**Supporting Information for**

# Asymmetric Fused Thiophenes for Field-Effect Transistors: Crystal Structure-Film Microstructure-Transistor Performance Correlations

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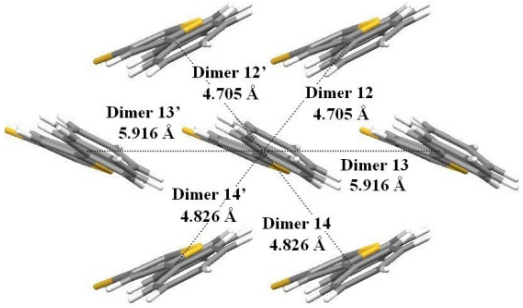
**Table S1.** Summary of Crystal Structure Data for compounds **1-4**.[a]

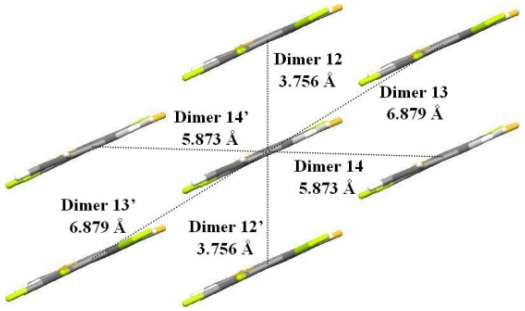
| Compound | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Empirical formula | C20H7F5S3 | C20H12S3 | C28H9F5S6 | C28H14S6 |
| Formula weight | 438.44 | 348.48 | 632.71 | 542.75 |
| Temperature (K)[b] | 100(2) | 200(2) | 296(2) | 296(2) |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | *P*21/*c* | *P*21/*c* | P-1 | P2(1)/c |
| Unit cell dimensions (Å) | a = 5.8734(2)<br>α = 90° | a = 7.468(4)<br>α = 90° | a = 3.8338(5)<br>α = 86.15(1)° | a = 5.9639(18)<br>α = 90° |
| | b = 36.1226(12)<br>β =91.677 (2)° | b = 5.916(3)<br>β =94.01(4)° | b = 5.8334(8)<br>β = 87.92(1)° | b = 7.509(2)<br>β = 92.83(1)° |
| | c = 7.4967(2)<br>γ = 90° | c = 34.719(15)<br>γ = 90° | c = 26.039(4)<br>γ = 87.04(1)° | c = 50.362(15)<br>γ = 90° |
| *V*, Å$^3$ | 1589.85(9) | 1530.15(449) | 579.93(49) | 2252.61(137) |
| *Z* | 4 | 4 | 1 | 4 |
| *d* (calc), g/cm3 | 1.832 | 1.5126 | 1.81154 | 1.60028 |
| Absorption coefficient (mm$^{-1}$) | 0.525 | 0.479 | 0.651 | 0.626 |
| F(000) | 880 | 720 | 318 | 1112 |
| $R_{All}$ | 0.1794 | 0.2708 | 0.1096 | 0.2014 |
| Crystal size (mm) | 0.44 × 0.20 × 0.04 | 0.60 x 0.46 x 0.01 | 0.33 x 0.14 x 0.01 | 0.28 x 0.19 x 0.01 |
| Reflections collected | 30972 | 8859 | 4776 | 12233 |
| Independent reflections | 3658 | 2642 | 2031 | 3592 |
| $R_{int}$ | 0.0554 | 0.1837 | 0.0598 | 0.1507 |
| Final R indices [I>2sigma(I)][c] | R1 = 0.0648<br>wR2 = 0.17 | R1 = 0.1599<br>wR2 = 0.3548 | R1 = 0.0692<br>wR2 = 0.1767 | R1 = 0.0698<br>wR2 = 0.1613 |
| R indices (all data) | R1 = 0.0706<br>wR2 = 0.1789 | R1 = 0.2708<br>wR2 = 0.4062 | R1 = 0.1096<br>wR2 = 0.2001 | R1 = 0.2014<br>wR2 = 0.2479 |

[a] CCD area detector diffractometer; Mo K$\alpha$ radiation; λ = 0.71073 Å. [b] Temperature for data collection. [c] Refinement method: Full-matrix least-squares on F2.

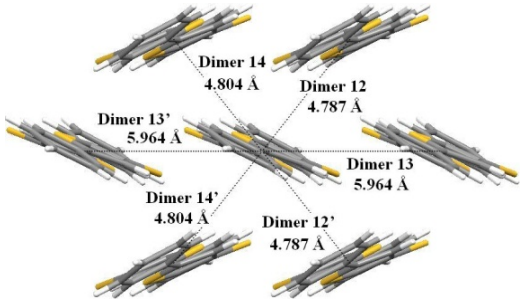
**Table S2.** Centroid-to-centroid distance ($L$) in the crystal strucutures, calculated reorganization energies ($\lambda^+$), electronic couplings ($t^+$), and mobilities ($\mu^+$) for hole transport.



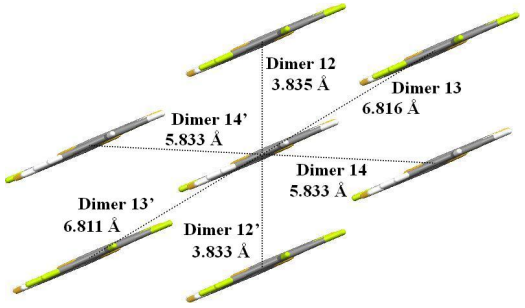

**DP-DTT**




**FPP-DTT**




**DP-BDTT**




**FPP-BDTT**

| Compound | Pair | $L$ (Å) | $\lambda^+$ (eV) | $t^+$ (eV) | $\mu^+$ ($cm^2\ V^{-1}\ s^{-1}$) |
|---|---|---|---|---|---|
| **FPP-DTT(1)** | Dimer12 | 3.76 | 0.258 | 0.178 | 2.35 |
| | Dimer13 | 6.88 | | 0.000 | 0.00 |
| | Dimer14 | 5.87 | | 0.006 | 0.01 |
| **DP-DTT (2)** | Dimer12 | 4.71 | 0.247 | 0.026 | 0.09 |
| | Dimer13 | 5.92 | | 0.001 | 0.00 |
| | Dimer14 | 4.83 | | 0.023 | 0.07 |
| **FPP-BDTT(3)** | Dimer12 | 3.84 | 0.239 | 0.140 | 1.89 |
| | Dimer12’ | 3.83 | | 0.153 | 2.26 |
| | Dimer13 | 6.82 | | 0.000 | 0.00 |
| | Dimer14 | 5.83 | | 0.004 | 0.00 |
| **DP-BDTT(4)** | Dimer12 | 4.79 | 0.237 | 0.025 | 0.10 |
| | Dimer13 | 5.96 | | 0.000 | 0.00 |
| | Dimer14 | 4.80 | | 0.025 | 0.10 |

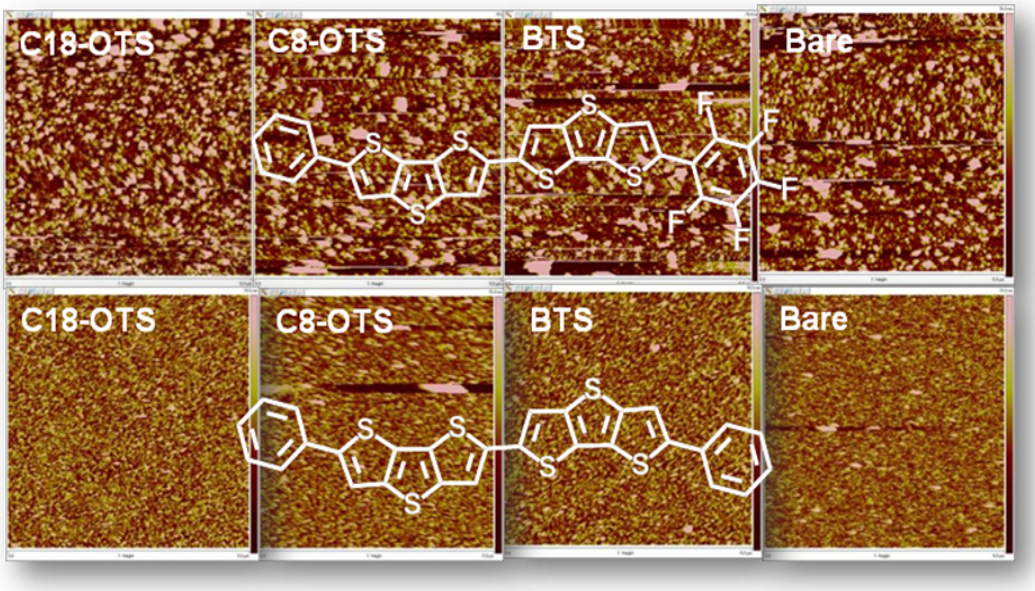



**Figure S1**. AFM images (5 × 5 μm$^2$) of films (50 nm) of **FPP-BDTT** (**3**) and **DP-BDTT** (**4**) on various substrates.

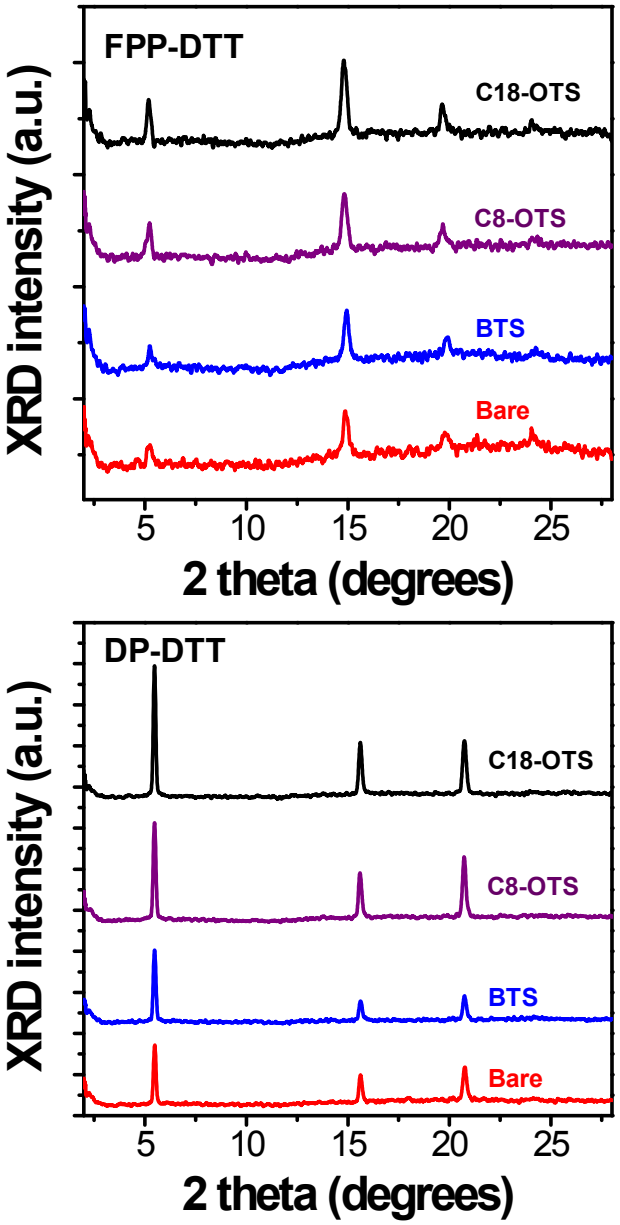



**Figure S2**. X-ray Diffraction pattern of thin films of **FPP-DTT** (**1**) and **DP-DTT** (**2**) on various substrates.