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TITLE (Include Security Classification)
ELECTRONIC AND IONIC TRANSPORT IN PROCESSABLE CONDUCTING POLYMERS

PERSONAL AUTHOR(S)
Martin Pomerantz, John R. Reynolds, Krishnan Rajeshwar, Dennis S. Marvnick

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COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) conducting polymers, composites, blends, ion transport, fibers, theoretical calculations
FIELD	GROUP	SUB-GROUP	

ABSTRACT (Continue on reverse if necessary and identify by block number)

A summary of the research carried out on this grant over the past year is given. This includes studies of water soluble polyelectrolyte/polypyrrole composites, conducting polymer/dopant ion interactions, symmetrically and asymmetrically substituted poly(di-2-heterocycle-2,5-disubstitutedphenylenes), poly(5-decylisothianaphthene), polypyrrole containing luminescent ions, the use of cyclic voltammetry coupled with UV-vis and Raman spectroscopy, the preparation of polypyrrole films containing nm-sized Pt particles, the neutral-polaron-bipolaron sequence of oxidation states of polypyrrole in the presence of O₂, melt spun fibers of blends of poly(3-decylthiophene) with polyethylene and the development of a new modification of the Extended Hückel band structure methodology which, when combined with geometries calculated by the PRDDO method, produces very accurate calculated band gaps.

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OFFICE OF NAVAL RESEARCH
END-OF-THE-YEAR REPORT
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

Grant N00014-90-J-1320

R&T Code a400008df

Electronic and Ionic Transport in Processable Conducting Polymers

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May 28, 1991



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OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: a400008df

Contract/Grant Number: N00014-90-J-1320

Contract/Grant Title: Electronic and Ionic Transport in Processable Conducting Polymers

Principal Investigator: Martin Pomerantz, Grant Administrator, John R. Reynolds, Krishnan

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- a. Number of papers submitted to refereed journals, but not published: 7 (not including 6 in press)
- b. Number of papers published in refereed journals (list attached)*: 18 (includes 6 in press and 3
- c. Number of books or chapters submitted, but not yet published: 0 acknowledging DARPA/ONR for
instrument purchases)
- d. Number of books or chapters published (list attached)*: 1
- e. Number of printed technical reports & non-refereed papers (list attached)*: 16
- f. Number of patents filed: 1
- g. Number of patents granted (list attached)*: 0
- h. Number of invited presentations at workshops or professional society meetings: 10
- i. Number of presentations at workshops or professional society meetings: 23
- j. Honors/Awards/Prizes for contract/grant employees (list attached)*: 3
(This might include Scientific Society Awards/Offices,
Promotions, Faculty Awards/Offices)
- k. Total number of Graduate Students and Post-Doctoral associates supported by at least 25% during this
period, under this R&T project number:
Graduate Students: 5
Post-Doctoral Associates: 9
including the number of,
Female Graduate Students: 1
Female Post-Doctoral Associates: 0
the number of
Minority* Graduate Students: 0
Minority* Post-Doctoral Associates: 1
and, the number of
Asian Graduate Students: 3
Asian Post-Doctoral Associates: 6
- l. Other funding (list agency, grant title, amount received this year, total amount, and period of
performance)*

* Use the letter and an appropriate title as a heading for your list, e.g.:

b. Published Papers in Refereed Journals, or, d. Books and Chapters published

* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

a) Papers Published in Refereed Journals

Reynolds, J. R.; Ruiz, J. P.; Child, A. D.; Marynick, D. S.; Nayak, K. "Electrically Conducting Polymers Containing Alternating Substituted Phenylene and Bithiophene Repeat Units," *Macromolecules* **1991**, *24*, 678-687. Other support: Robert A. Welch Foundation, Rockwell International, Texas Energy Research in Applications Program.

Basak, S.; Rajeshwar, K.; Kaneko, M. "In Situ Photogeneration of a Catalyst on a Chemically-Modified Electrode Surface: Application to a Mixed Valent Hexacyanoferrate System," *J. Electroanal. Chem.* **1990**, *295*, 403-407. Other support: Texas Advanced Technology Program, National Science Foundation.

Jolly, C. A.; Reynolds, J. R. "Mechanically Durable, Semiconducting and Optically Polarizing Poly(nickel tetrathiooxalate)/Poly(vinyl alcohol) Composites," *Chem. of Materials* **1990**, *2*, 479-480. Other support: Robert A. Welch Foundation.

Gieselman, M. G.; Reynolds, J. R. "Poly(*p*-phenyleneterephthalamido propane sulfonate): A New Polyelectrolyte for Application to Conducting Molecular Composites," *Macromolecules* **1990**, *23*, 3118-3124. Other support: General Dynamics, Inc.

Wang, F.; Reynolds, J. R. "Soluble and Electroactive Nickel Bis(dithiolene) Polymers Prepared Via Metal Complexation Polymerization," *Macromolecules* **1990**, *23*, 3219-3225. Other support: Robert A. Welch Foundation.

Basak, S.; Rajeshwar, K.; Kaneko, M. "Ion Binding by Poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulfonate]} Thin Films," *Anal. Chem.* **1990**, *62*, 1407-1413. Other support: National Science Foundation.

Krishna, V.; Ho, Y.-H.; Basak, S.; Rajeshwar, K. "A Luminescence Probe and Voltammetry Study of Ion Transport During Redox Switching of Polypyrrole Thin Films," *J. Am. Chem. Soc.* **1991**, *113*, 3325-3333.

Sundaresan, N. S.; Reynolds, J. R.; Ruiz, J. P. "Photocurrent Response of Poly(3-ethylmercapto-thiophene)," *J. Mat. Sci.* **1991**, *10*, 345-347. Other support: Texas Energy Research in Applications Program.

Qiu, Y. J. and Reynolds, J. R. "Dopant Anion Controlled Ion Transport Behavior of Polypyrrole," *Polym. Eng. and Sci.* **1991**, *31*, 417-421.

Papers in Press in Refereed Journals

Baker, C. K. and Reynolds, J. R. "Electrochemically Induced Mass Transport in Poly(pyrrole)/Poly(styrene sulfonate) Molecular Composites," *J. Phys. Chem.*, in press.

Pomerantz, M.; Tseng, J. J.; Zhu, H.; Sproull, S. J.; Reynolds, J. R.; Uitz, R.; Arnott, H. J.; Haider, M. I. "Processable Polymers and Copolymers of 3-Alkylthiophenes and Their Blends," *Synth. Met.*, in press.

Ruiz, J. P.; Child, A. D.; Nayak, K.; Marynick, D. S.; Reynolds, J. R. "Electrically Conducting Polymers Containing Substituted Phenylene and Heterocycle Repeat Units," *Synth. Met.*, in press. Other support: Robert A. Welch Foundation, Rockwell International, Texas Energy Research in Applications Program.

Prezyna, L. A.; Wnek, G. E.; Lee, J. J.; Reynolds, J. R.; Qiu, Y. J. "Interaction of Cationic Proteins with Electroactive Polypyrrole/Poly(styrene sulfonate) and Poly(*N*-methylpyrrole/Poly(styrene sulfonate) Films," *Synth. Met.*, in press.

Stickle, W. F.; Reynolds, J. R.; Jolly, C. A. "Surface Characterization of Electrically Conducting Nickel Tetrathiooxalate/Poly(Vinyl Alcohol) Composites," *Langmuir*, in press. Other support: Robert A. Welch Foundation.

Wang, F.; Qiu, Y. J.; Reynolds, J. R. "Synthesis and Characterization of Nickel Bis(dithiolene) Complex Polycarbonates and Polyurethanes," *Macromolecules*, in press. Other support: Robert A. Welch Foundation.

Papers in Refereed Journals Acknowledging DARPA/ONR Support for Instrumental Purchases

Pomerantz, M.; Levanon, M. "Carbene Addition to the 2,3-Bond of Naphthalene and Thermal Wolff Rearrangement of Bis(methoxycarbonyl)carbene," *Tetrahedron Lett.* **1991**, *32*, 995-998. Other support: U. S. Department of Energy, Robert A. Welch Foundation.

Pomerantz, M.; Levanon, M. "Bis(dimethyl Malonato)ketazine. Formation and Inversion/Rotation Barrier," *Tetrahedron Lett.* **1990**, *31*, 4265. Other support: U. S. Department of Energy, Robert A. Welch Foundation.

Brown, K. L.; Brooks, H. B.; Zou, X.; Victor, M.; Ray, A.; Timkovich, R. "Heteronuclear NMR Studies of Cobalamins. 11. ¹⁵N NMR Studies of the Axial Nucleotide and Amide Side Chains of Cyanocobalamin and Dicyanocobalamin," *Inorg. Chem.* **1990**, *29*, 4841-4844. Other support: National Institute of Diabetes and Digestive and Kidney Diseases, National Science Foundation.

d) Book Chapter Published

Reynolds, J. R.; Pomerantz, M. "Processable Electronically Conducting Polymers," in *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1991; Vol. 2, Chapter 4, pp. 187-256. Other support: Robert A. Welch Foundation.

e) Printed Technical Reports and Non-refereed Papers

Reynolds, J. R.; Pomerantz, M. "The International Conference on Science and Technology of Synthetic Metals," *ESN Information Bulletin* (ONR European Office), in press.

Reynolds, J. R.; Dharia, J. R. "Synthesis and Characterization of Conducting Poly(1,4-bis-(2-thienyl)benzenes) Containing Long Pendant Alkoxy Chains," *Proc. Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.* **1991**, *64*, 176-177.

Reynolds, J. R.; Child, A. D.; Ruiz, J. P.; Qiu, Y.-J. "Electrochemical Properties of Poly[2,5-dialkoxy-1,4-bis(2-thienyl)benzenes]," *Proc. Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.* **1991**, *64*, 182-183.

Reynolds, J. R.; Gieselmann, M. B.; Qiu, Y.-J.; Pyo, M. H. "Polypyrrole/Polyelectrolyte Composites: Versatile Material with Controllable Properties," *Proc. Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.* 1991, 64, 202-203.

Reynolds, J. R.; Wettermark, U. G.; Worrell, G. A.; Chen, C. S. "Polypyrrole Films and Epoxy Laminates: Electrical Conductivity, Mechanical Integrity and Environmental Stability," *Proc. Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.* 1991, 64, 267-268.

Reynolds, J. R.; Qiu, Y.-J. "Ion Binding on Poly(pyrrole cyclodextrin sulfate)," *Proc. Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.* 1991, 64, 343-344.

Pomerantz, M.; Reynolds, J. R.; Rajeshwar, K.; Marynick, D. S. "Electronic and Ionic Transport in Processable Conducting Polymers," End-of-the-Year Report; Technical Report No. 22, Grant No. N00014-90-J-1320, DARPA/ONR, May 25, 1990.

Pomerantz, M.; Reynolds, J. R.; Rajeshwar, K.; Marynick, D. S. "Electronic and Ionic Transport in Processable Conducting Polymers," Quarterly Technical Report No. 23, Grant No. N00014-90-J-1320, DARPA/ONR, October 5, 1990.

Pomerantz, M.; Reynolds, J. R. "Report on Travel to Attend the International Conference on Science and Technology of Synthetic Metals," Foreign Travel Report No. 1, Grant No. N00014-90-J-1320, DARPA/ONR, October 17, 1990.

Pomerantz, M.; Reynolds, J. R.; Rajeshwar, K.; Marynick, D. S. "Electronic and Ionic Transport in Processable Conducting Polymers," Quarterly Technical Report No. 24, Grant No. N00014-90-J-1320, DARPA/ONR, January 16, 1991.

Pomerantz, M.; Reynolds, J. R.; Rajeshwar, K.; Marynick, D. S. "Electronic and Ionic Transport in Processable Conducting Polymers," Quarterly Technical Report No. 25, Grant No. N00014-90-J-1320, DARPA/ONR, April 12, 1991.

Stickle, W. F.; Reynolds, J. R.; Jolly, C. A. "Surface Characterization of Electrically Conducting Nickel Tetrathiooxalate/Poly(vinyl alcohol) Composites," Technical Report No. 26, Grant No. N00014-90-J-1320, DARPA/ONR, April 12, 1991.

Baker, C. K.; Qiu, Y.-J.; Reynolds, J. R. "Electrochemically Induced Charge and Mass Transport in Polypyrrole/Poly(styrene sulfonate) Molecular Composites," Technical Report No. 27, Grant No. N00014-90-J-1320, DARPA/ONR, April 12, 1991.

Wang, F.; Qiu, Y.-J.; Reynolds, J. R. "Electroactive, Near Infrared Absorbing Nickel Bis(dithiolene) Complex Polycarbonates and Polyurethanes," Technical Report No. 28, Grant No. N00014-90-J-1320, DARPA/ONR, April 12, 1991.

Reynolds, J. R.; Pomerantz, M. "Processable Electronically Conducting Polymers," Technical Report No. 29, Grant No. N00014-90-J-1320, DARPA/ONR, April 12, 1991.

Pomerantz, M.; Tseng, J. J.; Zhu, H.; Sproull, S. J.; Reynolds, J. R.; Uitz, R.; Arnott, H. J.; Haider, M. I. "Processable Polymers and Copolymers of 3-Alkylthiophenes and Their Blends," Technical Report No. 30, Grant No. N00014-90-J-1320, DARPA/ONR, April 12, 1991.

j) Honors/Awards/Prizes

The following students won prizes for their papers presented at the 24th Annual Meeting-in-Miniature of the Dallas-Fort Worth Section of the American Chemical Society, Richardson, Texas, May 1990.

Andrew D. Child – First Prize – Graduate Division: Child, A. D.; Ruiz, J. P.; Hong, S. Y.; Marynick, D. S.; Reynolds, J. R. "Electrochemical Synthesis and Characterization of Substituted Bisfuranyl Phenylene Polymers."

Karl Zachary – First Prize – Undergraduate Division: Zachary, K.; Jolly, C. A.; Reynolds, J. R. "Transition Metal Tetrathiooxalate Composites."

Jimmy R. Rogers – Second Prize – Graduate Division: Rogers, J. R.; Marynick, D. S. "Conformational Floppiness in a Tetrathiolene Bridged Ditungsten Complex."

1) Other Funding

Agency	Title	Amount Recd. This Year	Total Amount	Period of Performance
Martin Pomerantz				
Robert A. Welch Foundation	"Synthesis and Study of Phosphorus and Nitrogen Compounds"	\$30,000	\$85,000	6/1/89 to 5/31/92
Alcon Laboratories, Inc.	"Synthesis of Some Organic Nitrogen Compounds"	\$6,000	\$22,000	1986-1991
LTV Aerospace and Defense Co.	"Preparation of Poly(3-alkyl- thiophenes)"	\$2,400	\$2,400	9/90 to 1/91
National Science Foundation (with R.J. Blau, PI and additional Chemistry Department faculty)	"An REU (Research Experiences for Undergraduates) Site in Chemistry at U. T. Arlington"	\$4,612	\$14,203	3/15/91 to 8/31/93
John R. Reynolds				
Robert A. Welch Foundation	"Synthetic Metals: Inorganic Complex and Conjugated Organic Polymers"	\$25,000	\$75,000	6/1/88-5/31/91
Energy Research in Applications Program (with K. Rajeshwar)	"High Performance Fuel Cells and Storage Batteries Based on Conducting Polymers"	\$62,005	\$233,017	2/1/89-1/31/93
Chronos Research Laboratory	"Conjugated Polymers with Polar or Polarizable Side Groups"	\$55,000	\$112,500	7/1/89-6/30/91
Rockwell Inter- national Science Center	"Oriented Conducting Polymers"	\$19,672	\$42,412	7/15/89-4/30/91
Army Research Office	"Copolymers and Blends with Enhanced Polymer Film Dielectric Properties"	\$58,426	\$119,173	6/11/90-6/10/93
General Dynamics, Fort Worth	"Synthesis and Characterization of Electrically Conducting Polymers"		\$4,000	4/1/90-12/31/90
National Science Foundation (with R.J. Blau, PI and additional Chemistry Department faculty)	"An REU (Research Experiences for Undergraduates) Site in Chemistry at U. T. Arlington"	\$4,612	\$14,203	3/15/91 to 8/31/93

Krishnan Rajeshwar

Texas Advanced Technology Program	"Photoelectrochemical Characterization and Processing of MBE-Grown Structures and Devices"	\$88,553	\$196,544	1/1/90-12/31/92
National Science Foundation	"Novel Approaches to Electrodeposition of Compound Semiconductors"	\$73,526	\$249,604	1/1/87-12/31/90
Energy Research in Applications Program (with J.R. Reynolds)	"High Performance Fuel Cells and Storage Batteries Based on Conducting Polymers"	\$62,005	\$233,017	2/1/89-1/31/93
National Science Foundation (with R.J. Blau, PI and additional Chemistry Department faculty)	"An REU (Research Experiences for Undergraduates) Site in Chemistry at U. T. Arlington"	\$4,612	\$14,203	3/15/91 to 8/31/93

Dennis S. Marynick

Texas Advanced Technology Program (with S. K. Estreicher, Texas Tech Univ.)	"Advanced Molecular Modeling Software for Quantum Biochemical Applications"	\$50,000	\$127,000	1/1/90 to 12/31/91
Cray Research, Inc.	"Molecular Orbital Techniques for Very Large Molecules"		\$47,800	4/1/91 to 3/31/92
Robert A. Welch Foundation	"Theoretical Studies of Inorganic Molecules"	\$35,000	\$105,000	6/1/91 to 5/31/94
National Science Foundation (with R.J. Blau, PI and additional Chemistry Department faculty)	"An REU (Research Experiences for Undergraduates) Site in Chemistry at U. T. Arlington"	\$4,612	\$14,203	3/15/91 to 8/31/93

Part II

a. Principal Investigators

Martin Pomerantz, Grant Administrator
John R. Reynolds
Krishnan Rajeshwar
Dennis S. Marynick

b. Current telephone numbers

817-273-3811 (Martin Pomerantz)
817-273-3813 (John R. Reynolds)
817-273-3810 (Krishnan Rajeshwar)
817-273-3914 (Dennis S. Marynick)

c. Cognizant ONR Scientific Officer

Dr. JoAnn Milliken

d. Brief Description of Project

We are preparing new electroactive and conducting processable polymers, polyelectrolytes, multicomponent blends, and composites, by both chemical and electrochemical methods, with improved properties. We are studying the effect of molecular structure on electrical conductivity, optical absorption, and luminescent emission, electrochemical switching rates, polymer-ion interactions, long range order and crystallinity. Also, strategies for improving environmental and thermal stability for applications are being probed. We are developing novel families of in-situ electrochemistry-spectroscopy probes for studying ion transport during redox switching of polypyrrole. We are mapping out new strategies for binding ionic species at chemically modified electrode surfaces and we are developing and characterizing polypyrrole/platinum nanocomposite electrodes for electrocatalysis and fuel cell applications. We are continuing our work in the preparation of soluble, processable small band gap, optically transparent conducting polymers. In addition, we are maintaining our on-going collaborative efforts with General Dynamics, Rockwell International and Hoechst-Celanese. We are continuing to develop and use theoretical methodology to guide and understand the properties and syntheses of many of these highly conjugated polymers.

e. Significant Results During Last Year

The following have been achieved or elucidated:

1. A series of water soluble polyelectrolytes has been prepared by derivatization of poly(*p*-phenyleneterephthalamide) (Kevlar) and polybenzimidazole (Celazole) and used to prepare molecular composites with rigid rod polymers and conducting composites and fibers with polypyrrole.

2. Conducting polymer-dopant ion interactions have been used to control ion transport during electrochemical switching such that either cations or anions are the dominant mobile species, while other ionic species are strongly entrapped.
3. A broad family of symmetrically and asymmetrically substituted poly(di-2-heterocycle-2,5-disubstituted phenylenes), utilizing thiophene, furan and pyrrole as the heterocycles with alkyl and alkoxy pendant substituents on the phenylene ring, have been synthesized and used to show that isoregic polymers exhibit higher degrees of order and higher doped electrical conductivities than their aregic counterparts.
4. Polypyrrole films have been utilized as the active elements in microwave dipole antennae and shown to perform nearly as well as copper in a collaborative program with General Dynamics, Inc.
5. Poly(5-decylisothianaphthene) has been prepared from 5-decyl-1,3-dihydroisothianaphthene and forms a dark blue-black solution which gives a "transparent" light yellow-brown solution upon doping with nitrosonium fluoborate.
6. Polypyrrole containing luminescent ions has been shown to be useful as in-situ probes of ion transport during redox switching of the polymer.
7. Cyclic voltammetric equivalents of processing UV-vis and Raman spectroscopic data for polypyrrole has been demonstrated and this technique provides much more molecular information than could be obtained with voltammetry.
8. The neutral-polaron-bipolaron sequence of the oxidation of polypyrrole has been shown to be sensitive to the O₂ content of the ambient, with the polaron state being unstable in the presence of O₂.
9. Polypyrrole thin films containing nm-sized Pt⁰ particles have been prepared and characterized using electrochemical quartz-crystal microgravimetry (EQCM).
10. Melt-spun fibers of blends of poly(3-decylthiophene) and low density polyethylene (collaborative program with Hoechst-Celanese Research Division) show very good conductivity (FeCl₃ doped) when electron microscopy shows good homogeneity and very poor conductivity when there is obvious phase separation. The blends are also much easier to spin than pure poly(3-decylthiophene).
11. A new modification of the Extended Hückel band structure methodology has been developed which, when combined with geometries calculated by the PRDDO method, produces very accurate calculated band gaps for a wide variety of conjugated polyheterocycles.

f. Brief Summary of Plans for Next Years Work

With completion of work on the poly(di-2-thienylphenylenes), we will examine a number of derivatized polyphenylenes for their photo- and electroluminescent properties while extending syntheses to encompass poly(di-2-pyrrolyl-2,5-disubstitutedphenylenes) which are expected to be solution processable and highly stable as doped electrically conducting polymers. Polymer-polymer and polymer-ion interactions will be examined via the ternary phase behavior of rigid rod-polyelectrolyte-solvent systems. Surface properties of electrically conducting polymer composites and blends will be examined microgravimetrically and spectroscopically and subsequently used to bind ionic and polymeric reagents at electrode surfaces. We will continue the development of

polypyrrole/naphthalene sulfonate thin films for sensor applications and develop quantitative models for the chemical reduction of these materials by reductive analytes including hydrazine. We will also continue studies on the polypyrrole/Pt nano-composites. Specifically, we will quantify the catalytic efficacy of these thin films towards dioxygen reduction. We plan to characterize conducting polymer solutions via redox probes as well as to develop flow methods for in-situ monitoring of ion transport. We will continue and expand our work on potentially transparent processable conducting polymers. These systems will include not only substituted poly(benzof[c]-thiophenes) (isothianaphthenes) and poly(thieno[3,4-b]pyrazines) but also poly(thieno[3,4-b]thiophenes), in addition to other systems. We also plan on continuing our very productive collaborations with General Dynamics and Hoechst-Celanese. Finally, we plan to make extensive use of our modified Extended Hückel method. Band gaps in many new systems will be calculated as an aid to the synthetic efforts now underway in our polymer group. Currently, our modified Extended Hückel method predicts one-dimensional band gaps ($\pi \rightarrow \pi^*$ transition energy, corresponding to the peak position of the optical spectrum of the polymer). Efforts will be made to develop and enhance the method to also estimate band edges.

g. Graduate Students Currently Working on Project

Chengchang Chen
Melinda B. Gieselman
Jimmy Rogers
Yong-Jian Qiu
Vepa Krishna

Postdoctorals Currently Working on Project

Sanjay Basak
Benjamin Chaloner-Gill
Larry Harding
Jayesh R. Dharia
Sung Hong
Panthappallil S. Zacharias