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Preface



It is our honor to present this special issue commemorating the 60th birthday of Professor Haruo Inoue of Tokyo Metropolitan University. This issue contains contributions from twenty of the leading research groups in the world in the area of photochemistry. Originally, we proposed the sub-title “supramolecular photoscience in nanoscale environments,” a topic that is close to Professor Inoue’s heart, and many of the contributions are indeed at least partially in line with this concept, but, as will become clear, the scope has broadened somewhat, and the full range of photochemistry and photophysics is now represented, providing a worthy tribute to a great photoscientist.

Let us first present a brief biographical sketch of Professor Inoue. Born in 1947 in Japan, he attended the University of Tokyo, graduating in 1969. After completing the graduate program, he joined the faculty of the Department of Applied Chemistry at Tokyo Metropolitan University in 1972, where he has spent his entire academic career. Currently he is a Professor in this Department and serves also as the Executive Director of the International Center. He has been playing a highly important leadership role in chemistry in Japan and Asia: he has served as the Vice President of the Chem-

ical Society of Japan (2004–2006), the President of the Japanese Photochemistry Association (2006–2007), and the President of the Asian and Oceania Photochemistry Association (2008–2010). In addition, he has been a member of the Editorial Board for four journals and the Advisory Board of a fifth journal. His major research interests are photochemistry, energy coupling among chemical reactions, selective energy flow in solution, anisotropic control of chemical reactions in the excited state, nano-layered compounds, metal complexes, photochemistry of supra-molecular systems in microenvironments, artificial photosynthesis, as well as others.

His lifetime scientific achievements are indeed impressive and include the following milestones: a photo-nucleophilic substitution reaction induced by visible light (Chem. Commun., 1347 (1971)), the efficient radiationless deactivation of excited states through inter-molecular hydrogen bonding (J. Phys. Chem., 86, 3184 (1982)) and the molecular mechanism through anisotropic specific interaction (J. Phys. Chem., 101, 8166 (1997), 102, 8657 (1998), J. Phys. Chem. A, 105, 8840 (2001)), the unique microstructure of polyfluorinated micelles and vesicles (J. Phys. Chem. B, 103, 9562 (1999), Phys. Chem. Chem. Phys., 1, 3135 (1999)), the efficient photochemical oxygenation sensitized by metalloporphyrins with water as both an electron and oxygen atom donor (Chem. Commun., 1681 (1987), J. Am. Chem. Soc. 118, 6311 (1996), 119, 8712 (1997), 125, 5734–5740 (2003) and their extension to the artificial photosynthetic system (Pure Appl. Chem. 77, 1019 (2005), J. Phys. Chem. C, 113, 11667 (2009)), and the unique photo-responsive nano-scroll formation from nano-sheets of layered compound (J. Am. Chem. Soc., 128, 684 (2006)) as well as many other studies. He received the Japanese Photochemistry Association Award in 1997, the honor of a Tallant Professorship at the University of Florida, USA, in 2007, and he served as a Visiting Professor at Tohoku University, Japan, in 2007. He has also served as an Adjunct Professor at fourteen Universities. He has been a Leader of a Core Research on Evolutional Science and Technology (CREST) and Solution Oriented Research (SORST) Project under the auspices of the Japan Science and Technology (JST) Agency to continue the research subject of “Construction of Artificial Photosynthesis with Water as an Electron Source.” Recently he has been appointed as the Research Supervisor of a Precursory Research for Embryonic Science and Technology Project (PRSETO/JST) on “Chemical Conversion of Light Energy.”

Indeed, his work has been an inspiration to many in the photochemistry and photoconversion fields, particularly from the point of view of novel chemical systems in nanoenvironments, mimicking natural photosynthetic systems. His approaches hold great

promise in present and future efforts to capture and make use of solar energy.

We now proceed to briefly introduce each of the contributions to this Special Issue. The first contribution is from the group of Professor David Whitten, with collaboration from the group of Professor Kirk Schanze. This is a brief report summarizing the authors' photophysical examination of a series of novel cationic oligomeric phenyleneethynylenes (OPEs), both in free solution and in the presence of added carboxymethyl cellulose or amylose. The OPEs can interact with the latter biopolymers electrostatically and hydrophobically.

The second paper is from the groups of Professor Hiroshi Masuhara and Professor Teruki Sugiyama. These authors report the highly intriguing result that fullerene C60 nanoparticles can be solubilized in water as a result of pulsed laser treatment, without chemical modification or additives. Such dispersions hold great promise in photodynamic therapy.

The third paper is from the group of Professor Akira Fujishima. This work involves the recently intensively studied photocatalyst nitrogen-doped titania. The authors have carefully examined the wavelength dependence of the quantum yields for the decomposition of phenol and chlorophenol and have mapped the changes in the absorption bands that appear in the 400–500 nm region as a result of the nitrogen doping. The authors make the case that the proper choice of reactant compounds can help to elucidate the photocatalytic mechanism.

The fourth paper is from the group of Professor Minjong Yoon. In this work, the authors investigated the Raman and fluorescence properties of oxo-titanium porphyrin bound to single molecules of natural and artificial DNA, using a novel confocal scanning microscope, which was correlated with atomic force microscopy. They were able to observe differences in DNA morphology depending upon the base pairs present, a result that holds promise for detection of cancer in single cells.

The fifth paper is from the group of Professor Masahiro Irie. In this work, the authors succeed in using a nano-cavitand as an encapsulating, water-solubilizing agent for a photochromic diarylethene derivative. The latter are highly favored photochromic compounds but lack water solubility.

The sixth paper is from the group of Professor Vaidhyanathan Ramamurthy. This work involves the study of photochemical reactions of benzoin ethers in the restricted space within a calixarene host molecule. The results are supported with theoretical calculations and are compared with results obtained in other types of organized media.

The seventh paper is from the group of Professor Jye-Say Yang. These authors report the synthesis and photophysical properties of a series of unique poly(*p*-phenyleneethynylene) compounds with bulky pentyptycene substituents. The latter induce energetic barriers to rotation about the axis of the rod-like backbone.

The eighth paper is from the group of Professor Laszlo Biczok. This paper describes fascinating work in which the authors were able to facilitate a photo-induced tautomerization reaction involving lumichrome by inserting the latter into a rigid macrocyclic host, cucurbit[7]uril.

The ninth paper is from the group of Professor Miguel Miranda. The authors have synthesized dyads composed of two drug molecules, flurbiprofen and carprofen, in order to study their photophysical interactions for the purpose of developing a novel technique of studying drug–protein and drug–drug interactions.

The 10th paper is from the group of Professor Guoqiang Yang. The authors present a thorough study of the optical and photophysical properties of a series of derivatized metal (Al, Ga, In) phthalocyanines. These compounds are highly promising in non-linear optical applications, including optical intensity-limiting materials.

The 11th paper is from the group of Professor Zhongze Gu. In this work, the authors report on the successful combination of photocatalytic and electrochemical approaches to decompose refractory synthetic dyes in wastewater. The electrochemical process makes use of the novel boron-doped diamond electrode, on which hydroxyl radicals are produced to a large extent.

The 12th paper is from the group of Professor Suresh Das. In this work, the authors synthesized several photoresponsive liquid-crystal-forming compounds based on a butadiene moiety linked to a cholesterol moiety. The pitches of the cholesteric helices, and thus the colors of the reflected light, were found to respond to changes in temperature and illumination.

The 13th paper is from the group of Professor Kirk S. Schanze. This work involves the synthesis and photophysical characterization of a series of novel acetylide oligomers that incorporate platinum centers, as well as 2,2'-bipyridyl moieties, in the backbone. Metal ions can be coordinated by the BP units—this is of interest, since the luminescence properties, particularly the phosphorescence properties, are modified dramatically as a result of binding with metal ions, making this system ideal for trace metal detection.

The 14th paper is from the group of Professor Russell Schmehl. This work involves the preparation and photophysical characterization, including generation of a long-lived charge-separated state, of a novel dyad composed of a terpyridyl-coordinated Pt(II) chromophore, acting as an electron donor, and a naphthalene diimide complex, acting as an acceptor.

The 15th paper is from the group of Professor Vivian W.W. Yam. This work involves the synthesis and characterization, including luminescence and electrochemical measurements, of a series of platinum and palladium bis-alkynyl compounds containing the carbazole moiety. The combination of organic components and metals, like the work of Professor Schanze's group, is particularly novel and interesting.

The 16th paper is from the group of Professor Noboru Kitamura. This work explores the spectroscopic and photophysical behavior of a series of interesting concatenated anthracene derivatives, in which up to three anthracene moieties are connected via either a benzene ring or a boron atom.

The 17th paper is from the group of Professor Osamu Ishitani. These authors report a series of new dyads based on Re(I) bipyridyl tricarbonyl and Ru(II) tris-bipyridyl complexes, which are connected with short alkyl linkages. With optimization of the spacer group, it is possible to optimize the interaction between the two metal centers and thus the CO₂ reduction quantum yield.

The 18th paper is from the group of Professor Hitoshi Tamiaki. In this work, the authors have prepared model compounds related to the J-aggregates of bacteriochlorophyll-d, which are present in the main light-harvesting assemblies of green photosynthetic bacteria. The self-aggregation behavior was found to depend upon the length of spacer units. One possible application of these chlorophyll–galactose conjugates is in photodynamic therapeutic treatment of cancer.

The 19th paper is from the group of Professor Hiroaki Misawa. In this work, the authors have constructed two different novel gold-based nanostructures and have studied the surface-enhancement of Raman spectra for organic compounds in contact with these structures. Using techniques that have been developed for nano-engineering, they have been able to design and build structures that are controllable down to the nanometer level. With these, it is possible to obtain measurable Raman signals even with non-laser light sources.

The 20th paper is from the group of Professor Katsuhiko Takagi. The authors have prepared layered structures based on titania nanosheets and mesoporous silica. In the former, they have inserted

methylviologen, while in the latter, they have inserted cationic tetra-pyridyl porphyrins. With these assemblies, they have studied the photochemical and photoelectrochemical response and observed the electron flow.

The 21st paper is a second contribution from the group of Professor Vaidhyanathan Ramamurthy. In this work, the authors explore the use of natural and chirally modified cyclodextrins as media for photoreactions involving a series of adamantyl acetophenones. The cyclodextrins are considered to hold promise as inexpensive molecular containers in which to induce chiral photo-products.

We hope that you will enjoy reading this Special Issue and that you will find inspiration from both the scintillating papers assembled herein and, of course, the groundbreaking work as well as the fine scientific and personal character of Professor Haruo Inoue.

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