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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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Abstract:

Bio-derived optoelectronic material is captivating and sustainable research as it reduces the environmental toxicity and comforting the wearable aspects. Our research involves the synthesis of series of bio-derived polyfluorene-*block*-poly(δ -decanolactone) (PF-*b*-PDL) conjugated block copolymers through smart one-pot procedure that involves simple purification for fabricating touch-responsive light-emitting diode (LED) devices. Compared with PF homopolymer, the block copolymers exhibit higher photoluminescence quantum yields and higher exciton binding energies. PF₁₈-*b*-PDL₁₃ specifically exhibits external quantum efficiency (EQE %) (~6 times higher than PF homopolymer). Moreover, because of coily PDL block inducing a highly stable bound state in block copolymer generating the increment in PL lifetime and exciton binding energies than the homopolymer. Furthermore, the diblock copolymers device exhibits fully solution processability, higher carrier recombination efficiency, flex-stretch stability, good structural integrity and mechanical endurance highlighting the brighter potential of our bio-derived block copolymers for fabricating highly durable wearable stretchable nano and microelectronic devices.

Keywords: *polyfluorene, rod-coil conjugated block copolymer, smart synthesis, light-emitting diode, flexible wearable device*

1. Introduction

Conjugated block copolymers (BCPs) have attracted a considerable amount of interest from academia and industry for their wide ranging applications in nano-microelectronics,[1] optoelectronics,[2-8] biotechnology,[9, 10] and environmental technology.[11] Given their nature to self-assemble into phase separated nanostructures, various types of morphologies such as spherical,[12, 13] cylindrical,[13, 14] bicontinuous,[13, 15] and lamellar nanostructures[13, 16] of conjugated BCPs have been reported thus far. The type and size of self-assembled nanostructures are controlled by overall molecular weight and volume fraction between the blocks. By taking this bottom-up approach in modifying the active-layer phase consisting of the conjugated block, the overall performance level of block copolymer devices can be fine-tuned for specific purposes. In particular, polyfluorene (PF) is a deep blue light-emitting conjugated polymer with a good photoluminescence quantum yield and an excellent thermal stability, and solution processability.[17-21] PF-based conjugated BCPs containing dielectric, coily blocks are reported to have enhanced PF crystallinity,[22, 23] structural ordering,[14, 22, 24] and stretchability.[24, 25] The control over domain size of nanostructures to achieve an exciton diffusion length of 20–50 nm is known to optimize device performance levels.[26, 27] In addition, coil blocks add stretchability to the overall BCPs and enable the construction of wearable devices.[28, 29] However, the insulating property of coil blocks considerably dampens the interchain charge transport properties, which is unfavorable for achieving efficient electroluminescent device. Therefore, a tradeoff exists in the molecular design of conjugated BCPs and it is of urgent need to solve this tradeoff to develop wearable stretchable

optoelectronics devices.

Typically, PF derivatives are synthesized through Suzuki–Miyaura polycondensation in a classical step-growth manner but it is unsuitable for producing BCPs. As an alternative, Suzuki–Miyaura catalyst transfer polymerization (SCTP) enables BCP synthesis through the controlled chain-growth of PF that is end-functionalized with chemically reactive groups for copolymerization.[2, 3, 30] In general, ethynyl or azido end groups are used to produce PF-based BCPs through click chemistry.[10, 25] However, the complex synthesis and stringent purification procedures involved in the aforementioned methods inhibit the mass production of BCPs. [2, 10, 22, 25, 30, 31] Despite the limitations, some studies have utilized those methods to demonstrate successful application of conjugated BCPs. Chen *et al.* reported the synthesis of poly[2,7-(9,9-di-*n*-hexylfluorene)]-*b*-poly(*n*-butyl acrylate) (PF-*b*-PBA) rod-coil diblock copolymers through a click reaction. These copolymers exhibit excellent fluorescence properties as well as high deformability, which demonstrate reliable high-performance wearable electronic devices.[22] Moreover, Chiu *et al.* designed intrinsically elastic PF-based copolymers through reversible addition–fragmentation chain transfer polymerization and it exhibited highly durable photoluminescence quantum yield (PLQY) even at 300% strain over 100 cycles.[24] Aforementioned studies have shown that conjugated BCPs exhibit higher PLQY than their respective homopolymers.[22, 24] Therefore, conjugated BCPs are potential candidates for light-emitting diode (LED) applications. However, in-depth investigation regarding higher PLQY in BCPs molecular systems has not been reported yet.

To address the limitations in synthetic strategy complication, purification and sustainable bio-

derived molecular blocks to construct conjugated BCPs with better PLQY, this study reports a smart scalable one-pot synthesis of poly(9,9-di-*n*-hexyl-2,7-fluorene)-*block*-poly(δ -decanolactone) (PF-*b*-PDL), poly(9,9-di-*n*-hexyl-2,7-fluorene)-*block*-[(phthalic anhydride)-*alternative*-(ethyl glycidyl ether)] (PF-*b*-(PA-*alt*-EGE)), and poly(9,9-di-*n*-hexyl-2,7-fluorene)-*block*-[(allyl succinic anhydride)-*alternative*-(ethyl glycidyl ether)] (PF-*b*-(AA-*alt*-EGE)) by using SCTP and ring-opening polymerization (ROP). High PLQY and exciton binding energy (EBE) were induced by a weak screening effect from PDL blocks in which their low dielectric constant increases the attractive force between electrons and holes interacting in PF blocks. The LED devices with PF-*b*-PDL as the emissive layer exhibit good mechanical robustness (stable 300 touch responses) and a greater external quantum efficiency (EQE % or 6 times higher) than devices with PF homopolymer. The results demonstrate conjugated BCP LED devices exhibiting superior performance over their conjugated homopolymer counterparts.

2. Experimental Section

2.1 Materials:

Potassium 2-(7-bromo-9,9-di-*n*-hexyl-9H-fluorene-2-yl) triolborate was prepared according to a previous report.[32] Tris-(dibenzylideneacetone) palladium (Pd₂(dba)₃, >97%), tetrahydrofuran (THF, anhydrous, \geq 99%), methanol (MeOH, \geq 99%), dichloromethane (CH₂Cl₂, anhydrous, \geq 99%), toluene (anhydrous, \geq 99%), chloroform (CHCl₃, anhydrous, \geq 99%), δ -decanolactone (δ -DL), phthalic anhydride (PA), ethyl glycidyl ether (EGE), tert-butylimino-tri(pyrrolidino)phosphorene (*t*-

BuP₁) and allyl succinic anhydride (AA), dec-5-ene (TBD, >98.0%), poly(9,9-di-*n*-octyl-2,7-fluorene) (PFO) ($M_n \sim 10,000$, $D \sim 2$), and poly(ethylene glycol) (PEO) were purchased from Sigma-Aldrich. Tri(*tert*-butyl)phosphine (*t*-Bu₃P, >96%) was obtained from Wako Pure Chemical Industries, Ltd. 4-Iodobenzyl alcohol (>99.0%) was bought from Tokyo Chemical Industry Co., Ltd. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT: PSS; high conductivity grade 1.1 wt% in H₂O) was purchased from Ossila, Ltd. Polyurethane (PU) was purchased from RainEmpire Taipei Co., Ltd. Silver nanowires (average diameter = 55-75 nm, average length = 20-40 μm) dispersed in IPA (0.66%) were purchased from Zhejiang Kechuang Advanced Materials Co., Ltd.

2.2 Synthesis of PF-based block with ROP monomer via smart procedure

The typical polymerization procedure is as follows: An appropriate amount of TBD (0.026 mmol, 1 equiv.), 4-iodobenzyl alcohol (0.026 mmol, 1 equiv.), and δ -DL (1.538 mmol, 60 equiv.) were added to an oven-dried Schlenk flask equipped with a magnetic stir (The PA or AA is 0.513 mmol, 20 equiv with EGE (1.026 mmol, 40 equiv) is added) The Schlenk flask was placed in an aluminum heating block with predetermined temperature of 25 °C to start the ROP (100°C for the PA or AA with EGE). During the ROP step, a crude aliquot was withdrawn from the system by pipette and monitor by ¹H NMR spectroscopy and size exclusion chromatography (SEC) to determine monomer conversion and molecular weight. After the defined time, Pd₂(dba)₃·CHCl₃ (0.010 mmol, 0.4 equiv.), *t*-Bu₃P (0.057 mmol, 2.2 equiv. as 0.5 mol L⁻¹ stock solution in tetrahydrofuran (THF)), and dry-THF (12 mL) were added to the reaction mixture, and stirred for 30 minutes to form Pd-

initiator complex. A solution of HexFL (0.466 mmol, 18 equiv.) in dry-THF (200 mL) was introduced to the Pd-initiator solution, which had been purged with argon and pre-cooled at -10°C , by a cannula to start the SCTP for 10 minutes. To terminate the polymerization, 12M hydrochloric acid (HCl) (10ml) was added to the reaction mixture and react for 30 minutes. SEC was performed to trace the final copolymers. The elution peaks of the copolymers shifted to a shorter elution time than those for the corresponding I-PDL_n, which indicated a successful chain extension of the PF block. After removing the solvent by evaporation, the residue was dissolved in CH₂Cl₂ and washed with brine. The organic layer was dried over MgSO₄ and purified by alumina column. The residue was diluted by adding THF and poured into cold acetone. The precipitate was collected by filtration and dried under reduced pressure to get PF₁₈-*b*-PDL₃₆ (yield: 63.1 %) as a dark green powder. $M_{n,\text{NMR}} = 12,800 \text{ g mol}^{-1}$; $D = 1.311$. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.71-7.83 (m, Ar-H of PF backbone), 5.18 (d, -CH₂OH): 2.29 (br, -CH₂(CH₂)₄CH₃ of PF side chain), 0.79-1.27 (m, -CH₂(CH₂)₄CH₃ of PF side chain), 4.87 (br, PDL backbone and side chain connection), 1.27-2.29 (br, PDL backbone), and 0.87-1.55 (br, pentyl side chain of PDL).

2.3 Touch-responsive light-emitting diode device fabrication

The PU substrates were prepared by being spin-coated onto the polytetrafluoroethylene (PTFE) substrate and being cured at 40 °C for 1 day. The PU substrates were oxygen plasma treated for 3 min and the PEDOT: PSS/ poly(ethylene glycol) (PEO) (5 wt%) solution was spin-coated onto the treated PU substrate at 1000 rpm for 30 s. Subsequently, the film was annealed at 80 °C for 15 min to remove

residual solvents. After being cooled down, the substrate was transferred into a nitrogen-filled glove box and spin-coated with the PF-based block copolymer, as an emissive layer. The emissive layer was prepared by spin coating at 3000 rpm for 60 s and annealed at 120 °C in vacuum for 1 day, and then, the spacer PET was introduced onto the emissive layer. The prepared PU@AgNWs electrode was then faced down and stacked onto the emissive layer that plays the role of cathode (upper electrode).

2.4 Characterization

^1H , ^{13}C , COSY, HMQC, and DOSY NMR spectra were measured with a JEOL JNM-ECS 400 (JEOL Ltd., Tokyo, Japan) at room temperature at 400 MHz in chloroform- d_1 , and chemical shifts are referenced to an internal standard. SEC analyses are using THF as the eluent at a flow rate of 1.0 mL min^{-1} at 40°C and measured by employing a JASCO (JASCO Co., Tokyo, Japan) high performance liquid chromatography system (PU-980 Intelligent HPLC pump, CO-2065 Plus Intelligent Column Oven, RI-2031 Plus Intelligent RI Detector, and DG-2080-53 Degasser) equipped with a Shodex KF-G guard column (4.6 mm×10 mm; particle size, 8 μm) and two Shodex KF-804L columns (linear; particle size, 7 μm ; 8.0 mm × 300 mm; exclusion limit, 4 × 10⁴) (Showa Denko K. K., Tokyo, Japan). The calculated number average molecular weight ($M_{n,\text{SEC}}$) and dispersity (D) of the polymers were calibrated with polystyrene (PSt) standards. UV-visible spectra were measured by Jasco V-370 spectrophotometer (JASCO Co., Tokyo, Japan). The PL spectra were measured by a Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon, Paris, France), and the polymer films were excited at wavelengths of 365 nm. The structure of the polymer thin films was imaged by Hitachi AFM5000II

(Hitachi Systems Co., Ltd., Tokyo, Japan) operating in tapping mode under an ambient atmosphere. The thin films for the AFM measurements were prepared by spin coating (3000 rpm, 60 s) from the polymer solutions in THF (5.0% w/w) onto a silicon substrate. The thin film samples were annealed under vacuum at 120 °C for one day. The AFM images were processed using Gwyddion software. DSC was measured to investigate thermal properties under a nitrogen atmosphere by Hitachi DSC 7000X (Hitachi High-Tech Science Co., Ltd., Tokyo, Japan) with a heating/cooling rate of 10 °C min⁻¹ from -100 °C to 250 °C under a nitrogen flow. TGA was performed through a Bruker AXS TG-DTA2010SAT (Bruker AXS, Billerica, USA) with a heating rate of 10 °C min⁻¹ from 100 °C to 500 °C under a nitrogen flow. Synchrotron GIWAXS measurements were conducted with an X-ray beam of wavelength (λ) 0.12359 nm at the 3C beamline[33-36] of the Pohang Accelerator Laboratory (PAL), Pohang, Korea. A 2D charge-coupled detector (model Eiger X 4M, DECTRIS Ltd., Baden-Daettwil, Switzerland) was used to measure all GIWAXS data. The incidence angle α_i of the X-ray beam with respect to the film sample surface was set in the range 0.093–0.196°, which is between the critical angle of the polymer film and the silicon substrate ($\alpha_{c,f}$ and $\alpha_{c,s}$). Aluminium foils were used as a semi-transparent beam stop. The sample-to-detector distance (SDD) was set to 208.3 mm. Each scattering pattern was collected for 30 s. The scattering angles were corrected according to the positions of the X-ray beams reflected from the silicon substrate as well as using precalibrated silver behenate standards (Tokyo Chemical Inc., Tokyo, Japan). Absolute PLQY measurement was recorded by using Enli Tech LQ-100X (Enli Technology Co., Ltd., Kaohsiung, Taiwan) for detecting all-polymer thin films under different strains or stretching cycles through the integrating sphere at a fixed

excitation wavelength at 365 nm. A measurement is done of the fluorescence emission (E_c) and the scatter (L_c) of the samples and also the emission and scatter of a blank (L_a and E_a). Finally, the absolute PLQY can be calculated from the equation of $\Phi_f = \frac{E_c - E_a}{L_a - L_c}$. The highest occupied molecular orbital (HOMO) energy levels were calculated from ultraviolet photoelectron spectroscopy (UPS), whereas the lowest unoccupied molecular orbital (LUMO) energy levels were estimated from the difference between the optical band gap and HOMO level based on the equation $LUMO \text{ (eV)} = HOMO + E_g^{opt}$. The OM observation was measured under a microscope by LSM 21 510 Meta (ZEISS Co., Ltd., Oberkochen, Germany) equipped with a 22 LCI Plan-Neofluar 40x 1.3⁻¹ NA immersion. The Commission Internationale de l'éclairage (CIE) color coordinates and correlated color temperature (CCT) of the LED spectra were measured by PR670 spectroradiometer (Titan Electro-Optics Co., Ltd., Taipei, Taiwan) under ambient air conditions at 25 °C. The calibration method was standard sunset light, which correlated to a color temperature of 2856 K, to confirm instrument correctness. The TR-PL spectra were coupled to a Horiba iHR320 spectrometer (HORIBA, Kyoto, Japan) with a Hamamatsu C10910 streak camera and an M10913 slow single sweep unit. Temperature-dependent photoluminescence was measured with a pulsed diode-laser by PicoQuant LDH-D-C-375 (PicoQuant, Berlin, Germany) at a repetition rate of 1 MHz.

2.5 Arrhenius formula simulation of the binding energy

Here, the photo-generated excitons are assumed to be depopulated only by thermal dissociation and radiative recombination. In the steady-state PL measurement, the n_{pg} refers to the

number of photo-generated excitons, n_{PL} is the number of the radiative emissions induced by the exciton recombination, which can be determined from the integrated PL intensity, and n_{td} is the number of thermally dissociated excitons. According to the Arrhenius formula, n_{td} is saturated when the T is not too high and the $n_{\text{td}} \propto Ae^{-E_b/kT}$ can get, in which E_b is the binding energy and k is the Boltzman constant. Assuming that when $T = \infty$ it has $n_{\text{PL}} = 0$, then $n_{\text{PL}} = n_{\text{pg}} - n_{\text{td}} = A(1 - e^{-E_b/kT})$. After fitting $n_{\text{td}}(T)$, we can determine A and E_b .

$$n_{\text{PL}} = n_{\text{pg}} - n_{\text{td}} = A(1 - e^{-E_b/kT}) \quad (1)$$

2.6 The time decay curve fitting by exponential function

The decays are fitted with the formula (2) where τ_1 is the time constant, which is attributed to the intrinsic recombination and A_1 is the fractions of the contribution. The first 1.0 ns following the laser excitation are used for fitting. The time constant of all the dots that have measured is around 0.0 ~ 1.0 ns. If the time constant is determined by a nonradiative channel, the distribution of exciton would expect a more rapid decline in time constant.

$$F(t) = A_1 e^{-t/\tau_1} \quad (2)$$

3. Results and Discussion

3.1 Synthesis and characterization of PF-based block copolymer

The details of the one-pot synthesis of PF-based BCPs are given in the **Supporting**

Information, and the molecular characteristics are summarized in **Table S1 (Supporting Information)**. The smart one-pot synthesis is a two-step process based on the ROP of bio-based sugar derived δ -decanolactone (δ -DL) and SCTP of potassium 2-(7-bromo-9,9-di-*n*-hexyl-9H-fluorene-2-yl) triolborate (HexFL) carried out in a sequential manner (**Figure 1a**). To realize the one-pot process, commercially available 4-iodobenzyl alcohol possessing hydroxyl and iodobenzene groups was chosen as the appropriate difunctional initiator. The hydroxyl group functions as the initiating site for ROP, and the iodobenzene group reacts with Pd(0) to form an initiating site for SCTP. First, ROP of δ -DL performed in bulk was carried out by using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a catalyst and 4-iodobenzyl alcohol as an initiator at 25 °C under a nitrogen atmosphere to produce iodo-end-functionalized PDLs [I-PDL_{*n*} (*n* = 13, 24, and 36; **Figure 1a,b**)]. The molecular weight of I-PDL_{*n*} was controlled by varying the reaction time and δ -DL/initiator ($[\delta\text{-DL}]_0/[I]_0$) ratio. The ROP monitored by performing SEC and ¹H nuclear magnetic resonance (NMR) analysis of aliquots at regular intervals produced a linear correlation between the evolution of the molecular weight ($M_{n,SEC}$) and monomer conversion, which demonstrated a living polymerization behavior (**Figures S1–S3 and Table S2, Supporting Information**). Subsequent addition of a mixture of a tris(dibenzylideneacetone) dipalladium (0)-chloroform adduct (Pd₂(dba)₃·CHCl₃) and tri-*tert*-butylphosphine (*t*-Bu₃P) resulted in the formation of a coordination complex with I-PDL_{*n*} for initiating a controlled chain-growth SCTP of HexFL. To understand the effect of the molecular weight balance between the conjugated rod and coil blocks on the LED performance, the PF blocks in all copolymers were synthesized with a fixed number average molecular weight ($M_{n,NMR}$) of 6,300 g

mol⁻¹ (i.e., 18 repeating units).[37]

On the other hand, the ring-opening alternating copolymerization (ROAC) of epoxides with cyclic anhydrides has been recognized as a promising approach to diversified polymers and allowing facile functional tunability. In view of achieving facile approach, the utilized commercially available initiator bridges two different catalytic reactions involving ring-opening alternating copolymerization (ROAC) of epoxide (EGE) and cyclic anhydrides (PA or AA) with SCTP of conjugated PF opens up the smart one pot synthetic strategy of PF-based conjugated BCPs (**Figure S4-7, Supporting Information**). Our synthetic strategy works efficiently in constructing diverse PF-based BCPs as it acts straightforward, and functions facile in regulating the molecular blocks with desired physical properties. Through smart synthetic approach, we synthesized series of PF-based BCPs namely PF₁₈-*b*-PDL₁₃, PF₁₈-*b*-PDL₂₄, PF₁₈-*b*-PDL₃₆, PF₁₈-*b*-(PA-*alt*-EGE)₂₀, and PF₁₈-*b*-(AA-*alt*-EGE)₂₀, which represents the ease and flexibility in attaining desired degree of polymerization without any purification steps. We believe that our smart synthetic approach reducing the synthesis cost, time, solvent toxicity, and these credible features adding limelight to the path of commercialization and facile solution-processable wearable electronics.

Although we prepared series of BCPs, we focus primitively on PF₁₈-*b*-PDL_{*n*} as our main theme of research is to fabricate bio-derived stretchable wearable LEDs. The chemical compositions of PF₁₈-*b*-PDL_{*n*} were analyzed and confirmed by ¹H, ¹³C, and 2D NMR spectra (**Figures S8–S13, Supporting Information**). In the ¹H NMR spectrum (**Figure 1c**), the proton signals originating from the hexyl side chain on the PF block (peaks a, b, and c) and the main chain of the PDL block (peaks

d, e, f, and g) were clearly observed for PF₁₈-*b*-PDL₃₆. The ¹H, ¹³C, and 2D NMR peak positions and their peak integration values for all the BCPs are in a good agreement with the chemical structures and target molecular weights. Diffusion ordered spectroscopy (DOSY) NMR analysis, a powerful tool for accurately identifying individual NMR spectra from a mixture of various chemical species, was performed to determine the capability of the novel synthesis for producing a single type of BCP. The representative DOSY NMR spectrum of PF₁₈-*b*-PDL₃₆ (**Figure 1d**) revealed only a single diffusion peak, which proves the smart one-pot synthesis only produced the copolymer virtually without side products. In contrast, two diffusion peaks were observed for a mixture of PF and PDL homopolymers (**Figure S14, Supporting Information**). The NMR spectra and SEC traces suggested that well-defined BCPs are produced through the novel smart synthesis process. The novel synthesis is a simple, high yielding (typically 65%–67%),^[2, 3, 24, 30, 31] and a short reaction (~2 h); thus, this method is beneficial for the mass production of bio-derived BCPs.

3.2 Morphologies and optical properties of PF-*b*-PDL thin films

The thermal behavior of PF₁₈-*b*-PDL_{*n*} were examined through thermogravimetric analysis (TGA) (**Figure S15, Supporting Information**) and differential scanning calorimetry (DSC) (**Figure S16, Supporting Information**) under a nitrogen atmosphere. The thermal parameters are summarized in **Table S3 (Supporting Information)**. The homopolymer of PDL and PF revealed glass transition temperatures (T_g) at -55.2 and 69.1 °C, respectively. As displayed in **Figure S16 (Supporting Information)**, each PF₁₈-*b*-PDL_{*n*} copolymers exhibited two T_g , which originated from

PDL and PF, respectively. The existence of individual phase transitions indicated the immiscibility of the PF and PDL blocks. Thus, PF and PDL segregated into separate domains.

The thin film morphology of PF₁₈-*b*-PDL_{*n*} copolymers was investigated through synchrotron grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements on as-cast and thermally annealed films (120 °C in vacuum for 1 day). As for PF homopolymer (PF₁₈), the as-cast film revealed a featureless data but the thermally annealed film revealed a set of weak crystalline peaks (**Figure S17a,b, Supporting Information**). BCPs crystalline peaks attributed to the formation of an orthorhombic crystalline structure similar to that of poly(9,9-di-*n*-octyl-2,7-fluorene) (PFO).^[28] In addition, a weak peak at approximately 16.8° in both out-of-plane and in-plane directions was observed with a *d*-spacing value of 4.2 Å, which evidenced the existence of π - π stacking between PF chains. However, the relatively weak peak intensities suggest low PF crystallinity inside the annealed film. A similar result is observed for PF₁₈-*b*-PDL₁₃ (**Figure S17c,d, Supporting Information**), with a minor difference in the annealed film that the scattering peaks are even weaker than PF homopolymer to suggest an even lower crystallinity. As for PF₁₈-*b*-PDL₂₄ and PF₁₈-*b*-PDL₃₆ (**Figure S17e-h, Supporting Information**), the as-cast films revealed scattering peaks appearing as halos suggesting the orientation of PF crystals is not controlled. Post-annealing, peaks begins to take similar appearance to that of PF homopolymer, with PF₁₈-*b*-PDL₃₆ revealing a relatively more similar scattering pattern. Atomic force microscopy (AFM) was performed to further investigate the phase separation behavior. As shown in **Figure S18-S19**, the as-cast films of PF homopolymer and copolymers were featureless but a fibrillar structure was clearly observed on the surface of thermally

annealed films for all BCPs. GIWAXS results ascertain the observed fibril morphological features originating from the tight packing of the PF blocks promoted by intermolecular π - π interaction, and linked PDL blocks offers amorphous matrix around the PF fibers.

To investigate the correlation between the conformation and optical properties of the studied polymers, the ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectra of the as-cast films were evaluated (**Figure 2a**) and summarized in **Table S4**. The UV-vis absorption spectra of the as-cast films revealed both PF homopolymer and PF_{18-b}-PDL_n copolymers to exhibit π - π^* transition occurring at a wavelength of \sim 403 nm. The PL spectra of PF homopolymer and PF_{18-b}-PDL_n copolymers did not reveal obvious differences between the as-cast and annealed states (**Figure S20**), which confirmed that the PF chain conformation in the BCPs and PF homopolymer remains unaffected by thermal annealing. To confirm the luminescence properties, PLQY of the as-cast thin films were evaluated (**Figure 2b**). The conjugated BCPs exhibited higher PLQY (32%–37%) than that of PF homopolymer (24%), which confirmed the superior luminescent property of the bio-derived BCPs. These results complied well with previous studies.[22, 24] A higher PLQY is correlated to a larger EBE,[38, 39] which indicates more frequent radiative recombination of excitons occurring in BCP films at room temperature.

3.3 The correlation between PLQY and EBE

Excitons are one of the important factors that determine the overall performance of an LED device.[40-42] PLQY increments with conjugated molecularly designed BCP systems dedicates EBE

modification and it is a critical factor in the LED device performance.[39, 43] Therefore, temperature-dependent PL measurements were conducted on PF homopolymer and BCPs to quantify their EBE. Both homopolymer and BCPs exhibited a rapid decrease in their PL intensities with increasing temperature from 100 to 300 K (**Figure S21**), which is governed by the strong screening effects eventually establishing a weak attractive force between electrons and holes in the exciton.[44, 45] Furthermore, the integrated PL intensity was fitted with the Arrhenius equation [Equation (1); see **Supporting Information**] to obtain exciton binding energies (EBE) of 42.29, 59.32, 64.99, and 71.91 meV for PF₁₈, PF₁₈-*b*-PDL₁₃, PF₁₈-*b*-PDL₂₄, and PF₁₈-*b*-PDL₃₆, respectively (**Figure 2c**). With decreasing molecular weight of PDL in the BCPs, EBE and PL is quenched causing detrimental effects on radiative recombination of photogenerated charges. The resulting PL and EBE trends are consistent with the PLQY results demonstrating the consistency of the as-synthesized bio-derived BCPs in terms of luminescence stability. Moreover, the time-resolved PL (TR PL) spectra (**Figure 2d**) and the kinetics were analyzed to investigate the exciton recombination dynamics. All studied samples showing the typical exponentially decay behavior of PL intensities. On fitting the exponential decay curve, PF homopolymer exhibited a lifetime (τ_{avg}) of 0.117 ns (**Table S5**). PF₁₈-*b*-PDL₁₃, PF₁₈-*b*-PDL₂₄, and PF₁₈-*b*-PDL₃₆ exhibited longer τ_{avg} of 0.137, 0.155, and 0.169 ns, respectively. Rapid dissociation and the separation of exciton recombination resulted in a rapid decline in the magnitudes of the fast component (τ_1) (consider correcting the fast component!) (the fitting of exponential function is shown in the **Supporting Information**). It is well known that declining τ_{avg} values implies the electrons in the excited state transitioned to the ground state, which enhanced the non-radiative

transition ratio.[46, 47] τ_{avg} of PF₁₈-*b*-PDL_{*n*} copolymers are longer than that of the PF homopolymer because their higher EBE stabilize the bound state. According to previous studies, extremely high EBE can be achieved in crystalline emissive materials by adding low-dielectric-constant (ϵ) organic components.[44] The presence of low-dielectric PDL blocks induces a weak screening effect and increases the attractive force between electrons and holes. In other words, bio derived PDL blocks significantly suppresses the non-radiative recombination and considerably enhance the magnitude of EBE. Therefore, these results indicate that EBE is considerably enhanced by incorporating PDL blocks, as illustrated in **Figure 2e**. From the above discussion, we claim that PLQY promotion in the conjugated BCP is attributed to the stable bound state for the excitons induced by low dielectric PDL block. Our finding reveals the potential of one pot synthesized sustainable bio-derived BCPs in generating better eco-friendly photoluminescence material with intrinsic flex-stretch endurance. Bio-derived BCPs qualified the major preliminary requirements such as good photoluminescence and mechanical robustness allowing them for stretchable wearable LED device fabrication.

3.4 Fabrication and investigation of a stretchable touch-responsive LEDs

The stretchable and touch-responsive LED devices of PF homopolymer and BCPs were fabricated based on the architecture of polyurethane (PU)/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT: PSS) with poly(ethylene glycol) (PEO) (PEDOT:PSS/PEO)/PF₁₈-*b*-PDL_{*n*}/poly(ethylene terephthalate) (PET)/PU with a silver nanowire electrode PU@AgNWs, as displayed in **Figure 3a** and energy level diagram was exhibited in **Figure S22**. The realization of

these devices involved the following concepts. First, only elastic materials capable of withstanding strain were used. Second, a PET spacer was implanted between the upper electrode and the emissive layer. Therefore, the device only emits light when pressure is applied to the upper electrode. As displayed in **Figure 3b**, the instantaneous light emission in the regions contacted by a wrench, and emission under 150% strain of PF_{18-*b*}-PDL₁₃ LED devices are observed. The as fabricated conformable device is patchable and easy to attach and peel without any device failure or degradation. Mechanically stable characteristics enabled stretchable and touch-responsive LEDs integration with finger joints which responds by lighting brilliantly on physical contact between the joint and device upon bending motion.

The luminescence–voltage (L – V), current density–voltage (J – V), and current efficiency–voltage (CE – V) characteristics are displayed in **Figures 3c,d** and **S16**. The performance of the optimized devices is summarized in **Table 1**. As-cast devices with PF_{18-*b*}-PDL_{*n*} as the emissive layer showed higher EQE (0.05%–0.10%) than using PF homopolymer ($EQE_{PF,as-cast} = 0.03\%$) and commercial PFO homopolymer ($EQE_{PFO,as-cast} = 0.034\%$), as presented in **Table 1**. Based on higher PLQY and EBE of PF_{18-*b*}-PDL_{*n*}, they possess more stable bound states and higher photon emission efficiencies than PF and PFO homopolymers. It is worth noting that both current density and EQE declines with increasing length of PDL block (**Figure S23, Supporting Information**). The decline in current density is unfavorable to the recombination event, which results in greatly suppressed emission of PF_{18-*b*}-PDL₂₄ and PF_{18-*b*}-PDL₃₆ devices. Interestingly, PF_{18-*b*}-PDL₂₄ and PF_{18-*b*}-PDL₃₆ devices stop emitting photons once thermally annealed. PF_{18-*b*}-PDL₂₄ and PF_{18-*b*}-PDL₃₆ devices

displays severely deteriorated emission and current density on thermal annealing due to the random orientations occurred with the crystalline block region which is evidenced with our AFM measurements. Hence, the overall resistance within the emission layer significantly increases and retards the device performance and operation. In contrast, PF_{18-*b*}-PDL₁₃, which has the shortest PDL block of all BCPs, possesses a relatively lower crystallinity. Among synthesized BCPs, the lower resistance offered by PF_{18-*b*}-PDL₁₃ emissive layer facilitates the current flow, and it additionally functions with intrinsically high EBE for optimal operation. Finally, the optimized device with thermal annealing treatment with the shortest PDL block (PF_{18-*b*}-PDL₁₃) exhibited a highly enhanced performance, with a maximum EQE of ~0.33% (at 18 V), which is 6 times higher than that of annealed PF (EQE = 0.05%) and annealed PFO (EQE = 0.05%) homopolymer LED devices.

To understand the correlation between mechanical stretch deformation and device performance based on PDL block lengths are characterized with optical microscopy (OM) of the annealed homopolymer and BCP emissive thin films (**Figure S24**). Furthermore, **Figure S25** displays the photographs of the annealed homopolymer and BCP devices emitting light at 19 V under 0% to 200% strain. Interestingly, only PF and PF_{18-*b*}-PDL₁₃ devices are functional whereas PF_{18-*b*}-PDL₂₄ and PF_{18-*b*}-PDL₃₆ devices, despite exhibiting improved deformability, suffer device failure due to overwhelming amount of PDL that induces high resistance. PF_{18-*b*}-PDL₁₃ devices works promising even under stretched states revealing the importance and reliability of the as synthesized bio-derived BCPs on comparison to homopolymer. Apart from stretchable performance, PF_{18-*b*}-PDL₁₃ device shows the rapid ultra-efficient touch-response performance along with greater mechanical endurance

which is affirmed by repetitive touch-response cycles. Our device demonstrates stable touch-responsive operation at nearly the same level for ~300 switch on–off cycles without any sudden decrease in luminance and EQE portrays the device structural integrity (**Figure 3e**). The uniaxial strain of 0%–100% representing the survivability of our device and it can be comfortably inlaid in an array of wearable electronics (**Figure 3f**). The device exhibits 13% decrease in luminance at 30% strain, and this indicates the device’s wide operational window under high strain. Mechanical stretch endurance (0%–20%) under repetitive 100 stretch cycles showed 39% luminance losses (**Figure S26**), which already exhibit more stability than current reports.[48-51] In particular, the device retains comparable performance to 40% strain with only 34% decrease in luminance for 50 stretching cycles, thereby demonstrating excellent stability and durability from highly repeated strain (**Figure S26**). Taking advantage of scalable one pot smart synthesized bio-derived BCPs, we successfully fabricated fully solution processable wearable LED device capable of working under higher strain % with outstanding flex-stretch endurance. Our future research direction involves preparing eco-friendly BCPs through one pot smart synthesis to employ them in a wide spectrum of eco-friendly wearable stretchable optoelectronics without sacrificing the device efficiency and stability.

4. Conclusions

In summary, we successfully prepared a series of PF-based bio-derived BCPs, namely PF₁₈-*b*-PDL_{*n*}, through a scalable smart one-pot synthesis. A commercially available difunctional initiator was used to induce both ROP and SCTP of PDL and PF blocks, respectively. The smart polymerization

procedure was used for quick and efficient synthesis of BCPs with various PDL lengths controlled by varying the polymerization time. Moreover, we determined that the BCP strategy can considerably enhance EBE compared to PF due to the incorporating of a short insulating PDL segment. The PF₁₈-*b*-PDL_{*n*} devices exhibited excellent radiative recombination because of their stable bound state induced by high EBE. Among synthesized BCPs, PF₁₈-*b*-PDL₁₃ achieves the highest EQE = 0.33%, which is 6 times higher than that of the PF and PFO homopolymers. Therefore, mechanically robust highly flexible and stretchable touch-responsive LEDs with ultra-high efficiency were fabricated with PF₁₈-*b*-PDL₁₃ capable of integrating with human finger, curved joints and smart garments. The findings of this study possibly elevated the conjugated BCPs importance with robust stretchable wearable LED fabrication and our one pot smart synthesis is anticipated to achieve impressive breakthroughs in forming diverse eco-friendly materials and wearable electronic fabrication.

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Supporting Information

The plots of M_n and D versus monomer conversion and the polymerization time versus conversion of PDL; ^1H , ^{13}C , COSY, and HMQC NMR spectra of studied polymers; the DOSY NMR spectrum of the PF₁₈ and PDL₃₆ blending sample; DSC and TGA curves of studied polymers; AFM phase images of as-cast and annealed state of studied polymers; PL emission spectrum compared to as-cast and annealed state of the studied polymers; exciton binding energy fitting curve; comparison of UPS for PF-*b*-PDL series polymer; exciton binding energy fitting curve; comparison of UPS for studied polymers of as-cast and annealed films; energy levels of the PF₁₈-*b*-PDL_{*n*}; device characteristics of studied polymers of as-cast thin film as an emissive layer; OM and LED images of PF-*b*-PDL series polymer at different strain from 0%-200%; luminance-stretching cycle characteristics of the touch-responsive LEDs at 20% strain.

Conflicts of Interest

The authors declare no conflict of interest.

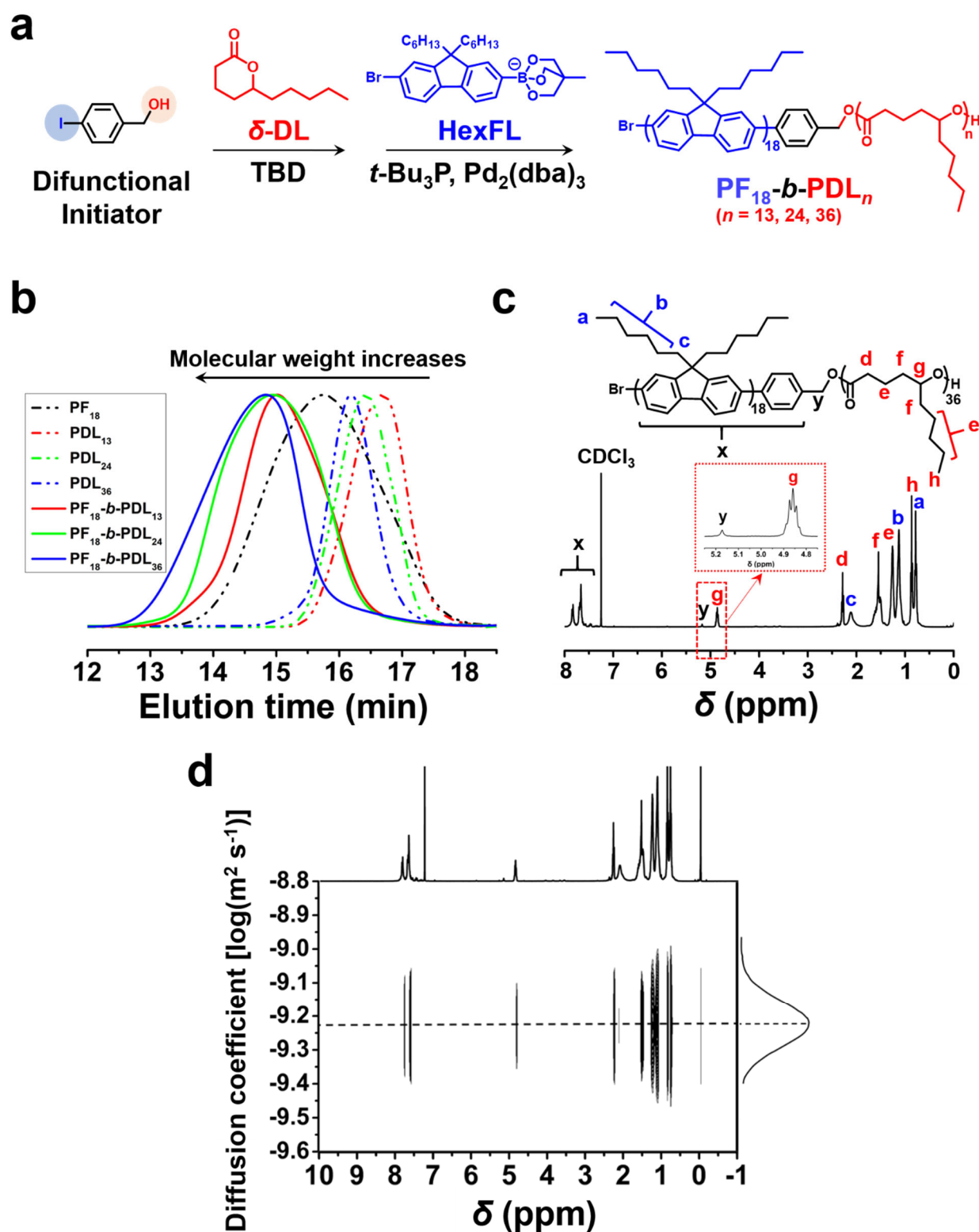


Figure 1. Formation and structure confirmation of $\text{PF}_{18}\text{-}b\text{-PDL}_n$ block copolymers. (a) Smart synthesis of $\text{PF}_{18}\text{-}b\text{-PDL}_n$ block copolymers by combining the ROP and SCTP mechanisms. (b) SEC trace of the studied polymers obtained through smart synthesis in THF calibrated with polystyrene standards. (c) ^1H NMR spectrum with peak designation and (d) DOSY NMR spectrum of $\text{PF}_{18}\text{-}b\text{-PDL}_{36}$ in CDCl_3 (The polymerization reactions were conducted in $[\text{TBD}]:[4\text{-iodobenzyl alcohol}]_0:[\delta\text{-DL}]_0:[\text{HexFL}]_0 = 1 : 1 : 60 : 18$ at 25°C in bulk for ROP and -10°C in THF for SCTP).

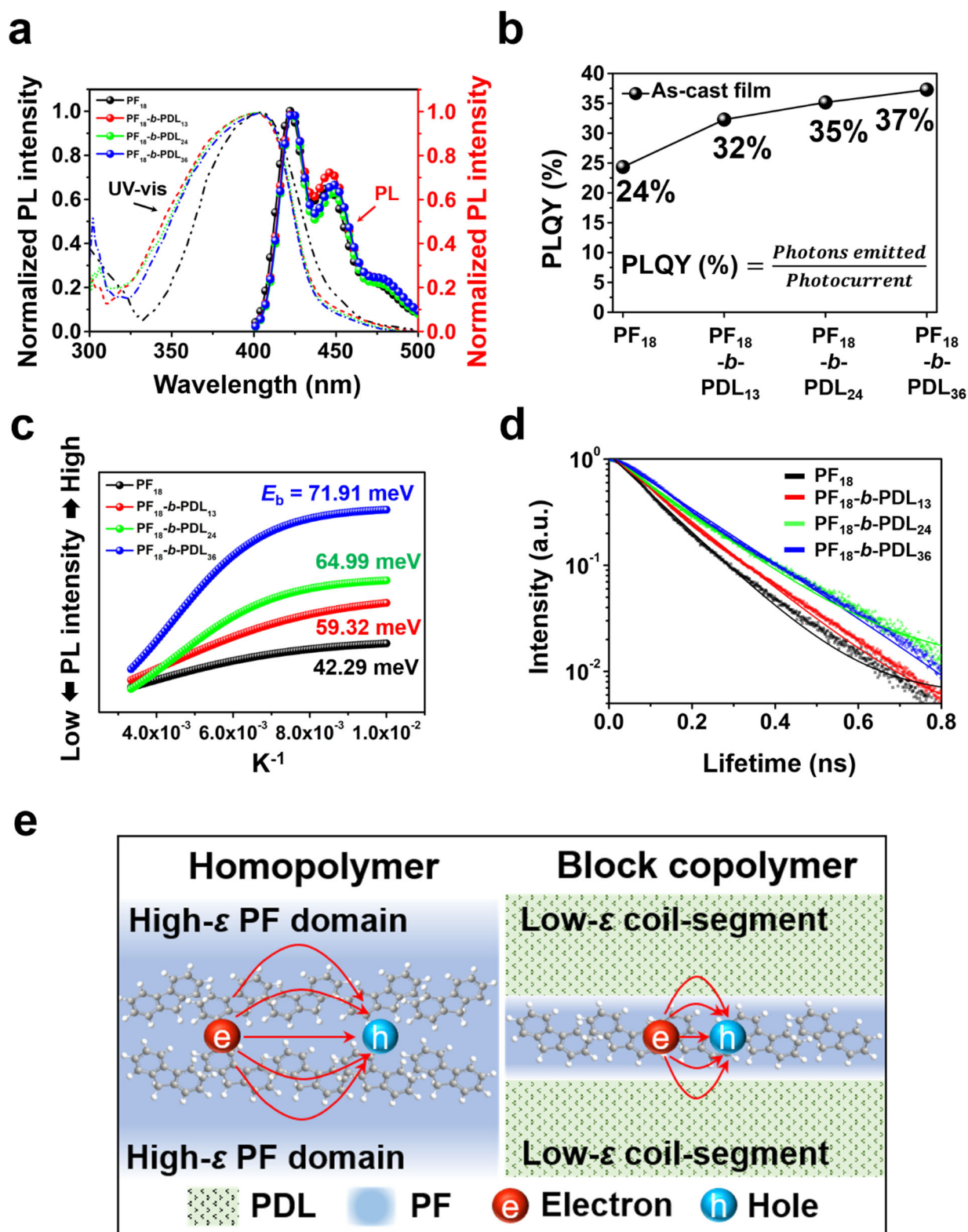


Figure 2. Composition-related photoluminescence for PF₁₈-b-PDL_{*n*} block copolymers. (a) UV-vis absorption, PL emission spectra, and (b) PLQY values of the studied polymers. (c) Correlation between the integrated PL intensity and temperature of the studied polymers, where the exciton binding energies (E_b) were extracted by fitting the curve with the Arrhenius equation. (d) TR PL decay and fitting curves of the studied polymers. (e) Explanation of the various dielectric constant (ϵ) effects in the stable bound state of excitons.

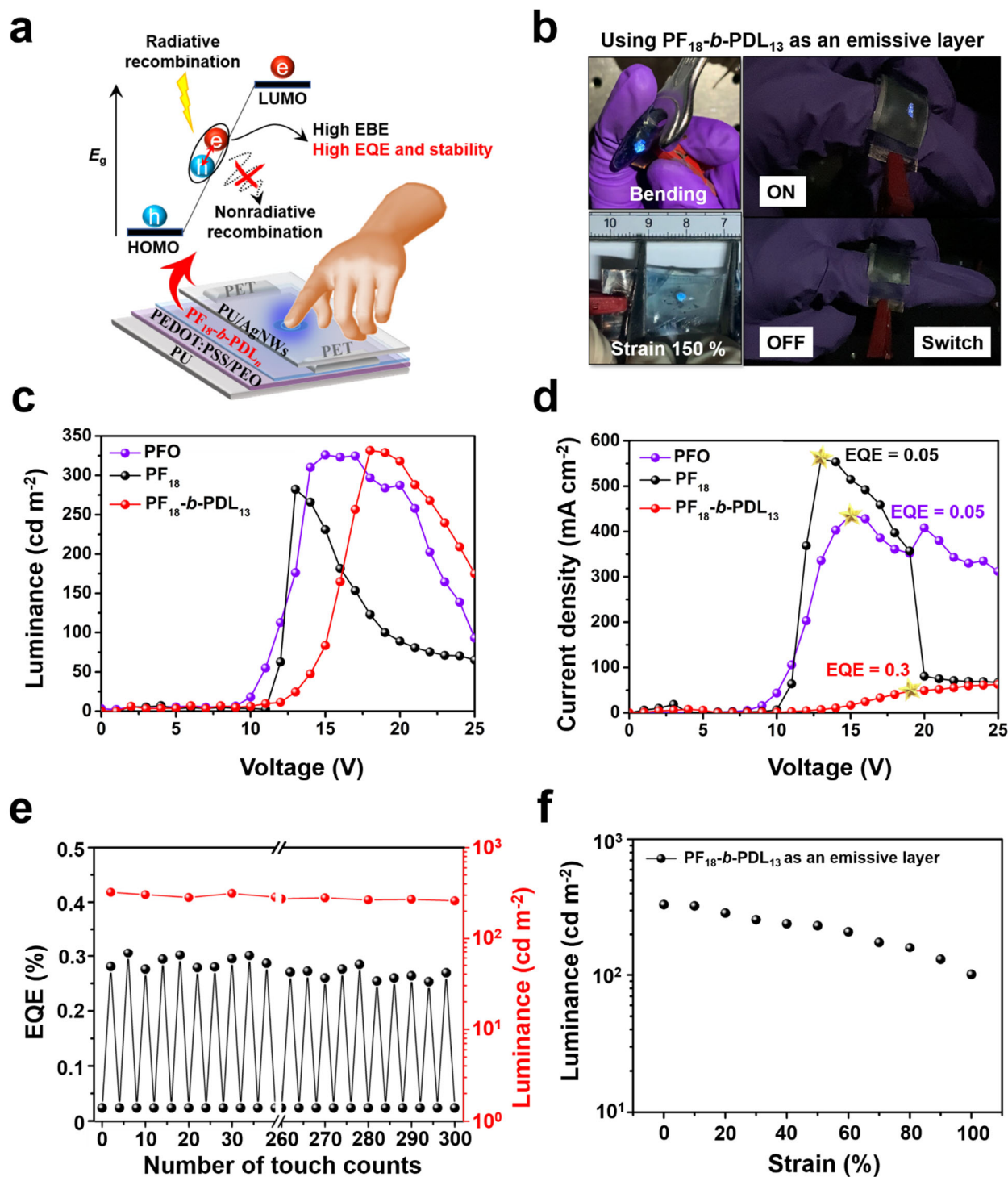


Figure 3. Schematic diagrams and electroluminescence spectra of touch-responsive LEDs. (a) Schematic of the touch-responsive LEDs. (b) Photograph of the bend in contact with the wrench (irregular complex surface), which was stretched to 150% strain, and attached by the finger using PF₁₈-b-PDL₁₃ as an emissive layer (at 19 V). (c) L - V and (d) J - V characteristics of the touch-responsive LEDs. (e) Durability results for the luminance and EQE characteristics and (f) luminance of the touch-responsive LEDs under a uniaxial strain of 0%–100% when using PF₁₈-b-PDL₁₃ as an emissive layer (at 19 V).

Table 1. The molecular characteristics, photoelectric properties, and device performance of studied samples.

Sample ^a	Molecular characteristics ^b			Photoelectric properties			Device performance (As-cast film) ^c			Device performance (Annealed film) ^c		
	$M_{n,NMR}$ (kDa)	\bar{D}	δ -DL (wt%)	PLQY (%)	EBE (meV)	τ_{avg}	L_{max} (cd m ⁻²)	CE_{max} (cd A ⁻¹)	EQE (%)	L_{max} (cd m ⁻²)	CE_{max} (cd A ⁻¹)	EQE (%)
PFO	10.0	~2.00	0	-	-	-	254	0.075	0.034	326	0.093	0.050
PF ₁₈	6.3	1.32	0	24.33	42.29	0.117	214	0.066	0.039	282	0.098	0.051
PF _{18-b} -PDL ₁₃	7.4	1.23	30	32.28	59.32	0.137	321	0.224	0.104	331	0.788	0.329
PF _{18-b} -PDL ₂₄	10.1	1.25	40	35.16	64.99	0.155	109	0.168	0.086	-	-	-
PF _{18-b} -PDL ₃₆	12.8	1.31	48	37.29	71.91	0.169	42	0.130	0.054	-	-	-

Abbreviations: δ -DL, δ -decanolactone; PLQY, photoluminance quantum yield; EBE, exciton binding energy; τ_{avg} , lifetime value; L_{max} , the maximum of luminance; CE_{max} , the maximum of current efficiency; EQE, external quantum efficiency. ^aThe samples were used as an emissive layer of the LED ^bThe polymerization reactions were conducted in [TBD]:[4-iodobenzyl alcohol]₀:[δ -DL]₀:[HexFL]₀ = 1 : 1 : 60 : 18 under 25°C in bulk for ROP and -10°C in THF for SCR. The molecular weights were determined from ¹H NMR spectra through a comparison of the relative intensities of the polymer and initiator peaks (δ (PF) = 2.21 ppm, δ (PDL) = 4.87 ppm, δ (initiator) = 5.18 ppm). ^cThe device performances were recorded at the highest EQE voltage. *Device structure: PU / PEDOT:PSS / sample / PET / PU @ AgNWs. *Annealing condition: annealing at 120 °C in vacuum for 1 day. *PFO is a commercial polymer as a control group in the experiment.

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