

Electronic supplementary information

SYNTHESIS OF WIDE BANDGAP CONJUGATED π -COPOLYMERS INCORPORATING 9H-CARBAZOL-3-YL DITHIENO[3,2-F:2',3'-H]QUINOXALINE UNITS

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Experimental section

Materials

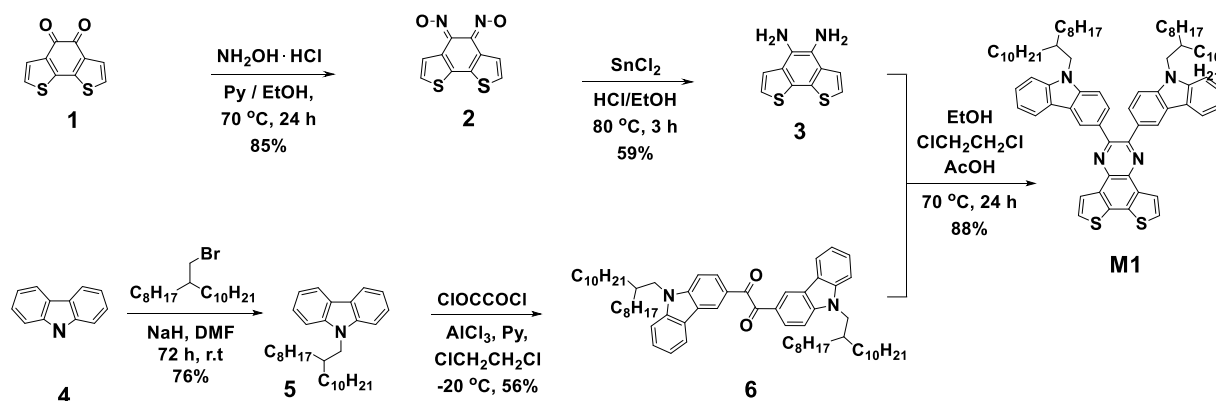
All chemicals and solvents were of reagent grade and were purchased from Aldrich. Toluene and tetrahydrofuran were distilled from sodium benzophenone ketyl under an argon atmosphere before use in the syntheses. 2,7-Ditrimethylsilylthieno[3,2-g][1]benzothiophene-4,5-dione is **M2** [1].

Instrumentation

The ¹H NMR and ¹³C NMR spectra were obtained on a Bruker Avance III 400 (400 MHz) NMR system. The MALDI-TOF MS spectra were measured on an Axima Confidence MALDI-TOF mass-spectrometer (Shimadzu, Japan). The UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. The TGA studies were carried out on a Perkin Elmer-7 thermal balance under nitrogen protection at a heating rate of 10 °C min. The DSC studies were performed on a Perkin-Elmer Pyris 1 differential scanning calorimeter. The oxidation and reduction potentials of the compounds under consideration were determined by cyclic voltammetry (CV) on a BioLogic SP-200 computer controlled potentiostat at a scan rate of 100 mV/s. The CV measurements were made using an ITO working electrode coated with a sample as a working electrode, a platinum wire as a counter electrode against an Ag/Ag⁺ reference electrode with a ferrocene/ferrocenium external standard. The measurements were carried out in a saturated solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) (0.1 M in anhydrous acetonitrile). The HOMO and LUMO energy levels were obtained from the equation: $E^{\text{HOMO}}/E^{\text{LUMO}} = -(E_{\text{ox}}/E_{\text{red}} + 4.44)$ (eV), where the oxidation/reduction onset potentials ($E_{\text{ox}}/E_{\text{red}}$) were determined from the position at which the current raised initially from the baseline.

Synthesis

Monomer **M1** was synthesized according to the following scheme [2]:



2,3-Bis[9-(2-octyldodecyl)-9*H*-carbazol-3-yl]dithieno[3,2-*f*:2'3'-*h*]quinoxaline (M1). 1,2-Bis[9'-(2''-octyldodecyl)carbazol-3'-yl]ethane-1,2-dione (4.28 g, 4.5 mmol) and thieno[3,2-*g*][1]benzothiophene-4,5-diamine (1.2 g, 5.4 mmol) were dissolved in a mixture of 5 mL of ethanol, 3 mL of 1,2-dichloroethane, and 1 mL of acetic acid. The reaction mixture was heated to 70 °C and kept at this temperature for 24 h. Upon the reaction completion, the mixture was cooled to room temperature, the volatiles were removed under vacuum, and the residue was dissolved in 100 mL of water and 100 mL of dichloromethane. After separation of the organic phase, the extract was dried over MgSO₄, concentrated under vacuum, and the resulting residue was subjected to chromatography in petroleum ether. Monomer **M1** was obtained as yellow crystals in 88% yield (4.50 g).

¹H NMR (400 MHz, CDCl₃): δ 8.69 (s, 2H), 8.55 (d, *J* = 5.2 Hz, 2H), 8.09 (d, *J* = 7.7 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 5.2 Hz, 2H), 7.49 (s, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 4H), 4.14 (d, *J* = 7.3 Hz, 4H), 2.19–2.03 (m, 2H), 1.33–1.16 (m, 64H), 0.89 (d, *J* = 4.7 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 151.93, 141.33, 141.29, 136.14, 135.03, 134.78, 130.00, 128.25, 125.77, 124.71, 124.57, 123.14, 123.05, 122.53, 120.59, 119.12, 109.15, 108.48, 47.79, 37.98, 31.94, 31.89, 31.82, 29.96, 29.64, 29.61, 29.55, 29.36, 29.26, 26.55, 22.72, 22.68, 14.15.

Anal. Calcd for C₇₆H₁₀₀N₄S₂: C, 80.51; H, 8.89; N, 4.94; S, 5.66. Found: C, 80.21; H, 8.69; N, 4.72; S, 5.21.

Synthesis of polymer P1. Monomer **M1** (0.5970 g, 0.5266 mmol), dibromide **M2** (0.4038 g, 0.527 mmol), K₂CO₃ (0.2400 g, 1.791 mmol), and pivalic acid (0.061 g, 0.5970 mmol) in toluene (2.6 mL) were combined, followed by the addition of Pd₂(dba)₃ (0.006 g, 0.0065 mmol). The reaction mixture was stirred at 110 °C for 20 h. Upon cooling to room temperature, 40 mL of chloroform were added, resulting in precipitation in methanol. The precipitate was filtered, and the crude product was then subjected to purification through Soxhlet extraction using acetone, hexane, and chloroform. The polymer-containing fraction was concentrated to 10 mL using a rotary evaporator and then added to 200 mL of methanol, resulting in the formation of a precipitate. The precipitate was filtered off and dried under vacuum at 50 °C for 24 h. Polymer **P1** was obtained in the form of a dark purple powder in 88% yield (0.81 g).

¹H NMR (500 MHz, CDCl₃): δ 8.68 (s, 2H), 8.50 (d, *J* = 5.3 Hz, 2H), 8.08 (d, *J* = 7.7 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.60 (d, *J* = 5.3 Hz, 2H), 7.51–7.38 (m, 5H), 7.24 (dd, *J* = 7.8, 4.9 Hz, 3H), 7.08 (t, *J* = 7.1 Hz, 2H), 4.15 (d, *J* = 7.3 Hz, 4H), 3.33 (dd, *J* = 11.7, 7.4 Hz, 4H), 2.11 (s, 2H), 1.84–1.13 (m, 88H), 0.91 (m, 18H).

Anal. Calcd for C₁₁₀H₁₃₆N₄O₂S₆: C, 75.99; H, 7.88; N, 3.22; S, 11.07. Found: C, 75.43; H, 7.56; N, 3.00; S, 10.48.

Device fabrication and characterization

The conventional binary and ternary OSCs with the structure of glass/ITO/PEDOT:PSS /binary or ternary active layer/PFN-Br/Ag were fabricated under ambient conditions. The patterned indium tin oxide (ITO) glass substrates were sequentially ultrasonicated with a detergent, deionized water, acetone, and isopropanol. The clean ITO substrates were treated with oxygen plasmas for 100 s. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) solution was filtered through 0.22 μm filter and spin coated on ITO substrates at 3500 rpm for 30 s to form a thin layer of 35 nm and heated at 120 $^{\circ}\text{C}$ for 10 min in air. The solutions of P1:Y6 and PM6:Y6 (with different weight ratios of the donor and acceptor, total concentration of 16 mg/mL) in chloroform were stirred at 40 $^{\circ}\text{C}$ for 1 h and then spin coated on the top of the PEDOT:PSS layer at the speed of 3000 rpm for 40 s to form a \sim 100 nm active layer. We found that the devices based on P1:Y6 (1:1.2 w/w) and PM6:Y6 (1:1.2 w/w) showed the best photovoltaic performance. After that the optimized active layers were subjected to solvent vapor annealing *via* exposing this active layer to THF vapors for 40 s. A solution of PM6:P1:Y6 (0.8:0.2:1.2) with a total concentration of 16 mg/mL in chloroform were spin coated and optimized in the same way as for the binary active layers. The cathode interlayer PFN-Br (1 mg/mL in methanol) was spin coated on the top of the active layer at the speed 3000 for 25 s to reach the thickness of 5 nm. Finally, 100 nm Ag were deposited under $1.0 \cdot 10^{-5}$ Pa vacuum condition. The current density–voltage (J – V) of all the organic solar cells were measured by a Keithley 2400 unit under ambient conditions. The AM1.5 G irradiation with illumination intensity (100 mW/cm²) was provided by a solar simulator (70 \times 70 mm² photobeam size). The external quantum efficiencies (EQEs) were analyzed using a Bentham IPCE measurement system. The hole and electron mobilities were measured by space-charge limited current (SCLC) methods with the device configuration ITO/PEDOT:PSS/active layer/MoO₃/Ag and ITO/ZnO/active layer/PFN-Br/Ag structure, respectively. The SCLC is described by the Mott–Gurney law: $J = 9\epsilon\mu V^2/(8L^3)$, where ϵ is the dielectric constant of the active layer, μ is the charge carrier mobility, V is the voltage drop across the device, and L is the thickness of the active layer. The transient photovoltage (TPV) and photocurrent (TPC) traces were measured on the oscilloscope (Tektronix make) and the background illumination was provided by the LED light source, and pulsed light was provided by a function generator.

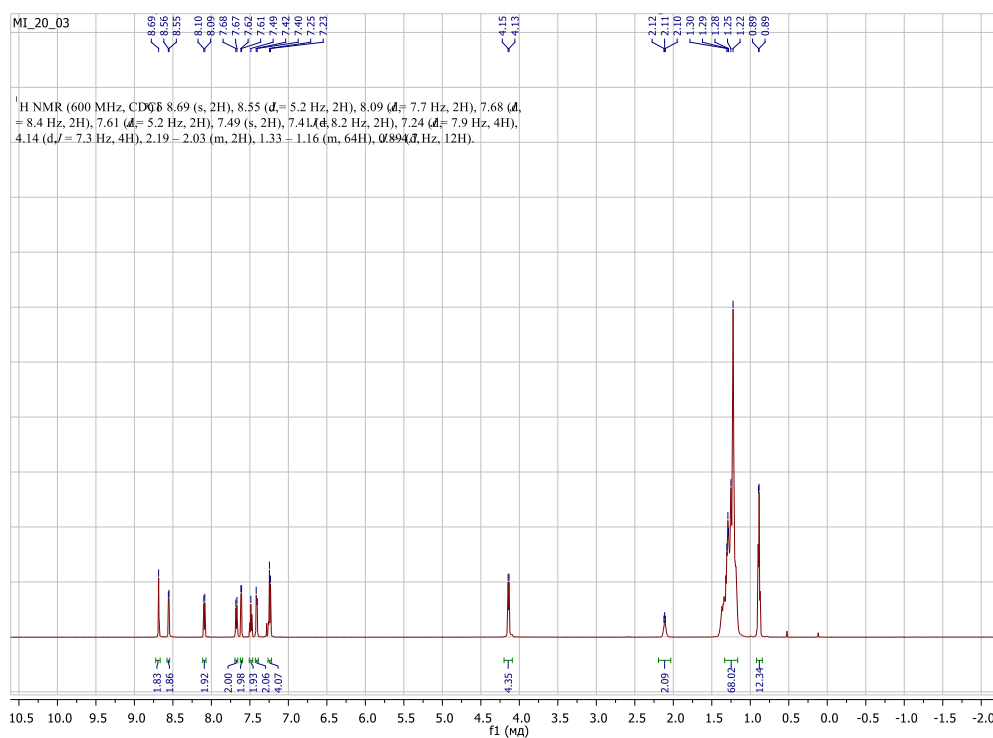


Figure S1. ^1H NMR spectrum of **M1** in CDCl_3 .

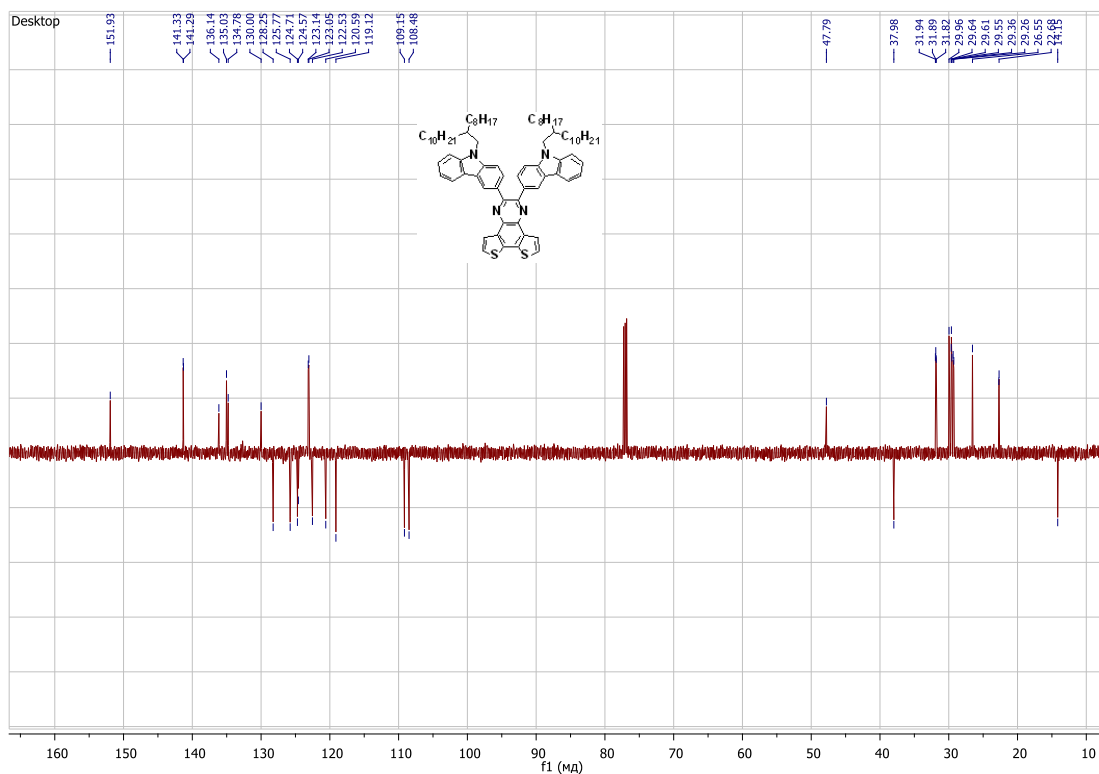


Figure S2. ^{13}C NMR spectrum of **M1** in CDCl_3 .

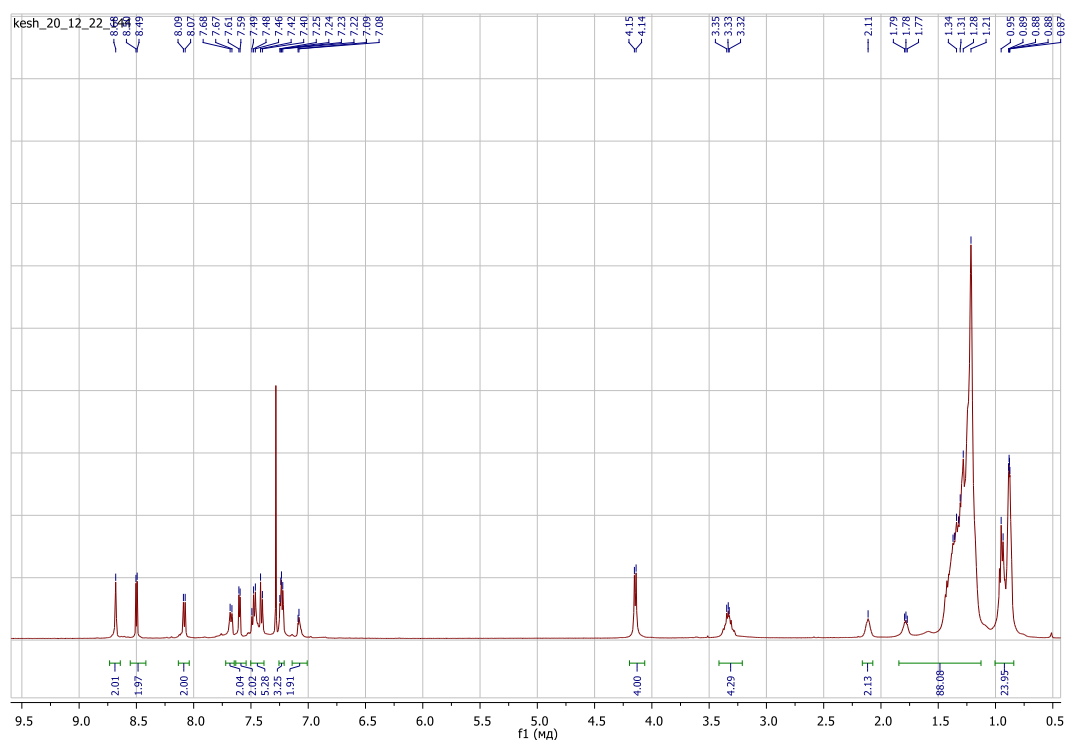


Figure S3. ^1H NMR spectrum of polymer **P1** in CDCl_3 .

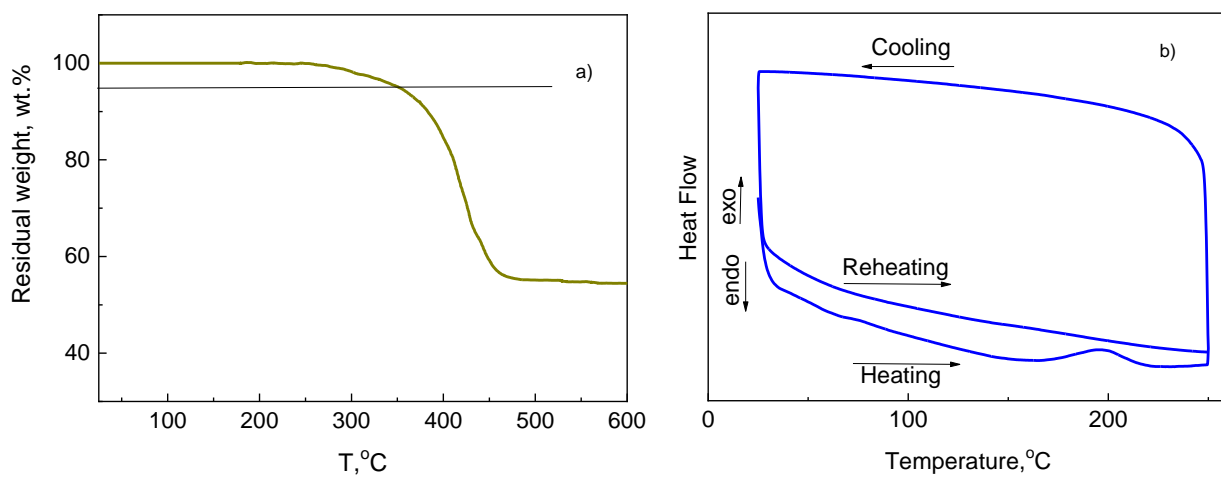


Figure S4. TGA (*a*) and DSC (*b*) curves of polymer **P1** at a heating rate $10\ ^\circ\text{C min}^{-1}$ under an inert atmosphere.

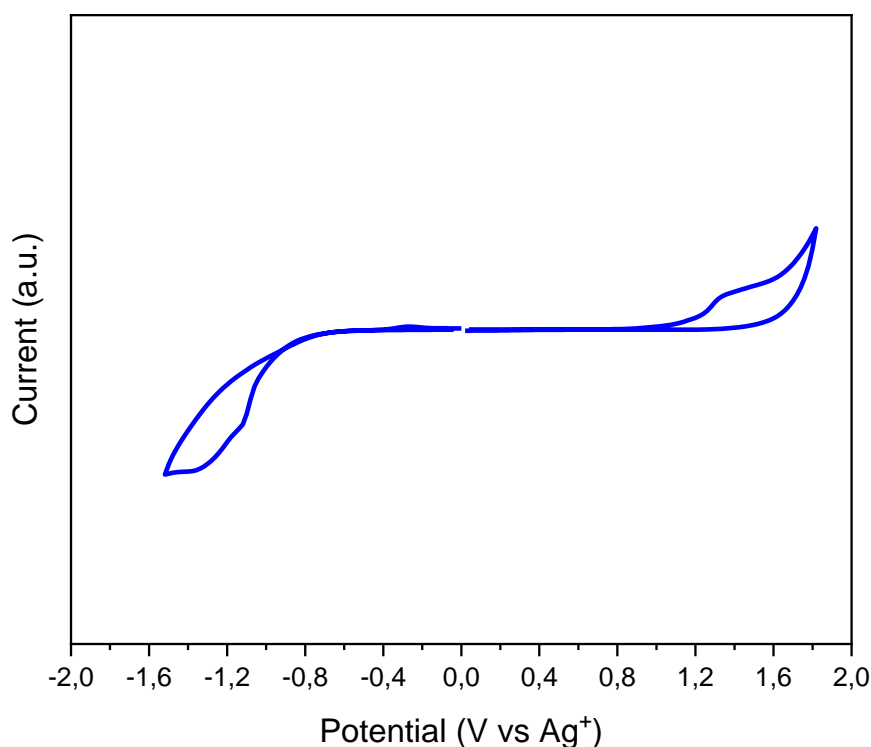


Figure S5. Cyclic voltammogram (CV) of the polymer P1 thin films in 0.1 M Bu₄NPF₆ in acetonitrile at a scan rate of 100 mV/s.

Table S1. Molecular weights and thermal properties of copolymer **P1**

Copolymer	Yield [%]	M_n^a [kDa]	M_w^a [kDa]	PDI [M_w/M_n]	T_g^b [°C]	T_d^c [°C]
P1	88	20.10	48.24	2.40	—	358

^a determined by GPC, polystyrene standards;

^b decomposition temperature according to the results of DSC studies;

^c decomposition temperature according to the results of TGA studies in nitrogen based on 5% weight loss.

References

1. Y. Zhang, J. Zou, H.-L. Yip, K.-S. Chen, J. A. Davies, Y. Sun, A. K.-Y. Jen, *Macromolecules*, **2011**, *44*, 4752–4758. DOI: 10.1021/ma2008699
2. M. L. Keshtov, S. A. Kuklin, I. O. Konstantinov, D. Yu. Godovskii, Y. Zou, I. E. Ostapov, E. E. Makhaeva, A. R. Khokhlov, *Dokl. Chem.*, **2018**, *482*, 195–200. DOI: 10.1134/S001250081809001X