

## Supporting Information

### **Blue Light-emitting Conjugated Polymer with Low Modulus and Better EL Spectra Stability**

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### **General characterization**

The  $^1\text{H}$  and  $^{13}\text{C}$ NMR spectra were recorded in  $\text{CDCl}_3$  using a Bruker 400 MHz spectrometer. The number-average molecular weights were obtained by gel permeation chromatography (GPC) analysis using THF as the eluent and linear polystyrene as the standard. The UV-visible absorption spectra were taken with a Shimadzu UV-1780 spectrometer at room temperature, and photoluminescence spectra were measured using Hitachi F-7100. Thermogravimetric analysis (TGA) was obtained using TGA2 (Mettler Instruments). Differential scanning calorimetry (DSC) data were measured by DSC214 Polyma (NETZSCH Instruments) at temperatures ranging from 25 to 300°C and at a rate of 10 K/min. The film morphology of the polymer film was measured with an AFM in tap mode (Bruker's size icon). PLQY measurements were performed with an Edinburgh FLSP980 fluorescence spectrophotometer equipped with an iso-arc lamp (Xe900) iso-lamp.

### **Transient Absorption Spectroscopy:**

Transient absorption measurements (visible) were performed using a Helios setup. The transient dynamics in fs-ns time region (50 fs-7 ns) was acquired by Helios that works in a nondegenerate pump-probe configuration. The pump pulses were generated from an optical parametric amplifier (OPerA Solo) that was pumped by a 1 kHz regenerative amplifier (Coherent Libra, 800 nm, 50 fs, 4 mJ). A mode lock Ti-sapphire oscillator (Coherent Vitesse, 80 MHz) was used to seed the amplifier. The probe pulses were a white light continuum generated by passing the 800 nm fs pulses through a 1 cm sapphire plate for the infrared part (840-1600 nm).

### **Nano-indentation test:**

The nano-indentation test was carried out by Hrysitron TI premier. A triangular based Berkovitch pyramid was chosen as the indenter, which has a nominal angle of 65.3° between the face and the vertical axis. The indenter is attached to a capacitive displacement transducer sensitive to movements of 0.2 nm, and the variable load is applied via a coil-and-magnet assembly with a resolution of around 2  $\mu\text{N}$ . The duration of the three processes, loading, holding and unloading in each test was set to 5 s, 2 s

and 5 s, respectively. The test samples were attached to a circular iron plate fixing on a magnet bracket. At least 3 sites were measured for each sample used for the nano-indentation test.

### **Tensile testing of free-standing films:**

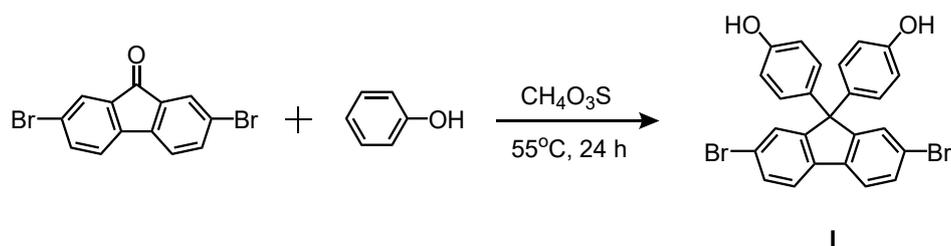
The sample preparation of free-standing films for tensile test is detailed description in our report previously.<sup>1</sup> The tensile test system was established referred to the tensile stage set-up reported before, which consists of a load cell, a linear stage and a DIC device on an anti-vibration table.<sup>2</sup> The tensile force is measured by load cells (LTS-50GA, KYOWA, Japan). An ultrahigh resolution linear DC motor (SGSP20-20, Japan) with a controller (PHSD-8353, AgeMotion) is used for linear displacement. Micro XYZ positioning stages are placed under the load cell and the linear stage for sample alignment. The system and stress-strain data are directly controlled by the programme of LabVIEW (National Instruments, USA). All samples were measured as cast without annealing.

### **PLED fabrication and characterization**

Patterned indium tin oxide (ITO) substrate ( $7-9 \Omega \text{ sq}^{-1}$ ,  $12 \times 12 \text{ mm}^2$ ) were cleaned in an ultrasonic bath with detergent, acetone, isopropanol and deionized water for 15 min each sequentially, then dried with flowed nitrogen atmosphere. Before preparing films, the surface of ITO substrates were treated with ultraviolet ozone for 15 min to achieve a hydrophilic surface. First, PEDOT:PSS (CLEVIOS P VP AI4083) was spin coated and annealed at  $120^\circ\text{C}$  for 20 minutes to form a 40 nm thickness hole transporting layer. Then, the emitting layer was spin coated at 1500 rpm from toluene solution (8 mg/mL). Subsequently, the substrates were transferred to nitrogen-filled glovebox and annealed at  $120^\circ\text{C}$  for 15 minutes. Finally, samples were moved to the vacuum chamber with a pressure below  $1 \times 10^{-5}$  mbar to sequentially deposit TPBi (20 nm,  $0.5 \text{ \AA/s}$ ), LiF (1 nm,  $0.2 \text{ \AA/s}$ ) and Al (100 nm,  $1 \text{ \AA/s}$ ) by thermal evaporating. The emitting area of PLEDs devices were  $4 \text{ mm}^2$ . The Current Density-Luminescence-Voltage curves and EL spectra were measured with a combination of Keithley 2400 source meter and QE65 Pro spectrometer (Ocean Optics). For the PLED with stretched emitting layer, we first

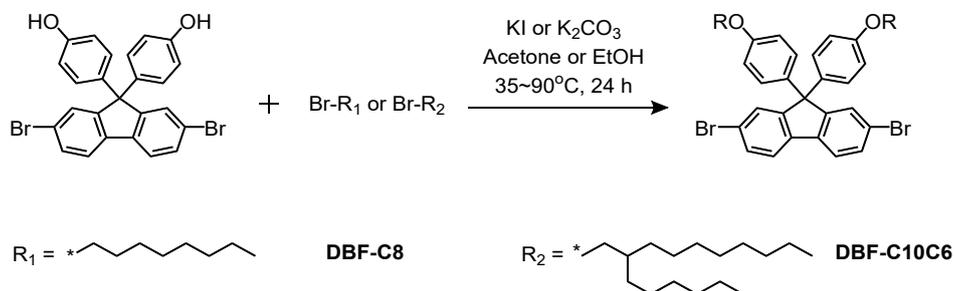
transferred the spin-coated light-emitting polymer film to the PDMS substrate, and stretched to a certain value, and then transferring the stretched emitting layer to the ITO-glass. The detailed fabrication procedures were referred to our previous report<sup>3</sup>.

**The detailed synthetic route of the studied polymers:**



**I (4,4'-(2,7-dibromo-9H-fluorene-9,9-diyl)diphenol):** First, 2,7-dibromofluorenone (4.0 g, 11.83 mmol) and phenol (8.2 g, 87.13 mmol) were put into a 250 mL round bottom flask, then methanesulfonic acid (30 mL) was injected. Then, the reaction was stirred at temperature of 55°C for 24 h. After the reaction completed, the product was extracted with dichloromethane for three times, and dried with anhydrous sodium sulfate. Then, the solvent was removed under reduced pressure, and the crude product was purified with silica gel column chromatography (petroleum ether:ethyl acetate = 4:1). The product was white powder (5.0 g, yield of 83%).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 9.38 (s, 2H), 7.86 (d, 2H), 7.54 (dd, 2H), 7.45 (d, 2H), 6.87 – 6.82 (m, 4H), 6.65 – 6.60 (m, 4H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 156.93, 154.41, 138.06, 134.99, 131.16, 129.17, 129.11, 123.30, 121.66, 115.82, 64.51.

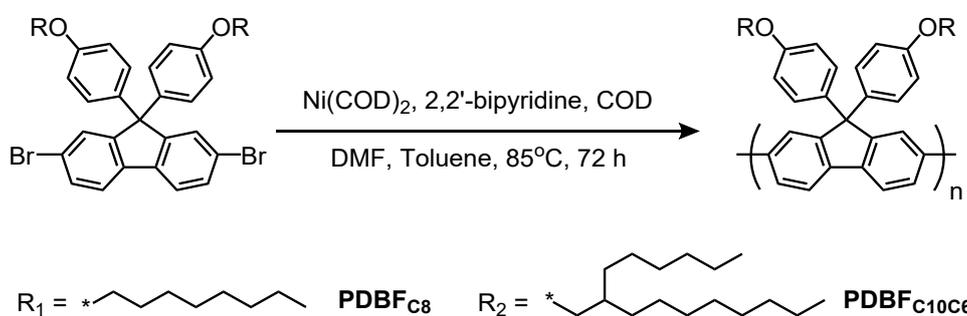


**DBF-C8 and DBF-C10C6:** The product I (2.0 g, 3.94 mmol) was put into a clean 250 mL round bottom flask with a clean magnet, K<sub>2</sub>CO<sub>3</sub> (1.0 g, 7.24 mmol), KI, (0.5 g, 3.01 mmol) was put into the flask to provide an alkaline environment, and then acetone (15 mL) or anhydrous ethanol (40 mL) was added as the solvent. Finally, 1-bromooctane

(1.9 g, 9.84 mmol) or 1-bromo-2-hexyldecane (3.0 g, 9.83 mmol) as the reaction material, was added to the flask, stirring was turned on, and the reaction temperature was set to 90°C with reflux. and the reaction was carried out for 24 h. The reaction progress was monitored by thin-layer chromatography. After the reaction was complete, the extraction was carried out by filtration. the crude product was purified by flash column chromatography, and the eluent was 4:1 petroleum ether: dichloromethane. The final product was waxy solid for DBF-C8 (2.2 g, yield of 76%) and transparent liquid for DBF-C10C6 (2.0 g, yield of 53%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) of DBF-C8: δ 7.56 (d, 2H), 7.48 – 7.44 (m, 4H), 7.04 (d, 4H), 6.76 (d, 4H), 3.90 (s, 4H), 1.75 (s, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) of DBF-C8: δ 158.32, 153.84, 136.35, 130.82, 121.62, 26.14.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) of DBF-C10C6: δ 7.57 (d, 2H), 7.47 (s, 4H), 7.04 (d, 4H), 6.77 (d, 4H), 3.78 (d, 4H), 1.74 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) of DBF-C10C6: δ 158.56, 153.89, 137.95, 136.26, 130.81, 129.06, 121.88, 70.81, 38.03, 31.44, 29.77, 26.93, 22.77.

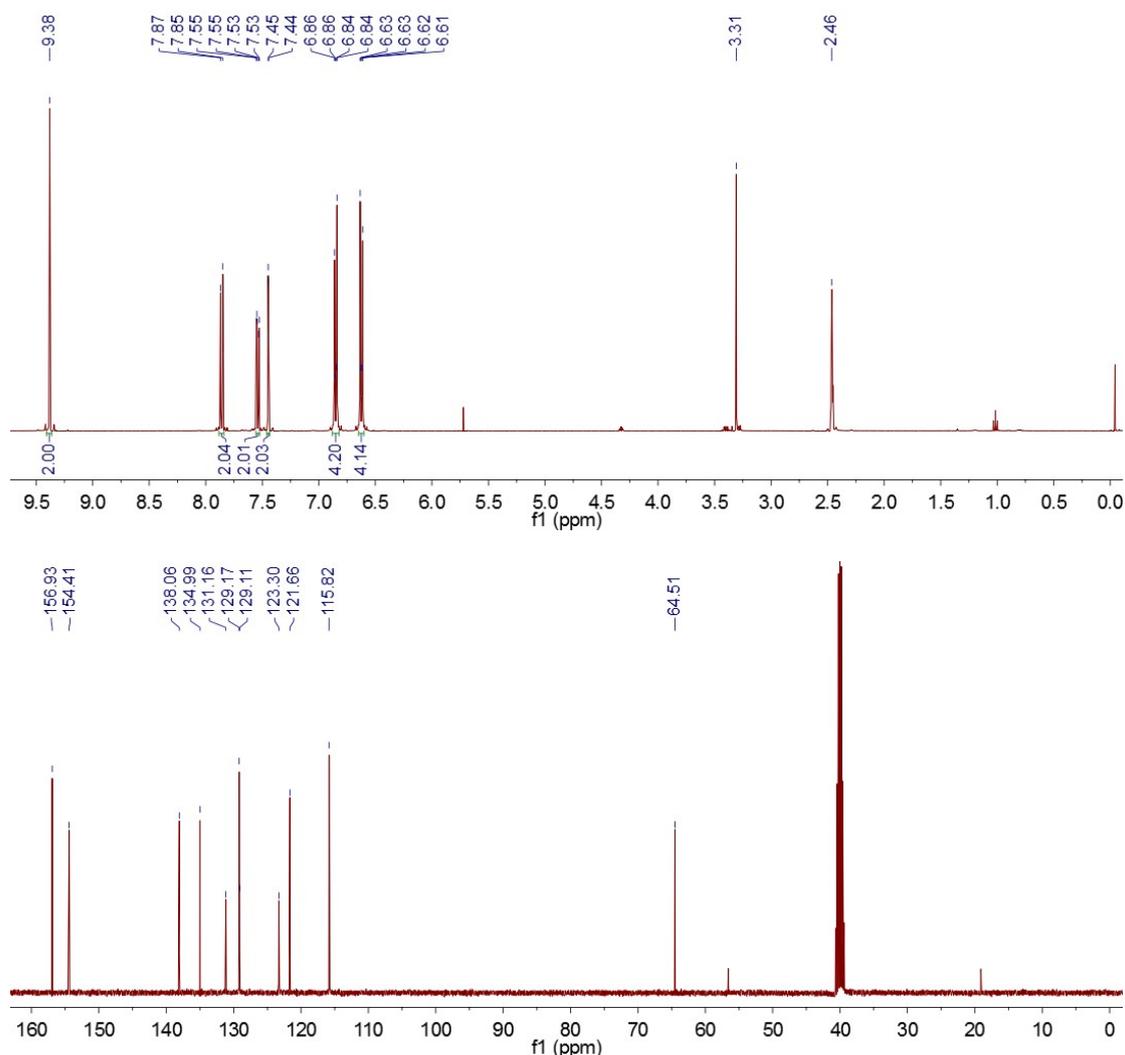


**Yamamoto polymerization of PDBF<sub>C8</sub> and PDBF<sub>C10C6</sub>:** The monomer of DBF-C8 or DBF-C10C6 (0.5 g), 2,2'-bipyridine (0.5 g), and bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)<sub>2</sub>) (1 g) were added successively in a Schlenk flask (25 mL) followed by degassing with N<sub>2</sub> adequately, sealing and protecting from light. Then, 1,5-cyclooctadiene (COD) (0.5 mL) and DMF (15 mL) were injected into the flask and stirred at 75°C for 30 min, in order to fully dissolved the monomer and catalysts. Then, toluene (15 mL) was injected, and the reaction mixture was stirred at 85°C under dark for 72 h. At last, bromobenzene (0.5 mL) was injected into the flask and stirred for 6 h in order to end the polymerization. After the flask cooling down, the mixture was

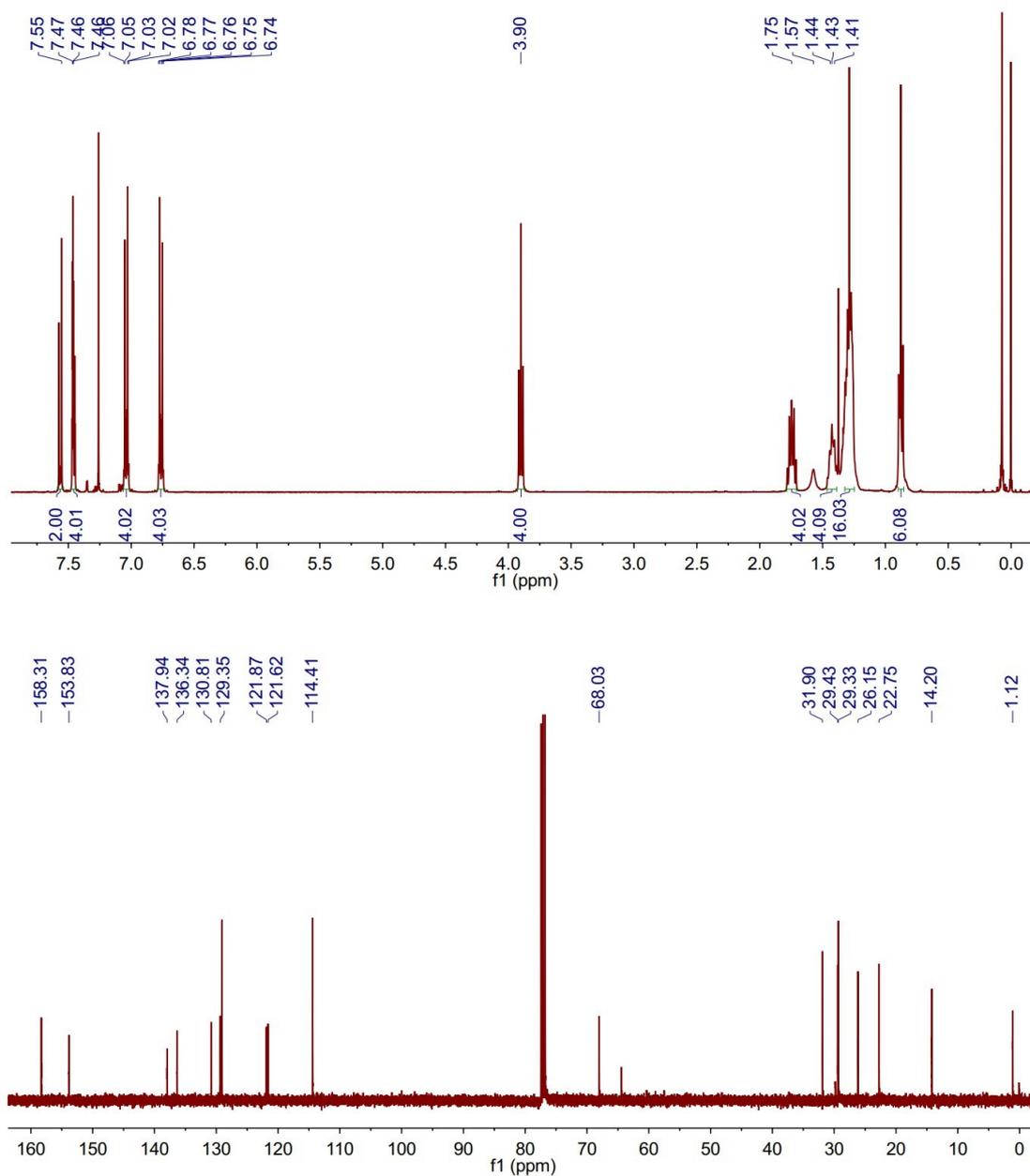
filtered and washed with DCM for several times, then the organic phase was purified by column chromatography ( $\text{Al}_2\text{O}_3$ ). Subsequently, the solution was concentrated to viscous, and precipitated in methanol followed with filtration. Further, the received polymer was washed through Soxhlet extraction using acetone and hexane as the eluent in order to remove oligomers and catalyst residues. At last, the polymer powder was dried under vacuum and used for this work (yields of ~60%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ) of  $\text{PDBF}_{\text{C}_8}$ :  $\delta$  7.86 - 7.67 (m, 2H), 7.53 (d, 4H), 7.16 (d, 4H), 6.76 (d, 4H), 3.97 - 3.81 (m, 4H), 1.79 - 1.68 (m, 4H).

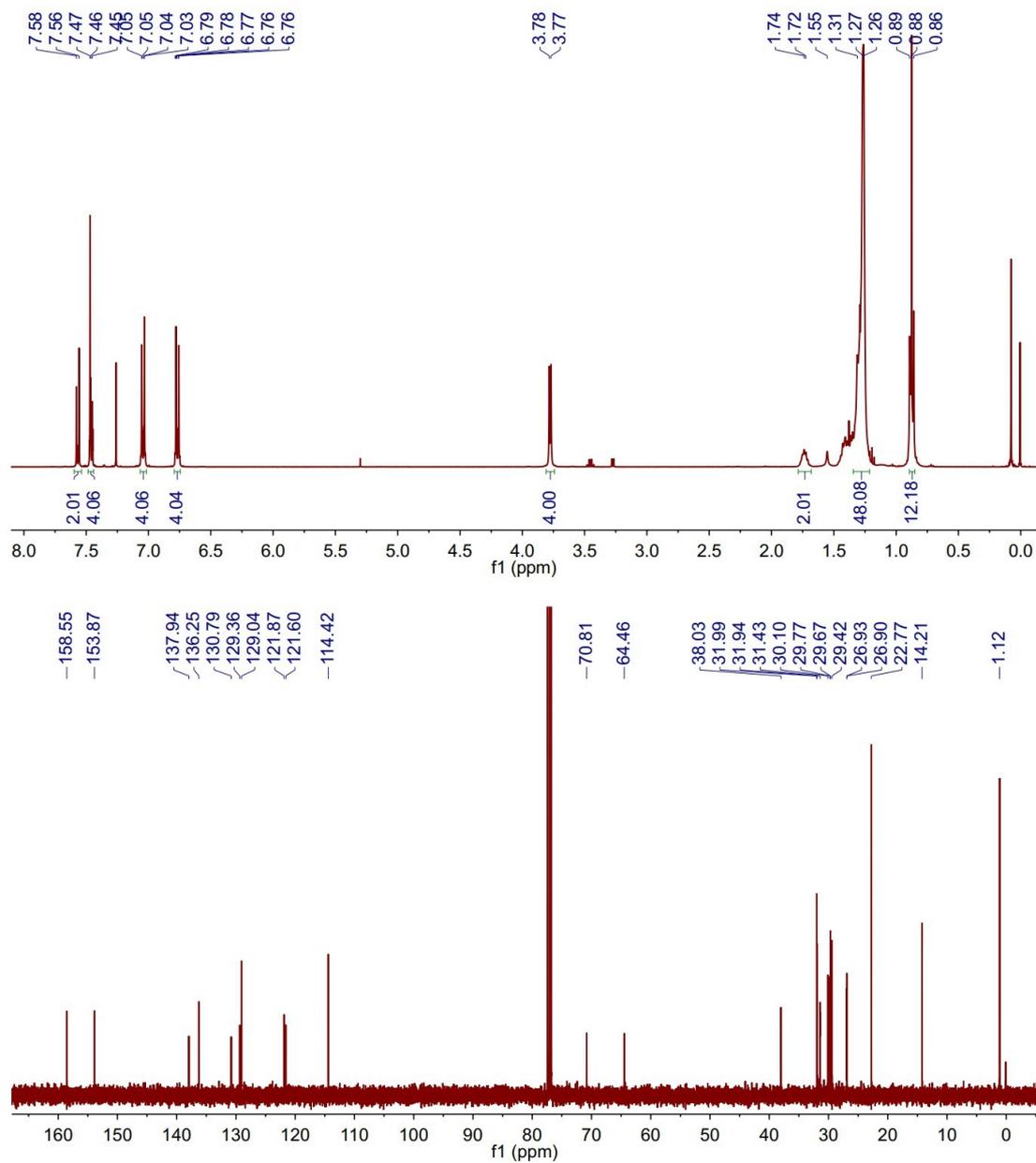
$^1\text{H}$  NMR ( $\text{CDCl}_3$ ) of  $\text{PDBF}_{\text{C}_{10}\text{C}_6}$ :  $\delta$  7.74 (d, 2H), 7.54 (d, 4H), 7.17 (d, 4H), 6.76 (d, 4H), 3.87 - 3.67 (m, 4H), 1.74 (s, 2H).



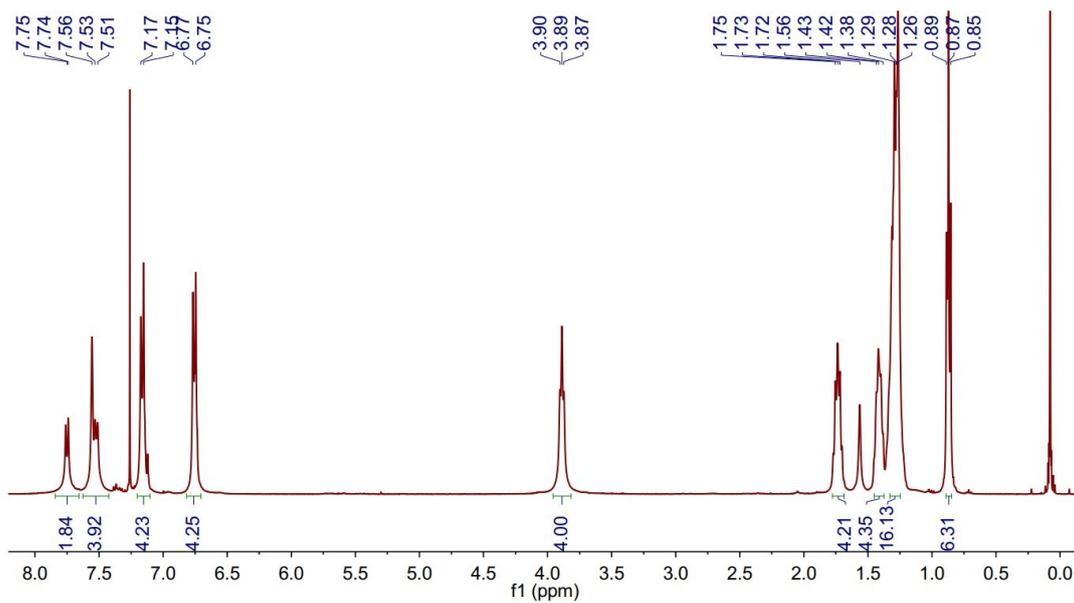
**Fig. S1.**  $^1\text{H}$  NMR (top) and  $^{13}\text{C}$  NMR (bottom) spectra of product I in  $\text{DMSO}-d_6$ .



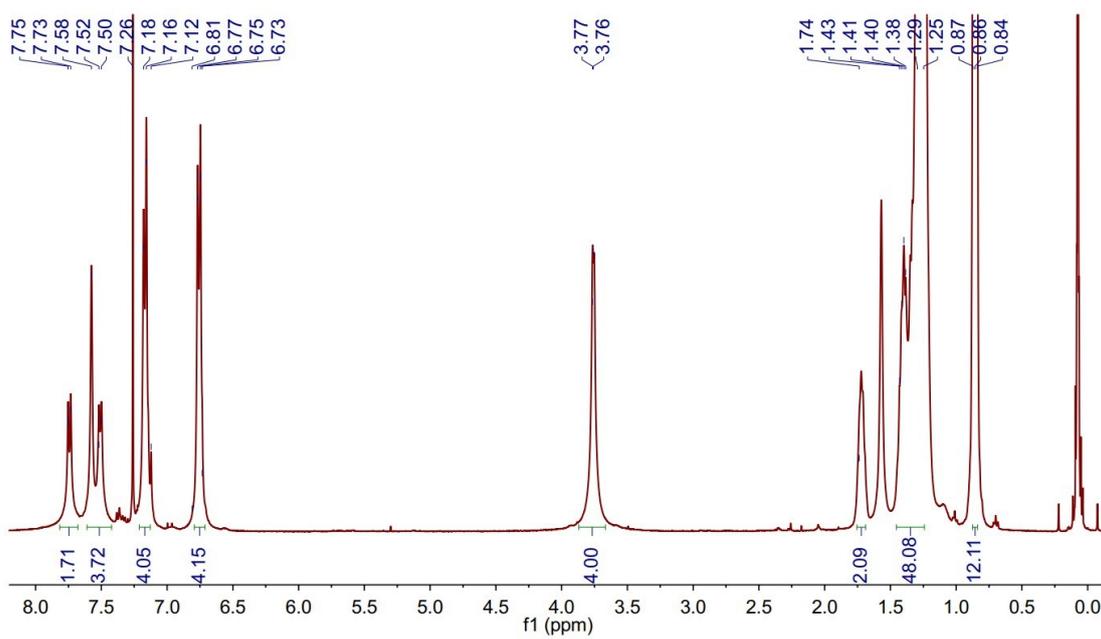
**Fig. S2.** <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of DBF-C8 in CDCl<sub>3</sub>.



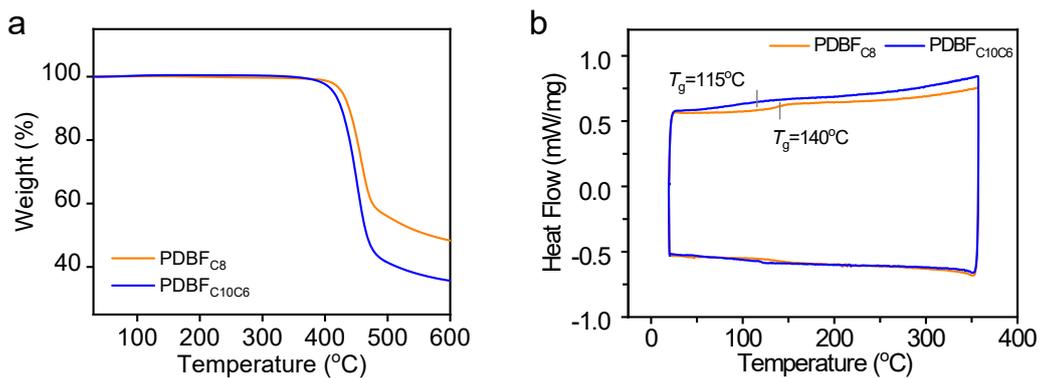
**Fig. S3.** <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of DBF-C10C6 in CDCl<sub>3</sub>.



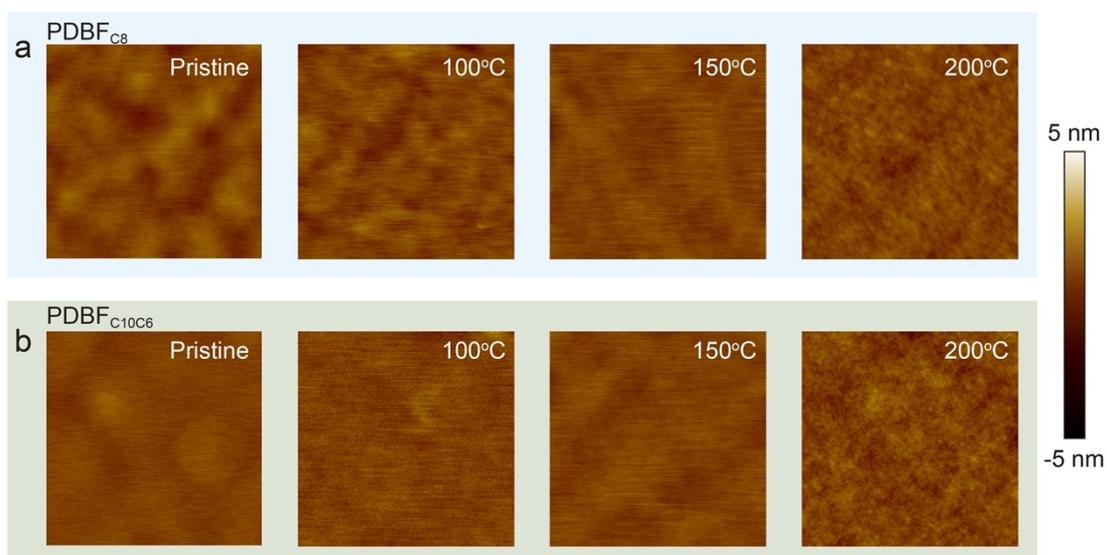
**Fig. S4.**  $^1\text{H}$  NMR spectra of  $\text{PDBF}_{\text{C}8}$  in  $\text{CDCl}_3$ .



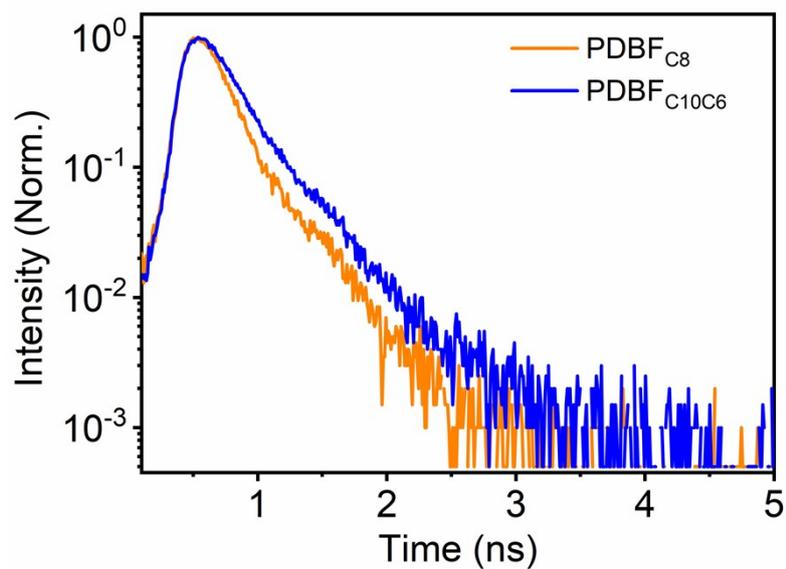
**Fig. S5.**  $^1\text{H}$  NMR spectra of  $\text{PDBF}_{\text{C}10\text{C}6}$  in  $\text{CDCl}_3$ .



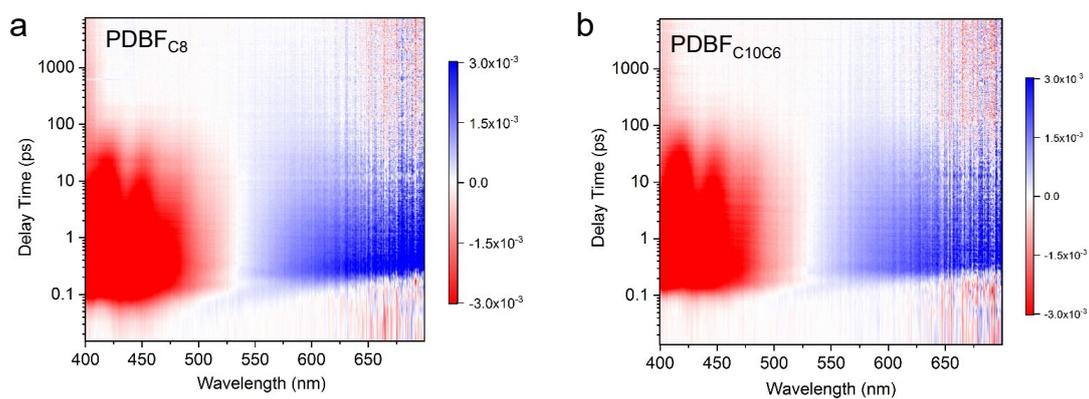
**Fig. S6.** (a) Thermogravimetric (TG) and (b) DSC curves of PDBF<sub>C8</sub> and PDBF<sub>C10C6</sub>. Heating rate was 10 K/min under nitrogen atmosphere.



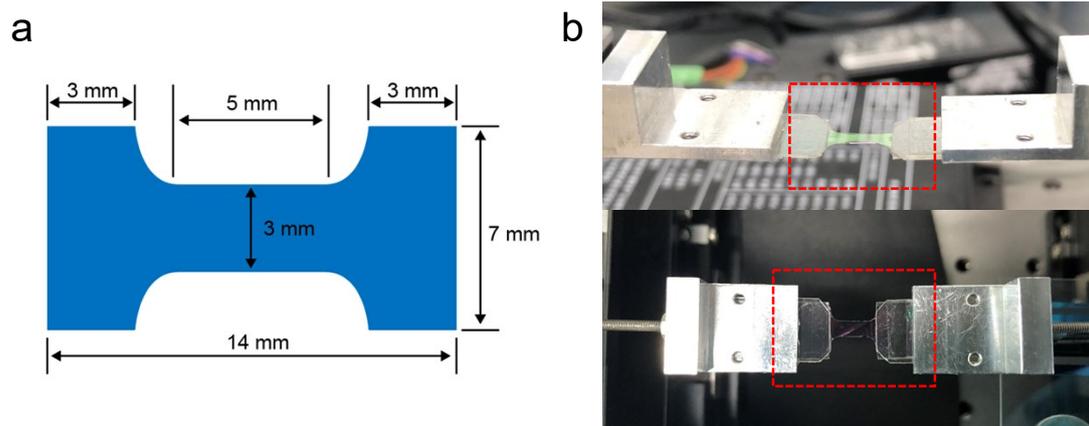
**Fig. S7.** Thermal stability of film morphology characterized by AFM tapping-mode with the scan size was  $5 \times 5 \mu\text{m}$ . The spin-coated films of PDBF<sub>C8</sub> (top) and PDBF<sub>C10C6</sub> (bottom) were thermal annealed at temperature of 100, 150, and 200°C for 20 min under N<sub>2</sub> atmosphere.



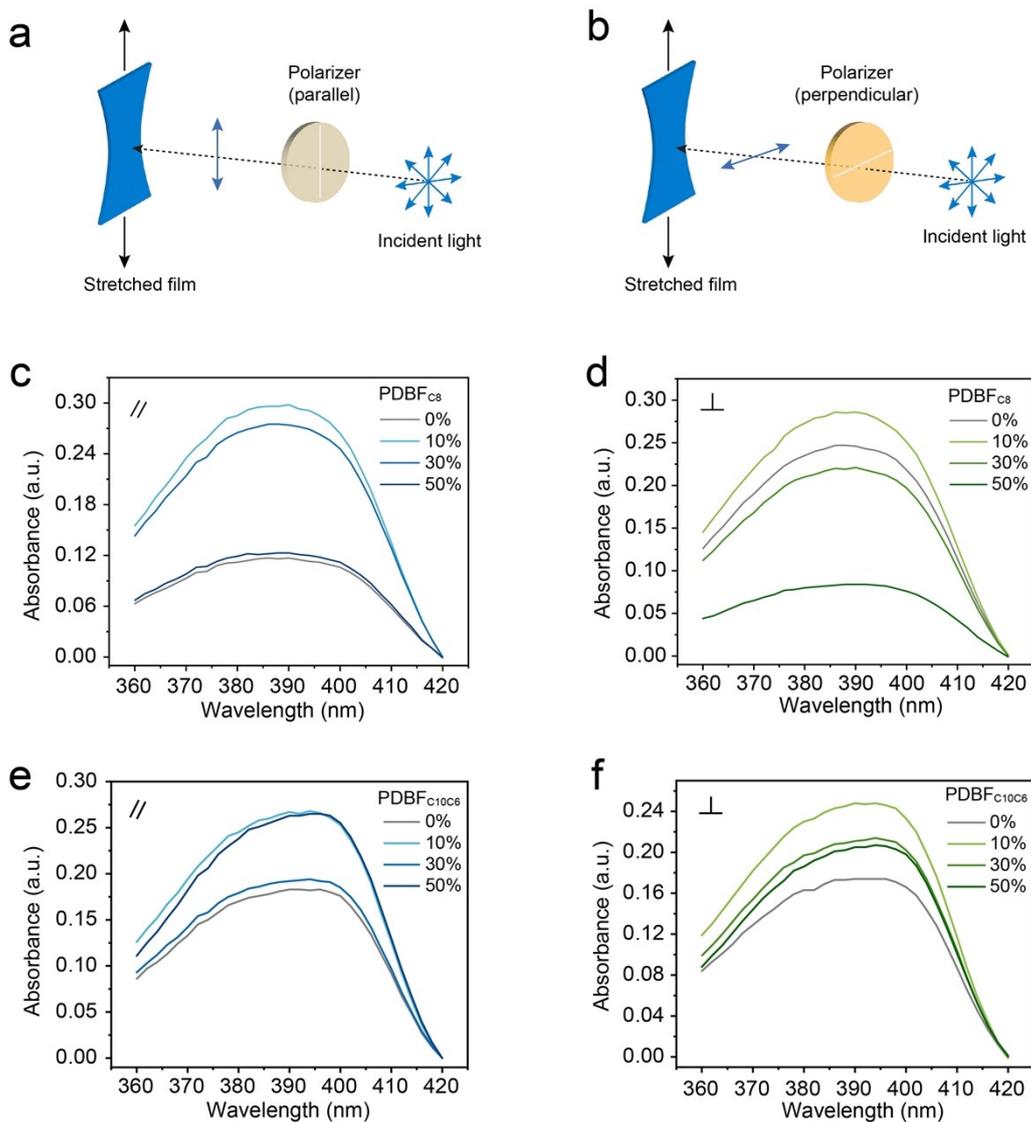
**Fig. S8.** Time-resolved fluorescence emission decays of spin-coated films. The lifetime of PDBF<sub>C8</sub> and PDBF<sub>C10C6</sub> were fitted to be 0.26 and 0.41 ns.



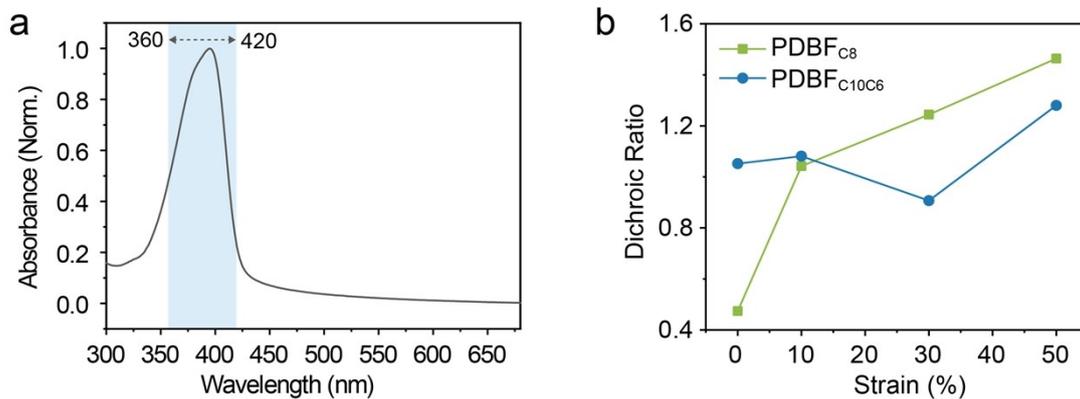
**Fig. S9.** Two-dimensional pseudocolor map of the TA spectra expressed in differential absorption ( $\Delta A$ ) versus of wavelength and pump-probe delay with the same scale bar.



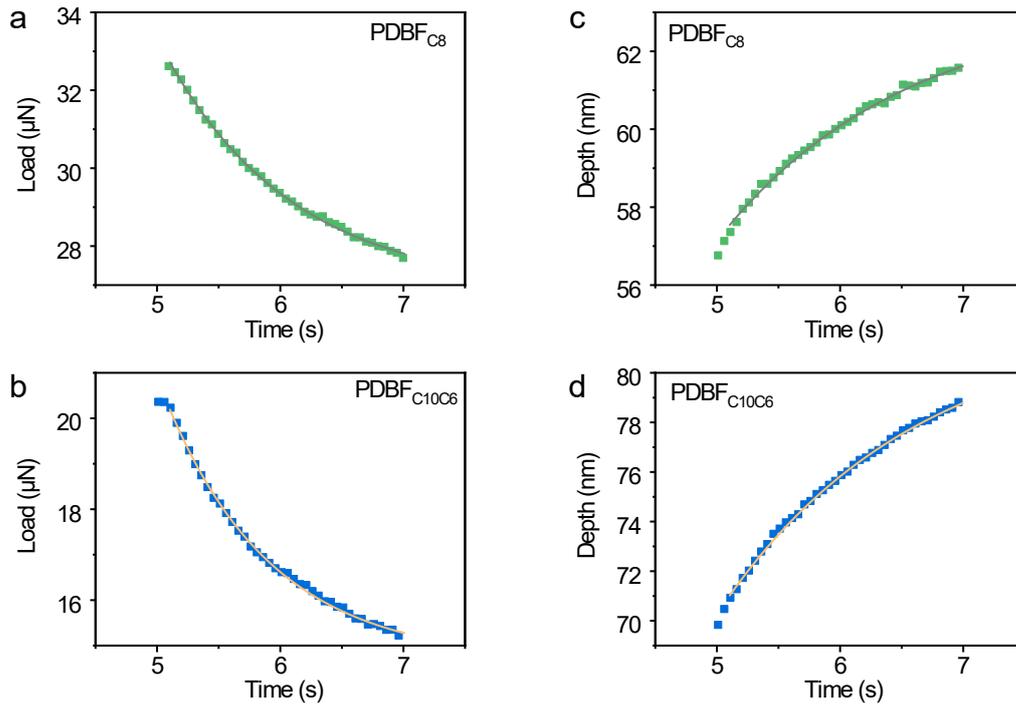
**Fig. S10.** (a) The design of the dog-bone sample. (b) Photographs of the free-standing thin film on the test stage.



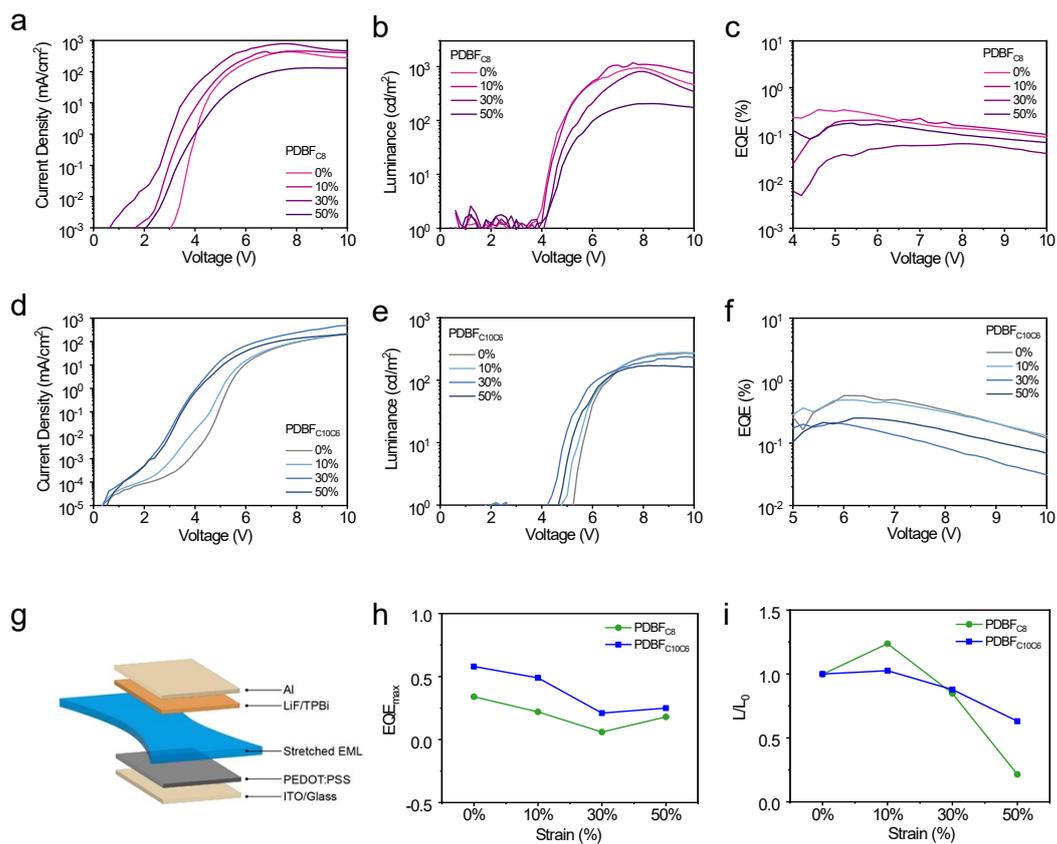
**Fig. S11.** Polarized UV-vis spectrum of PDBF<sub>C8</sub> and PDBF<sub>C10C6</sub> films under different strains. (a, b) Schematic illustration of parallel and perpendicular polarized UV-vis test on stretched films. Absorption spectra of PDBF<sub>C8</sub> films under different strains, which are parallel (c) and perpendicular (d) to the stretching direction. Absorption spectra of PDBF<sub>C10C6</sub> films under different strains, which are parallel (e) and perpendicular (f) to the stretching direction.



**Fig. S12.** (a) Polarized UV-vis spectra in the range of 360-420 nm were tested, due to the limitation of the polarized range of polarizer. (b) Change of the dichroic ratio of PDBF<sub>C8</sub> and PDBF<sub>C10C6</sub> under different strains.



**Fig. S13.** Three-parameter model fitting curves for the stress relaxation of (a) PDBF<sub>C8</sub> and (b) PDBF<sub>C10C6</sub> measured at mode of constant displacement. Three-parameter model fitting curves for the creep behavior of PDBF<sub>C8</sub> (c) and PDBF<sub>C10C6</sub> (d) measured at a constant displacement rate.



**Fig. S14.** The current density-voltage curves (a), luminance-voltage curves (b) and external quantum efficiency (EQE)-voltage curves (c) of devices based on stretched films of PDBF<sub>C8</sub>. The current density-voltage curves (d), luminance-voltage curves (e) and EQE-voltage curves (f) of devices based on stretched films of PDBF<sub>C10C6</sub>. (g) Device structure of the PLED fabricated with pre-stretched emitting layer. (h) EQE<sub>max</sub> and (i) relative luminance ( $L/L_0$ ) changes with the tensile strain.

## References

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2. J.-H. Kim, A. Nizami, Y. Hwangbo, B. Jang, H.-J. Lee, C.-S. Woo, S. Hyun and T.-S. Kim, *Nat. Commun.*, **2013**, 4, 2520.
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