Electronic Supporting Information

Oxidation Promoted Self-Assembly of π-Conjugated Polymers

*Garion E. J. Hicks, Charles N. Jarrett-Wilkins, Jenny R. Panchuk, Joseph G. Manion, and Dwight S. Seferos**

Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, M5S 3H6, Canada

Table of Contents

Figure S1. ^{1}H NMR spectrum of Thiophene Monomer S3
Figure S2. ^{1}H NMR spectrum of Tellurophene Monomer S4
Figure S3. ^{1}H NMR spectrum of PTh_{80}-*b*-PTe_{60} S5
Figure S4. GPC traces of block copolymer PTh_{80}-*b*-PTe_{60}. S6
Figure S5. PTe Homopolymer Solid State Optical Absorption Spectrum S7
Figure S6. UV-Vis-NIR of Oxidized PTh_{80}-*b*-PTe_{60}. S8
Figure S7. STEM of Partially Aggregated PTh_{80}-*b*-PTe_{60} S9
Figure S8. TEM of Oxidized PTh_{80}-*b*-PTe_{60} S10
Figure S9. Oxidized PTh_{80}-*b*-PTe_{60} Micelle Widths measured by AFM.....S11
Figure S10. PTh_{80}-b-PTe_{60} 15 min after $FeTs_3$ addition.....S12
Figure S11. Size Distribution of Oxidized Micelles Aged for 2 months S13
Figure S12. STEM of Oxidized Micelles Aged for 2 months.....S14
Figure S13. WAXS of Partially Aggregated (blue) and Oxidized PTh_{80}-*b*-PTe_{60} (red) samples. S15
Figure S14. UV-Vis-NIR Spectroscopy of Oxidized (red trace) and Reduced PTh_{80}-*b*-PTe_{60} (blue trace). S16
S1. Work Function Calculation for Oxidatively Doped PTe Films S17
Table S1. Differences in work function and conductivities of PTe thin films dip-doped with $FeTs_3$.....S18
References S18

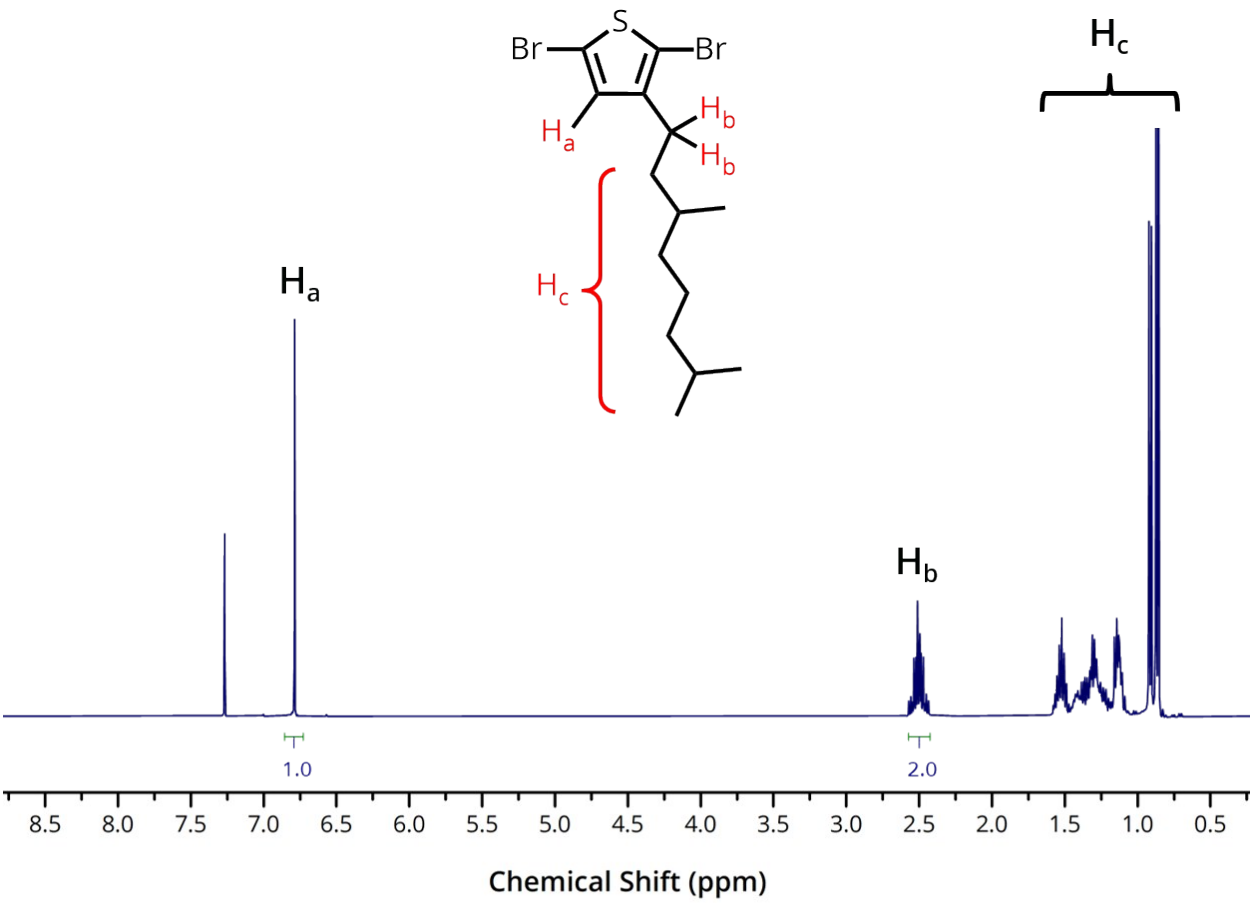

Figure S1. ^{1}H NMR spectrum of Thiophene Monomer in $CDCl_3$ at 25 °C, 500 MHz.

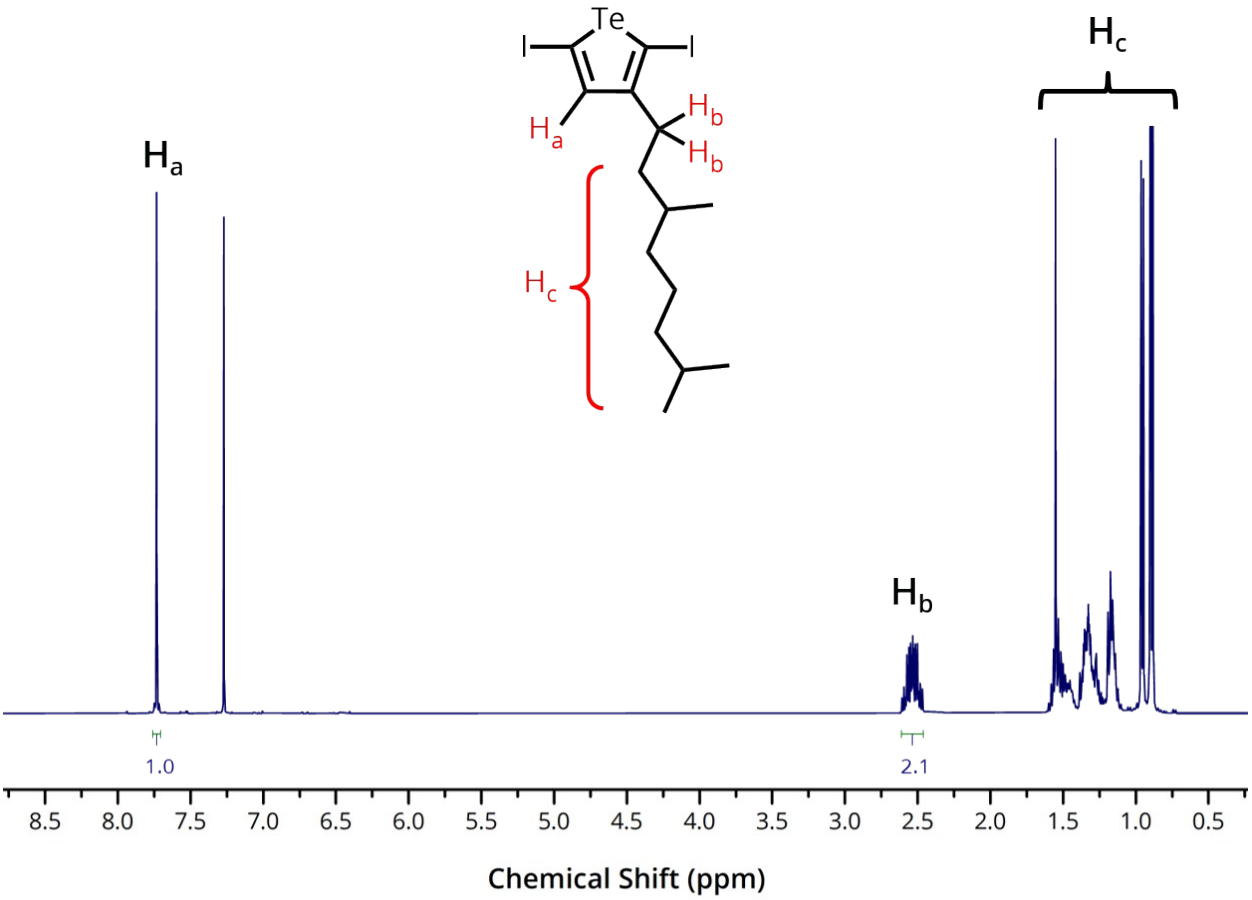

Figure S2. ^{1}H NMR spectrum of Tellurophene Monomer in $CDCl_3$ at 25 °C, 500 MHz.

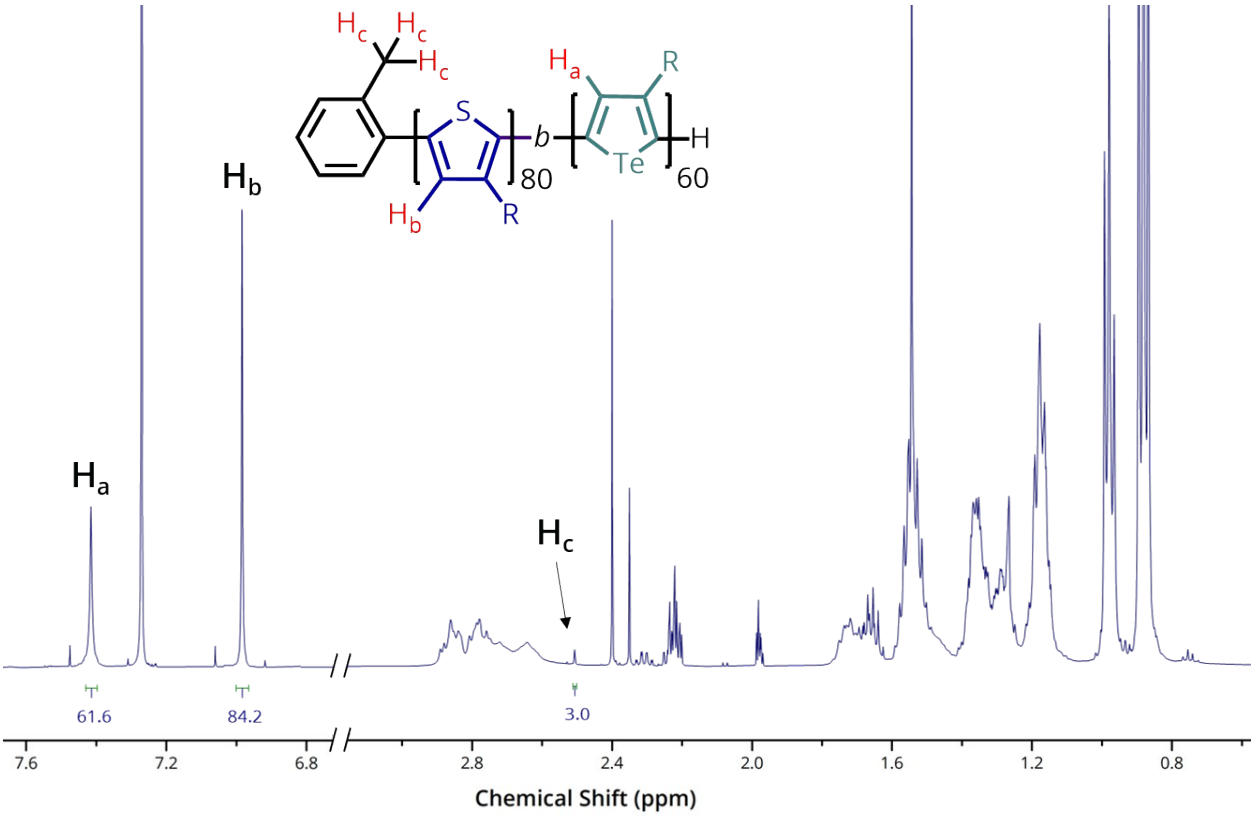

Figure S3. ^{1}H NMR spectrum of PTh_{80}-*b*-PTe_{60} in $CDCl_3$ at 25 °C, 500 MHz.

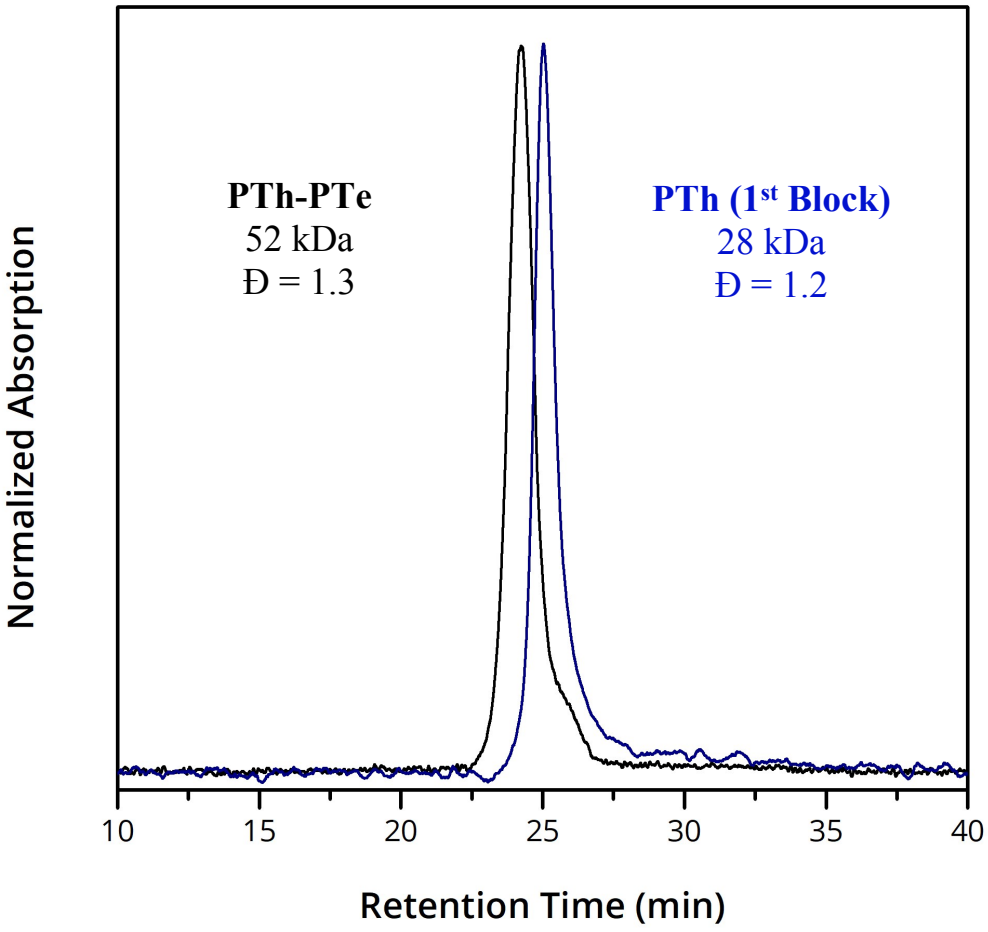

Figure S4. GPC traces of block copolymer PTh_{80}-*b*-PTe_{60}. M_n overestimation by a factor of 1.2 is typical due to the rigidity of polymer semiconductors relative to polystyrene standards.[1]

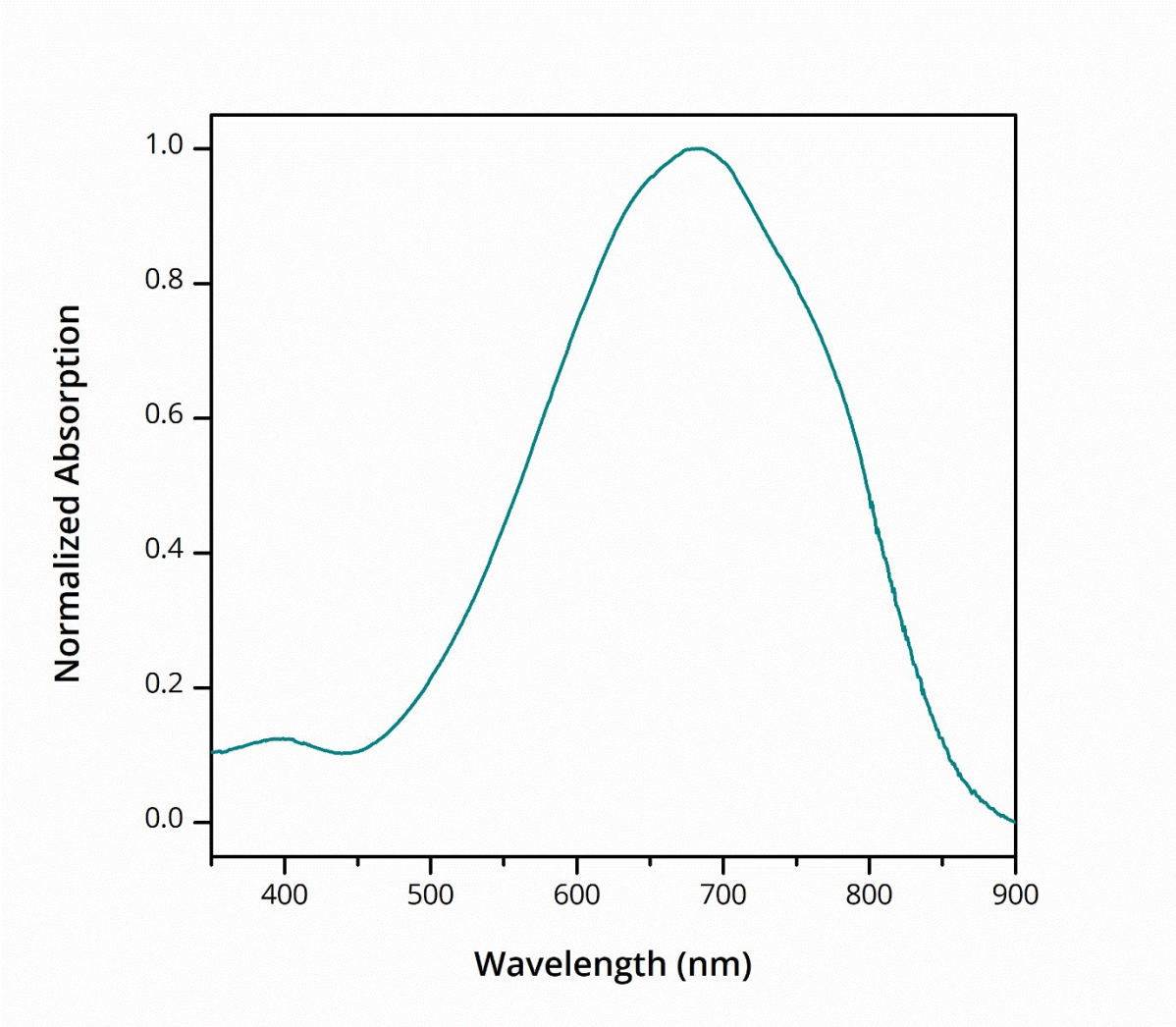

Figure S5. PTe Homopolymer Solid State Optical Absorption Spectrum

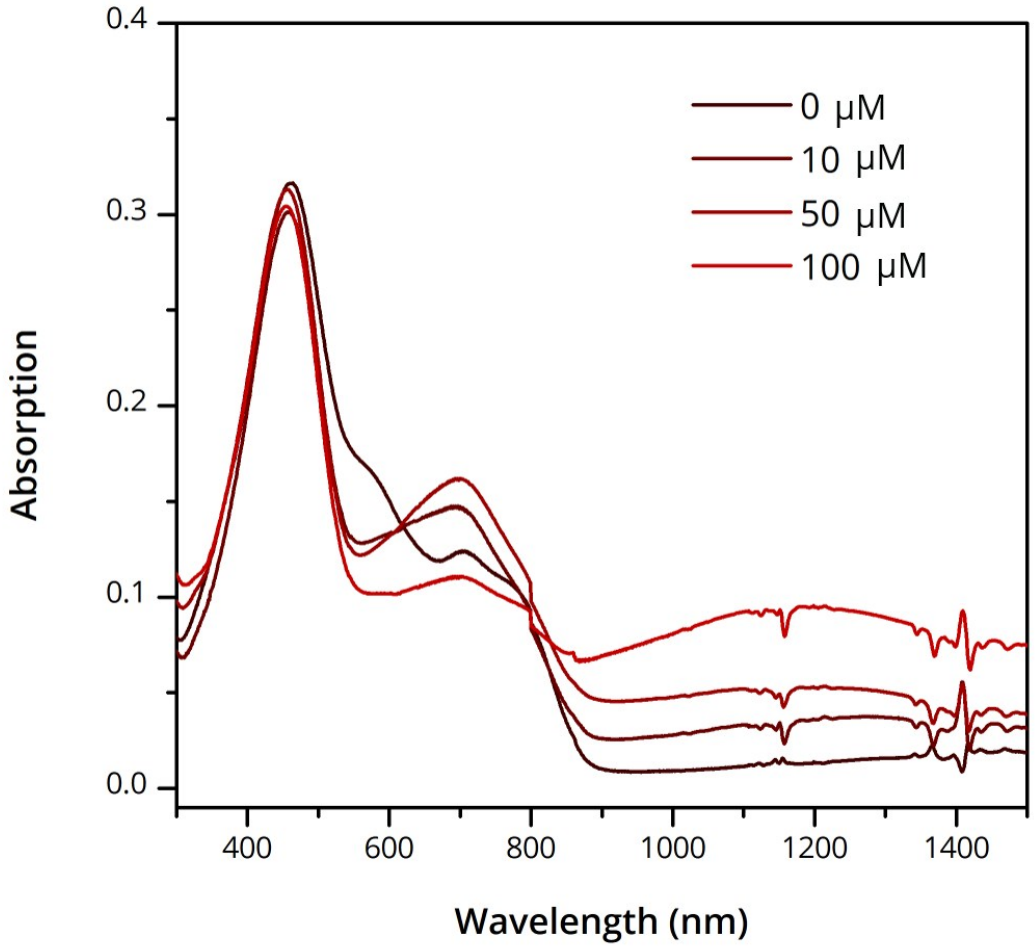

Figure S6. UV-Vis-NIR of Oxidized PTh_{80}-*b*-PTe_{60}. UV-Vis-NIR of PTh_{80}-*b*-PTe_{60} with different concentrations of $FeTs_3$. All samples prepared at 0.05 mg/mL in 95 % DCM, 5 % chloroform.

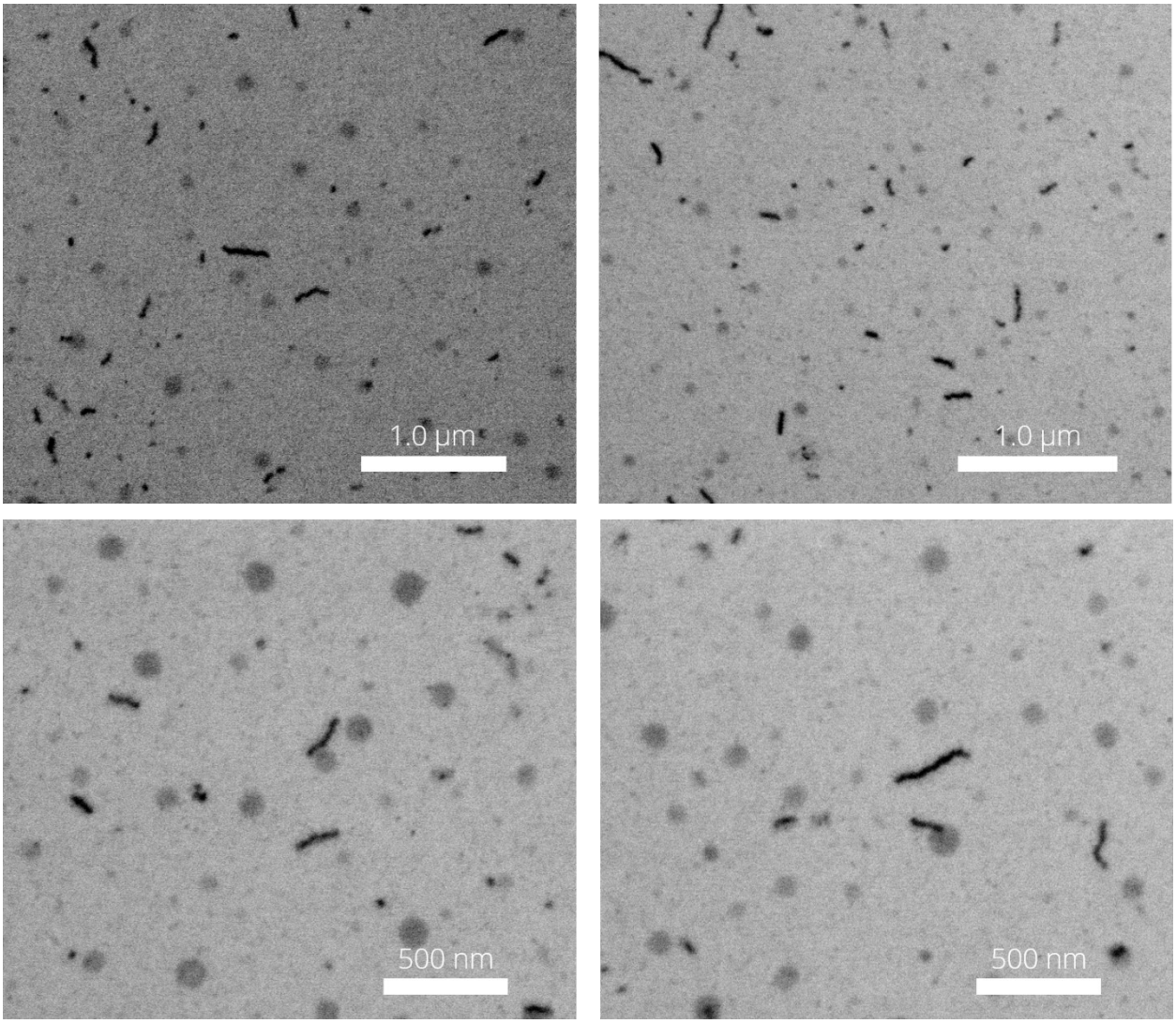

Figure S7. STEM of Partially Aggregated PTh_{80}-*b*-PTe_{60}. Partially aggregated PTh_{80}-*b*-PTe_{60} drop-cast onto a carbon film with Cu support grid. STEM utilized to improve the visualization of low contrast unimer film, which appear as amorphous, circular features.

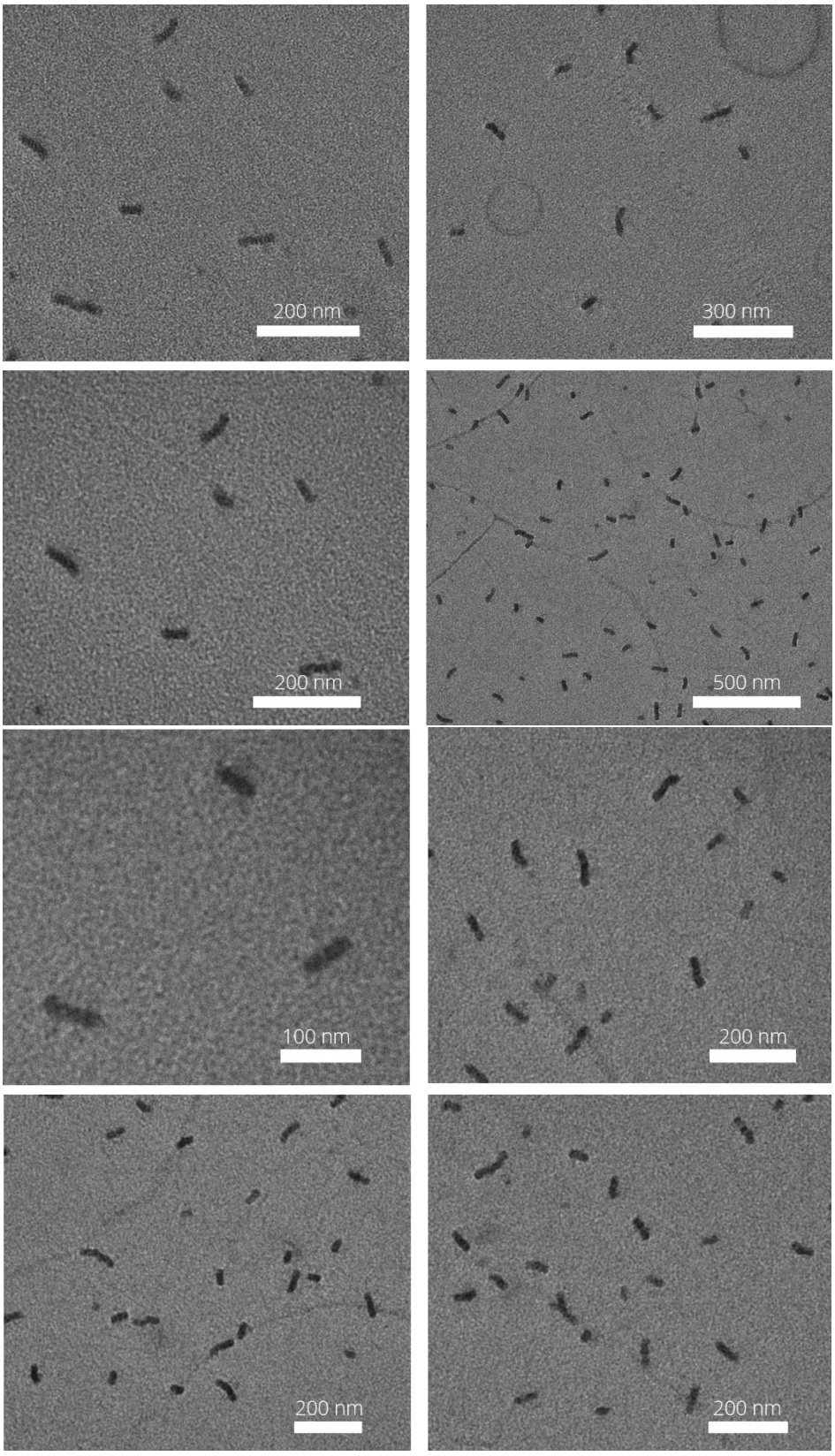

Figure S8. TEM of Oxidized PTh_{80}-*b*-PTe_{60}

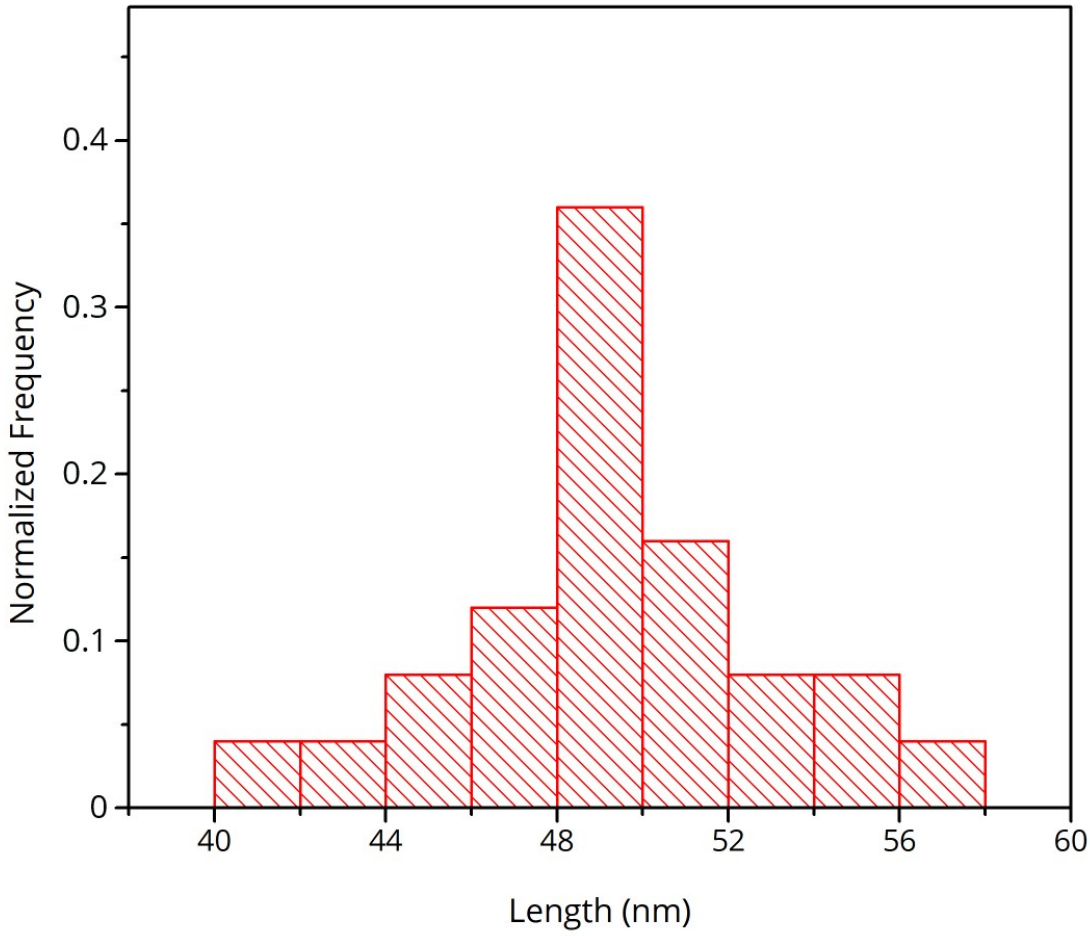

Figure S9. Oxidized PTh_{80}-*b*-PTe_{60} Micelle Widths measured by AFM

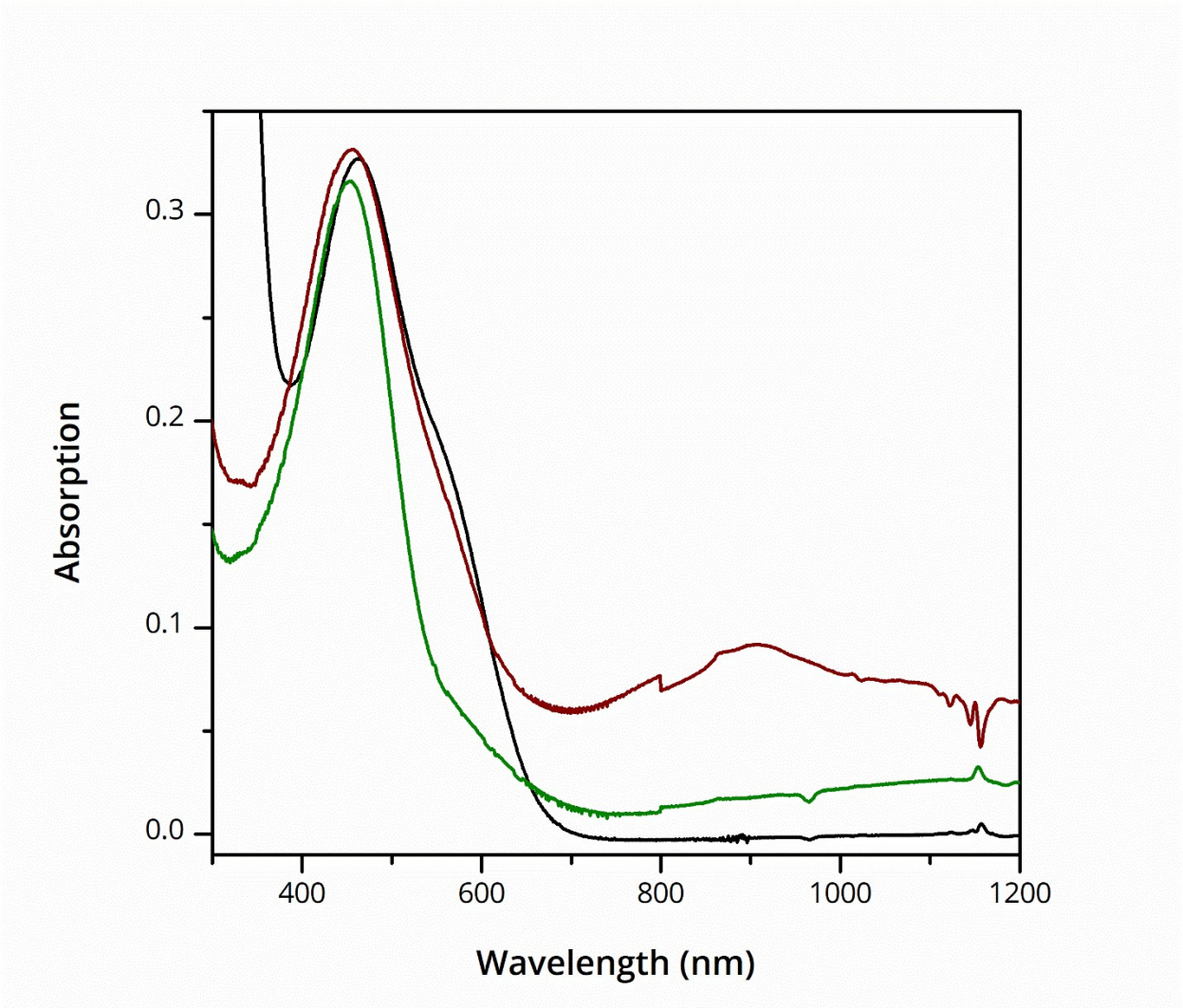

Figure S10. PTh_{80}-b-PTe_{60} 15 min after $FeTs_3$ addition in chloroform (green) and 95 % DCM, 5 % chloroform (red). Solvated PTh_{80}-b-PTe_{60} shown for reference (black).

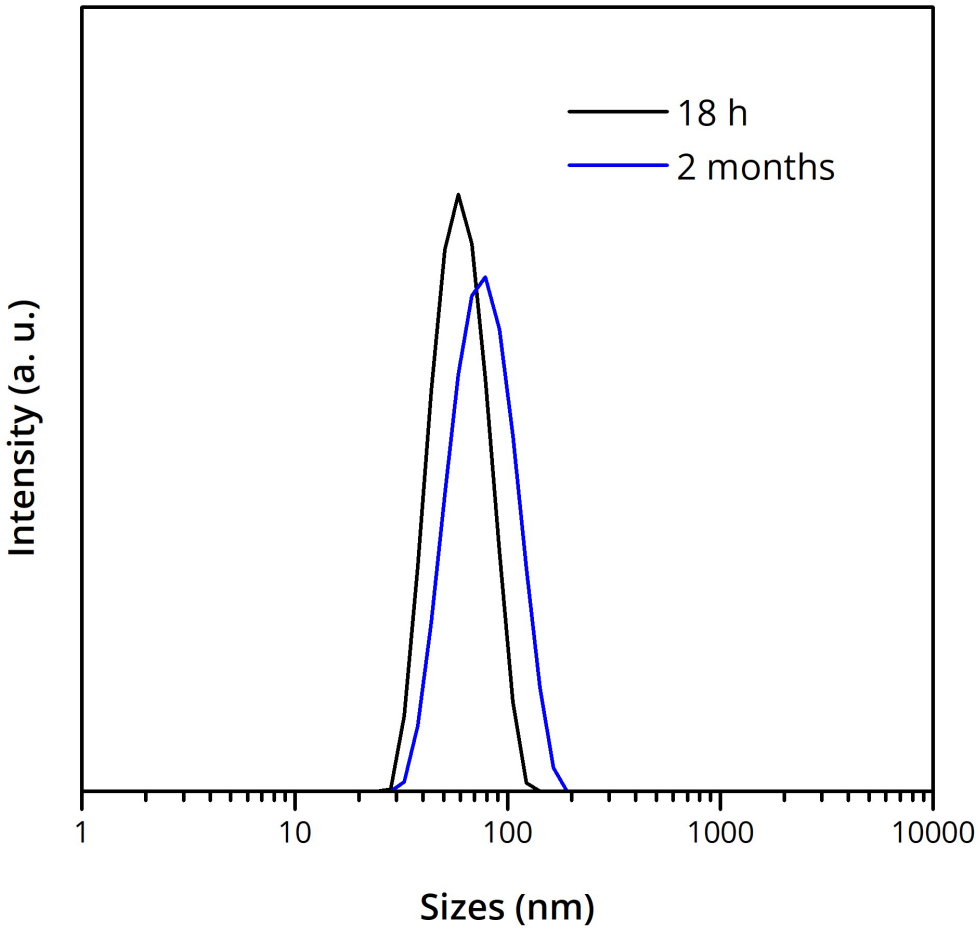

Figure S11. Size Distribution of Oxidized Micelles Aged for 2 months

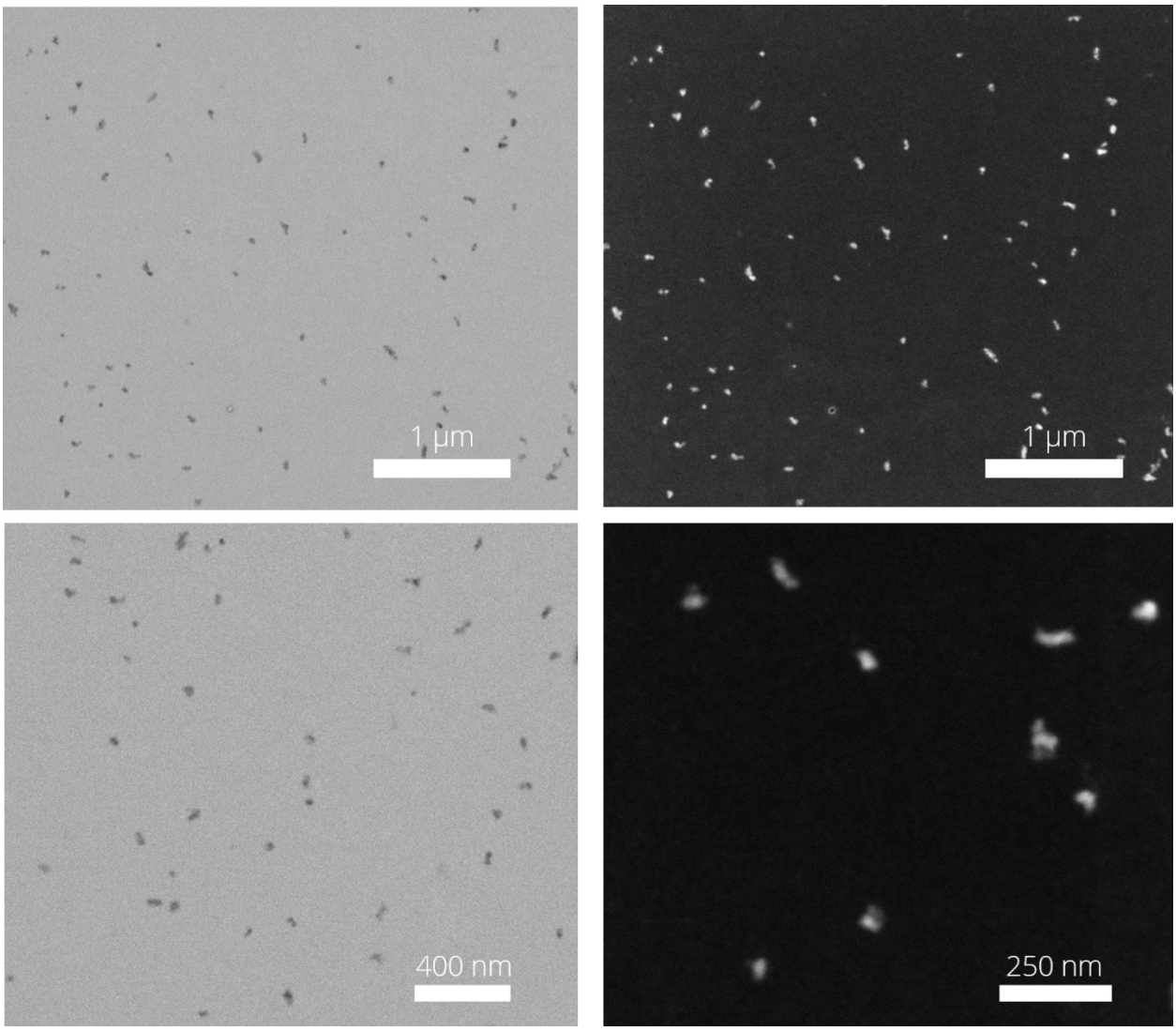

Figure S12. STEM of Oxidized Micelles Aged for 2 months. Oxidized micelles drop cast onto carbon film with Cu support grid after aging for 2 months. Bright field (left) and dark field (right) modes of STEM were used to visualize the sample, showing only oxidized micelles unchanged with aging.

.

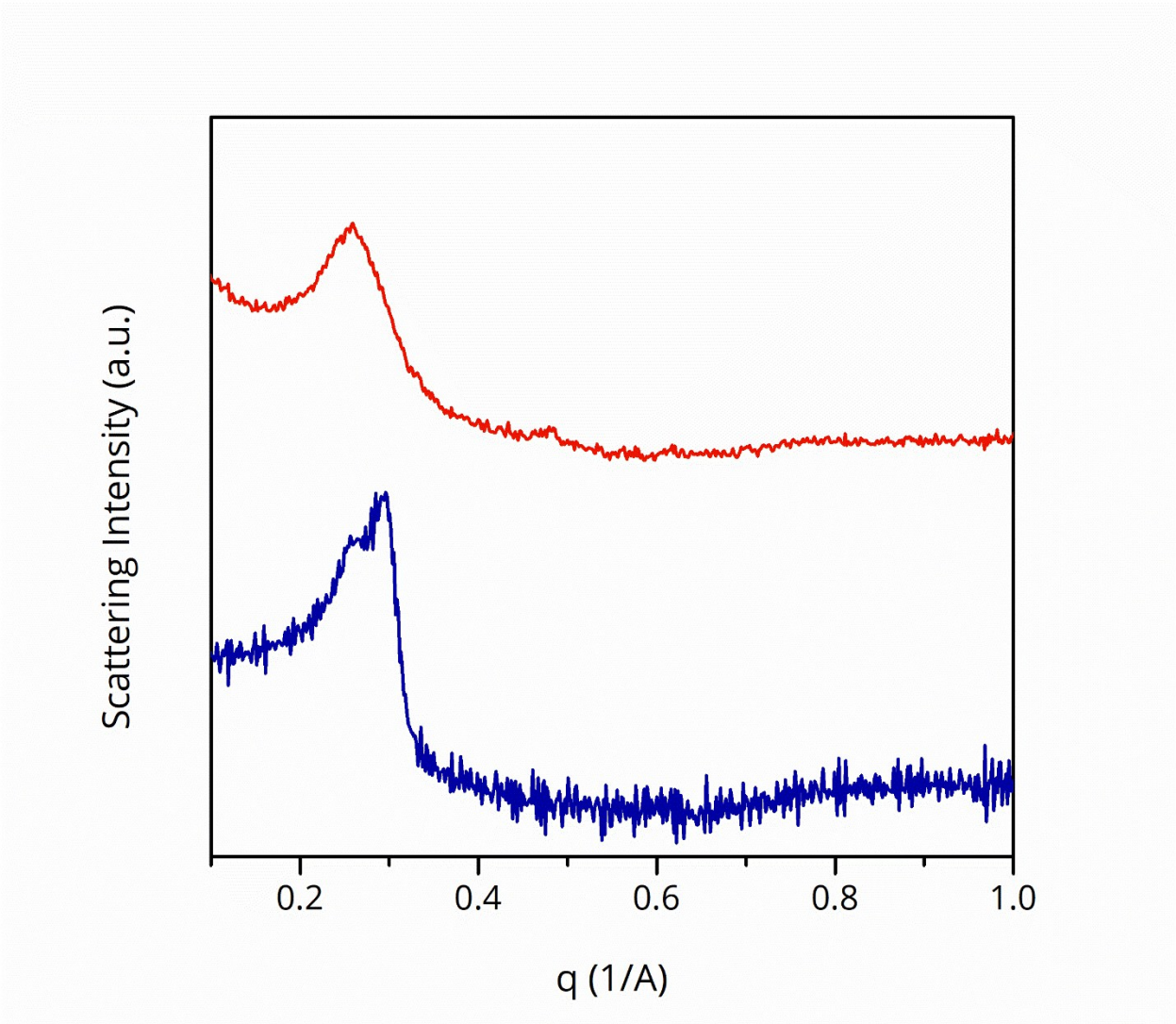

Figure S13. WAXS of Partially Aggregated (blue) and Oxidized PTh_{80}-*b*-PTe_{60} (red) samples.

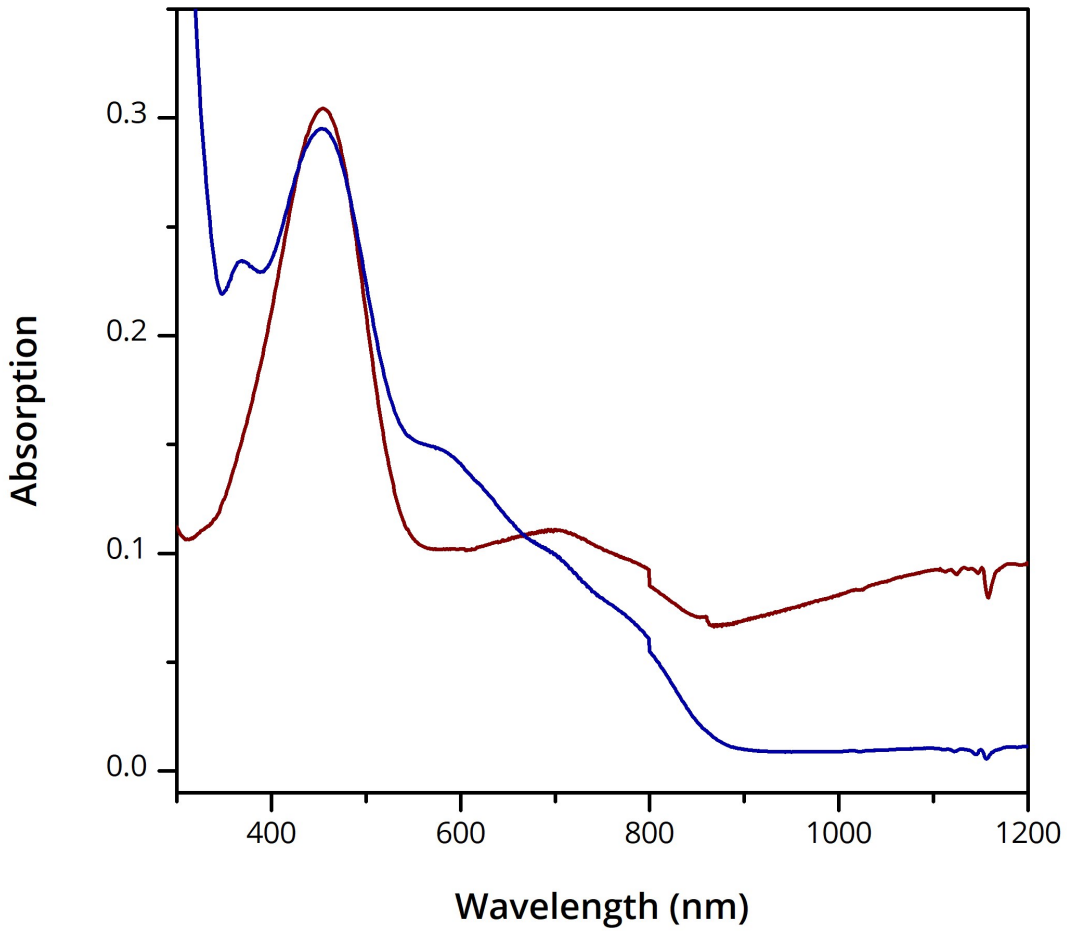

Figure S14. UV-Vis-NIR Spectroscopy of Oxidized (red trace) and Reduced PTh_{80}-*b*-PTe_{60} (blue trace).

S1. Work Function Calculation for Oxidatively Doped PTe Films

Difference in work function (Δφ) is an average of three measurements at different locations over two films. Films were scratched to expose the ITO to measure the contact potential difference (CPD) across the film surface and the CPD of the ITO surface using Kelvin probe force microscopy (KPFM). Δφ is calculated using the equations below where *e* is elementary charge.

$$\Delta\varphi = \varphi_{doped\ film} - \varphi_{pristine\ film}$$

where

$$CPD_{film} = \frac{\varphi_{film} - \varphi_{tip}}{e}$$

It should be noted that the CPD of the film is the relative difference of the CPD between the film surface and the CPD of the ITO surface. This difference is largely unaffected between measurements. Measuring the film surface without an ITO reference typically results in large differences in the CPDs of the film when measuring the same sample multiple times or when using different KPFM tips. Referencing the CPD of the film to the CPD of ITO eliminates this variability.

Concentration (mM)	Difference in Work Function (meV)	Conductivity (S cm^{-1})
1	240 ± 50	8.7 ± 3.4[2]
5	340 ± 50	6.0 ± 0.6[2]
10	400 ± 40	1.4 ± 0.4[2]

Table S1. Differences in work function and conductivities of PTh_{80}-*b*-PTe_{60} thin films dip-doped with $FeTs_3$

References

1 J. Liu, R. S. Loewe and R. D. McCullough, Employing MALDI-MS on Poly(alkylthiophenes): Analysis of Molecular Weights, Molecular Weight Distributions, End-Group Structures, and End-Group Modifications, *Macromolecules*, 1999, **32**, 5777–5785.

2 J. R. Panchuk, A. W. Laramée, J. G. Manion, S. Ye and D. S. Seferos, Heavy atom substitution — A strategy for improving conductivity in conjugated polymers, *Synth. Met.*, 2019, **253**, 57–61.