Supplementary material Ghazzali et al.

**Table S1 Bond lengths for 1-3**

| | **1** | **2** | **3** |
|---|---|---|---|
| S1A-C5A | 1.7099(16) | 1.713(2) | 1.714(7) |
| S1A-C2A | 1.7183(13) | 1.725(2) | 1.738(7) |
| N1A-C1A | 1.2840(18) | 1.283(3) | 1.295(9) |
| N1A-N1A$^{i}$, N1A-N1B | 1.406(2) | 1.403(2) | 1.410(8) |
| C1A-C2A | 1.4451(18) | 1.404(3) | 1.416(9) |
| C2A-C3A | 1.3758(19) | 1.374(3) | 1.363(9) |
| C3A-C4A | 1.421(2) | 1.418(3) | 1.418(9) |
| C4A-C5A | 1.353(2) | 1.359(3) | 1.342(9) |
| S1B-C5B | 1.7039(15) | 1.707(2) | 1.721(7) |
| S1B-C2B | 1.7288(14) | 1.7240(19) | 1.719(7) |
| N1B-C1B | 1.2882(18) | 1.286(3) | 1.304(9) |
| N1B-N1B$^{ii}$ | 1.398(2) | ------ | ----- |
| C1B-C2B | 1.4450(19) | 1.445(3) | 1.449(10) |
| C2B-C3B | 1.370(2) | 1.372(3) | 1.358(9) |
| C3B-C4B | 1.418(2) | 1.417(3) | 1.407(10) |
| C4B-C5B | 1.371(2) | 1.358(3) | 1.348(9) |
| C4A-C5A | 1.353(2) | 1.359(3) | 1.342(9) |
| BrA-CA | ---- | 1.882(2) | 1.871(7) |
| BrB-CB | ---- | 1.8884(19) | 1.871(7) |
| Symmetry transformations used to generate equivalent atoms: (i) -x,-y,-z (ii) -x,-y,-z+1 for **1**. | | | |

**Table S2: Bond angles for 1-3**

| | | | |
|---|---|---|---|
| **1:** | | | |
| C5A-S1A-C2A | 91.59(7) | C5B-S1B-C2B | 91.87(7) |
| C1A-N1A-N1A[i] | 111.73(13) | C1B-N1B-N1B[ii] | 111.77(14) |
| N1A-C1A-C2A | 121.25(12) | N1B-C1B-C2B | 120.30(13) |
| C3A-C2A-C1A | 126.42(13) | C3B-C2B-C1B | 126.94(13) |
| C3A-C2A-S1A | 111.20(10) | C3B-C2B-S1B | 111.20(12) |
| C1A-C2A-S1A | 122.33(10) | C1B-C2B-S1B | 121.83(10) |
| C2A-C3A-C4A | 112.42(14) | C2B-C3B-C4B | 112.44(15) |
| C5A-C4A-C3A | 112.24(13) | C5B-C4B-C3B | 112.56(14) |
| C4A-C5A-S1A | 112.55(11) | C4B-C5B-S1B | 111.92(12) |
| Symmetry transformations used to generate equivalent atoms: (i) -x,-y,-z (ii) -x,-y,-z+1 | | | |
| **2:** | | | |
| C5A-S1A-C2A | 92.16(11) | C5B-S1B-C2B | 91.96(9) |
| C1A-N1A-N1B | 111.23(16) | C1B-N1B-N1A | 112.40(16) |
| N1A-C1A-C2A | 122.12(18) | N1B-C1B-C2B | 119.87(17) |
| C3A-C2A-C1A | 125.92(19) | C3B-C2B-C1B | 127.48(17) |
| C3A-C2A-S1A | 111.22(15) | C3B-C2B-S1B | 111.63(14) |
| C1A-C2A-S1A | 122.80(16) | C1B-C2B-S1B | 120.87(14) |
| C2A-C3A-C4A | 111.7(2) | C2B-C3B-C4B | 111.24(17) |
| C5A-C4A-C3A | 113.88(19) | C5B-C4B-C3B | 114.00(17) |
| C5A-C4A-BrA | 123.77(16) | C5B-C4B-BrB | 121.86(15) |
| C3A-C4A-BrA | 122.30(17) | C3B-C4B-BrB | 124.12(14) |
| C4A-C5A-S1A | 111.00(16) | C4B-C5B-S1B | 111.17(14) |

| **3:** | | | |
|---|---|---|---|
| C5A-S1A-C2A | 90.7(3) | C1B-N1B-N1A | 110.9(6) |
| C1A-N1A-N1B | 112.0(6) | N1B-C1B-C2B | 120.9(7) |
| N1A-C1A-C2A | 122.2(6) | C3B-C2B-C1B | 126.8(7) |
| C3A-C2A-C1A | 127.9(6) | C3B-C2B-S1B | 111.5(5) |
| C3A-C2A-S1A | 110.8(5) | C1B-C2B-S1B | 121.6(5) |
| C1A-C2A-S1A | 121.3(5) | C2B-C3B-C4B | 113.3(6) |
| C2A-C3A-C4A | 113.3(6) | C5B-C4B-C3B | 111.8(6) |
| C5A-C4A-C3A | 111.8(6) | C4B-C5B-S1B | 112.8(5) |
| C4A-C5A-S1A | 113.4(5) | C4B-C5B-BrB | 127.6(5) |
| C4A-C5A-BrA | 127.3(5) | S1B-C5B-BrB | 119.6(4) |

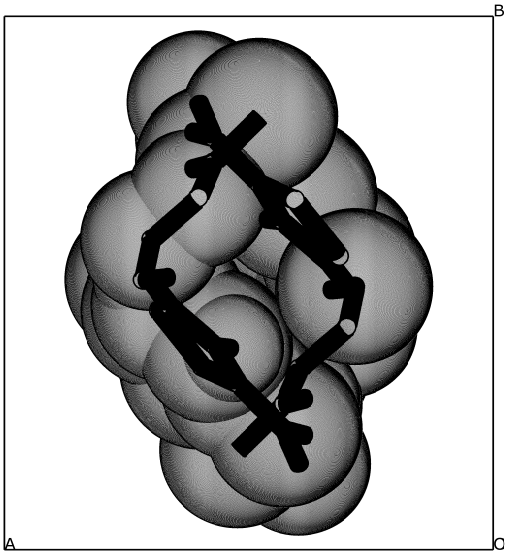


Figure S1. Plot of the van der Waals surfaces of the "walls" of the apparent "channels" in **3** showing that there are no voids in this structure.

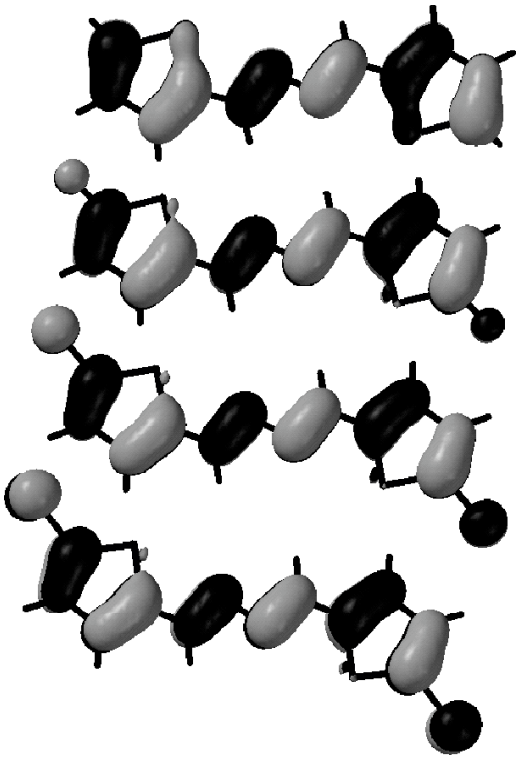

Figure S2. HOMO orbitals for thiophene **1**, and the fluoro **3b**, chloro **3c** and bromo **3** derivatives showing the increased contribution by the halogen orbitals. (Molecular orbital coefficients for the halogens also increase from 0.21 in **3b** to 0.29 in **3**.)

Table S3

**Cartesian coordinates (ångströms) for the DFT optimized structures of 1-3.**

**1**

| | | | | |
|---|---|---|---|---|
| H1 | 1 | 1.3689528 | -0.0094988 | -6.2016137 |
| H2 | 2 | -1.2821677 | -0.0286679 | -6.0372498 |
| C1 | 3 | -0.7262203 | -0.0034455 | 1.5314270 |
| C2 | 4 | 0.7262203 | 0.0034455 | -1.5314270 |
| H3 | 5 | -1.7859275 | -0.0187738 | 1.2053769 |
| S1 | 6 | 1.1667163 | 0.0193158 | 3.5826384 |
| C3 | 7 | -0.4600085 | 0.0035565 | 2.9433268 |
| C4 | 8 | 0.4600085 | -0.0035565 | -2.9433268 |
| H4 | 9 | -2.4788832 | -0.0109785 | 3.7881921 |
| S2 | 10 | -1.1667163 | -0.0193158 | -3.5826384 |
| C5 | 11 | -1.3976955 | -0.0003530 | 3.9736716 |
| C6 | 12 | 1.3976955 | 0.0003530 | -3.9736716 |
| H5 | 13 | 1.7859275 | 0.0187738 | -1.2053769 |
| H6 | 14 | 1.2821677 | 0.0286679 | 6.0372498 |
| C7 | 15 | -0.8058677 | 0.0093953 | 5.2614151 |
| C8 | 16 | 0.8058677 | -0.0093953 | -5.2614151 |
| H7 | 17 | 2.4788832 | 0.0109785 | -3.7881921 |
| N1 | 18 | -0.2322547 | -0.0057246 | -0.6494692 |
| C9 | 19 | 0.5760038 | 0.0199321 | 5.2009417 |
| C10 | 20 | -0.5760038 | -0.0199321 | -5.2009417 |
| N2 | 21 | 0.2322547 | 0.0057246 | 0.6494692 |
| H8 | 22 | -1.3689528 | 0.0094988 | 6.2016137 |

**2**

| | | | | |
|---|---|---|---|---|
| Br1 | 1 | -5.3980477 | 0.3874643 | 4.5356718 |
| Br2 | 2 | 5.4664044 | -0.1467878 | -4.5475454 |
| C1 | 3 | -1.2623677 | 0.2443905 | 1.0169937 |
| C2 | 4 | 1.3417862 | -0.5119526 | -0.9993320 |
| C3 | 5 | -2.1716622 | -0.2519438 | 2.0083846 |
| C4 | 6 | 2.2049978 | 0.0674760 | -1.9896519 |
| C5 | 7 | -3.1625267 | 0.4833732 | 2.6414854 |
| C6 | 8 | 3.2844637 | -0.5306808 | -2.6212847 |
| C7 | 9 | -3.9238237 | -0.3066361 | 3.5312448 |
| C8 | 10 | 3.9255186 | 0.3483575 | -3.5243652 |
| C9 | 11 | -3.5192656 | -1.6203137 | 3.5911922 |
| C10 | 12 | 3.3492402 | 1.5959444 | -3.5867776 |
| H1 | 13 | -1.3573501 | 1.3010662 | 0.7342425 |
| H2 | 14 | 1.5241160 | -1.5497748 | -0.6906816 |
| H3 | 15 | -3.3239719 | 1.5408297 | 2.4589023 |
| H4 | 16 | 3.5898683 | -1.5556914 | -2.4362628 |
| H5 | 17 | -3.9420439 | -2.4224883 | 4.1867325 |
| H6 | 18 | 3.6503052 | 2.4372811 | -4.2015756 |
| N1 | 19 | -0.3617554 | -0.5088576 | 0.4575802 |
| N2 | 20 | 0.3774343 | 0.1871523 | -0.4796119 |
| S1 | 21 | -2.1865528 | -1.9154667 | 2.5385534 |
| S2 | 22 | 1.9967535 | 1.7182812 | -2.5268778 |

**3**

| | | | | |
|---|---|---|---|---|
| H1 | 1 | 2.4422166 | -0.0095120 | -5.8627400 |
| Br1 | 2 | -0.5658357 | -0.0058339 | -6.8340515 |
| C1 | 3 | -1.0182963 | -0.0033496 | 1.3572786 |
| C2 | 4 | 1.0182963 | 0.0033496 | -1.3572786 |
| H2 | 5 | -1.9974149 | -0.0043185 | 0.8384385 |
| S1 | 6 | 0.5020337 | -0.0038779 | 3.6792121 |
| C3 | 7 | -1.0076956 | -0.0030581 | 2.7907509 |
| C4 | 8 | 1.0076956 | 0.0030581 | -2.7907509 |
| H3 | 9 | -3.1368821 | 0.0030003 | 3.2949983 |
| S2 | 10 | -0.5020337 | 0.0038779 | -3.6792121 |
| C5 | 11 | -2.1003199 | 0.0013828 | 3.6544413 |
| C6 | 12 | 2.1003199 | -0.0013828 | -3.6544413 |
| H4 | 13 | 1.9974149 | 0.0043185 | -0.8384385 |
| Br2 | 14 | 0.5658357 | 0.0058339 | 6.8340515 |
| C7 | 15 | -1.7388011 | 0.0044021 | 5.0236273 |
| C8 | 16 | 1.7388011 | -0.0044021 | -5.0236273 |
| H5 | 17 | 3.1368821 | -0.0030003 | -3.2949983 |
| N1 | 18 | -0.0959827 | 0.0004085 | -0.6801662 |
| C9 | 19 | -0.3669776 | 0.0023816 | 5.1790401 |
| C10 | 20 | 0.3669776 | -0.0023816 | -5.1790401 |
| N2 | 21 | 0.0959827 | -0.0004085 | 0.6801662 |
| H6 | 22 | -2.4422166 | 0.0095120 | 5.8627400 |