



Title	Facile one-pot synthesis of rod-coil bio-block copolymers and uncovering their role in forming the efficient stretchable touch-responsive light emitting diodes
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Supporting Information

Facile One-Pot Synthesis of Rod-Coil Bio-Block Copolymers and Uncovering Their Role in Forming the Efficient Stretchable Touch-Responsive Light Emitting Diodes

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Supplementary Materials

- **Figure S1.** The ^1H NMR spectrum of crude aliquots withdrawn from the reaction system for monitoring the conversion of δ -DL to form I-PDL.
- **Figure S2.** Polymerization time versus δ -DL conversion and $\text{Ln}([M]_0/[M]_t)$.
- **Figure S3.** The plots of $M_{n,\text{SEC}}$ and \bar{D} versus δ -DL conversion for indicating a controlled polymerization by TBD.
- **Figure S4.** The ^1H NMR spectrum of crude aliquots withdrawn from the reaction system for monitoring the conversion of EGE and the formation of alternative copolymer.
- **Figure S5.** Evolution of SEC traces after Suzuki–Miyaura catalyst transfer polymerization (SCTP) (a) $\text{PF}_{18}\text{-}b\text{-(PA-}alt\text{-EGE)}_{20}$ and (b) $\text{PF}_{18}\text{-}b\text{-(AA-}alt\text{-EGE)}_{20}$.
- **Figure S6.** The ^1H NMR spectrum of the resultant $\text{PF}_{18}\text{-}b\text{-(PA-}alt\text{-EGE)}_{20}$ via smart synthesis isolated from the mixture by precipitation in cold toluene.
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- **Figure S8.** The ^1H NMR spectrum of the resultant $\text{PF}_{18}\text{-}b\text{-PDL}_{13}$ via smart synthesis isolated from the mixture by precipitation in cold acetone (in CDCl_3).
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- **Figure S11.** The ^{13}C NMR with peak designation of the polymerization of $\text{PF}_{18}\text{-}b\text{-PDL}_{36}$ via smart synthesis (in CDCl_3).
- **Figure S12.** Representative COSY NMR spectrum of $\text{PF}_{18}\text{-}b\text{-PDL}_{36}$ in CDCl_3 .
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- **Figure S16.** 2nd heating DSC thermograms of studied polymers measured with a temperature ramping rate of 10 °C min⁻¹ under nitrogen atmosphere.
- **Figure S17.** Synchrotron GIWAXS data of thin films of block copolymers measured with SDD = 208.3 mm at room temperature using a synchrotron X-ray beam ($\lambda = 0.12359$ nm).
- **Figure S18.** AFM phase images of the thin films of block copolymers.
- **Figure S19.** AFM height images of the thin films of block copolymers.
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- **Figure S22.** Energy levels of the studied materials.
- **Figure S23.** Voltage dependent luminance and current properties of block copolymers.
- **Figure S24.** OM images of the studied polymers of as-cast film at the strain of 0%, 50%, 100%, 150% and 200%.
- **Figure S25.** Photographs of LED device at strains of 0%, 50%, 100%, 150%, and 200% respectively.
- **Figure S26.** Luminance-stretching cycle characteristics of the touch-responsive LEDs after repetitive stretching cycles at (a) 20% and (b) 40% strain.
- **Table S1.** Smart synthesis of conjugated block copolymer under organocatalysts using difunctional initiator.
- **Table S2.** Smart synthesis of PF-based conjugated block copolymer under TBD using difunctional initiator.
- **Table S3.** Thermal properties of studied polymers.
- **Table S4.** Optical properties of studied polymers.
- **Table S5.** The time-resolved PL spectra of PF₁₈-*b*-PDL_n thin films of as-cast state.

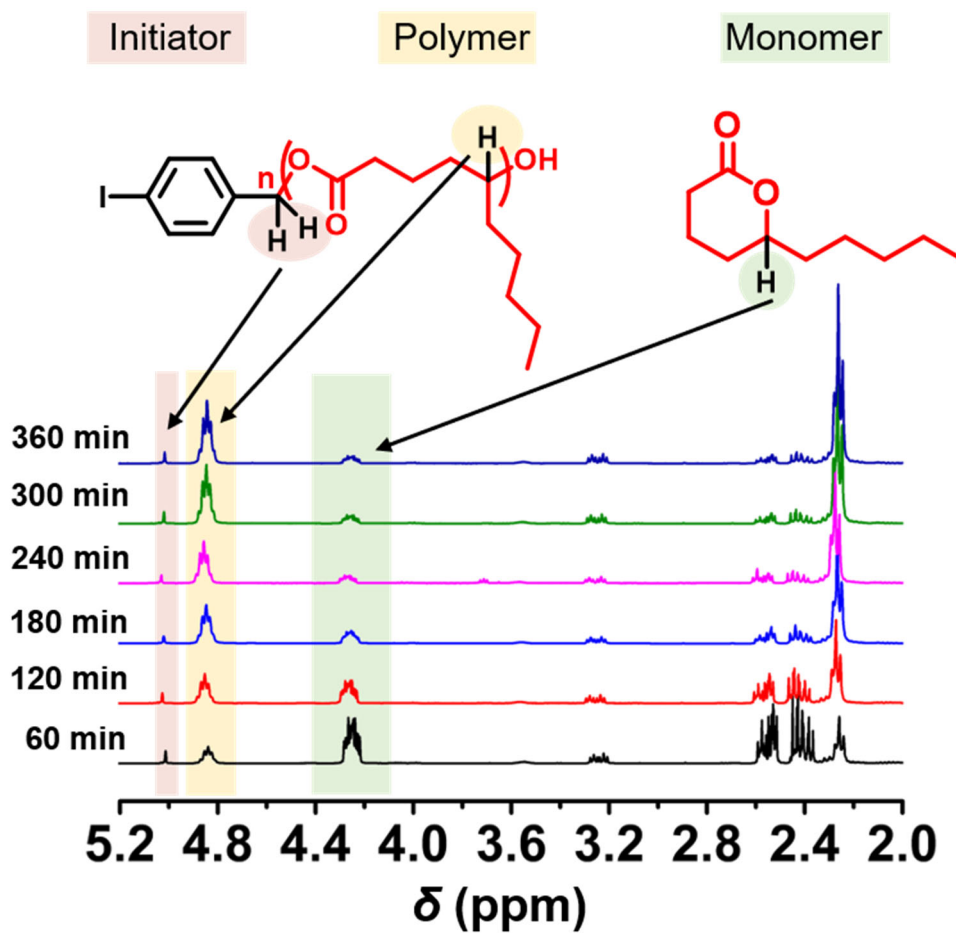


Figure S1. The ¹H NMR spectrum of crude aliquots withdrawn from the reaction system for monitoring the conversion of δ -DL to form I-PDL (The ROP is conducted in bulk at 25°C, [TBD]:[4-iodobenzyl alcohol]:[δ -DL] = 1 : 1 : 60).

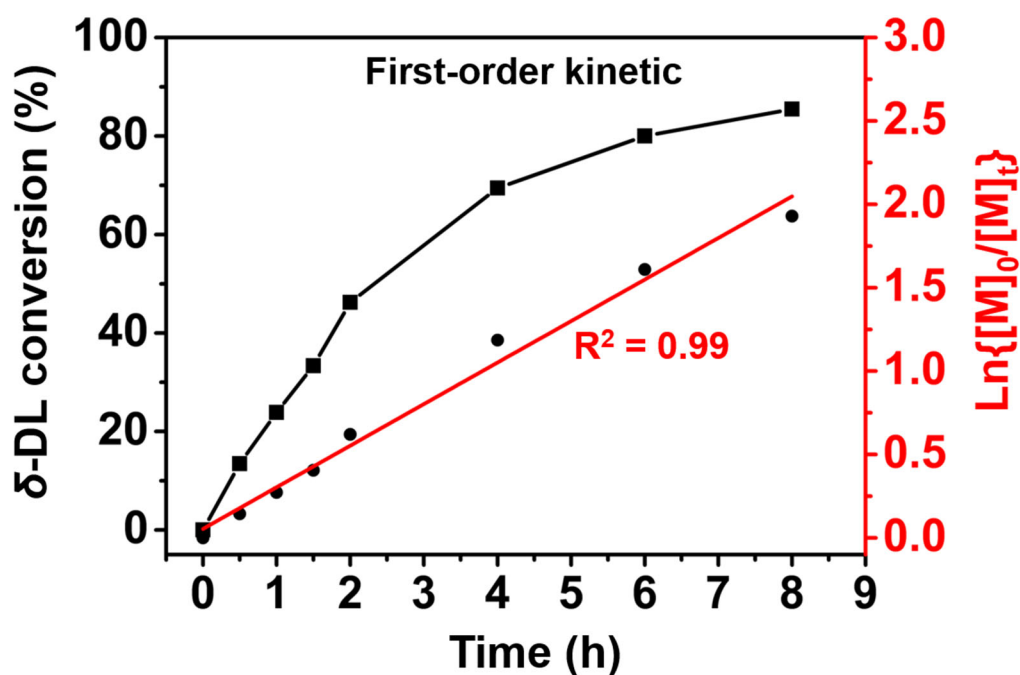


Figure S2. Polymerization time versus δ -DL conversion and $\ln\{[M]_0/[M]_t\}$ (The polymerization is conducted in bulk at 25°C, [TBD]:[4-iodobenzyl alcohol]₀:[δ -DL]₀ = 1 : 1 : 60).

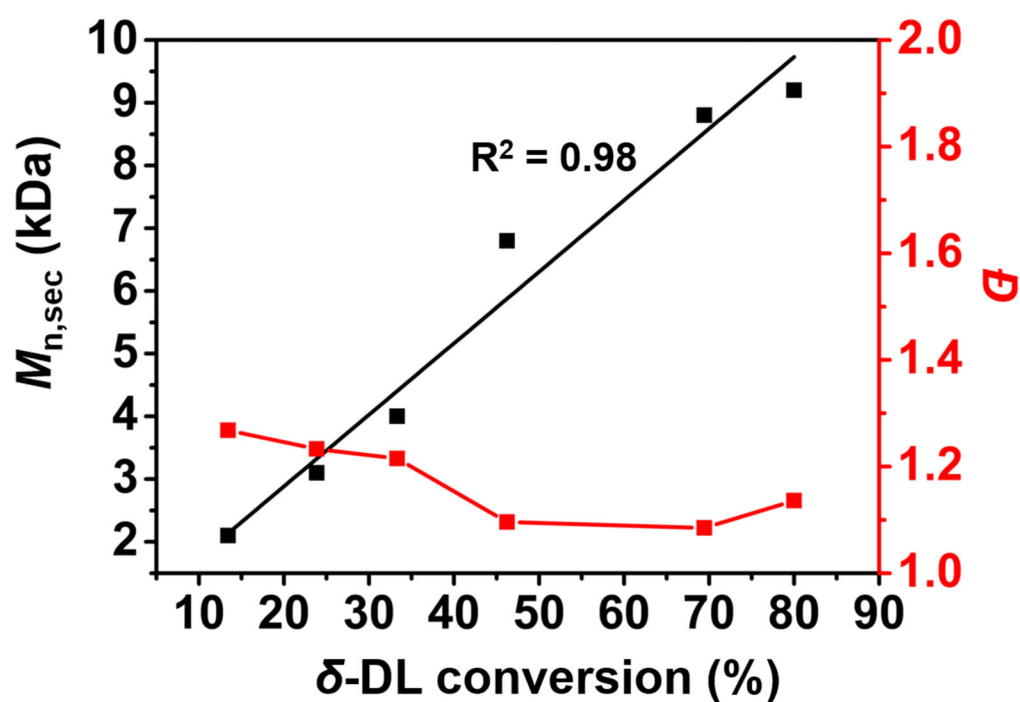


Figure S3. The plots of $M_{n,SEC}$ and D versus δ -DL conversion for indicating a controlled polymerization by TBD (The polymerization is conducted in bulk at 25°C, [TBD]:[4-iodobenzyl alcohol]₀:[δ -DL]₀ = 1 : 1 : 60).

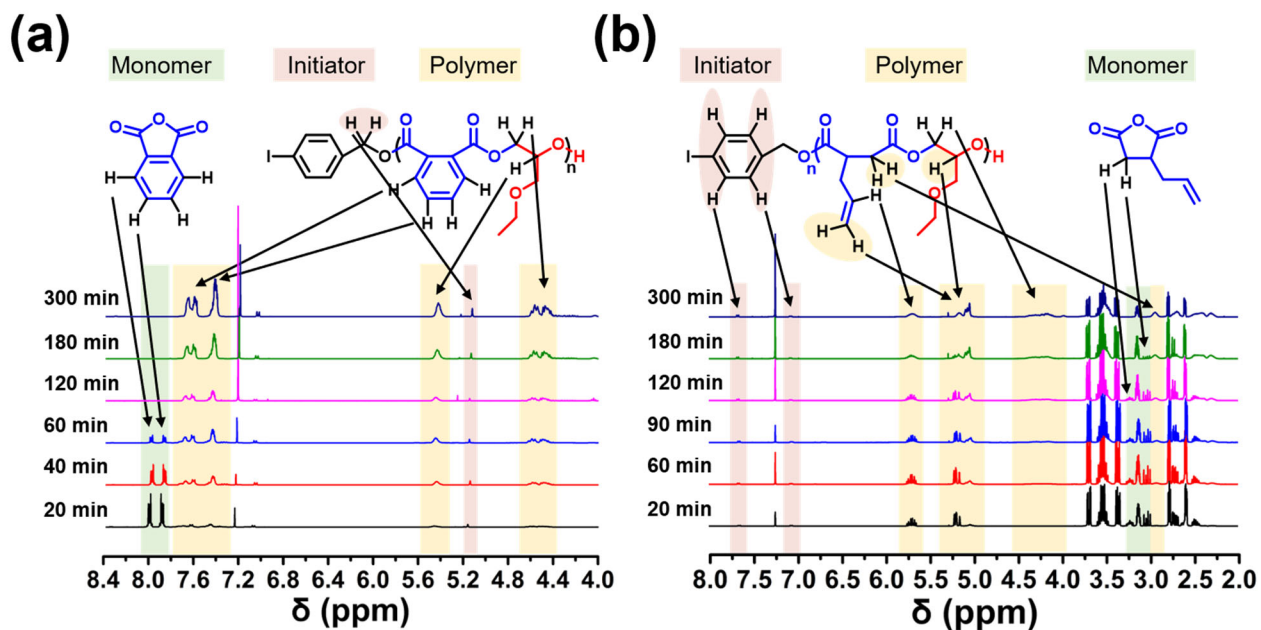


Figure S4. The ¹H NMR spectrum of crude aliquots withdrawn from the reaction system for monitoring the conversion of EGE and the formation of alternative copolymer (a) PA-*alt*-EGE and (b) AA-*alt*-EGE.

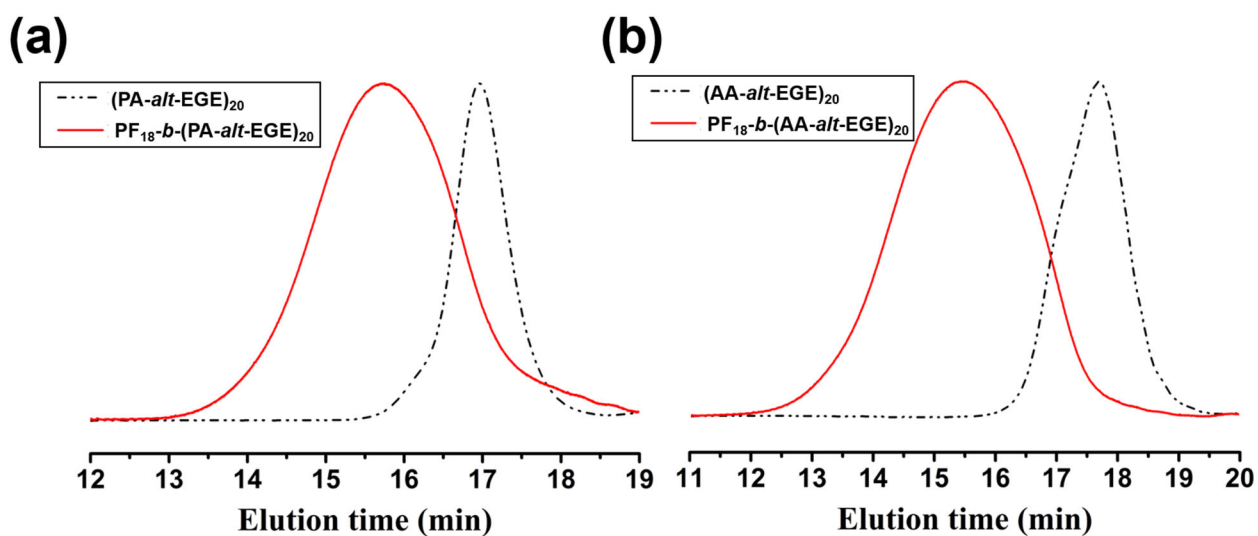


Figure S5. Evolution of SEC traces after Suzuki–Miyaura catalyst transfer polymerization (SCTP) (a) PF₁₈-*b*-(PA-*alt*-EGE)₂₀ and (b) PF₁₈-*b*-(AA-*alt*-EGE)₂₀.

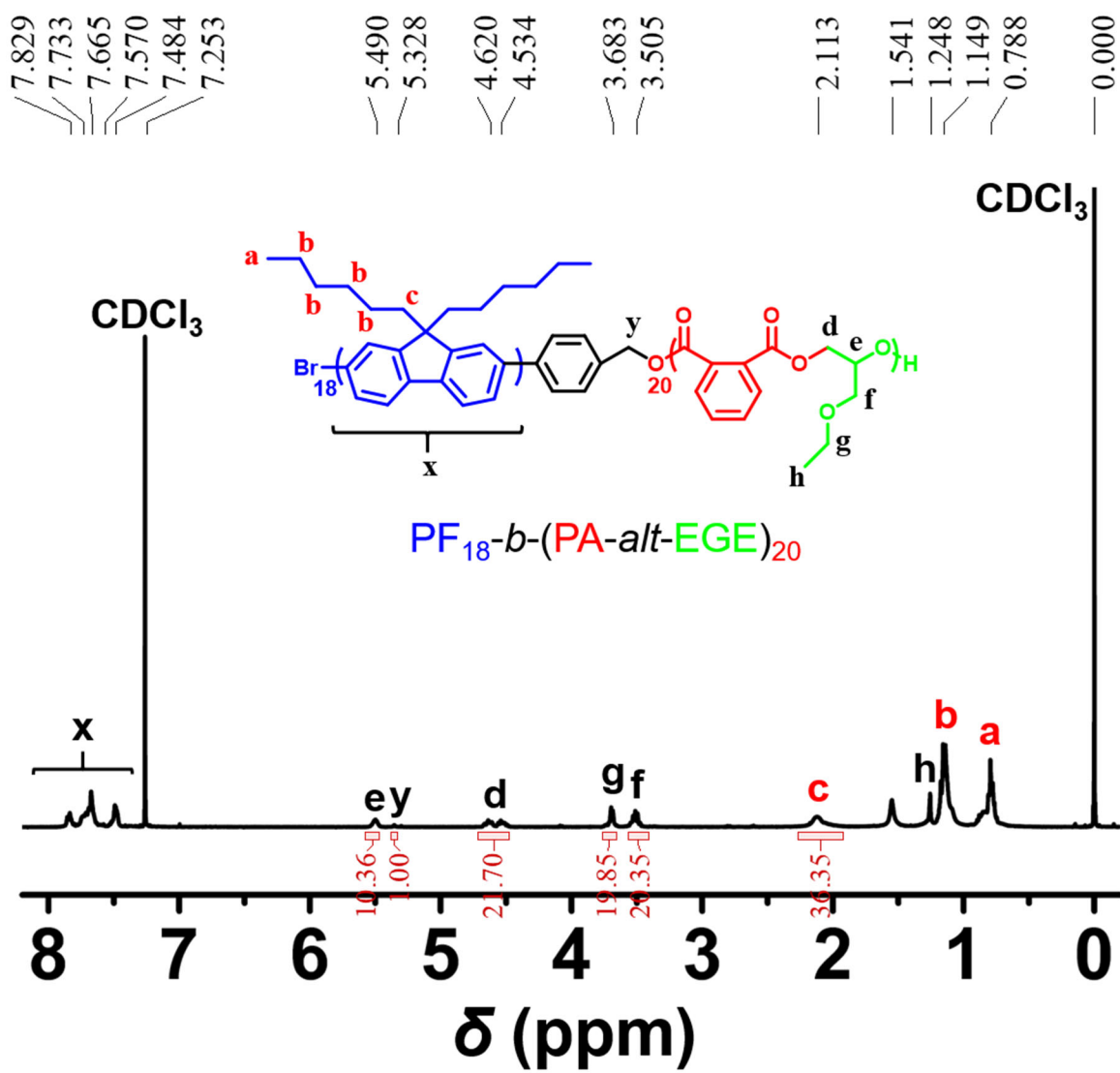


Figure S6. The ^1H NMR spectrum of the resultant $\text{PF}_{18}\text{-}b\text{-(PA-alt-EGE)}_{20}$ via smart synthesis isolated from the mixture by precipitation in cold toluene.

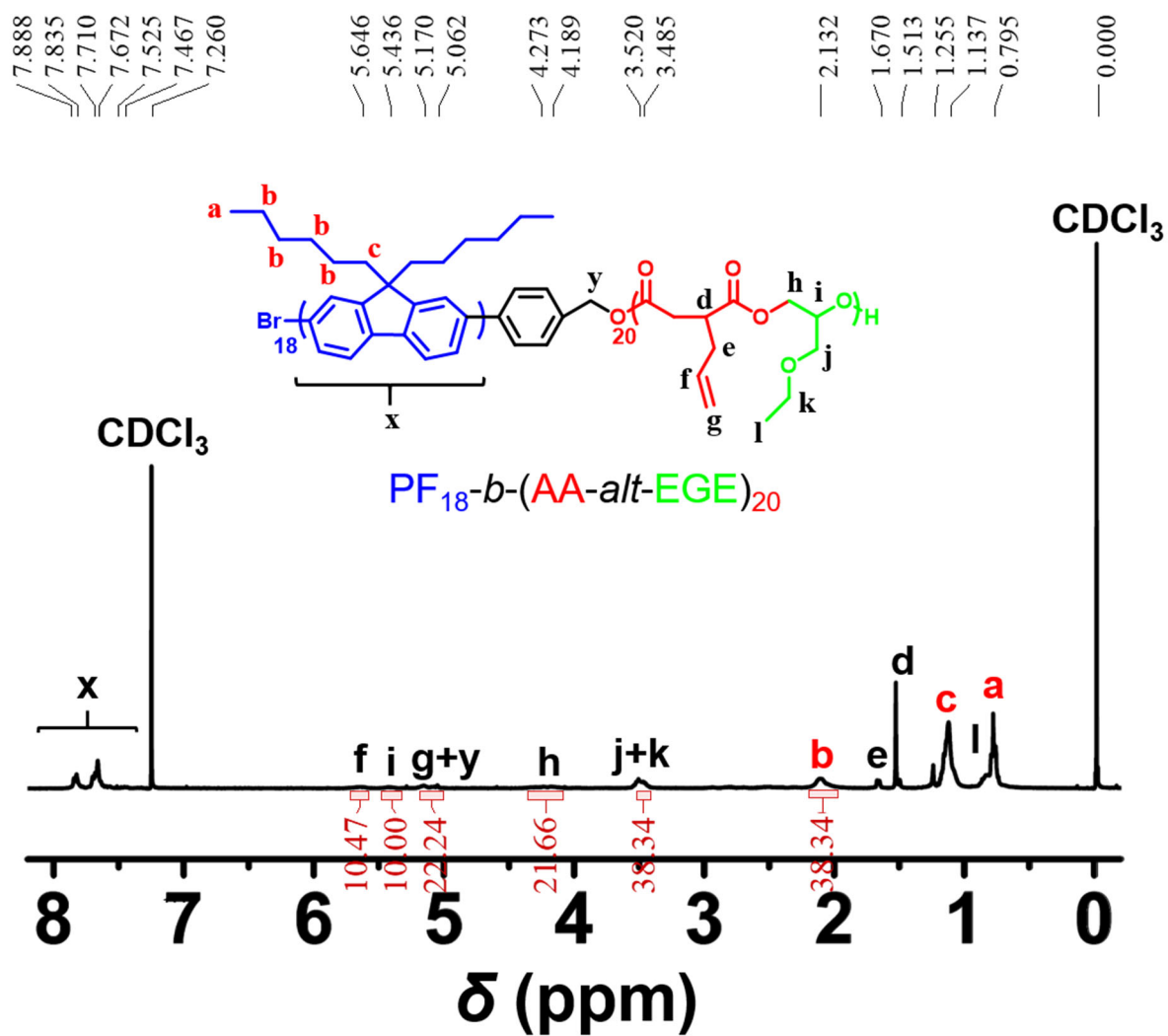


Figure S7. The ^1H NMR spectrum of the resultant $\text{PF}_{18}\text{-}b\text{-(AA-}i\text{alt-EGE)}_{20}$ via smart synthesis isolated from the mixture by precipitation in cold toluene.

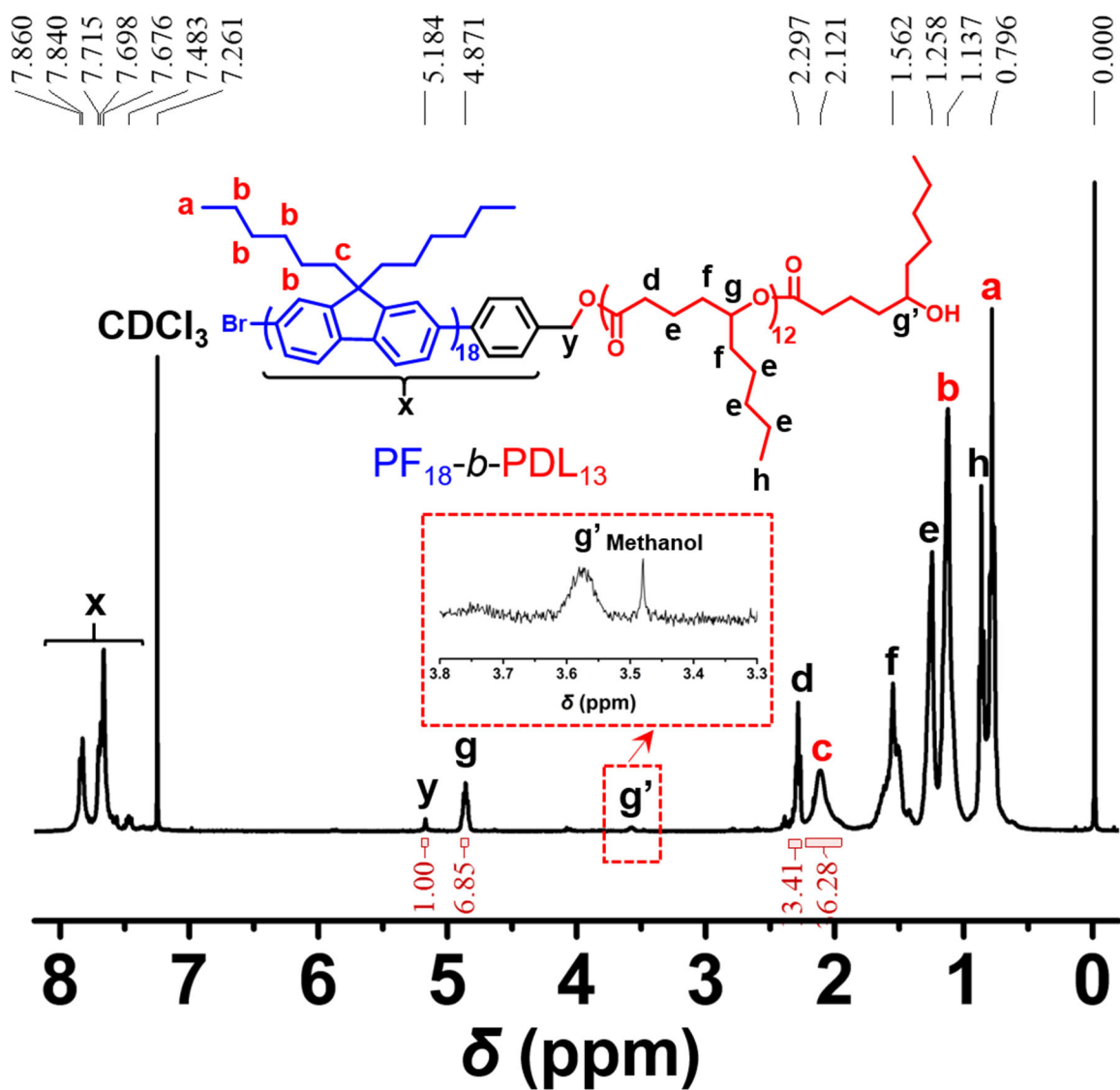


Figure S8. The ^1H NMR spectrum of the resultant $\text{PF}_{18}\text{-}b\text{-PDL}_{13}$ via smart synthesis isolated from the mixture by precipitation in cold acetone (in CDCl_3).

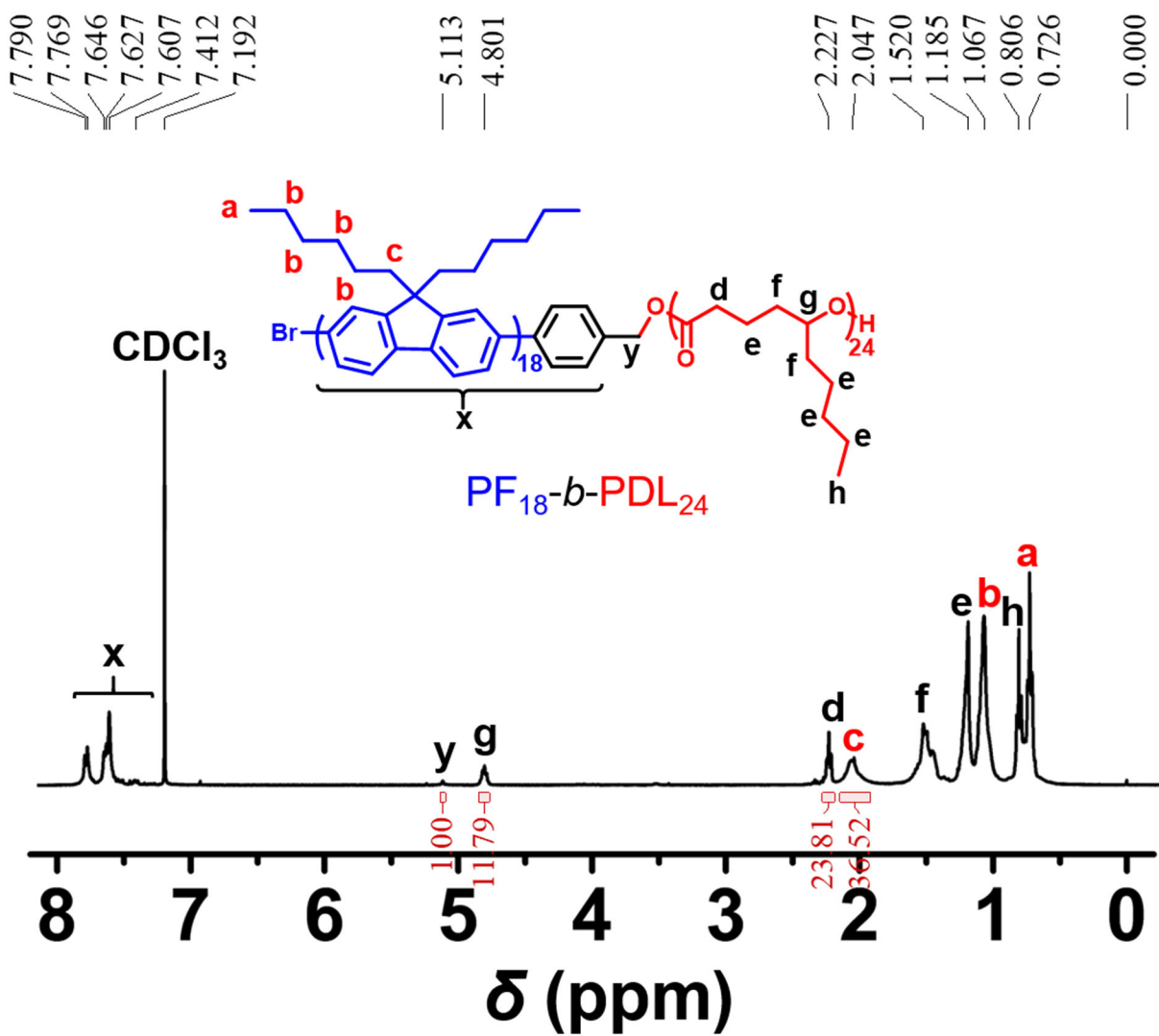


Figure S9. The ^1H NMR spectrum of the resultant $\text{PF}_{18}\text{-}b\text{-PDL}_{24}$ via smart synthesis isolated from the mixture by precipitation in cold acetone (in CDCl_3).

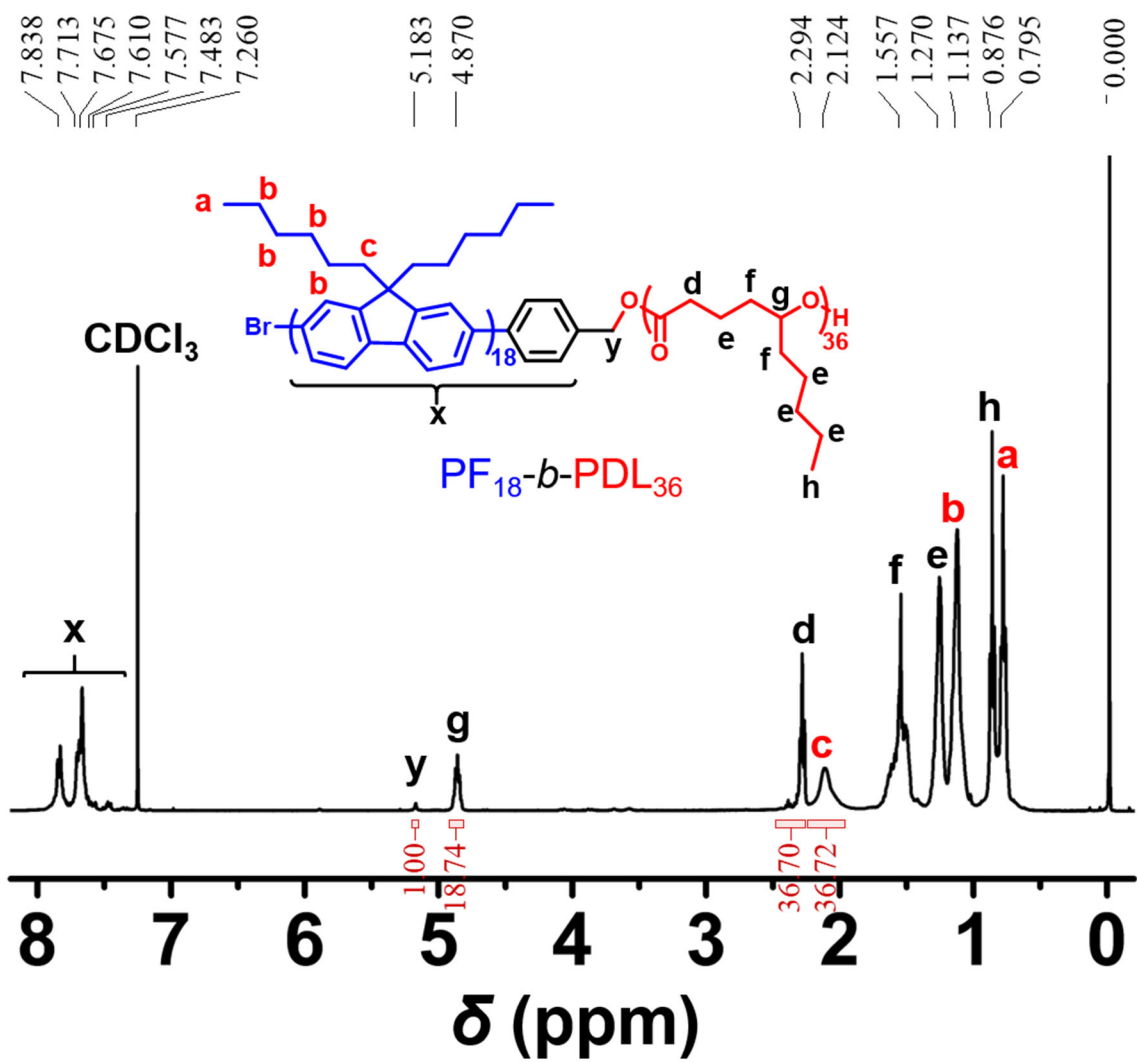


Figure S10. The ^1H NMR spectrum of the resultant $\text{PF}_{18}\text{-}b\text{-PDL}_{36}$ via smart synthesis isolated from the mixture by precipitation in cold acetone (in CDCl_3).

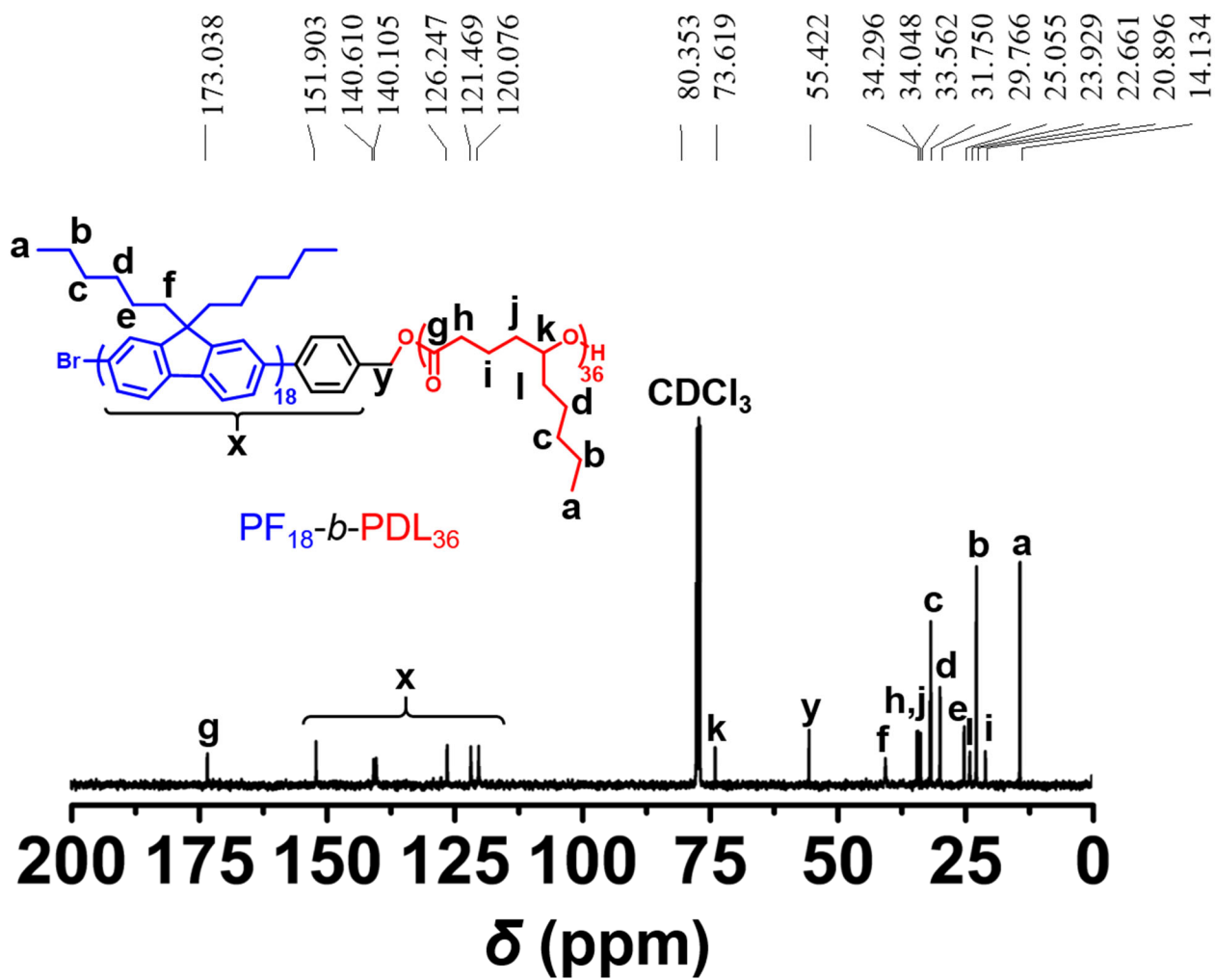


Figure 11. The ^{13}C NMR with peak designation of the polymerization of $\text{PF}_{18}\text{-}b\text{-PDL}_{36}$ via smart synthesis (in CDCl_3).

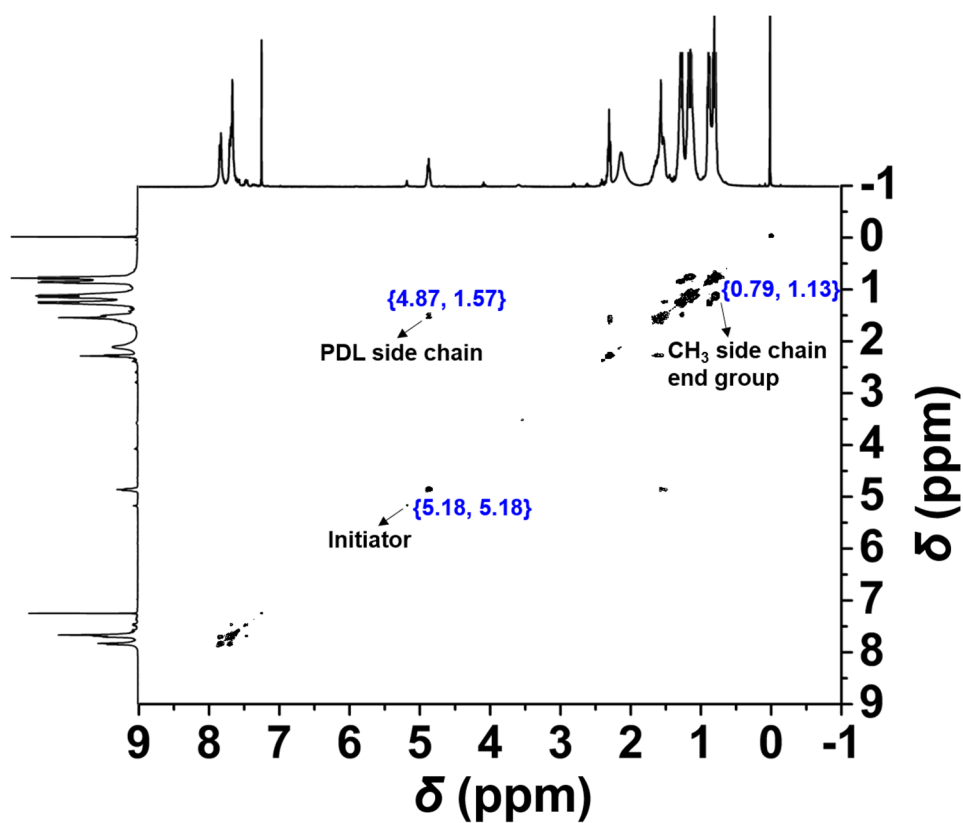


Figure S12. Representative COSY NMR spectrum of PF₁₈-*b*-PDL₃₆ in CDCl₃.

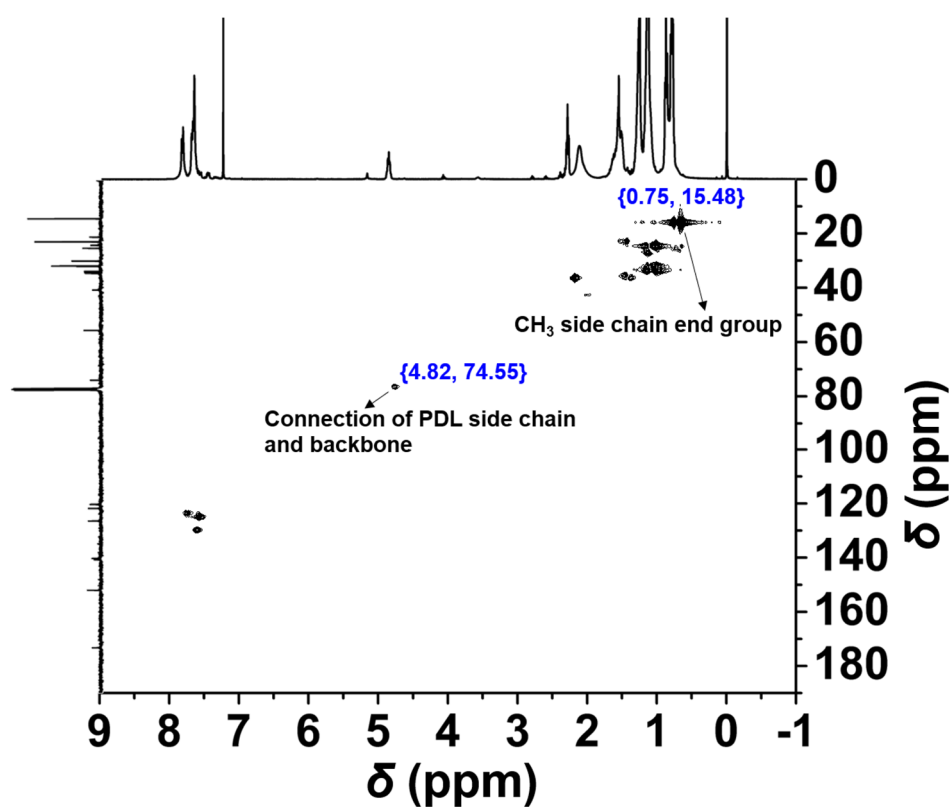


Figure S13. Representative HMQC NMR spectrum of PF₁₈-*b*-PDL₃₆ in CDCl₃.

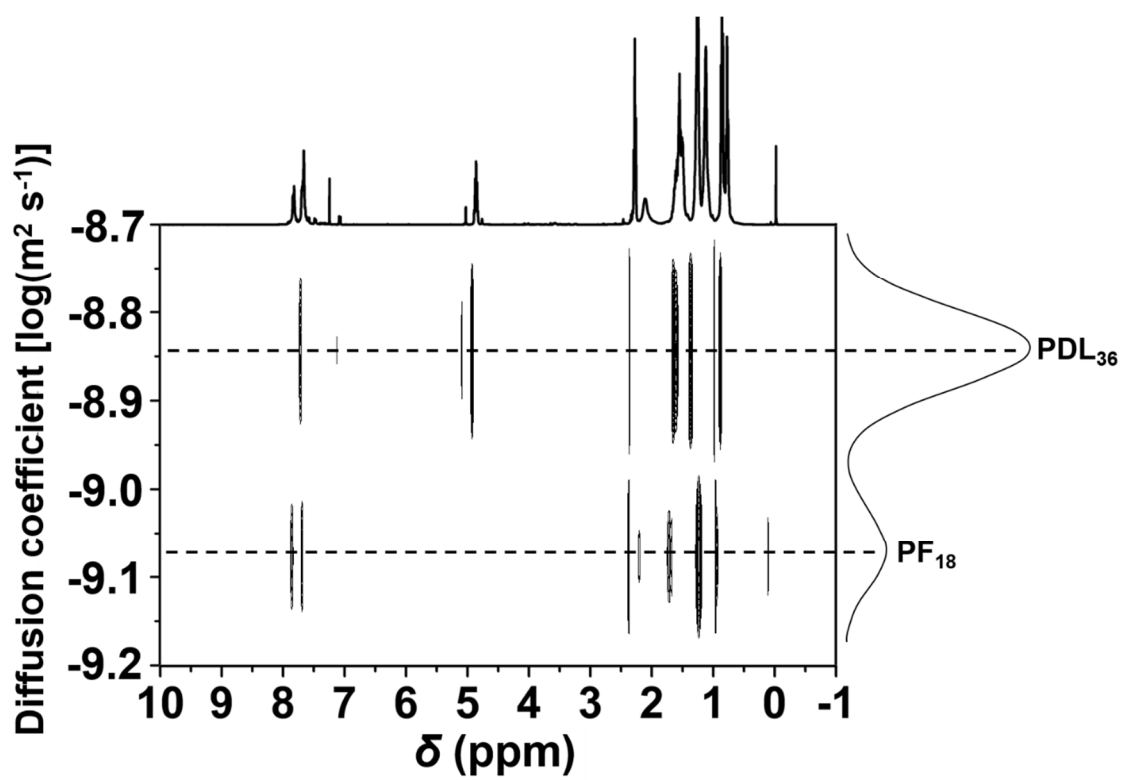


Figure S14. DOSY NMR spectrum of the polymer blend of PF₁₈ and PDL₃₆ in CDCl₃.

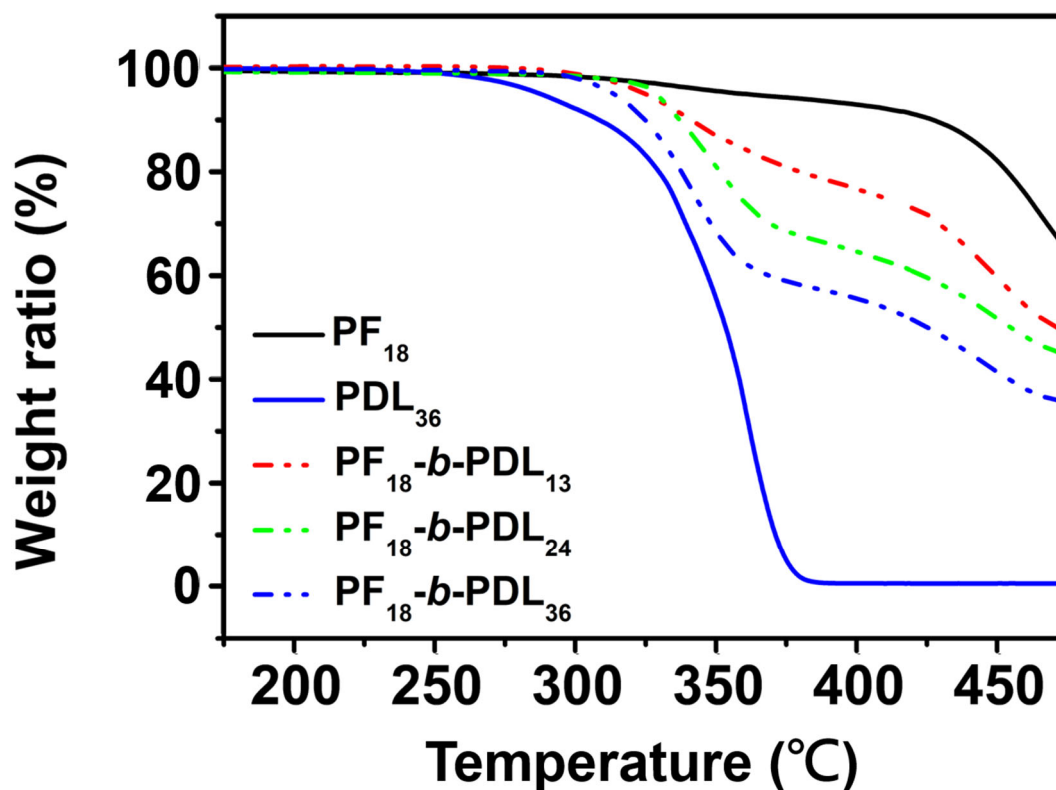


Figure S15. TGA curves of studied polymers measured with a temperature ramping rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere.

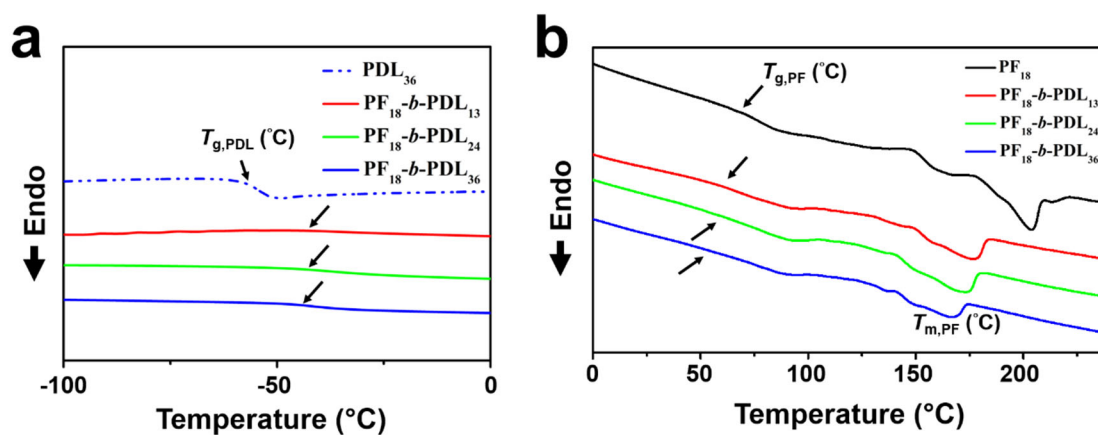


Figure S16. 2nd heating DSC thermograms of studied polymers measured with a temperature ramping rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere. The arrow from a and b show the expanded DSC curves for highlighting the T_g from PDL and PF block, respectively.

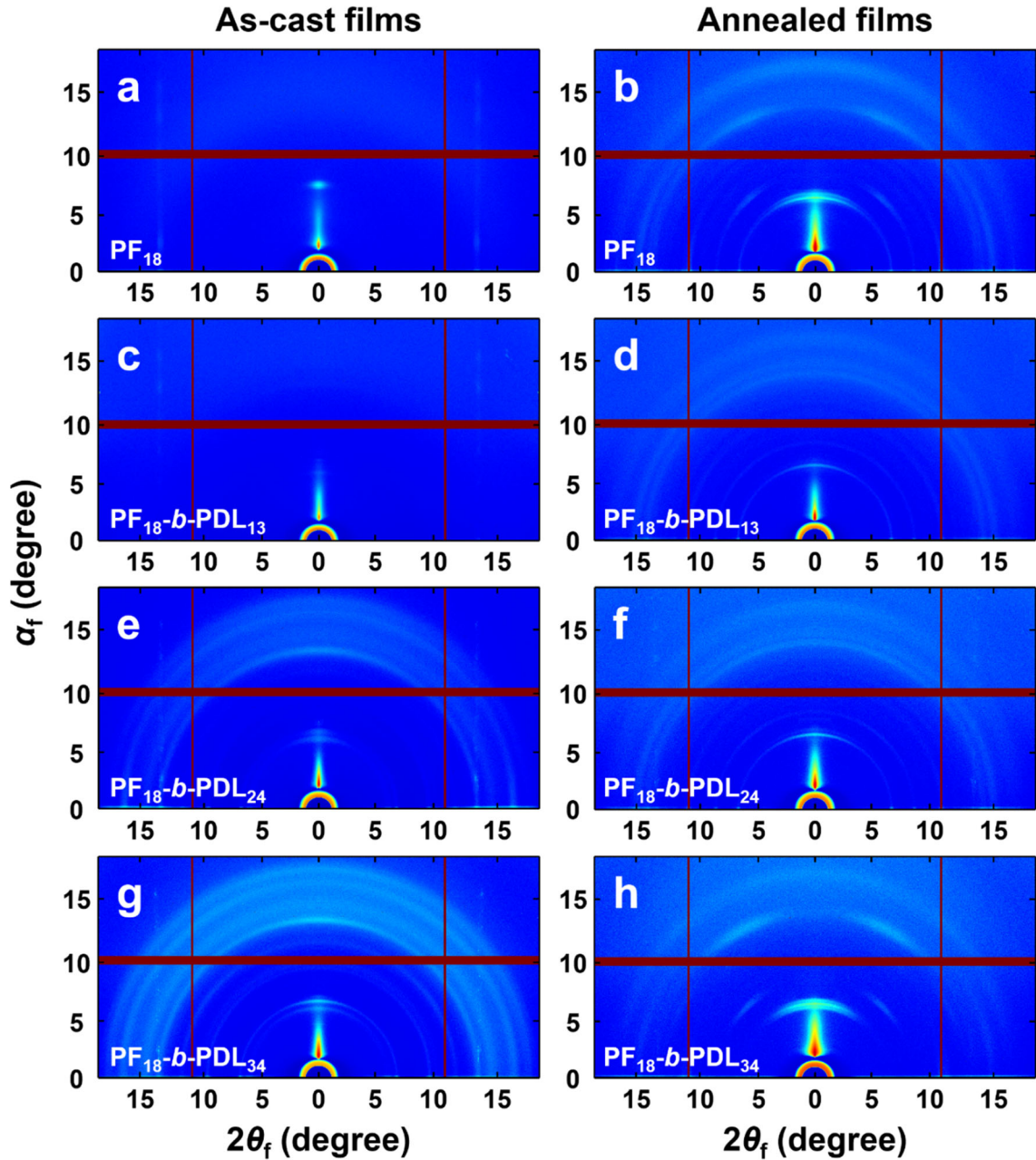


Figure S17. Synchrotron GIWAXS data of thin films of block copolymers measured with SDD = 208.3 mm at room temperature using a synchrotron X-ray beam ($\lambda = 0.12359$ nm). (a) PF₁₈ as-cast film ($\alpha_i = 0.144^\circ$). (b) PF₁₈ annealed film ($\alpha_i = 0.155^\circ$). (c) PF₁₈-*b*-PDL₁₃ as-cast film ($\alpha_i = 0.196^\circ$). (d) PF₁₈-*b*-PDL₁₃ annealed film ($\alpha_i = 0.155^\circ$). (e) PF₁₈-*b*-PDL₂₄ as-cast film ($\alpha_i = 0.134^\circ$). (f) PF₁₈-*b*-PDL₂₄ annealed film ($\alpha_i = 0.155^\circ$). (g) PF₁₈-*b*-PDL₃₄ as-cast film ($\alpha_i = 0.093^\circ$). (h) PF₁₈-*b*-PDL₃₄ annealed film ($\alpha_i = 0.165^\circ$).

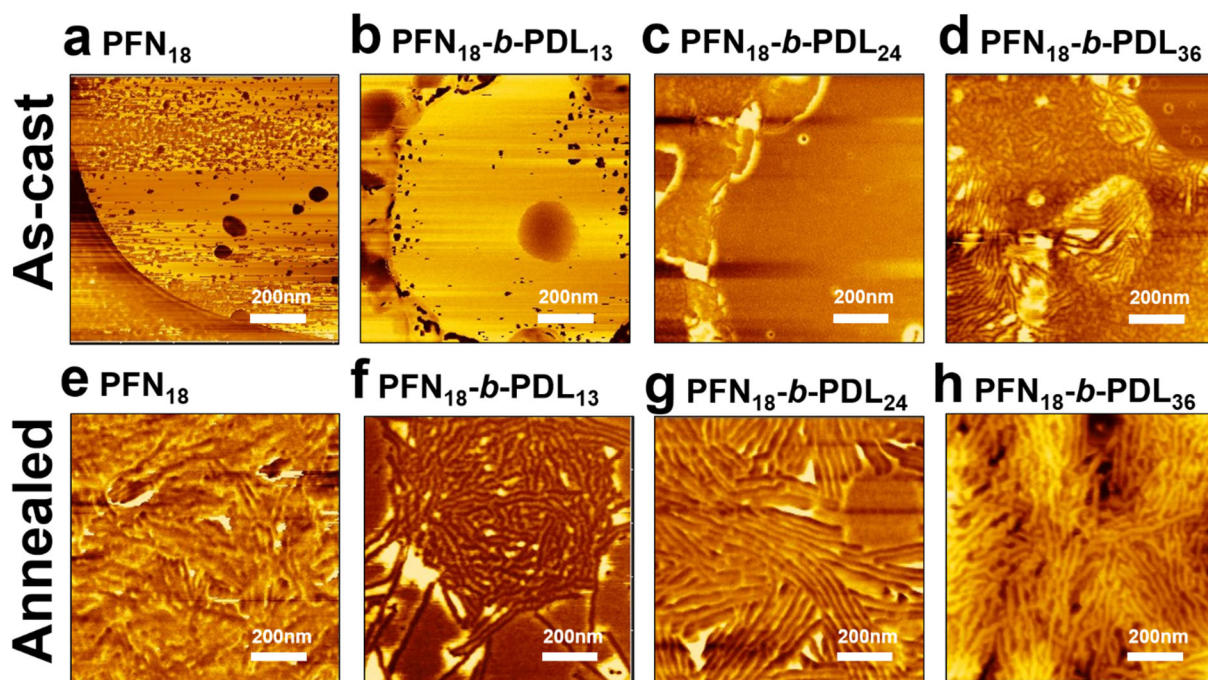


Figure S18. AFM phase images of the thin films of block copolymers. (a) PF₁₈ as-cast film. (b) PF₁₈-*b*-PDL₁₃ as-cast film. (c) PF₁₈-*b*-PDL₂₄ as-cast film. (d) PF₁₈-*b*-PDL₃₆ as-cast film. (e) PF₁₈ annealed film. (f) PF₁₈-*b*-PDL₁₃ annealed film. (g) PF₁₈-*b*-PDL₂₄ annealed film. (h) PF₁₈-*b*-PDL₃₆ annealed film.

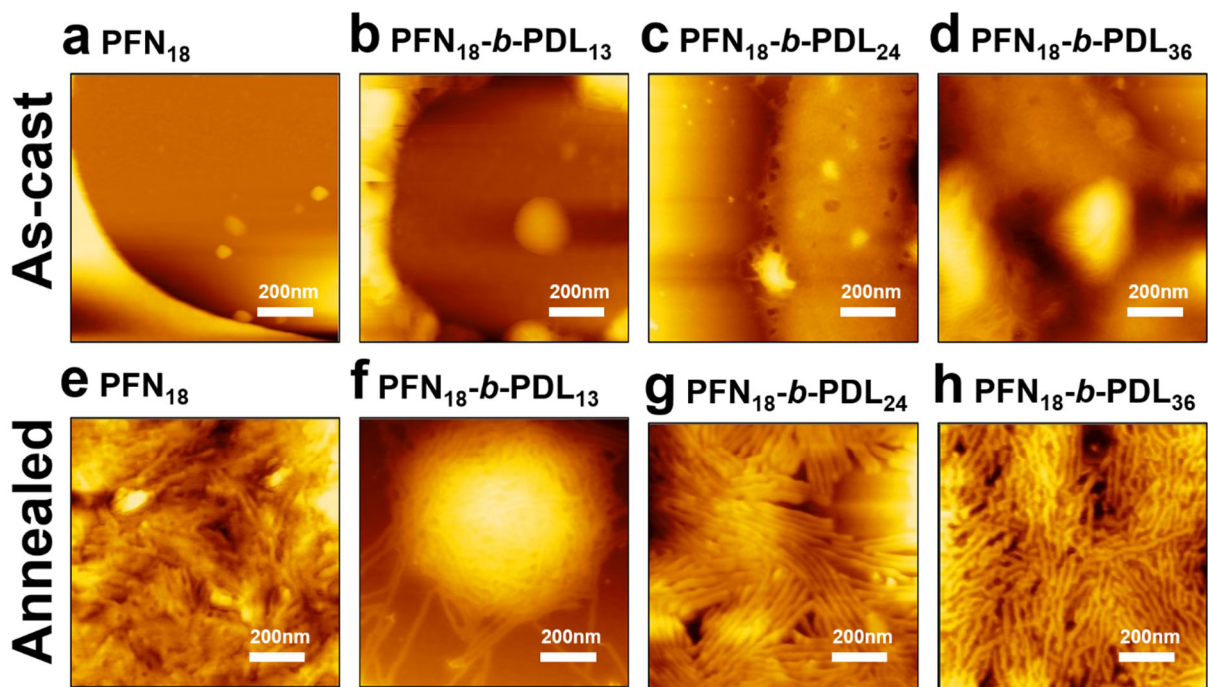


Figure S19. AFM height images of the thin films of block copolymers. (a) PF₁₈ as-cast film. (b) PF₁₈-*b*-PDL₁₃ as-cast film. (c) PF₁₈-*b*-PDL₂₄ as-cast film. (d) PF₁₈-*b*-PDL₃₆ as-cast film. (e) PF₁₈ annealed film. (f) PF₁₈-*b*-PDL₁₃ annealed film. (g) PF₁₈-*b*-PDL₂₄ annealed film. (h) PF₁₈-*b*-PDL₃₆ annealed film.

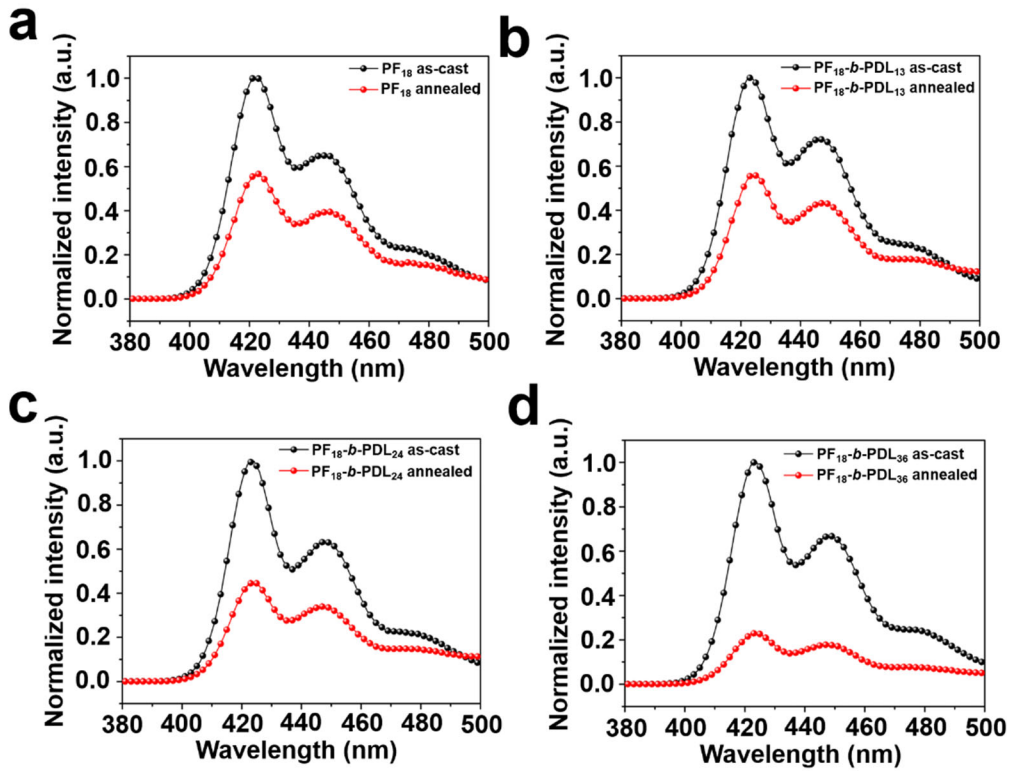


Figure S20. PL emission spectra of the as-cast and annealed film of block copolymers. (a) PF₁₈. (b) PF₁₈-*b*-PDL₁₃. (c) PF₁₈-*b*-PDL₂₄. (d) PF₁₈-*b*-PDL₃₆.

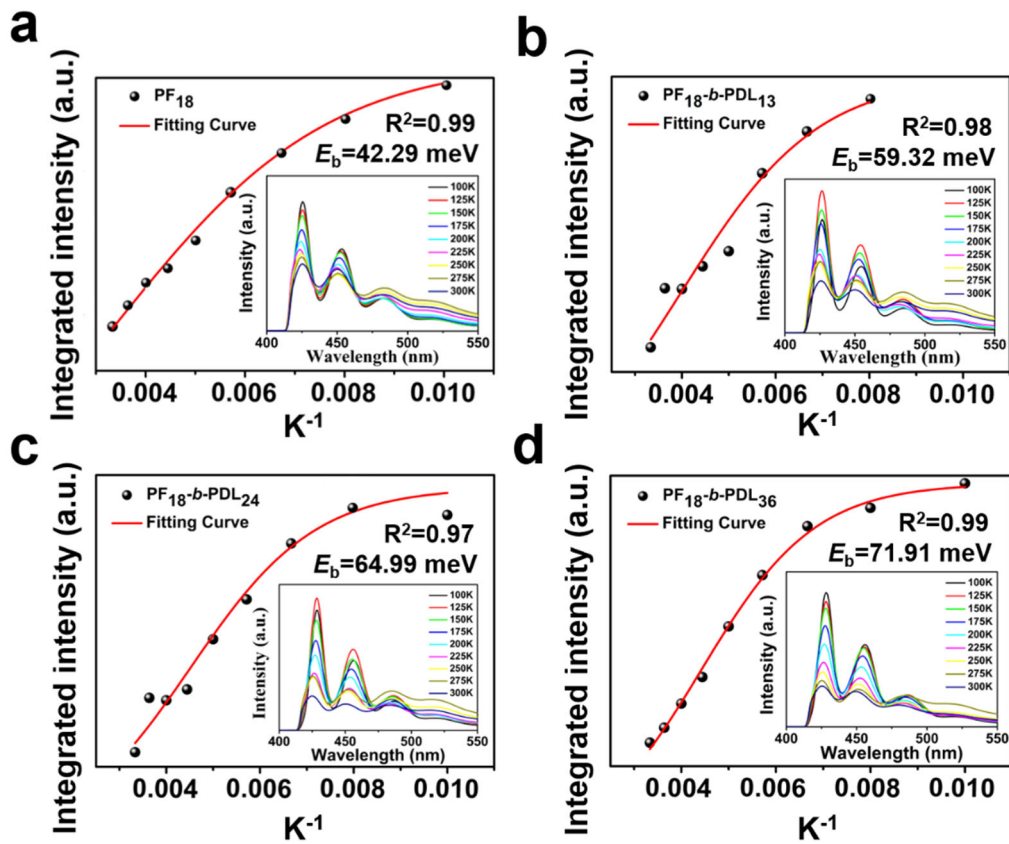


Figure S21. Correlation between integrated PL intensity and temperature. (a) PF₁₈. (b) PF₁₈-*b*-PDL₁₃. (c) PF₁₈-*b*-PDL₂₄. (d) PF₁₈-*b*-PDL₃₆. Exciton binding energy is extracted by fitting the curve.

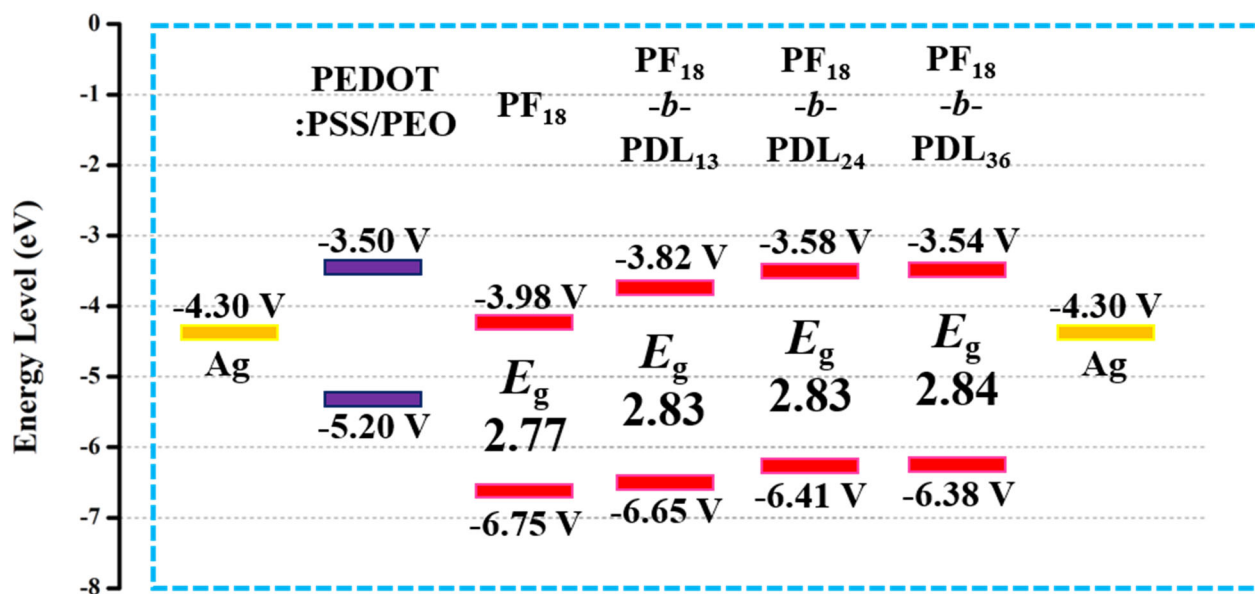


Figure S22. Energy levels of the studied materials.

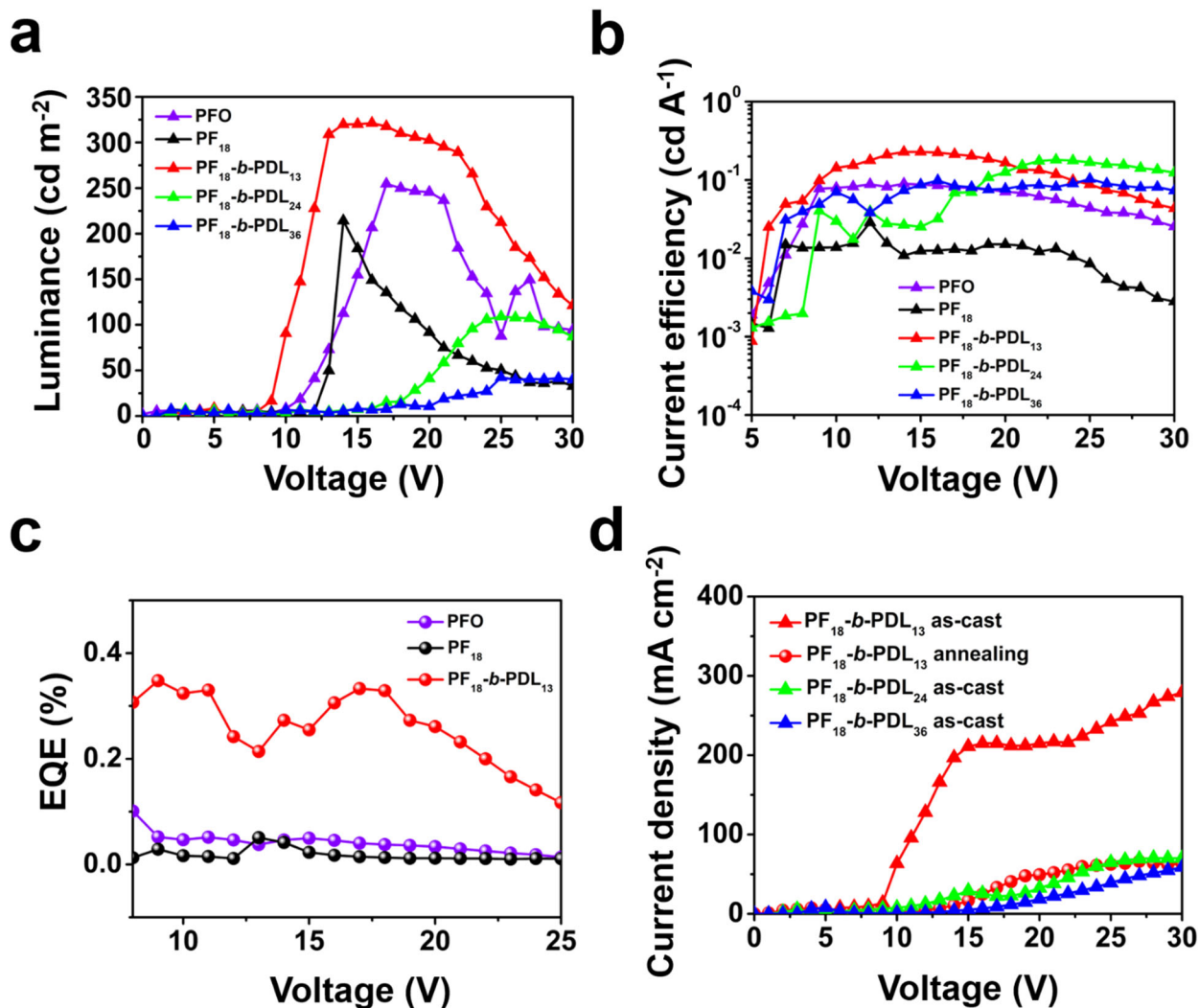


Figure S23. Voltage dependent luminance and current properties of block copolymers. (a) luminance-voltage plot characteristics of as-cast thin films of studied polymers. (b) current efficiency-voltage characteristics of as-cast thin films of studied polymers. (c) external quantum efficiency-voltage characteristics of annealed thin films of PFO, PF₁₈, and PF₁₈-*b*-PDL₁₃. (d) current density-voltage characteristics of PF₁₈-*b*-PDL_{*n*} block copolymers.

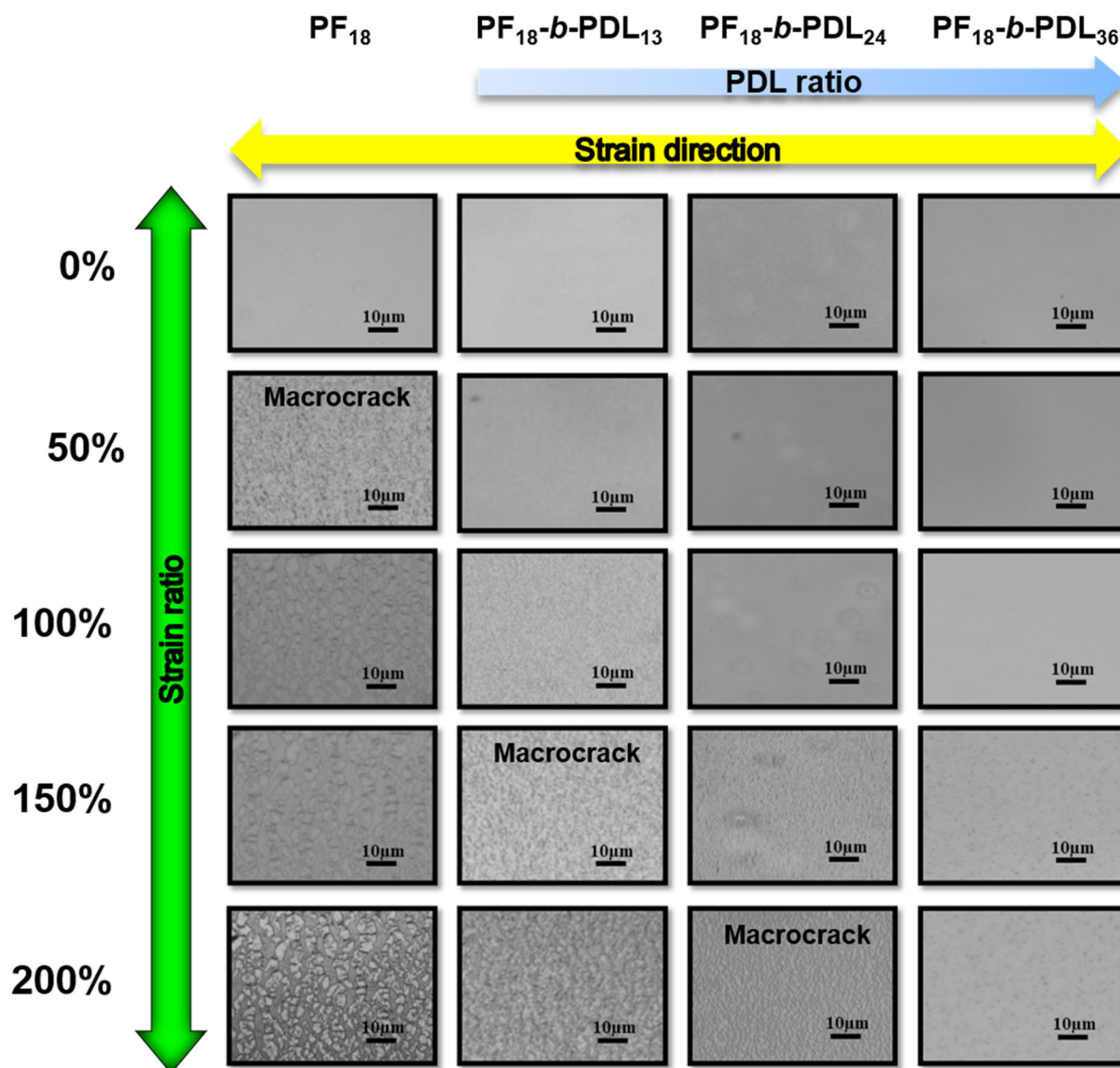


Figure S24. OM images of the studied polymers of as-cast film at the strain of 0%, 50%, 100%, 150% and 200%.

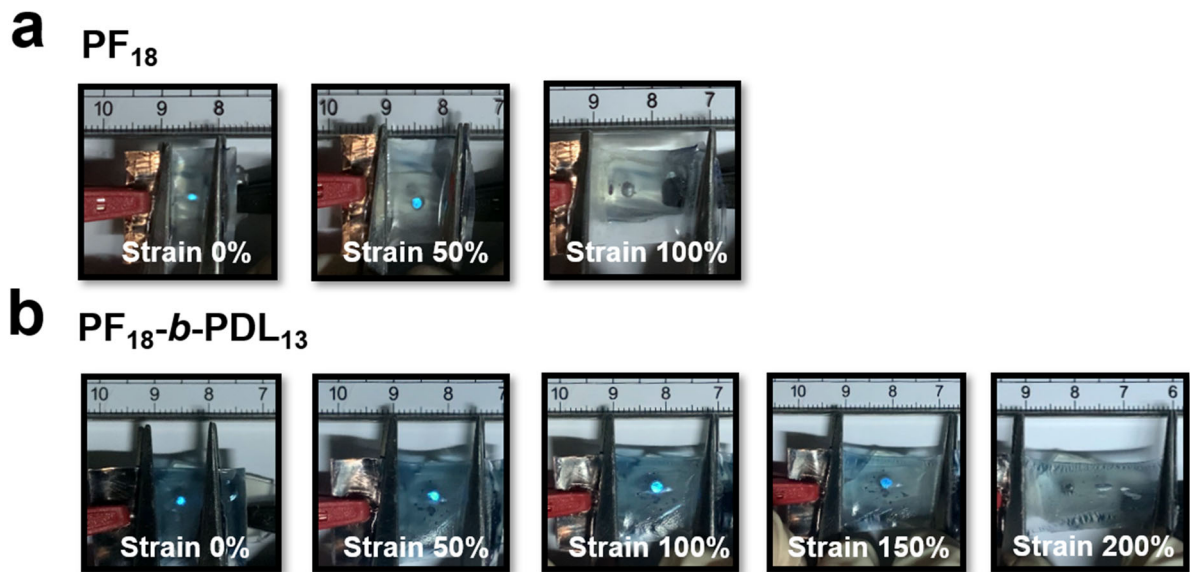


Figure S25. Photographs of LED device at strains of 0, 50, 100, 150%, and 200% respectively. (a) PF₁₈ (b) PF₁₈-*b*-PDL₁₃.

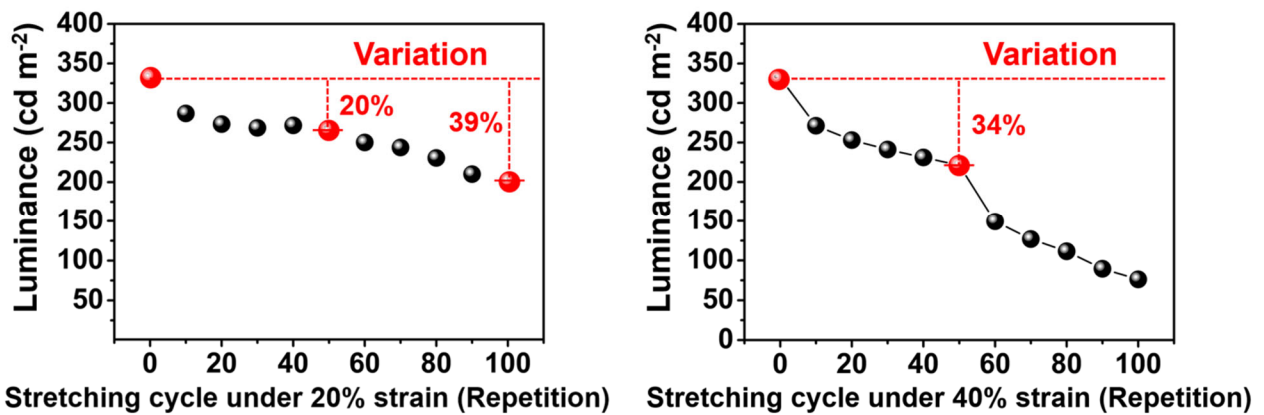


Figure S26. Luminance-stretching cycle characteristics of the touch-responsive LEDs after repetitive stretching cycles at (a) 20% and (b) 40% strain.

Table S1. Smart synthesis of PF-based conjugated block copolymer under TBD using difunctional initiator.

Run	Sample	[M] _{ROP} : [M] _{HexFL} : [Initiator] ₀ : [TBD] _{ROP}	Time (min)	T (°C) [ROP, SCP]	Conv. (%) (ROP)	Conv. (%) (HexFL)	$M_{n,NMR}^b$ (g mol ⁻¹)	$M_{n,SEC}^c$ (g mol ⁻¹)	\mathcal{D}^c	Yield (%)
1	PF ₁₈	0:18:1:0	10	-10	-	>99	6,300	11,000	1.327	82.1
2	PDL _{13, TBD}	60:0:1:1	30	rt	23.16	-	2,300	3,100	1.221	53.8
3	PDL _{24, TBD}	60:0:1:1	90	rt	39.06	-	3,900	5,000	1.099	75.2
4	PDL _{36, TBD}	60:0:1:1	120	rt	59.38	-	6,000	8,800	1.128	80.3
5	PF ₁₈ - <i>b</i> -PDL _{13, TBD} ^a	0:18:1:1	10	-10	-	>99	8,500	14,300	1.393	68.3
6	PF ₁₈ - <i>b</i> -PDL _{24, TBD} ^a	0:18:1:1	10	-10	-	>99	10,500	16,200	1.303	70.2
7	PF ₁₈ - <i>b</i> -PDL _{36, TBD} ^a	0:18:1:1	10	-10	-	>99	12,500	20,000	1.353	63.1
8	PF ₁₈ - <i>b</i> -PDL _{13, TBD}	60:18:1:1	40	rt, -10	22.47	>99	7,400	14,600	1.233	67.5
9	PF ₁₈ - <i>b</i> -PDL _{24, TBD}	60:18:1:1	100	rt, -10	38.41	>99	10,100	16,300	1.252	66.8
10	PF ₁₈ - <i>b</i> -PDL _{36, TBD}	60:18:1:1	130	rt, -10	59.47	>99	12,800	18,500	1.311	65.3
11	PF ₅₅ - <i>b</i> -PDL _{55, TBD}	80:55:1:1	210	rt, -10	68.24	>99	26,880	28,700	1.503	63.2
12	PF ₁₈ - <i>b</i> -(PA- <i>alt</i> -EGE) _{20, <i>t</i>-BuP1}	20:20:18:1:0.5	100	100, -10	>99	>99	10,860	12,200	1.326	73.5
13	PF ₁₈ - <i>b</i> -(AA- <i>alt</i> -EGE) _{20, <i>t</i>-BuP1}	20:20:18:1:0.5	160	100, -10	>99	>99	10,600	14,800	1.351	52.3

^aThe reaction conducted after purification (dialysis) of the PDL. ^bCalculated by ¹H NMR spectroscopy of the polymers in CDCl₃. ^cDetermined by SEC analysis in THF calibrated with polystyrene standards. (The ROP is conducted in bulk at 25°C, [TBD]:[4-iodobenzyl alcohol]:[δ -DL] = 1 : 1 : 60(80); SCTP is conducted in THF at -10°C, [Pd₂(dba)₃]:[*t*-Bu₃P]:[4-iodobenzyl alcohol]:[HexFL] = 0.4 : 2.2 : 1 : 18.

Table S2. The ROP of δ -DL catalyzed by TBD^a.

Run	Time (min)	Conv. ^b (%)	TOF (min ⁻¹)	$[M]_0/[M]_t$	$\text{Ln}\{[M]_0/[M]_t\}$	$M_{n,\text{SEC}}^c$ (g mol ⁻¹)	\mathcal{D}^c
1	30	13.44	0.45	1.15	0.14	2,100	1.268
2	60	23.86	0.40	1.31	0.27	3,100	1.233
3	90	33.33	0.37	1.51	0.41	4,000	1.215
4	120	42.23	0.35	1.85	0.62	6,800	1.096
5	240	69.44	0.29	3.29	1.19	8,800	1.085
6	360	80.00	0.22	6.89	1.93	9,200	1.136

^aThe polymerization reactions are conducted in [TBD]:[4-Iodobenzyl alcohol]:[δ -DL] = 1 : 1 : 60 under 25°C. ^bThe conversion of δ -DL is determined by ¹H NMR spectroscopy. ^c $M_{n,\text{SEC}}$ and \mathcal{D} are determined by SEC analysis in THF calibrated with polystyrene standards.

Table S3. Thermal properties of studied polymers.

Sample	T_d^a (°C)	T_g^b (°C)	T_m^c (°C)	T_c^d (°C)
PF ₁₈	341.7	69.1	203.8	143.9
PDL ₃₆	270.8	-55.2	--	--
PF ₁₈ - <i>b</i> -PDL ₁₃	302.3	65.3, -58.7	176.7	130.4
PF ₁₈ - <i>b</i> -PDL ₂₄	308.5	55.2, -57.3	172.9	122.3
PF ₁₈ - <i>b</i> -PDL ₃₆	292.5	52.6, -53.9	166.7	124.5

^aDegradation temperature at the heating/cooling rate of 10°C min⁻¹ in thermogravimetric analysis (TGA) in a nitrogen atmosphere. ^bMidpoint temperature of glass transition at a heating rate of 10°C min⁻¹ in differential scanning calorimetry (DSC) in a nitrogen atmosphere. ^cMelting temperature. ^dCrystallization temperature at a cooling rate of 10°C min⁻¹ in differential scanning calorimetry (DSC) in a nitrogen atmosphere.

Table S4. Optical properties of studied polymers.

Sample	Solution ^a		As-cast film ^d		Annealed film ^f	
	$\lambda_{\max}^{\text{abs}}$ ^b (nm)	$\lambda_{\max}^{\text{PL}}$ ^c (nm)	$\lambda_{\max}^{\text{PL}}$ (nm)	PLQY ^e (%)	$\lambda_{\max}^{\text{PL}}$ (nm)	PLQY (%)
PF ₁₈	383	420, 441	423, 445	24.33	423, 445	14.43
PDL ₃₆	--	--	--	--	--	--
PF ₁₈ - <i>b</i> -PDL ₁₃	383	420, 442	423, 448	32.28	423, 446	28.47
PF ₁₈ - <i>b</i> -PDL ₂₄	383	420, 442	423, 448	35.16	423, 448	25.58
PF ₁₈ - <i>b</i> -PDL ₃₆	383	420, 442	423, 447	37.29	423, 448	22.00

^aIn tetrahydrofuran. ^bAbsorption at the longest wavelength. ^cEmission wavelength, excited at 365 nm.

^dThe as-cast films of polymers were prepared on a glass substrate by spin-coating polymer solutions in tetrahydrofuran (1 mg mL⁻¹) at 3000 rpm. ^eAbsolute PL quantum yield (PLQY) was recorded at excitation wavelength of 365 nm. ^fThe films were annealed at 120 °C in vacuum for 1 day.

Table S5. The time-resolved PL spectra of PF₁₈-*b*-PDL_n thin films of as-cast state.

Sample	R ² ^a	A ₁ ^b	τ_1 ^c	τ_{avg} ^d
PF ₁₈	0.9966	1.0994	0.1171	0.1171
PF ₁₈ - <i>b</i> -PDL ₁₃	0.9972	1.0929	0.1372	0.1372
PF ₁₈ - <i>b</i> -PDL ₂₄	0.9971	1.0608	0.1547	0.1547
PF ₁₈ - <i>b</i> -PDL ₃₆	0.9965	1.1072	0.1692	0.1692

^aRegression analysis constant of the fitting by a single exponential reconvolution of Figure 2d.

^bNumber of photons at t = 0. ^cTime constant. ^dAn average lifetime.