Synthesis, characterization and photovoltaic properties of \( \pi \)-conjugated copolymers with thieno-imidazole units in main chain

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Synthesis of copolymers

2, 7- dibromobenz[2,1-b;4,5-b']dithiophene -4,5-dion (1): synthesized according to the method, analogous to reported in literature [1]. Dark violet crystals with yield is 0.47 g (92 %). T\(_\text{melt}\) = 235-238\(^\circ\)C. NMR -1H(CDCl\(_3\), 400 MHz, \(\delta\), ppm): 7.25 (c.2H). Found. % C 31.60; H 0.50; Br 42.15; for C\(_{10}\)H\(_2\)Br\(_2\)O\(_2\)S\(_2\), 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\(_\text{boil}\) = 190-193 \(^\circ\)C (2 mm Hg). NMR -1H(CDCl\(_3\), 400 MHz, \(\delta\), 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 C\(_{15}\)H\(_{22}\)O\(_2\), calculated 76.88; H 9.46.

5-(2-ethylhexyl)thiophene-2-carboxyaldehyde (3). Synthesized according to method [3][ Yield 7.8 g (63 %). T\(_\text{boil}\) = 142-145 \(^\circ\)C (2 mm.Hg.). NMR-1H (CDCl\(_3\), 400 MHz, \(\delta\), 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-
5,8-dibromo-2-{4-[(2-ethylhexyl)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-dibrombenzo[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 MgSO$_4$ 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%).

5,8-dibromo-2-[5-(2-ethylhexyl)thiophen-2-yl]-1H-bisthieno[3,2-e:2’,3’-g] benzimidazole (M$_2$). Synthesized analogous to compound 5. Yellow crystals. Yield 0.49 g (75%). T$_{\text{melt}}$ = 194-195 °C. NMR$^1$H (CDCl$_3$, 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$^{13}$C (CDCl$_3$, 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 C$_{25}$H$_{24}$Br$_2$N$_2$S$_2$O calculated, %: C 50.68; H 4.08; N 4.73; Br 27.48.

5,8-dibromo-2-[1’,1’,2’,2’,3’,3’,4’,4’-octafluorobutyl]-1H-bisthieno[3,2-e:2’,3’-g] benzimidazole (M$_3$). Synthesized analogous to compound 5. Yield (67%). NMR$^1$H ((CD$_3$)$_2$CO, 400 MHz, δ, ppm.): 13.36.85 (s, 1H), 7.87 (s, 1H), 7.83 (s, 1H), 6.91 (t, 1H. NMR $^{19}$F ((CD$_3$)$_2$CO, 100 MHz, δ, ppm.): -111.35, -124.32, -130.05, -139.03 ppm. Found, %:
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$_2$CO$_3$ (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%). 1HNMR (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$_2$N$_2$S$_2$: 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(0.5 mmol) 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-bis[c[5-(trimethylsilyl)thiophen-2il]2,1,3-benzothiadiazol 0.027 g Pd(Ph$_3$P)$_4$, added 20 ml of dry toluene. Reaction mixture was stirred at 110 °C during 48 hous in argon , thereafter 0.02 g of 2-bromthiophene was added and 0.02 g of 2-(tributylstannil)thiophene added and continued stirring during 5 hours. Than 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 Soxlett apparatus and dried in vacuum. Yield 75%. Calc. for C$_{29}$H$_{10}$N$_4$S$_5$F$_8$ %: 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$_4$S$_6$, %: 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$_4$S$_5$O$_1$, %: 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

Figure S1. $^1$H NMR spectra of monomer M1 in CDCl$_3$
Figure S2 (a) $^1$H NMR spectra  (b) $^{13}$C NMR of M2 in CDCl$_3$
Figure S3. (a) $^1$H NMR spectra of M3 in acetone –d and (b) $^{19}$F NMR spectra of M3
Figure S4. $^1$H NMR spectra of copolymer SB24