

Thiazolo[5,4-*d*]thiazoles with spirobifluorene moiety as the novel D- π -A type organic hosts: Design, synthesis, structure-properties relations and applications in electroluminescent devices

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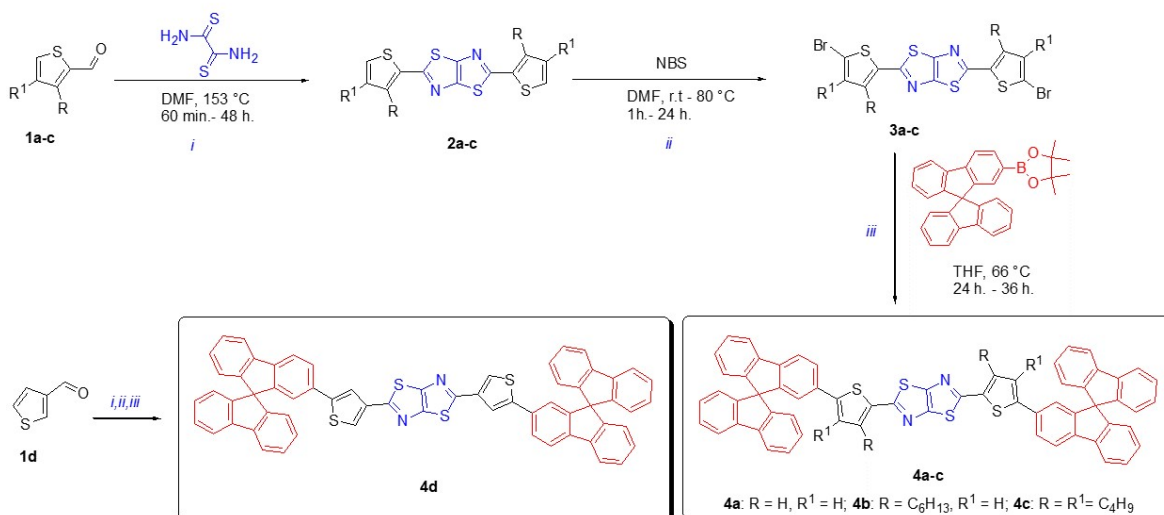
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Supplementary material

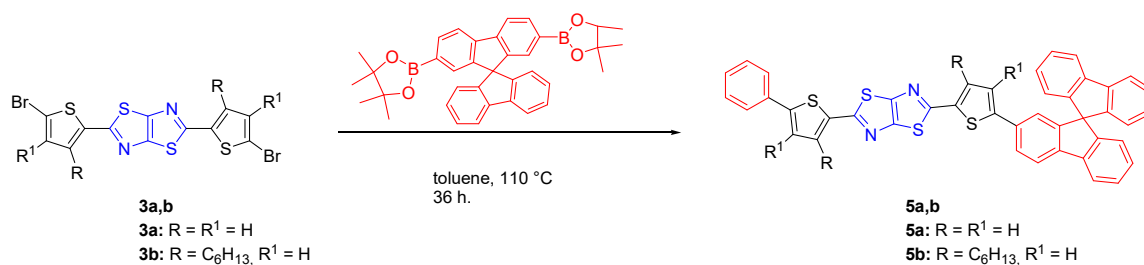
1. Synthetic approach and reaction schemes

The synthetic approach towards **4a-d** (Scheme 1) is a combination of three-step procedure: *i* - Ketcham reaction, *ii* - radical bromination, *iii* - Suzuki cross-coupling, according to the Scheme including the reaction conditions.

The synthetic approach towards **5a,b** (Scheme 2) is a combination of similar three-step procedure, differing from preparation of **4a-d** in a final *iii* step utilizing Suzuki-type polymerization, that in our case have been aborted upon quenching with phenylboronic acid upon creation of small-molecule with low molecular weight.



Scheme 1. Synthetic route for spirobifluorene-edged thiazolo[5,4-*d*]thiazoles **4a-c** starting from thiophene 2-carbaldehydes **1a-c**: (i) Ketcham reaction: DMF, 155 °C, 1 - 48 hours; (ii) Radical bromination: NBS, DMF; 80 °C, 1-24 hours; (iii) Suzuki coupling: Pd(PPh₃)₄, aliquat, THF, K₂CO₃, 66 °C, 24 - 36 hours and their structurally modified counterpart **4d** with different binding mode at the TzTz-thiophene position (C β) starting from thiophene-3-carbaldehyde (**1d**): (i) DMF, 155 °C, 90 min; (ii) NBS, DMF; 80 °C, 1 hour; (iii) Pd(PPh₃)₄, aliquat, THF, K₂CO₃, 66 °C, 36 hours.



Scheme 2. Suzuki-type polymerization: Pd(PPh₃)₄, aliquat, toluene, K₂CO₃, 110 °C, 36 hours, phenylboronic acid / brombenzene.

2.1 Materials and methods

Thiophene-2-carbaldehyde (**1a**), thiophene-3-carbaldehyde (**1d**), 3-hexylthiophene, 3,4-dibutylthiophene, dithioamide, *N*-bromosuccinimide, tetrakis(triphenylphosphine) palladium (0), Aliquat 336, 2-(9,9'-spirobi[fluoren]-7-yl)4,4,5,5-tetramethyl-1,3,2-dioxaborolane, poly(3,4-ethylene-dioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS, Heraeus Clevis Al 4083), poly(9-vinylcarbazole) (PVK), 2-(4-Biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), 1,3,5-tris(1-phenyl-1*H*-benzimidazol-2-yl)benzene, anhydrous *N,N*-dimethylformamide, acetone, and all the solvents were purchased from commercial suppliers (Sigma-Aldrich, Alfa-Aesar, TCI, Lancaster, Merck, Ossila, Ontario Chemicals) and used as received. ITO covered glass with 260 nm of indium tin oxide layer and surface resistivity < 7 ohm/sq was supplied from PGO GmbH. Starting materials: 3-hexylthiophene-2-carbaldehyde (**1b**) and 3,4-dibutylthiophene-2-carbaldehyde (**1c**) was prepared according to the previously described manner [1] under the standard Wilsmeier-Haack-Arnold protocol. All of the performed reactions were monitored by thin layer chromatography (TLC) on plates precoated with silica gel (Merck⁶⁰F₂₅₄) and visualized using a UV hand-lamp operating at 254/365 nm wavelengths. The synthesized compounds were fully characterized by ¹H, ¹³C NMR (Varian Unity 400), matrix-assisted laser desorption/time of flight (MALDI-TOF) mass spectroscopy (Bruker Daltonics) and/or elemental analysis (abundance % of C, H, N, S; Carlo Erba Elemental Analyzer 1108) and completed by IR vibrational spectroscopy (Agilent Cary 630 FTIR - diamond ATR).

2.2 General synthetic procedures

The detailed synthesis of the new derivatives **4a-d** including synthesis of precursors **2a-d** and **3a-d** is outlined in Scheme 1 and summarized in Table 1. The derivatives **2a** and **2b** were obtained by the Ketcham ring-closure reaction with a slight modification of reported procedures in [2] and the bromination towards **3a** was performed following the same procedure as in [3].

2,5-bis(3,4-dibutylthiophen-2-yl)thiazolo[5,4-d]thiazole (**2c** in Scheme 1, Table 1). The mixture of dithioamide (0.5 g, 4.1 mmol, 1 equiv.) and 3,4-dibutylthiophene-2-carbaldehyde (**1c**, 2.8 g, 12.5 mmol, 3 equiv.) in DMF (1 mL) was heated at 150 °C for 12 hours. The reaction mixture was cooled down to room temperature and poured into cold water. The solution was extracted into dichloromethane (3×15 mL). After evaporation of the solvent, the crude product was purified by sublimation (180 °C in an oil bath). Collected red crystals were isolated in a 35 % yield (0.76 g). ¹H NMR (400 MHz, CDCl₃) δppm 7.04 (s, 2 H, H_A), 2.93 (t, 4 H, *J* = 8 Hz, 2xCH₂), 2.56 (t, 4 H, *J* = 6.7 Hz, 2xCH₂), 1.68 – 1.40 (m, 16 H), 0.98 (q, 12 H, *J* = 6.7 Hz). For C₂₈H₃₈N₂S₄ (530.87 gmol⁻¹) *m/z*: calc. 530.19, found 530.20.

2,5-bis(thiophen-3-yl)thiazolo[5,4-d]thiazole (**2d** in Scheme 1). The mixture of dithioamide (0.657 g, 5.4 mmol, 1 equiv.) and excess of 3-thiophene carboxaldehyde (3.067 g, 27.2 mmol, 5 equiv.) was heated at 153 °C for 1.5 hours. Hot pyridine was added to dissolve the black solid arising during the reaction. After cooling the resulting rich purple crystalline solid was filtered off in 34 % yield (573 mg). ¹H NMR (400 MHz, CDCl₃) δppm 7.84 (s, 2H), 7.55 (dd, 2H, *J* = 5.1 Hz), 7.37 – 7.36 (m, 2H, *J* = 5.1 Hz). FTIR (ATR-Ge crystal) *v*: 3063, 1352, 1190, 842, 819, 777, 711, 648 cm⁻¹. For C₁₂H₆N₂S₄ (306.45 gmol⁻¹) calc. *m/z* 305.94, found 306.00.

2,5-bis(3-hexyl-5-bromothiophene-2-yl)thiazolo[5,4-d]thiazole (**3b** in Scheme 1). In a round bottom flask, **2b** (0.702 g, 1.47 mmol) was dissolved in DMF (10 mL). Then *N*-bromosuccinimide (1.052 g, 5.88 mmol) in DMF (16 mL) was added dropwise and stirred at room temperature for 24 hours. The reaction mixture was poured into cold water. The product was collected by filtration as a yellow solid in 42 % yield (0.530 g). ¹H NMR (400 MHz, CDCl₃) δppm 7.19 (s, 2H), 2.65 – 2.59 (m, 4H), 1.53 – 1.45 (m, 8H), 1.36 – 1.25 (m, 8H), 0.86 – 0.81 (m, 6H). For C₂₄H₂₈Br₂N₂S₄ (632.56 gmol⁻¹) *m/z*: calc. 631.95, found 634.00 (2H⁺).

2,5-bis(3,4-dibutyl-5-bromothiophene-2-yl)thiazolo[5,4-d]thiazole (**3c** in Scheme 1). *N*-Bromosuccinimide (0.145 mg, 0.8 mmol, 2.2 equiv.) was slowly added to the solution of **2c** (0.200 g, 0.37 mmol) in DMF (10 mL). The mixture was stirred at

80°C for 8 hours. The reaction mixture was cooled down to room temperature and poured into cold water. The precipitate was collected by filtration and washed with water and methanol. The product was isolated as yellow powder in 85 % yield (0.1799 g). ¹H NMR (400 MHz, DMSO-d₆) δppm 7.40 (s, 2H), 2.98 (t, 4H, *J* = 8.0 Hz, 2xCH₂), 2.54 (t, 4H, *J* = 7.8 Hz, 2xCH₂), 1.53 – 1.45 (m, 8H, *J* = 7.8 Hz 4xCH₂), 1.36 – 1.25 (m, 8H, *J* = 8.0 Hz 4xCH₂), 0.86 – 0.81 (m, 6H, 2xCH₃). For C₂₈H₃₆Br₂N₂S₄ (688.67 gmol⁻¹) m/z: calc. 688.01, found 688.00.

2,5-bis(2-bromothiophen-3-yl)thiazolo[5,4-d]thiazole (**3d** in Scheme 1). *N*-Bromosuccinimide (0.788 g 4.3mmol, 2.4 equiv.) was slowly added into a stirred solution of 2,5-bis(thiophen-3-yl)thiazolo[5,4-d]thiazole (**2d**, 0.566 g, 1.8 mmol, 1 equiv.) in DMF (15 mL). The mixture was heated at 80°C for 1 hour and then cooled down to room temperature. The precipitate was collected by filtration and washed with water. After drying yellow powder was isolated in 97 % yield (0.817 g). ¹H NMR (400 MHz, CDCl₃) δppm 7.62 (d, 2H, *J* = 5.8 Hz), 7.29 (d, 2H, *J* = 5.8 Hz). FTIR (ATR-Ge crystal) v: 3109, 3090, 1537, 1451, 1351, 1235, 1039, 840, 721 cm⁻¹. For C₁₂H₄Br₂N₂S₄ (464.24 gmol⁻¹) m/z: calc. 461.70, found 463.70 (2H⁺).

2-(5-(9,9'-Spirobi[fluoren]-2-yl)thiophen-2-yl)-5-(5-(9,9'-spirobi[fluoren]-3-yl)thiophen-2-yl)thiazolo[5,4-d]thiazole (**4a** in Scheme 1). 2,5-Bis(5-bromothiophen-2-yl)thiazolo[5,4-d]thiazole (**3a**, 0.075 g, 0.161 mmol, 1 equiv.), Pd(PPh₃)₄ (0.011 g, 9.5×10⁻³ mmol, 0.06 equiv) and 2-(9,9'-spirobi[fluoren]-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.150 g, 0.339 mmol, 2.1 equiv.) were dissolved in THF (20 mL). To the reaction mixture, three drops of Aliquat 336 and a water solution of K₂CO₃ (2M, 0.24 mL) were added, then the solution was stirred at 66 °C for 24 hours. Subsequently, the reaction mixture passed through a short neutral aluminum oxide column and the solvent was removed under reduced pressure. Then the solid residue (0.247 g) was dissolved in a small amount of THF and precipitated from methanol. The red precipitate was collected by filtration. Product was isolated as the red powder in 32 % yield (50 mg). ¹H NMR (400 MHz, CDCl₃) δppm 8.13 (s, 2H), 7.94-7.89 (m, 4H), 7.74 (dd, 2H, *J* = 6.4 Hz), 7.46 – 7.42 (m, 8H), 7.36 (d, 4H, *J* = 6.4 Hz), 7.33 (d, 2H, *J* = 6.4 Hz), 7.19-7.15 (m, 4H), 7.14-7.10 (m, 4H), 7.02 (s, 2H), 6.80 (t, 2H, *J* = 6.4 Hz). FTIR (ATR-Ge crystal) v: 3610, 2955 – 2926 (d), 1726, 1447, 1261, 1096 – 1019 (d), 803, 750, 729, 635 cm⁻¹. For C₆₂H₃₄N₂S₄ (935.21 gmol⁻¹) m/z: calc. 934.10, found 935.10 (H⁺).

2-(5-(9,9'-Spirobi[fluoren]-2-yl)-3-hexylthiophen-2-yl)-5-(5-(9,9'-spirobi[fluoren]-3-yl)-3-hexylthiophen-2-yl)thiazolo[5,4-d]thiazole (**4b** in Scheme 1). 2,5-Bis(5'-bromo-3'-hexylthiophen-2'-yl)thiazolo[5,4-d]thiazole (**3b**, 0.1028 g, 0.162 mmol, 1 equiv.), Pd(PPh₃)₄ (0.0248 g, 0.021 mmol, 0.06 equiv.) and 2-(9,9'-spirobi[fluoren]-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.157 g, 0.354 mmol, 2.19 equiv) were dissolved in THF (15 mL). To the reaction mixture, three drops of Aliquat 336 and the aqueous solution of K₂CO₃ (2M, 0.50 mL) were added. Subsequently, the solution was heated at 66 °C for 36 hours. The reaction mixture was passed through a short neutral aluminum oxide column and the solvent was removed under reduced pressure. Then the solid residue (0.340 g) was dissolved in a small amount of THF and precipitated from methanol. The precipitate was collected by filtration to give the product as a yellow powder in 86 % yield (154 mg). ¹H NMR (400 MHz, CDCl₃): δppm 7.80 - 7.70 (m, 8H), 7.40 (d, 2H, *J* = 6.2 Hz), 7.30 - 7.20 (m, 8H), 7.74 - 7.70 (m, 2H), 7.46 – 7.42 (m, 8H), 7.36 – 7.32 (m, 6H), 7.19 – 7.10 (m, 8H), 7.02 (s, 2H), 6.83 – 6.78 (m, 2H), 2.7 (t, 4H, *J* = 3.8 Hz), 2.3 (m, 4H), 1.2-1.0 (m, 12H), 0.8 (t, 6H, *J* = 1.2 Hz). ¹³C NMR (75 MHz, CDCl₃): δ_c 161.8, 159.7, 150.2, 149.7, 149.1, 148.3, 148.1, 145.6, 144.2, 142.1, 141.7, 140.9, 140.6, 139.2, 132.8, 130.8, 130.6, 128.7, 128.5, 127.9, 126.7, 125.6, 124.1, 124.0, 123.9, 121.2, 120.5, 120.2, 120.1, 120.0, 31.5, 31.4, 29.8, 29.3, 29.0, 22.5 ppm. FTIR (ATR-Ge crystal)v: 3610, 2955 – 2926 (d), 1726, 1447, 1261, 1096 – 1019 (d), 803, 750, 729, 635 cm⁻¹. For C₇₄H₅₈N₂S₄ (1103.53 gmol⁻¹) m/z: calc. 1103.53, found 1103.35.

2-(5-(9,9'-Spirobi[fluoren]-2-yl)-3,4-dibutylthiophen-2-yl)-5-(5-(9,9'-spirobi[fluoren]-3-yl)-3-hexylthiophen-2-yl)thiazolo[5,4-d]thiazole (**4c** Scheme 1). 2,5-Bis(5'-bromo-3',4'-dibutylthiophen-2'-yl)thiazolo[5,4-d]thiazole (**3c**, 0.1116 g, 0.162 mmol, 1 equiv.), Pd(PPh₃)₄ (0.0248 g, 0.021 mmol, 0.06 equiv) and 2-(9,9'-spirobi[fluoren]-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.157 g, 0.354 mmol, 2.19 equiv.) were dissolved in THF (15 mL). To the reaction mixture, three drops of Aliquat 336 and the aqueous solution of K₂CO₃ (2M, 0.50 mL) were added. Subsequently, the solution heated at 66 °C for 24 hours. The reaction mixture was passed through a short neutral aluminum oxide column and the solvent was removed under reduced pressure. Then the solid residue (0.340 g) was dissolved in a small amount of THF and precipitated from methanol. The precipitate was collected by filtration to give the product as a yellow powder in 72 % yield (135 mg). ¹H NMR (400 MHz, CDCl₃) δppm 7.90-7.82 (m, 8H), 7.49 (d, 2H, *J* = 10.4 Hz), 7.41 - 7.34 (m, 6H), 7.16 - 7.09 (m, 7H), 6.82 – 6.76 (m, 7H), 2.91 – 2.80 (m, 4H), 2.59 – 2.56 (m, 2H, *J* = 1.2 Hz), 2.38 – 2.33 (m, 2H, *J* = 1.2 Hz), 1.52-1.48 (m, 16H), 0.99 – 0.94 (m, 12H). ¹³C NMR (75 MHz, CDCl₃) δ_c 164.2, 158.8, 152.2, 150, 149.4, 148.1, 146.6, 144.8, 142.6, 141.3, 140.7, 140.1, 139.6, 135.2, 132.4, 131, 129.9, 128.4, 128.0, 127.4, 126.1, 126, 124.3, 124.0, 122.1, 120.8, 120.3, 120.1, 120.0, 31.2, 31, 29.7, 29.4, 29.1, 22.0 ppm. FTIR (ATR-Ge crystal) v: 3630, 2960, 1720, 1450, 1258, 1080 – 1041 (d), 810, 762, 733, 628 cm⁻¹. For C₇₈H₆₆N₂S₄ (1159.63 gmol⁻¹) calc. m/z 1158.41, found 1158.35.

2-(5-(9,9'-Spirobi[fluoren]-2-yl)thiophen-2-yl)-5-(5-(9,9'-spirobi[fluoren]-3-yl)thiophen-3-yl)thiazolo[5,4-d]thiazole (**4d** in Scheme 1). 2,5-Bis(5-bromothiophen-3-yl)thiazolo[5,4-d]thiazole (**3d**, 0.071 g, 0.155 mmol, 1 equiv.), Pd(PPh₃)₄ (0.010 g,

0.0093 mmol, 0.06 equiv) and 2-(9,9'-spirobi[fluoren]-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.133 g, 0.31 mmol, 2.1 equiv.) were dissolved in THF (10 mL). To the reaction mixture, one drops of Aliquat 336 and the aqueous solution of K_2CO_3 (2M, 2 mL) were added. Subsequently, the solution was heated at 66 °C for 36 hours. The reaction mixture was passed through a short neutral aluminum oxide column and the solvent was removed under reduced pressure. Then the solid residue was dissolved in a small amount of THF and precipitated from methanol. The precipitate was collected by filtration to give the product as a yellow powder in 86 % yield (90 mg). 1H -NMR (400 MHz, $CDCl_3$) δ ppm 7.90 (t, 4H, J = 12.0 Hz), 7.71 (d, 4H, J = 10.4 Hz), 7.53 (d, 2H, J = 7.2 Hz), 7.48 (dd, 2H, J = 10.4 Hz, 7.2 Hz), 7.43 - 7.37 (m, 2H), 6.9 (s, 2H), 7.25 - 7.20 (m, 6H), 7.15 (t, 2H, J = 12.0 Hz, 8.0 Hz), 7.03 (t, 4H, J = 8.0 Hz), 6.83 (s, 2H), 6.78 - 6.74 (m, 6H) ppm. FTIR (ATR-Ge crystal) ν : 361, 2955 - 2926 (d), 1726, 1447, 1261, 1096 - 1019 (d), 803, 750, 729, 635 cm^{-1} . For $C_{62}H_{34}N_2S_4$ (935.21 $gmol^{-1}$) m/z : calc. 934.16, found 935.10 (H^+).

2-(5-(9,9'-Spirobi[fluoren]-2-yl)thiophen-2-yl)-5-(phenylthiophen-2-yl)thiazolo[5,4-d]thiazole (**5a** in Scheme 2). 2,5-Bis(5-bromothiophen-2-yl)thiazolo[5,4-d]thiazole (**3a**, 0.050 g, 0.1 mmol, 1 equiv.), $Pd(PPh_3)_4$ (0.00056 g, 0.0048 mmol, 0.06 equiv.), 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-spirobis[9H-fluorene] (0.100 g, 0.21 mmol, 2.3 equiv.), 2M K_2CO_3 solution (4.0 mL), four drops of Aliquat 336 and 16 mL of toluene were loaded into a flame dried Schlenk tube under argon atmosphere. After that the reaction mixture was heated at 110 °C for 36 hours, then phenylboronic acid (0.038g, 0.21 mmol, 1 equiv.) was added and the solution was refluxed for 6 additional hours, after that bromobenzene (0.033 mL, 0.21 mmol) was added and refluxed for 6 hours. Then the reaction mixture passed through a short neutral aluminum oxide column and the solvent was removed under reduced pressure. Then the solid residue in small amount of tetrahydrofuran and precipitated to methanol. The red precipitate was collected by filtration to give the product as a red powder (0.205 g, 92%). 1H -NMR (400 MHz, $CDCl_3$) δ ppm 7.85-7.78 (m, J = 7.8, 8.0, 8.8 Hz, 4H), 7.60 - 7.58 (m, J = 4.4, 3.4 Hz, 2H), 7.37 - 7.30 (m, J = 7.8, 8.9 Hz, 2H), 7.20 (d, J = 6.0 Hz, 1H), 7.11 - 7.03 (m, J = 7.7, 4H), 6.98 (d, J = 4.0 Hz, 1H), 6.91 (d, J = 7.6 Hz, 2H), 6.74 (d, J = 7.6 Hz, 2H), 6.71 - 6.67 (m, J = 6.4, 7.3 Hz, 6H) ppm. FTIR (ATR-Ge crystal) ν : 3627, 3567, 3063, 2888, 1605, 1541, 1450, 1337, 1317, 1255, 1050, 869, 797, 731 cm^{-1} . For $C_{43}H_{24}N_2S_4$ (696.92 $gmol^{-1}$) m/z : calc. 696, found: 693.

2-(5-(9,9'-Spirobi[fluoren]-2-yl)-3-hexylthiophen-2-yl)-5-(phenyl)-3-hexylthiophen-2-yl)thiazolo[5,4-d]thiazole (**5b** in Scheme 1). 2,5-Bis(5'-bromo-3'-hexylthiophen-2'-yl)thiazolo[5,4-d]thiazole (**3b**, 0.1028 g, 0.162 mmol, 1 equiv.) $Pd(PPh_3)_4$ (0.0248 g, 0.021 mmol, 0.06 equiv.) and 2-(9,9'-spirobi[fluoren]-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.157 g, 0.354 mmol, 2.19 equiv.) were loaded into a flame dried one-neck Schlenk tube. Toluene (15 mL), three drops of Aliquat 336 and 2M K_2CO_3 solution (0.50 mL) were added, and the solution was heated at reflux for 36 hours. After that the reaction mixture was heated at 110 °C for 36 hours, then phenylboronic acid (0.038g, 0.21 mmol, 1 equiv.) was added and the solution was refluxed for 6 additional hours, after that bromobenzene (0.033 mL, 0.21 mmol) was added and refluxed for 6 hours. The reaction mixture was passed through a short neutral aluminum oxide column before removing the solvent under reduced pressure. Then the solid residue (0.340 g) was dissolved in small amount of tetrahydrofuran and precipitated from methanol. The red precipitate was collected by filtration to give the product as a yellow powder (0.154 g, 0.139 mmol, 86 %). 1H -NMR (400 MHz, $CDCl_3$) δ ppm 7.86-7.77 (m, 8H, J = 7.8, 7.8 Hz), 7.41 (m, 2H, J = 7.5 Hz), 7.36-7.29 (m, 4H, J = 7.1, 7.5 Hz), 7.08 (t, 2H, J = 8 Hz), 6.95 (s, 2H), 6.91 (d, 2H, J = 1.47 Hz), 6.74-6.68 (m, 4H, J = 7.7, 4.2 Hz), 2.78 (t, 2H, J = 8 Hz), 2.24 - 2.3 (m, 4H), 1.23 (m, 12 H), 0.81 (t, 6H) ppm. ^{13}C -NMR ($CDCl_3$) δ ppm 161.8, 159.7, 150.2, 149.7, 149.1, 148.3, 148.1, 145.6, 144.2, 142.1, 141.7, 140.9, 140.6, 139.2, 132.8, 130.8, 130.6, 128.7, 128.5, 127.9, 126.7, 125.6, 124.1, 124.0, 123.9, 121.2, 120.5, 120.2, 120.1, 120.0, 31.5, 31.4, 29.8, 29.3, 29.0, 22.5. FTIR (ATR-Ge crystal) ν : 3610, 2955, 2926, 1726, 1447, 1261, 1096, 1019, 803, 750, 729, 635 cm^{-1} . For $C_{55}H_{48}N_2S_4$ (865.24 $gmol^{-1}$) m/z : calc.: 864, found: 865 (H^+) (Figure 1).

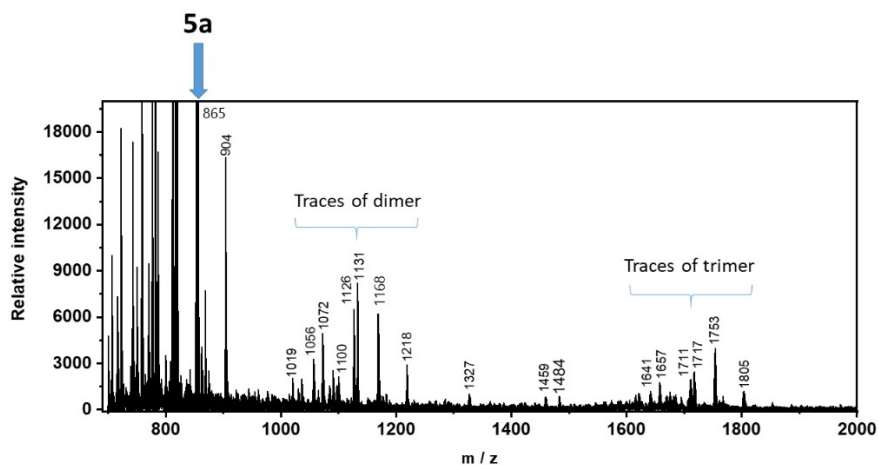


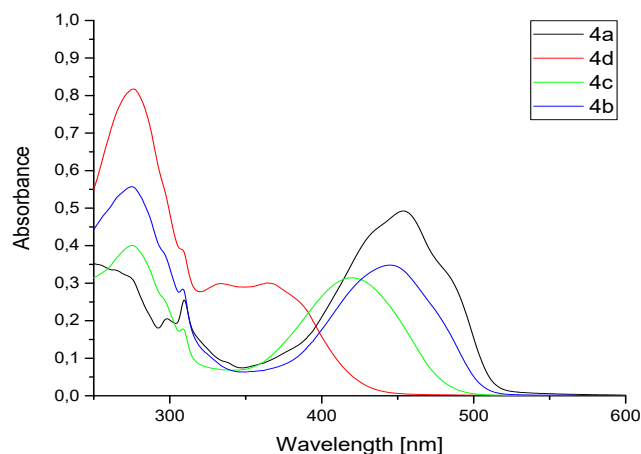
Figure 1. MALDI-TOF of **5b** accompanied by the traces of oligomeric forms

Lit.

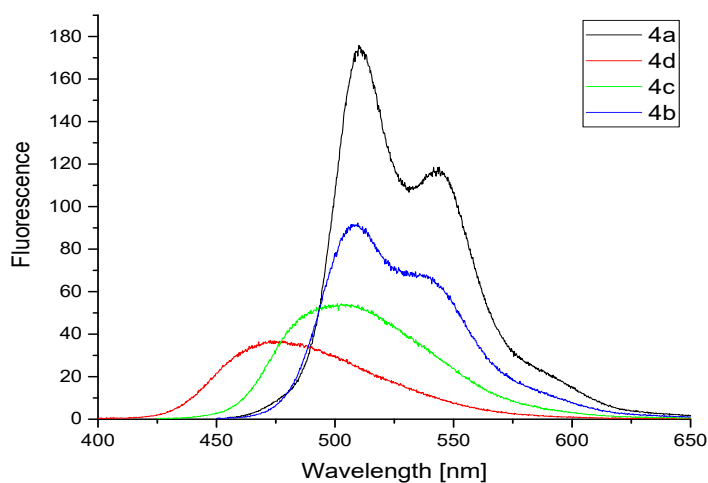
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3. Optical properties – UV-Vis and fluorescence

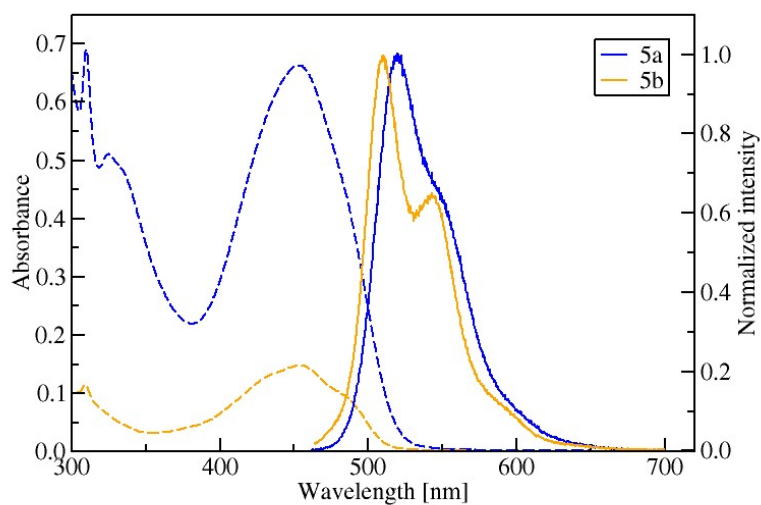
UV-visible (absorption) spectra were measured for solutions of appropriate compounds in chloroform ($c = 1 \times 10^{-5} \text{ molL}^{-1}$) revealing results presented at Graph 1 for **4a-d**. Fluorescence measurements were performed for the same dilute solutions in chloroform after illumination at the maximum absorbance revealing the behaviour represented by Graph 2. The UV-Vis and PL of unsymmetric compounds **5a,b** corresponds to Graph 3.



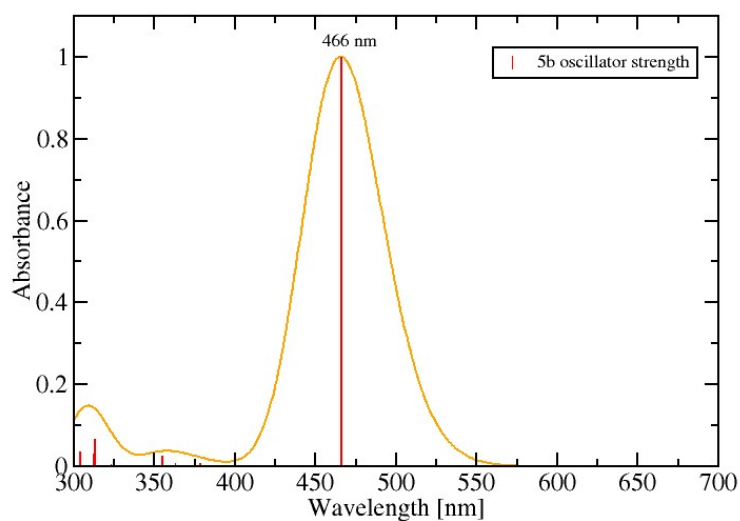
Graph 1 Ultraviolet-visible spectra of spirobifluorene-edged thiazolo[5,4-d]thiazoles measured in chloroform solutions with concentration $c = 1 \times 10^{-5} \text{ molL}^{-1}$.



Graph 2 Fluorescence spectra of compounds **4a-d** revealed for the chloroform solutions with concentrations $c = c = 1 \times 10^{-5} \text{ molL}^{-1}$.



Graph 3. Absorbance (dashed line) and photoluminescence of **5a,b** measured under the same environment as **4a-d**



Graph 4. Calculated normalized UV-vis absorbance and oscillator strengths of **5b** in acetonitrile from TD-DFT/B3LYP/TZV approximation.

4. Electrochemistry – cyclic voltametry (CV) and energy-resolved impedance spectroscopy (ER-EIS)

Cyclic voltammetry measurements were achieved from acetonitrile solutions with concentrations $1 \times 10^{-3} \text{ molL}^{-1}$ of target compounds with a content of tetrabutylammonium perchlorate (0.1 M) revealing the results according to **Figure 2**. Measurements were evaluated to all of novel compounds **4a-d** for the purposes of achievement of frontier molecular orbital energies (FMO).

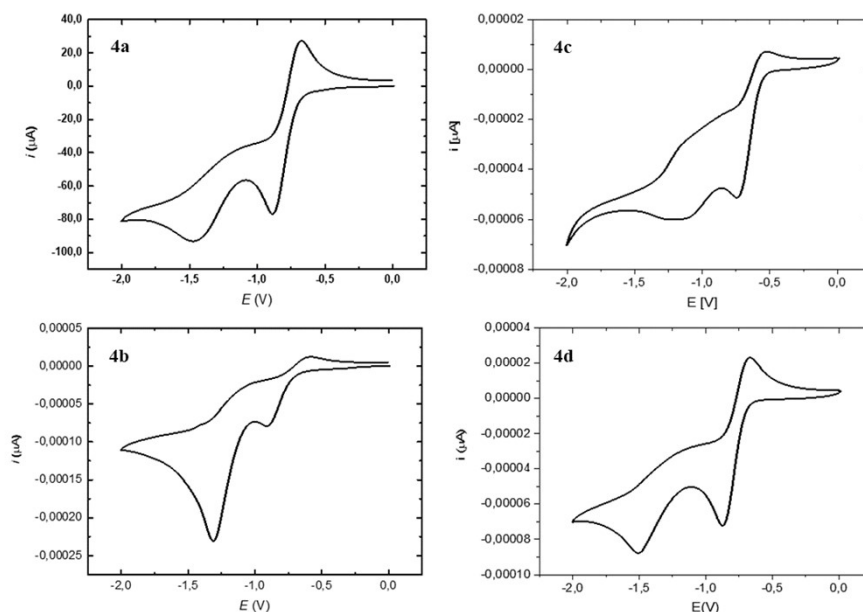


Figure 2. Cyclic voltammetry of bis-spirobifluorene-substituted thiazolo[5,4-d]thiazoles **4a-d** revealed for the acetonitrile solutions with concentrations $c = 1 \times 10^{-3} \text{ molL}^{-1}$.

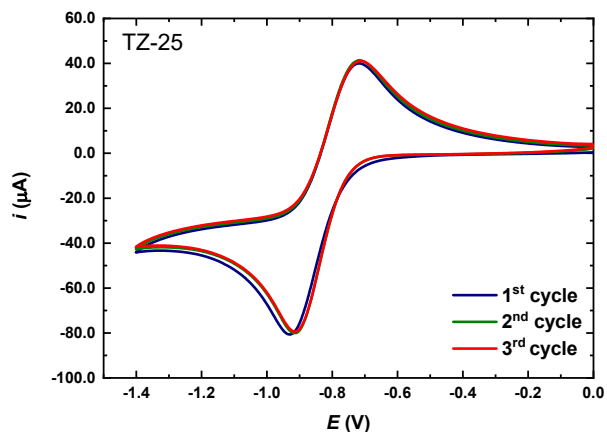


Figure 3. Cyclic voltammetry of mono spirobifluorene-substituted thiazolo[5,4-d]thiazole **5b** revealed for the acetonitrile solutions with concentrations $c = 1 \times 10^{-3} \text{ molL}^{-1}$

5. Density functional theory (DFT) computational details

First-principles calculations of electronic and vibrational properties of the molecules were performed in a frame of standard density functional theory (DFT). Molecules were considered in the gas phase approximation and electronic properties evaluated using the **GAMMESS (US)** package [4,5]. Molecular geometries were optimized in RHF pre-converged DFT procedures with B3LYP functional and 6-31g(d,p) localized basis set. The wavefunctions of molecules were investigated on optimized geometries at their B3LYP ground states treating various types of exchange-correlation functionals B3LYP, Coulomb-attenuating CAMB3LYP, meta-hybrid TPSSH and GGA parametrized M06-2X (the best fit achieved by TPSSH as listed in Table 1 for **5b**). The frontier Molecular Orbitals (FMO) and HOMO-LUMO energy gaps were projected out from the energy spectra of self-consistently converged wavefunction expanded in 6-31g(d,p) basis set. The plots of FMO distributions were adjusted in the **Avogadro 1.2.0** editing program [6] at 0.02 \AA^{-3} isosurface value.

Molecule **5b** (C₅₅H₄₈N₂S₄ 865.243 g/mol) electronic characteristics from simulations

Energy levels corresponding to FMO orbitals plots as calculated in Acetonitrile solvent (ACN), ionization potential (IP) and electron affinity (EA), fundamental/transport gap (E_t) in molecule from DFT, estimation of upper bound of exciton binding

energy as important characteristics for components design of OLED structures and their charge-transfer-functionality.

Table1 HOMO-LUMO Kohn-Sham levels of **5b** molecule calculated by DFT method in different localised bases of wave-function. The contribution of PCM model of the **Acetonitrile solvent (ACN)** is compared with gas phase setup.

DFT/basis	HOMO/eV	LUMO/eV	Eg /eV
TPSSH/6-311g(d,p)	-5.029	-2.498	2.531
B3LYP/6-311g(d,p)	-5.227	-2.218	3.010
B3LYP/cc-pVTZ *)	-5.230	-2.226	3.004
B3LYP/6-311g(d,p)/ACN**)	-5.322	-2.324	2.998
B3LYP/TZV ***)	-5.377	-2.294	3.083
B3LYP/TZV/ACN	-5.505	-2.438	3.067
CV (experiment)	-5.48	-3.36^{#)}	-

IP – ionization potential (vertical); EA – affinity energy (vertical); Et fundamental (transport) gap

*) Dunning-type Correlation Consistent basis;**) AN in CH₃CN acetonitrile;***) TZV triple-zeta valence basis; #) optical LUMO experimental.

Table2 Vertical ionization potential and electron affinity determined at B3LYP level with TZV basis set and PCM solvent model for ACN solvent. The difference between calculated potentials determines transport gap.

DFT/basis	IP/eV	EA/eV	Fundamental/transport gap Et/eV
B3LYP/TZV/ACN	5.407	2.562	2.845

Excitons binding energy estimation

Estimation (a rough) of localized **Frenkel exciton (electron-hole)** binding energy **E_b** on the molecule **C₅₅H₄₈N₂S₄** from theory and experimentally measured optical gap (CV/PL/UV-vis). Following works [1,2] in case of small conjugated molecules and using the CV/PL experimentally determined optical gap **E_{opt}=2.12 eV** along with ours best matched **DFT/B3LYP/TZV/AN** fundamental/transport gap **Et(DFT)=IP-EA** (as transport gap estimation **Table2**) [2,3]; the upper bound of exciton binding energy **E_b** in the studied molecule should be after formula:

$$E_b = Et(DFT) - E_{opt}(exp) = 2.845 - 2.120 = 0.725 \text{ eV} \sim 0.73 \text{ eV};$$

This binding energy value falls within interval determined for series of small organic molecules (0.4–1.4 eV) [2,3,4,5] and is approximately two time larger than in case of copolymers (0.09-0.44 eV) [6]. On the other hand, the TD-DFT/B3LYP/TZV/ACN calculated optical gap represented by first excited state **S₀ → S₁** is 2.664 eV (466 nm, see in **Graph 4**). Therefore pure DFT theoretically estimated excitonic energy yields **E_b(TD-DFT)=2.845 – 2.664= 0.181 eV**, what represents a lower bound of binding energy for exciton (**E_b=(0.18-0.73) eV**) in **5b** compound ACN solvated.

Refs to this part.

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6. Devices fabrication and characterization

Glass substrates patterned with indium tin oxide (ITO) stripe were cleaned ultrasonically in deionized water, acetone and twice in isopropyl alcohol. After 10 min of oxygen plasma treatment, poly(3,4-ethylene-dioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS, Heraeus Clevis AI 4083) was spincoated on the substrates through nylon filter (0.45 μm) creating a hole injecting layer with a thickness of 45 nm. Subsequently, the substrates were annealed at 100° C for 10 min inside nitrogen filled glovebox with 1 ppm of O₂ and H₂O. Afterwards, poly(9-vinylcarbazole) (PVK, 10⁶ g/mol, Sigma-Aldrich) was spincoated from chlorobenzene (10 mg/ml) and the substrates were annealed at 100° C for 30

minutes. The emitting layer had a composition 65% PVK : 30% PBD : 5% **4b** or **5b** (weight ratio) and was prepared from chloroform with concentration 16 mg/ml and rotation 2000 rpm. PVK denotes here poly(9-vinylcarbazole) with molecular mass 25.000-50.000 g/mol (Sigma-Aldrich) and PBD is 2-(4-Biphenyl)-5-(4-ter-butylphenyl)-1,3,4-oxadiazole (Aldrich). Subsequently, the devices were transferred to an organic molecular beam deposition (OMBD) system, where 30 nm of 1,3,5-tris(1-phenyl-1Hbenzimidazol-2-yl)benzene (TPBi, Ontario Chemicals, Inc.) electron transporting layer was evaporated with 0.2 Å/s rate at $2 \cdot 10^{-7}$ mbar pressure. Finally, a cathode consisting of 7 nm of barium and 100 nm of aluminum was deposited in metal evaporator at $1 \cdot 10^{-6}$ mbar pressure. An active area of the diodes was 6,1 mm².

Electroluminescence of the devices was registered with Spex 270M monochromator combined with liquid nitrogen cooled CCD by applying a constant bias. Electrical characterization was done by placing the OLED directly on a photodiode with known responsivity. External quantum efficiency (EQE) was calculated from the light emitted in the forward direction with Lambertian source assumption. Keithley 2602 served as a two channel sourcemeater. All measurements were done in nitrogen at room temperature.

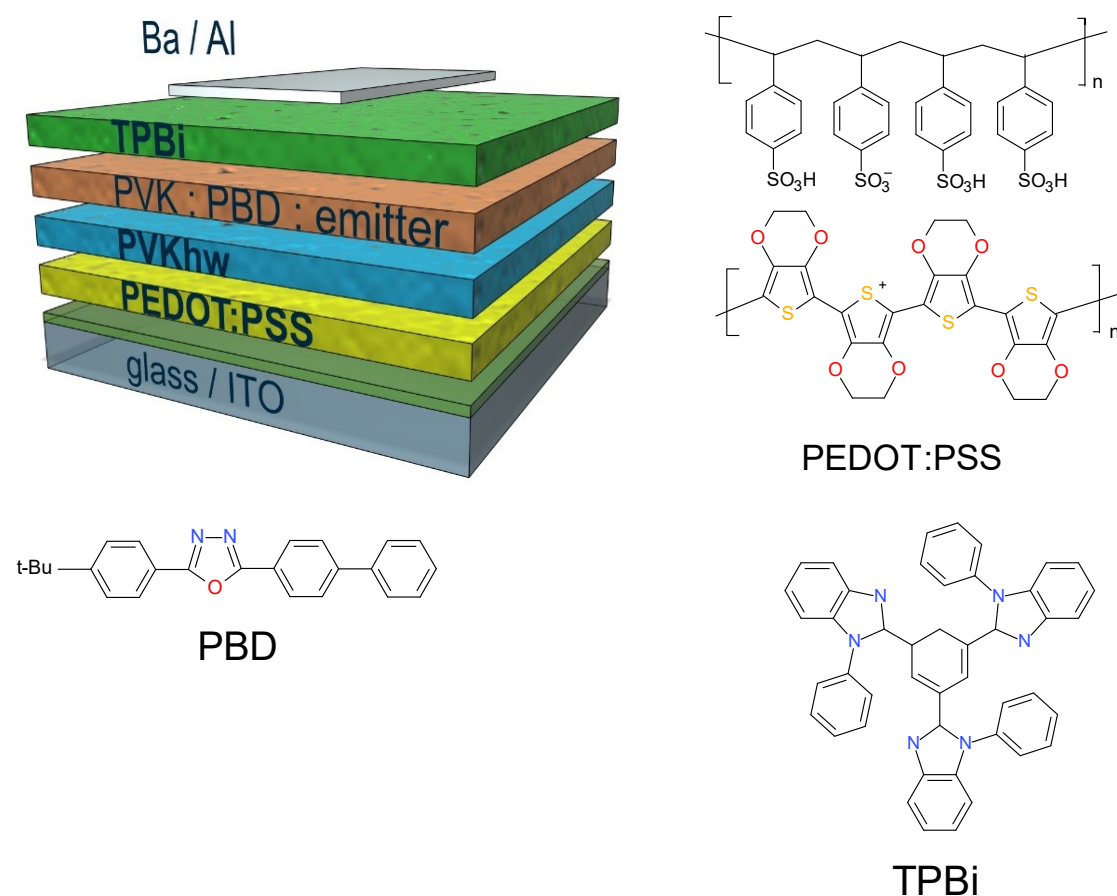


Figure 4. A structure of the device under discussion. The PEDOT:PSS, PVKhw and PVK:PBD: emitter **4b** or **5b** layers were prepared with spincoating, while TPBi organic layer and Ba/Al cathode were deposited with thermal evaporation. The structures of the materials used in the devices are also presented.

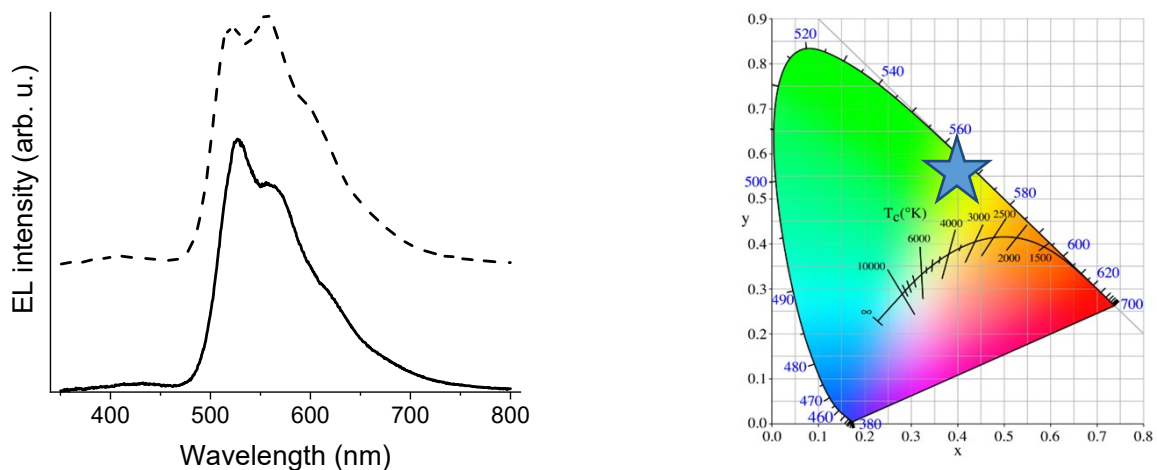


Figure 5. (left) A comparison of the EL at 16 V of the devices with unsymetric compound **5b** (solid line) and molecule **4b** (dashed line). (right) CIE 1931 chromaticity diagram with coordinates corresponding to the EL spectra.

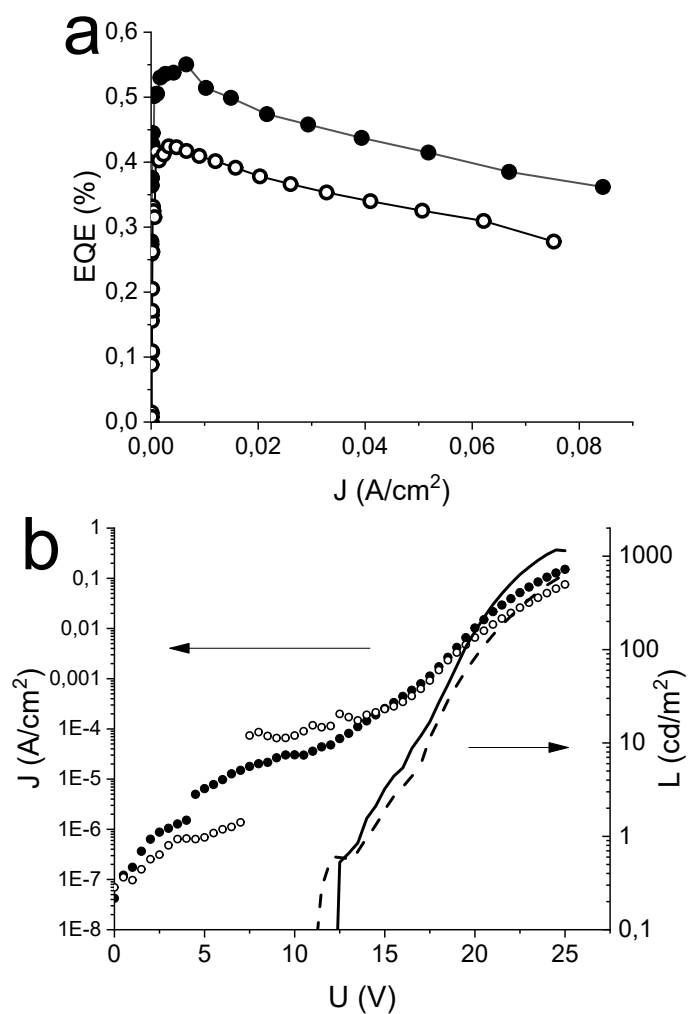


Figure 6. Performance of the devices with the molecules **4b** and **5b**. (a) External quantum efficiency; D/A type unsymmetrical monomer **5b** - full circles, D/AD-type symmetrical compound **4b** - empty circles. (b) Current density (J) - voltage (U) - luminance (L) curves; full circles and solid line - **5b**, empty circles and dashed line - **4b**.