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Supporting Information

Significant Alternation of Molecular Structures and Properties in Quinoidal Conjugated Polymers by Chalcogen Atom Substitution

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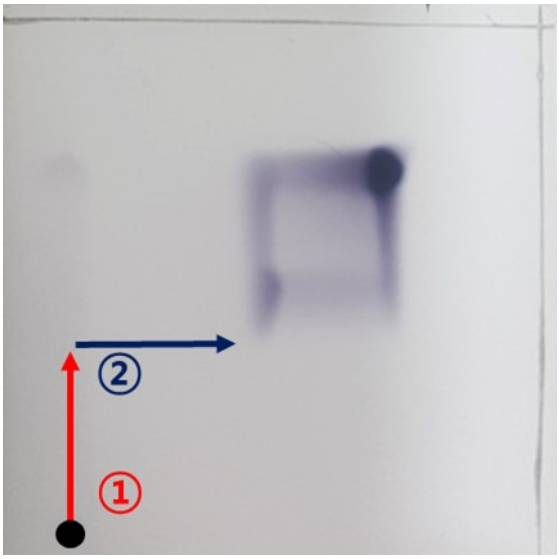

Fig. S1. Two dimensional TLC analysis of mQEDTT-T2 with chloroform/*n*-hexane = 6:4 (*v*/*v*) as the eluent.

Table S1. Total and relative total energies of quinoidal monomers mQEDOT-Br and mQEDTT-Br for each possible geometrical configuration obtained by density functional theory (DFT) calculations at B3LYP/6-311G (d, p) level

	Total energy (Hartree)	Relative total energy (kcal / mol)
mQEDOT-Br *(Z,Z)*	-6881.42707233	0
mQEDOT-Br *(Z,E)*	-6881.42113553	3.72
mQEDOT-Br *(E,E)*	-6881.41056024	10.4
mQEDTT-Br *(Z,E)*	-7527.37468504	0
mQEDTT-Br *(Z,Z)*	-7527.37205471	1.65
mQEDTT-Br *(E,E)*	-7527.37087468	2.39

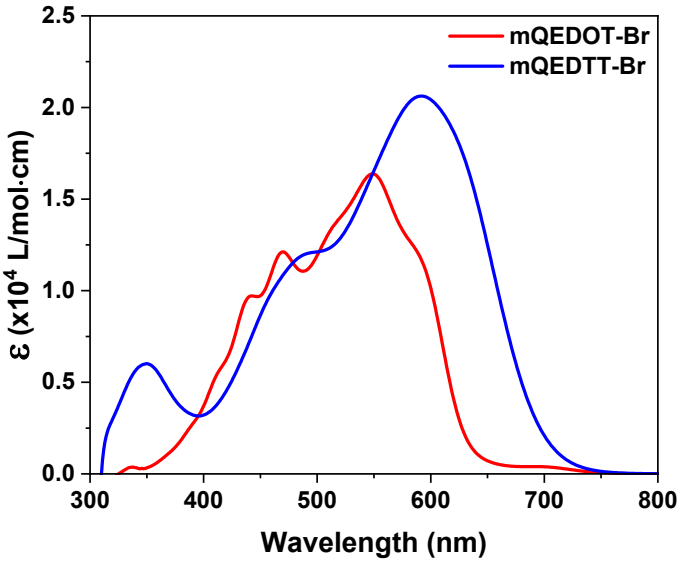

Fig. S2**.** UV-vis absorption spectra and absorption coefficient of mQEDOT-Br and mQEDTT-Br in TCE.

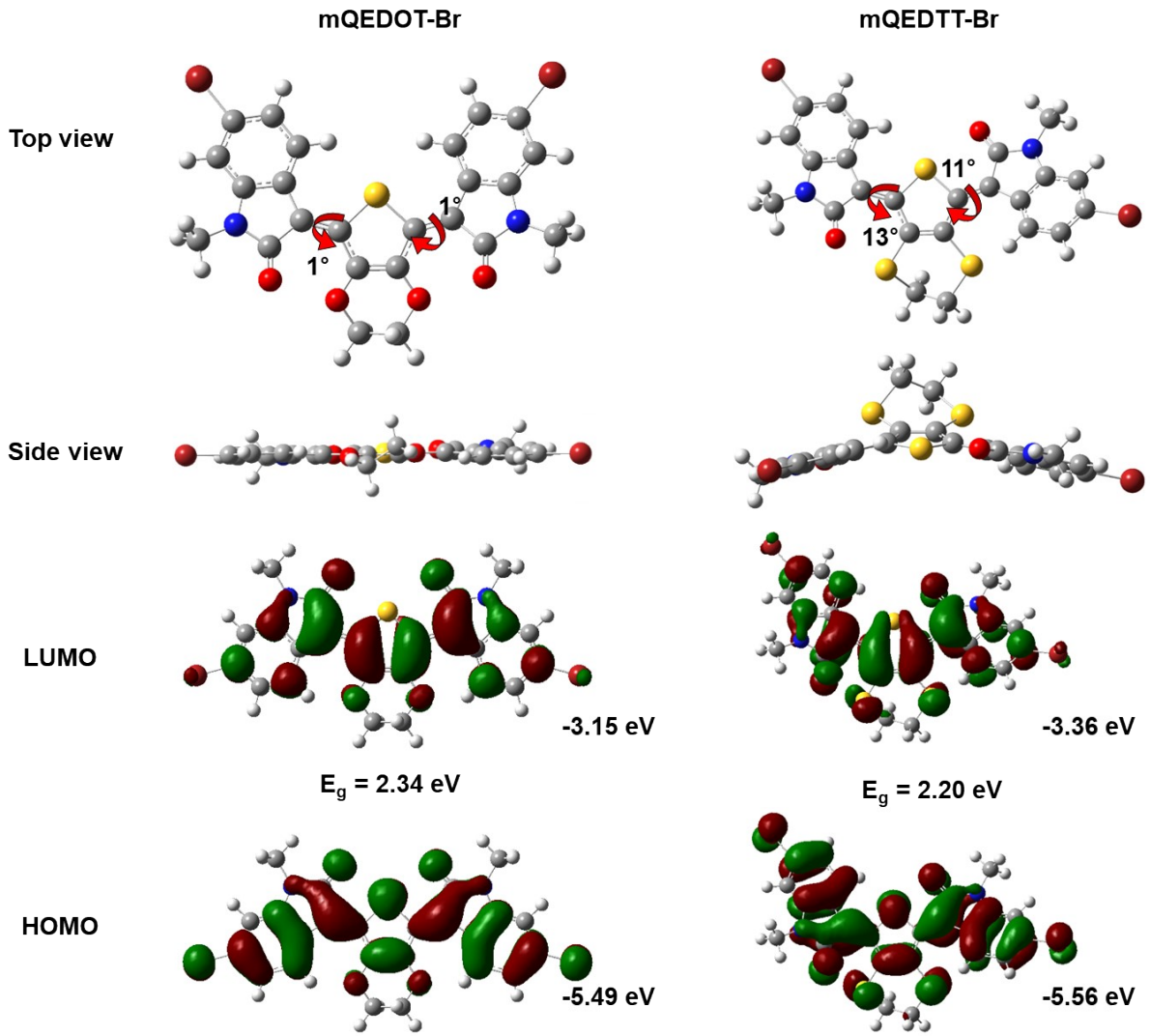

Fig. S3. Optimized molecular geometries of mQEDOT-Br and mQEDTT-Br obtained by DFT calculations at the B3LYP/6-311G (d, p) level.

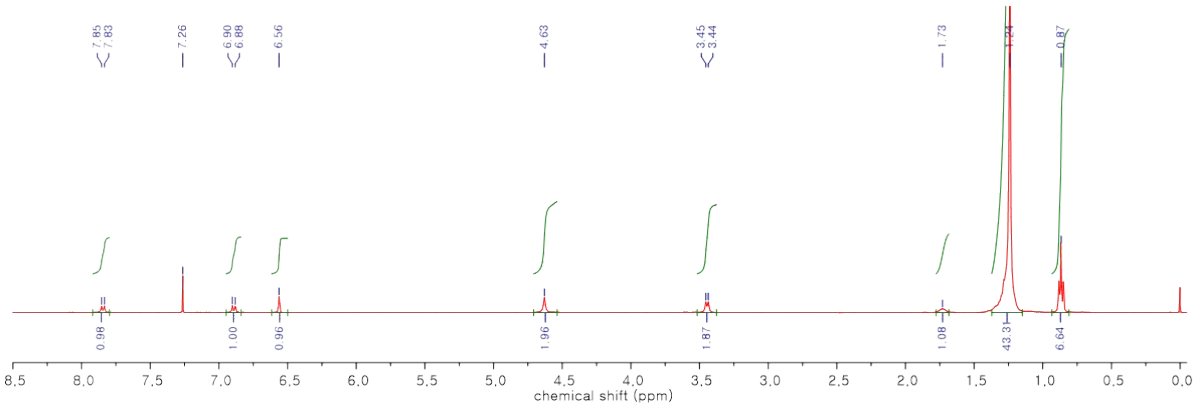

Fig. S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of mQEDOT-Br.

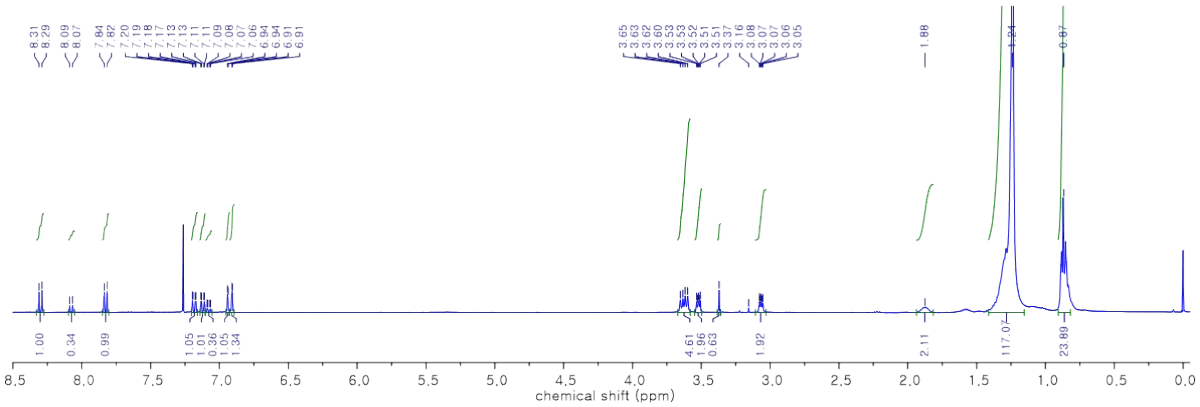

Fig. S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of mQEDTT-Br.

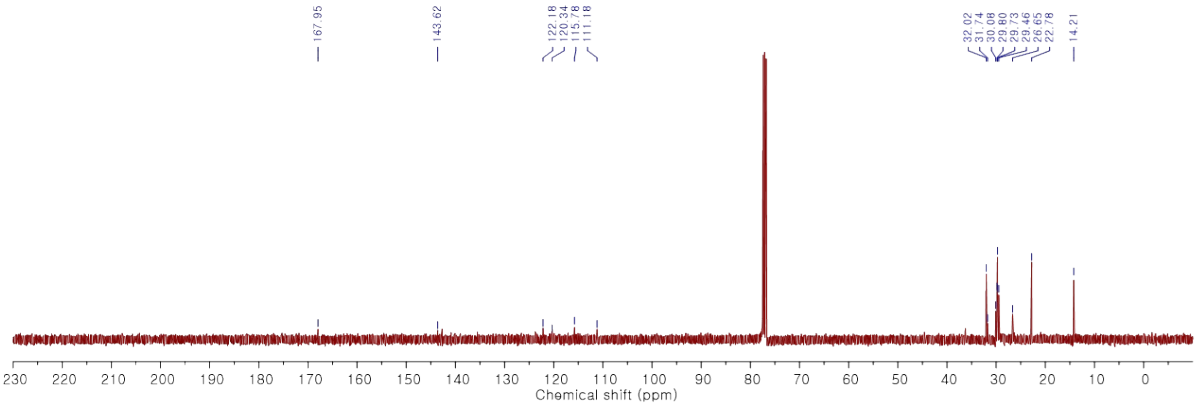

Fig. S6. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of mQEDOT-Br.

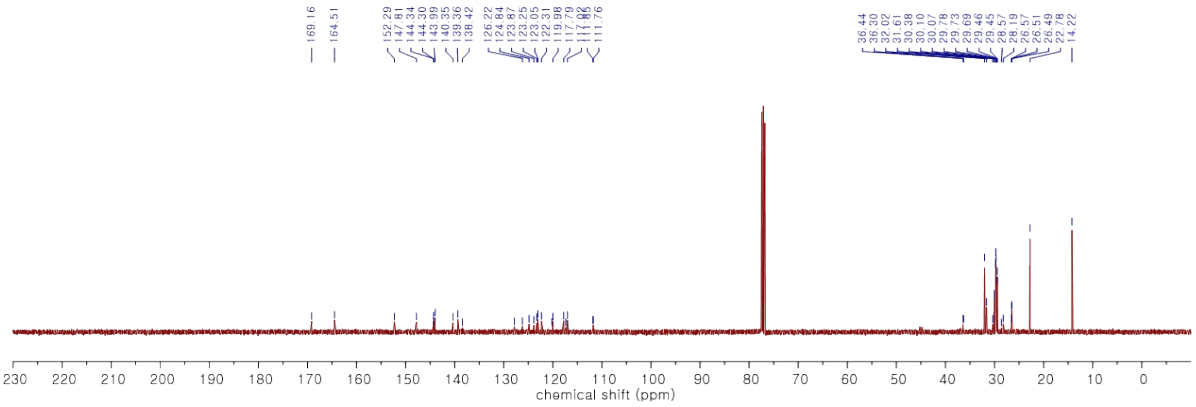

Fig. S7. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of mQEDTT-Br.

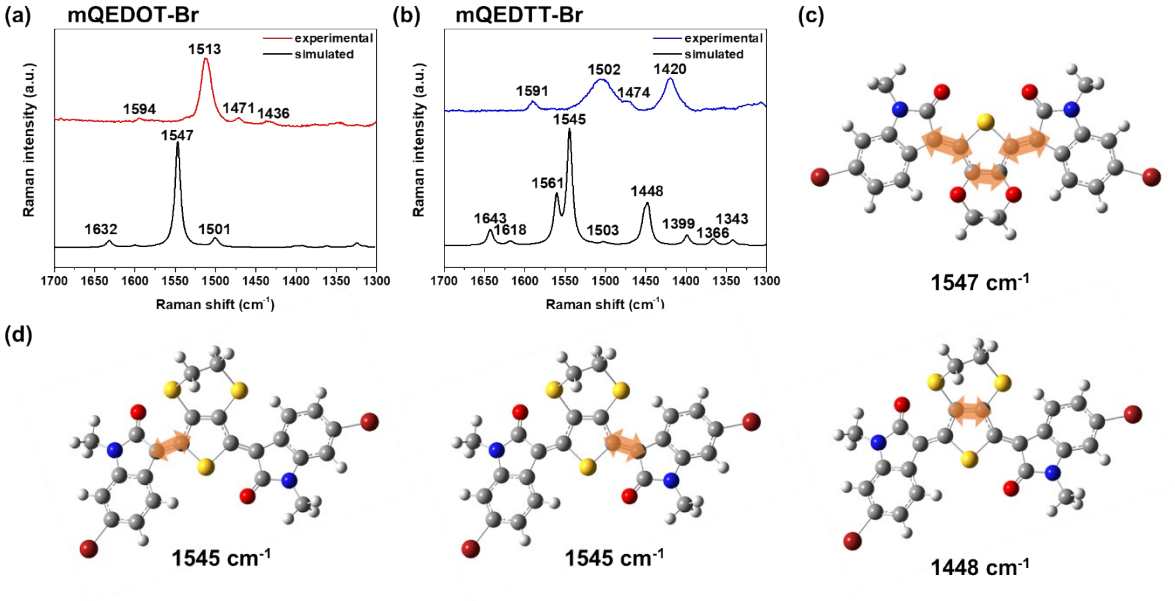

Fig. S8. Experimental and simulated resonant Raman spectra of (a) mQEDOT-Br and (b) mQEDTT-Br thin films. Theoretical eigenvectors of Raman vibration modes of (c) mQEDOT-Br and (d) mQEDTT-Br.

Table S2. Reaction conditions for the synthesis and physical properties of PmQEDOT-T2 and PmQEDTT-T2

Polymer	Entry	Catalyst	Ligand	Solvent	Temp. (℃)	Time (h)	M_n (kDa)	PDI	
PmQEDOT-T2	1	$Pd_2(dba)_3$	P(o-tolyl)$_3$	Toluene	110	72	30.1	2.01	CB fraction
	1	$Pd_2(dba)_3$	P(o-tolyl)$_3$	Toluene	110	72	2.70	1.31	Hex fraction
PmQEDTT-T2	2	$Pd_2(dba)_3$	P(o-tolyl)$_3$	Toluene/DMF = 9/1	110	72	4.57	1.34	CF fraction
	3	$Pd(PPh_3)_4$	-	Toluene/DMF = 4.5/1	120	25	20.3	3.06	CF fraction

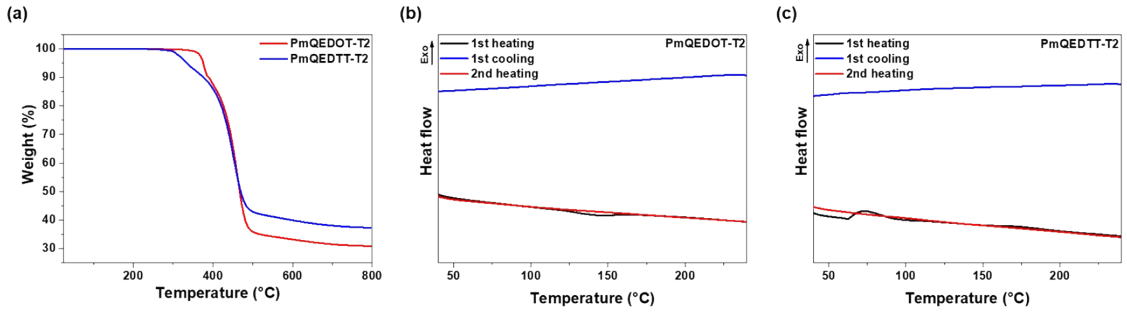

Fig. S9. (a) Thermogravimetric analyses and (b, c) differential scanning calorimetry curves of PmQEDOT-T2 and PmQEDTT-T2 polymers.

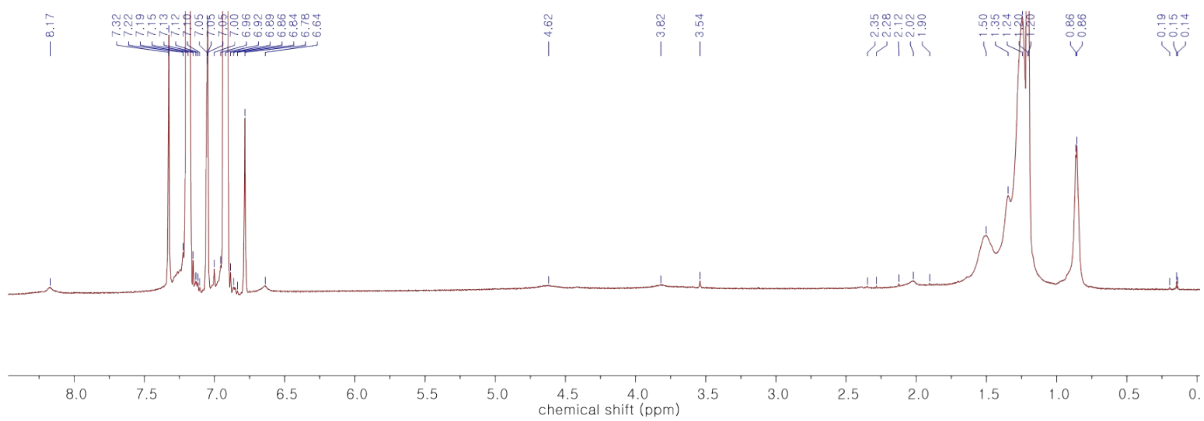

Fig. S10. ^{1}H NMR spectrum (600 MHz, $C_6D_4Cl_2$) of PmQEDOT-T2 polymer.

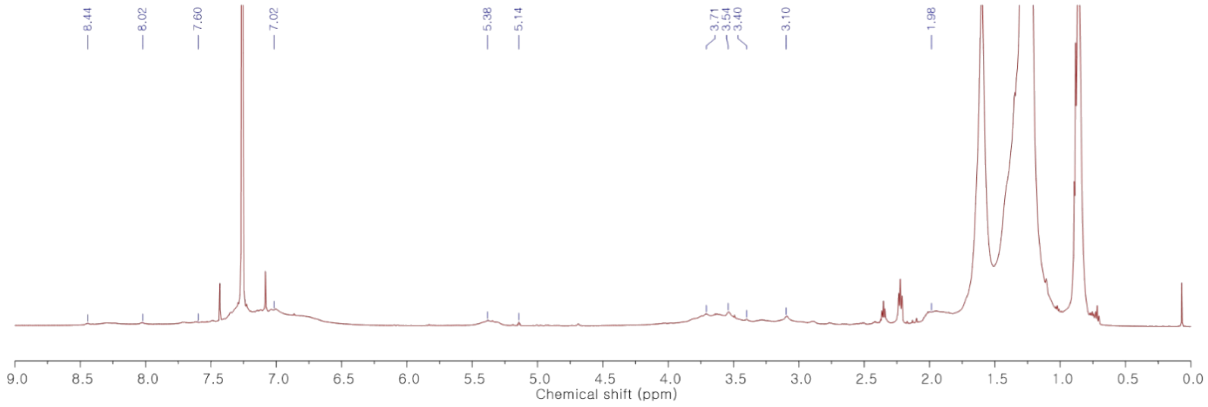

Fig. S11. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of PmQEDTT-T2 polymer.

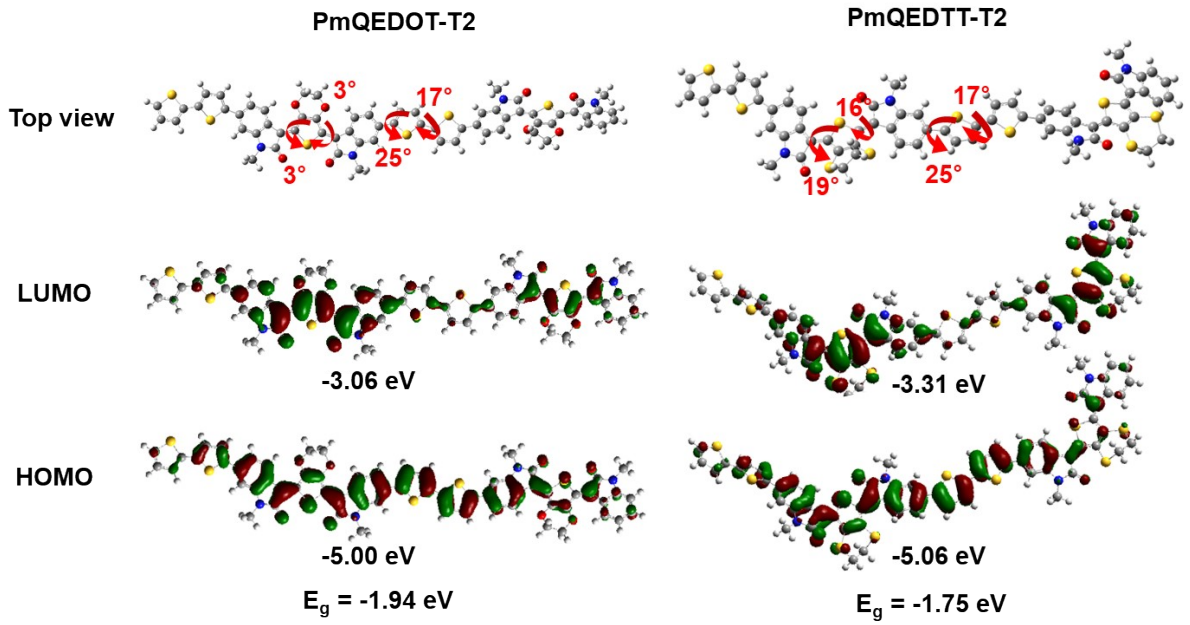

Fig. S12. Optimized molecular geometries of mQEDOT-T2 and mQEDTT-T2 dimers obtained by DFT calculations at the B3LYP/6-311G (d, p) level.

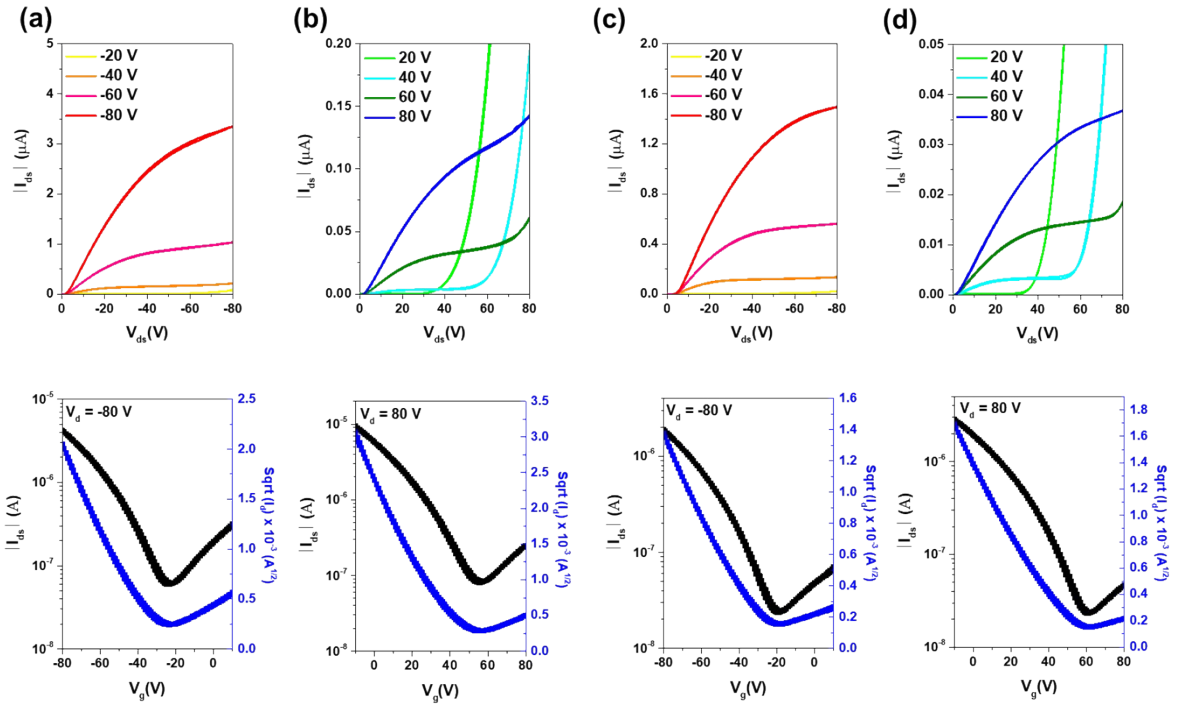

Fig. S13. Output and transfer curves of pristine (a, b) PmQEDOT-T2 and (c, d) PmQEDTT-T2- based OTFTs.

Table S3. Device performance parameters of pristine PmQEDOT-T2 and PmQEDTT-T2-based OTFTs

polymer	p-channel			n-channel		
	μ_h (cm^2/Vs)	V_{th} (V)	I_{on}/I_{off}	μ_e (cm^2/Vs)	V_{th} (V)	I_{on}/I_{off}
PmQEDOT-T2	1.4×10^{-2} (2.7×10^{-2})[a]	-43	10^2	6.3×10^{-4} (8.8×10^{-4})	35	10^2
PmQEDTT-T2	4.8×10^{-3} (5.5×10^{-3})[a]	-33	10^2	9.6×10^{-5} (1.0×10^{-4})	27	$< 10^1$

[a]Maximum mobility

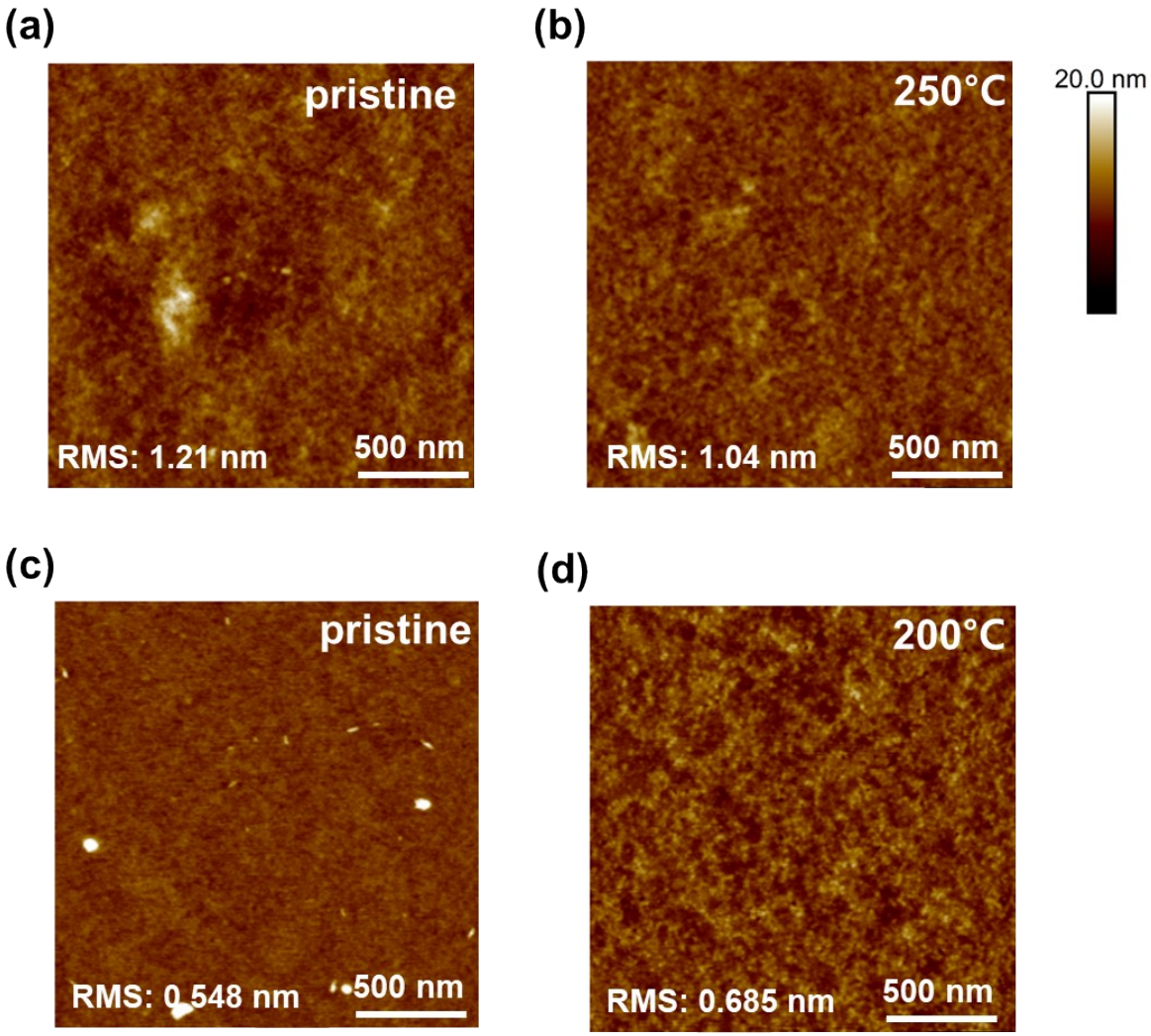

Fig. S14. AFM height images of (a, b) PmQEDOT-T2 and (c, d) PmQEDTT-T2 films.

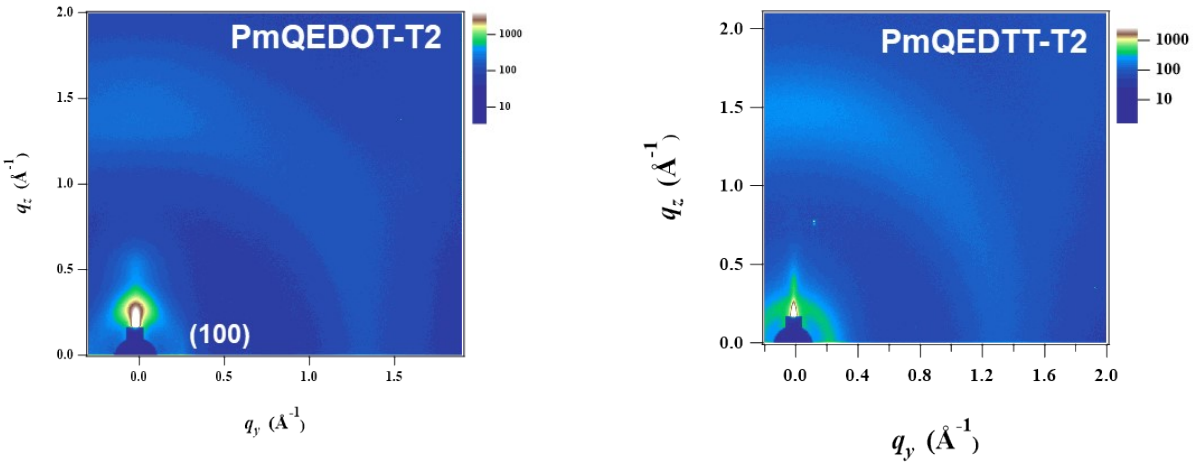

Fig. S15. 2D-GIWAXS images of pristine (a) PmQEDOT-T2 and (b) PmQEDTT-T2 films.

Table S4 Crystallographic information of PmQEDOT-T2 and PmQEDTT-T2 films obtained by 2D-GIWAXS

	Annealing temp. (°C)	In plane (Å)		Out of plane (Å)		
		d(100)	d(010)	d(100)	d(001)	d(001´)
PmQEDOT-T2	Pristine	23.0	-	-	-	-
	250	21.7	3.7	23.3	-	-
PmQEDTT-T2	Pristine	25.9	-	-	-	-
	200	21.4	-	-	20.9	9.2