Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Effects of incorporated pyrazine on the interchain packing and photovoltaic properties of wide-bandgap D–A polymers for non-fullerene polymer solar cells

Gururaj P. Kini, Jun Young Choi, Sung Jae Jeon, Il Soon Suh and Doo Kyung Moon*

Nano and Information Materials (NIMs) Laboratory,

Department of Chemical Engineering,

Konkuk University, 120, Neungdong-ro, Gwangjin-gu, Seoul 05029, Korea.

Experimental section

1.1 General Information:

Nuclear magnetic resonance (NMR) spectra were analyzed on a Bruker ARX 400 spectrometer instrument operating at 400 MHz for ^1H NMR and operating at 100 MHz for ^{13}C NMR. UV-vis absorption measurements were carried out with HP Agilent 8453 UV-Vis spectrophotometer with wavelength range 300-900 nm. All solution UV-vis experiments were measured in chloroform (CF) solutions and films were prepared by spin-coating CF solutions onto quartz substrates. Cyclic voltammograms (CV) were determined by using a Zahner IM6eX electrochemical workstation and at a scan rate of 50 mVs^{-1} at 25 ^oC under argon using 0.1 M tetrabutyl ammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile as the electrolyte. During measurement of CV, Pt wire was used as the counter electrode, Ag/AgCl electrode [Ag in 0.1 M KCl] was used as the reference electrode and polymer was drop casted on a carbon electrode used as the working electrode. The electrochemical potential was calibrated against ferrocene/ferrocenium (Fc/Fc^+) system. The highest occupied molecular orbital (HOMO) levels of the polymers were determined using the oxidation onset value. Whereas, LUMO levels were calculated from equation LUMO = E_g^{opt} – HOMO (where, E_g^{opt} is optical band-gap of polymer from the thin film state). Thermogravimetric analysis (TGA) measurements were performed on a NETZSCH TG 209 F3 thermogravimetric analyzer, where samples were run under N_2 and heated from room temperature to 400 °C at a rate of 10 °C/min. All gel permeation chromatography (GPC) analyses were performed using CF as an eluent and a polystyrene standard as a reference. Atomic force microscopy (AFM) measurements of size ($2 \times 2\ \mu m^2$) were obtained using a scanning probe XE-100 in a tapping mode. 2D-GIWAX measurements were performed on the PLS–II 3C beam line at the Pohang Accelerator Laboratory in South Korea. Active materials were coated on Silicon substrate with optimized device fabrication conditions. The monochromatic X-ray beam with intensity 11keV was adjusted with incident angle 0.110^o-0.140^o on sample with irradiation time 5-10 sec. The scattered X-ray patterns were recorded with charge coupled device (CCD) detector.

1.2 Fabrication and characterization of PSCs:

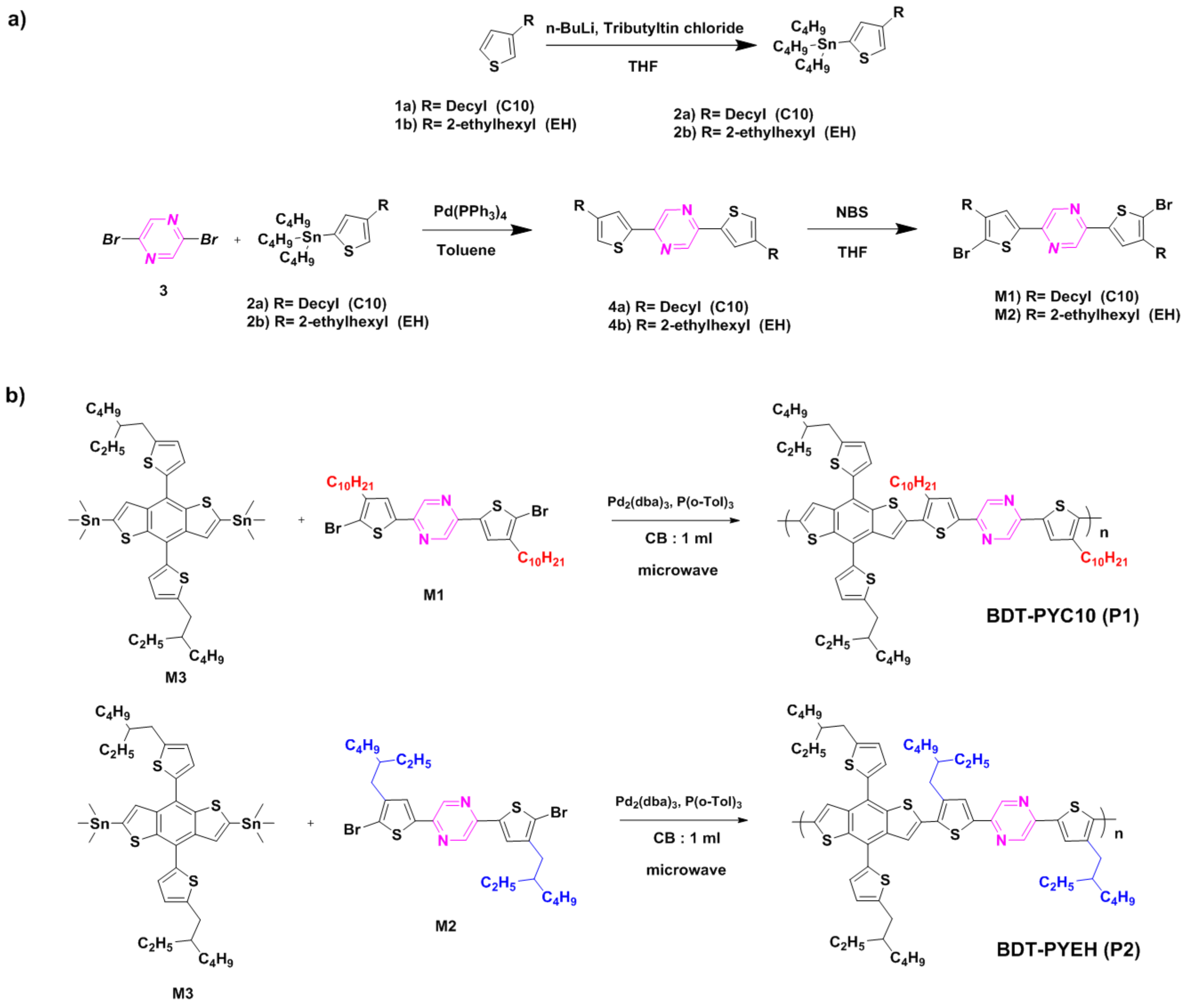
All the BHJ photovoltaic cells were prepared using inverted device fabrication procedure. Indium tin oxide (ITO) glass (10 Ω sq^{-1}, Samsung corning) was sequentially sonicated for a period of 10 min in order, detergent (Alconox in deionized water), acetone, isopropyl alcohol, and deionized water. To ensure the complete removal of the remaining water, the ITO glass was heated on a hot plate for 10 min at 120 °C. For the hydrophilic treatment of the ITO glass surface, the glass was cleaned for 15 min in a UVO cleaner. Then zinc oxide (ZnO) sol gel precursor[1] in 2-methoxy ethanol was spin coated on to the UVO-treated ITO to produce a 10 nm thick layer by spin-coating at 3000 rpm. The coated glass was then dried at 200 °C for 60 min on hot plate. Composite solutions of the polymer and ITIC were prepared using CB and 0.5 vol% DIO. The solutions were filtered through a 0.5 µm polytetrafluoroethylene (PTFE) filter and then spin coated (1000 - 4000 rpm, 30 s) on top of the ZnO layer. Then, the active layer was set above the hot plate at 130 °C for 10 mins, and then cooled to room temperature. Finally, inverted device fabrication was completed by depositing thin layers MoO_3 (5 nm) and Ag (100 nm) in vacuum (1026 Torr) using thermal evaporator. The active area of the device was 0.04 cm^2. The output photocurrent was adjusted to match the photocurrent of the Si reference cell to obtain a power density of 100 mW cm^{-2}.

1.3 Hole mobility measurements:

The hole mobility of polymer: $PC_{71}BM$ blends were measured by using space-charge limited current (SCLC) technique method. The hole only (ITO/PEDOT:PSS/active layer/MoO_3/Ag) devices were fabricated with optimum blend ratios in CB:DIO (0.5 vol% DIO). The charge carrier mobility were determined by fitting dark *J*-*V* measurements results in the 0-5 V range into space charge limited form and mobility (µ) calculated using Mott–Gurney equation $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, where J = current density, ε_r = dielectric constant of the transport medium, ε_0 = permittivity of free space (8.85×10^{-12} F m^{-1}), V = internal voltage and L = active layer thickness respectively.

1.4 Materials and Methods.

All chemicals and solvents were purchased from Aldrich, Alfa Aesar and TCI Chemical Co. companies and used as received. The monomers **2a** and **2b**[2] and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**M3**)[3] and were prepared according to previous reported methods.



Scheme 1. Synthetic routes of a) monomers and b) polymers.

General procedure for synthesis of pyrazine monomers:

Step 1: A mixture of 2-(trinbutylstannyl)-4-alkylthiophene (3 eq), 1,4-dibromopyrazine (**3**) (1 eq), and tetrakis(triphenylphosphine)palladium(0) (5 mol%) in toluene (25vol) was degassed twice with nitrogen (N2). The reaction mixture was then heated at 110 °C for 24 h; after cooling, the mixture was poured into water (100 mL) and extracted with chloroform. The organic layer was dried over anhydrous MgSO4. The crude compound was purified by silica gel chromatography. with dichloromethane (30%) in hexane.

2,5-bis(4-decylthiophen-2-yl)pyrazine (4a): (0.55 g, yield 75%), Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):** 8.80 (s, 2H), 7.49 (s, 2H), 7.05 (s, 2H), 2.63 (t, 4H), 1.62 (m, 4H), 1.35-1.24 (m, 28H) and 0.88 (t, 6H). **^{13}C NMR (100MHz, $CDCl_3$, δ ppm):**146.01, 144.86, 140.93, 139.38, 126.59, 123.40, 31.92, 30.55, 30.47, 29.63, 29.61, 29.47, 29.34, 29.31, 22.70, 14.13.

2,5-bis(4-(2-ethylhexyl)thiophen-2-yl)pyrazine (4b): (0.34 g, yield 69%), Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):** 8.80 (s, 4H), 7.46 (s, 2H), 7.03 (s, 2H), 2.58 (d, J = 6.87 Hz, 4H), 1.60 (m, 2H), 1.35-1.27 (m, 16H) and 0.89 (m, 12H). **^{13}C NMR (100MHz, $CDCl_3$, δ ppm):**146.01, 143.60, 140.76, 139.40, 127.06, 124.28, 40.32, 34.60, 32.46, 28.88, 25.62, 23.05, 14.15, 10.85.

Step 2: To the stirred solution of compound **4a** or **4b** (1eq) in THF (30 vol), N-Bromosuccinimide (NBS) (2.5 eq) was added at room temperature and reaction mass was stirred overnight under dark. After cooling, reaction mass was quenched with quenched with sodium bicarbonate solution and extracted with chloroform (50ml x 3). The organic extraction was dried over anhydrous magnesium sulfate and then concentrated. The crude product was purified by silica gel column with dichloromethane (20%) in hexane as eluent to obtain corresponding brominated product.

2,5-bis(5-bromo-4-decylthiophen-2-yl)pyrazine (M1): (0.6 g, 84%), Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):** 8.87 (s, 4H), 7.32 (s, 2H), 2.58 (t, 4H), 1.62 (m, 4H), 1.37-1.24 (m, 28H) and 0.88 (t, 6H). **^{13}C NMR (100MHz, $CDCl_3$, δ ppm):**145.36, 143.78, 140.68, 138.83, 125.94, 113.30, 31.91, 29.71, 29.69, 29.62, 29.58, 28.42, 29.34, 29.24, 22.70, 14.13.

2,5-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)pyrazine (M2): (0.37 g, yield 81%), Yellow solid. **^{1}H NMR (400 MHz, CDCl$_3$, δ ppm):** 8.72 (s, 4H), 7.29 (s, 2H), 2.52 (d, J = 7.16 Hz, 4H), 1.65 (m, 2H), 1.35-1.27 (m, 16H) and 0.89 (m, 12H). **^{13}C NMR (100MHz, CDCl$_3$, δ ppm):** 145.38, 142.99, 140.52, 138.87, 126.45, 113.94, 39.97, 33.95, 32.46, 28.77, 25.68, 23.05, 14.13, 10.84.

General procedure for synthesis of polymers:

To the clean dry 5 mL microwave vial pyrazine monomers (M1 or M2) (0.15 mmol), stannylated BDT monomers (M3) (0.15 mmol), Pd_2 (dba)$_3$ (3 mole%), and tri-(o-tolyl)phosphine (6 mole%) were added, followed by 1 mL of anhydrous chlorobenzene. The resulting reaction mixture was subsequently heated at 110 ^{o}C for 10 min, 130 ^{o}C for 10 min and then 140 ^{o}C for 60 min in a microwave reactor. Then polymer was end-capped by addition of 2-tributylstannylthiophene (0.1 equiv.) and the mixture was further reacted at 145 °C for 20 min. Similarly, 2-Bromothiophene (0.2 equiv.) was added by a syringe and the reaction solution was heated at 145 °C for another 20 min. Then reaction mixture was then cooled to room temperature, and the polymer was precipitated into methanol. Finally, crude precipitated polymer was purified by Soxhlet extraction using methanol 12h, acetone for 12h, hexane for 12h and chloroform (CF) 12 hours. The CF solution was then concentrated under reduced pressure and precipitated into methanol and filtered to give polymers P1 and P2. The polymer was dried in vacuum oven for 24 h before using to device fabrication.

Synthesis of poly-{2-(5-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-6-methylbenzo[1,2-b:4,5-b']dithiophen-2-yl)-4-decylthiophen-2-yl)-5-(4-decyl-5-methylthiophen-2-yl)pyrazine} (**P1**) **: M1** and **M3** monomers were reacted according to above reported process. The chloroform fraction (95 mg, 88%). **GPC analysis**: Mn = 44,308, Mw = 112,638, PDI = 2.5. **^{1}H NMR (400 MHz, CDCl$_3$, δ ppm):** 8.33 (br, 1H), 7.7-7.3 (br, 6H), 7.1-6.89 (br, 3H), 2.89 (br, 8H), 1.69-1.15 (m, 56H), 1.03-0.84 (m, 18). **T_d** = 410 ^{o}C.

Synthesis of poly-{2-(5-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-6-methylbenzo[1,2-b:4,5-b']dithiophen-2-yl)-4-(2-ethylhexyl)thiophen-2-yl)-5-(4-(2-ethylhexyl)-5-methylthiophen-2-yl)pyrazine} (P2) : M2 and **M3** monomers were reacted according to above reported process. The chloroform fraction (95 mg, 84%). **GPC analysis**: Mn = 52,639, Mw = 84,468, PDI = 1.6. **^{1}H NMR (400 MHz, CDCl$_3$, δ ppm):** 8.18 (br, 1H), 8.30 (br, 1H), 7.76 (br, 1H), 7.5-7.3 (br, 4H), 7.1 (br, 1H), 6.98-6.88 (br, 2H), 2.86 (br, 8H), 1.78-1.16 (m, 42H), 1.01-0.79 (m, 24). **T$_d$** = 426 °C.

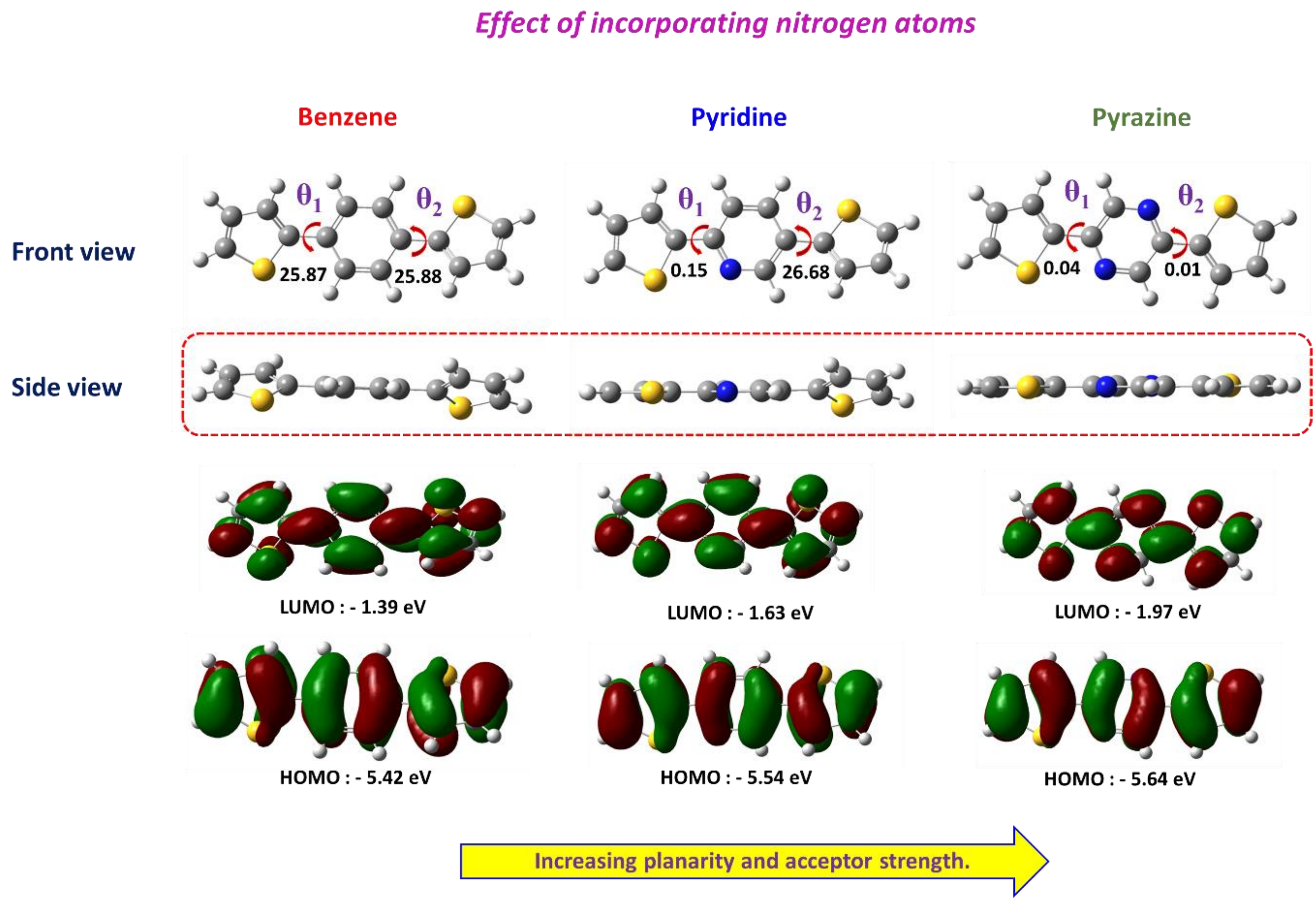


Fig. S1. The optimized HUMO/LUMO electron distribution diagrams and molecular geometries of (a) 1,4-di(thiophen-2-yl)benzene, (b) 2,5-di(thiophen-2-yl)pyridine and (c) 2,5-di(thiophen-2-yl)pyrazine as acceptor core. (Calculated using the Gaussian 09 package at the B3LYP/6–31G* level)

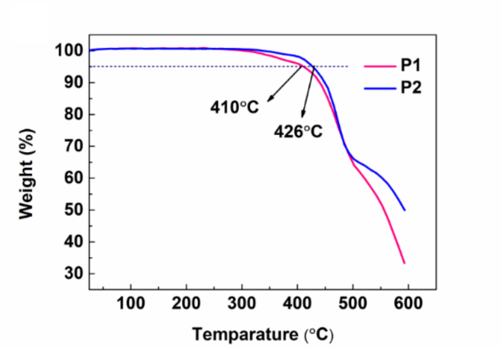


Fig. S2 TGA plots of polymers at a heating rate of 10 °C/min under nitrogen atmosphere.

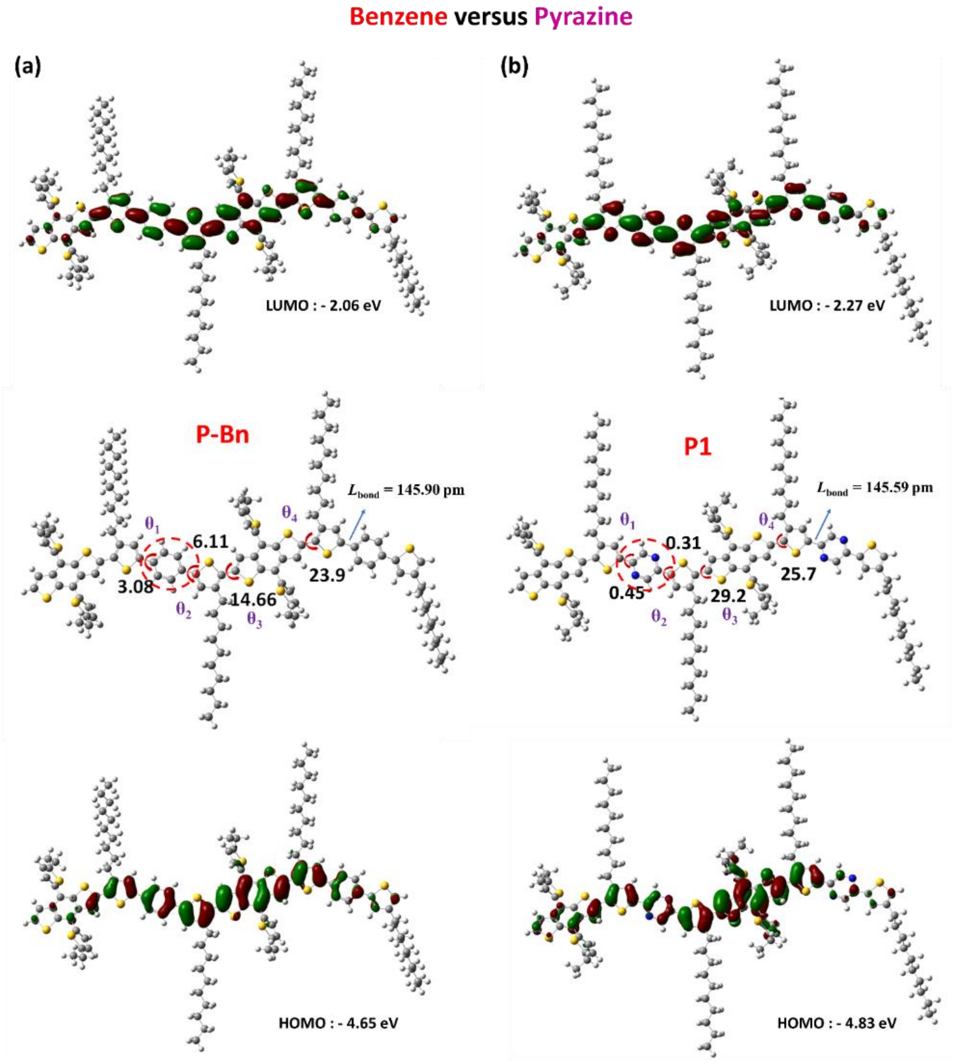


Fig. S3. The optimized molecular geometries and frontier molecular orbitals of polymer with (a) benzene and (b) pyrazine as acceptor core. (Calculated using the Gaussian 09 package at the B3LYP/6–31G* level).

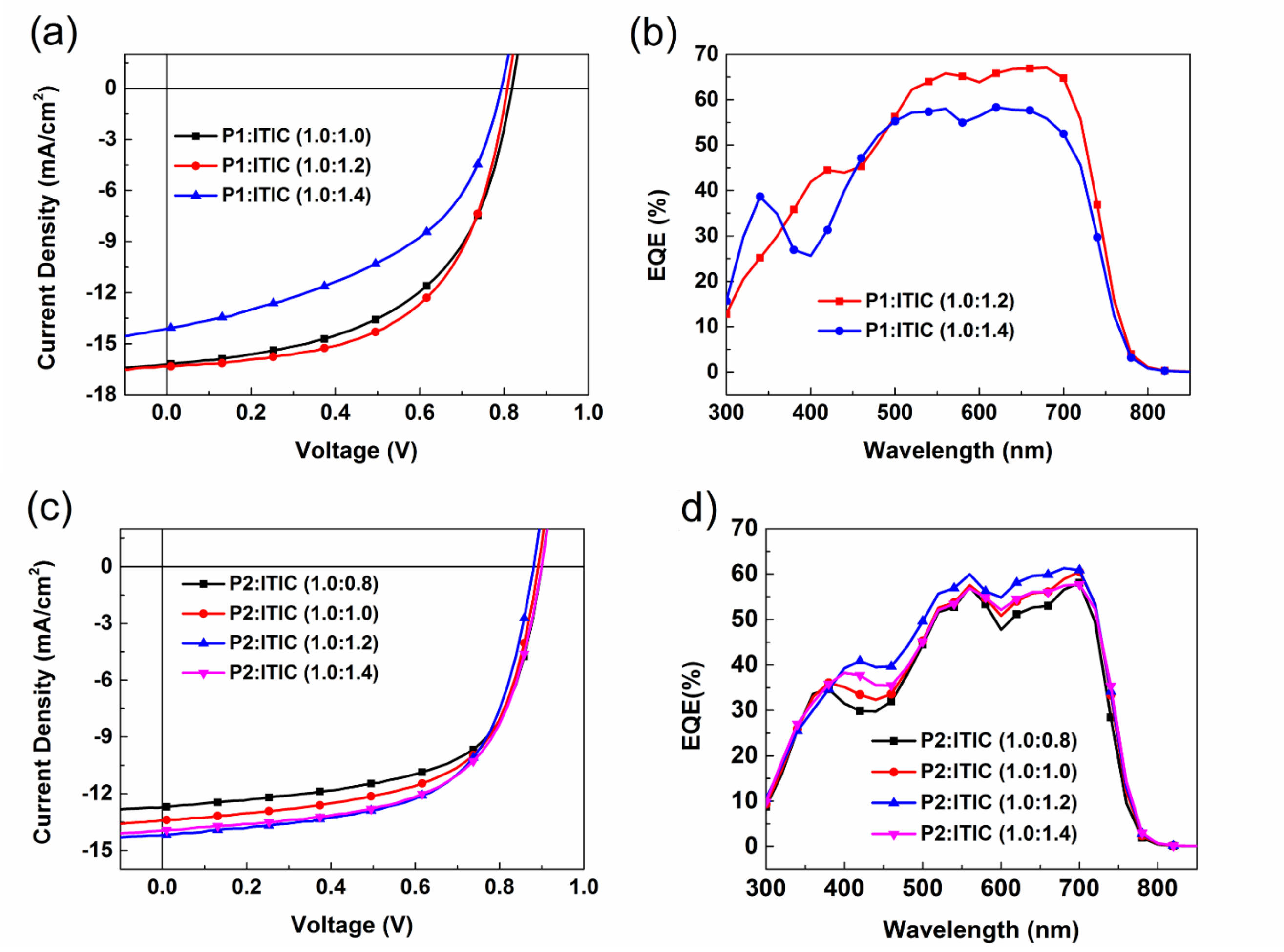


Fig. S4 (a) and (c) *J*-*V* characteristics and (c) and (d) EQE corresponding profiles **P1**:ITIC and (b) **P2**:ITIC based PSCs with different D:A blend ratios (CB/0.5 vol % DIO) under inverted device architecture ITO/ZnO/active layer/MoO3/Ag with thermal annealing 130 °C for 10 mins.

Table S1. Device characteristics of **P1**–ITIC and (b) **P2**–ITIC (CB/0.5 vol % DIO) PSCs processed with different blend ratios under optimized device fabrication conditions.

Polymer	**Polymer:ITIC blend ratio**	**Thermal annealing temperature [^oC]**	**V_{OC} [V]**	**J_{SC} [mA/cm^2]**	***FF* [%]**	**PCE [%]**
P1	**1.0:1.0**	130	0.818	16.2	54	7.2
	1.0: 1.2	130	0.798	16.3	58.1	7.6
	1.0:1.4	130	0.798	14.2	46.6	5.3
P2	**1.0:1.08**	130	0.919	13.0	62.6	7.5
	1.0: 1.0	130	0.919	13.9	62.2	7.9
	1.0:1.2	130	0.899	14.6	61.7	8.1
	1.0:1.4	130	0.899	14.0	61.4	7.7

The devices architecture is ITO/ZnO/active layer/MoO_3/Ag.

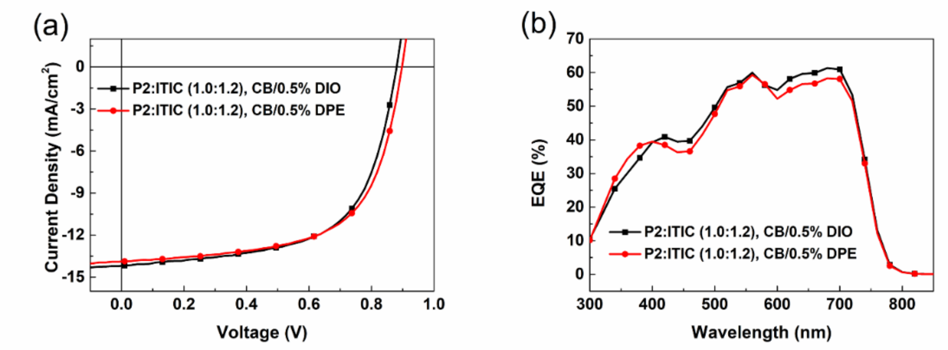


Fig. S5 *J-V* and EQE characteristics of P2 with different solvent additive conditions.

Table S2 Photovoltaic performance of **P2**:ITIC (1:1.2) solar cell devices processed with different solvent additive under AM 1.5G illumination at 100 mW cm^{-2}.

Polymer	Polymer: ITIC	Thermal annealing temperature [°C]	Solvent	V_{OC} [V]	J_{SC} [mA/cm^2]	*FF* [%]	PCE [%]
P2	1:1.2	130	CB/0.5%DIO	0.90	14.6	61.7	8.1
P2	1:1.2	130	CB/0.5%DPE	0.90	13.9	62.4	7.8

The devices architecture is ITO/ZnO/active layer/MoO_3/Ag.

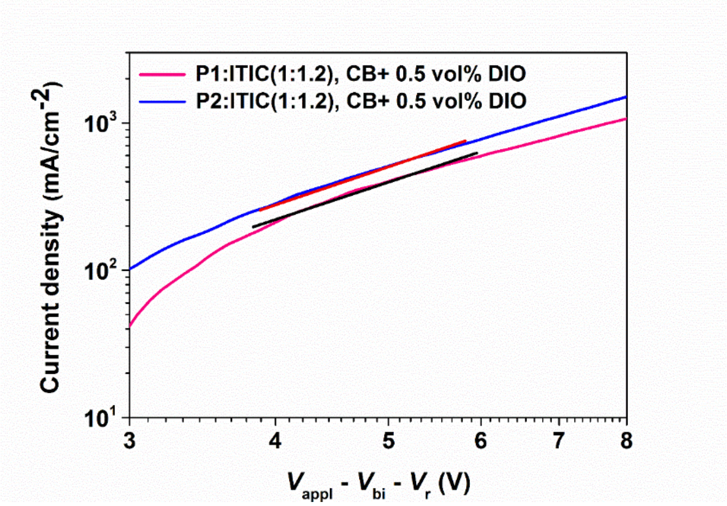


Fig. S6 *J-V* characteristics of (a) hole only devices for polymer: ITIC blends.

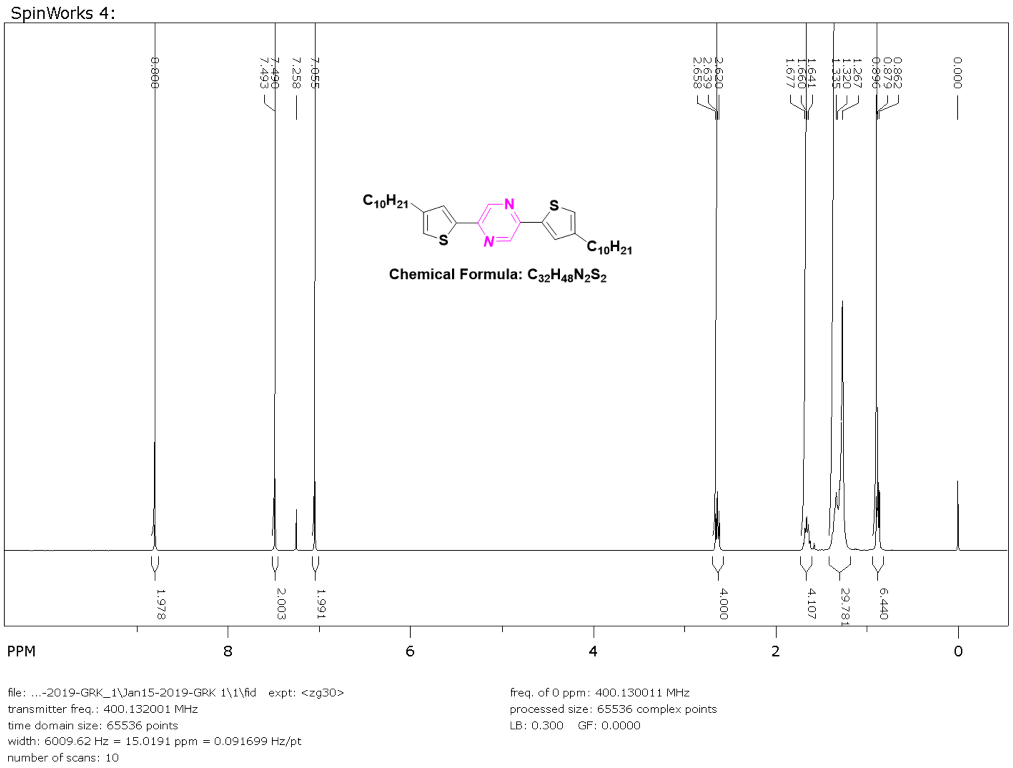
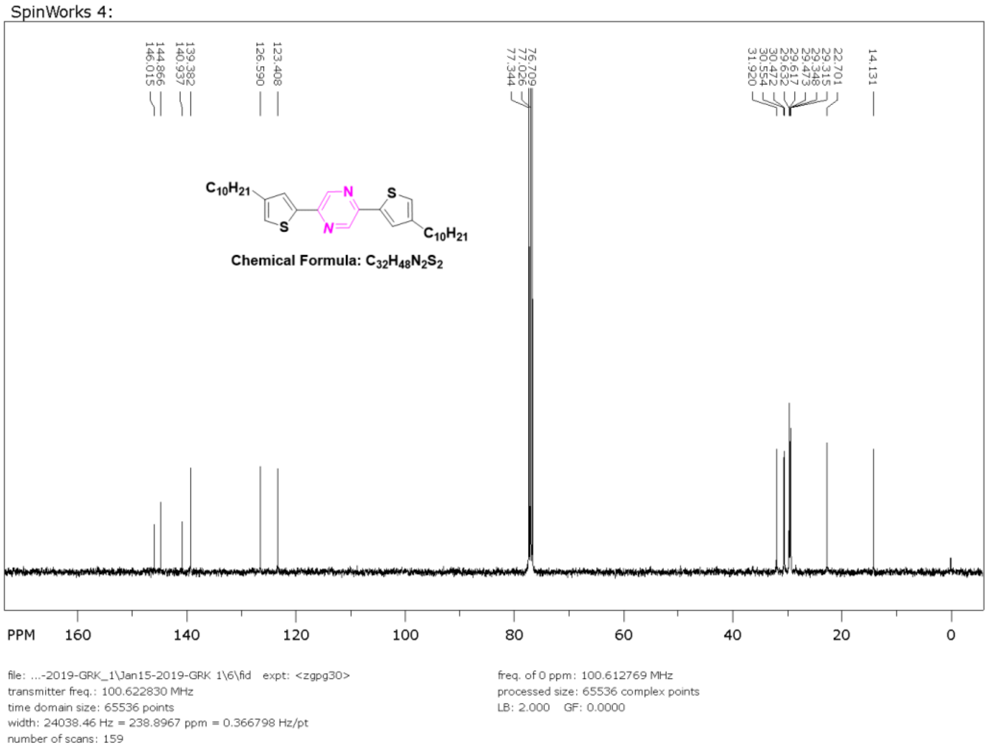


Fig. S7 ^{1}H NMR (top) and ^{13}C NMR (bottom) of monomer **4a**.



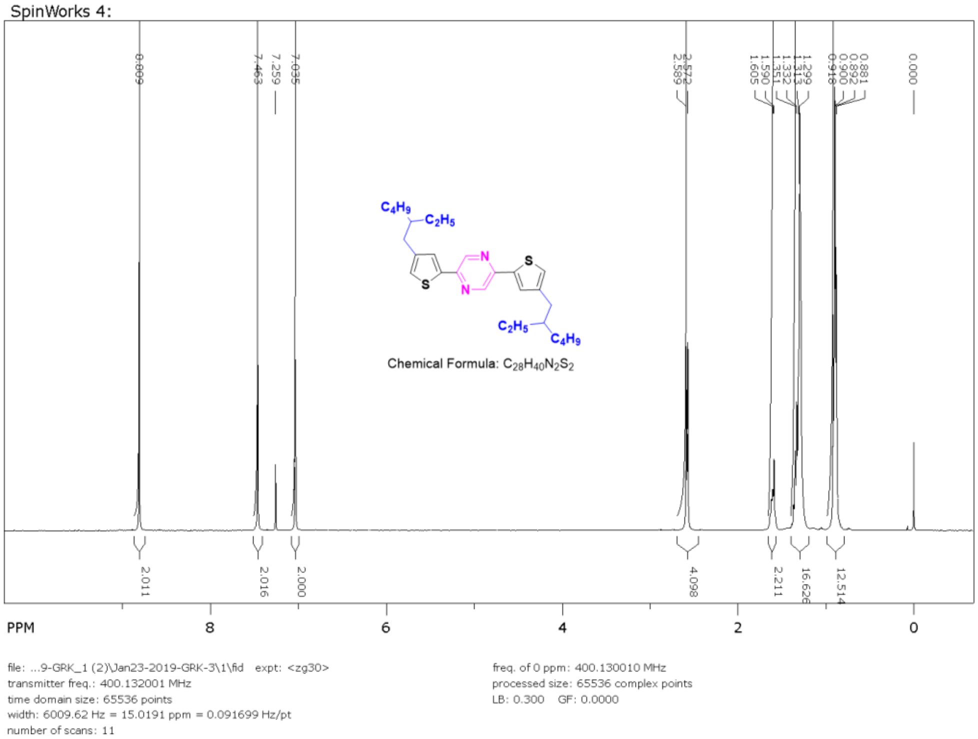
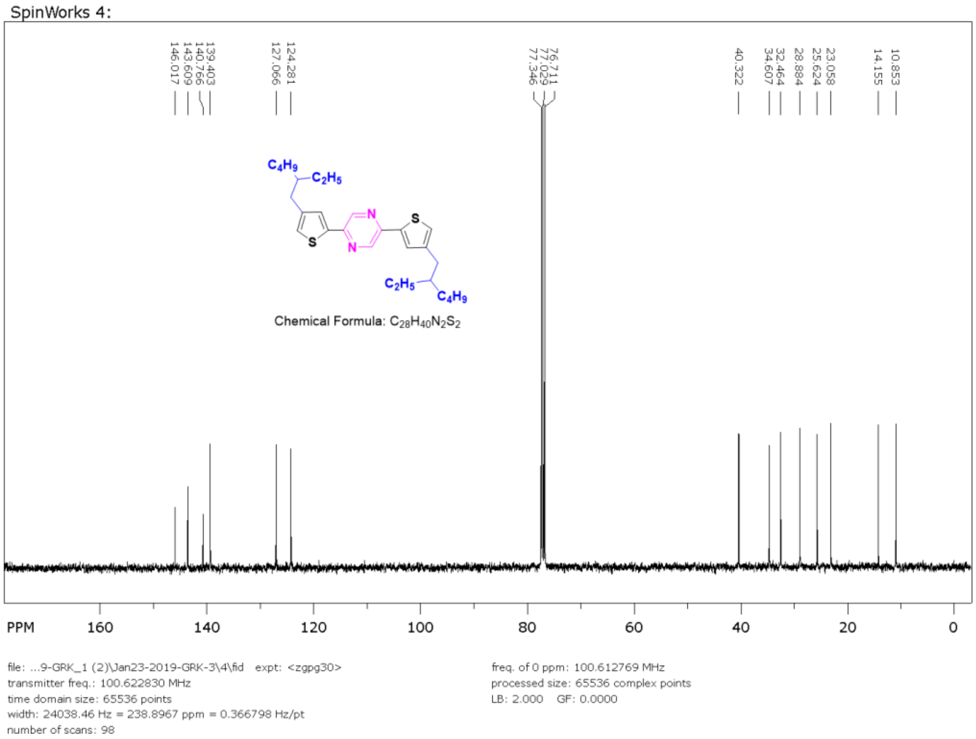


Fig. S8 ^{1}H NMR (top) and ^{13}C NMR (bottom) of monomer **4b**.



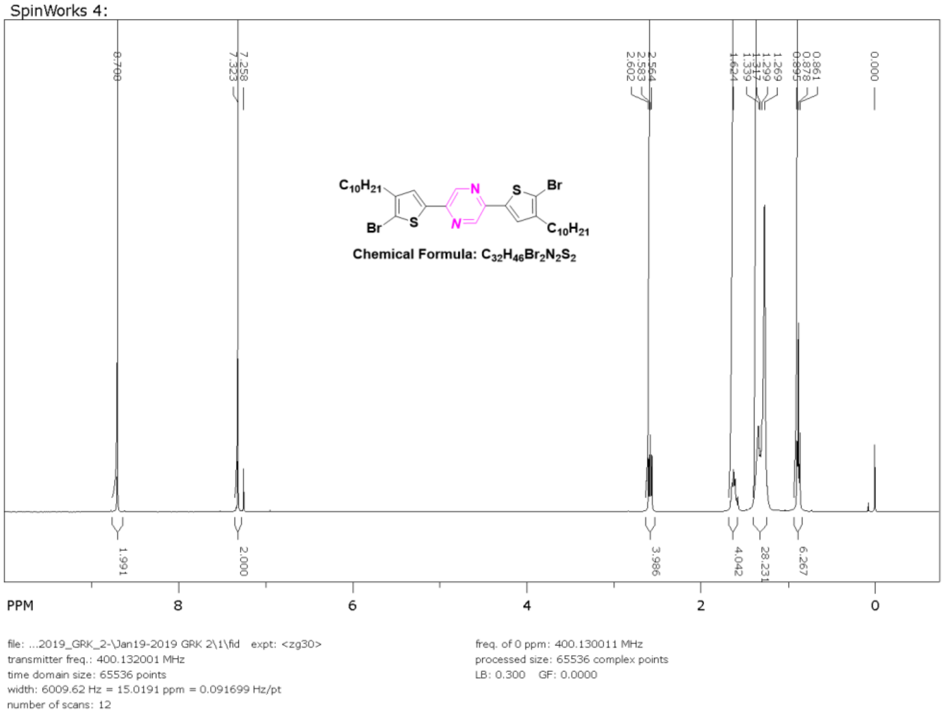
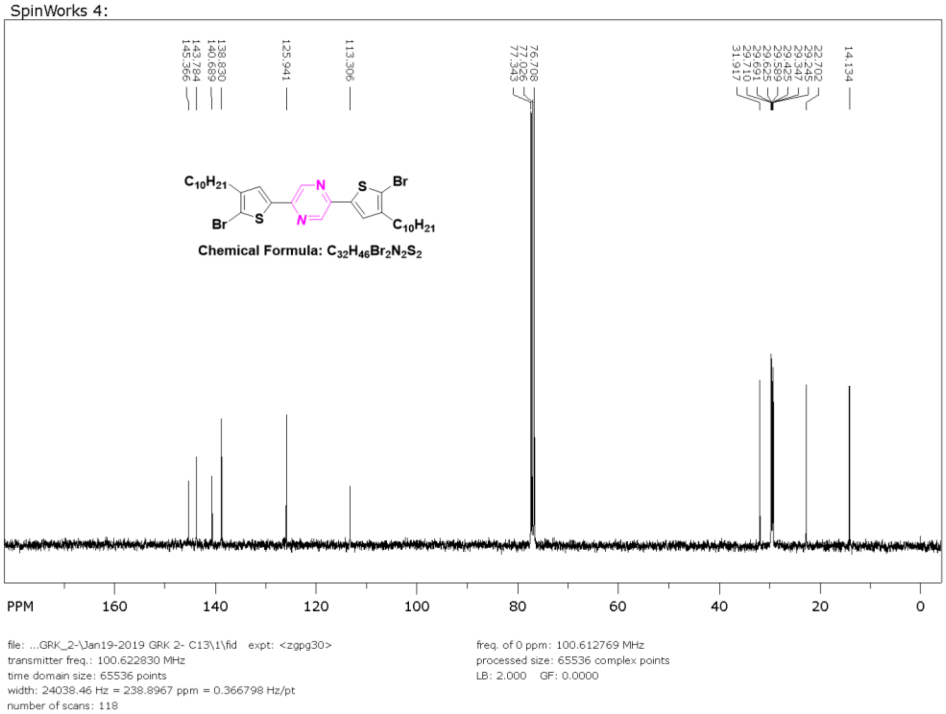


Fig. S9 ^{1}H NMR (top) and ^{13}C NMR (bottom) of monomer **M1**.



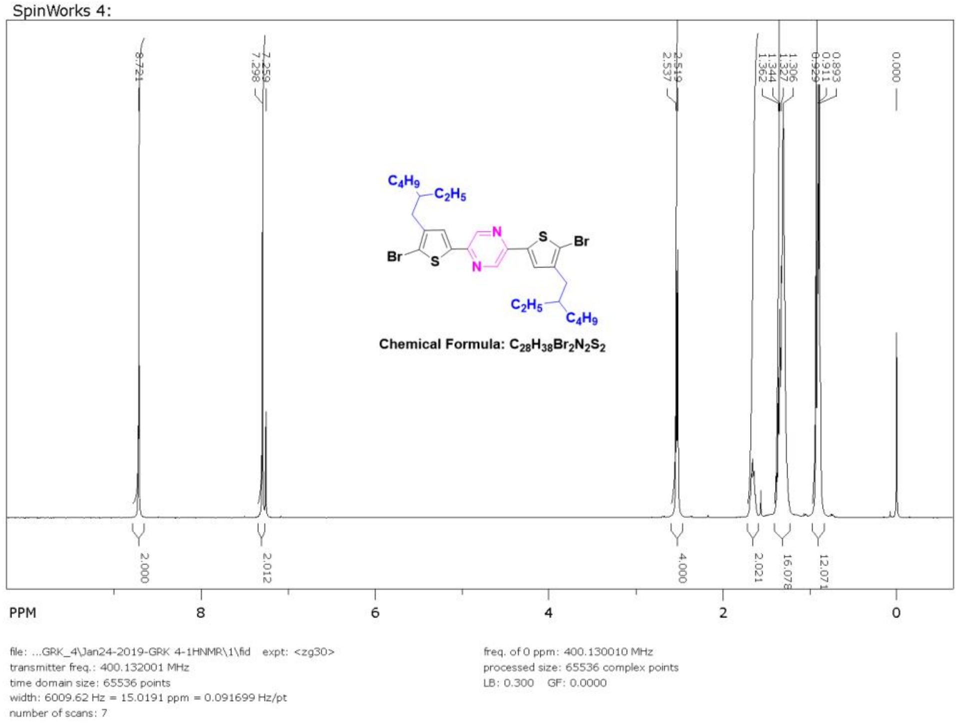
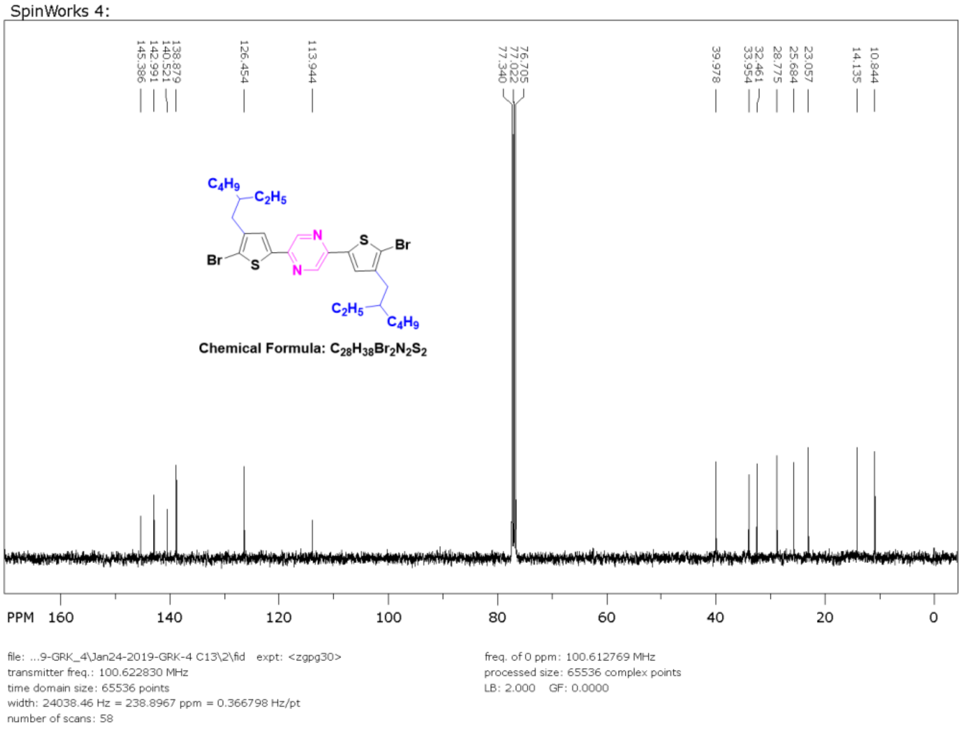


Fig. S10 ^{1}H NMR (top) and ^{13}C NMR (bottom) of monomer **M2**.



References:

(1) E. J. Lee, S. W. Heo, Y. W Han and D. K. Moon, J. Mater. Chem. C, 2016, **4**, 2463-2469.

(2) L. Biniek; S. Fall, C. L. Chochos; D. V. Anokhin; D. A. Ivanov; N. Leclerc and L. Patrick, Macromol., 2010*,* **43**, 9779–9786.

(3) N. J. Hong, H. Park, M.-J. Baek, S.-H. Lee, J. Jeong, J. H. Park and K. Zong, Org. Electron., 2016, **35**, 101-111.