Observations from the XXIst International Conference on Photochemistry (ICP21), Nara, Japan, July 26–31, 2003

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The XXIst International Conference on Photochemistry (ICP21) was held in the city of Nara, Japan, from July 26th to 31st, 2003. Scientific activities took place at Nara Public Hall in the middle of historic City Park, where modern facilities are tastefully integrated into a beautiful landscape full of *Shinta* shrines, *Buddhist* temples and traditional Japanese gardens. For a short time, 710–784 AD, Nara was Japan's capital, so stone and wood literally breathe history here (for more information see a website maintained by the prefecture: http://www.pref.nara.jp/nara_e/area01). The city park is also inhabited by thousands of domesticated yet vicious deer, known to beg unsuspecting tourists to death. Of the conferees, there was only one accident reported — a gang of deer ate half a copy of the scientific program (paperback) carelessly waved around by Bob Dunn of University of Kansas on his way to the lecture hall.

Further fatalities were prevented by the fact that the organizers (Mikhail V. Alfimov, Honorary Chairman of the International Organizing Committee and local organizers, Hiroshi Masuhara and Kinichi Obi, co-chairs; full list of organizers is below) did a superb job of putting together a diverse scientific program, which kept the conferees indoors and out of harms way from 9 am to 8:30 pm with short breaks for lunch and dinner. Except for the first three plenary lectures, the talks were held in four concurrent sessions, which made my task of reviewing them for this report a tad difficult. I, nevertheless, have a hope that my writeup will convey the spirit of this scientific gathering, which brought together 814 scientists from 31 countries and covered a wide variety of topics. According to the distributed participant list, the largest group of participants was, naturally, from Japan. The US followed with 33 conferees, then Korea (21), Russia (21), Germany (20), UK (12), Taiwan (9), Poland (8), France (7), Canada (6), India (6), Netherlands (6), Switzerland (6), Australia (5), Belgium (5), Ukraine (5), China (4), Finland (3), Spain (3), Sweden (3), Tailand (3), Belarus (2), Algeria (1), Denmark (1), Egypt (1), Hong Kong (1), Israel (1), Italy (1), Jordan (1), Nigeria (1), Turkey (1). There was also one participant from a country named *Other*, who actually came from University of Puerto Rico.

The conference kicked off with a special "Student Symposium" and a welcome party on Saturday, July 26th. The group photo from the party is posted at the conference website (http://www.pac.ne.jp/icp21). At the opening ceremony next day Hiroshi Masuhara proudly declared the conference the largest ICP meeting of them all. Kiyoshi Kurokawa, the chairman of the Science Council of Japan gave an inspiring speech and read a greeting telegram from the Prime Minister of Japan. Mikhail Alfimov, the honorary chairman and the host of the previous ICP meeting, found it symbolic that the conference on photochemistry is held in a country whose flag carries the image of world's largest UV/VIS source.

The opening ceremony was followed by three plenary lectures: by the 1986 Nobelist Yuan T. Lee, *Academia Sinica*, Toshio Yanagida, *Osaka U*, and Graham R. Fleming, *UC-Berkeley*. Lee briefly reviewed his method of crossed molecular beams, developed in his Berkeley days and then talked about two recent projects, one having to do with photochemistry of a *good guy (-YTL)*, ClO_2, and the other — with photoinduced scrambling of alkyl benzenes, which they proved involves cycloheptatrienes as intermediates. Toshio Yanagida had presented a spectacular lecture chock full of movies on molecular machines, manipulation of DNA with optical tweezers, single molecule fluorescence with evanescent wave excitation etc. He finished with his controversial stochastic model of myosin locomotion based on the premise that it is the Brownian motion and not the ATP, which is the energy source for myosin marching down the actin filaments. The ATP, he argues, is needed only to modulate the myosin-actin binding. The actual motion is Brownian, with the directionality biased by the asymmetric nature of myosin-actin binding (i.e., a thermal ratchet). On a lighter and somewhat philosophical note, Yanagida outlined the differences between the Western (*deterministic*) and Eastern (*ambiguity, stochastic*) understanding of various phenomena. Granted, he was not serious at all, but his comments underscored dramatic and irreconcilable differences between the "Western" and "Eastern" traditions, especially in the matters such as "to wear or not to wear" slippers, when presenting a lecture.

The podium in the Room "A" was a part of a traditional pagoda-like internal structure with a sort of tatami mat covering the stage. In addition to the usual "No food, No drinks, No smoking," there was another message displayed between the talks: "Please take off your shoes on stage. Please change to slippers." Apparently, this caught not only my attention — several people gave it some thought. The next plenary speaker, Graham Fleming, while climbing on stage, made a passing comment that this is the only talk you give, having to wonder if you have holes in your socks. Actually, after changing into traditional red slippers the speakers looked very homey and down to earth, in spite of all the formal attire, black suits, white shirts, ties and what not. In any event, Fleming's talk was on mechanisms and optimization of photosynthetic light harvesting. He summarized his seminal studies on energy transport in natural light harvesting systems and talked about studying ultrafast processes with the three-pulse photon echo peak shift technique. What also strikes me is that for systems as large and as complex as clusters of porphyrins outfitted with protein fragments or carotenoids, the Fleming group was able to run high level ab initio computations, both using Gaussian and in house programs, and some in collaboration with Martin Head-Gordon's group. The computed coupling matrix elements and the *transition density cube* made for a very realistic model of energy-transfer pathways in the photosystems.

After a brief lunch break the conference resumed in four concurrent sessions: (A) special session dedicated to late Professor George Porter "Elementary Processes in Photochemistry" at which among other things Frank Wilkinson of *Loughborough Univ.* covered George Porter's research at Cambridge and Sheffield; and David Phillips (*Imperial College London*) talked about Sir Porter's days at the Royal Institution and Imperial College; (B) "Laser Processing towards Nano-Technology"; (C) "Photofunction of Heterogeneous System"; (D) "Organic Photochemistry and Reactive Intermediate." The latter was organized jointly by Hideo Tomioka (*Mio U*) and Kazuhiko Mizuno (*Osaka Pref. U*). Invited lectures at this two-day mini-symposium included a talk by Daniel Falvey, *U Maryland*, on chemical and spectroscopic studies of photochemically generated nitrenium ions; Akihiko Ouchi (pronounced oh-`OO-chee, not ouchey!), *Natl Inst of Adv Industrial Science and Technology*, on photoinduced rearrangements of 1,6-(N-phenyl)aza[60]fulleroids; my lecture on photolabile scaffolds for molecular recognition; Takumi Oshima, *Osaka U*, on photosensitized E/Z isomerization of 1,2-dichloroethene with cation-recognized triplet sensitizers; UngChan Yoon, *Pusan Natl. U*, on synthetic strategy for the preparation of cyclic peptide mimetics based on SET-promoted photocyclizations; Teruo Shinmyozu, *Kyushu U*, on photochemical study of [3n]cyclophanes (with the objective of synthesizing hexaprismane derivatives); and Miguel A. Miranda, *U. Politecnica de Valencia*, on mechanistic studies in dyads containing benzoyl-thiophene and indoles or phenols. Diastereomeric dyads were synthesized and separated to investigate possible chiral discrimination in intramolecular hydrogen transfer from the indole or phenol fragment to benzoylthiophene. The day was concluded with poster session 1.

In addition to the second half of "Organic Photochemistry and Reactive Intermediates," several sessions were held on Monday, July 28th, including "Gas Phase Photodynamics," "Solar Light Energy Conversion: from Artificial photosynthesis to Solar Cell," "Anisotropic Control in Supramolecular Photochemistry," "Supramolecular Photochemistry," "Photochemistry of Biomolecules," "Photochemistry and Microscopy," "Atmospheric Chemistry" and "Reaction Dynamics and Spin Chemistry." As usual Michael Grätzel of *Swiss Federal Inst. of Technology* had delivered a stimulating lecture on molecular photovoltaics that mimic natural photosynthesis under "Solar energy conversion." Haruo Inoue of *Tokyo Metropolitan U.* opened the "Anisotropic Control…" session with a talk on anisotropic molecular interactions in supramolecular system and selective energy flow. This was followed by talks by Anthony Harriman, *U Newcastle* on conformational control of electronic coupling in molecular dyads and Robert Liu's (*U Hawaii*) photoisomerization by hula-twist (since Jack Saltiel decided not to go to Japan after the Gordon Research Conference, Bob's mechanism went largely uncontested). There were several talks in this session on semiconducting polymers and assemblies, including lectures by Sarah Tolbert, *UCLA*, on control of optical properties in semiconducting polymers through host/guest chemistry and inorganic/surfactant co-organization; Prashant Kamat, *U Notre Dame*, on photoinduced charging events in semiconductor-metal and metal-fluorophore hybrid nanoassemblies; Benjamin Schwartz, *UCLA*, on spatial distribution of interchain species in films of semiconducting conjugated polymers. Invited lectures in the "Supramolecular Photochemistry" session included a talk by Russell Schmehl, *U Tulane*, on photophysical behavior of Ru(II), Os(II) and Pt(II) complexes having multiple photoactive excited states; Seigo Yamauchi, *Tohoku U*, on controlling the lifetimes of excited states "by an electron spin"; and Kirk Schanze, *U Florida*, on triplet excited state in platinum-acetylide oligomers and polymers. Albert Brouwer, *U Amsterdam*, talked about photoinduced sub-molecular motion in rotaxanes.

In the "Photochemistry of Biomolecules" session Silvia Braslavsky, *MPI*, gave an invited lecture on

utilization of optoacoustic measurements to assess time-resolved thermodynamic parameters of biological photoreceptors.

On Monday afternoon a rather large audience was attracted to workshop on "Photochemistry and Microscopy" organized by M. Ishikawa, H. Fukumura, N. Tamai. Under scrutiny were singular quantities of molecules or, at most, nanocrystals. David Vanden Bout, *UT-Austin*, talked about single molecule studies of rotational dynamics in materials near their glass transition; Frans De Schryver, *KULeuven*, gave a talk on ensemble and single molecule photophysics of multichromophoric systems; Markus Sauer, *U Heidelberg*, discussed using electron transfer reactions to probe single-molecule conformational dynamics. After a short 25 min "coffee break with a snack," designed to substitute dinner, the talks continued into the evening, starting with a lecture by Stefan Hell of *Max Planck Inst for Biophys. Chemistry*. Using stimulated emission depletion (STED) microscopy in combination with 4Pi microscopy, Hell's group was able to overcome the Abbe's diffraction resolution barrier and achieve the order of 30 nm spatial resolution along the optic axis. If proved practical, the method may be the next BIG thing in far-field optical microscopy. Robert Dunn, *U Kansas*, gave a talk on utilization of a hybrid AFM/NSOM microscopy in single molecule studies of biological function. This session was concluded with a lecture by Paul Barbara, *UT-Austin*, who covered some selected issues related to single molecule spectroscopy of conjugated polymer and DNA isolated chains. Actually, there was a lot of new material on conjugated polymers to cover, so Paul only touched on the DNA issues at the end of his talk.

There were sessions on "Photochromism," "Organic Photochemistry," "Photochemistry and Photophysics of Porphyrin-Related Compounds" and "Synchrotron Radiation Chemistry" on Tuesday morning. The "Photochromism" session was held in Room A and the first few talks were chaired by Mr. Photochromism himself Masahiro Irie of *Kyushi U*. The first lecture was by Mikhail Krayushkin, *Russian Acad. Sci.*, who discussed several novel synthetic approaches to photochromic dihetarylethens. As was required of all the speakers in Room A, the renowned Russian scientist did change into red slippers. However, his drinking water during the stimulating talk did not come unnoticed by the presiding officer, who eventually sent his apprentice up the podium to seize the generic bottle of *Aqua*-something. As it turned out, the warning "No drinks" was strictly enforced in Room A (luckily, rooms B, C & D stayed less prohibitive). Yasushi Yokoyama, *Yokohama Natl. U*, who attended GRC on Photochemistry at Mount Holyoke and also managed to get to Nara on time, gave a lecture on novel photochromic systems based on 1,3-bisarylbutadienes. Several other lectures on various aspects of photochromism and optical switching were delivered by Kindo Uchida, *Ryukoku U*, Takahiro Seki, *Nagoya U*, Keitaro Nakatani, *Ecole Normale Superieure de Cachan*, Toshihiko Nagamura, *Shizuoka U*, and Valery Barachevsky, *Russian Acad. Sci.*

Tuesday afternoon was allocated for Noh performance, a half-day sightseeing tour and the Banquet, which was opened with a traditional ceremony of smashing the lid of a sake barrel with hatchets (performed by high ranking ICP officers dressed in traditional Japanese clothes) and also drinking sake from *petite* wooden boxes accompanied by shouting "Kanpai!" This certainly broke ice around many tables, so the banquet was a success. Countless variations of exquisite fish dishes were offered in addition to "first come first serve" sushi bar in the banquet hall. I personally enjoyed fish very much, although I should admit, in Nara I completely exhausted my annual quota of seafood intake. Our Japanese colleagues were extremely hospitable hosts. Masami Sakamoto of *Chiba U*, sharing table with us, patiently explained the customs and traditions of Japanese dining. A day before, the organizer of "Organic Photochemistry and Reactive Intermediates" Hideo Tomioka took several of us to a traditional restaurant, where we all enjoyed informal interaction with our Japanese colleagues. The organizers did a good job providing opportunities for such informal "mixing." Twice they organized Japanese-style-late-evening-bar mixers for the speakers, where we all were able to chat about scientific and not-so-scientific issues, consuming munchebles by the low tables and washing it down with ever-slightly-alcoholic beverages. Kanpai!

Wednesday, July 30[th], Room A (slippers!), "Asymmetric Photochemistry." The session was organized by Yoshihisa Inoue of *Osaka U*. Invited lectures included a talk by Kenso Soai, *Tokyo U Sci.*, on enantioselective synthesis with ee's exceeding 99.5% achieved by a combination of circularly polarized light and asymmetric autocatalysis; Richard Pagni, *U Tennessee*, on multiphoton chemistry with linear and circularly polarized light. Axel Griesbeck, *U Cologne*, summarized his work on spin effects in organic stereochemistry ("spin-mapping") and also talked about magnetic isotope effects in the absence of external magnetic fields — a new dimension in controlling the stereochemical outcome of photocyclizations by modulating SOC/HFC ratios. Norbert Hoffmann, *CNRS & U de Reims*, gave a talk on asymmetric photocycloadditions to furanones; Yasushi Yokoyama, *Yokohama Natl. U*, gave another lecture on chirality control in photocyclizations of diarylethenes and the morning session was concluded with an invited talk

by Thorsten Bach, *Tech. U Muenchen*, who reviewed his research efforts in achieving high enantioselectivity of intra- and intermolecular photocyclizations via H-bond templating with enantiomerically pure host molecules.

After lunch this session was continued with talks given by the organizer Yoshi Inoue, *Osaka U*, on photogeneration and properties of optically active *(E)*-diazacyclooctene, which racemizes much faster than its all-carbon counterpart, *trans*-cyclooctene; V. Ramamurphy, *Tulane U*, on the role of confinement and alkali metal ions in asymmetric photoreactions within zeolites. After coffee break Murphy took up the rains of session's chairman and the last two invited lectures in this workshop were delivered by John Scheffer, *U British Columbia*, on pre-organization of achiral molecules of photochirogenesis through crystallization-induced immobilization in homochiral conformations and Masami Sakamoto, *Chiba U*, on memory of chirality generated by spontaneous crystallization and asymmetric synthesis using the frozen chirality — a neat approach whereby achiral molecules trapped in chiral conformations (in chiral crystals) can be dissolved in cold solutions without racemization and then subjected to stereoselective transformations via all kinds of solution chemistries.

Other sessions this day included a workshop on "Photochemical and Photocatalytic Reactions within Zeolites," a special session "Photo-Catalytic Chemistry in Asia," and workshops "Molecules in Intense Laser Fields," "Electron Transfer and Energy Relaxation Dynamics I," and "Photochemistry of DNA." The latter drew a rather large crowd of participants and was opened with Fred Lewis' (*Northwestern U*) talk on dynamics and energetics of single step hole transport in DNA. Other invited talks at this session included a lecture by Tetsuro Majima, *Osaka U*, on hole transfer in DNA by adenine hopping mechanism; Kazuhiko Nakatani, *Kyoto U*, on charge transport in duplex DNA containing hole-trapping nucleotide bases; Hiroshi Sugiyama, *Kyoto U*, on photoreaction of 5-halouracil-containing Z-form DNA; and Masatsuga Shimomura, *Hokkaido U*, on aggregation behavior and photoisomerization of azobenzene DNA-mimetics formed at the air-water interface. Invited speakers at the "Electron transfer…" session included Monique Martin, *Ecole Normale Superieure*, speaking on ultrafast spectroscopy of p-coumaric acid in a quest to understand the primary photochemistry of the photoactive yellow protein; Klaas Zachariasse, *MPI for Biophys. Chem.*, with a lecture on intramolecular charge transfer with donor/acceptor molecules in solution, in crystals and with planarized systems; and Nobuhiro Ohta, *Hokkaido U*, speaking on electric field effects on excimer fluorescence of pyrene and generation of electroluminescence in a polymer film. The day ended with Poster Session II followed by a late night "bar mixer" for invited speakers.

Thursday, July 31[st]: in addition to the second section of "Asymmetric Photochemistry" chaired by John Scheffer, the last day of ICP saw the following sessions: "Photochemical Electron Transfer," "Electron Transfer and Energy Relaxation Dynamics II," "Nano-Scale New Technology," "Time- and Space-Resolved Vibrational Spectroscopy: State-of-the-Art and Photochemical Applications," "Spin photochemistry" and "Photochemistry and Function of Coordination Compounds." The latter was chaired by Kirk Schanze, Seigo Yamauchi, Russ Schmehl and Etsuko Fujita and covered a wide variety of topics, from bacteriochlorophyll, to optically switchable molecular solids, to light-to-electrical energy conversion. Gerald Meyer, *Johns Hopkins U*, gave a lecture on molecular control of photo-induced interfacial electron transfer. In his talk Jerry covered very fundamental issues related to electron injection at the TiO_2 interfaces. Joseph Hupp, *Northwestern U*, talked about supramolecular assemblies for photoelectrochemical light-to-electrical energy conversion. At the "Photochemical Electron Transfer" session Hiroshi Imahori, *Kyoto U*, talked about porphyrin and fullerene as a novel donor-acceptor couple in photoinduced electron transfer; Mikhail Kuzmin, *Moscow State U*, gave a talk on the nature of alternative mechanisms of excited-state electron transfer, elaborating the nature of medium reorganization. Also, a talk on femtosecond study of the photoinduced electron transfer in porphyrin-fullerene dyad was presented by Helge Lemmetyinen, *Tampere U Technology*. There were several interesting talks at the "Electron Transfer and Energy Relaxation Dynamics II," including a talk by Jacek Waluk entitled "In Search of cis Tautomeric Forms in Porphycene."

The Closing Ceremony was held shortly after 5 pm, after which it was time to say goodbye to Nara.

Well, what's left for me is to thank the organizers again for their hard work and congratulate them with all this success. I am particularly pleased with the fact that the program included more "organic" photochemistry than any previous ICP conference (granted I am biased!), making it a more diverse (and balanced) mix of mechanisms, photophysics, spectroscopy and practical applications.

Finally, a somewhat important note on raising public awareness and lobbying for fundamental science. Hiroshi Masuhara mentioned that Japanese government allocates special funds for no more than two chemistry conferences annually, but in spite of tough competition our local organizers were able to secure such support for ICP, underscoring the importance of photochemical sciences

in public view. In his tribute to Sir George Porter, Graham Fleming commended him on being not just a great scientist, but also a great showman, who was willing to talk about science with anyone (including Queen Elizabeth). That comment resonated with our conversation with Silvia Braslavsky, who suggested that every scientific conference should incorporate a popular science session open for general public for the same practical reason — to raise awareness and to (re)instill the idea that science is cool; — something for the future organizers to think about.

The next ICP meeting will take place in Australia in 2005.

Sayonara! (pronounced SA_YO-U_NA_RA). See you in Australia, mate! (pronounced m-EYE-t)

International Organizing Committee:

M. V. Alfimov (Russia): Honorary Chairman; A. K. Chibisov (Russia); G. R. Fleming (USA); M. Martin (France); H. Masuhara (Japan); D. Phillips (United Kingdom); J. C. Scaiano (Canada); J. D. Simon (USA); J. Waluk (Poland); K. Zachariasse (Germany)

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