

Supporting Information

Patternable Conjugated Polymers with Latent Hydrogen-bonding on the Main Chain

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General Method

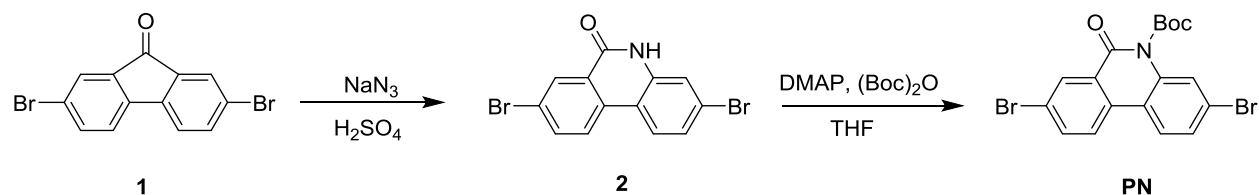
All the chemicals and solvents were used as received unless otherwise noted. Anhydrous tetrahydrofuran (THF) was distilled over sodium and freshly used. Nitrogen (N₂) protection was used for all oxygen and moisture-sensitive reactions. ¹H NMR spectra were performed on Varian Mercury 300 NMR (300 MHz) or 500 NMR (500 MHz) spectrometer. Molecular weight of polymers was measured by size exclusion chromatography (SEC) using Waters 150-C plus instrument equipped with three styragel HR columns (100 Å, mixed bed (50/500/10³/10⁴ Å) and mixed bed (10³, 10⁴, 10⁶ Å)) and a double detector [a differential refractometer (waters 410), a laser light scattering detector (Wyatt Technology, DAWN EOS λ=760 nm). All measurements were performed in THF with a flow rate of 1.0 ml/min at 30 °C. The columns were calibrated against commercially available polystyrene standards. Infrared spectra were obtained on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by casting films on KBr plates from solution with subsequent drying at 40–50 °C, the spectroscopic data were processed using

Win-IR software. UV/Vis spectra of monomer and polymer solutions were recorded on a Hewlett Packard Model 8453 UV/Vis Spectrophotometer. UV/Vis spectra of polymer films for all studies were measured on a in a CARY 100 Bio UV-visible spectrophotometer. Thermogravimetric analysis (TGA) was conducted on a TA Instrument Model Q500 at a heating rate of 10 °C/min under N₂ protection.

Cyclic voltammograms were recorded using an electrochemical analyzer from CH Instruments (CHI 608E). Thin films of the polymers were cast on an ITO electrode and cycled in CH₃CN containing 0.1 M *tetra*-n-butylammonium hexafluorophosphate (TBAPF₆) as an electrolyte salt at room temperature. Counter and reference electrode were platinum wires. Scan rate was 50mV · s⁻¹. All potentials were recorded versus Fc/Fc⁺ as reference. Onset potentials were determined from the intersection of two tangents drawn at the rising and background currents of the cyclic voltammograms curves. Spectroelectrochemical studies were carried out in a three electrode quartz cell that was placed in the UV-visible spectrophotometer.

Synthesis and Characterization

Monomer 1 (PN)

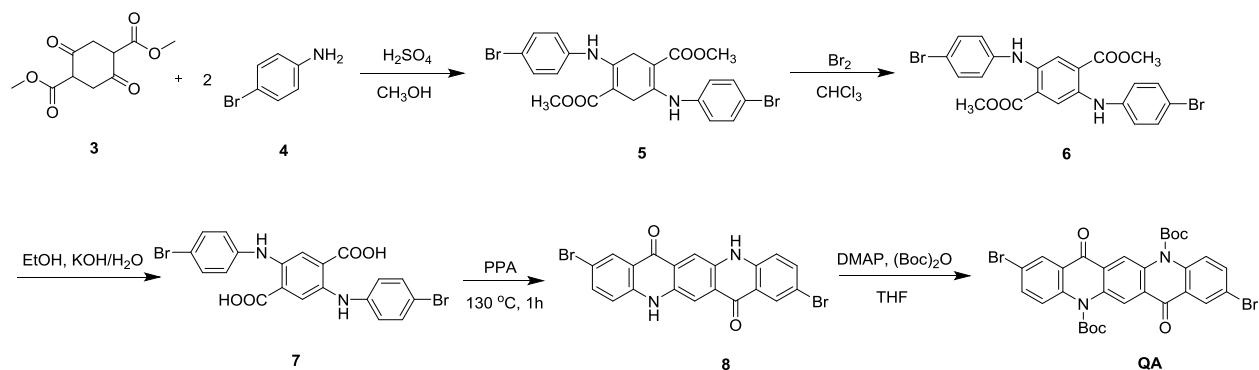


3,8-dibromophenanthridin-6(5H)-one (2).¹ To a solution of 8.1 g 2,7-dibromofluoren-9-one (Compound 1, 24 mmol Sigma-Aldrich, 99%) in 60 ml concentrated sulfuric acid (98%) at room temperature, 3.68 g sodium azide (NaN₃, 56.6 mmol) was added in small portions in half an hour under N₂ environment. After two hours reaction, the mixture was poured on ice with stirring. The

precipitated 3,8-Dibromophenanthridinone (2) was filtered off and washed with water and hexane, then dried under vacuum, affording 7.70 g product (91%). ^1H NMR (300 MHz, DMSO- d_6) δ 8.46 (d, 1H), 8.35 (q, 2H), 8.01 (q, 1H), 7.53 (d, 1H), 7.42 (q, 1H), 11.88 (s, 1H, N-H hydrogen bond).

***Tert*-butyl 3,8-dibromo-6-oxophenanthridine-5(6H)-carboxylate (PN).** To a solution of 4.23 g (12 mmol) compound 2 and 1.46 g 4-Dimethylaminopyridine (DMAP) (12 mmol, Sigma-Aldrich, 99%) in 70 ml anhydrous THF, 5.57 g di-*tert*-butyl dicarbonate (30 mmol, 2.5eq) in 15 ml anhydrous THF was added slowly at room temperature and under N_2 protection, allowing another 3 hours until TLC results show reaction finished. Reaction solution turned to clear during this process. Then the major part of the solvent was removed by rotary evaporator and remained mixture was mixed with about 40 ml 5% NaHCO_3 solution. Solid precipitates were filtered off and washed with water, then redissolved in CH_2Cl_2 and dried over anhydrous Na_2SO_4 . After solvent was removed using rotary evaporator, the obtained product was redissolved in minimum amount of CH_2Cl_2 and precipitated in 20 ml CH_3OH , affording 3.80 g pale yellow product (71%). ^1H NMR (300 MHz, CDCl_3) δ 8.60 (d, 1H), 8.05 (q, 2H), 7.89(q, 1H), 7.46 (q, 1H), 7.30 (d, 1H), 1.72 (s, 9 H).

Monomer 2 (QA)²



Dimethyl 2,5-bis(4-bromophenylamino)cyclohexa-1,4-diene-1,4-dicarboxylate (5). 4.56 g compound **3** (20 mmol) and 8.60 g compound **4** (50 mmol) was dissolved in 80 ml CH₃OH, refluxing at 65 °C for half an hour under N₂ protection. Concentrated H₂SO₄ (98%, 0.4 ml) was added as catalyst, allowing 3 hours reaction. Then reaction mixture was filtered off and washed with hot CH₃OH. The solid was dried under vacuum, yielding 9.25 g pale yellow product (86%). ¹H NMR (300 MHz, CDCl₃) δ 10.59 (s, 2H, N-H hydrogen bond), 7.46 (d, 4H), 6.97 (d, 4H), 3.67 (s, 6H), 3.33 (s, 4H).

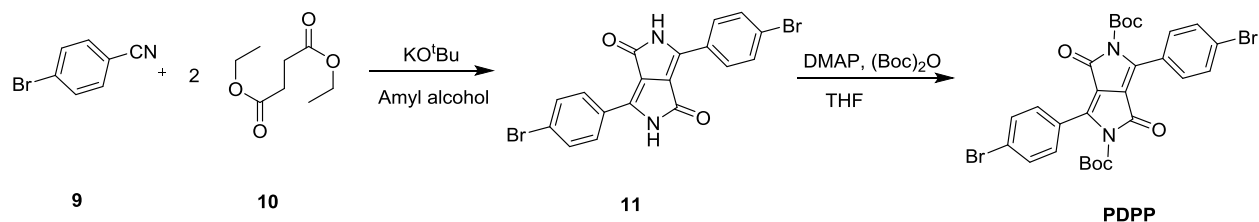
Dimethyl 2,5-bis(4-bromophenylamino)terephthalate (6). 11.25 g compound **5** (21 mmol) was suspended in 600 ml CHCl₃ for refluxing overnight under N₂ protection. Then the solution was cooled down and 1.13 ml Br₂ (22 mmol) in 30 ml CHCl₃ was added dropwisely in 0.5 hour. The reaction was allowed for another 0.5 hour and then the mixture was filtered. Solution phase was dried under vacuum, yielding 9.44 g red product (84%). ¹H NMR (300 MHz, CDCl₃) δ 7.93 (s, 2H), 7.42 (d, 4H), 7.06 (d, 4H), 3.87 (s, 6H).

2,5-bis(4-bromophenylamino)terephthalic acid (7). In a 500 ml 3-neck flask, 9.25 g compound **6** (17.3 mmol), 5.67 g KOH (100 mmol) and 6.39 g sodium-3-nitrobenzene sulphonate (28 mmol) were dissolved in 150 ml ethanol and 50 ml water and the mixture was refluxed overnight under N₂ protection. The ethanol was then distilled from the system for two hours by increasing the temperature to 110 °C. The reaction mixture was filtered in hot and hydrochloric acid (10%, 37.8 ml) was added into the solution phase dropwise. The resulted precipitation was filtered and washed with water until the pH of the filtrate reached 7. After drying under vacuum, 7.2 g product was obtained (82%). ¹H NMR (300 MHz, DMSO-d₆) δ 8.87 (s, 2H, N-H hydrogen bond) 7.93 (s, 2H), 7.80 (s, 2H), 7.44 (d, 4H), 7.10 (d, 2H).

2,9-dibromo-quinacridone (8). Compound **7** (7.2 g, 14 mmol) was suspended in 80 ml polyphosphoric acid (PPA) with strong stirring under N₂ protection. The mixture was heated to 135 °C and stirred for 3 h. After the reaction was finished, the mixture was poured into ice water (~500 ml) and was further stirred for 1 h. The dark red precipitation was filtered and washed with water until the pH of the filtrate reached 7. The product was dried under vacuum at 60 °C, yielding 6.4 g compound **8** (95%). The product was used for the next step without further NMR characterization due to the poor solubility.

2,9-dibromo-N,N'-di-*tert*-butoxycarbonyl quinacridone (QA). To a solution of 2 g (6.4 mmol) compound **8** and 1.56 g DMAP (12.8 mmol) in 60 ml anhydrous THF at room temperature under N₂ protection, 3.50 g di-*tert*-butyl dicarbonate (16.1 mmol, 2.5eq) in 10 ml anhydrous THF was added slowly, allowing reaction for overnight. The major part of the solvent was removed then by rotary evaporator and the reaction mixture was mixed with about 50 ml 5% NaHCO₃ solution. Solid precipitates were filtered off and washed with water, then redissolved in CH₂Cl₂ and dried over Na₂SO₄. After removing the solvent, solid product was redissolved in minimum amount of CH₂Cl₂ and precipitated in small amount of CH₃OH, affording 3.45 g yellow final product (80%).
¹H NMR (300 MHz, CDCl₃) δ8.74 (s, 2H), 8.52 (s, 2H), 7.78 (d, 4H), 1.74 (s, 18H).

Monomer 3 (PDPP)³

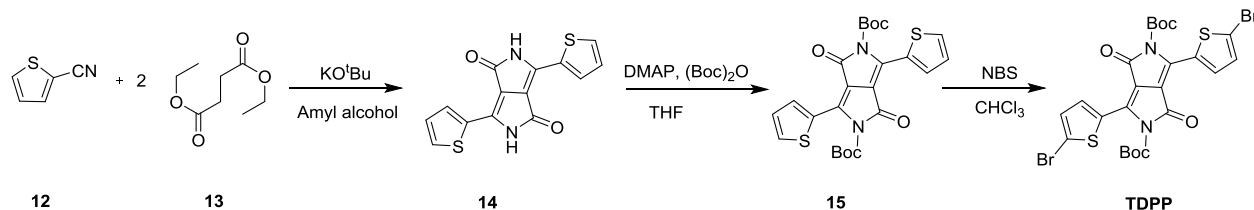


3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (11). KO^tBu (11.5 g, 102.5 mmol), 4-bromobenzonitrile (compound **9**, 18.2 g, 100mmol) was dissolved in 50 ml anhydrous *t*-amyl alcohol and heated to 90 °C under N₂ protection. Diethyl succinate (compound **10**, 6.625 ml, 40 mmol) in 5 ml *t*-amyl alcohol was added dropwise in 2 h. After extra two hours, the solution was cooled to 65 °C, and 50 ml CH₃OH was added. The reaction mixture was further neutralized with CH₃COOH and refluxing for 1 h. The red precipitates were filtered in hot (~50 °C). Then the solid was suspended in 150 ml CH₃OH and the mixture was stirred for 40 min. After filtration, the solid was washed with CH₃OH and water until the filtrate became colorless. The filter cake was dried at 80 °C in vacuum, affording 9.1 g product (51%). The product was used for the next step without further NMR characterization due to the pigment's poor solubility.

di-*tert*-butyl 3,6-bis(4-bromophenyl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1H,4H)-dicarboxylate (PDPP). To a solution of 1.96 g compound **11** (4.4 mmol) and 1.07 g DMAP (8.8 mmol) in 60 ml anhydrous THF at room temperature under N₂ protection, 2.40 g di-*tert*-butyl dicarbonate (11 mmol, 2.5eq) in 10 ml anhydrous THF was added slowly, allowing reaction for overnight. The major part of the solvent was removed then by rotary evaporator and remained mixture was mixed with 5% NaHCO₃ solution. Solid precipitates were filtered off and washed with water, then redissolved in CH₂Cl₂ and dried over Na₂SO₄. After the solvent was removed, the solid product was redissolved in minimum amount of CH₂Cl₂ and precipitated in small

amount of CH₃OH, affording 2.50 g yellow final product (88%). ¹H NMR (300 MHz, CDCl₃) δ7.63 (d, 8H), 1.46 (s, 18H).

Monomer 4 (TDPP)⁴



3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,6aH)-dione (14). In a 3-neck 500 ml flask, 125 ml *t*-amyl alcohol and KO^tBu (13.25 g, 118 mmol) were charged and stirred at 105 °C for 1.5 h under N₂ protection. Then 11.72 g 2-thiophene-carbonitrile (**11**, 10 ml, 107 mmol) was added dropwise in 0.5 h. After another 0.5 h, 6.23 g diethyl succinate (**12**, 5.95ml, 34 mmol) in 40 ml *t*-amyl alcohol was slowly added in 1 h at same temperature, allowing further stirring for 2 h. Then the reaction mixture was cooled to 50 °C, 60 ml methanol and 15 ml water was added and the solution was refluxed for 45 min. After cooled to room temperature, the reaction mixture was poured to 100 g ice/30 ml 35% HCl/150 ml methanol mixture and then stirred for 45 min. The dark purple precipitates were filtered and washed with methanol and water for 3 times. The solid was dried under vacuum at 80 °C, yielding 6.1 g product (57%). The product was used for the next step without further NMR characterization due to the poor solubility.

di-*tert*-butyl 1,4-dioxo-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-2,5(1H,4H)-dicarboxylate (15). To a solution of 3 g (10 mmol) compound **14** and 2.56 g DMAP (21 mmol) in 100 ml anhydrous THF, 5.61 g di-*tert*-butyl dicarbonate (30 mmol, 3eq) in 15 ml anhydrous THF was added slowly at room temperature under N₂ protection, allowing reaction for overnight. The

major part of the solvent was removed then by rotary evaporator and the reaction mixture was mixed with 5% NaHCO₃ solution. Solid precipitates were filtered off and washed with water, then redissolved in CH₂Cl₂ and dried over Na₂SO₄. After the solvent was removed, the solid product was redissolved in minimum amount of CH₂Cl₂ and precipitated in small amount of CH₃OH, affording 4.0 g dark red final product (80%). ¹H NMR (300 MHz, DMSO-d₆) δ8.11 (q, 2H), 8.07 (q, 2H), 7.33 (d, 2H), 1.44 (s, 18H).

di-tert-butyl 3,6-bis(5-bromothiophen-2-yl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1H,4H)-dicarboxylate (TDPP). Compound **15** (0.5 g, 1 mmol) was dissolved in 30 ml CHCl₃ under N₂ protection. N-bromosuccinimide (NBS) (0.374 g, 2.1 mmol) was charged in one portion and the reaction mixture was stirred in dark for 24 h. The reaction mixture was poured into 90 ml methanol and the resulted suspension was stirred for 20 min. The solid was filtered and washed with hot water and methanol. The filter cake was dried in vacuum and 0.49 g product was obtained (75%). ¹H NMR (300 MHz, CDCl₃) δ8.08 (d, 2H), 7.17 (d, 2H), 1.62 (s, 18H).

General Polymer Synthesis Procedure

200 mg of (0.44 mmol) **PN**, 228.98 mg 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (0.44mmol, 1.0 eq, Sigma-Aldrich, 97%), 15.37 mg Pd(PPh₃)₄ (3% eq) was charged in to a flask with 1 ml p-dioxane, 2 ml toluene. The mixture was degassed for 3 min using ultrasonication and then heated to 80 °C under N₂ protection. A degassed K₂CO₃/water (153 mg K₂CO₃, 2.5 eq in 1 ml water) solution was added in one portion and the temperature was raised to 105 °C for 2.5 hr. Then the reaction mixture was cooled down and 40 ml toluene was added. After washed with brine (30 ml × 2) and water (30 ml), the organic phase was dried over Na₂SO₄ and evaporated. The solid was dissolved in minimum amount of CH₂Cl₂ and precipitated

in small amount of methanol. The polymer was collected and dried under vacuum. 150 mg product (**P-PN-FLR**) was obtained with yellow color (54%). Mw: 30000, PDI: 2.0. ^1H NMR (300 MHz, CDCl_3) δ 8.92 (1H), 8.41 (1H), 8.19 (1H), 7.9-7.6 (8H), 7.50 (1H), 2.12 (4H), 1.83 (9H), 1.2-0.7 (22H).

Data for P-QA-FLR: Reaction time is 3 h, other protocol follow the same procedure. Mw: 14000, PDI: 1.5. Yield: 41%. ^1H NMR (500 MHz, CDCl_3): δ 8.86 (2H), 8.79 (2H), 8.10 (2H), 8.01 (2H), 7.83-7.82 (6H), 2.10 (4H), 1.80 (18H), 1.2-0.6 (22H).

Data for P-PDPP-FLR: Reaction time is 3 h, other protocol follow the same procedure. Mw: 9500, PDI: 1.3. Yield: 46%. ^1H NMR (500 MHz, CDCl_3): δ 7.91 (4H), 7.83 (6H), 7.68-7.65 (4H), 2.09 (4H), 1.54 (18H), 1.2-0.6 (22H).

Data for P-TDPP-FLR: Reaction time is overnight, other protocol follow the same procedure. Mw: 9400, PDI: 1.3. Yield: 30%. ^1H NMR (500 MHz, CDCl_3): δ 8.37-8.31 (1H), 7.76-7.61 (7H), 7.5-7.46 (2H), 2.04 (4H), 1.67 (18H), 1.2-0.7 (22H).

NMR spectra of all the polymers are shown in **Figure S1**.

Photo-patterning. Polymer solution (10 mg/ml **P-PN-FLR** in toluene) was filtered with a PTFE syringe filter (0.45 μm) and then was spin-casted on ITO glass (800 rpm, 45 s) or silicon wafer (1200 rpm, 45 s). Solution of photo-acid generator ((4-phenylthiophenyl)diphenylsulfonium triflate in methanol, 10 mg/ml) was spin-casted on the top of polymer films with same spin-casting condition in dark environment. The polymer film was irradiated by the UV flood exposure system (Newport, 1000 W Mercury-Xenon lamp with mid-range UV mirrors: 260~320 nm). The irradiation is conducted through a home-made “UA” stencil (for the patterns in Figure 5a, 5b and SI video S2), or a commercial (SPI supplies) TEM grid (for the patterns in Figure 5c and 5d), or a commercial (Photo Etch Technology) stainless steel mask (for the patterns in SI

Figure S8) under the controlled UV intensity (130 mW/cm^2 , with calibrator probe of 280 nm, exposure time = 30 s unless the case described below). After UV exposure, the film was soaked in toluene for 5 ~ 10 second to remove the non-irradiated polymer and then in methanol for 5 ~ 10 seconds to remove the photo-acid residues. The film was rinsed by clean methanol and then was blow-dried by air gun. The mask for the patterned “UA” letters (Figure 5) was prepared in the lab. In order to get a thick film for the better contrast in the videos, the polymer spin-casting process was repeated for three times with a time interval of one minute between each spin-coating process to make sure the previous spin-casted film is dry enough. The exposure time for such film is two minutes.

Figures and Tables

Table S1. Molecular weight and UV/Vis absorption information of polymers and monomers.

Polymer	Mw kDa	PDI	$\lambda_{\text{max}}/\text{nm}$ (monomer in THF)	$\lambda_{\text{max}}/\text{nm}$ (polymer in THF)	$\lambda_{\text{onset}}/\text{nm}$ (monomer in THF)	$\lambda_{\text{onset}}/\text{nm}$ (polymer in THF)	$\lambda_{\text{onset}}/\text{nm}$ (polymer film)	$\lambda_{\text{onset}}/\text{nm}$ (polymer film, annealed)
P-PN-FLR	30	2.0	329	395	353	420	431	435
P-QA-FLR	14	1.5	446	458	508	528	536	601
P-PDPP- FLR	9.5	1.3	441	482	488	544	569	604
P-TDPP- FLR	9.4	1.3	503	578	567	664	693	700

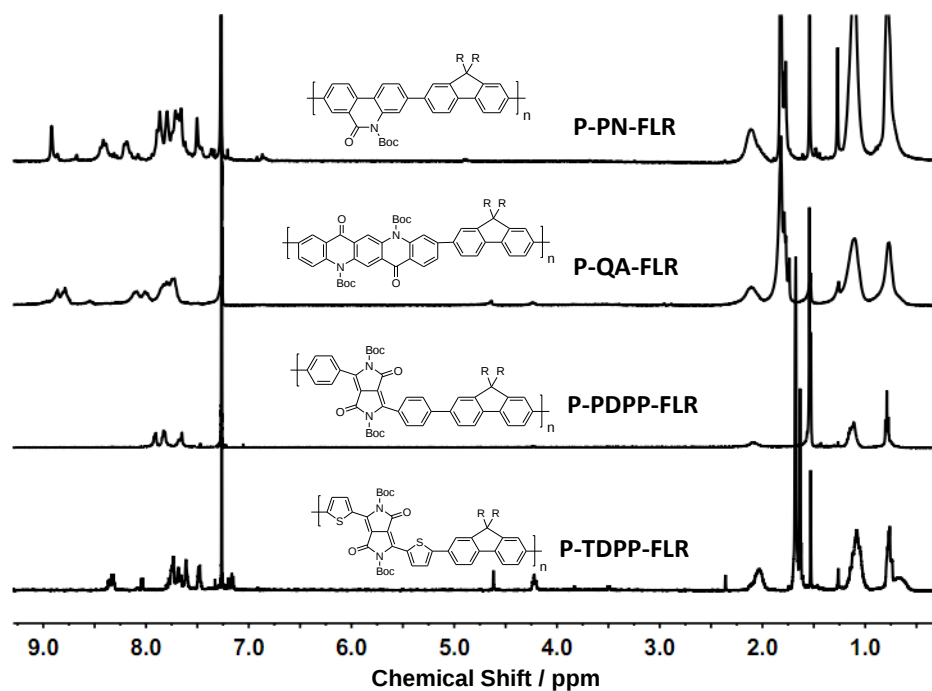


Figure S1. ^1H NMR spectra of polymers in CDCl_3 .

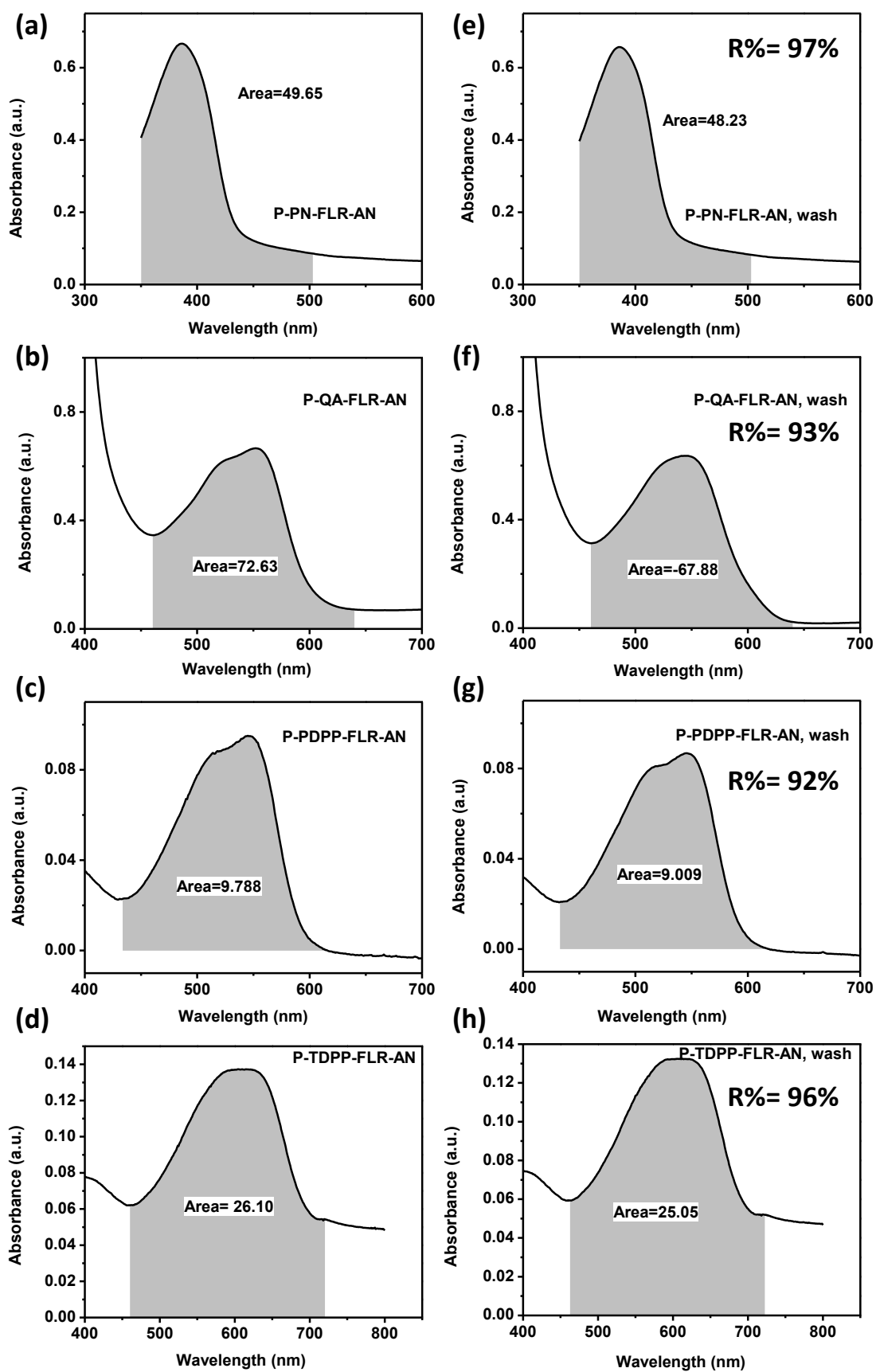


Figure S2. Integration area of UV/Vis absorption peaks of thermal annealed polymer thin films on glass substrates: a–d), before THF wash; e–h), after THF wash. The integration areas were calculated. Then the absorption retention ratio (R%) can be obtained by dividing the integration area of washed polymer films with the integration area of non-washed polymer films.

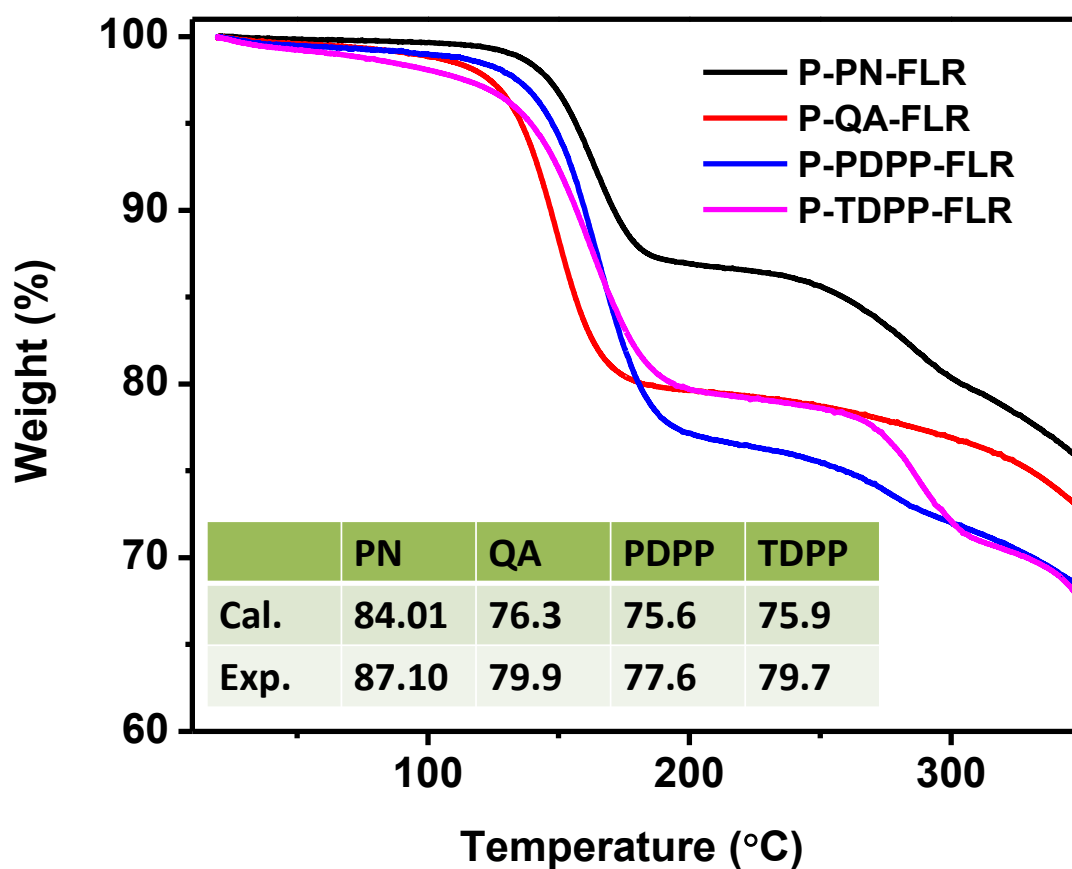


Figure S3. Thermogravimetric analysis (TGA) of polymers at a heating rate of 10 °C/min under N₂. The inset table concludes the theoretical and experimental mass loss of polymers after the removal of *t*-Boc group. The results indicate that the temperature for removing *t*-Boc group is around 180 °C.

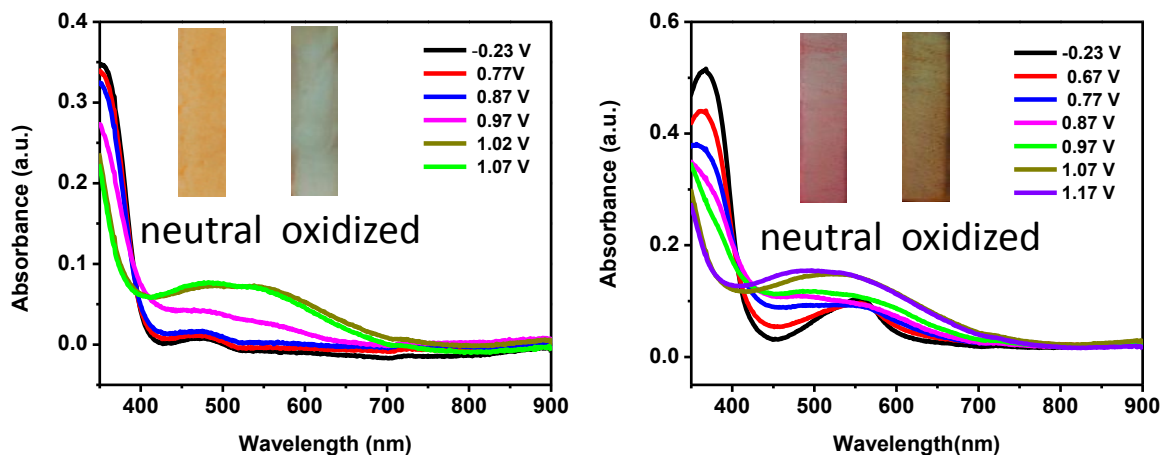


Figure S4. Spectroelectrochemical analysis of spin-casted **P-QA-FLR** films on an ITO anode before (Left) and after (Right) thermal annealed at 180 °C for 5 min. Electrolyte solution: 0.1 M TBAPF₆ in acetonitrile. Temperature: 25 °C. Potential from -0.23 V to 1.17 V versus Fc/Fc⁺. The samples of the neutral and fully oxidized films are shown in the insert.

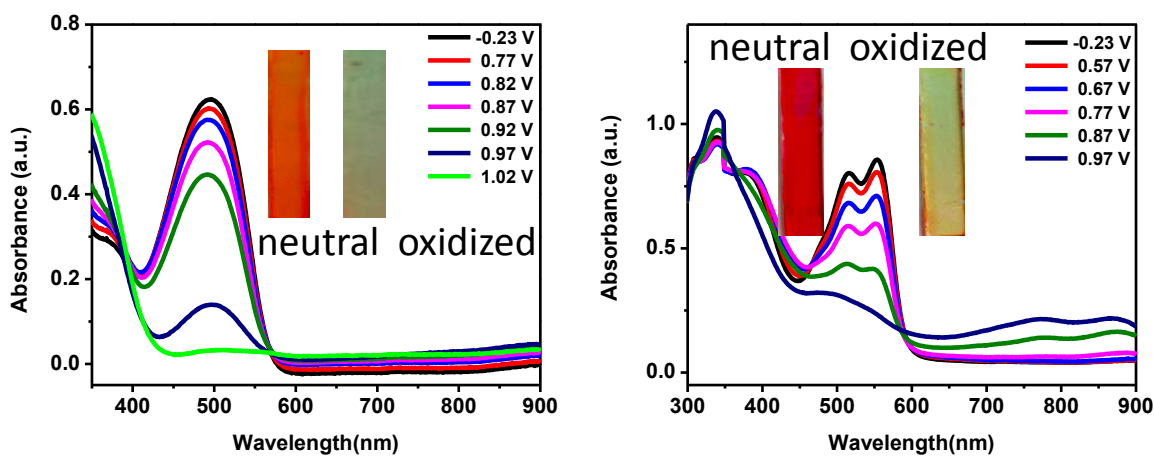


Figure S5. Spectroelectrochemical analysis of spin-casted **P-PDPP-FLR** film on an ITO anode before (Left) and after (Right) thermal annealed at 180 °C for 5 min. Electrolyte solution: 0.1 M TBAPF₆ in acetonitrile. Temperature: 25 °C. Potential from -0.23 V to 1.02 V versus Fc/Fc⁺. The samples of the neutral and fully oxidized films are shown in the insert.

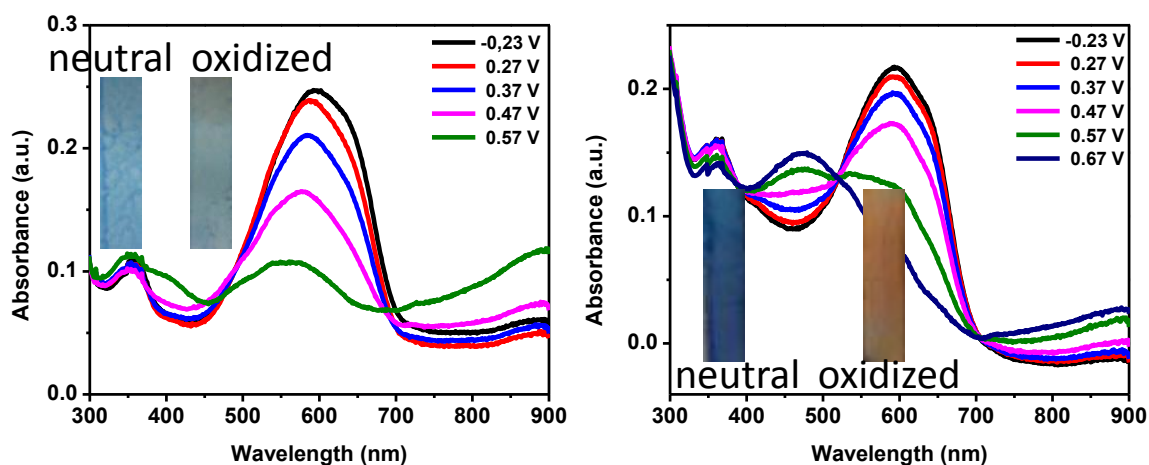


Figure S6. Spectroelectrochemical analysis of spin-casted **P-TDPP-FLR** film on an ITO anode before (Left) and after (Right) thermal annealed at 180 °C for 5 min. Electrolyte solution: 0.1 M TBAPF₆ in acetonitrile. Temperature: 25 °C. Potential from -0.23 V to 0.67 V versus Fc/Fc⁺. The samples of the neutral and fully oxidized films are shown in the insert.

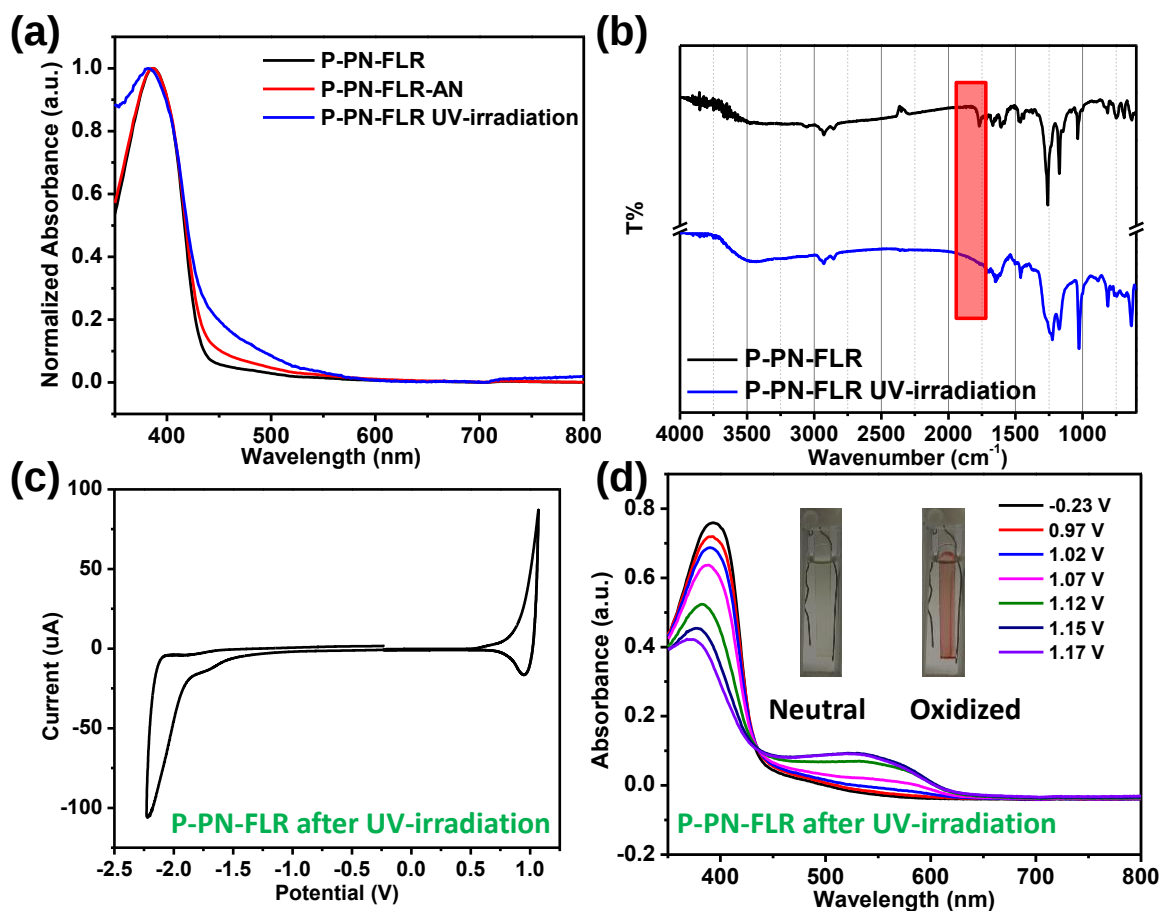


Figure S7. Characterization of UV irradiated polymer **P-PN-FLR** films. a) UV/Vis spectra of **P-PN-FLR** films (black), after thermal annealing (red) and after UV-irradiation. b) FTIR spectra of **P-PN-FLR** film before (black) and after (blue) UV-irradiation. The red frames indicate the region where the absorption peaks of *t*-Boc group appears. c) Cyclic voltammograms of UV-irradiated **P-PN-FLR** film. (Electrolyte: 0.1 M TBAPF₆/CH₃CN. Potential calculated versus Fc/Fc⁺. Scan rate: 50 mV/s; T = 25 °C) d) Spectroelectrochemical analysis of UV-irradiated **P-PN-FLR** film on an ITO anode. (Electrolyte: 0.1 M TBAPF₆/CH₃CN. Potential calculated versus Fc/Fc⁺) The samples of the neutral and fully oxidized films are shown in the insert.

Table S2. Optical and electrochemical properties of UV irradiated **P-PN-FLR** film.

Polymers	λ_{film}	$E_{\text{g,opt}}$	V_{ox}	E_{HOMO}	V_{red}	E_{LUMO}	$E_{\text{g,ec}}$
	[nm]	[eV]	[V]	[eV]	[V]	[eV]	[eV]
P-PN-FLR	431	2.88	1.08	-5.88	-2.07	-2.73	3.15
P-PN-FLR annealed	435	2.85	1.07	-5.87	-2.07	-2.73	3.14
P-PN-FLR UV irradiated	445	2.79	0.92	-5.72	-1.88	-2.92	2.80

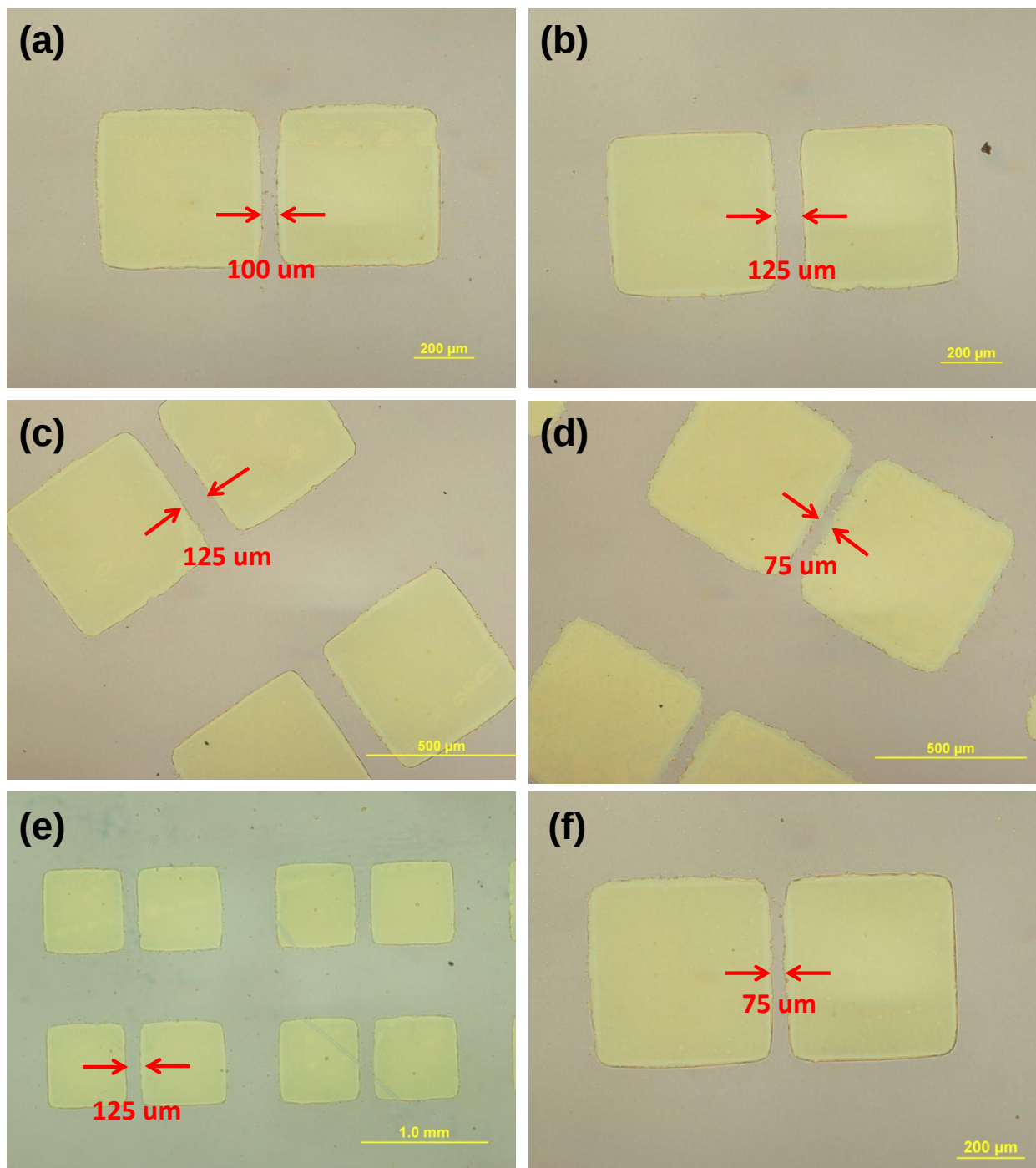


Figure S8. Optical images of patterned **P-PN-FLR** films.

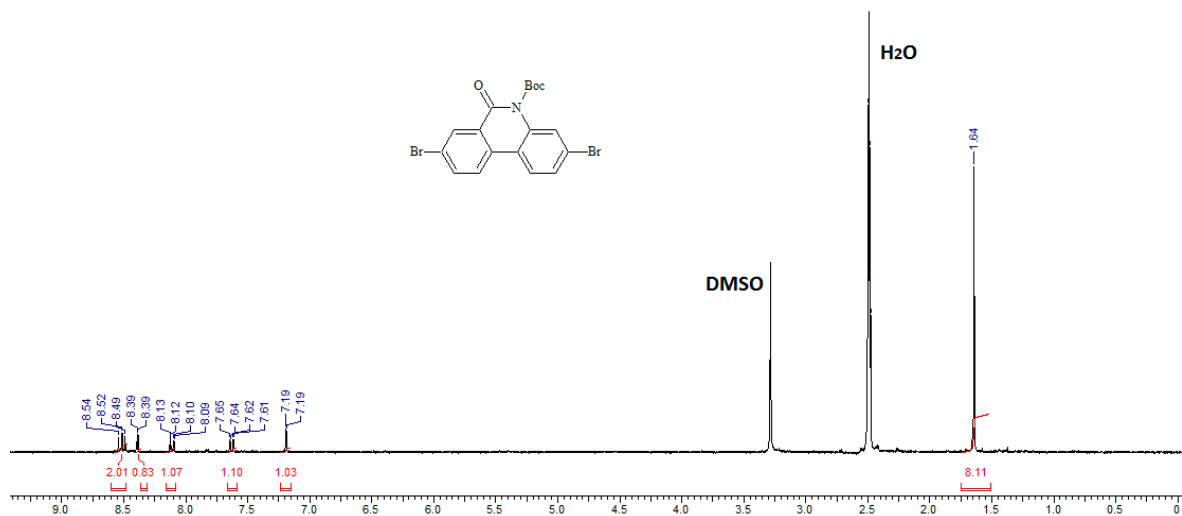


Figure S9. ^1H NMR spectrum of **PN** in dimethyl sulfoxide (DMSO)- d_6 .

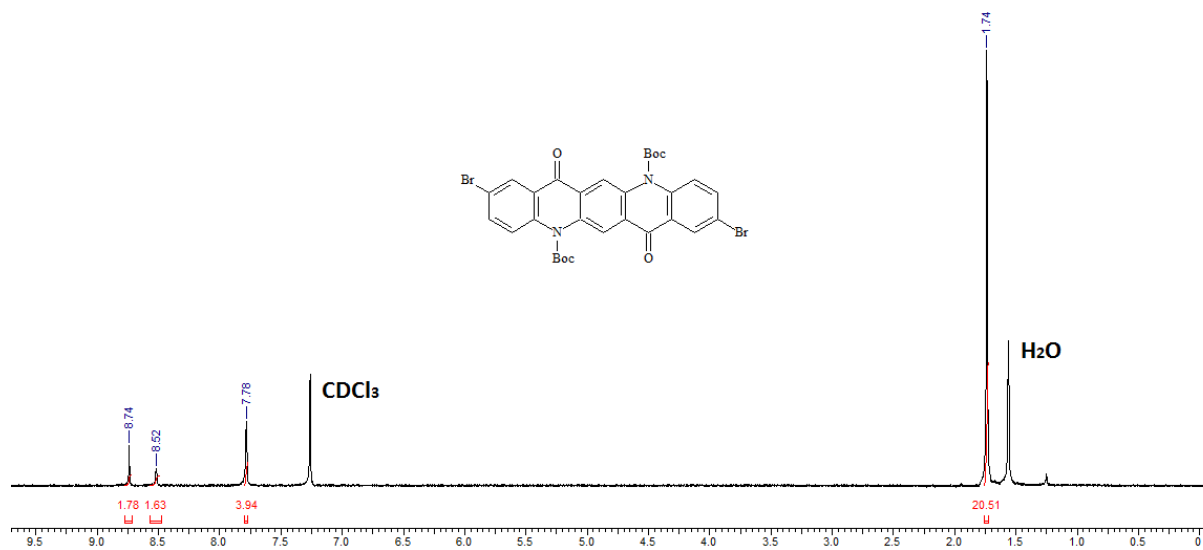


Figure S10. ^1H NMR spectrum of **QA** in CDCl_3 .

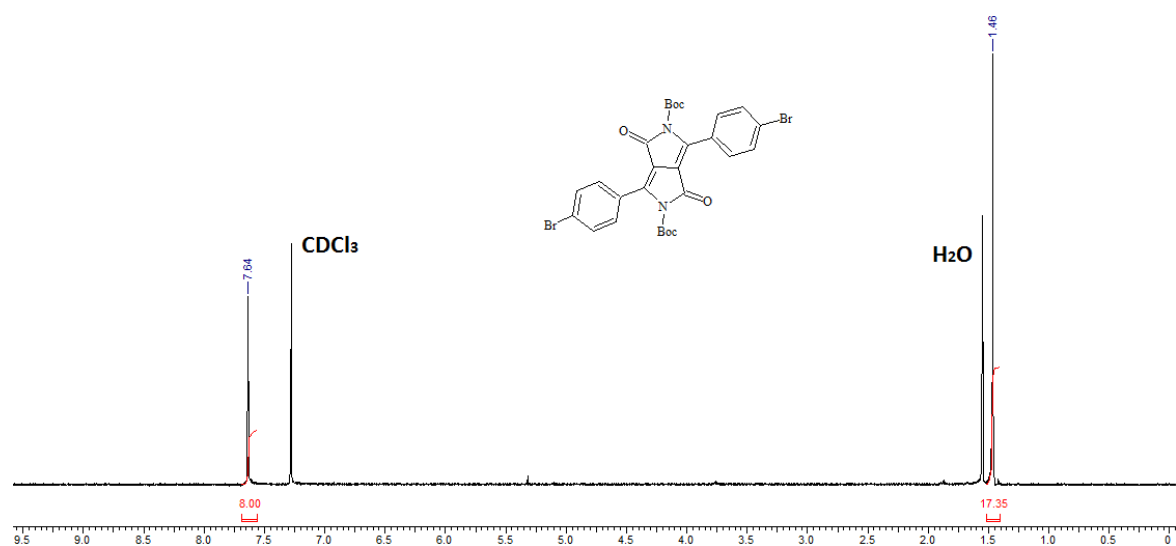


Figure S11. ¹H NMR spectrum of **PDPP** in CDCl₃.

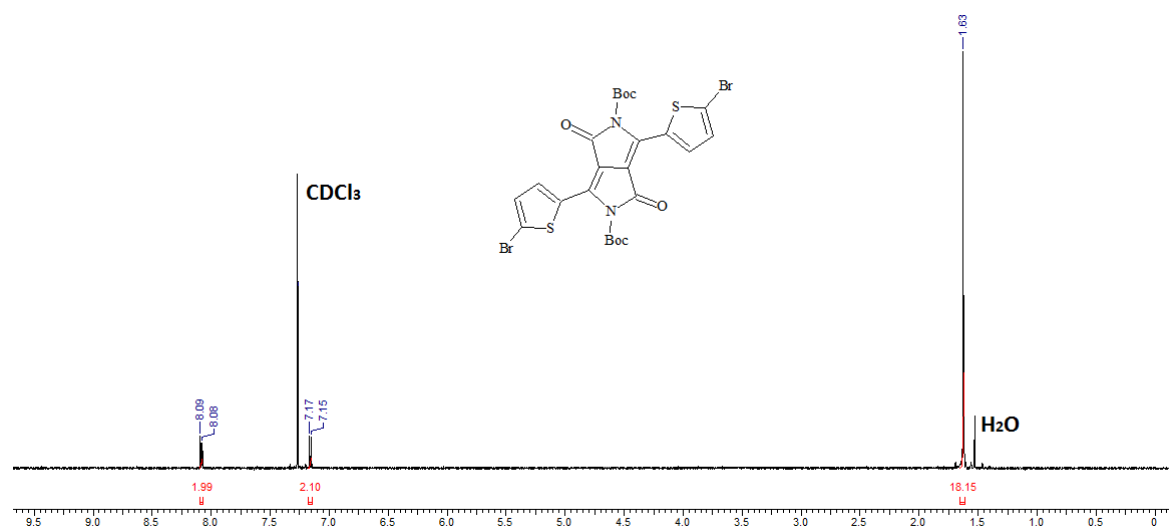


Figure S12. ¹H NMR spectrum of **TDPP** in CDCl₃.

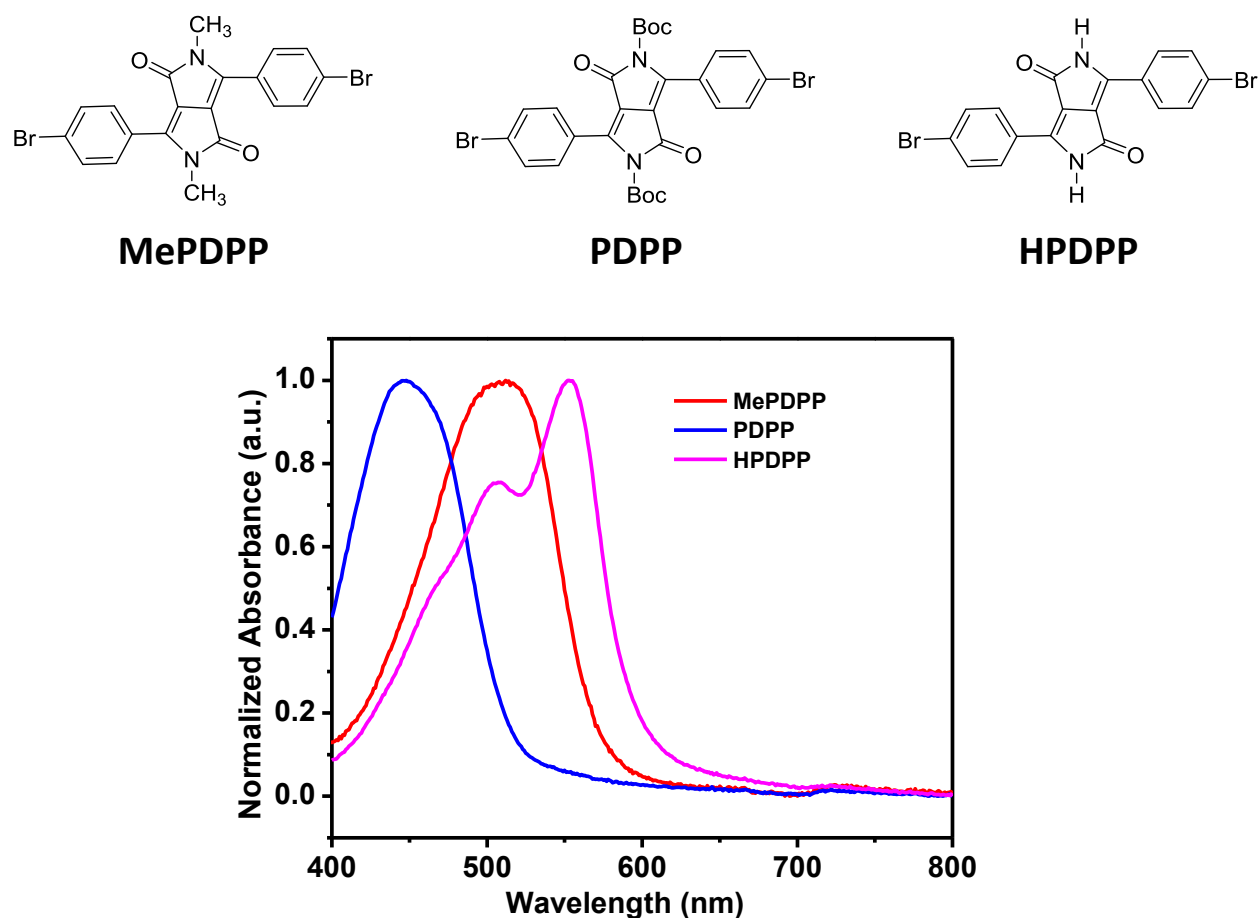


Figure S13. The UV/Vis spectra of the **MePDPP**, **PDPP** and **HPDPP** (annealed **PDPP**) films. It is clear that there is a bathochromic shift from **PDPP** (blue curve) to **MePDPP** (red curve). The reason for this shift is that the phenyl ring is tilted from the plane of **DPP** core in **PDPP** molecules. When the side groups were replaced with small unit like methyl group (**MePDPP**), the conjugation length of the molecule is extended because the phenyl rings and **DPP** core are in the same plane. However, in **HPDPP** (purple curve) spectrum, there are two peaks appeared. The shoulder peak around 506 nm is very close to the absorption of **MePDPP**, which originates from the absorption of conjugated structure (**DPP** core and two phenyl rings). The most prominent peak in **HPDPP** spectrum (554 nm) is likely from the hydrogen-bonding initiated packing effect.

References

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