Electronic Supplementary Material (ESI) for Materials Advances.

Supporting information

Highly crystalline and efficient red-emissive π-conjugated polymer film: Tuning of macrostructure for light-emitting properties

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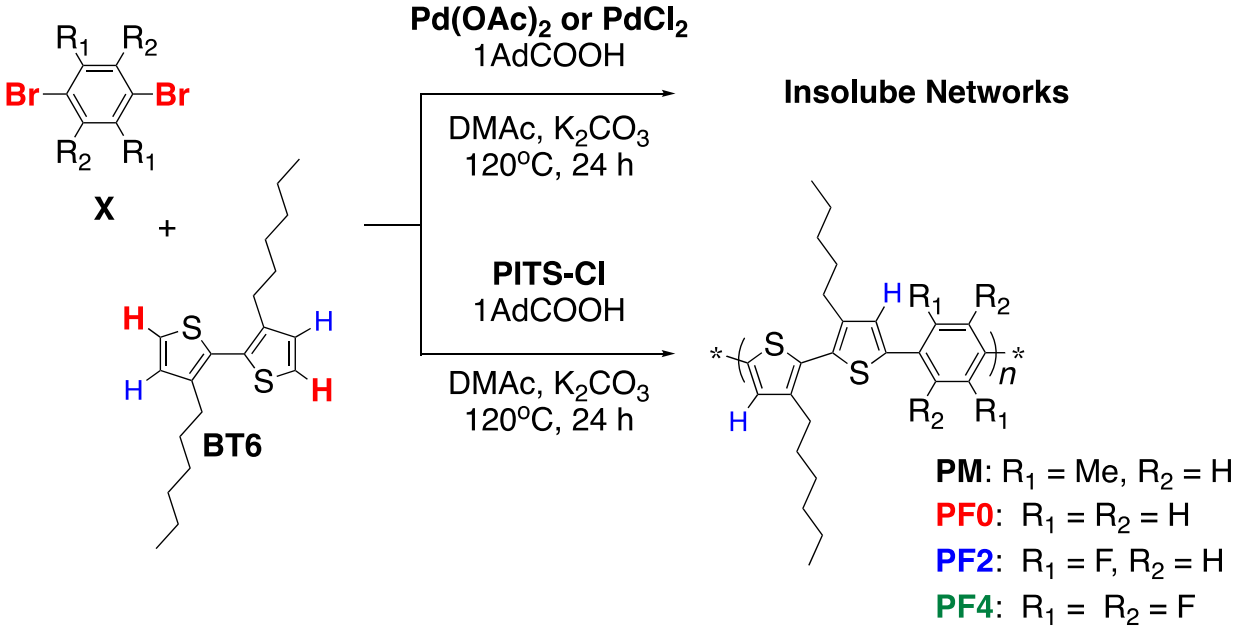
Scheme S1. Direct Arylation Polycondensation.



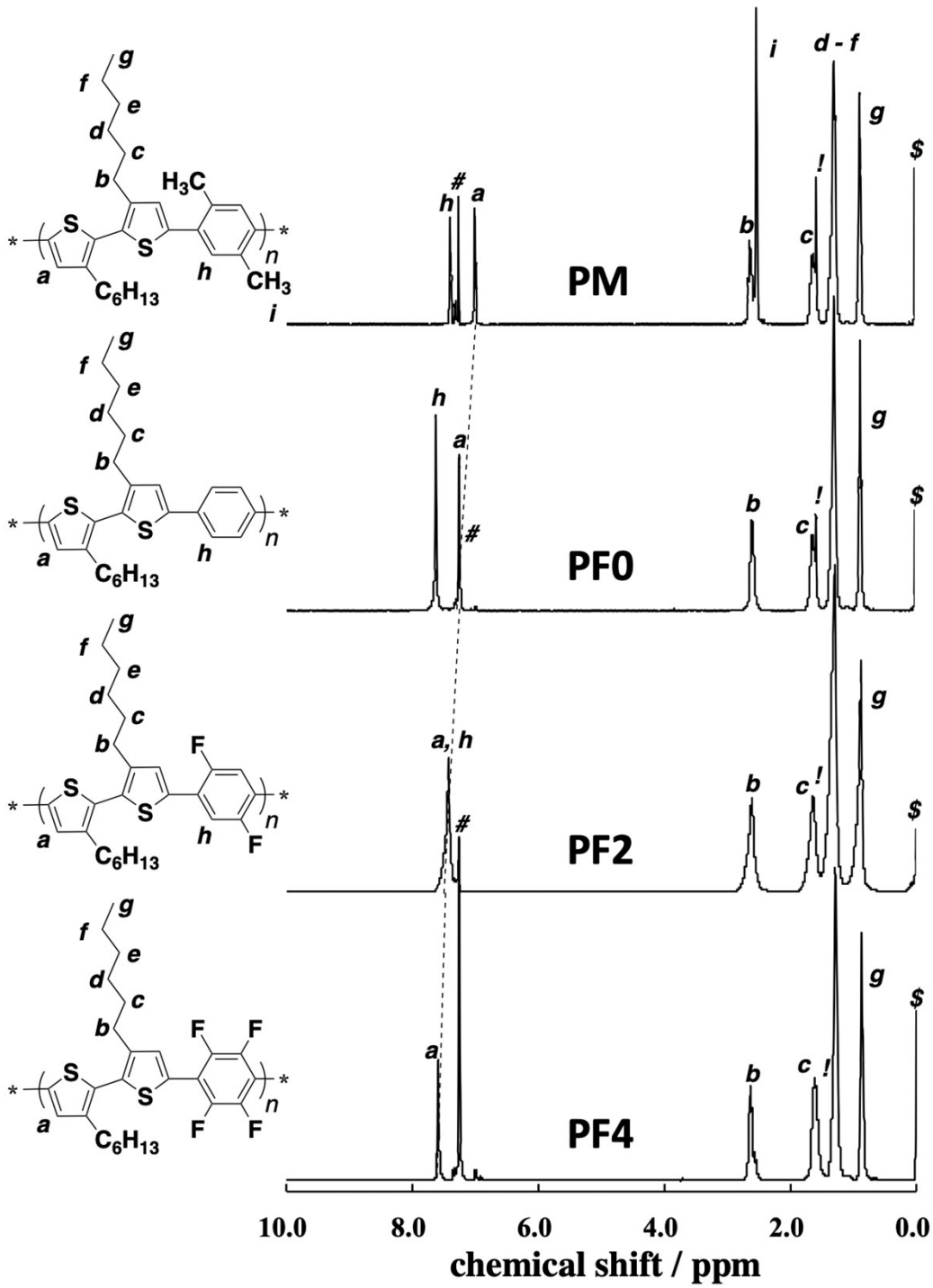


Fig. S1 ^{1}H NMR spectra of the polymers.

Table S1. Molecular Weight and Thermal Properties of the Polymers

Polymers	M_n[a]	M_w/M_n[a]	T_m[b]	$T_{d5\%}$[c]
PM	4400	1.63	-	387
PF0	16700	2.86	-	451
PF2	16300	3.78	-	386
PF4	6300[d]	1.22[d]	183	413

[a] Measured by GPC (standard: polystyrene, eluent: THF). [b] Measured by DSC. [c] Measured by TGA. [d] Insoluble in THF at 40 °C. GPC measurement was performed by soluble part in THF at room temperature.

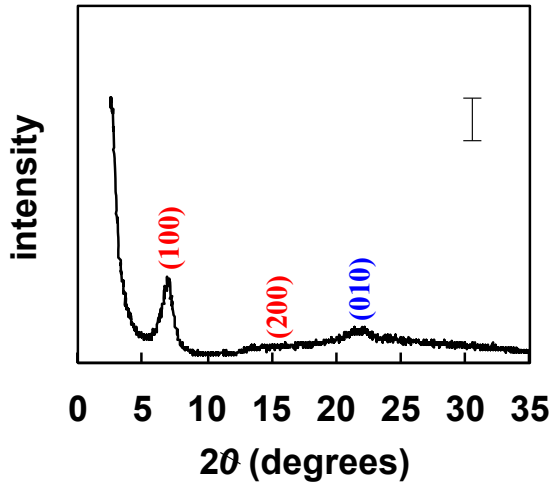


Fig. S2 XRD of **PF4**.

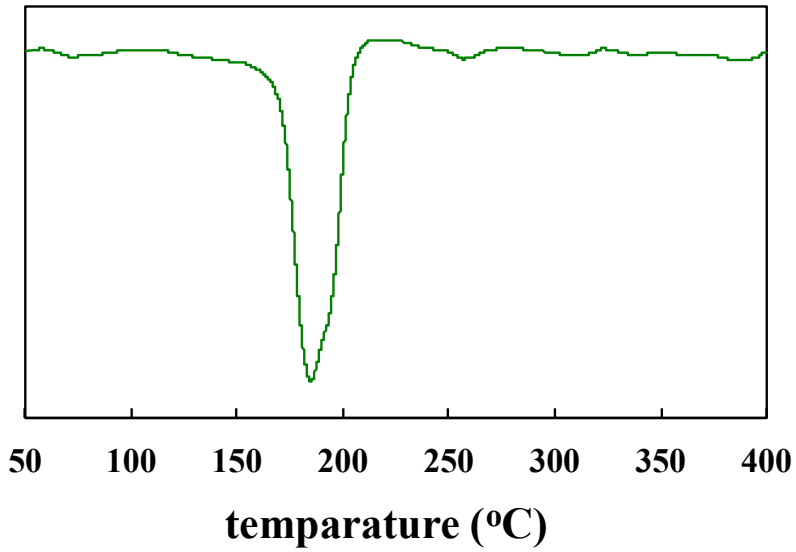


Fig. S3 DSC trace of **PF4**.

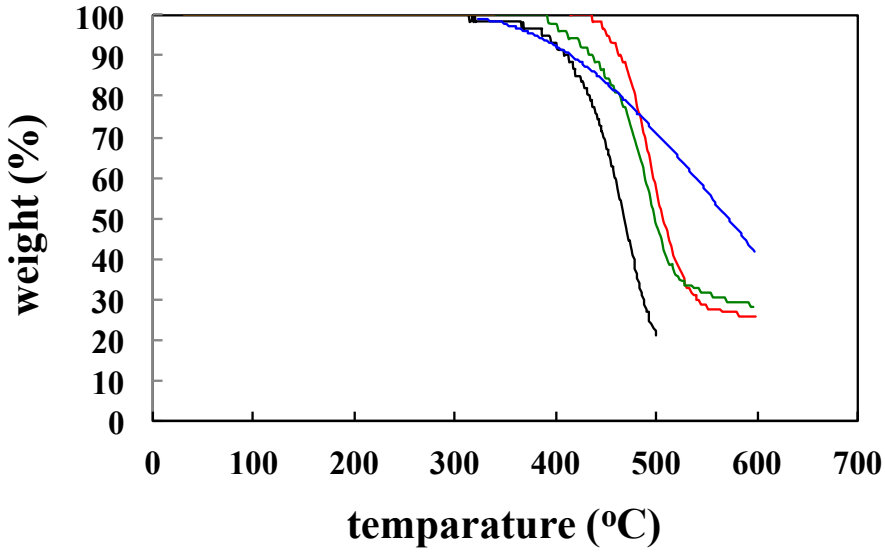


Fig. S4 TGA traces of the polymers. Black: **PM**. Red: **PF0**. Blue: **PF2**. Green: **PF4**.

Table S2. Results of Optical Properties

Polymers	λ^{ab} (nm)	λ^{fl} (nm)	λ^{ab} (nm)	λ^{fl} (nm)	Φ^{fl}		
	$CHCl_3$		Film		$CHCl_3$	Powder	Film
PM	340	501	340	499	15	14	13
PF0	380	505	384	505	12	12	16
PF2	391	502	398	511	24	25	16
PF4	382	506	484, 521	653	23	12	23

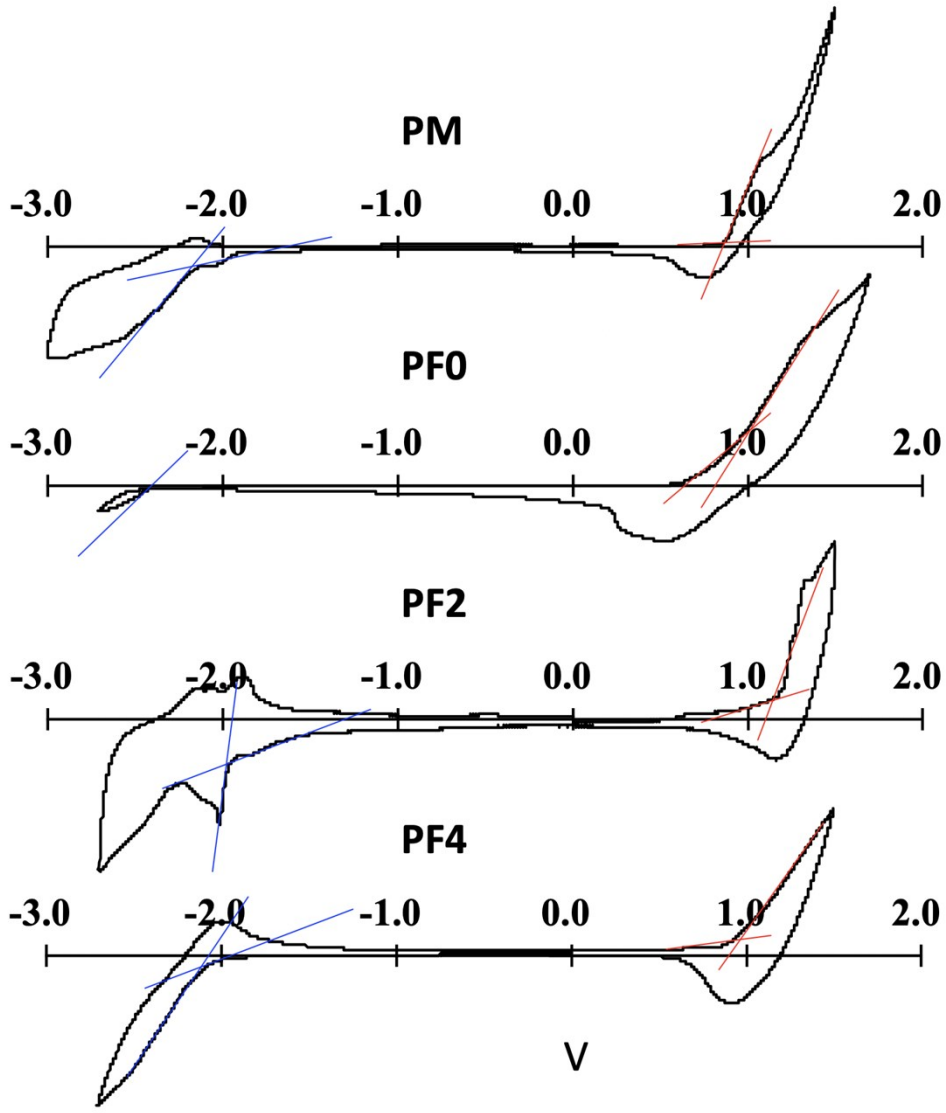


Fig. S5 CV of the polymer films.

Table S3. HOMO and LUMO levels of the polymers

Polymers	HOMO	LUMO	Eg
PM	5.26	2.15	3.11
PF0	5.37	1.85	3.52
PF2	5.62	2.40	3.22
PF4	5.35	2.31	3.04

$I_p(\text{LUMO}) = -(E_{onset,red} + 4.38)$ (eV)

$E_a(\text{LUMO}) = -(E_{onset,red} + 4.38)$ (eV)

$E_g = (E_a(\text{LUMO})-I_p(\text{HOMO}))$ (eV)

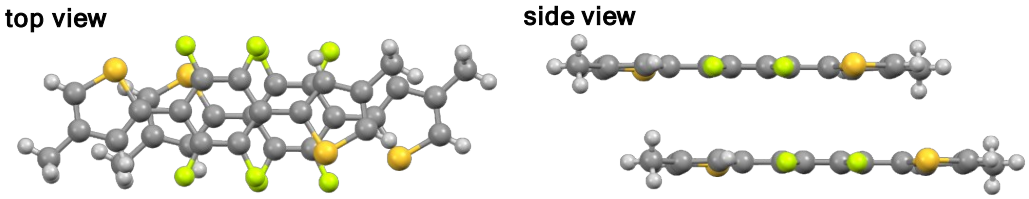


Fig. S6 Crystal structure (packing) of **B1PF4**.

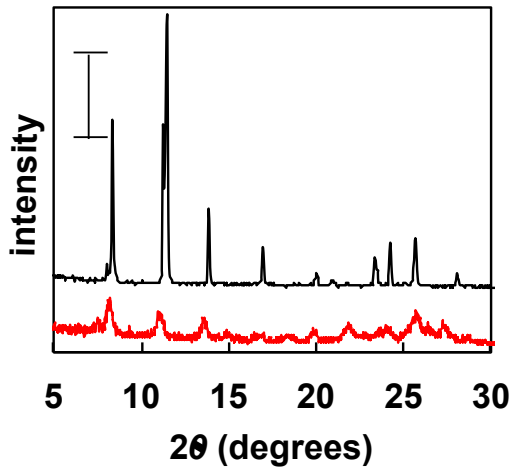


Fig. S7 XRD of **BT1PF4** crystal and powder.

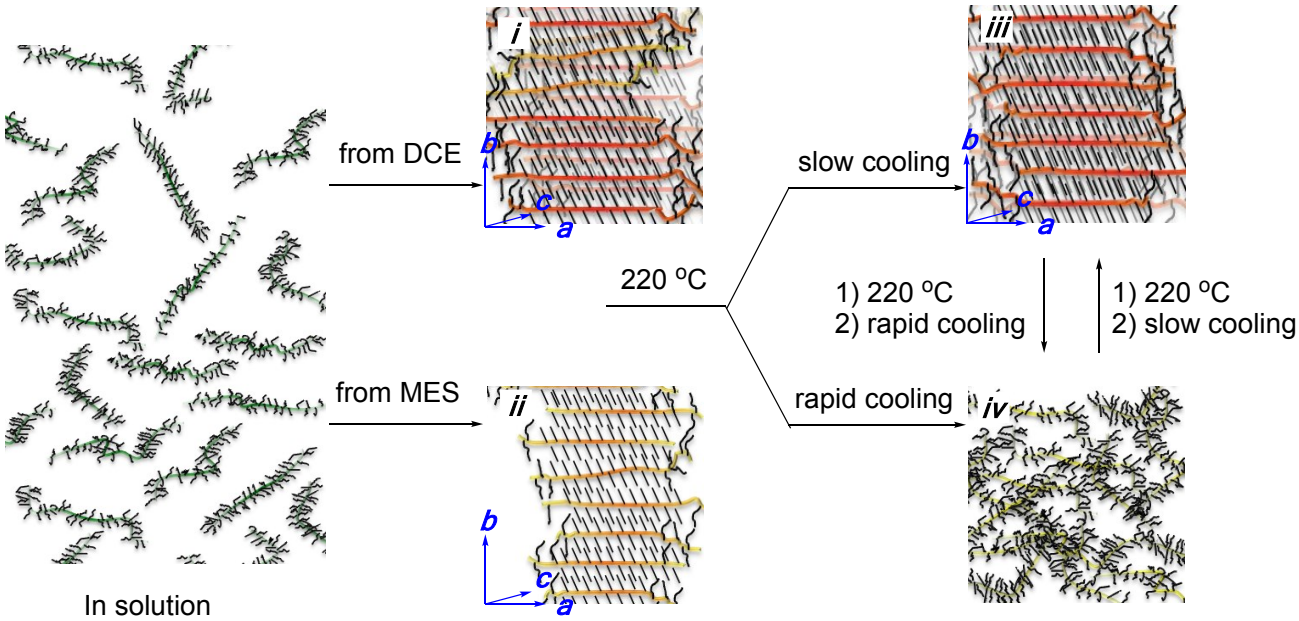


Fig. S8 Schematic illustration of plausible macrostructure of **PF4** chain. In solution and on macrostructure of ***Film***$_{DCE}$, ***Film***$_{MES}$, film after annealing then slow cooling, film after annealing then rapid cooling.