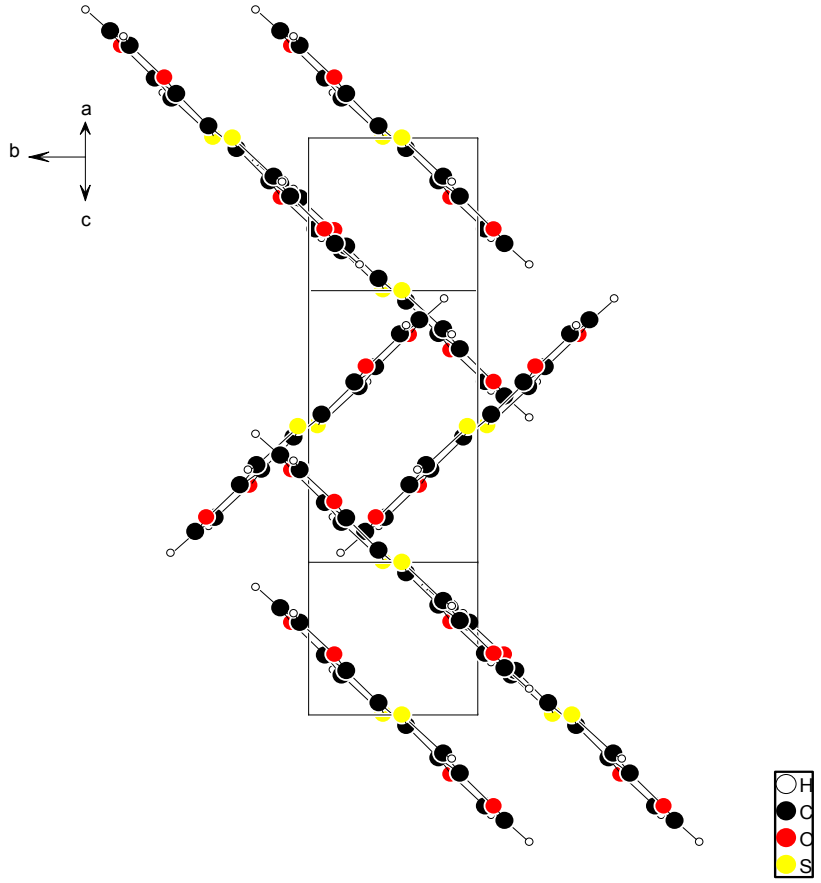
SPECTROSCOPIC DATA FOR 3-4

3: white solid; mp 86°C; ^{1}H NMR ($CDCl_3$): 6.28 (s, 2 H), 4.27 (t, ^{3}J=7.2Hz 4H), 3.44 (t, ^{3}J=7.2Hz 4H);^{13}C NMR ($CDCl_3$): 146.0, 99.5, 71.0, 0.48; EIMS calcd for $C_8H_{10}Cl_2O_2S$: 423.83; found: 423.8.

4: colorless oil; ^{1}H NMR ($CDCl_3$): 6.61 (dd, 3J=13.6Hz, ^{3}J=6.0Hz, 2H), 6.54 (s, 2H); 4.84 (dd, ^{3}J=13.6Hz, ^{2}J=2.0Hz 2H), 4.45 (dd, ^{3}J=6.2Hz, ^{2}J=2.0Hz 2H); ^{13}C NMR ($CDCl_3$): 148.7, 144.5, 104.1, 95.1; EIMS calcd for $C_8H_8O_2S$: 168.02; found: 197.99. Anal. for $C_8H_8O_2S$. Found (Calcd) : C, 56.84 (57.12); H, 4.86 (4.79); O, 20.04 (19.02); S, 18.67 (19.06).

X-RAY DATA FOR 2





Distance between 2 planar molecules = 3.444(4)Å

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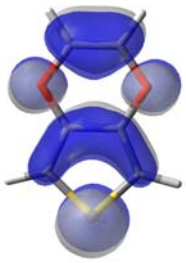
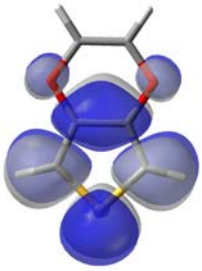
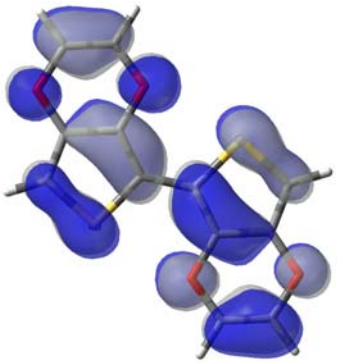
HOMO AND LUMO OF 1 AND 2, CALCULATED AND MEASURED (X-RAY) BOND LENGH FOR 2 AND BEDOT



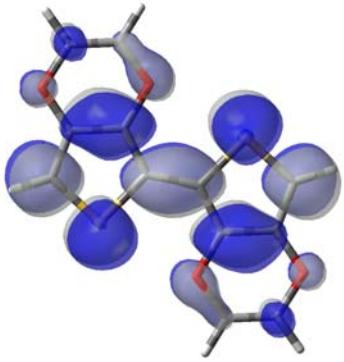
1, HOMO



1, LUMO



2, HOMO



2, LUMO

Table 6: Calculated and measured (X-ray diffraction bond length in BEDOT and BVDOT **2**)

	BEDOT		**BVDOT 2**	
	Calc.	X-ray	Calc.	X-ray
C2-C3	1.379	1.3733(3)	1.374	1.3790(2)
C3-C4	1.429	1.4205(3)	1.428	1.4067(3)
C4-C5	1.365	1.3467(3)	1.359	1.3455(2)
C5-S	1.738	1.7155(3)	1.742	1.7108(2)
S-C2	1.764	1.7316(2)	1.768	1.7404(3)
C2-C2’	1.443	1.4416(3)	1.444	1.4460(2)
C3-O2	1.370	1.36865”°	1.374	1.3790(2)
O1-C6	1.431	1.4500(4)	1.383	1.3948(2)
C6-C7	1.523	1.4829(5)	1.333	1.3023(2)
C7-O2	1.432	1.4351(3)	1.385	1.3846(2)
O1-C4	1.370	1.3740(3)	1.376	1.3830(2)

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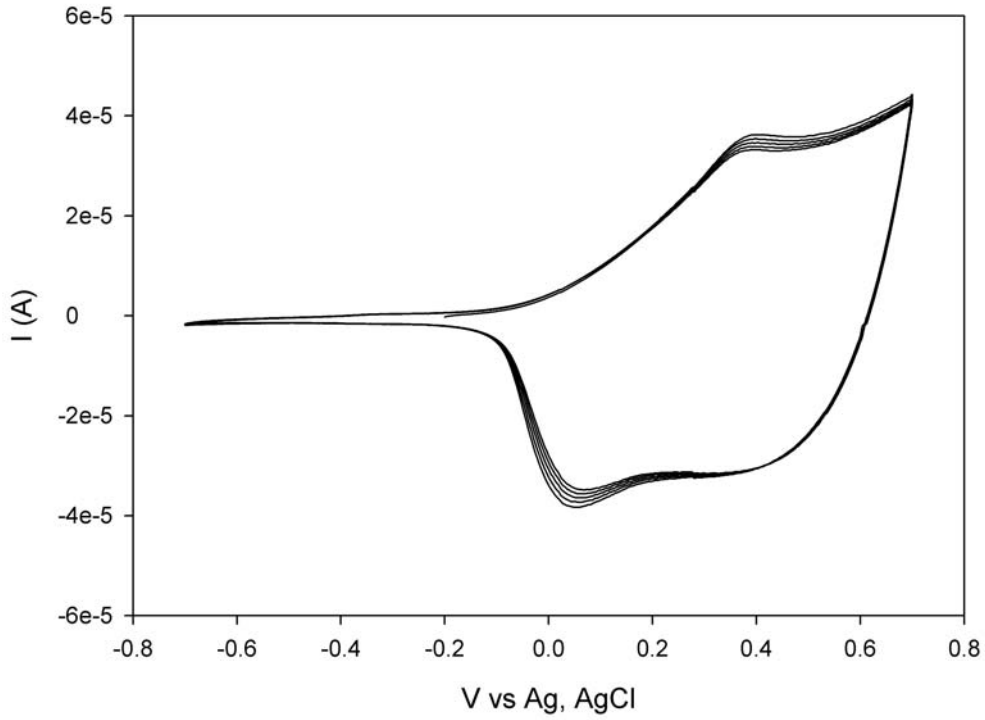
CYCLIC VOLTAMMETRY OF POLY(BVDOT)



Redox behaviour of poly(BVDOT) polymer in 10^{-1} M tetrabutylammonium hexafluorophosphate/methylene chloride solution (scan rate : 50 $mV.s^{-1}$).