Supporting Information

Synthesis of Furan-Based Conjugated Polymers with Tunable Bandgaps via Direct C-H Arylation of Oligofurans

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Experimental section

Materials

3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione, (E)-6,6'-dibromo-1,1'-bis(2-ethylhexyl)-[3,3'-biindolinylidene]-2,2'-dione and 4,7-dibromo-2-(2-hexyldecyl)isoindoline-1,3-dione were bought from SunaTech Inc (Suzhou, China). Cesium carbonate (Cs_2CO_3), palladium acetate, tris(o-methoxyphenyl) phosphine ($P(o\text{-}OMePh)_3$) were purchased from J&K Chemical Ltd. (Beijing, China). DSPE-PEG_{2000} were purchased from Aivituo Pharmaceutical Technology Co., Ltd. (shanghai, China). O-xylene was purchased from Sigma-Aldrich (St. Louis, MO, USA). DMEM, fetal bovine serum (FBS), penicillin, and streptomycin were provided by GibcoBRL (Invitrogen Corp., CA, USA). *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) were obtained from BeNa Culture Collection (Henan, China). Milli-Q water (18.2 MΩ cm^{-2} at 25°C) used throughout the study was purified by using a Millipore filtration system. Other solvents and reagents (analytical grade and spectroscopic grade) were obtained commercially and used as received unless indicated otherwise.

Instruments

The ^1H NMR spectra were recorded on a Bruker AV400 Spectrometer using tetramethylsilane (TMS) as an internal standard for NMR analyses. Number-average (Mn) and polydispersity index (PDI) were determined by Gel Permeation Chromatography (GPC) in tetrahydrofuran at 25 °C using Waters 1525 with Waters Styragel HT gel columns.

Ultraviolet-visible absorption spectra were measured with a PerkinElmer LAMBDA750 spectrophotometer. Fluorescence spectra were measured on a SPEX Fluorolog-τ3 fluorimeter (model FL- 321, 450 W Xenon lamp) using right-angle detection. Fluorescence quantum yields were tested in dichloromethane (DCM) using a Hamamatsu Quantaurus-QY spectrometer (C11347-11).

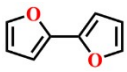
Cyclic voltammetry (CV) was performed on a CHI 660e electrochemical workstation in a three-electrode structure under a nitrogen atmosphere. A glassy carbon electrode,

Ag/AgCl electrode and a platinum electrode were used as the working, reference and counter electrodes, respectively. Bu_4NPF_6 (TBAF, 0.1 mol/L) in anhydrous acetonitrile was used as the supporting electrode. The ferrocene/ferrocinium redox couple served as an external reference for all measurements. The electrodes were polished with aluminum powder and cleaned with distilled water and acetonitrile. The polymer drop-cast film prepared with chloroform solution on the working electrode was scanned at a rate of 100 mV^{-1}. GPC

For DFT calculations, all DFT calculations were carried out using the Gaussian 09 program. The geometry optimizations and the spin density surfaces of the polymers were performed at the B3LYP/6-31G* method. Three repeating units were used and the side chains were replaced with methyl groups to reduce the computation time. All optimized structures were not imaginary frequency. Time-dependent DFT (TD-DFT) calculations were performed to estimate the UV/Vis absorption.

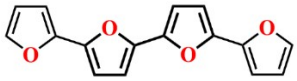
A FEI Tecnai G2 Spirit TWIN transmission electron microscope (Hillsboro, USA) was used to obtain the transmission electron microscopy (TEM) images of the synthesized nanoparticles. The DLS and zeta potential were measured at room temperature using a particle analyzer (Nano-ZS, Malvern, England). The surface morphologies of bacteria were observed with field emission scanning electron microscopy (SEM) FEI Quanta FEG 250 (FEI, USA).

Synthesis of 2F



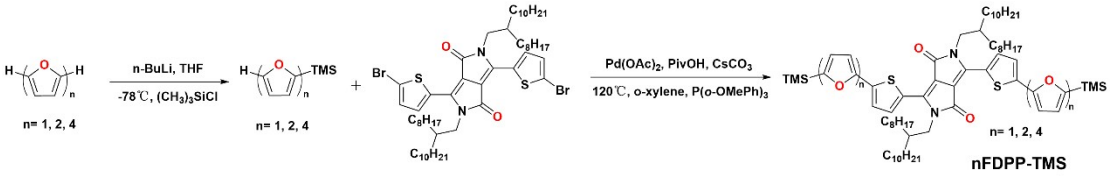
To a solution of furan (7.49 g, 110.0 mmol) and TMEDA (11.62 g, 100.0 mmol) in THF (130 mL) was added n-butyllithium (2.5 M, 40.0 mL, 100.0 mmol) at -78°C. The mixture was stirred at that temperature for 1 h, then anhydrous $CuCl_2$ (18.75 g, 110.0 mmol) was added and the mixture was allowed to warm up to room temperature overnight. Water (50 mL) and diluted HCl (50 mL) were added and the mixture was extracted with hexane (300 mL). The obtained crude product was purified by column chromatography (silica; hexane) to give 2F as a colorless oil. Yield: 5.57 g (41.5 mmol, 83 %). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 2H), 6.55 (s, 2H), 6.46 (s, 2H).

Synthesis of 4F



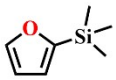
To a solution of 2F (3 g, 22.4 mmol) and TMEDA (2.56 g, 22 mmol) in THF (60 mL) was added n-butyllithium (2.5 M, 8.8 mL, 22 mmol) at -78 °C. The mixture was stirred at that temperature for 1 h, then anhydrous $CuCl_2$ (3.7 g, 22 mmol) was added and the mixture was allowed to warm up to room temperature overnight. Water (50 mL) and diluted HCl (50 mL) were added and the mixture was extracted with hexane (300 mL). The obtained crude product was purified by column chromatography (silica; hexane) to give 4F as a light-yellow solid. Yield: 1.3 g (4.9 mmol, 23%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 2H), 6.67 (s, 2H), 6.63 (s, 4H), 6.49 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.38 (s), 146.07 (s), 145.53 (s), 142.19 (s), 111.67 (s), 107.42 (s), 107.22 (s), 105.71 (s).

Synthetic Route for the Model Reaction



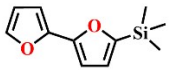
Scheme S1. Synthesis of nFDPP-TMS (n= 1, 2, 4)

Synthesis of 1F-1TMS



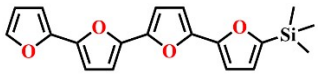
To a solution of n-butyllithium (2.5 M, 5.3 mL) in diethyl ether (50 mL) was added furan (1 g, 14.7 mmol) dropwise at 0 °C, and the mixture was stirred for 1h at that temperature, followed by 3 h at ambient temperature. Chlorotrimethylsilane (1.6 g, 14.8 mmol) was slowly added at 0 °C and the resulting mixture was stirred overnight. The colorless precipitate was removed by filtration. All volatiles were removed under reduced pressure. The crude product without further purified to give as a colorless liquid (0.88 g, 43%); ^{1}H NMR (400 MHz, DMSO) δ 7.85 (s, 1H), 6.73 (s, 1H), 6.46 (s, 1H), 0.23 (s, 9H).

Synthesis of 2F-1TMS



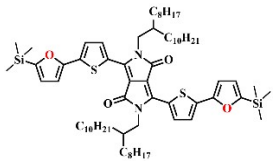
n-BuLi (2.5M, 1.5 mL) was added dropwise to a solution of 2F (0.5 g, 3.73 mmol) in dry THF (30 mL) at −78 °C under nitrogen. The mixture was stirred at −78 °C for 1h and at room temperature for 30 min. The solution was cooled again to −78 °C and chlorotrimethylsilane (0.24 g, 2.22 mmol) was added dropwise. After stirring for 3 h at room temperature, the mixture was quenched with water, extracted with hexane, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was further purified by column chromatography (hexane) to give as a light-yellow liquid (0.31 g, 40%); ^{1}H NMR (400 MHz, DMSO) δ 7.72 (s, 1H), 6.81 (s, 1H), 6.69 (s, 1H), 6.66 (s, 1H), 6.59 (s, 1H), 0.27 (s, 9H).

Synthesis of 4F-1TMS



The synthesis of 4F-1TMS is similar to 2F-1TMS. n-BuLi (2.5M, 0.75 mL) was added dropwise to a solution of 4F (0.5 g, 1.87 mmol) in dry THF (20 mL) at −78 °C under nitrogen. After stirred for 1h and at room temperature for 30 min. The solution was cooled again to −78 °C and the chlorotrimethylsilane (0.25 g, 2.34 mmol) was added dropwise. the mixture was allowed to warm up to room temperature overnight. And quenched with water, extracted with hexane, dried over Na_2SO_4, concentrated in vacuo. The crude product was further purified by column chromatography (hexane) to give as a light-yellow liquid (0.16 g, 25%). ^{1}H NMR (400 MHz, DMSO) δ 7.78 (s, 1H), 6.88 (s, 3H), 6.84 (s, 3H), 6.65 (s, 1H), 6.64 (s, 1H), 0.29 (s, 9H).

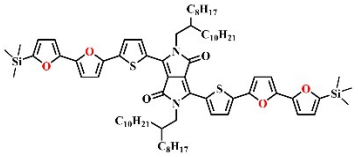
Synthesis of 1FDPP-TMS



The synthesis of 1FDPP-TMS using direct C-H arylation. 1F-1TMS (17 mg, 0.12 mmol) and 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (Br-DPP) (101.6 mg, 0.1 mmol), palladium

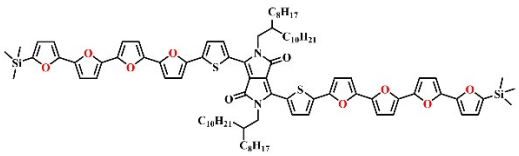
acetate (1.2 mg), tris(o-methoxyphenyl)phosphine (3 mg), cesium carbonate (30 mg) and pivalic acid (10 mg) were dissolved in anhydrous o-xlyene (3 mL) in a dried Schlenk tube under N_2 atmosphere. The reaction mixture was then heated at 120 ℃ under N_2 for 24 h. Then, the mixture was cooled to room temperature, extracted with dichloromethane, dried over Na_2SO_4, the crude product was further purified by column chromatography (hexane: dichloromethane =1:1) to give as a blue purple solid (15 mg; 14%); ^{1}H NMR (400 MHz, CD2Cl2) δ 8.93 (s, 2H), 7.47 (s, 2H), 7.40 (s, 2H), 6.73 (s, 2H), 4.04 (s, 4H), 3.25 (d, 2H), 1.25 (s, 72H), 0.92 (s, 18H), 0.31 (s, 18H).

Synthesis of 2FDPP-TMS



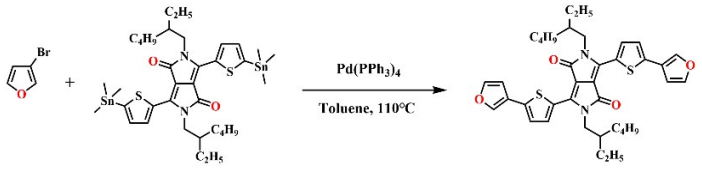
2F-1TMS (24 mg, 0.12 mmol) and Br-DPP (101.6 mg, 0.1 mmol), palladium acetate (1.2 mg), tris(o-methoxyphenyl)phosphine (3 mg), cesium carbonate (30 mg) and pivalic acid (10 mg) were dissolved in anhydrous o-xlyene (3 mL) in a dried Schlenk tube under N_2 atmosphere. The reaction mixture was then heated at 120 ℃ under N_2 for 24 h. Then, the mixture was cooled to room temperature, extracted with dichloromethane, dried over Na_2SO_4, the crude product was further purified by column chromatography (hexane: dichloromethane =1:1) to give as a blue solid (32 mg; 28.5%); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.98 (s, 2H), 7.47 (s, 2H), 6.79 (s, 6H), 6.52 (s, 2H), 4.06 (s, 4H), 3.26 (s, 2H), 1.26 (s, 72H), 0.88 (s, 12H), 0.30 (s, 16H).

Synthesis of 4FDPP-TMS



4F-1TMS (40.6 mg, 0.12 mmol) and Br-DPP (101.6 mg, 0.1 mmol), palladium acetate (10%), tris(o-methoxyphenyl)phosphine (15%), cesium carbonate (3 eq.) and pivalic acid (10 mg) were dissolved in anhydrous o-xlyene (5 mL) in a dried Schlenk tube under N_2 atmosphere. The reaction mixture was then heated at 120 ℃ under N_2 for 24 h. Then, the mixture was cooled to room temperature, extracted with dichloromethane,

dried over Na_2SO_4, the crude product was further purified by column chromatography (hexane: dichloromethane =1:1) to give as a blue green solid (61 mg; 34.2%); ^1H NMR (400 MHz, CD_2Cl_2) δ 8.91 (s, 2H), 7.38 (s, 4H), 6.74 (s, 4H), 6.65 (s, 8H), 6.46 (s, 2H), 3.99 (s, 5H), 3.18 (s, 2H), 1.24 (d, J = 47.3 Hz, 57H), 0.85 (s, 12H), 0.24 (s, 18H).



Scheme S2. Synthesis of β1F-DPP

3-bromofuran (14 mg, 0.1 mmol) and Sn-DPP (85 mg, 0.1 mmol) and Tetrakis(triphenylphosphine)palladium (8mg, 15%) were dissolved in anhydrous toluene (10 mL) in a dried Schlenk tube under N_2 atmosphere. The reaction mixture was then heated at 110 ℃ overnight. Then, extracted with dichloromethane, dried over Na_2SO_4, the crude product was further purified by column chromatography (hexane: dichloromethane =2:1) to give as a reddish-brown solid; ^1H NMR (400 MHz, CD_2Cl_2) δ 8.85 (s, 2H), 7.81 (s, 2H), 7.50 (s, 2H), 7.26 (s, 2H), 6.69 (s, 2H), 3.99 (s, 5H), 1.87 (s, 2H), 1.24 (s, 16H), 0.85 (s, 12H).

General Procedure for the Direct C-H Arylation Synthesis

The donor of oligofurans (0.1 mmol) and the acceptor of aryl bromides (0.1 mmol), palladium acetate (1.2 mg), tris(*o*-methoxyphenyl)phosphine (3 mg), cesium carbonate (30 mg) and pivalic acid (10 mg) were dissolved in anhydrous o-xlyene (3 mL) in a dried Schlenk tube under N_2 atmosphere. The reaction mixture was then heated at 120 ℃ under N_2 for 24 h. Then, the mixture was cooled to room temperature and drop into methanol. The precipitate was filtered and wash with methanol and chloroform. The polymer was recovered as a solid from the chloroform fraction by precipitation from methanol and dried under vacuum.

Polymerization of P1F-ISD

Same synthesis with general procedure, the polymer was concentration as a pale-yellow solid from the chloroform (yield: 44%, Mn: 6.1 kDa).

Polymerization of P2F-ISD

Same synthesis with general procedure, the polymer was concentration as earthy yellow

solid from the chloroform (yield: 49%, Mn: 9.3 kDa).

Polymerization of P4F-ISD

Same synthesis with general procedure, the polymer was concentration as a red solid from the chloroform (yield: 63%, Mn: 10.7 kDa).

Polymerization of P1F-IID

Same synthesis with general procedure, the polymer was concentration as a dark brown solid from the chloroform (yield: 38%, Mn: 7.2 kDa).

Polymerization of P2F-IID

Same synthesis with general procedure, the polymer was concentration as a brown solid from the chloroform (yield: 58%, Mn: 9.8 kDa).

Polymerization of P4F-IID

Same synthesis with general procedure, the polymer was concentration as a blue solid from the chloroform (yield: 67%, Mn: 12.5 kDa).

Polymerization of P1F-DPP

Same synthesis with general procedure, the polymer was concentration as a blue solid from the chloroform (yield: 42%, Mn: 7.6 kDa).

Polymerization of P2F-DPP

Same synthesis with general procedure, the polymer was concentration as a blue-green solid from the chloroform (yield: 53%, Mn: 11.4 kDa).

Polymerization of P4F-DPP

Same synthesis with general procedure, the polymer was concentration as a indigo solid from the chloroform (yield: 55%, Mn: 13.8 kDa).

Preparation of nanoparticle micelles (NPs): Polymers P1F-DPP, P2F-DPP and P4F-DPP were dissolved in tetrahydrofuran (1 mg, 2 mL), and the solution was then added into deionized water containing 1,2-distearoyl-sn-glycero-3-phosphoethanolamine-N-[methoxy-(polyethylene glycol)-2000] (mPEG(2000)-DSPE) (10 mg, 2 mL) under sonication. The resulted dispersion was sonicated for 1 h. After that, the mixture was placed on a rotary evaporator for two hours to slowly remove the organic solvents. Finally, the resultant solution was transferred to a 50 mL volumetric flask and diluted with deionized water to the volume to obtain the stock solution of polymers NPs with

a concentration of 200 μg mL^{-1}. The stock solution was stored in a refrigerator at 4 °C for later use.

ESR measurements of $^1O_2$: 2,2,6,6-Tetramethylpiperidine (TEMP) was employed as spin-trapping agents to detect $^1O_2$. NPs was dissolved in water at a dilution of 10 μM, and then 25 mM TEMP was added into water with US irradiation (1.0 MHz, 1.0 W cm^{-2}, 3min) or light irradiation (100 W, 3 min). The EPR signal was recorded at room temperature. As a comparison, the control group was detected too.

Antimicrobial Experiments: The antibacterial efficiency of P2F-DPP NPs was evaluated using a spread plate method. The bacteria were cultured in broth at 37 °C for 18 h. Then, bacteria were diluted with a culture medium for subsequent antibacterial experiments. 100 μL of the above bacterial solution was mixed with different concentrations of P2F-DPP NPs in 500 μL sterile water and then incubated at 37 °C for 30 min. The laser irradiation group was treated with white light irradiation for 6 min. Then, bacteria were gradually diluted 1×10^4-fold with sterile water, and 100 μL diluted bacterial solution was dispersed on a solid medium agar plate to form colonies. The plates were cultured at 37 °C for 16 h. The number of bacteria was counted using a counter. The bacteria with P2F-DPP NPs treatment in the dark was the control group. The diameter of the solid agar plate was 90 mm.

Morphological observation of bacteria：After the antibacterial experiments were completed, the samples were centrifuged (3500 rpm, 5 min) and washed with sterile water. The precipitate was fixed with 2.5% glutaraldehyde for 12 h at 4 °C, and glutaraldehyde was subsequently removed by centrifugation. The residue was washed twice with 10 mM of PBS buffer solution, dehydrated with different gradients of ethanol (30%, 50%, 70%, 85%, 95%, and 100%, respectively), and then dispersed in tert-butyl alcohol after centrifugation. The tert-butanol suspension of the sample was dropped on a silicon wafer.

Table S1. Reaction conditions for the direct C-H arylation using different palladium catalysts, ligands, bases and solvents.

Compound	[Pd]	Ligand	Base	Solvent	Yield (%)	Mn (Da)
P2F-DPP	$Pd(PPh_3)_4$	$P(2\text{-}MeOPh)_3$	Cs_2CO_3	toluene	NP	NP
P2F-DPP	$Pd_2(dba)_3$	$P(2\text{-}MeOPh)_3$	Cs_2CO_3	toluene	47	7356
P2F-DPP	$Pd(OAc)_2$	$P(2\text{-}MeOPh)_3$	Cs_2CO_3	toluene	51	8621
P2F-DPP	$PdCl_2(PPh_3)_2$	$P(2\text{-}MeOPh)_3$	Cs_2CO_3	toluene	43	4391
P2F-DPP	$Pd(OAc)_2$	$P(2\text{-}MeOPh)_3$	Cs_2CO_3	o-xylene	53	11299
P2F-DPP	$Pd(OAc)_2$	$P(2\text{-}MeOPh)_3$	K_2CO_3	o-xylene	28	6337
P2F-DPP	$Pd(OAc)_2$	$P(o\text{-}tol)_3$	Cs_2CO_3	o-xylene	NP	NP
P2F-DPP	$Pd(OAc)_2$	Pcy3	Cs_2CO_3	o-xylene	NP	NP

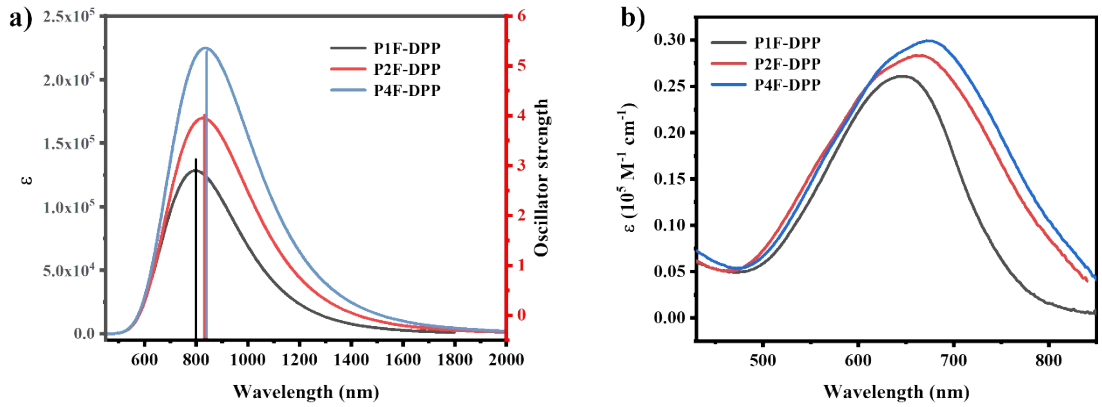


Figure S1. a) The absorption spectra and oscillator strength calculated by TD-DFT; b) UV−vis absorption at the same concentration.

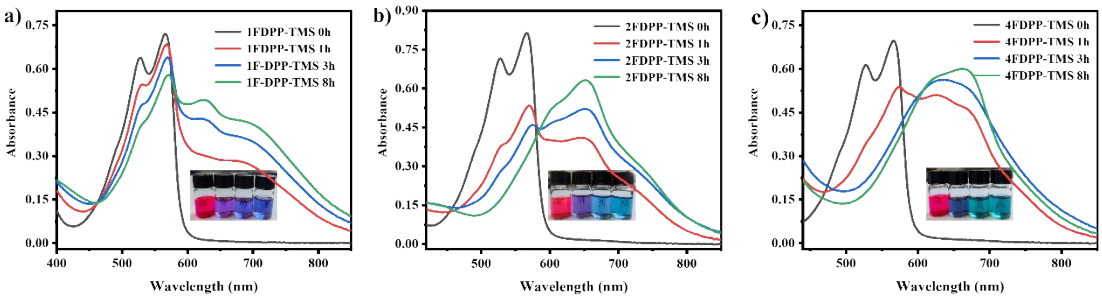


Figure S2. In-situ monitoring a) 1FDPP-TMS, b) 2FDPP-TMS and c) 4FDPP-TMS using UV-vis absorption spectra.

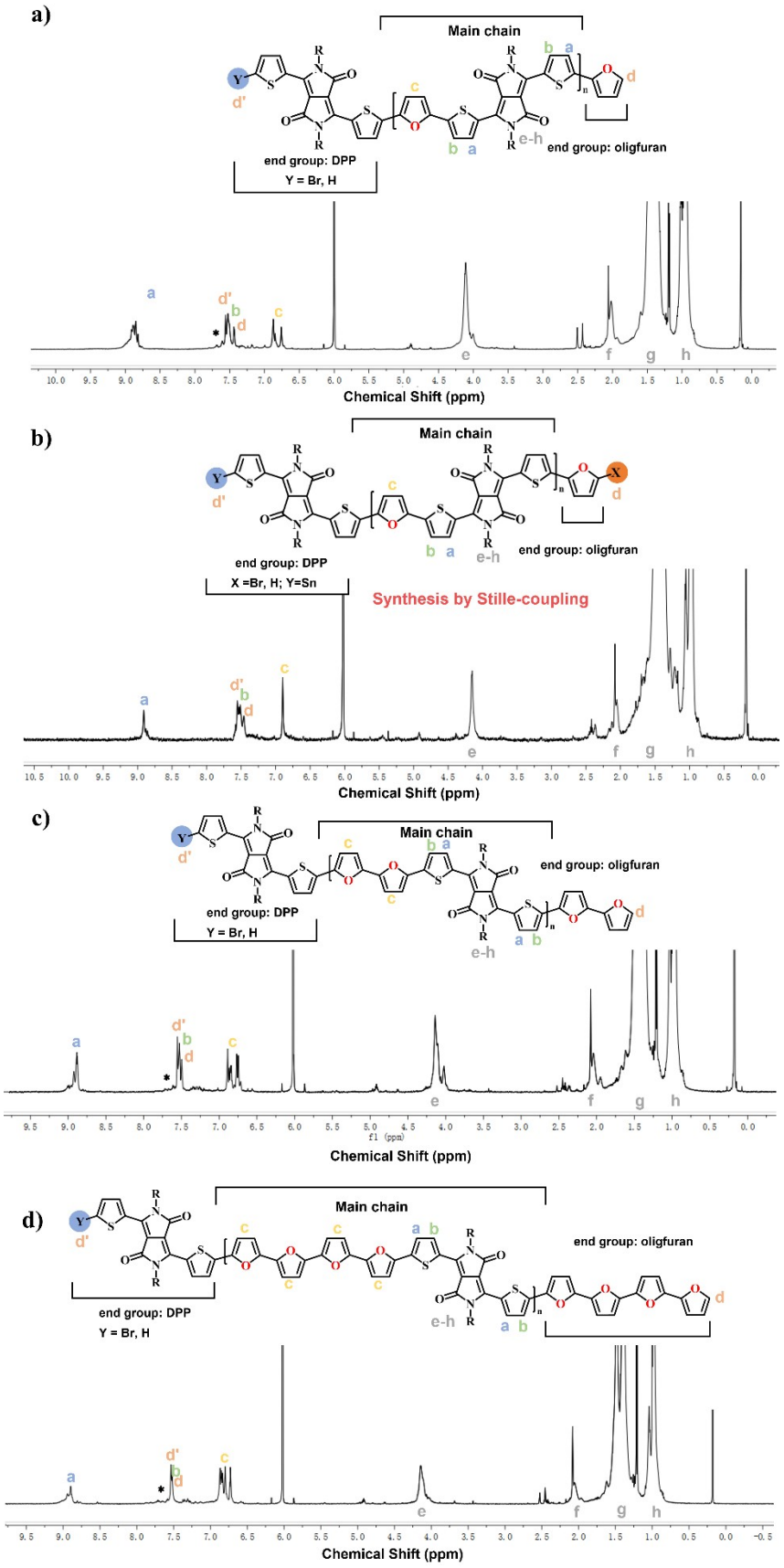


Figure S3. ^{1}H NMR spectra ($C_2D_2Cl_4$, 120 °C) of a) P1F-DPP, b) P1F-DPP polymer synthesis by Stille-coupling, c) P2FDPP and d) P4F-DPP.

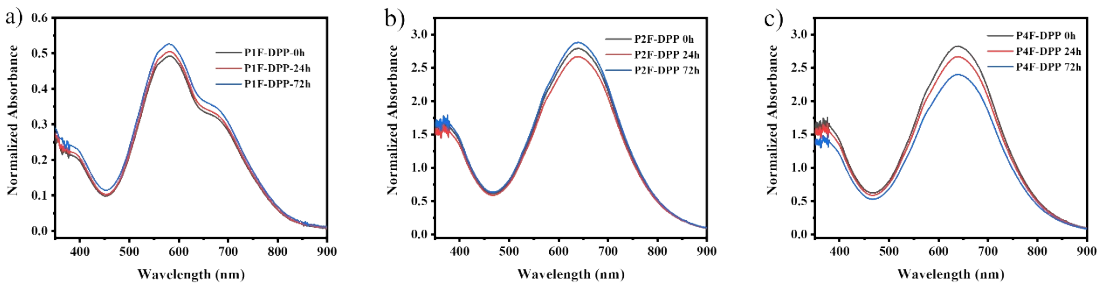


Figure S4. The long-term photostability in UV-vis absorption spectra of polymers a) P1F-DPP, b) P2F-DPP and c) P4F-DPP.

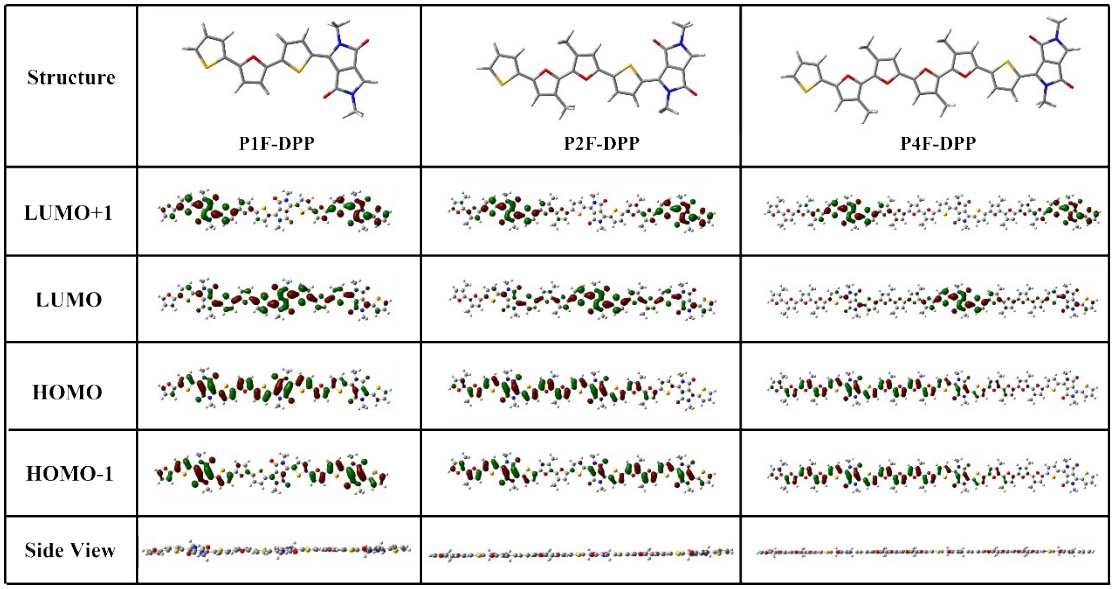


Figure S5. The optimized molecular conformation and electron density distributions of the polymers P1F-DPP, P2F-DPP and P4F-DPP, performed at the B3LYP/6-31G(d,p);

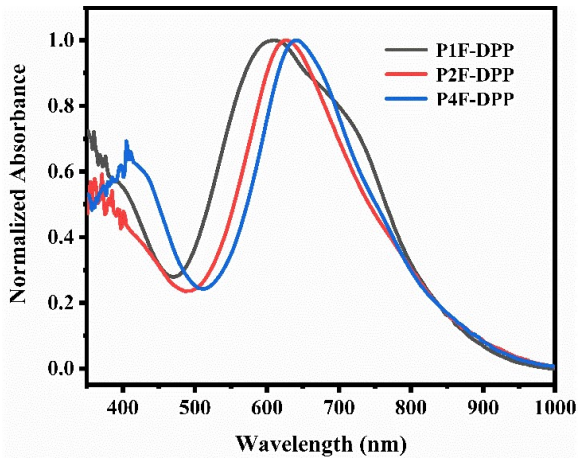


Figure S6. The UV–vis-NIR absorption spectrum of polymers nanoparticles in water.

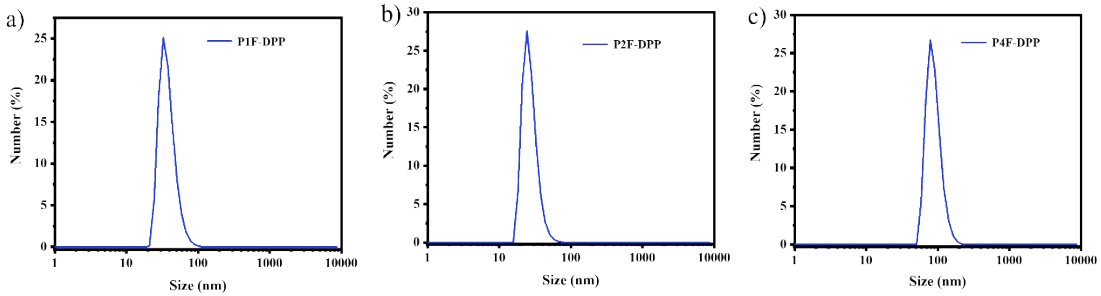


Figure S7. The number-averaged diameters of polymers a) P1F-DPP-NPs, b) P2F-DPP-NPs and c) P4F-DPP-NPs measured using dynamic light scattering (DLS) in water.

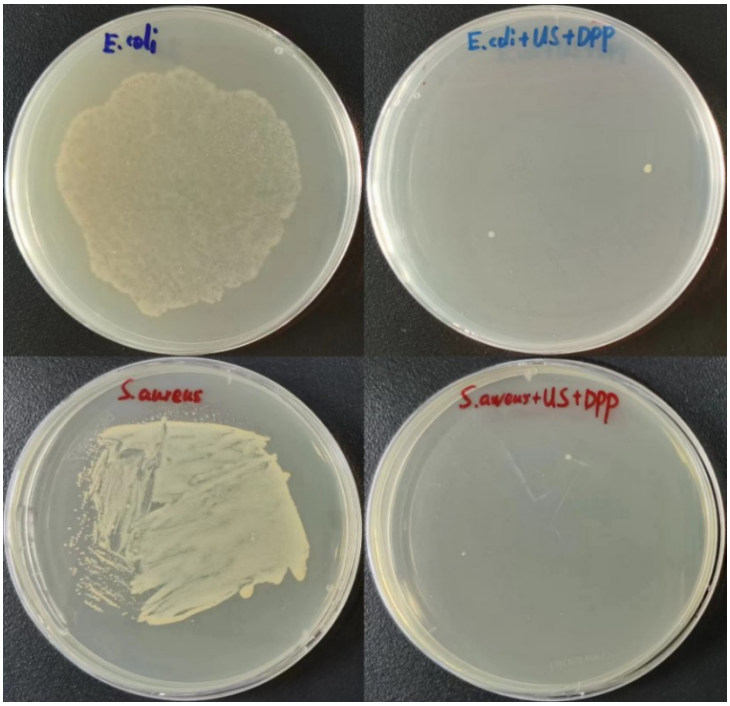


Figure S8. LB agar plate photographs of *E. coli* (top) and *S. aureus* (bottom) after treated with P2F-DPP NPs followed by ultrasound irradiation at 1.0 W cm^{-2}, 3 min.

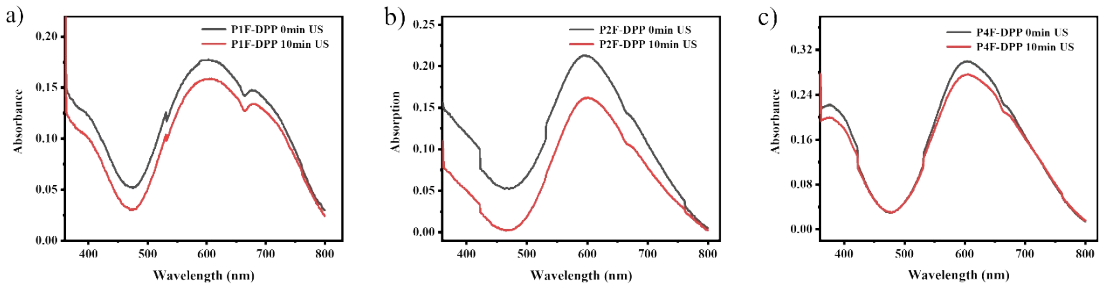


Figure S9. The UV-Vis absorption spectra of a) P1F-DPP-NPs, b) P2F-DPP-NPs and c) P4F-DPP-NPs, before and after ultrasound stimulation (1.0 MHz, 1.0 W cm^{-2},

10min).

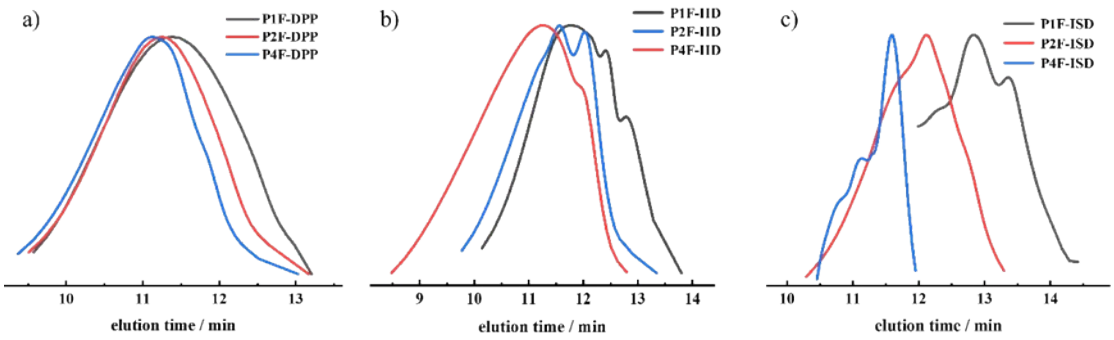


Figure S10. GPC trace of polymers.

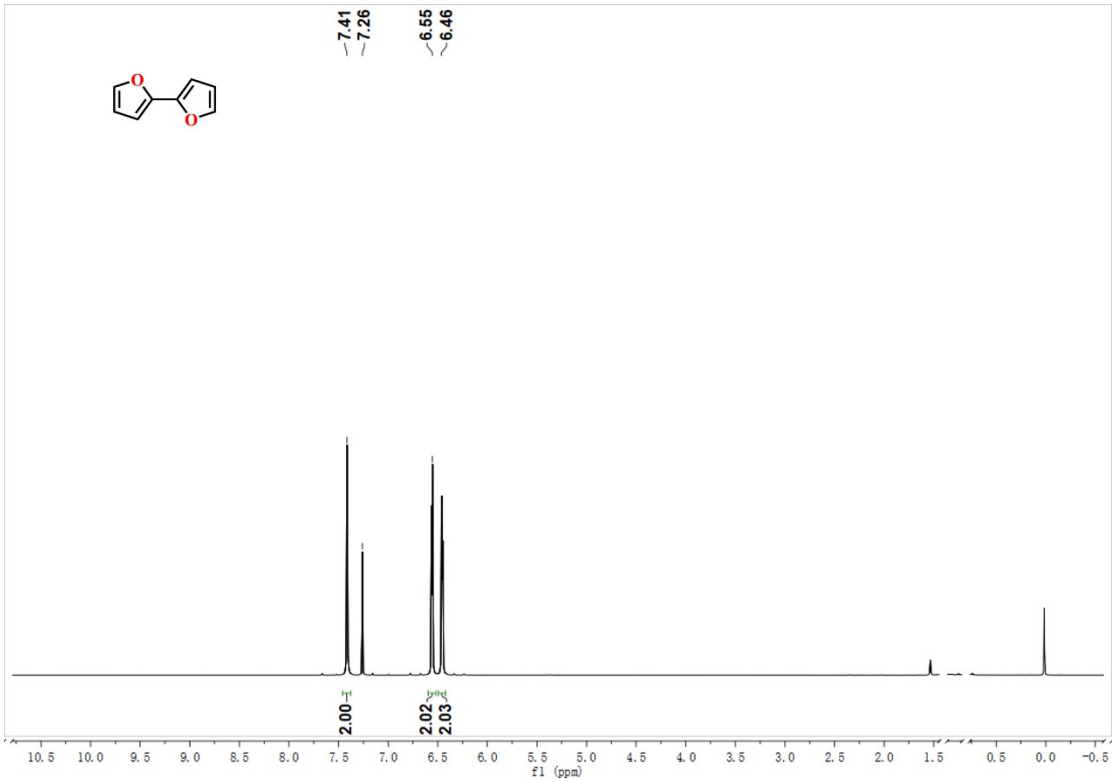


Figure S11. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 2F.

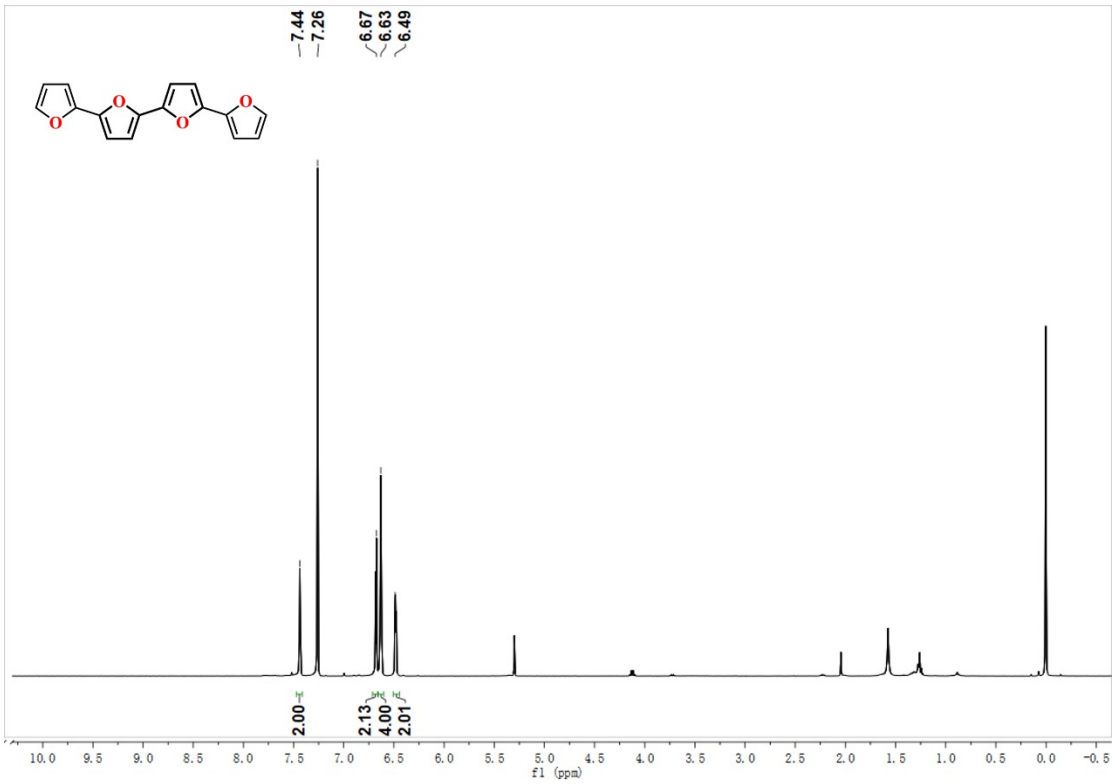


Figure S12. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 4F.

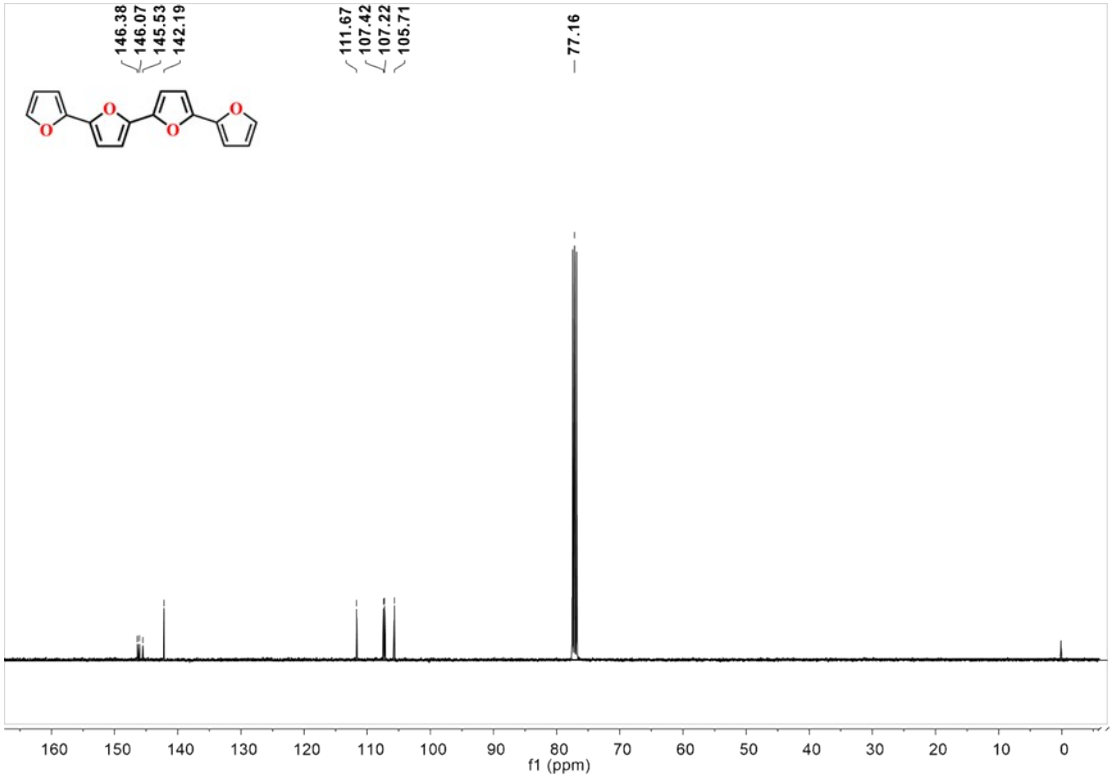


Figure S13. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 4F.

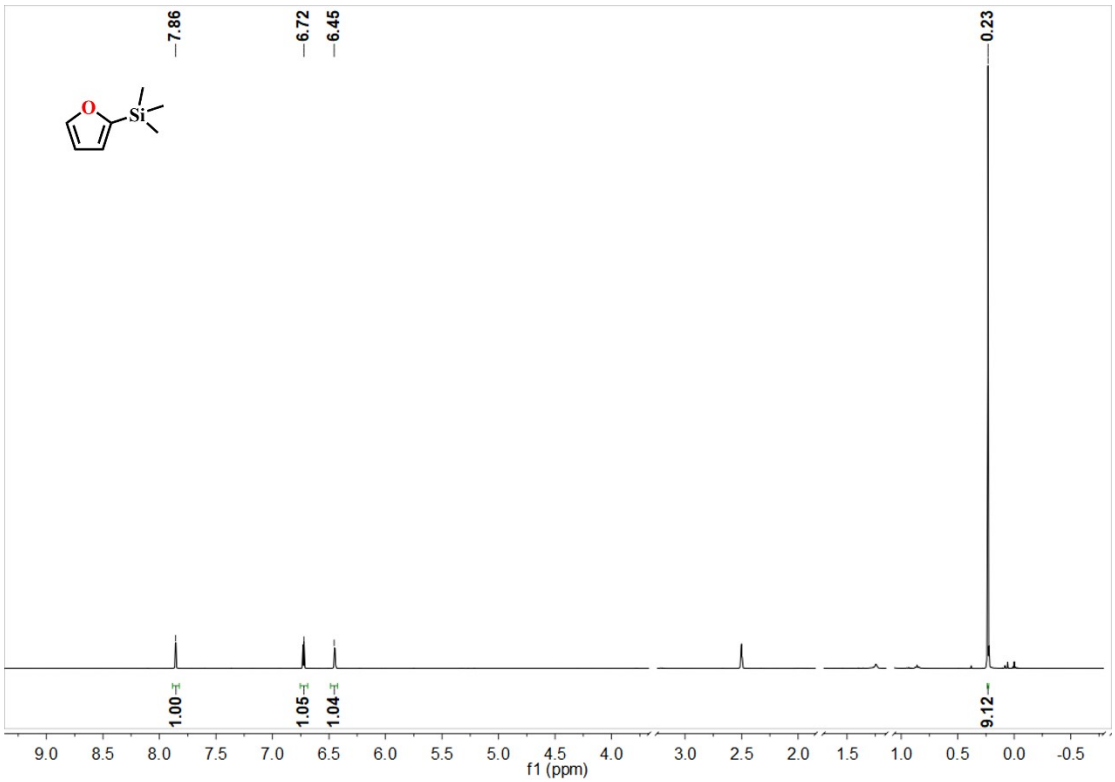


Figure S14. [1]H-NMR (400 MHz, DMSO) spectrum of 1F-1TMS.

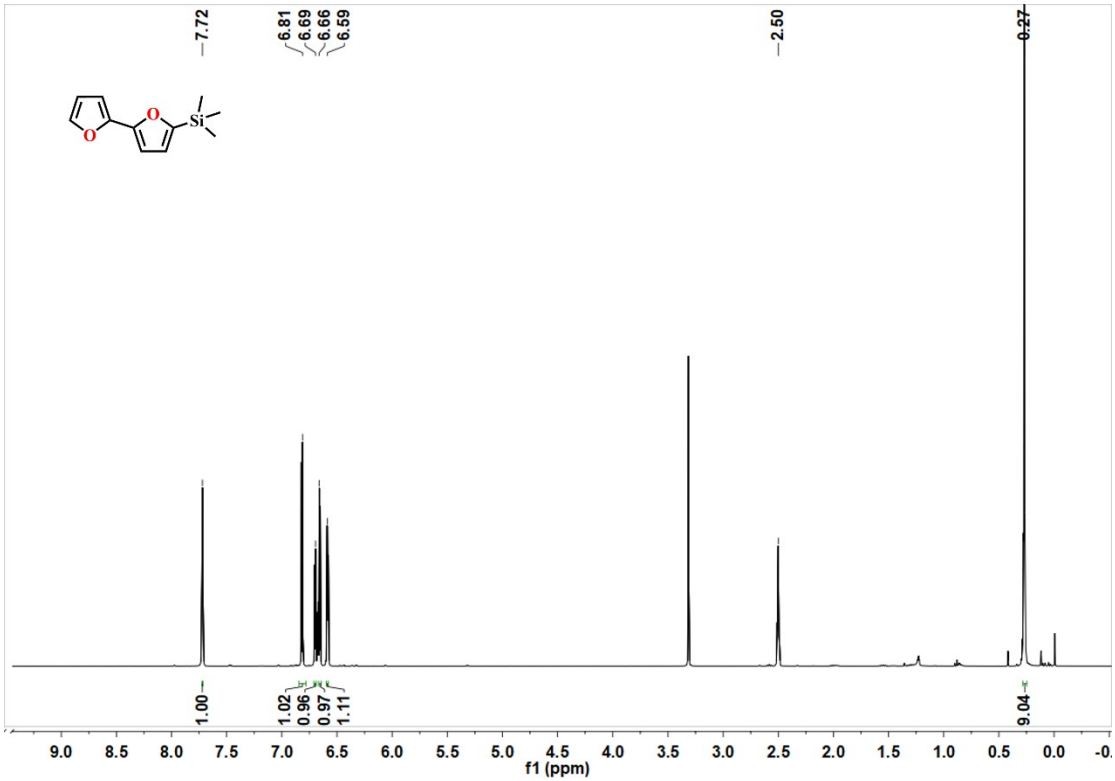


Figure S15. [1]H-NMR (400 MHz, DMSO) spectrum of 2F-1TMS.

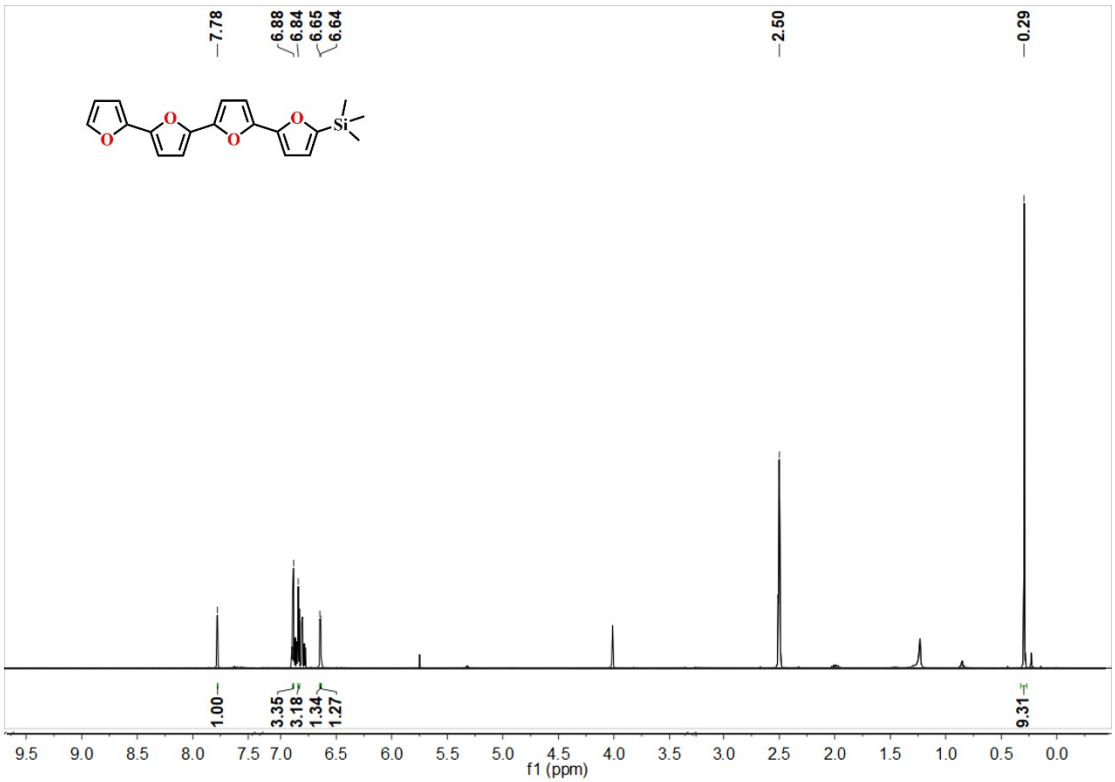


Figure S16. ^{1}H-NMR (400 MHz, DMSO) spectrum of 4F-1TMS.

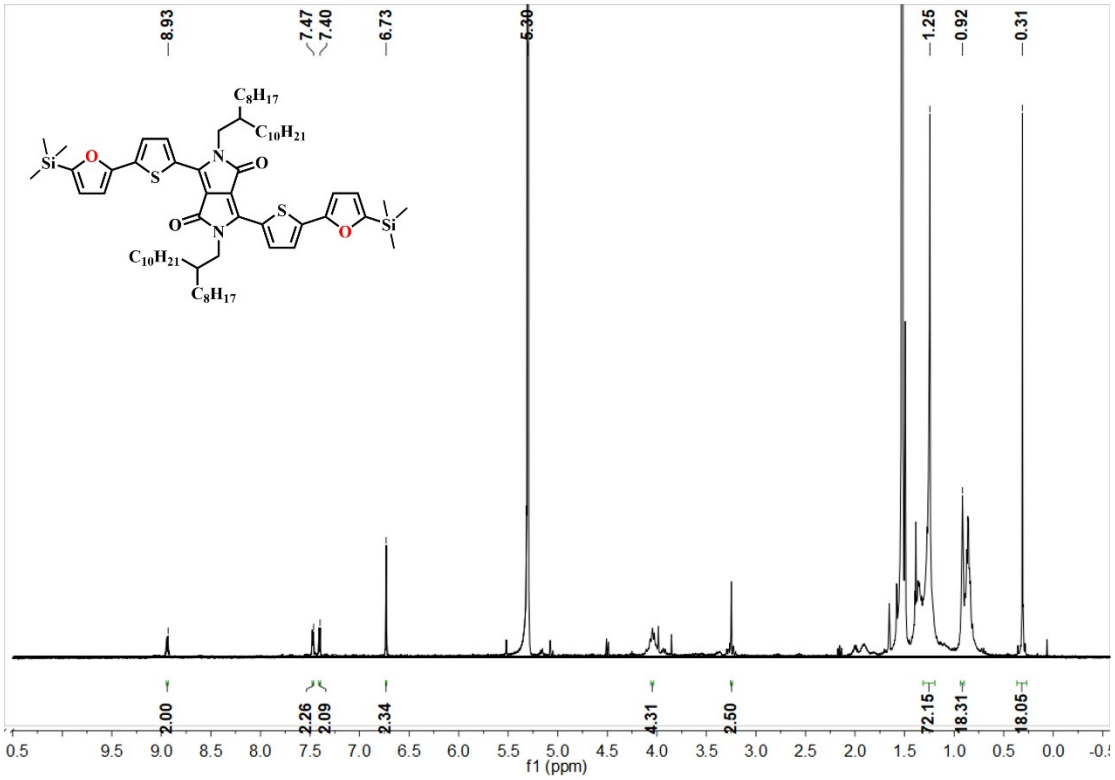


Figure S17. ^{1}H-NMR (400 MHz, CD_2Cl_2) spectrum of 1FDPP-TMS.

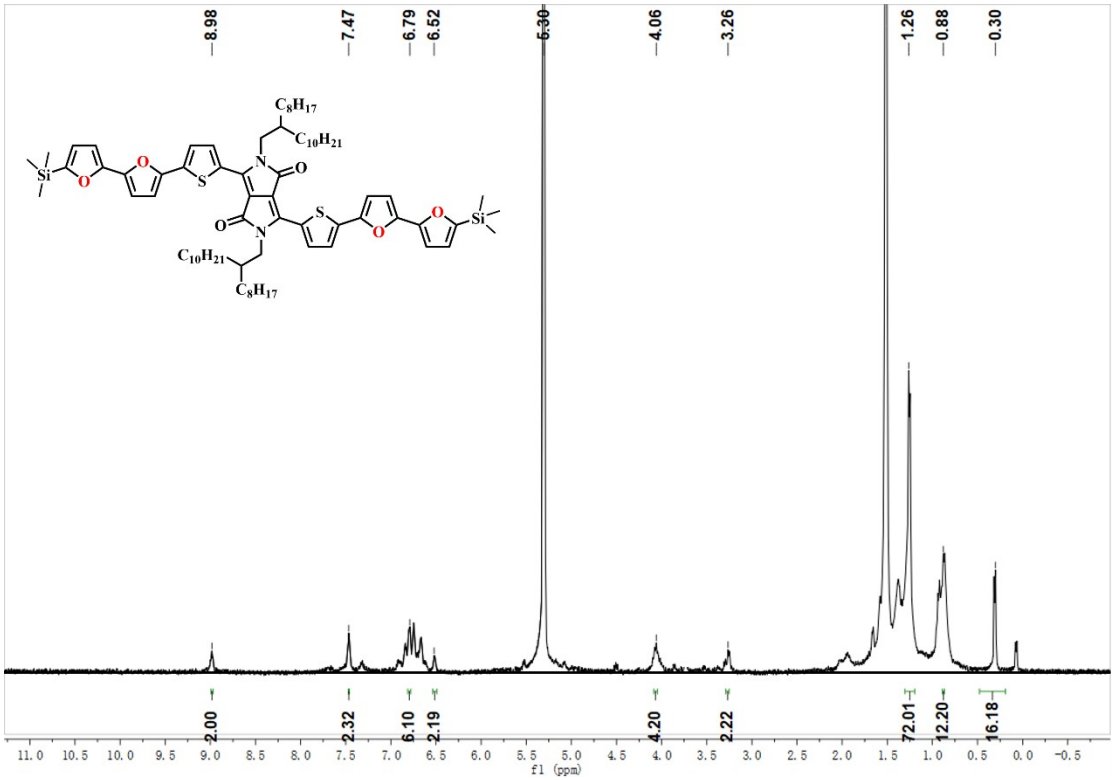


Figure S18. ^{1}H-NMR (400 MHz, CD_2Cl_2) spectrum of 2FDPP-TMS.

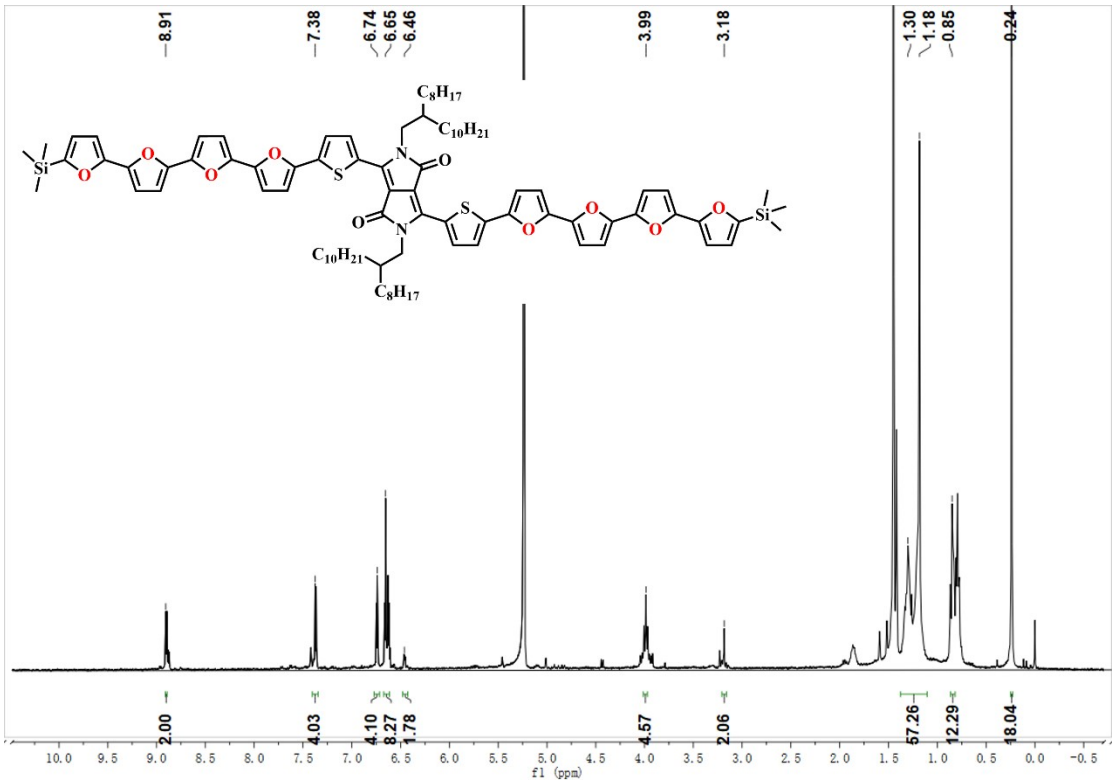


Figure S19. ^{1}H-NMR (400 MHz, CD_2Cl_2) spectrum of 4FDPP-TMS.

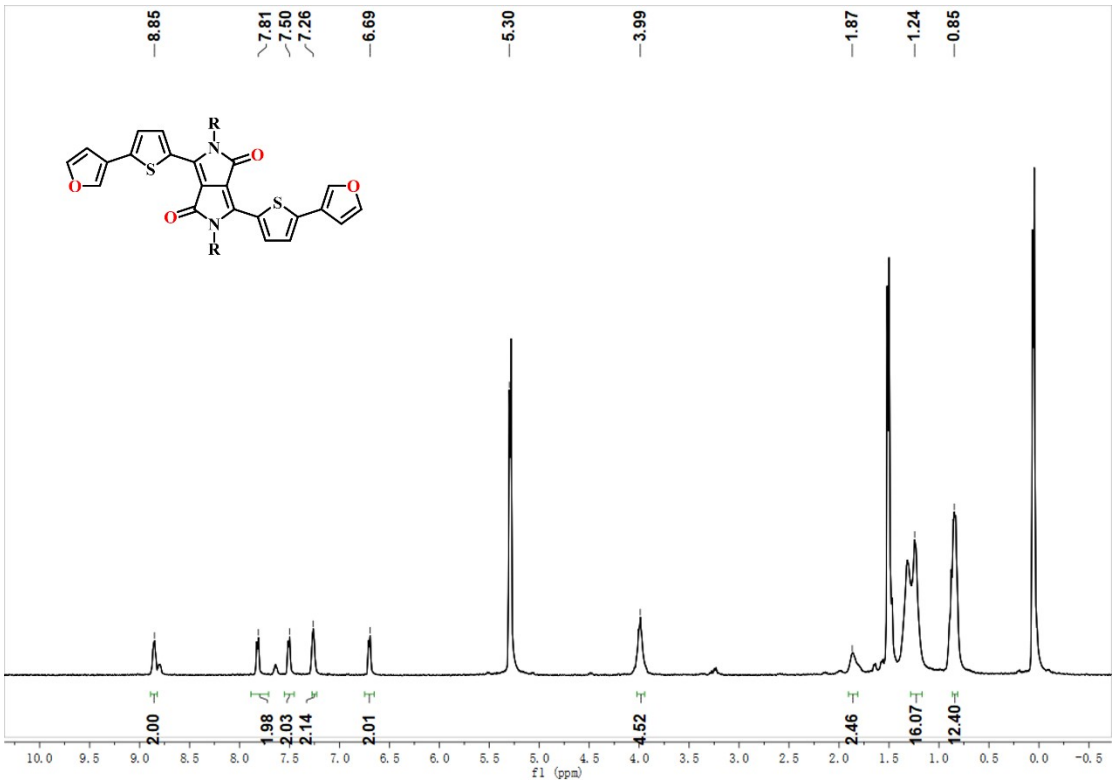


Figure S20. ^{1}H-NMR (400 MHz, CD_2Cl_2) spectrum of β1F-DPP.

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