EurJOC
European Journal of Organic Chemistry

Full Papers
doi.org/10.1002/ejoc.202001635

Chemistry Europe
European Chemical Societies Publishing

VIP *Very Important Paper*

Synthesis and Molecular Properties of Partially Fluorinated DNTTs**

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1,2,3,4-Tetrafluoro-dinaphthothienothiophene (F_4DNTT) and 1,2,3,4,8,9,10,11-octafluoro-dinaphthothienothiophene (F_8DNTT) were synthesized via bisthiomethyl alkene intermediates which were accessible by McMurry coupling or Wittig olefination of partially fluorinated naphthalene precursors. DFT-based electronic structure calculations, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and UV/Vis measurements were used for HOMO/LUMO gap determination and to analyze the electronic structures of the partially fluorinated DNTTs. Reduced exciton binding was observed in thin films.

Introduction

The promising potential of using π-conjugated molecules or polymers as active semiconducting material for flexible organic electronics applications such as e.g. rollable displays, cost-effective sensors, or electronic skin has triggered the synthesis of new organic materials suited for such applications.[1] Among the organic semiconductors, pentacene **1** (Figure 1) has long been considered a model system, as it forms well-ordered crystalline films with reasonably high charge carrier mobility that were commonly used to benchmark other organic semiconductors.[2] In addition, the electronic structure of this highly symmetric alternant hydrocarbon can be well-understood by Hückel theory,[3] while also the intermolecular coupling in molecular solids was analyzed theoretically in detail.[4] On the other hand, there are the disadvantages of the larger acenes such as their sensitivity to oxidation and light-induced dimerization of the central ring as well as their low solubility in organic solvents,[5] which complicates their processing in organic electronics. To address these problems, synthetic strategies such as the addition of functional side groups or heterosubstitutions have been developed to enhance chemical stability and processability.[6,7]

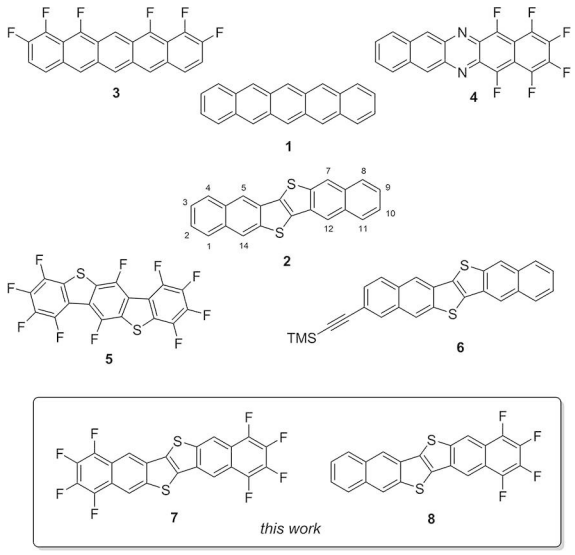

Figure 1. Examples for functionalized pentacenes, benzobisbenzothiophenes, and DNTTs.

A different approach is the substitution of the central ring by chemically more robust moieties such as thienothiophenes,[8] which has led to the synthesis of a new class of diacene-fused thienothiophenes (DAcTT).[9]

Among this new material class, the dinaphthothienothiophene (DNTT) **2** stands out because it combines superior charge carrier mobility with excellent stability against oxidation and chemical decomposition, making it one of the most stable organic semiconductors.[10–13] Increased solubility has also been realized for DNTTs by addition of peripheral side chains.[14] Adjustments of the electronic structure of such π-conjugated systems are possible either through modification of their length[15–17] or incorporation of further thiophene moieties.[9,18–20]

A different, for polycyclic aromatic hydrocarbons well-established, strategy is heteroatom substitution, which allows precise tailoring of the molecular properties.[5,21–23] In particular fluorination has become a common strategy to alter the electronic properties of organic semiconductors,[24] as the polar

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[**] *A previous version of this manuscript has been deposited on a preprint server (DOI: doi.org/10.26434/chemrxiv.13385351.v1)*

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejoc.202001635

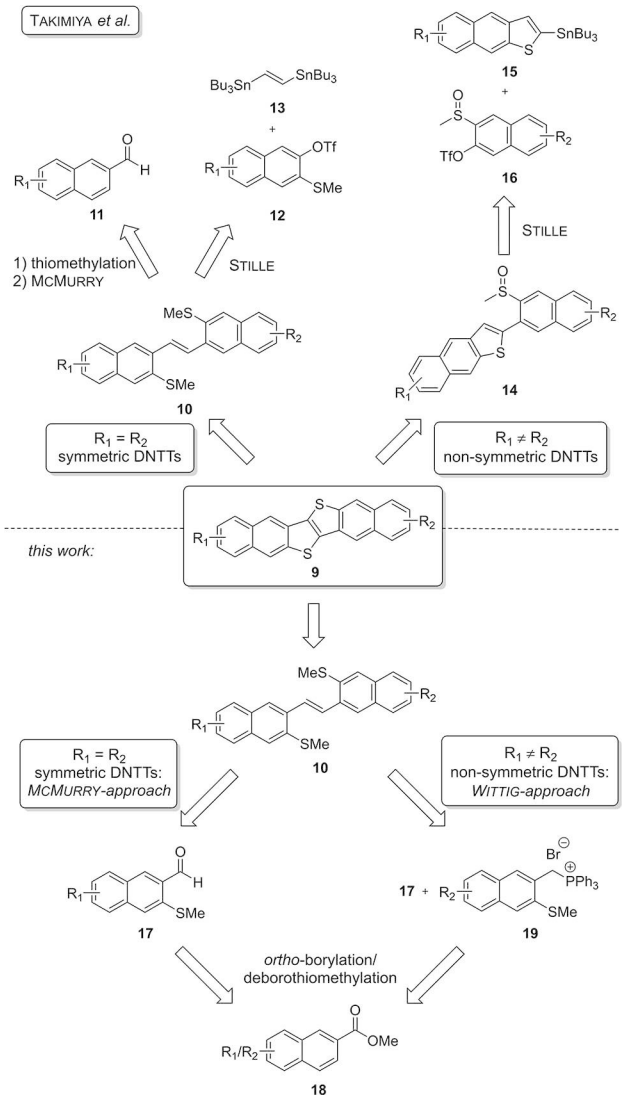
C–F bonds directly lower the energy levels of the π-system and simultaneously change the charge density distribution leading to electron accumulation at the fluorine atoms.[25–30] Partially fluorinated pentacenes **3** and azapentacenes **4** have been studied.[29,30] So far, however, fluorination has rarely been used to functionalize the vast class of thienoacene-based organic semiconductors with **5** as rare example.[31] Here, we introduce partially fluorinated DNTTs **7** and **8**.

We present new synthetic strategies to chemically alter the electronic properties of the more promising semiconductor DNTT by partial fluorination. For the symmetrically fluorinated F_8DNTT (**7**) we utilized a McMurry approach, while for the one-sidedly fluorinated F_4DNTT (**8**) we had to apply a Wittig approach. Using DFT-based electronic structure calculations, NEXAFS, and UV/Vis measurements we observe a similar reduction of the HOMO and LUMO levels, leaving the optical gap virtually unchanged. We also observe a reduced exciton binding energy in thin films. Last, we have analyzed the electronic structure of the DNTTs more in detail, revealing that the carbon K-edge NEXAFS signatures of the DNTTs exhibit characteristic naphthalene-, perfluoro-naphthalene- and thiophene-like features, which may serve as "fingerprints".[32]

Retrosynthetic pathways towards functionalized DNTTs of type **9** are shown in Scheme 1. The group of Takimiya developed different synthetic methods for symmetric as well as non-symmetric DNTTs.[10,14,33–36] For symmetric compounds, an olefinic precursor **10** is used, which can undergo an iodine-promoted double-ring-closing reaction to the corresponding DNTT **9**. In previous studies of Takimiya, the olefinic precursor **10** is built up in an *ortho*-thiomethylation/McMurry-sequence starting from aldehyde **11**.[10] While the McMurry-reaction of these compounds usually works smoothly, the *ortho*-thiomethylation of aldehyde **11** is very tedious, due to the formation of a regioisomer and difficult chromatographic isolation. In 2011, they reported a different strategy for the synthesis of the olefinic precursor **10**, utilizing a double Stille-reaction of triflate **12** with the bis-stannane **13**.[33] While the Stille-reaction gave good to excellent yield, this route also has the advantage, that the introduction of the thiomethyl moiety works with high selectivity in the desired 3-position.

A different strategy had to be developed for the selective synthesis of non-symmetric functionalized DNTT-derivatives. A possible pathway for this problem was shown by Takimiya when the final step of the synthesis is a thio-Friedel-Crafts-type ring-closure of the sulfoxide-precursor **14**.[34] This precursor can be synthesized *via* a Stille-coupling of the functionalized naphthothiophene **15** with triflate **16**, allowing the introduction of a non-symmetric substitution pattern. Takimiya showed the applicability of this route by the selective synthesis of 2-bromo-DNTT, which was derivatized in a late-stage functionalization into different non-symmetric DNTTs, including the TMS-acetylene-compound **6**.[34]

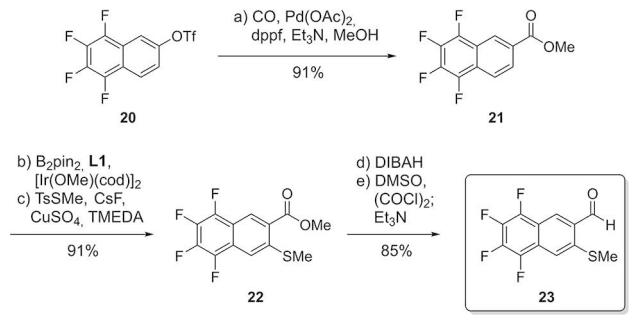
In this contribution, we demonstrate the synthesis of partially fluorinated DNTTs **7** and **8**. In the case of the symmetric F_8DNTT (**7**), we applied the McMurry-approach to build up the olefinic precursor **10**. The aldehyde **17** is, however, synthesized in a highly regioselective *ortho*-borylation/deborothiomethylation-sequence of ester **18**, based on a work by Hosoya.[37] For the synthesis of the non-symmetric F_4DNTT (**8**), a new route was developed, including the synthesis of the olefinic precursor **10** in a Wittig-reaction. The advantage of this route is, that the phosphoniumbromide **19** can also be synthesized utilizing the same strategy, starting from an ester of type **18**.



Scheme 1. Retrosynthesis of functionalized DNTTs.

Results and Discussion

The starting point of the syntheses was the known tetrafluoronaphthyltriflate **20**,[38] that was converted to aldehyde **23** in five steps, which served as a common precursor for both partially fluorinated DNTTs (Scheme 2). The first step was a carbonylative cross coupling[39] of **20** to methyl ester **21**, followed by an iridium catalyzed directed *ortho*-borylation.[40] The crude pinacolboronate was subjected to a deborothiomethylation-procedure[37] to provide thioether **22** in excellent yield



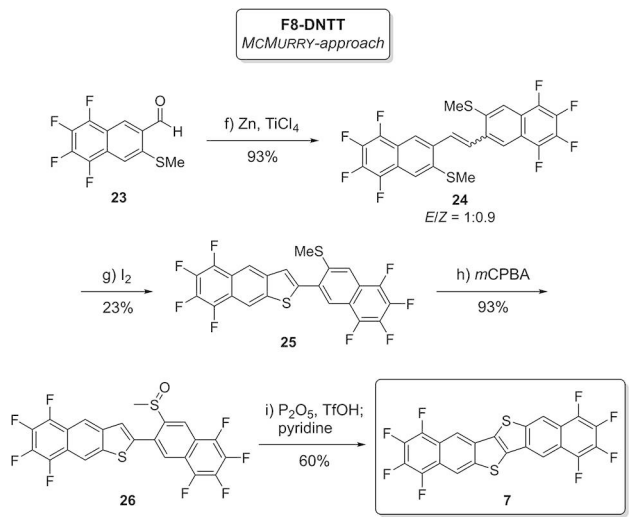
Scheme 2. Synthesis of aldehyde **23**. Reagents and conditions: a) CO (1 atm), $Pd(OAc)_2$ (5 mol%), dppf (10 mol%), Et_3N (2.0 eq), DMF/MeOH, 65 °C, 6 h; b) $[Ir(OMe)(cod)]_2$ (2.5 mol%), **L1** (5 mol%), B_2pin_2 (1.0 eq), THF, 55 °C, 2 h; c) TsSMe (1.2 eq), CsF (2.0 eq), $CuSO_4$ (0.1 eq), TMEDA (0.12 eq), MeOH, 50 °C, 26 h; d) DIBAH (3.0 eq), THF, 0 °C to rt, 20 min; e) $(COCl)_2$ (1.5 eq), DMSO (3.0 eq), CH_2Cl_2, −78 °C, 30 min; Et_3N (5.0 eq), −78 °C, 30 min; rt, 15 min.

and regioselectivity over two steps. Reduction of the ester to the alcohol using DIBAH and reoxidation under Swern-conditions gave aldehyde **23**.

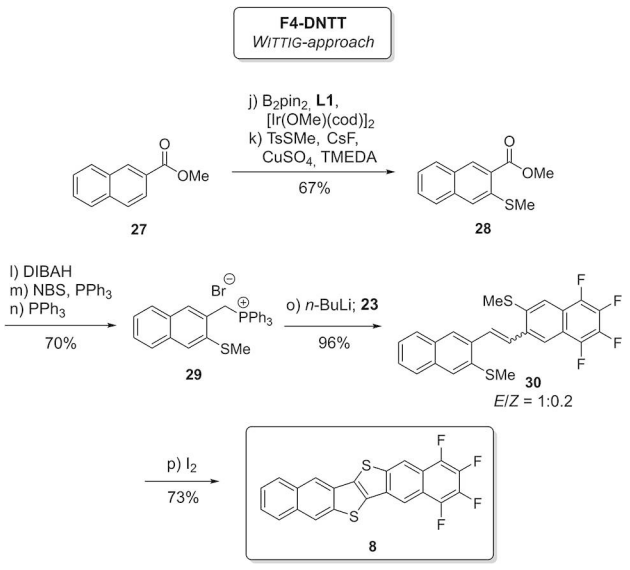
Since the F_8DNTT (**7**) is a symmetric compound, the carbon-backbone can be built up in a McMurry-reaction of aldehyde **23** (Scheme 3). The reaction worked smoothly in 93% yield to obtain the olefinic precursor **24**. Unfortunately, the final double-ring-closing reaction, using an excess of iodine in boiling dichloroethane or acetic acid, did not give the desired DNTT. The main product of the reaction was compound **25**, where only one of the thiophene rings was closed, with the other thiomethyl-group still intact. The thiomethyl-group was then oxidized to the corresponding sulfoxide **26** using *m*CPBA and cyclized in a thio-Friedel-Crafts type reaction[34] to obtain F_8DNTT (**7**).

A different strategy had to be developed for the synthesis of F_4DNTT (**8**). The non-symmetric olefinic precursor **30** could be built up in a Wittig-reaction. The corresponding phosphonium bromide **29** should be accessible in five steps, starting from ester **27**, using the same strategy to introduce the thiomethyl group. For this substrate the *ortho*-borylation/deborothiomethylation sequence to obtain **28** worked in 67% yield over two steps, indicating that the *ortho*-borylation works better for electron-deficient compounds. The ester moiety of **28** was then reduced to the corresponding alcohol and subjected to an Appel-reaction. The benzylic bromide was then refluxed in toluene with PPh_3 to obtain phosphonium bromide **29** in 70% yield over three steps. The following Wittig-reaction with aldehyde **23** worked smoothly, to give alkene **30** in 96% yield. This time, the iodine-promoted cyclization to F_4DNTT (**8**) worked fine in one step with 73% yield (see Scheme 4).

In addition to the chemical synthesis also the optoelectronic properties of the new compounds were analyzed and compared to the unsubstituted DNTT (**2**). At first, we studied the influence of partial fluorination on the electronic structure by means of DFT calculations. The results are visualized in Figure 2. As expected, the fluorine atoms prove to be strongly electron-withdrawing, which affects the charge density distribution within the molecule. In the case of DNTT (**2**) a high electrostatic potential (indicated by blue color) is present at the molecular rim and a low electrostatic potential (indicated by red color) and thus a high electron density appears in the center, while for the fluorinated species also the outer fluorine atoms exhibit a high electron density, yielding a nearly inverted electrostatic potential at the fluorinated aromatic subunits. For F_4DNTT (**8**) the asymmetric functionalization even leads to a permanent molecular dipole moment of $|\mathbf{p}| = 4.26$ D, which is slightly smaller than the dipole moment of related fluoroazaacenes (tetrafluorodiazatetracene: $|\mathbf{p}| = 4.31$ D, hexafluorodiaza-



Scheme 3. Synthesis of F_8DNTT **7**. Reagents and conditions: f) $TiCl_4$ (3.0 eq), Zn (3.0 eq), THF, 0 °C to 66 °C, 3 h; **23** (1.0 eq), rt to 66 °C, 14 h; g) I_2 (29.0 eq), $(CH_2Cl)_2$, 84 °C, 22 h; h) *m*CPBA (1.0 eq), CH_2Cl_2, 0 °C to rt, 26 h; i) P_2O_5 (1.0 eq), TfOH, rt, 3 d; pyridine, 115 °C, 23 h.



Scheme 4. Synthesis of F_4DNTT **8**. Reagents and conditions: j) $[Ir(OMe)(cod)]_2$ (2.5 mol%), **L1** (5 mol%), B_2pin_2 (1.0 eq), THF, 55 °C, 22 h; k) TsSMe (1.2 eq), CsF (2.0 eq), $CuSO_4$ (0.1 eq), TMEDA (0.12 eq), MeOH, 50 °C, 22 h; l) DIBAH (3.0 eq), THF, 0 °C to rt, 2 h; m) NBS (2.0 eq), PPh_3 (2.0 eq), CH_2Cl_2, 0 °C, 1 h; n) PPh_3 (1.2 eq), toluene, 110 °C, 17 h; o) **29** (1.1 eq), *n*-BuLi (1.09 eq), THF, 0 °C, 30 min; **23** (1.0 eq), 0 °C to rt, 15 min; p) I_2 (29.0 eq), AcOH, 118 °C, 21 h.

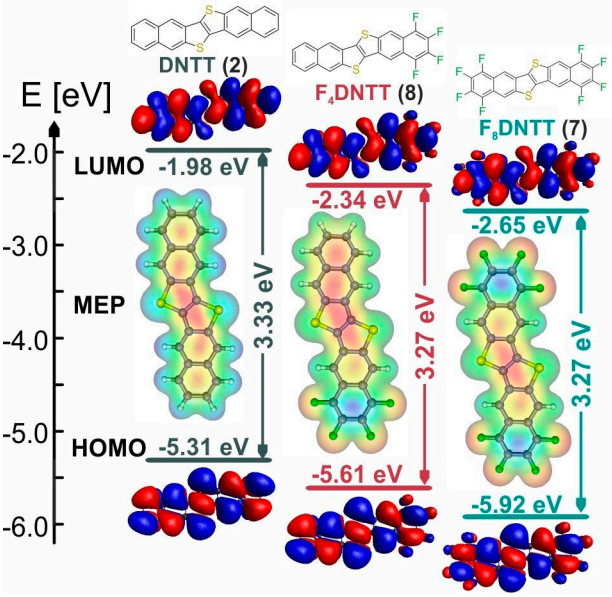


Figure 2. Comparison of calculated energy levels, frontier orbitals HOMO and LUMO, and molecular electrostatic potentials (MEPs) of DNTT (**2**), F_4DNTT (**8**), and F_8DNTT (**7**) obtained by DFT at the B3LYP/6-311G(d,p) level.

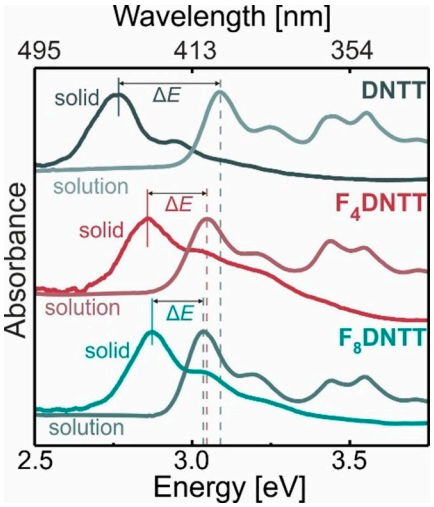


Figure 3. UV/Vis spectra of DNTT (**2**), F_4DNTT (**8**), and F_8DNTT (**7**) in solution (saturated solution in CH_2Cl_2) and as solid films evaporated onto quartz glass substrates. The dashed lines indicate the energy of the lowest absorption band (optical gap). Arrows visualize the exciton binding energies (ΔE).

pentacene **4**: $|\mathbf{p}| = 5.27$ D).[29] The electron withdrawing effect of the fluorine atoms leads to a reduction of the electron density at the carbon atoms that not only affects the electrostatic potential through the frontier orbitals but also increases the C1s binding energy upon fluorination, which transfers in the sense of Hückel theory to a larger Coulomb integral.[3] This leads to a lowering of the energy levels of the π-system, including the frontier orbitals HOMO and LUMO. Interestingly, in the case of the partially fluorinated DNTTs, the energy levels of both frontier orbitals are lowered almost equally, so that the optical gap changes only marginally. According to Hückel theory, this effect is expected for alternant hydrocarbons[25] and has been verified experimentally for other fluorinated organic semiconductors such as e.g. acenes, rubrene, and hexabenzocoronene.[26–30] The presently observed effect of an (approximately) equal energetically reduction of both frontier orbitals due to fluorination, even in the case of non-alternant hydrocarbons such as DNTT, suggests that partial fluorination generally leads to a reduction in both frontier orbitals for π-conjugated molecules.

The molecular HOMO-LUMO gap was experimentally obtained by optical spectroscopy. UV/Vis solution spectra (cf. Figure 3) yield HOMO-LUMO gaps of 3.09 eV (DNTT (**2**)), 3.04 eV (F_4DNTT (**8**)) and 3.03 eV (F_8DNTT (**7**)), respectively. Hence the experimental data show only a slight reduction of the HOMO-LUMO gap and are qualitatively consistent with the DFT calculations. Since for device applications the optical solid-state properties are more relevant, we also carried out UV/Vis absorption measurements on solid molecular thin films of about 50 nm evaporated under vacuum conditions onto quartz slides. As depicted in Figure 3, the transmission absorption spectra exhibit new bands below the HOMO-LUMO transition, which can be assigned to excitonic excitations in the solid. The exciton binding energies, which can be approximated by the difference between the lowest energy excitation in solution and in the solid (indicated as ΔE in Figure 3), are notably smaller for the partially fluorinated molecules when compared to the non-fluorinated pendent DNTT (**2**) (DNTT: 330 meV F_4DNTT (**8**): 180 meV, F_8DNTT (**7**): 160 meV). Hence the optical solid-state properties are modified notably upon fluorination, as also observed for partially fluorinated acenes, which could be attributed to a changed packing motif in the respective molecular solids.[30,41] Unfortunately, a crystal structure analysis that would rationalize this effect has not yet been possible, because the crystallites obtained so far are too small. This is in line with our observation that fluorinated aromatic molecules generally tend to crystallize in smaller crystallites than their non-fluorinated pendants.[30]

To obtain deeper insights into the nature of unoccupied electronic states, we have utilized NEXAFS spectroscopy. The carbon K- edge NEXAFS spectrum of F_4DNTT (**8**) (cf. Figure 4a) exhibits sharp π*-resonances, which can be assigned to excitations from C1s core levels into unoccupied molecular π-orbitals, and broad resonances corresponding to excitations in unoccupied σ-orbitals. The comparison of the magnified π* region of the differently fluorinated DNTTs (cf. Figure 4b) shows that some resonances appear at unchanged positions, while others occur only for the fluorinated species. This is particularly pronounced for F_4DNTT (**8**), which exhibits final states with mixed character, as it has also been observed also for unilaterally fluorinated acenes.[30] As DNTT topologically consists of naphthalene and thiophene units, a comparison of the corresponding signatures is useful. Indeed, the NEXAFS spectrum of DNTT can be well-described by the NEXAFS signatures of these units,[42,43] as indicated by the dashed lines (blue: naphthalene-like resonance, orange: thiophene-like resonance,

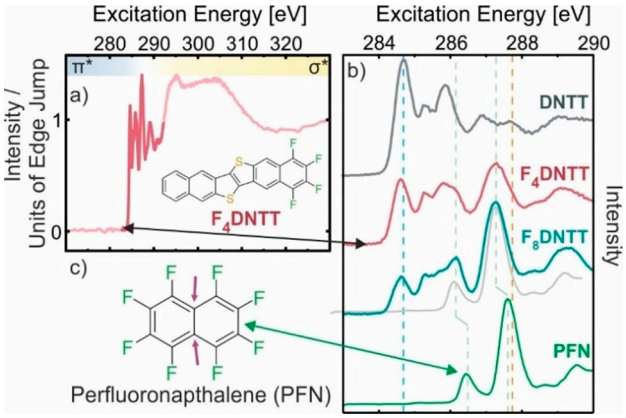


Figure 4. Summary of carbon K-edge NEXAFS data of the differently fluorinated DNTTs obtained for their solid films grown on SiO_2 substrates and recorded at an incident angle of 55°. a) NEXAFS spectrum of a thin film of F_4DNTT (**8**) prepared on SiO_2. b) Comparison of the leading NEXAFS resonances of DNTT (**2**), F_4DNTT (**8**), F_8DNTT (**7**), and perfluoronaphthalene (PFN, which is shown in c) and taken from ref. [44]). The gray line represents an energetically shifted PFN spectrum, which resembles the features of F_8DNTT at energies larger than 286 eV surprisingly well.

more details are given in Supp. Inf.). In addition, the carbon K-edge NEXAFS spectrum of F_8DNTT (**7**) can be well described by the spectra of DNTT and perfluoronaphthalene, since F_8DNTT (**7**) consists of thiophene units and semifluorinated naphthalene units, which impressively shows that more complex NEXAFS spectra can be understood by the analysis of characteristic NEXAFS signatures of subunits, which serve as "fingerprints". We note that the comparison of F_8DNTT (**7**) with perfluorobenzene would not be sufficient, as the resonance at 286.4 eV results from carbon atoms not directly bond to fluorine atoms (indicated by purple arrow in panel (c)).[44] More details on the comparison of DNTT NEXAFS spectra with naphthalene and thiophene NEXAFS spectra as well as a topological justification of the high chemical stability and low lying HOMO of DNTT-derivatives based on Hückel theory are presented in the supporting information.

Conclusion

In conclusion, the syntheses of two partially fluorinated DNTTs 1,2,3,4-tetrafluoro-dinaphthothienothiophene (F_4DNTT (**8**) and 1,2,3,4,8,9,10,11-octafluoro-dinaphthothienothiophene (F_8DNTT (**7**)) were accomplished via McMurry coupling or Wittig olefination of partially fluorinated naphthalene precursors and subsequent formation of the thienothiophene core. The electron-withdrawing character of the fluorine atoms strongly modifies the charge distribution and leads to a likewise reduction of both frontier orbital energy levels, thus only slightly reducing the optical bandgap. As DNTTs are non-alternant π-conjugated molecules, this appears to be a general effect of fluorination. Furthermore, the carbon K-edge NEXAFS spectra of these compounds can roughly be built up from the units naphthalene, thiophene, and perfluoronaphthalene, examining that the analysis of characteristic subunits can be used to shed a light on the electronic structure of such extended π-conjugated systems. The high chemical stability of the (partially fluorinated) DNTTs can be attributed to the low-lying HOMO originating from the topological structure of these molecules.

Experimental Section

General Information. All anhydrous reactions were carried out using flame-dried glassware under argon atmosphere. All solvents were distilled by rotary evaporation. THF for anhydrous reactions was dried with KOH and subsequently distilled from sodium/benzophenone and from Solvona® respectively. All other solvents employed under anhydrous and/or anaerobic conditions were bought in anhydrous form. All commercially available reagents and reactants were used without further purification unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) using MERCK Silica Gel 60 F254 and visualized by fluorescence quenching under UV-light. In addition, TLC-plates were stained using a cerium sulfate/phosphomolybdic acid stain or a potassium permanganate stain. Chromatographic purification of products was performed on MACHEREY-NAGEL Silica Gel 60 (230–400 mesh) using a forced flow of eluents. All crude products were adsorbed onto silica by dissolving in an appropriate solvent and removing the solvent under reduced pressure. Concentration under reduced pressure was performed by rotary evaporation at 40 °C and appropriate pressure and by exposing to high vacuum at room temperature if necessary.

NMR-Spectroscopy. NMR-spectra were recorded on a BRUKER AVIII HD250, AVII 300, AVIII HD300, AVIII 500, or AVIII HD500 spectrometer at room temperature unless otherwise mentioned. Chemical shifts are reported in ppm with the solvent resonance as internal standard. All reported ^{19}F-NMR spectra are proton decoupled ^{19}F{^{1}H}-measurements and referenced to external $CFCl_3$. Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet and combination thereof. All correlations of atoms from NMR spectra of new compounds could be achieved via additional 2D-NMR data (HSQC- and HMBC-spectra) which is not shown within these SI. All ^{13}C{^{19}F} spectra were recorded on AVIII 500 equipped with a 5 mm BBO (broadband observation) Cryo probe Prodigy. Due to the very low solubility in most routine solvents, some ^{13}C{^{1}H} and ^{13}C{^{19}F} spectra were taken in deuterated 1,1,2,2-tetrachloroethane at elevated temperatures, whereby ^{1}H and ^{13}C chemical shifts of 5.98 ppm and 73.8 ppm relative to TMS were used for internal calibration.

High Resolution Mass Spectrometry. HR-ESI and APCI mass spectra were acquired with a Finnigan LTQ-FT Ultra mass spectrometer (THERMO FISCHER SCIENTIFIC). EI mass spectra were acquired with an AccuTOF GCv (JEOL) mass spectrometer.

Infrared Spectroscopy. FT-IR spectra were recorded on a BRUKER IFS 200 spectrometer. Intensities are reported as follows: s = strong, m = medium, w = weak.

Melting Points. Melting points were determined on an MP70 (METTLER TOLEDO) using one end closed capillary tubes.

UV-Vis-Spectroscopy. The optical UV/Vis absorption spectra in solution have been acquired using an Agilent 8453 spectrometer. The absorption spectra of the thin films have been obtained using an OceanOptics HDX-HR spectrometer.

Ligands and Reagents. For the synthesis of TsSMe and ligand **L1**, see SI.

Thin film preparation. The organic thin films (DNTT, Sigma-Aldrich, purity 99%, and the synthesized fluorinated DNTTs) were grown under high vacuum conditions by organic molecular beam deposition (OMBD) from aluminium crucibles of resistively heated Knudsen cells. Transparent quartz substrates (MicroChemicals) were used for optical measurements, whereas natively oxidized Si(100) wafers (Siegert Wafers, referred to as SiO_2) were used as substrates for NEXAFS measurements. The substrates were cleaned by rinsing in ethanol and acetone and heated in vacuum before film deposition. The film growth rates were monitored by a quartz crystal microbalance (QCM) and processed at rates of about 4 Å min^{-1}.

NEXAFS-Spectroscopy. The NEXAFS measurements were carried out at the HE-SGM dipole beamline of the synchrotron storage ring BESSY II in Berlin (Germany), which provides linearly-polarized light (polarization factor = 0.91 and an energy resolution at the carbon K-edge of about 300 meV). All NEXAFS-spectra were recorded in partial electron-yield (PEY) mode at a sample orientation of 55° (magic angle) using a channel-plate detector with a retarding field of −150 V. The acquired spectra were normalized by considering the transmission of the beamline and energy-calibrated via a reference signal. All samples for the NEXAFS measurements were prepared without contact to air in order to prevent effects from contaminations. Details on the experimental setup and data evaluation of NEXAFS measurements are provided in literature.[45]

Quantum Chemical Calculations. The electronic structures of compounds DNTT, F_4DNTT (**8**) and F_8DNTT (**7**) have been analyzed theoretically in the frame of DFT-calculations carried out with an 6-311G(d,p) basis set, using the B3LYP functional as implemented in the US GAMESS-code.[46–47] In each case the structure of the individual molecules (i.e. gas phase) was optimized using the highest available symmetry. Based on these data precise energy levels and dipole moments, as well as frontier orbitals and molecular electrostatic potentials (MEPs) are derived. The orbital visualizations were performed with the MacMolPlt package,[48] whereas the MEPs are generated by Molekel.[49]

Synthesis of F_8DNTT (7)

5,6,7,8-Tetrafluoronaphthalen-2-yl trifluoromethanesulfonate (20)

n-BuLi (2.5 M in hexane, 1.60 mL, 4.00 mmol, 2.00 eq) was added dropwise to a solution of 3-methoxythiophene (0.20 mL, 2.00 mmol, 1.00 eq) and bromopentafluorobenzene (0.62 mL, 5.00 mmol, 2.50 eq) in *n*-pentane (10 mL) at −20 °C. The suspension was allowed to warm up to rt over 3 h and Et_2O (50 mL) was added. The mixture was washed successively with 2 M aq. HCl (20 mL), 13w % aq. NaOCl (20 mL), 1 M aq. NaOH (20 mL) and brine (15 mL). The organic layer was dried over $MgSO_4$ and the crude product was adsorbed onto silica and purified *via* column chromatography (*n*-pentane) to obtain 1,2,3,4-tetrafluoro-6-methoxy-naphthalene (255 mg, 1.11 mmol, 56%) as light yellow solid. The analytical data were in agreement with the literature.[38] R_f = 0.32 (*n*-pentane). ^{1}H-NMR (250 MHz, CD_2Cl_2): δ = 7.95 (d, *J* = 8.8 Hz, 1H, *H4*), 7.29–7.24 (m, 2H, *H1* & *H3*), 3.94 (s, 3H, O*Me*) ppm. ^{19}F-NMR (235 MHz, CD_2Cl_2): δ = −151.3 (dd, *J* = 19.1, 15.5 Hz, 1F), −152.5 (t, *J* = 16.7 Hz, 1F), −160.0 (t, *J* = 18.6 Hz, 1F), −164.6 (t, *J* = 18.9 Hz, 1F) ppm.

BBr_3 (1 M in CH_2Cl_2, 4.31 mL, 4.31 mmol, 4.00 eq) was added to a solution of 1,2,3,4-tetrafluoro-6-methoxy-naphthalene (248 mg, 1.08 mmol, 1.00 eq) in CH_2Cl_2 (15 mL) at 0 °C. The solution was allowed to warm to rt and was stirred for 22 h. The mixture was cooled to 0 °C before H_2O (50 mL) and Et_2O (100 mL) were added. The layers were separated and the aqueous layer was extracted with Et_2O (30 mL). The combined organic layers were washed with brine (30 mL) and dried over $MgSO_4$. The crude product was adsorbed onto silica and purified *via* column chromatography (*n*-pentane/EtOAc 5:1) to give 5,6,7,8-tetrafluoronaphthalen-2-ol (174 mg, 806 µmol, 75%) as brownish solid. The analytical data were in agreement with the literature.[38] R_f = 0.52 (*n*-pentane/EtOAc 5:1). ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 9.1 Hz, 1H, *H4*), 7.32–7.31 (m, 1H, *H1*), 7.20 (dd, *J* = 9.1, 2.2 Hz, 1H, *H3*), 5.23 (s, 1H, O*H*) ppm. ^{19}F-NMR (235 MHz, $CDCl_3$): δ = −150.3 (dd, *J* = 18.6, 15.8 Hz, 1F), −151.8 (dd, *J* = 17.3, 15.5 Hz, 1F), −158.4 (t, *J* = 18.6 Hz, 1F), −163.1 (t, *J* = 18.8 Hz, 1F) ppm.

Tf_2O (1.60 mL, 9.50 mmol, 1.30 eq) was added dropwise to a solution of 5,6,7,8-tetrafluoronaphthalen-2-ol (1.58 g, 7.31 mmol, 1.00 eq) and pyridine (0.89 mL, 11.0 mmol, 1.50 eq) in CH_2Cl_2 (28 mL) at 0 °C. The solution was stirred for 45 min at 0 °C before sat. aq. $NaHCO_3$ (50 mL) was added. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were washed with 2 M aq. HCl (50 mL) and dried over $MgSO_4$. The crude product was adsorbed onto silica and purified *via* column chromatography (*n*-pentane) to obtain triflate **20** (2.39 g, 6.86 mmol, 94%) as a colorless solid. The analytical data were in agreement with the literature.[38] R_f = 0.61 (*n*-pentane/EtOAc 50:1). ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 9.3 Hz, 1H, *H4*), 7.97 (s, 1H, *H1*), 7.52 (dd, *J* = 9.3, 2.2 Hz, 1H, *H3*) ppm. ^{19}F-NMR (235 MHz, $CDCl_3$): δ = −72.6 (s, 3F, C*F*$_3$), −147.9–−148.1 (m, 2F), −154.6–−154.8 (m, 1F), −155.6–−155.8 (m, 1F) ppm. m.p.: 74 °C (EtOAc).

Methyl 5,6,7,8-tetrafluoro-2-naphthoate (21)

Triflate **20** (1.05 g, 3.02 mmol, 1.00 eq), dppf (166 mg, 0.30 mmol, 0.10 eq) and $Pd(OAc)_2$ (33.7 mg, 0.15 mmol, 0.05 eq) were dissolved in DMF (5.0 mL) in a 100 mL Schlenk flask and Et_3N (0.84 mL, 6.04 mmol, 2.00 eq) and MeOH (2.8 mL) were added. The mixture was degassed and purged with CO (3×) and then stirred at 65 °C for 6 h. H_2O (50 mL) and brine (10 mL) were added and the mixture was extracted with Et_2O (3×60 mL). The combined organic layers were washed with 2 M aq. HCl (40 mL) and brine (30 mL) and dried over $MgSO_4$. The crude product was adsorbed onto silica and purified *via* column chromatography (*n*-pentane/EtOAc 29:1) to obtain ester **21** (706 mg, 2.73 mmol, 91%) as colorless solid. R_f = 0.46 (*n*-pentane/EtOAc 20:1). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.79 (s, 1H, *H1*), 8.18 (d, *J* = 8.9 Hz, 1H, *H3*), 8.11 (d, *J* = 8.9 Hz, 1H, *H4*), 4.01 (s, 3H, CO_2*Me*) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 166.1 (s, 1 C, *C*O_2Me), 142.2 (dddd, *J* = 252.4, 10.4, 5.0, 2.6 Hz, 1 C, *C*F), 143.0 (dddd, *J* = 253.8, 10.3, 5.0, 2.8 Hz, 1 C, *C*F), 139.5 (dtd, *J* = 256.1, 15.0, 3.0 Hz, 1 C, *C*F), 138.4 (dtd, *J* = 254.3, 15.6, 2.7 Hz, 1 C, *C*F), 129.3 (s, 1 C, *C2*), 127.1 (s, 1 C, *C3*), 123.2–123.1 (m, 1 C, *C1*), 121.7–121.5 (m, 1 C, C_q), 120.8–120.7 (m, 1 C, *C4*), 119.1 (dd, *J* = 14.6, 3.9 Hz, 1 C, C_q), 52.8 (s, 1 C, CO_2*Me*) ppm. ^{19}F-NMR (283 MHz, $CDCl_3$): δ = −147.4–−147.5 (m, 1F), −148.8–−149.0 (m, 1F), 154.3 (dt, *J* = 18.5, 2.0 Hz, 1F), −156.8–−156.9 (m, 1F) ppm. HRMS (EI^+): *m/z* calc. for $C_{12}H_6F_4O_2$ $[M]^+$: 258.03039, found: 258.02913. FT-IR: film; $\tilde{\nu}$ = 3098 (w), 3058 (w), 3022 (w), 2961 (w), 1723 (s), 1667 (w), 1617 (w), 1518 (w), 1492 (s), 1459 (m), 1422 (w), 1367 (s), 1299 (m), 1278 (w), 1249 (m), 1193 (w), 1132 (w), 1106 (m), 1037 (m), 995 (w), 954 (m), 910 (w), 853 (w), 816 (w), 772 (w), 753 (w), 715 (w), 672 (w), 637 (w), 536 (w), 448 (w) cm^{-1}. m.p.: 74 °C (EtOAc).

Methyl 5,6,7,8-tetrafluoro-3-(methylthio)-2-naphthoate (22)

A solution of ester **21** (323 mg, 1.25 mmol, 1.00 eq), B_2pin_2 (317 mg, 1.25 mmol, 1.00 eq), $[Ir(OMe)(COD)]_2$ (20.5 mg, 0.03 mmol, 0.025 eq) and ligand **L1** (23.3 mg, 0.06 mmol, 0.05 eq) in THF (1.6 mL) was degassed and purged with argon (3×) and stirred at 55 °C. After 2 h

sat. aq. NH_4Cl (30 mL) and H_2O (10 mL) were added and the mixture was extracted with EtOAc (3×30 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, and filtered over a short plug of celite and silica. The solvent was removed under reduced pressure and the crude methyl-5,6,7,8-tetrafluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthoate was used in the next step without further purification. ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 8.68 (s, 1H, *H1*), 8.18 (s, 1H, *H4*), 4.00 (s, 3H, CO_2*Me*), 1.47 (s, 12H, 4×CH_3) ppm. ^{19}F-NMR (235 MHz, $CDCl_3$): δ = −148.3 (t, *J* = 17.3 Hz, 1F), −149.3 (t, *J* = 17.3 Hz, 1F), −154.8 (t, *J* = 18.5 Hz, 1F), −156.7 (t, *J* = 18.4 Hz, 1F) ppm. ^{11}B-NMR (160 MHz, $CDCl_3$): δ = 22.31 (s, 1B) ppm. HRMS (EI$^+$): *m/z* calc. for $C_{18}H_{17}BF_4O_4$ [M]$^+$: 384.11560, found: 384.11594.

TMEDA (22.6 µL, 0.15 mmol, 0.12 eq) was added to a suspension of methyl-5,6,7,8-tetrafluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthoate (crude, ~1.25 mmol, 1.00 eq), TsSMe (303 mg, 1.50 mmol, 1.20 eq), $CuSO_4$ (21 mg, 0.13 mmol, 0.10 eq) and CsF (380 mg, 2.50 mmol, 2.00 eq) in MeOH (12.7 mL). The mixture was stirred at 50 °C for 26 h and was then filtered over a short plug of celite and rinsed with EtOAc (150 mL). The crude product was adsorbed onto silica and purified *via* column chromatography (*n*-pentane/EtOAc 49:1) to give thioether **22** (346 mg, 1.14 mmol, 91% over two steps) as light yellow solid. R_f = 0.58 (*n*-pentane/EtOAc 10:1). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.69 (d, *J* = 1.4 Hz, 1H, *H1*), 7.69 (s, 1H, *H4*), 4.00 (s, 3H, CO_2*Me*), 2.57 (s, 3H, S*Me*) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 166.0 (s, 1 C, *C*O_2Me), 142.8 (dddd, *J* = 254.3, 10.2, 5.2, 2.7 Hz, 1 C, *C*F), 141.8 (s, 1 C, *C3*), 141.2 (dddd, *J* = 251.5, 10.7, 4.7, 2.2 Hz, 1 C, *C*F), 140.0 (dtd, *J* = 256.3, 15.5, 3.4 Hz, 1 C, *C*F), 137.5 (dtd, *J* = 252.9, 15.4, 2.9 Hz, 1 C, *C*F), 127.6 (s, 1 C, *C2*), 124.8–124.7 (m, 1 C, *C1*), 121.5–121.4 (m, 1 C, $C_{q.}$), 115.8 (dd, *J* = 14.7, 4.1 Hz, 1 C, $C_{q.}$), 114.3–114.2 (m, 1 C, *C4*), 52.8 (s, 1 C, CO_2*Me*), 16.1 (s, 1 C, S*Me*) ppm. ^{19}F-NMR (283 MHz, $CDCl_3$): δ = −147.7–−147.8 (m, 1F), −150.4 (t, *J* = 16.9 Hz, 1F), −153.5 (td, *J* = 18.3, 2.9 Hz, 1F), −158.9 (t, *J* = 18.3 Hz, 1F) ppm. HRMS (EI$^+$): *m/z* calc. for $C_{13}H_8F_4O_2S$ [M]$^+$: 304.01811, found: 304.01533. FT-IR: film; $\tilde{\nu}$ = 3001 (w), 2960 (w), 2929 (w), 2848 (w), 1720 (s), 1665 (w), 1600 (m), 1505 (m), 1455 (m), 1437 (w), 1413 (w), 1384 (w), 1341 (m), 1290 (w), 1264 (w), 1232 (s), 1192 (w), 1130 (m), 1108 (w), 1068 (s), 1000 (w), 969 (w), 932 (w), 862 (w), 815 (w), 785 (w), 742 (w), 655 (w), 614 (w), 447 (w) cm^{-1}. m.p.: 149 °C (EtOAc).

5,6,7,8-Tetrafluoro-3-(methylthio)-2-naphthaldehyde (23)

DIBAH (1.0 M in CH_2Cl_2, 0.82 mL, 818 µmol, 3.00 eq) was added dropwise to a suspension of ester **22** (83 mg, 273 µmol, 1.00 eq) in THF (2.2 mL) at 0 °C. The solution was stirred for 20 min at rt before H_2O (5 mL) and 2 M aq. HCl (10 mL) were added. The mixture was extracted with CH_2Cl_2 (3×25 mL) and the combined organic layers were dried over $MgSO_4$. The crude product was adsorbed onto silica and purified *via* column chromatography (*n*-pentane/EtOAc 5:1) to obtain (5,6,7,8-tetrafluoro-3-(methylthio)naphthalen-2-yl) methanol (70 mg, 255 µmol, 93%) as colorless solid. R_f = 0.36 (*n*-pentane/EtOAc 5:1). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.06 (s, 1H, *H1*), 7.65 (s, 1H, *H4*), 4.88 (s, 2H, CH_2OH), 2.63 (s, 3H, S*Me*), 2.20 (s, 1H, O*H*) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 142.4 (dddd, *J* = 250.9, 10.1, 4.5, 3.0 Hz, 1 C, *C*F), 141.3 (dddd, *J* = 250.1, 10.5, 4.9, 2.2 Hz, 1 C, *C*F), 138.5 (s, 1 C, *C3*), 138.3 (s, 1 C, *C2*), 138.3 (dtd, *J* = 252.0, 15.4, 2.8 Hz, 1 C, *C*F), 137.4 (dtd, *J* = 251.2, 15.2, 2.8 Hz, 1 C, *C*F), 119.5 (dd, *J* = 14.4, 4.1 Hz, 1 C, $C_{q.}$), 118.0–117.9 (m, 1 C, *C1*), 117.0 (dd, *J* = 14.0, 4.1 Hz, 1 C, $C_{q.}$), 114.1–113.9 (m, 1 C, *C4*), 62.9 (s, 1 C, *C*H_2OH), 15.2 (s, 1 C, S*Me*) ppm. ^{19}F-NMR (283 MHz, $CDCl_3$): δ = −150.2 (dd, *J* = 18.3, 15.5 Hz, 1F), −151.6 (dd, *J* = 18.2, 15.6 Hz, 1F), −158.6 (t, *J* = 18.5 Hz, 1F), −160.4 (t, *J* = 18.6 Hz, 1F) ppm. HRMS (EI$^+$): *m/z* calc. for $C_{12}H_8F_4OS$ [M]$^+$: 276.02320, found: 276.02215. FT-IR: film; $\tilde{\nu}$ = 3306 (w), 2928 (w), 2886 (w), 2855 (w), 1668 (w), 1613 (m), 1508 (s), 1464 (m), 1418 (m), 1387 (w), 1363 (w), 1337 (m), 1252 (w), 1170 (w), 1122 (w), 1075 (w), 1052 (s), 993 (m), 959 (m), 886 (w), 855 (w), 785 (w), 737 (w), 709 (w), 672 (w), 641 (w), 530 (w), 438 (w) cm^{-1}. m.p.: 150 °C (EtOAc).

Oxalyl chloride (36.0 µL, 0.42 mmol, 1.50 eq) was added to a solution of DMSO (60.0 µL, 0.84 mmol, 3.00 eq) in CH_2Cl_2 (5.0 mL) at −78 °C. The solution was stirred for 10 min before it was added to a suspension of (5,6,7,8-tetrafluoro-3-(methylthio)naphthalen-2-yl) methanol (77 mg, 0.28 mmol, 1.00 eq) in CH_2Cl_2 (5.0 mL) at −78 °C. The mixture was stirred for 30 min and Et_3N (193 µL, 1.39 mmol, 5.00 eq) was added. After stirring for 30 min at −78 °C the cooling bath was removed and the solution was stirred for additional 15 min at rt. H_2O (20 mL) and brine (5 mL) were added and the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were dried over $MgSO_4$ and the crude product was adsorbed onto silica and purified *via* column chromatography (*n*-pentane/EtOAc 29:1) to obtain aldehyde **23** (70 mg, 255 µmol, 91%) as fluffy yellow solid. R_f = 0.55 (*n*-pentane/EtOAc 10:1). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 10.35 (s, 1H, C*H*O), 8.51 (d, *J* = 1.3 Hz, 1H, *H1*), 7.73 (s, 1H, *H4*), 2.61 (s, 3H, S*Me*) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 190.6 (s, 1 C, *C*HO), 143.1 (dddd, *J* = 254.9, 10.6, 4.5, 3.0 Hz, 1 C, *C*F), 141.3 (dddd, *J* = 252.0, 10.0, 5.0, 2.0 Hz, 1 C, *C*F), 141.1 (s, 1 C, *C3*), 140.5 (dtd, *J* = 257.1, 15.1, 3.1 Hz, 1 C, *C*F), 137.6 (dtd, *J* = 254.4, 15.3, 2.9 Hz, 1 C, *C*F), 132.5 (s, 1 C, *C2*), 128.5–128.4 (m, 1 C, *C1*), 122.1–122.0 (m, 1 C, $C_{q.}$), 116.1 (dd, *J* = 15.2, 4.1 Hz, 1 C, $C_{q.}$), 114.8–114.7 (m, 1 C, *C4*), 15.5 (s, 1 C, S*Me*) ppm. ^{19}F-NMR (283 MHz, $CDCl_3$): δ = −147.1–−147.3 (m, 1F), −150.1 (dd, *J* = 17.9, 16.5 Hz, 1F), −152.2–−152.3 (m, 1F), −158.6 (t, *J* = 18.5 Hz, 1F) ppm. HRMS (EI$^+$): *m/z* calc. for $C_{12}H_6F_4OS$ [M]$^+$: 274.00755, found: 274.00669. FT-IR: film; $\tilde{\nu}$ = 2927 (w), 2848 (w), 2734 (w), 1694 (s), 1668 (w), 1603 (m), 1507 (s), 1458 (s), 1420 (w), 1381 (w), 1343 (m), 1262 (w), 1184 (w), 1131 (w), 1077 (m), 1051 (w), 995 (m), 967 (w), 898 (w), 863 (w), 812 (w), 716 (w), 680 (w), 651 (w), 625 (w), 553 (w), 446 (w) cm^{-1}. m.p.: 151 °C (EtOAc).

1,2-Bis(5,6,7,8-tetrafluoro-3-(methylthio)naphthalen-2-yl)ethene (24)

$TiCl_4$ (0.12 mL, 1.09 mmol, 3.00 eq) was added dropwise to a suspension of zinc-powder (71 mg, 1.09 mmol, 3.00 eq) in THF (1.8 mL) at 0 °C. The mixture was stirred at 66 °C for 3 h and then cooled to rt. A solution of aldehyde **23** (100 mg, 365 µmol, 1.00 eq) in THF (1.2 mL) was added and the resulting mixture was stirred at 66 °C for 14 h. The reaction was carefully quenched by adding sat. aq. $NaHCO_3$ (2 mL) and the suspension was stirred vigorously for 1.5 h at rt. The mixture was filtered over a short plug of celite and rinsed with CH_2Cl_2 (200 mL). The solution was washed with brine (30 mL) and dried over $MgSO_4$. The crude product was adsorbed onto silica and purified *via* column chromatography (CH_2Cl_2) to obtain olefin **24** (88 mg, 170 µmol, 93%) as yellow solid with very low solubility. ^{1}H-NMR-spectroscopy showed an *E*/*Z*-ratio of 1:0.9. R_f = 0.69 (*n*-pentane/EtOAc 10:1). ^{1}H-NMR (300 MHz, CD_2Cl_2): *E-isomer:* δ = 8.21 (s, 2H, 2×$H_{ar.}$), 7.74 (s, 2H, 2×$H_{ar.}$), 7.61 (s, 2H, 2×$H_{olef.}$), 2.65 (s, 6H, 2×S*Me*) ppm. *Z-isomer:* δ = 7.68 (s, 2H, 2×$H_{ar.}$), 7.54 (s, 2H, 2×$H_{ar.}$), 7.04 (s, 2H, 2×$H_{olef.}$), 2.66 (s, 6H, 2×S*Me*) ppm. ^{13}C{^{19}F}-NMR (126 MHz, $C_2D_2Cl_4$): *Z-isomer:* δ = 141.7 (d, *J* = 3.8 Hz, 2 C, 2×*C8*), 140.9 (d, *J* = 3.8 Hz, 2 C, 2×*C5*), 140.2–140.1 (m, 2 C, 2×*C3*), 137.9 (s, 2 C, 2×*C6*), 136.7 (s, 2 C, 2×*C7*), 134.7 (dd, *J* = 12.1, 6.5 Hz, 2 C, 2×*C2*), 130.3 (d, *J* = 160.7 Hz, 2 C, 2×*C11*), 119.4 (d, *J* = 165.7 Hz, 2 C, 2×*C1*), 119.0 (d, *J* = 6.7 Hz, 2 C, 2×*C10*), 116.3 (d, *J* = 6.7 Hz, 2 C, 2×*C9*), 113.1 (d, *J* = 165.3 Hz, 2 C, 2×*C4*), 15.2 (q, *J* = 140.4 Hz, 2 C, 2×S*Me*) ppm. ^{19}F-NMR (235 MHz, CD_2Cl_2): *E-isomer:* δ =-150.7 (t, *J* = 17.0 Hz, 2F), -151.9 (t, *J* = 16.9 Hz, 2F), -159.1 (t, *J* = 18.3 Hz, 2F), -161.3 (t, *J* = 18.5 Hz, 2F) ppm. *Z-isomer:* δ =-151.4 (t, *J* = 17.0 Hz, 2F), -152.2 (t, *J* = 16.9 Hz, 2F), -159.6 (t, *J* = 18.3 Hz, 2F),

-162.0 (t, $J=18.5$ Hz, 2F) ppm. HRMS (EI^+): *m/z* calc. for $C_{24}H_{12}F_8S_2$ $[M]^+$: 516.02527, found: 516.02332. FT-IR: neat; $\tilde{\nu}=2962$ (w), 2924 (w), 1666 (w), 1599 (m), 1502 (s), 1456 (w), 1416 (m), 1383 (w), 1343 (m), 1314 (w), 1261 (w), 1233 (m), 1165 (w), 1148 (w), 1124 (w), 1070 (s), 1001 (s), 959 (m), 907 (w), 878 (w), 858 (w), 798 (w), 767 (w), 730 (w), 699 (w), 672 (m), 648 (w), 546 (w), 499 (w), 455 (w), 439 (w) cm^{-1}. m.p.: 262 °C (CH_2Cl_2).

5,6,7,8-Tetrafluoro-2-(5,6,7,8-tetrafluoro-3-(methylthio) naphthalen-2-yl)naphtho[2,3-b]thiophene (25)

A suspension of olefin **24** (44 mg, 85.2 μmol, 1.00 eq) and powdered iodine (627 mg, 2.47 mmol, 29.0 eq) in dichloroethane (2.7 mL) was stirred at 84 °C for 22 h under exclusion of light. After cooling to rt sat. aq. Na_2SO_3 (2 mL) was added and the suspension was stirred vigorously for 15 min. Additional sat. aq. Na_2SO_3 (18 mL) was added and the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were dried over $MgSO_4$ and the crude product was adsorbed onto silica and purified *via* column chromatography (*n*-pentane/EtOAc 19:1) to obtain naphthothiophene **25** (10 mg, 20.0 μmol, 23%) as light yellow solid. $R_f=0.25$ (*n*-pentane/CH_2Cl_2 30:1). ^{1}H-NMR (300 MHz, CD_2Cl_2): $\delta=8.61$ (s, 1H, $H_{ar.}$), 8.57 (s, 1H, $H_{ar.}$), 8.16 (d, $J=1.3$ Hz, 1H, $H_{ar.}$), 7.80 (s, 1H, $H_{ar.}$), 7.76 (s, 1H, $H_{ar.}$), 2.61 (s, 3H, S*Me*) ppm. ^{19}F-NMR (235 MHz, CD_2Cl_2): $\delta=$-150.2 (t, $J=17.1$ Hz, 1F), -151.0 (t, $J=16.5$ Hz, 1F), -151.5 (t, $J=16.9$ Hz, 1F), -151.6 (t, $J=16.1$ Hz, 1F), -157.6 (t, $J=18.4$ Hz, 1F), -160.3 (t, $J=17.4$ Hz, 1F), -160.5 (t, $J=18.6$ Hz, 1F), −161.2 (t, $J=17.7$ Hz, 1F) ppm. HRMS (EI^+): *m/z* calc. for $C_{23}H_8F_8O_2S_2$ $[M]^+$: 499.99397, found: 499.99125. FT-IR: neat; $\tilde{\nu}=2957$ (w), 2921 (w), 2851 (w), 1714 (w), 1667 (w), 1592 (m), 1499 (m), 1464 (m), 1402 (w), 1379 (w), 1347 (s), 1255 (m), 1173 (w), 1117 (w), 1071 (s), 1007 (w), 966 (m), 883 (m), 860 (w), 800 (w), 741 (w), 709 (w), 657 (w), 634 (m), 537 (w), 432 (m) cm^{-1}. m.p.: 237 °C decomposition (CH_2Cl_2).

5,6,7,8-Tetrafluoro-2-(5,6,7,8-tetrafluoro-3-(methylsulfinyl) naphtha-lene-2-yl)naphtho[2,3-b]thiophene (26)

CH_2Cl_2 (2.0 mL) was added to a mixture of naphthothiophene **25** (28 mg, 56.0 μmol, 1.00 eq) and *m*CPBA (77%, 13 mg, 56.0 μmol, 1.00 eq) at 0 °C. The suspension was stirred for 5 min at 0 °C and then additional 26 h at rt. The mixture was poured into 1 M aq. K_2CO_3 (20 mL) and extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with 1 M aq. K_2CO_3 (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude sulfoxide **26** (27 mg, 52.3 μmol, 93%) was used in the next step without further purification. ^{1}H-NMR (300 MHz, CD_2Cl_2): $\delta=8.86$ (d, J=1.3 Hz, 1H, $H_{ar.}$), 8.63 (s, 1H, $H_{ar.}$), 8.60 (s, 1H, $H_{ar.}$), 8.32 (d, J=1.1 Hz, 1H, $H_{ar.}$), 7.74 (s, 1H, $H_{ar.}$), 2.55 (s, 3H, OS*Me*) ppm. ^{19}F-NMR (235 MHz, CD_2Cl_2): $\delta=-147.5$ (t, $J=16.9$ Hz, 1F), −148.6 (t, $J=16.9$ Hz, 1F), −150.6 (t, $J=16.4$ Hz, 1F), −151.3 (t, $J=16.3$ Hz, 1F), −155.4 (t, $J=18.2$ Hz, 1F), −155.7 (t, $J=18.3$ Hz, 1F), −159.4 (t, $J=17.4$ Hz, 1F), −160.5 (t, $J=17.5$ Hz, 1F) ppm. HRMS (EI^+): *m/z* calc. for $C_{23}H_8F_8O_2S_2$ $[M]^+$: 515.98888, found: 515.98944.

1,2,3,4,8,9,10,11-Octafluoronaphtho[2,3-b]naphtha[2′,3′:4,5] thieno-[2,3-d]thiophene (F_8DNTT, 7)

TfOH (0.69 mL) was added to sulfoxide **26** (32 mg, 62.0 μmol, 1.00 eq) and P_2O_5 (8.8 mg, 62.0 μmol, 1.00 eq), and the suspension was stirred at rt for 3 d. The mixture was cooled to 0 °C and ice-water (1.0 mL) was added. The precipitate was centrifuged (13.000 rpm, 2 min), washed with H_2O (1.0 mL), and dried under reduced pressure. Pyridine (0.57 mL) was added and the suspension was stirred at 115 °C for 23 h. The mixture was cooled to rt and MeOH (2 mL) was added. The precipitate was centrifuged (13.000 rpm, 2 min) and washed successively with MeOH (1.0 mL), H_2O (2×1.0 mL), acetone (2×1.0 mL), *n*-hexane (1.0 mL), and CH_2Cl_2 (4×1.0 mL) to obtain F_8DNTT **7** (18 mg, 37.2 μmol, 60%) as green solid. ^{1}H-NMR (500 MHz, 343 K, $C_2D_2Cl_4$): $\delta=8.70$ (s, 2H, 2×$H_{ar.}$), 8.60 (s, 2H, 2×$H_{ar.}$) ppm. ^{13}C{^{19}F}-NMR (126 MHz, 343 K, $C_2D_2Cl_4$): $\delta=$ 142.2, 141.4, 137.7, 137.4, 123.5, 120.2 ppm. *Due to the low solubility of 7, not all expected ^{13}C-signals could be observed.* ^{19}F-NMR (471 MHz, 343 K, $C_2D_2Cl_4$): $\delta=-149.7$ (t, $J=16.4$ Hz, 2F), −150.3 (t, $J=16.4$ Hz, 2F), −157.8 (t, $J=17.5$ Hz, 2F), −158.7 (t, $J=17.6$ Hz, 2F) ppm. HRMS ($APCI^+$): *m/z* calc. for $C_{22}H_4F_8S_2$ $[M]^+$: 483.9627, found: 483.9626. FT-IR: neat; $\tilde{\nu}=3085$ (w), 1667 (m), 1609 (w), 1592 (w), 1501 (w), 1475 (w), 1460 (m), 1411 (w), 1353 (s), 1303 (w), 1250 (m), 1199 (w), 1177 (w), 1127 (m), 1065 (m), 1006 (s), 970 (s), 913 (w), 863 (m), 801 (m), 726 (w), 664 (w), 635 (m), 549 (m), 434 (m) cm^{-1}. m.p.: >350 °C (CH_2Cl_2).

Synthesis of F_4DNTT (8)

Methyl 3-(methylthio)-2-naphthoate (28)

A solution of ester **27** (248 mg, 1.33 mmol, 1.00 eq), B_2pin_2 (338 mg, 1.33 mmol, 1.00 eq), $[Ir(OMe)(COD)]_2$ (22 mg, 0.03 mmol, 0.025 eq) and ligand **L1** (25 mg, 0.07 mmol, 0.05 eq) in THF (1.7 mL) was degassed and purged with argon (3×) and stirred at 55 °C. After 2 h sat. aq. NH_4Cl (30 mL) and H_2O (10 mL) were added and the mixture was extracted with EtOAc (3×30 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, and filtered over a short plug of celite and silica. The solvent was removed under reduced pressure and the crude methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthoate was used in the next step without further purification. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta=8.49$ (s, 1H, $H_{ar.}$), 7.99 (s, 1H, $H_{ar.}$), 7.92–7.84 (m, 2H, 2×$H_{ar.}$), 7.60–7.50 (m, 2H, 2×$H_{ar.}$), 3.97 (s, 3H, CO_2*Me*), 1.46 (s, 12H, 4×CH_3) ppm. ^{11}B-NMR (160 MHz, $CDCl_3$): $\delta=22.29$ (s, 1B) ppm. HRMS ($APCI^+$): *m/z* calc. for $C_{18}H_{22}BF_4O_4$ $[M+H]^+$: 313.1609, found: 313.1614.

TMEDA (24.7 μL, 0.16 mmol, 0.12 eq) was added to a suspension of methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthoate (crude, ~1.33 mmol, 1.00 eq), TsSMe (324 mg, 1.60 mmol, 1.20 eq), $CuSO_4$ (21 mg, 0.13 mmol, 0.10 eq) and CsF (404 mg, 2.66 mmol, 2.00 eq) in MeOH (14 mL). The mixture was stirred at 50 °C for 22 h and was then filtered over a short plug of celite and rinsed with EtOAc (60 mL). The crude product was adsorbed onto silica and purified *via* column chromatography (*n*-pentane/EtOAc 29:1) to give thioether **28** (207 mg, 891 μmol, 67% over two steps) as light yellow solid. $R_f=0.23$ (*n*-pentane/EtOAc 29:1). ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta=8.54$ (s, 1H, *H1*), 7.85 (d, $J=8.2$ Hz, 1H, *H8*), 7.76 (d, $J=8.1$ Hz, 1H, *H5*), 7.57–7.54 (m, 2H, *H4* & *H7*), 7.46–7.42 (m, 1H, *H6*), 3.98 (s, 3H, CO_2*Me*), 2.57 (s, 3H, S*Me*) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): $\delta=167.1$ (s, 1 C, *C*O_2Me), 138.1 (s, 1 C, *C3*), 135.4 (s, 1 C, *C9*), 132.8 (s, 1 C, *C1*), 129.5 (s, 1 C, *C10*), 129.0 (s, 1 C, *C8*), 129.0 (s, 1 C, *C7*), 126.6 (s, 1 C, *C5*), 125.8 (s, 2 C, *C2* & *C6*), 122.6 (s, 1 C, *C4*), 52.4 (s, 1 C, CO_2*Me*), 16.1 (s, 1 C, S*Me*) ppm. HRMS (EI^+): *m/z* calc. for $C_{13}H_{12}O_2S$ $[M]^+$: 232.05580, found: 232.05643. FT-IR: film; $\tilde{\nu}=3054$ (w), 2990 (w), 2949 (w), 2919 (w), 1716 (s), 1625 (w), 1584 (w), 1488 (w), 1435 (w), 1347 (w), 1314 (w), 1276 (s), 1226 (w), 1201 (m), 1136 (w), 1110 (m), 1018 (w), 951 (w), 902 (w), 874 (w), 842 (w), 812 (w), 782 (w), 746 (w), 608 (w), 474 (w) cm^{-1}. m.p.: 75 °C (EtOAc).

((3-(Methylthio)naphthalen-2-yl)methyl) triphenylphosphonium-bromide (29)

DIBAH (1.0 M in CH_2Cl_2, 2.4 mL, 2.36 mmol, 3.00 eq) was added dropwise to a suspension of ester **28** (183 mg, 788 μmol, 1.00 eq) in THF (6.4 mL) at 0 °C. The solution was stirred for 2 h at rt before

H_2O (10 mL) and 2 M aq. HCl (10 mL) were added. The mixture was extracted with CH_2Cl_2 (4×20 mL) and the combined organic layers were dried over $MgSO_4$. The crude product was adsorbed onto silica and purified *via* column chromatography (*n*-pentane/EtOAc 5:1) to obtain (3-(methylthio)naphthalen-2-yl)methanol (143 mg, 700 μmol, 89%) as colorless solid. R_f = 0.29 (*n*-pentane/EtOAc 5:1). ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = \delta$ = 7.82 (s, 1H, *H1*), 7.79 (d, J = 8.1 Hz, 1H, *H8*), 7.75 (d, J = 8.1 Hz, 1H, *H5*), 7.60 (s, 1H, *H4*), 7.48–7.45 (m, 1H, *H7*), 7.44–7.41 (m, 1H, *H6*), 4.89 (s, 2H, CH_2OH), 2.60 (s, 3H, S*Me*), 2.25 (s, 1H, O*H*) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 136.8 (s, 1 C, *C2*), 135.2 (s, 1 C, *C3*), 133.5 (s, 1 C, *C9*), 131.4 (s, 1 C, *C10*), 127.9 (s, 1 C, *C8*), 126.8 (s, 1 C, *C1*), 126.6 (s, 2 C, *C5* & *C7*), 125.7 (s, 1 C, *C6*), 124.2 (s, 1 C, *C4*), 63.7 (s, 1 C, CH_2OH), 16.0 (s, 1 C, S*Me*) ppm. HRMS (EI$^+$): *m/z* calc. for $C_{12}H_{12}OS$ $[M]^+$: 204.06089, found: 204.06125. FT-IR: film; $\tilde{\nu}$ = 3348 (m), 3051 (w), 2983 (w), 2918 (w), 2873 (w), 1626 (w), 1592 (w), 1490 (w), 1431 (s), 1390 (w), 1314 (w), 1273 (w), 1205 (w), 1158 (w), 1131 (m), 1053 (w), 1029 (m), 1006 (w), 954 (w), 891 (w), 868 (s), 746 (s), 600 (w), 476 (m) cm^{-1}. m.p.: 63 °C (EtOAc).

NBS (787 mg, 4.42 mmol, 2.00 eq) was added in portions over 3 min to a solution of (3-(methylthio)naphthalen-2-yl)methanol (451 mg, 2.21 mmol, 1.00 eq) and PPh_3 (1.16 g, 4.42 mmol, 2.00 eq) in CH_2Cl_2 (10.6 mL) at 0 °C. The solution was stirred at 0 °C for 1 h before H_2O (50 mL) and brine (15 mL) were added. The mixture was extracted with CH_2Cl_2 (3×50 mL) and the combined organic layers were dried over $MgSO_4$ and filtered through a short plug of silica. The crude product was adsorbed onto silica and purified *via* column chromatography (*n*-pentane/EtOAc 49:1) to obtain (3-(bromomethyl)naphthalen-2-yl)(methyl)sulfane (486 mg, 1.82 mmol, 82%) as colorless solid. R_f = 0.73 (*n*-pentane/EtOAc 10:1). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.85 (s, 1H, *H1*), 7.78–7.74 (m, 2H, *H5* & *H8*), 7.63 (s, 1H, *H4*), 7.50–7.46 (m, 1H, *H7*), 7.44–7.41 (m, 1H, *H6*), 4.80 (s, 2H, CH_2Br), 2.64 (s, 3H, S*Me*) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 136.3 (s, 1 C, *C3*), 134.0 (s, 1 C, *C2*), 133.8 (s, 1 C, *C9*), 131.2 (s, 1 C, *C10*), 129.9 (s, 1 C, *C1*), 127.9 (s, 1 C, *C8*), 127.3 (s, 1 C, *C7*), 126.7 (s, 1 C, *C5*), 125.9 (s, 1 C, *C6*), 124.9 (s, 1 C, *C4*), 32.2 (s, 1 C, CH_2Br), 16.4 (s, 1 C, S*Me*) ppm. HRMS (EI$^+$): *m/z* calc. for $C_{12}H_{11}BrS$ $[M]^+$: 265.97648, found: 265.97453. FT-IR: film; $\tilde{\nu}$ = 3050 (w), 3019 (w), 2986 (w), 2965 (w), 2918 (w), 2855 (w), 1622 (w), 1586 (w), 1489 (w), 1432 (m), 1315 (w), 1275 (w), 1246 (w), 1208 (s), 1174 (w), 1151 (w), 1134 (w), 1115 (w), 1018 (m), 952 (w), 917 (w), 896 (w), 867 (m), 836 (w), 802 (w), 748 (s), 697 (w), 598 (w), 582 (m), 521 (w), 507 (w), 474 (m), 449 (w) cm^{-1}. m.p.: 106 °C (*n*-pentane).

A solution of (3-(bromomethyl)naphthalen-2-yl)(methyl)sulfane (486 mg, 1.82 mmol, 1.00 eq) and PPh_3 (572 mg, 2.18 mmol, 1.20 eq) in toluene (20.6 mL) was stirred at 111 °C for 17 h. After cooling to rt, the precipitate was filtered, washed with toluene (3× 10 mL), and dried under reduced pressure. Phosphonium bromide **29** (929 mg, 1.75 mmol, 96%) was obtained as a colorless solid. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 7.93–7.89 (m, 3H, 3×$H_{ar.}$), 7.87 (d, J = 8.2 Hz, 1H, $H_{ar.}$), 7.79 (s, 1H, $H_{ar.}$), 7.74–7.70 (m, 6H, 6×$H_{ar.}$), 7.65–7.61 (m, 6H, 6×$H_{ar.}$), 7.57–7.51 (m, 3H, 3×$H_{ar.}$), 7.44–7.41 (m, 1H, $H_{ar.}$), 5.23 (d, J = 14.6 Hz, 2H, CH_2PPh_3), 2.26 (s, 3H, S*Me*) ppm. ^{13}C-NMR (126 MHz, DMSO-d_6): δ = 137.4 (d, J = 5.0 Hz, 1 C, $C_{q.}$), 135.2 (d, J = 2.6 Hz, 3 C, 3×$C_{ar.}$), 134.1 (d, J = 9.9 Hz, 6 C, 6×$C_{ar.}$), 133.1 (d, J = 2.0 Hz, 1 C, $C_{q.}$), 130.5 (d, J = 7.0 Hz, 1 C, $C_{ar.}$), 130.2 (d, J = 13.0 Hz, 6 C, 6×$C_{ar.}$), 130.2–130.1 (m, 1 C, $C_{q.}$), 127.4 (s, 1 C, $C_{ar.}$), 127.2 (s, 1 C, $C_{ar.}$), 126.8 (s, 1 C, $C_{ar.}$), 126.3 (s, 1 C, $C_{ar.}$), 125.6 (d, J = 2.0 Hz, 1 C, $C_{ar.}$), 124.2 (d, J = 9.0 Hz, 1 C, $C_{q.}$), 117.5 (d, J = 85.4 Hz, 3 C, 3×$C_{q.}$P), 26.9 (d, J = 48.2 Hz, 1 C, CH_2PPh_3), 16.2 (s, 1 C, S*Me*) ppm. ^{31}P-NMR (202 MHz, DMSO-d_6): δ = 23.1 (s, 1P, *P*Ph_3) ppm. HRMS (ESI$^+$): *m/z* calc. for $C_{30}H_{26}PS$ $[M–Br]^+$: 449.1487, found: 449.1485. FT-IR: neat; $\tilde{\nu}$ = 3041 (w), 3004 (w), 2988 (w), 2928 (w), 2914 (w), 2843 (w), 2775 (w), 1585 (w), 1486 (w), 1436 (m), 1404 (w), 1316 (w), 1191 (w), 1162 (w), 1108 (s), 1014 (w), 995 (w), 974 (w), 929 (w), 893 (w), 867 (w), 841 (w), 771 (w), 757 (w), 740 (s), 716 (w), 690 (s), 626 (w), 550 (m), 511 (s), 481 (w), 444 (w), 425 (w) cm^{-1}. m.p.: 262 °C decomposition (toluene).

Methyl(5,6,7,8-tetrafluoro-3-(2-(3-(methylthio)naphthalen-2-yl) vinyl)-naphthalen-2-yl)sulfane (30)

n-BuLi (2.5 M in *n*-hexane, 0.32 mL, 795 μmol, 1.09 eq) was added dropwise to a suspension of phosphonium bromide **29** (425 mg, 802 μmol, 1.10 eq) in THF (58 mL) at 0 °C. The orange solution was stirred at 0 °C for 30 min before a pre-cooled solution of aldehyde **23** (200 mg, 729 μmol, 1.00 eq) in THF (5.0 mL) was added dropwise. The ice-bath was removed and the solution was stirred at rt for 15 min before H_2O (50 mL) and brine (10 mL) were added. The mixture was extracted with CH_2Cl_2 (3×60 mL) and the combined organic layers were washed with brine (30 mL) and dried over $MgSO_4$. The crude product was adsorbed onto silica and purified *via* column chromatography (*n*-pentane/CH_2Cl_2 29:1) to obtain olefin **30** (311 mg, 700 μmol, 96%) as a light yellow solid. ^{19}F-NMR-spectroscopy showed an *E*/*Z*-ratio of 1:0.16. R_f = 0.30 (*n*-pentane/EtOAc 50:1). ^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 7.70 (d, J = 7.9 Hz, 1H, $H_{ar.}$), 7.65 (s, 1H, $H_{ar.}$), 7.59–7.59 (m, 2H, 2×$H_{ar.}$), 7.40–7.35 (m, 3H, 3×$H_{ar.}$), 7.25–7.21 (m, 1H, $H_{ar.}$), 7.10 (dd, J = 11.8, 0.7 Hz, 1H, $H_{olef.}$), 6.94 (d, J = 11.8 Hz, 1H, $H_{olef.}$), 2.65 (s, 3H, S*Me*), 2.64 (s, 3H, S*Me*) ppm. ^{19}F-NMR (283 MHz, CD_2Cl_2): δ = −151.0 (dd, J = 18.5, 15.3 Hz, 1F), −152.1 (t, J = 16.9 Hz, 1F), −159.7 (t, J = 18.4 Hz, 1F), −161.8 (t, J = 18.3 Hz, 1F) ppm. HRMS (EI$^+$): *m/z* calc. for $C_{24}H_{16}F_4S_2$ $[M]^+$: 444.06295, found: 444.06325. FT-IR: film; $\tilde{\nu}$ = 3053 (w), 2987 (w), 2921 (w), 2853 (w), 1666 (w), 1600 (m), 1504 (s), 1459 (w), 1419 (m), 1344 (m), 1317 (w), 1248 (w), 1204 (w), 1175 (w), 1128 (w), 1071 (s), 1018 (w), 993 (m), 963 (w), 898 (w), 870 (w), 841 (w), 797 (w), 745 (m), 691 (w), 666 (w), 643 (w), 599 (w), 475 (w), 440 (w) cm^{-1}. m.p.: 167 °C (CH_2Cl_2).

1,2,3,4-Tetrafluoronaphtho[2,3-b]naphtho[2′,3′:4,5]thieno [2,3-d]thio-phene (F_4DNTT, 8)

A suspension of olefin **30** (40 mg, 90.0 μmol, 1.00 eq) and powdered iodine (662 mg, 2.61 mmol, 29.0 eq) in AcOH (2.8 mL) was stirred at 118 °C for 21 h. The mixture was cooled to rt and sat. aq. Na_2SO_3 (1 mL) was added and the suspension was stirred vigorously for 5 min. The precipitate was centrifuged (13.000 rpm, 2 min) and successively washed with sat. aq. Na_2SO_3 (1.0 mL), H_2O (1.0 mL), acetone (1.0 mL) and CH_2Cl_2 (2×1.0 mL) to obtain F_4DNTT **8** (27 mg, 65.5 μmol, 73%) as green solid. ^{1}H-NMR (500 MHz, 343 K, $C_2D_2Cl_4$): δ = 8.66 (s, 1H, $H_{ar.}$), 8.54 (s, 1H, $H_{ar.}$), 8.48 (s, 1H, $H_{ar.}$), 8.43 (s, 1H, $H_{ar.}$), 8.08–8.07 (m, 1H, $H_{ar.}$), 7.99–7.97 (m, 1H, $H_{ar.}$), 7.59–7.58 (m, 2H, 2×$H_{ar.}$) ppm. ^{13}C-NMR (126 MHz, 343 K, $C_2D_2Cl_4$): δ = 128.2, 127.2, 126.4, 125.9, 123.5, 122.6, 120.6, 120.2 ppm. *Due to the low solubility of* ***8****, not all expected* ^{13}*C-signals could be observed.* ^{19}F-NMR (471 MHz, 343 K, $C_2D_2Cl_4$): δ = −150.0 (t, J = 16.4 Hz, 1F), −150.6 (t, J = 16.1 Hz, 1F), −158.8 (t, J = 17.9 Hz, 1F), −159.3 (t, J = 17.4 Hz, 1F) ppm. HRMS (EI$^+$): *m/z* calc. for $C_{22}H_8F_4S_2$ $[M]^+$: 412.00035, found: 412.00176. FT-IR: neat; $\tilde{\nu}$ = 3259 (w), 1673 (w), 1592 (w), 1499 (m), 1463 (w), 1413 (w), 1383 (w), 1345 (m), 1247 (w), 1212 (w), 1121 (s), 1066 (w), 1031 (w), 1009 (m), 971 (m), 913 (w), 862 (m), 803 (w), 745 (m), 706 (w), 619 (s), 585 (w), 567 (w), 540 (w), 496 (w), 470 (w), 426 (w) cm^{-1}. m.p.: > 350 °C (CH_2Cl_2).

Acknowledgements

We acknowledge support by the German Science Foundation (Grant SFB 1083, TP A2 and A8) and thank the Helmholtz Center Berlin (electron storage ring BESSY II) for the provision of

synchrotron radiation at the beamline HE-SGM. The authors thank Dr. Xiulan Xie for helpful discussions for the measurement and assignment of the NMR spectra. Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Conjugated systems · Electronic structure · Fluorination · Polycycles · Synthesis design

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Manuscript received: December 18, 2020
Revised manuscript received: January 7, 2021
Accepted manuscript online: January 11, 2021