Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Selective dispersion of single-walled carbon nanotubes with electron-rich fluorene-based copolymers

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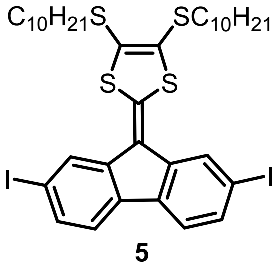
General

As produced HiPco Single-walled carbon nanotubes (SWNTs) were purchased from Carbon Nanotechnologies, Inc. (Batch #: R0-513). All other reagents were purchased from Aldrich Chemical Co. and Acros Organics. NMR spectra were measured on a Bruker 600 MHz spectrometer. High-resolution MALDI-TOF MS measurements were performed on Bruker Ultraflextreme MALDI-TOF/TOF instrument. Instrument settings were: pulsed ion extraction=100 ns, laser frequency=1000 Hz, number of shots per sample=2500 (random walk, 500 shots per raster spot). A saturated solution of dithranol was prepared in THF. The samples were dissolved in THF to a concentration of 1 mg/mL and mixed in a ratio of 1:1 with the matrix solution. 0.5 μL was spotted on the target plate. Spectra were acquired from m/z 600 to 1700 in reflectron mode. UV-vis and UV-vis-NIR spectra were measured on Cary 5000 spectrometer using a 10 mm quartz cuvette. Photoluminescence excitation (PLE) mapping was performed using a Jobin-Yvon SPEX Fluorolog 3.22 equipped with a 450 W Xe arc lamp, and fitted with a liquid-nitrogen cooled InGaAs photodiode detector. Slit widths were set to 10 nm band-pass on both excitation and emission, and samples were illuminated in a quartz cell using 5 nm wavelength steps. Polymer molecular weight and polydispersity index (PDI) were estimated by gel permeation chromatography (GPC) using a Waters 2695 Separations Module equipped with a Waters 2996 photodiode array detector, a Waters 2414 refractive-index detector, and two Jordi Labs Jordi Gel DVB fluorinated mixed bed columns. Polystyrene standards were used for calibration, and THF was used as the eluent at a flow rate of 3.0 mL/min. Thermogravimetric analysis (TGA) was carried out on a TA Instruments Q50 thermogravimetric analyzer. All measurements were done under Ar. Ultrasonication was carried out in a Branson Ultrasonics a B2500 bath sonicator. A Beckman Allegra[TM] X-22R Benchtop centrifuge was used for centrifugation. Raman spectra were collected at room temperature with a Renishaw InVia Laser Raman spectrometer, equipped with a 500 mW HeNe Renishaw laser (633 nm, 1800 L/mm grating) and a 300 mW Renishaw laser (785 nm, grating 1200 L/mm). The lasers were set at less than 10% power. Cyclic voltammetric (CV) experiments were carried out in a standard three-electrode setup controlled by a BASi Epsilon workstation. Experimental conditions: analyte concentration: ca. 10^{-3} M; supporting electrolyte: Bu_4NBF_4 (0.1 M); solvent: CH_2Cl_2; working: glassy carbon; counter: Pt wire; reference: Ag/AgCl; scan rate: 0.2 Vs^{-1}.

Synthesis

DTF 5



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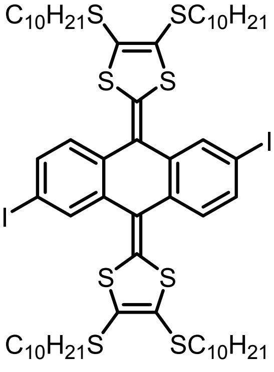
In a round bottom flask equipped with a stir bar, fluorenone **3**[1] (2.43 g, 5.62 mmol) was dissolved in $P(OEt)_3$ (120 mL), and the solution was degassed with Ar for 0.5 h and then heated to 120 °C under N_2. To the solution was slowly added a solution of thione **4**[2] (2.69 g, 5.62 mmol) in $P(OEt)_3$ (30 mL) over a period of 20 min. After the addition was completed, the reaction mixture was kept stirring for another 2 h at 120 °C, and then it was concentrated *in vacuo* to remove $P(OEt)_3$. The residue was subjected to silica gel column chromatography (CH_2Cl_2/hexanes 1:9) to afford **5** as a yellow solid (3.86 g, 4.47 mmol, 80%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04 (d, *J* = 1.1 Hz, 2H), 7.63 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 2.98 (t, *J* = 7.4 Hz, 4H), 1.74-1.69 (m, 4H), 1.49-1.44 (m, 4H), 1.35-1.23 (m, 24H), 0.86 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 141.8, 138.4, 136.2, 134.3, 131.6, 129.6, 121.3, 118.0, 92.5, 36.9, 32.0, 30.0, 29.73, 29.70, 29.48, 29.33, 28.7, 22.8, 14.3; HR–MALDI–TOF MS Calc'd for $C_{36}H_{48}I_2S_4$ $[M]^+$ m/z = 862.0728, found $[M]^+$ m/z = 862.0740.

TTFAQ 9



9

In a round bottom flask equipped with a stir bar, 2,6-diiodoanthraquinone **8**[3] (1.00 g, 2.17 mmol) was dissolved in $P(OEt)_3$ (50 mL), and the solution was degassed with Ar for 0.5 h and then heated to 120 °C under N_2. To the solution was slowly added a solution of thione **4**[2] (2.59 g, 5.42 mmol) in $P(OEt)_3$ (30 mL) over a period of 20 min. After the addition was completed, the reaction mixture was kept stirring for another 2 h at 120 °C, and then it was concentrated *in vacuo* to remove $P(OEt)_3$. The residue was subjected to silica gel column chromatography (CH_2Cl_2/hexanes 0.5:9.5) to afford **9** as a yellow oil

(1.61 g, 1.21 mmol, 56%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.85 (d, *J* = 1.7 Hz, 2H), 7.59 (dd, *J* = 8.2, 1.8 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 2.85-2.77 (m, 8H), 1.66-1.59 (m, 8H), 1.43-1.35 (m, 8H), 1.30-1.25 (m, 48H), 0.87 (m, 12H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 136.7, 135.2, 134.12, 133.95, 133.84, 126.9, 126.61, 126.51, 120.4, 91.3, 36.54, 36.44, 32.1, 29.90, 29.83, 29.69, 29.5, 29.3, 28.70, 28.66, 22.8, 14.3; HR–MALDI–TOF MS Calc'd for $C_{60}H_{90}I_2S_8$ [M]$^+$ m/z = 1320.2897, found [M]$^+$ m/z = 1320.2911.

DTF-PF

A 50 mL Schlenk tube equipped with a magnetic stir bar was charged with DTF **5** (150 mg, 0.173 mmol), 9,9-bis(dodecyl)fluorene-2,7-diboronate ester **6**[4] (131 mg, 0.173 mmol), Cs_2CO_3 (676 mg, 2.07 mmol), DMF (2 mL), and toluene (5 mL). The mixture was degassed via sonication under continuous bubbling with Ar for 30 min. Then a catalytic amount of $Pd(PPh_3)_4$ (20.0 mg, 0.017 mmol) was added and the mixture was stirred at 95 °C under Ar atmosphere for 24 h. The reaction mixture was poured into methanol (150 mL), which resulted in a yellow precipitate that was collected by vacuum filtration, and then washed with methanol (150 mL). The solid was dissolved in THF (5 mL), and re-precipitated in methanol (200 mL), filtered and washed with acetone (50 mL). The solid was dried under vacuum for 24 h at 50 °C, giving **DTF-PF** as a brown solid (222 mg, 79%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 8.12 (b, 2H), 7.97 (b, 2H), 7.89 (b, 2H), 7.78 (b, 2H), 7.75 (b, 2H), 7.70 (b, 2H), 3.01 (b, 4H), 2.14 (b, 4H), 1.76 (b, 4H), 1.49 (b, 4H), 1.15 (b, 58H), 0.84 (b, 18H). GPC: Mn = 14,600 g mol^{-1}, Mw = 35,600 g mol^{-1}, PDI = 2.4.

TTFAQ-PF

A 50 mL Schlenk tube equipped with a magnetic stir bar was charged with TTFAQ **9** (107 mg, 0.081 mmol), 9,9-bis(dodecyl)fluorene-2,7-diboronate ester **6**[4] (61.1 mg, 0.081 mmol), Cs_2CO_3 (316 mg, 0.970 mmol), DMF (2 mL), and toluene (4 mL). The mixture was degassed via sonication under continuous bubbling with Ar for 30 min. Then a catalytic amount of $Pd(PPh_3)_4$ (9 mg, 0.007 mmol) was added and the mixture was stirred at 95 °C under Ar atmosphere for 24 h. The reaction mixture was poured into methanol (150 mL), which resulted in an orange precipitate that was collected by vacuum filtration, and then washed with methanol (150 mL). The solid was dissolved in THF (5 mL), and re-precipitated in methanol (200 mL), filtered and washed with acetone (50 mL). The solid was dried under vacuum for 24 h at 50 °C, giving **TTFAQ-PF** as a yellow solid (119 mg, 71%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94 (b, 2H), 7.83 (b, 2H), 7.74 (b, 2H), 7.68 (b, 6H), 2.85 (b, 8H), 2.08 (b, 4H), 1.66 (b, 8H), 1.42 (b, 8H), 1.26-1.02 (m, 88H), 0.89-0.74 (m, 18H). GPC: Mn = 20,200 g mol^{-1}, Mw = 29,200 g mol^{-1}, PDI = 1.4.

Table S1. Molecular weights and polydispersity of fluorene copolymers determined by GPC analysis

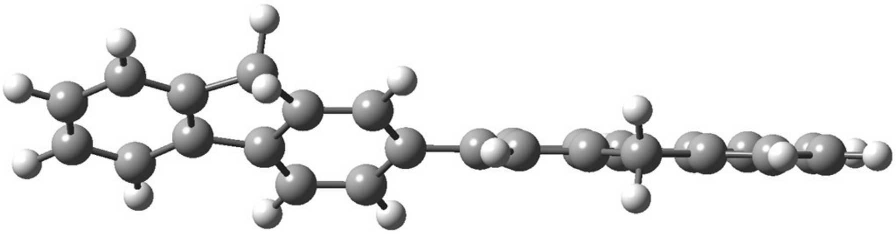
Polymer	**Mn (g mol^{-1})**	**Mw (g mol^{-1})**	**PDI**	**DP**
PF	11,100	22,400	2.0	22
DTF-PF	14,600	35,600	2.4	13
TTFAQ-PF	20,200	29,200	1.4	13

Computational Details

Density Functional Theory (DFT) Calculations

DTF calculations on structures **11-13** were performed using the B3LYP functional and 6-31+G(d,p) or 6-31G(d) basis sets implemented in the *Gaussian 09* software package.[5] For each of the structures, geometry optimization was first conducted followed by frequency check to validate that it was the global minimum (zero imaginary frequency). The molecular structures and frontier molecular orbitals (FMOs) were visualized by *GaussView 5*.[6]

*Optimized structure and Cartesian coordinates of **11***

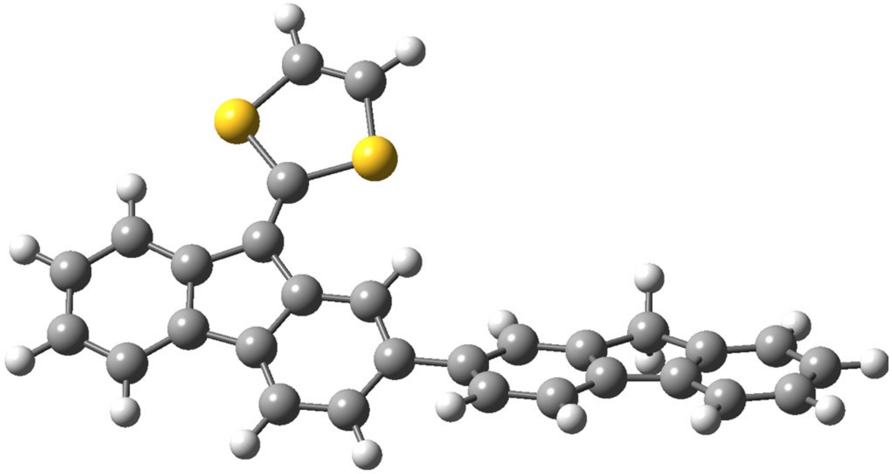


E(RB3LYP) = -1001.71303784 a.u., RMS gradient morm = 0.00000870 a.u., imaginary freq = 0, dipole moment = 1.0080 Debye

C	-7.38082500	0.56567000	-0.34632100
C	-6.09229300	1.09220400	-0.47401700
C	-4.99777300	0.28847300	-0.13999900
C	-5.19417500	-1.03207500	0.32014200
C	-6.47920600	-1.55136700	0.44530400
C	-7.57485500	-0.74507100	0.10902200
H	-8.24049800	1.17826000	-0.60269300
H	-5.94950800	2.10950900	-0.82794100
H	-6.63708700	-2.56742600	0.79854000
H	-8.58279600	-1.13897200	0.20230900
C	-3.55504500	0.56121800	-0.17292200
C	-2.86694900	-0.59055700	0.26335100
C	-2.83708000	1.70210200	-0.54206400
C	-1.47987700	-0.60461900	0.33439900
C	-1.44390000	1.68128600	-0.47117400
H	-3.34783000	2.59544000	-0.89102500
C	-0.74185300	0.53891700	-0.03443800
H	-0.95814900	-1.48568700	0.69887800
H	-0.88439000	2.55746200	-0.78459800
C	0.74185300	0.53891700	0.03443800
C	1.44390000	1.68128600	0.47117200
C	1.47987700	-0.60461900	-0.33439800
C	2.83708000	1.70210300	0.54206200

H	0.88439000	2.55746300	0.78459500
C	2.86694900	-0.59055700	-0.26335000
H	0.95814900	-1.48568800	-0.69887600
C	3.55504500	0.56121800	0.17292100
H	3.34783000	2.59544100	0.89102100
C	4.99777300	0.28847300	0.13999900
C	5.19417500	-1.03207500	-0.32014000
C	6.09229300	1.09220500	0.47401600
C	6.47920600	-1.55136800	-0.44530200
C	7.38082500	0.56567000	0.34632100
H	5.94950800	2.10951000	0.82793900
C	7.57485500	-0.74507100	-0.10902100
H	6.63708700	-2.56742700	-0.79853700
H	8.24049800	1.17826100	0.60269200
H	8.58279600	-1.13897300	-0.20230700
C	3.85717100	-1.68443900	-0.61289700
H	3.70087300	-2.58719700	-0.00733600
H	3.77318800	-1.99184800	-1.66391300
C	-3.85717100	-1.68443800	0.61289900
H	-3.70087300	-2.58719700	0.00733900
H	-3.77318800	-1.99184600	1.66391500

Optimized structure and Cartesian coordinates of ***12***



E(RB3LYP) = -1912.38549854 a.u., RMS gradient norm = 0.00001189 a.u., imaginary freq = 0, dipole moment = 3.1228 Debye

C	6.23126600	-2.75067500	0.33559000
C	4.86329300	-3.03546600	0.30427200
C	3.95279600	-1.98644700	0.18210500
C	4.39030300	-0.63651500	0.08839500
C	5.76533500	-0.36809900	0.12180800

C	6.67367600	-1.42619800	0.24501300
H	6.95192400	-3.55764000	0.43031100
H	4.51576400	-4.06253600	0.37441300
H	6.15710800	0.63856000	0.05507200
H	7.73783100	-1.21028400	0.26989500
C	2.49554100	-2.00424400	0.12569800
C	2.02981700	-0.66806900	-0.00081000
C	1.59779100	-3.06890100	0.17353400
C	0.65365600	-0.43207100	-0.07939500
C	0.22805200	-2.81568500	0.09693100
H	1.95507700	-4.08952900	0.27971200
C	-0.26206600	-1.50169900	-0.03030100
H	0.25537000	0.56558100	-0.20789200
H	-0.47297900	-3.64200500	0.16281800
C	-1.72245200	-1.24073500	-0.11116700
C	-2.56743400	-2.09520900	-0.84870200
C	-2.29426000	-0.13283900	0.54766400
C	-3.94121900	-1.86830600	-0.93809200
H	-2.13316700	-2.93561100	-1.38183700
C	-3.66102800	0.09903900	0.46046800
H	-1.66340600	0.52102600	1.14427800
C	-4.49363400	-0.76547700	-0.28084400
H	-4.56369800	-2.54057800	-1.52231300
C	-5.87637600	-0.27874800	-0.19160100
C	-5.89188800	0.88400200	0.60970200
C	-7.06148900	-0.77238500	-0.74593900
C	-7.08619800	1.55414300	0.85692800
C	-8.25827300	-0.09517800	-0.49463600
H	-7.05798800	-1.66652500	-1.36323400
C	-8.27282500	1.05869000	0.29984100
H	-7.10468700	2.44975700	1.47311500
H	-9.18648400	-0.46681300	-0.91933800
H	-9.21141900	1.57290500	0.48543000
C	-4.48851600	1.20571900	1.08505300
H	-4.41651100	1.20130400	2.18096100
H	-4.16121900	2.19985000	0.75225900
C	3.20129100	0.23634900	-0.03050600
C	3.18813700	1.60245100	-0.14133900
S	4.65497400	2.61248900	-0.16487100
S	1.70363300	2.57710700	-0.27942300
C	3.83467300	4.15365800	-0.31718200
H	4.45153800	5.04303900	-0.36295000
C	2.49627300	4.13784400	-0.36890900
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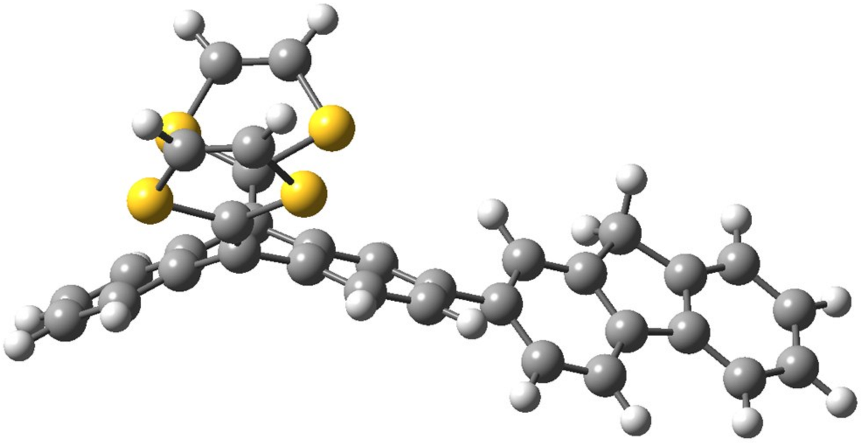
Optimized structure and Cartesian coordinates of ***13***



E(RB3LYP) = -2862.28846818 a.u., RMS gradient norm = 0.00000846 a.u., imaginary freq = 0, dipole moment = 2.1721 Debye

C	5.33132900	0.81518000	2.90727700
C	4.87309700	-0.21260400	2.08293300
C	3.75203200	-0.03715000	1.26044500
C	3.05971500	1.20262100	1.29483400
C	3.51804800	2.21439500	2.14934700
C	4.65233400	2.03175900	2.94044700
H	6.20086100	0.65296500	3.53822900
H	5.37225500	-1.17608900	2.11047200
H	2.96076500	3.14259700	2.22824500
H	4.98565400	2.83030400	3.59749600
C	1.72886600	-1.14017100	0.36221300
C	1.03506300	0.09804300	0.39520500
C	0.98025000	-2.32433400	0.35855500
C	-0.36317200	0.09887600	0.42552400
C	-0.41158800	-2.30294700	0.36035400
H	1.48973200	-3.28248400	0.38278900
C	-1.11330400	-1.08859400	0.39495500
H	-0.88835100	1.04175900	0.53841000
H	-0.95735200	-3.24139900	0.33096100
C	-2.59578200	-1.05307100	0.42463000
C	-3.32653000	-2.03102600	1.12805000
C	-3.30354200	-0.03910000	-0.25117300
C	-4.71919800	-2.01665400	1.16581200
H	-2.78893400	-2.79870200	1.67700100
C	-4.69006700	-0.01910900	-0.21579100
H	-2.75679700	0.70902200	-0.81970600
C	-5.40750900	-1.00642000	0.49075900
H	-5.25493200	-2.78037100	1.72392500

C	-6.84337100	-0.73723900	0.34971300
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C	-7.95696600	-1.41240500	0.85524900
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C	-9.23212700	-0.92774700	0.55773800
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H	-8.41294200	1.78034200	-1.35557400
H	-10.10739700	-1.44298900	0.94458800
H	-10.39392300	0.57902300	-0.45582200
C	-5.65374300	0.95383300	-0.86709600
H	-5.49491300	1.98416700	-0.51931300
H	-5.53960600	0.97558000	-1.95995100
C	1.84713800	1.33549100	0.45444900
C	1.55751400	2.45501600	-0.26851700
S	2.59547400	3.91553600	-0.30832500
S	0.16033600	2.59301500	-1.38268300
C	1.78194900	4.67958000	-1.66764300
H	2.20168600	5.60871100	-2.03576400
C	0.68708100	4.08500500	-2.15129900
H	0.08453200	4.45857600	-2.97121600
C	3.99041600	-1.91249300	-0.38348600
C	3.20775800	-1.10360300	0.38787300
S	5.77748500	-1.80157500	-0.45608100
S	3.34440600	-3.12524800	-1.53369900
C	5.96773800	-2.84617100	-1.85815200
H	6.97068900	-2.96892200	-2.25050700
C	4.87356800	-3.44147300	-2.34270100
H	4.85455800	-4.12034000	-3.18750700

Molecular Mechanics (MM) Simulations of SWNT-Polymer Complexes

Molecular modeling of the fluorene polymers wrapping around SWNTs was done using the Spartan'10 software.[7] A segmental (6,5) SWNT was first built by the Tubegen program,[8] and then imported into Spartan. Trimeric fluorene copolymers (n = 3) were then set around the SWNT respectively and the initial geometries were subjected to optimization with the *MMFF* force field implemented in *Spartan*.

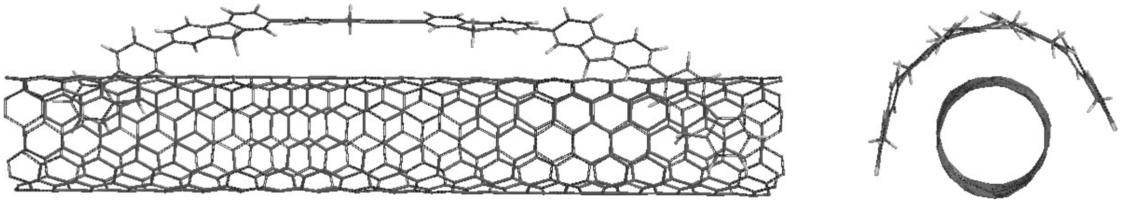

Fig. S-1 Optimized geometry of a trimer of **PF** wrapping around a (6,5) SWNT.

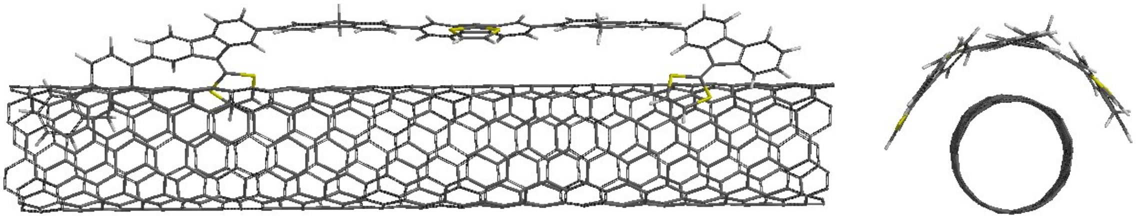

Fig. S-2 Optimized geometry of a trimer of **DTF**-**PF** wrapping around a (6,5) SWNT.

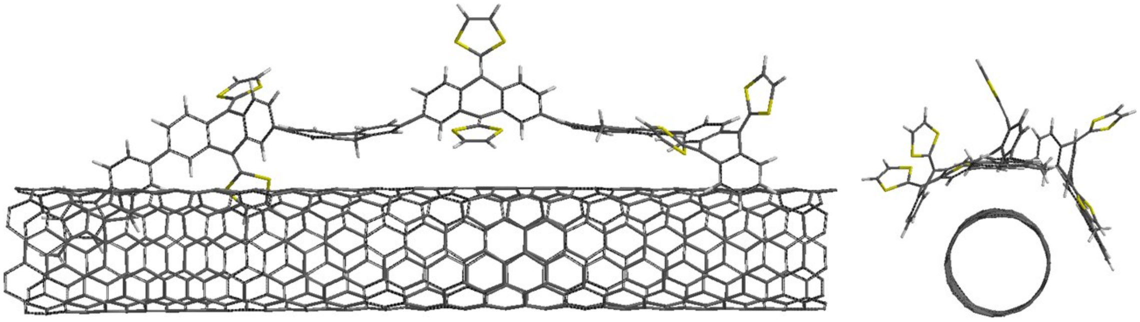

Fig. S-3 Optimized geometry of a trimer of **TTFAQ**-**PF** wrapping around a (6,5) SWNT.

References

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