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Research Area：Microchemistry, Photochemistry, Microspectroscopy

Research Project: A Study on Laser Microchemistry

Academic Carrier

1976: Bachelor Degree, Tokyo Metropolitan University
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Research Background

1. Studies on Microchemistry

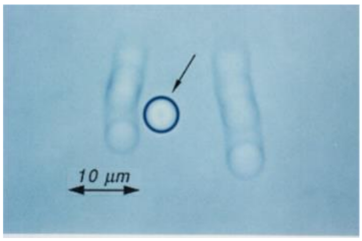

Fig. 1. Laser manipulation of a single microparticle in water.

1.1. Laser Trapping Microspectroscopy of Single Microparticles in Solution: We have developed laser trapping – microspectroscopy (absorption/fluorescence/Raman) techniques of various single microparticles in solution. As shown in Fig. 1, one can manipulate single microparticles (polymer beads, droplets, biological cells, and so forth) by a laser beam under an optical microscope. On the basis of this particular technique, we have demonstrated 1) *in situ* observation of the ion diffusion processes in single ion-exchange resin microparticles, 2) the mass/electron transfer processes across single microdroplet/water interfaces, 3) the photochemical cyanation reaction of an aromatic hydrocarbon across a single droplet/water interface.

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1.2. Simultaneous Extraction Detection of an Analyte Based on a Laser-Induced Microparticle Formation Technique: Some of an aqueous oil solution shows temperature-dependent phase separation. As an example, an aqueous butanol (BuOH) solution undergoes phase separation at around room temperature. On the other hand, water (H_2O) absorbs 1064 nm light through the overtone bands of the OH-vibration mode of water. Based on such phenomena, one can produce a single BuOH microdroplet by focused 1064 nm laser irradiation to an aqueous BuOH solution: Fig. 2. Similarly, focused continuous-wave 1064 nm laser irradiation to an aqueous poly(*N*-isopropyl acrylamide) (PNIPAM)/alcohol solution under an optical microscope can produce single PNIPAM/alcohol microparticle and the produced microparticle is trapped simultaneously by the incident laser beam. In the presence of a fluorescent dye, rhodamine B (RhB), RhB is extracted to the microparticle produced by laser irradiation. Our preliminary study has demonstrated that RhB in an aqueous PNIPAM/butanol (BuOH) solution as low as 10^{-15} mol/L is extracted to the PNIPAM/BuOH microparticle as demonstrated by in situ fuluorescence microspectroscopy of the microparticle. In practice, we have confirmed laser-induced extraction of RhB to the PNIPAM/BuOH microparticle at a single molecule level.

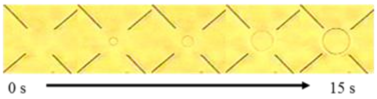

Fig. 2. Laser-induced single microdroplet formation in an aqueous butanol solution (7.1 wt%).

1.3. Laser Trapping of Single aerosol roplets in Air: We have succeeded in laser trapping of single aerosol water droplets levitated in air. Furthermore, we have demonstrated that aerosol water droplets in air do not freeze down to –60 °C since the water droplet levitated in air without physical contact other than air is not likely to form a freezing nucleus: see Fig. 3. Similar to the aerosol water droplets, single aerosol dimethyl sulfoxide (DMSO) or *tert*-BuOH droplets with the bulk freezing temperature (f_p) being +18.5 and +25.7 °C, respectively, does not freeze in air down to –60 and ca.

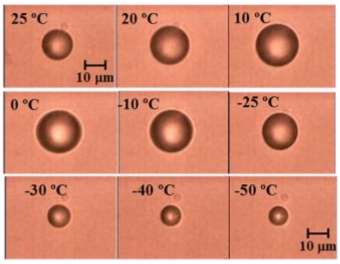

Fig. 3. Laser trapping of a single aerosol water droplets at several temperatures.

0 °C, respectively. Furthermore, we have demonstrated that the solution viscosity of aerosol DMSO, water, or ethanol droplets increased with a decrease in the aerosol droplet diameter.

1.4 Development of Pulsed Laser Shock Wave Technique for Mechanochemical Phenomena: We reported triboluminescence of *N*-alkylcarbazole crystals. Triboluminescence of crystals is in general induced by manual grinding of the crystals by a glass rods or spatula and, therefore, such experiments cannot afford quantitative information of triboluminescence. For quantitative discussion on triboluminescence, we proposed a pulsed laser shock wave (PLSW) method. In the PLSW method, a shock wave generated by irradiation of a pulsed laser beam to a solid substrate is employed as mechanical force for triboluminescence. In practice, we have succeeded in determining the threshold laser power to induce triboluminescence of *N*-isopropyl carbazole crystals by the PLSW method.

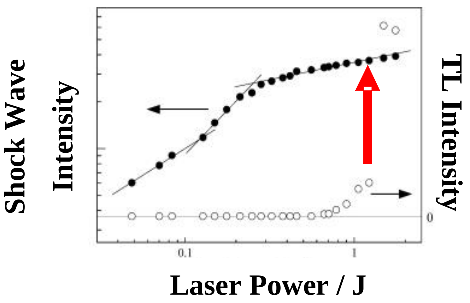

Fig. 4 Triboluminescence of *N*-isopropylcarbazole crystals by a pulsed laser shock wave technique.

2. Photochemistry of Organic and Transition Metal Compounds: We reported the spectroscopic and photophysical properties of various organic (triarylboranes) and transition metal complexes (Ru(II), Pt(II), Re(I), Mo(II), W(II), etc). As an example, we have found that octahedral hexanuclear metal cluster complexes whose general structure is shown in Fig. 5 show intense and long-lived phosphorescence both in solution and solid phases at room temperature. In order to elucidate such unique emission properties of a hexanuclear metal complex, we recently conducted a systematic study on the spectroscopic and photophysical properties of a series of hexanuclear Mo(II) clusters in the temperature (T) range of 3 ~ 300 K. The study has demonstrated the emitting excited triplet state of an Mo(II) cluster splits in energy as large as ca. 1000 cm^{-1} and the splitting energies in the excited triplet state of Mo(II) complexes (ΔE_{1n}) are shown to be correlated linearly with the forth power of the atomic number of the atom composed of the cluster (Z(X)): $\Delta E_{1n} \propto [Z(X)]^4$, Figure 6. This is the first demonstration for the Z^4 power dependence of the zero-magnetic-field splitting in the excited triplet state.

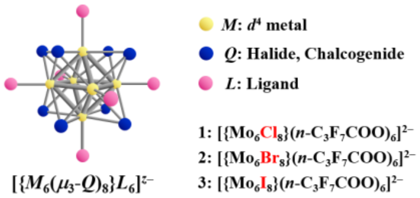

Fig. 5. Structure of an octahedral hexanuclear molybdenum(II) cluster.

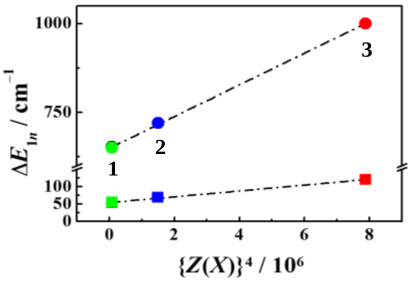

Fig. 6. Correlation between ΔE_{1n} and $[Z(X)]^4$ of a series of hexanuclear Mo(II) clusters.

Publication List

Selected original papers

1. Terminal Ligand (L) Effects on Zero-Magnetic-Field Splitting in the Excited Triplet States of $[\{Mo_6Br_8\}L_6]^{2-}$ (L = Aromatic Carboxylates), S. Akagi, T. Horiguchi, S. Fujii, and **N. Kitamura**. ***Inorg. Chem.***, **2019**, *58*, 703 – 714.
2. Emission Tuning of Heteroleptic Arylborane-Ruthenium(II) Complexes by Ancillary Ligands: Observation of Strickler-Berg Relation, A. Nakagawa, A. Ito, E. Sakuda, S. Fujii, and **N. Kitamura**. ***Inorg. Chem.*** **2018**, *57*, 9055 – 9066.
3. Zero-Magnetic-Field Splitting in the Excited Triplet States of Octahedral Hexanuclear Molybdenum(II) Clusters: $[\{Mo_6X_8\}Y_6]^{2-}$ (X, Y = Cl, Br, I), S. Akagi, S. Fujii, and **N. Kitamura**. ***J. Phys. Chem. A***, **2018**, *122*, 9014 – 9024.
4. A Study on the Redox, Spectroscopic, and Photophysical Characteristics of a Series of Octahedral Hexamolybdenum(II) Clusters: $[\{Mo_6X_8\}Y_6]^{2-}$ (X, Y = Cl, Br, I), S. Akagi, S. Fujii, and **N. Kitamura**. ***Dalton Trans.***, **2018**, *47*, 1131 – 1139.
5. Laser-Induced Single Microdroplet Formation and Simultaneous Water-to-Single Microdroplet Extraction/ Detection in Aqueous 1-Butanol Solutions, **N. Kitamura**, K. Konno, and S. Ishizaka. ***Bull. Chem. Soc. Jpn.***, **2017**, *90*, 404 – 410.
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11. Dual Emissions from Ruthenium(II) Complexes Having 4-Arylethynyl-1,10-phenanthroline at Low Temperature, E. Sakuda, C. Matsumoto, Y. Ando, A. Ito, K. Mochida, A. Nakagawa, and **N. Kitamura**. ***Inorg. Chem.***, **2015**, *54*, 3245 – 3252.
12. Reversible Control of the Equilibrium Size of a Single Aerosol Droplet by Change in Relative Humidity, S. Ishizaka, K. Yamauchi, and **N. Kitamura**. ***Anal. Sci.***, **2014**, *30*, 1075 – 1079.
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