Electronic Supplementary Material (ESI) for Chemical Science.

Tetrathiafulvalene-Containing Polymers for the Electronic Modification of MoS_2 Nanomaterials

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Supporting Information

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ADDITIONAL DATA

Synthesis

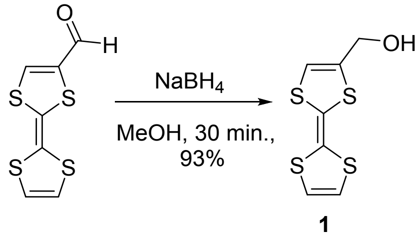


Figure S1. Synthesis of TTF-alcohol **1**.

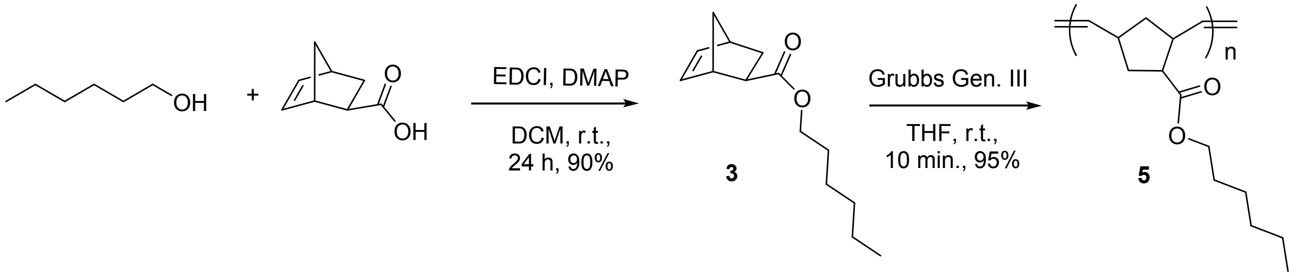


Figure S2. Synthesis of hexyl ester **3** and polynorbornene **5**.

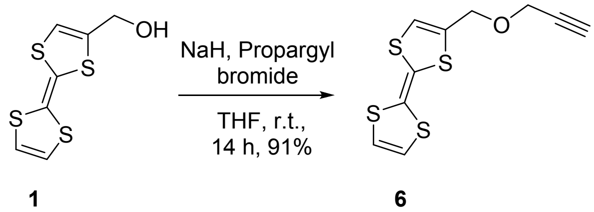


Figure S3. Synthesis of TTF-alkyne **6**.

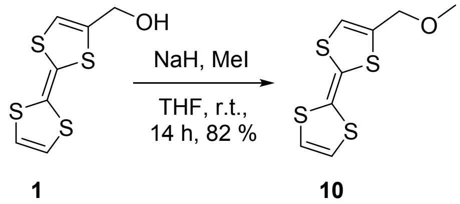


Figure S4. Synthesis of TTF-ether **10** as a model compound for electrochemical comparison.

Table S1. Characterization of the **poly(TTF-norbornene)** series.

Compound	**Target TTF incorporation**	**Actual TTF incorporation**	**% Conversion (^{1}H NMR)**	**M_n (GPC)**	**PDI**	**Yield**
PolyHexNB (5)	0	0%	95	50 kDa	1.20	80
PolyTTFNB-10 (4a)	10%	9%	60	25 kDa	1.26	85
PolyTTFNB-20 (4b)	20%	17%	90	52 kDa	1.16	76
PolyTTFNB-30 (4c)	30%	27%	93	42 kDa	1.12	58
PolyTTFNB-40 (4d)	40%	37%	85	40 kDa	1.22	76
PolyTTFNB-50 (4e)	50%	48%	82	38 kDa	1.20	85

M_n and PDI values were estimated by GPC; TTF incorporation and percent conversion values were determined by ^{1}H NMR spectroscopy.

Table S2. Characterization of the p**olyTTF-methacrylate and butylacrylate** copolymer series.

Compound	**Target TTF incorporation**	**Actual TTF incorporation**	**M_n (GPC)**	**PDI**	**Yield**
PolyTTFMMA-1 (9a)	1%	1%	36 kDa	1.14	63
PolyTTFMMA-10 (9b)	10%	12%	37 kDa	1.23	66
PolyTTFMMA-25 (9c)	25%	29%	31 kDa	1.28	79
PolyTTFMMA-50 (9d)	50%	55%	43 kDa	1.26	60
PolyTTF-b-MMA-35 (9e)	20%	30%	19 kDa	1.14	57%
PolyTTFBMA-10 (9f)	10%	10%	47 kDa	1.17	51
PolyTTFBMA-25 (9g)	25%	27%	50 kDa	1.23	75
polyTTFBMA-50 (9h)	50%	52%	42 kDa	1.27	86

M_n and PDI values were estimated by GPC; TTF incorporation values were determined by ^{1}H NMR spectroscopy.

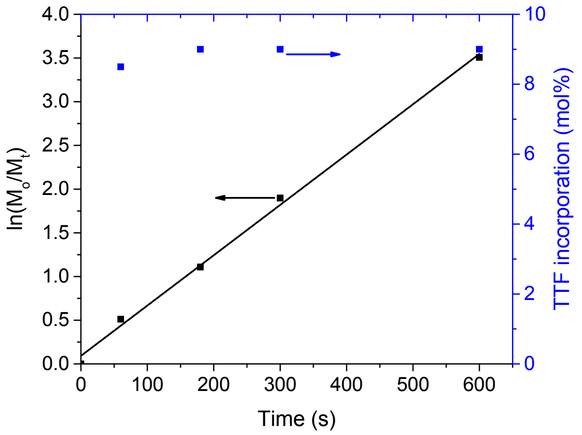


Figure S5. Kinetic data and mole% TTF incorporation for the preparation of **polyTTFNB-10** (**4a**).

Electrochemistry

Table S3. Cyclic voltammetry results for **polyTTFMMA** (**9a-e**), **polyTTFBMA** (**9f-h**), and **polyTTFNB** (**4a-e**), as well as **TTF** and **2-methoxymethylTTF** (**10**) at a scan rate 100 mV/s.

Compound	$E^1_{1/2}{}^{OX}$ (V)	$E_2{}^{OX}$ (V)
TTF	0.21	0.45
2-MethoxymethylTTF (10)	0.24	0.48
PolyTTFMMA-1 (9a)	0.21	-
PolyTTFMMA-10 (9b)	0.21	-
PolyTTFMMA-25 (9c)	0.21	0.45[a]
PolyTTFMMA-50 (9d)	0.20	0.47[a]
PolyTTF-b-MMA-35 (9e)	0.25	0.52[a]
PolyTTFBMA-10 (9f)	0.22	-
PolyTTFBMA-25 (9g)	0.21	0.46[a]
PolyTTFBMA-50 (9h)	0.20	0.47[a]
PolyTTFNB-10 (4a)	0.22	-
PolyTTFNB-20 (4b)	0.23	-
PolyTTFNB-30 (4c)	0.24	-
PolyTTFNB-40 (4d)	0.24	-
PolyTTFNB-50 (4e)	0.24	-

[a] Due to the quasi-reversible nature of the second oxidation transition for the polymers noted, the potentials are given for the forward oxidation peak only.

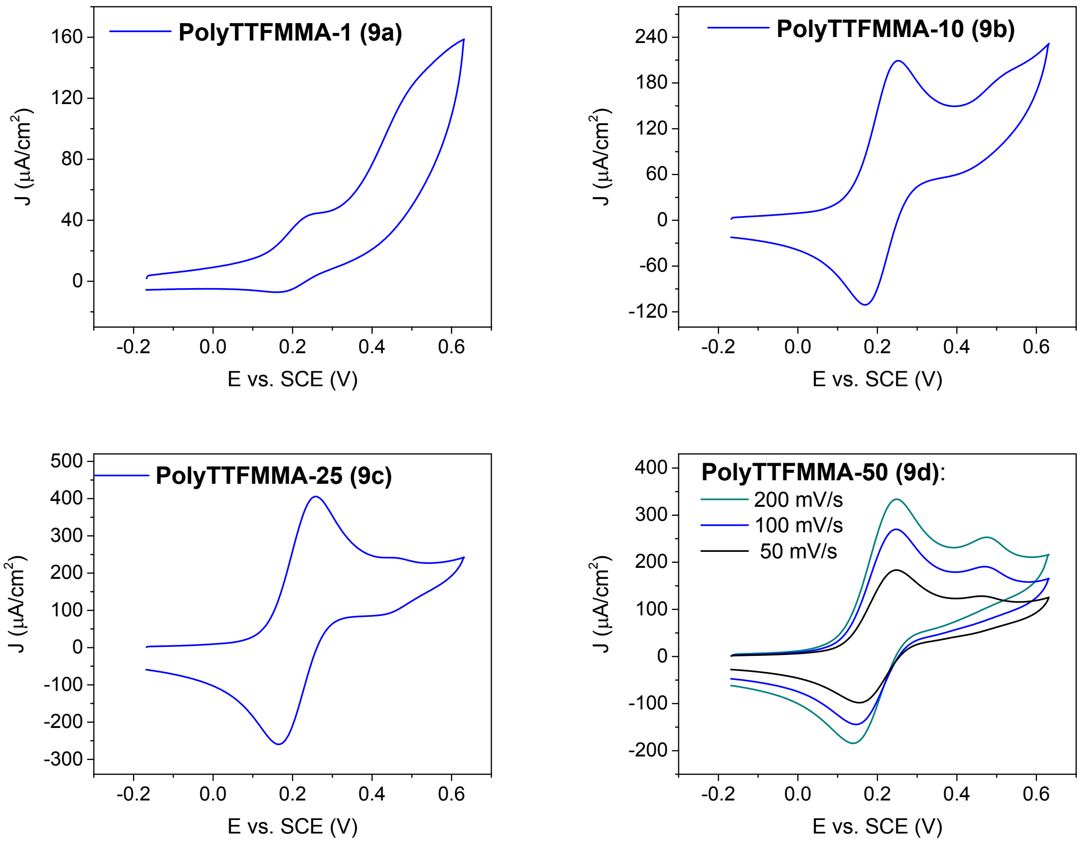


Figure S6. Cyclic voltammograms of the **polyTTFMMA (9a-d)** series in 0.1 M Bu_4NPF_6 solution in NMP at a 100 mV/s scan rate. Cyclic voltammograms for **9d** at scan rates of 50, 100 and 200 mV/s illustrate the increasing definition of the second oxidation peak with increasing scan rate. Platinum button, platinum flag and non-aqueous Ag/Ag^+ electrode (calibrated versus the Fc/Fc^+ standard redox couple) were used as the working, counter and reference electrodes, respectively.

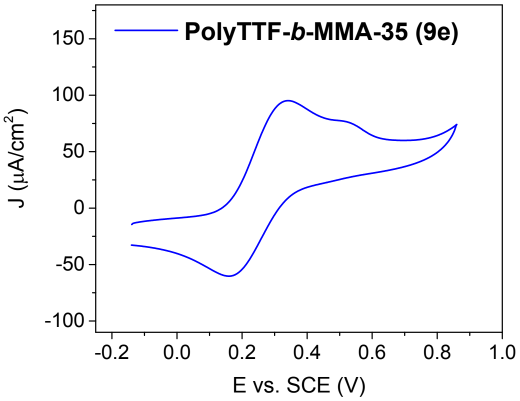


Figure S7. Cyclic voltammogram of **PolyTTF-*b*-MMA-35** (**9e**) in 0.1 M TBAPF$_6$ solution in NMP at a 100 mV/s scan rate. Platinum button, platinum flag and non-aqueous Ag/Ag$^+$ electrode (calibrated vs. Fc/Fc$^+$) were used as the working, counter and reference electrodes, respectively.

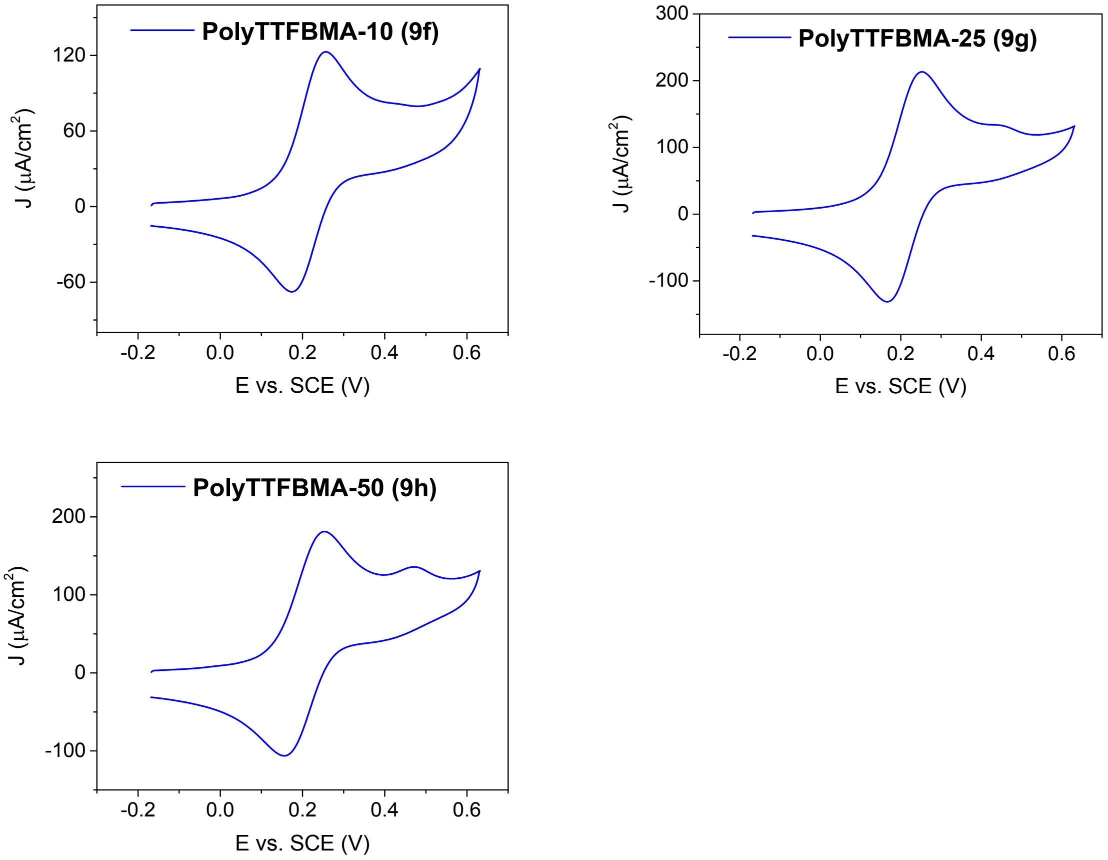


Figure S8. Cyclic voltammograms of the **PolyTTFBMA (9f-h)** series in 0.1 M TBAPF$_6$ solution in NMP at a 100 mV/s scan rate. Platinum button, platinum flag and non-aqueous Ag/Ag$^+$ electrode (calibrated vs. Fc/Fc$^+$) were used as the working, counter and reference electrodes, respectively.

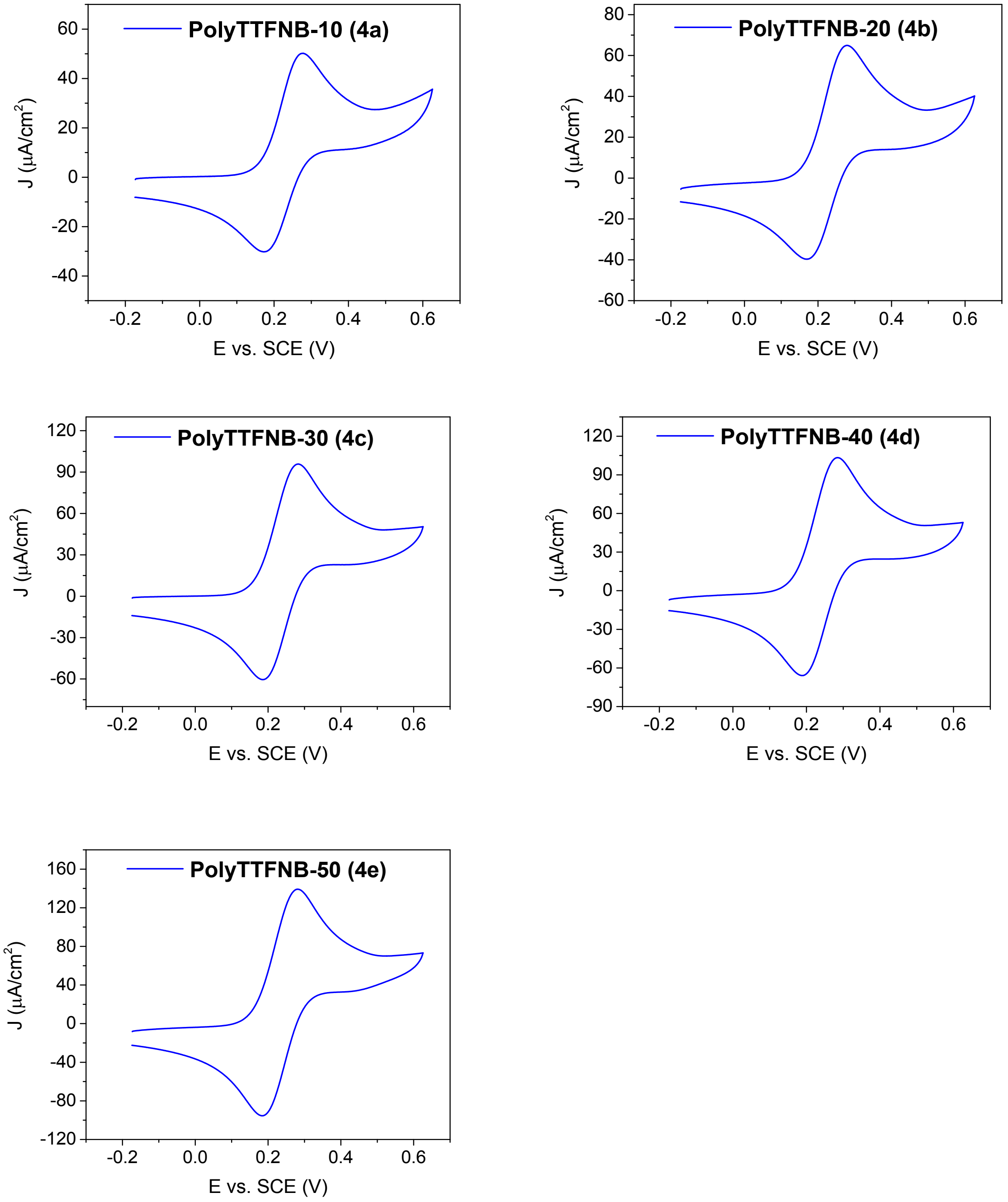


Figure S9. Cyclic voltammograms of the **PolyTTFNB (9a-e)** series in 0.1 M TBAPF$_6$ solution in NMP at a 100 mV/s scan rate. Platinum button, platinum flag and non-aqueous Ag/Ag$^+$ electrode (calibrated vs. Fc/Fc$^+$) were used as the working, counter and reference electrodes, respectively.

MoS$_2$ Characterization

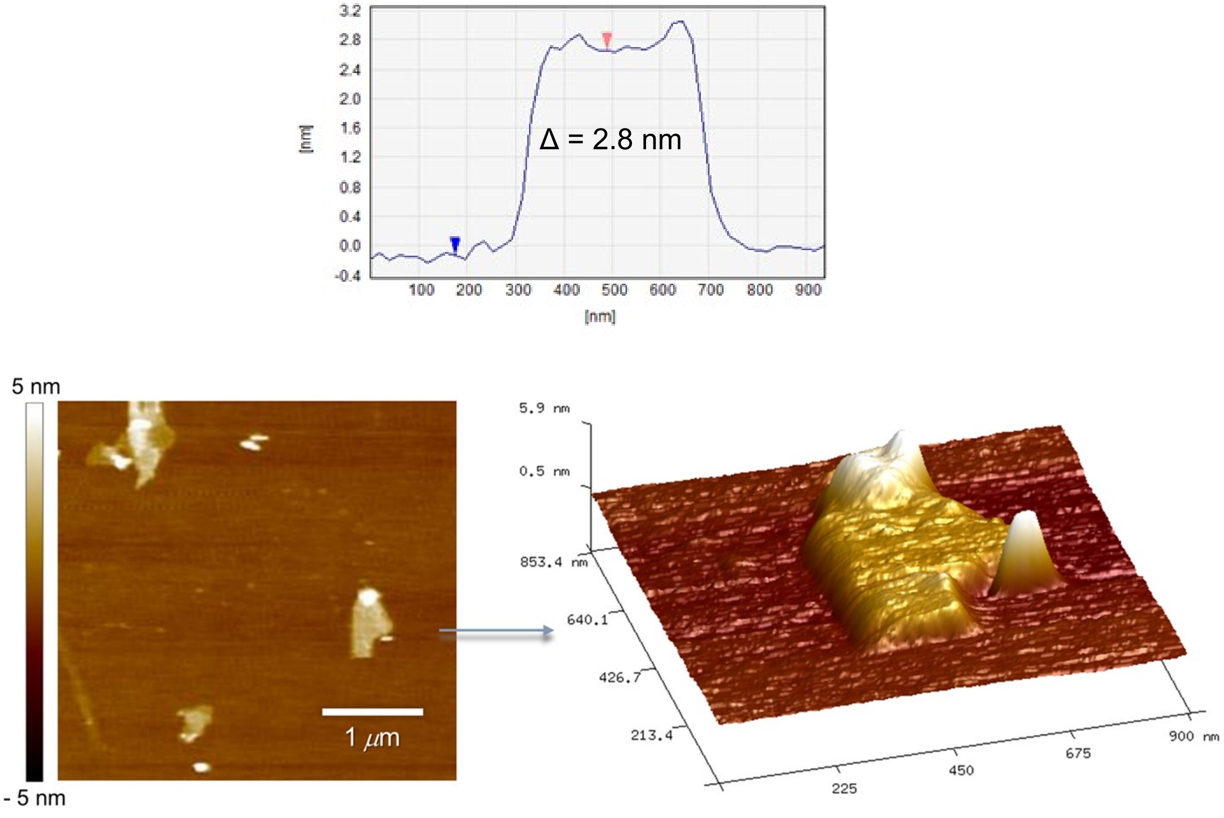


Figure S10. AFM height images of chemically exfoliated MoS$_2$ nanosheets.

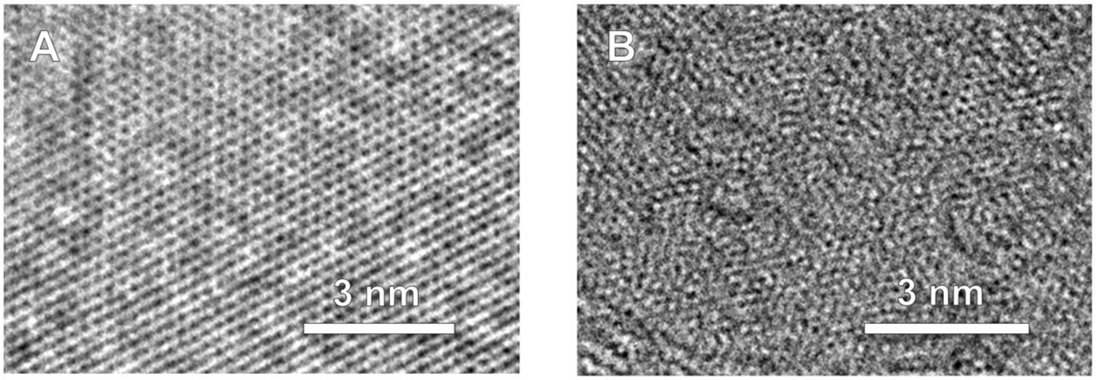


Figure S11. High resolution TEM images of (a) MoS_2 nanosheets exfoliated via sonication that feature a pristine 2H lattice; (b) chemically exfoliated MoS_2 nanosheets with a disordered 1T lattice.

MoS_2 – TTF interactions

Suspension Stabilization

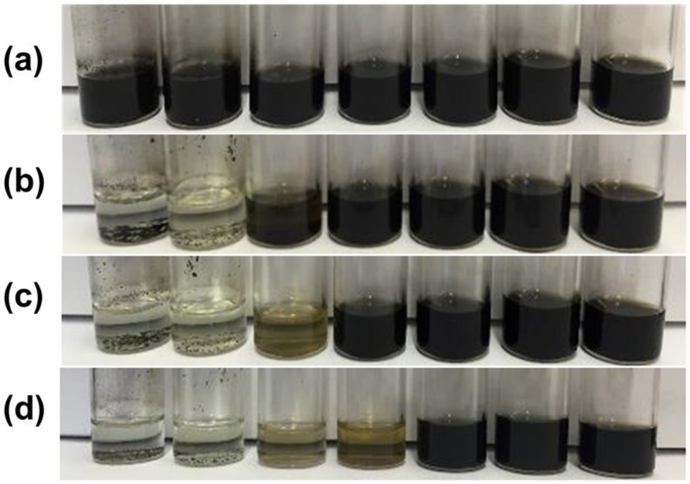


Figure S12. Photographs of chemically exfoliated MoS_2 nanosheet/**PolyTTFNB (4a-e)** suspensions in THF. From left to right the samples are MoS_2 (native), **PolyHexNB (5), 4a, 4b, 4c, 4d,** and **4e.** The different times are (a) immediately after suspension in THF, (b) 2 days, (c) 4 days, and (d) 8 days.

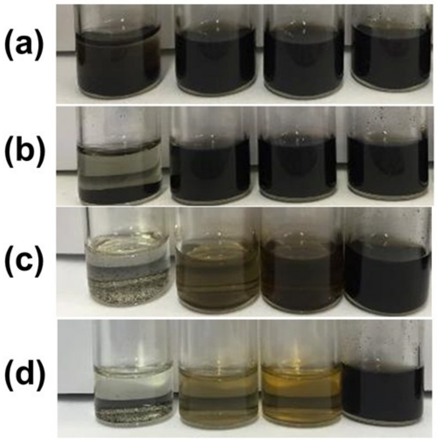


Figure S13. Photographs of chemically exfoliated MoS_2 nanosheet/**PolyTTFBMA (9f-h)** suspensions in THF, taken over time. From left to right the samples are PBMA, **9f, 9g, 9h**. The different times are (a) immediately after suspension in THF, (b) 1 day, (c) 3 days, and (d) 8 days.

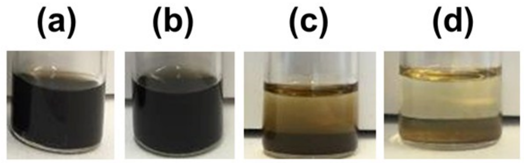
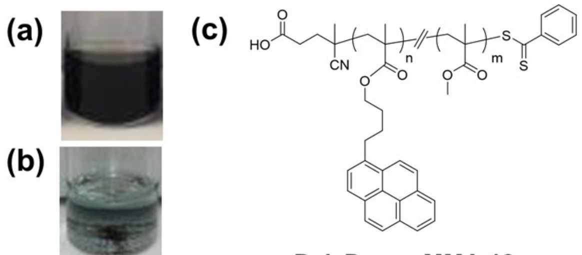


Figure S14. Photographs of chemically exfoliated MoS_2 nanosheet/**PolyMMA-b-TTF-35 (9e)** suspensions in THF, taken over time**.** The different times are (a) immediately after suspension in THF, (b) 3 days, (c) 11 days, and (d) 15 days.



PolyPyreneMMA-12

Figure S15. Photographs of chemically exfoliated MoS_2 nanosheet/**PolyPyreneMMA-12** suspensions in THF, taken over time**.** The different times are (a) immediately after suspension in THF, and (b) 12 hours; (c) chemical structure of the pyrene-functionalized methacrylic polymer **PolyPyreneMMA-12** (M_n = 18.1, PDI = 1.1, polymer contains ca. 12% of pyrene-based repeat units).

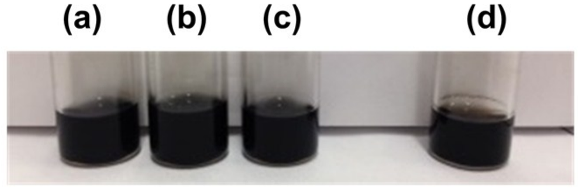


Figure S16. Photographs of chemically exfoliated MoS_2 nanosheet suspensions in THF after 2 months. The remaining stable suspensions are ones prepared with polymers (a) **4c**, (b) **4d**, (c) **4e**, and (d) **9d**.

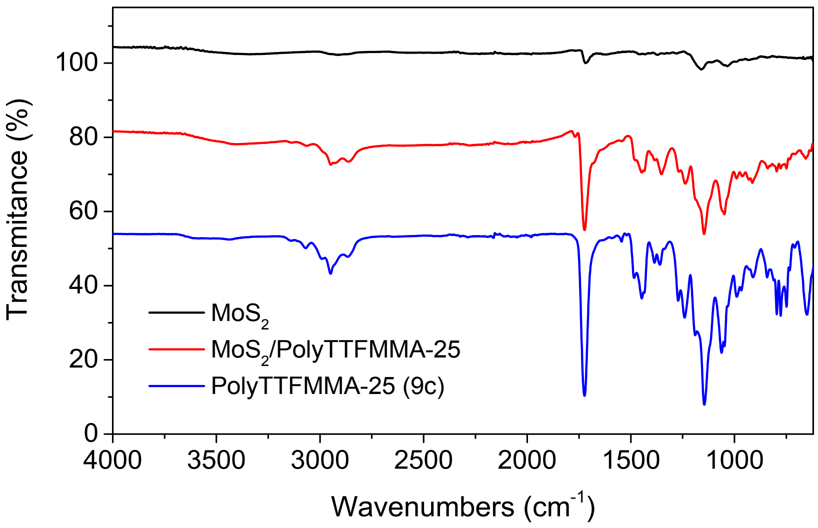


Figure S17. FT-IR spectra of chemically exfoliated MoS$_2$, MoS$_2$/**PolyTTFMMA-25** conjugates, and **PolyTTFMMA-25 (9c)**.

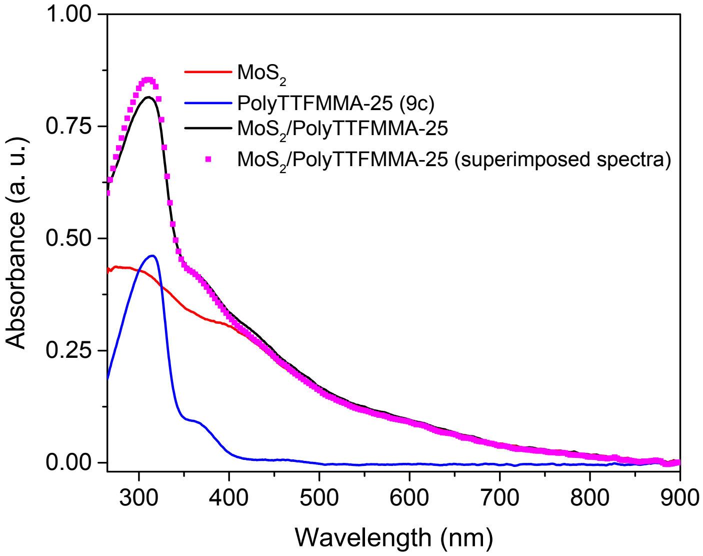


Figure S18. UV-Vis spectra of chemically exfoliated MoS$_2$, MoS$_2$/**PolyTTFMMA-25**, and **PolyTTFMMA-25 (9c)** in NMP and the superimposition of MoS$_2$ and **PolyTTFMMA-25 (9c)** spectra.

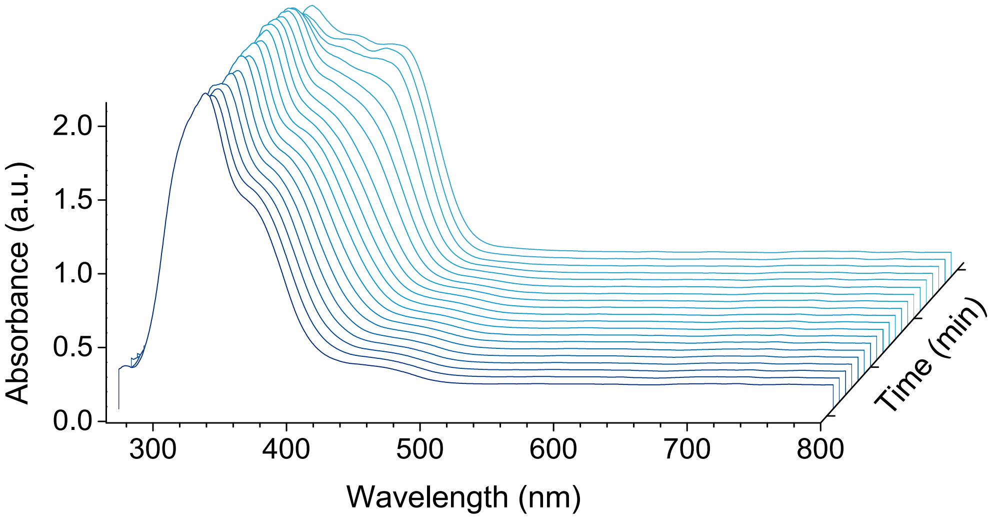


Figure S19. UV-VIS spectra of NMP exfoliated, pristine MoS_2 nanosheets and **PolyTTFNB-50 (4e)** taken over a period of *ca.* 10 min, showing the temporal evolution of the spectral signal at 405 nm, indicative of TTF dimer formation.

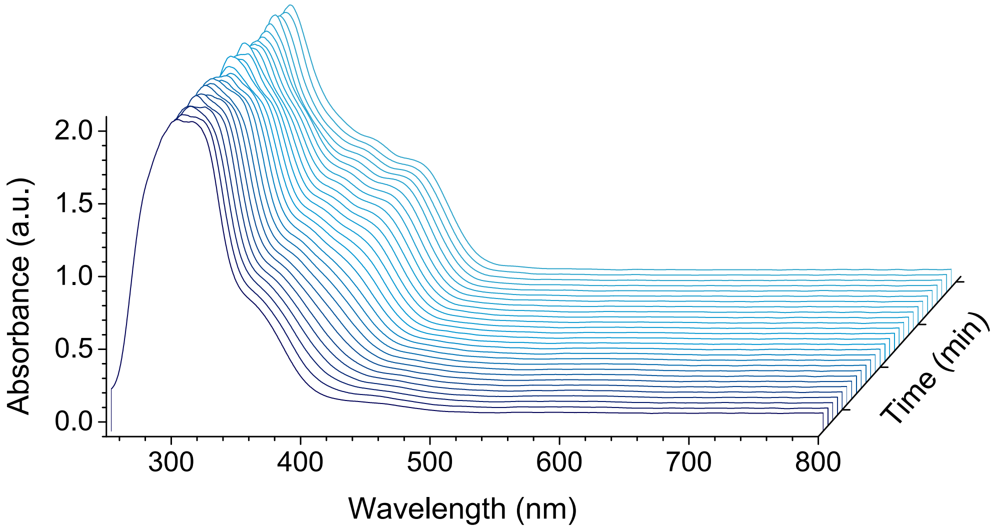


Figure S20. UV-VIS spectra of NMP exfoliated, pristine MoS_2 nanosheets and **PolyTTFMMA-10 (9c)** taken over a period of *ca.* 10 minutes, showing the temporal evolution of the spectral signal at 405 nm, indicative of TTF dimer formation.

Computational Considerations

Comparison of optB86b and HSE Functionals. While the optB86b-vdW functional[1] provides a better description of vdW interactions, this semi-local DFT functional is prone to excessive electron delocalization due to self-interaction errors.[2,3,4] This leads to errors in electronic structure with deleterious consequences for predicting observables such as charge transfer and work function shifts. The inclusion of a fraction of exact exchange within DFT (hybrid DFT) provides a computationally tractable means of decreasing the self-interaction error. Thus, the Heyd-Scuseria-Ernzerhof (HSE) hybrid-DFT functional[2] was employed, which is more accurate than standard DFT across a range of gapped and molecular systems.[3,4] Due to its computational expense, the HSE functional was employed solely to study TTF on a 4×4 MoS_2 monolayer, and the trends identified were consistent with the optB86b studies detailed below.

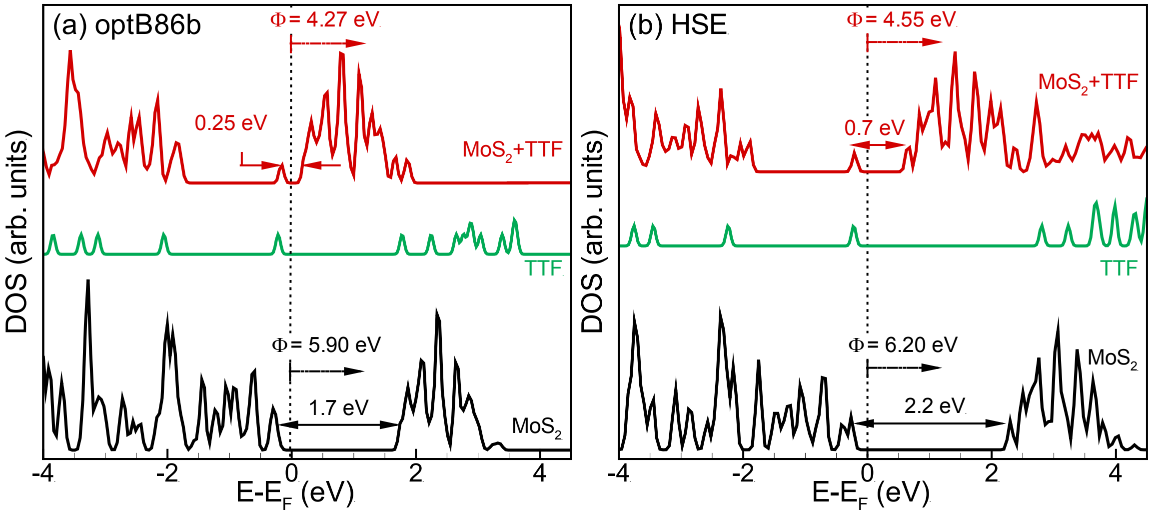


Figure S21: Density of states for monolayer MoS_2, TTF, and MoS_2+TTF composite using (a) optB86b-vdW and (b) HSE functionals. The adsorbed TTF molecule introduces a defect level at 0.25 eV and 0.7 eV from the conduction band edge of pristine MoS_2 as calculated using the optB86b-vdW and HSE functional, respectively. Work functions (Φ) for the MoS_2 monolayer and the MoS_2+TTF composite are indicated from which we note a decrease in work function upon TTF functionalization of MoS_2.

Figure S21 displays the density of states obtained from the optB86b-vdW and the HSE functional for a TTF molecule adsorbed on a 4×4 MoS_2 monolayer. The optB86b-vdW functional predicts about double the charge transfer from TTF to MoS_2 as compared to the HSE functional (see **Table S4**), which is likely due to excessive electron delocalization for the former functional. Note that the TTF adsorbate introduces a defect level within the MoS_2 band gap at 0.25 and 0.7 eV from the conduction band edge of pristine MoS_2 as calculated using the optB86b-vdW and HSE functional, respectively. As expected, with *n*-doping of the MoS_2 monolayer, we find a decrease in the overall work-function of the TTF-MoS_2 composite the optB86b-vdW and HSE results being nearly similar (~1.6 eV work function shift).

Comparison of Adsorption Energies, Charge Transfer, and Work-Function Shifts. Table S4 displays results for the various adsorption scenarios and exchange-correlation functionals. In addition to the 4×4 monolayer MoS_2 supercell cases, we also report the results for a larger 8×8 supercell. Adsorption energies were calculated by subtracting the ground-state total energies of the MoS_2 monolayer and the adsorbate (or adsorbate complex) from the total energy of the composite. Work functions were calculated as the difference between the vacuum level, obtained from the planar-averaged Hartree potential, and the Fermi level. Dipole corrections introduce a step discontinuity in the Hartree potential; the work function in this case is reported as an average of the values calculated on the TTF and non-TTF sides of the composite. The net charge transferred between the two constituents was estimated from a Bader analysis.

Table S4: Results from DFT calculations of TTF adsorbed on monolayer MoS$_2$

	optB86b-vdW		**HSE**
Pristine MoS$_2$ + TTF	***4×4 MoS$_2$***	***8×8 MoS$_2$***	***4×4 MoS$_2$***
Adsorption Energy	-1.04 eV	-1.13 eV	--
Work function shift	-1.63 eV	-1.53 eV	-1.65 eV
Electrons transferred *to* MoS$_2$	8.0×10^{12}/cm^{-2}	2.7×10^{12}/cm^{-2}	3.3×10^{12}/cm^{-2}
MoS$_2$ with sulfur vacancy + TTF	***4×4 MoS$_2$***		
Adsorption Energy	-1.20 eV		
Work function shift	-1.20 eV		
Electrons transferred *to* MoS$_2$	1.8×10^{13}/cm^{-2}		
Pristine MoS$_2$ + TTF dimer	***4×4 MoS$_2$***		
Adsorption Energy	-1.08 eV		
Work function shift	-2.33 eV		
Electrons transferred *to* MoS$_2$	1.1×10^{13}/cm^{-2}		

EXPERIMENTAL PROCEDURES

Materials

Sodium borohydride (98%), Grubbs generation I catalyst (97%), exo-5-norbornene carboxylate (97%), triphenylphosphine (99%), dimethylaminopyridine (DMAP) (98%), sodium hydride (60% suspension in mineral oil), sodium azide (99.5%), copper(I) bromide (99.99%), N,N,N',N',N''–pentamethyldiethylenetriamine (PMDETA) (99%), ethyl-2-bromoisobutyrate (98%), 4-Cyano-4-(thiobenzoylthio)pentanoic acid (97%), ethyl vinyl ether (99%), tetrabutylammoniumhexafluoro phosphate (TBAPF$_6$) (98%), Molybdenum (IV) sulfide (99%), n-butyl lithium (1.6M in hexanes), hexanol (98%), anhydrous anisole (99.7%), and anhydrous N,N-dimethylformamide (99.8%) were purchased from Aldrich. Methyl methacrylate (99%), n-butyl methacrylate (99%), 2-formyltetrathiafulvalene (98%)

and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (98%) were purchase from TCI. Trishydroxymethyl phosphine (95%) was purchased from Strem Chemicals. Propargyl bromide (95%), 18-crown-6 (98%) and 2-chloroethyl methacrylate (97%) were purchased from Alfa Aesar. Azobisisobutyronitrile (AIBN) was recrystallized from methanol prior to use. Methyl methacrylate, n-butyl methacrylate and 2-chloroethyl methacrylate were run through a plug of alumina prior to use to remove inhibitors present in the commercial source. All other chemicals were used as received. Dichloromethane was distilled over calcium hydride and tetrahydrofuran was distilled over sodium/benzophenone prior to use.

2-Hydroxymethyltetrathiafulvalene (**1**).[5] To a stirring solution of 2-formyl tetrathiafulvalene (1.24 g, 5.31 mmol) and methanol (120 mL) was added sodium borohydride (0.37 g, 10 mmol) over a period of 5 minutes. The mixture was allowed to stir for 30 minutes, and the bright yellow solution was concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel, eluting with dichloromethane, to afford a bright yellow solid upon drying. Yield: 1.15 g, 93%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 6.27 (d, *J* = 35.4 Hz, 2H), 4.41 (s, 2H), 1.72 (t, *J* = 6.3 Hz, 1H).

Exo-5-norbornene-3-(hydroxymethyltetrathiafulvalene)ester (2). Exo-5-norbornene-3-carboxylic acid (0.55 g, 4.0 mmol), EDCI (0.7 g, 4.5 mmol), DMAP (0.045 g, 0.35 mmol), and anhydrous dichloromethane (20 mL) were combined in a roundbottom flask, degassed for 15 min with nitrogen gas, and cooled to 0 ^oC. To the resulting mixture was added, dropwise, a degassed solution of compound **1** (0.86 g, 3.7 mmol) in anhydrous dichloromethane (10 mL). The reaction mixture was allowed to warm to room temperature and stirred overnight under a nitrogen atmosphere. The resulting solution was washed with saturated aqueous $NaHCO_3$ solution followed by 3 washes with water. The organic layer was separated, dried over $MgSO_4$ and the excess solvent was removed by rotary evaporation. Purification of the residue was performed by column chromatography on silica gel using a dichloromethane:hexanes mixture (1:1 volume ratio) as the mobile phase, followed by drying under vacuum to afford the product as yellow crystals. Yield: 1.06 g, 75%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 6.32 (d, *J* = 2.3 Hz, 3H), 6.18 – 6.08 (m, 2H), 4.83 (s, 2H), 3.07 (s, 1H), 2.94 (s, 1H), 2.26 (dd, *J* = 10.0, 4.5 Hz, 1H), 1.93 (dt, *J* = 11.7, 4.0 Hz, 1H), 1.52 (d, *J* = 8.9 Hz, 1H), 1.45-1.31 (m, 2H); ^{13}C (126 MHz, $CDCl_3$) 30.4, 41.7, 43.0, 46.4, 46.7, 60.8, 109.3, 111.7, 118.9, 119.0, 119.1, 131.4, 135.7, 138.2, 175.7. ESI-MS: m/z calculated for C15H14O2S4 [M+]: 353.9877, found: 353.9863.

Exo-5-norbornene-3-hexyl ester (3).[6] Exo-5-norbornene-3-carboxylic acid (2.0 g, 14.5 mmol), EDCI (2.9 g, 15.0 mmol), DMAP (0.065 g, 0.35 mmol), and 20 mL of anhydrous DCM were combined in a roundbottom flask, degassed for 15 min (N_2 purging) and cooled to 0 °C. To the resulting mixture, a degassed solution of 1-hexanol (1.6 g, 15.0 mmol) in dichloromethane (10 mL) was added dropwise by syringe. The reaction mixture was then allowed to warm to room temperature and stirred overnight. The solution obtained was washed with saturated $NaHCO_3$ solution followed by three washes with water. The organic layer was separated, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel, eluting with hexanes:ethyl acetate (7:3 volume ratio) to afford a clear liquid after evaporation of excess solvent. Yield: 2.9 g, 90%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 1.91 (dt, *J* = 11.8, 4.0 Hz, 1H), 1.61 (p, 2H), 1.51 (d, *J* = 8.4 Hz, 1H), 1.38 – 1.28 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H).

Typical procedure for ring-opening metathesis polymerization (ROMP) of TTF-substituted norbornenes. Compounds **2** and **3**, PPh_3, and 0.5 mL of anhydrous THF were combined in a 20 mL vial and equipped with a septum. In a separate 20 mL vial, equipped with a septum and a stir bar, the ruthenium benzylidene catalyst (Grubbs Generation I catalyst) was dissolved in anhydrous THF (0.5 mL). Both solutions were subjected to three freeze-pump-thaw cycles, then allowed to return to room temperature. The monomer solution was added to the catalyst solution by syringe, and the mixture was stirred for 10 min. The polymerization was terminated by the addition of excess ethyl vinyl ether (EVE) (0.2 mL), and a solution of tris(hydroxymethyl)phosphine (0.10 g, 0.75 mmol) in THF (0.5 mL) was added as a ruthenium scavenger 30 minutes after termination with the vinyl ether. This mixture was allowed to stir overnight, and the resultant solution was precipitated twice into a large excess of MeOH to give a bright yellow tacky solid.

Poly-n-hexylNB 5 was synthesized using compound **3** (0.2 g, 0.9 mmol)**,** PPh_3 (0.004 g, 0.015 mmol), and Grubbs Generation I catalyst (0.013 g, 0.016 mmol) in anhydrous THF (1 mL): Yield: 0.16 g, 84%. GPC (estimated against polystyrene standards and eluting in THF): M_n = 50 kDa, PDI = 1.20. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 5.35 (broad, s, 2H *trans* from polymer backbone), 5.15-5.25 (broad, m, 2H *cis* from polymer backbone), 2.70-2.90 (broad, m, 3H), 2.35-2.50 (broad, m, 2H), 1.70-1.95 (broad, m, 6H), 1.25-1.45 (broad, m, 4H), 0.90-1.10 (broad, m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 176.48, 133.70-134.50 (multiple), 132.9-133.5 (multiple), 64.77, 49.80-51.00 (multiple), 43.62, 43.34, 42.94, 42.29, 41.55, 38.85, 38.61, 33.33, 32.56, 32. 39, 31.65, 28.91, 25.81, 22.75.

PolyTTFNB-10 (**4a**) was synthesized from **2** (0.035 g, 0.1 mmol), **3** (0.2 g, 0.9 mmol), PPh_3 (0.004 g, 0.015 mmol), and Grubbs Generation I catalyst (0.013 g, 0.016 mmol) in anhydrous THF (1 mL). Monomer conversion from ^{1}H NMR: 60%. Yield: 0.12 g, 85%. GPC (*versus* PS in THF): M_n = 25 kDa, PDI = 1.26. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 6.31(s, 2H from TTF ring), 6.29 (s, 1H from TTF ring), 5.30-5.50 (m, 4H *trans* from polymer backbone) 5.15-5.28 (m, 4H *cis* from polymer backbone), 4.72-4.87 (broad, m, 2H TTF methylene spacer), 4.00-4.10 (broad, m, 2H), 3.08 (broad, s, 4H, *cis*), 2.96 (broad, s, 4H, *cis*), 2.45-2.80 (broad, m, 10H), 2.01-2.15 (broad, m, 2H), 1.89-2.00 (broad, m, 2H), 1.54-1.73 (broad, m, 4H), 1.25-1.39 (broad, m, 6H from hexyl chain), 1.09-1.22 (broad, m, 2H), 0.88 (t, 3H, J = 6.2Hz, from hexyl chain). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 176.14, 175.47, 130.60-133.80 (multiple), 128.65, 126.14, 119.29, 119.18, 111.79, 109.40, 64.67, 60.86, 51.05, 50.46, 50.16, 49.00-50.05 (multiple), 47.00-48.10 (multiple), 43.15, 42.10, 41.29, 37.37, 36.36, 31.60, 28.84, 25.77, 22.72, 14.25.

PolyTTFNB-20 (**4b**) was synthesized from **2** (0.070 g, 0.2 mmol), **3** (0.18 g, 0.8 mmol), PPh_3 (0.004 g, 0.015 mmol), and Grubb's Generation I catalyst (0.013 g, 0.016 mmol) in anhydrous THF (1 mL). Monomer conversion from ^{1}H NMR: 90%. Yield: 0.16 g, 76%. GPC (*versus* PS in THF) M_n: 55 kDa, PDI = 1.16. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 6.31(s, 2H from TTF ring), 6.29 (s, 1H from TTF ring), 5.29-5.50 (m, 4H *trans* from polymer backbone) 5.10-5.27 (m, 4H *cis* from polymer backbone), 4.73-4.87 (broad, m, 2H TTF methylene spacer), 4.00-4.10 (broad, m, 2H), 3.08 (broad, s, 4H, *cis*), 2.96 (broad, s, 4H, *cis*), 2.45-2.80 (broad, m, 10H), 2.00-2.15 (broad, m, 2H), 1.88-1.99 (broad, m, 2H), 1.54-1.72 (broad, m, 4H), 1.25-1.38 (broad, m, 6H from hexyl chain), 1.11-1.23 (broad, m, 2H from hexyl chain), 0.88 (t, 3H, J = 6.2Hz). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 176.14, 175.47, 130.80-133.84 (multiple), 128.65, 126.14, 119.29, 119.18, 111.79, 109.40, 64.67, 60.86, 51.05, 50.46, 50.16, 49.10-49.71 (multiple), 47.00-48.20 (multiple), 43.15, 42.10, 41.29, 37.37, 36.36, 31.60, 28.84, 25.77, 22.72, 14.25.

PolyTTFNB-30 (**4c**) was synthesized from **2** (0.11 g, 0.3 mmol), **3** (0.15 g, 0.7 mmol), PPh_3 (0.004 g, 0.015 mmol), and Grubbs Generation I catalyst (0.014 g, 0.017 mmol) in anhydrous THF (1 mL). Monomer conversion from ^{1}H NMR:

93%. Yield: 0.14 g, 58%. GPC (*versus* PS in THF) M_n: 42 kDa, PDI: 1.12. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 6.31(s, 2H from TTF ring), 6.29 (s, 1H from TTF ring), 5.29-5.48 (m, 4H *trans* from polymer backbone) 5.13-5.27 (m, 4H *cis* from polymer backbone), 4.72-4.86 (broad, m, 2H TTF methylene spacer), 3.98-4.08 (broad, m, 2H), 3.08 (broad, s, 4H, *cis*), 2.96 (broad, s, 4H, *cis*), 2.44-2.77 (broad, m, 10H), 1.98-2.14 (broad, m, 2H), 1.88-1.97 (broad, m, 2H), 1.53-1.71 (broad, m, 4H), 1.23-1.38 (broad, m, 6H from hexyl chain), 1.08-1.22 (broad, m, 2H), 0.87 (t, 3H, J = 6.2Hz, hexyl). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 176.13, 175.46, 130.50-134.50 (multiple), 128.66, 126.13, 119.28, 119.15, 111.89, 109.40, 64.66, 60.86, 51.05, 50.46, 49.00-49.78 (multiple), 46.90-48.10 (multiple), 43.19, 42.07, 41.24, 37.27, 37.02, 36.37, 31.60, 28.87, 25.76, 22.72, 14.23.

PolyTTFNB-40 (**4d**) was synthesized from **2** (0.14 g, 0.4 mmol), **3** (0.13 g, 0.6 mmol), PPh_3 (0.005 g, 0.019 mmol), and Grubbs Generation I catalyst (0.015 g, 0.018 mmol) in anhydrous THF (1 mL). Monomer conversion ^{1}H NMR: 85%. Yield: 0.17 g, 74%. GPC (*versus* PS in THF) M_n: 40 kDa, PDI: 1.22. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.31 (s, 2H from TTF ring), 6.29 (s, 1H from TTF ring), 5.28-5.47 (m, 4H *trans* from polymer backbone) 5.13-5.27 (m, 4H *cis* from polymer backbone), 4.72-4.86 (broad, m, 2H, TTF methylene spacer), 3.98-4.08 (broad, m, 2H), 3.08 (broad, s, 4H, *cis*), 2.96 (broad, s, 4H, *cis*), 2.40-2.80 (broad, m, 10H), 1.99-2.15 (broad, m, 2H), 1.87-1.96 (broad, m, 2H), 1.53-1.74 (broad, m, 4H), 1.23-1.36 (broad, m, 6H, from hexyl chain), 1.07-1.22 (broad, m, 2H), 0.87 (t, 3H, J = 6.2Hz, from hexyl chain). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 176.13, 175.46, 130.40-134.80 (multiple), 128.65, 126.13, 119.28, 119.16, 111.87, 109.39, 64.66, 60.85, 51.04, 50.45, 49.10-50.50 (multiple), 47.00-48.20 (multiple), 43.23, 42.09, 41.20, 37.26, 37.02, 36.34, 31.59, 28.83, 25.76, 22.71, 14.24.

PolyTTF-NB-50 (**4e**) was synthesized from **2** (0.18 g, 0.5 mmol), **3** (0.11 g, 0.5 mmol), PPh_3 (0.005 g, 0.019 mmol, and (0.016 g, 0.019 mmol) Grubbs Generation I catalyst in anhydrous THF (1 mL). Monomer conversion estimated by ^{1}H NMR: 82%. Yield 0.20 g, 84%. GPC (*versus* PS in THF) M_n: 38 kDa, PDI: 1.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.31(s, 2H from TTF ring), 6.29 (s, 1H from TTF ring), 5.30-5.47 (m, 4H *trans,* from polymer backbone) 5.14-5.28 (m, 4H *cis,* from polymer backbone), 4.72-4.86 (broad, m, 2H, TTF methylene spacer), 3.98-4.08 (broad, m, 2H), 3.08 (broad, s, 4H, *cis*), 2.96 (broad, s, 4H, *cis*), 2.45-2.78 (broad, m, 10H), 2.00-2.14 (broad, m, 2H), 1.88-1.99 (broad, m, 2H), 1.54-1.74 (broad, m, 4H), 1.24-1.38 (broad, m, 6H, from hexyl chain), 1.10-1.23 (broad, m, 2H), 0.88 (t, 3H, J = 6.2Hz, from hexyl chain). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.14, 175.47, 130.50-134.50 (multiple), 128.65, 126.14, 119.29, 119.18, 111.79, 109.40, 64.67, 60.86, 51.05, 50.46, 49.00-50.50 (multiple), 47.00-48.40 (multiple), 43.15, 42.10, 41.29, 37.37, 36.85, 36.36, 31.60, 28.84, 25.77, 22.72, 14.25.

2-Propargyloxymethyltetrathiafulvalene (6). Sodium hydride (38 mg, 1.6 mmol) was added under a nitrogen blanket to a dry, nitrogen purged flask, and the flask was cooled to 0 °C. Anhydrous THF (45 mL) was added by syringe, and the resulting suspension stirred for 5 minutes. A solution of **1** (500 mg, 2.13 mmol) in dry THF (3 mL) was then added dropwise. The solution obtained was stirred for 15 minutes, followed by the dropwise addition of propargyl bromide (80% wt in toluene, 0.34 g, 2.3 mmol). The mixture was allowed to warm to room temperature and stirred for 12 hours. The mixture was quenched with methanol (3 mL) and extracted using dichloromethane and water. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated by rotary evaporation. The residue was purified by column chromatography over silica gel, eluting with dichloromethane to afford the desired compound as an orange solid upon drying. Yield: 91% 0.53 g ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 2.45 (t, 1H); 4.17 (d, 2H); 4.33 (s, 2H); 6.25 (s, 1H); 6.28 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 56.88, 66.17, 75.56, 77.23, 78.98, 109.62, 111.58, 117.79, 119.16, 119.32, 133.43. . FAB-MS: m/z calculated for $C_{10}H_8OS_4$ [M+]: 271.9458, found: 271.9486.

2-Methoxymethyltetrathiafulvalene (3). Sodium hydride (0.0143 g, 0.5975 mmol) was added under a nitrogen blanket to a dry, nitrogen-purged flask. The flask was cooled to 0 °C, anhydrous tetrahydrofuran (30 mL) was added and the resulting suspension stirred for 5 minutes. A solution of **1** (0.1000 g, 0.427 mmol) in dry tetrahydrofuran (1 mL) was then added drop-wise, and the solution was stirred for 15 minutes, followed by the drop-wise addition of methyl iodide (133 µL, 2.134 mmol). The content of the flask was allowed to warm to room temperature and stirred for 12 hours. The reaction mixture was quenched with 3 mL of methanol, and extracted using dichloromethane/water. The organic fractions were combined and dried over magnesium sulfate, filtered, and brought to dryness by rotory evaporation. The resulting residue was purified by silica flash chromatography, eluting with dichloromethane to afford the desired compound as an orange solid (stored at -20^{o}C, under N_2). Yield: 82% (0.872 g). ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 3.19 (s, 3H); 4.18 (s, 2H); 6.21 (s, 1H); 6.31 (s, 2H).

Preparation of chloroethyl-functionalized polymer precursors (7a-h) via reversible addition-fragmentation chain-transfer polymerization (RAFT). 2-Chloroethyl methacrylate, methyl methacrylate or butyl methacrylate 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid, azobisisobutyronitrile (AIBN), and anisole were combined in a flask equipped with a septum and degassed for 25 min (N_2 purging). The reaction mixture was immersed in an oil bath preheated to 80 °C. The flask was sealed and the content stirred for 8 hours (ca. 50% monomer conversion was targeted to circumvent any radical transfer by chloroethyl functionalities). The reaction was quenched by immersion in liquid nitrogen, and the mixture precipitated twice in methanol. The resulting pale pink polymers were collected by centrifugation, and dried under vacuum

7a was synthesized using methyl methacrylate (2.9736 g, 29.700 mmol), 2-chloroethyl methacrylate (0.0446 g, 0.300 mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (14.1 mg, 0.0503 mmol), AIBN (1.7 mg, 0.010 mmol) , and anisole (6 mL). Monomer conversion by ^{1}H NMR: 59.4%. Yield of light pink powder: 71%, 1.2640 g. GPC (versus PMMA in THF): M_n = 35 kDa, PDI = 1.13. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.65-1.48 (m, 6H from methacrylate backbone); 1.56-2.12 (m, 4H from methacrylate backbone); 3.55 (s, 3H from methyl methacrylate pendent group); 3.69 (s, 2H from 2-chloro-ethylmethacrylate) 4.17 (s, 2H from 2-chloro-ethylmethacrylate pendent group) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 16.63 (broad), 18.89, 19.14, 41.42, 41.61, 44.71, 45.06, 45.69, 51.99, 54.37 (broad), 54.60 (broad), 64.71, 64.86, 177.14 (broad), 177.29, 177.96 (broad), 178.25 (multiple).

7b was synthesized using methyl methacrylate (2.7032 g, 27.000 mmol), 2-chloroethyl methacrylate (0.4458 g, 3.000 mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (14.7 mg, 0.053 mmol), AIBN (1.7 mg, 0.011 mmol) , and anisole (6 mL). Monomer conversion by ^{1}H NMR: 55.7%. Yield of light pink powder: 76%, 1.3235 g. GPC (versus PMMA in THF): M_n = 33 kDa, PDI = 1.14. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.66-1.52 (m, 6H from methacrylate backbone); 1.64-2.11 (m, 4H from methacrylate backbone); 3.58 (s, 3H from methyl methacrylate pendent group); 3.69 (s, 2H from 2-chloro-ethylmethacrylate); 4.20 (s, 2H from 2-chloro-ethylmethacrylate pendent group) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 16.62 (broad), 18.85 (multiple), 41.41, 41.59, 44.89 (multiple), 45.69, 51.97, 54.45 (broad), 64.71, 64.86, 176.41, 177.11, 177.27, 177.95, 178.24.

7c was synthesized using methyl methacrylate (2.2527 g, 22.500 mmol), 2-chloroethyl methacrylate (1.1144 g, 7.500 mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (15.7 mg, 0.0561 mmol), AIBN (1.8 mg, 0.011 mmol) , and anisole (6 mL). Monomer conversion by ^{1}H NMR: 55.6%. Yield of light pink powder: 69%, 1.2961 g. GPC (versus PMMA in THF): M_n = 34 kDa, PDI = 1.14. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.63-1.55 (m, 6H from methacrylate backbone); 1.62-2.19 (m, 4H from methacrylate backbone); 3.58 (s, 3H from methyl methacrylate pendent group); 3.70 (s, 2H from 2-chloro-ethylmethacrylate); 4.20 (s, 2H from 2-chloro-ethylmethacrylate pendent group) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 16.64 (broad), 18.88 (multiple), 41.43, 41.61, 44.91 (multiple), 45.70, 51.99, 54.53 (broad), 64.58, 64.76, 64.90, 176.46, 177.12, 177.30, 177.59, 177.96, 178.26, 178.54.

7d was synthesized using methyl methacrylate (1.5018 g, 15.000 mmol), 2-chloroethyl methacrylate (2.2289 g, 15.000 mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (17.4 mg, 0.0622 mmol), AIBN (2.0 mg, 0.012 mmol) , and anisole (6 mL). Monomer conversion by ^{1}H NMR: 59.3%. Yield of light pink powder: 75%, 1.6670 g. GPC (versus PMMA in THF): M_n = 38 kDa, PDI = 1.19. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.67-1.55 (m, 6H from methacrylate backbone); 1.64-2.16 (m, 4H from methacrylate backbone); 3.59 (s, 3H from methyl methacrylate pendent group); 3.71 (s, 2H from 2-chloro-ethylmethacrylate); 4.21 (s, 2H from 2-chloro-ethylmethacrylate pendent group) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 16.64 (broad), 18.83 (multiple), 41.43, 41.61, 44.92 (multiple), 45.52, 52.04, 54.38 (broad), 64.77, 64.581, 64.92, 176.35, 176.54, 177.24, 177.54, 177.87, 178.18.

7f was synthesized using butyl methacrylate (3.8394 g, 27.000 mmol), 2-chloroethyl methacrylate (0.4458 g, 3.00 mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (20.0 mg, 0.0714 mmol), AIBN (2.3 mg, 0.013 mmol) , and anisole (6 mL). Monomer conversion by ^{1}H NMR: 78.2%. Yield of light pink amorphous solid: 84%, 2.0679 g. GPC (versus PMMA in THF): M_n = 42 kDa, PDI = 1.11. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.76-1.29 (m, 6H from methacrylate backbone and 3H from butyl pendent group); 1.40 (s, 2H from butyl pendent group); 1.61 (s, 2H from butyl methacrylate pendent group); 1.71-2.11 (m, 4H from methacrylate backbone); 3.69 (s, 2H from 2-chloroethylmethacrylate); 3.94 (s, 2H from butyl methacrylate pendent group); 4.19 (s, 2H from 2-chloroethylmethacrylate pendent group) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 13.91, 16.67 (broad), 18.55 (broad), 19.51, 30.39, 41.43 (multiple), 44.91, 45.30, 52.47 (broad), 54.36 (broad), 64.90 (broad), 177.01 (multiple, broad), 177.70 (multiple, broad), 178.04 (multiple, broad).

7g was synthesized using butyl methacrylate (3.1995 g, 22.500 mmol), 2-chloroethyl methacrylate (1.1144 g, 7.500 mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (20.1 mg, 0.0719 mmol), AIBN (2.4 mg, 0.014 mmol) , and anisole (6 mL). Monomer conversion by ^{1}H NMR: 73.7%. Yield of light pink amorphous solid: 93%, 2.3173 g. GPC (versus PMMA in THF): M_n = 45 kDa, PDI = 1.15. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.78-1.29 (m, 6H from methacrylate backbone and 3H from butyl pendent group); 1.39 (s, 2H from butyl pendent group); 1.61 (s, 2H from butyl methacrylate pendent group); 1.69-2.10 (m, 4H from methacrylate backbone); 3.69 (s, 2H from 2-chloroethylmethacrylate); 3.93 (s, 2H from butyl methacrylate pendent group); 4.20 (s, 2H from 2-chloroethylmethacrylate pendent group) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 13.91, 16.69 (broad), 18.72 (broad), 19.51, 30.39, 41.44 (multiple), 44.95, 45.92, 52.43 (broad), 54.34 (broad), 64.91 (broad), 176.99 (multiple, broad), 177.67 (multiple, broad), 178.04 (multiple, broad).

7h was synthesized using butyl methacrylate (2.1330 g, 15.000 mmol), 2-chloroethyl methacrylate (2.2289 g, 15.000 mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (20.3 mg, 0.0727 mmol), AIBN (2.4 mg, 0.015 mmol) , and anisole (6 mL). Monomer conversion by ^{1}H NMR: 72%. Yield of light pink amorphous solid: 97%, 2.5992 g. GPC (versus PMMA in THF): M_n = 40 kDa, PDI = 1.20. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.79-1.30 (m, 6H from methacrylate backbone and 3H from butyl pendent group); 1.36 (s, 2H from butyl pendent group); 1.58 (s, 2H from butyl methacrylate pendent group); 1.72-2.21 (m, 4H from methacrylate backbone); 3.70 (s, 2H from 2-chloroethylmethacrylate); 3.94 (s, 2H from butyl methacrylate pendent group); 4.20 (s, 2H from 2-chloroethylmethacrylate pendent group) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 13.92, 16.80 (broad), 18.80 (multiple), 19.51, 30.37, 30.45, 41.48 (multiple), 44.98, 45.29, 45.92, 52.50 (broad), 54.35 (broad), 64.94 (broad), 176.70 (multiple, broad), 177.24 (multiple, broad).

7e Methyl methacrylate (3.0036 g, 30.000 mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (0.0140 g, 0.050 mmol), and azobisisobutyronitrile (0.0016 g, 0.010 mmol) were combined in a round-bottom flask equipped with a septum and degassed for 25 min (N_2 purging). The reaction mixture was immersed in an oil bath preheated to 80 °C and stirred 2 hours. The reaction was quenched by immersion in liquid nitrogen, and precipitated twice in methanol. The resulting pale pink polymer was collected by centrifugation, and dried under vacuum. To achieve chain extension, the methacrylate polymer obtained (0.8300 g), 2-chloroethyl methacrylate (1.010 g, 6.800 mmol), AIBN (0.0016 g, 0.010 mmol), and anisole (2 mL) were added to a round-bottom flask (equipped with a septum) and degassed for 25 min (N_2 purging). The flask was immersed in an oil bath preheated to 80 °C and stirred for 2 additional hours, quenched by immersion in liquid nitrogen, and precipitated twice in methanol. The resulting pale pink polymer was collected by centrifugation, and dried under vacuum. Monomer conversion by ^{1}H NMR: poly(methyl methacrylate) block - 29.9%; poly(2-chloroethyl methacrylate) block - 47.7%. Yield: 69%, 0.9520 g. GPC (versus PMMA in THF): M_n = 29 kDa, PDI = 1.17 (PMMA block: M_n = 20.0 kDa, PDI=1.09). ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.66-1.58 (m, 6H from methacrylate backbone); 1.63-2.18 (m, 4H from methacrylate backbone); 3.57 (s, 3H from methyl methacrylate pendent group); 3.69 (s, 2H from 2-chloro-ethylmethacrylate); 4.20 (s, 2H from 2-chloro-ethylmethacrylate pendent group) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 16.66 (broad), 16.93 (broad), 18.90 (broad), 19.15 (broad), 41.50, 41.66, 44.73 (multiple), 45.04, 45.31, 52.01, 54.37, 54.61, 64.85, 65.00, 176.33 (multiple), 176.53, 177.15, 177.32 (multiple), 177.45 (multiple), 177.99, 178.27 (multiple), 178.58.

Preparation of azidoethyl-functionalized polymer precursors 8a-h. Chloroethyl-functionalized polymers **7a-h**, sodium azide, a catalytic amount of 18-crown-6, and N,N-dimethylformamide (DMF) were combined in a 20 mL scintillation vial, stirred at 65 °C for 72 hours, and precipitated in a 1:1 mixture of methanol and water. The resulting powder was collected by centrifugation, washed with methanol, dried, and redissolved in chloroform (3 mL). The solution obtained was reprecipitated in a 1:1 mixture of methanol and water. The resulting white solid was collected by centrifugation and dried under vacuum.

8a was synthesized using **7a** (0.1500 g), sodium azide (0.5000 g, 7.700 mmol), 18-crown-6 (2 mg, 0.0139 mmol), and DMF (8 mL). Yield: 69%, 0.1047 g. GPC (versus PMMA in THF): M_n = 37 kDa, PDI = 1.15. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.71-1.51 (m, 6H from methacrylate backbone); 1.74-2.10 (m, 4H from methacrylate backbone); 3.50 (s, 2H from 2-azido-ethylmethacrylate); 3.60 (s, 3H from methyl methacrylate pendent group); 4.11 (s, 2H from 2-azido-ethylmethacrylate pendent group) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 16.48 (broad), 18.73, 18.97, 44.56, 44.89, 51.87, 53.43 (broad), 54.22 (broad), 54.43 (broad), 63.80, 176.18, 176.30, 176.99, 177.15, 177.81, 178.10 (multiple), 178.39, 178.43.

8b was synthesized using **7b** (0.1500 g), sodium azide (0.5000 g, 7.700 mmol), 18-crown-6 (2 mg, 0.0139 mmol), and DMF (8 mL). Yield: 75%, 0.1120 g. GPC (versus PMMA in THF): M_n = 37 kDa, PDI = 1.18. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.70-1.53 (m, 6H from methacrylate backbone); 1.56-2.15 (m, 4H from methacrylate backbone); 3.49 (s, 2H from 2-azido-ethylmethacrylate); 3.59 (s, 3H from methyl methacrylate pendent group); 4.11 (s, 2H from 2-azido-ethylmethacrylate pendent group) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 16.65 (broad), 18.89 (multiple), 44.71, 44.87, 45.05, 45.20, 49.67 (multiple), 49.81, 51.99 (multiple), 52.71 (broad), 54.47 (broad), 63.81, 63.96, 176.48 (multiple, broad), 177.14, 177.31 (multiple, broad), 177.96 (multiple), 178.26 (multiple).

8c was synthesized using **7c** (0.1500 g), sodium azide (0.5000 g, 7.700 mmol), 18-crown-6 (2 mg, 0.0139 mmol), and DMF (8 mL). Yield: 70%, 0.1039 g. GPC (versus PMMA in THF): M_n = 37 kDa, PDI = 1.20. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.70-1.54 (m, 6H from methacrylate backbone); 1.60-2.21 (m, 4H from methacrylate backbone); 3.49 (s, 2H from 2-azido-ethylmethacrylate); 3.59 (s, 3H from methyl methacrylate pendent group); 4.11 (s, 2H from 2-azido-ethylmethacrylate pendent group) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 16.68 (broad), 18.89 (multiple), 44.71, 44.90, 45.05, 45.20, 49.65 (multiple), 49.78, 51.99 (multiple), 52.71 (broad), 54.37 (broad), 63.90 (multiple), 176.46 (broad), 177.12, 177.26, 177.34, 177.64, 177.95 (multiple), 178.25.

8d was synthesized using **7d** (0.1500 g), sodium azide (0.5000 g, 7.700 mmol), 18-crown-6 (2 mg, 0.0139 mmol), and DMF (8 mL). Yield: 75%, 0.1128 g. GPC (versus PMMA in THF): M_n = 43 kDa, PDI = 1.26. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.73-1.52 (m, 6H from methacrylate backbone); 1.78-2.21 (m, 4H from methacrylate backbone); 3.50 (s, 2H from 2-azido-ethylmethacrylate); 3.60 (s, 3H from methyl methacrylate pendent group); 4.12 (s, 2H from 2-azido-ethylmethacrylate pendent group) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 16.81 (broad), 18.99 (multiple), 44.78, 44.95, 45.09, 45.25, 49.68 (multiple), 49.81, 52.07 (multiple), 52.79 (broad), 54.33 (broad), 64.01 (multiple), 176.43, 177.29, 177.63, 177.89, 178.23.

8e was synthesized using **7e** (0.1500 g), sodium azide (0.5000 g, 7.700 mmol), 18-crown-6 (2 mg, 0.0139 mmol), and DMF (8 mL). Yield: 66%, 0.0986 g. GPC (versus PMMA in THF): M_n = 36 kDa, PDI = 1.16. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.67-1.56 (m, 6H from methacrylate backbone); 1.74-2.27 (m, 4H from methacrylate backbone); 3.50 (s, 2H from 2-azido-ethylmethacrylate); 3.59 (s, 3H from methyl methacrylate pendent group); 4.12 (s, 2H from 2-azido-ethylmethacrylate pendent group) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 16.62, 17.07, 18.88, 19.03, 44.70, 44.91, 45.04, 45.24, 49.61 (multiple), 49.73, 51.98 (multiple), 52.74 (broad), 54.33, 54.58, 63.88, 64.02, 176.25 (multiple), 176.46, 177.12 (multiple), 177.29, 177.42 (multiple), 177.96 (multiple), 178.25 (multiple).

8f was synthesized using **7f** (0.1500 g), sodium azide (0.5000 g, 7.700 mmol), 18-crown-6 (2 mg, 0.0139 mmol), and DMF (8 mL). Yield: 73%, 0.1095 g. GPC (versus PMMA in THF): M_n = 46 kDa, PDI = 1.15. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.79-1.30 (m, 6H from methacrylate backbone and 3H from butyl pendent group); 1.38 (s, 2H from butyl pendent group); 1.60 (s, 2H from butyl methacrylate pendent group); 1.76-2.09 (m, 4H from methacrylate backbone); 3.47 (s, 2H from 2-azido-ethylmethacrylate); 3.93 (s, 2H from butyl methacrylate pendent group); 4.09

(s, 2H from 2-azido-ethylmethacrylate pendent group) ^{13}C NMR (125 MHz, CDCl$_3$), δ (ppm): 13.90 (multiple), 16.86 (broad), 18.65 (broad), 19.01 (broad) 19.45, 30.36 (multiple), 44.94, 45.26, 45.91, 49.66, 49.79, 52.54 (broad), 54.34 (broad), 63.81 (broad), 64.93 (broad), 177.51 (multiple, broad), 177.51 (multiple, broad).

8g was synthesized using **7g** (0.1500 g), sodium azide (0.5000 g, 7.700 mmol), 18-crown-6 (2 mg, 0.0139 mmol), and DMF (8 mL). Yield: 73%, 0.1095 g. GPC (versus PMMA in THF): M_n = 48 kDa, PDI = 1.23. ^{1}H NMR (500 MHz, CDCl$_3$), δ (ppm): 0.73-1.30 (m, 6H from methacrylate backbone and 3H from butyl pendent group); 1.38 (s, 2H from butyl pendent group); 1.59 (s, 2H from butyl methacrylate pendent group); 1.71-2.11 (m, 4H from methacrylate backbone); 3.47 (s, 2H from 2-azido-ethylmethacrylate); 3.92 (s, 2H from butyl methacrylate pendent group); 4.09 (s, 2H from 2-azido-ethylmethacrylate pendent group) ^{13}C NMR (125 MHz, CDCl$_3$), δ (ppm): 13.89 (multiple), 16.68 (broad), 18.58 (broad), 19.50, 30.37 (multiple), 44.90, 45.27, 45.92, 49.64, 49.77, 52.71 (broad), 54.31 (broad), 63.84 (broad), 65.03 (broad), 176.76, 176.96, 177.41, 177.53, 177.69 (multiple), 178.02.

8h was synthesized using **7h** (0.1500 g), sodium azide (0.5000 g, 7.700 mmol), 18-crown-6 (2 mg, 0.0139 mmol), and DMF (8 mL). Yield: 76%, 0.1140 g. GPC (versus PMMA in THF): M_n = 49 kDa, PDI = 1.28. ^{1}H NMR (500 MHz, CDCl$_3$), δ (ppm): 0.73-1.30 (m, 6H from methacrylate backbone and 3H from butyl pendent group); 1.38 (s, 2H from butyl pendent group); 1.59 (s, 2H from butyl methacrylate pendent group); 1.70-2.10 (m, 4H from methacrylate backbone); 3.47 (s, 2H from 2-azido-ethylmethacrylate); 3.92 (s, 2H from butyl methacrylate pendent group); 4.09 (s, 2H from 2-azido-ethylmethacrylate pendent group) ^{13}C NMR (125 MHz, CDCl$_3$), δ (ppm): 13.89 (multiple), 16.66 (broad), 18.53 (broad), 19.50, 30.41 (multiple), 44.91, 45.27, 45.91, 49.67, 49.79, 52.60 (broad), 54.32 (broad), 63.78 (broad), 64.89 (broad), 176.98, 177.15, 177.52, 177.68 (multiple), 178.03 (multiple, broad).

Preparation of TTF-containing polymers 9a-h via "click" chemistry. Polymers **8a-h**, 2-propargyloxymethyltetrathiafulvalene **6**, N,N,N',N'',N''-pentamethyldiethylenetriamine, and tetrahydrofuran, were combined in a round bottom flask and degassed for 20 min (N_2 purging). Under a nitrogen blanket, copper(I) bromide was added, and the solution degassed for additional 20 min. The reaction mixture was stirred at 40 °C for 4 h (FT-IR control: disappearance of the azide stretch at 2140 cm^{-1}). The solution was precipitated in hexanes, centrifuged, dissolved in THF, and passed through a short basic alumina column into another solution of hexanes. The resulting yellow powder was collected by centrifugation, and dried under reduced pressure.

PolyTTFMMA-1 (9a) was synthesized using **8a** (0.1453 g), **6** (0.0047 g, 0.020 mmol), copper (I) bromide (0.0020 g, 0.0139 mmol), N,N,N',N'',N''-pentamethyldiethylenetriamine (20 µL, 0.0166 g, 0.096 mmol), and tetrahydrofuran (6 mL). Yield: 63%, 0.0945 g. GPC (versus PMMA in THF): M_n = 36 kDa, PDI = 1.14. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.66-2.10 (m, 10H from methacrylate backbone); 3.59 (s, 3H from methyl methacrylate pendent group); 4.35 (m, 2H from methylene adjacent to TTF group and 2H from ethylmethacrylate pendent group); 4.63 (s, 2H from ethylmethacrylate pendent group); 4.72 (2H from propargyl methylene); 6.33 (3H aryl protons from TTF moiety); 7.68-7.78 (m, 1H from triazole ring) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 16.65, 18.92, 19.18, 29.71, 44.74, 45.08, 52.01, 52.89, 53.62, 54.41, 54.63, 63.35, 67.37, 117.27, 119.27, 119.36, 123.78, 134.18, 145.09, 177.18, 177.33, 177.99 (multiple) 178.28 (multiple), 178.57.

PolyTTFMMA-10 (9b) was synthesized using **8b** (0.1146 g), **6** (0.0354 g, 0.151 mmol), copper (I) bromide (0.0020 mg, 0.0139 mmol), N,N,N',N'',N''-pentamethyldiethylenetriamine (20 µL, 0.0166 g, 0.096 mmol), and tetrahydrofuran (6 mL). Yield: 66%, 0.0951 g. GPC (versus PMMA in THF): M_n = 37 kDa, PDI = 1.23. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.51-2.10 (m, 10H from methacrylate backbone); 3.59 (s, 3H from methyl methacrylate pendent group); 4.34 (m, 2H from methylene adjacent to TTF group and 2H from ethylmethacrylate pendent group); 4.65 (s, 2H from ethylmethacrylate pendent group); 4.71 (2H from propargyl methylene); 6.33 (3H aryl protons from TTF moiety); 7.69-7.84 (m, 1H from triazole ring) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 13.93, 13.97, (broad), 19.53, 30.41, 30.49, 44.93, 45.32, 48.77, 49.95, 54.36, 54.81 63.25 (multiple), 64.94 (multiple), 67.31, 109.91, 111.21, 117.19, 119.22, 119.37, 123.83, 134.20, 144.92, 145.06, 176.98, 177.49, 177.73 (multiple) 178.06 (multiple).

PolyTTFMMA-25 (9c) was synthesized using **8c** (0.0874 g), **6** (0.0626 g, 0.267 mmol), copper (I) bromide (0.0020 g, 0.0139 mmol), N,N,N′,N′′,N′′-pentamethyldiethylenetriamine (20 µL, 0.0166 g, 0.096 mmol), and tetrahydrofuran (6 mL). Yield: 79%, 0.1103 g. GPC (versus PMMA in THF): M_n = 31 kDa, PDI = 1.28. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.41-2.19 (m, 10H from methacrylate backbone); 3.59 (s, 3H from methyl methacrylate pendent group); 4.34 (m, 2H from methylene adjacent to TTF group and 2H from ethylmethacrylate pendent group); 4.67 (m, 2H from ethylmethacrylate pendent group and 2H from propargyl methylene); 6.33 (3H aryl protons from TTF moiety); 7.69-7.87 (m, 1H from triazole ring) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 13.93, 13.97, (broad), 19.53, 30.41, 30.49, 44.93, 45.32, 48.77, 49.95, 54.36, 54.81 63.25 (multiple), 64.94 (multiple), 67.31, 109.91, 111.21, 117.19, 119.22, 119.37, 123.83, 134.20, 144.92, 145.06, 176.98, 177.49, 177.73 (multiple) 178.06 (multiple).

PolyTTFMMA-50 (9d) was synthesized using **8d** (0.0658 g), **6** (0.0842 g, 0.359 mmol), copper (I) bromide (0.0020 g, 0.0139 mmol), N,N,N′,N′′,N′′-pentamethyldiethylenetriamine (20 µL, 0.0166 g, 0.096 mmol), and tetrahydrofuran (6 mL). Yield: 60%, 0.0816 g. GPC (versus PMMA in THF): M_n = 20 kDa, PDI = 1.29. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.69-1.32 (m, 6H from methacrylate backbone and 3H from butyl pendent group); 1.39 (s, 2H from butyl pendent group); 1.60 (s, 2H from butyl methacrylate pendent group); 1.66-2.05 (m, 4H from methacrylate backbone); 3.93 (s, 2H from butyl methacrylate pendent group); 4.34 (m, 2H from methylene adjacent to TTF group and 2H from ethylmethacrylate pendent group); 4.67 (m, 2H from ethylmethacrylate pendent group and 2H from propargyl methylene); 6.33 (3H aryl protons from TTF moiety); 7.69-7.87 (m, 1H from triazole ring) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 13.91, 13.97, (broad), 19.51, 30.40, 30.53, 44.98, 45.35, 48.74, 49.93, 54.37, 54.77 63.30 (multiple), 64.99 (multiple), 67.35, 109.96, 111.27, 117.18, 119.19, 119.44, 123.87, 134.33, 144.93, 145.02, 176.98, 177.48, 177.66 (multiple) 178.10 (multiple).

PolyTTF-*b*-MMA-35 (9e) was synthesized using **8e** (0.0500 g), **6** (0.0502 g, 0.214 mmol), copper (I) bromide (0.0020 g, 0.0139 mmol), N,N,N′,N′′,N′′-pentamethyldiethylenetriamine (20 µL, 0.0166 g, 0.096 mmol), and tetrahydrofuran (4 mL). Yield: 57%, 0.0523 g. GPC (versus PMMA in THF): M_n = 19 kDa, PDI = 1.14. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.42-2.11 (m, 10H from methacrylate backbone); 3.59 (s, 3H from methyl methacrylate pendent group); 4.32 (broad, m, 2H from methylene adjacent to TTF group and 2H from ethylmethacrylate pendent group); 4.66 (broad, m, 2H from ethylmethacrylate pendent group and 2H from propargyl methylene); 6.33 (3H aryl protons from TTF moiety); 7.86 (broad), 1H from triazole ring) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 16.70, 18.92, 19.53, 44.76, 45.03 (multiple), 54.40, 54.63, 63.25 (multiple), 64.94 (multiple), 67.31, 109.91, 111.21, 117.19, 119.22, 119.37, 123.83, 134.20, 144.92, 145.06, 177.20, 177.35, 178.02 (multiple) 178.31 (multiple).

PolyTTFBMA-10 (9f) was synthesized using **8f** (0.1222 g), **6** (0.0278 g, 0.119 mmol), copper (I) bromide (0.0020 g, 0.0139 mmol), N,N,N′,N′′,N′′-pentamethyldiethylenetriamine (20 µL, 0.0166 g, 0.096 mmol), and tetrathydrofuran (6 mL). Yield: 50%, 0.0737 g. GPC (versus PMMA in THF): M_n = 47 kDa, PDI = 1.17. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.69-1.32 (m, 6H from methacrylate backbone and 3H from butyl pendent group); 1.39 (s, 2H from butyl pendent group); 1.60 (s, 2H from butyl methacrylate pendent group); 1.66-2.05 (m, 4H from methacrylate backbone); 3.93 (s, 2H from butyl methacrylate pendent group); 4.33 (s, 2H from methylene adjacent to TTF group); 4.35 (broad s, 2H from ethylmethacrylate pendent group); 4.63 (s, 2H from ethylmethacrylate pendent group); 4.71 (s, 2H from propargyl methylene); 6.33 (3H aryl protons from TTF moiety); 7.68-7.86 (m, 1H from triazole ring) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 13.93, 13.97, (broad), 19.53, 30.41, 30.49, 44.93, 45.32, 48.77, 49.95, 54.36, 54.81 63.25 (multiple), 64.94 (multiple), 67.31, 109.91, 111.21, 117.19, 119.22, 119.37, 123.83, 134.20, 144.92, 145.06, 176.98, 177.49, 177.73 (multiple) 178.06 (multiple).

PolyTTFBMA-25 (9g) was synthesized using **8g** (0.0961 g), **6** (0.0539 g, 0.230 mmol), copper (I) bromide (0.0020 g, 0.0139 mmol), N,N,N′,N′′,N′′-pentamethyldiethylenetriamine (20 µL, 0.0166 g, 0.096 mmol), and tetrathydrofuran (6 mL). Yield: 75%, 0.1058 g. GPC (versus PMMA in THF): M_n = 51 kDa, PDI = 1.23. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.43-1.28 (m, 6H from methacrylate backbone and 3H from butyl pendent group); 1.39 (s, 2H from butyl pendent group); 1.60 (s, 2H from butyl methacrylate pendent group); 1.70-2.13 (m, 4H from methacrylate backbone); 3.93 (s, 2H from butyl methacrylate pendent group); 4.33 (s, 2H from methylene adjacent to TTF group); 4.37 (broad s, 2H from ethylmethacrylate pendent group); 4.65 (s, 2H from ethylmethacrylate pendent group); 4.69 (s, 2H from propargyl methylene); 6.33 (3H aryl protons from TTF moiety); 7.69-7.89 (m, 1H from triazole ring) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 14.00 (broad), 19.56, 30.42, 30.50, 44.94, 45.31, 48.81, 54.40, 63.31 (multiple), 65.07 (multiple), 67.33, 109.86, 111.27, 117.31, 119.37, 123.95, 134.22, 144.96, 177.75 (multiple).

PolyTTFBMA-50 (9h) was synthesized using **8h** (0.0715 g), **6** (0.0785 g, 0.335 mmol), copper (I) bromide (0.0020 g, 0.0139 mmol), N,N,N′,N′′,N′′-pentamethyldiethylenetriamine (20 µL, 0.0166 g, 0.096 mmol), and tetrathydrofuran (6 mL). Yield: 86%, 0.1177 g. GPC (versus PMMA in THF): M_n = 42 kDa, PDI = 1.27. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 0.39-1.29 (m, 6H from methacrylate backbone and 3H from butyl pendent group); 1.38 (s, 2H from butyl pendent group); 1.59 (s, 2H from butyl methacrylate pendent group); 1.70-2.09 (m, 4H from methacrylate backbone); 3.92 (s, 2H from butyl methacrylate pendent group); 4.32 (s, 2H from methylene adjacent to TTF group); 4.37 (broad s, 2H from ethylmethacrylate pendent group); 4.68 (m, 2H from ethylmethacrylate pendent group, 2H from propargyl methylene); 6.33 (3H aryl protons from TTF moiety); 7.68-7.91 (m, 1H from triazole ring) ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 14.04 (broad), 19.56, 30.41, 30.49, 44.90, 45.22, 48.79, 54.31, 63.36 (multiple), 65.13, 67.39, 109.83, 111.32, 117.40, 119.44, 124.11, 134.23, 144.83, 176.12 (multiple, broad), 177.20 (multiple, broad).

Chemical Exfoliation of MoS_2. MoS_2 nanosheets were prepared according to the method previously reported by Joenson *et al.* with minor modifications[7]. MoS_2 powder (0.3 g) was added to a flame-dried 50 mL round-bottom flask, equipped with a magnetic stir bar and a septum, and purged with N_2. N-butyllithium (3.0 mL, 1.6 M in hexanes) was then added, and the resulting mixture was stirred for 2 days at room temperature. The solution was then diluted to *ca.* 40 mL with anhydrous hexanes and the suspension was filtered under a nitrogen nitrogen blanket (Millipore 0.45µm pore size). The Li-intercalated MoS_2 was then carefully introduced to 300 mL of Milli-Q water and sonicated at low power for 1 hour resulting in a black homogeneous suspension. The nanosheets were then dialyzed (10 kDa cutoff, Spectra/Por® (Spectrum Labs) regenerated cellulose) against deionized water for 5 days to remove residual salts. The sheets were used immediately to minimize restacking.

MoS_2 suspension stabilization: To remove water, MoS_2 nanosheets were centrifuged at 11.2k rcf for 30 min. (1.5 mL per sample). The samples were decanted and polymers **PMMA**, **PBMA**, **PolyHexNB**, **4a-e**, and **9a-f** in THF were added to the remaining solid. The samples were then sonicated at low power for 30 min., after which the samples were monitored over the following days to assess the solution stability (OM and photographs).

Liquid exfoliation of MoS_2: In a procedure by Neill and Khan[8], MoS2 powder (0.3 g) was suspended in NMP (30 mL). The solution was sonicated using a bath sonicator at high power for 1 hour. The resulting suspension was centrifuged at 1000 rcf for 10 min and the supernatant decanted which contained pristine MoS_2 nanosheets in low concentration. The homogeneous suspensions were used in further experiments as prepared.

Instrumentation and Measurements

Materials Characterization. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz), spectra were obtained using a Bruker Ascend™ 500 spectrometer equipped with a Prodigy cryoprobe. High resolution fast atom bombardment (FAB) mass spectrometry was performed on a double focusing magnetic sector mass-spectrometer JEOL-700 MS station at the UMass Amherst Mass Spectrometry Center. The FTIR spectra were obtained with a Perkin-Elmer Spectrum One FTIR spectrometer. Gel permeation chromatography (GPC) was carried out in THF at 40 °C using a flow rate of 1.0 mL/min on an Agilent 1260 infinity system with a G1362A refractive index detector and G1310B isocratic pump, equipped with a PLgel 5 µm mixed-c (7.5 × 300 mm), a PLgel 5 µm mixed-d (7.5 × 300 mm), and a 5 µm guard column (7.5 × 50 mm) calibrated against poly(methyl methacrylate) (PMMA) and polystyrene (PS) standards.

Ground State Absorption. UV-Visible spectra were recorded on an Ocean Optics USB2000+XR spectrophotometer using a 1.0 cm quartz cuvette. Ground state electronic interactions between MoS_2 and TTF-based systems were studied *in situ*: to a suspension of MoS_2 nanosheets in NMP (prepared by sonication), a TTF-based analyte solution in NMP (1 mg/mL) was added, and spectra were taken over a period of *ca.* 10 minutes. TTF, as well as polymers **9b**, **9d**, and **4e** were used for these experiments. For clarity, decay curves were smoothed using Origin Adjacent Averaging function.

Electrochemistry. Electrochemical studies were performed using a single-compartment three-electrode cell with a platinum flag as the counter electrode, a non-aqueous Ag/Ag+ reference electrode (calibrated versus ferrocene/ferrocenium (Fc/Fc^+) standard redox couple as an external standard), and a platinum button (0.02 cm^2) as the working electrode. Cyclic voltammetry measurements were carried out in 0.1 M $TBAPF_6$ NMP electrolyte solution with the analyte concentration of ca. 1-3 mg/mL. All potentials are reported vs. standard calomel electrode (SCE), assuming SCE is 0.31 V vs Fc/Fc^+. Electrochemical measurements were performed under nitrogen using inlets fed into the electrochemical cell.

Spectroelectrochemistry. *In situ* spectroelectrochemical data acquisition was performed on an Ocean Optics USB2000+XR spectrophotometer coupled with a BASi Epsilon potentiostat scanninf voltage from -0.10 to 1.00 V. Spectral data were collected upon linear sweep voltammetry scans (50 mV/s scan rate) of the polymer films (drop-cast from a 10 mg/mL solution in toluene) on indium tin oxide (ITO)-coated glass slides (7 × 50 × 0.7 mm, sheet resistance, $R_s = 8–12\ \Omega/cm^2$, purchased from Delta Technologies, Ltd.) in a 1 cm quartz cuvette. The experiments were performed in 0.1 M $TBAPF_6$ solution in acetonitrile under a nitrogen atmosphere using the ITO/glass slide as the working electrode, a silver wire pseudoreference electrode, and a platinum wire as the counter electrode. For clarity, the absorption spectra obtained were smoothed using OriginPro 7.5 Adjacent Averaging function.

Transmission Electron Microscopy. High-resolution transmission electron microscopy (HRTEM) was performed on a JEOL JEM-2200FX microscope using samples prepared on 400 square mesh holey carbon-coated copper grids (Electron Microscopy Sciences).

Atomic Force Microscopy. Chemically exfoliated MoS_2 nanosheets were imaged by a scanning force microscope (Nanoscope III, Digital Instrument Co., Santa Barbara, CA) in tapping mode.

Optical Microscopy Measurements. Optical microscopy measurements were performed on an inverted optical microscope (Zeiss Axiovert 200) equipped with a QImaging camera (Retiga-2000R Fast 1394 Mono Cooled). Chemically exfoliated MoS_2 or MoS_2/polymer conjugate samples were prepared by drop-casting on glass slides from the respective suspensions in THF.

Kelvin Probe Force Microscopy. Kelvin probe force microscopy (KPFM) is a technique that measures the local surface potential by the contact potential difference between a metal-coated tip and the surface. KPFM experiments were conducted on a Digital Instruments AFM/KPFM in non-contact tapping mode, under ambient atmospheric conditions. The AFM probes were platinum-coated silicon (ANSCM-PT) used as supplied by App Nano. For these measurements, MoS_2 (purchased from SPI Supplies) flakes were mechanically exfoliated on a glass substrate using the Scotch tape method[9] and located using photoluminescence imaging (ProEM512 camera, Princeton Instrument). AFM/KPFM measurements were then conducted on the selected MoS_2 nanosheets before and after polymer doping, recording the differences in surface potential. Polymer doping was achieved by drop-casting a thin **PNB-50TTF** film from 0.001 mg/ml solution in THF. The glass substrates for KPFM were prepared plasma cleaning, rinsing with DI water, and subjecting to a NRD Static Control LLC. deionizer to remove the static charges.

Computational Methods. Density functional theory (DFT) calculations were performed using the Vienna *Ab Initio* Simulation Package (VASP).[10] The projector-augmented wave method was employed to represent core and valence electrons.[11,12] From convergence tests, a plane-wave cutoff of 400 eV was employed with a Brillouin zone sampling equivalent to a Γ-centered 8×8×1 mesh for the MoS_2 primitive cell. Electronic wavefunctions were converged to within 10^{-4} eV in conjunction with a Gaussian smearing 0.05 eV. As semi-local DFT functionals do not account for van der Waals interactions, which we expect to be significant for adsorption of TTF molecules on MoS_2, we employed a non-local functional (optB86b-vdW [1], which is designed to capture van der Waals (vdW) interactions more accurately. Cell vectors for the MoS_2 monolayer were optimized with a force tolerance of 0.01 eV/Å using the optB86b-vdW functional; in subsequent calculations of adsorbed TTF, only atomic positions were relaxed with a force tolerance of 0.01 eV/Å keeping the cell vectors fixed at the optB86b-vdW-optimized value of 3.173 Å. These optB86b-optimized atomic positions were used without further relaxation for additional calculations using the Heyd-Scuseria-Ernzerhof (HSE) functional,[2] which is known to be more accurate for electronic structure calculations than semilocal functionals across a range of gapped and molecular systems[2,3]. Periodic images were separated by a minimum of 10 Å of vacuum normal to the MoS_2 sheet to prevent spurious interlayer coupling. Work functions were obtained as the difference between the vacuum level, calculated from the planar-averaged local potential (excluding the exchange-correlation potential), and the Fermi level. Dipole corrections[13] were found to be necessary only for the case of MoS_2 with a basal-plane sulfur vacancy; the work function in this case is reported as an average of the work functions calculated on the TTF and non-TTF sides of the structure. A Bader analysis was used to partition charge between the TTF molecule and MoS_2 monolayer from which the net charge transferred between the two constituents was estimated.[14,15] A 4×4 monolayer MoS_2 supercell was used in all calculations unless explicitly noted otherwise.

Appendix

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