Learning It From Manny

By Jack Hess L. Baricuatro*

It's only 9:00 AM but the Texas sun had already been blistering every moving creature outside. Drought was in the extended forecast that year, and temperatures were expected to be in the triple digits for the next two days. My feet were cold. I primped myself up and fidgeted around, as if it mattered, and for the first time I stepped into the office of *Professor Manuel P. Soriaga.*

The room was august in its order and simplicity. Books on the shelves were perfectly aligned from spine to spine. Definitely a family man, I surmised, as I saw pictures of his wife and three children, bedecked along with his plaques and certificates. My eyes wandered to a shiny, yellow M&M mascot by the corner table, blissfully waiting for an eternal high-five. *Manny* gazed at me with poker-face intensity and started to explain the rubrics of his laboratory. The declarations were concise but powerful: *You work hard. You cooperate with members who need your help. You can work on any topic we agree upon. You take short vacations*. Years later, these would be the same rules I would gratefully reiterate to many high-school, undergraduate, and graduate trainees I had the pleasure to work with in his laboratory. Manny stood up, shook my hand, wished me luck – and then gave me my first quiz that broke the ice of that encounter: *How do you get your candies from the M&M mascot?*

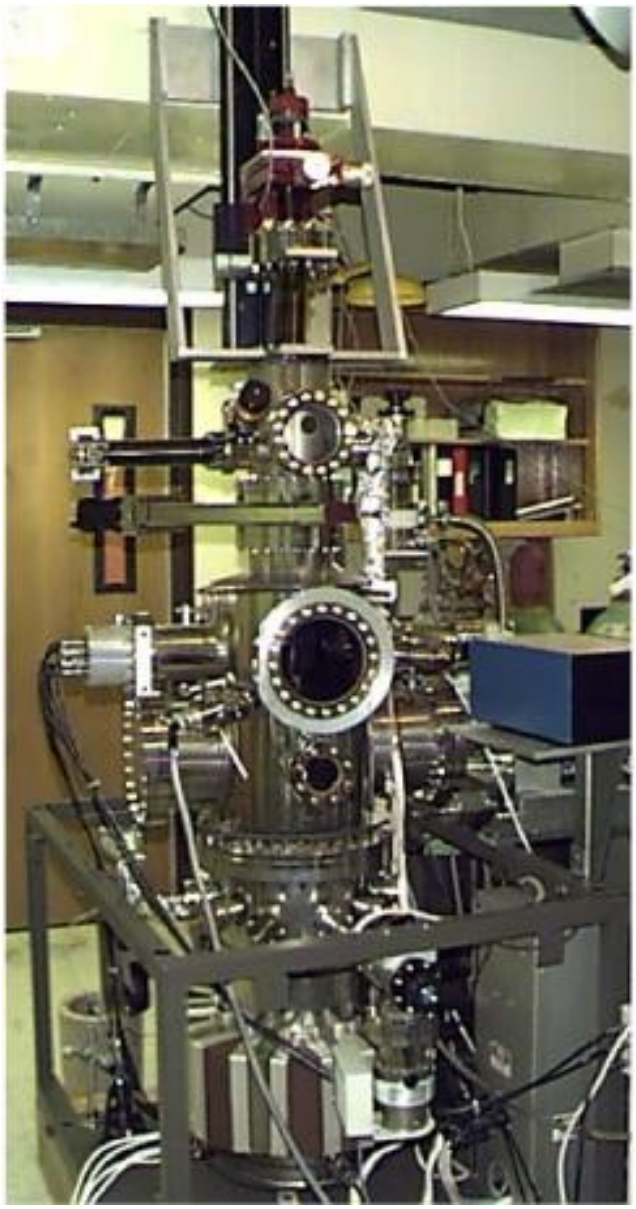
* Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, CA 91125

Manny's induction into Chemistry took deep roots at home: his father was a highly esteemed professor of Chemistry at the University of San Carlos in Cebu, where Manny finished his B. S. in Chemistry in 1970. Upon their father's prompting, all six siblings, regardless of their chosen field of specialization, had to take Chemistry courses. After a two-semester teaching stint at his *Alma Mater* and at St. Theresa's College, Manny left for the US as an East-West Center scholar to pursue graduate studies in Chemistry at the University of Hawaii. Manny briefly returned to the Philippines to marry Elizabeth Binamira, who later earned her Ph. D. degree in Inorganic Chemistry at the University of California at Santa Barbara; she is presently a Senior Lecturer at Texas A&M University. They have three children, all steeped in the sciences and engineering: Joseph (B. S. Electrical Engineering, California Institute of Technology; Ph. D. Electrical Engineering, University of California at San Diego), Angela (B. A., Biophysical Chemistry, Dartmouth College; Ph. D., Biochemistry, University of California at Los Angeles) and Christine (B. A., Chemistry, Texas A&M University).

After completion of his doctoral studies on lattice dynamics and solid-state vibrational spectroscopy under the tutelage of George Andermann, Manny served as a Visiting Assistant Professor at the University of Hawaii. He then joined the laboratory of Arthur T. Hubbard at UCSB as an American Chemical Society Petroleum Research Fund research fellow. There, he diverted his research attention to electrochemical surface science. Later, as a research chemist in the same laboratory, he published 50-odd papers that focused on structure-composition-reactivity relationships at platinum electrocatalyst

surfaces. His prolific work became the genesis of his research at Texas A&M University.

Manny combines both theory and experiment in his studies. The computational work makes use of *ab initio* density functional theory. The experimental strategies rely on the integration of traditional electrochemical techniques with modern surface spectroscopic methods. Techniques available at his Electrochemical Surface Science Laboratory include: scanning tunneling microscopy, atomic-force microscopy, low energy electron diffraction, Auger electron spectroscopy, X-ray photoelectron spectroscopy, high resolution electron energy loss spectroscopy, Fourier transform infrared reflection-absorption spectroscopy, temperature-programmed desorption-mass spectrometry, low-energy ion scattering spectroscopy and thin-layer electrochemistry. He has also availed of the National Synchrotron Light Source at Brookhaven National Laboratory. Projects currently under investigation are: the surface science of electrocatalysis; electrochemistry of nanostructured interfaces; electrode-surface organometallic chemistry; electrochemical hydrogen storage; mixed-metal fuel-cell electrocatalysts; and green electroanalytical chemistry. His group is also active in collaborative projects: enzyme-inspired heterogeneous catalysts; surface redox capacity and cellular toxicity of nanoparticles, Ni-metal hydride batteries; multi-megawatt batteries; and artificial photosynthesis. The studies find relevance in several technological areas such as renewable energy sources, heterogeneous catalysis, corrosion inhibition, materials science, microelectronics, electroanalysis and sensors.



One of three ultrahigh vacuum surface spectroscopy-electrochemistry instruments at the Electrochemical Surface Science Laboratory (ESSL) and the Center for Electrochemical Systems and Hydrogen Research (CESHR) at Texas A&M University; Dr. M. P. Soriaga is the Director of both research facilities. This particular apparatus is equipped for low-energy electron diffraction, Auger electron spectroscopy, thermal desorption mass spectrometry, high-resolution electron-energy loss spectroscopy and electrochemistry. Other accessible instruments include Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, low-energy ion scattering spectroscopy, atomic force microscopy and electrochemical scanning tunneling microscopy.

To date, Manny has generated 225 publications, including five books that he wrote or co-edited and a handful of papers in *Philippine Science Letters* and *The Philippine Scientist*. Manny's tour de force impact on both electrochemistry and surface science can be gleaned from a string of early influential papers that unveiled critical conceptual parallels between the chemical properties of organic molecules chemisorbed on noble-metal surfaces and those of homogeneous organometallic complexes (Soriaga et al. 1985, Soriaga et al. 1985, Schardt et al. 1985); as a measure of both the productivity and impact of his published work, his current *h-index* is 35. Manny is the Director of the Center for Electrochemical Systems at Texas A&M University. He has been a two-term National President of Phi Lambda Upsilon, the National Chemistry Honors Society. He is a member of the American Chemical Society, The Electrochemical Society, Society of Electroanalytical Chemists, and the Philippine-American Academy of Science and Engineering. He is also part of the editorial board for the journals *Electrocatalysis*, *Physics and Chemistry of Surfaces*, *Philippine Science Letters*, *The Philippine Scientist* and *Reports in Electrochemistry.* Early in his academic career, he was awarded

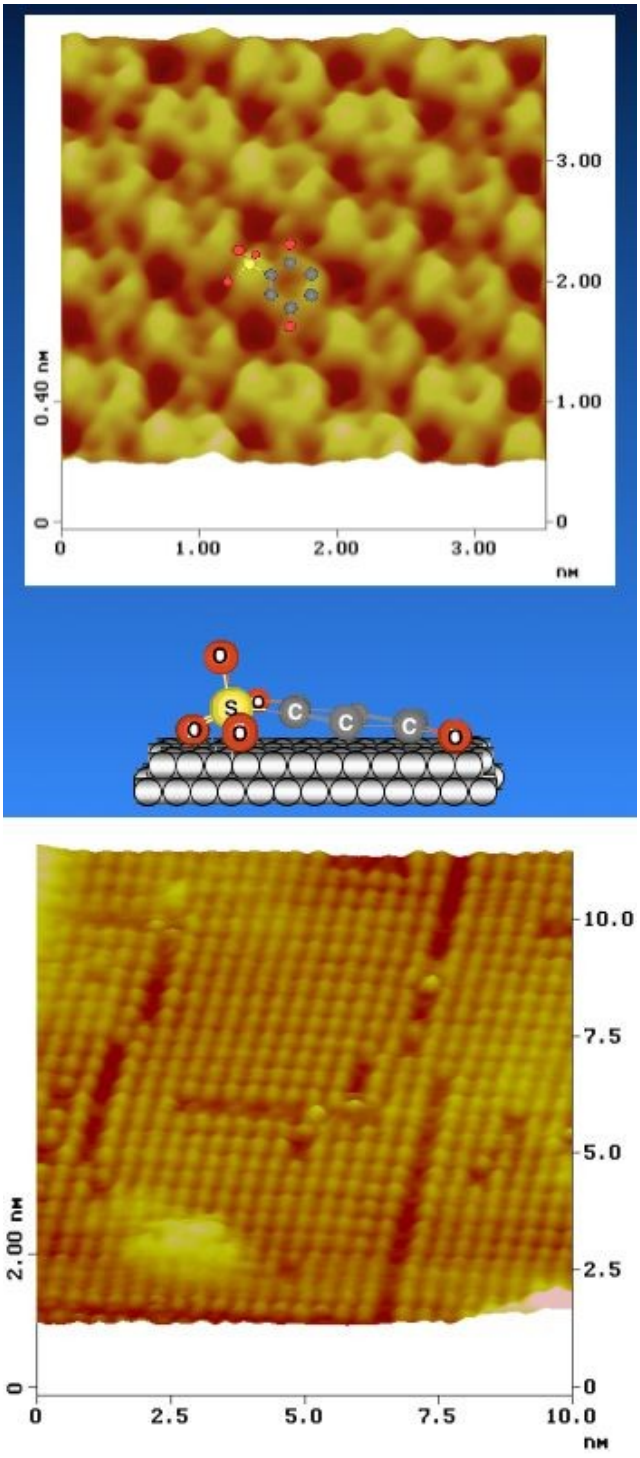
the *Presidential Young Investigator* award by the National Science Foundation.

You work hard.

One cannot simply question the fidelity of purpose of a scientist like Manny who has relentlessly documented the electrode-surface organometallic chemistry of hundreds of organic molecules at noble metals. In his laboratory, a suite of cryogenic and turbomolecular pumps interminably hummed along with a constant shuffling of feet from graduate students who were about to embark on the experimental protocols prescribed for tandem electron spectroscopy and electrochemistry. As a fledgling member of his group, I remember how I was initially envious of friends outside my circle who worked on researches that quickly gratified the senses with a bountiful yield, a multi-peaked spectrum or a lustrous precipitate, while I, even after week-long sessions of intense laboratory lucubration, always seemed to be empty-handed, ever pining for my sample surface to be clean and ordered, at the atomic level, before even the most routine voltammetric experiment could be initiated. Manny made me see the wisdom in the slow, the repetitive, the evasive and the insurmountable. Work hard and work will love you back.

Manny's *laissez-faire* non-interventionist approach to his students' professional growth showed his trust in the unique strength of each of his students to succeed. He insisted on "not running an empire." There were no minions and there were no kings. But the Friday-afternoon group meetings can daunt the habitually ill-prepared. One question that subtly intimidated: *Why is it that I know more about your own research than you?* Then, the blunt disapproval: *Your work is insignificant; it has not taught me anything that I did not already know.* The mild tantrum-like outbursts, however, never linger, and he is quick to revert to his good-natured self. The group members eventually learn how to cope with Manny's hilariously random sense of humor, borne out of two "creeds": (i) *No one deserves the right answer the first time around*; so we all adapted to ignore his first reply and simply wait for the second response. (ii) *For every situation in life, there is a corresponding joke*; and, he tells us, *your sense of humor depends on whether you find it or not.*

Twenty-five years of academic mentorship has spawned thirty-three doctoral and masteral degree holders spread around the globe; probe any of his former students, and you will discover stories rich with pride and gratitude for a mentor who knows when to crack the whip and when to let go. Manny has



Electrochemical scanning tunneling microscope (EC-STM) images obtained at the ESSL. The top image is that of benzoquinone sulfonate chemisorbed on Pd(111) at potentials in the double-layer region. The bottom demonstrates the anisotropic corrosion of a Pd(100) surface pretreated with a monolayer of iodine.

indeed successfully built a community dedicated to the tenets of superior science wrought in the dignity of hard work, tempered with equal force of creative freedom and critical thinking, and duly sealed with a bond of lifelong friendship.

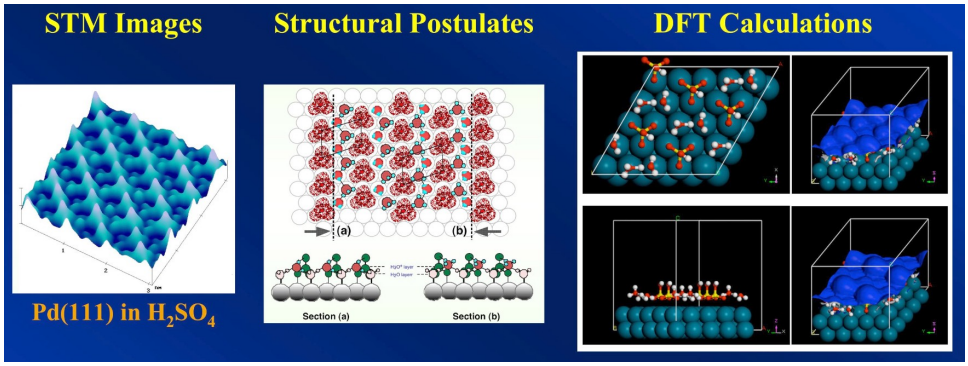
You cooperate with members who need your help.

The marriage of ultrahigh-vacuum surface science and in-solution electrochemistry was never an easy proposition. The pressure gap between the domains of electron spectroscopy and traditional electrochemistry necessitated a custom-built transfer system that permits shuttling the single-crystal electrode of choice between the near-ambient conditions of electrochemical methods and the ultrahigh vacuum environment needed for surface-sensitive tools. Manny's experimental excursions into the atomically resolved details of electron-transfer events, particularly on the palladium surface that many would consider too idiosyncratic for electrochemical surface science, were unmatched at the time his experiments were launched in the late eighties. The complexity of the operation demanded meticulous care to details that could only be perfected after months of practice in the hands of an experienced user. A novice can easily lose track of his experiment, and can do more harm than good in the absence of a mentor. In Manny's lab, everyone starts at the lowest rung of the so-called experimental ladder by working with a partner; everyone departs from the group with a team by his side. Much of the success of Manny's experiments is a transubstantiation of the spirit of *bayanihan* – a Filipino value of collective effort manifested in the act of moving a house by literally placing it on the shoulders of helpful participants.

You can work on any topic we can agree upon.

Manny's collaboration with numerous research groups attest to his ever-expanding sphere of research endeavors. A quick trip to Japan in the mid-nineties led to a collaboration with Kingo Itaya at Tohoku University, which ushered in experiments with John L. Stickney at the University of Georgia that demonstrated the complementary nature of the traditional ambient-air scanning tunneling microscopy (STM) and its electrochemical counterpart (EC-STM) (Soriaga et al. 1998). For the first time, various stages of the adsorbate-catalyzed dissolution of the Pd surface were imaged. Results for the iodine-on-Pd adlattices depicted a process akin to electrochemical digital etching whereby corrosion transpired faster on disordered (step) sites than that at the ordered planes; the dissolution occurred in layer-by-layer fashion, leading to the formation of a wide area of smooth, stable low-index planes (Soriaga et al. 1995).

A long standing interest on the surface chemistry of diphenolic compounds as electrochemical tags for platinum and palladium resulted in collaborative work with Perla Balbuena (Texas A&M University) who uses state-of-the-art first-principles computational chemistry methods to understand thermodynamic and kinetic properties of nanoscale materials. Manny's signature arsenal of integrated techniques, along with results from density functional theory, revealed unprecedented atomic details on the chemisorption of various species such as benzoquinone sulfonate at Pd(111) (Javier et al. 2010). Recognizing the remarkable capabilities of differential electrochemical mass spectrometry (DEMS) in characterizing the surface intermediates and products of electrolysis, Manny forged research ties with Helmut Baltruschat at the University of Bonn. With the use of DEMS, the electrochemical hydrogenation of prototypical aromatic compounds was investigated on various surfaces, specifically polycrystalline and Pt(*hkl*) (Sanabria-Chinchilla et al. 2006); as well as on terraces and step sites of Au(332) and Au(111) surfaces decorated with Pd ultrathin films (Sanabria-Chinchilla et al. 2007).



Ab initio density functional theory has recently been employed by the Soriaga group to help resolve compositional and structural issues related to EC-STM images. The work illustrated here is that of a well-defined Pd(111) electrode surface immersed in aqueous sulfuric acid solution at open-circuit potentials.

Many of Manny's friends in the electrochemistry and surface science community often jestingly kvetch over his seeming *idée fixe* on palladium and platinum. The reasons were self-evident to any practitioner in the field but all questions were readily quelled when Manny co-wrote papers, with John F. Garst at the University of Georgia, on the surface science of magnesium in Grignard-reagent formation (Garst and Soriaga 2004); and with Marcetta Y. Darensbourg at Texas A&M University on the electrocatalytic production of hydrogen using enzyme-inspired di-iron complexes (Chong et al. 2003). Noble-metal surfaces, however, still predominate the landscape of Manny's work, especially in his continuing quest

for high-performance electrocatalysts. Fruitful ties with D. Wayne Goodman (Texas A&M University) led to the characterization of thin-film mixed-metal catalysts for oxygen reduction (Axnanda et al. 2010). The investigation partly involved cobalt, a metal that introduced me to the liberal nature of selecting a research topic in Manny's laboratory. As impish as its Germanic etymology, cobalt almost cost me two apparently fruitless years in graduate school as I tried ambitiously to electrodeposit Co-Pd superlattices for magneto-optical devices. I remain grateful to Manny for summoning me to his office one afternoon, advising me to jettison the project in favor of more productive experiments. The release of his recent report on Co-Pt surface alloys gave me a frisson of vicarious satisfaction from knowing that dreams do not readily die under Manny's supervision; they simply metamorphose into new advanced themes.

You take short vacations.

General Chemistry is a core-curriculum course at Texas A&M University and is required of all students, regardless of academic major, for graduation. Manny would usually spend a summer term teaching freshman chemistry in order to keep himself on his "pedagogical toes". Meeting the demands of teaching and the rigors of research always required a balancing act, and Manny took both responsibilities in stride. Having served as his teaching assistant for many terms made me realize how his pedagogical style can drive students to do more in order to be more. Issue no formulaic exams. Raise questions that always probe. Deliver lectures that equally instruct and entertain. His classes were never popular with tepid students who did not intend to learn and to learn truly. His classes were never meant for the benchwarmers and lollygaggers. For one who had taught himself electronics in graduate school for lack of such training in his undergraduate education, learning did not necessarily require a formal university lecture. I was not surprised when he expected the same intellectual maturity and responsibility from his graduate students.

He constantly made all his students teach during their entire graduate program. The assignment provided an opportunity for students to strengthen their fundamentals in chemistry despite the specialized knowledge and skills afforded by his laboratory. The arrangement was also a blessing for someone who did a lot of hurrying-up and waiting for an ultrahigh vacuum chamber to work optimally. Semestral breaks were the busiest of times in the research laboratory, when one would get the quiet from the maddening din of querying students. But in this self-imposed desert of labor, Manny's words would always glisten like an oasis every time he declared: *It's time for a vacation. No longer than two weeks. Just keep me posted.* This was, of course, in addition to the *obligatory* two-week Christmas break.

Manny is currently a Visiting Faculty at the Joint Center for Artificial Photosynthesis (JCAP) at the California Institute of Technology where he serves as the Project Leader of the Heterogeneous Catalysis group. JCAP is the largest research program in the US dedicated to the development of an artificial solar fuel-generation technology. Established as an Energy Innovation Hub by the Department of Energy, JCAP has the missison to invent an economically viable device for the synthesis of fuels using only sunlight, water, and carbon dioxide.

So, how do you get your candies from the M&M mascot?

Facetiously, Manny cautioned me during my first formal interview in his office that nobody becomes a member of the group without correctly answering the M&M mascot mystery. Grapevine stories had it that one prospective student failed to get his candies from the mascot and did not make it to the group. I trust it was just plain rumor. But in case you are interested: just swing the mascot's arm and you will get your treat.

REFERENCES

Axnanda S, Cummins K, He T, Goodman DW, Soriaga MP. "Structural, Compositional and Electrochemical Characterization of Pt–Co Oxygen-Reduction Catalysts." Chem. Phys. Chem. 2010; 11: 1468

Chong D, Georgakaki IP, Mejia-Rodriguez R, Sanbria-Chinchilla J, Soriaga MP, Darensbourg MY. "Electrocatalysis of Hydrogen Production by Active Site Analogues of the Iron Hydrogenase Enzyme: Structure/Function Relationships." Dalton Trans. 2003;4158.

Garst JF, Soriaga MP. "Grignard Reagent Formation." Coord. Chem. Rev. 2004; 248: 623.

Javier A, Li D, Balbueno PB, Soriaga MP. "Density Functional Study of Benzoquinone Sulfonate Adsorbed on a Pd(111) Electrode Surface." Electrocatal. 2010; 1: 159.

Sanabria-Chinchilla J, Soriaga MP, Brussar R, Baltruschat H. "A DEMS Study of the Electrocatalytic Hydrogenation and Oxidation of Dihydroxybenzene at Polycrystalline and Monocrystalline Platinum Electrodes." J. Appl. Electrochem. 2006; 26: 1253

Sanabria-Chinchilla J, Baricuatro JH, Soriaga MP, Hernandez F, Baltruschat H. "Electrocatalytic Hydrogenation and Oxidation of Aromatic Compounds Studied by DEMS: Benzene and p-Dihydroxybenzene at Ultrathin Pd Films Electrodeposited on Au(hkl) Surfaces." J. Coll. Interfac. Sci. 2007; 314: 152.

Schardt BC, Stickney JL, Stern DA, Frank DG, Katekaru JY, Rosasco SD, Salaita GN, Soriaga MP. "Surface Coordination Chemistry of Well-Defined Platinum Electrodes: Surface Polyprotic Acidity of Pt(111)–CNH." Inorg. Chem. 1985; 24: 1419.

Soriaga MP, Binamira-Soriaga E, Hubbard AT, Benziger JB, Pang KWP. "Surface Coordination Chemistry of Platinum Studied by Thin-Layer Electrodes. Adsorption, Orientation and Mode of Binding of Aromatic and Quinonoid Compounds." Inorg. Chem. 1985; 24: 65.

Soriaga MP, Itaya K, Stickney JL. "In Situ STM and UHV-EC: Complementary, Noncompeting Techniques." In W. Lorenz and W. Plieth, Eds. "Electrochemical Nanotechnology." Springer-Verlag: Berlin, Germany (1998).

Soriaga MP, Schimpf JA, Carrasquillo A, Jr., Abreu JB, Temesghen W, Barriga RJ, Jeng JJ, Sashikata K, Itaya K. "Electrochemistry of the I-on-Pd Single-crystal Interface: Studies by UHV-EC and In Situ STM." Surf. Sci. 1995; 273.

Soriaga MP, White JH, Chia VKF, Song D, Arrhenius PO, Hubbard AT. "Surface Coordination Chemistry of Platinum Studied by Thin-Layer Electrodes. Surface Chemical Reactivity of Aromatic and Quinonoid Compounds Adsorbed in Specific Orientation States." Inorg. Chem. 1985; 24: 73.