Organic semiconductors for field-effect transistors (FETs). Tuning of spectroscopic, electrochemical, electronic and structural properties of naphthalene bisimides *via* substituents containing alkylthienyl moieties.

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SUPPORTING INFORMATION

Semiconducting naphthalenebisimides synthesized in the framework of this research are depicted below (**Chart 1**).

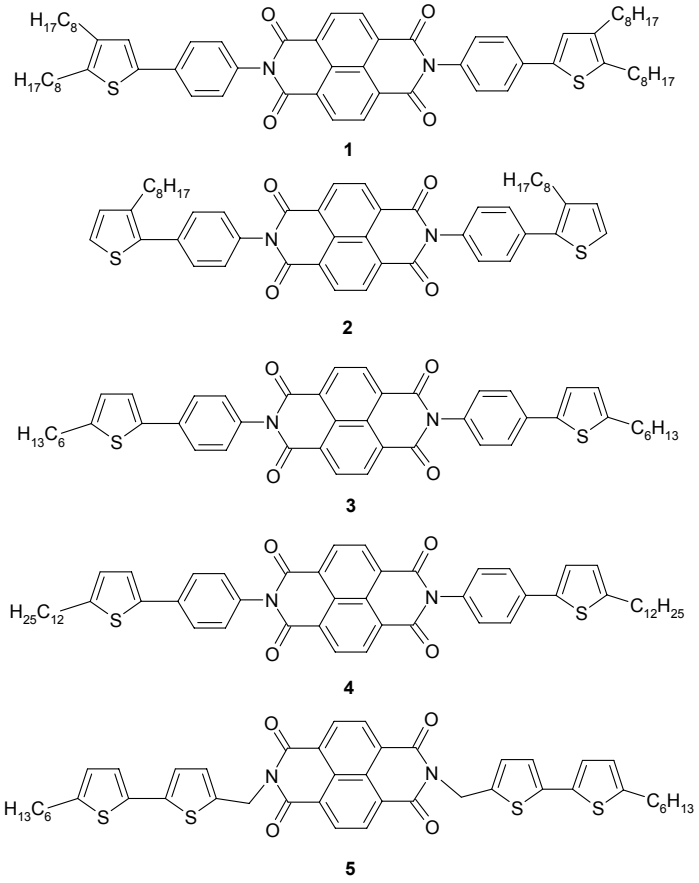


Chart 1

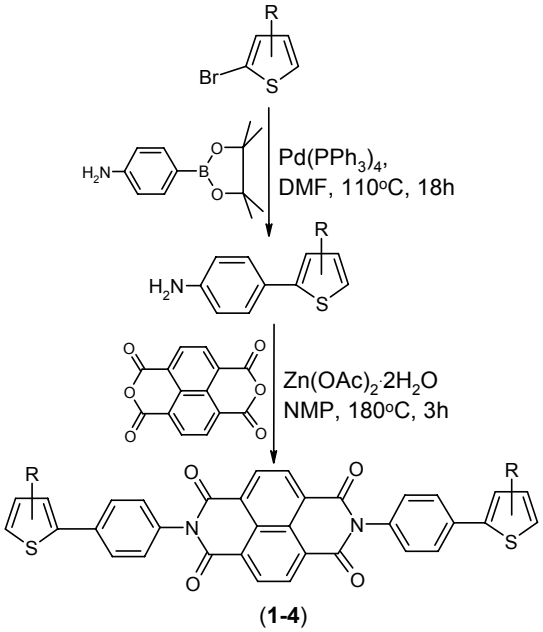
Reagents

NMP, 2-thienylmethylamine, 1-bromooctane, 4-aminophenylboronic acid pinacol ester, 1,4,5,8-naphthalenetracarboxylic acid bisanhydride tetrakis(triphenylphosphine)palladium, [1,3-bis(diphenylphosphino)propane]dichloronickel(II) were purchased form Sigma Aldrich Co. and used as received. Diethyl ether was dried and stored over sodium. Dry DMF, zinc acetate dihydrate and potassium phosphate were purchased form Fluka and used as received. N-bromosuccinimide (Fluka) was crystallized from water before use. 2-bromo-3-octylthiophene, 2-bromo-5-dodecylthiophene and 2-bromo-5-hexylthiophene were prepared

according to methods already described[1]. 5-hexyl-2-thienylboronic acid neopentyl glycol ester was prepared according to modified method already described[2].

Preparation of alkylthienylphenyl naphthalenebisimides

Alkylthienylphenyl bisimides were prepared using the reaction sequence depicted in **Scheme S1:**



Scheme S1

Synthesis of 2,3-dioctylthiophene *via* Kumada coupling[3]

To a stirred mixture of 0.38 g (15.9 mmol) of magnesium turnings and 7 mL of dry diethyl ether a solution of n-octyl bromide (3.07 g; 15.9 mmol) in 8 mL of dry diethyl ether was added dropwise, under argon atmosphere and then stirred for 1 hour at RT The resulting solution of the Grignard reagent formed was then slowly added, at RT, to a solution of 2-bromo-3-octylthiophene (3.98 g; 14.5 mmol) and 30 mg of [1,3-bis(diphenylphosphino)propane]dichloronickel(II) in 8 mL of dry diethyl ether. The obtained mixture was stirred for 12 hours at RT, and then it was cooled to 0°C with an ice bath. In the next step 25 mL of 1M HCl were carefully added, the obtained biphasic mixture was shaken with diethyl ether and finally its organic phase was separated, washed with water and dried over anhydrous magnesium sulphate. The solvent was removed in a rotary evaporator and the crude product was purified using a chromatographic column (silica gel, hexane). Further purification was carried out by distillation in Kugelrohr vacuum oven, yielding 2 g (45%) of colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.02 (d, 2H, J=5.2 Hz), 6.81 (d, 2H, J=5.2 Hz), 2.71 (t, 2H, J=7.8 Hz), 2.47 (t, 2H, J=7.8 Hz), 1.50-1.68 (m, 4H), 1.22-1.40 (m, 20H), 0.88 (apparent triplet, 6H, J=6.8 Hz).

[1] (a) P. Bauerle; F. Wurthner, G. Gotz, F. Effenberger, *Synthesis*, 1993, 1099-1103.; (b) C. Xia, X. Fan, J. Locklin, R. C. Advincula *Org. Lett.*, 2002, **4**, 2067–2070.
[2] D. Didier, S. Sergeyev, Y. H. Geerts, *Tetrahedron* 2007, **63**, 941–946.
[3] K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S.-I. Kodma ,I, Nakajima, A. Minato, M. Kumada, *Bull. Chem. Soc. Jpn.* 1976, **49**, 1958-1969.

^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 138.8; 137.7; 128.7; 120.9; 32.0; 31.9(2C); 30.9; 29.5 (2C); 29.4 (2C); 29.3; 29.2; 28.2; 27.7; 22.7; 14.1.

Synthesis of 2-bromo-4,5-dioctylthiophene

To a stirred solution of 2,3-dioctylthiophene (1.03 g; 3.35 mmol) in 10 mL of dry DMF a solution of N-bromosuccinimide (0.61 g (3.35 mmol) in 10 mL of dry DMF was added dropwise, under argon atmosphere and stirred for 1 hour at RT. Then, the reaction mixture was poured onto ice water. The resulting biphasic mixture was shaken with diethyl ether and the resulting organic phase was washed with brine and water, and then dried over anhydrous magnesium sulphate. The solvent was then removed using a rotary evaporator. In the final step the crude product was purified using a chromatographic column (silica gel, hexane) yielding 0.97 g (75%) of colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 6.74 (s, 1H), 2.64 (t, 2H, J=7.6 Hz), 2.43 (t, 2H, J=7.8 Hz), 1.46-1.62 (m, 4H), 1.22-1.38 (m, 20H), 0.88 (apparent triplet, 6H, J=6.8 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 140.6; 138.4; 131.3; 107.0; 31.9; 31.8; 31.7; 30.7; 29.4 (2C); 29.3; 29.2 (2C); 28.1; 27.8; 22.7; 14.1.
HRMS (M+ found = 386.15869; calcd. = 386.16428).

General procedure for the synthesis of alkylthienylanilines via Suzuki coupling[4]

To a solution of 10 mmol of appropriate bromoalkylthiophene in 30 mL of dry DMF 0.29g (0.5 mmol) of tetrakis(triphenylphosphine)palladium was added under argon atmosphere and then stirred for 10 minutes at RT. Next, 2.31 g (8.23 mmol) of potassium phosphate were added, followed by immediate addition of 4-aminophenylboronic acid pinacol ester (2.4 g; 10.97 mmol). The resulting mixture was heated at 110^{o}C for 18 hours. After cooling to RT it was poured onto 100 mL of chloroform. DMF was then removed by several extractions with water. The organic phase was dried with anhydrous magnesium sulphate which was followed by evaporation of chloroform in a rotary evaporator. The crude product was then purified using a chromatographic column (silica gel, methylene chloride + 1 % vol. triethylamine). The samples of new amines were also kept in ambient conditions for 3 months. ^{1}H NMR analysis did not show signs of significant decomposition. The signal from NH_2 group broadened due to moisture intrusion.

4-(4,5-dioctyl-2-thienyl)aniline (41 %).
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.35-7.40 (m, 2H), 6.89 (s, 1H), 6.70-6.74 (m, 2H), 4.2 (broad, 2H), 2.70 (t, 2H, J=7.8 Hz), 2.47 (t, 2H, J=7.6 Hz), 1.52-1.68 (m, 4H), 1.22-1.42 (m, 20H), 0.88 (apparent triplet, 6H, J=6.8 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 144.5; 139.8; 138.6; 137.1; 126.5 (2C); 123.1; 115.6; 31.9 (3C); 30.8; 29.5 (2C); 29.4; 29.3 (2C); 29.2; 28.4; 27.8; 22.7; 14.1.
HRMS (M+ found = 399.29424; calcd. = 399.29597).

4-(3-octyl-2-thienyl)aniline (57 %)[4]
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.22-7.25 (m, 2H), 7.15 (d, 1H, J=5.2 Hz), 6.95 (d, 1H, J=5.2 Hz), 6.74-6.79 (m, 2H), 4.10 (broad, 2H), 2.61 (t, 2H, J=7.8 Hz), 1.54-1.64 (m, 2H), 1.20-1.34 (m, 10H), 0.88 (t, 3H, J=6.8 Hz).

[4] D. Aldakov, C. Querner, Y. Kervella, B. Jousselme, R. Demadrille, E. Rositto, P. Reiss, A. Pron, *Microchimica Acta* 2008, **160**, 335-344.

4-(5-dodecyl-2-thienyl)aniline (32%)
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.34-7.39 (m, 2H), 6.95 (d, 1H, J=3.6 Hz), 6.65-6.70 (m, 1H+2H), 3.70 (broad, 2H), 2.78 (t, 2H, J=7.2 Hz), 1.63-1.71 (m, 2H), 1.22-1.42 (m, 18H), 0.88 (t, 3H, J=7.0 Hz).

4-(5-hexyl-2-thienyl)aniline (35 %)
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.34-7.39 (m, 2H), 6.95 (d, 1H, J=3.6 Hz), 6.65-6.70 (m, 1H+2H), 3.70 (broad, 2H), 2.79 (t, 2H, J=7.6 Hz), 1.64-1.72 (m, 2H), 1.28-1.42 (m, 6H), 0.88 (t, 3H, J=7.0 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 145.4; 143.9; 142.2; 126.7; 125.7; 124.7; 120.1; 115.3; 31.6 (2C); 30.2; 28.8; 22.6; 14.1.
HRMS (M+ found = 259.13996; calcd. = 259.13947).

Condensing of alkylthienylanilines and naphthalene bisanhydride[5]
In this step a modification of the methods already described in the literature was used. In a typical preparation 1.96 mmol of amine and 0.20 g (1.86 mmol) of zinc acetate dihydrate were added to a stirred suspension of 0.25 g (1.86 mmol) of 1,4,5,8-naphthalenetracarboxylic acid bisanhydride in 30 mL of dry NMP. The resulting mixture was stirred at the temperature of 180^{o}C for 3 hours, and then was poured onto 100 ml of water. The obtained precipitate was filtered off, washed with water and dried in air. In the next step the crude product was vigorously stirred with 50 mL of acetone for 2 hours to remove the excess of the primary amine and remaining zinc acetate. The obtained bisimides were next purified using a chromatographic column (silica gel, chloroform) (twice), which was followed by drying in vacuum at 65^{o}C for 12 hours. Due to its low solubility, purification of larger amounts of **3** was tedious. In the case of **4** no chromatographic purification was carried out, the product precipitated while cooling the reaction mixture. The obtained solid was filtered off, washed with acetone and dried.

N, N'- bis[(4,5-dioctyl-2-thienyl)phenyl]-1,4,5,8-naphthalenetetracarboxylic-1,4:5,8-bisimide (**1**)(42%).
Orange solid.
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.86 (s, 4H), 7.72-7.76 (m, 4H), 7.30-7.34 (m, 4H), 7.12 (s, 2H), 2.75 (t, 4H, J=7.6 Hz), 2.53 (t, 4H, J=7.6Hz), 1.54-1.72 (m, 8H), 1.24-1.46 (m, 40H), 0.89 (apparent triplet, 12H, J=6.8 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 163.0; 139.9, 139.1; 138.2; 135.9; 132.7; 131.5; 128.7; 127.2; 127.0; 126.4; 125.8; 31.9 (2C); 31.8; 30.8; 29.5; 29.4 (2C); 29.3; 29.2; 28.3; 28.0; 22.7; 14.1.
FTIR (KBr, cm^{-1}): 3073, 2954, 2920, 2851, 1713, 1675, 1580, 1511, 1467, 1445, 1345, 1250, 1193, 1137, 1118, 1106, 980, 854, 830, 768, 751.
UV-vis ($CHCl_3$) λ_{max} = 237 nm, 314 nm, 340 nm, 360nm, 381 nm.
Elemental analysis: Calcd for $C_{68}H_{82}N_2O_4S_2$: C, 76.85, H, 8.01, N, 2.72, S, 6.22. Found: C, 76.85, H, 8.09, N, 2.75, S, 5.95.
Melting point: 171°C.

[5] (a) A. Rademacher, S. Markle, H. Langhals, *Chem. Ber.* 1982, **115**, 2927-2934. (b) H. Langhals, *Chem. Ber.* 1985, **118**, 4641-4645. (c) S. Demmig, H. Langhals, *Chem. Ber.* 1988, **121**, 225-230. (d) H. Langhals, H. Jaschke, *Chem. Eur. J.* 2006, **12**, 2815-2824.

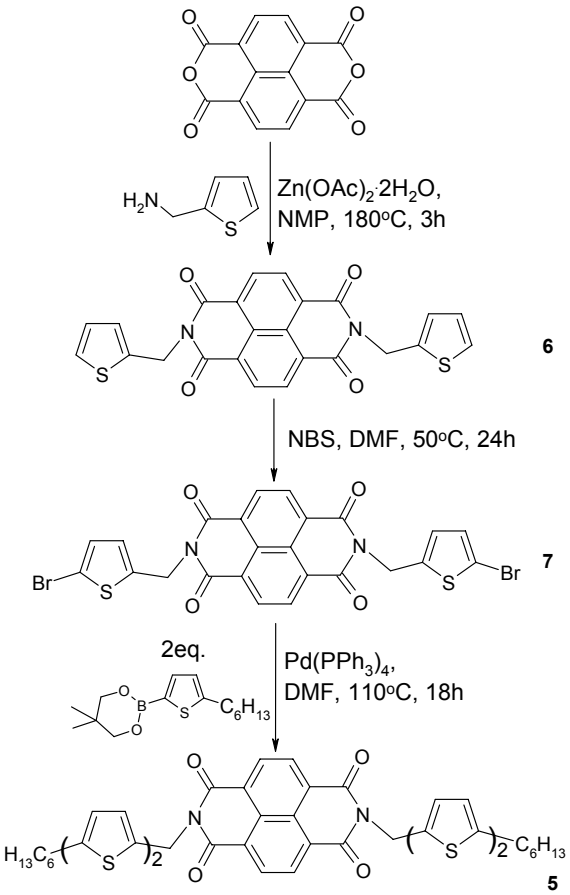
N, N'- bis[(3-octyl-2-thienyl)phenyl]-1,4,5,8-naphthalenetetracarboxylic-1,4:5,8-bisimide (**2**) (52 %).
Orange fluorescent solid.
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.89 (s, 4H), 7.62-7.65 (m, 4H), 7.37-7.41 (m, 4H), 7.29 (d, 2H, J=4.8 Hz), 7.03 (d, 2H, J=5.6 Hz), 2.73 (t, 4H, J=8.0 Hz), 1.62-1.72 (m, 4H), 1.22-1.40 (m, 20H), 0.88 (t, 6H, J=7.8 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 163.0; 139.4, 136.5; 135.9; 133.3; 131.5; 130.4; 129.6; 128.5; 127.2; 127.0; 124.3; 31.8 ; 31.1; 29.5; 29.3; 28.8 ; 22.7; 14.1.
FTIR (KBr, cm^{-1}): 3079, 3062, 3039, 2954, 2921, 2850, 1708, 1669, 1580, 1529, 1448, 1347, 1248, 1191, 1142, 1121, 983, 923, 886, 856, 845, 835, 771, 764, 751, 721, 709.
UV-vis ($CHCl_3$) λ_{max} = 237 nm, 282 nm, 343 nm, 360nm, 380 nm.
Elemental analysis: Calcd for $C_{50}H_{50}N_2O_4S_2$: C, 74.41, H, 6.24, N, 3.47, S, 7.95. Found: C, 74.26, H, 6.30, N, 3.52, S, 7.64.
Melting point: 217°C.

N, N'- bis[(5-hexyl-2-thienyl)phenyl]-1,4,5,8-naphthalenetetracarboxylic-1,4:5,8-bisimide (**3**)(53%)
Pink-red solid.
^{1}H NMR ($CDCl_3$+CF_3COOD, 400 MHz, ppm): 8.95 (s, 4H), 7.74-7.80 (m, 4H), 7.30-7.35 (m, 4H), 7.22 (d, 2H, J=3.6 Hz), 6.80 (d, 2H, J=3.6 Hz), 2.86 (t, 4H, J=7.6 Hz), 1.59-1.88 (m, 4H), 1.30-1.46 (m, 12H), 0.91 (t, 6H, J=7.2 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 164.3; 147.4; 139.7; 137.0; 132.7 (2C); 131.5; 128.6; 127.2; 126.9; 125.3; 124.1; 31.6 (2C); 30.3; 28.8; 22.6; 14.0.
FTIR (KBr, cm^{-1}): 3068, 2947, 2922, 2848, 1719, 1676, 1583, 1512, 1467, 1449, 1349, 1251, 1196, 1139, 1118, 980, 951, 882, 855, 834, 814, 767, 749.
UV-vis ($CHCl_3$) λ_{max} = 237 nm, 311 nm, 340 nm, 360nm, 381 nm.
Elemental analysis: Calcd for $C_{46}H_{42}N_2O_4S_2$: C, 73.57, H, 5.64, N, 3.73, S, 8.54. Found: C, 72.00, H, 5.12, N, 3.84, S, 8.41.
Melting point: >340 °C, gradually darkens upon heating.

N, N'- bis[(5-dodecyl-2-thienyl)phenyl]-1,4,5,8-naphthalenetetracarboxylic-1,4:5,8-bisimide (**4**)(41%)
Orange solid.
^{1}H NMR ($CDCl_3$+CF_3COOD, 400 MHz, ppm): 8.94 (s, 4H), 7.74-7.79 (m, 4H), 7.29-7.34 (m, 4H), 7.22 (d, 2H, J=3.6 Hz), 6.80 (d, 2H, J=3.6 Hz), 2.85 (t, 4H, J=7.4 Hz), 1.54-1.78 (m, 4H), 1.22-1.46 (m, 36H), 0.89 (t, 6H, J=6.8 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 164.2; 147.4; 139.8; 136.9; 132.5 ; 131.6; 128.6; 127.2, 126.9; 126.8; 125.3; 124.1; 32.0 ; 31.6; 30.3; 29.7(3C), 29.6, 29.4 (2C), 29.1, 22.7; 14.0.
FTIR (KBr, cm^{-1}): 3073, 3042, 2955, 2919, 2850, 1714, 1670, 1579, 1513, 1468, 1446, 1344, 1248, 1208, 1194, 1187, 1138, 1109, 980, 951, 882, 854, 835, 800, 767, 749.
UV-vis ($CHCl_3$) λ_{max} = 238 nm, 305 nm, 342 nm, 360nm, 380 nm.
Elemental analysis: Calcd for $C_{58}H_{66}N_2O_4S_2$: C, 75.78, H, 7.24, N, 3.05, S, 6.98. Found: C, 75.61, H, 7.06, N, 3.14, S, 7.20.
Melting point: >340 °C, gradually darkens upon heating.

Preparation of alkylbithiophenemethyl naphthalenenebisimide (5)

Compound **5** was synthesized using the reaction sequence presented in **Scheme2**:



Scheme 2

Synthesis of *N, N'*- bis[(2-thienyl)methyl]-1,4,5,8-naphthalenetetracarboxylic-1,4:5,8-bisimide (6)

1.266 g (11.19 mmol) of 2-thienylmethylamine and 0.81g (3.73 mmol) of zinc acetate dihydrate were added to a stirred suspension of 1g (3.73 mmol) of 1,4,5,8-naphthalenetracarboxylic acid bisanhydride in 40 mL of dry NMP. The resulting mixture was stirred at the temperature of 180°C for 3 hours and then cooled to RT. Upon this cooling the obtained bisimide precipitated. The precipitate was filtered off and washed with acetone. As prepared, bisimide is pure enough to be used for the next step. Analytical sample was dried for the sake of elemental analysis. Yellow solid. 1.34 g (73%).

^{1}H NMR ($CDCl_3$+CF_3COOD, 400 MHz, ppm): 8.86 (s, 4H), 7.27-7.29 (m, 2H), 7.24-7.27 (m, 2H), 6.95-6.98 (m, 2H), 5.58 (s, 4H).
^{13}C NMR ($CDCl_3$+CF_3COOD, 100 MHz, ppm): 163.4, 136.7, 132.1, 129.1, 126.8, 126.7, 126.6, 126.5, 39.0.
FTIR (KBr, cm^{-1}): 3080, 2963, 1703, 1669, 1581, 1450, 1419, 1357, 1320, 1253, 1158, 1104, 995, 884, 857, 770, 714.
UV-vis ($CHCl_3$) λ_{max} = 237 nm, 340 nm, 361nm, 381 nm.
Elemental analysis: Calcd for $C_{24}H_{14}N_2O_4S_2$: C, 62.87, H, 3.08, N, 6.11, S, 13.95. Found: C, 62.75, H, 3.00, N, 6.21, S, 13.80.
Melting point: 329-331 °C, partial decomposition.

Synthesis of *N, N'*- bis[(5-bromo-2-thienyl)methyl]-1,4,5,8-naphthalenetetracarboxylic-1,4:5,8-bisimide (7)

0.3 g (0.65 mmol) of **6** and 0.25g (0.133 mmol) of NBS were suspended in 40 mL of dry DMF and stirred at 50°C for 24 hours. After cooling, the reaction mixture was poured onto 100 mL of water. The obtained yellow precipitate was filtered off and washed with water and finally dried. The crude product was purified with a chromatography column (silica gel, methylene chloride). Pale yellow solid. 0.3 g (74%).

^{1}H NMR ($CDCl_3$+CF_3COOD, 400 MHz, ppm): 8.78 (s, 4H), 7.05 (d, 2H, J=3.6 Hz), 6.95 (d, 2H, J= 4.0 Hz), 5.44 (s, 4H).
^{13}C NMR ($CDCl_3$+CF_3COOD, 100 MHz, ppm): 162.8, 138.7, 131.7, 129.5, 129.4, 126.7, 126.5, 113.2 (C-Br), 38.8.
FTIR (KBr, cm^{-1}): 3079, 2961, 1706, 1668, 1581, 1453, 1441, 1372, 1329, 1247, 1222, 1161, 1107, 998, 962, 890, 797, 771.
UV-vis ($CHCl_3$) λ_{max} = 238 nm, 340 nm, 361nm, 381 nm.
Melting point: 272-273 °C, partial decomposition.

Synthesis of *N, N'*- bis[(5'-hexyl-2,2'-bithiophen-5-yl)methyl]-1,4,5,8-naphthalenetetra-carboxylic -1,4:5,8-bisimide (5)

To a suspension of 0.24 g (0.39 mmol) of **7** in 30 mL of dry DMF at 40°C, 10 mg of tetrakis(triphenylphosphine)palladium was added under argon atmosphere and then stirred for 5 minutes. In the next step 0.282 g (1.33 mmol) of potassium phosphate and 0.282 g (1 mmol) of 5-hexyl-2-thienylboronic acid neopentyl glycol ester were consecutively added. The resulting mixture was heated at 110°C for 18 hours. After cooling to RT the reaction mixture was poured onto 100 mL of chloroform. DMF was then removed by repeated extractions with water. The organic phase was dried with anhydrous magnesium sulphate which was followed by evaporation of chloroform. The crude product was then purified using a chromatographic column (silica gel, methylene chloride) to yield 0.13 g of pink powder. Careful rinsing of the product with 50 mL of acetone/methylene chloride (1:1 v/v), followed by drying, yielded 0.122 g of light grey solid (40%).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.78 (s, 4H), 7.15 (d, 2H, J=3.6 Hz), 6.89 (apparent doublet, 4H, J=3.6 Hz), 6.61 (d, 2H, J=3.6 Hz), 5.47 (s, 4H), 2.73 (t, 4H, J=7.4 Hz), 1.58-1.66 (m, 4H), 1.24-1.38 (m, 12H), 0.86 (t, 6H, J=6.8 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 162.4, 145.5, 138.7, 135.9, 134.4, 131.2, 130.0, 126.7, 126.6, 124.6, 123.4, 122.2, 38.6, 31.5, 31.4, 30.1, 28.7, 22.5, 14.1.
FTIR (KBr, cm^{-1}): 3071, 2958, 2927, 2855, 1705, 1668, 1581, 1451, 1411, 1368, 1325, 1245, 1190, 1102, 1044, 884, 838, 796, 771, 697.
UV-vis ($CHCl_3$) λ_{max} = 237 nm, 326 nm, 339 nm, 361nm, 381 nm.
Elemental analysis: Calcd for $C_{44}H_{42}N_2O_4S_4$: C, 66.81, H, 5.35, N, 3.54, S, 16.21. Found: C, 66.54, H, 5.48, N, 3.53, S, 16.44.
Melting point: 252-253 °C, partial decomposition.

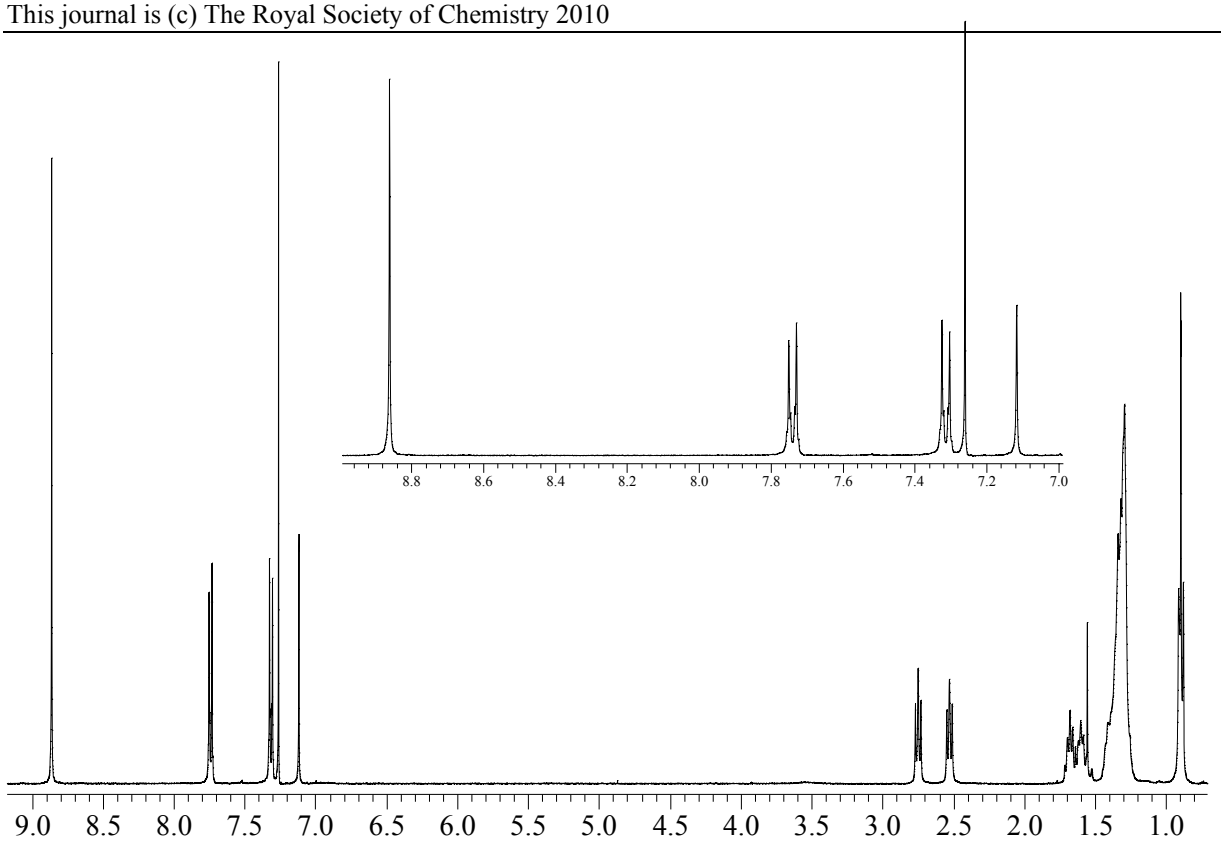


Fig. S1 ^{1}H NMR spectrum of **1** (400MHz, $CDCl_3$)

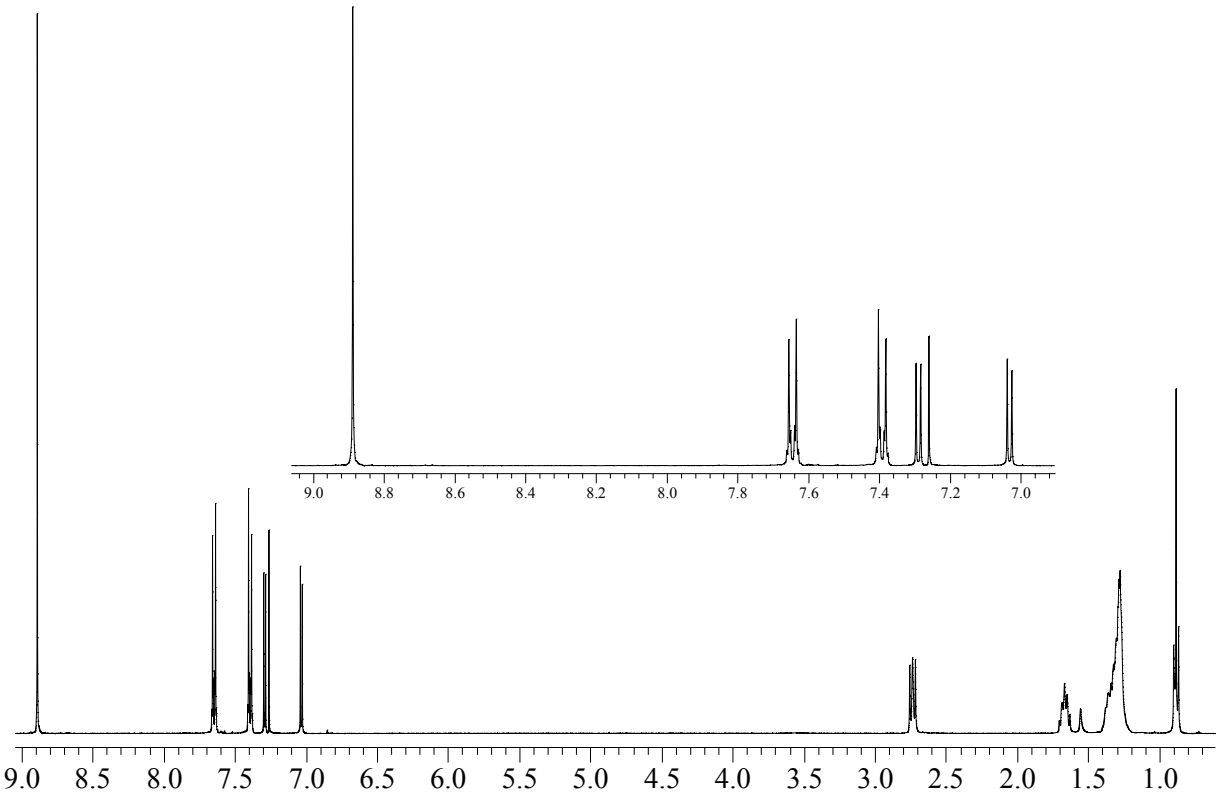


Fig. S2 ^{1}H NMR spectrum of **2** (400MHz, $CDCl_3$)

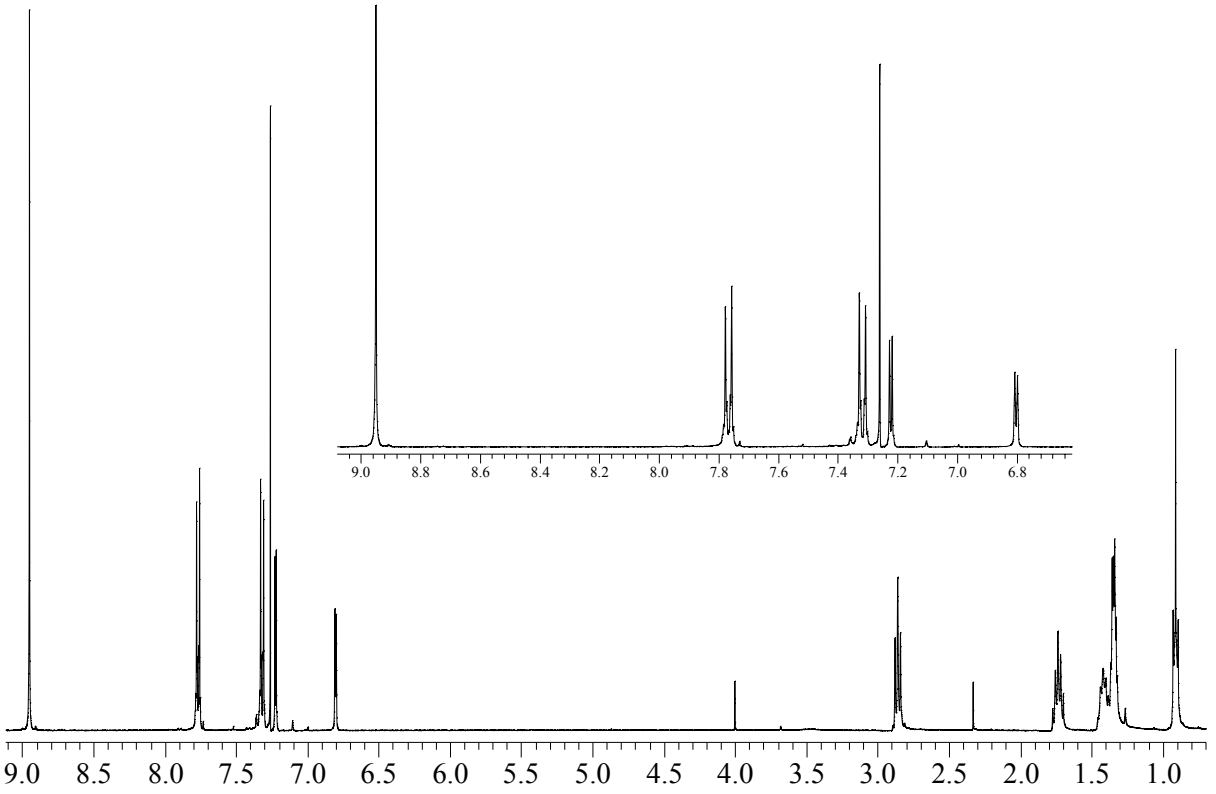


Fig. S3 ^{1}H NMR spectrum of **3** (400MHz, $CDCl_3$ + CF_3COOD)

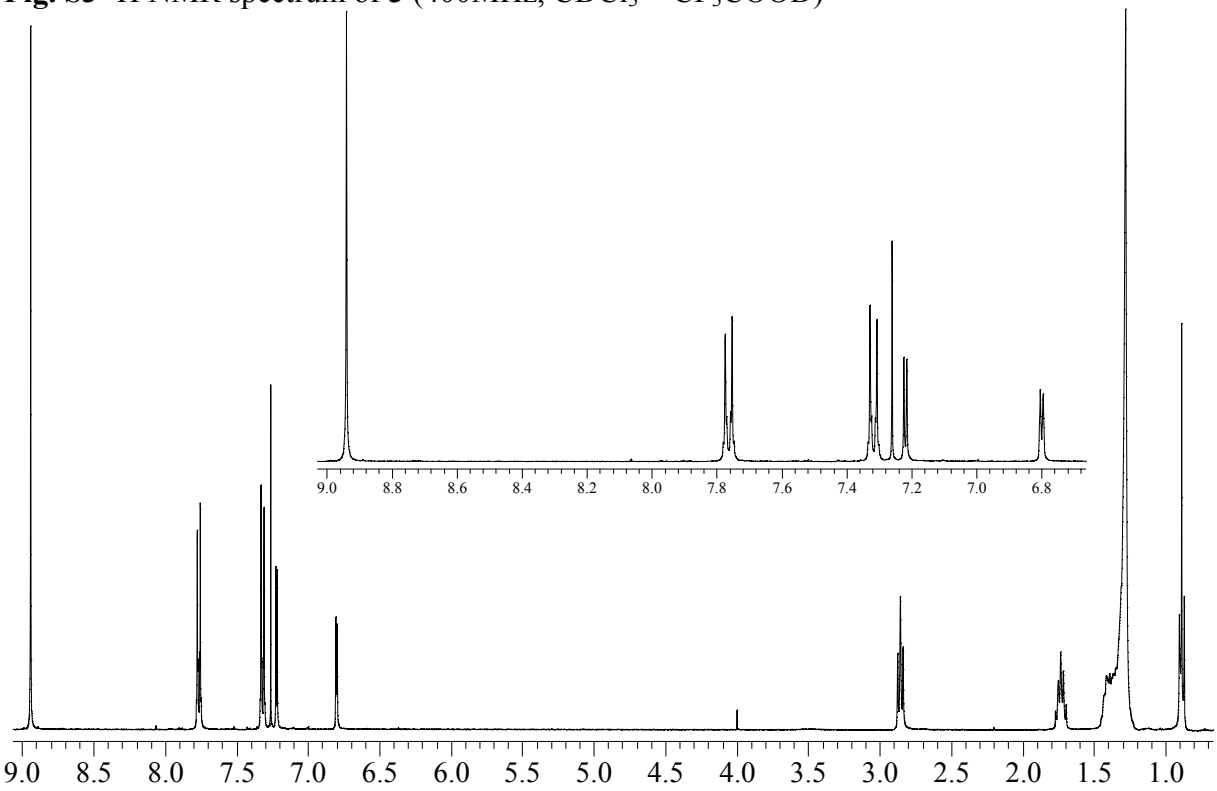


Fig. S4 ^{1}H NMR spectrum of **4** (400MHz, $CDCl_3$ + CF_3COOD)

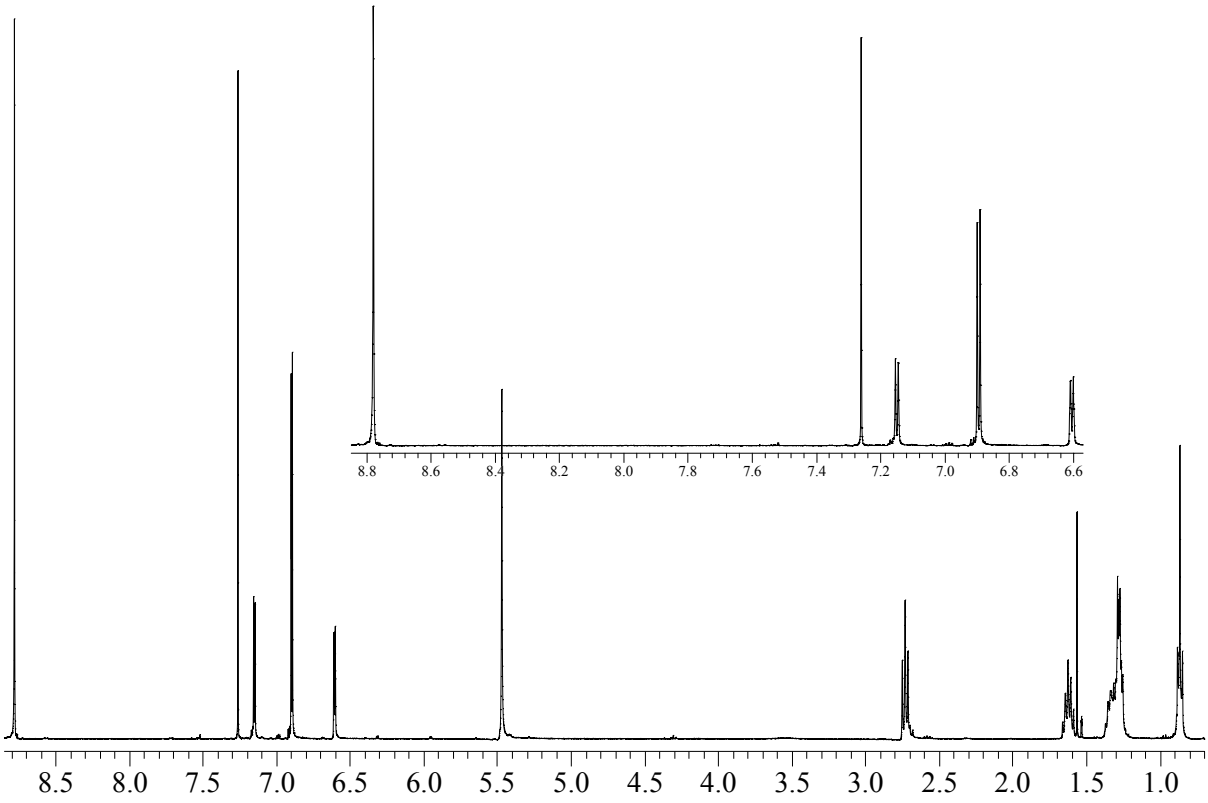


Fig. S5 ^{1}H NMR spectrum of **5** (400MHz, $CDCl_3$)

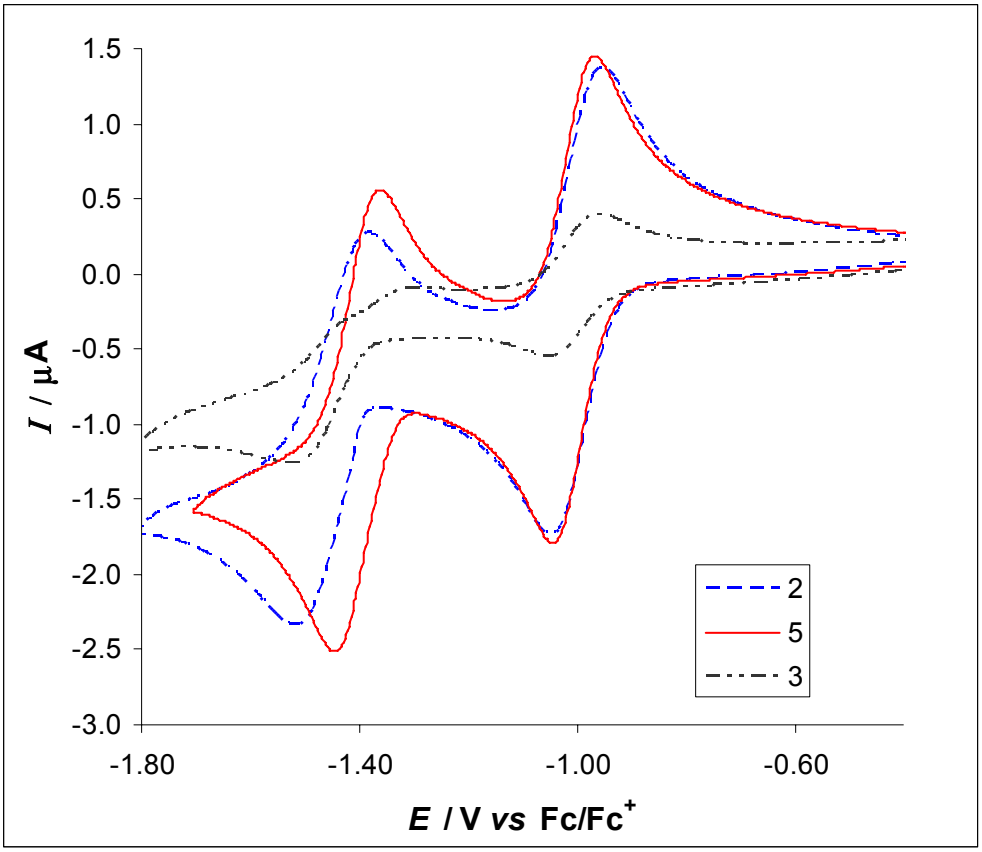


Fig. S6 Cyclic voltammograms of solutions of **5** ($5x10^{-4}$M), **2** ($5x10^{-4}$M) and **3** (~$2x10^{-4}$M, saturated). *E vs* Fc/Fc^{+}; scan rate of 50 mV/s; electrolyte 0.1 M Bu_4NBF_4 in CH_2Cl_2.

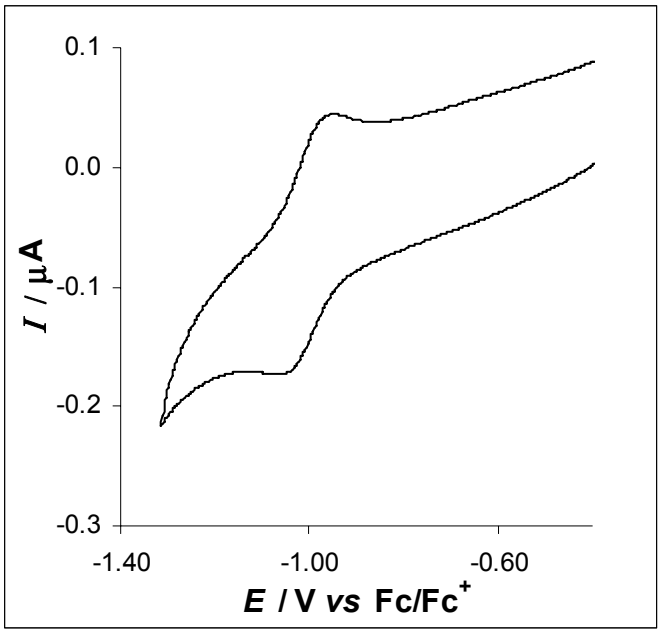


Fig. S7 Cyclic voltammogram of saturated solution of **4** (<0.5x10^{-4}M)**.** *E vs* Fc/Fc^{+}; scan rate of 50 mV/s; electrolyte 0.1 M Bu_4NBF_4 in CH_2Cl_2. The concentration of the bisimide was too low for appropriate recording of CV at lower potentials.

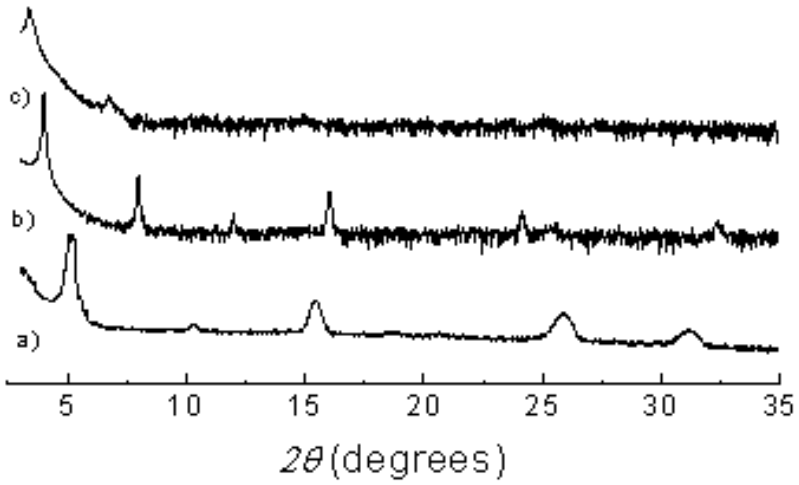


Fig. S8: X-ray profiles obtained in Bragg-Brentano geometry of a) **2** (with no receiving slit), b) **1** and c) **5** (Intensity is in log scale).

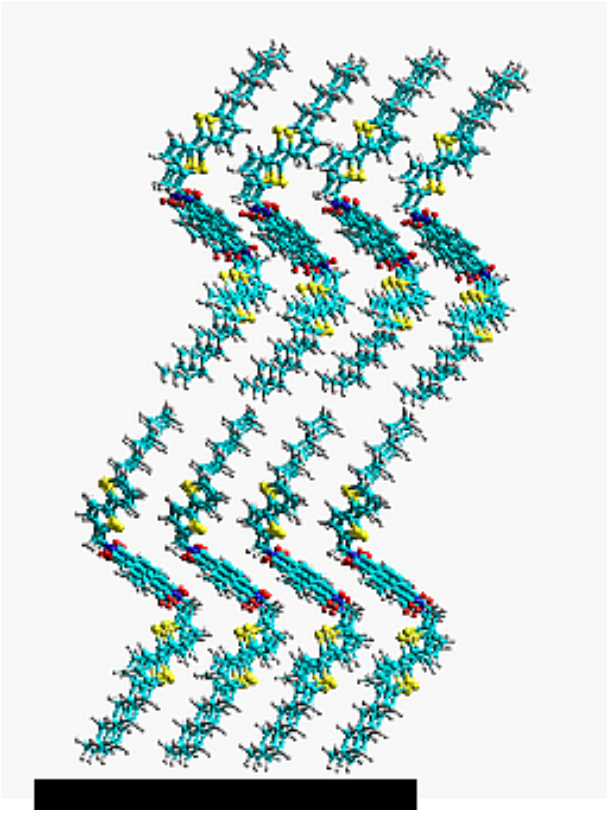


Fig. S9 Molecular stacking of **5** molecules with chair-like conformation.

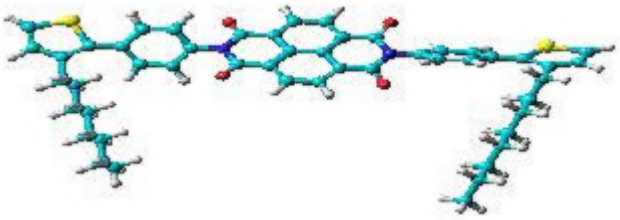


Fig. S10 Optimized geometry of an isolated **2** molecule resulting from MM^{+} calculations (Hyperchem® software).