Final Report
**New Sensing Platforms for Explosives, Nerve Agents, and
Radionucleotides**

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The purpose of this project was to build on successful past work synthesizing new families of materials and apply these to biological, chemical, and radiological detection. Our primary objectives were to exploit the fluorescence and conductivity properties of metal nanowires and the mechanical and conductivity properties of polymeric helicenes to form prototype sensors that can improve WMD proliferation detection capabilities. We focused on the following tasks:

1. Synthesis of polymeric helicenes and metal nanowires;
2. Processing materials;
3. Characterization material response;
4. Fabrication sensor devices

TASK 1: SYNTHESIS

Polymeric helicenes could serve as surrogates for CNTs, with similar dimensions and electronic properties. The mechanical properties will, however, be complimentary – the helicenes will be elastic, not stiff. The synthesis relies on the ring closing metathesis (RCM) of a precursor polymer, poly(2,4-dipropenyl)-*meta*-phenylene (Scheme 1). The key feature of this strategy is that the structure of precursor polymer dictates the structure of the helicene.

Scheme 1. Conversion of a precursor polymer to a polymeric helicene by RCM.

Our first aim was to demonstrate in model systems the viability the RCM step. The formation of arenes by RCM had received little attention in the literature. The reaction worked in quantitative yield in models systems. The requisite monomer was prepared on gram scale (Scheme 2), and its polymerization (Scheme 1) was effective. The precursor polymer was characterized by mass spectrometry and NMR spectroscopy.

Scheme 2. Monomer synthesis.

The key step, RCM to afford the helicene, was challenging and required much optimization. We ultimately found that treatment of the precursor polymer with the second generation Grubbs-Hoveyda metathesis catalyst under an atmosphere of ethylene produced an insoluble material. Deuterium labeling experiments demonstrated complete consumption of all propenyl groups. The product was identified as the desired helicene by the appearance of a characteristic infrared at 800 cm^{-1} , corresponding to $\text{CH}=\text{CH}$ out of plane wagging. The $\text{CH}=\text{CH}$ feature is only present in the product and is the result of the RCM reaction. Solid-state NMR and nanoscale probing microscopy experiments are planned to confirm the structure.

The second synthetic target was to produce a series of luminescent materials based on the synthetic and structural motif depicted below (Scheme 3). The premise was that the luminescence of the Au–Ag chain would be altered upon interaction with the desired substrate. Results from this work established that this premise was sound; however, very early on in the project we discovered that the polymeric structural motif was, in fact, unique to the original ligand system thereby preventing us from developing the necessary homologues needed to address the material science, specificity, and device requirements.

Scheme 3. Preparation of metal nanowires.

We therefore focused our attention on developing a series of luminescent materials that would lend themselves to this project. Regrettably, we were unsuccessful. Our first

endeavor looked at simple modifications to the NHC backbone while keeping all other structural and electronic aspects as similar as possible. Simply replacing the uncoordinated pyridyl ring with a methyl group does indeed produce luminescent polymers; however, their structural motifs are considerably different from each and very different from the prototype (Figure 1). Interestingly, the luminescence of these polymers does not appear to follow any simple trend related to metal-metal separation, angles or auxiliary donor ligand electronics. These data suggest that the nature of the excited state has considerable ligand and metal character, and to generate a predictable luminescence shift upon induction of a structural change requires a truly homologous series of compounds.

Figure 1. Some metal nanowires

The discovery of the coordinated nitrate polymer (bottom figure 1) suggested that benzoate ligands could be incorporated which could be substituted with electron donating and withdrawing groups residing away from the metal core thereby producing a homologous series. Instead of forming nearly linearly coordinated --Au--Ag--Au-- motifs, these new polymers contain a $\text{Ag}_2(\text{O}_2\text{CPhR})_2$ dimer coordinated perpendicularly to the Au(I) centers forming a tetrametallic repeating unit. Each tetranuclear cluster is aurophilically attracted to another in the solid state (shown bottom in Scheme 4 below). Alternatively, replacing an electronegative R group for a proton reproducibly generates a similar series of polymers except each tetranuclear Au_2Ag_2 core is bridged by a linearly coordinated $\text{Ag}_2(\text{O}_2\text{CPhR})_2$ dimer as in the top part of the figure below. Interestingly, these materials are not photoluminescent at room temperature. This is quite remarkable in that several highly luminescent Ag_2Au_2 tetrametallic clusters have been reported by Laguna and coworkers.

Scheme 4. Formation of tetranuclear clusters.

We returned to the original ligand system and tried to build a series of usable polymers. Once again we explored the benzoate addition to the dipyriddy-substituted NHC. However, as shown below, the reaction between the dipyriddy-NHC and silver benzoates reproducibly leads only to the known helical polymeric system. This was true for a variety of silver benzoates.

Scheme 5: Benzoates give helical polymers.

TASK 2: DEVICE FABRICATION

Running parallel to the compound development aspect of this proposal was a project to explore physical properties in order to build a workable device. We quickly learned that simple evaporative coating of substrate and spincoating were not working. Although the complexed polymers are stable to air and light, prolonged exposure of light to the dissolved materials leads to photodecomposition and deposition of metallic gold or silver. To circumvent this problem, we blended several of these coordination polymers into a polystyrene matrix. The overall samples were luminescent, yet the bulk blended materials did respond to added substrate. The polymeric helicenes were obtained as an insoluble, intractable polymer that was not amenable to incorporation into a device.

The development of nanofibers as sensor components was another key aspect of this project. An effective experimental setup to produce nano-scale fibers is electrospinning. The common setup used in electrospinning process has a capillary with polymer and/or other polymer-composite solution with an electrode inserted into it. The capillary is placed with some inclination with the horizontal to have polymer drop at the tip. Aluminum foil collector is placed at a fixed distance from the tip. As can be seen in Figure 1, a syringe is often used in place of capillary with a 22 gauge needle. The power supply is connected to the needle instead of inserting into solution. In our experimental setup a high voltage electrode (Gamma High Voltage Research Inc, Model ES30P-5W, Florida) was used as the power supply. During electrospinning using the above setup it was observed that the fibers were deflected to surrounding metal surfaces other than collector and deposited on them. To avoid this, a plastic box was made. The box acted as a shield against effect of surrounding metal parts. Figure 2 shows the electrospinning setup built. The top polycarbonate sheet has a small hole in the center to insert the needle. The needle protrudes through this hole, and the power supply is connected from the inner side of the box. The collector is placed on a lab stand that can be moved up and down to control the distance from tip of needle to collector. A syringe pump (Razel Scientific Instruments, Connecticut) was used to control the flow rate precisely. Programmed flow rate can be applied using computer interface with an overall accuracy of 2% and repeatability of 0.5%. To measure the electric current flowing in the system, a high value resistor (20 M Ω) was connected between the collector and ground, and the voltage drop across the resistor was monitored in real time using a data acquisition system.

Figure 2: Illustration of an electrospinning setup

Baseline experiments with polyacrylonitrile (PAN) and nanoparticles: Initially, the polymer solution was made by dissolving polyacrylonitrile(PAN) in dimethylformamide(DMF). PAN was dissolved in DMF at an elevated temperature and cooled to room temperature before electrospinning. PAN solutions of different weight percentage (4-10 wt %) were made. Other important parameters including surface tension and dynamic viscosity of the polymer solutions were controlled. By using a syringe

pump, a variable flow rate was applied. By using electric current as a control parameter a stable jet was produced leading to the fiber mat having the radius of the fibers changing along its thickness, which results in better distribution of pore size and better characteristics (like mechanical properties etc). Finally we were able to produce controllable PAN nanofibers (Figure 3(a)). Also, polymer/titanium dioxide nanocomposite fibers were also electrospun using a sol-gel technique. The precursor solution was prepared from titanium tetraisopropoxide (Aldrich Chemical Co., USA) in acetic acid and ethanol by stirring. Its concentration was in the range of 0.04 g/ml to 0.16 g/ml. Polyvinyl pyrrolidone (PVP, Mw=1,300,000) dissolved in ethanol was added to the TiO₂ precursor solution by weight to provide the viscosity of the solution. The concentration of PVP was within 0.02 g/ml and 0.1 g/ml. The presence of a polymer matrix is the basic requirement for the formation of jet and subsequently fibers in an electrospinning. PVP was chosen in the present study as the polymer matrix. The solutions were mixed and stirred for 1 hour at room temperature prior to electrospinning. This practice is important for us to understand electrospinning processes for fluid/solid systems. Figure 3(b) shows electrospun PAN/TiO₂ fibers.

Figure 3: A photograph of electrospinning setup. 1-High voltage power supply; 2-Syringe pump; 3-Grounded collector; 4-Polycarbonate sheet box; and 5-Black paper for background

Figure 4: (left) electrospun 6 wt% PAN/DMF solution (SEM micrograph); (right) Electrospun titanium dioxide/PVP fibers made from sol-gel precursor (optical micrograph). Note that the electric field strength and flow rate were 1 kV/cm and 0.5 mL/h, respectively.

Electrospinning of an ionomer, Nafion, in a liquid form: DuPont developed NafionTM, the first perfluoro-sulfonated ionomer, in the early 1970s. Typically, these are manufactured from polytetrafluoroethylene (PTFE) as an effective backbone and sidechains ending with active ion-exchange sites such as sulfonate or carboxylate. The starting monomer is the perfluorinated alkenes with appropriate substituents. An important consideration is the length of the sidechain that determines the properties of the final product. One example is to introduce weave fabric to improved mechanical strength. Generally speaking, the term *Liquid NafionTM* refers to solutions of NafionTM Perfluoro-Sulfonated Ionomers (NPSI). Commercially available NPSI membranes are (as-received membranes) are semicrystalline and have ionic aggregates. Therefore, they are not melt-processable since such supermolecular structures are resistive to flow. The adopted technique for obtaining Liquid NafionTM is to dissolve the as-received NafionTM membrane at an elevated temperature (approximately 250°C) under pressure of a 50/50 mixture of aliphatic alcohols and water. The recasted film can be obtained but is generally mechanically poor (cracked and brittle) and is also easily dissolved in polar solvents including water and alcohol. A number of answers to this problem have been proposed. Typically, the processes are to include additive solvents such as triethyl phosphate, dimethyl sulfoxide, dimethyl formamide (DMF) or ethylene glycol so as to obtain good insoluble recasted NafionTM films. However, such recasted NafionTM exhibit morphological differences relative to as-received NafionTM. An important issue to be addressed could be its micellar structure of the recasted NafionTM. Another issue to electrospin Nafion is its high conductivity relative to most polymer solutions. In this experiment we used PVP as a carrier solution (Figure 4). Figure 5 shows electrospun Nafion nanofibers.

Figure 5: Illustrative process of making Nafion/PVP solution

Figure 6: Electrospun Nafion (ionomer) fibers. Note: Fiber diameter is approximately 2 micron. A good shape without branching or twisting was observed.

TASK 3: RESPONSE CHARACTERIZATION

A major outcome of this work is the first accurate estimation of the expected gas-phase binding energy of TNT with aromatic molecules. Nitroarenes are the largest class of conventional explosives and their detection is important for military and civilian security. We report the interaction energies of nitroarenes, including TNT and picric acid, with arenes, calculated using state-of-the-art quantum mechanical methods.

Sandwich complex	Binding Energy (kcal/mol)	Eq. separation (Å)
$C_6H_6/C_6H_6^{(a)}$	-1.81	3.80
$p-C_6H_4(NH_2)_2/C_6H_6^{(a)}$	-3.20	3.60
$C_6H_5NO_2/C_6H_6$	-3.67	3.64
$m-C_6H_4(NO_2)_2/C_6H_6$	-5.60	3.56
$p-C_6H_4(NO_2)_2/C_6H_6$	-5.73	3.55

$s\text{-C}_6\text{H}_3(\text{NO}_2)_3/\text{C}_6\text{H}_6$	−7.62	3.49
$1,2,4,5\text{-C}_6\text{H}_2(\text{NO}_2)_4/\text{C}_6\text{H}_6$	−9.68	3.47
$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{CH}_3/\text{C}_6\text{H}_6$	−8.12	3.49
$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}/\text{C}_6\text{H}_6$ (C_s)	−8.38	3.46
$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}/\text{C}_6\text{H}_6$ (C_1)	−8.09	3.48
$p\text{-C}_6\text{H}_4(\text{NO}_2)_2/p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ ($C_{2v}, +$)	−9.71	3.38
$p\text{-C}_6\text{H}_4(\text{NO}_2)_2/p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ (C_{2v}, II)	−9.06	3.43
$[p\text{-C}_6\text{H}_4(\text{NH}_2)_2]_2$ ($D_{2d}, +$)	−5.01	3.43
$[\text{C}_6\text{H}_5\text{NO}_2]_2$ ($C_{2v}, \uparrow\uparrow$)	−3.44	3.62
$[\text{C}_6\text{H}_5\text{NO}_2]_2$ ($C_2, +$)	−4.80	3.56
$[\text{C}_6\text{H}_5\text{NO}_2]_2$ ($C_{2h}, \downarrow\uparrow$)	−5.15	3.57
$[p\text{-C}_6\text{H}_4(\text{NO}_2)_2]_2$ ($D_{2d}, +$)	−6.75	3.45
$[p\text{-C}_6\text{H}_4(\text{NO}_2)_2]_2$ (D_{2h}, II)	−5.01	3.54
$[s\text{-C}_6\text{H}_3(\text{NO}_2)_3]_2$ (D_{3d})	−6.10	3.43

The long history of picrate co-crystals and the computational results for other electron-poor arenes led us to expect significant binding energies of nitroarenes to arenes. We calculated a benchmark for the *s*-trinitrobenzene/benzene system (CCSD(T)/CBS limit//MP2/cc-pVTZ, C_{3v} symmetry) following the methodology of Hobza and co-workers. Our expectations were met: the binding energy is −8.04 kcal/mol, which is 1.72 kcal/mol more binding than the hexafluorobenzene/benzene complex (−6.32 kcal/mol).

The benchmark validated a somewhat more affordable model chemistry, developed by Sherrill and co-workers, in which the binding energy of an arene sandwich complex relative to benzene dimer can be reliably calculated at the MP2/aug-cc-pVDZ level. The MP2 binding energy was −7.62 kcal/mol, 0.42 kcal/mol less binding than the benchmark. These results for a series of nitroarene/arene complexes are given in the table.

The interaction of nitroarenes with benzene strengthens with additional nitro groups. A plot of binding energy against number of the nitro groups reveals that their influence is additive ($r = 0.99942$). The intercept, which is the benzene/benzene dimer interaction

energy, is -1.66 kcal/mol, in agreement with the best calculated value and definition in this model (-1.81 kcal/mol).⁵ The slope, which is the nitro group increment, is -2.00 kcal/(group $\cdot$ mol). The position of the nitro groups has little influence: *p*-dinitrobenzene and *m*-dinitrobenzene bind to benzene with nearly identical energies, -5.73 and -5.60 kcal/mol, respectively, despite the lack of a dipole moment in the para isomer. The linearity of the plot is surprising because the crowded nitro groups in 1,2,4,5-tetranitrobenzene are twisted (44°) which should diminish their mesomeric electron withdrawal. This result contradicts somewhat available solution data, therefore suggesting that solvent plays a role in determining acceptor strength in solution.

TASK 4: FABRICATION OF SENSOR DEVICES

The Colorimeter may be a useful tool for detecting the absorbance and % transmission of the test samples. Figure 6 shows a mobile colorimeter (CO7500, WPA, UK; with the reference wavelength in the range from 440 to 680 nm in this case). We repackaged a mobile sensor box that can house the samples size of 1 cm (width) x 1 cm (height). This set up allows us to investigate the electro-spun nano-fibers or other small samples while the electric field is applied.

Figure 6: (from left to right) a sensor box setup. Dimension: 7.5 inch x 5 inch x 4.5 inch