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AFOSR-Final Report
Award FA9550-10-1-0395, "Chain-Growth Methods for the Synthesis of High Molecular Weight Conducting and Semiconducting Polymers"
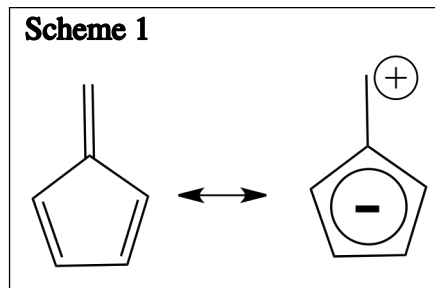Timothy M. Swager, Massachusetts Institute of Technology

Under funding from FA9550-10-1-0395 we published 6 papers that have appeared in top peer reviewed journals:

1. Andrew, T. L.; Cox, J. R.; Swager, T. M. "Synthesis, Reactivity and Electronic Properties of 6,6-Dicyanofulvenes" *Org. Letters* **2010**, *12*, 5302-5305.
2. VanVeller, B.; Schipper, D. J.; Swager, T. M. "Polycyclic Aromatic Triptycenes: Oxygen Substitution Cyclization Strategies" *J. Am. Chem. Soc.* **2012**, *134,* 7282–7285.
3. Cox, J. R.; Igarashi, T.; Kang, H.; Swager, T. M. "Norbornadiene Endcapping of Cross-Coupling Polymerizations: A Facile Route to Triblock Polymers" *ACS Macro Letters*, **2012**, *1*, 334-337.
4. Cordovilla, C.; Swager, T. M. "Strain Release in Organic Photonic Nanoparticles for Protease Sensing" *J. Am. Chem. Soc.* **2012**, *134*, 6932–6935.
5. Bonillo, B.; Swager, T. M. "Chain-Growth Polymerization of 2-Chlorothiophenes Promoted by Lewis Acids" *J. Am. Chem. Soc.* **2012**, *134*, 18916-18919.
6. Den Boer, D.; Krikorian, M.; Esser, B.; Swager, T. M. "STM Study of Gold(I) Pyrazolates: Distinct Morphologies, Layer Evolution, and Cooperative Dynamics" *J. Phys. Chem. C*. **2013,** *117*, 8290–8298.
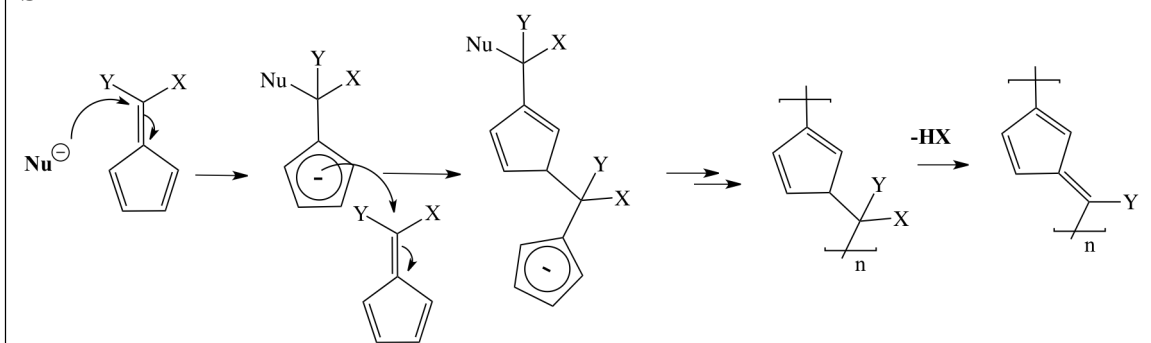
Our accomplishments under this award include the synthesis of materials with novel electronic structures and properties and the organization of materials in particles and at interfaces. In this report we briefly summarize our various accomplishments.
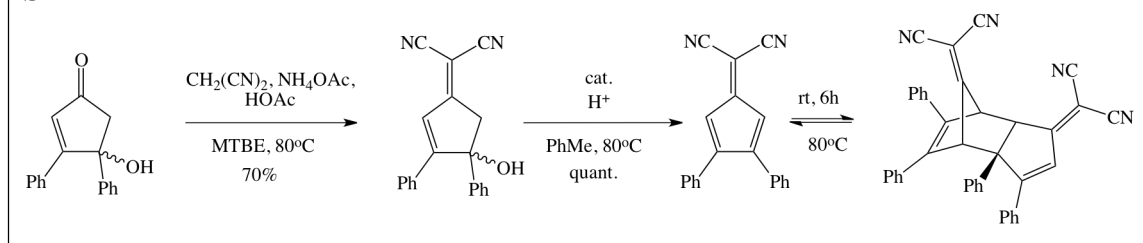
Fulvene Chemistry (Publication 1)

Fulvenes are a class of non-aromatic molecules that have a number of unique properties. They have low-lying zwitterionic excited states stabilized by aromaticity (Scheme 1). In spite of the fact that they can be synthesized readily from very inexpensive starting materials, there have been very few examples of these structures used in materials science. This stems from the fact that the non-aromatic reactive character complicates their chemistry. Our group has therefore endeavored to develop key materials that serve to empower materials applications of this intriguing structure.

Scheme 1

Fulvenes are known to add nucleophiles to the exocyclic carbon to generate the aromatic cyclopentadienyl anion and we anticipated that such a reaction could be the basis of an anionic polymerization (Scheme 2). To produce a conjugated system a leaving group "X" is required and the acidity of the cyclopenadiene C-H bond enhances the final elimination reaction. To facilitate polymerization we considered that both substituents "X" and "Y" should be electron withdrawing to increase the electrophilicity of the exocyclic carbon center.

Scheme 2

We envisioned that X=Y=CN would be the appropriate substituents to produce the desired polymerization in analogy to the well-known "super glue" anionic polymerization. Although there are abundant examples of fulvenes with X=Y= Donor, we found that there were no examples of fulvenes with electron nitriles in this position. These structures were further anticipated to be highly reactive because the electron withdrawing groups will produce antiaromatic character in the ring system in analogy to cyclopentadienone. As a result, we initiated a synthetic study designed to investigate the potential of this substitution pattern (Scheme 3, Pub. 1). To access these structures we introduced the nitriles through a condensation reaction in the diphenyl substituted cyclopentadienone precursor. Acid catalyzed dehydration yielded the target compound, which was prone to reversible Diels-Alder self-dimerization reaction. This dimerization can be blocked with further substitution of the fulvene ring systems and we conducted detailed characterization of these systems (X-ray crystal structures, optical spectroscopy and electrochemical analysis).
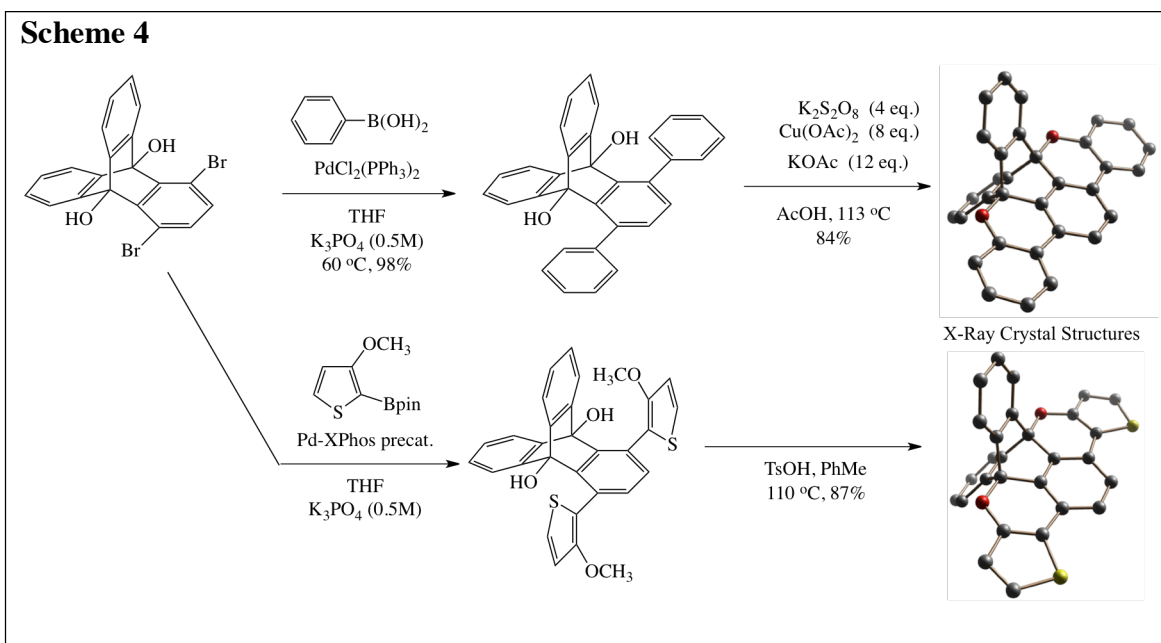
Scheme 3

We made numerous attempts to polymerize the dicyanofulvene shown in Scheme 3. However, the diphenyl groups appear to be very effective at blocking the reactivity of that center on the cyclopentadiene ring system. This fact is not surprising and indeed we had largely considered this structure more of a model system than a viable monomer. In our ongoing proposed research we detail an approach to monomers that are likely to undergo polymerization that makes use of the Diels-Alder reactivity and seeks to create the polyfulvene structure through a precursor method.

New Fused Ring Aromatic Monomers

Conformational flexibility can lead to disorder and dispersion of the energy levels in conjugated polymers. As a result, we have had a long-term interest in the creation of ladder polymer structures and monomers with fused aromatic ring systems. We had previously reported on a facile method to create functional triptycene systems by a [2+2+2] transition metal catalyzed cyclization reaction.[1] The triptycene group has a shape persistent structure that is highly effective at creating high solubility, enhanced stability, and optimal solid state luminescent quantum yields. As a result, we have been interested in creating monomers that incorporate this functional group into a very well defined conformational structure that is electroactive.

Scheme 4 (Pub. 2) shows two representative examples of this chemistry using a novel oxidation to create a terphenyl structure and an acid catalyzed substation to form a phenylene thiophene system. The chromophores of both monomers have completely planar structures. The enforced rigidity produces high quantum yields and these materials are under active investigation as building blocks to create new emissive materials for sensors and photovoltaics.

Scheme 4

X-Ray Crystal Structures

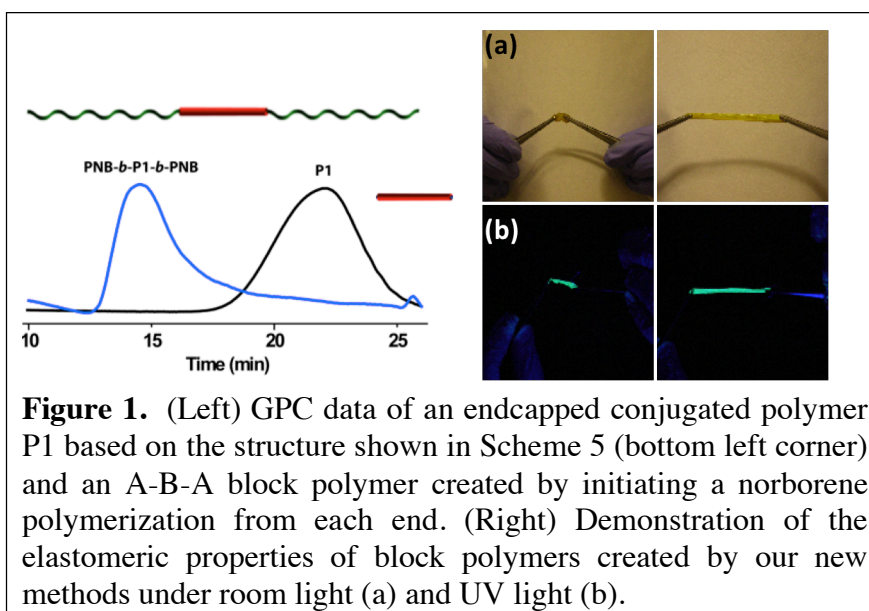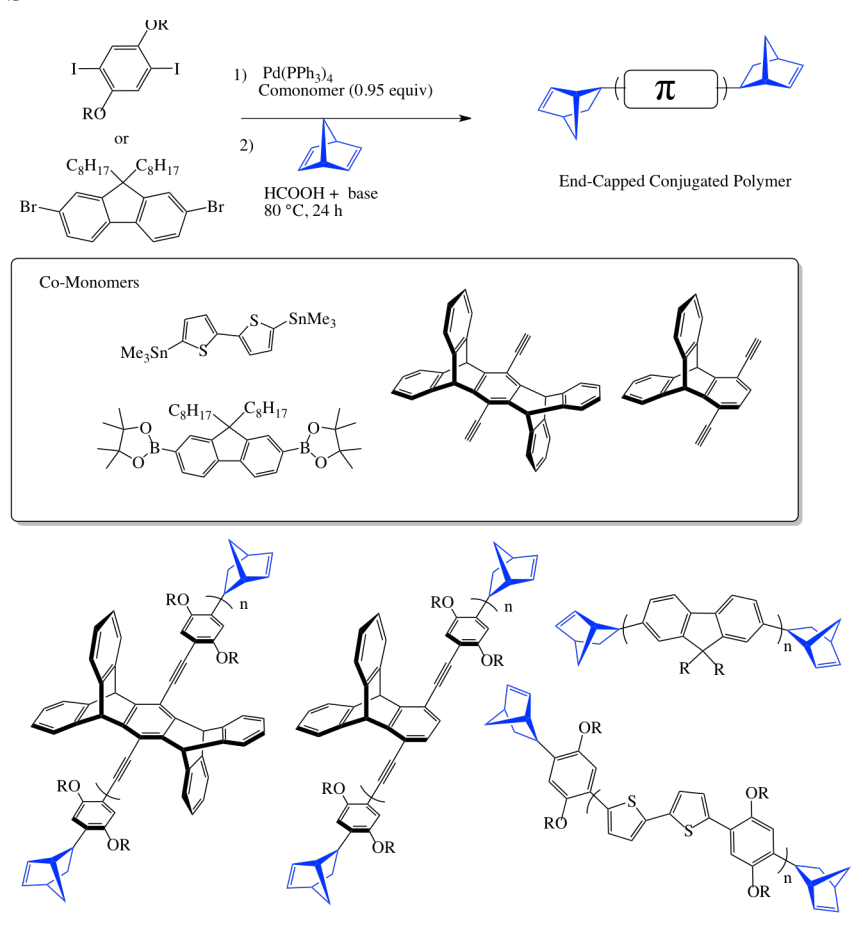**Block Co-Polymers of Semiconducting Organic Polymers (Publications 3 and 4)**

There are limited routes to the synthesis of block co-polymers of semiconductive polymers. We have developed (Pub. 3) a new broadly applicable method that is compatible with all common palladium catalyzed cross-coupling polymerizations.

The method (Scheme 5) involves the endcapping of these standard step-growth polymerizations with norboradiene in the presence of formic acid and base. The high reactivity of the norboradiene results in quantitative Heck-type insertion reactions and the formic acid serves to generate a metal hydride that can undergo facile reductive elimination. The result is the quantitative placement of norborene rings at the termini of the semiconductive polymers. These groups are the typical monomers for ring opening olefin

Scheme 5

Co-Monomers

End-Capped Conjugated Polymer

metathesis polymerizations (ROMP). As a result, we can apply the full power of ROMP methods to the creation of complex block polymers.

We have produced a number of A-B-A triblock polymers (B = π-conjugated polymer) by reacting the endcapped conjugated polymers with a generation 1 Grubbs catalyst to create macro-initiators. As can be seen from the gel permeation chromatography (GPC) data in Figure 1, all of the conjugated polymers

Figure 1. (Left) GPC data of an endcapped conjugated polymer P1 based on the structure shown in Scheme 5 (bottom left corner) and an A-B-A block polymer created by initiating a norborene polymerization from each end. (Right) Demonstration of the elastomeric properties of block polymers created by our new methods under room light (a) and UV light (b).

are further functionalized and block polymers formed with polynorborene have elastomeric properties.

The controlled assembly and processing of semiconductive polymers into precise structures is far from being understood. These processes are more complex than the now textbook examples of the nanostructure phase diagrams of block polymers based on? low persistence length coiled polymers. Complexities originate not only from the rigid nature of the π-block, but also the tendency to have strong and directional associations. The strong aggregation results in kinetic trapping of these materials in metastable structures/morphologies.

Considering that assembly of block copolymers into organized 3-D, 2-D, or even 1D structures is particularly challenging, we have focused on making functional structured nanoparticles that can be considered as 0-D. With the goal of generating functional nanoparticles we prepared complex ABCBA penta-block copolymers, wherein the central C-block is the semiconductive polymer (Pub. 4). These complex block copolymers can be self-assembled into responsive nanoparticles (Figure 2). Aqueous dispersions of the nanoparticles can be "fixed" in a collapsed less emissive (OFF) state by crosslinking the reactive B-block. Addition of a small amount of a good solvent for the central C-block can then "stress" the complex particle. Specifically, the C-block would like to swell in response to the solvent, but is prevented from expanding by the crosslinked B-block. Cleavage of these crosslinks allows for nanoparticle expansion and restores the fluorescence (i.e. ON-state). This general method was demonstrated with peptide crosslinks that can be cleaved by exposure to an appropriate protease. Future particles can be developed that respond to a broad range of biological, chemical, radiation, and electromagnetic signals.
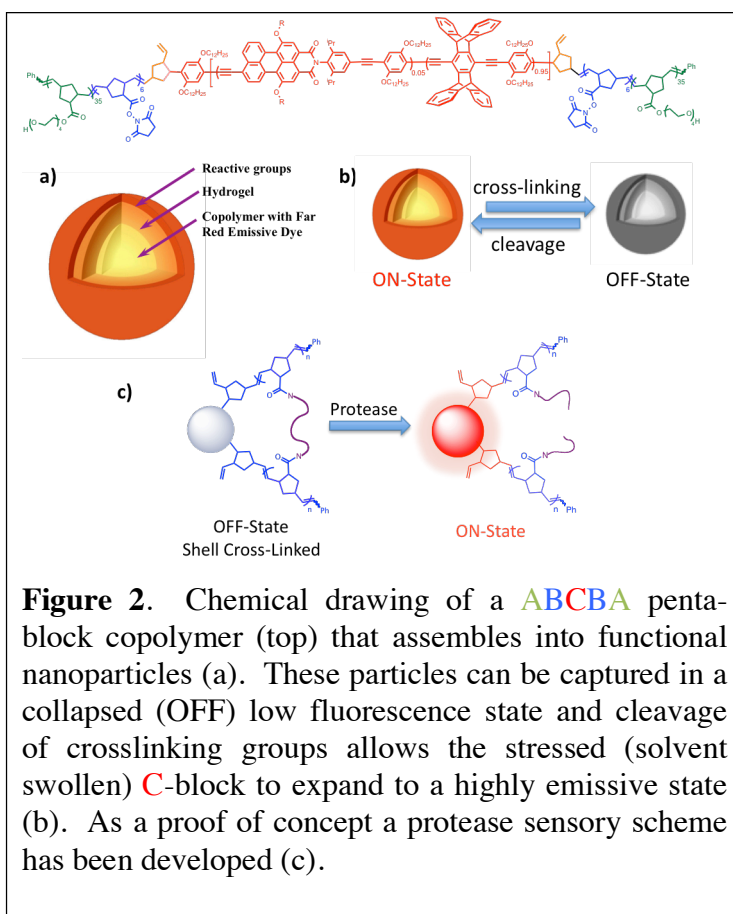

Figure 2. Chemical drawing of a ABCBA penta-block copolymer (top) that assembles into functional nanoparticles (a). These particles can be captured in a collapsed (OFF) low fluorescence state and cleavage of crosslinking groups allows the stressed (solvent swollen) C-block to expand to a highly emissive state (b). As a proof of concept a protease sensory scheme has been developed (c).

A New Living Chain-Growth Polymerization for Polythiophenes
We have also developed a powerful new method for the synthesis of polythiophenes through the cationic activation of monomers by Lewis or Brønsted acid catalysts (Pub. 5). The method is a paradigm shift because with addition of each new monomer in the

polymerization ?formally must disrupt its aromatic character. Consequently, this process would have nominally not been expected to be highly efficient. However, the polymerization is made possible by the formal elimination of hydrochloric acid (HCl) from the de-aromatized intermediates. This elimination reaction reconstitutes the aromatic stabilization of the thiophene repeating groups and results in a controlled living polymerization (Figure 3). Polythiophenes are certain to be a dominant materials platform in emerging and future electronic polymer technologies.

The power of a living polymerization is the ability to control the molecular weight, initiate polymerizations from a specific location (i.e. a surface or particle), and create complex block copolymers. The MIT team has shown that this new method can be applied to the synthesis of a variety of thiophene monomers and have produced block and endcapped polymers. This represents the first chain growth synthesis of the technologically important electron-rich alkoxy-thiophenes as well as their endcapped and block copolymer forms. A sampling of materials that can be synthesized with this controlled polymerization are shown in Chart 1. It is expected that similar living polymerizations can be developed for other families of aromatic monomers.

Figure 3. Polymerization of a thiophene monomer by a Lewis acid (SnCl$_4$) promoted chain-growth mechanism. The photographs under incandescent (top) and UV (bottom) light show the evolution of the band gap of the polymer with increasing molecular weight. The plot on the right shows the molecular weight and polydispersity index of each of these fractions relative to the monomer conversion. The linear correlation of the conversion and M$_n$ confirms a living chain growth polymerization.

The cationic nature of the polymerization also is ideally suited for the generation of regioregular polythiophenes wherein the chain propagating cation is directed by unsymmetric electron donor groups. Indeed, the polymer in the lower right corner of Chart 1 is formed in a completely regioregular fashion.
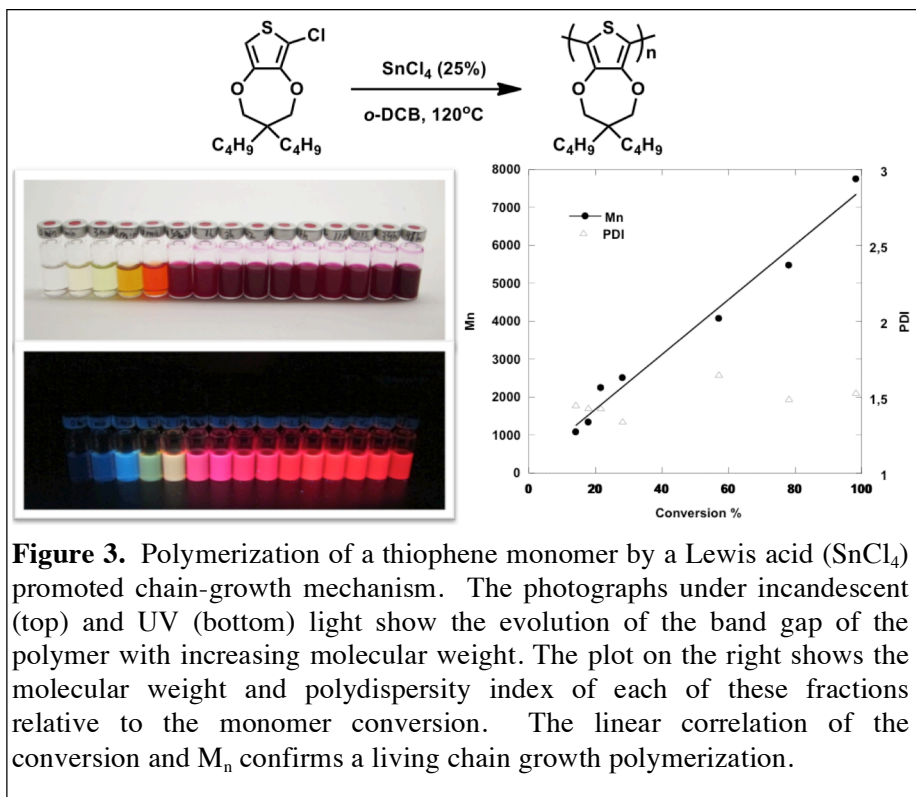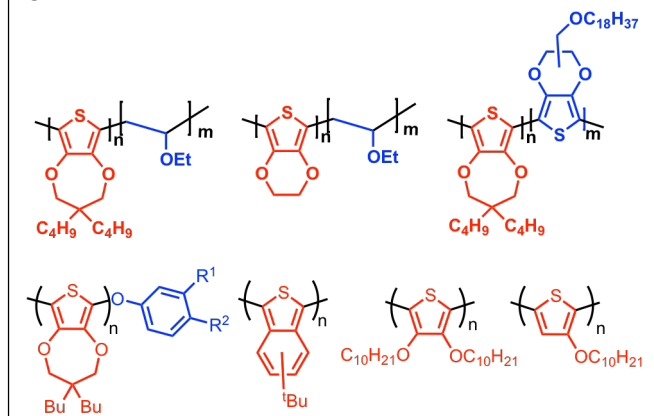

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Nanostructure Organization and Analysis

To realize our longer-term goals of creating organized structures we have initiated a program to analyze the complex organization of materials at interfaces. To get molecular information these studies are generally performed using scanning tunneling microscopy (STM) at conductive substrates. We have investigated a number of polymers and expect that this method will be useful in understanding structure formation of polymers that could be relevant to the generation of large Faraday rotations. As an initial study (Pub. 6), we focused on understanding the assembly of the highly polarizable trinuclear gold(I) pyrazolates (Figure 4). On the graphite/1-octanoic acid interface dodecyl functionalized gold pyrazolates formed concentration-controlled morphologies. We found two types of monomeric packing and one dimeric type with two trinuclear gold pyrazolates next to each other on the surface. For an octadecyl functionalized derivative all studied concentrations resulted in a dimeric morphology (Figure 4). However, different concentrations led to different transient states during the layer evolution. At low concentrations, a transient monomeric state was present with the alkyl chains in a gauche-conformation that subsequently converted to a more optimized anti-conformation. At higher concentrations a less stable "line" polymorph was observed.

Figure 4. Structures of compounds analyzed (a, b) and the preferred organization of a graphene surface (c). The bottom images show scanning induced reorientation of dimeric unites of AuC18.

The confinement of the molecules to the surface led to cooperative dynamics, in which two molecules in a dimer moved as if they were one particle. Furthermore, in a higher level of cooperativity, the rotation of one dimer appears to induce rotations in coupled neighboring dimers.
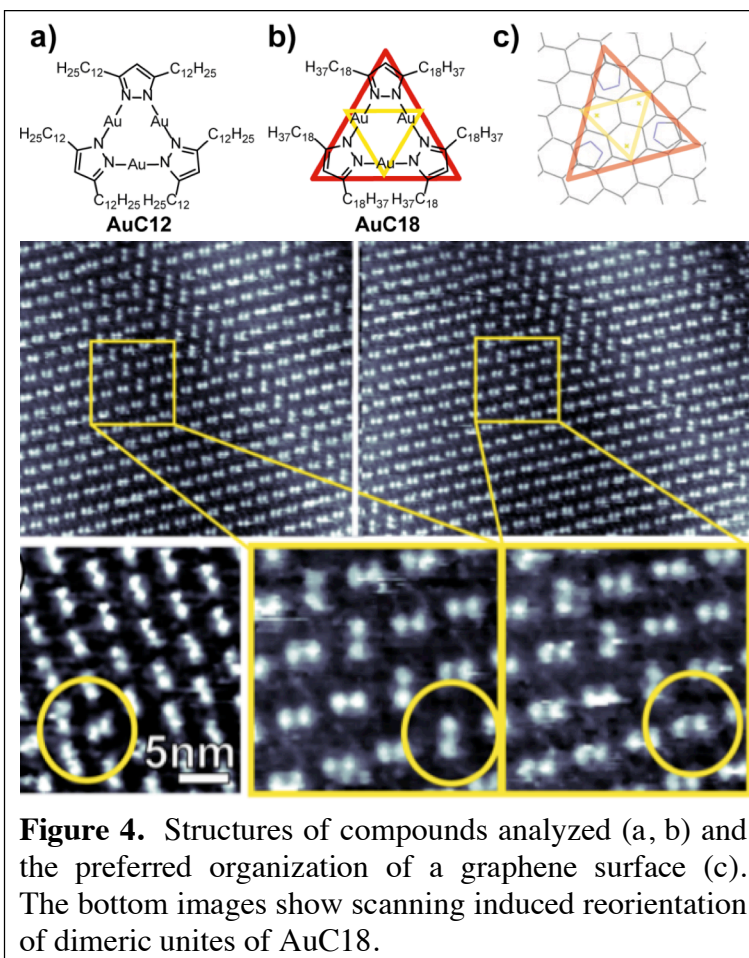
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[1] Taylor, M. S.; Swager, T. M. "Triptycenediols by Rhodium-Catalyzed [2+2+2] Cycloaddition" *Org. Lett.* **2007**, *9*, 3695-3697.