Effect of substituents on redox, spectroscopic and structural properties of conjugated diaryltetrazines – a combined experimental and theoretical study†

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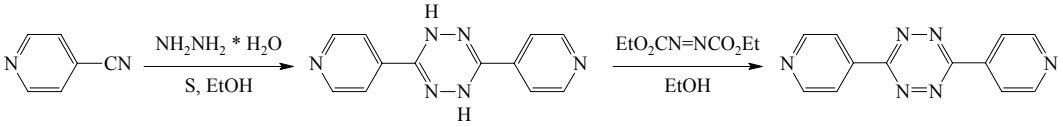
Chemicals and reagents

Most of chemicals and reagents were purchased from Aldrich and used as received. Diethyl azodicarboxylate was purchased from Alfa Aesar. Dry DMF, and potassium phosphate were purchased from Fluka and used as received. Diethyl ether was dried and stored over sodium. N-bromosuccinimide (Fluka) was crystallized from water before use.
2-bromo-3-octylthiophene, 2-bromo-5-hexylthiophene, 5-bromo-2,2'-bithiophene, 5-bromo-5'-hexyl-2,2'-bithiophene, 5-hexyl-2-thienylboronic acid neopentyl glycol ester and 5-octyl-2-thienylboronic acid neopentyl glycol ester were prepared according to the methods already published[1,2,3]. Synthesis of 2,3-dioctylthiophene and 2-bromo-4,5-dioctylthiophene was described recently in [4].

Synthesis of compounds

1. Synthesis of 3,6-di(4-pyridyl)-1,2,4,5-tetrazine (1)

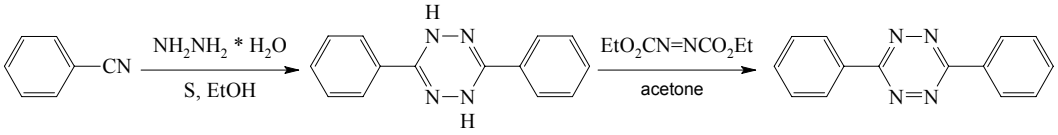


1.021 g (9.82 mmol) of 4-cyanopyridine, dissolved in 5 mL of 99.8% ethyl alcohol, was added to 0.198 g (6.17 mmol) of sulfur under constant argon flow. In the next step 1.0 mL (20.64 mmol) of hydrazine hydrate was added drop-wise to the stirred solution, previously heated to 80°C. A brown powder precipitated from the solution after 1 hour of heating. After 2 additional hours the evolution of H_2S stopped and the reaction mixture was cooled down. The precipitate was separated from the solution and dried.

The obtained crystals of 3,6-di(4-pyridyl)-1,4-dihydro-1,2,4,5-tetrazine (1.168 g, 4.91 mmol) were dissolved in 96% ethanol with gentle heating, then 1.039 g (5.97 mmol) of diethyl azodicarboxylate was carefully added drop-wise. In the next step the reaction mixture was heated for 3 hours and then concentrated to ½ of its initial volume and cooled. The crude product **(1)** was purified by column chromatography and repeated crystallization from $CHCl_3$.
^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.51 (dd, 4H, J_1=1.6 Hz, J_2=4.4 Hz), 8,96 (dd, 4H, J_1=1.6 Hz, J_2=4.4 Hz)
^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 121.39, 138.62, 151.31, 163.76.
IR (KBr, cm^{-1}): 560, 716, 831, 919, 992, 1055, 1065, 1111, 1190, 1203, 1218, 1263, 1389, 1412, 1495, 1558, 1589, 3033

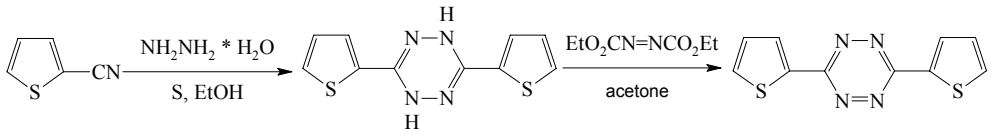
Elemental analysis: Calcd for $C_{12}H_8N_6$: C, 61.02; H, 3.39; N 35.59. Found: C, 60.44; H, 3.95; N, 35.44.
Melting point = 257°C

2. Synthesis of 3,6-diphenyl-1,2,4,5-tetrazine (2)



3,6-diphenyl-1,4-dihydro-1,2,4,5-tetrazine was synthesized according to[5] (88% yield), then oxidized with diethyl azodicarboxylate in the same way as described for compound **1** and purified by crystallization from acetone (yield 65%).
^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.61-7.64 (m, 6H), 8.64-8.67 (m, 4H)
^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 127.96, 129.30, 131.75, 132.69, 163.97
IR (KBr, cm^{-1}): 588, 688, 767, 773, 856, 919, 931, 1023, 1052, 1075, 1104, 1177, 1188, 1308, 1392, 1456, 1599, 3073
Elemental analysis: Calcd for $C_{14}H_{10}N_4$: C, 71.80; H, 4.27; N 23.93. Found: C, 71.71; H, 4.20; N, 23.72.
Melting point = 197°C

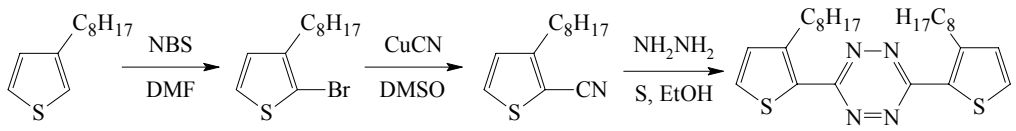
3. Synthesis of 3,6-di(2-thienyl)-1,2,4,5-tetrazine (3)



1.355 g (12.43 mmol) of 2-cyanothiophene, dissolved in 2.5 mL of 99.8% ethyl alcohol was added to 0.198 g (6.19 mmol) of sulfur under constant argon flow. In the next step 2.5 mL (51.6 mmol) of hydrazine hydrate was added drop-wise to the stirred solution, previously heated to 80°C. The reaction mixture turned from yellow to dark red and a brown powder precipitated from the solution after 1 hour of heating. After 3 additional hours the evolution of ammonia stopped and the reaction mixture was cooled down. The precipitate was separated from the solution and re-dissolved in 220 mL of 96% ethyl alcohol with gentle heating. The crude product was purified by crystallization yielding 1.378 g of pure 3,6-di(2-thienyl)-1,4-dihydro-1,2,4,5-tetrazine (89% reaction yield).
Crystals of 3,6-di(2-thienyl)-1,4-dihydro-1,2,4,5-tetrazine (0.609 g, 2.46 mmol) were dissolved in warm acetone. Then 0.428 g (2.46 mmol) of diethyl azodicarboxylate was carefully added. In the next step the reaction mixture was gently heated for 3 hours and then concentrated to ½ of its initial volume and cooled. The resulting precipitate was separated from the solution and then recrystallized from ethanol yielding 0.552 g of pure 3,6-di(2-thienyl)-1,2,4,5-tetrazine (91% reaction yield).
^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.27 (dd, 2H, J_1=5.1Hz, J_2=3.8Hz), 7.69 (dd, 2H, J_1=5.1Hz, J_2=1.1Hz), 8.28 (dd, 2H, J_1=3.8 Hz, J_2=1.1Hz)
^{13}C NMR ($CDCl_3$, 100MHz) δ: 129.00, 130.94, 132.48, 135.92, 161.49
IR (KBr, cm^{-1}): 607, 716, 729, 850, 913, 1003, 1052, 1073, 1083, 1384, 1443, 1534, 3079, 3102

Elemental analysis: Calcd for $C_{10}H_6N_4S_2$: C, 48.78; H, 2.44; N, 22.76, S, 26.02. Found: C, 48.60; H, 2.21; N, 22.35; S, 26.33.
Melting point: 205°C.

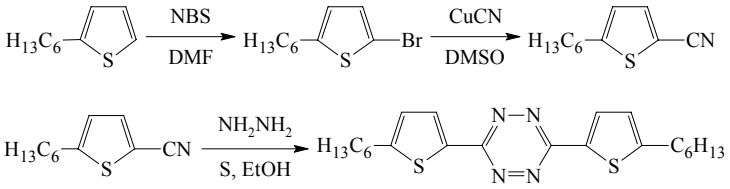
4. Synthesis 3,6-bis(3-octyl-2-thienyl)-1,2,4,5-tetrazine (4)



2-cyano-3-octylthiophene: 1.002 g (3.64 mmol) of 2-bromo-3-octylthiophene dissolved in 15 mL of DMSO was added to 0.516 g (5.77 mmol) of CuCN under constant argon flow. The reaction mixture was then heated to 185 °C, kept at this temperature for 8 hours with constant stirring. Then the reaction mixture was cooled down to room temperature and 20 mL of 25% aqueous solution of NH_3 was added. In the next step the product was extracted with ethyl acetate, then washed with brine and water and finally dried over anhydrous $MgSO_4$. The solvent was removed using a rotary evaporator and the crude product was purified using a chromatographic column (silica gel, n-hexane/ethyl acetate 2:1) yielding 0.755g of pure 2-cyano-3-octylthiophene (94% reaction yield).
^{1}H NMR ($CDCl_3$, 400MHz) δ: 0.88 (t, 3H, J=6.8 Hz), 1.27-1.32 (m, 10H), 1.61-1.68 (p, 2H), 2.78 (t, 2H, J=7.8 Hz), 6.96 (d, 1H, J=4.8 Hz), 7.47 (d, 1H, J=5.2 Hz)

3,6-bis(3-octyl-2-thienyl)-1,2,4,5-tetrazine: The synthetic procedure was essentially the same as in the case of **3**, using 0.053 g (1.66 mmol) of sulfur, 0.743 g (3.36 mmol) of 2-cyano-3-octylthiophene and 0.7mL (14.44 mmol) of hydrazine hydrate. The reaction was carried out at 80^{o}C for 6 hours. The crude product was purified using a chromatographic column (silica gel, n-hexane/methylene chloride 4:1) yielding 0.072 g of pure 3,6-bis(3-octyl-2-thienyl)-1,2,4,5-tetrazine **(4)** (9% reaction yield). In the synthesis of **4,** the step involving the of oxidation of 3,6-bis(3-octyl-2-thienyl)-1,4-dihydro-1,2,4,5-tetrazine) to 3,6-bis(3-octyl-2-thienyl)-1,2,4,5-tetrazine using diethyl azodicarboxylate was omitted. The intermediate product spontaneously oxidized to **4** in air during the preparation and purification steps as confirmed by NMR data.
^{1}H NMR ($CDCl_3$, 400MHz) δ: 0.87 (t, 6H, J=6.8 Hz), 1.26-1.43 (m, 20H), 1.66-1.74 (m, 4H), 3.24 (t, 4H, J=7.6 Hz), 7.10 (d, 2H, J=5.2 Hz), 7.55 (d, 2H, J=4.8 Hz)
^{13}C NMR ($CDCl_3$, 100MHz) δ: 14.11, 22.67, 29.26, 29.46, 29.48, 30.38, 30.43, 31.89, 129.26, 130.71, 132.00, 149.26, 161.76
IR (KBr, cm^{-1}): 575, 614, 670, 705, 720, 745, 843, 921, 932, 1069, 1365, 1449, 1467, 1536, 2852, 2923, 2955, 3069, 3071, 3114
Elemental analysis: Calcd for C_{26} H_{38} N_4S_2: C, 66.38; H, 8.09; N, 11.91; S, 13.62. Found: C, 65.21; H, 8.40; N, 11.55; S, 12.90.
Melting point: 135°C.

5. Synthesis of 3,6-bis(5-hexyl-2-thienyl)-1,2,4,5-tetrazine (5)

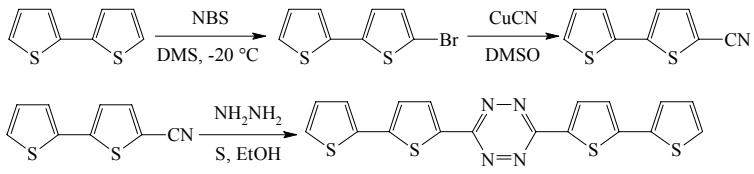


2-cyano-5-hexylthiophene: The synthetic procedure and purification of the product was the same as in the case of 2-cyano-3-octylthiophene**,** using 0.574 g (6.41 mmol) of CuCN and 0.999 g (4.04 mmol) of 2-bromo-5-hexylthiophene dissolved in 20 mL of DMSO. 0.706g (91% reaction yield) of pure 2-cyano-5-hexylthiophene was obtained.
^{1}H NMR ($CDCl_3$, 400MHz) δ: 0.89 (t, 3H, J=7.0 Hz), 1.28-1.38 (m, 6H), 1.66-1.72 (p, 2H), 2.84 (t, 2H, J=7.6 Hz), 6.79 (d, 1H, J=3.6 Hz), 7.45 (d, 1H, J=3.6 Hz)

3,6-bis(5-hexyl-2-thienyl)-1,2,4,5-tetrazine: The synthesis was carried out in a similar manner to that of **3** and **4,** using 0.042g (1.31 mmol) of sulfur, 0.700 g (3.63 mmol) of 2-cyano-5-hexylthiophene dissolved in 6 mL of 99.8% ethyl alcohol and 0.74 mL (15.28 mmol) of hydrazine hydrate. The reaction was carried out at 80^{o}C for 4 hours. The crude product was purified by crystallization from ethyl alcohol yielding 0.310 g of pure 3,6-bis(5-hexyl-2-thienyl)-1,2,4,5-tetrazine (41% reaction yield). Similarly as in the case of **4** the intermediate product spontaneously oxidized in air during the preparation and purification steps.
^{1}H NMR ($CDCl_3$, 400MHz) δ: 0.90 (t, 6H, J=6.8 Hz), 1.30-1.43 (m, 12H), 1.71-1.77 (p, 4H), 2.91 (t, 4H, J=7.4 Hz), 6.93 (d, 2H, J=2.8 Hz), 8.06 (d, 2H, J=3.6 Hz)
^{13}C NMR ($CDCl_3$, 100MHz) δ: 14.06, 22.55, 28.73, 30.59, 31.40, 31.51, 126.37, 130.92, 133.14, 154.24, 161.09
IR (KBr, cm^{-1}): 608, 666, 725, 818, 920, 926, 989, 1080, 1389, 1443, 1466, 1485, 1545, 2848, 2927, 2954, 3104, 3110
Elemental analysis: Calcd for $C_{22}H_{30}N_4S_2$: C, 63.77; H, 7.24; N, 13.53; S, 15.46. Found: C, 62.67; H, 7.16; N, 13.27, S, 14.61.
Melting point: 158°C.

6. Synthesis of 3,6-bis(2,2'-bithien-5-yl)-1,2,4,5-tetrazine (6)

Method 1

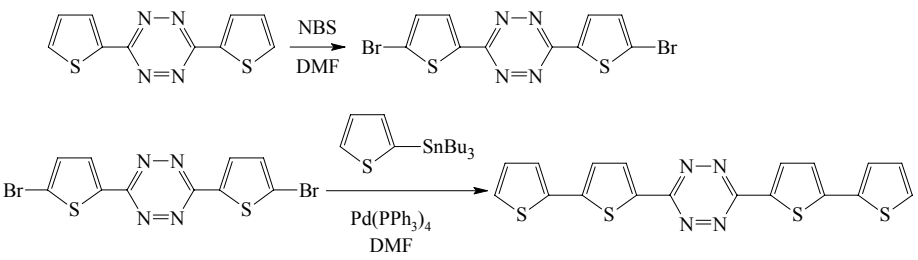


5-cyano-2,2'-bithiophene: The synthesis was carried out in a similar manner to that of 2-cyano-3-octylthiophene, using 0.295 g (3.30 mmol) of CuCN and 0.512 g (2.09 mmol) of 5-bromo-2,2'-bithiophene dissolved in 10 mL of DMSO. The reaction mixture was heated at 200 °C for 5 hours with constant stirring. The separation and purification of the reaction product gave 0.366 g of pure 5-cyano-2,2'-bithiophene (92% yield).
^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.07 (dd, 1H, J_1=4.0 Hz, J_2=5.0 Hz), 7.14 (d, 1H, J=4.0 Hz), 7.29 (dd, 1H, J_1=1.0 Hz, J_2=3.6 Hz), 7.35 (dd, 1H, J_1=1.2 Hz, J_2=4.8 Hz), 7.53 (d, 1H, J=4.0 Hz)

3,6-bis(2,2'-bithien-5-yl)-1,2,4,5-tetrazine: The synthesis of **6** was carried out in a similar manner to that of **1**, using 0.135 g (4.22 mmol) of sulfur, 1.248 g (6.53 mmol) of 5-cyano-2,2'-bithiophene dissolved in 6 mL of 99.8% ethyl alcohol, and 0.97 mL (20.02 mmol) of hydrazine hydrate.The reaction mixture was stirred at 80^{o}C for 1.5 hour.

The produced precipitate of 3,6-bis(2,2'-bithien-5-yl)-1,4-dihydro-1,2,4,5-tetrazine [0.635 g (1.55 mmol)] was dissolved in 100 mL of acetone with gentle heating and 0.27 g (1.55 mmol) of diethyl azodicarboxylate was added. Within 0.5 h a precipitate started to separate from the solution. The obtained suspension was cooled down to room temperature and then put in a refrigerator were the precipitation continued. The crude product was purified using a chromatographic column (silica gel, n-hexane/methylene chloride 1:1) yielding 0.300 g (22% reaction yield) of pure product (3,6-bis(2,2'-bithien-5-yl)-1,2,4,5-tetrazine) whose spectroscopic characteristics were in agreement with the literature [6].

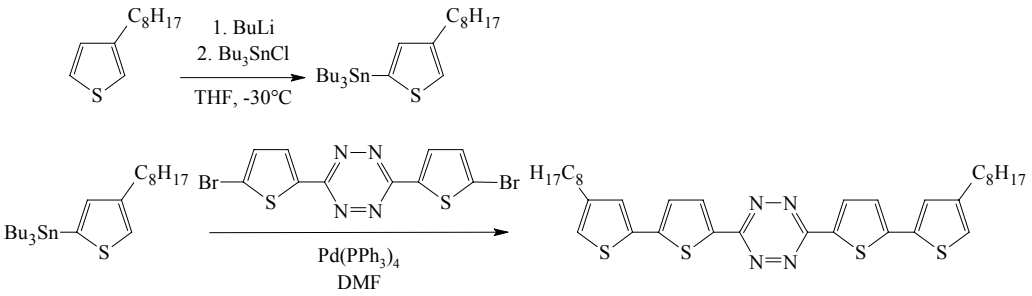
Method 2



Synthesis of 3,6-bis(5-bromo-2-thienyl)-1,2,4,5-tetrazine: To a stirred solution of 3,6-di(2-thienyl)-1,2,4,5-tetrazine (**3**) (0.820 g, 3.33 mmol) in 30 mL of DMF, a solution of NBS (1.874 g, 10.53 mmol) in 15 mL of DMF was slowly added drop-wise at 75°C under constant argon flow. The reaction was carried out for 2.5 hours in the darkness. The product was extracted with methylene chloride, then washed with water and finally dried over $MgSO_4$. The obtained powder was purified by crystallization from methylene chloride yielding 1.196 g of 3,6-bis(5-bromo-2-thienyl)-1,2,4,5-tetrazine (89% reaction yield).
^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.23 (d, 2H, J=4.0 Hz), 8.01 (d, 2H, J=4.0 Hz)
^{13}C NMR ($CDCl_3$, 100MHz) δ: 120.97, 131.29, 132.10, 137.01, 160.71.

3,6-bis(2,2'-bithien-5-yl)-1,2,4,5-tetrazine: A solution of 3,6-bis(5-bromo-2-thienyl)-1,2,4,5-tetrazine (1.18 g, 2.92 mmol) in 65 mL of DMF and 0.183 g (0.158 mmol) of $Pd(PPh_3)_4$ catalyst were placed in a reaction flask under constant argon flow. Next, a solution of 2-tributyltinthiophene (2.212 g, 5.93 mmol) in 25 mL of DMF was added drop-wise at 90°C. The reaction was carried out for 2.5 h, then the reaction mixture was allowed to cool down to room temperature. The precipitate was separated by filtration and the product was extracted from the filtrate with methylene chloride, then it was washed with brine and water and finally dried over $MgSO_4$. The crude product was purified using a chromatographic column (silica gel, methylene chloride/n-hexane/ 4:1) yielding 1.008 g of pure 3,6-bis(2,2'-bithien-5-yl)-1,2,4,5-tetrazine (84% reaction yield).
^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.09 (dd, 2H, J_1=3.6 Hz, J_2=5.2 Hz), 7.32 (d, 2H, J=4.0 Hz), 7.35 (dd, 2H, J_1=0.8 Hz, J_2=5.2 Hz), 7.38 (dd, 2H, J_1=1.2 Hz, J_2=3.6 Hz), 8.17 (d, 2H, J=4.4 Hz)
^{13}C NMR ($CDCl_3$, 100MHz) δ: 125.21, 125.45, 126.28, 128.27, 131.76, 133.93, 136.42, 144.44, 161.01
IR (KBr, cm^{-1}): 593, 607, 692, 707, 776, 794, 811, 814, 838, 887, 916, 1050, 1066, 1078, 1357, 1388, 1422, 1459, 1517, 1550, 3054, 3093
Elemental analysis: Calcd for $C_{18}H_{10}N_4S_4$: C, 52.68; H, 2.44; N, 13.66; S, 31.22. Found: C, 53.13; H, 2.39; N, 13.25; S, 30.03.

7. Synthesis of 3,6-bis(4'-octyl-2,2'-bithien-5-yl)-1,2,4,5-tetrazine (7)

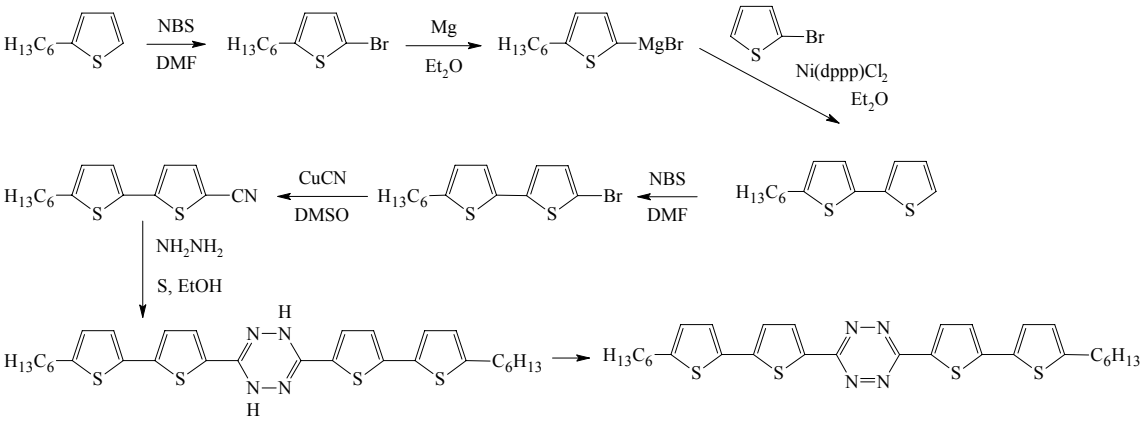


2-tributyltin-4-octylthiophene: Under constant argon flow 2 mL of 2.5 M BuLi in hexane (5.0 mmol) was drop-wise added at -30°C to a stirred solution of 3-octylthiophene (1.073 g, 5.47 mmol) in 7 mL of THF. The reaction mixture was stirred at -30°C for 2 hours, then tributyltin chloride (1.56 g, 4.79 mmol) was added drop-wise. After additional one hour the reaction mixture was warmed to RT and transferred to a saturated aqueous solution of $NaHCO_3$. In the next step the product was extracted with diethyl ether and consecutively washed with brine and water. It was then dried over anhydrous Na_2SO_4. The crude product was purified using a chromatographic column (Al_2O_3, n-hexane). In the final step it was distilled in a vacuum Kugelrohr oven at 110°C to yield 1.624 g of 2-tributyltin-4-octylthiophene (70% reaction yield).
^{1}H NMR ($CDCl_3$, 400MHz) δ: 0.90 (t, 12H, J=7.4 Hz), 1.07-1.11 (m, 4H), 1.27-1.35 (m, 18H), 1.54-1.59 (m, 8H), 2.63-2.67 (m, 2H), 6.97 (s, 1H), 7.19 (s, 1H)

3,6-bis(4'-octyl-2,2'-bithien-5-yl)-1,2,4,5-tetrazine: The synthesis an of **7** was carried out in a similar manner to that of **6** (second method), using a solution of 0.040 g (0.1 mmol) of 3,6-bis(5-bromo-2-thienyl)-1,2,4,5-tetrazine in 5 mL of DMF, 0.04 g (0.035 mmol) of $Pd(PPh_3)_4$ and 0.112 g (0.023 mmol) of 2-tributyltin-4-octylthiophene dissolved in 6 mL of DMF. The reaction was carried out at 90°C for 2 hours. The crude product was purified using a chromatographic column (silica gel, methylene chloride/n-hexane/4:1) yielding 0.03 g of pure 3,6-bis(4'-octyl-2,2'-bithien-5-yl)-1,2,4,5-tetrazine (48 % reaction yield).
^{1}H NMR ($CDCl_3$, 400MHz) δ: 0.86-0.90 (m, 6H), 1.27-1.35 (m, 20H), 1.61-1.67 (p, 4H), 2.62 (t, 4H, J=7.8 Hz), 6.93 (d, 2H, J=1.2 Hz), 7.20 (d, 2H, J= 1.2 Hz), 7.28 (d, 2H, J=4.4 Hz), 8.15 (d, 2H, J=4.0 Hz)
^{13}C NMR ($CDCl_3$, 100MHz) δ: 14.10, 22.66, 29.26, 29.28, 29.41, 29.70, 30.40, 31.87, 124.83, 126.79, 128.26, 131.71, 133.68, 136.01, 144.66, 144.86, 160.99
IR (KBr, cm^{-1}): 580, 603, 725, 764, 803, 829, 865, 921, 999, 1063, 1079, 1397, 1420, 1430, 1465, 1529, 1548, 2848, 2869, 2925, 2954, 3093
HRMS (EI); Calc for $C_{34}H_{42}S_4N_4$ 634.2292, found m/z 634.2313.
Melting point: 171°C

8. Synthesis of 3,6-bis(5'-hexyl-2,2'-bithien-5-yl)-1,2,4,5-tetrazine (8)

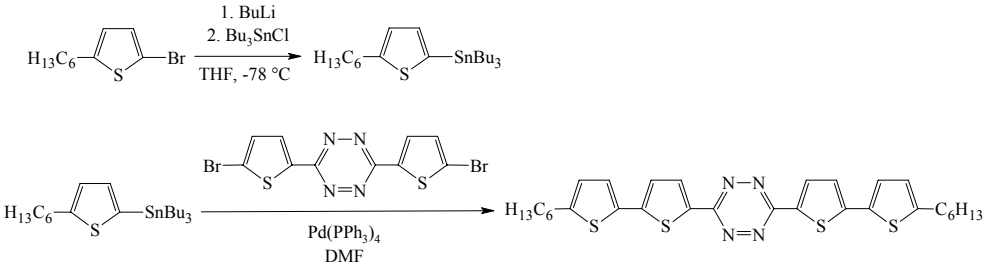
Method 1



5-cyano-5'-hexyl-2,2'-bithiophene: The synthesis and the purification of 5-cyano-5'-hexyl-2,2'-bithiophene was carried out in similar manner as 2-cyano-3-octylthiophene, using 0.510 g (5.70 mmol) of CuCN and 1.183 g (3.60 mmol) of 5-bromo-5'-hexyl-2,2'-bithiophene dissolved in 17 mL of DMSO. The reaction was carried out at 170^{o}C for 7 hours. 0.628 g (63 % reaction yield) of pure 5-cyano-5'-hexyl-2,2'-bithiophene was obtained.
^{1}H NMR ($CDCl_3$, 400MHz) δ: 0.89 (t, 3H, J=7.0 Hz), 1.29-1.40 (m, 6H), 1.64-1.72 (p, 2H), 2.81 (t, 2H, J=3.8 Hz), 6.72 (dt, 1H, J_1=0.8 Hz, J_2=3.6 Hz), 7.03 (d, 1H, J=3.6 Hz), 7.10 (d, 1H, J=3.6 Hz), 7.49 (d, 1H, J=4.0 Hz).

3,6-bis(5'-hexyl-2,2'-bithien-5-yl)-1,2,4,5-tetrazine: The synthesis of **8** was carried out in a similar manner to that of **1**, using 0.052 g (1.63 mmol) of sulfur, 0.628 g (2.28 mmol) of 5-cyano-5'-hexyl-2,2'-bithiophene in 4 mL of 99,8% EtOH and 0.258 g (5.16 mmol) of hydrazine hydrate. The reaction was carried out at 80^{o}C for 6 hours. The precipitate of 3,6-bis(5'-hexyl-2,2'-bithien-5-yl)-dihydro-1,2,4,5-tetrazine was separated by filtration on a Buchner funnel and dissolved in 200 mL of acetone with gentle heating. Then 0.206 g (1.18 mmol) of diethyl azodicarboxylate were slowly added. The reaction mixture was then heated for 3 h. In the next step it was concentrated to *ca.* half of its initial volume and then the precipitate formed was separated by filtration. The crude product was purified by crystallization from ethanol yielding 0.107 g of 3,6-bis(5'-hexyl-2,2'-bithien-5-yl)- 1,2,4,5-tetrazine (16% reaction yield).

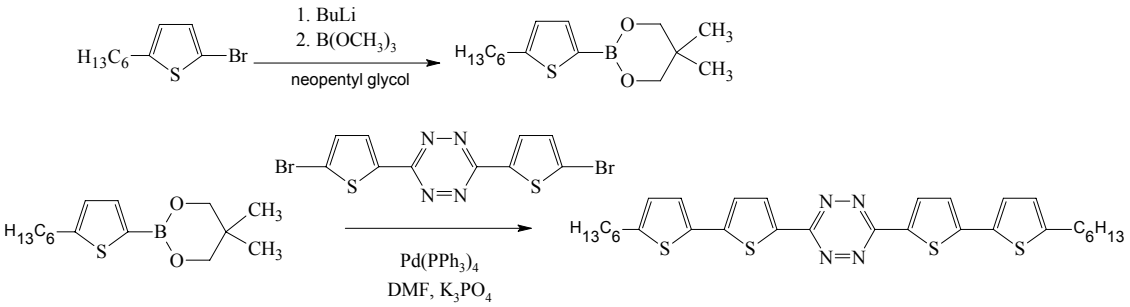
Method 2



2-tributyltin-5-hexylthiophene: Under constant argon flow 0.95 mL (2.38 mmol) of 2.5 M BuLi solution in hexane was drop-wise added at –78°C to a stirred solution of 0.266 g (1.08 mmol) of 2-bromo-5-hexylthiophene in 10 mL of THF. In the next step, after 1 h, tributyltin chloride (0.73 mL, 2.69 mmol) was added drop-wise. The cooling bath was removed after an additional hour and the reaction mixture was allowed to warm up to RT. The reaction as carried out for additional 18 h. In the next step 15 mL of water were added, then the product was extracted with methylene chloride, washed with water and finally dried over anhydrous Na_2SO_4. Since the obtained butyltin derivative decomposes in contact with SiO_2 and Al_2O_3 gels, it could not be purified chromatographically. Thus, the crude product was purified by distillation in a vacuum Kugelrohr oven at 120°C.
^{1}H NMR ($CDCl_3$, 400MHz) δ: 0.87-0.93 (m, 12H), 1.05-1.13 (m, 6H), 1.30-1.37 (m, 12H), 1.54-1.64 (m, 8H), 2.85 (t, 2H, J=7.8 Hz), 6.89 (d, 1H, J=2.8 Hz), 6.98 (d, 1H, J=3.2 Hz)

3,6-bis(5'-hexyl-2,2'-bithien-5-yl)-1,2,4,5-tetrazine: The synthesis of **8** was carried out in a similar manner to that of **6** (second method), using a solution of 0.219 g (0.54 mmol) of 3,6-bis(5-bromo-2-thienyl)-1,2,4,5-tetrazine in 7 mL of DMF, 0.096 g (0.083 mmol) of $Pd(PPh_3)_4$ and 0.494 g (1.08 mmol) of 2-tributyltin-4-hexylthiophene dissolved in 5 mL of DMF. The reaction was carried out at 90°C for 5 hours. The crude product was purified using a chromatographic column (silica gel, methylene chloride/n-hexane/4:1) yielding 0.152 g of pure of 3,6-bis(5'-hexyl-2,2'-bithien-5-yl)-1,2,4,5-tetrazine (50 % reaction yield).

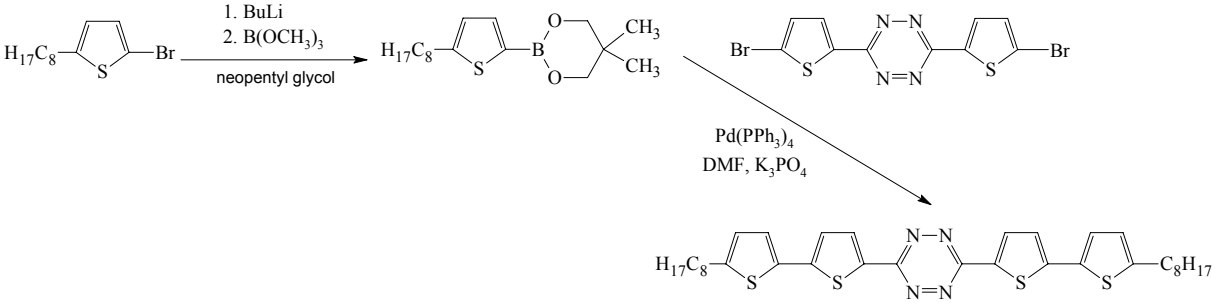
Method 3

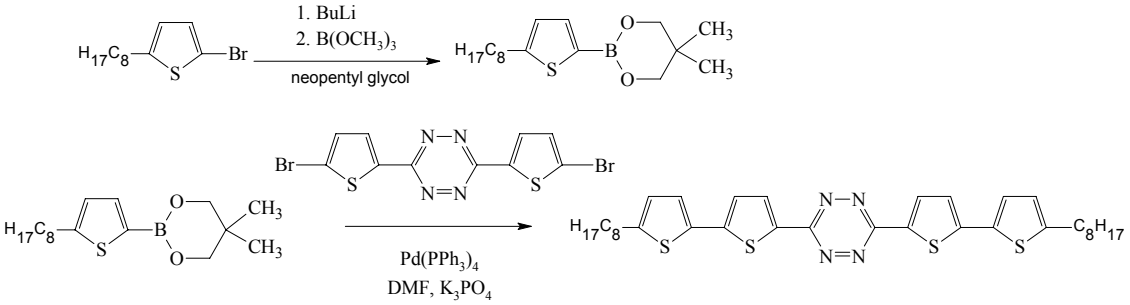


3,6-bis(5-bromo-2-thienyl)-1,2,4,5-tetrazine (0.3 g, 0.743 mmol) in 10 mL of DMF and $Pd(PPh_3)_4$ (0.1 g, 0.087 mmol) was stirred under constant argon flow for 10 min. Then, 0.316 g (1.49 mmol) of K_3PO_4 and 0.541 g (1.49 mmol) of 5-hexyl-2-thienylboronic acid neopentyl glycol ester were added. The resulting mixture was heated at 110°C for 24 hours. The precipitated product was collected, and washed with CH_2Cl_2. After the purification using a chromatographic column (silica gel, $CHCl_3$) 0.332 g of 3,6-bis(5'-hexyl-2,2'-bithien-5-yl)-1,2,4,5-tetrazine was obtained (77% reaction yield).

^{1}H NMR ($CDCl_3$, 400MHz) δ: 0.90 (t, 6H, J=7.0 Hz), 1.31-1.40 (m, 12H), 1.67-1.73 (p, 4H), 2.82 (t, 4H, J=7.6 Hz), 6.75 (d, 2H, J=3.6 Hz), 7.18 (d, 2H, J=3.6 Hz), 7.22 (d, 2H, J=4.0 Hz), 8.13 (d, 2H, J= 4.0 Hz)
^{13}C NMR ($CDCl_3$, 100MHz) δ: 14.07, 22.55, 28.74, 30.27, 31.53 (2C), 124.37, 125.23, 125.29, 131.66, 133.24, 133.82, 145.03, 147.71, 160.92,
IR (KBr, cm^{-1}): 609, 672, 722, 784, 796, 821, 874, 926, 1005, 1069, 1085, 1367, 1392, 1450, 1481, 1530, 1556, 2853, 2870, 2924, 2953, 3095
Elemental analysis: Calcd for $C_{30}H_{34}N_4S_4$: C, 62.28; H, 5.88; N, 9.69; S, 22.15. Found: C, 61.80; H, 6.19; N, 9.63; S, 21.81.
Melting point: 198°C

8a. Synthesis of 3,6-bis(5'-octyl-2,2'-bithien-5-yl)-1,2,4,5-tetrazine (8a)

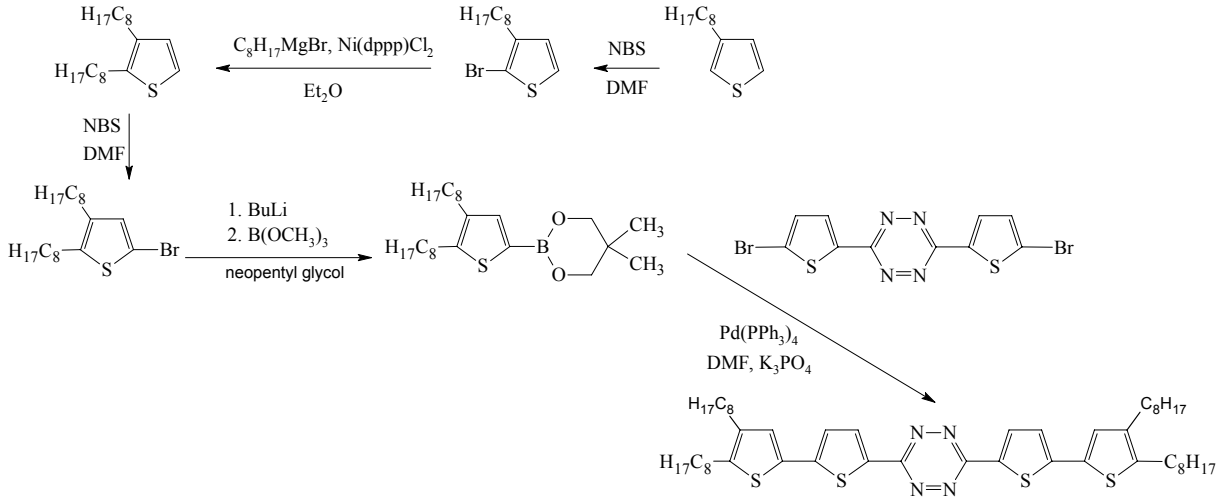




The synthesis of **8a** was carried out in a similar manner to that of **8** (method 3) using 0.222 g (0.55 mmol) of 3,6-bis(5-bromo-2-thienyl)-1,2,4,5-tetrazine in 8 mL of DMF, 0.074 g (0.064 mmol) of $Pd(PPh_3)_4$, 0.339 g (1.1 mmol) of 5-octyl-2-thienylboronic acid neopentyl glycol ester, 0.241 g (1.14 mmol) of K_3PO_4. The reaction yield was 53%.

^{1}H NMR ($CDCl_3$, 400MHz) δ: 0.89 (t, 6H, J=9.0 Hz), 1.28-1.39 (m, 20H), 1.66-1.74 (p, 4H), 2.82 (t, 4H, J=7.6 Hz), 6.75 (d, 2H, J=3.6 Hz), 7.19 (d, 2H, J=3.6 Hz), 7.23 (d, 2H, J=4.4 Hz), 8.13 (d, 2H, J=3.6 Hz)
^{13}C NMR ($CDCl_3$, 400MHz) δ: 14.10, 22.65, 29.07, 29.20, 29.30, 30.26, 31.57, 31.84, 124.38, 125.25, 125.32, 131.69, 133.82, 145.05, 147.74, 160.93
IR (KBr, cm^{-1}): 594, 609, 672, 721, 785, 796, 821, 876, 925, 1005, 1070, 1085, 1366, 1393, 1451, 1481, 1530, 1556, 2851, 2871, 2922, 2955, 3094
Elemental analysis: Calcd for $C_{34}H_{42}N_4S_4$: C, 64.35; H, 6.62; N, 8.83; S, 20.20. Found: C, 64.38; H, 6.24; N, 8.87; S, 21.38.
Melting point 182^{o}C

9. Synthesis of 3,6-bis(4',5'-dioctyl-2,2'-bithien-5-yl)- 1,2,4,5-tetrazine (9)



Synthesis of 4,5-dioctyl-2-thienylboronic acid neopentyl glycol ester: Under constant argon flow 3 mL (7.5 mmol) of 2.5 M BuLi solution in hexane was drop-wise added at –70^{o}C to a stirred solution of 2 g (5.17 mmol) of 2-bromo-4,5-dioctylthiophene in 15 mL of THF. Then, the reaction mixture was allowed to warm up slowly to the room temperature. In the next step, it was cooled down again to –70^{o}C and 4.5 mL (40.36 mmol) of $B(OCH_3)_3$ was added. Once this addition was completed the reaction mixture was left with stirring and allowed to reach the room temperature. After additional 1 hour 4.72 g (45.35 mmol) of neopentyl glycol was added. In the final step the reaction mixture was stirred at room temperature for additional 12 hours and then 30 mL of CH_2Cl_2 and 40 mL of water was added. The aqueous phase was extracted with CH_2Cl_2. The combined organic phases was washed with water and dried over $MgSO_4$. The crude product was purified using a chromatographic column using first n-hexane to remove unreacted substrate and then methylene chloride to yield 0.618 g of 4,5-dioctyl-2-thienylboronic acid neopentyl glycol ester (39% reaction yield).
^{1}H NMR ($CDCl_3$; 400 MHz): δ: 0.88 (t, 6H, J=6.8 Hz), 1.02 (s, 6H), 1.2 - 1.4 (m, 20H), 1.5 - 1.68 (m, 4H), 2.48 (t, 2H, J=7.8 Hz), 2.72 (t, 2H, J=7.6 Hz), 3.74 (s, 4H), 7.26 (s, 1H)

3,6-bis(4',5'-dioctyl-2,2'-bithien-5-yl)-1,2,4,5-tetrazine:3,6-bis(5-bromo-2-thienyl)-1,2,4,5-tetrazine (0.370 g, 0.91 g mmol) in 10 mL of DMF and $Pd(PPh_3)_4$ (0.096 g, 0.083 mmol) was stirred under constant argon flow for 10 min. Then, 0.39 g (1.84 mmol) of K_3PO_4 and 0.8 g (1.9 mmol) of 4,5-dioctyl-2-thienylboronic acid neopentyl glycol were added. The resulting mixture was heated at 110^{o}C for 24 hours. After cooling to RT the reaction mixture was poured to 50 mL of CH_2Cl_2. The organic phase was washed with brine and water and dried over $MgSO_4$. The crude product was purified using a chromatographic column twice (silica gel, methylene chloride/n-hexane/1:1) yielding 0.365 g of 3,6-bis(4',5'-dioctyl-2,2'-bithien-5-yl)-1,2,4,5-tetrazine (46 % reaction yield).
^{1}H NMR ($CDCl_3$; 400 MHz): δ: 8.11 (d, 2H, J=4.4 Hz), 7,20 (d, 2H, J=3.6 Hz), 7,09 (s, 2H), 2.73 (t, 4H, J=7.8 Hz), 2.50 (t, 4H, J=7.8 Hz), 1.56 – 1,.70 (m, 8H), 1.24 – 1.42 (m, 40H), 0.89 (t, 12H, J=6.8 Hz)
^{13}C NMR ($CDCl_3$; 100 MHz): δ (arom): 160.9, 145.3, 141.1, 139.4, 133.0, 131.9, 131.6, 127.2, 124.1.
IR (KBr, cm^{-1}): 721, 791, 1237, 1377, 1392, 1481, 1450, 1537, 2919, 2853, 2956

Elemental analysis: Calcd for $C_{50}H_{74}N_4S_4$: C, 69.93; H, 8.62; N, 6.53; S, 14.92. Found: C, 69.85; H, 8.72; N, 6.51; S, 15.04.
Melting point 108^{o}C

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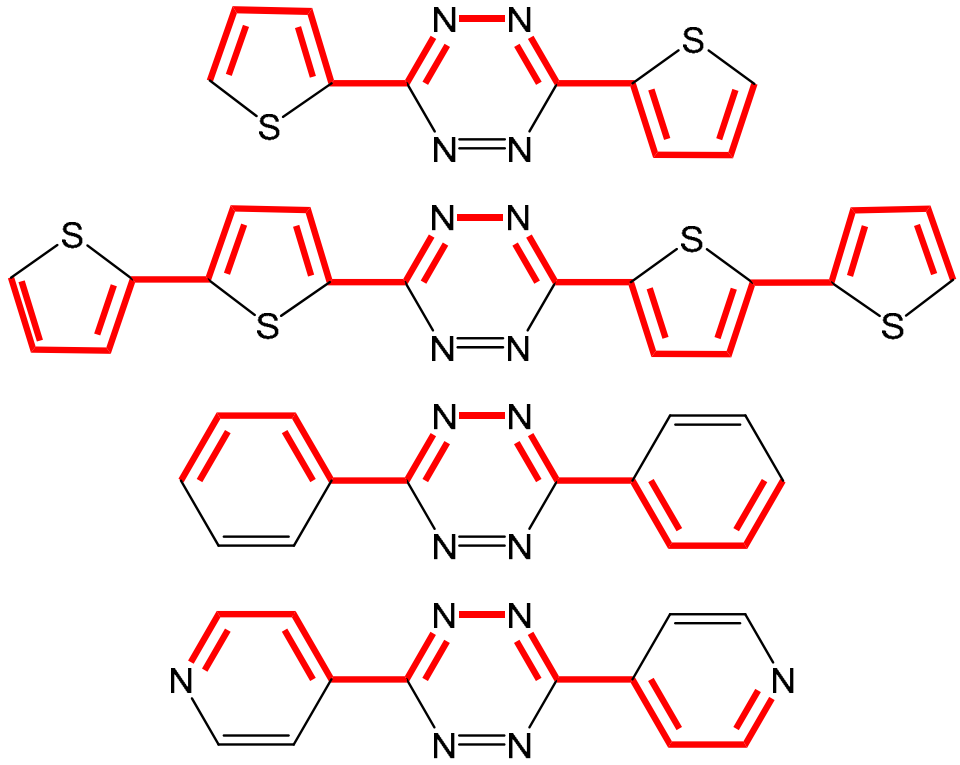

Fig. S1 The highlighted (red colour) bonds forming the main conjugated backbone. These bonds were used for the BLA* calculation.

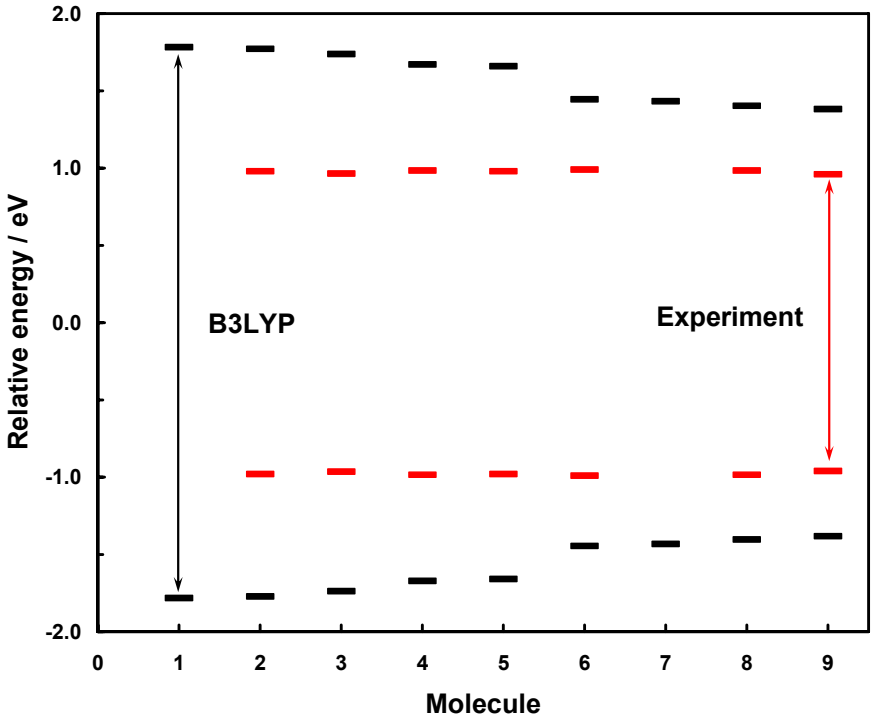

Fig. S2 Schematic representation of the relative energy between HOMOs and LUMOs for the molecules studied. Red lines stand for the experimentally determined values (from cyclic voltammetry) and the grey lines indicate the B3LYP/6-31G* results.

Table S1 TD-B3LYP optical transitions for studied molecules.

Molecule	*k*	Energy (eV)	Oscillator strength
1	1	2.14	0.0039
	2	2.67	0.0000
	3	3.51	0.0000
	4	3.56	0.0000
	5	3.58	0.0000
	6	3.62	0.0021
	7	3.67	0.0022
	8	3.69	0.0000
	9	3.74	0.0088
	10	4.05	0.0294
	11	4.06	0.0000
	12	4.23	0.9861
	13	4.50	0.0000
	14	4.59	0.0000
	15	4.85	0.0000
2	1	2.13	0.0038
	2	2.80	0.0000
	3	3.30	0.0045
	4	3.76	0.0291
	5	3.78	0.0000
	6	3.97	0.0000
	7	3.98	1.0456
	8	4.25	0.0191
	9	4.26	0.0000
	10	4.62	0.0000
	11	4.74	0.0000
	12	4.87	0.0000
	13	5.27	0.0000
	14	5.31	0.0000
	15	5.32	0.0001
3	1	2.23	0.0040
	2	2.83	0.0000
	3	2.92	0.0065
	4	3.52	0.8096
	5	3.66	0.0000
	6	3.83	0.0000
	7	3.85	0.1603
	8	4.26	0.0000

	9	4.30	0.0478
	10	4.38	0.0000
	11	4.57	0.0000
	12	4.85	0.0000
	13	5.04	0.0000
	14	5.35	0.0000
	15	5.54	0.0000
4	1	2.18	0.0032
	2	2.79	0.0087
	3	2.85	0.0009
	4	3.41	0.6091
	5	3.45	0.0005
	6	3.58	0.2798
	7	3.64	0.0007
	8	4.06	0.0291
	9	4.07	0.0489
	10	4.30	0.0001
	11	4.56	0.0001
	12	4.80	0.0001
	13	4.95	0.0003
	14	5.07	0.0008
	15	5.15	0.0015
5	1	2.23	0.0039
	2	2.77	0.0060
	3	2.84	0.0000
	4	3.34	1.1925
	5	3.47	0.0000
	6	3.82	0.0000
	7	3.83	0.1218
	8	4.14	0.0007
	9	4.27	0.0295
	10	4.28	0.0000
	11	4.56	0.0001
	12	4.84	0.0000
	13	4.85	0.0033
	14	5.34	0.0000
	15	5.52	0.0012
6	1	2.24	0.0039
	2	2.40	0.0025
	3	2.68	1.6334
	4	2.71	0.0000

	5	2.85	0.0000
	6	3.18	0.0000
	7	3.71	0.0000
	8	3.89	0.0619
	9	3.92	0.0000
	10	4.00	0.0001
	11	4.06	0.0406
	12	4.09	0.0005
	13	4.11	0.1535
	14	4.20	0.0246
	15	4.21	0.0282
7	1	2.24	0.0038
	2	2.38	0.0022
	3	2.65	1.7206
	4	2.72	0.0000
	5	2.81	0.0000
	6	3.15	0.0004
	7	3.70	0.0006
	8	3.85	0.0311
	9	3.86	0.0020
	10	3.91	0.0084
	11	3.93	0.0014
	12	3.94	0.0433
	13	4.01	0.0000
	14	4.04	0.0011
	15	4.07	0.2051
8	1	2.24	0.0039
	2	2.33	0.0016
	3	2.57	1.8308
	4	2.71	0.0000
	5	2.74	0.0468
	6	3.06	0.0129
	7	3.61	0.0755
	8	3.89	0.0043
	9	3.89	0.0604
	10	3.96	0.2283
	11	4.00	0.0008
	12	4.05	0.0045
	13	4.05	0.0071
	14	4.10	0.0594
	15	4.15	0.0053

9	1	2.24	0.0038
	2	2.29	0.0020
	3	2.54	1.9948
	4	2.69	0.0000
	5	2.72	0.0000
	6	3.02	0.0001
	7	3.59	0.0001
	8	3.83	0.0390
	9	3.84	0.0001
	10	3.88	0.0308
	11	3.90	0.0015
	12	3.91	0.1100
	13	3.94	0.1850
	14	4.01	0.0000
	15	4.03	0.0002