Electronic Supporting Information for the paper

Towards crystal engineering of solid-state polymerization in dibromothiophenes

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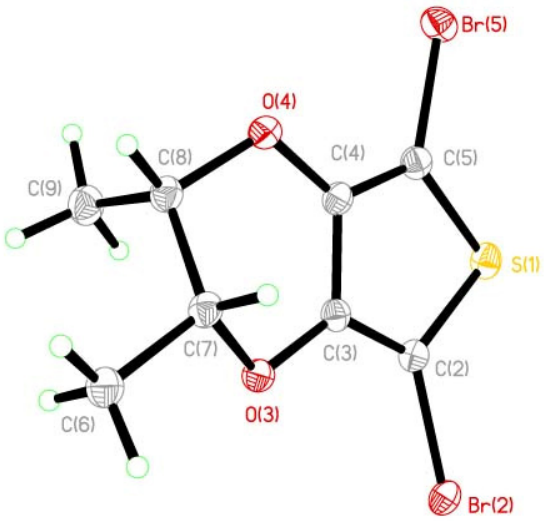

Figure S1. Molecular structure of **4a**

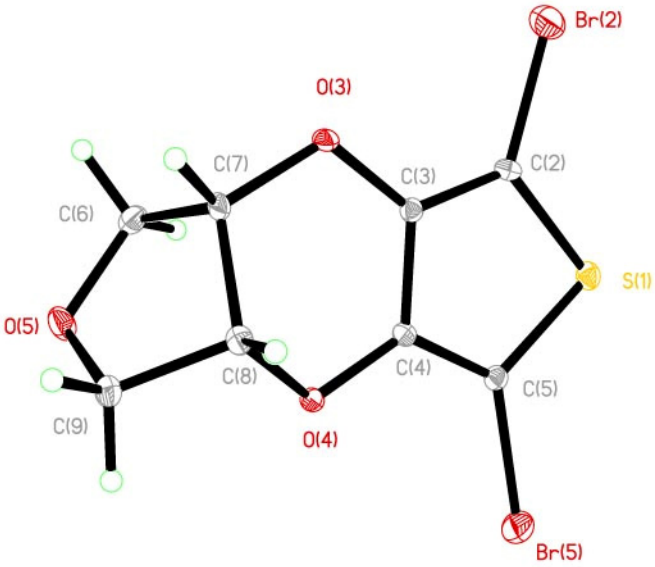

Figure S2. Molecular structure of **4b**

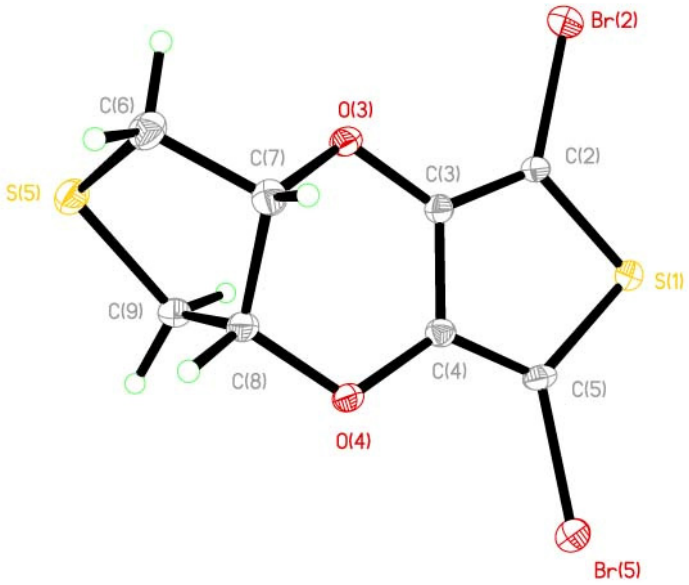

Figure S3. Molecular structure of **4c**

Table S1. List of X-ray crystallographic data for **4a, 4b, 4c**

	4a	**4b**	**4c**
Empirical formula	C8 H8 Br2 O2 S	C8 H6 Br2 O3 S	C8 H6 Br2 O2 S2
Formula weight	328.02	342.01	358.07
Temperature (K)	150	150	150
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pbca	Pbca	Pbca
a (Å)	8.7321(3)	7.3511(2)	9.3142(3)
b (Å)	14.2816(4)	12.1366(4)	11.3466(4)
c (Å)	16.6582(5)	21.9075(7)	19.4858(7)
Volume ($Å^3$)	2077.42(11)	1954.53(10)$Å^3$	2059.35(12)$Å^3$
Z	8	8	8
D_{calc} (g/cm^{-3})	2.098	2.325	2.310
μ(CuKα)(cm^{-1})	11.515	12.363	13.546
F(000)	1264	1312	1376
Crystal size (mm)	0.08 x 0.08 x 0.03	0.08 x 0.08 x 0.07	0.20 x 0.06 x 0.04
Collected reflections	42435	23675	24995
Unique reflections	2026 [R_{int} = 0.035]	1916 [R_{int} = 0.042]	2010 [R_{int} = 0.069]
Observed data [I>2σ(I)]	1949	1809	1940
Goodness-of-fit	1.186	1.182	1.229
R_1	0.0226	0.0471	0.0492
*w*R2	0.0638	0.1644	0.1418
final max/min Δρ ($eÅ^{-3}$)	0.38/-0.79	1.15/-2.12	1.46/-1.28

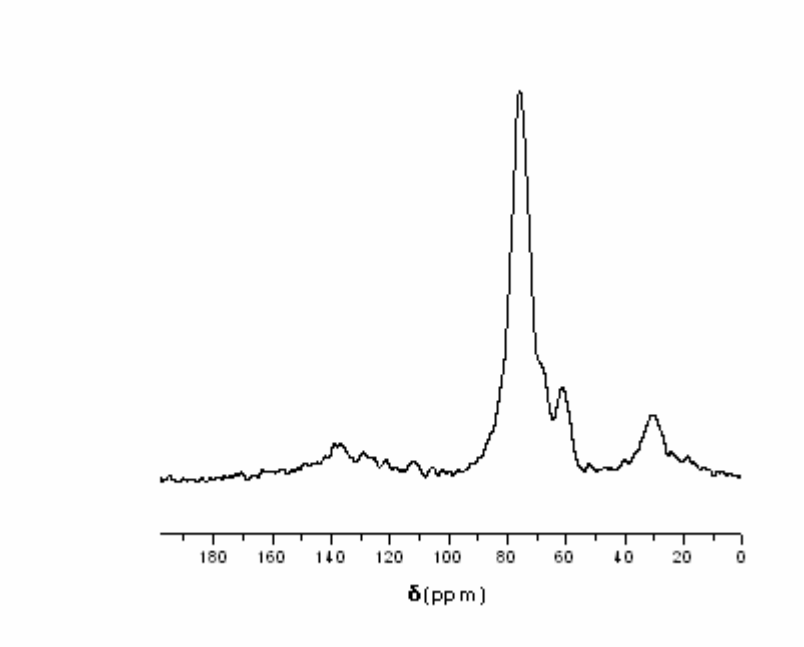

Figure S4. CP-MAS ^{13}C NMR spectrum of poly-**4b**.

Explanation: There is a strong paramagnetic broadening of aromatic carbons (due to unusually facile doping by air); however, the ring-opening of the furan moiety by bromine is evident: the peak at 62ppm (OCH(CH)*C*H_2O) is reduced in intensity (relative to that of O*C*H(CH)CH_2O at 78ppm) and an extra peak appears at ~30 ppm (*C*H_2-Br).

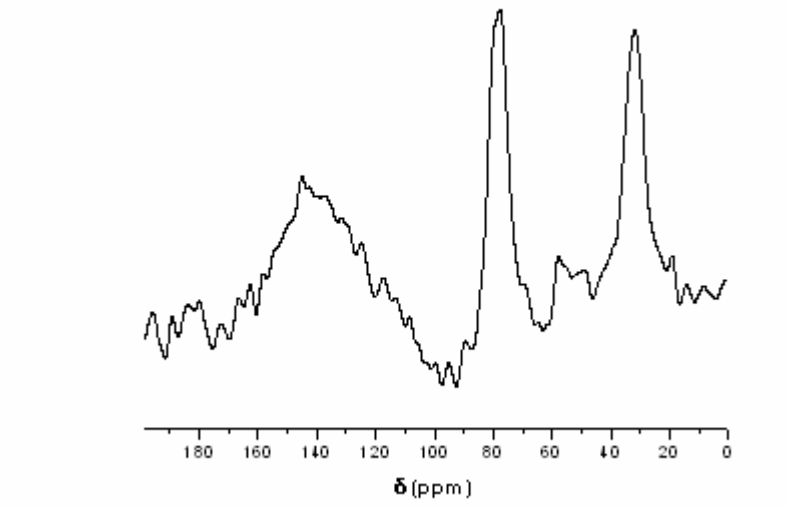

Figure S5. CP-MAS ^{13}C NMR spectrum of SSP **C**.

Explanation: There is a strong paramagnetic broadening of aromatic carbons (due to facile doping by air); however, the bromination of the tetrahydrothiophene moiety is evident from an extra peak appears at ~55 ppm (*C*H_2S=O).

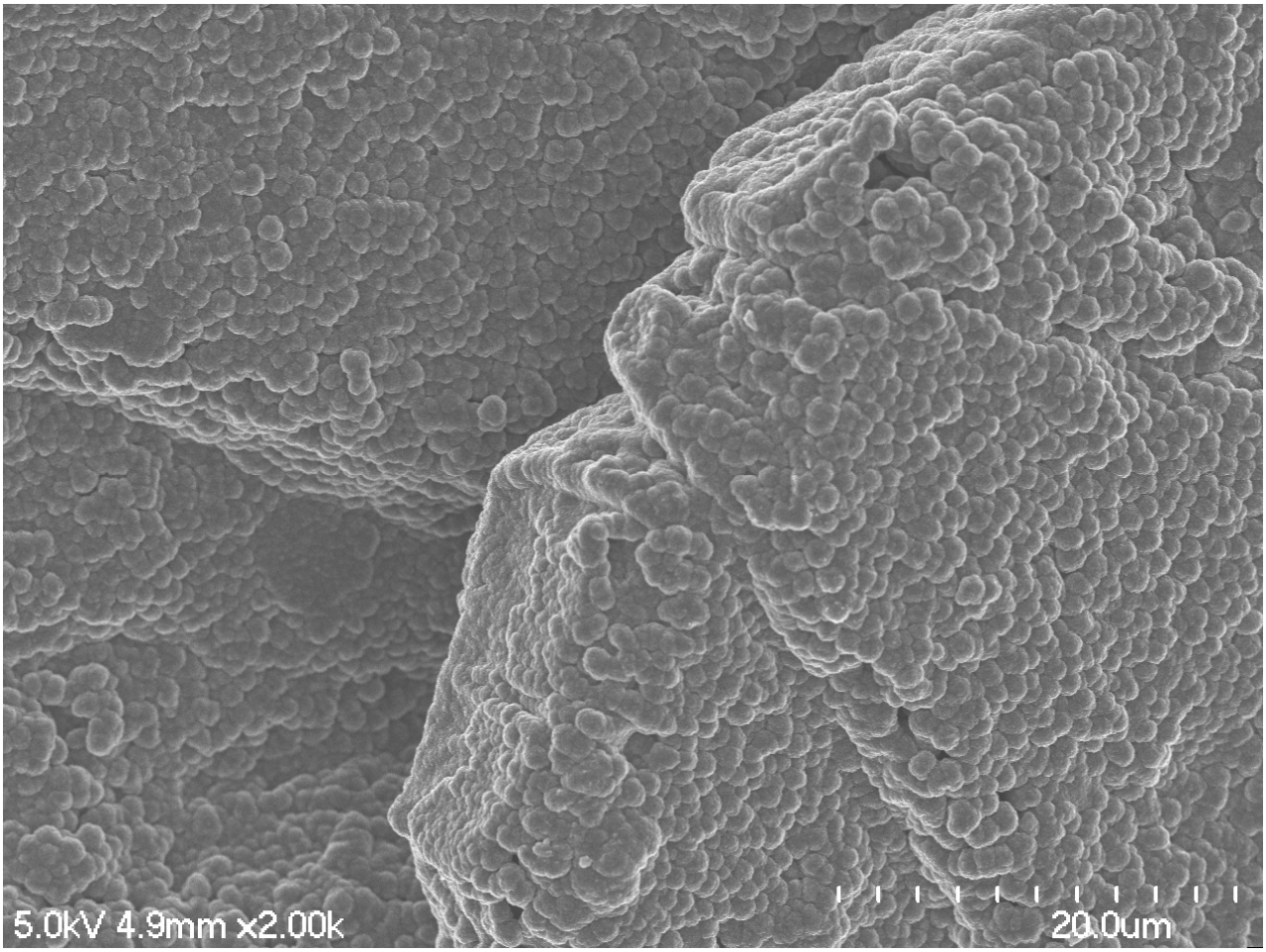

Figure S6. FE-SEM image of polymer **A** prepared by SSP of crystalline **4c**, showing substantial morphological changes to the crystal surface.