Research Facilities and Resources Available for Hunter's Research

H1. Laboratory Facilities

The Youngstown State University Chemistry Department is located on the 5th and 6th floors of the Ward Beecher Science Hall. It was originally built in the mid-1960s, was extensively upgraded in the mid-1980s, and plans are currently in place for the building of a substantial extension starting in 2005. The labs and instrumentation rooms to be used by PI's and Co-PI's coworkers in this project are all located adjacent to one another and include:

- A chemistry majors/research student computer lab having twelve Windows NT workstations loaded with conventional software, including: NMR prediction software, PC Spartan Pro and other molecular graphics/modeling/orbital software, SHELX-TL software, etc., for diffraction analysis, Data analysis software for the FT-IR, DSC/TGA, NMR, etc., Online access to the holdings of OhioLink (i.e., the Ohio universities shared card catalogue and internet access to almost all chemistry journals), Remote software to operate the university's LC-MS and X-ray diffractometer (by the summer of 2001) instruments.
- Hunter has four dedicated research labs and 1/3 of another which are suitable for 10-12 students and directly opens onto the adjacent Advanced Synthesis Lab in which he has space for additional students. There is at least 6" of fume hood space per student.
- The YSU Chemistry Department has a BAS CV-27 and CV-100 electrochemical instrumentation with Dr. L. S. Curtin in a lab which is next to their research space. We are also receiving funding in NSF 0111511 for a new BAS 100B/W electrochemical system. *This project will use this instrumentation extensively for the electrochemical studies, especially cyclic voltammetry and bulk electrolysis.* Hunter recently received an NSF grant that includes funding for an advanced Electrochemistry System for his Group.
- The Small Instruments Rooms have doors to the Advanced Synthesis Lab and have the following small instrumentation: a TA Instruments 2910 DSC and a 2050 TGA, a Cannon CT-518 constant temperature bath for viscometry measurements, a GBC Instruments/Polymer Labs GPC-SEC-HPLC system (i.e., autosampler, isocratic/gradient pump, column oven, RI and diode array UV-visible detectors, and data system), a Jasco 410 FT-IR (0.9 cm^{-1} resolution), and a GC.
- Two basic Vacuum Atmospheres HE-43-2 inert atmosphere glove boxes, one in each of the PI's and Co-PI's labs. Hunter has recently received a grant to purchase 2 additional high end glove boxes with O2/H20 sensors, refrigerators, etc.

H2. Youngstown State University Instrumentation Facilities

Youngstown State University has two closely related instrumentation centers. The YSU Center for Biomedical and Environmental Research, YSU-CBER, is housed on the 4th floor of the Ward Beecher science hall and specializes in instrumentation for the characterization of biological materials. The YSU Structure & Chemical Instrumentation Center, YSU-S&CIC, is housed on the 5th floor of the Ward Beecher science hall and specializes in the characterization of non-biological materials. The two centers work closely together, sharing both staff, faculty participants, and instrumentation funding. Both centers were established to serve the teaching and research needs of faculty and students from YSU and other PUIs and to help meet the needs of users from local governmental organizations and industry (in that priority). They have a full time PhD Scientist, Bruce Levison (with a PhD in chemistry and nearly 15 years of post-graduate experience with analytical instrumentation) to assist with data collection and analysis, 0.75 of a full time Instrumentation Service Specialist, Ray Hoff (with a BS in Physics and a dozen years university instrumentation service experience), pending permission to hire an additional electronics instrumentation maintenance technician and two instrument operators, trained undergraduate and MS student assistants to run the instruments and collect data. The major instruments in these centers are all research grade and were purchased with a combination of NSF,

Foundation, State, and internal funds with the PI on the current RUI proposal as either the PI or as a co-PI in each case. In addition to the smaller chromatographic, electrochemical, spectroscopic, physical, and analytical instruments expected at any MS level institution, the centers are equipped with the following modern instrumentation. There is plentiful instrument time available which means that the students can spend the time on the instrument needed to get to know it well and to push it to its full capabilities. The students learn to use all of this instrumentation in their Junior and Senior labs which means that research time is spent primarily on honing skills and collecting data.

- A Bruker Daltonics Esquire LC-MS instrument with an autosampler and a Solid Phase Micro Extraction, SPME, interface and both Electro-Spray, ESI, and Atmospheric Pressure Chemical Ionization, APCI, inlets. This instrument can be run from remote locations over the WEB. YSU was the first Bruker Esquire customer to accomplish the remote control of this LC-MS instrument. This instrument is ideal for analyzing organometallics too involatile for a conventional direct insertion MS. In particular, they are excellent for high molecular weight species and oligomers and for materials ranging from relatively non-polar species to hydrogen bonding or even ionic materials. Indeed, they are ideal for acquiring the mass from the sorts of high molecular weight, often ionic, species to be prepared in this project. *They will be used for characterizing both the neural and cationic rigid-rods and their $(MS)^n$ capabilities will be used to provide structural information.* Where more advanced capabilities are required, they are available to us from Ohio's research institutions via our participation in the Ohio MS Consortium, including: MALDI-TOF, high field ICR, high resolution MS, Field Desorption, etc. *In addition, our collaborator at York University in England, Dyson, has the expertise, students, and facilities for studying gas phase reactivity.*
- A substantially upgraded Varian Gemini-2000 400 MHz multinuclear NMR with four probes (i.e., 5 m and 10 mm VT broadband probes, a Quadruply Tuned PFG probe for $^{1}H/^{13}C/^{19}F/^{31}P$, and an Inverse Detection probes), Variable Temperature, VT, Inverse Detection, and Pulsed Field Gradient, PFG, accessories, and several work stations. This instrument is ideal for routine solution phase characterization studies for several reasons, including its high sensitivity and the solvent suppression capabilities provided by the inverse detection and Z-gradient PFG system. In addition, the students have plentiful NMR time available. Thus, having 24 hours of uninterrupted NMR time on our 400 MHz system allows a student to get results that they would never obtain in a 15 minute time slot on a triple channel 500 MHz system. The new $^{1}H/^{13}C/^{19}F/^{31}P$ Quadruply Tuned PFG probe allows our students to collect data on all of the nuclei of routine interest without having to retune the probe (unless they want to collect ^{29}Si, etc.). The Inverse probe allows them to collect the spectra of particularly insensitive nuclei such as nitrogen and metals (including via ^{1}H or ^{19}F inverse detection where appropriate). Where more advanced capabilities are required, they are available to us from Ohio's research institutions via our participation in the Ohio NMR Consortium, including: NMR systems optimized at up to 800 MHz and optimized for solid state or solution studies. *The YSU 400 MHz NMR will be extensively used to characterize the starting materials and rigid rod products in solution with the higher field and solids NMRs at remote sites being used to characterize the high oligomers in solution and the solid state structures of these materials.*
- Three automated GC-MS systems (both with autosamplers, one with a solids probe and one with an SPME interface). One of these is optimized for synthetic samples and one for trace environmental samples. *The direct insertion probe will be useful for the characterization of the more volatile organic, phosphine, and organometallic starting materials.* The Chemistry Department has also just received the donation of a older but highly functional high resolution mass spectrometer (i.e., it was upgraded last year at a cost of $200,000) and it will be installed at YSU by January of 2002.
- A TA Instrument model 2910 DSC (with quench cooling accessory for temperatures down to ≈ -160 °C) and a model 2050 TGA. *These thermal analysis instruments will be critical for monitoring the phase changes and decomposition reactions of our new organometallic materials. We also have access to advanced "hyphenated" thermal analysis techniques (e.g., TGA-FTIR and TGA-MS) though our*

ongoing relationship with the analytical division of Packard Electric in Youngstown.

- Dr. Jeff Carroll of the YSU Physics Department has a 3 year old Mossbauer spectrometer. *This will be used to collect the appropriate data on the iron redox properties with his assistance and that of one of his undergraduate research students.* If required, a new cobalt source will be purchased with the budgeted operating funds.
- A 40 node Beowulf supercomputer cluster is now being set up at YSU and will be available as needed to the participants at no charge.
- Less relevant to Hunter's projects, these centers have a new Bruker-Nonius X-Ray Fluorescence, XRF, system and multiple GC, HPLC, IR, UV-Vis, etc., systems.

H3. YSU Diffraction Facility

The Youngstown State University Structure & Chemical Instrumentation Center, YSU-S&CIC, Diffraction Facility is currently located in a 400 square foot lab. This lab contains two 6 year old Bruker-AXS P4 diffractometers. One has a X-1000 multiwire area detector and a Cu tube and is used primarily for powder studies. The other has a serial detector, a LT2 low temperature system, and a Mo tube and is used for the large majority of single crystal samples. We have just had a proposal funded by NSF (i.e., NSF DUE-CCLI-A&I 0087210) and by the Ohio Board of Regents Action Fund (i.e., OBoR-AF #491): "WEB Accessible Single Crystal X-Ray Diffractometer for Undergraduate Instruction at a Consortium of Predominantly Undergraduate Institutions"), **A. Hunter** (PI), L. M. Hoistad, Alan J. Jircitano, T. R. Wagner, and E. P. Zovinka. The following text is taken verbatim from the funded proposal and describes its goals. We are currently expect delivery of an Oxford Cryostream equipped Bruker-Nonius APEX system on July 1st. It is now installed and operational.

"During the summer of 2001, the YSU Structure Center Diffraction Facility will be moved to a 1,200 square foot room to allow additional space for the new Bruker APEX CCD instrument (or an analogous model from a different vendor) and, especially, more instructional space near the instruments. With the grant and matching funds, this lab will be set up so that anyone in the world with WEB access will be able to watch lab and instrument operations via fixed and pan/tilt/zoom WEB cameras. If they have a WEB camera on their own computer, they will also be able to video conference with the operators or faculty and students in this lab. The new stereo polarizing microscope to be placed in this lab will be equipped with a color WEB camera so that students in the attached instructional space or at remote sites will be able to view the crystal selection and mounting operations. With funds from this grant, the two current P4 diffractometers will be upgraded with new computer hardware and software so that they can be remotely controlled over the WEB. Similarly, the new CCD instrument will be made WEB accessible for both the diffractometer control software and the crystal centering scope. The current LT2 system will be upgraded to the LT3 standard to improve its low temperature performance (which is marginal below -80° in Ohio's summer humidity) and to make it compatible with the PLATFORM goniometer on the Bruker APEX CCD system."

A Bruker-Nonius D8 Powder Diffractometer is now on order (equipped with optics optimized for high resolution/Rietveld work) for February 2002 delivery.

This project will be dependent on access to diffraction data to structurally characterize all crystalline products and to evaluate the 3-D shapes of the nanomaterials. Almost all of our seniors get several different exposures to these instruments during their laboratory courses. In addition, many take a senior level course dedicated to diffraction methods taught by the PI. As each student synthesizes new organometallic building blocks and oligomers, they will attempt to grow crystals of them. All new single crystalline samples will be characterized by single crystal diffraction methods and powder samples will be qualitatively analyzed by powder diffraction methods (i.e., using the GADDS software and the area detectors) to characterize the phases that are present. Some of the crystallographically better behaved single crystal samples will also be characterized by charge density diffraction methods (the PI is spending part of his current sabbatical gaining familiarity with these

methods) in collaboration with the Hansen/Lecomte group in France.

H4. External Facilities

Being an undergraduate institution, YSU does not have all of the requisite facilities and expertise for carrying out all of the materials testing parts of this project "in house." Where needed, these will be accessed through access to those at regional PhD granting institutions, at regional companies, and at DOE National Labs (described above) and especially through the international collaborations which are central to this proposal (described below and in Sections C, I2, and I3). These European collaboration were developed while the PI was on sabbatical in Scotland and represent ongoing interactions with some of the best materials groups in Europe.

H4a. Charge Density Diffraction Facilities and Collaborators

The PI has been spending part of his sabbatical this year increasing his diffraction skills (he is currently best know to the crystallographic community for his work on crystallographic education) and has ongoing relationships with three of the most well know charge density diffraction groups in the world, namely those of: Phillip Coppens at SUNY Buffalo, Simon Coles and Michael Hursthouse in Southampton (UK), and *Niels Hansen and Claude Lecomte in Nancy (France)*. The PI and his students will continue developing their skills in diffraction and charge density methods while collaborating with these groups using the new state of the art APEX CCD diffractometer to be placed at YSU this summer. Where shorter wavelengths, higher luminosities, and/or liquid He temperature data are needed, these will be collected using the shared access times at the NSLS and APS and using the synchrotron access of our collaborators in France. *The group in Nancy will play the lead role in the charge density diffraction studies for this RUI proposal while helping the YSU team develop their expertise in this area of growing importance to materials science.* For access to powder diffraction data at variable temperatures and pressures and at high resolutions, we will use the facilities at the Oakridge High Temperature Materials Lab, with Camden Hubbard, the lab director as our contact.

H4b. ESR Facilities and Collaborators

We have local (to an older instrument, installation planned this Summer/Fall for the Co-PI) and regional access to more modern 10 GHz ESR facilities (including at the University of Vermont where the Co-PI was a postdoctoral fellow with W. Geiger). *For access to cutting edge ESR facilities, we will use the very high field ESR lab at St. Andrews University in Scotland (i.e., operating at up to 200GHz) via our collaboration with Riedi/Smith in Physics.*

H4d. Bulk and Molecular Conductivity Facilities and Collaborators

Electrical conductivities of the bulk materials will be qualitatively evaluated using 4-point conductivity methods. *Quantitative bulk measurements and the measurement of molecular conductivities will be done in collaborations with the groups at St. Andrews University including Richardson in Chemistry and Riedi in Physics. This group also has the capability to use "Break Junction" methods to measure the electrical behavior of single molecules (esp. by Dr. Thomas Bitzer) and this capability will be heavily used.*

H4e. Electronic/Optical Device Fabrication and Testing Facility and Collaborators

The St. Andrews Physics Department Photonics Innovation Center is equipped to fabricate integrated electronic and/or optical circuits (i.e., device elements) in its new clean room and to test their electronic and optical properties, their compatibilities with conventional device elements and manufacturing techniques (e.g., spin coating), and their suitability for practical applications (e.g., response times, energy consumption, and lifetimes).

H4f. NLO Facilities and Collaborators

All NLO measurements will be done in collaborations with the group at the Photonics Innovation Center in the St. Andrews Physics Department.

H4g. Theoretical Collaborators

Theoretical calculations on the isolated and solid state materials will be performed by our current collaborators Frank Blockhuys and Christian Van Alsenoy of Antwerp University and John McGrady of York University, using multiple high level approaches, including Density Functional Theory and combinations of DFT and Molecular Mechanics, respectively.

H4i. Surface Structure Analysis

Through his Collaboration with Professor Mark Foster at the U. of Akron Polymer Science Department, Hunter has access to his facilities, including: Foster has a total of 1740 sq. ft. of lab space in three labs. One small lab is devoted to Langmuir-Blodgett film deposition requiring a clean environment. The second laboratory houses a 12kW rotating anode X-ray generator with attached X-ray reflectometer and an 18kW rotating anode with attached custom small angle X-ray spectrometer and surface X-ray spectrometer. The surface spectrometer (Molecular Metrology) combines capabilities for performing specular reflectivity, diffuse scattering (in-plane and out-of-plane), and Evanescent Wave Induced X-ray Fluorescence or X-ray Standing Wave Induced X-ray Fluorescence. The third lab contains a Gaertner variable angle, two wavelength ellipsometer, Headway Research spin coater, fume hood, exhausting laminar flow hood, vacuum ovens, high vacuum oven, three scanning probe microscopes, and assorted items suited to the fabrication and characterization of thin films. A Park Scientific M5 SPM allows the study of comparatively large samples in many modes. A Park Scientific Autoprobe CP, capable of operating in many modes is located in an environmental chamber in which humidity and temperature can be controlled. This microscope has also been modified to perform nanoscale mechanical measurements on surfaces using x-modulation. The third microscope is a Thermal Microscopes Explorer with a stage allowing the heating and cooling of samples.