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Jian He[a], Kyle J. Myerson[a] and Matthew B. Zimmt[a]

Triphenyleneethynylene (TPE) monolayers at the solution - HOPG interface are oligomerized by oxidation of pendant thioethers to form disulfide cross-links. Oligomerized TPE monolayer adheres strongly to HOPG. Disulfide reduction unzips oligomers to form monomeric TPE monolayer with pendant thiols. Subsequent oxidation and reduction treatments zip and unzip the monolayer.

Monolayers self-assembled on graphite and other planar surfaces can express complex molecular patterns with nanometer features.[1,2,3,4,5] Molecule exchange between monolayer and solution is required for high fidelity pattern self-assembly,[6,7,8] but can hinder use of monolayers in applications requiring durable surface adhesion, e.g, for object capture, storage or as nanometer scale templates. Various in-situ reactions have been used to alter monolayer structure and properties,[9] e.g., diyne side chains within monolayers may be converted to polydiacetylene to increase molecular size and monolayer durability.[10,11] Here we describe a post-assembly disulfide cross-linking strategy that "zips" together monolayer monomers. The resulting, oligomeric monolayer adheres strongly to HOPG and is much more durable than the initially assembled, monomeric monolayer. When desired, the oligomeric monolayer may be "unzipped" by reducing disulfides to thiols, thus reforming monomeric monolayer. Cycles of oxidation and reduction enable repeated zipping and unzipping of the monolayer, interconverting the oligomeric, cross-linked disulfide and monomeric, molecular thiol forms.

Thiol – disulfide redox interconversion modulates protein structure / function[12] and engenders dynamic covalent polymers distinct properties in cross-linked and uncross-linked forms.[13,14,15] To investigate the feasibility of, and impact of, thiol - disulfide interconversion on physisorbed monolayer properties, monolayers were self-assembled from **1** at the HOPG - solution interface. Molecule **1** is comprised of (i) two

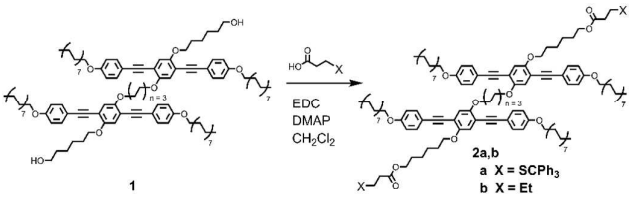

Fig. 1 Structure of **1,** the TPE_2 molecule applied to HOPG, and the surface reactions used to prepare bis-(tritylthio ester) monolayer **2a** and bis-(pentanoate ester) **2b**.

triphenyleneethynylene cores (TPE_2), (ii) four morphology determining hexadecyloxy side chains, one on each terminal phenylene ring, (iii) one (6-hydroxyhexyl)oxy chain on each central phenylene ring and (iv) a (6-oxyhexyl)oxy chain linking the two cores' central phenylene rings (Fig. 1). STM images collected from drop cast monolayers of **1** on HOPG (3 µL of 12 µM **1** in 25% $CHCl_3$ / phenyloctane, Fig. 2, SI-1) exhibit columns of yellow (higher tunnelling) rods assigned as TPE cores. Adjacent cores are shifted from each column's midline, in opposite directions, by ~ 0.3 nm. CPK models with close-

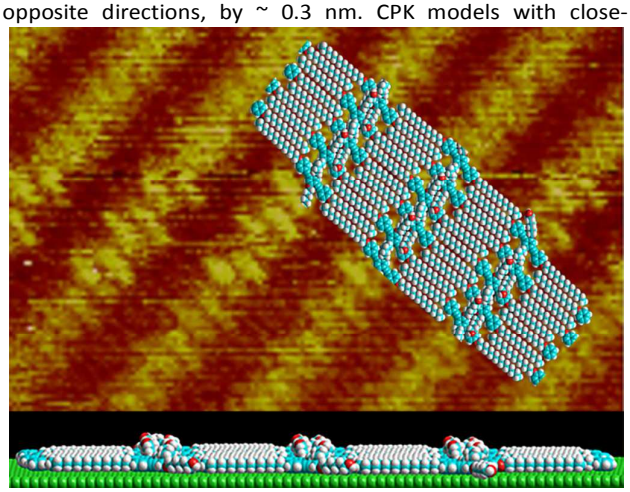

Fig. 2. STM image (-1.4 V, 42pA, 25nm x 15.5nm) of a monolayer of **1** (12µM in 25% $CHCl_3$ / phenyloctane). TPE cores (yellow rods) in each aryl column are spaced by 1 nm (unit cell; a = 2.0±0.2 nm, b = 4.0±0.5 nm, α = 98±5°). Overlay: CPK model of molecular mechanics minimized monolayer (ML) section. Inset: Side view of ML section showing $O(CH_2)_6OH$ chains' location off the graphene sheet (green).

[a] Department of Chemistry, Brown University, Providence, RI 02912
Electronic Supplementary Information (ESI) available: [Synthesis of **1**, Mass spectra of monolayers following each surface reaction / incubation, statistical summaries of mass spectral intensities from independent samples, STM image of annealed **1** monolayer, image of THAP coated monolayer on **1** on HOPG after recording mass spectra]. See DOI: 10.1039/x0xx00000x

packed hexadecyloxy side chains lack space for the (6-hydroxyhexyl)oxy and (6-oxyhexyl)-oxy chains to adsorb fully to graphite (Fig. 2 CPK overlay and inset). These chains extend above the TPE cores.

Monolayers of **1** on HOPG were characterized by time-of-flight mass spectrometry (TOF-MS).[16] Mass spectra were collected after applying a thin film[17] of the MALDI matrix 2,4,6-trihydroxyacetophenone (THAP) to increase signal intensity.[16] Spectra collected from 50 μm spots (Fig. SI-2) spanning the HOPG substrate exhibit strong molecular ion signal for **1** (m/z = 1864.4 [**1** + H]$^+$)[18,19]) and for THAP.[20] Lower intensity peaks (m/z = 791, 891) are fragment with one TPE core. The intensity of [**1** + H]$^+$ is fairly uniform across an HOPG substrate (Int. = 49 ± 11 x 10^3). The mean [**1** + H]$^+$ intensity from independently prepared monolayers of **1** varies less than 35% (Fig. SI-2).

Monolayers of the oligomerization precursor, bis-(tritylthio ester) **2a** (Fig. 1), were prepared in-situ by immersing a mono-layer of **1** on HOPG in dichloromethane (DCM) solution containing β-(tritylthio)propanoic acid (β-TTP), EDC coupling agent[21] and dimethylaminopyridine (DMAP; each 40 mM) for 30 minutes. Mass spectra were collected from the HOPG substrate after rinsing to remove reagents / side products and applying a THAP thin film. Post reaction mass spectra exhibit very strong trityl ion signal (m/z = 243, Int. = 78 ± 2. x 10^3), greatly reduced [**1** + H]$^+$ intensity (Int. < 0.5 x 10^3) and faint peaks assignable as **2a** (m/z = 2527, Int. < 0.1 x 10^3) or as the mono β-TTP ester of **1** (m/z = 2195 < 0.2 x 10^3).[22] (Fig. SI-3). Facile fragmentation of the tritylthio group reduces the intensity of **2a** molecular ion and generates large trityl ion signal. Two control experiments demonstrate that ester formation with β-TTP causes the 50-100 fold drop of **1** molecular ion intensity and the intense trityl ion signal in post-incubation mass spectra. (i) A monolayer of **1** on HOPG was immersed for 30 minutes in DCM containing 40 mM β-TTP but lacking the EDC and DMAP required for esterification. Mass spectra collected after rinsing and THAP film application exhibit [**1** + H]$^+$ intensities (Int. = 39 ± 10. x 10^3, Fig. SI-4) comparable to unreacted monolayers of **1** (Fig. SI-2) and trityl ion intensity (Int. = 3.8±2.3 x 10^3) that is 15-20 fold less intense than following reaction using EDC, DMAP and β-TTP. Thus, residual, physisorbed β-TTP reagent contributes less than 6 % of trityl ion signal when β-TTP ester (**2a**) is synthesized at the surface. (ii) A monolayer of **1** was immersed for 30 minutes in DCM containing EDC, DMAP and valeric acid, in place of β-TTP. After rinsing and THAP film application, mass spectra (Fig. SI-5) exhibit moderate bis-(valerate ester) ion [**2b** + H]$^+$ signal (m/z = 2032.3, Int. = 11 ± 4. x 10^3)[23], 3-fold smaller mono-valerate ester ion signal (m/z = 1948.5, Int. = 3.3 ± 1.4 x 10^3) and [**1** + H]$^+$ ion signal (Int. = 1.2±0.4 x 10^3) that is less than 5% of the [**1** + H]$^+$ signal from unreacted monolayers of **1.** After 30 minutes, valerate diester is the most intense TPE_2 ion peak, despite being the heaviest of the three detected TPE_2.[24]

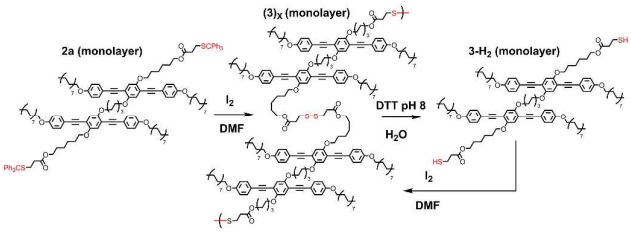

Fig. 3. Reactions used to form crosslinked disulfides from bis-thioester **2a** and bis-thiol **3-H_2** monolayers (zipping) and to form thiols from disulfide **(3)x** monolayers (unzipping).

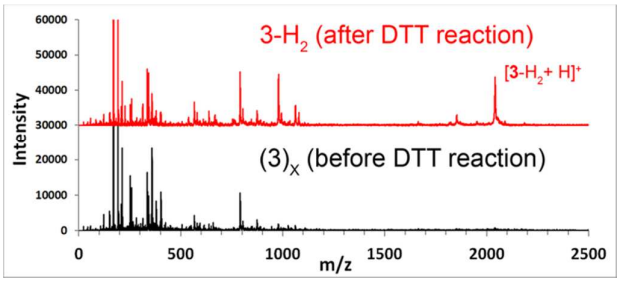

Fig. 4. TOF mass spectra (THAP thin film applied) of (bottom) $(\mathbf{3})_X$ monolayer formed by I_2 / DMF treatment of **2a** monolayer; (top) **3-H_2** monolayer formed by DTT reduction of $(\mathbf{3})_X$ monolayer. The top spectrum is shifted vertically by 30000.

Tritylthioethers may be oxidized to disulfide using I_2, with concomitant removal of trityl groups.[25,26] To promote TPE_2 oligomerization on HOPG via disulfide formation (Fig. 3), monolayers of **2a** were reacted with I_2 (10 mM) in dimethyl-formamide (DMF) for 1 minute, then rinsed with DMF to remove reagents. Mass spectra acquired after applying a THAP thin film (Fig. 4, SI-6) exhibit strong peaks from THAP, a moderate intensity fragment ion with one TPE core (m/z = 791.1, Int. = 9.0±3.4 x 10^3), but very low intensity peaks associated with reaction precursors: trityl ion (Int. < 0.2 x 10^3), reactant **2a** (Int. < 0.1 x 10^3) or **1** (Int., < 0.9 x 10^3). A faint peak observed at (m/z = 2040, Int. < 0.7 x 10^3)[27] is assigned, tentatively, as [M+H]$^+$ of **3**, the repeat unit of $(\mathbf{3})_\mathbf{x}$ monolayer. Immersion of **2a** monolayer in DMF lacking I_2 does not reduce trityl ion intensity, confirming **2a** monolayer's stability to DMF. The absence of nearly all trityl and TPE_2 ion peaks following I_2 oxidation of **2a** monolayer is attributed (Fig. 3) to formation of disulfide oligomers $(\mathbf{3})_\mathbf{x}$ that are too heavy and too strongly adsorbed on HOPG to be detected. The $(O(CH_2)_6O_2C(CH_2)_2S)$ chains attached to carbons (C_P) of the central phenylene units are long enough to form disulfide cross-links between adjacent ($r(C_P - C_P) \leq 2$ nm) or next nearest neighbor ($r(C_P - C_P) \leq 2.5$ nm) TPE_2 molecules within the same aryl column (Fig. 5, SI-7). These chains are too short to form disulfide links between TPE_2 molecules ($r(C_P - C_P) \geq 3.5$ nm) in different aryl columns. Formation of cyclic disulfide by I_2 induced reaction of the two tritylthio groups on one TPE_2 molecule also can occur, and is one of two reasonable sources of the faint m/z = 2040 peak.[28]

Reduction of disulfide cross-links within an oligomeric $(\mathbf{3})_\mathbf{x}$ monolayer should form monomeric bis-thiol TPE_2 molecules, **3-H_2**, (Fig. 3) that are more readily detected by mass spectrometry. To attempt reduction, HOPG bearing the putative $(\mathbf{3})_\mathbf{x}$ monolayer was incubated with dithiothreitol.[29] Mass spectra collected after applying a thin THAP film (Fig. 4, 6, SI-8) exhibit intense signals from THAP and moderate intensity signal at (m/z = 2040.4, Int. = 9.1±2.5 x 10^3) assigned as the bis-thiol TPE_2 protonated molecular ion ([**3-H_2**+H]$^+$).[30] Additional moderate intensity peaks at (m/z = 979.4, Int. = 8.6±1.9 x 10^3) and (m/z = 791.5, Int. = 10.±2. x 10^3) are assigned as protonated, single-TPE fragments that have lost one or both

aliphatic chains, respectively, from the central phenylene ring. (Fig. SI-8b). Weaker peaks at (m/z = 1954, Int. < 1.0 x 10^3) and (m/z = 1854., Int. < 2.5 x 10^3) are protonated TPE_2 fragments missing parts of one aliphatic chain on a central phenylene ring (Fig. SI-8b). Faint peaks at m/z = 2090. and at 2138 are assigned as protonated TPE_2 ions (Fig. 6) in which one thiol (**3-H(O$_3$H)**) or both thiols (**3-(O$_3$H)$_2$**), respectively, have been oxidized to sulfonic acids.[31] Observation of moderately intense **3-H$_2$** TPE_2 ion in the mass spectrum following DTT reduction of "TPE_2 silent" **(3)$_X$** monolayer confirms that disulfide oligomerized TPE_2 units comprise **(3)$_X$** monolayer.

DTT reduction converts *internal* TPE_2 units of **(3)$_X$** oligomer to **3-H$_2$** molecules by reducing two disulfide cross-links. Terminal TPE_2 units of **(3)$_X$** oligomer have only one disulfide cross-link. I_2 oxidation of the other tritylthio group yields sulfenic (SOH), sulfinic (SO_2H) and, ultimately, sulfonic acid terminated side chain. DTT reduces disulfides, but not sulfonic acids, to thiols. Thus, DTT reduction converts *terminal* TPE_2 units of **(3)$_X$** oligomer to **3-(H)(O$_3$H)** molecules. The dithiol [**3-H$_2$**+H]$^+$ peak is 10-fold more intense than the thiol / sulfonic [**3-H(O$_3$H)**+H]$^+$ peak and 18-fold more intense than the bis-sulfonic acid [**3-(O$_3$H)$_2$**+H]$^+$ peak (Fig. 6, SI-8).

Monolayers of **3-H$_2$** were prepared independently by a two-step surface reaction that avoids I_2 oxidation. A monolayer of **1** on HOPG was incubated with the mono-ethyl ester of 3,3'-dithiobispropanoic acid,[32] EDC and DMAP (Fig. SI-10). The resulting disulfide monolayer (**3-(SR')$_2$**) was reduced with DTT to prepare a monolayer of **3-H$_2$**. Mass spectra collected after rinsing and applying a thin THAP film exhibit moderate intensity from the dithiol molecular ion [**3-H$_2$**+H]$^+$ (m/z = 2040.4, Int. = 10.9±3.4 x 10^3) and trace intensity from unreacted bis-disulfide molecular ion (m/z = 2305, Int. < 0.4 x 10^3) and thiol / disulfide (half-reduced) molecular ion (m/z = 2173, Int. = 1.0 ± 0.3 x 10^3). These spectra exhibit negligible intensity at m/z corresponding to oxidation products **3-H(O$_3$H)** and **3-(O$_3$H)$_2$**. The [**3-H$_2$**+H]$^+$ ion intensity from **3-H$_2$** monolayer prepared by the non-oxidative, two-step route is 20-25% larger than from **3-H$_2$** monolayer prepared by the three-step route involving oxidative monolayer cross-linking, **2a→(3)$_X$**. Oxidation of **2a** with I_2 effects disulfide oligomerization, but siphons a fraction of the sulfur bearing functional groups onto a parasitic SO_XH path.

Reoxidation of thiols to disulfide could allow cycling of TPE_2 monolayers between monomeric **3-H$_2$** and oligomeric **(3)$_X$** forms (Fig. 3). Immersion of **3-H$_2$** monolayer in 10 mM I_2 / DMF for one minute followed by rinsing leads to nearly complete disappearance of TPE_2 molecules from mass spectra.[33] Reduction with DTT, rinsing and application of a THAP film yields TOF-MS molecular ion intensities of **3-H$_2$** (4.9±1.4 x 10^3), **3-H(O$_3$H)** (0.5±0.2 x 10^3) and **3-(O$_3$H)$_2$** (0.3±0.1 x 10^3) that are 55%, 100% and 55% of their respective intensities following one oxidation / reduction cycle of **2a** monolayer (Fig. 6, SI-8, SI-10). The second zip / unzip cycle, comprising oxidation to **(3)$_X$** and reduction, yields a "product" **3-H$_2$** monolayer with roughly half the dithiol TPE_2 as the "reactant" **3-H$_2$** monolayer. Performing a third cycle of I_2 oxidation / DTT reduction generates TOF-MS signal intensities of **3-H$_2$** (2.7±0.7 x 10^3), **3-H(O$_3$H)** (0.4±0.1 x 10^3) and **3-(O$_3$H)$_2$** (0.6±0.2 x 10^3) that are 55%, 80% and 230% of their respective intensities following two oxidation / reduction cycles of **2a** monolayer (Fig. 6, SI-10, SI-13). The third oxidation / reduction cycle also reduces the monolayer's **3-H$_2$** content by half. After three cycles, the dithiol [**3-H$_2$**+H]$^+$ peak is 5-6 times larger than the bis-sulfonic acid [**3-(O$_3$H)$_2$**+H]$^+$ and thiol / sulfonic [**3-H(O$_3$H)**+H]$^+$ peaks. After three oxidation / reduction cycles, the monolayer contains 25% as much bis-thiol TPE_2 as in **3-H$_2$** monolayers prepared without oxidation (Fig. SI-9). The decrease of **3-H$_2$** surface content following each pair of zipping / unzipping reactions limits the number of cycles a monolayer can undergo.

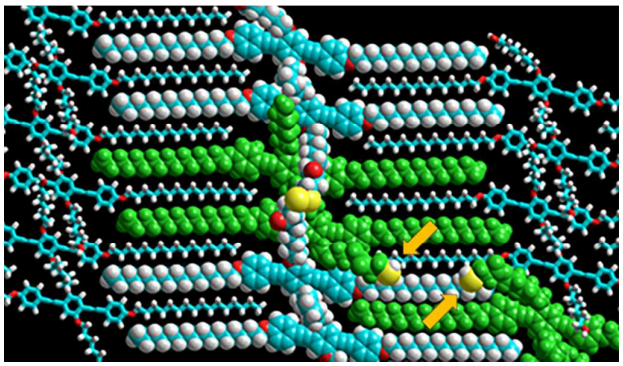

Fig. 5. Minimized molecular mechanics model of a monolayer section with disulfide cross-linked next-nearest neighbor TPE_2 molecules (CPK, center aryl column). Arrows point to sulfur atoms (yellow) from $(O(CH_2)_6O_2C(CH_2)_2SH)$ chains on TPE_2 molecules (green CPK) in different aryl columns. These two sulfurs are separated by > 1.3 nm.

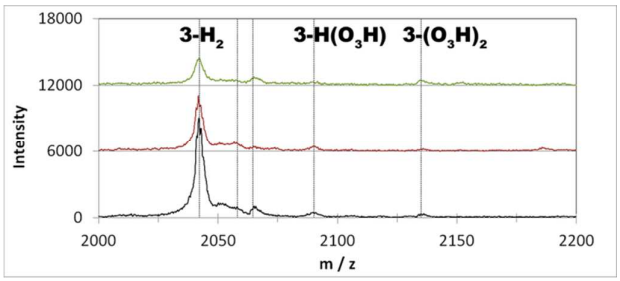

Fig. 6. TPE_2 regions of TOF mass spectra (THAP film applied) after exposing a mono-layer of **2a** to one (bottom), two (middle) or three (top) oxidation / reduction cycles consisting of (i) I_2 in DMF (forming oligomerized **(3)$_X$** monolayer) then (ii) DTT pH 7.8 (forming **3-H$_2$** monolayer). The vertical lines at m/z = 2042, 2058, 2064, 2090 and 2138 mark calculated average masses of [**3-H$_2$** + H]$^+$, mono-sulfenic acid [**3-H(OH)** + H]$^+$, [**3-H$_2$** + Na]$^+$, [**3-H(O$_3$H)** + H]$^+$ and [**3-(O$_3$H)$_2$** + H]$^+$. Each spectrum is an average of five sample locations (See Figs. SI-8, 10, 11). Spectra are shifted vertically by 6000.

Desorption of monomeric and oligomerized TPE_2 molecules during surface reactions and surface rinses may contribute to the loss of **3-H$_2$** from monolayers. The durability of monolayers assembled by single-core TPE molecules, monomeric dual-core TPE_2 molecules and oligomeric dual-core TPE_2 molecules was tested using o-dichlorobenzene (oDCB). oDCB more effectively desorbs TPE monolayers from HOPG than the DCM, DMF, ethanol, water and hexane solvents used in these monolayer reaction procedures. Single-core molecule **TPE-4**, with one hexadecyloxy chain on each terminal phenylene ring and two hexyloxy chains on the central phenylene ring, assembles monolayers on HOPG (Fig. SI-14).[16] Rinsing HOPG substrates (1.2 x 1.2 cm) bearing **TPE-4** monolayer with 20 µL oDCB removes 98+% of the molecules as determined by laser desorption ionization TOF-MS (Fig. SI-14). Monolayers assembled by monomeric dual-core TPE_2 molecules are somewhat more durable. A monolayer of **1** survives rinsing with 20 µL oDCB but is desorbed extensively (<30% retained) by immersion in 1 mL oDCB at 19°C for 3 hours (Fig. SI-15). A monolayer of **1** is desorbed almost fully (<10% retained) after 18 hours in oDCB at 19°C (Fig. SI-

15). The durability of oligomeric, dual-core TPE_2 **$(3)_X$** monolayer was evaluated by incubation in oDCB at 19°C or 60°C for 20+ hours. After rinsing to remove oDCB, the oligomeric **$(3)_X$** monolayer was reduced with DTT. The amount of monomeric **$3\text{-}H_2$** present on the HOPG was evaluated by TOF-MS after applying a thin THAP film. Immersion of **$(3)_X$** monolayer in 1 mL oDCB at 19°C for 20 hours, followed by DTT reduction, yielded $[3\text{-}H_2+H]^+$ molecular ion signal comparable (> 90%) to a **$3\text{-}H_2$** monolayer prepared by DTT reduction of **$(3)_X$** monolayer that was not exposed to oDCB (reference **$3\text{-}H_2$** monolayer). Immersion of **$(3)_X$** monolayer in oDCB at 60°C for 21 hours, followed by DTT reduction, produced more than 80% of the $[3\text{-}H_2+H]^+$ molecular ion signal found in the reference **$3\text{-}H_2$** monolayer (Fig. SI-16). Compared to dual-core TPE_2 molecule **1**, oligomerized **$(3)_X$** monolayer exhibits 10-fold, at minimum, slower desorption and improved desorption resistance in ambient and heated oDCB. Desorption of **$(3)_X$** is not a source of significant **$3\text{-}H_2$** loss. Monomeric **$3\text{-}H_2$** desorption may contribute, albeit slightly. Most likely, over oxidation of **$(3)_X$** and **$3\text{-}H_2$** by I_2 is the main cause of **$3\text{-}H_2$** loss.

These experiments demonstrate quasi-reversible zipping and unzipping between monomeric and oligomeric forms of TPE_2 monolayers by way of redox based thiol - disulfide chemistry. As disulfide-linked TPE_2 oligomers adhere much more strongly to graphite than monomeric TPE_2 molecules, this chemistry provides a means to reversibly switch monolayer adhesion; a capability that may find use in surface capture and release applications. The large difference in monomer / oligomer adhesion impacts TOF-MS analyses, which can detect, intact, TPE_2 molecules present in monomeric monolayer adsorbed on graphite but observe only fragments of the oligomeric monolayer. Fortunately, disulfide to thiol unzipping allows indirect assessment of oligomeric monolayer composition. Greater reversibility of the zipping / unzipping process will require decreasing the over oxidation of sulfur a thiol to disulfide cross-linking.

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[19] For assignment of m/z value from peaks lacking isotopic patterns see K. Biemann in Methods in Enzymology, **1990**, *193*, 295-305.
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[23] 2032.3 (2033.6) is the observed monoisotopic mass (most intense mass) in the pattern for $[\mathbf{2b}+H]^+$. Calculated values of the mono-isotopic and average masses are 2032.6 and 2034.1, respectively.
[24] Increased molecular weight is one factor that reduces TOF-MS signal intensities from TPE molecules on HOPG.[16].
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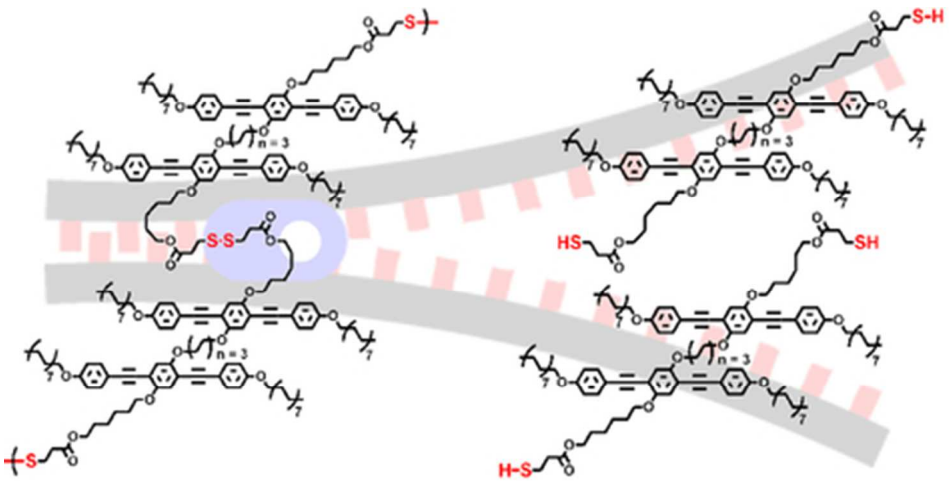
[31] 2090 and 2138 are the most intense m/z values of the two observed peaks. Isotopic patterns are not resolved. Calculated values of $[\mathbf{3}\text{-}H(O_3H)+H]^+$ and $[\mathbf{3}\text{-}(O_3H)_2+H]^+$ average masses are 2090.1 and 2138.1, respectively
[32] For preparation of (3-((3-ethoxy-3-oxopropyl)disulfaneyl)-propanoic acid) see J. Zhao, Y. Zhou, Y. Li, X. Pan, W. Zhang, N. Zhou, K. Zhang, Z. Zhang and X. Zhu, *Polym. Chem.*, **2015**, *6*, 2879-2891.
[33] Trace peaks assigned as $[M+H]^+$ of **3** and **$3\text{-}(O_3H)_2$** are present in the TPE_2 region (see Fig. SI-11). The spectra are collected after applying a THAP thin film.



39x19mm (300 x 300 DPI)