

Supporting information

Synthesis, characterization and photovoltaic properties of π -conjugated copolymers with thieno-imidazole units in main chain

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Synthesis of copolymers

2, 7 –dibromobenzo[2,1-b;4,5-b']dithiophene -4,5-dione (1): synthesized according to the method, analogous to reported in literature [1]. Dark violet crystals with yield is 0.47 g (92 %). $T_{melt} = 235-238^\circ \text{C}$. NMR -¹H(CDCl₃, 400 MHz, δ , ppm): 7.25 (c, 2H). Found. % C 31.60; H 0.50; Br 42.15; for C₁₀H₂Br₂O₂S₂, calculated, % C 31.77, H 0.53; Br 42.27.

4-(2-ethylhexyloxy)benzaldehyde (2): Synthesized according to the method [2]. Yield 11.7 g (87 %), $T_{boil} = 190-193^\circ \text{C}$ (2 mm Hg), NMR-¹H(CDCl₃, 400 MHz, δ , ppm): 9.86 (c, 1H), 7.81 (d, J=8.7 Hz, 2H), 6.98 ((d, J=8.7 Hz, 2H), 3.91 (d, J=5.8 Hz, 2H), 1.74 (m, 1H), 1.54-1.28 (m, 8H), 0.99-0.82 (m, 6H). Found, % C 76.47, H 9.37, for C₁₅H₂₂O₂, calculated 76.88; H 9.46.

5-(2-ethylhexyl)thiophene-2-carboxyaldehyde (3). Synthesized according to method [3][Yield 7.8 g (63 %). $T_{boil} = 142-145^\circ \text{C}$ (2 mm.Hg.). NMR-¹H (CDCl₃, 400 MHz, δ , ppm): 9.80 (c, 1H), 7.59 (d, J = 3.7 Hz, 1H), 6.87 (d, J = 3.7 Hz, 1H), 2.79 (d, J = 6.8 Hz, 2H), 1.66-

1.55 (m, 1H), 1.37-1.20 (m, 8H), 0.87 (t, J = 7.4 Hz, 6H). Found, %: C 69.27; H 8.86; S 14.01. For C₁₃H₂₀OS calculated, %: C 69.59; H 8.98; S 14.29.

5,8-dibromo-2-{4-[(2ethylhexyl)oxy]phenyl}-1H-bisthieno[3,2-e:2',3'-g] benzimidazole (5). Into three neck flask with the volume of 25 ml, reversible refrigerator, input for argon and magnetic mixer placed 0.5 g (1.32 mmol) 2,7-dibromobenzo[2,1-b;4,5-b']dithiophen-4,5-dion (1), 0.31 g (1.32 mmol) 4-(2-ethylhexyloxy)benzaldehyde (2), 1.02 g (13.22 mmol) ammonium acetate and 10 g of ice acetic acid, thereafter the mixture was stirred at boiling in the flow of Argon during 7 hours. Reaction mass was cooled down to room temperature and casted into 100 ml of distilled water, product was extracted by chloroform. Extract was washed by saturated water solution of NaCl, dried by MgSO₄ and steamed using rotor evaporator. Product was purified by column chromatography (silicagel, eluent – hexane/ethylacetate=1:1). Obtained beige crystals. Yield 0.58 g (74%) T_{melt} = 202-204 °C. NMR¹H (CDCl₃, 400 MHz, δ, ppm.): 8.07 (d, J = 8.7 Hz, 2H), 7.78 (c, 2H), 7.05 (d, J = 8.7 Hz, 2H), 3.97 (d, J = 5.6 Hz, 2H), 2.05 (m, 1H), 1.76 (m, 1H), 1.60-1.33 (m, 8H), 0.98-0.89 (m, 6H). NMR-¹³C (CDCl₃, 100 MHz, δ, ppm.): 160.79, 149.84, 148.21, 128.77, 127.67, 123.70, 123.17, 121.51, 114.89, 113.03, 70.58, 39.18, 30.34, 28.96, 23.68, 22.94, 14.00, 11.01. Found, %: C 50.49; H 4.00; N 4.58; Br 26.84. For C₂₅H₂₄Br₂N₂S₂O calculated, %: C 50.68; H 4.08; N 4.73, Br 26.98.

5,8-dibromo-2-[5-(2ethylhexyl)thiophen-2-yl]-1H-bisthieno[3,2-e:2',3'-g] benzimidazole (M₂). Synthesized analogous to compound 5. Yellow crystals. Yield 0.49 g (75 %). T_{melt} = 194-195 °C. NMR-¹H ((CD₃)₂CO, 400 MHz, δ, ppm.): 9.85 (c, 1H), 7.79 (c, 2H), 7.56 (d, J = 3.6 Hz, 1H), 6.89 (d, J = 3.5 Hz, 1H), 2.84 (d, J = 6.6 Hz, 2H), 1.66 (m, 1H), 1.45 – 1.23 (m, 8H), 0.97 – 0.83 (m, 6H). NMR-¹³C ((CD₃)₂CO, 100 MHz, δ, ppm.): 148.08, 146.50, 132.21, 128.80, 127.31, 126.82, 125.47, 113.26, 112.96, 112.69, 42.41, 34.69, 33.21, 29.65, 26.33, 23.75, 14.48, 11.23. Found, %: C 47.18; H 3.64; N 4.48; Br 27.14. For C₂₃H₂₂Br₂N₂S₃ calculated, %: C, 47.43; H, 3.81; N, 4.81 ; Br, 27.44.

5,8-dibromo-2-[1',1',2',2',3',3',4',4'-octafluorobutyl]-1H-bisthieno[3,2-e:2',3'-g] benzimidazole (M₃). Synthesized analogous to compound 5. Yield (67 %). NMR-¹H ((CD₃)₂CO, 400 MHz, δ, ppm.): 13.36.85 (s, 1H), 7.87 (s, 1H), 7.83 (s, 1H), 6.91 (t, 1H). NMR ¹⁹F ((CD₃)₂CO, 100 MHz, δ, ppm.): -111.35, -124.32, -130.05, -139.03 ppm. Found, %:

C 30.21; H 0.64; N 4.48; Br 26.84. For $C_{15}H_4Br_2N_2F_8S_2$ calculated, %: C, 30.63; H, 0.68; N, 4.76; Br, 27.17.

5,8-Dibromo-2-(4-((2-ethylhexyl)oxy)phenyl)-1-octyl-1H-dithieno[2',3':3,4;3'', 2'':5,6] benzo[1,2-d]imidazole (M₁) [4]. To a solution of **5** (g, 9.31 mmol) in DMF (50 mL), K_2CO_3 (3.08 g, 22.34 mmol) was added and heated to 95 °C for 2 hours. Then cooled to room temperature. To it 1-iodooctane (g, 12.19 mmol) was added slowly. Reaction mixture was heated to 95°C overnight. After cooling to room temperature the reaction mixture was poured in water (300mL). Organic phase was extracted by ethyl acetate via repeated washing in water. Dried over $MgSO_4$, solvent was removed under rotary evaporation. Crude product was purified by silica gel column chromatography (Hexane as eluent) to give a brown solid (g, 88%). ¹H NMR ($CDCl_3$, 400 MHz): 8.00 (s, 1H), 7.62 (d, 2H), 7.59 (s, 1H), 7.06 (d, 2H, 8.7Hz), 4.42 (t, 2H, 7.8 Hz), 3.95 (d, 2H, 5.7 Hz), 1.55-0.85 (m, 30H). Calcd for $C_{33}H_{40}Br_2N_2OS_2$: C, 56.25; H, 5.72; N, 3.98; Found: C, 55.99; H, 5.45; N, 3.56.

Synthesis of polymer P1. Into three neck flask with the volume of 25 ml, connected to inverse refrigerator and magnetic mixer placed in the flow of 0.2940(0.5mmol) 5,8-dibromo-2-[1',1',2',2',3',3',4',4'-octafluorobutyl]-1H-bisthieno[3,2-e:2',3'-g] benzimidazole (M₃). 0.3102g (0.5 mmol) 4,7-bisc[5-(trimethylsilyl)thiophen-2il]2,1,3-benzothiadiazol 0.027 g $Pd(Ph_3P)_4$, added 20 ml of dry toluene. Reaction mixture was stirred at 110 °C during 48 h in argon, thereafter 0.02 g of 2-bromothiophene was added and 0.02 g of 2-(tributylstannil)thiophene added and continued stirring during 5 hours. Then the mixture was cooled down to room temperature, product was precipitated in 200 ml of methanol and filtered. Polymer was then dissolved in chloroform and re-precipitated in methanol, afterwards it was purified by extraction by methanol, hexane and chloroform in Soxhlet apparatus and dried in vacuum. Yield 75%. Calc. for $C_{29}H_{10}N_4S_5F_8$, %: C, 47.93; H, 1.39; N, 7.71; S, 22.06; F, 20.91 Found: C, 47.98; H, 1.27; N, 7.64; S, 22.36; F, 20.41. ¹H NMR (400 MHz, $CDCl_3$, δ , ppm): 7.74-7.30 (6H, Ar), 7.10-6.89 (2H, alk).

Copolymer P2: **P2** was synthesized analogous to **P1**. Yield 81%. Calc. for $C_{37}H_{28}N_4S_6$, %: C, 61.63; H, 3.91; N, 7.77; S, 26.68. Found: C, 61.91; H, 3.83; N, 7.54; S, 26.38. ¹H NMR (400 MHz, $CDCl_3$, δ , ppm): 8.25-7.50 (10H, Ar), 3.75(2H, aliph), 2.50-0.55 (15H, alk).

Copolymer P3: **P3** was synthesized analogous to **P1**. Yield 87 %. Calc. for $C_{47}H_{46}N_4S_5O_1$, %: C, 66.95; H, 5.50; N, 6.64; S, 19.01. Found: C, 67.05; H, 5.47; N, 6.40; S, 18.81. ¹H NMR (400 MHz, $CDCl_3$, δ , ppm): 7.80-7.50(12H, Ar), 3.90-0.55(34H, alk).

References

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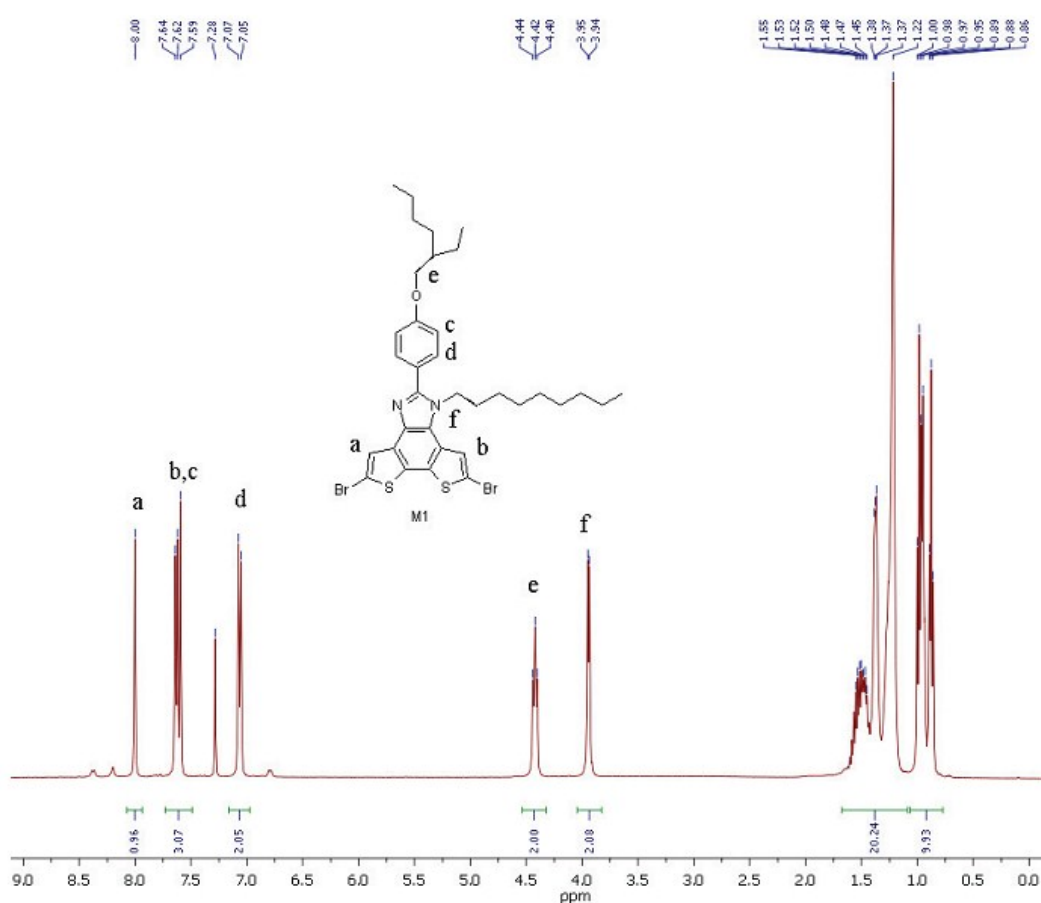


Figure S1. ¹H NMR spectra of monomer **M1** in CDCl₃

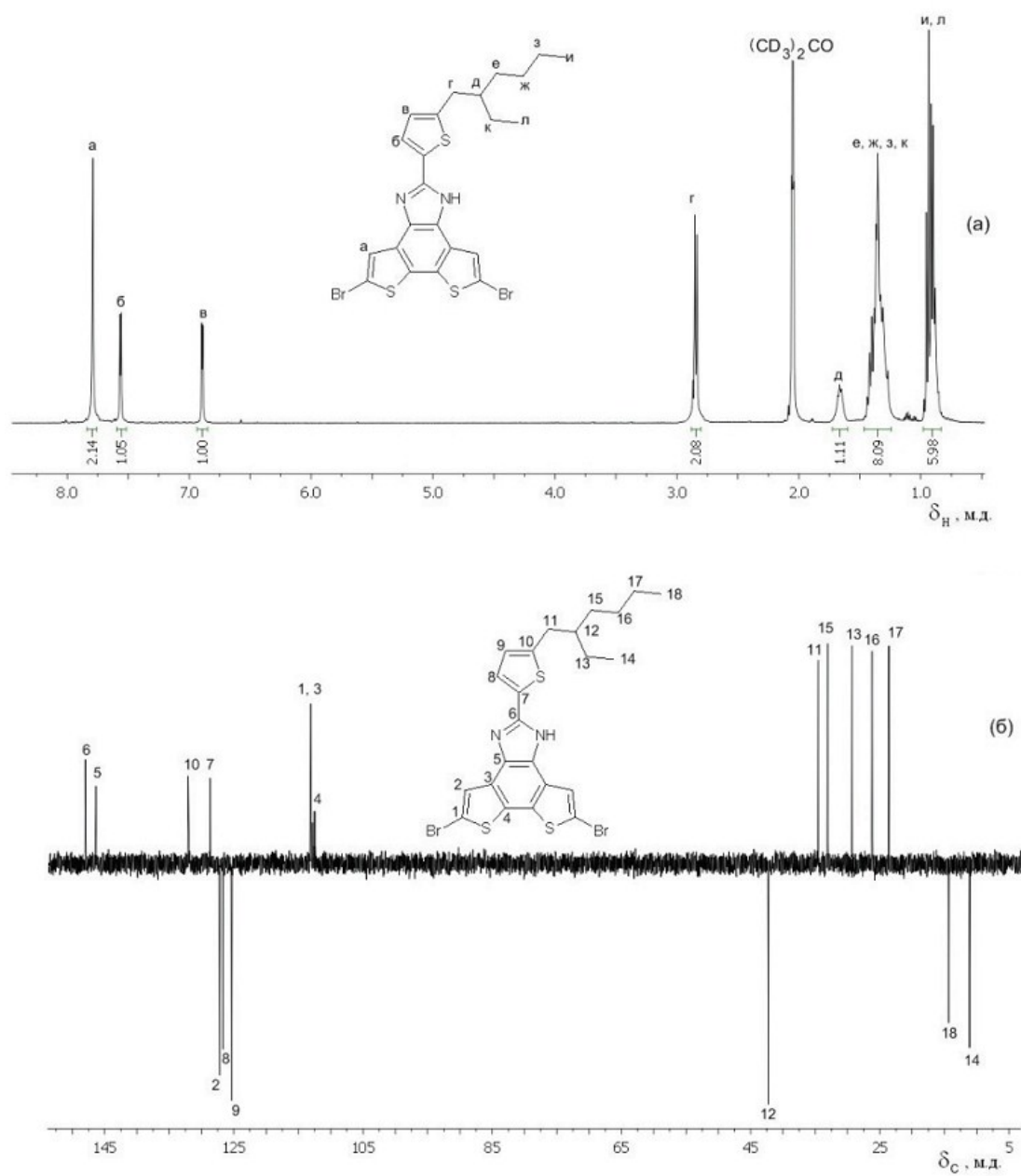


Figure S2 (a) ^1H NMR spectra (b) ^{13}C NMR of **M2** in CDCl_3

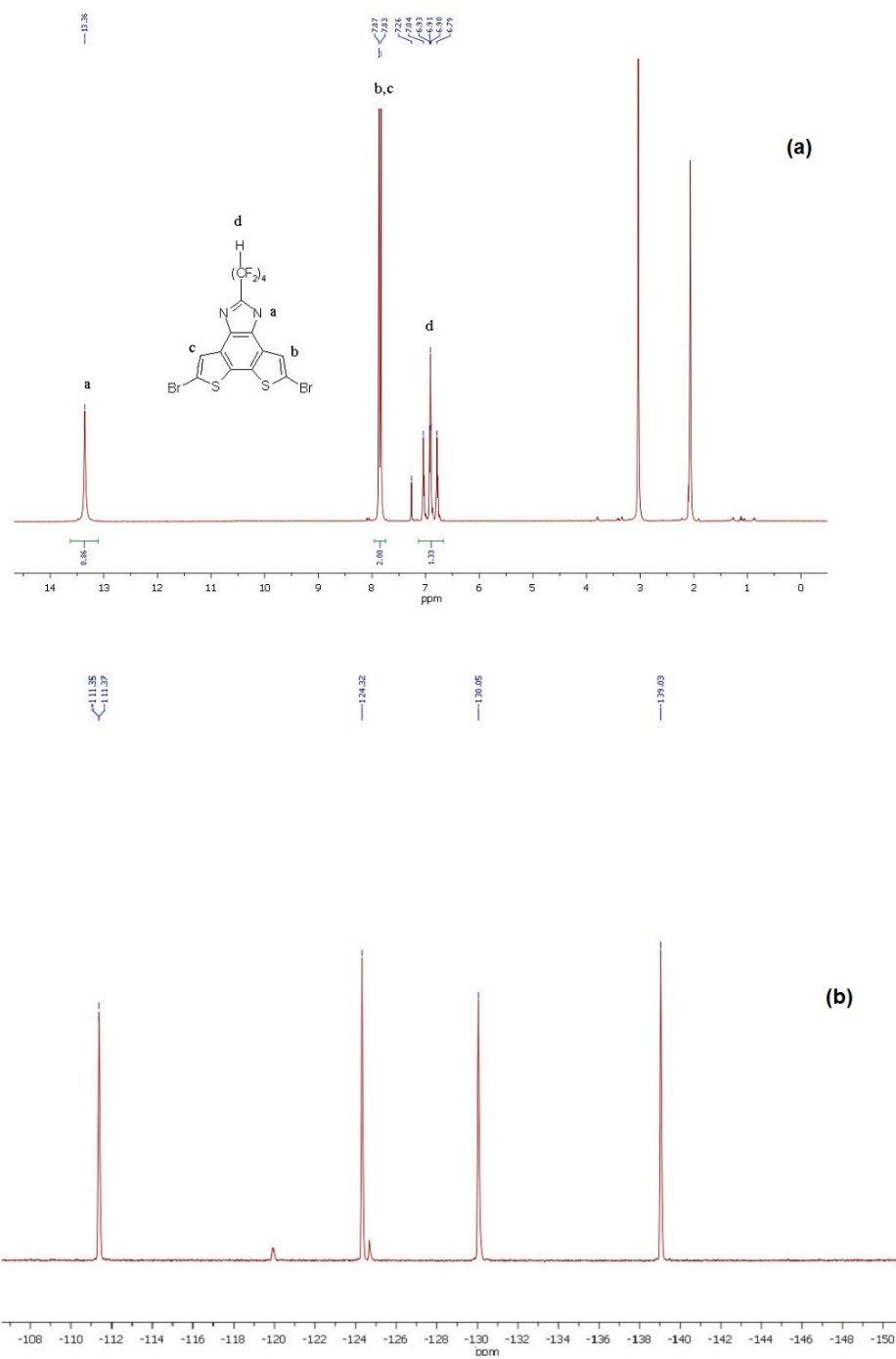


Figure S3. (a) ^1H NMR spectra of **M3** in acetone- d_6 and (b) ^{19}F NMR spectra of **M3**

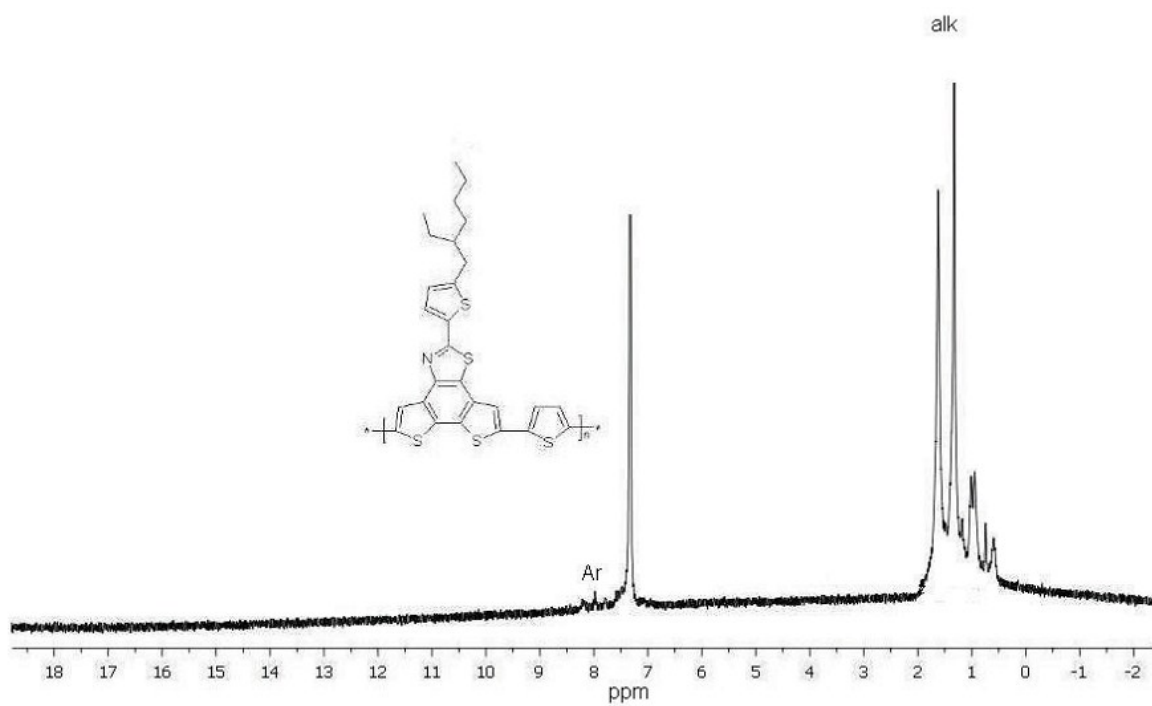


Figure S4. ^1H NMR spectra of copolymer **SB24**